ECN

Energy research Centre of the Netherlands

GASASH

Improvement of the economics of biomass/waste gasification by higher carbon conversion and advanced ash management

J.R. Pels

D.S. de Nie

J.H.A. Kiel

ECN-C--06-038

Revisions		
A		
B		
Made by: J.R. Pels Checked by: J.H.A. Kiel	Approved/Issued by: J.W. Erisman	ECN Biomass, Coal & Environmental Research

Acknowledgement/Preface

This report is the final report of the project "Improvement of the economics of biomass/waste gasification by higher carbon conversion and advanced ash management (GASASH)", sponsored by SenterNovem, project nr. 2020-02-12-14-006. The work encompasses ECN's share of the EU Fifth Framework Project with the same title (ENK5-CT-2002-00635). Public reports of the EU project are included as annexes.

Abstract

Gasification of biomass and waste in circulating-fluidised-bed systems produces carbon-rich fly ash. How to deal with this fly ash in an economic way was the key question in the GASASH project. Landfill was not considered as an option, since it is prohibited in many countries due to the high calorific value of the fly ash. A parametric study showed that optimisation of the gasification process itself may decrease the amount of fly ash to some extent by increasing the carbon conversion and thus decreasing the carbon content in the fly ash. However, process optimisation will still not lead to a fly ash quality that allows utilisation options in building materials as developed for fly ash from pulverised-coal combustion. Direct utilisation of the fly ash appears to be limited to use as a (secondary) fuel or as filler in asphalt or asphalt-like products. For other utilisation options, after-treatment is needed, e.g., to lower the carbon content and to remove or immobilise contaminants like chlorine and heavy metals. Fly ash combustion tests at different temperature levels revealed that the resulting material can be used as (component in the manufacturing of) building materials. Leaching tests showed that several products comply with the lower limits of the Dutch Building Materials Decree, which means unrestricted use. Examples are synthetic basalt and heat-treated fly ash (as filler in cement). In general, consistency of quantity and quality is crucial for all forms of utilisation. Local factors strongly influence the technical and economic feasibility of various options. For the Netherlands, the most promising option is direct utilisation as secondary fuel, followed by utilisation as building material, directly in asphalt or after combustion in various building products.

Keywords

Ash utilisation, fly ash, carbon-rich fly ash, leaching, gasification, biomass, waste

Contents

List of tables 6

List of figures 8

Summary 9

Samenvatting 11

1. INTRODUCTION 13
   - 1.1 Objectives of the overall project 13
   - 1.2 Introduction to work packages 13
   - 1.3 Structure of this report 13

2. OPTIMISATION OF THE GASIFICATION PROCESS (WP 1) 15
   - 2.1 Introduction 15
     - 2.1.1 Parametric study to optimise carbon conversion 15
     - 2.1.2 HSD-CFB Principle 15
     - 2.1.3 Gasification of demolition wood with and without fines 16
   - 2.2 Experimental 16
     - 2.2.1 Fuel selection 16
     - 2.2.2 Gasifier 17
     - 2.2.3 The HSD-CFB concept and other measures 17
     - 2.2.4 Runs with sewage sludge and sewage sludge/wood pellets 17
     - 2.2.5 Runs with demolition wood with and without fines 18
   - 2.3 Results and discussion 18
     - 2.3.1 Air ratio, temperature and application of the HSD-CFB principle 18
     - 2.3.2 Combining sewage sludge with wood pellets 19
     - 2.3.3 Removal of fines from demolition wood 23
   - 2.4 Conclusions on optimisation of the gasification process (WP 1) 25

3. DEVELOPMENT OF NEW TECHNOLOGY (WP 2) 26
   - 3.1 Introduction 26
   - 3.2 Experimental 27
     - 3.2.1 Sample of carbon-rich fly ash from EEP's 80 MW_{th} gasifier 27
     - 3.2.2 Dry separation of carbon-rich fly ash 27
     - 3.2.3 Low-temperature combustion 27
     - 3.2.4 High-temperature combustion 27
     - 3.2.5 Pelletisation 28
     - 3.2.6 Controlled leaching 28
     - 3.2.7 Immobilisation 28
     - 3.2.8 Up scaling of smelting experiments 28
   - 3.3 Results and Discussion 29
     - 3.3.1 Review on the "strategy on staged cooling and particle removal" 29
     - 3.3.2 Literature review on screening techniques 29
     - 3.3.3 Sample of carbon-rich fly ash from EEP's 80 MW_{th} gasifier 29
     - 3.3.4 Dry screening of carbon-rich fly ash 31
     - 3.3.5 Low-temperature combustion of carbon-rich fly ash 33
     - 3.3.6 High-temperature combustion of carbon-rich fly ash in a coal burner 35
     - 3.3.7 High-temperature combustion of carbon-rich fly ash in a smelter 36
     - 3.3.8 Immobilisation of carbon-rich fly ash in C-Fix construction blocks 38
     - 3.3.9 Controlled leaching and analysis of the washing fluids 39

3.3.10 Pelletisation of carbon-rich fly ash 39
3.3.11 Comparison of results of explorative techniques 40
3.3.12 Up-scaling of high-temperature combustion 41
3.4 Conclusions from development of new technology (WP 2) 41

4. CHARACTERISATION OF ASHES AND THE DEVELOPMENT OF ASH UTILISATION METHODS (WP 3) 43
4.1 Introduction 43
4.1.1 Characterisation 43
4.1.2 Leaching tests 43
4.1.3 Comparison of leaching results to limits in established legislation 43
4.1.4 Development of new and existing utilisation routes 45
4.2 Characterisation of Fly Ashes 45
4.2.1 Characterisation of ashes derived from gasification of sewage sludge 45
4.2.2 Characterisation of fly ash from gasification of demolition wood with and without fines 46
4.2.3 Characterisation of fly ash samples of EEP's 80 MW_{th} gasifier 47
4.2.4 Ash characteristics after combustion at low temperature 49
4.2.5 Characterisation of fly ash after combustion at high temperatures 50
4.2.6 Characterisation of C-Fix block 52
4.2.7 Characterisation of synthetic basalt 52
4.2.8 Effect of pH control on leaching of Pb and other elements in washing of ashes 54
4.3 Utilisation Options for Carbon-rich Fly Ash 55
4.3.1 Building material 55
4.3.2 Fertiliser 55
4.3.3 Fuel 55
4.3.4 Niche applications 56
4.4 Most promising routes for utilisation of gasification ashes 56

5. TECHNO-ECONOMIC EVALUATION (WP 4) 58

6. CONCLUSIONS 59
6.1 Technical and economical conclusions 59
6.2 Outlook for utilisation of carbon-rich gasification ashes in the Netherlands 60

Appendix A Public Summary of Consolidated Final Report 63

Appendix B Deliverable 1 Report on Selection of Test Fuels and Test Program 95

Appendix C Deliverable 4&5 Report on Methods to Improve Carbon Conversion of Fluidised Bed Gasification and on Technical Possibilities to Reduce Ash Volume 103

Appendix D Deliverable 15 Identification of the Most Promising Ash Utilisation Options and Ash Treatment Needed 175

Appendix E Deliverable 16 Report on Technically Potential Gasification Ash Utilisation Options 191

Appendix F Deliverable 17 Report on a detailed Characterisation of Different Gasification Ashes 203

Appendix G Deliverable 20 Report on the Influence of Optimised Ash Management of the Economy of the Gasification Process 219

Appendix H Deliverable 23 Comparison of the Results from Different Ash Treatment Methods 251

List of tables

Table 1.1 Deliverable reports where ECN contributed a significant part of the work..... 14
Table 2.1 Comparison of the effect of different measures on the carbon conversion in gasification of biomass 18
Table 2.2 Composition of wood pellets, sewage sludge and ashes from combustion of wood pellets and sewage sludge; all data on dry base, moisture as received 20
Table 2.4 Data of ash collection in gasification runs with 100% sewage sludge 20
Table 2.5 Composition of sewage sludge and ash collected in gasification runs with 100% sewage sludge; moisture content as received, all other data on dry basis..... 21
Table 2.6 Composition of demolition wood and fly ash in runs with and without fines; moisture content as received, all other data on dry basis..... 24
Table 3.1 Proximate and ultimate analysis of fly ash obtained from AMER-CFB (September 2003)..... 30
Table 3.2 Trace elements in carbon-rich fly ash obtained from AMER-CFB (September 2003); all data in mg/kg original material, dry basis 30
Table 3.3 Composition of sieve fractions; background colours indicate the deviation from average: yellow = within 10% of the average value, light green = between 10% and 50% lower than average; dark green = lower than 50% of the average value; pink = between 10 and 100% higher than the average value; red = more than 100% above the average value; <d.l. = below detection limit 33
Table 3.4 Composition of fly ash recovered from combustion of AMER-CFB high-carbon fly ash at 700°C; all data in mg/kg on dry basis 34
Table 3.5 Composition of fly ash recovered from high-temperature combustion of AMER-CFB high-carbon fly ash in a simulated coal burner; all data in mg/kg on dry basis 35
Table 3.6 Composition of ash samples prepared by heating at a high temperature and compared to the original AMER-CFB high-carbon fly ash normalised to 100% ash; all data in mg/kg (dry); '< d.l.' = below detection limit 37
Table 3.7 Washing of elements at L/S=2 and L/S=10 from AMER-CFB fly ash (September 2003); 'L/S' in litre water per kg original material 38
Table 4.1 Overview of samples from WP1 and WP2 subjected to leaching tests 43
Table 4.2 Maximum values at L/S=10 in constituent release for acceptance of waste in 3 categories: inert, non-hazardous and hazardous, according to the European Landfill Directive (2002); data in mg/kg (dry material) 44
Table 4.3 Limits of Cat. 1 and Cat. 2 applications in the Dutch Building Materials Decree for a layer thickness of 0.7 m and for shaped monolithic building material..... 45
Table 4.4 Leaching results (L/S=10) of percolation tests NEN 7343 on fly ash samples from gasification of demolition wood, AMER-CFB fly ash (September 2003) and two BIVKIN runs with and without fines; all data in mg/kg dry basis..... 46
Table 4.5 Cumulative release (PrEN 14405) of constituents (L/S=10) from gasification fly ash of demolition wood compared to the EULFD acceptance criteria of non-hazardous and hazardous waste and limits of Cat 1. and Cat 2. applications in the Dutch Building Materials Decree for a layer thickness of 0.7 m; data are in mg/kg (dry material) 47
Table 4.6 Cumulative release of constituents (L/S=10) from gasification fly ash of demolition wood in mg/kg dry matter, compared the European Landfill Directive (EULFD acceptance criteria of non-hazardous and hazardous waste and to the limits of cat 1 and cat 2 applications in the Dutch Building Materials Decree (DBMD) for a layer thickness of 0.7 m; data in mg/kg (dry material)..... 49
Table 4.7 Cumulative release of constituents (L/S=10) from ash samples prepared by high-temperature combustion of gasification fly ash of demolition wood,

compared the European Landfill Directive (EULFD acceptance criteria of non-hazardous and hazardous waste and to the limits of cat 1 and cat 2 applications in the Dutch Building Materials Decree (DBMD) for a layer thickness of 0.7 m; data in mg/kg (dry material) 50
Table 4.8 Constituent release (mg/m^2/64 days) from C-fix material compared to limit values for eluate concentrations in shaped monolithic building materials in a category 1 application in the Dutch Building Materials Decree (DBMD). 52
Table 4.9 Results from a tank test on 1 kg sample synthetic basalt (90% AMER-CFB fly ash and 10% alumina) 53
Table 4.10 Results from availability test on 5 kg sample of synthetic basalt 53

List of figures

Figure 1.1 Schematic of interactions between work packages 14
Figure 2.1 Diagram of the bottom part of the riser in a CFB gasifier designed according to HSD-CFB principle 16
Figure 2.2 Distribution of elements in the three ash fractions produced in the gasification of 100% sewage sludge at 800°C; total mass distribution is 77% in hot cyclone, 17%% in cold cyclone and 7% in filter at ambient conditions 22
Figure 2.3 Distribution of elements in the three ash fractions produced in the gasification of 100% sewage sludge at 900°C; total mass distribution is 85% in hot cyclone, 12% in cold cyclone and 3% in filter at ambient conditions 22
Figure 2.4 Total ash and element content of fly ash from gasification of demolition wood with and without fines and from AMER-CFB gasifier (log-scale in mg/kg dry basis) 23
Figure 3.1 Particle size distribution (incl. cumulative) of fly ash and bottom ash of AMER 80 MW_{th} circulating fluidised bed gasifier, measured with Malvern Mastersizer 2000 30
Figure 3.2 SEM photographs, SEI (a) and COMPO (b) of carbon-rich fly ash from the AMER 80 MW_{th} circulating fluidised bed gasifier 31
Figure 3.3 Particle size distribution of the fly ash obtained from AMER-CFB fly ash (Sept. 2003). The distribution is per size fraction, so that the surface area of each rectangle represents the mass of the sieve fraction. Sieves at 20, 38, 45, 63, 90 and 180 µm. 32
Figure 3.4 Concentration of elements in fly ash after combustion in a BFB and of the carbon-rich fly ash (used as fuel) normalised to total ash content; all data in mg/kg (dry) 34
Figure 3.5 Photographs from high-temperature combustion of AMER-CFB high-carbon, a) agglomerate (about 3 cm long) from high-temperature combustion in a simulated coal burner, b) fragment of the molten ash layer from incineration at 1450°C. 36
Figure 4.1 pH dependent release of lead (Pb) from gasification fly ash of demolition wood in leaching test (PrEN 14429) 48
Figure 4.2 SEM pictures of fly ash samples from high-temperature combustion of AMER-CFB high-carbon a) in a simulated coal burner at 1400°C, b) powder in crucible at 1100°C, c) smelt in crucible at 1400°C, d) smelt in crucible at 1550°C 51
Figure 4.3 pH dependent release of several elements from gasification fly ash of demolition wood in pH dependence leaching test (PrEN 14429). 54
Figure 4.4 Preferences for Waste Treatment 56

Summary

Gasification of biomass and waste in circulating fluidised bed systems produces a black, carbon-rich fly ash. In the GASASH project, utilisation options have been investigated for this particular material. Landfill was not considered as an option, since it is prohibited in many countries due to the high calorific value of the fly ash. Moreover, it jeopardises the green image of energy production from biomass. The general objective of the project was to find economic ways to manage the carbon-rich fly ash. Specific goals were addressed in three work packages. Firstly, the gasification process should be optimised not only for energy production, but also for ash quality and ash quantity. With respect to the latter, the carbon conversion should be maximised. The second work package aimed at development of new techniques for after-treatment to condition carbon-rich fly ash for certain forms of utilisation. The third work package consisted of a search for existing and new utilisation routes. The fourth work package - with a relatively small contribution from ECN - comprised a techno-economic evaluation of the utilisation routes.

In the first work package, ECN performed several tests in its 500 kW_{th} circulating fluidised bed gasifier (BIVKIN) and used data from older runs and background information to determine the influence of several process parameters. The main conclusion (supported by results from the other project partners) was, that practical measures manipulating the parameters of existing gasification plants cannot increase the burnout level of gasification ash to a degree, where the ash can be used directly in applications established for fly ash of pulverised-coal combustion. Significant changes in the design of the gasifier might accomplish this goal, but those are still in an early development stage.

In the second work package, various after-treatment techniques have been explored to upgrade the ashes and make them better suitable for utilisation. *Dry screening* allows separation of a small ash fraction with a relatively low level of contaminants, but the bulk of the material cannot be treated this way. *Pelletisation* can significantly improve logistics. *Immobilisation* with heavy petroleum residue was found to be effective in improving leaching behaviour, producing a material suitable for utilisation as building material. *Low-temperature combustion* converts carbon-rich fly ash into a low-carbon fly ash that is nearly identical to fly ash from combustion. *High-temperature combustion* is a technically acceptable way to convert carbon-rich biomass into sintered material that is suitable for utilisation as building material. *Controlled leaching* can be used to remove chlorine and alkali salts, but heavy metals are largely retained. Smelting (high temperature combustion) was selected for more elaborate investigations. Several kilograms of synthetic basalt blocks and granulate were made. Each complied with the limits of category 1 building material of the Dutch Building Materials Decree, which means that it can be used without restrictions.

In the third work package, new different utilisation options were searched and evaluated. This included comparison of fly ash characteristics with the specifications of each utilisation route, mainly from a Dutch perspective. The overall conclusion is that there is no universal solution and that for each kind of fly ash an optimal route should be defined. Technical and economic feasibility depend on the local situation. When criteria are used that apply to the situation in the Netherlands, it becomes clear that fly ashes with high carbon content should preferably be utilised as a fuel. There are applications possible, where the calorific value of the remaining combustible material is valued, e.g. co-firing in coal-fired plants, smelters or cement kilns. Direct utilisation of carbon-rich fly ash as building material (although possible for bottom ash) is not likely. Carbon-rich fly ash is not an attractive material and in case of fly ash from demolition wood or other contaminated fuels. It is unlikely to comply with the limits of the Dutch Building Materials Decree (DBMD). Indirect utilisation as building material is possible

for carbon-rich fly ash in asphalt and asphalt-like products, e.g. C-fix. After combustion, oxidised fly ash from biomass may be used directly as building material, e.g. in road construction or in special cement products. Utilisation as fertiliser or as raw material for fertiliser products is very unlikely. Typically, the ratio of nutrients versus contaminants is unfavourable. In Scandinavia and elsewhere, fly ash from uncontaminated wood, can be recycled ash to the forests where the wood was harvested. The geographic conditions in the Netherlands determine that ash recycling is nearly irrelevant subject. There are no large production forests or energy plantations. Dutch legislation has not been updated to allow ash recycling. Landfill of carbon-rich fly ash is prohibited; landfill of oxidised fly ash is possible, but expensive. The most promising routes are 1) direct utilisation as fuel, 2) direct utilisation in asphalt and asphalt-like products and 3) application - after combustion - as building material or utilisation as raw material in cement.

In a fourth work package, a techno-economic study was performed (mainly by other project partners). The main conclusion is that all forms of fly ash utilisation are associated with costs, ranging from close to zero to over € 300 per tonne. Only metal recovery from bottom ash can produce a profit. The most economic way to utilise gasification ashes is as secondary fuel. Oxidation (combustion) forming a low-carbon ash is the next best option in combination with utilisation in cement or - when possible - as fertiliser. Combustion also enables landfill. Smelting is the most expensive option that was evaluated. For all options, the actual costs depend on the ash quality and are strongly influenced by local conditions related to logistics and legislation.

Based on the results and conclusions of the GASASH project an outlook was formulated for the situation in the Netherlands. One of the basic conclusions is that fly ash from gasification of biomass and waste is a difficult material. There are no obvious solutions and production of it should be avoided, e.g., by integrating combustion in the gasification system. Chlorine, alkali metals, heavy metals and the high carbon content are most troublesome. Bulk utilisation of high-carbon fly ashes is effectively limited to use as secondary fuel or as filler in asphalt. The potential is determined by local factors. E.g., transportation distances should be short and power plants must be licensed to burn waste. Small-scale applications depend even more on local circumstances.

Combustion as after-treatment enlarges the options for utilisation. Direct utilisation as building material is possible and logical for bottom ash, not for fly ash. Utilisation as a raw material for the manufacture of building materials has the best prospects, but depends on matches between specific ash characteristics and specifications needed for cement, bricks and other building materials. For the Netherlands, utilisation as fertilisers appears to be not feasible because of unfavourable ratio between nutrients and contaminants. Exceptions may exist, e.g. by using chicken litter as a fuel. Recycling of ashes to the original soils is currently not an option in the Netherlands.

Finally, it has become clear that consistency in quality and quantity is of the highest importance. Users will only contemplate fly ash as a raw material when it has a guaranteed quality and is available in predictable and sufficiently large amounts. This emphasises the need to be careful with the fuels used in the gasification process, because they have a direct effect on the fly ash composition.

Samenvatting

Vergassing van biomassa en afval in een circulerend wervelbed produceert als bijproduct een zwarte koolstofrijke vliegas. In het GASASH project zijn de mogelijkheden tot hergebruik van dit specifieke materiaal onderzocht. Storten is meegenomen als optie, omdat in diverse landen het storten van hoogcalorisch materiaal in vele landen verboden is. Verder is storten slecht voor het groene imago van de productie van energie uit biomassa. Hoofddoel van het project was het vinden van economisch aantrekkelijke manieren om met deze koolstofrijke vliegas om te gaan. Specifieke doelen waren gesteld voor drie werkpakketten. Ten eerste (werkpakket WP1) zou het vergassingsproces geoptimaliseerd kunnen worden, niet alleen voor energieproductie, maar ook voor de kwaliteit en omvang van de as, d.w.z. maximale koolstofconversie. Het tweede werkpakket (WP2) had tot doel de ontwikkeling van nieuwe technieken voor de nabehandeling van koolstofrijke vliegas om deze geschikt te maken voor hergebruik. Het derde werkpakket (WP3) betrof het zoeken naar bestaande en nieuwe routes voor hergebruik. Een vierde werkpakket (WP4), waar ECN slechts een kleine bijdrage aan heeft geleverd, omvatte een techno-economische evaluatie van de diverse routes voor hergebruik.

In WP1 heeft ECN een aantal testen uitgevoerd in haar 500 kW_{th} circulerend wervelbed vergasser (BIVKIN). De resultaten van de runs, alsmede data van oude runs en achtergrond informatie zijn gebruikt om de invloed van de diverse procesparameters te bepalen. De voornaamste conclusie was (ondersteund door resultaten van de andere projectpartners) dat praktische maatregelen in bestaande vergassers niet kunnen leiden tot een koolstofgehalte in de vliegas, wat zo danig laag was, dat het in de bestaande routes voor gebruikt van steenkool vliegas zou passen. Ingrijpende veranderingen in het ontwerp zouden dit mogelijk wel kunnen bereiken, maar dat werk is nog in een pril ontwikkelingsstadium.

In WP2 zijn diverse nabehandelingstechnieken zijn onderzocht, die stuk voor stuk tot verbetering van bepaalde askarakteristieken kunnen leiden en assen geschikter kunnen maken voor hergebruik. Door *droog zeven* kan een kleine asfractie van grove deeltjes worden afgescheiden met een relatief laag gehalte verontreinigingen. De bulk van de as wordt hier echter niet mee aangepakt. *Pelletiseren* kan tot belangrijke verbeteringen in opslag en transport van vliegas leiden. *Immobilisatie* met petroleum residu resulteert in een materiaal met sterk verbeterd uitlogingsgedrag, wat als bouwmateriaal inzetbaar is. *Verbranding bij lage temperatuur* zet koolstofrijke vliegas om in koolstofarme vliegas, die vergelijkbaar is met vliegas van directe verbrandingsprocessen. *Verbranding bij hoge temperatuur* is een technisch acceptabele manier om de vliegas om te zetten in steenachtig bouwmateriaal, wat onbeperkt toegepast kan worden. *Gecontroleerde uitloging* kan gebruikt worden om chloor en alkali metalen te verwijderen, maar zware metalen blijven grotendeels achter. Uiteindelijk is smelten geselecteerd om nader onderzocht te worden. Enige kilogrammen synthetisch basalt zijn gemaakt in de vorm van blokken en granulaat. Elk van deze producten voldoet aan de criteria voor categorie 1 van het Bouwstoffenbesluit (BSB), nl. toepasbaar in onbeperkte hoeveelheden.

In WP3 is er gezocht naar technisch haalbare vormen van hergebruik, bestaand of nieuw. Dit omvatte o.a. een vergelijking van de askarakteristieken met de specificaties van elke gevonden route voor hergebruik, voornamelijk vanuit een Nederlands perspectief. De algemene conclusie is, dat er geen universele oplossing bestaat en dat voor elke soort vliegas apart een optimale route moet worden gevonden. Technische en economische haalbaarheid is afhankelijk van de lokale situatie. Wanneer we de Nederlandse wet- en regelgeving toepassen, kan gesteld worden dat koolstofrijke vliegas bij voorkeur ingezet moet worden als brandstof. Dat is een vorm van hergebruik waarbij de relatief hoge calorische waarde van de droge, koolstofrijke vliegas nuttig gebruikt wordt. De brandstof kan o.a. worden toegepast als meestookbrandstof in kolencentrales, of in smelters en cementovens. Direct hergebruik als bouwmateriaal is niet goed

mogelijk voor de koolstofrijke vliegas (maar wel voor bodemas). De vliegas heeft geen aantrekkelijke technische eigenschappen, wanneer sloophout of een andere vervuilde brandstof gebruikt wordt. De kans is groot, dat de as niet voldoet aan de eisen van het Bouwstoffenbesluit (BSB). De vliegas zou wel als vulstof in asfalt of asfaltachtige producten gebruikt kunnen worden. Na verbranding zou de koolstofarme vliegas wel gebruikt kunnen worden als bouwmateriaal, o.a. voor de aanleg van wegen, mits wordt voldaan aan het BSB en andere (civiel)technische eisen. Ook bestaan er mogelijkheden om na verbranding koolstofarme vliegas in bouwmaterialen te verwerken, mogelijk in speciale cementproducten. Toepassing als meststof (direct of indirect als grondstof) is onwaarschijnlijk. Bijna altijd is de verhouding tussen nutriënten en verontreinigingen ongunstig. Misschien zou vliegas van schoon hout teruggebracht kunnen worden naar het bos waar het hout is geoogst. In Scandinavië en elders is dat mogelijk, maar onder Nederlandse omstandigheden is asrecycling nauwelijks relevant. Er zijn geen grootschalige productiebossen of energieplantage en de Nederlandse wet- en regelgeving biedt geen mogelijkheden daartoe. Storten van koolstofrijke vliegas is niet toegestaan in Nederland. Uitgebrande vliegas kan wel gestort worden, maar dat is duur. De technisch meest kansrijke routes voor hergebruik van koolstofrijke vliegas zijn uiteindelijk: 1) direct gebruik als brandstof, 2) gebruik in asfalt en asfaltachtige producten en 3) toepassing - na verbranding - als bouwstof in de wegenbouw of als grondstof voor cement.

In WP4 is een techno-economische studie verricht, grotendeels door andere projectpartners in een breder, Europees perspectief. De voornaamste conclusie is dat alle vormen van hergebruik van vliegas geld kosten, variërend van bijna niets tot meer dan € 300 per ton. Alleen terugwinning van metaal uit bodemas kan een positief economisch resultaat opleveren. In Europees perspectief is hergebruik als (secondaire) brandstof economisch het meest aantrekkelijk. Daarna komt naverbranding, waarbij een koolstofarme as wordt gevormd, die als bouwmateriaal of misschien als meststof gebruikt kan worden. Naverbranding opent ook de weg naar storten. Smelten is de meest kostbare van de onderzochte vormen van hergebruik. Voor elke optie geldt, dat de uiteindelijke kosten niet alleen sterk afhankelijk zijn van de askwaliteit, maar ook van de lokale situatie m.b.t. logistiek en regelgeving.

Op basis van de bredere conclusies van het GASASH project is een vooruitblik voor de situatie in Nederland geformuleerd. Eén van de eerste conclusies is, dat koolstofrijke vliegas van vergassing van biomassa en afval een lastig materiaal is. Er zijn geen voor de hand liggende oplossingen en het beste zou zijn om productie ervan te voorkomen, b.v. door verbranding in het vergassingsproces te integreren. Chloor, alkalimetalen, zware metalen en het hoge koolstofgehalte zijn allen problematisch. Direct hergebruik in bulkhoeveelheden is in feite beperkt tot gebruik als (secondaire) brandstof of als vulstof in asfalt, maar het is afhankelijk van lokale factoren. Transportafstanden moeten kort blijven en gebruikers moeten een vergunning hebben voor het verbranden/verwerken van afval. Hergebruik op kleine schaal is nog sterker afhankelijk van toevallige, gunstige omstandigheden.

Naverbranding van koolstofrijke vliegas vergroot de mogelijkheden tot nuttig hergebruikt in bulktoepassingen. Direct gebruik als bouwstof is in principe mogelijk, maar ligt niet voor de hand voor vliegas (wel voor bodemas). Gebruik als grondstof voor bouwstoffen biedt betere perspectieven, maar hangt af van specifieke aseigenschappen en de eisen die worden gesteld voor productie van o.a. cement en bakstenen. Gebruik als meststof lijkt voor Nederland niet mogelijk omdat de verhouding tussen nutriënten en verontreinigingen te slecht is, maar uitzonderingen zijn denkbaar, b.v. voor as van kippenmest. Recycling naar de bodem is door de geografische omstandigheden in Nederland geen serieuze optie.

Tenslotte is duidelijk geworden dat een constante samenstelling en voorspelbare hoeveelheden van het allergrootste belang zijn. Gebruikers zullen alleen overwegen om vliegas te gebruiken als zowel kwaliteit als voldoende kwantiteit gegarandeerd zijn. Dit impliceert dat men ook zorgvuldig moet zijn bij de keuzes voor brandstoffen die gebruikt worden in vergassingsinstallaties, want deze hebben direct effect op de samenstelling van de assen.

1. INTRODUCTION

1.1 Objectives of the overall project

The overall objective of the project was to develop sustainable and economic systems for ash management in biomass/waste gasification and gas cleaning processes. More specific objectives were to reduce ash volume and to improve ash quality. The latter enables utilisation or recycling of ashes as raw material. The work in the GASASH revolved around enhancement of the carbon conversion by adjustment of the gasification process and development of ash treatment technologies. The project was co-ordinated by VTT. Other partners were PVO, Foster Wheeler Energy, AICIA, Casella en Essent Energie Productie.

1.2 Introduction to work packages

The project was divided into four Work Packages. Each of the work packages interacted with the other, see also Figure 1.1. ECN was involved in all work packages.

- **WP1 Optimisation of the gasification and gas cleaning** produced information on the technical possibilities to optimise ash management and improve carbon conversion of the gasification process. The aim was to create realistic overall understanding on the possibilities and limitations for improving the carbon conversion and ash quality by different methods
- **WP2 Development of new technology** aimed at development of new technology to improve the overall ash management, using existing know-how and results from WP1. Project partners implemented and tested several advanced concepts to improve the ash quality, to minimise difficult ash volumes and to improve the overall carbon conversion of the process.
- **WP3 Characterisation of ashes and development of ash utilisation methods** involved characterisation of ashes and a search for existing and new routes for utilisation of ashes. The criteria for utilisation routes were used as guidelines for WP 2. Most efforts were directed towards construction materials, but material recovery has also been studied.
- **WP4 Techno-economic evaluation** contained evaluation of the technical and economic feasibility on industrial scale of the different methods to utilise gasification ashes and to improve the quality of these ashes.

1.3 Structure of this report

In the following chapters, results and conclusions of ECN's work in the GASASH Project are presented. Each chapter corresponds to a Work Package of the project. The introduction of each chapter gives some background information of the Work Package as a whole and identifies ECN's part of the work. Only ECN work and publicly available results from other partners are included. Each chapter ends with intermediate conclusions.

The primary form of reporting in the GASASH Project was done by means of Deliverables and a Final Report. The public part of the final report is reproduced in Appendix A. Public deliverables, 1, 4&5, 15, 16, 17, 20 and 23 have significant contributions from ECN and are included as appendices to this report as well.

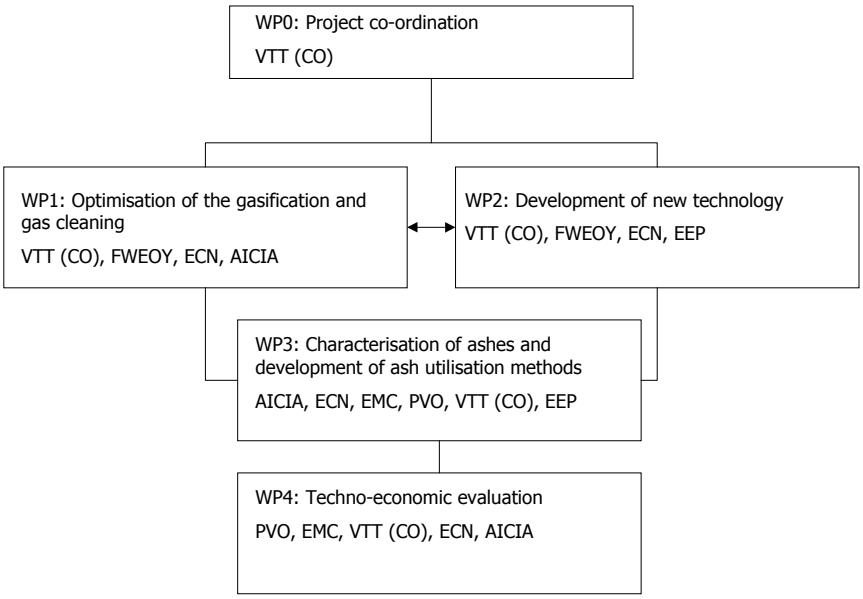


Figure 1.1 Schematic of interactions between work packages

Table 1.1 Deliverable reports where ECN contributed a significant part of the work

No	Title	Task	Status
1	Report on selection of test fuels and test program	1.1	Public
2&3	Draft report on methods to improve carbon conversion of fluidised bed gasification and on technical possibilities to reduce ash volume	1.2, 1.3	Conf.
4&5	Report on methods to improve carbon conversion of fluidised bed gasification and on technical possibilities to reduce ash volume	1.2, 1.3	Public
8	Report on the potential of staged cooling and particle removal	2.2	Conf.
11	Report on performance of separation and ash conditioning of fractions	2.2	Conf.
15	Identification of the most promising ash utilisation options and ash treatment needed	3.2, 3.3	Public
16	Report on technically potential gasification ash utilisation options	3.2	Public
17	Report on a detailed characterisation of different gasification ashes	3.1	Public
18&19	Technical and economical feasibility of gasification ash quality improvement and ash utilisation and estimate of the economical impacts of gasification ash management on the economy of the plant	4.1	Conf.
20	Report on the influence of optimised ash management of the economy of the gasification process	4.1	Public
23	Comparison of the results from different ash treatment methods	2.4	Public
24	Potential ash utilisation routes for further testing	3.2, 3.3	Conf.
28	Report on available separation techniques potentially applicable to gasification fly ash	2.2	Conf.

2. OPTIMISATION OF THE GASIFICATION PROCESS (WP 1)

2.1 Introduction

The first objective of the GASASH project was to reduce ash volume and to enhance the carbon conversion by adjusting and optimising the gasification process. Increased carbon conversion leads directly to lower ash volumes. It also improves ash quality, because in biomass-fired gasification systems, the unburnt carbon content of ashes varies strongly, depending on the fuel. It ranges from 20-80 wt%. This is far from the desired limit of 5-10 wt% that is used in the EN-450 standard for fly ashes from coal-fired plants.

The investigations in WP 1 comprised an evaluation of the process parameters of gasification that may influence the carbon conversion and hence the ash volumes produced. The effects of temperature, air ratio and cooling were investigated, as well as application of the HSD-CFB concept (see below). Besides carbon content, other aspects of ash quality were assessed, in particular the distribution of contaminants (heavy metal, chloride, etc.) and leaching behaviour. The focus was on combinations of wood fuels with sewage sludge and on removing contaminants from demolition wood by excluding the finest fuel fraction.

2.1.1 Parametric study to optimise carbon conversion

Many parameters have an influence on the carbon conversion in a gasification process. In practice, the number of measures that can be taken to manipulate biomass gasification is limited, often influencing multiple parameters. The effect on the carbon conversion of the following measures has been investigated:

- Separation of the air inlet and the fuel inlet and introduction of a flow restriction (HSD-CFB principle)
- Increasing of temperature by increasing the air/fuel ratio
- Enhanced heat loss (not lowering the temperature) by increasing the air/fuel ratio combined with non-preheating of air, dilution with nitrogen or heat sink in reactor wall
- Smaller or coarser sand as bed material
- Specific elimination of the finest size fraction (0-3 mm) from demolition wood as fuel
- Addition of regular wood to low caloric fuel (sewage sludge)

Optimised carbon conversion does not necessarily mean maximised carbon conversion. In regular circulating fluidised bed systems, increasing the carbon conversion improves the efficiency of any gasification process. However, when a certain level of carbon conversion - typically 90-95% - is reached, further conversion requires a high air ratio, which will lead to producer gas with a lower calorific value and a drop in cold-gas efficiency[1]. Also, temperatures are getting close to the maximum temperature allowable in fluidised bed installations. Therefore, technically and economically, gasification installation operate already close to the optimum carbon conversion, but not to the maximum carbon conversion.

2.1.2 HSD-CFB Principle

Work at ECN identified the HSD-CFB concept (High Solids Density in a Circulating Fluidised-Bed) as an attractive way to increase carbon conversion in biomass gasification with negligible effects on cold gas efficiency[2]. The focus of the HSD-CFB Project was on optimisation of the

[1] The ratio between the calorific value of the product gas and the fuel, thus excluding thermal energy.
[2] The final report of the HSD-CFB Project is a public document (in Dutch): A. van der Drift et al., "Hogere koolstofconversie in CFB-biomassavergassers", ECN Report ECN-C--03-053, June 2003.

cold gas efficiency, but its results were re-interpreted to formulate conclusions related to improvements in ash quality suitable for serving as background knowledge for WP 1 of the GASASH project.

The HSD-CFB concept as applied at ECN is a modification of a regular circulating fluidised bed gasifier. It has been tested in the BIVKIN by moving the fuel injection halfway up in the riser and inserting a ring in the riser. In Figure 2.1 is a graphic representation of the changes at the bottom of the riser. The essence of the modification is to create a separation of the fuel inlet and the air inlet that creates two gasification zones. Air and char from the down-comer enter the lower zone, which enables faster char oxidation reactions due to the presence of O_2. Fuel is introduced in the upper zone, where there is no O_2 left, which limits the direct reaction of volatiles to reactions with H_2O and CO_2. The insert also interrupts the downward flow along the walls.

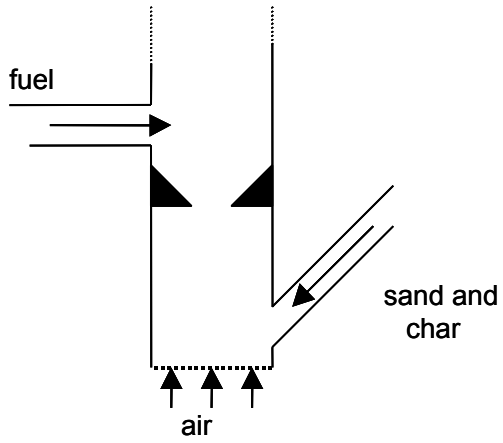


Figure 2.1 Diagram of the bottom part of the riser in a CFB gasifier designed according to HSD-CFB principle

2.1.3 Gasification of demolition wood with and without fines

The current situation is that Essent Energie Productie (EEP) uses fuel with fine dust included. However, during fuel preparation the finest fraction is separated and later added. It would be easy to use fuel without the finest fraction, by not adding it to the bulk of the fuel. The finest fraction was expected to have relatively large concentrations of paint chips and other materials that contain problem elements like Pb and Ba. Arguing along these lines it can be expected that the concentration of problem elements in the producer gas that is fed to the combustion chamber of the coal-fired plant will diminish, when the finest fraction is omitted. On the other hand, the fuel price increases, because the fuel supplier must find ways to sell the fine dust, most likely at an unfavourable price. In the worst case it needs to be treated as chemical waste at considerable costs. The option to use demolition wood with or without fine dust is essentially a decision based on practicality and economics.

2.2 Experimental

2.2.1 Fuel selection

Clean wood, sewage sludge and demolition wood ware selected as fuels. Clean wood in the form of wood pellets was selected as a reference point, since many runs have been done at ECN using this fuel. The clean wood pellets have a constant quality and composition, but a very low ash content. Therefore they are very good for researching carbon conversion, but not suitable for research on ash. Demolition wood was selected, because it is the fuel used in EEP's Circulating Fluidised-Bed gasifier at the AMER-9 power station. It is also one of the most commonly available biomass fuels in the Netherlands. Sewages sludge was selected because it is a fuel with a high ash content and high, easy to measure contents of problem elements.

2.2.2 Gasifier

For the test runs, ECN's circulating fluidised bed gasifier (BIVKIN) has been used. The BIVKIN (Biomassa Vergassings en Karakeriserings Installatie) is an atmospheric circulating fluidised bed gasifier of 500 kW_{th} (typical fuel rate is 100 kg/hr). The BIVKIN is in principle also suitable for combustion experiments. The CFB gasifier has several fuel bunkers and it is possible to mix fuels. The riser is 6 m high and has a diameter of 20 cm. The gasifier has an air and a steam supply. The recycling loop is composed of a cyclone for ash/sand separation and a loop seal. A second (hot) cyclone is present directly after the gasifier to extract ash at the same temperature as the gasifier is operated. A third (cold) cyclone is present after a cooler. Alternatively, a ceramic filter can be used for solids removal. The hot cyclone can be switched off, so that the cooler is fed with dust loaded gas and all the solids are collected in the cold cyclone. The fuel gas is cleaned further using water and oil-based scrubbers. The clean fuel gas is fed to either a gas engine or a boiler.

In all runs, quartz sand of 0.4-0.6 mm is used as bed material. Gasification temperature is varied from 800 to 900°C. The primary air feed is 75-90 Nm^3/h, pre-heated to 350°C. Air to the seal pot is 23 Nm^3/h. Linear gas velocity is 6.5 to 7.0 m/s. Typical feed rates vary from 75 to 120 kg/h, depending on the calorific value of the fuel.

2.2.3 The HSD-CFB concept and other measures

Several measures that can be taken when operating a fluidised bed gasifier, were investigated for their effect on the carbon burnout level. The runs were done using clean wood pellets with a low ash content and a known, constant composition[3]. The fuel characteristics are included in Table 2.3. The measures investigated are:

- separation of the air inlet and the fuel inlet and introduction of a flow restriction (HSD-CFB principle)
- increasing of temperature by increasing the air/fuel ratio
- enhanced heat loss (not lowering the temperature) by increasing the air/fuel ratio combined with non-preheating of air, dilution with nitrogen or heat sink in reactor wall

The effect of each measure and some combination of measures was determined in comparison to a standard run at 850°C and an air/fuel ratio of 0.22 (equivalence ratio = E.R.), resulting in a carbon conversion of 92% and a cold gas efficiency of 69%.

2.2.4 Runs with sewage sludge and sewage sludge/wood pellets

Two BIVKIN runs with a mixture of sewage sludge and wood pellets were performed. Wood pellets were added to lower the air/fuel ratio and improve the fuel gas quality. Objective of the runs was to improve the gasification behaviour and study the effect on the ash composition. One run was done with 25% sewage sludge and 75% clean wood pellets. The other run was done with 50% sewage sludge and 50% wood pellets. The sewage sludge was dried to a moisture content of 7 wt%. The wood pellets are made from clean wood having a very low ash content of only 0.3 wt%. Details of the composition of the wood pellets and the sewage sludge can be found in Table 2.3. Gasification temperature was 900°C and the air/fuel ratio was 0.3. Gas velocity was 7 m/s. Bed material was sand of 0.4-0.6 mm. The hot cyclone was switched off. Ash was collected in the cold cyclone at 200°C.

Two BIVKIN runs were performed with sewage sludge that was dried biologically (heat from composting) to 19%. Details of the composition of the sewage sludge can be found in Table 2.5.

[3] The technical details of the various runs are summarised in the ECN Report ECN-C--03-053.

Gasification took place at 800 and 900°C with air/fuel ratios of 0.41 and 0.54, respectively. Gas velocity was 6.5 m/s. The objective was to collect ash at several temperature levels and compare the composition. The bulk of the ash was collected from the hot cyclone directly after the gasifier at either 800 or 900°C. The second ash fraction was collected from the cold cyclone at 200°C. The remainder of the ash was collected in the filter.

2.2.5 Runs with demolition wood with and without fines

Two BIVKIN runs have been performed using demolition wood. The fuel was prepared by Meer Recycling. Regular demolition wood was shredded and sieved over a 15 mm screen. The wood that passed this screen was labelled as "demolition wood 0-15 mm" and used in one run. A similar batch of demolition wood was made in the same way, but an additional screen of 3 mm was placed after the shredder. In this way the fraction 0-3 mm was removed from the demolition wood. This batch was labelled as "demolition wood 3-15 mm" and used in the other run. BIVKIN settings were kept identical for both runs. Quartz sand 0.4- 0.6 mm was used as bed material. Gasification temperature set at 850°C. Primary air supply was 85 Nm^3/hr, air supply to the seal pot was 20 Nm^3/hr. Fuel supply rate was slightly lower for demolition wood 0-15, 88 kg/hr, compared to 96 kg/hr for demolition wood 3-15 kg/hr. The hot cyclone was switched off. Ash was collected in the cold cyclone at 310°C.

2.3 Results and discussion

2.3.1 Air ratio, temperature and application of the HSD-CFB principle

The effects of changes in air ratio, temperature and of application of the HSD-CFB principle on carbon conversion and cold-gas efficiency are summarised in Table 2.1. There is a strong correlation between the air ratio and the carbon conversion. This is especially clear from runs 3a/c and 5a/d, where the carbon conversion increases when the air ratio increases. This not only happens when the temperature increases as well (run 3a/c), but also when the temperature is kept constant (5a/d). Apparently, it is not the temperature, but the availability of oxygen from air that is enhancing carbon conversion.

Table 2.1 Comparison of the effect of different measures on the carbon conversion in gasification of biomass

run	measure	temperature*	air ratio	carbon conversion	cold gas efficiency
ref	reference	850°C	0.22	92%	69%
3a/c	higher temperature	880°C	0.26	93%	68%
		900°C	0.27	92%	68%
		930°C	0.30	96%	67%
5a/d	no preheating +	830°C	0.35	99%	61%
	wall cooling	840°C	0.32	96%	64%
		840°C	0.29	92%	65%
		850°C	0.28	87%	67%
6a/b	no pre heating +	850°C	0.32	96%	62%
	nitrogen addition	850°C	0.29	94%	67%
6c	no preheating	850°C	0.26	92%	68%
8a/b	HSD-CFB	810/880°C	0.23	95%	70%
		820/920°C	0.26	99%	69%

* For 8a/b, temperatures of upper and lower zone are given, respectively

The carbon conversion is significantly higher when the air ratio is above 0.30, but the effect of a higher air ratio is complex and not limited to the carbon conversion. With a higher air ratio, more producer gas and more heat are produced (independent of the actual temperature). The higher amount of oxygen also means that in the producer gas is further oxidised than at a lower

air ratio. The overall effect is that the cold gas efficiency (caloric value of the combustibles in the producer gas) is constant when the air ratio is below 0.3 and there is no adverse or beneficial effect for the production of syngas or applications in gas engines or gas turbines there is no beneficial effect. However, when the carbon conversion significantly increases, i.e, when the air ratio exceeds 0.30, the cold gas efficiency decreases.

In the runs where the HSD-CFB principle is tested (8a/b), the carbon conversion and the cold gas efficiency are increased compared to the reference case. The air ratio is higher, achieving hither carbon conversion, but the negative effect of putting more oxygen in the gasifier (a lower cold-gas efficiency) is avoided. This observation makes application of the HSD-CFB principle the most effective measure that can be taken to improve carbon conversion and/or cold gas efficiency at the same time. Carbon conversion of up to 99% is achieved. This is remarkably high for gasification. However, it should be kept in mind that with an ash content of 3 wt% in the fuel (an average value for biomass), this still means about 25 wt% unburnt carbon in the fly ash. When gasifying clean wood pellets with 0.3 wt% ash content, the percentage unburnt carbon is about 75 wt%. Both numbers are far from the 5-10 wt%, which means that despite all efforts, fly ash from gasification is still carbon-rich and not suitable for existing applications in construction materials.

The HSD-CFB concept (see section 2.1.2) is the most effective measure for increasing the carbon conversion in the gasification of biomass, when taking the cold-gas efficiency into account. The retrofit as done in the BIVKIN is simplistic and merely approaches the HSD-CFB principle, but already a significant improvement in carbon conversion was found. The full potential of this principle should be investigated more thoroughly, but it should first be done at an academic level, outside the scope of the GASASH project. The design of a new type gasifier based on the HSD-CFB principle must address potential problems with pressure drops, and the scale-up of the narrow passage between the two sections.

2.3.2 Combining sewage sludge with wood pellets

The runs with a mixture of sewage sludge and wood pellets produced ashes that are dominated by the ashes from sewage sludge. This is valid for both runs (with 25% and 50% sewage sludge). The composition of the ash and the fuel is presented in Table 2.2. The ash compositions reflect the composition of sewage sludge. There is hardly any correlation with the composition of the wood pellets. This result can be expected, because the sewage sludge has a total ash content of about 33% (dry) while the clean wood pellets have an ash content of only 0.3%. The conclusion is that for the ash composition it is not important how much wood is co-fired. Mixing of sewage sludge may influence other gasification parameters, e.g. tar emission, but during our tests there were no differences that attracted attention.

The two runs where only sewage sludge was gasified used a different kind of sewage sludge, which was dried biologically. Ashes were extracted at three different temperature levels in the gasifier. Data of the ash collection are summarised in Table 2.3. The bulk of the ash is collected in the hot cyclone. The mass balance of the total amount of ash (sum of ash extracted versus ash introduced in fuel) closed within 5%. Most element balances closed as well, with noted exceptions. The recovery of Hg and S in the ash was too low, 6 and 45%, respectively in the run at 800°C. This is explained by a preference of these elements to stay in the gas phase. Recovery of K, F, Ti, Ni and Cr was too high, 182, 7286, 662, 195 and 141%, respectively, in the run at 800°C. In the case of F and Ti, this is probably the result of a problem in the fuel analysis. Both elements are notoriously difficult to analyse. The high recovery of Ni and Cr can be explained by corrosion or wear of stainless steel. The reason why K levels in ash are higher than expected remains uncertain.

All ashes were analysed for trace elements, presented in Table 2.4. For each element the distribution between the ash fractions is calculated and compared to the overall mass distribution of the ashes for both runs. The results can be found in Figure 2.2 and Figure 2.3.

The distribution is normalised on the total amount of this element in the ash fractions; the fraction emitted in the gas phase is excluded, but this is only a major issue for the elements Hg, S, Cl, Se and Te, which are known to form species that remain in the gas phase even at ambient conditions.

Table 2.2 Composition of wood pellets, sewage sludge and ashes from combustion of wood pellets and sewage sludge; all data on dry base, moisture as received

material		wood pellets	sewage sludge	25% sewage sludge	50% sewage sludge
type		fuel	fuel	ash	ash
ash(815°C)	wt% (dry)	0.3	33.2	70.5	88.7
volatile	wt% (dry)	82.1	53.5	0.3	0.2
moisture	wt% (a.r.)	8.0	7.2	0.7	0.2
C	wt% (dry)	48.3	34.8	31.9	12.8
H	wt% (dry)	6.0	4.9	0.2	<0.1
N	wt% (dry)	45.2	27.0	2.4	2.7
O	wt% (dry)	0.1	5.1	<0.1	<0.1
Cl	mg/kg (dry)		1057	748	294
Al	mg/kg (dry)	65	18443	33831	45851
As	mg/kg (dry)		7.3	13.5	16.9
B	mg/kg (dry)	3	39	76	82
Ba	mg/kg (dry)	14	339	683	866
Ca	mg/kg (dry)	1303	29233	57477	79020
Cd	mg/kg (dry)	0.2	1.1	3.9	1.7
Co	mg/kg (dry)	0.1	5.2	15.8	17.3
Cr	mg/kg (dry)	5	42	486	361
Cu	mg/kg (dry)	5	371	517	811
Fe	mg/kg (dry)	83	35782	59648	55046
K	mg/kg (dry)	380	4777	15524	15641
Li	mg/kg (dry)		5.5	10.1	13.0
Mg	mg/kg (dry)	136	5386	10624	14286
Mn	mg/kg (dry)	115	487	1817	1629
Mo	mg/kg (dry)	0.4	12.8	36.2	26.5
Na	mg/kg (dry)	70	1739	3977	5105
Ni	mg/kg (dry)	3	24	687	777
P	mg/kg (dry)	85	32446	53435	64282
Pb	mg/kg (dry)		130	373	263
S	mg/kg (dry)	10	1419	430	409
Sb	mg/kg (dry)	0.8	3.7	5.7	0.4
Se	mg/kg (dry)		5.4	7.9	8.6
Si	mg/kg (dry)	209	33555	78651	100169
Sn	mg/kg (dry)	0.9	21.0	11.3	8.3
Sr	mg/kg (dry)	5	294	541	752
Ti	mg/kg (dry)	7	1303	2570	3397
V	mg/kg (dry)	0.1	18.4	35.7	49.1
Zn	mg/kg (dry)	15	899	1802	2422

Table 2.3 Data of ash collection in gasification runs with 100% sewage sludge

run	800°C	800°C	800°C	900°C	900°C	900°C
location	hot cyclone	cold cyclone	dust filter	hot cyclone	cold cyclone	dust filter
temperature [°C]	800	200	ambient	900	200	ambient
fraction [wt%]	77	17	7	85	12	3

Table 2.4 Composition of sewage sludge and ash collected in gasification runs with 100% sewage sludge; moisture content as received, all other data on dry basis

material		sewage sludge*	ash hot cyclone	ash cold cyclone	ash filter	ash hot cyclone	ash cold cyclone	ash filter
run		both	800°C	800°C	800°C	900°C	900°C	900°C
moisture	wt%	19	0.0	1.2	2.5	0.0	5.8	6.3
ash	wt%	43	97	92	91	100	93	82
Al	mg/kg	21583	50885	54669	52442	56272	54229	46735
As	mg/kg	8	9	34	91	15	125	160
B	mg/kg		56	116	307	71	353	448
Ba	mg/kg	359	861	919	886	935	936	829
Be	mg/kg		0.8	0.8	0.8	0.8	0.9	0.8
Ca	mg/kg	36750	75297	104949	144277	89410	123250	137117
Cd	mg/kg	1	0.3	8.5	15.2	0.1	22.9	27.2
Cl	mg/kg	1942	580	9891	16073	219	5105	35023
Co	mg/kg	7	16	20	22	20	24	21
Cr	mg/kg	67	197	192	187	258	235	183
Cu	mg/kg	519	921	1272	1890	1064	2011	2051
F	mg/kg	2	87	625	739	107	1123	1479
Fe	mg/kg	53813	110532	122680	119669	129137	114948	101911
Hg	mg/kg	1	0.0	0.2	1.7	0.0	2.0	27.3
K	mg/kg	3892	14244	16894	14445	15182	13174	11406
Li	mg/kg		18	20	15	46	19	14
Mg	mg/kg	4658	10364	11775	11729	11439	12054	10739
Mn	mg/kg	684	1363	1458	1417	1482	1447	1212
Mo	mg/kg	9	21	31	90	22	114	139
Na	mg/kg		5558	4919	3884	5566	4329	3497
Ni	mg/kg	33	113	203	184	524	633	378
P	mg/kg	35200	73112	77173	72525	79979	74840	64799
Pb	mg/kg	173	246	558	619	143	1637	1719
S	mg/kg	14000	10014	20533	27605	4684	11286	17925
Sb	mg/kg	7	11	25	28	12	49	37
Se	mg/kg	27	1.4	6.2	8.6	6.9	10.2	9.1
Si	mg/kg		149840	84704	65048	139656	77207	60743
Sn	mg/kg	22	43	87	86	30	284	228
Sr	mg/kg		485	526	513	529	528	455
Te	mg/kg	4	5.2	4.5	2.0	4.7	4.3	1.9
Ti	mg/kg	287	3865	4067	4447	4116	3959	3885
V	mg/kg	23	47	49	51	51	54	52
Zn	mg/kg	1074	1965	2204	2406	1964	2133	2046

* data on composition supplied with delivery of sewage sludge

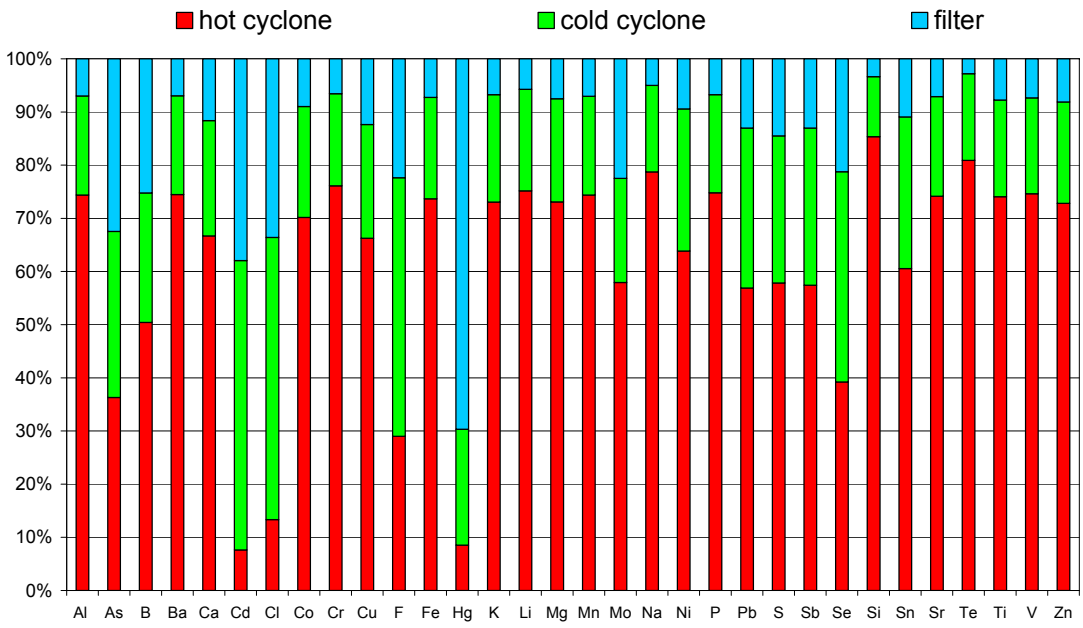


Figure 2.2 Distribution of elements in the three ash fractions produced in the gasification of 100% sewage sludge at 800°C; total mass distribution is 77% in hot cyclone, 17%% in cold cyclone and 7% in filter at ambient conditions

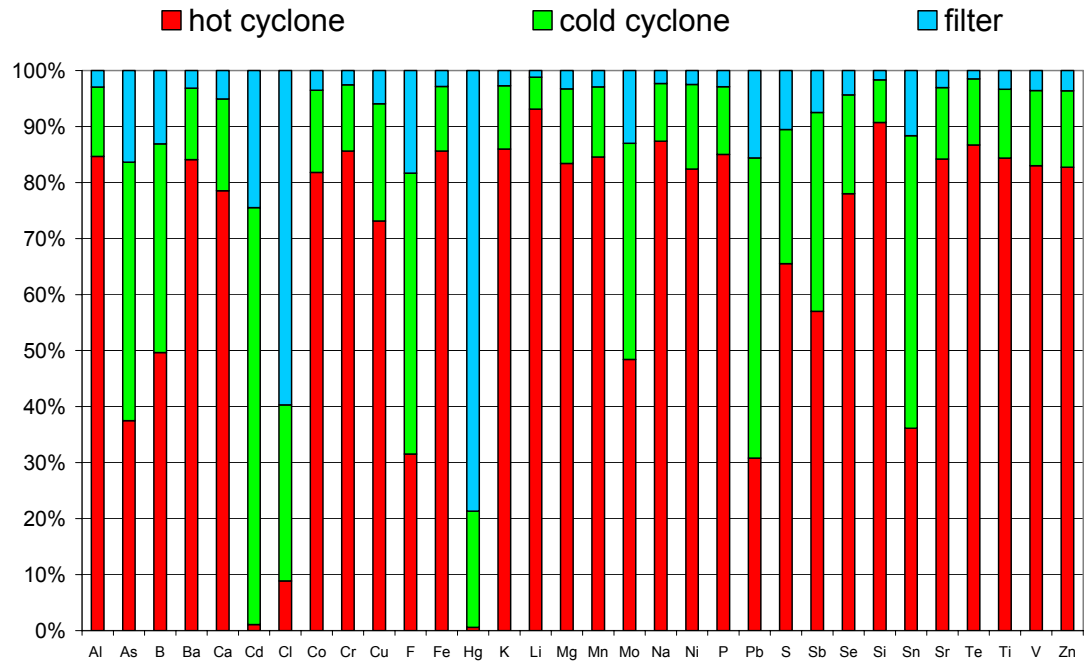


Figure 2.3 Distribution of elements in the three ash fractions produced in the gasification of 100% sewage sludge at 900°C; total mass distribution is 85% in hot cyclone, 12% in cold cyclone and 3% in filter at ambient conditions

The data in Figure 2.2 and 2.3 are very similar. Nearly all elements are recovered in the hot cyclone at levels that are comparable to the total mass fraction. This means that the bulk of the elements is not affected by temperature of ash collection. Elements that are found in significantly lower levels are Se, Cd, and Cl. This could be expected based on the volatility of the compounds that these elements form. At the temperature level in the hot cyclone these elements are preferably in the gas phase and not in the ash. When the flue gas is cooled these elements condense into the solid phase and are found in the ash of the cold cyclone and the filter

in larger proportions. A number of elements, As, B, Mo, Ni, Pb, S, Sb and Sn shows a small concentration in the ash of the cold cyclone and the filter. These elements are noticeably affected by the temperature of ash extraction, but the shift is not dramatic.

Sand is preferentially found in the hot cyclone. The sand is either from the fuel or from attrition of the bed material. The sand dilutes the material in the hot cyclone making the overall mass fraction relatively large, but it does not influence the distribution of the elements.

The results from the runs with sewage sludge indicate that it is not possible to concentrate all problem elements in one small ash fraction, by removing of the bulk of the ash at a high temperature level. The set of problem elements that can be removed in this way is limited to Se, Cd and Cl. Some problem elements are somewhat depleted, including Pb, Mo, As and Sb. Other problem elements like Cr, Cu and - surprisingly - Zn are not affected and equally distributed. The conclusion is that extracting ash at high temperature levels cannot be used to improve the ash quality of the bulk of the ash. This conclusion was one of the main reasons to reconsider the strategy of "Staged cooling and particle removal" in WP 2.

2.3.3 Removal of fines from demolition wood

In two runs in the BIVKIN gasifier, two batches of demolition wood were used which only differed in the presence or absence of the size fraction 0-3 mm. The fuel was prepared under identical conditions (except for the presence of 3 mm screen). The gasification took place under nearly identical conditions, so that differences in ash composition could only be attributed to the presence of fines (in this case 0-3 mm).

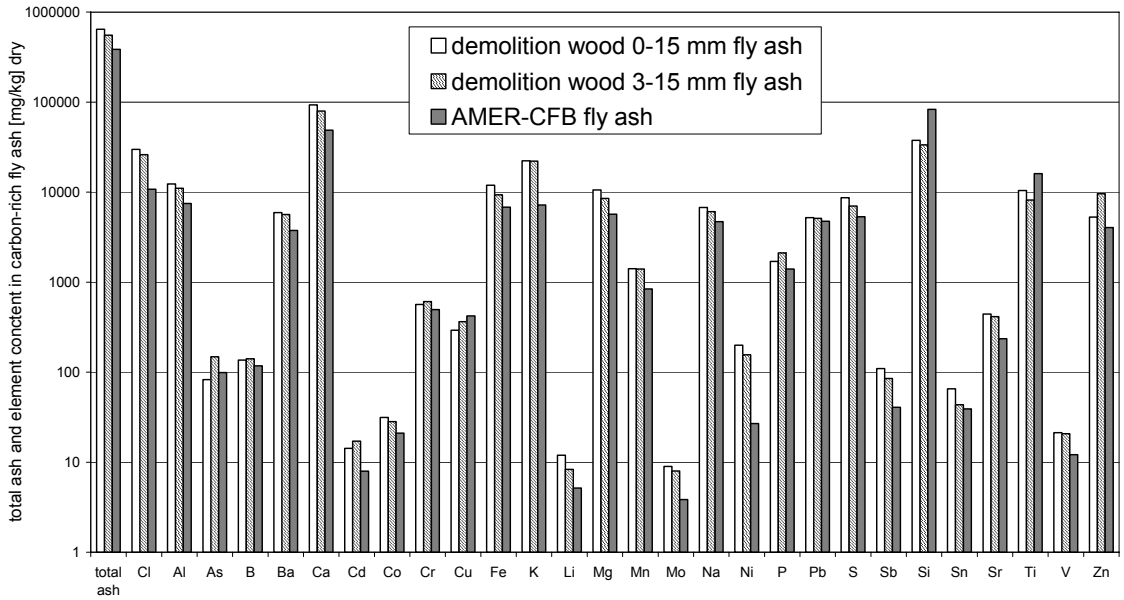


Figure 2.4 Total ash and element content of fly ash from gasification of demolition wood with and without fines and from AMER-CFB gasifier (log-scale in mg/kg dry basis)

The compositions of both fuel batches and the fly ash collected in a cold cyclone at 310°C are presented in Table 2.5. The fly ash composition (total ash and element concentrations) of the runs with and without fines is presented in a bar graph in Figure 2.4. For comparison, the composition of the AMER-CFB fly ash is included. The differences between the three ashes are small. The total ash content of the fly ash from the run with fines is slightly higher than from the run without fines, but the magnitude of the difference, 64 wt% versus 55 wt%, respectively, is too small to be of significance. Both are higher than the 39 wt% total ash of the AMER-CFB.

Table 2.5 Composition of demolition wood and fly ash in runs with and without fines; moisture content as received, all other data on dry basis

material		demolition wood 0-15 mm "with fines"		demolition wood 3-15 mm "without fines"	
type		fuel	fly ash	fuel	fly ash
Ash (550°C)	wt%	8.4	64.4	4.9	55.2
Ash (815°C)	wt%	8.0	58.9	4.6	51.1
Volatile	wt%	72.5	8.7	75.5	6.8
Moisture	wt% (a.r.)	16.3	2.7	15.3	2.1
C	wt%	45.5	39.7	47.5	50.0
H	wt%	5.7	0.7	6.0	0.8
N	wt%	1.8	0.7	1.3	0.7
O	wt%	39.9	8.1	40.8	7.0
Cl	mg/kg	709	29871	711	26008
HHV	MJ/kg	18609	11784	19538	14567
Al	mg/kg	1648	12344	1168	11033
As	mg/kg	10	83	15	148
B	mg/kg	18	136	14	141
Ba	mg/kg	516	5918	392	5627
Ca	mg/kg	7731	92905	6119	79639
Cd	mg/kg	1.0	14.3	1.5	17.2
Co	mg/kg	3.0	31.5	2.2	28.3
Cr	mg/kg	59	565	49	607
Cu	mg/kg	48	293	38	364
Fe	mg/kg	1197	11907	754	9319
K	mg/kg	1030	22255	887	22034
Li	mg/kg	1.4	11.9	1.2	8.3
Mg	mg/kg	1042	10580	707	8513
Mn	mg/kg	114	1414	96	1398
Mo	mg/kg	<d.l.	9.0	<d.l.	8.0
Na	mg/kg	1568	6743	1085	6073
Ni	mg/kg	103	199	51	156
P	mg/kg	130	1698	120	2110
Pb	mg/kg	408	5218	355	5105
S	mg/kg	1600	8649	1131	7004
Sb	mg/kg	<d.l.	110	<d.l.	85
Se	mg/kg	<d.l.	<d.l.	<d.l.	<d.l.
Si	mg/kg	7242	37634	4567	33445
Sn	mg/kg	3.2	65.3	2.7	43.5
Sr	mg/kg	39	443	33	415
Ti	mg/kg	1197	10420	563	8141
V	mg/kg	3.6	21.3	2.1	20.8
Zn	mg/kg	659	5272	839	9579

Knowing the differences in total ash content, it is logical to observe that nearly all elements are present in slightly higher concentrations in the fly ash produced from fuel with fines compared to fuel without fines. Exceptions are Zn, As and Cd, which were exactly those elements where a higher content was found in the fuel. When both are compared to the AMER-CFB fly ash, it is again clear that the differences are rather small in particular, when the lower total ash content of the AMER-CFB fly ash is taken into account. Only Si (sand) and Ti are noticeably higher in AMER-CFB fly ash, while Mo, Cl and Ni are present in significantly lower concentrations.

A significant difference was expected based on the presumption that fuel without fines has less ash-forming components, in particular small paint chips. This should have been clearly visible

in the form of difference in Pb concentration. However, this is not the case. Apparently, paint chips are evenly distributed in all fuel fractions. It can be concluded that removing the fines does not improve the fly ash quality by lowering the concentrations of specific elements. The opposite is true. Differences between ashes are smaller than the differences between fuels

The fly ash composition of the runs with and without fines can be compared to the fly ash from the AMER-CFB. The latter has a noticeable lower total ash content. This is reflected in a lower caloric value for the carbon-rich fly ash produced in the BIVKIN. Apparently, the burnout is better in the BIVKIN. The reason must be found in the operational conditions, because the demolition wood used in both installations is not significantly different. E.g., the ash content of demolition wood fed to the AMER-CFB is about 6 wt% ash (dry basis), which is between the ash contents of the demolition wood with and without fines used in the BIVKIN tests.

The main difference between using fuel with and without fines is found in the bottom ash. The material collected at the bottom of the BIVKIN was in both runs composed of inorganic particle, stone, concrete, tiles, etc, materials. In the run with fines these materials were found insignificantly larger quantities. In the material collected at the bottom of the BIVKIN also large numbers of agglomerated particles were found. These were composed of a molten piece of glass covered with sand particles.

The overall conclusion is that removal of fines (0-3 mm) from demolition wood is not significantly affecting the ash quality of the fly ash. Differences between installations or between separate fuel suppliers are larger.

2.4 Conclusions on optimisation of the gasification process (WP 1)

Improvement of ash quality by optimisation of the gasification parameters is possible, but the changes will be limited. Certainly, it is not possible to guarantee a carbon content in the range of 5-10 wt%. Only modifications of the gasification process, e.g. changes in design of the gasifier, may lead to significant lowering of the carbon content in gasification of biomass. One of those process modifications is application of the HSD-CFB principle.

Dramatic lowering of the carbon content of fly ash can be accomplished by combining the gasifier with a combustor. One option is the Integrated Oxidiser of VTT, which is part of WP2 of the GASASH project. It produces ashes with very low carbon content. See appendix A for public information. The integrated gasification-combustion system developed by ECN, known as MILENA, is another improved process design, which produces ashes that are essentially combustion ashes, with a very low carbon content.

In gasification of demolition wood, inclusion or exclusion of the smallest fuel size fraction (0-3 mm) has only a minor effect on the fly ash composition. The strongest influence is found on the bottom ash, not on fly ash. When sewage sludge is used as fuel, the inorganic components from sewage sludge dominate the ashes. Mixing with clean wood can influence gasification behaviour, but does not have a significant influence on ash composition.

For re-use of the gasification ash as a fuel, optimisation of carbon conversion does not necessarily mean maximisation of carbon conversion. In that case, the carbon content of the fly ash should be more than 35%.

3. DEVELOPMENT OF NEW TECHNOLOGY (WP 2)

3.1 Introduction

The second objective of the GASASH project is to develop new technology aimed at improving ash quality from gasification of biomass and waste. This chapter presents results related to the strategies of "*Staged gas cooling and particulate separation"* and "*Separation of ash and conditioning of fractions"*. The latter strategy was formulated when it became clear that the former strategy is not likely to find an application in the near future in gasification systems, although it is experimentally proven to be effective in biomass combustion systems. The two reasons to pursue alternative roads are:

1. The strategy of "staged cooling and particle removal" results in significant extraction of ash before the end of the cooler. This is in conflict with the requirements of a "self-cleaning cooler". This is a cooler-type where the ductwork is kept (relatively) clean by scouring the walls and pipes with entrained ash particles, which is very useful in the case of gasification of biomass. Removal of (part of) the ash prior to the end of the cooler is unwanted, because a) the larger particles are the first to be removed but these are also the most effective in keeping the deposition low and b) the scouring is most needed at the end in the colder parts of the cooler, so most particles must remain entrained by the gas until the end of the cooler. The benefits of the "self-cleaning cooler" are preferred above "staged cooling and particle removal and both ECN's BIVKIN and the AMER-CFB are equipped with such a cooler.
2. From a few gasification runs using sewage sludge, it appears that the strategy of "staged cooling and particle removal" is only effective for a limited number of elements. In the experiments, ash was collected at 200 and 800°C. Some elements were concentrated in the "cold" ash fraction, e.g. Pb, Cd and Cl, but most elements, including Ni, Cr, Cu and Zn, showed no significant preference to concentrate in a certain fraction. One can expect that in the narrower temperature ranges in cooler, 400-600°C, the differences in ash composition will be even smaller.

Despite these arguments, the strategy of "staged cooling and particle removal" should not be regarded as useless. The second argument is based on results with sewage sludge as fuel and application in biomass gasification in a CFB. Using other fuels, the conclusions may be different, but the first argument is still strong. Only in systems where a "self-cleaning cooler" is not needed, there might be room for a staged cooler.

In the newly formulated work plan, based on "*Separation of ash and conditioning of fractions"*, specific objectives were to investigate the potential of ash separation and to explore several forms of after-treatment that are suitable for certain ash fractions. Each of these techniques should modify one or more of the characteristics of the ash to improve its quality. The six forms of after-treatment that were explored were:

- Dry separation of carbon-rich fly ash using screen sieves
- Low-temperature combustion of carbon-rich fly ash in a lab-scale 5 kW bubbling fluidised bed (BFB).
- High-temperature combustion, directly in a simulated coal burner (LCS) and as a batch in a smelter furnace (vitrification)
- Immobilisation as a filler material in C-Fix construction blocks,
- Controlled leaching and analysis of the washing fluids
- Pelletisation using several binder materials, with strength tests.

The basis for the work was a batch of gasification fly ash produced by the 80 MW_{th} Circulating Fluidised Bed Gasifier located at the AMER-9 power plant of Essent Energy Productions (the AMER-CFB). Based on the results of the explorative tests, high-temperature combustion (smelting) was selected as the preferred method for up scaling.

3.2 Experimental

3.2.1 Sample of carbon-rich fly ash from EEP's 80 MW_{th} gasifier

On 16 September 2003, a singular batch of 45 kg carbon-rich fly ash was collected at the 80 MW_{th} Circulating Fluidised Bed Gasifier at the AMER-9 power plant, owned by Essent Energie Productie (EEP). The ash was produced in the week prior to the sampling. The gasifier was fuelled with shredded demolition wood and the fly ash was representative for the situation in 2003, during the GASASH project. In this report, the ash is labelled as "AMER-CFB fly ash" and used for nearly all tests in WP2. Four samples were taken for proximate and ultimate analysis as well as analysis for trace elements using ICP-AES. For Si and Ti separate digestion was used. Also, mercury content was separately analysed. The particle size distribution was measured using a Malvern Mastersizer 2000 using ethanol as dispersant. The results of the particle size distribution may not be completely reliable, because part of the ash (in particular the salts) could have been dissolved in the alcohol, but this is not expected to be a significant effect. A sample of the AMER-CFB fly ash was subjected to SEM analysis. Two samples of AMER-CFB fly ash were subjected to leaching tests, see section 4.2.4.

3.2.2 Dry separation of carbon-rich fly ash

Dry screening was performed for separating a sample of AMER-CFB fly ash into several fractions, using laboratory screens (20 cm diameter). Objective was to identify size fractions that have beneficial characteristics and that are suitable for utilisation options that are not attractive for the bulk fly ash. Based on the particle size distribution a selection of screen sieves was made: 20, 38, 45, 63, 90 and 180 μm. The chemical composition of each fraction was determined using proximate, ultimate and ICP-AES analysis of trace elements. The characteristics of the size fractions obtained in this part of the work are used to draw conclusions with regard to potential of after-treatment techniques.

3.2.3 Low-temperature combustion

A sample of AMER-CFB fly ash was combusted in a lab-scale 5 kW_{th} BFB installation. Objective is to make fly ash suitable for utilisation in cement products or for landfill at low gate fee. In short tests, the temperature range between 550-700°C was explored, with 5% O_2 in the flue gas. Feed rates were 45 g/h for the experiment at 550°C and 79 g/h for 700°C. Ash samples were collected and carbon content was analysed. Based on these results, a long duration test was done at 700°C in order to produce a large amount of ash under stable conditions during 4 days. The fuel feed rate was 70 g/h, air supply 9 l/min, keeping O_2 in the flue gas at 6%. In all BFB tests feeding and hence the combustion process fluctuated but never uncontrollably. The ash was analysed using proximate and ultimate analysis as well as trace elements using ICP-AES. The ash was also subjected to a leaching test, see section 4.2.5.

3.2.4 High-temperature combustion

High temperature combustion was tested in two ways. Firstly in ECN's Lab-scale Coal-burner Simulator (LCS), AMER-CFB fly ash was co-fired in a flame at 1400°C (made with natural gas) that simulates a coal-burner. Objective is to make sintered fly ash that is similar to coal fly ash, e.g., resistant to leaching and with good flow characteristics. On a cooled collector plate, about 10 g ash was collected. For this ash sample, chemical analysis (trace elements) and SEM analysis are scheduled. Also, the sample must be tested for compliance to EN 450 criteria for inclusion in cement.

Secondly, batches of AMER-CFB fly ash have been combusted in SiC pots at 1350-1450°C, a temperature range where the ashes melt. The resulting molten and solidified ash is being subjected to chemical analysis for trace elements. Combinations of AMER-CFB fly ash and fluxing agents were investigated in an effort to lower the melting point of the ash. A 1 kg block, prepared from AMER-CFB fly ash with 10% alumina (in the end product) was made and subjected to a leaching in a tank test (NEN 7375) , see section 4.2.6.

3.2.5 Pelletisation

From small batches of AMER-CFB fly ash, pellets were made one by one in a die by compression. Objective is to make (fractions of) fly ash suitable for utilisation as fuel by improving the handling (e.g., reducing the risk of dust explosion). Test pellets were about 1 cm high and had diameters of 1 cm or 4 cm. Various amounts of water and binder were added. Binders included starch, sugar, paraffin, tar and cement. The 4 cm diameter pellets were made in a uni-axial isostatic press. The 1 cm diameter pellets were made in a heated uni-axial isostatic press. Pellets were subjected to strength on an Instron 4505 workbench, with applied pressure to a maximum of 100 kN.

3.2.6 Controlled leaching

For assessment of controlled leaching as a viable ash conditioning technique tests were performed in the laboratory equipment normally in use for pH dependence testing (PrEN14429) and column leaching tests (PrEN 14405). Objective is to remove soluble salts from the ash so that it can be utilised without typical problems associated with leaching of salts from biomass ashes. The washing liquids were analysed for dissolved components.

3.2.7 Immobilisation

AMER-CFB fly ash was tested as a filler material in two C-fix test blocks. Objective is to determine the suitability as filler in construction products that can be used without the leaching problems typical for fly ash originating from biomass. C-fix was originally developed by Shell Global Solutions, but is now being developed further in a private company by the name of C-fix BV. C-fix is a material with properties between asphalt and concrete. One block was composed of 7% filler (biomass ash), 36% sand (0-2 mm), 50% aggregates (2-8 mm) and 7% binder (petroleum residue). The other block had less sand (26%) and more aggregate material (61%). Both blocks were subjected to strength tests (flexural and compressive). The block that passed the strength tests was subjected to leaching in a tank test (NEN 7375), see section 4.2.7.

3.2.8 Up scaling of smelting experiments

First a recipe was developed for making synthetic basalt from AMER-CFB fly ash. Ash combusted at 1100°C was used as starting material to produce a block of approximately 1 kg. The block was made in a laboratory furnace (the largest size of such a material that can be produced in the ECN laboratories). A total of 10 wt% alumina (based on mass of the end product) was added to lower the melting point to 1250-1300°C. The synthetic basalt was subjected to a tank leaching test (NEN 7375) , see section 4.2.8.

In an up-scaled test an amount of 5 kg synthetic basalt was prepared. The material used in this test was about 15 kg fly ash from the 80 MW_{th} Circulating Fluidised Bed Gasifier located at the AMER-9 Power Plant of Essent Energy (AMER-CFB). The pilot test was done off-line from the gasifier to avoid interruption of the power-plant operation. The conditions reflected the situation of full-scale smelter to such an extent, that it is expected that the end product will be representative for full-size smelting operation with respect to material characterisation. The fly ash was pre-treated by combustion at 1100°C. The resulting ash was largely a powder and sintered parts were pulverised. Alumina was used as a fluxing agent, 10 wt% of end product. A total of 4.5 kg ash (with 10% alumina powder) was then heated in a smelter pot at 1300°C for 24 h under slight oxidising conditions. The smelt was removed from the pot and broken into granulate of 0-40 mm.

3.3 Results and Discussion

3.3.1 Review on the "strategy on staged cooling and particle removal"

A review of the potential of the strategy of "staged cooling and particle removal" has been written. The objective was to assess the potential of staged cooling for application in gasification, despite the growing understanding that it is very unlikely to find an application in a commercial installation.

Staged cooling and particle removal is successfully applied to in combustion for a limited number of elements. It is expected to work also in gasification in a similar way. Calculations indicate that it is possible to concentrate problem elements like Cd, Zn and Pb in certain ash fractions. However, the same calculations indicate that the strategy does not work for other problem elements like Ba Cr, Cu, Co and Ni. The fate of elements like S, Cl and Se depends on the metals they combine with. The temperature history and the particle sizes in an ash fraction determine the distribution of elements. The fuel composition determines the absolute level. The unsuccessful removal of contaminants from the bulk of the ashes is one reason why staged cooling and particle removal is unlikely to find an application in the near future. The other main reason is that removal of the bulk of the ash at a high temperature results in unacceptable fouling of the cooler: Staged cooling and particle removal conflicts with application of a self-cleaning cooler. Improvement of fly ash quality should preferably be done by means of some kind of after-treatment.

3.3.2 Literature review on screening techniques

A review of screening techniques was made which may be used for separating carbon-rich fly ash into several fractions. For separation of carbon-rich fly ash, both dry and wet techniques are available. For dry systems, screening using an electric vibrating screen is the most obvious method. The particle size of carbon-rich fly ash is small making screening difficult, but not impossible. Sieving with small apertures (e.g., 20 μm) is time consuming. For smaller sizes relatively large screen surface areas are required, which on a larger scale may not be practical. Cohesiveness of fly ash particles is an uncertain factor. Electrostatic separation or cyclones in series are not viable alternatives.

For separation of carbon-rich fly ash, both dry and wet techniques are available. For dry systems, screening using an electric vibrating screen is the most obvious method. The particle size of carbon-rich fly ash is small making screening difficult, but not impossible. Sieving with small apertures (e.g., 20 μm) is time consuming. For smaller sizes relatively large screen surface areas are required, which on a larger scale may not be practical. Cohesiveness of fly ash particles is an uncertain factor. Electrostatic separation or cyclones in series are not viable alternatives. Wet systems perform potentially better than dry systems. In particular, liquid cyclones and froth flotation are promising techniques. However, wet systems have serious disadvantages. Firstly, the need to dry the solids afterwards and secondly, the contamination of the liquid with leached compounds. Only when wetting of the solids and/or controlled leaching are part of the processing of the ash, wet techniques may be good choice.

3.3.3 Sample of carbon-rich fly ash from EEP's 80 MW_{th} gasifier

Four samples of AMER CFB fly ash from the singular batch collected on 16 September 2003, were subjected to proximate and ultimate analysis as well as analysis of trace elements. The averaged results are presented in Tables 3.1 and 3.2. Most important is the finding that it has 60% combustible material. The ash content between the four samples varies from 33 to 45%, which is due almost exclusively due to variations of the Si content. The likely explanation is, that spilled over sand (from attrition of the bed material) is not evenly mixed with the char particles, containing the bulk of the other elements.

Table 3.1 Proximate and ultimate analysis of fly ash obtained from AMER-CFB (September 2003)

proximate analysis		ultimate analysis	
moisture (as received)	< 0.1 wt %	C	56.6 wt% (dry)
ash (dry, at 550°C)	37.5 wt%	H	0.5 wt% (dry)
ash (dry, at 815°C)	33.8 wt%	N	0.7 wt% (dry)
		O	4.7 wt% (dry)
HHV	24.9 MJ/kg	S	0.9 wt% (dry)

Table 3.2 Trace elements in carbon-rich fly ash obtained from AMER-CFB (September 2003); all data in mg/kg original material, dry basis

	content in fly ash		content in fly ash		content in fly ash
Al	7473	Fe	6858	S	5366
As	101	K	7239	Sb	41
B	119	Li	5	Se	5
Ba	3776	Mg	5722	Si	76492
Ca	48909	Mn	848	Sn	39
Cd	8	Mo	4	Sr	237
Cl	10710	Na	4731	Ti	16077
Co	21	Ni	27	V	12
Cr	501	P	1418	Zn	4011
Cu	427	Pb	4736		

When comparing these data to the composition of a comparable fly ash originating from gasification of clean biomass, the ash composition is not much different. Ba, Pb, Zn and Ti are present in significantly larger amounts. These elements originate from paint residues. The content of Si is significantly larger in clean biomass, while Mo is somewhat higher. The reason for the large Si content is the presence of inert sand in clean biomass, particularly from park waste and harvested wood.

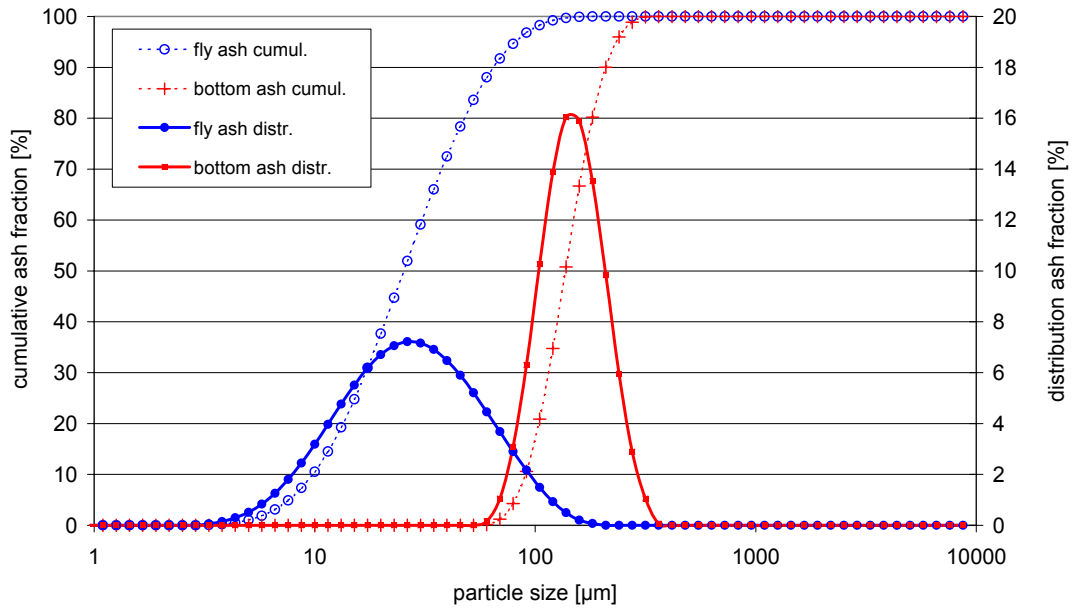
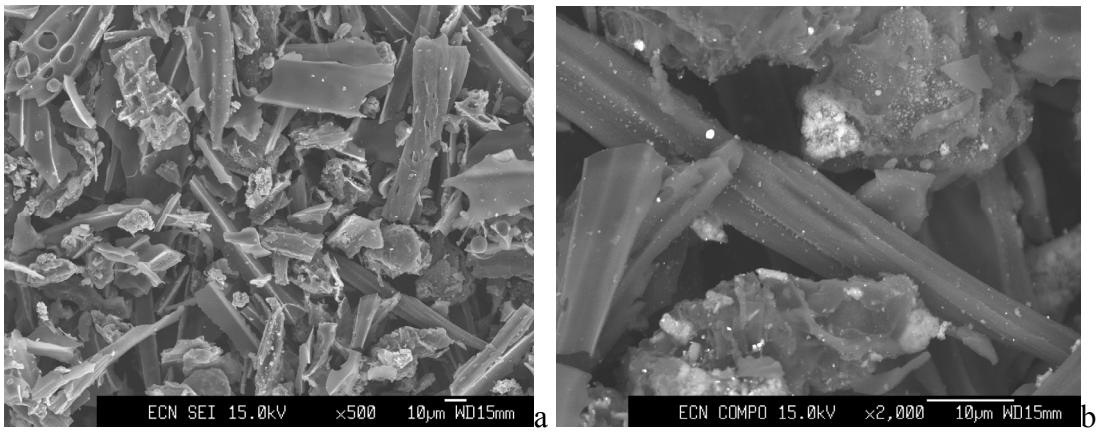


Figure 3.1 Particle size distribution (incl. cumulative) of fly ash and bottom ash of AMER 80 MW_{th} circulating fluidised bed gasifier, measured with Malvern Mastersizer 2000

The particle size distribution was determined using a Malvern Mastersizer 2000 with ethanol as solvent. The results (of fly ash and bottom ash) can be seen in Figure 3.1. It can be seen that there is a unimodal size distribution with a peak at about 30 μm. The bulk of the particles in the fly ash is found in the range 10-100 μm. Bottom ash is coarser, because it is primarily composed of inert sand, used as bed material.

In figure 3.2a, a SEM picture of AMER-CFB fly ash is presented. It is a regular SEI photograph that shows the morphology of the particles that form the fly ash. All particles are primary char particles. Some of the particles resemble the structure of the original wood. There are small particles (< 1 μm) visible. The identity of these particles is better presented in Figure 3.2b (detail of Figure 3.2a in COMPO mode). In this picture, the brightness indicates the atomic mass of the elements. The dark areas are mainly C and O (H is not visible). The bright spots are mainly inorganic materials. The irregular white spots in the centre and at the bottom of the picture are composed of contains Ca, Al, Mg, Ti and Cl. Two of the rectangular particles in the bottom left quadrant were identified as CaS. The small, bright white spots (0.5 μm), e.g. in the upper left corner, are TiO_2 particles. Titania (TiO_2) is added as a whitener to paint. The tiny white specs found all over the material are too small to be identified. Heavy metals, Pb and Zn, are found in the irregular white spots.



a b

Figure 3.2 SEM photographs, SEI (a) and COMPO (b) of carbon-rich fly ash from the AMER 80 MW_{th} circulating fluidised bed gasifier

3.3.4 Dry screening of carbon-rich fly ash

A small batch of the high-carbon fly ash was subjected to mechanical sieving on a series of laboratory screen sieves. From Figure 3.1 it became apparent that screening is most effective in the size fractions ranging from 10-100 μm. For the lab-scale screening, sieves of 20, 38, 45, 63, 90 and 180 μm were used. None of the particles was larger than 300 μm. The thus obtained particle size distribution gives a good indication of the fractions that large scale screen sieving can yield. The particle size distribution obtained by the mechanical sieving is presented in Figure 3.3. The obtained particle size distribution is presumed representative and gives a good indication of the size fractions that large-scale screen sieving can yield. The distribution matches with the results as presented in Figure 3.1. The sieving on the smallest screen (20 μm) was time consuming. On a larger scale it may not be practical to use such a small screen. Already on the 38 μm screen, complete separation was hard to achieve. Since 90 wt% of the particles is below 45 μm, screening is not very effective when only the practical sieves (45 μm and larger) are used. The practical conclusion is that sieving is possible and simple, but time consuming and requires rather large installations. Only a clear distinction of chemical composition of the size fraction can justify the costs of sieving.

The seven fractions obtained in the lab-scale sieving experiment were subjected to chemical analysis. The results are presented in Table 3.3. The deviations from the average values are displayed in colours (see caption for explanation). Most elements are concentrated in the

smallest fraction and depleted in the larger fractions, except for Si, which is strongly concentrated in the larger fractions. Ash content is slightly higher for the smallest fraction (below 20 μm), but not much compared to the average ash content. All elements (except Si) are enriched in the smallest fraction even when normalised for the total ash content. The concentrations of problem elements in the smallest fraction are never larger than two times the average. Combined with the fact that the smallest fraction is nearly half of the total amount it means that separating the fraction < 20 μm from the bulk will not result in concentration of the bulk of problematic elements in a small fraction.

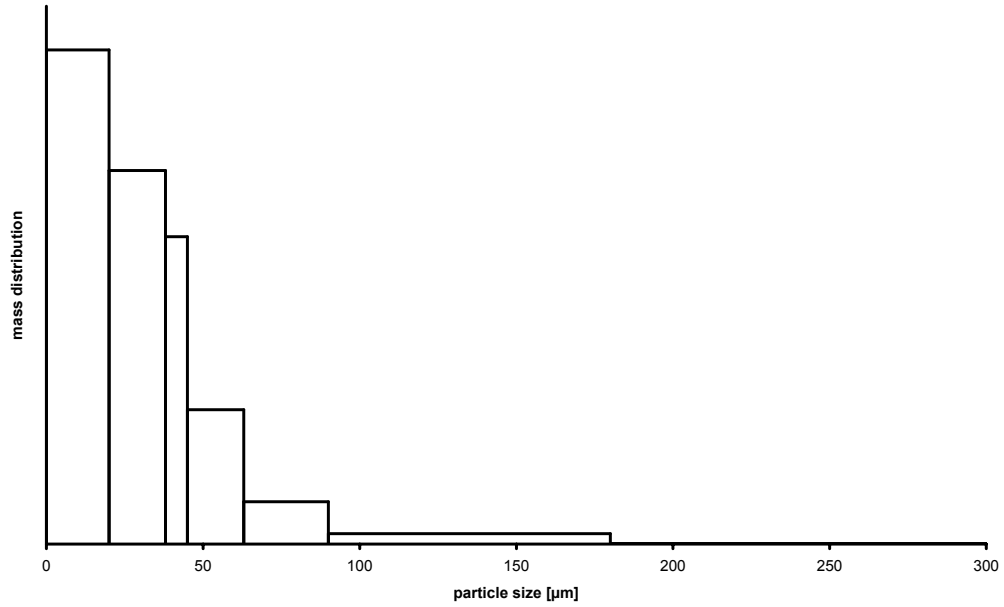


Figure 3.3 Particle size distribution of the fly ash obtained from AMER-CFB fly ash (Sept. 2003). The distribution is per size fraction, so that the surface area of each rectangle represents the mass of the sieve fraction. Sieves at 20, 38, 45, 63, 90 and 180 μm.

In the larger fractions all elements (except Si) are depleted and for nearly all elements by at least by a factor two. This means that the larger fractions are less contaminated and contain mainly sand as ash. The measurement of the total ash content of the largest ash fraction is not reliable. The conclusion is that separating the largest 10 to 20 % from the fly ash will yield an ash fraction lower in contaminants and high in inert sand. Unfortunately, the gain is small, because the bulk of the ash remains. The material contains concentrations of Ba, Pb, Zn and other problematic elements that exceed the average levels in demolition wood, typically by about a factor four.

The overall conclusion is that in principle, dry screening can be applied to the carbon-rich fly ash to separate the material into fractions with unequal composition. Based on the analysis of the sieve fractions obtained from screening a sample of AMER-CFB fly ash, it can be concluded that extracting the largest 10% of the particles is a viable option to create a small, but relatively clean ash fraction. This requires a screen sieve at 63 μm with a surface area of a few square meters. Separation of the smallest fraction, below 20 μm, is not a promising route to pursue. There is no significant concentration of problem elements and it requires a large screen surface area (estimated 50 m^2).

Analysis of the chemical composition of four samples of AMER-CFB fly ash revealed that variations in the ash content are caused by variations in Si content. The concentrations of the other trace elements do not vary much. The data in Table 3.3 indicate that Si is concentrated in the larger size fractions, which is consistent with the explanation that these are spilled-over sand

particles. Dry sieving at 90 µm removes about 20% of Si in 5% of the mass. The remaining 95% contains Si at an average concentration of 42000 mg/kg. Differences between the compositions of the four carbon-rich fly ash samples become insignificant when the Si concentration is artificially set at 42000 mg/kg, which would be the case after sieving out the largest 5% of particles. In other words, sieving out the particles larger than about 100 µm removes the (broken) sand particles (and also large char particles) that cause the fluctuations in ash composition. Similar results can be obtained by sieving at 63, 45 or even 38 µm, but sieving is increasingly cumbersome at smaller apertures.

The conclusion is that sieving at a particle size around 100 µm produces a) a small size fraction of larger particles with a lowered content of contaminants, suitable for utilisation as fuel, and b) a large fraction of small particles with a predictable composition. Consistency is a great advantage in *all* utilisation routes.

Table 3.3 Composition of sieve fractions; background colours indicate the deviation from average: yellow = within 10% of the average value, light green = between 10% and 50% lower than average; dark green = lower than 50% of the average value; pink = between 10 and 100% higher than the average value; red = more than 100% above the average value; <d.l. = below detection limit

size	µm	<20	20-38	38-45	45-63	63-90	90-180	>180	average
mass	wt%	42%	29%	9%	10%	5%	4%	0%	100%
ash*	wt%	33	29	19	18	24	52	6	29
Cl	mg/kg (dry)	13833	13047	9066	7619	7455	6915	6108	11908
As	mg/kg (dry)	130	103	75	72	47	19	23	102
Ba	mg/kg (dry)	6013	3702	1522	1355	1334	1340	1337	4019
Ca	mg/kg (dry)	63441	54321	31618	27576	27733	16918	17114	50397
Cd	mg/kg (dry)	10	7	4	3	2	1	0	7
Co	mg/kg (dry)	28	20	13	14	13	8	9	21
Cr	mg/kg (dry)	641	466	314	264	208	151	164	479
Cu	mg/kg (dry)	557	433	315	288	238	145	199	438
Fe	mg/kg (dry)	10233	6619	3660	3282	3120	2125	2395	7166
K	mg/kg (dry)	8671	7330	5753	5771	6465	4516	4409	7426
Mg	mg/kg (dry)	7223	5658	3812	3638	3544	2169	2244	5687
Mo	mg/kg (dry)	3	3	*<d.l.*	*<d.l.*	*<d.l.*	*<d.l.*	3	3
Na	mg/kg (dry)	6309	4632	3026	2839	2998	3175	3224	4865
Ni	mg/kg (dry)	40	24	16	14	11	6	8	28
Pb	mg/kg (dry)	6911	4221	2487	2023	1428	685	668	4683
S	mg/kg (dry)	6945	5838	3718	3234	2663	1041	1080	5478
Sb	mg/kg (dry)	77	49	35	27	21	9	154	54
Se	mg/kg (dry)	*< d.l.*	*<d.l.*	*<d.l.*	5	*<d.l.*	*<d.l.*	*<d.l.*	
Si	mg/kg (dry)	39966	44231	40185	38007	63486	233493	207123	50454
Sr	mg/kg (dry)	331	254	142	131	132	96	101	251
Ti	mg/kg (dry)	22394	13915	9239	7355	8074	4998	2968	15718
Zn	mg/kg (dry)	5966	3314	1721	1416	1163	1066	1183	3891

* determined at 815°C

3.3.5 Low-temperature combustion of carbon-rich fly ash

AMER CFB fly ash contains about 60% combustible material. Tests show that combustion of carbon-rich fly ash is possible at 550-700°C in a lab-scale BFB. Due to the low temperatures, agglomeration of the bed was prevented. The combustion ash has a low carbon content: LOI of about 8% for combustion at 700°C, LOI of about 15% for combustion at 550°C. The carbon

content of the low-carbon fly ash is in the same range as the carbon content of fly ash from coal-fired plants. The fly ash produced at 700°C complies with specifications set in the EN-450 (5-10% LOI) for using combustion fly ash in cement. However, the chemical content is quite different from coal fly ash and does not comply with other criteria of the EN-450.

Table 3.4 Composition of fly ash recovered from combustion of AMER-CFB high-carbon fly ash at 700°C; all data in mg/kg on dry basis

element	low-carbon fly ash	bed material (after use)	element	low-carbon fly ash	bed material (after use)
Al	26816.9	22762.9	Mo	125.5	130.1
As	218.6	108.7	Na	9905.6	8102.1
B	278.8	162.1	Ni	1206.3	3574.5
Ba	10210.1	6841.0	P	3908.7	3034.0
Ca	106941.7	79401.8	Pb	13882.1	11789.5
Cd	16.1	14.7	S	11531.0	6301.3
Cl	32976.5	24155.5	Sb	156.7	84.7
Co	68.9	63.1	Se	6.3	1.3
Cr	3249.9	6369.3	Si	157579.8	222135.2
Cu	1002.4	839.1	Sn	53.0	30.7
Fe	29351.0	45921.4	Sr	604.9	429.4
K	25479.1	29814.7	Ti	52319.7	34096.6
Mg	16293.4	12720.3	V	46.0	56.3
Mn	2362.3	2113.9	Zn	8849.1	5829.3

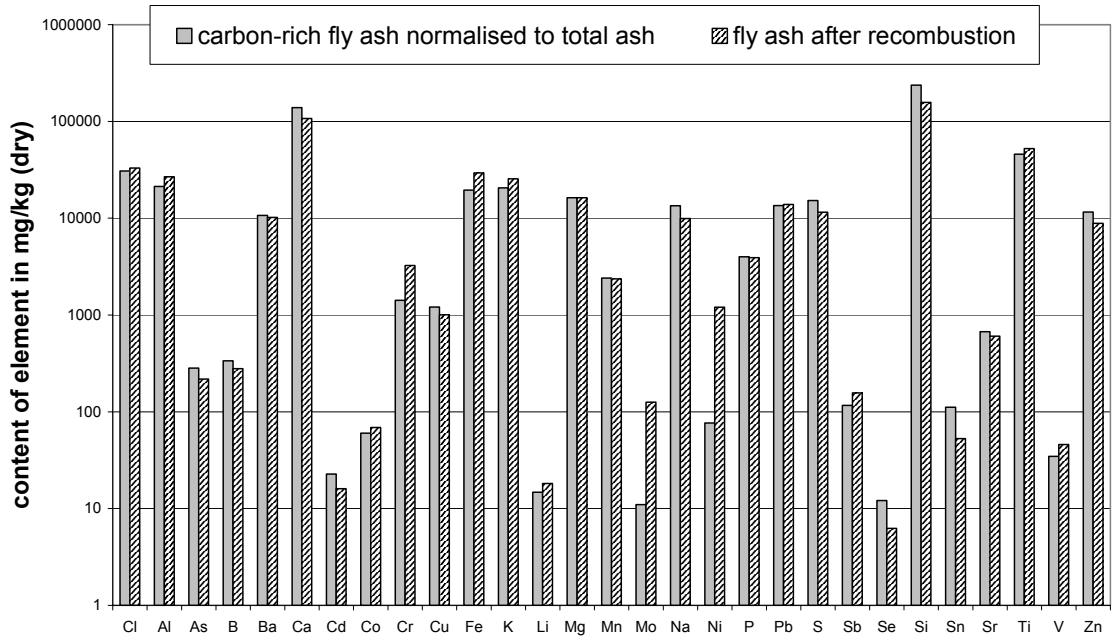


Figure 3.4 Concentration of elements in fly ash after combustion in a BFB and of the carbon-rich fly ash (used as fuel) normalised to total ash content; all data in mg/kg (dry)

In a long-duration run (4 days) at 700°C, the BFB system became saturated with ash and the mineral balance could be closed at 95%, of which 48% in the filter at the reactor outlet and 47% accumulated in the bed. The fly ash and bottom ash were subjected to chemical analysis and leaching tests (fly ash only), see section 4.2.5. The fly ash after combustion closely resembles the ash composition of the high-carbon fly ash normalised on its total ash content, see Figure 3.4. A few elements show a larger difference. Some volatile elements are present in smaller quantities in the low-carbon fly ash, e.g., Cd, Se and Sn. These elements are partially emitted in

the gas phase. The significantly increased presence of Ni, Mo and Cr in the low-carbon fly ash is most likely an artefact of the test method. The ash has become contaminated with stainless steel, either from wear of the screw feeder or from scaling of the walls of the reactor.

The fly ash from low-temperature combustion in a BFB is comparable to ash that is produced in the 85 MW_{th} BFB combustion facility in Cuijk (owned by EEP) with a few exceptions. Certain elements, Pb, Ba, etc. that are typical for paint residues are present in larger quantities in the fly ash from the AMER-CFB. On the other hand the ash from the Cuijk BFB contains more K, P and other elements that are typical for growing parts of plants. The causes for these differences can be found in the fuel composition. The Cuijk BFB is fuelled with clean biomass, mainly wood, but including park waste and grass-like plants. The AMER-CFB is fuelled with demolition wood. The conclusion is that the fly ash from combustion of carbon-rich fly ash from gasification will produce a low-carbon fly ash that is very well comparable to the fly ash that would be produced in a BFB, when the fuel was directly combusted.

The leaching test results (see Appendix A) used to characterise ashes show that Pb release from the carbon-rich gasification fly ash was very high due to the high mobility of Pb at high pH (natural pH=12.5). After low temperature combustion the Pb release decreases to levels that comply with acceptance of hazardous waste at landfill sites according to the European Landfill Directive (EULFD). The leaching test results also indicate that after combustion of the ashes, the Cr release increases significantly, but are still within limits of acceptance at a hazardous waste landfill. The low-carbon fly ash does not comply with Dutch regulations to be applied as a bulk building material, but its potential for being used as a raw material in cement-like products is larger. Application as a bulk building material is also limited by the physical properties of the ashes. Contrary to the CFB and MSWI bottom ashes that are often used as a replacement for sand in construction works, the gasification ash after combustion in a BFB is still a very fine, powdery substance.

Chlorine is the most troublesome element that limits the use of these ashes as a bulk building material (according to the Dutch Building Materials Decree in a category 2 application).

3.3.6 High-temperature combustion of carbon-rich fly ash in a coal burner

High-carbon fly ash from the AMER-CFB can be used as a fuel in a coal-fired burner. The simulated burner (LCS) produced a fine dust that was collected on a cold plate. The chemical analysis is given in Table 3.5. Visual inspection showed that the particles form loose agglomerates that fall apart when touched. A photograph of the agglomerate and some loose powder is presented in Figure 3.5a.

Table 3.5 Composition of fly ash recovered from high-temperature combustion of AMER-CFB high-carbon fly ash in a simulated coal burner; all data in mg/kg on dry basis

element		element		element	
Al	15829.0	Fe	12777.9	Sb	40.1
As	51.6	K	7395.1	Se	2.1
B	81.0	Mg	10059.1	Si	290126.7
Ba	6628.9	Mn	1330.8	Sn	25.6
Ca	85949.7	Mo	13.5	Sr	415.5
Cd	1.8	Na	5201.1	Ti	29056.5
Cl	2952	Ni	65.0	V	20.6
Co	33.4	P	2055.3	Zn	2070.1
Cr	597.1	Pb	1620.4		
Cu	246.4	S	891.0		

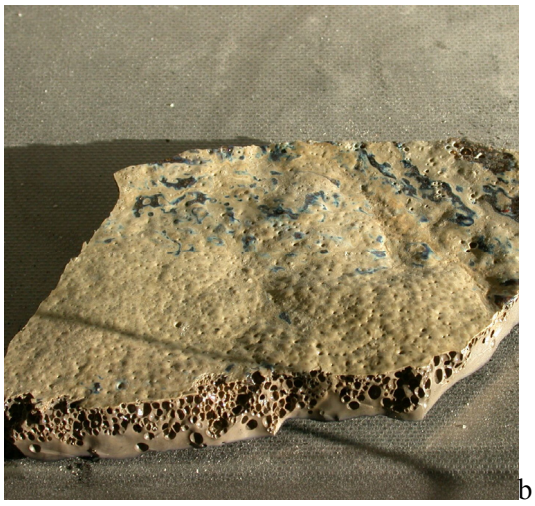

a

b

Figure 3.5 Photographs from high-temperature combustion of AMER-CFB high-carbon, a) agglomerate (about 3 cm long) from high-temperature combustion in a simulated coal burner, b) fragment of the molten ash layer from incineration at 1450°C.

The simulated burner test demonstrated, that carbon-rich fly ash from gasification is a fuel that can replace part of pulverised coal in boilers without major changes to feeding systems. It is expected that it is technically possible to modify a coal burner so that it will even be able to fire 100% carbon-rich fly ash. However, the low-carbon fly ash is not likely to fulfil the criteria of the EN-450. When comparing the characteristics of the fly ash from combustion of AMER-CFB fly ash in to the specifications of the EN-450, it becomes clear that the chlorine content is too high (0.3 wt% instead of < 0.1 wt%) and that the sum of SiO_2, Al_2O_3 and Fe_2O_3 is too small (67 wt% instead of > 70 wt%). The alkali content is well within limits.

Co-firing of carbon-rich fly ash from gasification of demolition wood in coal-fired plants is possible up to a certain level unless it is acceptable that fly ash exceeds the specifications of EN 450. Other fuels may produce carbon-rich fly ashes with different characteristics, but chloride is expected to be problematic in nearly all cases. After-treatment of the carbon-rich fly ash aimed at removing chloride and other components other than Si, Al and Fe may help. Washing can be considered, but wet fly ash will need drying before it can be used in a PF burner.

3.3.7 High-temperature combustion of carbon-rich fly ash in a smelter

The carbon-rich fly ash can be combusted at high temperature producing a molten ash phase that solidifies when cooled. Combustion of 3-5 kg of AMER-CFB fly ash was done at 1350 and 1450°C in SiC crucibles. After cooling, the ash layer found in the crucibles was broken into fragments. Figure 3.5b shows a picture of the largest fragment. The yellowish material is burnt-out ash, molten and solidified. The thickness of the layer was on average 2 cm. The molten ash is not completely solid but contains bubbles. These are gas bubbles that were trapped during cooling. Despite high temperatures and long durations (up to 24 hours) the carbon-rich ash was not completely burnt out.

The formation of a seal is a problem, because burned-out AMER-CFB fly ash liquefies partly at a certain temperature between 1100-1400°C and simultaneously a gaseous component is formed. The loss of the gaseous component results in a shift to a higher melting point of the remaining material. The effect is, that ash expands like a foam and solidifies. The resulting porous ash has a melting point between 1500-1550°C and is inhibiting contact between carbon-rich ash at the bottom of the pot and air

The formation of a sealing layer of foam was avoided by burning and melting the AMER-CFB fly ash in stages. First the ash was combusted in a crucible at 1100°C then the ash was heated to different temperatures. The ash produced at 1100°C was completely burnt-out, but not molten.

The ash was partially sintered, but the material could be pulverised by grinding it in a mortar. Heating the molten ash to 1400°C resulted in solidified foam that did not melt again below 1550°C. The chemical composition of the ashes produced at different temperatures is presented in Table 3.6. For comparison the composition of AMER-CFB ash normalised for total ash content is given. Clearly, the more volatile elements, e.g. Cl, Cd and Pb decrease at higher temperatures. Some of the ashes produced at temperatures of 1100°C and higher were subjected to leaching tests; see next chapter. Comparing the leaching results to the criteria of the Dutch Building Materials Decree it was found that not only vitrified ash complied with the requirements for category 1 building material (unlimited use), but also the ash produced at 1100°C, which is mostly a fine powder. This is caused mainly by evaporation of the elements that are causing problems in the ashes produced at lower temperatures. The other problem elements, Ba and Cr, are apparently immobilised already at 1100°C

The first conclusion is that it is technically possible to transform the AMER-CFB fly ash into a synthetic rock, although the melting point is rather high. The second conclusion is, that it can be expected that material produced from AMER-CFB fly ash, which is heated above 1100°C for a sufficiently long time to evaporate problem elements, may be utilised as a building material of category 1, i.e. unlimited use.

Table 3.6 Composition of ash samples prepared by heating at a high temperature and compared to the original AMER-CFB high-carbon fly ash normalised to 100% ash; all data in mg/kg (dry); '< d.l.' = below detection limit

sample	normalised AMER-CFB fly ash	foam prepared at 1350°C	foam prepared at 1450°C	powder prepared at 1100°C	foam prepared at 1400°C	solid prepared at 1550°C
Al	21334	19242	22555	15207	16176	42390
As	283	< d.l.	< d.l.	104	70	< d.l.
B	336	860	264	2449	2355	1550
Ba	10701	6780	6712	6291	6928	6693
Ca	138926	83023	83210	81626	89578	85713
Cd	23	1	0	0	0	< d.l.
Cl	30792				12	< d.l.
Co	60	1513	745	31	122	515
Cr	1420	648	631	598	784	564
Cu	1208	172	41	457	491	470
Fe	19506	12957	10507	11584	13916	14328
K	20564	8221	6964	3467	3582	2948
Li	15	85	67	19	19	18
Mg	16259	9786	10309	9840	10805	10872
Mn	2404	1749	1600	1288	1479	1466
Mo	11	< d.l.	< d.l.	3	280	606
Na	13448	12035	6067	2425	2413	2214
Ni	77	33	19	40	50	50
P	4000	2082	856	1766	2447	2338
Pb	13536	< d.l.	< d.l.	20	17	< d.l.
S	15263	100	133	1580	115	< d.l.
Sb	117	94	52	17	85	124
Se	12	37	26	5	6	30
Si	236806	273817	295775	286830	295571	295318
Sn	112	< d.l.	< d.l.	< d.l.	6	6
Sr	672	393	397	375	443	406
Ti	45825	26063	27747	27424	29353	28775
V	35	38	30	15	23	23
Zn	11563	210	17	16	54	39

3.3.8 Immobilisation of carbon-rich fly ash in C-Fix construction blocks

Carbon-rich fly ash from gasification of biomass and waste was successfully tested for utilisation as a constituent in a novel building material (C-fix). C-fix was originally developed by Shell Global Solutions, but is now the product of a private company by the name of C-fix BV. C-fix is a material with properties between asphalt and concrete. It is made from a heavy residue of the oil refinery, which is usually added to ship fuel or combusted for electricity. From an environmental point of view, C-fix contributes to reduction of the greenhouse gas CO_2 problem by acting as a carbon sink. In addition, C-fix has very beneficial properties like high flexural and compressive strength, easy handling, low permeability and the possibility to fully recycle the material. The material is applied in pilot-scale projects.

Table 3.7 Washing of elements at L/S=2 and L/S=10 from AMER-CFB fly ash (September 2003); 'L/S' in litre water per kg original material

element	total in ash (mg/kg dry)	dissolved at L/S=2 (mg/kg dry ash)	percentage dissolved at L/S=2	dissolved at L/S=2 (mg/kg dry ash)	percentage dissolved at L/S=10
Al	7473.2	0.19	0%	14.30	0%
As	100.5	0.01	0%	0.02	0%
B	118.6	0.32	0%	0.50	0%
Ba	3776.4	24.5	1%	127.00	3%
Ca	48909.1	4341	9%	5921	12%
Cd	7.9	0.0002	0%	0.0007	0%
Cl	10709.7	8235	77%	9713	91%
Co	21.1	0.0001	0%	0.001	0%
Cr	501.2	0.002	0%	0.004	0%
Cu	427.4	0.02	0%	0.049	0%
Fe	6857.9	0.018	0%	0.021	0%
K	7238.9	2217	31%	3100	43%
Li	5.2	0.12	2%	0.25	5%
Mg	5722.4	0.088	0%	0.25	0%
Mn	847.9	0.0009	0%	0.001	0%
Mo	4.2	0.29	7%	0.52	12%
Na	4730.9	1129	24%	1481	31%
Ni	27.1	0.0008	0%	0.002	0%
P	1417.5	0.041	0%	0.077	0%
Pb	4736.3	581.4	12%	708.8	15%
S	5366.3	575.3	11%	1096	20%
Sb	41.4	0.004	0%	0.25	1%
Se	4.6	0.042	1%	0.1	2%
Si	76491.7	9.21	0%	37.5	0%
Sn	39.3	0.001	0%	0.002	0%
Sr	236.9	23.5	10%	35.6	15%
Ti	16077.1	0.002	0%	0.002	0%
V	12.2	0.003	0%	0.005	0%
Zn	4011.0	9.62	0%	11.7	0%

Carbon-rich AMER-CFB fly ash was tested as filler material in two C-fix test blocks. One of the blocks fulfilled the physical requirements for C-fix blocks. This block had a flexural strength of 6.4 mPa, surpassing the minimum of 6.0 mPa. The compressive strength was 14 mPa. The other block (with less sand and more aggregates) had a flexural strength of 5.1 mPa. The leaching test (tank test) was done only on the first block (with more sand). The block qualified as a category 1 building material and is thus acceptable for unlimited use. Data of the leaching results are presented in WP 3. The C-fix blocks made with fly ash from gasification of biomass performed better - both in strength tests and leaching tests - than similar blocks made

with fly ash from biomass combustion. Actually, it was - even without optimisation of recipe - among the best test blocks made so far by C-fix using biomass ashes. Acting as filler in C-fix is a technically feasible solution for utilisation of carbon-rich fly ash.

The results show that immobilisation is a technically viable option for utilisation of gasification ashes. It is expected that after optimisation of the manufacturing process, C-fix blocks made with gasification ashes will have a high quality. At the moment, the future of C-fix blocks no longer depends on improvement of the technology. The challenge is to find a market and producing C-fix blocks at a lower price. Application of fly ash from gasification depends on the competition with other filler materials, e.g. residues from waste incineration.

In C-fix, the petroleum-based binder that inhibits contact between fly ash and water is the key factor. This can be extended to any kind of asphalt or asphalt-like products that have a water-repellent binder. The overall conclusion that is that immobilisation is a successful form of after treatment.

3.3.9 Controlled leaching and analysis of the washing fluids

The potential of controlled leaching was estimated from the leaching tests done on a sample of AMER-CFB fly ash (September 2003). In Table 3.7, the results at L/S=2 and L/S=10 are presented. L/S=2 represents a more practical situation where two litres of water are used per kg fly ash. L/S=10 represents a situation where thorough washing has taken place. The washing liquid is strongly alkaline having a pH of about 12. The dominant mechanism is the pH-controlled solubility of the salts, although binding of metals to the (activated) carbon matrix may play a role as well. Simple salts of alkali with chloride and sulphate are easily removed. Chloride is almost completely removed, already to a large extent at L/S=2. K and Na are partly removed, indicating that some of K and Na are bound as silicates and/or aluminates. Sulphur is removed for only up to 20%, indicating that a large fraction of S is present as sulphide or poorly soluble $CaSO_4$.

Washing at L/S=2 or L/S=10 does not result in significant removal of total sum of metals, except for Pb, which is soluble as a complex at high pH. Generally, the pH dependent solubility of heavy metals shows a typical V- shaped curve. Especially the solubility of Zn and Pb at pH ranges above 10 increases significantly. A minimum of Pb solubility can be found at the pH close to 10. When measures are taken to control the pH during washing, heavy metal removal can be minimised. One of the possibilities is to wash with slightly acidic water. Another measure could be carbonation or aging of the fly ash, which is treatment with CO_2 to convert metal oxides to carbonates, resulting in less OH^- ions being released during washing. In a continuous process, counter current scrubbing can be considered as well.

Work on washing of carbon-rich fly ash from combustion of SRF at a scale of 15000 kg/h was presented by PVO at the progress meeting in Amsterdam, 18 March 2005. Chloride was effectively removed at L/S=3, while heavy metals are not dissolved, so that the washing liquid was of sufficient quality to be discharged into the regular waste water system. The results are similar and complementary to the results obtained by ECN. The only difference is that in the case of PVO's experiments, the amounts of Pb were very low in the washing liquid. Gasification ashes from waste wood and from SRF are different, which may result in differences in the leaching of heavy metals, e.g. because the pH of the washing of SRF gasification ash was kept closer between 10 and 11.

3.3.10 Pelletisation of carbon-rich fly ash

Pelletisation of the carbon-rich fly ash was successful. A large reduction in volume was achieved. Compacting also prevents dusting, so the risk of dust explosions during handling is minimised. The fly ash pellets are similar to charcoal pellets. For sufficient strength addition of a binder is needed in the case of fly ash from the AMER-CFB. Seven biomass-based binders

have been tested. Most binders were effective in the manufacture of strong pellets, but only a few binders produced pellets that did not stain or form dust when scratched. Other carbon-rich fly ashes require less binder material. In some cases only addition of water is needed, because components in already present in the fly ash act as a binder, e.g. salts and lime.

Pelletisation is best suited for combination with other utilisation options, in particular when the fly ash is utilised as a fuel and needs transportation. The pellets can be used as solid fuel with a very low volatile content. They are best suited for application where they replace charcoal or high-grade coal, but other applications are possible. When the original fuel was demolition wood, the pellets contain significant amounts of heavy metals, which limits utilisation to combustion systems with adequate flue gas cleaning. The conclusion is that it is technically a viable option, but that the challenge is to find a market for the pellets. In this sense, the best way to look at pelletisation is to regard it as a fuel preparation technique, not an utilisation option. It should be done only when the end user of the carbon-rich fly ash wants to improve the logistics of the fly ash.

3.3.11 Comparison of results of explorative techniques

The six forms of after-treatment that have been tested for carbon-rich fly ash are partially successful. Dry screening is capable of producing a small ash fraction with relatively low content of contaminants. The bulk of the material cannot be treated this way. Success for this route is limited, but not zero.

Pelletisation of the fly ash is possible and produces fuel pellets, which have improved characteristics for logistics and storage, but which still contain contaminants. Success depends on finding a buyer for the pellets, which has an installation with effective flue gas cleaning. The potential for fuel pellets or briquettes is better when the fly ash is produced from gasification of clean wood, but even then heavy metal content and other contaminants may be present in unacceptable amounts.

Immobilisation in carbonaceous material like C-fix produces building material that can be used in unlimited amounts. It is a technically a viable form of after-treatment, that is expected to be applicable to all utilisation options where a water repelling binder is used.

Low-temperature combustion is a possible form of after-treatment. It converts carbon-rich fly ash into a low-carbon fly ash that is nearly identical to fly ash from combustion. Hence, all applicable utilisation options for fly ash from combustion of biomass can be used.

After-treatment in the form of high-temperature combustion is a technically acceptable way to convert carbon-rich biomass into building material, either directly as a molten and solidified artificial rock, or as a raw material for cement and/or concrete. This conclusion requires confirmation from chemical analysis and leaching tests. The economical perspectives of utilisation options that include high-temperature combustion are not very good. In principle, the ash has enough caloric value to give a substantial contribution to temperature increase needed to reach the temperature where the ashes are molten, e.g. in a smelter. The economics of this kind of process are typically unfavourable. Further investigation into this matter is needed

Controlled leaching is promising after-treatment technique. Technically it is challenging to apply it to the small particles that constitute high-carbon fly ash. The attractive part of the technique is that it removes Cl and alkalis, which are the components that are most often listed as showstoppers for utilisation options. On the other hand, the general understanding is that washing of ash is too expensive

.

Based on the conclusions listed above, high-temperature combustion and controlled leaching are the best selection for further research. Dry screening is not a viable technique. Immobilisation and pelletisation are viable techniques, but not suitable for further technical research. Low-

temperature combustion and consecutive processes are promising, but stay outside the scope of the ECN's part of the GASASH project.

Knowing the progress made by PVO on washing, in fact proving that it is a viable technique, it was concluded that further research efforts should be directed towards the high-temperature combustion of vitrification of high-carbon fly ash from gasification. The decision was made to select high-temperature combustion as the after treatment technique for up scaling in the final year of GASASH with the objective to transform carbon-rich fly ash into a category 1 building material.

The decision to continue with high-temperature treatment is partly based on the expectation that in the future, the gate fees for landfill can only increase. This will improve the economics of vitrification techniques, generally presumed to be difficult. Finding ways to combine utilisation of carbon-rich fly ash with incineration of difficult or hazardous wastes (already with high gate fees) is another way to improve the economics.

3.3.12 Up-scaling of high-temperature combustion

The first step towards up scaling of high-temperature combustion was to make a block of synthetic basalt from AMER-CFB fly ash of more than 1 kg. The block was made in a laboratory furnace. It is the largest size of such a material that can be produced in the ECN laboratories. Alumina was added as a fluxing agent to lower the melting point. It was found that a sufficiently low melting point of 1250-1300°C was obtained when 10% alumina was added (based on the mass of the end product). The synthetic basalt was subjected to a tank leaching test. The preliminary results show that all emissions are below the limits of category 1 building material of the DBMD, i.e. unrestricted used.

In the up-scaled test an amount of 5 kg synthetic basalt was prepared. The conditions reflected the situation of full-scale smelter to such an extent, that it is expected that the end product will be representative with respect to material characteristics. The synthetic basalt was recovered from the smelter pot and broken into particles of 0-40 mm (granulate). The appearance of the material is the same as the lab-scale test: a black, glass-like material. In the large-scale test, part of the material has been spilled over the edge of the ceramic pot, despite the fact that it was filled less than half full and at least 20 cm below the rim. This is certainly an effect that must be investigated in further research on vitrification of ashes from biomass and waste. Further testing of the material is in progress. It is expected to prove that the granulate prepared from the 5 kg sample complies with the requirements of category 1A limit of the DBMD.

3.4 Conclusions from development of new technology (WP 2)

Six forms of after-treatment have been tested using explorative tests. *Dry screening* was found to be capable of producing a small ash fraction with relatively high carbon content and a lower content of contaminants. However, the bulk of the material remains more or less as it is. Techno-economic assessment should determine whether screening out this fraction is attractive for using it as a fuel. *Pelletisation* of the fly ash was found to be possible and produces fuel pellets, which have improved characteristics for logistics and storage. The composition is not changed. Success depends on finding a buyer for the fuel and then deciding whether turning the ash into pellets is useful. *Immobilisation* in a carbonaceous material like C-fix was found to produce building material that can be used in unlimited amounts. It is a technically viable form of after-treatment, which is expected to be applicable to all utilisation options where a water repelling binder is used. Competition from other waste materials is expected. *Low-temperature combustion* was found to be a possible form of after-treatment converting carbon-rich fly ash into a low-carbon fly ash that is nearly identical to fly ash from fluidised-bed combustion with improved potential for utilisation in cement products and with lower costs when land filled. *High-temperature combustion* was found to be a technically acceptable way to convert carbon-rich biomass into building material, either by producing a fly ash similar to coal fly ash or by

vitrification. *Controlled leaching* was found to be a promising after-treatment technique, suitable for removing salts. When the pH is controlled, heavy metals are precipitated and the washing liquid can be disposed at low cost, in particular when discharged to the sea.

Based on the results of the explorative tests, it was decided to concentrate further research in the GASASH Project at ECN on vitrification of the ashes with special attention to co-incineration with other waste streams. The production of vitrified ash from AMER-CFB fly ash with alumina was performed on a 1 kg scale in a laboratory furnace and on a 5 kg scale in a batch reactor. The resulting material can be regarded as synthetic basalt. The preliminary results of a tank test on the 1 kg sample showed that it complies with the requirements of category 1A building material of the Dutch Building Materials Decree, i.e. unlimited use. A test on pilot-scale using 5 kg of material yielded material nearly identical to the material obtained from lab-scale vitrification tests. It was found that processing conditions must be carefully controlled when scaling up, in particular foaming.

4. CHARACTERISATION OF ASHES AND THE DEVELOPMENT OF ASH UTILISATION METHODS (WP 3)

4.1 Introduction

Carbon-rich fly ash from gasification of biomass and waste is a material without established utilisation routes. Objective of this part of the work is to find existing and new utilisation routes for this material. This requires thorough characterisation of fly ash samples and comparisons with the criteria for various utilisation options. This part of the work was done in close co-operation with other partners of the GASASH project. To a large extent the results presented in this work are shared results.

4.1.1 Characterisation

Characterisation of ash samples (from ECN and from other partners) included total composition and leaching behaviour in standardised tests, plus additional tests, e.g. strength test for pellets and particle size distributions. Some characterisation results, e.g., simple chemical analyses of composition, were already presented in the previous chapters, because they were used to determine the effectiveness of various after-treatment methods.

4.1.2 Leaching tests

Various national and international regulations are based on leaching test results. Table 4.1 presents an overview of the leaching tests that were performed in the GASASH project. Leaching characteristics are in essence a reflection of the behaviour of the material in a wet environment. They are used for the assessment of their suitability for various utilisation routes, notably utilisation as (raw material for) building materials and the classification of landfill.

Table 4.1 Overview of samples from WP1 and WP2 subjected to leaching tests

sample	test method
gasification ash using sewage sludge (4 samples)	EN12457-3
carbon-rich AMER CFB fly ash	2 x column test PrEN 14405:2003
carbon-rich fly ash from gasification of demolition wood with or without fines	percolation test NEN 7343*
fly ash of BFB combustion 700°C	2 step compliance test EN12457-3 and pH stat PrEN 14429:2003
simulated coal burner 1450°C	pH stat PrEN 14429:2003
powder at 1100°C	pH stat PrEN 14429:2003
smelt at 1400°C	pH stat PrEN 14429:2003
synthetic basalt with 10% alumina	tank test NEN 7375:2004
C fix block	tank test NEN 7375:2004

* percolation test NEN 7343 is identical to column test PrEN-14405:2003

4.1.3 Comparison of leaching results to limits in established legislation

The leaching results of ash samples were compared to the limits of the European Land Fill Directive (EULFD) and the Dutch Building Materials Decree (DBMD). Comparisons to the EULFD waste acceptance limits were made because it is a European wide accepted standard and enabled international comparison between ash samples from various project partners.

When evaluating materials for landfill, bulk materials are subjected to percolation leaching tests in a column, according to standardised methods PrEN 14405:2003 or NEN 7343. The column

leaching test gives information on the release of contaminants from the ash in time. During the test 10 litre water is percolated through a column of 1 kg material, a liquid to solid ratio of L/S=10. The leachates are analysed and total leached amounts are calculated. The total amounts at L/S=10 are compared to limits from the EULFD as presented in Table 4.2.

Table 4.2 Maximum values at L/S=10 in constituent release for acceptance of waste in 3 categories: inert, non-hazardous and hazardous, according to the European Landfill Directive (2002); data in mg/kg (dry material)

element	inert	non-hazardous	hazardous
As	0.5	2	25
Ba	20	100	300
Cd	0.04	1	5
Cr (total)	0.5	10	70
Cu	2	50	100
Hg	0.01	0.2	2
Mo	0.5	10	30
Ni	0.4	10	40
Pb	0.5	10	50
Sb	0.06	0.7	5
Se	0.1	0.5	7
Zn	4	50	200
Cl	800	15000	25000
F	10	150	500
SO_4	1000	20000	50000
phenol index	1	-	-
DOC	500	800	1000
TDS (Total Dissolved Solids)	4000	60000	100000

When evaluating the potential for utilisation as a bulk building material, compliance tests were done as prescribed by the Dutch Building Materials Decree (DBMD). For bulk materials percolation leaching tests were done according to standardised methods PrEN 14405:2003 or NEN 7343. (The same tests as used for the EULFD.) Results are compared to the limits of the DBMD for a layer of 0.7 metre thickness, see Table 4.3. For shaped materials tank leaching tests were done using standardised method tank test NEN 7375:2004. In this test a sample of monolithic building material is put in a tank filled with water. The water is refreshed after 7 consecutive intervals, each with longer equilibrium time. After 64 days the cumulative concentrations in the leachate can be compared with the Dutch Building Materials Decree. The DBMD limits for category 1 (unlimited use) of shaped material are presented in Table 4.3. In addition, pH stat tests (PrEN 14429:2003) were performed. This pH-dependence test gives information on the behaviour of the ash in various controlled pH conditions. The results can also be used as an indication for compliance to the DBMD by comparison of the emission at the native pH of the material. Furthermore a quick availability test was used which yields maximum leachable amounts using unfavourable conditions. When these concentrations in the leachate are below the Category 1 limits, the material is classified as Category 1 building material and further (expensive, elaborate) testing is not necessary.

The DBMD applies only to end products. The leaching behaviour of ashes using as a raw material in building products, e.g. as filler in cement, is irrelevant. Only the end product must be subjected to compliance tests. The DBMD classifies building materials into two categories. Category 1 is unlimited use; category 2 is utilisation shielded from water (above the highest ground water level and insulated from rainwater.

During the course of the GASASH project, some leaching criteria in the Dutch Building Materials Decree have changed. A general dispensation of 3x the maximum allowable

*im*mission into the soil was granted as of 29th Oct 2004 for Sb, Ba, Mo, Se, V, F and SO_4. Results of leaching tests performed on the ash are compared to these new criteria. The critical elements mentioned in this report may therefore differ from the critical elements identified in earlier deliverables in the GASASH project.

Table 4.3 Limits of Cat. 1 and Cat. 2 applications in the Dutch Building Materials Decree for a layer thickness of 0.7 m and for shaped monolithic building material.

element	DBMD Category 1, layer of 0.7 m thickness	DBMD Category 2, layer of 0.7 m thickness	DBMD Category 1, shaped monolithic materials
unit	mg/kg (dry material)	mg/kg (dry material)	limit in mg/m^2/64days
As	0.88	7	41
Ba	5.5	58	600
Cd	0.032	0.066	1.1
Cl	599	8807	18000
Co	0.42	2.5	29
Cr	1.3	12	140
Cu	0.72	3.5	51
Hg	0.018	0.076	0.43
Mo	0.28	0.91	14
Ni	1.1	3.7	50
Pb	1.9	8.7	120
SO_4	1136	22027	27 000
Sb	0.045	0.43	3.7
Se	0.044	0.1	1.4
Sn	0.27	2.4	29
V	1.6	32	230
Zn	3.8	15	200
Br	2.9	4.1	29
F	13	102	1300
CN (free)	0.013	0.076	1.4
CN (complex)	0.067	0.38	7.1

4.1.4 Development of new and existing utilisation routes

The search for existing utilisation routes and the formulation of new forms of utilisation include direct utilisation as a carbon-rich powder or indirect use after combustion or another form of after-treatment. First, potential ash utilisation routes for further testing were collected. These were critically assessed, which resulted in Deliverable 16 "Report on technically potential gasification ash utilisation options". Subsequently, the most promising routes were selected from the technically potential routes and presented in Deliverable 15 "Identification of the most promising ash utilisation options and ash treatment needed". The public reports (Deliverable 15 and 16) are reproduced in Appendix D and E, respectively. This chapter presents only a summary of Deliverable 15, which was prepared by ECN. Deliverable 16 was prepared by AICIA, but it must be emphasised that all reports had significant contributions from all project partners.

4.2 Characterisation of Fly Ashes

4.2.1 Characterisation of ashes derived from gasification of sewage sludge

Fly ashes from gasification of sewage sludge in ECN's BIVKIN gasifier were collected at different temperatures. The chemical analyses are discussed in Chapter 2. The compositions showed a depletion of certain elements, most notably Cd, in the ash collected at high temperature.

Four fly ash samples were characterised by two-step compliance leaching tests (EN12457-3). The results are compared to the limits of the EULFD and the Dutch Building Materials Decree (DBMD). The general conclusion is that the ashes collected at high temperature have lower levels of leaching of most elements. However, Mo and Se were identified as problem elements in all ash fractions. The leached amounts of Mo and Se make all ash fractions unsuitable as bulk building material. Also, Mo and Se leaching exceeds the level of hazardous waste. Leaching of Hg was not analysed, although it is a known problem element in sewage sludge.

4.2.2 Characterisation of fly ash from gasification of demolition wood with and without fines

Two runs with the pilot-scale 500 kW_{th} gasifier (BIVKIN) were performed in Work Package 1, using demolition wood with or without the finest fraction. Objective of these tests was to investigate whether a small adjustment to the fuel (removal of fines) is having a significant effect on the ash quality. The experimental conditions and the effects on composition of fly ash and bottom ash are presented Chapter 2. With respect to the fly ash, only small differences were found. Major differences are only found in the bottom ash.

Table 4.4 Leaching results (L/S=10) of percolation tests NEN 7343 on fly ash samples from gasification of demolition wood, AMER-CFB fly ash (September 2003) and two BIVKIN runs with and without fines; all data in mg/kg dry basis

element	AMER CFB fly ash (average of 2 tests)	BIVKIN test with fines (0-15 mm)	BIVKIN test without fines (3-15 mm)	DBMD cat 1 [@]	DBMD cat 2 [@]	EULFD non-hazardous	EULFD hazardous
pH	11.3	11.4	11.9				
As	0.02	0.02	0.02	0.88	7	2	25
Ba	151.1	47.4	111.3	16.4	172.7	100	300
Cd	0.0005	0.0005	0.0001	0.032	0.066	1	5
Cr	0.01	0.01	0.01	1.3	12.3	10	70
Co	0.001	0.094	0.022	0.42	2.5	-	-
Cu	0.05	0.18	0.03	0.72	3.5	50	100
Hg	-	-	-	0.018	0.076	0.2	2
Mo	0.56	0.83	1.40	0.85	2.74	10	30
Ni	0.003	0.005	0.016	1.1	3.7	10	40
Pb	764.4	111.9	23.2	1.9	8.7	10	50
Sb	0.66	0.49	0.24	0.045	0.43	0.7	5
Se	0.06	0.05	0.03	0.14	1.28	0.5	7
Sn	0.005	0.003	0.005	0.27	2.4	-	-
V	0.008	0.009	0.003	4.7	96.9	-	-
Zn	11.77	0.52	7.05	3.8	14.7	50	200
Br	35.4	58.8	42.8	2.9	4.1	-	-
Cl	10100	24014	16753	240	8807	15000	25000
F	22.14	-	-	39	306	150	500
SO_4*	3289	8494	3493	1728	22027	20000	50000

* indicative based on the assumption that all S (measured by ICP-AES) is present as SO_4
[@] maximum allowed emission for granular materials with an assumed application height of 0.7 m

The results of leaching tests of the fly ash samples are presented in Table 4.4. The data from percolation tests at L/S=10 (NEN-7343) of BIVKIN demolition wood "with fines" and BIVKIN demolition wood "without fines" are compared to the data from AMER-CFB fly ash. Generally, lower leaching amounts are found when the fines are removed, but the differences are not dramatic and exceptions exist, notably Ba and Zn. The amount of Pb leached from the ash without fines is below EULFD criteria for hazardous waste, but still above the limit for category

2 of the DBMD. For Ba and Zn, the release from the sample without fines is higher than from the sample with fines. The observed phenomena are complex and not well understood. The pH is also playing an important role. A comparison with AMER-CFB fly ash is difficult; there is no match between AMER-CFB fly ash and BIVKIN fly ash with or without fines.

In any case, it can be concluded that removal of the finest fuel fraction is not improving the fly ash quality very much. The second conclusion is that differences between ash fractions from two installations, both fired with demolition wood are larger than the differences between fly ashes from one installation with or without fines in the fuel.

4.2.3 Characterisation of fly ash samples of EEP's 80 MW_{th} gasifier

The fly ash derived in a singular batch in 2003 from EEP's full-scale gasifier was characterised by means of a column percolation test (in duplicate), performed according to the draft European standard PrEN 14405. The ash was also subjected to batch pH dependence test, described in the draft European standard PrEN 14429.

Table 4.5 presents cumulative release of relevant elements (except SO_4, Hg, F, CN free and CN complex) from EEP's gasification fly ash and the criteria of the EULFD and the DBMD. A comparison to the DBMD shows that the Cat. 1 limits (at a layer thickness of 0.7 m.) are exceeded for: Ba, Cl, Pb, Mo, Sb, Se, Zn and Br. The cat. 2 limits are exceeded for: Ba, Cl, Pb, Zn and Br. This demonstrates that this carbon-rich fly ash cannot be directly used as bulk building material. Largest bottleneck is Pb, a known problem element in demolition wood originating from old paint and from fragments of metallic lead (slabs and pipes) that remain in demolition wood.

Table 4.5 Cumulative release (PrEN 14405) of constituents (L/S=10) from gasification fly ash of demolition wood compared to the EULFD acceptance criteria of non-hazardous and hazardous waste and limits of Cat 1. and Cat 2. applications in the Dutch Building Materials Decree for a layer thickness of 0.7 m; data are in mg/kg (dry material)

element	release from fly ash	DBMD Category 1	DBMD Category 2	EULFD non-haz. waste	EULFD hazardous waste
As	0.020	0.88	7	2	25
Ba	151.14	5.5	58	100	300
Cd	0.0005	0.032	0.066	1	5
Cl	10100	599	8807	15000	25000
Co	0.0013	0.42	2.5	-	
Cr	0.007	1.3	12	10	70
Cu	0.046	0.72	3.5	50	100
Hg	-	0.018	0.076	0.2	2
Mo	0.56	0.28	0.91	10	30
Ni	0.003	1.1	3.7	10	40
Pb	764.4	1.9	8.7	10	50
SO_4	-	1136	22027	2000	50000
Sb	0.658	0.045	0.43	0.7	5
Se	0.063	0.044	0.1	0.5	7
Sn	0.0052	0.27	2.4	-	-
V	0.0082	1.6	32	-	-
Zn	11.77	3.8	15	50	200
Br	35.38	2.9	4.1	-	-
F	-	13	102	150	500
CN (free)	-	0.013	0.076	-	-
CN (complex)	-	0.067	0.38	-	-

Lead release also exceeds the limit of hazardous waste of the EULFD. Barium release is also high and exceeds non-hazardous waste limits. Other elements, like Cr, As, Cu and Zn do not lead to increased leached concentrations, despite relatively high total concentrations. This means that the ash cannot be accepted at any landfill site and needs some kind of after-treatment that lowers leaching of Pb and preferably also Ba. In addition, it is prohibited to land fill high calorific waste. Carbon-rich fly ashes with caloric values comparable to wood, will certainly be excluded from landfill for this reason.

Figure 4.1 shows the pH dependent release of Pb from demolition wood derived fly ash. The Pb release reaches a minimum at pH=10. The natural pH of the EEP's gasification fly ash in an aqueous solution is pH=12.5), resulting in an increased mobility of Pb and Zn. Lowering the pH to about 10, will decrease the release of lead significantly to approximately 1 mg/kg dry material. This would solve any problems regarding leaching of Pb, because it is below the limit of Category 1 building material.

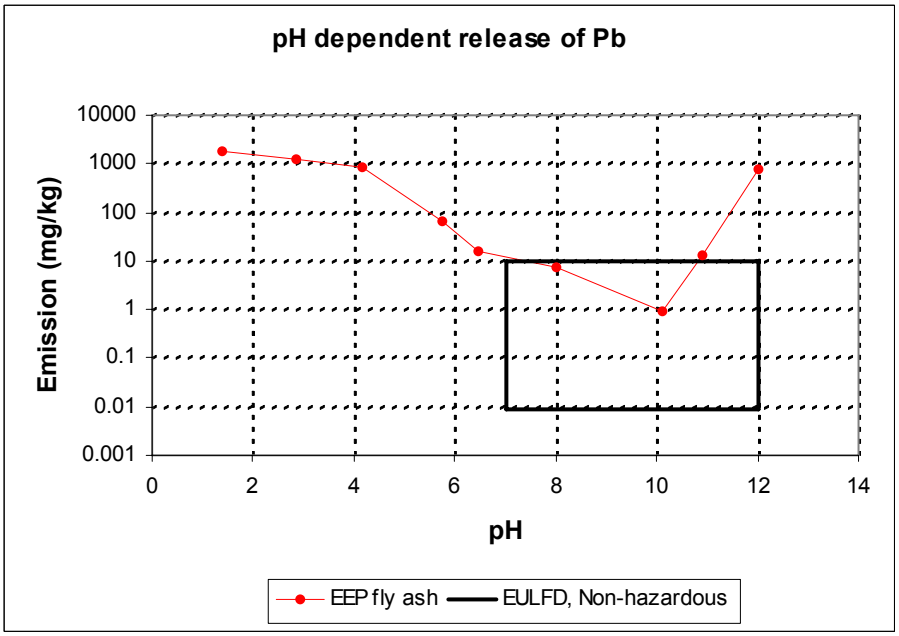


Figure 4.1 pH dependent release of lead (Pb) from gasification fly ash of demolition wood in leaching test (PrEN 14429)

The graph in Figure 4.1 demonstrates clearly that total concentration of a component cannot be used as an indication for the release in leaching tests. Contaminant release is driven by a several interacting forces: pH conditions, redox conditions, chemical speciation and mineral solubility. Only for alkali and halogenides the total composition is well correlated to the leaching behaviour. Chlorine, sodium and potassium are released easily in the leaching tests but most other elements are retained and do not leach to a great extent from the ash.

Cr release complies with the European Landfill Directive limits (2002) of non-hazardous waste, despite the high total Cr levels in the ash. This is caused by the redox state of the ashes after the gasification process. Chromium is present as Cr(III), rather than the oxidised Cr(VI) form, which is much more mobile at high pH conditions.

Based on these leaching results it is not likely that EEP's high-carbon fly ash will be used directly as building material. This is not a problem, because the physical characteristics make it unattractive (if not impossible) to use this fine powder as a building material. The material can be used as a component in the manufacture of building materials. Only the leaching characteristics of the end product must be compared to the limits of the DBMD for compliance.

4.2.4 Ash characteristics after combustion at low temperature

Leaching characteristics of AMER-CFB fly ash combusted at 700°C in a BFB were tested using the European Standard EN12457-3. Results can be compared directly to the European Landfill Directive standards and Dutch Building Materials Decree, as presented in Table 4.6.

Table 4.6 Cumulative release of constituents (L/S=10) from gasification fly ash of demolition wood in mg/kg dry matter, compared the European Landfill Directive (EULFD acceptance criteria of non-hazardous and hazardous waste and to the limits of cat 1 and cat 2 applications in the Dutch Building Materials Decree (DBMD) for a layer thickness of 0.7 m; data in mg/kg (dry material)

element	release from carbon-rich fly ash	release from combusted fly ash	DBMD Cat. 1	DBMD Cat. 2	EULFD non-haz. waste	EULFD hazardous waste
As	0.020	0.0095	0.88	7	2	25
Ba	151.14	1.848	5.5	58	100	300
Cd	0.0005	0.0005	0.032	0.066	1	5
Cl	10100	14155	599	8807	15 000	25 000
Co	0.0013	0.001	0.42	2.5	-	
Cr	0.007	22.5	1.3	12	10	70
Cu	0.046	0.002	0.72	3.5	50	100
Hg	-	-	0.018	0.076	0.2	2
Mo	0.56	10.96	0.28	0.91	10	30
Ni	0.003	0.002	1.1	3.7	10	40
Pb	764.37	4.718	1.9	8.7	10	50
SO_4	-	-	1136	22027	20 000	50 000
Sb	0.658	0.247	0.045	0.43	0.7	5
Se	0.063	0.152	0.044	0.1	0.5	7
Sn	0.0052	0.152	0.27	2.4	-	-
V	0.0082	0.0025	1.6	32	-	-
Zn	11.77	0.003	3.8	15	50	200
Br	35.38	66	2.9	4.1	-	-
F	-	-	13	102	150	500
CN (free)	-	-	0.013	0.076	-	-
CN (complex)	-	-	0.067	0.38	-	-

The test on low-carbon fly ash demonstrated a change in pH from pH=12.4 to pH=10 compared to original, carbon-rich fly ash. This resulted in a strongly reduced mobility of lead (Pb). The release of Pb is within the non-hazardous waste limits of the European Landfill Directive. The leaching of Pb is also below the Cat. 2 limit of the DBMD, but - unfortunately - it is still above the Cat. 1 limit.

The change in redox conditions was clearly illustrated by a strongly enhanced release of Cr, now exceeding the EULFD limits for non-hazardous waste. This increase in mobility of chromium (Cr) was expected, because hexa-valent Cr formed after oxidation is more mobile than tri-valent Cr. Carbon-rich fly ash has no problem with leaching of Cr. The release of Cr stays within limits of hazardous waste acceptance criteria, but exceeds the limits for Cat. 2 of the DBMD. The same applies to molybdenum (Mo). Finally, it was found that chlorine release is increased (compared to carbon-rich fly ash) to levels close to the limits of hazardous waste.

The overall conclusion is that combustion at 700°C in a BFB can improve the quality of fly ash, because its classification in terms of the EULFD is improved. Low-carbon fly ash does not comply to the requirements of category 2 of the DBMD making it still unfit for utilisation as a bulk building material, but it can be used as a raw material for building materials, e.g., cement products, because only the leaching behaviour of the end product is relevant for the DBMD. In

the manufacture of cement and concrete, potential Cr leaching is a known problem and measures exist to immobilise Cr in the end product. Also, the total concentration of hexa-valent Cr in the dry mixture must be below 2 ppm.

4.2.5 Characterisation of fly ash after combustion at high temperatures

Three samples from ashes prepared by high temperature combustion of AMER-CFB fly ash (in WP 2) have been subjected to pH stat leaching tests. The ashes were subjected to pH stat leaching tests. The equilibrium concentrations at a fixed pH have been determined. The results at a pH closest to the natural pH of the material are summarised in Table 4.7. These values are compared to the leaching behaviour of the original gasification ash and the limits for the Dutch Building Materials Decree and the EU Landfill Directive.

Table 4.7 Cumulative release of constituents (L/S=10) from ash samples prepared by high-temperature combustion of gasification fly ash of demolition wood, compared the European Landfill Directive (EULFD acceptance criteria of non-hazardous and hazardous waste and to the limits of cat 1 and cat 2 applications in the Dutch Building Materials Decree (DBMD) for a layer thickness of 0.7 m; data in mg/kg (dry material)

element	release from ash from simulated coal burner (LCS)	release ash combusted at 1100°C	release of ash from smelt at 1400°C	DBMD Cat. 1	DBMD Cat. 2	EULFD non-haz. waste	EULFD haz. waste
Leaching test	CEN test at L/S=10	L/S=10 in pH stat test at natural pH	L/S=10 in pH stat test at natural pH				
pH	11.5	8.5	7.5				
As	0.02	0.43	0.15	0.88	7	2	25
Ba	4.9	3.9	3.2	16.4	172.7	100	300
Cd	0.0004	0.00025	0.0001	0.032	0.066	1	5
Cl	4860	*	< 12 *	240	8807	15 000	25 000
Co	0.003	0.0002	0.01	0.42	2.5	-	
Cr	**42.5**	0.03	0.22	1.3	12.3	10	70
Cu	0.022	0.0011	0.045	0.72	3.5	50	100
Hg	-	-	-	0.018	0.076	0.2	2
Mo	**3.56**	0.12	0.17	0.85	2.74	10	30
Ni	0.0001	0.01	0.03	1.1	3.7	10	40
Pb	0.05	0.0036	0.007	1.9	8.7	10	50
SO_4 (#)	1100	218	40	1728		20 000	50 000
Sb	1.42	0.019	0.132	0.14	1.28	0.7	5
Se	0.061	0.0014	0.0271	0.13	0.3	0.5	7
Sn	0.0044	0.0022	0.0044	0.27	2.4	-	-
V	0.016	0.034	0.042	4.7	96.9	-	-
Zn	0.007	0.001	0.539	3.8	14.7	50	200
Br	7	0.45	2	3.47	44.2	-	-
F	-	0.48	0.6	39		150	500

* chloride not reliable; total Cl content of sample below DBMD cat. 1 limit
# indicative based on the assumption that all S is present as SO4

Fly ash from combustion in a simulated coal fired burner (LCS) has a series of elements that are leached at too high concentrations: Cr and Mo exceed the limits for category 2 of the DBMD, which means that it cannot be used as building material. It can still be used as a raw material for building materials. In particular, it should be considered to use it in the same way as powder coal fly ash or comparable applications

The powder resulting from slow combustion of ash at 1000°C shows very good leaching behaviour. All emissions are below the category 1 limits of the DBMD, which means that it can be used in unlimited quantities. This result also indicates that materials prepared at even higher temperatures are also likely to comply with cat. 1 of the DBMD, giving good perspectives for samples prepared.

The smelt sample prepared at 1400°C was ground to a very fine powder and tested at its natural pH=7.5. Under these conditions, all elements were still below the category 1A limits of the DBMD. Antimony - although below category 1 limits - is the critical component in this material. It can be expected (also based on the leaching results of the powder prepared at 1000°C) that the leaching of Sb will be lower when the material is used as a shaped building block or in bulk at a much larger particle size, e.g. as granulate 0 - 40 mm. It can be safely predicted that under these more favourable conditions material prepared by smelting at 1400°C will comply with the limits of category 1A of the DBMD, i.e. unlimited use.

These results can be compared to the leaching characteristics (EN12457-3) of the low-carbon fly ash produced by combustion of AMER-CFB fly ash in a laboratory BFB unit at 700°C. Leaching of Pb is below the Cat. 2 limit of the DBMD, but still above the Cat. 1 limit; Cr leaching is very high, exceeding the EULFD limits for non-hazardous waste, which is the result of presence of highly mobile hexa-valent Cr formed after oxidation; Cl release is close to the limits of hazardous waste.

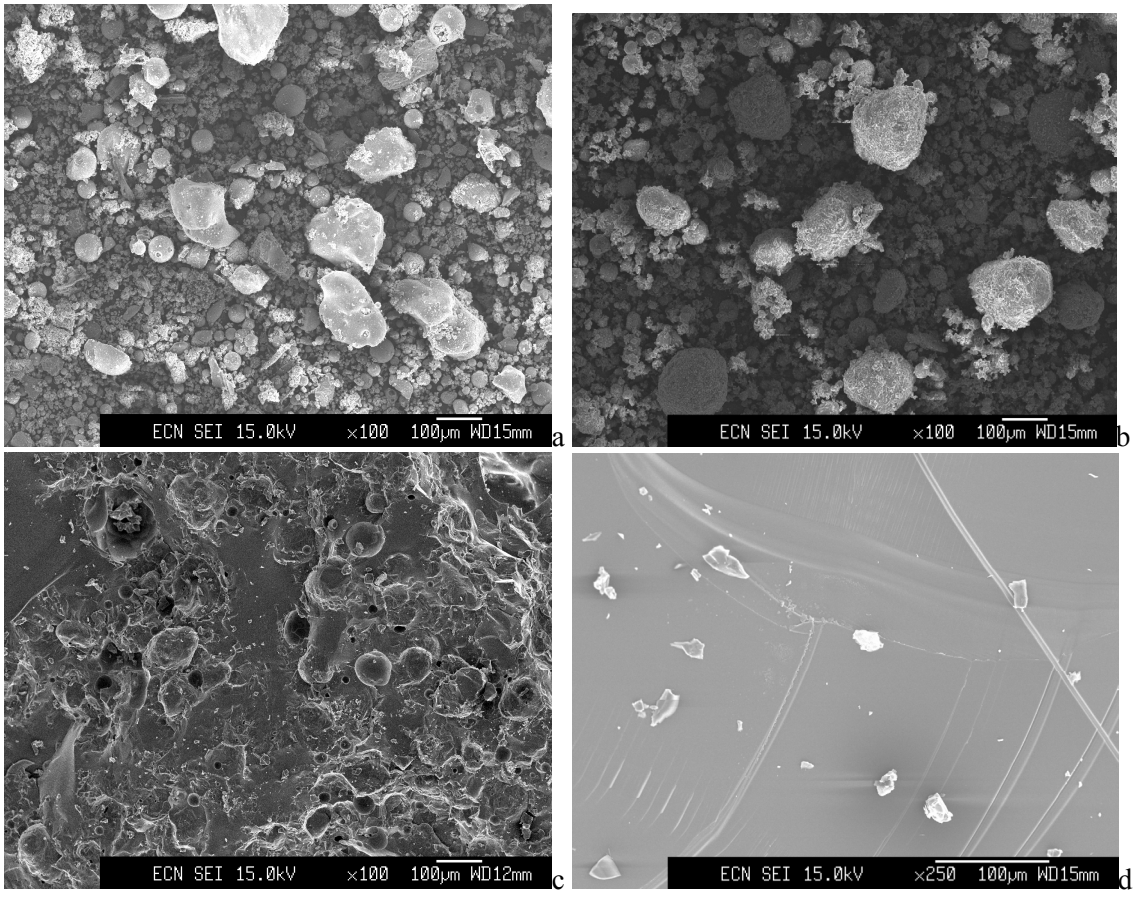


Figure 4.2 SEM pictures of fly ash samples from high-temperature combustion of AMER-CFB high-carbon a) in a simulated coal burner at 1400°C, b) powder in crucible at 1100°C, c) smelt in crucible at 1400°C, d) smelt in crucible at 1550°C

The SEM photographs (Figure 4.2) clearly illustrate that with high temperature treatment, the surface area is greatly reduced. When the vapour containing heavy metals and chloride is removed during heat treatment, or when ashes are extracted at elevated temperature, a nice and clean product is obtained that can be used as building material or in the manufacture of building materials.

The overall conclusion is that combustion improves the quality of fly ash, because its classification in terms of the EULFD is improved. For bulk utilisation, high temperature treatment at 1000°C or more is needed; fly ash from BFB combustion at 700°C does not comply with the requirements of the DBMD. It appears to be the case that when sufficiently high temperature is reached, the exact form of combustion is not relevant.

4.2.6 Characterisation of C-Fix block

Carbon-rich ash from gasification of biomass, can be used as a filler material in the manufacture of C-Fix building blocks. EEP's fly ash from a full-scale CFB gasifier have been applied to produce two C-fix test blocks. One of the blocks also fulfilled the requirements for compressive and flexural strength. For acceptance as a building material, it must also comply with the DBMD for 'shaped' materials. Therefore, the block was subjected to a tank leach test (NEN 7375). The cumulative concentrations in the leachate are presented in Table 4.8 and compared to the Dutch Building Materials Decree. From the leaching tests it was concluded that a C-fix block made with gasification fly ash is acceptable as building material category 1A, which means that it can be used without restrictions in unlimited quantities.

Table 4.8 Constituent release (mg/m^2/64 days) from C-fix material compared to limit values for eluate concentrations in shaped monolithic building materials in a category 1 application in the Dutch Building Materials Decree (DBMD).

element	DBMD Cat. 1	Cumulative release C-fix sample (L/S=10)
As	41	0.86
Ba	600	21.4
Cd	1.1	0.041
Cl	18000	3605
Co	29	0.037
Cr	140	2.34
Cu	51	0.17
Hg	0.43	-
Mo	14	0.82
Ni	50	0.21
Pb	120	0.88
SO_4	27 000	-
Sb	3.7	0.38
Se	1.4	0.35
Sn	29	0.091
V	230	0.071
Zn	200	3.52
Br	29	24.7
F	1300	-
CN (free)	1.4	-
CN (complex)	7.1	-

4.2.7 Characterisation of synthetic basalt

A block of about 1 kg synthetic basalt was produced from 90% AMER-CFB ash heat treated at 1000°C and 10% alumina. The block was subjected to a tank leaching test (NEN 7375). The results presented in Table 4.9 show clearly that leaching is well below the limits of category 1 building material of the DBMD, i.e. unrestricted used.

Table 4.9 Results from a tank test on 1 kg sample synthetic basalt (90% AMER-CFB fly ash and 10% alumina)

ELEMENT		**E(64d)**	**calculated immission (I_c)**		**I_{max}**	**Result:**
1. Metals		**[mg/m^2]**	**catg.1A**	**catg.1B/2**	**[mg/m^2]**	
Antimony	Sb	0.69	7.2	2.3	117	catg.1A
Arsenic	As	0.4	5	1	435	catg.1A
Barium	Ba	0	4	1	18900	catg.1A
Cadmium	Cd	0.04	0.4	0.1	12	catg.1A
Chromium	Cr	0	0	0	1500	catg.1A
Cobalt	Co	0.1	1	0	300	catg.1A
Coper	Cu	4.3	45	14	540	catg.1A
Mercury	Hg	--	--	--	4.5	--
Lead	Pb	0.5	5	2	1275	catg.1A
Molybdenium	Mo	0.07	1	0	450	catg.1A
Nickel	Ni	0.5	5	2	525	catg.1A
Selenium	Se	0.87	9.1	2.9	45	catg.1A
Tin	Sn	0.2	2	1	300	catg.1A
Vanadium	V	0.1	1	0	7200	catg.1A
Zinc	Zn	6	58	18	2100	catg.1A
2. Other inorganics						
Bromide	Br	--	--	--	90	--
Chloride	Cl	29	48	15	30000	catg.1A
Fluoride	F	--	--	--	42000	--
Sulfate	SO4	--	--	--	135000	--

Table 4.10 Results from availability test on 5 kg sample of synthetic basalt

ELEMENT		**U^*_{bes}**	**Test against**	**Result**
Metals		**[mg/kg]**	**I_{max}**	
Antimony	Sb	18.82	*> Imax*	NOT APPLICABLE
Arsenic	As	3.3	*> Imax*	catg.1A
Barium	Ba	27	*catg.1*	catg.1A
Cadmium	Cd	0.01	*catg.1*	catg.1A
Chromium	Cr	0	*catg.1*	catg.1A
Cobalt	Co	43.5	*> Imax*	NOT APPLICABLE
Copper	Cu	40.5	*> Imax*	NOT APPLICABLE
Mercury	Hg	--	--	--
Lead	Pb	0.6	*catg.1*	catg.1A
Molybdenium	Mo	0.36	*catg.1*	catg.1A
Nickel	Ni	11.3	*> Imax*	catg.1B
Selenium	Se	0.01	*catg.1*	catg.1A
Tin	Sn	0.0	*catg.1*	catg.1A
Vanadium	V	0.1	*catg.1*	catg.1A
Zinc	Zn	15	*> Imax*	catg.1A
Other inorganics				
Bromide	Br	--	--	--
Chloride	Cl	113	*catg.1*	catg.1A
Fluoride	F	--	--	--
Sulfate	SO4	50	*catg.1*	catg.1A

The material, produced in the 5 kg test was subjected to a quick availability test, a leaching test on finely ground material, done at pH=7 and pH=4. This resulted in compliance to criteria for category 1A building material, with exception of Sb, Ni, Co and Cu, see Table 4.10. The increased leaching of these four is the result of the very unfavourable conditions in the availability test (Sb, Ni and Cu) or an artefact (Co). Antimony is the only element that may cause real problems in compliance tests (DBMD), but comparing with the results of the tank test of the 1 kg sample, it can be concluded that it is highly probable that the material of the 5 kg

smelt, when tested in a tank test (block) or in a percolation test (granulate 0-40 mm), will pass without difficulty and comply to the requirements of category 1A limit of the DBMD.

4.2.8 Effect of pH control on leaching of Pb and other elements in washing of ashes

From the leaching tests, it became clear that in the case of ashes from demolition wood, Pb and other heavy metals are problematic elements. The pH of the leachate is a crucial factor in the release of these elements. Therefore, in the washing of ashes, pH control is an extra parameter that enables the release or retainment of heavy metals.

The results of the column leaching test at a liquid to solid (L/S) ratio of 10 show that the cumulative release of Pb exceeds the limits of acceptance at a landfill for hazardous waste. The high release of lead is caused by the nature of the material (Pb is a constituent in paint). The pH of the EEP's gasification fly ash in an aqueous solution is very high (pH=12.5), indicating a very high mobility of Pb. Figure 4.3 shows the pH dependent release of Pb from demolition wood derived fly ash. The Pb release reaches a minimum at pH=10. It can be concluded that when the pH is reduced from 12.5 to around pH=10 the release of lead would decrease immensely (by approximately a factor 1000) and the fly ash would then comply with non-hazardous waste limits.

Zinc displays a similar leaching behaviour, i.e. a minimum around pH=10. For Ba, the emission is less dependent on pH, but in Figure 4.3 a maximum is found at pH=12. Lowering the pH to 10-11 will lower the release of Ba to about 40 mg/kg, which is below the EULFD non-hazardous waste limit and the DBMD Cat. 2 limit. The only element that may cause problems when the pH is lowered is Sb, which is below all limits at pH=12, except DBMD cat. 1, but it exceeds DBMD cat. 2 and EULFD non-hazardous waste limit at pH=11 and lower.

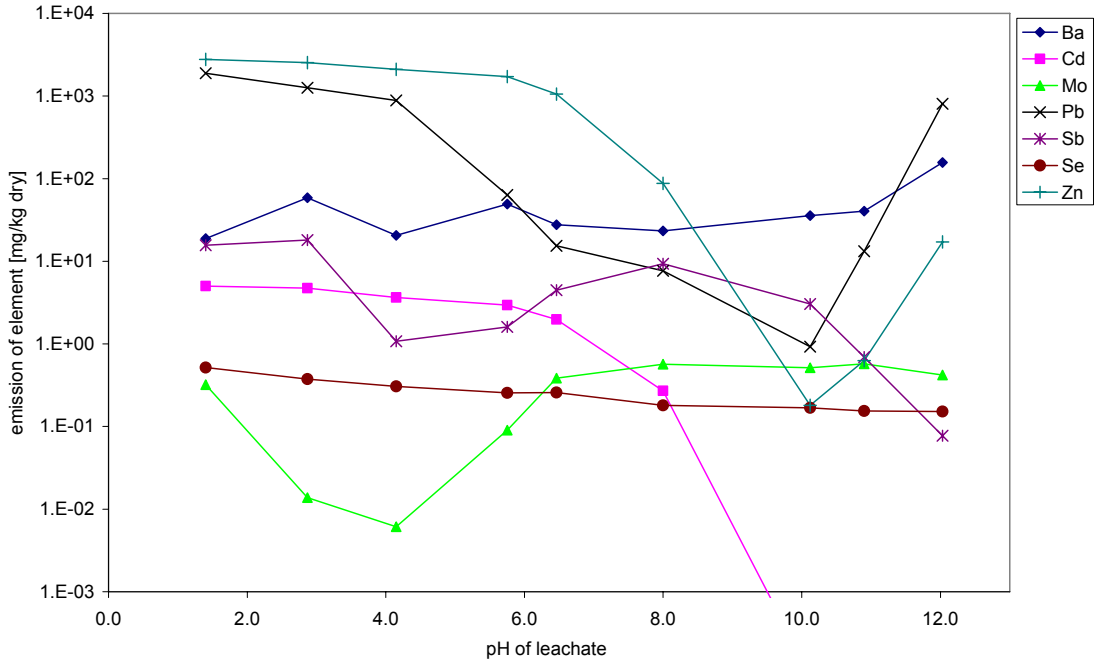


Figure 4.3 pH dependent release of several elements from gasification fly ash of demolition wood in pH dependence leaching test (PrEN 14429).

From the pH controlled leaching behaviour, it was concluded that bringing the natural pH of the material in the range of 10 to 11 should make land filling of the ashes easier. Emission of Pb, Ba and Zn decrease. However, leaching of Sb might become a problem. Improvements towards utilisation as building material are less relevant.

For washing of ashes, it was concluded that pH control in a range of 10-11 minimises the release of heavy metals. Low metal content improves the quality of the water and may enable discharge in sewer systems.

4.3 Utilisation Options for Carbon-rich Fly Ash

The bulk of fly ash can - in general - be utilised in three ways: building material, fertiliser or fuel (only for carbon-rich fly ash). In this section, the potential for bulk utilisation of carbon-rich fly ash from EEP's CFB gasifier are discussed and criteria that apply to the Netherlands are used. For other ashes and other countries, the results may be different. Niche applications are discussed briefly as well.

4.3.1 Building material

Utilisation as bulk building material, according to the Dutch Building Materials Decree DBMD is limited by the leaching. In the case of carbon-rich fly ash produced from demolition wood, Ba, Cl, Pb, Zn and Br prevent direct utilisation (see above). Application as a bulk building material is also limited by the physical properties of the ashes. Contrary to the CFB and MSWI bottom ashes that are often used as a replacement for sand in construction works, the gasification ash is very fine, powdery substance. It was never the objective to use it directly. One way of using it as a component in building material is presented in the preceding section (C-fix). Other options are under investigation.

4.3.2 Fertiliser

In principle, carbon-rich fly ash from gasification can be used as a fertiliser. It contains nutrients, K, Ca and S. In the Netherlands, when a material is used as a fertiliser, it must be listed on the "Meststoffenlijst"; the list of approved fertilisers. Applicability of a material to be used as a fertiliser is based on assessment of nutrients content versus contaminants. The applicability of combustion fly ashes from clean wood in the Netherlands has been assessed (NMI, 2003, confidential report). The nutrient value of a material is determined from the total or available content of N, P, K, Ca, S and other elements, resulting in a minimum required load (in kg per hectare per year). The environmental impact is calculated from the total contents of Cd, Cr, Cu Hg, Ni, Pb, Zn and As, and maximum limits of the Dutch regulations for agricultural use of sewage sludge (the Dutch Decree of Other Organic Fertilisers), resulting in a maximum allowed load. Only when the maximum allowable load exceeds the minimum required load a material can be allowed as a fertiliser.

In the fly ash from combustion of clean wood the nutritious elements were found to be Ca (varying between 12-15 %) and K (over 30%). Other elements were not regarded as nutrients since their concentrations were too low. Unfortunately, contaminants were present in such concentrations that the maximum allowed load was in all cases well below the minimum required load. In practice the Cd content is the limiting factor. Acceptance of other biomass ash from combustion of wood on the list of approved fertilisers is highly unlikely. Only for specific fuels, e.g. chicken litter, a potential for utilisation as fertiliser exists.

Gasification ash from demolition wood contains too many contaminants compared to nutrients. Also in this case, the ratio of nutrients to contaminants is not high enough. Another reason may be that the ash is a black powder that stains the environment. In other countries the situation may be different, in particular in locations where the soil is significantly depleted of carbon.

4.3.3 Fuel

Given the fact that the carbon-rich ash has a significant caloric value, utilisation as fuel is the most obvious solution. It is important to keep in mind that the ash contains relatively large amounts of pollutants, so combustion facilities must have adequate flue gas cleaning. Also, combustion will produce a certain amount of ash for which (again) a solution must be found.

The key questions are to find a buyer for the ash, establish a price and find a solution for the combustion ash. ECN has approached several potential buyers and is discussing their needs. The ash residues after combustion of the gasification ashes are presented in the next paragraph.

4.3.4 Niche applications

For small ash volumes, niche applications are possible. These will always depend on specific combinations of ash characteristics and utilisation criteria. E.g., ash from combustion of chicken litter may be used for certain kinds of fertiliser. Ashes that can bind considerable amounts of water can be used in fire retarding materials. And particular combinations of carbon-rich ashes and other waste materials may be used to make synthetic basalt, fire-proof stones or insulation materials.

4.4 Most promising routes for utilisation of gasification ashes

ECN collected information from all project partners to identify the most promising routes for utilisation of gasification ashes were identified. Only a summary is presented here. A thorough discussion is presented in Appendix D.

The various forms of utilisation, emerging from the GASASH project, were technically verified to be viable: Does the ash quality fulfil known criteria? Then the options were ranked using the EU Strategy for Waste Management of 1989 (SEC(89) 934 Final 1989) as illustrated by Figure 4.4. Reuse, including utilisation as a fuel has a high priority, disposal is low on the ladder.

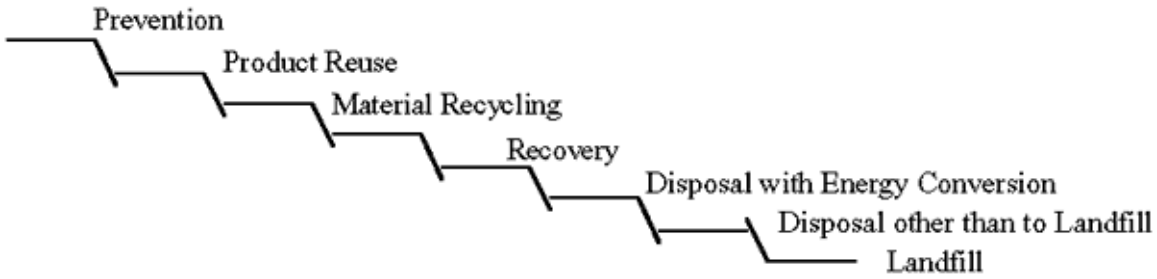


Figure 4.4 Preferences for Waste Treatment

Utilisation options for gasification ashes were divided into at least 6 categories with a hierarchy in ranking:

- Direct application/utilisation of the material without treatment
- Direct application/utilisation of the material with pre-treatment
- Use as a raw material/utilisation as component without prior treatment
- Use as a raw material/utilisation as component with prior treatment
- Disposal with energy recovery
- Alternative disposal (other than landfill)

Putting "direct application/utilisation of material with pre-treatment" hierarchically above "use as a raw material/utilisation as component without prior treatment" is open for discussion.

The conclusions were, that based on the available data, the following utilisation options may be regarded as the most promising routes for the carbon-rich fly ashes that have been investigated with the GASASH project:

- Direct application as an alternative fuel
- Filler in asphalt or asphalt-like products
- (Lightweight) aggregates
- Filler/binder in concrete mortars after low temperature treatment (combustion)
- High temperature treatment for the production of category 1 building material

Potentially promising utilisation options are

- Solidification/stabilisation of waste
- Component in manufacture of fire proof plates

Some form of after-treatments may be found attractive. Always the (economic) advantages and disadvantages of after-treatment must be balanced against direct utilisation. The most promising forms of after-treatment are

- Washing to remove chloride (and alkali)
- Heat-treatment to lower carbon-content

It should be noted that these routes are not "most promising" for all ashes and all fuels, but generalised suggestions based on the technical potential of the routes. The following issues should always be included the discussion:

- Different routes are the optimal alternative for different fuels, depending on specific characteristics of the ashes.
- Routes become more or less attractive, depending on local conditions. In particular gate fees and emission regulations for combustion.
- Lucky matches may always be found outside the presented selections, e.g., gasification ash from chicken litter utilised in manufacture of fertiliser.

The most promising routes, among several others were used for the techno-economic evaluation done by PVO.

5. TECHNO-ECONOMIC EVALUATION (WP 4)

Potential options for utilisation of carbon-rich fly ash from gasification of biomass and waste have been identified in the previous chapters. The most promising routes have been selected and were used in a techno-economic evaluation. This work was performed by PVO after collecting information from all project partners. Their work resulted in a confidential report (Deliverable 18&19) with extensive information and details on the technical and economic feasibility of the various utilisation routes. In addition, a public report (Deliverable 20) was prepared on the influence of optimised ash management on the economy of the gasification process. This Deliverable is reproduced in Appendix G. Since ECN made limited contributions to the techno-economic evaluation, only the main conclusions are presented here:

- For fly ash, utilisation as fuel emerged as being not only technically, but also economically most attractive, although net profit of this form of utilisation is about zero.
- For bottom ash, recovery of metals is most economic. It is even possible to make a profit.
- Utilisation in asphalt and asphalt-like products is attractive in those cases where fly ash is not replacing other waste products as a filler. Unfortunately, in the Netherlands, residues from waste incineration are used in this particular application, which have a negative value. When similar costs are involved when using gasification ashes it is not an economically attractive route.
- Oxidising smelting followed by use as aggregate was identified as the most expensive of the forms of utilisation that have been investigated. The costs figures of € 200-350 per ton are based on existing processes for smelting oxidised ashes, notably the processes used in waste management in Japan. However, ECN's point of view is that carbon-rich gasification ashes should not be equalled to oxidised ashes from waste incineration. In ECN's view, carbon-rich ashes can be utilised in smelting processes making use of its caloric value, thus replacing a large part of the fuel needed in smelting processes, hence providing a substantial cost reduction. Preferably, the gasification ash should be combined with other waste materials to optimise the manufacture of synthetic basalt (viscosity, melting point, etc.). This is different from the Japanese processes. Recently, the final report[4] of a project on smelting of biomass and waste residues has been published outlining this vision. Calculations done in the framework of that project yielded costs in the order of €100 per ton ash, including costs for flue gas cleaning. Unfortunately, this view was not shared by most partners, who insisted on using economic data of established processes.

[4] Boersma, A.R., Pels, J.R., Oudhuis, A.B.J. en Lotens, J.P., "Smelten van biomassa-reststromen en afval tot (duurzame) energie en grondstoffen: een onderzoek naar mogelijke brandstofmengsels en een smeltervoorontwerp", ECN Report ECN-C--06-013

6. CONCLUSIONS

The GASASH Project has made clear that fly ash from gasification of biomass and waste is difficult material for utilisation and no obvious or universal solutions have been found. In this chapter, specific technical conclusions from ECN's part of the GASASH project are presented together with general conclusions from the overall project regarding the economics. Finally, an outlook or strategy for management of gasification fly ashes is given for the situation in the Netherlands.

6.1 Technical and economical conclusions

Technical conclusions on optimisation of the gasification process:

- Practical measures manipulating the parameters of existing gasification plants cannot increase the burnout level of gasification ash to a level, where the ash can be directly used in the same application as for fly ash of coal combustion. Significant changes in the design of the gasifier may accomplish this goal, but those are still in an early stage of development.
- Removal of the smallest fraction (0-3 mm) of demolition wood used as a fuel does not significantly influence the fly ash quality. Bottom ash has much less debris when the smallest fraction is removed.
- When sewage sludge is used as fuel, the inorganic components from sewage sludge dominate the ashes. Mixing with clean wood can influence gasification behaviour, but does not have a significant influence on ash composition.

Technical conclusions on after-treatment and the development of new techniques:

- Various after-treatment techniques can be employed to improve ash characteristics. *Dry screening* can separate a small ash fraction with relatively low content of contaminants, but the bulk of the material cannot be treated this way. *Pelletisation* can significantly improved logistics. *Immobilisation* in carbonaceous material like C-fix was found to produce building material that can be used in unlimited amounts. *Low-temperature combustion* converts carbon-rich fly ash into a low-carbon fly ash that is nearly identical to fly ash from combustion. *High-temperature combustion* is a technically acceptable way to convert carbon-rich biomass into building material that can be used in unlimited amounts. *Controlled leaching* can be used to remove chlorine and alkali salts; heavy metals are largely retained.
- Prospects for implementing the strategy of "staged cooling and particle removal" in gasification are not good enough to design a new plant with such a system in place.

Technical conclusions on the search for new and existing utilisation routes:

- Fly ashes with a high carbon content should preferably be utilised as a fuel. There are applications possible, where the calorific value of the remaining combustible material is valued, e.g. co-firing in coal-fired plants, smelters or cement kilns.
- Direct utilisation as building material is possible for bottom ash.
- Direct utilisation of carbon-rich fly ash is unlikely. Technically, it is not an attractive material and in case of fly ash from demolition wood, it does not comply with limits of the Dutch Building Materials Decree (DBMD). After combustion, oxidised fly ash may be used directly as building material, e.g., in road construction, when the ash characteristics comply with the criteria of the DBMD.
- Indirect utilisation as building material is possible for carbon-rich fly ash in asphalt and asphalt-like products (e.g. C-Fix). After combustion, oxidised fly ash may be used in various building materials, e.g., special cement products.

- Utilisation as fertiliser or as raw material for fertiliser products in the Netherlands is very unlikely. Typically, the ratio of nutrients versus contaminants is unfavourable.
- For clean fly ashes from uncontaminated wood, the possibility exists to recycle the ash to the forests where the wood was harvested. In Scandinavia and elsewhere this is already taking place. In the Netherlands, absence of large production forests and energy plantations make ash recycling nearly irrelevant.
- Landfill of carbon-rich fly ash is prohibited; landfill of oxidised fly ash is possible, but expensive.
- The most promising routes are:
  - Direct utilisation as fuel
  - Direct utilisation in asphalt and asphalt-like products
  - Application - after combustion - as building material or utilisation as raw material in cement

Techno-economic conclusions in co-operation with all project partners:

- All forms of fly ash utilisations are associated with costs, ranging from close to zero to over € 300 per ton.
- Only metal recovery from bottom ash can result in an economic profit.
- The most economical way of utilisation of gasification ashes is as secondary fuel.
- Utilisation of fly ash in asphalt and asphalt-like products is economically attractive, only when does not replace other waste materials.
- Oxidation (combustion) forming a low-carbon ash is the next best option in combination with utilisation in cement or - when possible - as fertiliser.
- Combustion enables landfill. Costs vary strongly between countries.
- Smelting is the most expensive option that was evaluated. The general conclusion is that smelting costs are € 300 per ton. ECN's calculations indicate € 100 per ton.
- The actual costs depend on the ash quality, e.g. washing of salts or pelletisation, add to the cost per ton ash.

6.2 Outlook for utilisation of carbon-rich gasification ashes in the Netherlands

Typically, fly ash from CFB gasification of biomass and waste is produced as a by-product of production of clean producer gas. The objective to remove contaminants by means of ash extraction makes it a difficult material to manage, because problem elements are concentrated in the material. Chlorine, alkali and heavy metals are most troublesome. Moreover, the powdery nature and the high carbon-content are problematic, because it makes the ash easily combustible. The high carbon-content also prohibits landfill as a worst-case solution.

Bulk utilisation of high-carbon fly ashes is effectively limited to use as filler in asphalt or as secondary fuel. The options are strongly determined by local factors. Transportation distances should not exceed 100 km or pelletisation should be considered, but this is also expensive. The owners of thermal installations must be licensed to burn waste and this makes the number of potential buyers relatively small. Potential buyers may have problems with the chlorine content and they have competitive negatively priced fuels like meat and bone meal or sewage sludge. Small applications may exist as well. The project has shown that carbon-rich fly ash can be used as filler in C-Fix blocks. However, it is economically not attractive if it is replacing other waste materials like residues from waste incineration that have a large negative price.

When direct utilisation is not possible, the preferred way to enlarge the number of options is to drastically lower the carbon content of the fly ash. Optimisation of the CFB gasification process alone cannot accomplish this goal. Combustion as after-treatment in a separate reactor is possible and enables manipulation of the combustion system to produce ash fractions with different qualities, using the strategy of “staged cooling and particle removal”, which cannot be

applied to the gasification process. The objective to lower carbon content of the fly ash can be accomplished in new process designs integrating gasification with combustion of the char. VTT's Integrated Oxidiser and ECN's MILENA concept are examples. The resulting ashes are combustion ashes rather than gasification ashes.

Combustion ashes may be used in various bulk applications. For the Netherlands, utilisation as fertilisers appears to be impossible. Exceptions may exist, e.g. by using chicken litter as a fuel. In other countries, recycling of ashes to the original soil is possible. Utilisation in building materials has the best prospects. Direct utilisation as building material is possible and logical for bottom ash, not for fly ash. The potential uses in building materials will depend on specific ash characteristics and specifications needed for cement, bricks and other building materials.

Finally, it has become clear that consistency of quality and quantity is of the highest importance. Users will only contemplate fly ash as a raw material when it has a guaranteed quality and is available in predictable amounts. This emphasises the need to be careful with the fuels used in the gasification process, because they have a direct effect on the fly ash composition.

Appendix A Public Summary of Consolidated Final Report

FINAL TECHNICAL REPORT

CONTRACT N° : ENK5-CT-2002-00635

PROJECT N° : NNE5-2001-00598

ACRONYM : GASASH

TITLE : Improvement of the economics of biomass/waste gasification by higher carbon conversion and advanced ash management

PROJECT CO-ORDINATOR : VTT Processes

PARTNERS: VTT Processes (VTT)
Foster Wheeler Energia Oy (FWEOY)
Energy Research Centre of the Netherlands (ECN)
Asociación de Investigación y Cooperación Industrial de Andalucía (AICIA)
Pohjolan Voima Oy (PVO)
EMC Environment Engineering Limited (EMC)
Essent Energie Productie B.V. (EEP)

REPORTING PERIOD : FROM November 2002 TO October 2005

PROJECT START DATE : 1 November 2002 DURATION : 36 months

Date of issue of this report : 21.12.2005

	Project funded by the European Community under the 'EESD' Programme (1998-2002)

TABLE OF CONTENTS

Part 1: Publishable Final Report	**Non confidential**
1.1. Executive publishable summary	3
1.2. Publishable synthesis report	4
1.2.1 Introduction	4
1.2.2 Improvement of carbon conversion and effects of bed materials	4
1.2.3 Process developments related to gasification and gas cleaning	8
1.2.4 Utilisation of fly ashes	17
1.2.4.1 Characterisation of ashes produced	17
1.2.4.2 Fly ash utilisation methods and utilisation of treated ashes	18
1.2.5 Techno-economic evaluation of different ash management chains	22
1.2.6 Conclusions	27

Part 1: Publishable Final Report	**Non confidential**

1.1. Executive publishable summary

Gasification technology offers an attractive way to use low-grade fuels in energy production with high efficiency particularly when the product gas is cleaned. The gasification and gas cleaning technology exists already today but the economic competitiveness of large-scale gasification has to be improved in order to be able to compete with advanced combustion technology. Fly ash disposal related cost represent significant share of overall operation cost of gasification based energy production. It is also expected that landfilling cost will increase in near future.

The primary objective of the project was to develop sustainable and economic methods for ash management of gasification and gas cleaning process. This was done by optimising gasification and gas cleaning process in order to reduce volume of fly ash and improve ash quality, characterising large variety of different gasification ashes to enable assessment of suitability of potential utilisation methods, developing several upgrading methods for carbon rich fly ashes, developing different utilisation methods for different qualities of ashes and finally evaluating the economy of 15 different utilisation routes in order to assess their feasibility.

Results showed that optimisation of the operation of the gasifier and gas cleaning process is technically possible way to reduce slightly produced volume of ash and to achieve some improvement in ash quality but simultaneously technical risks will increase. In large industrial scale this has direct impact on availability of the plant, which is more important factor than ash related disposal cost. In practice, it means that potential of this optimisation route is relatively limited and in any case its feasibility has to be assessed case by case.

Development of fly ash upgrading methods was very successful producing several applicable methods to reduce carbon content, reduce soluble chloride content and stabilise ash by oxidising fly ash. Fluidised bed oxidation of fly ash proved to be very efficient and feasible and final product was very similar than conventional combustion fly ash. Fly ash oxidation reactor can be stand-alone plant or it can be integrated to gasifier. Integration enables avoiding of additional flue gas cleaning facilities and simultaneously overall carbon conversion is increased close to 100 %. Fly ash washing was also developed for reduction of leachability of fly ash and reduction of chlorides. High temperature treatment methods were also developed. Benefits of high temperature methods are related to final product, which is enables utilisation of fly ash in many construction applications. However, economy of high temperature treatment is not attractive compared to lower temperature oxidation.

Finally, 15 different fly ash treatment and utilisation routes were selected for techno-economic assessment in order to evaluate their feasibility in industrial scale. Large variety of different treatment and utilisation routes is needed because quality of fly ash depends very strongly on the composition and contaminants of the fuel of the gasifier. Cost of these routes were compared to landfilling cost, which was assumed to be 150 Euro/ton and 14 of assessed these routes proved to be economically feasible. In the best case contaminant free fly ash from for example gasification of clean wood can be utilised as an alternative fuel in energy production. The economy of stand-alone or integrated fluidised bed oxidation was also proved to be feasible as well as washing of chlorides out and utilising cleaned carbon-rich fly ash as a fuel. It was estimated that economic impact of ash treatment and utilisation on the production cost of fuel gas varied from 0 to 3 Euro/MWh (gas) when alternative disposal is based on landfilling with 150 Euro/ton.

1.2. Publishable synthesis report

1.2.1 Introduction

Ash disposal cost for biomass or waste gasification process has a significant impact on the feasibility of biomass/waste gasification based energy production. Fly ash (filter dust) in particular might contain high concentrations of unburned carbon and harmful compounds restricting further utilisation, or normal disposal.

Ash related costs could be reduced by reducing ash volumes, improving the quality of ashes and developing products and technologies for the utilisation of ash as a raw material. These were the key topics of the GASASH project, which focused on improving the overall economics of biomass/waste gasification by higher carbon conversion and advanced ash management. The final objective was to develop different alternative treatment and utilisation routes for gasification fly ash and preliminary assess feasibility of these routes.

The project focused on three topics. The first task of the project concentrated on further development and improvement of fluidised-bed gasification process in order to reduce ash volumes and improve ash quality.

The second task focused on the development of new techniques for gasification and gas cleaning process. Three different methods were studied and developed: 1) thermal treatment (separate combustion) of gasification ashes, 2) fly ash oxidation process integrated to the gasifier and 3) conditioning of fly ash. All three developments were targeted reduce the carbon content of the ash, reduce ash volume or improve ash quality.

The third task focused on screening of present combustion fly ash utilisation methods and development of gasification fly ash specific utilisation routes. The most promising methods and routes were selected for more detailed evaluation and experimental studies in order to be able to assess industrial scale feasibility of them.

Finally, the technical and economic feasibility of the developed improvements was evaluated in order to define the optimal ash management procedure.

1.2.2 Improvement of carbon conversion and effects of bed materials

The objectives were related to improvement of carbon conversion, reduction of ash volumes and effects of bed additives in order to reduce cost related to disposal of solid residues. Work contained optimisation of bubbling fluidised bed (BFB) and circulating fluidised bed (CFB) gasification of clean waste wood, clean wood pellets, demolition wood, solid recovered fuel (SRF), orujillo and sewage sludge. Different bed materials (sand, limestone, ofita) were used in order to optimise the gasification process. Most of the gasification test trials were carried out with air but wood pellet gasification test trials with CFB gasification pilot-plant were also carried out with oxygen enriched air.

VTT carried out gasification optimisation test trials with process development unit-scale (PDU) circulating fluidised bed gasification and gas cleaning test facility and with pilot-scale bubbling fluidised bed gasification and gas cleaning test rig. Used fuels were clean waste wood and solid recovered fuel (SRF). Both fuels were gasified with both test facilities. Bed material was in all

cases mixture of sand and limestone and gasification agent was air and 10-20 % steam. Gasification temperature varied from 860°C to 895°C.

High carbon conversion was achieved in all test trials. Carbon conversion in BFB gasification of clean waste wood varied from 94,4 % to 98,7 % when target was 96 %. In CFB gasification of clean waste wood carbon conversion was 98, which also was the target.

Solid recovered fuel (SRF) is typically rich in plastic and paper, which are both very reactive and produce only little char. High reactivity leads typically to high carbon conversion. In BFB gasification of SRF carbon conversion 97,5 % was achieved (target 96 %) and in CFB gasification carbon conversion varied from 96,1 to 98,0 % (target 98 %). All carbon conversions were high and technically gasification process was always stable.

The primary aim related to improved carbon conversion was to improve the quality of fly ash and reduce volume of difficult carbon containing fly ash. Table 1 summarises composition of ash fractions from bubbling fluidised bed gasification of clean waste wood. Fly ash contained 50-60 % carbon, which is still high because in most ash utilisation applications carbon content should be lower than 10...15 % or even lower.

In BFB gasification of SRF most of the fly ash was removed by the filter. Typical bulk compositions of solid mass streams are presented in Table 2. These data show that bottom ash is primarily composed of sand additive and contains no combustible material. Filter dust contained only 10.6 % of carbon, which is very low compared to waste wood derived filter dust. Low carbon content of filter dust was achieved by high reactivity of the feedstock and successful operation of the gasifier.

Table 1. Composition of different ash products in BFB gasification of clean waste wood.

Set point	**BFB 0250A**	**BFB 0250B**	**BFB 0250C**	**BFB 0250D**
Filter dust, wt% (d.b.)				
C	51.5	53.9	60.7	56.0
H	0.8	0.8	0.8	0.8
N	0.2	0.3	0.3	0.2
O (difference)	5.2	5.9	3.6	8.6
Ash	42.4	39.3	34.8	34.4
Bottom ash, wt% (d.b.)				
Ash	99.7	99.8	99.6	99.6

Table 2. Composition of different ash products in CFB gasification of clean waste wood and solid recovered fuel.

Set point	**CFB 0323A**	**CFB 0323B1**	**CFB 0323B2**	**CFB 0323C**
Feedstock	Clean waste wood	SRF	SRF	SRF
Filter dust, wt% (d.b.)				
C	40.9	13.3	12.1	13.4
H	0.5	0.36	0.2	0.5
N	0.1	0.1	0.1	0.1
O (difference)	9.9	2.6	8.0	0.8
Ash	48.1	80.8	76.6	81.6
Bottom ash, wt %				
Ash	99.5	99.9	99.8	99.7

ECN focused on improvement of carbon conversion based on modified bottom of fluidised bed gasifier. ECN carried out gasification test trials with clean biomass (wood), demolition wood and sewage sludge. Sewage sludge gasification test trial was related to optimised gasification but also on fractionating of fly ash by staged cooling and particulate removal. Clean biomass and demolition wood waste gasification test trials were carried out in a 500 kW CFB gasification test facility with so called High Solids Density Circulating Fluidised Bed (HSD-CFB) facility installed. Principle of this test facility is based on separation of fuel inlet and air inlet into two different zones in order to increase char reaction with air. Figure 1 illustrates the principle of HSD-CFB gasification test rig.

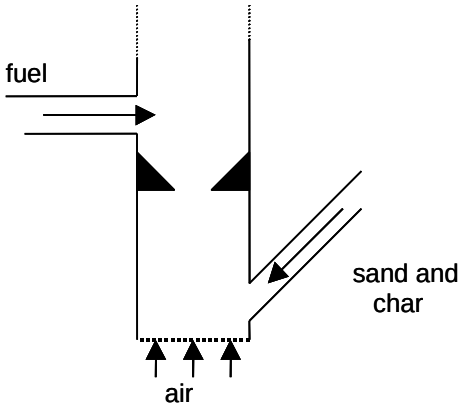


Figure 1. A schematic figure of the bottom part of the riser in a CFB designed according to HSD-CFB principle.

From gasification point of view gasification test trials with sewage sludge were successful but fractionating of fly ash did not work as planned. Carbon conversion of sewage sludge gasification was 99 %, which was based on high air ratio and high gasification temperature.

HSD-CFB gasification reference fuel was clean biomass (wood). Gasification test trial resulted in relatively high carbon conversion, 96 %, without further changes to the gasification conditions. Test trials with demolition wood waste resulted in carbon conversion 92 %.

One way to optimise ash management in gasification of demolition wood waste could be separation of finest fraction of fuel prior gasification. The finest fraction of demolition wood contains relatively large amounts of problematic elements. If removal of finest fraction can be done successfully it would improve ash quality as well as reduce ash volume. This was studied by carrying out gasification tests with two different demolition wood fractions. The first fraction represented demolition wood as such (0-15 mm). The second fraction was prepared from demolition wood waste by separating finest fraction by sieving (3-15 mm). After sieving the second fraction contained significantly less visible impurities and dust, which had positive effect on handling, operation of feeding and bottom ash discharge systems. Most of the concentrations of metal impurities in fly ash were decreased when finest fraction was removed. However, some elements enriched, especially Cu and Zn. From ash quality and reduction of ash volume point of view effect was not significant.

The list of fuels studied in the GASASH project contained one agrobiomass, orujillo, which is available in large quantities in Southern European countries. Orujillo is a residue of the olive oil

extraction industry with high heating value but it is rich in alkali metals (primarily potassium), which can cause serious deposit formation and agglomeration in FB gasification or combustion. AICIA carried out the work related to fluidised bed gasification of orujillo.

The first test trials were carried out with sand bed but tests were not successful. The bed suffered of severe defluidisation due to bed agglomeration even at low gasification temperatures. Bed material was changed from sand to ofita, which is a sub-volcanic rock (a silicate with formula ($(Ca, Mg, Fe, Ti, Al)_2(SiAl)_2O_6$). Test trials with ofita bed were successful and bed agglomeration was successfully avoided. Carbon conversion (without taking into account the tars in the gas produced) varied between 73.4% and 86.1% (no reliable tar measurement system was available). Although orujillo was the most difficult fuel used in this project it was successfully gasified and carbon conversion was reasonable or even good.

Largest gasification test trials were carried out by Foster Wheeler Energia. Test trials were carried out with atmospheric pressure CFB gasification pilot plant (1.5 MW ACFBG pilot) and the main variable oxygen content of fluidisation air. The heating value of product gas can be increased by oxygen enrichment but the effects on carbon conversion are not clear: the partial pressure of oxygen is higher but on the other hand, temperature control requires lower air coefficient. Effects of different bed materials were also studied. Fuel of all test trials was pelletised wood. Test matrix contained three different oxygen levels of fluidization air, three different bed materials and two different levels of bed inventory.

Applying oxygen did not cause any significant difficulties but the effects on the process appeared quite clear: fuel feeding had to be increased to keep bed temperature constant, there was less circulation due to less primary air, temperature at the top of the reactor was reduced and the share of combustible components of the syngas was increased.

Three different bed materials were tested: magnesium oxide, 50 % sand / 50 % coarse limestone and 50 % sand / 50 % fine P6 limestone (the same as P3 but finer fraction). The feed rate was generally 4 - 5 kg/h but with the fine limestone it was 10 kg/h.

The oxygen content of gasification air was about 23 % (m), 30 % or 40 % during most of the tests but finally it was raised to 50 %, which was the maximum level with the available equipment.

Only moderate amounts of bottom ash were removed from the gasifier during steady-state test runs. No signs of bed sintering related to fuel alkalis were observed. The bottom ash contained mostly bed make-up materials because the fuel was virtually free of solid impurities and the fine fuel ash is obviously elutriated from the reactor.

The filter ash consisted of calcium hydroxide fed after the gas cooler, elutriated bed make-up (mainly Ca or Mg), unburned carbon from the fuel and fuel ash. The unburned carbon content of filter ash seemed to increase with oxygen enrichment level of the fluidization air, as illustrated in Figure 2. Oxygen enrichment has several direct and indirect effects on gasification process but final conclusion was that oxygen enrichment of air did not decrease the unburned carbon content of filter ash to levels required for direct utilisation or landfilling.

The CO, H_2 and CH_4 contents of syngas increased with oxygen enrichment, as expected. The differences between limestone types were very small, but with MgO bed the CO and H_2 contents

rose slightly higher than with limestone / sand bed as the oxygen content was increased. The tar contents of syngas were very low with MgO bed.

The carbon conversion decreased slightly with increasing oxygen content. However, it should be noted that the primary objective was to find out potential effects of the tested parameters.

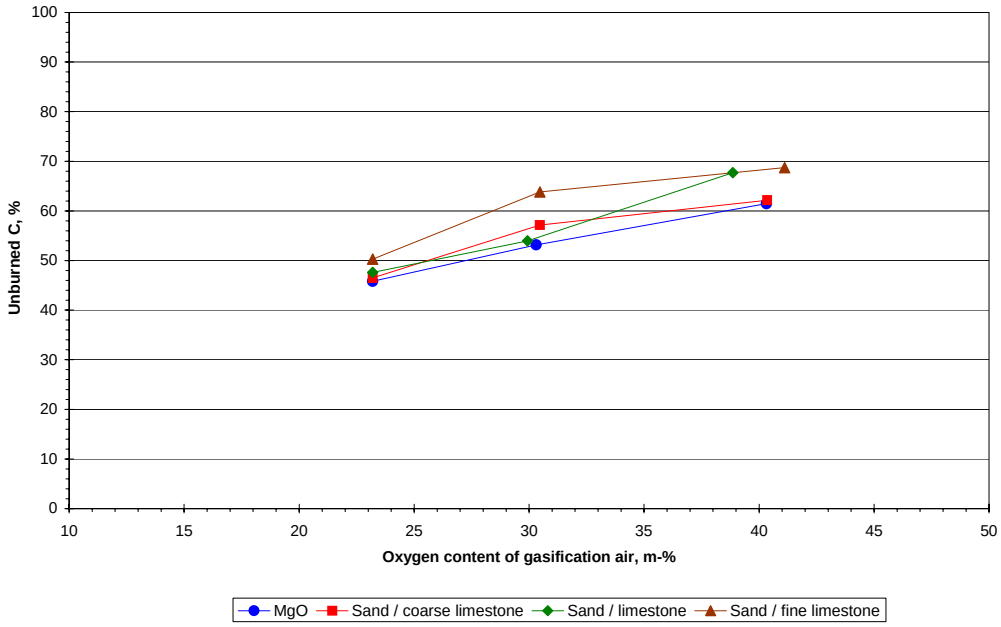


Figure 2. Unburned Carbon Content of Filter Ash.

A common conclusion related to optimisation of gasification and gas cleaning process conditions is that no universal solution can be defined but final optimisation has to be done case by case. Carbon conversion can be increased, but this does not necessarily mean that the carbon content in the fly ash is low enough for convenient utilisation options. It is expected that for many regular fuels carbon content in the fly ash cannot be lowered enough without significant drawbacks for the efficiency gasification process. Final optimisation has to be done case by case. Optimal solution depends on type of fuel and local conditions. In addition, oxygen enrichment might offer one way to have positive effect on carbon conversion but this needs further optimisation.

1.2.3 Process developments related to gasification and gas cleaning

The objective of process development activities was to develop technical solutions in order to reduce volume of fly ash and upgrade its quality. Efforts were focused on development of further treatment processing of fly ash and development of new components to gasification and gas cleaning process.

Development of fly ash treatment methods

FWE concentrated on development of further treatment of biomass- and waste-derived gasification fly ash. Primary aims of ash treatment were to reduce ash volume, improve ash quality and utilise the energy bound in the combustible fraction of ash.

In recent years, several types of ash treatment methods have been commercialised, e.g. fluidised bed combustion, thermal stabilisation, separation methods, chemical stabilisation and solidification. Ash treatment techniques have mainly been developed for fly ashes originating from combustion. Most of the commercial methods cannot be applied for gasification fly ashes

as such due to the different ash properties, e.g. high contents of unburned carbon and PAH compounds. However, an environmentally acceptable solution can also be found for gasification ashes by combining different treatment techniques. The following ash treatment processes were considered potential for gasification fly ashes:

- CFB combustion (carbon, PAH) + solidification / encapsulation with water or chemicals (Cl, heavy metals)
- Water wash (Cl) + wet separation (carbon) + chemical stabilisation (heavy metals)
- Pelletisation + sintering (carbon & PAH destruction; Cl vaporisation; heavy metals vaporisation / stabilisation)
- Thermal stabilisation = vitrification, fusion, sintering (carbon & PAH destruction; Cl vaporisation; heavy metals vaporisation / stabilisation)

The first and third processes were selected for experimental studies. Melting methods have been found technically feasible in Japan, but due to high costs they have not been considered viable in Europe.

In the first investigation line, the objective of ash treatment was to reduce the contents of organic matter and solubility of inorganic impurities to an environmentally acceptable level. It was essential to retain inorganic elements in ash.

Gasification fly ashes were oxidised in a CFB combustor, after which combusted fly ash samples were solidified by adding some water or chemicals. In addition, after-treatment of combusted gasification fly ash through pelletisation was tested. Some encapsulation tests for solidified fly ash samples were also performed (Figure 3).

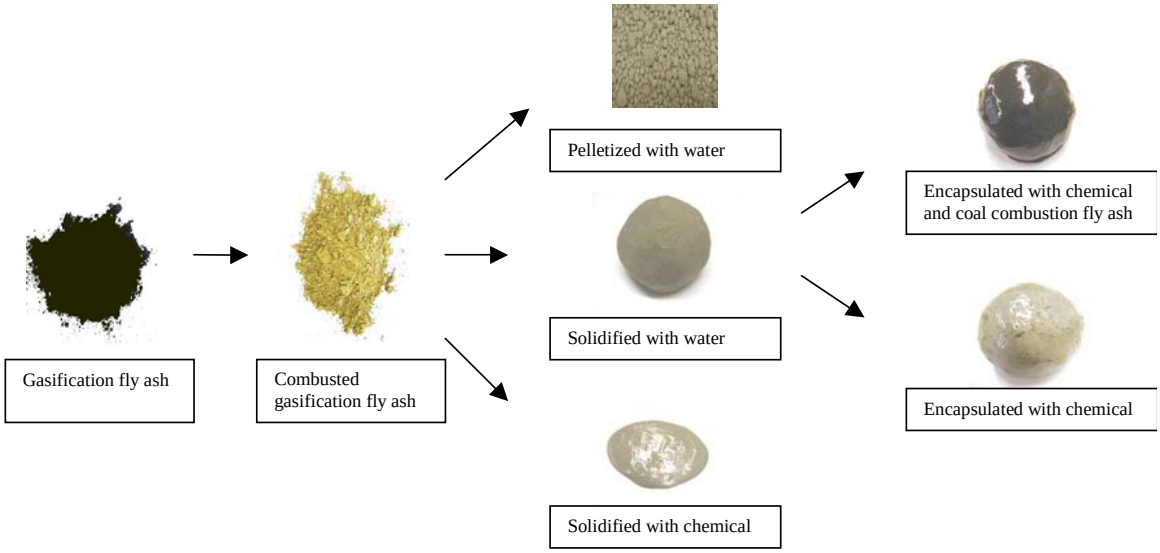


Figure 3. Ash samples from CFB combustion and solidification/encapsulation.

Combustion of gasification fly ash was studied in an atmospheric circulating fluidized bed test unit with a diameter of 100 mm and height of 3.8 m. Sand without any additives was used as the bed material. The average combustor temperature was in the range from 770 °C to 870 °C, and the flue gas was cooled near to 200 °C before filtration.

The gasification fly ashes contained enough unburned carbon to be burnt very effectively without additional energy sources. The carbon contents decreased markedly in all the ash

combustion tests, from about 40 % below a limit of 2.5 %. The carbon conversions were excellent, above 98 % in all tests. Additionally, the decomposition of PAH compounds was almost complete (99.9 %). The mass of gasification fly ash could be decreased in half and very good heat recovery from the residual carbon could be achieved by fluidised bed combustion. Flue gas analyses showed very low levels of HCl and SO_2, while the small height of the test facility and the resulting short residence time at high temperatures presumably contributed to the fairly high levels of CO and NO_x. Nevertheless, the combustion efficiency was 96 % or higher in all the test runs.

The chemical analyses and flue gas contents indicated that the most part of chlorine, barium, sulphur and heavy metals left the CFB combustion process with the combustion fly ash. Especially the leaching values of chlorine and barium were relatively high in the combusted gasification fly ash. When the results of leaching tests and chemical analyses are compared with national regulations and EU criteria on the acceptance of waste at landfills, it can be concluded that oxidised gasification fly ash derived from waste fractions can be dumped into landfills for hazardous waste. Additional treatment is required before disposal at landfills for non-hazardous waste.

Due to the high leaching values of chlorine and some heavy metals in the oxidized fly ash, experimental research was continued. Because of high calcium content of the combustion fly ash, solidification of it with water was studied. Several different ash-water mixtures were prepared and compressed into the shape of cylinders and balls, which were dried up at room temperature. However, the achieved reductions in leaching values were not significant: even if the leaching value of barium decreased below the limit value, high solubility of chlorine remained problematic.

Pelletisation of combusted fly ash was also tested. In the last solidification test, a chemical additive (TKR) was mixed with oxidised gasification fly ash in the ratio of 1:2. TKR is an environmentally safe, vegetable oil based polymer normally used as a protection material on the surfaces of concrete, metal and wood materials. TKR coating could easily solidify the combusted ash, but it had little effect on leaching of chlorine. Producing a coating from a mixture of TKR and coal combustion fly ash (filling material) turned out to be the technically and economically best solution but within a longer time period chlorine leached also from these encapsulated ash samples.

Therefore, it seems that especially preventing the leaching of chlorine is a very difficult task to be carried out by chemical or mechanical treatment methods. All results from after-treatment methods of combusted gasification fly ashes are of course specific to the tested chemicals and treatment techniques.

In the second investigation line sintering of pelletised gasification fly ash samples was studied. The objectives of the sintering studies were as follows:

- Oxidise unburned carbon and destroy other harmful organic matter.
- Evaporate chlorine and highly volatile heavy metals.
- Reduce leaching values of other inorganic impurities.

The particle size of the produced pellets ranged from 5 mm to 15 mm. Only water was used as binder in the first ash pelletising test. In the other test runs, the effects of various additives, i.e. sodium lignosulfonate, bentone and sodium silicate were studied. Tests showed that sintering of pelletised gasification fly ash requires high temperatures, 1350 °C or higher.

In the ash sintering methods, most of the problematic chlorine and highly volatile heavy metals, such as zinc, vaporize. In addition, unburned carbon oxidises very effectively. According to the available data from Japanese ash melting methods for waste-derived ashes, harmful organic matters, such as PAH compounds, dioxins and furans are completely destroyed. Presumably these compounds are not problematic in ash sintering either. In addition, the results of leaching tests indicated that sintering has a stabilising effect on some heavy metals, such as barium. According to the results of this study, sintered gasification fly ash can be disposed at landfills for non-hazardous waste. Even utilisation or inert waste category might be achievable.

The objective of work of ECN was to investigate the potential of ash separation and to explore several forms of after-treatment that are suitable for certain ash fractions. Each of these techniques should improve one or more of the characteristics of the ash to improve its quality. The basis for the work was the gasification fly ash as produced by the 80 MW(th) Circulating Fluidised Bed Gasifier located at the AMER-9 power plant of Essent Energy Productions. The gasifier is fuelled with shredded demolition wood.

Work was divided in three subtasks:

- *Exploration of separation techniques using physical characteristics of fly ash*
- *Exploration of after-treatment techniques for different fly ash fractions*
- *Pilot-scale application of selected forms of ash conditioning*

A review of screening techniques was made which may be used for separating carbon-rich fly ash into several fractions. For separation of carbon-rich fly ash, both dry and wet techniques are available. For dry systems, screening using an electric vibrating screen is the most obvious method. The particle size of carbon-rich fly ash is small making screening difficult, but not impossible. For smaller sizes relatively large screen surface areas are required, which on a larger scale may not be practical. Cohesiveness of fly ash particles is an uncertain factor. Electrostatic separation or cyclones in series are not viable alternatives.

Wet systems perform potentially better than dry systems. In particular, liquid cyclones and froth flotation are promising techniques. However, wet systems have serious disadvantages. Firstly, the need to dry the solids afterwards and secondly, the contamination of the liquid with leached compounds. Only when wetting of the solids and/or controlled leaching are part of the processing of the ash, wet techniques may be good choice.

Six forms of after-treatment were tested using explorative tests.

Dry screening was found to be capable of producing a small ash fraction with relatively high carbon content and a lower content of contaminants. The sieve fractions that were relatively clean were the larger particles: 90-180 µm mainly consisting of fractured sand particles (bed material) and >180 µm, mostly char particles. Unfortunately, these cleaner fractions are small in mass. Even if the fraction 63-90 µm is included, less than 10% of the total ash can be regarded as significantly cleaner than the rest. The two smallest (and most difficult to sieve) fractions form 70% of the total ash amounts. Thus, it is not possible to create by dry screening a cleaner bulk fraction with better perspectives for utilisation.

Pelletisation of the fly ash is possible and produces fuel pellets, which have improved characteristics for logistics and storage. It strongly increases the density (factor 4 or more) and lowers risks of handling, e.g. dust explosions and health effects. For making good pellets,

AMER-CFB fly ash needed addition of water and a binder material; traditional starch is good enough. Other fly ashes can be compressed into pellets by only adding water. Pelletisation is of particular interest when the ash is used as fuel and requires transportation and storage.

Immobilisation as a filler material in a carbonaceous material like C-fix was found to produce a category 1 building material, i.e. unrestricted use, when tested in a tank test (NEN 7375). It is a technically a viable form of after-treatment, that is expected to be applicable to all utilisation options where a water repelling binder is used. Filler in asphalt is an example of this form of utilisation. Competition from other waste materials is expected.

Controlled leaching was found to be a promising after-treatment technique, suitable for removing salts. Technically it is challenging to apply it to the small particles that constitute high-carbon fly ash, but it is possible, as proven by VTT/PVO. The attractive part of the technique is that it removes Cl and alkalis, which are the components that are most often listed as showstoppers for utilisation options. When the pH is controlled, heavy metals are precipitated and the washing liquid can be disposed at low cost, in particular when discharged to the sea.

Low-temperature combustion was found to be a possible form of after-treatment converting carbon-rich fly ash into a low-carbon fly ash that is nearly identical to fly ash from combustion. Hence, all applicable utilisation options for fly ash from combustion of biomass can be used.

High-temperature combustion was found to be a technically acceptable way to convert carbon-rich biomass into building material, either by producing a clean burned-out fly ash or by producing a molten synthetic rock, also known as vitrification. Chemical analyses and leaching tests have confirmed that it is possible to produce building material that can be used in unlimited quantities according to the Dutch Building Materials Decree (DBMD).

Carbon-rich fly ash, burned and heat-treated at 1000°C was found to be strongly reduced in alkali, chlorine and heavy metal content, contaminants that are typical for limiting utilisation options. The material is still a powder and it was demonstrated in a pHstat test (PrEN 14429) that it complies to the limits of category 1 building material. Given its composition, it has a potential to be used similar to coal fly ash; potential utilisation as a raw material for cement and/or concrete. A general conclusion is, that it can be expected that material produced from AMER-CFB fly ash, which is heated above 1100°C for a sufficiently long time to evaporate problem elements, may be utilised as a building material of category 1, i.e. unlimited use. This conclusion can probably be extended to many more fly ashes from both gasification and combustion.

Fly ash was vitrified at 1400°C (and higher). It is technically possible to transform this fly ash into a synthetic rock, although the melting point is rather high. Adding fluxing agents proved that the melting point can be easily lowered to 1250-1350°C. Leaching tests showed that it is a category 1 building material, when used as gravel or as shaped building material..

Co-firing of carbon-rich gasification ash in powder coal burners is technically possible. The burned-out ashes become mixed with the coal ashes. Given the fact that the gasification ashes contain relatively large amounts of alkali and chloride, it can be calculated that they can only partly replace coal. Fly ash quality standards (EN 450), emission regulation and corrosion preventions can all act as limiting factor for co-firing.

Based on the results of the explorative tests, high-temperature combustion was selected as the after treatment technique for further research and up-scaling with the objective to transform carbon-rich fly ash into a category 1 building material.

Unmixed AMER-CFB fly ash produces two phases upon heating, one glass-like material melting at 1400°C and a stone-like material at 1550°C. To avoid formation of foam, the carbon-rich fly ash was pre-treated at 1000°C to remove carbon and chloride, both compounds that may lead to gas formation when heated further. Addition of 10-15% alumina to the burned-out fly ash was found to produce a single-phase smelt with a sufficiently low melting point of 1250-1300°C, which solidifies into a block of glass-like material. The material looks more like obsidian than basalt. A 1 kg block of burned-out AMER-CFB fly ash with 10% added alumina, based on the mass of the end product, was made in a laboratory furnace. The block of vitrified ash was subjected to a tank leaching test (NEN 7375). The results show that all emissions are well below the limits of category 1 building material of the DBMD, i.e. unrestricted used.

In the up-scaled test, an amount of 5 kg synthetic basalt was prepared in a silicon-carbide smelter pot from pre-treated carbon-rich fly ash and 10% alumina (based on the end product). The conditions reflected the situation of full-scale smelter to such an extent, that it is expected that the end product will be representative with respect to material characteristics. The solidified smelt was recovered from the smelter pot and broken particles of 0-40 mm (granulate). The appearance of the material is the same as the lab-scale test: a black, glass-like material. In the large-scale test, part of the material has been spilled over the edge of the ceramic pot, despite the fact that it was filled less than half full and at least 20 cm below the rim. The loss due to foaming is certainly an effect that must be investigated in further research on vitrification of ashes from biomass and waste. Thus for up-scaling of vitrification, silicon-carbide pot may not be the best selection.

The material, produced in the 5 kg test was subjected to a quick availability test, a leaching test on finely ground material, done at pH = 7 and pH = 4. This resulted in compliance to criteria for category 1A building material, with exception of Sb, Ni, Co and Cu. The increased leaching of these four is the result from the very unfavourable conditions in the availability test or an artefact (Co). Antimony is the only element that may cause problems in compliance tests (DBMD), but comparing with the results of the tank test of the 1 kg sample, it can be concluded that it is highly probable that the material of the 5 kg smelt, when tested in a tank test (block) or in a percolation test (granulate 0-40 mm), will pass without difficulty and comply to the requirements of category 1A limit of the DBMD.

Developments related directly to gasification and gas cleaning process

ECN and VTT carried out development work related directly to gasification and gas cleaning process. ECN focused on optimised selective particle separation and VTT on integrated fly ash oxidation.

Staged cooling and particle separation

Selective particle separation was based on staged cooling and particle removal. The principal idea is to extract the bulk of the fly ash directly after the gasifier at a high temperature. Under those conditions notorious contaminants like Cd, Pb and Zn are in the gas phase and the extracted ashes are supposed to be relatively clean and better suited for utilisation. The unwanted gaseous elements will deposit during cooling on a small ash fraction, which may be utilised separately (or land filled). The strategy of staged cooling and particle removal is based on work by Obernberger and co-workers who have published a series of papers on this principle when applied to combustion installations. These publications prove that a bulk ash fraction can be

obtained with strongly depleted concentrations of Pb, Cd and Zn, when extracting ash at high temperatures.

However, early results of the project indicated that staged cooling and particle removal is not likely to find an application in commercial gasifiers. In principle, it is a valid strategy, but there are two reasons to pursue alternative roads:

1. The strategy of “staged cooling and particle removal” results in significant extraction of ash before the end of the cooler. This is in conflict with the requirements of a “self-cleaning cooler”. This is a cooler-type where the ductwork is kept (relatively) clean by scouring the walls and pipes with entrained ash particles, which is very useful in the case of gasification of biomass. Removal of (part of) the ash prior to the end of the cooler is unwanted, because a) the larger particles are the first to be removed but these are also the most effective in keeping the deposition low and b) the scouring is most needed at the end in the colder parts of the cooler, so most particles must remain entrained by the gas until the end of the cooler. As a result, application of the latter is unlikely under the current conditions.

2. From a few runs using sewage sludge, it appears that the strategy of “staged cooling and particle removal” is only effective for a limited number of elements. In the experiments, ash was collected at 200 and 800°C. Some elements were concentrated in the “cold” ash fraction, e.g. Pb, Cd and Cl, but most elements, including Ni, Cr, Cu and Zn, showed no significant preference to concentrate in a certain fraction. One can expect that in the narrower temperature ranges in cooler, 400-600°C, the differences in ash composition will be even smaller.

To illustrate the latter, results are presented from one of the test runs in ECN's 500 kW(th) biomass gasifier using sewages sludge as fuel. Ashes were collected in a "hot" cyclone at gasification temperature (800°C), a "cold" cyclone at about 200°C and an ESP filter at ambient temperature. The temperature difference is large, so it was expected to find large differences in the distribution of many elements, in particular heavy metals. The main conclusion from these tests was that most elements show no sensitivity to the temperature of ash collection. Only for Cd, Hg, Cl and F a significantly different distribution is found, compared to the overall mass distribution. Problem elements like Ba, Ni, Cr, Cu, Pb and Zn are not significantly depleted in the bulk of the ash. The behaviour of Ba, Ni, Cr and Cu was predicted using thermodynamic equilibrium calculations, but the even distribution of Pb and Zn came as a surprise.

The overall conclusion is that the strategy of “staged cooling and particle removal” is not likely to find an application in gasification systems. It is not fully effective and conflicts with application of a self-cleaning cooler. “Staged cooling and particle removal” should not be regarded as useless. In combustion systems it is a valid approach, as well as in gasification systems where tar is not a problem and a self-cleaning cooler is not needed. For gasification, it may also be successful when only a limited number of elements, notably Cd, Zn and Pb, need to be removed. In addition, when carbon-rich fly ashes from gasification are subjected to combustion as a form of after-treatment, the combustion process can be designed with staged cooling and particle removal.

Integrated fly ash oxidiser

Fly ash or filter dust is usually rich in carbon and impurities. Oxidation (combustion) of filter dust reduces very efficiently volume by oxidising carbon and simultaneously most of metal impurities are oxidised to more stable compounds. Oxidation can be done in a separate combustion unit or using so called integrated oxidiser. The basic principle of integrated oxidiser is oxidation of filter dust in a fluidised bed oxidiser and utilisation of released heat energy by using hot flue gas as a secondary air of fluidised bed gasifier. This integration of the oxidiser to the gasifier enables avoiding of heat exchange surfaces in oxidiser and in addition, no additional flue gas facilities are needed and simultaneously the overall carbon conversion increases very close to 100 %.

In the work of VTT integrated oxidiser was designed and constructed. Oxidiser was preliminary tested and optimised without integration to gasifier and finally the performance of the integrated oxidiser was tested by carrying out test trials with complete integration to 1 MW_{th} fluidised bed gasifier.

During development of the integrated oxidiser a specific attention was focused on the following topics:

- Successful operation of the oxidiser
- The effect of the oxidiser on the product gas.
- Verification of the gasification and gas cleaning performance of the entire process concept
- Stabilisation of gasification fly ash applying integrated oxidiser

The main component of the oxidiser is a fluidised bed oxidation reactor fluidised by air. The oxidiser was designed to be operated at 700-900^{o}C. The lower end of this temperature window is limited by carbon conversion efficiency and upper end by risk of bed sintering. The design bed material was sand but other bed materials can also be used if needed.

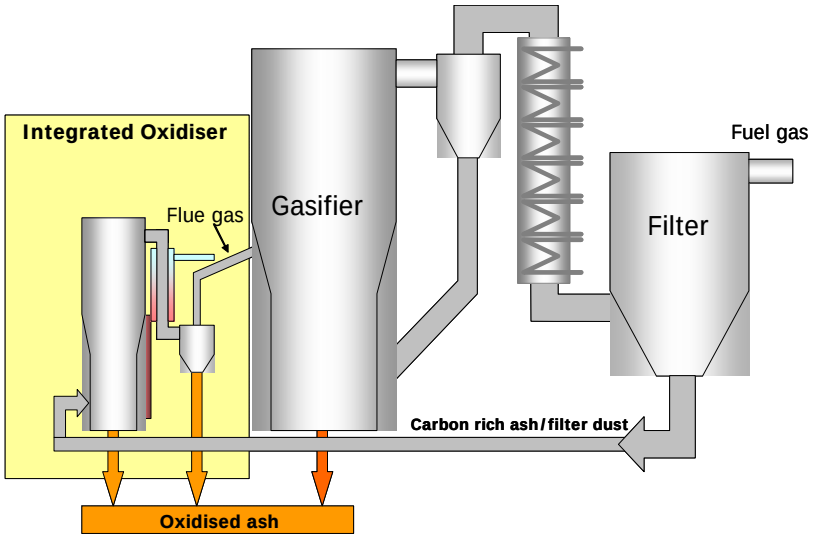


Figure 4. Integrated Oxidiser and the atmospheric pressure bubbling Fluidised-Bed (BFB) gasification pilot plant.

The bottom of the oxidiser is designed so that even some bed agglomerates can be discharged without shutting down the oxidiser. In addition to the bottom ash, ash is also removed by cyclone

from flue gas of the oxidiser. Flue gas is slightly cooled prior cyclone but no efficient gas cooling can be done because of high risk of deposit formation. In large-scale application gas cooler can be operated as a gasification air preheater. The produced heat from oxidiser was led directly to the FB gasifier as a secondary air.

The constructed oxidizer was equipped with an automatic data collection of temperatures and pressures measured at different locations. The flow rate of air was continuously measured and recorded. The feeding rate of fly ash was controlled too. In addition, on-line analysers monitored the combustion gas constituents.

The final verification test trial was carried out with complete integration to the pilot-scale BFB gasifier. The two different feedstocks used in the gasifier were (1) mixture of forest residue and wood pellets and (2) SRF (Solid Recovered Fuel) pellets. A mixture of sand and limestone P3 was used as a bed material in the gasifier at all set points.

Two feedstocks of the oxidiser were fly ash from wood gasification and from SRF gasification. Carbon content of wood gasification fly ash was reasonably high (52%) whereas fly ash from SRF gasification test contained fewer than 10% carbon.

The test programme contained a total of three set point periods during one week test trial. During two set point periods the gasifier was operated with integrated oxidiser and one set point period was a reference test without oxidiser.

Operation of the oxidiser integrated to the gasifier was very smooth and steady state. The reactor temperatures and fuel feedings of the process concept were stable. No major problems occurred during the test runs. High **carbon conversion** was achieved at all tests. **The lower heating values** of wet product gas varied from 4.0 to 4.4 MJ/m^3n when oxidiser was used. and during the reference test with SRF the lower heating value was 5.2 MJ/m^3n.

Chlorine content of mixed forest residue fuel was 0.02% and SRF fuel 0.5%. Limestone was added to the bed but specific chlorine removal sorbent was not used. The measured HCl-content was almost negligible (0.6-1.4 ppmv) with mixed forest residue. HCl content varied between 34-67 ppmv with SRF.

Heavy metals listed in WID (Waste Incineration Directive) were measured from the product gas after the gas cleaning. The following elements were analysed: As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Sn, Tl, V and Zn. The sampling point was located after the filter, which was operated in the range of 425-436^{o}C. Heavy metals except mercury are typically captured efficiently by filter in temperature below 450 ^{o}C. The results showed that very low concentration (<0.02 mg/m^3_n dry) of heavy metal emission were analysed from product gas.

Filter dust from wood gasification was rich on carbon (61 wt %). In SRF gasification tests, the carbon content of filter ash was lower (19-27 wt %). Bottom ash was primarily composed of bed material and contained almost no combustible material.

The primary objective in development of oxidiser was efficient reduction of carbon content of filter dust. This objective was achieved and residual organic carbon content was very low, below 0.2 %. In test trial BFB 05/23A total carbon content of oxidised ash was higher (3.2 %) but most of this (2.9 %) was bound to inorganic carbonate.

The overall conclusion was that integrated filter dust oxidiser could be operated in stable conditions without any significant impact on performance of the gasifier. Carbon of filter dust was oxidised almost completely and final quality of oxidised filter dust was very close to fly ash from conventional combustion, as targeted. These results showed clearly that integrated oxidiser can be used for very efficient upgrading of gasification filter dust.

1.2.4 Utilisation of fly ashes

1.2.4.1 Characterisation of ashes produced

Nine main fuels were selected for the investigation of the gasification fly ashes, two of them coming from full-scale gasifiers (from Lahti and Amer gasifiers). Lahti ashes are fly ashes collected in a 50-80 MWth CFB gasifier at Lahti during 100% REF (Recovered Fuel) gasification. The REF is produced from origin-classified refuses, coming from households, offices, shops and construction sites. Amer-CFB is the 80 MW(th) Circulating Fluidised Bed Gasifier located at the AMER-9 Power Plant of Essent Energy (AMER-CFB) The rest of ashes has been obtained from different partners pilot-scale plants.

Table 3. Main elements in different ashes.

			%w/w									
ASH	**Moisture**	**LOI**	**Fe_2O_3**	**CaO**	**MgO**	**SiO_2**	**Al_2O_3**	**Na_2O**	**K_2O**	**P_2O_5**	**Cl**	**S**
Orujillo	1.8	20.3	5.3	26.1	8.6	41.0	8.0	1.3	8.3	1.5	0.6	0.1
MBM	2.1	16.6	2.9	44.5	3.6	12.5	3.5	4.1	1.5	18.0	-	0.2
Waste wood	3.7	63.7	11.0	45.1	4.0	21.4	6.2	0.6	0.7	1.2	1.2	-
SRF	1.5	23.8	3.0	39.0	3.3	27.9	21.5	1.5	0.7	-	2,8/4,6	-
RDF Lahti		33,2***	2.1	44.6	2.9	19.1	13.4	1.6	1.4	0,8 (0,7**)	4,3/2,1	0.3
Straw		37,5***	0.3	14.4	1.2	32.3	0	0.2	6.1	0,4 (0,5**)	0.8	0.1
RDF Karhula		20,9***	7.6	31.8	2.1	21	18.2	0.3	0.7	2,4 (2,5**)	8.9	0.3
AMER-CFB	0	65	0.97	6.8	0.94	17.8	1.4	0.6	0.9	0.3	1.07	-
Sewage Sludge	-	65	15.79	10.54	1.73	32.1	9.6	0.8	1.7	16.8	0.06	1

Table 4. Metal concentrations in different ashes

							Metals in mg/kg									
SAMPLES	**As**	**Hg**	**Se**	**Mo**	**Zn**	**Pb**	**Cd**	**Co**	**Ni**	**Cr**	**V**	**Cu**	**Ba**	**Sb**	**Mn**	**Sn**
ORUJILLO ashes	<160	<100	<100	<100	210.5	<160	<16	<10	<100	761.5	83	146	289	<200	-	-
ORUJILLO Fuel	<160	<100	<100	<100	182	<160	<16	<10	<100	646	60	182	270	<200	-	-
MBM	<100	<100	<100	<20	398	100	<10	<10	864	636	<20	212	134	<20		
SRF	20				1500	920	14	19	96	530	41	2100		180	860	150
SRF	<100	<100	<100	<20	1660	426	<10	<10	122	786	<20	1474	1560	<20		
Waste wood	1430	<100	<100	<20	8412	1832	<10	<10	190	1212	<20	1436	2644	<20		
RDF Lahti	46.2	0.0077	<2	8.27	5340	722	5.88	21.1	47.9	83	15	1900	1345	362	766	-
AMER-CFB	99.2	-	4.2	3.8	4045	4736	8.0	21.0	26.9	497	12.1	423	3744	41	841	39
Sewage Sludge	9.26	0.02	1.44	21.06	1965	246	0.28	15.51	113.22	197	47.48	921	861	11	1363	43

Table 5. DIN 38414 leaching test results of some ashes

			Leachate DIN (mg/L)									
SAMPLES	**pH**	**As (ppb)**	**Zn**	**Pb**	**Cd**	**Ni**	**Cr**	**V**	**Cu**	**Ba**	**K**	**P**
ORUJILLO	12.59	<1	0.1	0.1	< 0,03	0.1	<0,05	<1,9	0.09	1.83	27.35	0.02
MBM	10.25		0.07	<0.1	<0.02	<0,05	<0.05	<1,9	<0.05		100.0	0.01
Waste wood	9.12	44	<0,02	<0,1	< 0,03	<0,05	<0,05	<1	<0,05	1.1		
SRF	11.47	<1	0.03	0.13	0.03	0.12	<0,05	<1	<0,05	24.5		
RDF Lahti	12.17	1	0.04	0.1	< 0,03	0.08	<0,05	<1	<0,05	49.5		
Straw	12.93	<1	0.17	0.14	< 0,03	0.11	<0,05	<1	0.05	2.7		
RDF Karhula	10.10	<1	0.05	0.18	0.04	0.22	<0,05	<1	0.07	17.7		
AMER-CFB*	11.2	2	1.18	76.4	0.00005	0.0003	0.0007	0.0008	0.0046	15.1	310	0.029
Sewage sludge*	11.7	< d.l.	0.0046	0.007	0.00003	0.001	0.004	< d.l.	0.064	0.12	6.9	0.012

** leaching percolation test (PrEN 14405) at L/S=10; content in leachate in mg/L*

The calorific value of Lahti and Amer gasification fly ashes ranges from 14 to 25 MJ/kg. These values are comparable to the heating values of peat and wood, despite of the high ash content. For the ashes analysed in GASASH-project the loss-on-ignition (LOI), mainly carbon, ranges from 7 to 60 wt%. Leaching properties were analysed by several different methods (DIN 38414, TCLP, column tests).

1.2.4.2 Fly ash utilisation methods and utilisation of treated ashes

Some of the investigated utilisation methods can be regarded as niche applications, e.g. filler in C-Fix. This is perfectly acceptable for the small production volumes that currently exist. Moreover, in small gasification units often specific fuels are used resulting in ashes with unique characteristics, which can match with specific forms of small-scale utilisation. These "lucky matches" should also be investigated, but they do not offer solutions for all gasification ashes. Bulk utilisation options are needed, when multiple large-scale gasifiers are built in Europe. Gasification ashes *direct* bulk utilisations are not easily found. Therefore ash treatment technologies are included in the assessment of utilisation options.

Three main utilisation categories have been identified for the gasification ashes derived from biomass/waste.

1. Use as fuel: co-firing in coal/biomass-fired power plants; firing in a dedicated boiler; replacement fuel in smelters/incinerators (best option for highly polluted fly ash); firing in cement kiln
2. Use in construction: filler in asphalt or asphalt-like products (C-Fix); additives in concrete manufacturing; bulk construction / raw building material; lightweight bricks; fire-resistant material; stabilisation/solidification
3. Use in agriculture: directly as fertilizer or soil improver; as raw material

Landfill is not considered as a form of utilisation, but as an alternative to utilisation, more like a backup method. The current policy in the EU is to discourage the landfill of high calorific waste. Implementation is different in the member countries. In some countries, e.g. The Netherlands, it has become nearly impossible to landfill high-calorific waste. In the UK there are no regulations that refer specifically to high calorific value waste, but the requirements of landfill acceptance criteria set limits to the (organic) carbon content of materials for disposal.

Identification of most promising options

Application as a fuel is regarded as direct application and is not the same as disposal with energy recovery, but is in fact a higher-grade application. This is supported by the fact that the aim to use gasification ash as an alternative fuel is not the need of disposal, but the need to replace fossil fuels in the same way as the original intention of the biomass before gasification: energy production. The Commission supports this concept, see the revised version of the EU waste strategy adopted by the Commission in July 1996.

Criteria for utilisation as fertilizer/soil improver: In European Union Member States, the application of fertilisers and soil improvers is restricted with respect to the maximum allowed addition of contaminants to the soil. The 1986 Directive (EEC, 1986) included restrictions on the metals content of the sludge, each Member State setting their own limit values. These limit values for sewage sludge are often used as a reference for other materials as well.

Criteria for utilisation as building materials: With regard to direct utilisation in building materials, each Member State of the EU has its own regulations concerning the application of recycled materials in landscaping and road construction. In the Netherlands the application of waste streams (limited to stony material or soil-like material) in landscaping / road construction is regulated by maximum allowed leaching of contaminants. Within this document (and much of the GASASH project) the Dutch Building Materials Decree (DBMD) is used as a reference, but it was tried to minimise the bias and leave room for regulations from other member countries. A harmonized European Construction Products Directive (CPD) is being developed. This directive will be based on much of the same principles as the current DBMD, in which leaching of contaminants and long-term impact is guiding in the risk assessment for the application of construction products.

Criteria for utilisation as fuel: There are no specific regulations for the use of fuel, other than legislation based on the fact that ashes from gasification are being regarded as a waste product. The potential for utilisation as fuel is to be decided by the prospective buyer, who needs to take into consideration the calorific value, permits for firing waste and sufficient flue gas cleaning. Since carbon-rich fly ash has a low density, logistics will be a dominating factor. Compression (pelletisation) should be considered when utilisation does not take place in the vicinity of the location where the fly ash was produced.

Direct application/utilisation of the material without treatment

The feasibility of application of ash as a fertiliser depends on local conditions, but in a wider perspective it can be can concluded that none of the ashes used in the GASASH project have a great potential to be applied directly as fertilizer. This is caused by the generally low nutritional value of available nutrients compared to the relatively high content of contaminants. Exceptions are possible for specific fuels. When the strict Dutch limit values for fertilizers are used, it is found that none of the gasification ashes comply, whereas according to Spanish limitations, the Orujillo ashes meet the criteria. The most critical components for application as a fertilizer are Cd, As, Cu, Zn and Pb.

When comparing the leaching behaviour of ashes with the criteria of the Dutch Building Materials Decree, the conclusion is that studied fly ashes cannot be *directly* used as building material, mainly due to high leaching of contaminants. Chlorine is a problem element for all ashes; Pb, Cd, Mo, Cr, Br, Se and Sb are typical problem elements for many ashes.

Some of the ashes have a high enough heating value to allow utilisation as replacement fuel (up to 25 MJ/kg). Combustion can be integrated, which has the advantage that no separate flue gas treatment is needed. This also applies to utilisation in separate installations that already have a sufficient flue gas treatment system before alternative fuels were introduced. Utilisation as an alternative fuel is one of the most promising routes for gasification ashes with a carbon content above 35 wt%. Limitations will be emissions and end-of-pipe fly ash quality if the fly ash has an established utilization that requires a certain quality (e.g. in cement production).

Direct application/utilisation of the material with pre-treatment

Quality improvement of the gasification ash will have to concentrate on the elimination or reduction of critical components. Which component is critical differs for various combinations of fly ash and application. In fertilizer applications, the only way to improve the ash quality is to reduce the total amounts of contaminants, which is not easily done. As a result, utilisation as fertilizer after treatment is not a likely route.

In applications that are regulated by leaching limits (building materials), the possibility exists to reduce leachable amounts of contaminants by washing the ash, since this specifically eliminates soluble compounds; 75% removal of Cl is easily achieved. Other components can be made less easy to leach by manipulating the pH, e.g. by converting oxides into carbonates. Washed gasification ash could be used in direct utilisation routes towards construction products, because it eliminates the most problematic element: chloride. Still, it remains questionable whether the washed gasification ashes will be used as a building material in direct applications because of its mechanical properties. Washing may also be used to improve the potential for utilisation as a fuel, by removing chlorine, a notorious corrosive component.

Combustion in a fluidised-bed at 600-900°C converts the characteristics of the ashes completely. The composition of the fly ashes produced in the GASASH project at these conditions was found to be not suitable for direct utilisation. The ratio of nutrients compared to contaminants is still unfavourable for utilisation as fertiliser and the leaching behaviour of several samples indicates that the ashes after combustion do not comply with category 1 (unrestricted use) of the DBMD. However, some ashes comply with category 2, *i.e.* use as bulk material, shielded from contact with water.

High-temperature treatment can convert biomass ashes into synthetic basalt that complies with the limits of category 1 building material of the DBMD (unlimited use). Typically, when the temperature exceeds 1000°C, the material is sintering and problem elements (Cl, K, Pb, Zn) have been evaporated or are encapsulated into the bulk. The remaining ash is free of carbon and can be cast into moulds or broken into granulate. Technically, vitrification processes offer one of the most promising options for the utilization of gasification ashes from biomass, but the economics are unfavourable.

Use as a raw material/utilisation as component without prior treatment

Several options for utilisation as a component in the production or manufacture of products have been identified. One promising route is to use the gasification ash in asphalt or asphalt-like products (like C-fix), which is an established route for MSWI fly ash in The Netherlands. The key factor is that a non-porous, organic binder is used, which minimises contact with water. High carbon gasification fly ashes have been tested successfully as fine filler (7% w/w) in C-fix, a material with properties between asphalt and concrete. The carbon-rich ash performed better than

the combustion fly ashes. In contrast to most other forms of utilisation as filler, low pozzolanic properties are not a problem.

Another form of utilisation of carbon-containing ashes from gasification of biomass or waste can be the production of (lightweight) aggregates. Biomass ashes are part of the raw material that Lytag uses to produce lightweight aggregates (fly ash from a coal-fired power plant that co-fires several kinds of biomass). The Lytag process is based on granulating and sintering at 1300 °C. The surface area is strongly reduced and potentially toxic elements are evaporated or bound into the sintered material. In the process both the inorganic fraction of the ash and the caloric value of the carbon fraction are used. Lightweight aggregates can be used to replace natural gravel in (lightweight) concrete and other applications.

A third way of using fly ash from gasification of biomass is to replace cement or cement-like products in waste stabilization[1]. In particular the ashes with a high Ca-content and a low carbon content and showing pozzolanic properties are promising. E.g. Orujillo ashes have good mechanical properties and are susceptible to be used as partial replacement for cement; other ashes (SRF and wood waste) have shown good leaching properties, but display poor mechanical properties. Although potentially promising, more research is needed before this route can be identified as one of the "most promising utilisation options".

Use as a raw material/utilisation as component with prior treatment

Utilisation as a component after prior treatment opens countless opportunities. The most relevant option is the use of gasification fly ash after combustion as a filler or binder in concrete, cement or special mortars. Reduction of the carbon content and obtaining physical properties that resemble powder coal fly ash are needed. Most likely, the combusted gasification ash itself does not comply with required properties, but can be made part of a blend, whose quality depends on the application of the concrete (high grade, low grade). Good pozzolan properties are a good indicator, e.g., those ashes that have a high Ca content, either by themselves or due to the use of lime or dolomite in the gasification or combustion process. Guaranteeing a constant and predictable composition and the physical properties (loss on ignition, size fraction < 63 µm, water demand, hollow spaces, etc.) is of great concern for successful application in cement making. All ashes assessed in the GASASH project have the potential to be used as filler after thermal treatment that lowers the carbon content. Possible restrictions in this route are the high SO_4 and Cl contents and possibly alkali content of the ash after combustion.

Based on the available data, it can be concluded that the following utilisation options may be regarded as the most promising routes for the carbon-rich fly ashes that have been investigated with the GASASH project:

- Direct application as an alternative fuel
- Filler in asphalt or asphalt-like products
- Component in manufacture of lightweight aggregates
- Filler/binder in concrete mortars after low temperature treatment (combustion)
- High temperature treatment (vitrification) for the production of category 1 building material

Potentially promising utilisation options are

- Solidification/stabilisation of waste

[1] For solidification/stabilization no separate criteria are available. Landfill criteria have been adopted.

- Component in manufacture of fire proof plates
- Component in manufacture of lightweight bricks

Some form of after-treatments may be found attractive. Always the (economic) advantages and disadvantages of after-treatment must be balanced against direct utilisation. The most promising forms of after-treatment are

- Washing to remove chloride (and alkali)
- Heat-treatment to lower carbon-content

It should be noted that there is a large variation in ashes and ash qualities. The routes listed here are classified as "most promising" when the ashes as used in the GASASH project are taken as typical gasification ashes. The options are generalised suggestions based on the technical potential of the routes. The following issues should always be included the discussion:

- Different routes are the optimal alternative for different fuels, depending on specific characteristics of the ashes.
- Routes become more or less attractive, depending on local conditions. In particular gate fees and emission regulations for combustion.
- Lucky matches may always be found outside the presented selections, e.g., gasification ash from chicken litter utilised in manufacture of fertilizer.

Finally, it must be noted that consistency is the key factor for successful utilisation of gasification ashes. Ash must be generated in predictable quantities with guaranteed minimum quality. If that cannot be accomplished, landfill of ashes is nearly inevitable.

1.2.5 Techno-economic evaluation of different ash management chains

Several potential methods were identified and developed for the management of gasification ashes. Those methods and ash management routes which fulfilled the operational and environmental criteria in up-scaled size were evaluated economically. In this working method the sub-task results prompted in many cases new ideas for further development as the work packages were elaborated by the project partners partly separately and partly jointly together.

Identification of principal alternatives and specific methods

Several of the routes were found to be potential and were up-scaled and evaluated. The general workflow of the development testing and evaluation of methods was iterative as illustrated in the Figure 5.
Figure 6, Figure 7 and Figure 8 give an overview of the identified management routes for gasification fly ashes. Several of the routes were found to be potential and were up-scaled and evaluated further. Some identified routes were however estimated not to be potential because of environmental, technical or economical reasons.

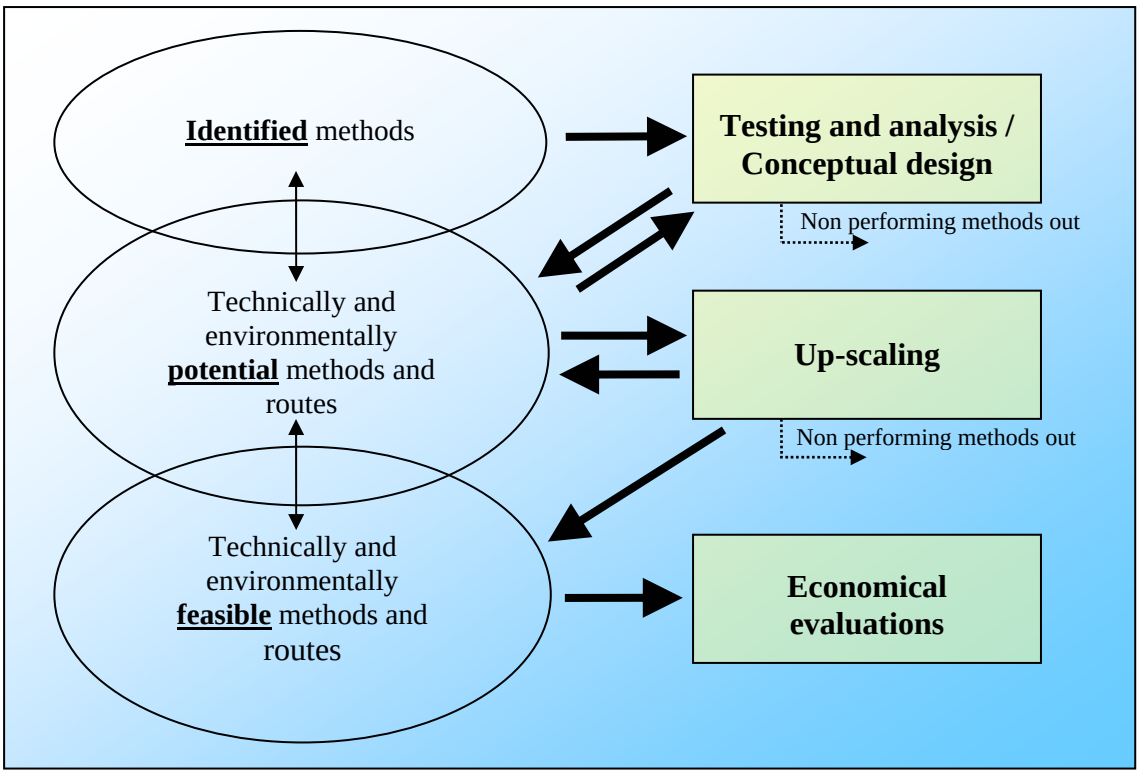


Figure 5. The iterative interactive work flow of method development, testing and evaluation.

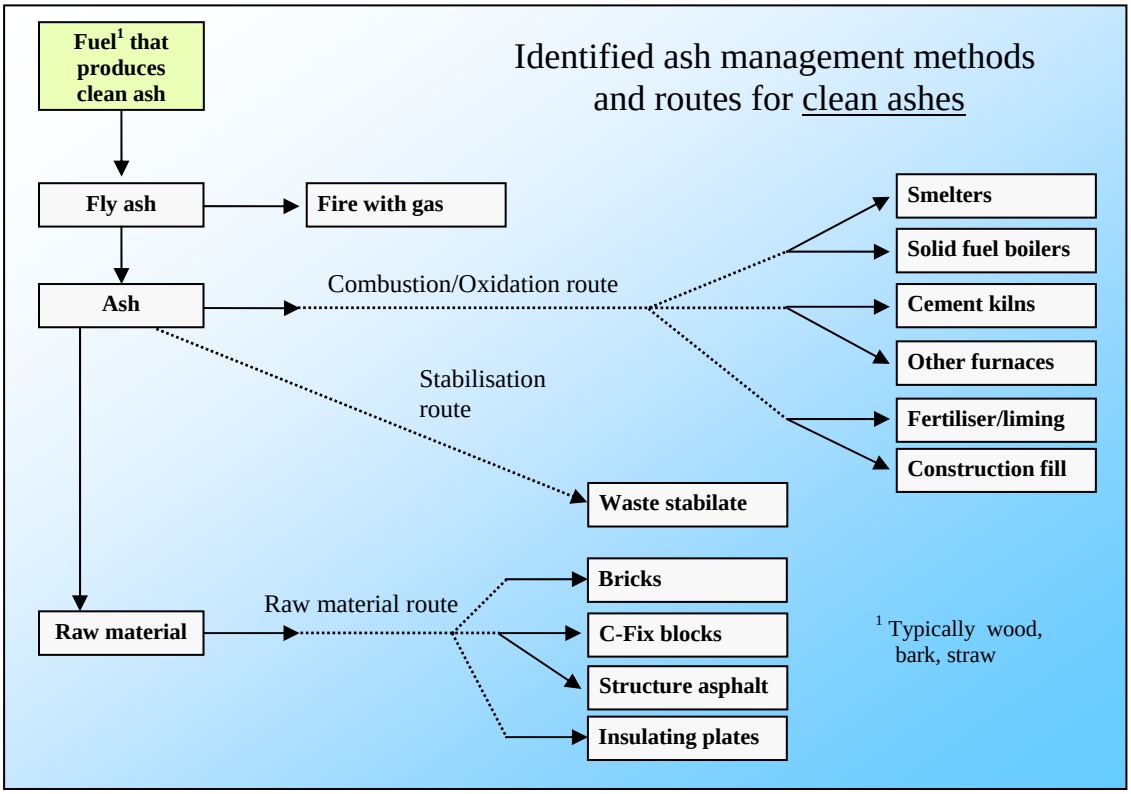


Figure 6. The identified methods and management routes for clean gasification fly ash. The figure illustrates the routes in a simplified form.

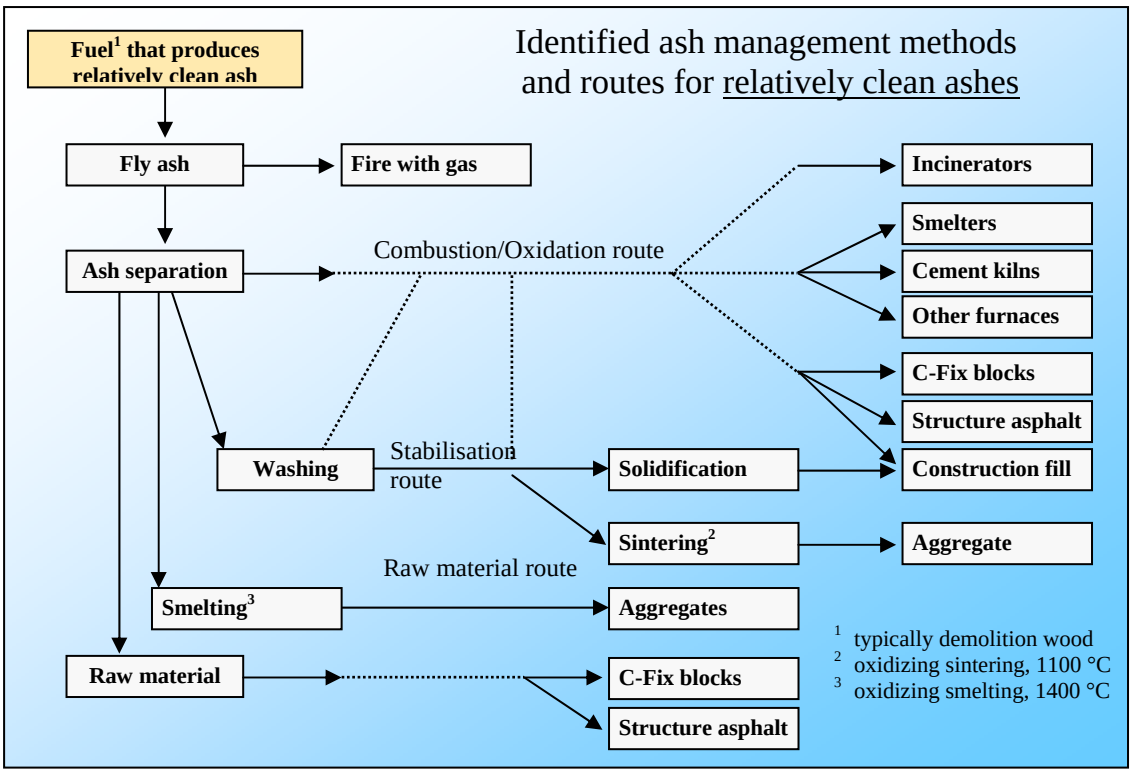


Figure 7. The identified methods and management routes for relatively clean gasification fly ash.

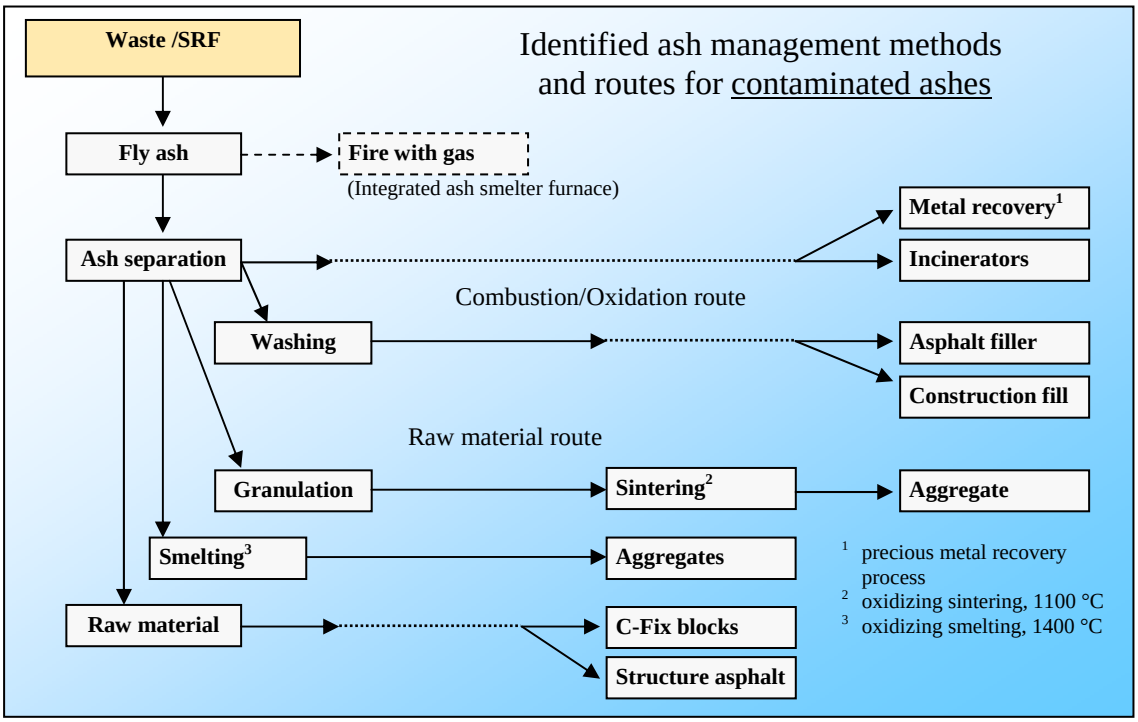


Figure 8. The identified methods and management routes for contaminated gasification fly ash.

Conceptual design and up-scaling and evaluations

The identified ash treatment methods and utilisation routes were evaluated and most of them were also tested. Those methods and routes that were estimated to be potential were taken into

the next phase for conceptual design, which included the process and special equipment designs. This phase was done in many cases in co-operation with equipment manufacturers. The technical feasibility, emissions and environmental effects were evaluated during the design work. The methods which were found operationally feasible were accepted for continuation.

The operational feasibility covers in this context functionality and scalability of the method as well as environmental performance. The methods which were evaluated to convert the gasification ash into an acceptable product or raw material or to utilise the energy content of the ash were considered to meet the required functionality. The possibility to utilise a method technically in an industrial scale was used as the criteria for scalability.

Environmental performance was also one key criterion in selection of the methods for analysis. The present and known future regulations for emissions and safety were used when evaluating the environmental performance. The directives for waste incineration and landfilling were used as criteria for environmental feasibility on many cases. Also the regulations for occupational health and safety as well as present and anticipated future building material requirements were used in evaluations.

An ash production of 1 500 kg/hour for fly ash and 250 kg/hour for bottom ash (after 75 % internal circulation) were selected as the basis of up-scaling and evaluations. These capacities were estimated to be relevant for an anticipated industrial gasification plant with fuel capacity of 80 MW. Smaller scale methods can offer feasible solutions at individual cases but in general a quite large capacity is needed for economical operation.

The following methods and routes (and different combinations) were selected for economical analysis:

- **Use of fly ash as fuel** in boilers and process furnaces
- **Granulation** to improve the ash properties for further processing or utilisation as fuel
- **Washing** to improve the ash properties for further processing or utilisation as fuel
- **Fluid bed combustion** to recover the energy content of ash and to improve the ash properties
- **Integrated fluid bed oxidation** to recover the energy content of ash and to improve the ash properties
- Production of aggregate with **oxidising sintering process**
- Production of aggregate with **oxygen smelting**
- **Fertiliser and soil improvement** use of clean ash
- **Metal recovery** from bottom ash of SRF gasification

Cost and economic impacts of ash treatment and utilisation

Table 6 and Table 7 summarise the estimated ash handling costs of different methods. The cost estimates should be considered as ranges to indicate the cost level rather than exact values as there are many assumptions and uncertainties. The tables however show the relative differences for evaluation of the usefulness of different methods.

Table 6. Estimates of the ash management cost levels for alternative methods and routes ash.

Treatment method/route **Fly ashes**	**Ash management cost; eur/t** Low – Mean – High	**Products of the method**
Landfilling at a special site, 0-case	150	None
Use as fuel without treatment	0	Low grade fuel
Granulation and use as fuel	17....24....31	Low grade fuel
Washing and use as fuel	14....20....29	Low grade fuel
Combustion of clean ash in integrated CFB, use as construction material	21....29....39	Secondary construction material + energy
Combustion of clean ash in integrated CFB + granulation, use as forest fertiliser	38…53…70	Low grade fertiliser + energy
Combustion of clean ash in integrated BFB, use as construction material	28....40....55	Secondary construction material + energy
Washing + combustion in integrated CFB, use as construction material	35…49…68	Secondary construction material + energy
Combustion of clean ash in stand-alone CFB, use as construction material	22....31....42	Secondary construction material + energy
Combustion of contaminated ash in stand-alone CFB, use in construction	38....54....72	Secondary construction material + energy
Combustion of clean ash in stand-alone BFB, use as construction material	29....43....58	Secondary construction material + energy
Combustion of contaminated ash in stand-alone BFB, use in construction	45....65....89	Secondary construction material + energy
Oxidising sintering of clean ash, use as aggregate	34....61....94	Aggregate
Oxidising sintering of contaminated low chloride ash, use as aggregate	79....130....179	Aggregate
Washing + oxidising sintering of contaminated ash, use as aggregate	93…150…208	Aggregate
Oxidising smelting, use as aggregate	203....274....351	Aggregate

Table 7. Estimates of the ash management cost levels with alternative methods and routes for bottom ash.

Treatment method/route **SRF gasification bottom ash**	**Ash management cost; eur/t** Low – Mean – High	**Products of the method**
Basic case, landfilling	50	None
Use as construction material without treatment	0	Low grade construction material
Metal recovery + landfilling	-175…-93...-8 (profit per ton of ash)	Metals

It should be noted that the ash handling cost is a relatively large cost item if the ash has to be landfilled in a special landfill. The ash management cost of an industrial scale gasifier is with the assumed landfilling cost of 150 eur/t for fly ash and 50 eur/t for bottom ash about 1,3 M eur/year. This is clearly a major cost item for a gasifier plant. However it is not always only a cost question, but in some cases there is no possibility to deposit large amount of ash in special landfills as there may not be such capacity available.

The estimated effect of the improvement of carbon conversion on production cost of fuel gas was also estimated. If alternative method is landfilling with 150 euro/t the economic impact of ash treatment and utilisation proved to be very attractive. The highest reduction of production cost was estimated to be 3.0 eur/MW_h(gas) when carbon-rich and contaminant-free fly ash is used as an alternative fuel. For contaminated ashes, which can be upgraded by washing, reducing impact on production cost of fuel gas was estimated to be 2.7 eur/t. Even sintering of low chloride SRF ash and use of the product as an aggregate was estimated to have 0.4 eur/t reducing impact on production cost of energy. Cost of washing of high chloride SRF ash, sintering and use of product as an aggregate was estimated to be more or less the same than landfilling cost having no

impact on production cost of fuel gas energy. In the fact, 14 of 15 studied ash treatment and utilisation routes had reducing or zero impact on energy production cost and only oxygen smelting of ash and using product as an aggregate had 2.7 eur/MW_h(gas) increasing impact on fuel gas production cost.

Finally, the economic impact of ash treatment and utilisation on production cost of electricity was estimated. Reduction of production cost of electricity was highest (8.5 euro/MWh(e) when carbon-rich and contaminant-free fly ash is used as an alternative fuel.

1.2.6 Conclusions

The objective of the GASASH project was to develop further gasification and gas cleaning process, ash treatment and ash utilisation methods in order to improve the economy of gasification based energy production. Work was focused on optimisation of process conditions, development of new components and methods and development of ash treatment and utilisation methods especially suitable for high carbon containing gasification fly ash.

Optimisation of gasification and gas cleaning process could be done successfully and carbon conversion could be slightly increased. However, the results were achieved in pilot-scale environment, which does not guarantee that results could be as successfully applied directly in large-scale industrial applications. In addition, in industrial applications availability of the plant has higher priority than slightly increased carbon conversion and slightly reduced volume of ash.

Development of fly ash treatment methods produced several technically feasible methods for upgrading of fly ash. Developed methods were focused primarily on reduction of carbon and chlorine content and leachability of heavy metals. Most of technically feasible methods were based on oxidation of fly ash but fly ash washing was developed in order to remove most of chlorine of fly ash. High temperature treatment was also studied and technically it proved to be efficient method to upgrade fly ash to high quality product for construction purposes. However, cost related to high temperature treatment of fly ash was very significant.

Development of utilisation routes for any ash qualities is extremely challenging because large quantities of coal derived combustion fly ash is available in most of EU countries. Quality of combustion ashes is usually significantly better than quality of gasification fly ashes. Practically the only application, in which gasification fly ash does not compete with combustion ashes, is use of high-carbon fly ash as an alternative fuel. Most of other studied applications were based on utilisation of inorganic part of fly ash. However, potential of gasification fly ash can be improved by upgrading quality of fly ash by oxidation, washing, etc.

The most promising ash treatment and utilisation routes were finally evaluated from economic point of view. The basic case was landfilling with 150 euro/t disposal cost. Most of developed routes were estimated to be economically feasible. The most feasible was direct use of contaminate free fly ash as an alternative fuel. Combustion and especially combustion in an integrated oxidiser was assessed to be very feasible, as well as even some more complicated upgrading and utilisation routes. The only evaluated route, which did not look feasible (when alternative route is landfilling with 150 euro/t), was oxygen blown smelting and vitrification. On the other hand, final product of this route was very high quality construction material with very low leachability.

The overall conclusion was that several technically feasible alternative ash treatment and utilisation routes were developed. The economic feasibility depends on cost of an alternative disposal method. When alternative disposal method is landfilling with 150 euro/t most of the developed ash treatment and utilisation routes will be feasible also from economic point of view.

Appendix B Deliverable 1 Report on Selection of Test Fuels and Test Program

DELIVERABLE REPORT NUMBER 1

CONTRACT N° : ENK5-CT-2002-00635

PROJECT N° : NNE5-2001-00598

ACRONYM : GASASH

TITLE : Improvement of the economics of biomass/waste gasification by higher carbon conversion and advanced ash management

PROJECT CO-ORDINATOR : VTT Processes

PARTNERS : VTT Processes (VTT)
Foster Wheeler Energia Oy (FWEOY)
Energy Research Centre of the Netherlands (ECN)
Asociación de Investigación y Cooperación Industrial de Andalucía (AICIA)
Pohjolan Voima Oy (PVO)
EMC Environment Engineering Limited (EMC)
Essent Energie Productie b.v. (EEP)

REPORTING PERIOD : From 1 November 2002 to 30 April 2003

PROJECT START DATE : 1 November 2002 DURATION : 36 months

Date of issue of this report : June 2003

Project funded by the European Community under the 'EESD' Programme (1998-2002)

DELIVERABLE REPORT NUMBER 1

CONTRACT No:	ENK5-CT-2002-00635
PROJECT No:	NNE5- 2001-00598
ACRONYM:	GASASH
TITLE:	Improvement of the economics of biomass/waste gasification by higher carbon conversion and advanced ash management

REPORT ON SELECTION OF TEST FUELS AND TEST PROGRAM

WP-1 Optimisation of the gasification process in order to increase carbon conversion and to reduce the amount of problematic fly ash

1 Introduction

This Deliverable No 1 concentrates on selection of test fuels and test program and is linked to Work Package 1 '*Optimisation of the gasification process in order to increase carbon conversion and to reduce the amount of problematic fly ash'* in this project.

Feedstocks for the tests of Work Package 1 will represent different biomass and waste derived fuels from North, Middle and South Europe. The main focus is on biomass fuels and agro residues.The selected fuels are wood, agricultural residues, demolition wood and different waste-derived fuels, which are potential fuels of atmospheric-pressure gasifiers connected to coal-fired power plants. In addition, co-gasification tests with coal/biomass and coal/waste will possibly be carried out aiming primarily to high-efficiency power cycles.

Fuels will represent different local conditions (Finland, the Netherlands and Spain) with commercial and environmental value. The feedstocks will also represent different gasification behaviour (volatile matter content, char reactivity, ash sintering behaviour, contents of contaminants), which have great effects on possible operating condition window of fluid-bed gasifiers. Fuels have been selected primarily by partners (VTT, FWEOY, ECN, AICIA and EEP) carrying out gasification and gas cleaning tests. PVO has also had an activie role in selecting test fuels. Total number of test fuels will be 7-10.

2 Selection of test fuels and test program

2.1 Fuel selection

Within the first six-month period, selection of different test fuels has been accomplished. Fuels have been selected primarily by partners *(VTT, FWEOY, ECN, AICIA)* carrying out gasification and gas cleaning tests. Total number of the test fuels will be 7-10. List of fuels to be used in gasification tests will be the following:

- clean wood residue (VTT)
- SRF (solid recovered fuel) (VTT)
- clean wood (ECN)
- demolition wood (ECN) Demolition wood will be delivered by EEP.
- clean biomass mixed with sewage sludge (ECN)

- orujillo (olive stone and pulp) (AICIA)
- olive pruning residue (AICIA)
- other optional fuels MBM, coal + residual edible oil and rice husk (AICIA)
- 2-3 fuel blends of biomass and waste (REF) and RDF (FWEOY)

Furthermore, PVO has given power producer viewpoint into the selection of feedstocks. Interaction with partners regarding to fuel selection has been active and essential in this subject. Partners have set up a schedule of the gasification test runs with selected fuels. All selected fuels to be used are listed in *Table 1*.

Table 1. Fuel selection list.

Partner	Fuel	basic characteristics
VTT	Woody fuel,	contamination free demolition wood chips; represents clean biomass
	Waste derived fuel/SRF pellets	commercial waste derived fuel; represents one of the design fuels of planned commercial gasification plants
ECN	clean biomass	wood
	demolition wood	wood taken from demolition and construction work; chipped; contains limited contaminations: traces of paint; nails, concrete, etc.
	biomass + sewage sludge	type of biomass not yet decided, probably wood pellets (with a constant and controlled composition)
EEP	*demolition wood*	*EEP will deliver demolition wood to ECN*
AICIA	Orujillo	PCI 4600 kcal/kg Humidity 8% Ashes 10% (DB) Volatile 72% (DB)
	Olive pruning residue	PCI 4300 kcal/kg Humidity 13% Ashes 10% (DB) Volatile 72% (DB)
AICIA **Optional fuels**	MBM (meat and bone meal)	PCI 4880 kcal/kg Humidity 3,5% Ashes 18% (DB) Volatile 72% (DB)
	Coal+residual edible oil	
	Rice husk	
FWEOY	2-3 different fuel blends of biomass and waste (REF) - RDF	pilot scale tests will be replaced at least partly by gasification and slip stream gas cleaning tests in commercial scale (Lahti gasifier); actual tests will be implemented by other project but ash related issues will be reported to this project; collected ashes will be used in the project (raw material)

2.2 Test program

The operated parameters of both CFB and BFB gasification will be optimised for the selected fuels. The parameters to be studied will include: operating temperatures, air/steam feed, use of bed additives, fluidising velocity, recycling of fines. Gasification optimisation tests will be carried out with existing test rigs from lab-scale to pilot plants. The test program of the Work Package 1, task 1.1 is presented in Table 2.

The test program includes both shorter set points of 3 to 12 hours for parametric studies and extended time tests of 30 to 100 hours for verifying the technical operability under selected optimal conditions. All test facilities are already existing, however some modifications and maintenance work are required. Test facilities are large enough for producing relevant information to be used in design of commercial-scale gasifiers.

Table2. Test program

Partner	Schedule	Fuel	Objectives	Test rig	Other comments
VTT	November 2002 - 2004	woody fuel, waste derived fuel	effects of temperature, fluidising velocity, gasification agent, bed materials, gas cleaning	CFB (350 kW_{th}) / BFB (1 MW_{th})	
AICIA	March 2003 - November 2003	Orujillo Olive prune residue Other	To relate gasification conditions to ashes characteristics	Lab scale BFB (6 kW_{th}) 9 tests (gross analysis) 9 tests (fine analysis)	In according to results, additional tests will be carried out
	July 2003 - November 2003	Orujillo Olive prune residue Other	Analysis of bed material role on ash quality	Lab scale BFB 3 tests	In according to results, additional tests will be carried out
	December 2003 - June 2004	Orujillo Other	Optimisation of gasification conditions to reach higher carbon conversion	Pilot scale BFB (195 kW_{th}) 6 tests	In according to results, additional tests will be carried out
	March 2004 - November 2004	Orujillo Other	Analysis of bed material role on ash quality	Pilot scale BFB 2 tests	In according to results, additional tests will be carried out
	March 2004 -November 2004	To determine	Long duration tests	2 tests	
ECN	3 runs before 1/5/2003	each of the three fuels	reference runs; influence of additive; creating large ash samples for distribution	BIVKIN:500 kW CFB	1)
	between 1/5/2003 and 1/12/2003	demolition wood	testing minature versions of coolers and cyclones; aim is to find optimum configuration on small scale	WOB: 0.5 kW BFB	number of tests is expected to be a few dozen.
	1 run, between 1/11/2003 and 1/4/2004	demolition wood	reference run; comparison with previous runs;	BIVKIN:500 kW CFB	if wanted: large ash samples for distribution
	5 runs, between 1/11/2003 and 1/4/2004	demolition wood	parametric study; aimed at maximising carbon conversion	BIVKIN:500 kW CFB	2)
	3 runs between 1/1/2004 and 1/7/2004	all three fuels	testing optimum configuration of coolers and cyclones on large scale	BIVKIN:500 kW CFB	
FWEOY	June 2003 - 2004	2-3 different fuel blends of biomass and waste (REF) - RDF	carbon conversion, ash quality	CFB gasifier, Lahti slipstream CFB (100 kW_{th}) CFB pilot (1 MW_{th})	

1) The BIVKIN will undergo major revision between 1/5/2003 - 1/9/2003. The gas cleaning section will be rebuilt. Part of the reconstruction is installation of a new cooler with multiple ports for sampling an extraction of ash and gas all temperatures.
2) The parametric study is shifted to a time after the revision of BIVKIN. With the new cooler a much more sophisticated sampling of ash can be performed which is profitable for understanding the effects of varying parameters.

3 Summary

The results to be obtained by VTT, FWEOY, ECN and AICIA for CFB and BFB gasification of a wide range of different European biomass and waste fuels will be evaluated. Evaluation will be done in co-operation with project partners. The aim is to create a realistic overall understanding on the possibilities and limitations for improving the carbon conversion and ash quality by the different methods studied in the project.

All of these gasification tests separately and together will support the overall objective for the Work Package 1. In addition, fuels have been carefully selected to eliminate overlapping.

Appendix C Deliverable 4&5 Report on Methods to Improve Carbon Conversion of Fluidised Bed Gasification and on Technical Possibilities to Reduce Ash Volume

DELIVERABLE REPORT NO 4 &5

CONTRACT N° : ENK5-CT-2002-00635
PROJECT N° : NNE5-2001-00598
ACRONYM : GASASH
PROJECT TITLE : Improvement of the economics of biomass/waste gasification by higher carbon conversion and advanced ash management

PROJECT CO-ORDINATOR : VTT Processes
PARTNERS : VTT Processes (VTT)
Foster Wheeler Energia Oy (FWEOY)
Energy Research Centre of the Netherlands (ECN)
Asociación de Investigación y Cooperación Industrial de Andalucía (AICIA)
Pohjolan Voima Oy (PVO)
EMC Environment Engineering Limited (EMC)
Essent Energie Productie b.v. (EEP)

PROJECT START DATE : 1 November 2002 **DURATION : 36 months**

Date of issue of this report : June 2005

Project funded by the European Community under the 'EESD' Programme (1998-2002)

TABLE OF CONTENTS

1 Introduction 2
2 Work package 1 2
3 Gasification test trials 3
3.1 Gasification test trials of VTT 3
3.2 Gasification test trials of ECN 7
3.2.1 Principle of HSD-CFB 7
3.2.2 Gasification of sewage sludge and mixed sewage sludge/wood pellets 7
3.2.3 Gasification of demolition wood with and without fines 8
3.2.4 Fuels 8
3.2.5 Equipment 8
3.2.6 Runs with clean wood testing HSD-CFB concept and a other measures 9
3.2.7 Runs with sewage sludge and mixed sewage sludge/wood pellets 9
3.2.8 Runs with demolition wood with and without fines 10
3.2.9 Results 10
3.2.10 Conclusions 20
3.3 Gasification test trials of AICIA 20
3.3.1 Gasification test trials 20
3.3.2 Test facility 22
3.3.3 Test procedure and sampling 23
3.3.4 Gasification pilot plant test results 24
3.3.5 MBM gasification tests 27
3.3.6 Conclusions related to AICIA's gasification test trials 30
3.4 Gasification test trials of FWE 30
3.4.1 Test facility 31
4.4.2 Gasification test trials 34
4.4.3 Results 37
4 Conclusions 45

DELIVERABLE REPORT NUMBER 4 & 5

CONTRACT No:	ENK5-CT-2002-00635
PROJECT No:	NNE5-2001-00598
ACRONYM:	GASASH
DELIVERABLE TITLE:	REPORT ON METHODS TO IMPROVE CARBON CONVERSION OF FB GASIFICATION AND ON TECHNICAL POSSIBILITIES TO REDUCE ASH VOLUMES

REPORT ON METHODS TO IMPROVE CARBON CONVERSION OF FB GASIFICATION AND ON TECHNICAL POSSIBILITIES TO REDUCE ASH VOLUMES

1 Introduction

This report is combination of deliverables 4 and 5, reports related to optimization of fluidised bed gasification and gas cleaning process. Technically improved carbon conversion is one of the key factors having effect on reduced ash volume. In addition, experimental work related to both titles has been carried out simultaneously. Deliverable is related to WP1 *Optimisation of the gasification process in order to increase carbon conversion and to reduce the amount of problematic fly ash*. Results presented in this report are based on experimental work carried out by VTT, Foster Wheeler Energia, ECN and AICIA.

The overall objective of WP1 is to minimise ash related cost by reducing volume of difficult fly ash primarily. The primary way to reduce volume of fly ash is improvement of carbon conversion. Improved carbon conversion results directly in decreased carbon content of fly ash, which has positive effect on volume of fly ash as well as quality of fly ash. However, it has to be kept in mind that although improved carbon conversion leads to reduced ash volume highest priority is always on reliable operation of the process.

2 Work package 1

The objectives of WP 1 were related to improvement of carbon conversion, reduction of ash volumes and effects of bed additives. The overall objective was to reduce cost related to disposal of solid residues. Work contained optimisation of BFB and CFB gasification of clean waste wood, clean wood pellets, demolition wood, solid recovered fuel (SRF), orujillo and sewage sludge. In addition, different bed materials have been used in order to optimise the gasification process. Most of gasification test trials were carried out with air but wood pellet gasification test trials with CFB gasification pilot plant were carried out with oxygen enriched air. Used bed materials were sand, sand and limestone and ofita.

3 Gasification test trials

Test trials were carried out by VTT, Foster Wheeler Energia, ECN and AICIA. In addition, Foster Wheeler carried out 3 MW_{th} slipstream tests in connection to 50-70 MW_{th} Lahti gasifier. One target of this slip stream testing was to optimise fly ash removal process and to collect fly ash for further studies of GASASH project.

3.1 Gasification test trials of VTT

Gasification test trials, feedstocks and results have been reported in details separately in combination with the first progress report of the GASASH project and therefore only summary is reported in this report. The previous report is also appended to this report.

VTT carried out gasification test trials with process development unit (PDU) circulating fluidised bed gasification and gas cleaning test facility (Figure 1.) and with pilot-scale bubbling fluidised bed gasification and gas cleaning test rig (Figure 2.). Used fuels were clean waste wood and solid recovered fuel (SRF). Both fuels were gasified with both test facilities. Bed material was in all cases mixture of sand and limestone and gasification agent was air and 10-20 % steam. Gasification temperature varied from 860°C to 895°C.

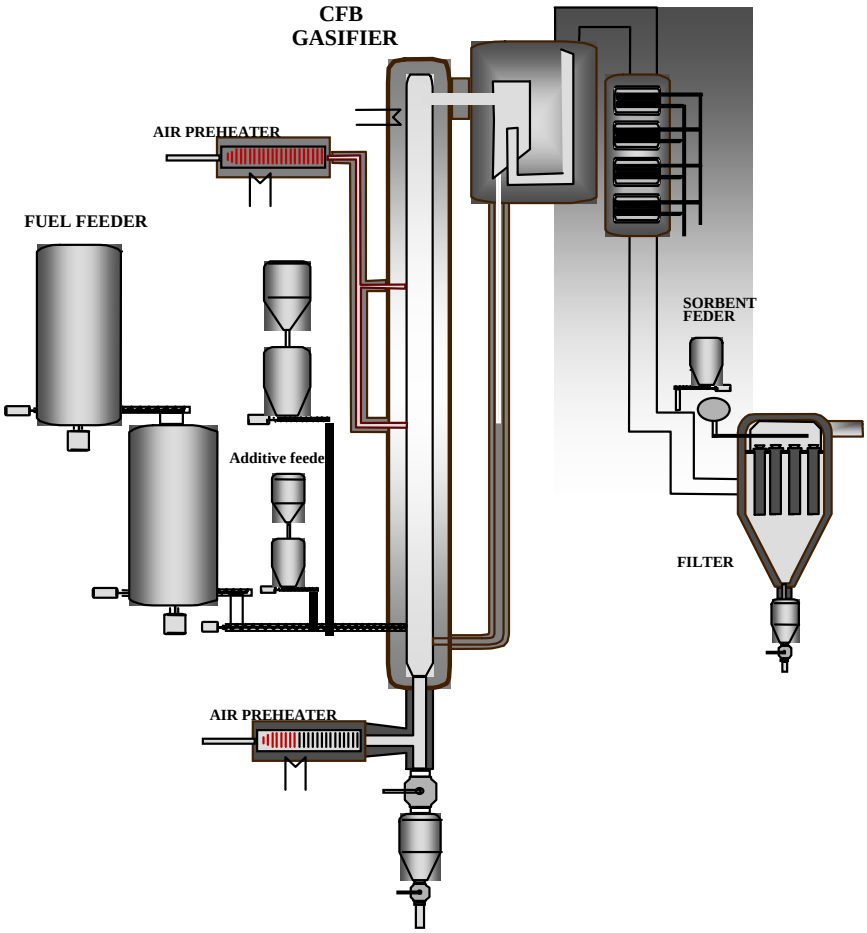


Figure 1. PDU-scale CFB gasification and gas cleaning test rig of VTT.

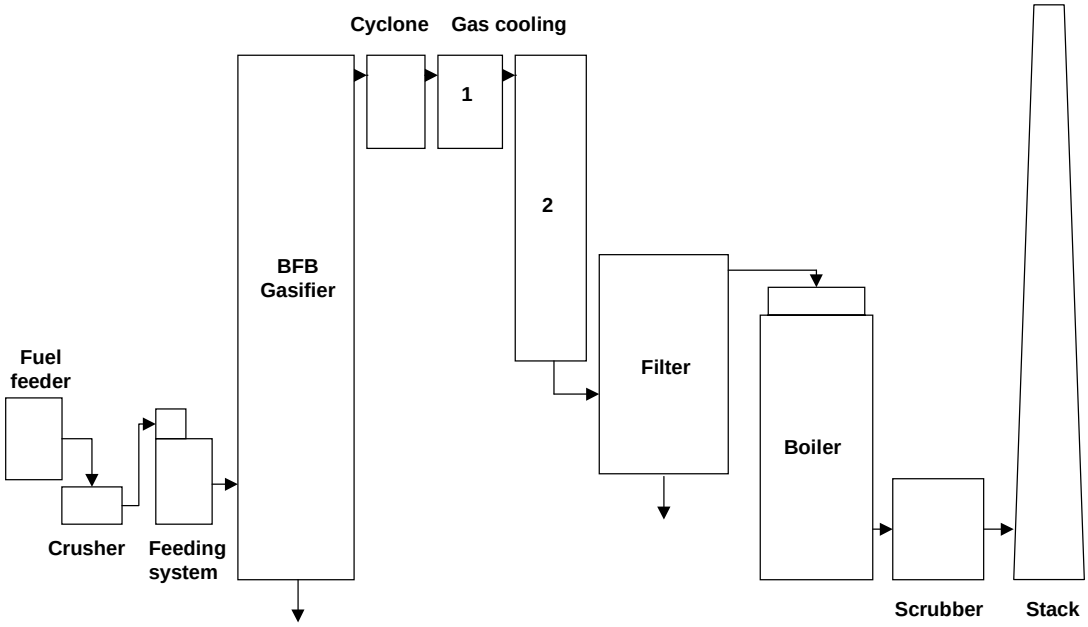


Figure 2. BFB gasification and gas cleaning pilot plant of VTT.

All test trials were technically successful and they all resulted in high carbon conversion. Carbon conversion in BFB gasification of clean waste wood varied from 94,4 % to 98,7 % when target was 96 %. In CFB gasification of clean waste wood carbon conversion was 98, which also was the target.

Solid recovered fuel is typically rich in plastic and paper, which are both very reactive and produce only little char. High reactivity results typically in high carbon conversion. In BFB gasification of SRF carbon conversion 97,5 % was achieved (target 96 %) and in CFB gasification carbon conversion varied from 96,1 to 98,0 % (target 98 %). All carbon conversions were high and technically gasification process was always stable.

The primary aim related to improved carbon conversion was to improve the quality of fly ash and reduce volume of difficult carbon containing fly ash. Table 1 summarises composition of ash fractions from bubbling fluidised bed gasification of clean waste wood. Fly ash contained 50-60 % carbon, which is still high. In most ash utilisation applications carbon content should be lower than 10...15 % or even lower. However, if fly ash does not contain harmful contaminants (heavy metals, etc.) it could be used s a fuel in power production process. Bottom ash was almost completely carbon free as expected. Heat exchanger dust represents fly ash collected by heat exchanger. This fraction contains typically some heavier particles than fly as collected by filter and thus carbon content of this fraction is lower.

In bubbling fluidised bed gasification of SRF main part of the fly ash was removed by filter unit. Typical bulk compositions of different solid streams (filter dust, bottom ash, heat exchanger dust) are presented in Table 2. These data show that bottom ash is primarily composed of sand additive and contains no combustible material. Filter dust contained only 10.6 % of carbon, which is very low compared to waste wood derived filter dust. Low

carbon content of filter dust was achieved by high reactivity of the feedstock and successful operation of the gasifier. The carbon content of heat exchanger dust was 3.2 wt%.

Table 1. Composition of different ash products in BFB gasification of clean waste wood.

Set point	BFB 0250A	BFB 0250B	BFB 0250C	BFB 0250D
Filter dust [1], wt% (d.b.)				
C	51.5	53.9	60.7	56.0
H	0.8	0.8	0.8	0.8
N	0.2	0.3	0.3	0.2
O (difference)	5.2	5.9	3.6	8.6
Ash	42.4	39.3	34.8	34.4
Bottom ash, wt% (d.b.)				
Ash	99.7	99.8	99.6	99.6
Heat exchanger dust, wt% (d.b.)				
C	24.4	26.6	30.5	25.2
H	0.9	0.2	0.5	0.7
N	0.1	0.1	0.1	0.1
O (difference)	15.3	10.6	7.8	13.1
Ash	59.3	62.5	61.1	60.9

[1] dry sample

Table 2. Composition of different ash products in BFB gasification of solid recovered fuel.

Set point	BFB 0310C
Filter dust [1], wt% (d.b.)	
C	10.6
H	0.26
N	0.08
O (difference)	4.3
Ash	84.8
Heat exchanger dust, wt% (d.b.)	
C	3.2
H	0.04
N	0.02
O (difference)	4.2
Ash	92.5
Bottom ash, wt %	
Ash	100

[1] dry sample

CFB gasification of clean waste wood resulted in lower carbon content of fly ash than was achieved in BFB gasification. Carbon content of fly ash from CFB gasification of SRF was close to that achieved in BFB gasification of SRF. Bulk compositions of different solid streams (filter dust, bottom ash) are presented in Table 3. These data show that bottom ash is primarily composed of sand additive and contains almost no combustible material.

Table 3. Composition of different ash products in CFB gasification of clean waste wood and solid recovered fuel.

Set point	CFB 0323A	CFB 0323B1	CFB 0323B2	CFB 0323C
Feedstock	Clean waste wood	SRF	SRF	SRF
Filter dust [1], wt% (d.b.)				
C	40.9	13.3	12.1	13.4
H	0.5	0.36	0.2	0.5
N	0.1	0.1	0.1	0.1
O (difference)	9.9	2.6	8.0	0.8
Ash	48.1	80.8	76.6	81.6
Bottom ash, wt %				
Ash	99.5	99.9	99.8	99.7

[1] dry sample

Conclusions related to VTT's gasification test trials (WP1)

Fluidised test gasification test trials carried out in WP1 focused on developing and improving the gasification process for woody biomass and solid recovered fuel (SRF). The objective was to optimise the fluidised bed gasification process in order to increase carbon conversion and to reduce the amount of problematic fly ash. Both circulating fluidised bed and bubbling fluidised bed gasification process were considered.
The following conclusions can be made on the basis of test trials:

- All tests were successful and good material balances could be calculated.
- Operation of the bubbling fluidised bed gasifier with woody biomass was stable and woody fuel could be gasified successfully in the extended test of 90 hours of continuous operation.
- Very good carbon conversions were achieved in BFB gasification of woody fuels at 862-893°C. The carbon conversion to gas and tars were higher than 95 % in all set points and highest carbon conversion was 98.7 %.
- Operation of the bubbling fluidised bed gasifier with solid recovered fuel was stable and SRF could be gasified successfully.
- Very good carbon conversion was achieved in BFB gasification of SRF at 870°C. The carbon conversion to gas and tars was (about 98 %).
- Optimised operation of the gasifier resulted in low carbon content of filter dust (10.6 wt %).
- Operation of the circulating fluidised bed gasifier with woody biomass was stable and waste wood could be gasified successfully.
- Good carbon conversion was achieved. The carbon conversion to gas and tars was 97 %.
- Carbon content of filter dust was relatively low for woody fuel (40.9 %).

The effects of different compositions of bed materials were studied by carrying out gasification test trials using different mixtures of bed materials. The aim was to optimise carbon conversion, minimise tar formation and minimise volume of harmful fly ash.

3.2 Gasification test trials of ECN

ECN's contribution consists of results from experimental work and background knowledge. In the framework of Work Package 1, several runs with ECN's pilot-scale 500 kW(th) CFB gasifier (BIVKIN) have been performed using clean wood pellets, sewage sludge and demolition wood as fuel. Ash composition of the fly ash was determined for all runs. Gasification test trials carried out by ECN were not only related to improved carbon conversion and reduction of ash volumes but also to improvement of ash quality in order to enable further utilisation..

3.2.1 Principle of HSD-CFB

The High Solids Density Circulating Fluidised-Bed (HSD-CFB) principle is in essence a separation of the fuel inlet and the air inlet that creates two gasification zones. Air and recycled char enters the lower zone, which enables faster char oxidation reactions due to the presence of O_2. Fuel is introduced in the upper zone, where there is no O_2 left, which limits the direct reaction of volatiles to reactions with H_2O and CO_2. In addition, a flow restriction is made to interrupt a downward flow along the walls. The HSD-CFB principle was been tested by moving the fuel injection halfway up in the riser and inserting a ring in the riser. In Figure 3graphic representation of the changes is displayed.

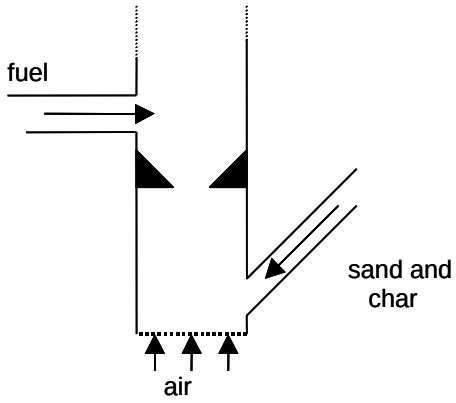


Figure 3. Diagram of the bottom part of the riser in a CFB designed according to HSD-CFB principle.

3.2.2 Gasification of sewage sludge and mixed sewage sludge/wood pellets

Four runs using sewage sludge were performed with the BIVKIN. Two runs were done using only dried sewage sludge. In these runs the objective was to collect ash at several temperature levels and compare the composition. The bulk of the ash was removed in a hot cyclone directly after the gasifier, at gasification temperature. Another ash fraction was collected in a cold cyclone placed after the cooler, at about 200°C. Finally, a dust filter was used to collect the remaining ash. In two other runs, a mixture of dried sewage sludge and clean wood pellets was used. Wood pellets were added to lower the air/fuel ratio and improve the fuel gas quality. Objective of the runs was to improve the gasification behaviour and study the effect on the ash composition. In this case ash was only collected in the cold cyclone.

3.2.3 Gasification of demolition wood with and without fines

Two runs with the pilot-scale 500 kW gasifier (BIVKIN) were done using demolition wood with or without the finest fraction. Objective of these tests is to investigate whether a small adjustment to the fuel (removal of fines) is having a significant effect on the ash quality.

The current situation is that EEP uses fuel with fine dust. The option to use demolition wood with or without fine dust is essentially a decision based on practicality. There will certainly be an impact of using fuel without fine dust on the quality of the carbon-rich fly ash. The concentration of problem elements in the producer gas that is fed to the combustion chamber of the coal-fired plant will certainly diminish. Both may have positive effects. On the other hand, the fuel price increases, because the fuel supplier must find ways to sell the fine dust, most likely at a lower price. In the worst case it needs to be treated at chemical waste at considerable costs. It is easy to predict, that implementation of the measure (fuel without fines) will need a solution for utilisation of the fine dust in a useful way.

The BIVKIN gasifier was used as a simulation of the AMER gasifier. Two batches of demolition wood were shipped from one company producing fuels from recycled wood. The two batches were produced in exactly the same way, but one of the batches was sieved to remove wood particles smaller than 3 mm. During both gasification runs several kilograms of ash were collected for future use.

3.2.4 Fuels

Table 4. List of fuel used by ECN in GASASH project.

Fuel	basic characteristics	links to other partners/projects	Other background information related to fuels
clean wood	clean wood pellets of known and stable composition	fuel is used in most ECN Biomass projects, including HSD-CFB Project	comparable fuel is used in Cuijk Fluid Bed Combustor
demolition wood	wood taken from demolition and construction work; chipped; contains limited contaminations: traces of paint; nails, concrete, etc.	fuel of choice for EEP in their AMER-CFB	important fuel, widely used in Netherlands; Locally, known as "class 2 wood" or "B-hout"
sewage sludge (also mixed with clean wood)	dried sewage sludge has a relatively stable composition independent of the source; clean wood pellets (see above)	mixtures of fuels, including sewage sludge are used in other ECN projects	dried sewage sludge is a large unused resource of biomass, with a high social interest

3.2.5 Equipment

For the test runs, ECN's 500 kW circulating fluidised-bed gasifier (BIVKIN) has been used. The BIVKIN (Biomassa Vergassings Karakeriserings Installatie) is an atmospheric circulating fluidized-bed gasifier of 500 kW_{th} (max. fuel rate 100 kg/hr). The BIVKIN is in principle also suitable for combustion experiments. The CFB gasifier has several fuel bunkers and it is possible to mix fuels. The riser is 6 m high and has a diameter of 20 cm. The gasifier has an air and a steam supply. The recycling loop is composed of a cyclone for ash/sand separation and a loop seal. A second (hot) cyclone is present directly after the

gasifier to extract ash at the same temperature as the gasifier is operated. A third (cold) cyclone is present after a cooler. Alternatively, a ceramic filter can be used for solids removal. The hot cyclone can be switched off, so that all solids are entrained through the cooler and collect in the cold cyclone. The fuel gas is cleaned using water and oil based scrubbers. The clean fuel gas is fed to either a gas engine or a boiler.

At standard conditions, quartz sand of 0.4-0.6 mm is used as bed material. Gasification temperature is varied from 800 to 900°C. The primary air feed is 75-90 Nm^3/h, pre-heated to 350°C. Air to the seal pot is 23 Nm^3/h. Linear gas velocity is 6.5 to 7.0 m/s. Typical feed rates vary from 75 to 120 kg/h, depending on the caloric value of the fuel. The fuel and air supply are fixed to obtain the gasification temperature.

3.2.6 Runs with clean wood testing HSD-CFB concept and a other measures

The effect on the carbon burnout level of several measures that can be taken operating a fluidised bed gasifier was investigated in the HSD-CFB project. The runs (relevant to the GASASH project) are done using clean wood pellets with a low ash content and a very reliable composition. The fuel characteristics are included in Table 4 The measures investigated are:

- separation of the air inlet and the fuel inlet and introduction of a flow restriction (HSD-CFB principle)
- increasing of temperature by increasing the air/fuel ratio
- enhanced heat loss (not lowering the temperature) by increasing the air/fuel ratio combined with non-preheating of air, dilution with nitrogen or heat sink in reactor wall
- smaller or coarser sand as bed material

The effect of each measure and some combination of measures was determined in comparison to a standard run at 850°C and an air/fuel ratio of 0.22 (equivalence ratio = E.R.), resulting in carbon conversion of 92% and a cold gas efficiency of 69%. The technical details of the various runs done under a parallel project are summarised in the ECN Report ECN-C--03-053.

3.2.7 Runs with sewage sludge and mixed sewage sludge/wood pellets

Two BIVKIN runs with a mixture of sewage sludge and wood pellets were performed. One run was done with 25% sewage sludge and 75% clean wood pellets. The other run was done with 50% sewage sludge and 50% wood pellets. The sewage sludge was dried to a moisture content of 7 wt. The wood pellets are made from clean wood having a very low ash content of only 0.3 wt%. Details of the composition of the wood pellets and the sewage sludge can be found in Table 3.1. Gasification temperature was 900°C and the air/fuel ratio was 0.3. Gas velocity was 7 m/s. Bed material was sand of 0.4-0.6 mm. The hot cyclone was switched off. Ash was collected in the cold cyclone at 200°C.

Two BIVKIN runs were performed with sewage sludge that was dried biologically (heat from composting) to 19%. Details of the composition of the sewage sludge can be found in Table 4. Gasification took place at 800 and 900°C with air/fuel ratios of 0.41 and 0.54, respectively. Gas velocity was 6.5 m/s. The bulk of the ash was collected from the hot

cyclone at either 800 or 900°C. The second ash fraction was collected from the cold cyclone at 200°C. The remainder of the ash was collected in the filter.

3.2.8 Runs with demolition wood with and without fines

Two BIVKIN runs have been performed using demolition wood. The fuel was prepared by Meer Recycling. Regular demolition wood was shredded and sieved over a 15 mm screen. The wood that passed this screen was labelled as "demolition wood 0-15 mm" and used in one run. A similar batch of demolition wood was made in the same way, but an additional screen of 3 mm was placed after the shredder. In this way the fraction 0-3 mm was removed from the demolition wood. This batch was labelled as "demolition wood 3-15 mm" and used in the other run. BIVKIN settings were kept identical for both runs. Quartz sand 0.4- 0.6 mm was used as bed material. Gasification temperature set at 850°C. Primary air supply was 85 Nm^3/hr, air supply to the seal pot was 20 Nm^3/hr. Fuel supply rate was slightly lower for demolition wood 0-15, 88 kg/hr, compared to 96 kg/hr for demolition wood 3-15 kg/hr. The hot cyclone was switched off. Ash was collected in the cold cyclone at 310°C.

3.2.9 Results

In principle, many parameters have an influence on the carbon conversion in a gasification process. In practice, the number of measures that can be taken to manipulate biomass gasification is limited, often influencing multiple parameters. The effect on the carbon conversion of the following measures has been investigated.

- separation of the air inlet and the fuel inlet and introduction of a flow restriction (HSD-CFB principle)
- increasing of temperature by increasing the air/fuel ratio
- enhanced heat loss (not lowering the temperature) by increasing the air/fuel ratio combined with non-preheating of air, dilution with nitrogen or heat sink in reactor wall
- smaller or coarser sand as bed material
- specific elimination of the finest size fraction (0-3 mm) from demolition wood as fuel
- addition of regular wood to low caloric fuel (sewage sludge)

The conclusions of the runs is that physical separation of the fuel inlet and the air inlet, the HSD-CFB Concept, is the most effective measure for increasing the carbon conversion in the gasification of biomass. In the following sections some of the measures are discussed in detail.

Effect of air ratio and temperature

The most important data from the HSD-CFB project, relevant for the GASASH project are reproduced in Table 5. A complete set of data can be found in the final report of the HSD-CFB project. These include the effects of varying the air ratio, the temperature and application of the HSD-CFB principle.

Table 5. Comparison of the effect of different measures on the carbon conversions in gasification of biomass with taken.

run	measure	temperature	air ratio	carbon conversion	cold gas efficiency
ref	reference	850°C	0.22	92%	69%
3a/c	higher temperature	880°C 900°C 930°C	0.26 0.27 0.30	93% 92% 96%	68% 68% 67%
5a/d	no preheating + wall cooling	830°C 840°C 840°C 850°C	0.35 0.32 0.29 0.28	99% 96% 92% 87%	61% 64% 65% 67%
6a/b	no pre heating + nitrogen addition	850°C 850°C	0.32 0.29	96% 94%	62% 67%
6c	no preheating	850°C	0.26	92%	68%
8a/b	HSD-CFB	810/880°C* 820/920°C*	0.23 0.26	95% 99%	70% 69%

*) temperatures for bottom and top part of the riser, respectively

There is a strong correlation between the air ratio and the carbon conversion. This is especially clear from runs 3a/c and 5a/d, where the carbon conversion increases when the air ratio increases. This not only happens when the temperature increases as well (run 3a/c), but also when the temperature is kept constant (5a/d). Apparently, it is not the temperature, but the reaction with oxygen from air that is enhancing the carbon conversion.

The carbon conversion is significantly higher when the air ratio is above 0.30, but the effect of a higher air ratio is complex and not limited to the carbon conversion. With a higher air ratio, more producer gas and more heat are produced (independent of the actual temperature). The higher amount of oxygen also means that in the producer gas is further oxidised than at a lower air ratio. The overall effect is that the cold gas efficiency (caloric value of the combustibles in the producer gas) is constant when the air ratio is below 0.3 and there is no adverse or beneficial effect for the production of syngas or applications in gas engines or gas turbines there is no beneficial effect. However, when the carbon conversion significantly increases, i.e., when the air ratio exceeds 0.30, the cold gas efficiency decreases.

Application of the HSD-CFB principle

In the runs where the HSD-CFB principle is tested (8a/b), the carbon conversion and thecold gas efficiency are increased, but the overall air ratio is not higher than in the reference case. The negative effect of putting more oxygen in the gasifier are avoided and the cold gas efficiency is increased. This observation makes application of the HSD-CFB principle the most effective measure that can be taken to improve carbon conversion and/or cold gas efficiency at the same time.

The retrofit as done in the BIVKIN is simple and merely approaches the HSD-CFB principle, but already a significant improvement in carbon conversion was found. The full potential of this principle should be investigated more thoroughly, but it should first be done at an academic level, outside the scope of the GASASH project. The design of a new type gasifier based on the HSD-CFB principle must address potential problems with pressure drops, and the scale-up of the narrow passage between the two sections.

Combining sewage sludge with wood pellets

The carbon conversion of the runs with a mixture of sewage sludge and clean wood pellets was 94-95%, comparable to runs with 100% clean wood pellets at an air/fuel ratio at 0.3. The runs produced ash that is dominated by the ashes from sewage sludge. This is valid for both runs (with 25% and 50% sewage sludge). The composition of the ash and the fuel is presented in Table 6. The ash compositions reflect the composition of sewage sludge. There is hardly any correlation with the composition of the wood pellets. This observation is not a surprise, because the sewage sludge has a total ash content of about 33% (dry) while the clean wood pellets have an ash content of only 0.3%. The conclusion is that for the ash composition it is not important how much wood is co-fired. Mixing of sewage sludge may influence other gasification parameters, e.g. tar emission, but during our tests there were no differences that attracted attention.

The two runs where only sewage sludge was gasified used a different kind of sewage sludge, which was dried biologically. This did not seem to affect the overall performance in the gasifier. Ashes were extracted at three different temperature levels in the gasifier. The carbon conversion was deterimined to be 96% for the run at 800°C and 99% for the run at 900°C. This is rather high, caused by the high air/fuel ratio (0.41 and 0.54, respectively). Data of the ash collection are summarized in Table 7. The bulk of the ash is collected in the hot cyclone. The mass balance of the total amount of ash (sum of ash extracted versus ash introduced in fuel) closed within 5%. Most element balances closed as well, with noted exceptions. The recovery of Hg and S in the ash was too low, 6 and 45%, respectively in the run at 800°C. This is explained by a preference of these elements to stay in the gas phase. Recovery of K, F, Ti, Ni and Cr was too high, 182, 7286, 662, 195 and 141%, respectively, in the run at 800°C. In the case of F and Ti, this is probably the result of a problem in the fuel analysis. Both elements are notoriously difficult to analyse. The high recovery of Ni and Cr can be explained by corrosion or wear of stainless steel. The reason why K levels in ash are higher than expected remains uncertain. For the run at 900°C very similar results were found.

Table 6. Composition of wood pellets, sewage sludge and ashes from combustion of wood pellets and sewage sludge; all data on dry base, moisture as received

Material Type		wood pellets fuel	sewage sludge fuel	25% sewage sludge ash	50% sewage sludge ash
Ash(815°C)	wt% (dry)	0.3	33.2	70.5	88.7
Volatile	wt% (dry)	82.1	53.5	0.3	0.2
Moisture	wt% (a.r.)	8.0	7.2	0.7	0.2
C	wt% (dry)	48.3	34.8	31.9	12.8
H	wt% (dry)	6.0	4.9	0.2	<0.1
N	wt% (dry)	45.2	27.0	2.4	2.7
O	wt% (dry)	0.1	5.1	<0.1	<0.1
Cl	mg/kg (dry)		1057	748	294
Al	mg/kg (dry)	65	18443	33831	45851
As	mg/kg (dry)		7.3	13.5	16.9
B	mg/kg (dry)	3	39	76	82
Ba	mg/kg (dry)	14	339	683	866
Ca	mg/kg (dry)	1303	29233	57477	79020
Cd	mg/kg (dry)	0.2	1.1	3.9	1.7
Co	mg/kg (dry)	0.1	5.2	15.8	17.3
Cr	mg/kg (dry)	5	42	486	361
Cu	mg/kg (dry)	5	371	517	811
Fe	mg/kg (dry)	83	35782	59648	55046
K	mg/kg (dry)	380	4777	15524	15641
Li	mg/kg (dry)		5.5	10.1	13.0
Mg	mg/kg (dry)	136	5386	10624	14286
Mn	mg/kg (dry)	115	487	1817	1629
Mo	mg/kg (dry)	0.4	12.8	36.2	26.5
Na	mg/kg (dry)	70	1739	3977	5105
Ni	mg/kg (dry)	3	24	687	777
P	mg/kg (dry)	85	32446	53435	64282
Pb	mg/kg (dry)		130	373	263
S	mg/kg (dry)	10	1419	430	409
Sb	mg/kg (dry)	0.8	3.7	5.7	0.4
Se	mg/kg (dry)		5.4	7.9	8.6
Si	mg/kg (dry)	209	33555	78651	100169
Sn	mg/kg (dry)	0.9	21.0	11.3	8.3
Sr	mg/kg (dry)	5	294	541	752
Ti	mg/kg (dry)	7	1303	2570	3397
V	mg/kg (dry)	0.1	18.4	35.7	49.1
Zn	mg/kg (dry)	15	899	1802	2422

All ashes were analysed for trace elements, presented in Table 8. For each element the distribution between the ash fractions is calculated and compared to the overall mass distribution of the ashes for both runs. The results can be found in Figure 4 and Figure 5. The distribution is normalized on the total amount of this element in the ash fractions; the fraction emitted in the gas phase is excluded, but this is only a major issue for the elements Hg, S, Cl, Se and Te which are known to form species that remain largely in the gas phase even at ambient conditions.

The data in Figure 4 and 5 are very similar. Nearly all elements are recovered in the hot cyclone at levels that are comparable to the total mass fraction. This means that the bulk of the elements is not affected by temperature of ash collection. Elements that are found in

significantly lower levels are Se, Cd, and Cl. This could be expected based on the volatility of the compounds that these elements form. At the temperature level in the hot cyclone these elements are preferably in the gas phase and not in the ash. When the flue gas is cooled these elements condense into the solid phase and are found in the ash of the cold cyclone and the filter in larger proportions. A number of elements, As, B, Mo, Ni, Pb, S, Sb and Sn shows a small concentration in the ash of the cold cyclone and the filter. These elements are noticeably affected by the temperature of ash extraction, but the shift is not dramatic.

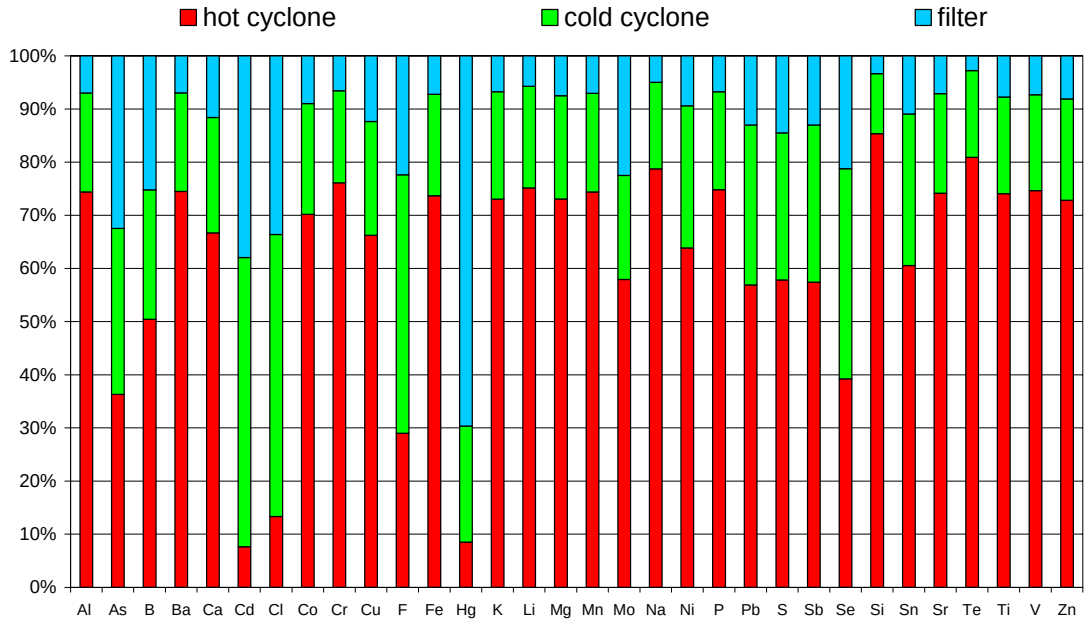


Figure 4. Distribution of elements in the three ash fractions produced in the gasification of 100% sewage sludge at 800°C; total mass distribution is 77% in hot cyclone, 17%% in cold cyclone and 7% in filter at ambient conditions

Sand is preferentially found in the hot cyclone. The sand is either from the fuel or from attrition of the bed material. The sand dilutes the material in the hot cyclone making the overall mass fraction relatively large, but it does not influence the distribution of the elements.

Table 7. Data of ash collection in gasification runs with 100% sewage sludge

run	800°C	800°C	800°C	900°C	900°C	900°C
location	hot cyclone	cold cyclone	dust filter	hot cyclone	cold cyclone	dust filter
temperature [°C]	800	200	ambient	900	200	ambient
fraction [wt%]	77	17	7	85	12	3

Table 8. Composition of sewage sludge and ash collected in gasification runs with 100% sewage sludge; moisture content as received, all other data on dry basis.

Material		sewage sludge*	ash hot cyclone	ash cold cyclone	ash filter	ash hot cyclone	ash cold cyclone	ash filter
Run		both	800°C	800°C	800°C	900°C	900°C	900°C
moisture	wt%	19	0.0	1.2	2.5	0.0	5.8	6.3
ash	wt%	43	97	92	91	100	93	82
Al	mg/kg	21583	50885	54669	52442	56272	54229	46735
As	mg/kg	8	9	34	91	15	125	160
B	mg/kg		56	116	307	71	353	448
Ba	mg/kg	359	861	919	886	935	936	829
Be	mg/kg		0.8	0.8	0.8	0.8	0.9	0.8
Ca	mg/kg	36750	75297	104949	144277	89410	123250	137117
Cd	mg/kg	1	0.3	8.5	15.2	0.1	22.9	27.2
Cl	mg/kg	1942	580	9891	16073	219	5105	35023
Co	mg/kg	7	16	20	22	20	24	21
Cr	mg/kg	67	197	192	187	258	235	183
Cu	mg/kg	519	921	1272	1890	1064	2011	2051
F	mg/kg	2	87	625	739	107	1123	1479
Fe	mg/kg	53813	110532	122680	119669	129137	114948	101911
Hg	mg/kg	1	0.0	0.2	1.7	0.0	2.0	27.3
K	mg/kg	3892	14244	16894	14445	15182	13174	11406
Li	mg/kg		18	20	15	46	19	14
Mg	mg/kg	4658	10364	11775	11729	11439	12054	10739
Mn	mg/kg	684	1363	1458	1417	1482	1447	1212
Mo	mg/kg	9	21	31	90	22	114	139
Na	mg/kg		5558	4919	3884	5566	4329	3497
Ni	mg/kg	33	113	203	184	524	633	378
P	mg/kg	35200	73112	77173	72525	79979	74840	64799
Pb	mg/kg	173	246	558	619	143	1637	1719
S	mg/kg	14000	10014	20533	27605	4684	11286	17925
Sb	mg/kg	7	11	25	28	12	49	37
Se	mg/kg	27	1.4	6.2	8.6	6.9	10.2	9.1
Si	mg/kg		149840	84704	65048	139656	77207	60743
Sn	mg/kg	22	43	87	86	30	284	228
Sr	mg/kg		485	526	513	529	528	455
Te	mg/kg	4	5.2	4.5	2.0	4.7	4.3	1.9
Ti	mg/kg	287	3865	4067	4447	4116	3959	3885
V	mg/kg	23	47	49	51	51	54	52
Zn	mg/kg	1074	1965	2204	2406	1964	2133	2046

* data on composition supplied with delivery of sewage sludge

Objective in the project was to investigate whether problem elements can be concentrated in a small ash fraction, by removal of the bulk of the ash at a high temperature level. The results from the runs with sewage sludge indicate that this cannot be achieved. The set of problem elements that can be removed is limited to Se, Cd and Cl. Some problem elements are somewhat depleted, including Pb, Mo, As and Sb. Other problem elements like Cr, Cu and - surprisingly - Zn are not affected equally distributed. The conclusion is that extracting ash at high temperature levels cannot be used to improve the ash quality of the bulk of the ash. This conclusion was one of the main reasons to reconsider the strategy of "Staged cooling and particle removal" in WP 2.

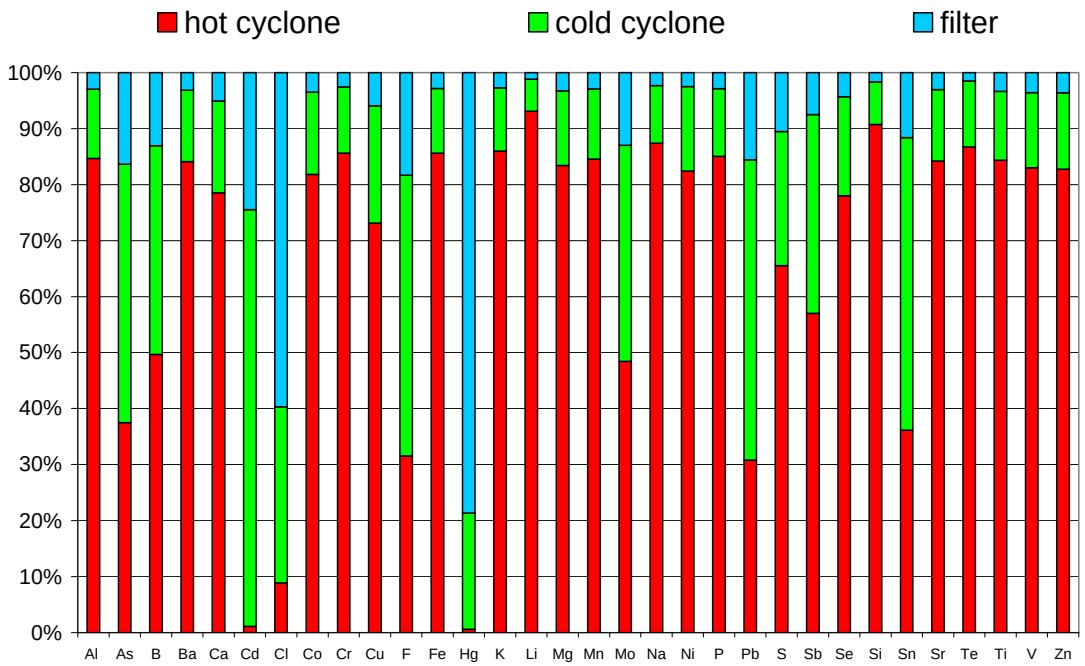


Figure 5. Distribution of elements in the three ash fractions produced in the gasification of 100% sewage sludge at 900°C; total mass distribution is 85% in hot cyclone, 12% in cold cyclone and 3% in filter at ambient conditions.

Removal of fines from demolition wood

In two runs in the BIVKIN gasifier, two batches of demolition wood were used which only differed in the presence or absence of the size fraction 0-3 mm. The fuel was prepared under identical conditions (except for the presence of 3 mm screen). The gasification took place under nearly identical conditions, so that differences in ash composition could only be attributed to the presence of fines (in this case 0-3 mm). The carbon conversions of the run with fines was 98.4%, for the run without fines 97.6%. No difference within error margins. The carbon conversion is rather high, probably due to the fact that the wood was relatively dry and shredded to small pieces (after sieving). This enhances reaction kinetics. Using finely ground fuel is not a very practical measure because it will cost considerable amounts of energy to pre-treat fuel in this way and may add extra Cr, Mo, etc. due to wear of the metal cutting tools.

The compositions of both fuel batches and the fly ash collected in a cold cyclone at 310°C are presented in Table 9. In Figure 6 the concentrations of total ash and trace elements is presented in a bar graph. There is a significant difference in the total ash content, which is reflected in the caloric value of the fuel. Demolition wood with fines has a lower caloric value and an ash content that is about 50% larger than the ash content of the demolition wood without fines. The same trend is found for nearly all individual elements. Some exceptions are found: Zn, As and Cd, which have a higher content in the demolition wood without fines. Based on these results it cannot be concluded that removal of particles of 0-3 mm is results in a fuel where specific elements associated with paint (Pb, Ba, Zn and Ti) are removed. Visual inspection of the fuels confirmed that conclusion. Sieving a sample of demolition wood with fines over a 3 mm screen resulted in removal of several kinds of particles, including wood, sand, stone, concrete and glass. There was no concentration of paint chips in this fraction. Apparently, paint remains bound to the wood and is

proportionally distributed over all particle sizes and the amount of paint that gets dislodged during size reduction of the wood is insignificant. The difference between demolition with and without fines is mainly the amount of glass splinters and fractured bricks, tiles, concrete, etc.

The total ash content of the carbon-rich fly ashes is higher than for the carbon-rich fly ash collected at the AMER-CFB. This is also reflected in a lower caloric value for the carbon-rich fly ash produced in the BIVKIN. Apparently, the burn-out is better in the BIVKIN. The reason must be found in the operational conditions, because the demolition wood used in both installations is not significantly different. E.g., the ash content of demolition wood fed to the AMER-CFB is about 6 wt% ash (dry basis), which is between the ash contents of the demolition wood with and without fines used in the BIVKIN tests.

The fly ash composition (total ash and element concentrations) of the runs with and without fines is presented in a bar graph in Figure 7. The difference between both ashes is not significantly different. The total ash content of the fly ash from the run with fines is slightly higher than from the run without fines. The difference was expected based on the presumption that fuel without fines has less ash-forming components. However, the magnitude of the difference, 64 wt% versus 55 wt%, respectively, is too small to be of significance for the ash quality. It is surprising to see that, the differences between ashes is smaller than the difference between fuels.

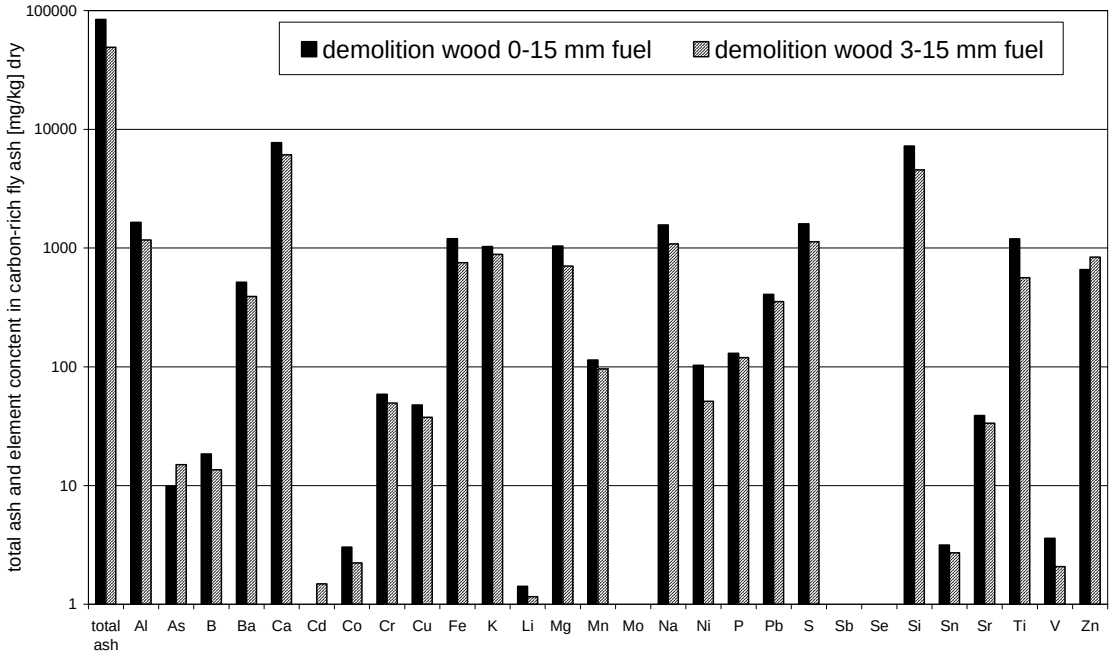


Figure 6. Total ash and element content of demolition wood with and without fines (logarithmic scale in mg/kg dry basis).

Trends found for the total ash composition are the same for nearly all trace elements. Concentrations of nearly all elements are higher in the fly ash from the run using demolition wood with fines. Exceptions are Zn, As and Cd, which were exactly the same elements where this was found in the fuel. It seems that the distribution of elements in fly ash is an excellent reflection of the fly ash composition of the fuel composition. As with the total ash content, the differences between element compositions is small and not very

significant. Moreover, the differences seem to have diminished in fly ash composition compared to fuel composition.

Table 9. Composition of demolition wood and fly ash in runs with and without fines; moisture content as received, all other data on dry basis.

Material		demolition wood 0-15 mm "with fines"		demolition wood 3-15 mm "without fines"	
Type		fuel	fly ash	fuel	fly ash
Ash (550°C)	wt%	8.4	64.4	4.9	55.2
Ash (815°C)	wt%	8.0	58.9	4.6	51.1
Volatile	wt%	72.5	8.7	75.5	6.8
Moisture	wt% (a.r.)	16.3	2.7	15.3	2.1
C	wt%	45.5	39.7	47.5	50.0
H	wt%	5.7	0.7	6.0	0.8
N	wt%	1.8	0.7	1.3	0.7
O	wt%	39.9	8.1	40.8	7.0
Cl	mg/kg	709	29871	711	26008
HHV	MJ/kg	18609	11784	19538	14567
Al	mg/kg	1648	12344	1168	11033
As	mg/kg	10	83	15	148
B	mg/kg	18	136	14	141
Ba	mg/kg	516	5918	392	5627
Ca	mg/kg	7731	92905	6119	79639
Cd	mg/kg	1.0	14.3	1.5	17.2
Co	mg/kg	3.0	31.5	2.2	28.3
Cr	mg/kg	59	565	49	607
Cu	mg/kg	48	293	38	364
Fe	mg/kg	1197	11907	754	9319
K	mg/kg	1030	22255	887	22034
Li	mg/kg	1.4	11.9	1.2	8.3
Mg	mg/kg	1042	10580	707	8513
Mn	mg/kg	114	1414	96	1398
Mo	mg/kg	<d.l.	9.0	<d.l.	8.0
Na	mg/kg	1568	6743	1085	6073
Ni	mg/kg	103	199	51	156
P	mg/kg	130	1698	120	2110
Pb	mg/kg	408	5218	355	5105
S	mg/kg	1600	8649	1131	7004
Sb	mg/kg	<d.l.	110	<d.l.	85
Se	mg/kg	<d.l.	<d.l.	<d.l.	<d.l.
Si	mg/kg	7242	37634	4567	33445
Sn	mg/kg	3.2	65.3	2.7	43.5
Sr	mg/kg	39	443	33	415
Ti	mg/kg	1197	10420	563	8141
V	mg/kg	3.6	21.3	2.1	20.8
Zn	mg/kg	659	5272	839	9579

It can be concluded that removing the fines from the fuel improves the ash quality by lowering the total emission of the inorganic part of the ash. Removing the fines does not improve the fly ash quality by lowering the concentrations of specifically elements, in particular Pb and Zn, which are associated with paint.

The difference between using fuel with and without fines is found in the bottom ash. During a run, bottom ash can not be removed from the BIVKIN, which means that larger particles, that are not entrained by the gas flow in the riser, settle on the bottom and build up. Eventually, this immobile material will block the fuel feed. In the run without fines, this moment came after 18 hours, in the run using fuel with fines it took just 6 hours. This operational problem is not expected in large-scale installations where bottom ash can be removed during operation. The material collected at the bottom of the BIVKIN was in both cases composed of inorganic particle, stone, concrete, tiles, etc, materials that were already identified as component of the fines when the fuel was sieved on a 3 mm screen. In the material collected at the bottom of the BIVKIN also large numbers of agglomerated particles were found. These were composed of a molten piece of glass covered with sand particles.

The overall conclusion is that removal of fines (0-3 mm) from demolition wood is not affecting the ash quality of the fly ash. The inorganic components in this size fraction end up in the bottom ash as inert particles or as agglomerates.

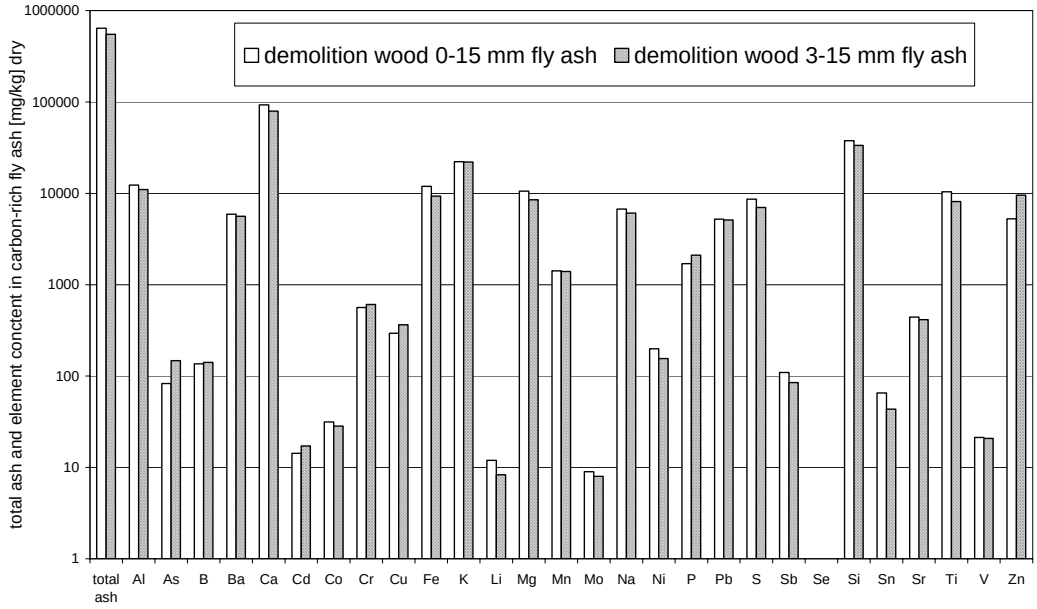


Figure 7. Total ash and element content of fly ash from gasification of demolition wood with and without fines (logarithmic scale in mg/kg dry basis).

3.2.10 Conclusions

With respect to the objective of increasing the carbon conversion by adjusting the gasification parameters, the conclusion can be drawn that practical measures can increase the burnout level of gasification ash. However, it is not possible to achieve such a low carbon content in the ash that the ash can be used directly in applications similar to fly ash of coal combustion. Using fuel in very small particle sizes will also increase carbon conversion, but it is a measure that has negative consequences for the fuel price.

When sewage sludge is used as fuel, the inorganic components from sewage sludge dominate the ashes. Mixing with clean wood can influence gasification behaviour, but not ash composition. In gasification of demolition wood, inclusion of the smallest fuel size fraction (0-3 mm) has only a minor effect on the fly ash composition. The strongest influence is found on the bottom ash, not on fly ash.

Accomplishment of significantly improving the quality of gasification ash, both in terms of a very low carbon content (making in suitable for applications in building material and/or being able to land fill it after the EU Waste Incinerator Directive has become active) requires more than simply optimisation of the gasification parameters. One solution is to drastically changes the design of the gasifier, e.g. innovative reactor design, which is currently better suited for development at an academic level, otherwise after treatment of fly ash from gasification of wood is inevitable. The after treatment can be integrated in the system (VTT's oxidiser) or not. Alternatively, the gasification ash could be used as a fuel. In that case, optimisation of carbon conversion does not necessarily mean maximisation, but a carbon of more than 35%.

3.3 Gasification test trials of AICIA

3.3.1 Gasification test trials

AICIA has focussed bubbling fluidised bed gasification activities on two fuels: (1) a agricultural residue called orujillo, and (2) Meat and Bone Meal (MBM). Orujillo is a residue of the olive oil extraction industry. Heating value of orujillo is high but it contains high amount of alkali metals (primarily potassium), which can cause serious deposit formation and agglomeration in high temperature processes like fluidised bed gasification or combustion. Orujillo is also available in large quantities. MBM is a residue difficult to dispose and gasification could be a plausible method for processing it. Table 10**,** presents typical analysis of the orujillo and MBM used in these tests.

Table 10. Chemical characterization of the fuels.

	Orujillo		**MBM**	
LHV (MJ/kg)	17.55		19.75	
	% (w.b.)	% (d.b)	% (w.b.)	% (d.b)
C	-	41.01	-	45.04
H	-	4.16	-	6.4
N	-	1.13	-	7.47
S	-	-	-	0.64
O	-	30.64	-	21.58
Moisture	10.82	-	6.91	-
Ashes	20.41	22.88	17.57	18.87
Volatile Matter	53.34	59.81	67.05	72.03
Fixed carbon	15.44	17.31	8.47	9.1

The primary objective of this work was to study the effect of operating conditions (fuel rate and air to biomass ratio) and bed material on the reduction of generated ash volume and quality (mainly carbon conversion). With these data the final aim was to optimise these conditions for achieving maximum carbon conversion and to reduce the volume of ashes.

The test trials have used several bed materials: silica sand, ofite (a silicate with formula $(Ca, Mg, Fe, Ti, Al)_2(SiAl)_2O_6)$), limestone and mixtures thereof. The gasification tests using sand as a bed material were not technically successful since the defluidization problems caused by the prompt sintering resulting from the high alkali content of ashes (mainly K). Thus, these tests are not reported here. Test trials with ofite bed were successful and bed agglomeration was successfully avoided. Further, the impact of the addition of limestone mixed with ofite in different percentages has also been studied. The main characteristics of the ofite used in the tests are reported in Table 11.

Table 11. Chemical and physical characterization of the ofite.

Major Analysis (wt%)			
Si as SiO_2	53.93	Na as Na_2O	3.49
Al as Al_2O_3	13.61	K as K_2O	0.48
Fe as Fe_2O_3	9.15	Moisture at 105 ºC	0.47
Ca as CaO	11.15	Weight loss at 750ºC	0.64
Mg as MgO	7.90		

Size Distribution (wt %)									
Size (µm)	2500	1900	1410	1000	500	250	125	100	62
Wt (%)	100	98	74.3	45.6	17.9	8.54	5.9	5.47	3.8

3.3.2 Test facility

Gasification trials were conducted at a pilot scale bubbling fluidized bed reactor designed to process up to 30 kg/hr of solid biomass and suitable for combustion and gasification studies. Figure 8 presents respectively, a schematic diagram and the more relevant operating parameters and data of the pilot plant.

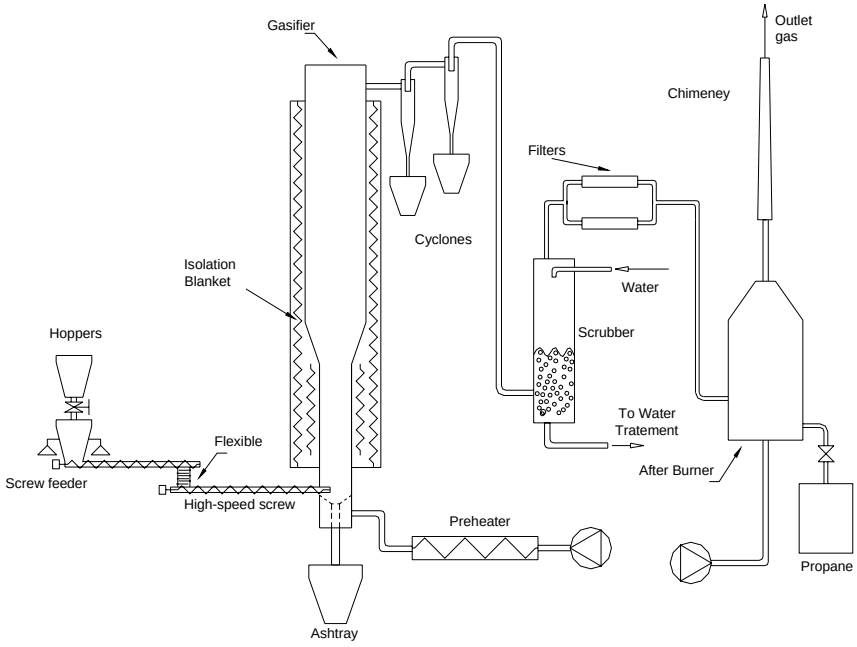


Figure 8. AICIA BFB 150 kW_{th} pilot plant facility.

The biomass is injected at the bottom of the gasifier where a slightly positive pressure exists. The feed system consists of two hoppers with a knife valve between them. There are also two screws, the feeder screw placed immediately after the metering hopper and the high-speed water-cooled injection screw. The air for combustion or gasification can be preheated in a 7 kW electrical heater and enters the reactor at the plenum located just under the gas distributor.

The BFB gasifier consists of a refractory stainless steel reactor AISI •310 (150 mm ID), fitted with a distributor plate drilled with 37 holes (1 mm diameter) in a square arrangement with 20 mm triangular pitch. It has a total height of 4,2 m and two sections, the bed zone of 150 mm ID and the freeboard of 250 mm ID. The system is provided with an isolation blanket, which cover completely both reactor and freeboard. Temperatures and pressures are measured along the bed and freeboard which is equipped with eight thermocouple probes. Three pressure taps are located along the side of the reactor (PT1-PT3) to monitor the fluidisation conditions of the bed.

The gas leaving the freeboard section passes through two cyclones in series to collect entrained particles and through a wet scrubbing system to remove the condensable tars. Char, ash and inert bed material particles are collected in bins placed under the cyclones and under the system to extract ash from the bed bottom. The gas sampling point is located downstream from the scrubber. A slipstream of the fuel gas is taken out by an Inconel

probe with a filter to remove particles. The sampling line is electrically heated to avoid condensation of organic compounds within the probe. The composition of produced gas is measured continuously (CO, CO2, CH4, H2 and O2). Finally, the producer gas flowrate is measured by a rotameter.

After leaving the analysing section, the producer gas passes through a tar and particle filter system in series. After being blown, the produced gas enters into a post-combustion chamber, which has been included into the system to keep away from environmental problems derived from smells and emissions. The post-combustion chamber is a refractory lined horizontal cylinder, allowing work at temperatures up to 900°C. The heat power of the burner is 85 kWth.

During normal operation, the biomass input is held constant and the bed temperature is controlled with a PID that manipulates the air flowrate. The temperature of the inlet air is controlled by another PID, which manipulates the power input to the electrical preheater. The signals of all the measuring instruments are transmitted to the computerized data acquisition system, where they are monitored and registered with a sampling period of 0.5 s.

3.3.3 Test procedure and sampling

At the very beginning of each test run, the material in the bed was heated with the preheated air. After about an hour of heating, the temperature exceeds 200°C, and then a small amount of biomass is fed. In this oxidising atmosphere, the biomass is combusted and the reactor rapidly heated up to the desired process temperature. The computer-based data acquisition system is activated to monitor and record the temperature, the pressure drop and the feed rate values. The transition from combustion to gasification is made by increasing the feeding of biomass and thus by decreasing the ratio between air and biomass flow rate.

In every test an initial transitory period of around 4 hours is followed by a steady state period of 5 hours, which ends with the shutdown of the gasifier. The operating pressure increases with time, due to the progressive clogging of the gas filter located at the mouth of the induced-draft fan. After each test both the two cyclone bins and the extraction ash bin under the reactor were sampled. The three locations were sampled twice and analysed for each run. Finally, one temperature probe is located after the cyclones and one just before the blast enters the scrubber. This protocol of taking samples allowed us to have further details of the ash properties obtained at different operating conditions. Table 12 shows the main design characteristics and operating conditions of the fluidised bed gasification system used for these tests.

Table 12. Technical and operating data of Pilot Plant facility

Bed inside diameter	0.15 m
Bed height	1.7 m
Freeboard inside diameter	0.25 m
Freeboard height	2.5 m
Fluidization velocity	0.8-1.4 m/s
Bed material	Ofite
Fuel feed rate	18-35 Kg/h
Gasification agent	Air
Operation temperature	700-820 ºC
Operation pressure	Atmospheric
Regime of fludisation	Bubbling
Maximun thermal capacity	150 kW_{th}

3.3.4 Gasification pilot plant test results

Results with orujillo

AICIA has carried out several valid tests in its pilot-scale atmospheric air blown bubbling fluidised bed gasifier using orujillo and ofite as fuel and bed material, respectively. Table 13, presents the main inputs to the system together the most relevant parameters for the analysis of the gasifier.

In the tests presented here the effect of ER was analysed using two air flowrates (18 and 20 Nm^3/h) and several fuel feeding rates ranging from 15 to 30 kg/h, which establish an air/biomass mass ratio within the range 0.57-1.02 (Nm3 air/kg biomass). With these air and biomass flowrates the equivalence ratio ER ranges from 0.17 to 0.31, which falls within the typical range analysed by other authors with other biomasses. This arrangement gives a weight hourly space velocity (WHSW), expressed as the ratio of the biomass mass flowrate to the weight of the fluidised bed material, which is kept within the range 0.5-1, also typical of this units.

Table 13. Main variables obtained from orujillo Pilot Plant Gasification Tests.

Run number	1	2	3	4	5	6	7
Air /orujillo	0,57	0,66	0,74	0,76	0,81	0,98	1,02
Air flowrate (Nm^3/h)	20	18	19	18	20	18	18
Orujillo flowrate (Kg/h)	35	27	26	24	25	18	18
Tbed (ºC)	700	740	750	760	785	780	820
Tfreeboard (ºC)	530	540	550	600	600	590	650
Produced gas flowrate (Nm3/h)	n.a.	n.a.	32	31	n.a.	n.a.	n.a.
%(v/v*) CH_4	6	6	7	7	7	5	5
%(v/v*) CO	14	12	12	9	10	13	14
%(v/v*) CO_2	18	17	20	17	17	16	16
%(v/v*) H_2	12	11	12	12	8	10	9
ER	0,17	0,20	0,22	0,23	0,24	0,29	0,31
Gas LHV (MJ/Nm^3)	5,21	4,85	5,31	4,93	4,63	4,51	4,52
Thermal Efficiency	33,8	32,3	37,1	35,5	31,7	28,6	27,7
Produced gas flowrate (Nm^3/h) (c.f.b.)	45,2	36,8	37,4	33,2	39,2	31,3	30,5
Gas yield (kg/kg)	1,56	1,62	1,75	1,68	1,90	2,05	2,09
Carbon conversion	74,3	73,4	82,7	79,2	86,1	85,1	85,7
Gasification Efficiency	52,7	52,4	65,0	59,8	60,4	58,6	57,7

*Notes: c.f.b. (calculated from balances), n.a. (not available), *Dry basis*

Table 14. Typical ash analysis (%) of orujillo ashes for the different sample Location.

	Fuel (orujillo)		**Cyclone 1**		**Cyclone 2**		**Overflow**		**Bottom-ash**	
	% (w.b.)	% (d.b)	% (w.b.)	% (d.b)	% (w.b.)	% (d.b)	% (w.b.)	% (d.b)	% (w.b.)	% (d.b)
C	-	41,01	-	8,61	-	11,81	-	9,45	-	0,44
H	-	4,16	-	<0,05	-	0,14	-	0,48	-	<0,05
N	-	1,13	-	0,29	-	0,5	-	0,22	-	0,08
O	-	30,64	-	5,08	-	6,96	-	6,23	-	0,27
Moisture	10,82	-	0,98	-	2,81	-	1,13	-	0,15	-
Ash	20,41	22,88	85,17	86,02	78,32	80,59	82,68	83,62	99,06	99,21
Volatile matter	53,34	59,81	7,79	7,86	11,05	11,37	10,99	11,12	0,96	0,97
Fixed carbon	15,44	17,31	6,06	6,12	7,81	8,04	5,2	5,26	0	0

Table 14 and 15 show the characteristic of the ashes sampled in the tests above. Specifically, Table 14 shows the elemental and ultimate analysis of the ashes from cyclones, ashtray and overflow for a typical test. Also, for comparison, the first row of Table 5 includes the fuel analysis. Table 15, displays the carbon content of the ashes for the tests considered here. Also it is reported the different composition depending of the sampled location. In Figure 9 is clearly illustrated how the carbon content of ashes decreases as temperature increases (or equivalently, when ER decreases since they are linearly correlated).

Table 15. Total Carbon Content (%) of orujillo ashes for the different sample Location.

Test	**Tbed (ºC)**	**ER**	**%C Ashtray**	**%C Cyclone 1**	**%C Cyclone 2**
1	700	0.17	37.54	20.18	22.08
2	740	0.20	20.77	12.00	15.24
3	750	0.22	37.44	15.78	18.08
4	760	0.23	29.85	14.51	19.51
5	785	0.24	19.85	14.03	15.86
6	780	0.29	8.24	11.58	9.66
7	820	0.31	5.33	9.09	12.04

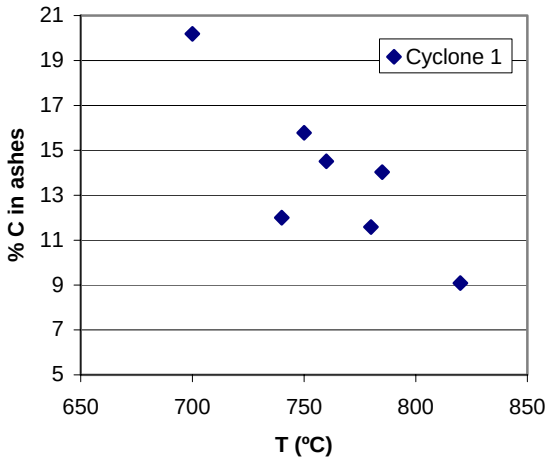


Figure 9. Carbon content of ashes in cyclone 1 as a function of T.

The carbon conversion, defined as the degree to which the carbon in the fuel has been converted into gaseous products, is presented in Figure 10. As known, carbon conversion is a key parameter in any biomass conversion process since achieving a high carbon conversion is important for overall plant efficiency and consequently for economical operation and also this permits the utilisation of the gasification ashes.

We have focussed this study in the most practical ER for biomass gasification, i.e. in the range 0.20 to 0.40. Lower values of ER produce a high tar content gas and are therefore just allowed when the produced gas is going to be used as fuel gas in a furnace or in a boiler without previously cooling it. On the other hand, high values of ER give higher operating temperatures and lower amounts of tar in the gas but at the cost of reducing the produced gas heating value. Specifically, the ER range studied was 0.17–0.31 and the carbon conversion varied between 73.4% and 86.1%.

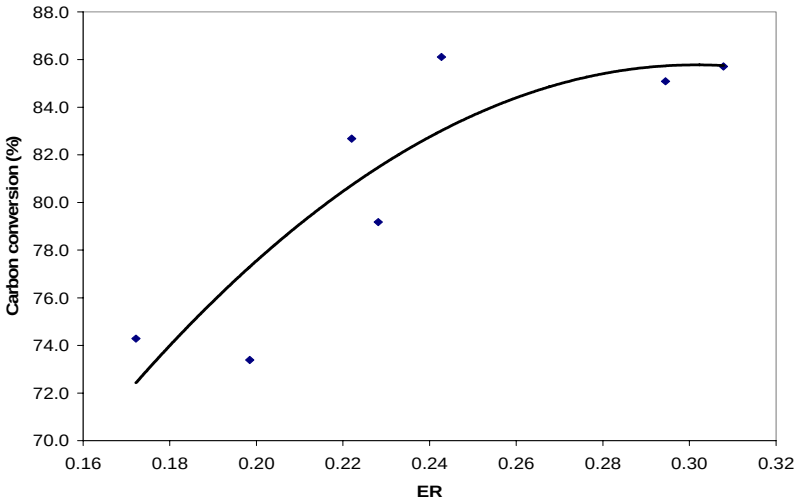


Figure10. Carbon conversion as a function of ER

The so low carbon conversion of some gasification tests can be explained by considering that it has not taken into account the tars in the gas produced. In spite of this, as Figure 11 shows, we have optimised the carbon conversion properly by observing that there exist and optimum of the gasification efficiency range. This is compatible with the fuel, since the strong restriction derived from the high alkalis lead to reduce the gasifying temperature for long-term enough tests.

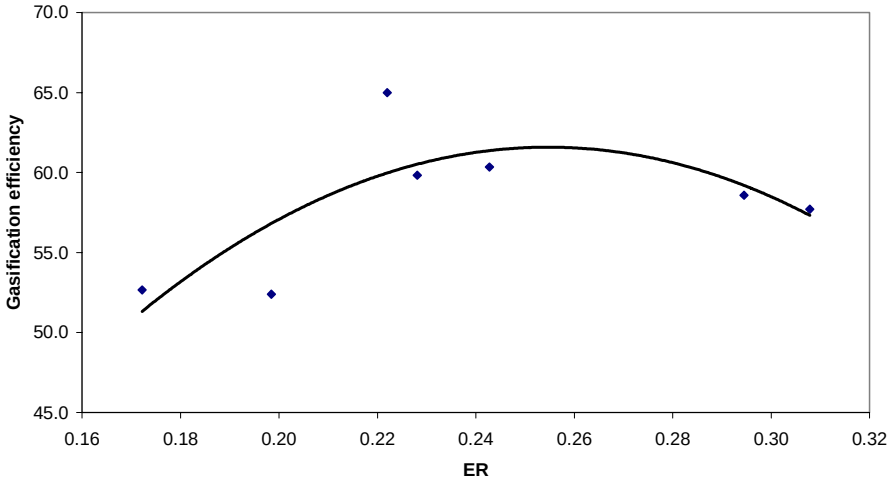


Figure 11. Gasification Efficiency as a function of ER.

As summary, the use of ofite has allowed us to optimise the gasification by operating at higher temperature. However, higher conversion than 90% has not been possible to be achieved because of the agglomeration problems caused by the severe sintering. Therefore it has been selected a range of ER which permits having a relatively acceptable carbon conversion with a maximum efficiency, which takes into account the compromise between LHV of the produced gas and the gas yield.

3.3.5 MBM gasification tests

Lesson learned by handling and feeding MBM

Thermal decomposition of MBM in feed bins has lead to solids sticking to the walls. This phenomenon was due to the propagation of heat from the gasifier to the feeding system, i.e. screws and bin. Therefore, care had to be taken to prevent this phenomenon such as partial filling up of the bin and controlled injection of N_2 to keep cool the feeding system. Measures such as the redesign of the screws to adapt the MBM together with the selection of a coarser MBM (from 1 to 3 mm) were undertaken. New gasification trials were tried but these measures were not entirely satisfactory and low solid rate of feeding and non-enough long tests were obtained. The problems above together with the particular cohesivety of MBM led us to decide the pelletization of the MBM. At the beginning AICIA tried to pelletise several tonnes of MBM in their installation but various technical problems led to ask a specialised manufacturer to do the work. The pellets were manufactured with constant diameter of 4 mm and a variable length ranging between 5 and 20 mm. Finally, re-calibration of the screw for the new feed and for various temperatures for getting the exact

correlation at the actual operating conditions. After these last modification the pilot plant was ready for a proper operation. The results are given bellow.

Operational conditions: pilot plant modifications

A complete set of successfully tests have been carried out using MBM as fuel and ofite as bed material. No cleaning additives were used. In all cases the gasification agent was air at atmospheric pressure. As with Orujillo, two factors or independent variables were used in that set of tests: the air / biomass ratio with 3 levels and the air flowrate with 3 levels. Additionally these tests have been done with a 25 kW_{th} refractory lined oven recently installed and so, a additional degree of freedom has been introduced into the system, the heat supply. However we used this heat just for simulating real losses in higher scale systems. Thus we just supply the heat necessary to compensate the natural heat losses. We therefore consider our tests almost adiabatic.

MBM gasification tests: general performance and gas composition

The gasification tests with MBM have shown very good fluidised behaviour. Also, low "natural" (without external heat supply) bed temperature and "slow" gasification reactivity has been identified from the tests. The results presented in Table 16 indicate that MBM is not a good "gasifiable" feedstock since the SynGas composition obtained has a low CO and H_2 concentrations. Additionally, a rather high CH_4 has been detected which is probably due to the very low gasification temperature, this latter when the oven has been used just to provide the heat losses.

With regard to fly ashes generated by MBM gasification a very low carbon content (< 3 %) has been measured in the tests. The bed with lime or percentages of lime has shown a reduction on tar content up to 50 % (no major differences were found regarding composition with these additives).

Additionally, high quantity of P and Ca (typical of bones) has been detected. This fact together with the low C (low PAH) led us to think about the possibility of the MBM ashes to be a good candidate for agriculture use at least as amendment since the solubility (of P and Ca) are not good enough. In spite of this good ash-related properties for ash utilisation MBM gasification does not present good gas producer quality and in principle, MBM does not seem to be an interesting fuel for gasification purposes.

Table 16. Data of MBM gasification tests.

Test	**MBM 6.4-0**	**MBM 7.3-0**	**MBM 8.2-0**
Bed material	Ofite	CaO	Ofite+20%CaO
Air Flowrate (Nm3/h)	14	14	14
Superficial air velocity (m/s)	0.95	0.93	0.93
Biomass Flowrate (kg/h)	10.2	9.7	9.4
Air/Biomass ratio (Nm3/kg d.a.f.)	1.82	1.91	1.97
ER	0.29	0.31	0.32
Bed temperature (ºC)	840	825	815
Set point bed furnace (ºC)	800	800	800
Tar (mg/Nm3)	n.a.	n.a.	n.a.
Particles (mg/Nm3)	n.a.	n.a.	n.a.
%v/v CH4	3.6	3.1	2.8
%v/v CO	6.1	5.5	4.4
%v/v CO2	14.3	14.6	15.7

%v/v H2	3.9	3	2.1
Gas Flowrate (Nm3/h)	18.5	19.7	20.3
Ash Flowrate (kg/h) (mean run)	0.69	0.79	1.19
Ash/Biomass ratio (kg ash/kg d.a.f.)	0.09	0.11	0.17
LHV (kcal/Nm3)	592.7	508.6	426.5
Gas yield (Nm3/kg d.a.f.)	2.40	2.69	2.86
% C ashes	3.40	3.97	4.10
Carbon conversion	96.21	95.18	92.73
Cold efficiency	0.30	0.29	0.26

Table 17. Effect of additive on gas produced and analysis of volume and quality of ash generated for MBM gasification (Ofite 100% and ofite/CaO=80/20).

	WITHOUT CaO	**WITH 20% CaO**
Tar Content (mg/Nm3, dry)	17000 – 21000	8000 – 13000
Particle Content (mg/Nm3, dry)	200 – 900	2000 – 4000
Carbon Cyclone 1 (%w)	4	8
Carbon Cyclone 2 (%w)	12	9
W/F (kg inert/kg fuel·h-1)	1.25	1.3
C1/F (kg ash/ kg fuel)	0.07	0.13
C2/F (kg ash/ kg fuel)	$1.52 \cdot 10^{-3}$	$1.16 \cdot 10^{-3}$

A comparison between the two fuels gasified here can be found in Table 18. As shown in the table, a favourable behaviour of MBM gasification ashes as far as its carbon content (typically 4% for MBM vs. 7-12 % for orujillo). In spite of this the gasification characteristics of MBM are rather poor, mainly concerning the LHV of the gas and gasification efficiency of the process.

Table 18. Comparison of mayor parameters between MBM and orujillo gasification in AICIA BFB pilot Plant.

	MBM	**ORUJILLO**
Air Ratio (Nm3 air/kg fuel)	1.4 – 2.8	0.6 – 1.1
Gasification Temperature (ºC)	750 – 850	700 – 820
Gas Yield (Nm3 air/kg fuel)	2.1 – 3.6	1.3 – 1.8
LHV (MJ/Nm3)	1.5 – 3	4.5 – 5.5
Gasification Efficiency (cold)	0.25 – 0.4	0.5 – 0.65
Carbon Conversion	0.80-0.97	0.7 – 0.85
Gas Composition (%v/v, dry):		
H_2	1 – 6	8 – 12
CO	3 – 8	9 – 14
CH_4	2 – 5	2.5 – 4
CO_2	12 - 16	16 – 20

3.3.6 Conclusions related to AICIA's gasification test trials

Two fuels, orujillo and MBM have been successfully gasified. The searching of bed materials (ofite) has finally allowed us to operate the fluidised-bed gasifier at higher temperatures (up to 820ºC) when gasifying orujillo. However, at this thermal level higher conversion than 90% has not been possible to be achieved because of the agglomeration problems caused by the severe sintering, mainly due to the high potassium content of the orujillo. Therefore it has been selected a range of ER (around 0.25) which has permitted to obtain a relatively acceptable carbon conversion (90%) with a maximum efficiency. This takes into account the compromise between LHV of the produced gas and the gas yield. Moreover, despite this relative low carbon conversion, carbon content of ashes are not very high (around 12%) if compared with other biomasses and consequently its ashes are not "difficult" as far as utilisation purposes is concerned. In addition, at calculating the carbon conversion, the tar content has not been take into account in this values and therefore, it is expected to have real carbon conversion up to 95-97% in the best cases (tar content around 20.000 mg/Nm^3).

The other biomass included here (MBM) is a residue difficult to dispose and gasification could be a plausible method for processing it. In this investigation carbon conversion of 97% (target 96%) has been reached for MBM gasification test. The carbon content (around 3%) and volume of ashes are very low (0.1 kg/kg biomass) and thus the gasification ashes is not of major problem for this biomasses. In addition high quantity of P and Ca (typical of bones) has been detected in MBM ashes. This fact together with the low C (low PAH) lead us to think about the possibility of the MBM ashes to be a good candidate for agriculture use at least as amendment since the solubility (of P and Ca) are not good enough.

In spite of this, the gas produced by gasifying MBM is rather poor. The main reason is that MBM has very low oxygen content and the proper air to biomass ratio for gasifying this biomass is rather high. Consequently the dilution of N_2 is very high and the LHV low. Typical gasification efficiency reaches around 30% has been found.

In principle, the ash characterisation of both fuel fly ashes showed rather good quality of the gasification ashes with regard to heavy metals and chlorine content for both kinds of ashes. This leads (subject to further restrictions analysed in WP3) to the potential use of this ashes in several applications as have been analysed within the WP3 of this project.

3.4 Gasification test trials of FWE

Largest gasification test trials were carried out by Foster Wheeler Energia. Test trials were carried out with atmospheric pressure CFB gasification pilot plant (1.5 MW ACFBG pilot). The main variable of the test trials was oxygen level of fluidisation air. The heating value of product gas can be increased by oxygen enrichment but the effects on carbon conversion are not clear: the partial pressure of oxygen is higher but on the other hand, temperature control requires lower air coefficient. Different bed materials varying in quality and particle size were included in the test plan as a secondary variable. Bed materials that grind easily increase the volume of fly ash but may also have positive effects on downstream

components. Moreover, the catalytic effects of different bed materials may result in varying carbon conversion to syngas and tars. Test trials were carried out in late fall 2004.

3.4.1 Test facility

The main components of the ACFBG test facility are circulating fluidized bed gasifier, syngas cooler and hot gas filter. Part of the syngas produced in the gasifier is burned at a syngas combustion facility and the rest is led to a flare; the ratio is adjustable. The process flow scheme shown in Figure 12 gives an overview of the plant. Table 19 shows the major technical details of the test facility.

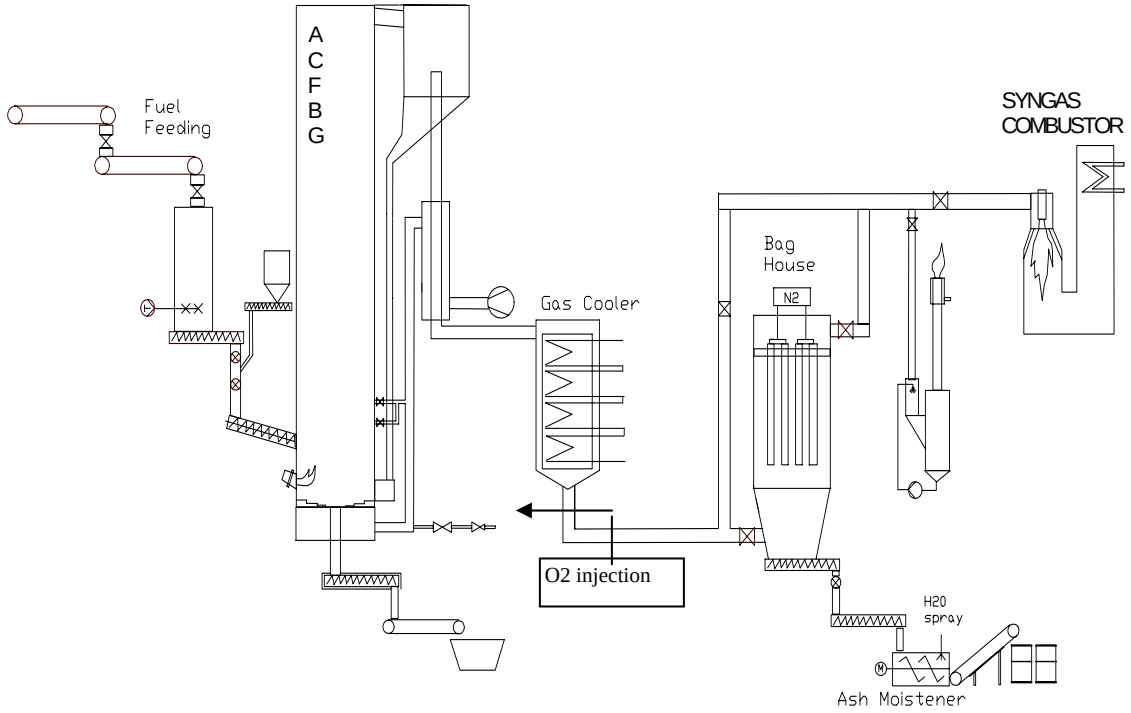


Figure 12. ACFBG Test Facility – Process Flow Scheme.

Table 19. Technical Details of the ACFBG Gasifier.

Year of construction	1980, modified 1997, 2002
Reactor inside diameter height	 400 mm 10.5 m
Operating temperature Gas flow velocity in the reactor Air flow rate Operating pressure Fuel feed rate Thermal capacity	600 - 1000 ^{o}C 1.5 - 5 m/s 0 - 0.25 m^3n/s 0 - 100 mbar(g) 0 - 500 kg/h 1.5 MW

Fuel and Bed Material Handling Systems

Fuel is loaded by a tractor shovel onto a drag-chain conveyor, which is carrying the fuel through two conveyors to a weighted fuel silo. The silo is shut off from the transporting line by a lock plate. From the silo, fuel is discharged by a hydraulically driven screw feeder into a vertical drop pipe and further to a reactor screw, which penetrates the wall of the reactor and feeds the fuel into the gasifier.

Sand, limestone and other possible bed materials are fed manually as premixed and weighed batches into a vertical pipe, which discharges into the reactor screw.

Gasifier Reactor

The refractory-lined reactor is inside a 10 m high gas-tight steel shell. The bed is fluidized by air coming through the air distribution grid at the bottom of the reactor. Air is fed by a Roots blower, the capacity of which is 0.25 m^3n/s of 1.4 bar air. Part of the total air is fed as secondary air. The solid matter, entrained from the reactor, is separated in a uniflow cyclone and recycled back to the bottom of the reactor. A start-up burner fuelled by natural gas is located above the grid.

As a novelty of these tests runs, equipment for oxygen injection into the fluidization air was installed. The injection point is shown in Fig. 12. The main components of the system required for the supply of gaseous oxygen included a 7-m^3 storage tank for liquid oxygen, evaporator, pipelines and instrumentation. A similar system was installed to supply nitrogen for pulse cleaning and inertisation purposes. The equipment was leased from AGA that also delivered the liquid oxygen and nitrogen used during the test runs. The main measurements and actuators were connected to the plant DCS to enable follow-up, control and interlocks related to oxygen injection.

Hot syngas, leaving the reactor at 850 – 950 °C, is cooled in the gasifier air preheater to about 550 – 650 °C. The air preheater is a double-pipe shell-and-tube heat exchanger, in which the preheated air flows in an annulus over the inner syngas pipe.

Syngas Cooling and Filtration

After the air preheater, syngas is cooled further in the water-tube syngas cooler to about 300 °C. From the closed cooling water system, heat is transferred into river water in heat exchangers.

Sorbents such as calcium hydroxide can be injected into the syngas stream between the gasifier and hot gas filter. Sorbents are typically fine powders and they have to be fed in small quantities but continuously. The device used for the purpose is provided an adjustable speed screw feeder, and in these test runs it was connected to the outlet pipe of the syngas cooler.

After the gas cooler, gas is cleaned in a bag house-type hot filter unit. The unit is designed for high-temperature filter bags, which were replaced with low-density candle filters for these test runs. The candle filters were Tenmat "Big Tube" elements, which had previously been used for up to 3300 hours in long-term exposure testing in a slipstream installation at the Lahti gasifier. They were vacuum-cleaned prior to installation at the test facility.

The shell of the filter housing is provided with electrical heating to prevent condensation of tar compounds and deposit formation in the filter unit.

After the hot filter, most of the syngas is led to the syngas combustion facility. Part of the syngas - even all of it, such as during start-up - is normally led via a venturi scrubber to flare.

Ash Handling Systems

Bottom ash is discharged from the grid through a vertical pipe, which the takes ash to a water-cooled screw. The screw cooler reduces the ash temperature to 100 - 200 °C and discharges it to a drag-chain conveyor, which takes it to a 1-m^3 container. Hot gas filter ash is conveyed from the bottom of the filter housing by a screw, a rotary feeder and another transport screw to the same room as the bottom ash. The transport screw discharges ash to a closed 200 l barrel, which is weighed and replaced intermittently.

Syngas Combustion

Normally the syngas flow from the hot gas filter is divided for the syngas combustor and flare, and the flow split can be adjusted. The syngas combustion facility includes an insulated, refractory-lined combustion chamber provided with a syngas burner and a flue gas cooling section.

Syngas combustion and continuous emission measurements of the generated flue gas provide information of the gas burning properties and emissions.

Plant Operation Procedure

Operation of the ACFBG test facility is started by igniting the start-up burner fuelled by natural gas. In the first phase, the refractory linings of the furnace are warmed up with natural gas firing. Gradually the feeding of the bed material is initiated. When the desired furnace temperature has been achieved, combustion of solid fuel can be started. This continues the heating of the gasifier. After sufficient heating, rapid changeover from solid fuel combustion to solid fuel gasification is made. The fuel feed rate is increased in one step by changing the speed of the screw feeder.

Process Measurements and Sampling

The main compounds of syngas: H_2, CO, CO_2, CH_4, C_2H_4 and C_2H_6 were analyzed automatically semi continuously by a gas chromatograph. The sampling interval was 30 minutes. The CO, H_2, CO_2, O_2 and CH_4 contents in syngas were also analyzed by

continuously operated gas analyzers. The main sampling points were located before the gas cooler and after the gas cooler.

The flue gas composition after the syngas combustion was also analyzed. The O_2, CO, CO_2, SO_2, NO_x and HCl contents of the flue gas were analyzed by continuously operated gas analyzers.

In addition to these gas analyses, VTT carried out the periodical composition measurements for syngas during test runs 9 - 17. The measurements carried out by VTT are listed in Table 20.

Table 20. Measurements Carried out by VTT.

Test run	Light tars and benzene	Gaseous hydrocarbons	Main gas components	Moisture	HCN	NH_3
Test 9	X	X	X	X	X	X
Test 10	X	X	X	X	X	X
Test 11	X	X	X	X	X	X
Test 14B	X	X	X	X	X	X
Test 15	X	X	X	X	X	X
Test 16	X	X	X	X	X	X
Test 17	X	X	X	X	X	X

Samplings of polyaromatic hydrocarbons (PAH) or other organic compounds, heavy metals or particulate matter in the syngas were not carried out in these test runs.

During the test runs, run-time solids samples were taken from all input and output streams. The sampling frequency was typically 1 sample every 2 - 4 hours. The bed makeup (sand, limestone, MgO) and additive (calcium hydroxide) samples were taken less frequently, typically once per test run. The samples of each test were collected in buckets, mixed and divided into samples for analyses and samples for later storing. The particle size of filter ash and calcium hydroxide were measured by dry laser diffraction analysis (Malvern), whereas the particle size of the bed materials, bottom ash and circulating material were measured by mechanical sieving.

4.4.2 Gasification test trials

Wood pellets were gasified for a total of 341 hours in November - December 2004. The test period included two five-day test weeks (48 / 2004 and 49 / 2004) and one longer run in week 51 / 2004, with an extension through the weekend to the beginning of week 52.

In the GASASH project, the test runs were related to two tasks, "Optimization of gasification conditions to reach higher carbon conversion" and "Role of bed materials and gas cleaning additives on ash volume and quality". In air-blown fluidized bed gasification

of biofuels, the chances to reduce carbon content of fly ash are limited. For the pilot tests, level of oxygen enrichment of fluidization air was selected as the main test parameter. Different bed materials were included in the planned scope of testing as a secondary variable. Steam was planned to be used mainly if required for temperature control. The aim was to run the bed at about 900 °C in all the tests and also keep the flow rate of product gas constant.

Tests in Week 48 / 2004 (November 22 - 26, 2004)

Sand and P3 limestone were used as bed material, and they were mixed in 1:1 ratio before feeding in batches. Feeding of calcium hydroxide downstream of the syngas cooler was commenced at an approximate rate of 4 kg/h. Gasification of wood pellets was started at first in the normal air-blown mode.

Oxygen enrichment testing was planned to be started as follows: oxygen feed rate is increased in steps and primary air flow rate reduced simultaneously, and fuel feed rate is increased as required to keep the bed temperature constant at about 900 °C. The possible operational window would be studied this way, and actual longer steady state operating periods would be planned based on the experiences. These scoping tests were named similar to the actual steady state tests (Test 1 - 3), but closer evaluation of the data was not carried out.

After the scoping tests, the basic test matrix was chosen to contain three different oxygen levels of fluidization air, three different bed materials and two different levels of bed inventory. Steam injection remained as a potential test parameter. Bed temperature would be adjusted at about 900 °C with fuel feeding. According to initial estimates, the syngas flow rate would remain about constant regardless of the oxygen enrichment level.

Totally five steady-state test runs (Tests 4, 5, 6, 7 and 8) were performed during the first test week. Applying oxygen did not cause any significant difficulties but the effects on the process appeared quite clear: fuel feeding had to be increased to keep bed temperature constant, there was less circulation due to less primary air, temperature at the top of the reactor was reduced and the share of combustible components of the syngas was increased.

For the last test of the week, the bed material was changed to magnesium oxide (MgO).

Tests in Week 49 / 2004 (November 29 - December 3, 2004)

Inspections and maintenance work were carried out before starting up the gasifier. Visual inspection did not reveal any damages or deposit formation as a result of operation with oxygen enrichment.

Gasification tests were continued using MgO as bed material and calcium hydroxide was fed downstream of the syngas cooler. Three steady-state test runs (Tests 9, 10 and 11) were performed during the second test week.

VTT was carrying out syngas sampling after the hot gas filter during the tests to determine the contents of tars, benzene, NH_3, HCN, H_2O and C_2 - C_5 hydrocarbon gases. Even though

actual particle sampling was not carried out, the syngas was noticed to be free of particulate matter.

Operation was once interrupted in the middle of the week due to difficulties in steam feeding to the gasifier. Steam was not used normally but the effects of it were planned to be tested. However, the available steam generator was found to produce too wet steam. This resulted in unstable operation and finally a trip due to high temperatures, and testing of steam injection was interrupted.

Tests in Weeks 51 - 52 / 2004 (December 12 - 21, 2004)

The test facility was found to be in good shape in the inspection following the second test week. Testing was again started with MgO as bed material. The first gasification period remained short due to freezing problems in fuel conveyors, stopping the fuel flow to the feed bin. After solving the initial problems, the facility was run in gasification mode without interruptions until the planned conclusion of testing.

One of the targets of the test week was testing of a new syngas combustor, but it was also possible to continue testing of the gasifier with different bed materials and oxygen enrichment. Three different bed materials were tested: magnesium oxide, 50 % sand / 50 % coarse limestone and 50 % sand / 50 % fine P6 limestone (the same as P3 but finer fraction). The feed rate was generally 4 - 5 kg/h but with the fine limestone it was 10 kg/h. On the other hand, feeding of calcium hydroxide was stopped when fine limestone was used, while with the other bed materials it was fed at the rate of 3 - 4 kg/h.

Nine steady-state test runs (Tests 14A, 14B, 15, 16, 17, 18, 19, 20 and 21) were performed during the third test week. The oxygen content of gasification air was about 23 % (m), 30 % or 40 % during most of the tests, as in the previous test weeks, but during the last test the oxygen level was raised to 50 %, which was the maximum level with the available equipment.

VTT was carrying out syngas sampling after the hot gas filter during four different tests (one with MgO bed and three with coarse limestone bed) to determine the contents of tars, benzene, NH_3, HCN, H_2O and C_2 - C_5 hydrocarbon gases.

Post-Test Inspection

Some maintenance work and inspections were carried out in the beginning of January, 2005. The grid was removed for inspection. There was only some dark material that had fallen from the return pipe, but no lumps. The reactor and return pipe appeared clean, and also the cyclone was almost clean with a small amount of loose material on the bottom. Trouble-free operation seemed to be possible with all the tested bed material combinations and with oxygen enrichment of gasification air at least to the 50 % level tested.

The filter system was found to be in very good condition, with a thin dust cake on the filter elements and no traces of dust leaks or deposits anywhere.

4.4.3 Results

The main process data for the gasifier is presented in Table 21. The fuel feed rate is based on on mass and energy balance calculations. When the bed make-up consisted of sand and limestone, the share of each was always 50 %. Because of the clean fuel, there was little need to feed bed make-up to remove solid impurities from the fluidized bed. The feed rate ranged from about 1 to 6 % of the fuel feeding, and even at the lowest feed rates there were no signs of bed quality problems. The filter ash consisted of unreacted carbon from the fuel, fuel ash, elutriated bed make-up and the calcium hydroxide fed after the gas cooler to increase dust loading of the filter.

Table 21. Main Process Data.

Test run	**-**	**5**	**7**	**6**	**9**	**10**	**11**
Start date	dd.mm.yy	24-11-04	25-11-04	25-11-04	01-12-04	02-12-04	02-12-04
Start time	hh:mm	17:00	12:00	0:30	7:00	7:00	21:30
Test duration	hh:mm	5:00	10:00	8:00	10:00	10:00	15:00
Fuel feed rate, wet	g/s	54.4	50.2	75.9	46.2	58.5	79.3
Primary air feed rate	g/s	76.9	44.9	39.4	78.2	55.1	39.0
O2 content of total air	%	23	30	38	23	30	40
Bed make-up type	-	sand / limest.	sand / limest.	sand / limest.	MgO	MgO	MgO
Bottom ash discharge rate	g/s	0.4	0.2	1.0	0.3	0.6	0.7
Filter ash discharge rate	g/s	3.7	4.3	4.8	3.4	3.8	5.1
Bed temperature	°C	900	896	877	904	902	903
Temperature inside filter	°C	291	276	296	323	284	287

Test run	**-**	**15**	**16**	**17**	**18**	**19**	**20**	**21**
Start date	dd.mm.yy	15-12-04	15-12-04	16-12-04	17-12-04	18-12-04	19-12-04	20-12-04
Start time	hh:mm	0:30	20:00	22:00	23:00	17:00	12:00	15:30
Test duration	hh:mm	14:30	20:00	17:00	14:30	16:00	6:00	13:00
Fuel feed rate, wet	g/s	76.8	63.0	49.2	49.4	64.4	75.2	105.0
Primary air feed rate	g/s	38.5	54.0	75.0	75.0	54.0	38.0	38.0
O2 content of total air	%	39	30	23	23	30	40	49
Bed make-up type	-	sand / coarse limest.	sand / coarse limest.	sand / coarse limest.	sand / fine limest.	sand / fine limest.	sand / fine limest.	MgO
Bottom ash discharge rate	g/s	0.5	0.4	0.4	1.1	1.2	2.2	0.9
Filter ash discharge rate	g/s	4.8	4.0	3.2	3.2	3.5	3.7	8.2
Bed temperature	°C	897	900	899	887	889	901	893
Temperature inside filter	°C	302	309	309	304	310	316	340

Input Materials

The fuel used during the gasification test runs was Finnish wood pellets. The fuel was generally homogenous, but it originated from two different pellet manufacturing mills producing pellets with a different diameter, 6 mm and 8 mm nominally. Also small variations in moisture were observed. Table 22 shows the analyses of the wood pellets used during different tests.

Table 22. Fuel Analyses.

Order code			S2004/011	S2004/011	S2004/011	S2004/013	S2004/013	S2004/013	S2004/013	S2004/013
Sample code			FUWO/28	FUWO/30	FUWO/31	FUWO/26	FUWO/27	FUWO/28	FUWO/29	FUWO/30
Test run			5 - 7	9	10 - 12	14	15	16	17	18 - 21
Date			24.-25.11. 2004	1.12. 2004	2.-3.12. 2004	14.12. 2004	15.12. 2004	15.-16.12. 2004	17.12. 2004	18.-21.12. 2004
Moisture[2]	as received	%	8.25	7.95	8.15	8.77	8.1	8.43	8.34	8.14
Volatiles	in d.s.	%	--	85.4	85.5	--	85.7	85.0	85.5	--
Ash 575 °C	in d.s.	%	--	0.32	0.31	--	0.36	0.31	0.30	--
Ash 815 °C	in d.s.	%	0.23	0.23	0.23	0.23	0.27	0.23	0.23	0.24
Fixed carbon	in d.s.	%	--	14.4	14.3	--	14.0	14.8	14.3	--
C	in d.s.	%	50.4	50.3	50.4	50.7	50.4	50.6	50.6	50.5
H	in d.s.	%	6.25	6.19	6.21	6.19	6.21	6.21	6.23	6.18
N	in d.s.	%	0.12	0.11	0.11	0.15	0.13	0.09	0.12	0.11
S	in d.s.	%	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
O	in d.s.	%	43.0	43.2	43.0	42.7	43.0	42.9	42.8	43.0
HHV	in d.s.	MJ/kg	--	20.45	20.63	--	20.68	20.6	20.64	--
LHV	in d.s.	MJ/kg	--	19.09	19.27	--	19.32	19.24	19.27	--
	as received	MJ/kg	--	17.38	17.50	--	17.56	17.41	17.46	--
Bulk density	as received	kg/m3	--	598	--	--	528	--	--	--
Cl total	in d.s.	mg/kg	--	< 100	< 100	--	< 100	--	--	--
F total	in d.s.	mg/kg	--	< 100	< 100	--	< 100	--	--	--
Na total[1]	in d.s.	mg/kg	--	14	--	--	21	--	--	--
K total[1]	in d.s.	mg/kg	--	288	--	--	367	--	--	--
Na acid soluble	in d.s.	mg/kg	--	0	--	--	0	--	--	--
K acid soluble	in d.s.	mg/kg	--	338	--	--	353	--	--	--
Ca	in d.s.	%	--	0.08	0.07	--	0.08	0.08	0.07	--
Sintering Index[3]	Na equiv. in ash	%	--	8.6	--		7.7	--	--	--

Notes:
1) Results from XRF, not accurate values
2) Average of the individual samples of a combined sample
3) <4.5 low agglomeration potential; 4.5 - 9 medium; >9 high

Bed make-up material consisted either of a mixture of limestone and sand (50 % sand and 50 % limestone) or of magnesium oxide (MgO) only. Three different limestone types were tested: fine Parfill P6 limestone, P3 that is a coarser fraction of the same material, and a third limestone which was coarser than normally used in circulating fluidized bed reactor, named "coarse limestone". Table 23 shows the analyses of different limestones and MgO. P6 was not analyzed chemically as it is the same material as P3.

Table 23. Limestone and MgO Analyses.

Order code			S2004/011	S2004/011	S2004/013
Sample code			LI/14	BM/06	LI/07
Test run			4 - 7	8, 11	15 - 17
Sampling date			24.-25.11. 2004	26.11.; 2.12. 2004	15.-17.12.2004
Type			P3	MgO	Coarse
MAIN COMPONENTS					
Moisture	as received	%	0.06	0.49	1.2
CaCO3	in d.s.	%	91.5		93.5
MgCO3	in d.s.	%	2.3		2.7
Inert	in d.s.	%	6.3		3.8
REACTIVITY TEST Chemical analysis of fraction 0.125 - 0.25 mm before reaction					
Ca	in d.s.	%	34.6	1.9	34.6
Mg	in d.s.	%	0.65	46.3	0.77
C_total	in d.s.	%	11.3	0.28	13.0
C_CO3	in d.s.	%	--	--	11.6
S	in d.s.	%	0.0	0.19	0.75
Chemical analysis of calcined and sulphated limestone after reaction					
C	in d.s.	%	0.15	0.07	0.07
S	in d.s.	%	7.74	1.17	17.2
The reactivity index (RI) and capacity index (CI)					
RI		mol/mol	4.89	1.52	1.72
CI		g S / kg limestone	57	10	161
Characterization of limestones					
Grade	RI mol/mol	CI g S / kg limestone			
excellent	< 2.5	> 120		RI	RI, CI
good	2.5 - 3.0	100 - 120			
average	3.0 - 4.0	80 - 100			
fair	4.0 - 5.0	60 - 80	RI		
low	> 5.0	< 60	CI	CI	

Bottom Ash

Only moderate amounts of bottom ash were removed from the gasifier during steady-state test runs. The fuel was free of solid impurities, and therefore, accumulation of stones, metals etc. in the bed did not occur. Furthermore, no signs of bed sintering related to fuel alkalis were observed. During several tests, bottom ash was removed practically only for the material sampling purpose. Chemical analyses of the bottom ash samples are presented in Table 24.

Samples of the bottom and fly ash were collected during the tests and the total content of carbon and the content of carbonate-bound carbon were analyzed in order to determine the content of unburned carbon in ash. The bottom ash contained mostly bed make-up materials because the fuel was virtually free of solid impurities and the fine fuel ash is obviously elutriated from the reactor. The content of unburned carbon in bottom ash varied in the range from 2 to 20 %, which is higher than usual (< 1 %) at the test facility. The reason was quite obvious: the samples contained a varying amount of "char pellets", i.e. part of the fuel got into the bottom ash discharge pipe soon after entering the reactor, before

carbon burn-out took place. Even so, the flow rates were so small that the effect on carbon conversion remained negligible. Figure 13 shows the appearance of a typical bottom ash sample.

Table 24. Chemical analyses of bottom ash.

BOTTOM ASH ANALYSES

Order code			S2004/011	S2004/011	S2004/011	S2004/011	S2004/011	S2004/011	S2004/013	S2004/013	S2004/013	S2004/013	S2004/013	S2004/013	S2004/013
Sample code			BAGA/44	BAGA/45	BAGA/46	BAGA/48	BAGA/49	BAGA/50	BAGA/50	BAGA/51	BAGA/52	BAGA/53	BAGA/54	BAGA/55	BAGA/56
Test run			5	6	7	9	10	11	15	16	17	18	19	20	21
C_total	in d.s.	%	5.16	3.85	4.58	5.47	8.60	16.10	7.74	5.60	2.95	3.65	7.26	6.52	21.90
C_carbonate	in d.s.	%	0.77	1.00	0.69	0.98	1.10	2.17	1.64	0.35	0.49	0.44	0.63	0.48	1.65
C_combustable	in d.s.	%	4.39	2.85	3.89	4.49	7.50	13.93	6.10	5.25	2.46	3.21	6.63	6.04	20.25
H	in d.s.	%	--	--	--	0.07	--	0.06	0.02	0.01	0.01	--	--	--	--
S	in d.s.	%	0.01	0.01	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.00	0.01	0.01	0.01
Ca, HCl soluble	in d.s.	%	11.0	12.9	10.9	3.5	1.8	1.2	11.3	11.3	12.0	7.4	7.4	10.9	1.8
Mg, HCl soluble	in d.s.	%	--	--	--	35.8	39.9	38.6	--	--	--	--	--	--	31.9
N	in d.s.	%	--	--	--	0.03	--	0.04	0.03	0.02	0.01	--	--	--	--
Cl	in d.s.	mg/kg	--	--	--	< 1000	--	--	< 1000	--	--	--	--	--	--
Na, acid soluble	in d.s.	%	--	--	--	0.02	--	0.00	0.05	0.10	0.09	--	--	--	--
K, acid soluble	in d.s.	%	--	--	--	0.06	--	0.05	0.12	0.19	0.14	--	--	--	--
Bulk density		kg/m3	--	--	--	830	--	901	892	--	--	--	--	--	--
Major components as elements															
Na	in ash	%	0.6	0.5	0.6	0.0	0.0	0.0	0.3	0.4	0.4	0.6	--	--	0.0
K	in ash	%	2.5	2.2	2.5	0.4	0.2	0.1	1.9	2.4	2.5	2.6	--	--	0.4
Ca	in ash	%	21.0	24.3	19.7	4.6	2.3	1.6	22.3	19.8	26.7	14.5	--	--	2.4
Mg	in ash	%	0.8	0.8	0.7	44.1	44.1	40.0	4.2	3.1	2.1	1.4	--	--	32.9
Al	in ash	%	2.7	2.7	2.7	0.0	0.0	0.0	1.9	2.2	2.2	2.7	--	--	0.0
Fe	in ash	%	1.3	1.3	1.1	0.4	0.3	0.2	1.1	1.0	1.1	1.2	--	--	0.2
Si	in ash	%	23.6	21.9	25.0	5.1	5.2	4.1	19.1	23.7	20.8	28.5	--	--	6.8
P	in ash	%	0.1	0.1	0.1	0.0	0.0	0.0	0.1	0.1	0.1	0.1	--	--	0.0
Ti	in ash	%	0.1	0.2	0.1	0.0	0.0	0.0	0.1	0.1	0.1	0.1	--	--	0.0
S	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
Cl	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
Major components as oxides															
Na2O	in ash	%	0.9	0.7	0.8	0.0	0.0	0.0	0.5	0.6	0.6	0.9	--	--	0.0
K2O	in ash	%	3.0	2.7	3.0	0.5	0.3	0.2	2.3	2.9	3.1	3.2	--	--	0.5
CaO	in ash	%	29.4	34.1	27.6	6.4	3.2	2.2	31.2	27.7	37.4	20.2	--	--	3.3
MgO	in ash	%	1.3	1.3	1.1	73.1	73.1	66.4	7.0	5.2	3.5	2.3	--	--	54.5
Al2O3	in ash	%	5.0	5.1	5.1	0.0	0.0	0.0	3.6	4.1	4.1	5.1	--	--	0.0
Fe2O3	in ash	%	1.8	1.8	1.6	0.5	0.4	0.3	1.6	1.4	1.6	1.7	--	--	0.3
SiO2	in ash	%	50.4	46.8	53.6	10.9	11.2	8.8	40.9	50.6	44.6	61.1	--	--	14.6
P2O5	in ash	%	0.2	0.2	0.2	0.0	0.0	0.0	0.2	0.3	0.2	0.2	--	--	0.0
TiO2	in ash	%	0.2	0.3	0.2	0.0	0.0	0.0	0.2	0.2	0.2	0.2	--	--	0.0
SO3	in ash	%	-	-	0.0	0.0	0.0	0.0	-	-	-	0.0	--	--	-
Minor components as elements															
Mn	in ash	%	0.1	0.1	0.1	0.0	0.0	0.0	0.1	0.1	0.1	0.0	--	--	0.0
Zn	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
Cu	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
Pb	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
Cr	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
Sn	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
Sb	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
Co	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
Ni	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
V	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
Light components analyzed by other methods															
CO2	in ash	%	7.2	6.5	6.4	8.1	11.5	21.9	12.1	6.5	4.3	4.8	--	--	26.3
SUM calculated as oxides															
	in ash	%	99.7	99.6	99.8	99.6	99.7	99.7	99.7	99.7	99.8	99.6	--	--	99.6

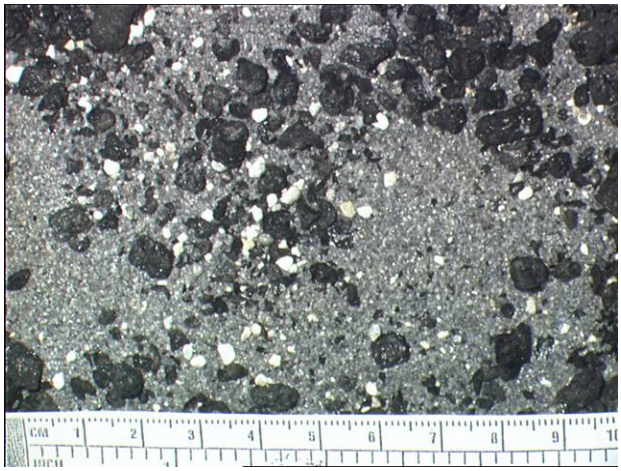


Figure 13. Bottom Ash Sample.

Filter Ash

The filter ash consisted of calcium hydroxide fed after the gas cooler, elutriated bed make-up (mainly Ca or Mg), unburned carbon from the fuel and fuel ash. Chemical analyses of the filter ash samples are presented in Table 25. The unburned carbon content of filter ash seemed to increase with oxygen enrichment level of the fluidization air, as illustrated in Figure 14**.** The carbon content is normally higher with wood-based fuels when compared with for instance waste-derived fuels tested at the same facility, and using higher gasification temperatures would decrease the carbon contents. The rise with increasing oxygen enrichment may be attributed to a lower air coefficient required for bed temperature control and to lower temperatures at the upper part of the reactor. Furthermore, the share of additives of the total solids feed into the system decreased with increasing fuel feeding, i.e. with increasing oxygen enrichment, hence increasing the percentage of carbon. But even without more detailed analysis, it became evident that oxygen enrichment of air will not decrease the unburned carbon content of filter ash to levels required for direct utilisation or landfilling.

Table 25. Chemical analyses of filter ash.

FILTER ASH ANALYSES

Order code			S2004/011	S2004/011	S2004/011	S2004/011	S2004/011	S2004/011	S2004/013	S2004/013	S2004/013	S2004/013	S2004/013	S2004/013	S2004/013
Sample code			FAGS/46	FAGS/47	FAGS/48	FAGS/50	FAGS/51	FAGS/52	FAGS/50	FAGS/51	FAGS/52	FAGS/53	FAGS/54	FAGS/55	FAGS/56
Test run			5	6	7	9	10	11	15	16	17	18	19	20	21
C_total	in d.s.	%	49.4	68.4	55.0	47.5	53.7	62.4	66.3	61.4	50.2	55.6	68.7	75.0	75.2
C_carbonate	in d.s.	%	1.82	0.69	0.99	1.64	0.51	0.96	4.13	4.25	3.72	5.32	4.87	6.27	4.43
C_combustable	in d.s.	%	47.61	67.70	53.97	45.81	53.14	61.48	62.17	57.15	46.48	50.28	63.83	68.73	70.77
H	in d.s.	%	1.2	1.0	1.3	0.88	0.9	0.9	0.94	1.03	1.22	0.75	0.68	0.72	0.67
S	in d.s.	%	0.05	0.04	0.04	0.08	0.04	0.04	0.07	0.06	0.06	0.04	0.03	0.04	0.05
Ca, HCl soluble	in d.s.	%	22.3	12.8	19.1	14.1	12.7	11.5	13.2	15.9	20.1	19.0	11.7	8.4	6.5
Mg, HCl soluble	in d.s.	%	--	--	--	11.2	9.6	5.3	0.59	--	--	--	--	--	3.15
N	in d.s.	%	0.27	0.46	0.28	0.20	0.27	0.34	0.44	0.42	0.26	0.26	0.36	0.40	0.39
Cl	in d.s.	mg/kg	--	--	--	1900	--	--	< 1000	--	--	--	--	--	--
Na, acid soluble	in d.s.	%	--	--	--	0.01	--	--	0.02	0.02	0.03	--	--	--	--
K, acid soluble	in d.s.	%	--	--	--	0.15	--	--	0.09	0.07	0.07	--	--	--	--
Bulk density		kg/m3	--	--	--	381	--	--	337	324	350	396	--	--	--
Ash 575 °C	in d.s.	%	59.9	35.3	51.2	57.6	50.6	40.4	38.2	45.0	57.1	53.2	35.1	26.3	26.1
HHV	in d.s.	MJ/kg	--	--	--	16.20	18.65	--	22.5	20.7	16.5	18.74	--	--	25.74
LHV	in d.s.	MJ/kg	--	--	--	16.01	18.46	--	22.3	20.4	16.2	18.57	--	--	25.6
Major components as elements															
Na	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
K	in ash	%	0.5	1.0	0.6	0.6	0.7	0.8	0.9	0.9	0.7	0.5	--	--	1.6
Ca	in ash	%	40.4	39.6	40.2	26.4	25.5	29.8	40.0	41.0	40.0	44.4	--	--	30.1
Mg	in ash	%	0.7	0.9	0.7	20.7	21.5	15.2	2.0	1.3	1.3	1.8	--	--	13.8
Al	in ash	%	0.1	0.1	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.4	--	--	0.0
Fe	in ash	%	0.6	0.5	0.4	0.3	0.2	0.2	0.5	0.4	0.5	0.8	--	--	0.3
Si	in ash	%	0.1	0.2	0.1	0.6	0.6	0.5	0.6	0.2	0.4	0.8	--	--	0.8
P	in ash	%	0.1	0.2	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	--	--	0.2
Ti	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	--	--	0.0
S	in ash	%	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.0	--	--	0.1
Cl	in ash	%	0.2	0.4	0.2	0.4	0.2	0.2	0.2	0.0	0.0	0.0	--	--	0.4
Major components as oxides															
Na2O	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
K2O	in ash	%	0.6	1.2	0.7	0.7	0.8	1.0	1.1	1.1	0.9	0.7	--	--	2.0
CaO	in ash	%	56.6	55.4	56.3	36.9	35.6	41.6	56.0	57.4	55.9	62.1	--	--	42.1
MgO	in ash	%	1.1	1.5	1.2	34.3	35.6	25.2	3.4	2.2	2.1	3.1	--	--	22.8
Al2O3	in ash	%	0.1	0.1	0.0	0.0	0.0	0.0	0.2	0.1	0.2	0.7	--	--	0.0
Fe2O3	in ash	%	0.9	0.7	0.6	0.4	0.3	0.3	0.8	0.6	0.7	1.1	--	--	0.5
SiO2	in ash	%	0.2	0.4	0.1	1.2	1.4	1.0	1.2	0.4	0.8	1.7	--	--	1.6
P2O5	in ash	%	0.2	0.4	0.3	0.2	0.2	0.2	0.6	0.3	0.3	0.2	--	--	0.4
TiO2	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	--	--	0.0
SO3	in ash	%	0.2	0.2	0.1	0.3	0.2	0.2	0.4	0.3	0.3	0.1	--	--	0.3
Minor components as elements															
Mn	in ash	%	0.2	0.3	0.2	0.2	0.2	0.2	0.3	0.3	0.2	0.2	--	--	0.4
Zn	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
Cu	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
Pb	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
Cr	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
Sn	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
Sb	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
Co	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
Ni	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
V	in ash	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--	--	0.0
Light components analyzed by other methods															
CO2	in ash	%	39.3	39.1	39.9	25.0	25.2	29.8	35.6	36.8	38.2	29.6			28.9
SUM calculated as oxides															
	in ash	%	99.6	99.7	99.7	99.7	99.8	99.8	99.6	99.6	99.6	99.6			99.5

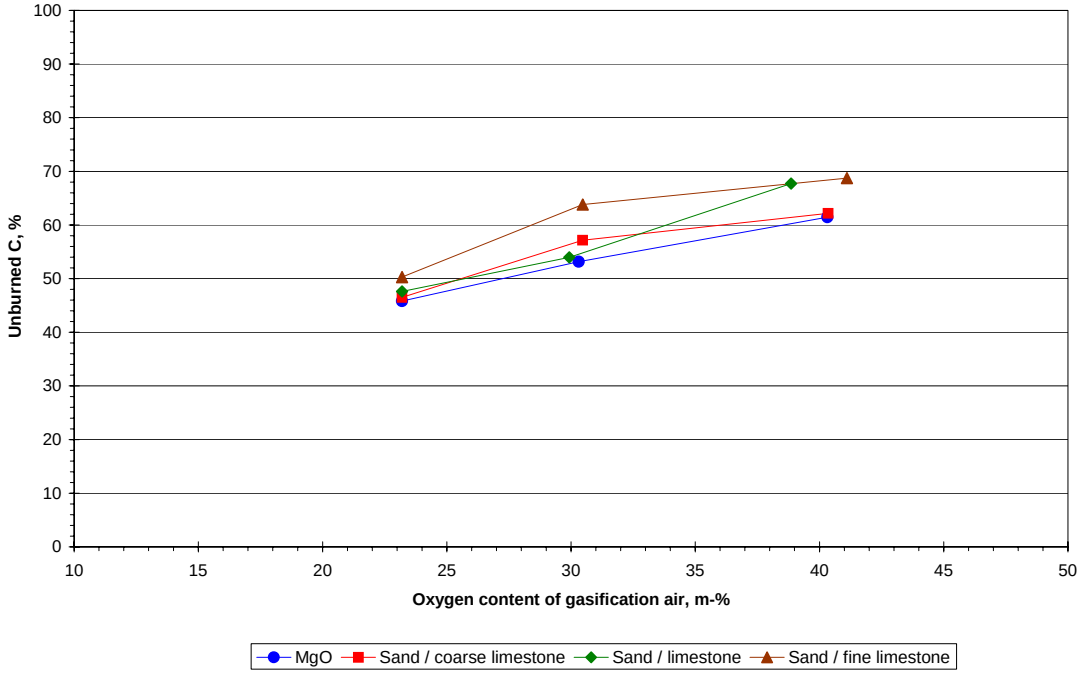


Figure 14. Unburned Carbon Content of Filter Ash.

Syngas composition

Figure 15 illustrates the effect of bed material and oxygen enrichment on the syngas tar and benzene contents. The tar contents turned out to be very low with MgO bed. However, with both bed materials the tar contents increased with oxygen enrichment, as naturally did the other combustible fractions as well.

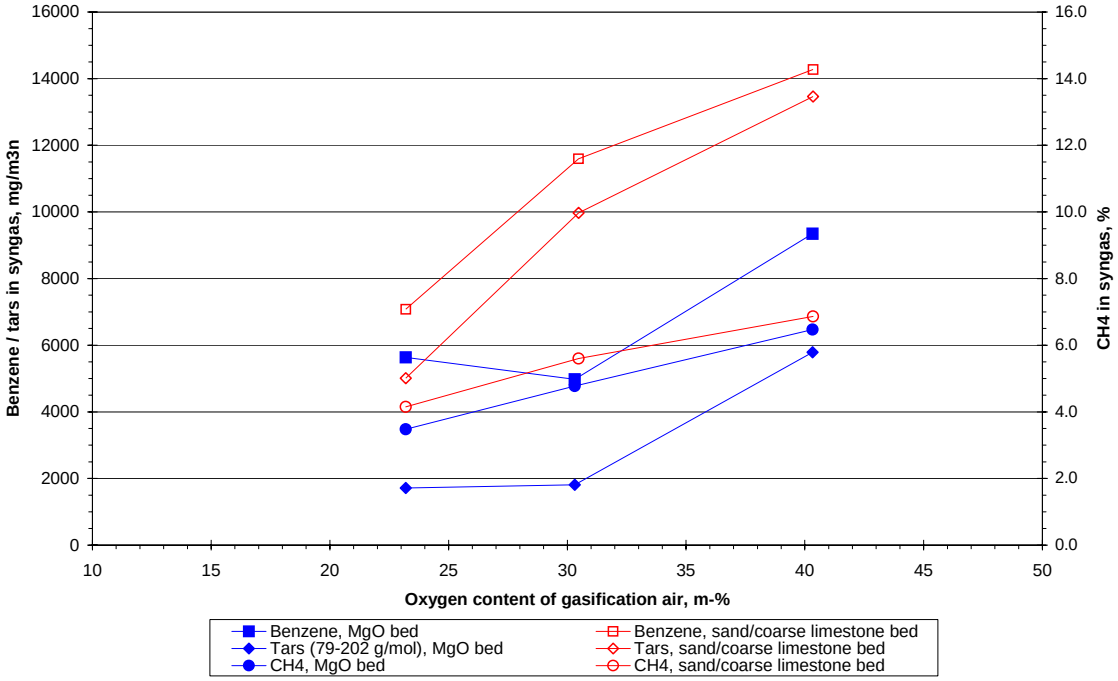


Figure 15. Tars and Benzene in Syngas.

The CO, H_2 and CH_4 contents of syngas with different bed materials, measured with continuously operating analyzers are shown in Figure 16. The contents increased with oxygen enrichment, as expected. The differences between limestone types were very small, but with MgO bed the CO and H_2 contents rose slightly higher than with limestone / sand bed as the oxygen content was increased.

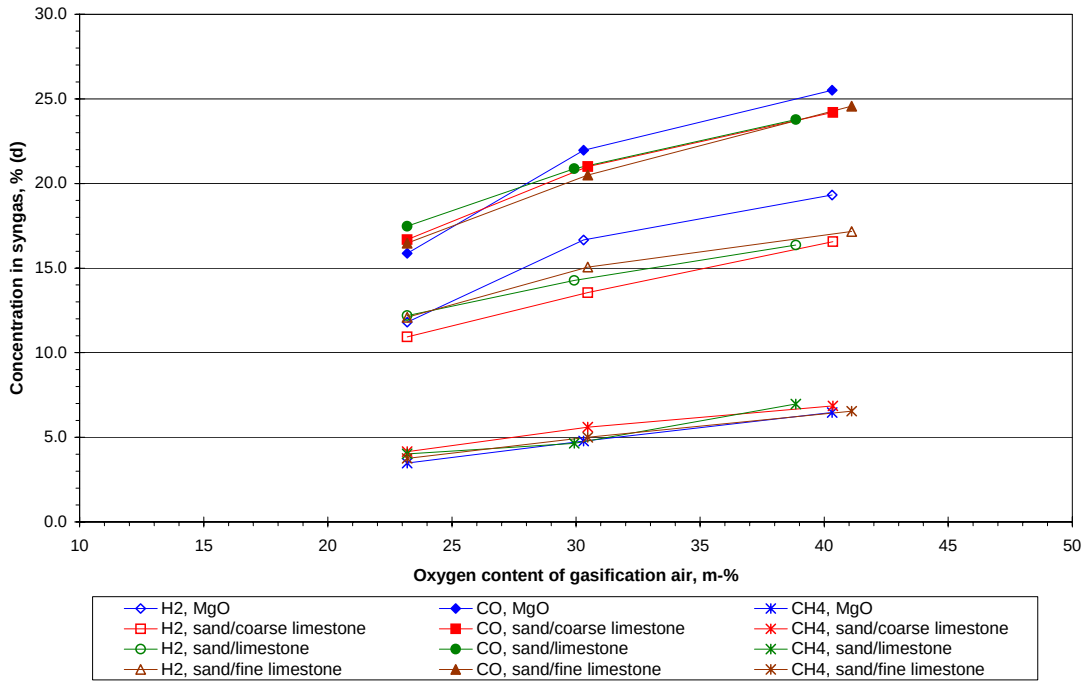


Figure 16. Combustible Syngas Components.

Carbon Conversion

Carbon conversion was calculated based on the measured material streams and their analyzed carbon contents, using the following equation:

$$\text{Carbon conversion} = \frac{\text{C_fuel} - \text{C_ash}}{\text{C_fuel}}$$

where C_fuel is carbon input in the fuel, g/s
C_ash is unburned carbon output in bottom and fly ashes, g/s

The results with different bed materials and levels of oxygen enrichment are summarized in Figure 17. Differences between the bed materials were small. Generally the carbon conversion decreased slightly with increasing oxygen content. When evaluating the figures, it should be noted that the operation was not tried to be optimized regarding carbon conversion but the main objective was to find out potential effects of the tested parameters.

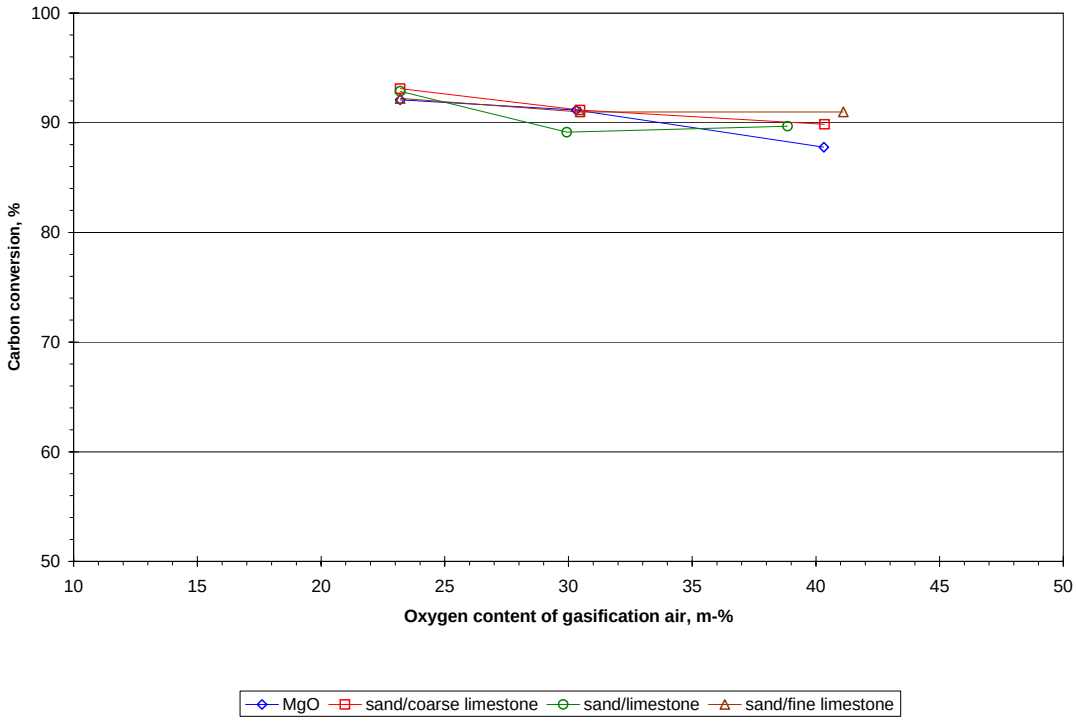


Figure 17. Carbon Conversion.

4 Conclusions

Carbon conversion is one of the factors having influence on economy of the gasification based (heat and) power production. Carbon conversion has direct effect on the efficiency of energy production process. In addition, low carbon conversion leads to enrichment of carbon in gasification residues, especially in fly ash. Carbon in fly ash increases mass of fly ash but carbon can also restrict further utilisation of fly ash in many applications. However, air-blown fluidised bed gasification of wood or other char producing fuel leads always (in practice) to rather high carbon content (30-80 %-m) of fly ash. In practice, this high carbon content means necessarily some further treatment in order to eliminate problems related to carbon. One of the most evident ways to treat carbon rich fly ash is combustion (oxidation). If fly ash does not contain any hazardous or harmful components (heavy metals etc.) it can be utilised as a fuel in combustion processes. If fly ash is utilised as a fuel high carbon content is an advantage, not a disadvantage. Therefore optimisation of gasification process has to be done keeping in mind the further treatment, utilisation or disposal of fly ash. Using other words, high carbon conversion is not always best possible solution.

Optimisation of gasification conditions without any significant modifications in design of the gasifier results in relatively limited improvement of carbon conversion. This was achieved using test facilities, which does not necessarily mean that same results could be achieved in commercial operation of large scale gasifier. One of the key issues related to operation of commercial scale gasifier is availability, which means minimisation of all technical risks. In practice, this means that even higher carbon content of filter dust and lower carbon conversion is accepted if availability of the plant can be maximised.

Carbon conversion could also be improved by HSD-CFB principle but simultaneously technical risks are increased. In practice, this led to conclusion that this technological solution is not yet ready for large scale and commercial operation.

Oxygen enrichment was indicated to be one way to improve carbon conversion and reduce ash volumes. However, the test trials carried out in this project did not show clearly any improvements related to these targets. The main reason for this was that simultaneously when oxygen content of primary air is increased temperature tends to increase and fuel feed has to be increased in order to compensate this effect. This means that oxygen content is not such an independent variable which could be optimised independently from other variables and parameters. However, the number of oxygen enrichment related gasification test trials was limited and therefore all potential process conditions could not be studied and tested in details. Further optimisation might result in improved carbon conversion without any significant disadvantages.

Conventional combustion of fly ash is not potential solution for fly ash from gasification of waste derived fuels or any fuels containing heavy metals or other harmful components. In this case minimisation of volume of fly ash is essential in order to reduce ash-related cost. Solid recovered fuel (SRF), studied in this work, has high reactivity and carbon content of fly ash could be reduced by optimising gasification conditions and improving carbon conversion. Fly ash from gasification of SRF contains high concentration of chlorine as well as heavy metals and it can not be combusted in conventional combustion process equipped with conventional flue gas cleaning. Therefore this improvement of carbon conversion is very essential in order to reduce fly ash related cost.

Some biofuels, like straw and orujillo, are usually rich in alkali metals, which have direct effect on bed agglomeration tendency, especially when bed consists of sand. Serious agglomeration means always unstable process that should be avoided. In this case stability of the process has always higher priority than ash related cost and therefore even reasonable carbon conversion can be accepted. In this study carbon conversion in gasification of orujillo was reasonable when agglomeration was avoided by optimising bed material.

Composition of bed material was also optimised especially in gasification of SRF and orujillo. Fluidised bed gasification of SRF was done with bed containing sand and limestone. Limestone has several positive effects on gasification and gas cleaning process. Limestone has positive effect on reduction of tar formation, it reacts with sulphur (in-bed sulphur removal) and fine calcined particles elutriate from the reactor and react with HCl in filter dust cake. Negative effects related to use of limestone are primarily cost related to use of limestone and increase of mass of filter dust.

Fluidised bed gasification of orujillo caried out using different bed materials but only use of ofite resulted in successful gasification test trials i.e. avoiding of serious agglomeration of the bed. Orujillo is rich in potassium, which leads easily to sintering of bed material and finally leads to serious agglomeration and poor fluidisation.

A common conclusion related to optimisation of gasification and gas cleaning process conditions is that no universal solution can be defined but final optimisation has to be done case by case. Optimal solution depends on type of fuel and local conditions. In addition,

oxygen enrichment might offer one way to have positive effect on carbon conversion but this needs further optimisation.

ANNEX 1

(Reported preiviously in combination with the 1st Progress Report)

VTT

CONTRACT N° : ENK5-CT-2002-00635

PROJECT N° : NNE5-2001-00598

ACRONYM : GASASH

TITLE : Improvement of the economics of biomass/waste gasification by higher carbon conversion and advanced ash management

REPORTING PERIOD : From 1 November 2002 to 31 October 2003

PROJECT START DATE : 1 November 2002 DURATION : 36 months

Date of issue of this report : June2005

Project funded by the European Community under the 'EESD' Programme (1998-2002)

PREFACE

This report presents VTT's activities and results of GASASH project during the first year of the project. Largest activities were related to the gasification tests carried out in the bubbling fludised bed pilot-plant test facility of VTT Processes. The other activities were related to CFB gasification tests, design and construction of integtrated oxidiser and prelimianry characterisation of gasification ashes.

The main objective of the gasification tests was to develop and improve the BFB gasification process for woody fuels. The objective was to optimise the BFB gasification process in order to increase carbon conversion and to reduce the amount of problematic fly ash. In addition, a special attention was focused on studying the effects on operation conditions on the tar contents and heating value of the product gas, which are very important characterististics of fuel gas.

The experiments of this report are related to an EC-financed project: Improvement of the economics of biomass/waste gasification by higher carbon conversion and advanced ash management, *(GASASH, contract no ENK5-CT-2002-00635),* started in November 2002.

CONTENTS

1 INTRODUCTION 4

2 WORK PACKAGE 1 4
2.1 BFB GASIFICATION TEST TRIAL 0250 4
2.1.1 Test programme and objectives 4
2.1.2 Test facility 4
2.1.3 Feedstock 6
2.1.4 Experiences from operation 7
2.1.5 Gasification results 7
2.1.6 Conclusions (BFB gasification of waste wood) 11
2.2 BFB GASIFICATION test trial 0310 11
2.2.1 Feedstock 11
2.2.2 Experiences from operation (BFB 0310C) 12
2.2.3 Gasification results 12
2.2.4 Conclusions (BFB gasification of SRF) 14
2.3 CFB GASIFICATION test trial 0323 15
2.3.1 Test facility 15
2.3.2 Feedstock 17
2.3.3 Experiences from operation (CFB 0323A) 18
2.3.4 Gasification results 18
2.3.5 Conclusions (CFB gasification of waste wood) 20
2.4 Conclusions related to WP1 21

3 REFERENCES 21

1 INTRODUCTION

One of the worst disadvantages of air blown gasification process is related to disposal of solid residues. Solid residues of air blown fluidised bed gasification are bottom ash and residues from gas cleaning. This project is focused on air blown fluidised bed gasification with hot gas cleaning. Hot gas cleaning can be based on cyclones and hot gas filter or on both of these. Bottom ash is usually easier to dispose because it is almost carbon free and usually it contains only minor amounts of soluble compounds. Fly ash from filter is significantly more difficult to dispose. The main focus of this project is mainly on fly ash.

Project has 4 workpackages focusing on (1) further development of gasification and gas cleaning process, (2) development of new components in order to reduce ash volume and improve ash quality, (3) develop methods for ash utilisation and (4) economic evaluation of different routes to reduce overall ash related cost. This report describes activities of VTT focused primarily on work package 1.

2 WORK PACKAGE 1

The objectives of WP 1 were related to improvement of carbon conversion, reduction of ash volumes and effects of bed additives. The overall objective was to reduce cost related to disposal of solid residues. Work contained optimisation of BFB and CFB gasification of waste wood and solid recovered fuel (SRF).

2.1 BFB GASIFICATION TEST TRIAL 0250

2.1.1 Test programme and objectives

The main aim of the tests was to develop and improve the BFB gasification process for woody fuels. The objective was to optimise the BFB gasification process in order to increase carbon conversion and to reduce the amount of problematic fly ash. The target was to improve total carbon conversion of woody fuels > 96 %. In addition, a specific attention was focused on the following topics:

- Operation of the gasifier: the effects of operating parameters on gasifier performance especially on carbon conversion and tar contents.
- Modification and optimisation of bed additives (sand and limestone).

2.1.2 Test facility

The gasification tests were carried out with atmospheric pressure Bubbling Fluidised-Bed (BFB) gasification pilot plant facility. A schematic figure of the test facility is shown in Figure 1.

The gasification air is electrically preheated and can be divided into primary fluidisation air as well as secondary air feeds. The tests of this report were carried out using primary

air and steam as a gasification agent. In addition, a small amount of secondary air was fed above the fluidised bed.

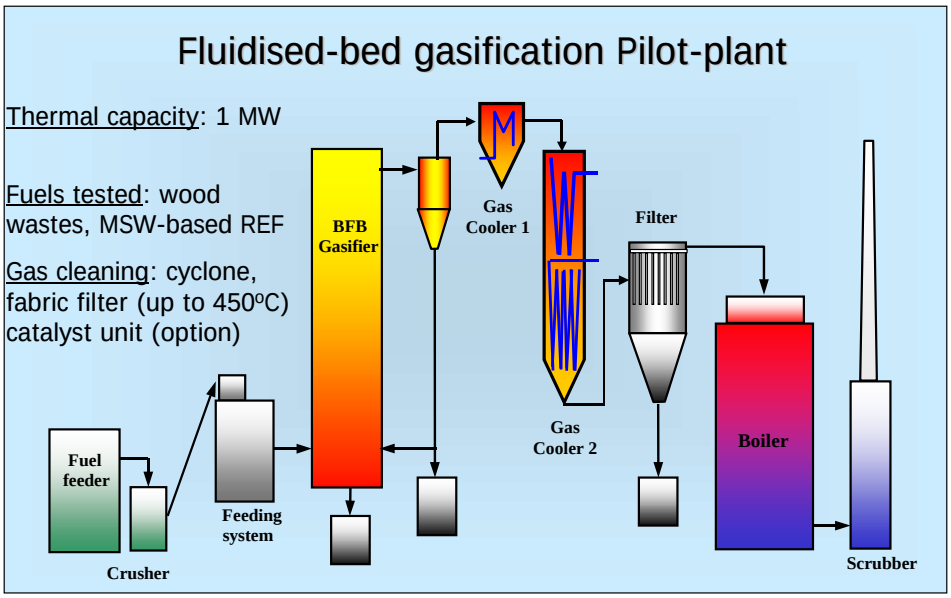


Figure 1. Bubbling Fluidised Bed (BFB) gasification test rig of VTT Processes.

The test rig is equipped with feedstock hoppers of live bottom type suitable to low bulk density bio fuels and with a separate hopper for bed additives. Screw feeders were used for both metering and feeding purposes. In the test rig the product gas was firstly cleaned in the primary (recycling) cyclone. After the cyclone the product gas was cooled close to the target filtration temperature. The product gas was filtered with high temperature bag filter. The tests of this campaign were carried out at a filter temperature of 368-373 °C. The bag filter contained 36 bags of FB900 supplied by 3M company.

The test rig is equipped with an automatic data collection of temperatures and pressures measured at different locations. The flow rates of gasification agents (air, steam, nitrogen) are continuously measured and recorded as well. The fuel feed rate is controlled on the basis of the screw calibration curve and the rotating speed of the metering screw is continuously measured. The main gas constituents, CO, H_2, CH_4, CO_2 were monitored by on-line analysers. In addition, the contents of permanent gas components including C_2H_x-C_5H_y were analysed by a process gas chromatography.

A representative fuel sample for each of the set points were analysed for moisture content, ultimate and proximate composition, LHV, volatile matter and ash content. All separated bottom ashes, filter and heat exchanger dusts were weighed and sampled throughout the tests. One or more representative samples for each set point were analysed for the C, H, N, (S) and ash.

2.1.3 Feedstock

The feedstock in test BFB 0250 was a wood waste (Figure 2). Representative samples of the wood fuel were taken from each set point and these were analysed for moisture content, elemental composition as well as for ash composition. The proximate and ultimate analyses of the woody fuel are presented in Table 1.



Figure 2. Feedstock conveyor (left) and woody fuel crushed below 20-mm sieve size (right).

A mixture of sand and limestone P3 was used as a bed material at all set points. A calcium-based bed additive was used in order to reduce tar content of the gas and thereby to avoid tar related problems in downstream components. During the set points continuous feeding of bed additive was used in order to maintain a stable operation fluidised bed.

Table 1. Average composition of feedstock used in gasification test BFB 0250.

Feedstock	**Woody fuel**				
Set point	**BFB 0250A**	**BFB 0250B**	**BFB 0250C**	**BFB 0250D**	*Average*
Moisture content, wt%	26.8	27.1	24.3	23.3	*25.4*
Proximate analysis, wt% (d.b.)					
Volatile matter	79.4	79.9	80.4	81.5	*80.3*
Ash	3.0	2.7	2.1	1.3	*2.3*
Ultimate analysis, wt% (d.b.)					
C	49.9	49.6	49.8	50.1	*49.9*
H	6.0	6.0	6.0	6.1	*6.0*
N	0.5	0.4	0.4	0.4	*0.4*
S	0.01	nm	nm	nm	nm
O (as difference)	40.6	41.3	41.7	42.1	*41.4*
Ash	3.0	2.7	2.1	1.3	*2.3*
LHV (d.b.), MJ/kg	18.7	18.8	18.8	18.9	*18.8*

2.1.4 Experiences from operation

The operation conditions of the set points carried out with woody fuel are presented in Table 2. The whole test programme could be carried out without major operational problems.

The main variables studied in the tests were as follows:

- The operation temperature of the gasifier
- Bed additive (the amount of sand/limestone in bed mixture)
- The distribution of primary/secondary air feeding and steam

Table 2. Gasification BFB 0250 set points with 100 % woody fuel. Filter was operated at 370℃ in all set points.

Set point date	Fuel	Bed material	T_{gasif} [1], °C	Length [2], h
BFB 0250A 10.-11.12.02	woody fuel	50 %Sand (0.1-0.6mm) + 50 % P3 limestone	882 / 916	10.0
BFB 0250B 11.-12.12.02	woody fuel	2/3 sand + 1/3 P3 limestone	892 / 908	18.2
BFB 0250C 12.12.02	woody fuel	2/3 sand + 1/3 P3 limestone	862 / 904	10.0
BFB 0250D 13.12.02	woody fuel	1/3 sand (0.5-1.0 mm) + 2/3 P3 limestone	893 / 887	12.1

[1] Average temperature at bed/freeboard of the gasifier
[2] Duration of the steady state set point

2.1.5 Gasification results

CARBON CONVERSION AND TAR YIELDS

The average operation conditions and main results of the process measurements at the different set points are presented in Table 3.

The carbon conversion efficiencies determined for different set points were calculated both directly from the gas yields (carbon in gaseous products divided by the input carbon) and indirectly on the basis of carbon loss determined on the basis of mass flows and carbon contents of the solid samples (filter dust, bottom ash heat exchanger dust). The results are illustrated in Figure 3. The first two bars (from left) show the amount of carbon in dry gas and in dry gas and tars divided by the input carbon of the woody fuel. The third conversion efficiency includes also the carbon of $CaCO_3$ in the total carbon input. Finally the fourth bar is calculated indirectly on the basis of the carbon content of filter dust, bottom ash and heat exchanger dust. These different conversion efficiencies are defined in detail in reference [1].

Table 3. Results of the process measurements at the set points in test BFB 0250.

Set point	BFB 0250A	BFB 0250B	BFB 0250C	BFB 0250D
T(beb), °C	882	892	862	893
T(freeboard), °C	916	908	904	887
Bed additives [1]	1/2 S+ 1/2 P3	2/3 S+1/3 P3	2/3 S+1/3 P3	1/3 S+2/3 P3
Fuel moisture content, wt%	26.8	27.1	24.3	23.3
Fuel feed rate, g/s	36	38	35	34
Primary air feed rate, g/s	56	56	50	56
Secondary air feed rate, g/s	6.6	3.4	7.7	3.1
Steam feed rate, g/s	4.2	4.1	4.1	4.3
Air ratio	0.39	0.36	0.37	0.37
Gas flow rate, m^3n/h (wet)	340	335	318	324
Dry gas composition, %				
CO	9.6	10.5	10.1	10.4
CO_2	17.9	17.3	17.3	17.7
H_2	11.0	11.3	11.3	12.4
N_2 (+Ar)	57.8	56.6	57.3	55.7
CH_4	3.1	3.3	3.1	3.2
C_2Hy	0.65	0.82	0.82	0.66
C_3-C_5Hy	-	-	-	-
NH_3	-	0.16	0.17	-
H_2O in wet gas vol%	21.9	22.8	21.6	20.4
Wet product gas LHV, MJ/m3n	3.4	3.7	3.6	3.7
Dry product gas LHV, MJ/m3n	4.4	4.9	4.7	4.7
Tars + benzene, g/m^3n	7.8	9.7	7.4	7.3
Tar yield, g/kg daf fuel	22.6	26.2	20.0	20.2
C-conversion, wt%				
to dry gas	95.8	93.0	91.6	94.4
to gas and tars	99.9	97.7	95.3	98.1
to gas and tars [2]	98.7	96.8	94.4	96.6
Carbon losses [3], wt%	1.2	3.3	5.6	2.4
Mass balance closures (out/in)				
C-balance	1.00	1.00	1.00	0.99
O-balance	1.02	1.01	1.01	1.01
Ash balance	1.04	0.78	1.01	1.02

[1] S + P3 = The mixture of sand and Parfil 3 limestone, [2] Including limestone-C in the input carbon, [3] Incl. C in filter dust, heat exchanger dust and bottom ash /Fuel C

The following conclusions can be made on the basis of carbon conversion results:

- Very high carbon conversion could be achieved in all set points. Carbon conversion to dry gas (without tars) in all tests varied from 91 to 96 % and carbon conversion to gas and tars varied from 95 to 99.9 %.
- The carbon conversion was slightly lower in set point BFB 0250C when the secondary air feed rate was higher and gasification temperature was lower (862°C).

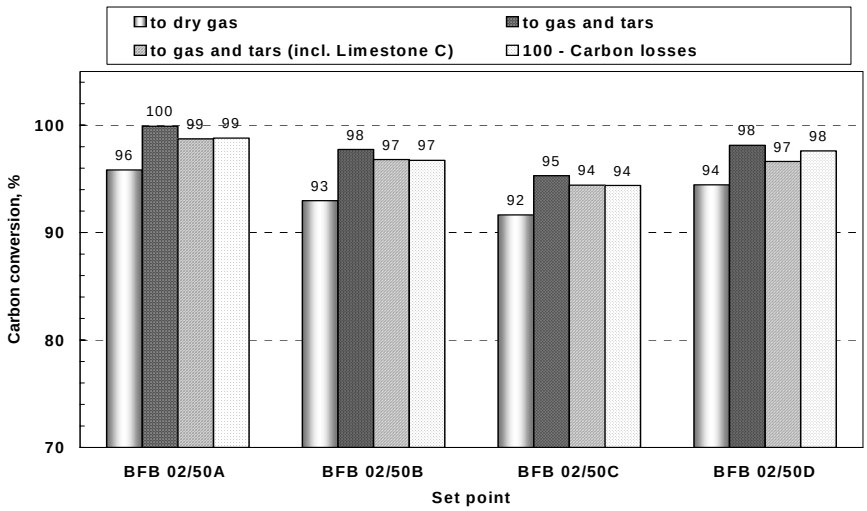


Figure 3. The carbon conversion at different set points in test run BFB 0250.

The tar contents of the product gas were determined at all set points. The results for benzene and tar contents are presented in Table 4. Figure 4 shows the measured tar concentrations divided into four groups: benzene, light oils, naphthalene and the sum of polyaromatic compounds (PAC) heavier than naphthalene.

Table 4. Benzene and tar contents of the product gas, mg/m3n (in dry gas) in test run BFB 0250.

Set point	**BFB 0250A**	**BFB 0250B**	**BFB 0250C**	**BFB 0250D**
Benzene, g/m^{3}n	5.5	6.5	4.8	5.4
Tars, mg/m^{3}n	2.4	3.2	2.6	1.9

Clearly more tars were produced in set point BFB 0250B (secondary air feed was reduced, bed additive feed was highest). In set point BFB 0250D feeding more limestone into the bed could reduce the concentration of heavier PACs. Generally, the tar results were very similar as reported [2] earlier for the test runs of wood residues.

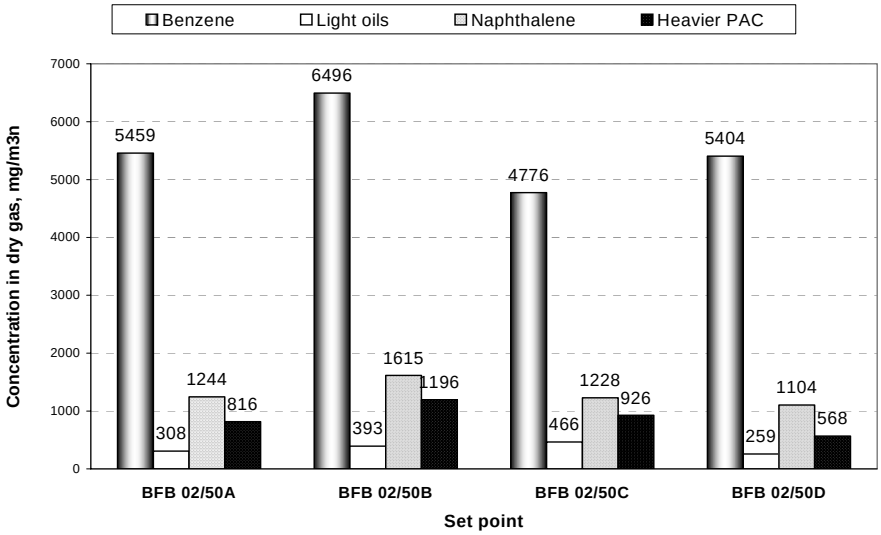


Figure 4. The concentrations of tar components at different set points in test run BFB 0250.

COMPOSITION OF SOLID RESIDUES

The main part of the fly ash was removed from filter unit. Typical bulk compositions of different solid streams (filter dust, bottom ash, heat exchanger dust) are presented in Table 5. These data show that bottom ash is primarily composed of sand additive and contains almost no combustible material, whereas filter dust contain considerable amounts of unburned carbon. The carbon content of heat exchanger dust was 24 - 31 wt%.

Table 5. Composition of different ash products.

Set point	**BFB 0250A**	**BFB 0250B**	**BFB 0250C**	**BFB 0250D**
Filter dust [1], wt% (d.b.)				
C	51.5	53.9	60.7	56.0
H	0.8	0.8	0.8	0.8
N	0.2	0.3	0.3	0.2
O (difference)	5.2	5.9	3.6	8.6
Ash	42.4	39.3	34.8	34.4
Bottom ash, wt% (d.b.)				
Ash	99.7	99.8	99.6	99.6
Heat exchanger dust, wt% (d.b.)				
C	24.4	26.6	30.5	25.2
H	0.9	0.2	0.5	0.7
N	0.1	0.1	0.1	0.1
O (difference)	15.3	10.6	7.8	13.1
Ash	59.3	62.5	61.1	60.9

[1] dry sample

2.1.6 Conclusions (BFB gasification of waste wood)

These BFB gasification tests focused on developing and improving the gasification process for woody fuels. The objective was to optimise the BFB gasification process in order to increase carbon conversion and to reduce the amount of problematic fly ash.

The following conclusions can be made on the basis of BFB 0250 test runs with woody fuel:

- All tests were successful and good material balances could be calculated.
- Operation of the bubbling fluidised bed gasifier was stable and woody fuel could be gasified in the extended test of 90 hours of continuous operation.
- Very good carbon conversions were achieved in gasification of woody fuels at 862-893°C. The carbon conversion to gas and tars were higher than 95 % in all set points.

2.2 BFB GASIFICATION TEST TRIAL 0310

Gasification test trials BFB 0310 were carried out in co-operation with other projects of VTT. Total number of set point periods was 3 and one of these was carried for Gasash project. Test focused on improvement of carbon conversion when waste derived fuel is gasified.

2.2.1 Feedstock

The feedstock in test BFB 0310 was crushed SRF pellet (Figure 5). Representative samples of the crushed fuel were taken from each set point and these were analysed for moisture content, elemental composition as well as for ash composition. The proximate and ultimate analyses of the crushed SRF fuel are presented in Table 6.



Figure 5. SRF pellets before crushing (left) and after crushing (right).

Table 6. Average composition of feedstock used in gasification test BFB 0310.

Feedstock	**BFB 0310C**
Set point	100 % EWA-REF
Moisture content, wt%	1.9
Proximate analysis, wt% (d.b.)	
Volatile matter	80.4
Ash	10.1
Ultimate analysis, wt% (d.b.)	
C	53.9
H	7.8
N	0.7
S	0.14
Cl	0.61
O (as difference)	26.8
LHV (d.b.), MJ/kg	22.6

2.2.2 Experiences from operation (BFB 0310C)

The operation conditions of the set point carried out with SRF fuel are presented in Table 7. Test programme could be carried out without major operational problems.

Table 7. Gasification BFB 0310 set point with crushed SRF pellets.

Set point date	Fuel	Bed material	T_{gasif} [1], °C	Length [2], h
BFB 0310C	crushed SRF pellet	50 %Sand + 50 % P3 limestone	870 / 873	7.0

[1] Average temperature at bed/freeboard of the gasifier
[2] Duration of the steady state set point

Set point **BFB 0310C** was carried out at a bed temperature of about 870°C and the temperature at the freeboard was 873°C. A 50/50 wt-% mixture of sand and limestone was used as the bed additive. Operation temperature of the filter was 392°C. No problems were seen during this set point and all necessary measurements were carried out (tars, nitrogen compounds, gas analysis) and solid samples were taken.

2.2.3 Gasification results

CARBON CONVERSION AND TAR YIELDS

The average operation conditions and main results of the process measurements at the set point BFB 0310C are presented in Table 8.

Table 8. Results of the process measurements at the set point BFB 0310.

Set point	**BFB 0310C**
T(bed), °C	870
T(freeboard), °C	873
Bed material [1]	50% H+50% P3
Fuel moisture content, m-%	1.9
Fuel feed rate, g/s	27
Primary air, g/s	55.0
Secondary air, g/s	4.8
Steam, g/s	6.1
Air ratio	0.29
Gas flow rate, m^3n/h	285
Dry gas composition, %	
CO	7.4
CO_2	16.3
H_2	9.0
N_2 (+Ar)	59.3
CH_4	5.0
C_2Hy	2.6
C_3-C_5Hy	0.04
NH_3	0.38
H_20 in wet gas, vol %	16.4
Wet product gas LHV, MJ/m3n	5.7
Dry product gas LHV, MJ/m3n	6.9
Tars + benzene, g/m^3n	31.9
Tar yield, g/kg PA daf	89.7
C-conversion, m-%	
to dry gas	85.0
to gas and tars	98.8
to gas and tars [2]	97.5
Carbon losses [3], m-%	1.5
Mass balance closure(out/in)	
C-balance	0.99
O-balance	1.03
Ash balance	1.03

[1] S + P3 = The mixture of sand and Parfil 3 limestone, [2] Including limestone-C in the input carbon, [3] Incl. C in filter dust, heat exchanger dust and bottom ash /Fuel C

The carbon conversion efficiencies were calculated both directly from the gas yields (carbon in gaseous products divided by the input carbon) and indirectly on the basis of carbon loss determined on the basis of mass flows and carbon contents of the solid samples (filter dust, bottom ash heat exchanger dust). The value shows the amount of carbon in dry gas and second in dry gas and tars divided by the input carbon of the fuel. The third conversion efficiency includes also the carbon of $CaCO_3$ in the total carbon input. These different conversion efficiencies are defined in detail in reference [1].

The determined carbon conversion was very high. High conversion is primarily based on high reactivity of SRF and optimised process conditions.

The tar content of the product gas was also determined. The results for benzene and tar content are presented in Table 9

Table 9 Benzene and tar contents of the product gas , mg/m3n (in dry gas) in test run BFB 0310C.

Set point	BFB 0310C
Benzene, g/m^{3}n	18.6
Tars, mg/m^{3}n	13.3

Tar content of product gas was significantly higher than in waste wood derived product gas. This was caused by high plastic content of SRF. It is known that high plastic content of feedstock results usually in high tar loading of product gas. However, filter was operated successfully in stable conditions during the test trial.

COMPOSITION OF SOLID RESIDUES

The main part of the fly ash was removed from filter unit. Typical bulk compositions of different solid streams (filter dust, bottom ash, heat exchanger dust) are presented in Table 10These data show that bottom ash is primarily composed of sand additive and contains no combustible material. Filter dust contained only 10.6 % of carbon, which is very low compared to waste wood derived filter dust. Low carbon content of filter dust was achieved by high reactivity of the feedstock and successful operation of the gasifier. The carbon content of heat exchanger dust was 3.2 wt%.

Table 10 Composition of different ash products.

Set point	BFB 0310C
Filter dust [1], wt% (d.b.)	
C	10.6
H	0.26
N	0.08
O (difference)	4.3
Ash	84.8
Heat exchanger dust, wt% (d.b.)	
C	3.2
H	0.04
N	0.02
O (difference)	4.2
Ash	92.5
Bottom ash, wt %	
Ash	100

[1] dry sample

2.2.4 Conclusions (BFB gasification of SRF)

This BFB gasification test focused on developing and improving the gasification process for waste derived fuel (SRF). The objective was to optimise the BFB

gasification process in order to increase carbon conversion and to reduce the amount of problematic fly ash.

The following conclusions can be made on the basis of BFB 0310 test run with solid recovered fuel:

- Test trial was successful and good material balances could be calculated.
- Operation of the bubbling fluidised bed gasifier was stable and SRF could be gasified successfully.
- Very good carbon conversion was achieved in gasification of SRF at 870°C. The carbon conversion to gas and tars was (about 98 %).
- Optimised operation of the gasifier resulted in low carbon content of filter dust (10.6 wt %).

2.3 CFB GASIFICATION TEST TRIAL 0323

Gasification test trials CFB 0323 were carried out in co-operation with other projects of VTT. Total number of set point periods was 3 and one of these was carried out for Gasash project. Test was focused on improvement of carbon conversion of CFB gasification of waste wood.

2.3.1 Test facility

Test trials were carried out with an atmospheric pressure Circulating Fluidised-Bed (CFB) gasification Process Development Unit (PDU) at VTT Processes. A schematic figure of the test rig is shown in figure 6. The key dimensions and the technical data of the test rig is presented in the Table 11 The test rig is equipped with feedstock hoppers of live-bottom type suitable for low-bulk-density fuels and with lock hopper type of feeder for coal or pellets. In addition, the test rig is equipped with a separate feeder for bed additive. Gasifier has two alternative feeding ports located in the bottom of the reactor and above the dense bed. These tests were carried out using the lower feeding port. The recycling material from the cyclone is introduced close to the distributor.

The gasification air is electrically preheated and can be divided into primary fluidisation air, as well as secondary and tertiary air feeds. Steam can be added to the fluidisation air. Only primary air and steam were used in these tests.

The gasifier reactor tube, the recycling cyclone and the recycling line are electrically heated in order to minimise heat losses, which otherwise would be very high due to the small size of the test rig. The use of electrical heaters together with rather high circulation rates makes it possible to maintain relatively uniform temperature distribution over the whole reactor.

The product gas is cleaned in the recycling cyclone followed by a gas cooler and a hot gas filter. The gas cooler has four independent cooling zones to improve the adjustment of heat exchange/gas cooling. Each of the four cooling zones is equipped with independent steam purging systems to remove dust and other loosely bound impurities/deposits.

Test trial was carried out with a high temperature candle filter unit. The filter consists of ceramic candle elements (calcium silicate fibres). Candles are located in four clusters and each of them is equipped with pulse ejector and pulse cleaning tube. The number of candle elements was 12. The used candles were about 60 mm in diameter and 1000 mm in length. The filter can be operated in a wide temperature range, maximum operation temperature is 800 – 900 ^{o}C.

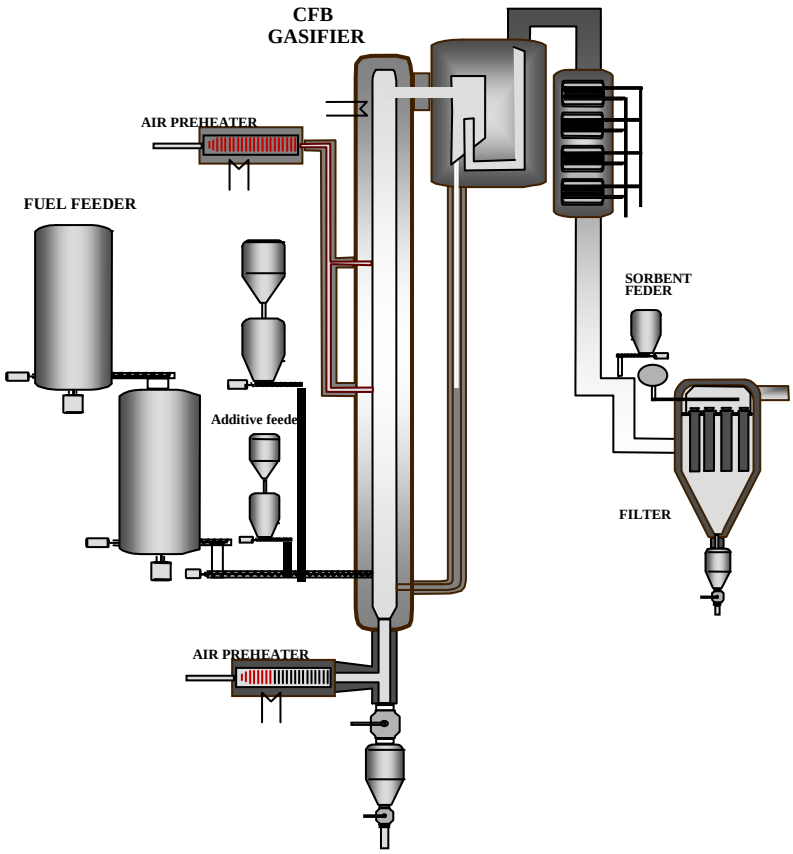


Figure 6. A schematic figure of the Circulating Fluidised-Bed (CFB) gasification test rig of VTT Processes (Process Development Unit, PDU).

The test rig is equipped with an automatic data collection of temperatures and pressures measured at different locations. The flow rates of gasification agents (air, steam, purging nitrogen) are continuously measured and recorded. The main gas constituents CO, H_2, CH_4 and CO_2, and in addition O_2 are monitored by on-line analysers. The contents of main gas components, nitrogen and hydrocarbon components including

C_2H_x - C_5H_y are analysed automatically by process gas chromatography hourly. In addition the analyses of gas components were confirmed by analysing some gas samples by the laboratory GC.

Table 11 Technical data on the CFB gasification test rig of VTT Processes.

Reactor diameter	154 mm
Reactor height	7.9 m
Operation temperature	600 - 1 000°C
Superficial gas flow rate in the reactor	1 - 5 m/s
Operation pressure	1.0 - 1.3 bar (abs)
Maximum fuel feed rate	80 kg/h
Maximum thermal capacity	about 350 kW
Gas cleaning equipment	recycling cyclone, 2nd cyclone (option) ceramic candle filter (12 elements) option: bag filter (max. 16 bags)
Research applications	Gasification, combustion, heat treatment

All mass streams were measured except product gas, which was calculated based on the other mass streams and product gas composition. All solid residues were collected and characterised.

2.3.2 Feedstock

The feedstock in test BFB 0323A was crushed waste wood (Figure 6). Representative samples of the crushed fuel were taken and these were analysed for moisture content, elemental composition as well as for ash composition. The proximate and ultimate analyses of the crushed waste wood fuel are presented in Table 12



Figure 6. Crushed waste wood fuel used in the test trial CFB 0323A.

Table 12 Average composition of feedstock used in gasification test BFB 0323A.

Feedstock	**BFB 0323A**
Set point	100 % waste wood
Moisture content, wt%	18.8
Proximate analysis, wt% (d.b.)	
Volatile matter	81.5
Ash	1.4
Ultimate analysis, wt% (d.b.)	
C	50.0
H	6.1
N	0.3
S	0.03
Cl	0.02
O (as difference)	42.2
LHV (d.b.), MJ/kg	18.8

2.3.3 Experiences from operation (CFB 0323A)

The operation conditions of the test trial carried out with waste wood are presented in Table 13 Test programme could be carried out without major operational problems.

Table 13 Gasification BFB 0323A set point with waste wood.

Set point date	Fuel	Bed material	T_{gasif} [1], °C	Length [2], h
BFB 0323A	waste wood	50 %Sand + 50 % P3 limestone	883 / 887	13.0

[1] Average temperature at bottom/top of the riser
[2] Duration of the steady state set point

Set point **CFB 0323A** was carried out at a temperature of about 885°C. A 50/50 wt-% mixture of sand and limestone was used as the bed material. Operation temperature of the filter was 496°C. No problems were detected during this set point and all necessary measurements were carried out and solid samples were taken.

2.3.4 Gasification results

CARBON CONVERSION AND TAR YIELDS

The average operation conditions and main results of the process measurements at the set point BFB 0310C are presented in Table 14

Table 14 Results of the process measurements at the set point CFB 0323A.

Set point	**BFB 0310C**
T(bottom), °C	883
T(top), °C	887
Bed material [1]	50% H+50% P3
Fuel moisture content, m-%	18.7
Fuel feed rate, g/s	7.6
Primary air, g/s	14.2
Steam, g/s	1.6
Air ratio	0.38
Dry gas composition, %	
CO	9.1
CO_2	17.2
H_2	11.4
N_2 (+Ar)	58.4
CH_4	2.8
C_2Hy	1.1
C_3-C_5Hy	0.002
H_20 in wet gas, vol %	20.6
Wet product gas LHV, MJ/m3n	3.7
Dry product gas LHV, MJ/m3n	4.7
Tars + benzene, g/m^{3}n	9.2
Tar yield, g/kg PA daf	26.1
C-conversion, m-%	
to dry gas	93.3
to gas and tars	98.0
to gas and tars [2]	96.9
Carbon losses [3], m-%	2.4
Mass balance closure(out/in)	
C-balance	0.99
O-balance	1.03
Ash balance	1.03

[1] S + P3 = The mixture of sand and Parfil 3 limestone, [2] Including limestone-C in the input carbon, [3] Incl. C in filter dust and bottom ash /Fuel C

The carbon conversion efficiencies were calculated both directly from the gas yields (carbon in gaseous products divided by the input carbon) and indirectly on the basis of carbon loss determined on the basis of mass flows and carbon contents of the solid samples (filter dust, bottom ash heat exchanger dust). The value shows the amount of carbon in dry gas and second in dry gas and tars divided by the input carbon of the fuel. The third conversion efficiency includes also the carbon of $CaCO_3$ in the total carbon input. These different conversion efficiencies are defined in detail in reference [1].

The determined carbon conversion was high. High conversion was primarily based on relatively high air ratio and optimised process conditions.

The tar content of the product gas was also determined. The results for benzene and tar content are presented in Table 15 Tar content of product gas was very low. This was mainly caused by high air ratio and optimised gasification conditions.

Table 15 Benzene and tar contents of the product gas , mg/m3n (in dry gas) in test run BFB 0323A.

Set point	BFB 0310C
Benzene, g/m^{3}n	6.1
Tars, mg/m^{3}n	3.2

COMPOSITION OF SOLID RESIDUES

The fly ash was removed from filter unit. Bulk compositions of different solid streams (filter dust, bottom ash) are presented in Table 16 These data show that bottom ash is primarily composed of sand additive and contains almost no combustible material. Filter dust contained only 40.9 % of carbon, which is lower compared to carbon content of waste wood derived filter dust from BFB gasification test trial 0250.

Table 16 Composition of different ash products.

Set point	BFB 0323A
Filter dust [1], wt% (d.b.)	
C	40.9
H	0.5
N	0.1
O (difference)	9.9
Ash	48.1
Bottom ash, wt %	
Ash	99.5

[1] dry sample

2.3.5 Conclusions (CFB gasification of waste wood)

This CFB gasification test focused on developing and improving the gasification process for woody biomass. The objective was to optimise the CFB gasification process in order to increase carbon conversion and to reduce the amount of problematic fly ash.

The following conclusions can be made on the basis of CFB 0323A test run with waste wood:

- Operation of the circulating fluidised bed gasifier was stable and waste wood could be gasified successfully. God material balances could be calculated.
- Good carbon conversion was achieved. The carbon conversion to gas and tars was 97 %.
- Carbon content of filter dust was relatively low for wood fuel (40.9 %).

2.4 CONCLUSIONS RELATED TO WP1

Fluidised test gasification test trials carried out in WP1 focused on developing and improving the gasification process for woody biomass and solid recovered fuel (SRF). The objective was to optimise the fluidised bed gasification process in order to increase carbon conversion and to reduce the amount of problematic fly ash. Both circulating fluidised bed and bubbling fluidised bed gasification process were considered.

The following conclusions can be made on the basis of test trials:

- All tests were successful and good material balances could be calculated.
- Operation of the bubbling fluidised bed gasifier with woody biomass was stable and woody fuel could be gasified successfully in the extended test of 90 hours of continuous operation.
- Very good carbon conversions were achieved in BFB gasification of woody fuels at 862-893°C. The carbon conversion to gas and tars were higher than 95 % in all set points and highest carbon conversion was 98.7 %.
- Operation of the bubbling fluidised bed gasifier with solid recovered fuel was stable and SRF could be gasified successfully.
- Very good carbon conversion was achieved in BFB gasification of SRF at 870°C. The carbon conversion to gas and tars was (about 98 %).
- Optimised operation of the gasifier resulted in low carbon content of filter dust (10.6 wt %).
- Operation of the circulating fluidised bed gasifier with woody biomass was stable and waste wood could be gasified successfully.
- Good carbon conversion was achieved. The carbon conversion to gas and tars was 97 %.
- Carbon content of filter dust was relatively low for woody fuel (40.9 %).
- The effects of different compositions of bed materials were studied by carrying out gasification test trials using different mixtures of bed materials. The aim was to optimise carbon conversion, minimise tar formation and minimise volume of harmful fly ash.

3 REFERENCES

1. Kurkela, E., Ståhlberg, P., Laatikainen, J, Pressurized fluidized-bed gasification experiments with wood, peat and coal at VTT in 1991 - 1992. Part 1. Test facilities

and gasification experiments with sawdust, 1993. VTT, Espoo. 55 p. + app. 2 p. (VTT Publications : 161).

2. Kurkela, E., Laatikainen, J., Progress report on CFB gasification tests with wood residues from Värnamo carried out in 1997-98, Confidential project report ENE1/22/98, VTT Energy, Espoo, 17 p. + app. 15 p.

Appendix D Deliverable 15 Identification of the Most Promising Ash Utilisation Options and Ash Treatment Needed

DELIVERABLE REPORT No 15

CONTRACT N° : ENK5-CT-2002-00635
PROJECT N° : NNE5-2001-00598
ACRONYM : GASASH
PROJECT TITLE : Improvement of the economics of biomass/waste gasification by higher carbon conversion and advanced ash management

PROJECT CO-ORDINATOR : VTT Processes
PARTNERS :VTT Processes (VTT)
Foster Wheeler Energia Oy (FWEOY)
Energy Research Centre of the Netherlands (ECN)
Asociación de Investigación y Cooperación Industrial de Andalucía (AICIA)
Pohjolan Voima Oy (PVO)
EMC Environment Engineering Limited (EMC)
Essent Energie Productie b.v. (EEP)

PROJECT START DATE : 1 November 2002 **DURATION : 36 months**

Date of issue of this report : August 2005

Project funded by the European Community under the 'EESD' Programme (1998-2002)

DELIVERABLE REPORT NUMBER 15

CONTRACT No: ENK5-CT-2002-00635
PROJECT No: NNE5- 2001-00598
ACRONYM: GASASH
DELIVERABLE TITLE: "Identification of the most promising ash utilisation options and ash treatment needed"

REPORT ON THE IDENTIFICATION OF THE MOST PROMISING ASH UTILISATION OPTIONS AND ASH TREATMENT NEEDED - (WP-3 Utilisation of Fly Ashes)

1 INTRODUCTION AND SCOPE

1.1 Background of deliverable 15

This report presents the progress of WP3 *Utilisation of Fly Ashes,* identifying the most promising ash utilization options. A summary is made of existing and potential utilisation options, as well as the effects of after-treatment. Contributions from all other project partners (VTT, FWE, PVO (NOVOX), AICIA and EEP) are included. The deliverable is a follow-up of Deliverable 16 *Report on technically potential gasification ash utilization options*. The conclusions will serve as input for the remaining work in WP4 *Techno-economic evaluation of different methods to improve the quality of ashes and to utilize ashes*.

The overall objectives of WP3 are to characterize ash samples from WP1 and WP2, to screen potential options of utilization, material recycling and disposal and to develop new methods for utilization. The objective of Deliverable 15 is to identify the most promising routes from all the information that has been collected on existing and potential utilization options. The identification is based on technical aspects and on compliance to requirements (legal and technical) for the various utilization options. The economic aspects of utilization options are not included - to be done in WP 4 - but it is noted when exceptional economic factors are expected.

The most relevant aspects of gasification fly ashes are that they contain unburned carbon, water soluble components and organic components such as PAHs. In the case of ashes derived from waste gasification most often also chlorides and heavy metals are found in large quantities. These compounds may prevent the use of these materials in most large-scale applications unless the ashes are treated prior to utilisation.

Generally, it can be stated that high-grade applications are economically more attractive routes than low-grade applications. However, if the ashes need treatment for quality improvement to fit into the high-grade applications, the situation becomes more complex. Also, in low-grade applications the margins are small and logistic costs (storage, transportation) can make the difference whether a certain route is viable in practice or

not. Also, small ash streams are difficult to divert to other utilisation options than landfill. There should be a production of at least 1000 tonnes annually, unless a very specific and highly profitable application is possible.

One of the foremost conclusions of the GASASH project is, that fly ashes from gasification of biomass and waste are very diverse in composition and behaviour, resulting from the large variety in fuels and of specific operational parameters, such as limestone addition in the gasification process. The large diversity in fly ashes makes it impossible to identify most promising utilization options that apply to *all* fly ashes. Each kind of fly ash will have its own optimal utilization option. Therefore, this report is set up as an algorithm where the main kinds of fly ashes used in the GASASH project are taken as examples and checked for suitability for options with a decreasing rank.

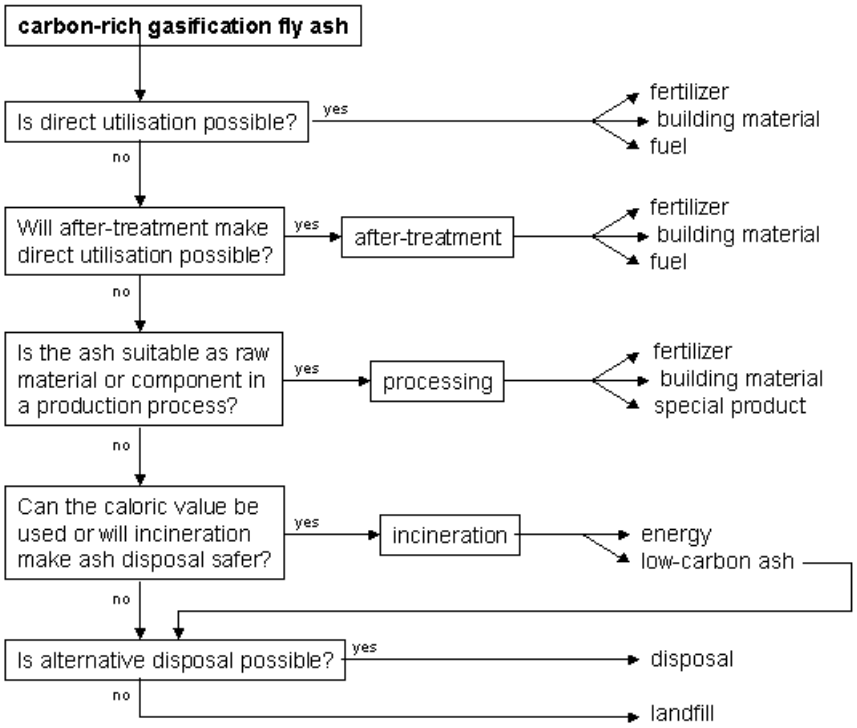


Figure 1 General algorithm for determining the best utilization option for gasification ashes

1.2 High grade applications versus low grade applications

The European Commission initially set out its Community-wide waste policy in the Community Strategy for Waste Management of 1989 (SEC(89) 934 Final 1989). This document forms the cornerstone of European waste policy. As well as many detailed measures, the strategy contains the following points:

- The establishment of a hierarchy of waste management. This prioritises the prevention of waste then its reuse and recycling and lastly the optimisation of its final disposal through, for example, energy recovery (Figure 1).
- Confirmation of the 'Proximity Principle'. This requires that waste is dealt with as near as possible to its source.

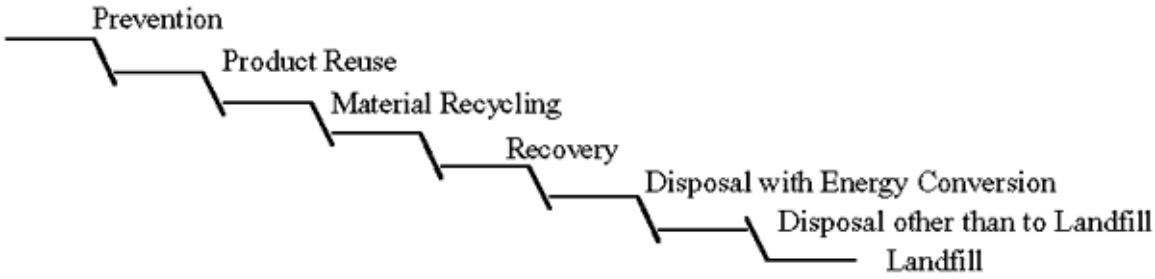


Figure 2 Preferences for Waste Treatment

The concept behind this Strategy for Waste Management is that when a product is discarded (e.g. a PET-bottle), the most sustainable route would be to reuse the product, preferably in the same way it was originally intended (as a bottle). When it is not possible to do so, alternative re-utilisation options are sought. When complete product reuse is not possible, material recycling (partial recycling) and recycling and recovery (e.g. meltdown the bottle and produce a new bottle) is the next preferred step. Next comes disposal with energy recovery (e.g. MSWI), followed by alternative disposal and landfill.

The utilization options for biomass ashes can be ranked based on this waste management concept. Applying the concept to gasification ashes is, however, not as straightforward as it seems.

Utilisation options for gasification ashes can be divided into at least 6 categories with an hierarchy in ranking (based on the waste management concept) as follows:

- direct application/utilisation of the material without treatment
- direct application/utilisation of the material with pre-treatment[1]
- use as a raw material/utilisation as component without prior treatment
- use as a raw material/utilisation as component with prior treatment
- disposal with energy recovery
- alternative disposal (other than landfill)

It can be argued that the application as dedicated fuel of gasification ash with a high calorific value is not the same as disposal with energy recovery, but is in fact a higher-grade application. This can be supported by the fact that the aim to use gasification ash as an alternative fuel is not driven by the need of disposal, but by the need to replace fossil fuels. The waste stream is being used in the same way as the original intention of the biomass before gasification: energy production. This concept is supported by the Commission, because subsequent to the Treaty on European Union entering into force in 1993 (establishing the European Union), a revised version of the EU waste strategy was

[1] Putting "direct application/utilization of material with pre-treatment" above "use as a raw material/utilization as component without prior treatment" is open for discussion.

adopted by the Commission in July 1996. The 1996 strategy has added the following points:

- Energy recovery may in some cases be environmentally superior to recycling within the hierarchy.
- The EU will investigate possible actions on incineration and the implications of using waste as a fuel at installations not originally designed for this.
- The Commission will introduce targets to substantially reduce the amount of waste generated and to generally achieve high waste recovery objectives.

In practice; policy instruments have been developed to divert waste streams with a high calorific value from landfill to energy recovery or other uses. The Directive's requirement for the progressive reduction of biological waste would also progressively exclude such high calorific material. More Member States have developed instruments discourage the landfill of biological degradable waste and promote recycling above energy recovery (box 1). The current policy in The Netherlands is to discourage the landfill of high calorific waste. In the UK there are no regulations that refer specifically to high calorific value waste, but the requirements of landfill acceptance criteria set limits to the (organic) carbon content of materials for disposal

Box 1 *Overview of instruments to divert the landfill of biodegradable waste and encourage recycling rather than energy recovery (year 2000)*[2].

- Denmark – landfill tax is currently set at €50. Landfill of MSW is banned, however in practice bulky waste still goes to landfill
- Netherlands – landfill tax is set at Dfl 144.21 (€ 65.44) per tonne for waste less than 1,100kg/m3 for specific waste streams, and Dfl 27.78 (€ 12.61)per tonne for non municipal waste more than 1,100kg/m3 (non combustible). Landfill of MSW is banned although where there is insufficient incineration capacity there is an annual exemption from the ban of 3 million tonnes.
- Ireland - £15 per tonne (€ 19)
- Sweden – SEK 290 (€ 31.34) per tonne from 2002
- France – the 1999 landfill tax rate was 60 FF FF (€ 9.15). It is the intention that landfill of unprocessed waste would be banned from landfill by 2002
- Switzerland – introduced a tax in 2001
- Austria – for MSW the tax is €43.6 per tonne, and MSW can only be landfilled if it has been pre-treated through MBT in such a way as a) certain EMISSION limit values are adhered to and b) the landfilled fraction has respirometric index below a certain level and c) the volatile organic solids content is less than 5%. also, calorific value has to below 6mj/kg).

source: http://www.number-10.gov.uk/su/waste/report/downloads/ai.pdf

The calorific value of the gasification fly ashes studied within the scope of GASASH range from 14 to 25 MJ/kg. These values are comparable to the heating values of peat and wood, despite the high ash content. Loss-on-ignition (LOI), mainly carbon, ranges from 7 to 60 wt%. This implies that energy recovery is preferred over land filling. All efforts are directed towards useful utilization options, including utilization as an

[2] An update of these numbers will be part of the final report. Gate fees continually increase and will make any form of utilization more attractive. The level of gate fees does not influence the potential of utilization routes compared to each other and has not influenced the identification of certain utilization options as "most promising".

alternative fuel. In the following review, it is examined of the main ashes studied within the GASASH project to what extent they fit into identified routes, starting with the higher-grade applications.

2 Identification of potential routes

2.1 Direct application/utilization of gasification ash

The routes that have been examined for direct application is are:

- direct application as a fertiliser / soil improver
- direct application as a construction material (replacement of sand in landscaping projects / road construction)
- direct application as a fuel

Agricultural application

With regard to agricultural applications, a difference can be made between fertilisers and soil improvers. Generally, fertilisers provide useful macronutrients (NPK) and in some cases Ca, Mg, Na and SO_4. Soil improvers are used to increase the buffer capacity of soils, usually by addition of lime or to increase the cation exchange capacity and water storing capacity of the soil by adding (organic) carbon.

Of the useful macronutrients (N,P,K) N is not available in gasification ash, and the total content of P and K is relatively low. For K_2O the total content ranges from 0.5 to 11 % w/w. Generally, for potassium fertilizers these values should be about 30 or 40%. For phosphorous (P_2O_5) the total contents of the gasification ashes range from 0.5 to 17 % w/w. Ash from wood has a few percent and from SRF/RDF typically 0.4-0.6 wt% P_2O_5 and on top of that phosphorous in ash is usually not readily soluble. In contrast, MBM ashes are relatively rich in phosphorous (about 50% P_2O_5), but P-solubility of the MBM ashes has not been established.

The calcium content of some of the gasification ashes (generally those that are derived from a process of gasification using dolomite / CaO in the process) are relatively high. CaO contents range from 7 to 40 % w/w. The CaO content of some of the ashes (VTT's waste wood and SRF, FWE's RDF and AICIA's MBM) is high enough to be interesting as a soil improver (liming agent)

In nearly European Member States, the application of fertilisers and soil improvers is restricted with respect to the maximum allowed addition of contaminants to the soil. The members of the European Community have varying levels of restrictions on the use of sludge as a soil amendment (Disposal and recycling routes for sewage sludge. European Commission, http://europa.eu.int/comm/environment/waste/sludge/sludge_disposal.htm). The 1986 Directive (EEC, 1986) included restrictions on the metals content of the sludge, each Member State setting their own limit values (Table 1). These limit values for sewage sludge are often used as a reference for other materials as well.

When applying the stricter Dutch limit values it is found that none of the gasification ashes comply, whereas according to Spanish limitations, the Orujillo ashes meet the

limitations for sludge. The most critical components for application as a fertilizer in clean biomass ashes is Cd, closely followed by As, Cu, Zn. For the ash derived from waste streams the critical components depend on the specific origin of the fuel. E.g., in the case of demolition wood, the most critical element is Pb. The Cr and Ni contents analysed in the ashes produced at laboratory conditions can be artificially increased due to wear of reactor walls or the feeding screws.

Table 1 Examples of differences between Member States in limit values for the application of sludges or other organic fertilisers.

Element	Agricultural application in the Netherlands	Agricultural application in Spain		Maximum allowed dosage in NL (g/ha/yr)	Maximum allowed dosage in Spain (g/ha/yr))
		acid soils (pH<7)	basic soils (pH<7)		
Cd	1.25	20	40	2.5	150
Cr	75	1000	1500	150	3000
Cu	75	1200	1750	150	12000
Hg	0.75	16	25	1.5	100
Ni	30	300	400	60	3000
Pb	100	750	1200	200	15000
Zn	300	2500	4000	600	30000
As	15	-	-	30	-

source: "BOOM 30 januari 1998- Besluit Overige Organische Meststoffen." and "REAL DECRETO 1310/1990, DE 29 DE OCTUBRE - MINISTERIO DE AGRICULTURA, PESCA Y ALIMENTACION."

In general, the feasibility of application of ash as a fertiliser is influenced by local conditions, but in a wider perspective it can be can concluded that none of the ashes used in the GASASH project have a great potential to be applied *directly* as fertilizer. This is caused by the generally low nutritional value of *available* nutrients compared to the relatively high content of contaminants. Exceptions are possible for specific fuels, but in general direct application as fertilizer cannot be regarded as one of the most promising options for utilization.

Construction products

Similarly, each Member State of the EU has its own regulations concerning the application of secondary materials[3] in landscaping and road construction. However, a harmonized European Construction Products Directive (CPD) is being developed. This directive will be based on much of the same principles as the current Dutch Building Materials Decree, in which leaching of contaminants and long-term impact is guiding in the risk assessment for the application of construction products.

In the Netherlands the application of waste streams (limited to stony material or soil-like material) in landscaping / road construction is regulated by maximum allowed leaching of contaminants. Within this document (and much of the GASASH project) the Dutch Building Materials Decree (DBMD) is used as a reference, but it was tried to minimise the bias and leave room for regulations from other member countries.

From the leaching data available in the GASASH project it can be concluded that, none of the ashes comply with the Dutch Building Materials Decree, neither in category 1

[3] In this document secondary materials are materials from other sources than primary sources. Secondary does not imply that the material is of a lower quality.

(unlimited use) nor in category 2 (shielded use) applications. Critical components that hamper utilisation of gasification ashes in construction works have been identified and summarised in Table 2.

Table 2 Identified critical elements (in bold) in gasification ash and oxidised gasification ash limiting direct application in construction works. Between brackets the elements of concern and limiting cat 1 application

	Fuel type	Critical elements in gasification ash	Critical elements in oxidised gasification ash
EEP	demolition wood	**Pb, Cl** (Sb, Ba, Zn, Br)	**Cr, Mo, Br, Cl** (Sb, Se Pb, SO_4)
VTT	waste wood (untreated)	**Cd, Br, Cl** (Sb)	**Pb, Cl, Br** (Ba, Se)
	SRF	**Cd, Br, Cl** (Sb, Se, Mo)	**Cr, Cl, Br** (Mo, Ba, Sb)
AICIA[4]	Orujillo	**Cd** (Ba, Ni, V), *non measured constituents*	?
	MBM	**Cd Ni** (Ba) *non measured constituents*	?
FW	100% RDF Lahti	**Cl**, (Sb, Se, Ba)	**Sb, Ba, Se, Cl** (Mo)

The conclusion is that fly ashes used in the GASASH project cannot be *directly* used as building material, mainly due to high leaching of contaminants. Such direct utilization routes are often available for bottom ashes from fluidised bed combustion, because these are largely composed of sand or other inert material.

Direct application as a fuel
The application of gasification ash as an alternative fuel is considered as a direct application. This is based on the fact that:

- Utilisation of biomass gasification ashes as an alternative fuel is in line with the original concept of what the product (the biomass) was intended for.
- The ashes are technically suitable to be used as fuel.
- The oxidation/combustion may take place in the vicinity of the location where the fly ash was produced.

Out of the ashes that have been assessed within the project, some have a high enough carbon content and heating value to allow them as replacement of primary fuels. The application of gasification ash as an alternative fuel can be on-site combustion/oxidation, as a replacement of powder coal or as part of a fuel/waste mix (e.g. in cement kilns or smelters). Integrated oxidation has the advantage that no separate flue gas treatment is needed. This also applies to utilisation in separate installations that already have a sufficient flue gas treatment system before alternative fuels were introduced.

Utilisation as an alternative fuel is one of the most promising routes for gasification ashes with high heating values and carbon contents above 35 wt. Ideally, this will be done at the plant or in the direct neighbourhood of the plant. Limitations will be emissions and

[4] AICIA's analyses were initially not aimed at testing for compliancy to the DBMD. Updated analyses will become available in the final report . At the moment, ashes can be assessed on limited measurements. It is expected that Orujillo and MBM ashes will also have several elements that will prevent direct utilisation as building material.

end of pipe fly ash quality if this fly ash has an established utilization that requires a certain quality (e.g. in cement production).

When utilising gasification ash as a fuel (rather than regarding combustion as a form of after-treatment or waste incineration), the question what to do with the ashes is the responsibility of the buyer of the fuel and has to be incorporated in the value of the ashes. In general, it can be stated that the fuel should be applied in such a way that the specifications of the product where the ash components go (cement, coal fly ash) should not exceed limits, thus limiting the quantities that can be used.

2.2 Direct application of gasification ash after treatment or quality improvement

Quality improvement of the gasification ash will have to concentrate on the elimination or reduction of critical components. Which component is critical differs for various combinations of fly ash and application (fertilizer, construction product or fuel). The critical components in fertilizers are based on total concentration. Hence, the only way to improve ash quality to fit in this route is to reduce total amounts of contaminants, which is not easily done and utilisation as fertilizer after treatment is not a likely route.

In applications that are regulated by leaching limits (application in landscaping / road base, or construction products and land filling), there are more possibilities to reduce leached amounts of contaminants. Leaching of contaminants can be reduced by washing the ash (and so remove highly soluble critical components) or they can be made less easier to leach by manipulating the pH, e.g. by converting oxides into carbonates. Controlling the pH of ashes can reduce leaching of heavy metals that generally show pH dependent release (e.g. Zn, Pb). At high pH, heavy metals are mobile, lowering the pH (to around pH 9-10) decreases solubility. After treatments can be different for the various ashes (even combinations of after-treatment techniques are conceivable).

Work done by PVO and VTT showed the technical feasibility of washing gasification fly ash and removing large fractions of salt. A reduction of about 75 % of the chlorine content of high carbon/high chloride SRF fly ash was achieved at the tests carried out by PVO and VTT. The tests were done in pilot scale using fly ash from gasification of SRF originating from domestic waste. The Cl-content of the this type of ash varies typically in the area of 4 – 10 % which largely restricts it's utilisation possibilities. The leaching of other components than the most soluble chlorides was low when L/S = 3 in cascade arrangement was used. Washing of the SRF fly ash does not in practice alter the carbon content of the ash. According to the work done by VTT and PVO, washing would be a feasible component in a total treatment route for SRF ash utilisation if it is combined with thermal removal of carbon and carbon compounds.

Work done at ECN reaches the same conclusion. Washing could be applied to gasification ash from the AMER-CFB. A key factor in washing is pH control to suppress dissolution of heavy metals into the washing liquid. It appears to be technically feasible to wash/neutralise the ash to improve the chemical quality of the residue so that it complies with the DBMD category 2 applications (usage shielded from water). What

remains is the question whether the physical characteristics of the material are acceptable and comply with regulations regarding health issues when handling the ash.

Depending on the foreseen utilization route for oxidized ashes the gasification ashes can receive treatment prior to oxidation. Specifically, critical elements that cause problems in too high leaching values or even influence performance of oxidizers (e.g. corrosion due to high chlorine contents) can be reduced. Washing the gasification ashes prior to thermal treatment or energy recovery can provide an opportunity. Washing the ashes can remove soluble compounds like Cl and Br that are problematic elements in all oxidized ashes (table 2). Also, at very high pH, Cd is very soluble and can be removed with the wash water. ECN has used leached concentrations of contaminants measured at various liquid to solid ratios (L/S) to estimate the achievable quality improvement. Complete data sets are available for only for VTT's and EEP's gasification ashes.

Calculations by ECN and pilot-scale experimental work shows that washing removes about 70-90% of the total Cl content. Also fractions of the total bromide and sulphates together with alkali's and oxy-anions are removed with the wash water. The leaching of chlorine, bromide and cadmium of VTT's wood ashes can be reduced sufficiently by washing at L/S = 1 to comply to the DBMD. The treatment reduces leached concentrations of Br by an estimated 75%, of Cl by 85% and of Cd by 95%. Sb leaching remains critical in utilization as construction product. VTT's SRF ashes contain such high amounts of chlorine, bromide and fluoride that washing at L/S = 1 does not provide the required quality improvement. Increasing the L/S to 2 does is expected to remove sufficient Cl, however, to remove bromide to acceptable levels, the expected needed LS is close to 5, which is not realistic in an industrial process.

The washed gasification ash could be used in direct utilisation routes as construction products. A combined washing/neutralisation step can improve the quality of the material that it complies to category 2 applications in the DBMD, but the barium leaching remains critical in the case of gasification of demolition wood.

Table 3 Improvement of environmental quality by washing of gasification ashes

	Fuel type	After treatment	Technically possible application	Threats
EEP	demolition wood	Washing (salt removal) and combined pH neutrilization to pH 9-10	Construction product that complies to required environmental quality DBMD cat 2	Physical characteristics (fly ash handling), high carbon content, high storage volume, bad fluidity
VTT	waste wood (untreated)	Washing at L/S 1 removes high percentage of Cd, Cl and Br	Construction product that complies to required environmental quality of DBMD cat 2, but Sb remains critical	Physical characteristics (fly ash handling), high carbon content, high storage volume, bad fluidity.
PVO/ VTT	SRF originating from domestic waste	Washing at L/S 3	Low chloride, high carbon ash for utilisation as fuel	Variation of the SRF fly ash quality.

High-temperature treatment and vitrification
High-temperature treatment (to the level that it can be called vitrification), performed at ECN on EEP's high-carbon fly ash from gasification of demolition wood, has been demonstrated to convert biomass ashes into synthetic basalt that complies with the limits of category 1 building material of the DBMD (unlimited use). Typically, when the temperature exceeds 1100°C, the material is sintering en problem elements (Cl, K, Pb, Zn) have been evaporated or are encapsulated into the bulk. The remaining ash is free of carbon and can be cast into molds or broken into granulate.

Technically, vitrification processes offer one of the most promising options for the utilization of gasification ashes from biomass, but the economics are unfavourable. Partly because of the high energy consumption, partly because of the flue gas treatment needed. Vitrification is possible for all kinds of ashes (from gasification and combustion) but best suited for ashes with high carbon content, which deliver most of the energy needed in the process. Other ways to improve the situation is to make combinations with disposal of other hazardous waste with very high gate fees.

2.3 Re-use of gasification ash as a raw material without prior treatment

Filler in asphalt or asphalt like materials (C-fix)
A promising route is to use the gasification ash in asphalt or asphalt-like products (like C-fix). The application of MSWI fly ash in asphalt is an established route in The Netherlands. It is reasonable to assume that gasification fly ash can follow the same route as MSWI fly ash. The chemical composition or content of Cl is not limiting (Cl is abundantly present in MSWI fly ash) but physical characteristics, like size fraction, flowability are more important.

High carbon gasification fly ashes have been tested successfully as fine filler (7% w/w) in C-fix, a material with properties between asphalt and concrete. The test blocks showed sufficiently high flexural and compressive strength. The carbon-rich ash performed better than the combustion fly ashes. Gasification ashes that qualify to be used as a filler material in asphalt or asphalt-like products must show certain physical characteristics. The size fraction should be < 63 μm, the ash should preferably show low LOI (exceptions possible). Depending on local conditions, competition with other materials and logistics, it is possible that some of the gasification ashes (e.g., wood ash, Orujillo ash) and possibly also the oxidized gasification ashes can be used as filler materials in asphalt or asphalt-like products. In contrast too most other forms of utilisation as filler, low puzzolanic properties are not a problem.

Lightweight aggregates
Carbon-containing ashes from gasification of biomass or waste can be used in the production of (lightweight) aggregates in a similar way as powder coal fly ashes are used for over 30 years. Among the various methods for producing aggregates, there are basically two processes to produce lightweight aggregates: a cold bonded process (e.g., Aardelite/Eurolite) and hot sintering process (e.g., Lytag process). The Aardelite technology is based on the puzzolanic properties of the residue to be treated. By adding a binder, for example lime, the silica and alumina in the residue are transformed into

cementitious minerals. This transformation takes place at a temperature of 90° C. The cementitious minerals form a matrix in which potential toxic trace elements like heavy metals are encapsulated. The Lytag process is based on granulating and sintering at 1300 °C. Surface area is strongly reduced and potentially toxic elements are bound into the sintered material. In the process both the inorganic fraction of the ash and the caloric value of the carbon fraction are used. Both lightweight aggregates can be used to replace natural gravel in (lightweight) concrete and other applications.

The use of (blends of) gasification ashes is specific per plant. In both kinds of processes, consistency in composition is the most equally important as the chemical/physical composition of the material. In the hot process, carbon content is a key parameter and should be well controlled in ranges 5-10 wt%. This is lower than most gasification ashes, but blending of low-ash material may remedy the situation.

In general, in cold processes the puzzolanic properties determine whether they are suitable; in hot processes, the carbon content is critical. Both properties vary strongly for several kinds of biomass ash and the suitability depends on individual case. Since the aggragates are used as (component in) building material, the criteria for the construction process (mechanical and environmental) determine ultimately whether acceptable light weight aggregates can be made from biomass ashes. It is possible that many gasification ashes (and ashes after oxidation) in the GASASH project are suitable and production of lightweight aggregate production can be identified as one of the most promising utilisation options.

Solidification/ Stabilization of hazardous waste
Since gasification ashes can have puzzolanic properties, the ashes can be used to replace cement or cement-like products in waste stabilization. Some ashes used in the GASASH project have shown (unquantified) puzzolanic properties and can be useful. Currently, fly ash from combustion of clean wood is used in a similar application in the Netherlands (stabilisation of hazardous waste for landfill). In particular the ashes with a high Ca-content and a low carbon content are promising. AICIA's reports that Orujillo ashes have good mechanical properties and are susceptible to be used as partial replacement for cement, and that other ashes (SRF and wood waste) have shown good leaching properties, but display poor mechanical properties. ECN found that high-carbon fly ash from EEP's AMER gasifier shows no sign of puzzolanic activity..

Solidification/stabilisation appear to be more attractive for ashes from combustion than from gasification. Leaching characteristics of heavy metals are unclear and probably depend on the pH of the final product. Although potentially promising, more research is needed before this route can be identified as one of the "most promising utilisation options"[5].

Fireproof plates
Ashes can be used as a component in the low-cost manufacture of fireproof plates. The functionality is based on water release when exposed to fire and thus keeping the

[5] For solidification/stabilization no separate criteria are available. Landfill criteria have been adopted.

temperature at 100°C for a certain amount of time. In particular chemically bound water as in gypsum is useful. Ashes with a high carbon content are less likely to be suitable, while ashes from combustion appear to be more appropriate choices. AICIA's results show that Orujillo ashes are acceptable and can be used without previous treatment. The unburned content is not a good property but also not a problem with respect to the objective: to retain water. Other ashes need more research.

Table 4 Improvement of environmental quality of gasification ashes

Raw material for	Ashes		Threats
Aspalt and asphalt-like materials (filler)	EEP VTT AICIA	wood ash wood ash Orijullo ash	fluidity, content of salts (Cl, Br, SO_4), content, PAH's*.
Lightweight aggregates	all		heavy metals, high carbon content
S/S hazardous waste	AICIA	Orujillo (?)	carbon content, pH control
Fireproof plates	AICIA	Orujillo	mechanical properties, unburnt carbon content

* data on PAHs are not complete, but given the nature of the product it is unlikely that PAHs will become problem components.

2.4 Re-use of gasification ash as a raw material with prior treatment

Filler/ binder in concrete and cement mortars

The use of gasification fly ash as a filler or binder in concrete (and hence as a replacement of raw materials) is only possible after reduction of the carbon content, and after obtaining physical properties that resemble powder coal fly ash. The environmental quality (concerning the amount of contaminants in heavy metals) is based on the characteristics of the end product and not of its components. Optimisation of recipes can compensate for many risks. The blending of secondary materials is specific and dependent on many local factors. Guaranteeing a constant and predictable composition and the physical properties (loss on ignition, size fraction < 63 μm, water demand, hollow spaces, etc.) is of greater concern for successful application in cement making. Actually, consistency of the raw products is of the utmost importance for any kind of bulk processing manufacturing process. All ashes regarded in the GASASH project have too high carbon contents to be interesting for this route. However, after thermal treatment the carbon content is lowered, so that use in a concrete mortars becomes a more viable solution.

Provided that a gasification fly ash with very low carbon content is produced, then possible restrictions in this route are the high SO_4 and Cl contents of the ash after combustion. The 100% combusted (oxidized) gasification ash itself does not comply to required properties, but can be made part of a blend, whose quality depends on the application of the concrete (high grade, low grade).

Burning off the carbon from gasification ashes may improve their potential, in particular applications where ashes with a low heating values (low carbon contents) but with good puzzolane properties may benefit. E.g., those ashes that have a high Ca content, either by

themselves or due to the use of lime or dolomite in the gasification or combustion process. Possible utilization options are that to replace cement as a binder in mortars or in other cement based applications (i.e. solidification/stabilization of hazardous waste and fire proof plates, see previous section) or in the production of lightweight aggregates.

2.5 Energy recovery from gasification ash

All other explored routes in the GASASH project can be regarded as energy recovery. This application is comparable to waste incineration. The utilization of gasification ash as replacement of powder coal, the utilization of gasification in cement kilns and the utilization of ash in smelt products are all covered here.

3 CONCLUSIONS

Based on the available data, the following utilisation options may be regarded as the most promising routes for the carbon-rich fly ashes that have been investigated with the GASASH project:

- Direct application as an alternative fuel
- Filler in asphalt or asphalt-like products
- (Lightweight) aggregates
- Filler/binder in concrete mortars after low temperature treatment (combustion)
- High temperature treatment for the production of category 1 building material

Potentially promising utilisation options are

- Solidification/stabilisation of waste
- Component in manufacture of fire proof plates

Some form of after-treatments may be found attractive. Always the (economic) advantages and disadvantages of after-treatment must be balanced against direct utilisation. The most promising forms of after-treatment are

- Washing to remove chloride (and alkali)
- Heat-treatment to lower carbon-content

It should be noted that these routes are not "most promising" for all ashes and all fuels, but generalised suggestions based on the technical potential of the routes. The following issues should always be included the discussion:

- Different routes are the optimal alternative for different fuels, depending on specific characteristics of the ashes.
- Routes become more or less attractive, depending on local conditions. In particular gate fees and emission regulations for combustion.
- Lucky matches may always be found outside the presented selections, e.g., gasification ash from chicken litter utilised in manufacture of fertilizer.

Appendix E Deliverable 16 Report on Technically Potential Gasification Ash Utilisation Options

DELIVERABLE REPORT NO 16

CONTRACT N° : ENK5-CT-2002-00635
PROJECT N° : NNE5-2001-00598
ACRONYM : GASASH
PROJECT TITLE : Improvement of the economics of biomass/waste gasification by higher carbon conversion and advanced ash management

PROJECT CO-ORDINATOR : VTT Processes
PARTNERS : VTT Processes (VTT)
Foster Wheeler Energia Oy (FWEOY)
Energy Research Centre of the Netherlands (ECN)
Asociación de Investigación y Cooperación Industrial de Andalucía (AICIA)
Pohjolan Voima Oy (PVO)
EMC Environment Engineering Limited (EMC)
Essent Energie Productie b.v. (EEP)

PROJECT START DATE: 1 November 2003 **DURATION: 36 Months**

Date of issue of this report : April 2005

Project funded by the European Community under the 'EESD' Programme (1998-2002)

DELIVERABLE REPORT NUMBER 16

CONTRACT No: ENK5-CT-2002-00635
PROJECT No: NNE5-2001-00598
ACRONYM: GASASH
DELIVERABLE TITLE: REPORT ON TECHNICALLY POTENTIAL GASIFICATION ASH UTILISATION OPTIONS

REPORT ON TECHNICALLY POTENTIAL GASIFICATION ASH UTILISATION OPTIONS

1. INTRODUCTION

The most remarkable aspects on gasification fly ashes is that they contain unburned carbon, water soluble components and organic components such as PAH's. In the case of ashes derived from waste gasification most often also chlorides and heavy metals are found. These compounds prevent the use of these materials in most large scale applications unless the ashes are treated prior utilisation. Practical measures cannot easily reduce the carbon content of biomass/waste derived gasification ash to a level where the ash can directly be used in applications similar for coal fly ash. Fluidised bed gasification of waste derived fuels in optimised gasification conditions may produce fly ash with as low as 5-20 % of carbon. However, this low carbon content does not solve ash disposal problem because typical waste derived fuels contain chlorine and hazardous metals, which are enriched in fly ash. Therefore, careful studies of the screened methods for these ashes provide technical and realistic utilisation options.

This report presents the preliminary results found after screening of present combustion (and gasification) fly ash utilisation methods. Up to now, most of the ash utilisation options have been evaluated. The characterisation of ashes has permitted to screen and preliminary tested different utilisation methods for these ashes. Furthermore, new concept of utilisation and ash treatment options are being assessed.

While the work developed within the GASASH project has allowed us to broaden the know-how of specific utilisation routes for gasification ashes from technical point of view, the final results of the project are far apart from the economical point of view. This deliverable describes the main conclusions related to potential ash utilisations options. It completes the information reported at month 18 in Deliverable 24 where the existing (combustion) utilisation options were screened and assessed. In addition, deliverable 15 at month 34 will complete the whole concept by incorporating the identification of the most promising ash utilisation options and ash treatments needed.

This report contemplates those applications that seem more appropriate to be developed from the gasification ashes studied in this project. Clearly it is not possible to develop general methods suitable for all ash types, since the ash characteristics are quite different depending on the type of biomass/waste gasified. Thus the utilization routes cannot be expected to be the same for a clean biomass than for urban waste, which usually gives much higher concentration of chlorine and heavy metals. This point makes the problem somewhat complex.

At this moment the project is focussed on fly ashes since bottom ashes have much similarities with those from combustion, which are better known. This type of ashes has widely found utilisation in construction materials and thus, gasification bottom ashes could be utilised in similar ways than biomass or waste combustion ashes. This could mean in practice mineral substitution in construction. Also in this project material recovery has also been technically studied and the final option should be assessed within the frame of WP4.

2. CLASSIFICATION OF TECHNICALLY POTENTIAL GASIFICATION ASH UTILISATION OPTIONS

Three main utilisation categories have been identified for the gasification ashes derived from biomass/waste: Use as fuel, use in construction material and use in agriculture. Obviously, there are a few different routes included in each group and in some cases with notorious differences. However, the use of these three main concepts allows us to compare and assess different routes within a suitable common frame. Bellow we split each category into different routes and in the next paragraph we discussed in some detail each option.

1. Use as fuel.
   1.1. Co-firing in coal/biomass-fired power plants
   1.2. Firing in a dedicated boiler
   1.3. Replacement fuel in smelters/incinerators (best option for highly polluted fly ash)
   1.4. Firing in cement kiln
   1.5. Reshaping into a fuel.

2. Use in construction
   2.1. Filler in asphalt (CFix)
   2.2. Additives in concrete manufacturing
   2.3. Bulk construction / Raw building material
   2.4. Light-weight Bricks
   2.5. Fire-proof material
   2.6. Stabilisation/Solidification

3. Use in agriculture:

Use in agriculture:
Further, although landfilling could be considered as an alternative to an utilisation option, this project is aimed at searching for more promising routes and thus, landfilling is just considered to be included as a backup method.

3. USE AS FUEL

The high-C fly ash has in theory enough caloric value to be combusted at high-temperature without supplemental fuel. Therefore, untreated fly ashes could be used as fuel in suitable boilers if the carbon content is high enough, which is often the case. There are many ways to use it as fuel, including lime kiln, co-firing in coal powered plants, co-firing in waste incinerators, industrial furnaces and other. The technical and economical potentials of each "use as fuel" vary widely. The likelihood for utilisation depends on the composition of the high-C fly ash.

3.1 Co-firing in existing biomass or coal fired boilers

In a coal power plant it is possible and will affect the quality of the fly ash. There are some restrictions for the amount of ashes that can be used in coal-fired plants. For instance, in the Netherlands, its use is limited by the certification of the fly ash.

This option seems to be a plausible when heavy metal contents are low. Also, in existing facilities firing biomass it is possible to re-use these high carbon-content ashes without any previous treatment. For example, in Andalusia there are some plants firing orujillo. It is best possible to think of firing orujillo ashes within these plants.

3.2. Firing in a dedicated boiler

Firing in a dedicated boiler is theoretically possible. However, the success of this route will depend on the flue-gas cleaning and the corrosion problems in the boiler, not the ash quality. These aspects are currently being further investigated.

3.3. Firing in a smelter

The best chance is to use it as a supplemental fuel in metallurgical smelters.

3.4. Fuel in cement kilns

This route (fuel in cement kilns) significantly differs from the other fuel applications since it allows a material valorisation in addition of the energetic one. In principle, this is a good option when Cl and S are low, or even after a pre-washing treatment.

The manufacture of cement is an energy intensive process and energy demand can account for between 30% and 40% of the production cost. Substitute fuels have been explored by the cement industry, including tyres, waste paper, waste oils, waste wood, paper sludge, sewage sludge, plastics and spent solvents. Therefore, biomass gasification ash would naturally be competing with other low grade fuels. On the other hand, there are often some restrictions with respect to the maximum amounts that can be used that are closely related with the type of biomass/waste.

For example, in Andalusia, Spain, there is an agreement between the some regional regulators (i.e. Junta de Andalusia) and the cement makers, which establishes a minimum heating value of the supporting fuel of about 6 MJ/kg. This agreement also regulates the maximum fuel flow rate which is allowed to burn, as well as some restriction with regard the limits of chlorine, fluorine and heavy metals. Thus, in this application fly ashes with carbon content above about 15-25 % could fulfil this restriction. AMER-CFB fly ashes, for instance, has a caloric value of about 25 MJ/kg, which is well above the required 6 MJ/kg. In principle, the ashes coming from gasification of biomass could preferably be processed at the high temperature zone (camera) situated in the rotary kiln. This allows an energetic as well as material valorisation of the ashes.

In addition, there are some restrictions which should be taken into account. The chlorine content limits plausible use of these ashes due to the associated erosion and corrosion process, mainly at the lower cyclones of the heat exchanger. Some cement manufactures have overcome this problem to some extent by incorporating a chlorine by-pass. This allows the manufactures to operate with higher chlorine content in the feed. In conclusion, the use of high or medium carbon-content biomass gasification fly/filter ashes in cement kilns seems to be a technically

possible route. In any case, the ash would have to be available in sufficient quantities and of predictable quality to interest a cement maker.

3.5. Reshaping into fuel

The carbon-rich ash is by itself a fuel. Technically, it is possible to use it as a fuel because it has a caloric value comparable to peat, despite the high ash content. Additionally, this method allows the ash volume to be reduced up to ten times giving to all imaginable fuel shapes. This use has many advantages derived from the volume reduction such as saving in transportation and storages costs.

The main handicaps are, however, the impact of the pelletisation process and the need of binder on the extra cost. Savings in logistics depend on the actual situation, e.g. distance from gasification plant, transported amounts and means of transportation (road, train, and ship). The cost of pelletisation depends on the type and the amount of binder. This regard will be part of the future negotiation with the potential buyer but also with transporters, who may have specific requirements, e.g. stability, dusting.

Also, the market is needed to be sought and the end use is not still fixed. Thus, there is need to look for potential buyers, and to find potentially interested buyers. ECN is currently under negotiation stage but this is beyond the scope of the GASASH project.

4. USE IN CONSTRUCTION

This concept covers different applications including the well-known uses as filler in asphalt, raw building material, additives in concrete manufacturing, and light bricks, but also some other less investigated such as material for fire-proof material manufacturing as well as stabilisation and/or solidification. The details and main conclusions derived from characterisation and testing worked out within this project are discussed bellow.

4.1. Filler in asphalt (C-Fix)

One of the existing non-fuel applications found possible for untreated gasification fly ashes was the use in structural asphalt mass as fine filler. Fillers are used to strengthen structural asphalt. The small particles fill in the gaps in the stone – sand – bitumen-matrix and make it stronger. The ash particle size of 5 to 20 μm is ideal for this purpose. Also the bitumen is a good binder to minimise the leachability of metals and could even fix the chlorides into the matrix. This type of application has been studied by ECN with promising technical results. The material should be used in non-wearing applications to avoid formation of harmful dust or sludge. To reach the necessary volumes in an economic way is likely to be a challenge.

EEP's fly ashes from a full-scale gasifier have been applied in a novel building material called C-fix. C-fix was originally developed by Shell Global Solutions, but is now being developed further in a private company by the name of C-fix BV. C-fix is a material with properties between asphalt and concrete. It is made from a heavy residue of the oil refinery, which is usually added to ship fuel or combusted for electricity. From an environmental point of view, C-fix contributes to reduction of the greenhouse gas CO2 problem by acting as a carbon sink. In addition, C-fix has very beneficial properties like high flexural and compressive strength, easy handling, low permeability and the possibility to fully recycle the material. The material is now being applied in pilot-scale projects. A large scale market introduction is in preparation.

In addition to the carbon rich binder, filling materials in various fractions are needed, from fine to sand to coarse gravel. The gasification fly-ash is added as fine filler (7% w/w). An extra advantage of using carbon rich fly ash from gasification is that the CO_2 sink will be even greater.

The material must comply with the DBMD for 'shaped' materials. The appropriate way to test this compliance is by performing a tank leach test (PrEN 14405). In this test a sample of monolithic building material is put in a tank filled with water. The water is refreshed after 7 consecutive intervals, each with longer equilibrium time. After 64 days the cumulative concentrations in the leachate can be compared with the Dutch Building Materials Decree.

The results for gasification fly ash applied in C-fix are good. None of the measured elements exceed the limits for the DBMD cat. 1 application (no limitations in application). Cyanide, fluoride, mercury and SO4 were not measured. All other elements were within limits. So this is a very promising route to explore further.

Based on the above results, it can be said that application of EEP's high-carbon fly ash in C-fix is a possible utilisation. Possibly, other building products can be found where the ash can be utilised.

4.2. Additives in concrete manufacturing

It has been demonstrated that for the ashes analysed in this project, none of them are susceptible to be used as concrete or cement additions without any previous treatment. The concept of mixing the gasification ashes with other “good ashes”, namely coal combustion fly ashes, rest on the concept of diluting the ashes with other with the final aim at obtaining a overall ashes that fulfil the requirements for the final use: in cement kilns and to concrete manufacturing. With regard to the former, one possibility is to be used as support fuel, as said above.

The route of mixing ashes can be a good concept for concrete manufacture. Also, the new version EN 450 fulfilment should be fulfilled by the mixed ashes. With this restriction the amount (and type) of gasification ashes could be determined and thus, the viability of this route to be properly assessed. This should be further assessed within the frame of WP4.

Extra benefit can be identified by the use of mixed ashes in concrete manufacturing. In particular, the use of "mixed/overall" gasification ashes as mineral agents in concrete manufacture is a possibility subject to the location issues discussed above (EN 450). This standard allows some degree of flexibility regarding the additives which can be added. Moreover, the revised version of this standard is going to arise soon and it is hoped to include other ashes such those coming from co-combustion processes. Obviously, the amount and type of gasification ashes which can potentially be mixed with the combustion ones depend of its composition. In principle, only ashes with low content in Cl and S seem to be susceptible to be applied within this concept.

4.3.Bulk construction / Raw building material

Fill is an application where alternative material is used as an inert, bulking agent in place of standard materials such as soil. Fly ash without pozzolanic activity can be used to replace earthen fills. Engineered fills are described as those applications where the filling material is used to construct embankments, dykes or as general site fills. In such applications, the fills are usually in thin layers and compacted to produce relatively incompressible support. There are a number of physical requirements for fills which are covered by relevant standards in some

countries. For example ASTM E 1861 was issued in the USA for guidance on the use of fly ash, bottom ash and FGD materials in fills.

Utilisation as bulk building material is usually limited by the leaching. For instance, the case of carbon-rich fly ash produced from demolition wood, Ba, Cl, Pb, Zn and Br prevent direct utilisation. Application as a bulk building material is also limited by the physical properties of the ashes. The ashes are fluffy and have a high leaching. He gasification ashes cannot be used as a replacement for sand in construction works, because their very fine size. One way of using it as component in building material is presented in the section 4.1. as filler asphalts (C-fix). Other options (by previous treatments) are under investigation.

4.4. Light weight bricks

In spite of the high alkali and chlorine content that may be problematic, especially when evaporation takes place in a high-temperature environment, most brickworks are apparently well equipped to reduce emissions of HF, and this may be a solvable problem with the right gas scrubbing procedures. Also, there is the important concern of knowing whether biomass-ashes have a technical advantage over other raw materials in manufacturing.

AICIA has sent a batch of orujillo ashes produced within this project for further testing. As soon as the ashes have been chosen we will proceed to their analysis in this laboratory. As a summary, this could be a potential utilisation route for some ashes. However, the amount that could be used seems to be rather limited.

4.5. Application in fire-proof materials

Thermal (Differential scanning calorimeter and Thermogravimetry) and mechanical properties (compressive and bending strength, surface hardness and elasticity modulus) have been studied in relation to possible applications of plates or panels manufactured using gasification ashes. Up to now, the ashes from Orujillo, VTT (CFB) and Lahti have been tested.

RDF (CFB Lahti, FW), SRF (CFB, VTT) and Orujillo (BFB, AICIA) ashes have been tested in blends containing ash 60-80 wt%, gypsum and additives used to manufacture fireproof plates. The maximum carbon (or organic content) of the tested ashes included in the investigation are: Orujillo (LOI between 10 and 20%), from full-scale FW ashes (Lahti): 30% organic carbon and from SRF (VTT) 20% LOI.

The preliminary results allow us to say that some positive properties from biomass gasification fly ashes have been found. For example, the high potassium content of the orujillo ashes lead to the formation of different water absorbent compounds which are of great utility for materials of this kind. On the other hand, VTT and FW ashes with a lower K content than orujillo ashes can provide the panels with higher porosity and lower weight.

In addition, the presence of unburned matter is not a serious handicap for this application to succeed. This feature is rather different in the rest of utilisation routes (except in applications as a fuel) where high carbon content is one of the major obstacles. Additionally, a comparison between the properties of as-received ashes with those coming from a previous (improving) treatment such as post-combustion, thermal oxidation or other, is one interesting aspect to be tested in this application.

Environmental impact of orujillo plates has been carried out, submitting test probes to the tank leaching test (NEN 7345, diffusion test) and analysing for metals: As, Ba, Cr, Cu, Ni, Pb, V and Zn. All the metals are in all subsamples under detection limits (ICP-OE) except Ba. After 64 days the accumulated Ba concentration was 11 mg/m^2 (the limit of the Dutch Building Materials Decree, BMD, for Category 1 is 600 mg Ba/m^2)

AICIA is working on products which include more than 50% of ashes. Taking 50 wt% as reference and 800-900 kg/m^3 as the density of the plates, a rough estimation of ash utilisation in this route, defined as ashes content per unit of area and unit of thickness, is around 6 kg /m^2/cm. The market on this respect might be studied or sought within WP4.

4.6. Stabilisation/Solidification (S/S) of hazardous wastes

The principle of the stabilisation of hazardous wastes rests on that the alkaline components in the fly ashes reduce the leachability of the metals in a high pH matrix. There is a pH window that gives the lowest metal concentration in the leachate. This window depends on the metal element but for a given fly ash, it can be found an optimum for minimising the final product leachability.

The currently tests are trying to stabilise an arc furnace dust waste, which is a dust that results from the collecting systems of particulate material in a carbon–steel electric arc furnace (EAF). The hazardous metals normally found in EAF dust are: lead; cadmium and chromium. In addition, the dust usually has a high zinc content (typical values are normally around 20%) resulting from the use of galvanized scrap. Because of its heavy metal content, s-WA is classified as hazardous waste.

Nr 1 Lahti (F-W), CFB (VTT) and orujillo ashes have been tested as potential immobilising agents of an EAF dust. Blends containing 45 wt% EAF dust, 45 wt% ash and 10 wt% of Portland cement have tested so far. After 28 days of curing, mechanical (compressive strength) and leaching properties (DIN 38414 and TCLP) have been measured in the resulting solids. The main results are:

- At 28 days, F-W and VTT ash blends presented better leaching properties for the metals tested (Ba, Cd, Cr, Cu, Ni, Pb, V and Zn) than AICIA (orujillo ash) blends, both in DIN and TCLP leachates. This is probably due to an excess of alkalinity in AICIA solids.

- Conversely, the mechanical resistance of F-W and VTT solids was very bad reaching compressive strength values at 28 days of 0.15 (Nr1) and 1 kg/cm^2 (CFB), whereas AICIA solids reached 6 kg/cm^2 at the same time. Moreover, F-W and VTT solids presented difficulties to set, showing a non-uniform setting at 21 days, while AICIA samples set in 1 hour.

- In order to better define new stabilising blends, we have applied the Generalized Acid Neutralization Capacity (GANC) leaching test to CFB and BFB ashes (VTT), Lahti Nr1 (F-W) and orujillo ashes. The results show that, though orujillo ashes give the higher pH value in water (pH > 12), both CFB and Nr1 have a greater acid neutralization capacity.

- The study of the pozzolanic activity of CFB, Lahti Nr1 and orujillo ashes through thermo gravimetric techniques did not allow us to bear conclusions so far.

- The immobilized solids have also been submitted to the tank leaching test NEN 7345 (diffusion test). The metals analysed were: As, Ba, Cd, Cr, Cu, Ni, Pb, V and Zn. All the metal is in all sub samples under detection limits (ICP) except Cr, Zn and Ba. The most problematic metal in all the cases is Cr, especially in the orujillo ash solids. As it is well known, Cr in its

hexavalent form is a species difficult to stabilize. For that reason many wastes need a previous reduction step before an immobilization process. After 64 days the accumulated Cr concentration in the orujillo ash solids was 500 mg/m^2 (the limit of the Dutch Building Materials Decree, BMD, for Category 1 is 140 mg Cr/m^2). Moreover, in addition to regulatory aims, the tank leaching test is also useful to study the metal immobilization mechanism.

- A study of the evolution with time of the above mentioned solids has been carried out. Mechanical properties improve with time, especially for the orujillo ash solids: The compressive strength goes from 6 kg/cm^2 at 28 days, 20 kg/cm^2 at 3 months and 52 kg/cm^2 at 9 months. During this period the other two solids tested reached a resistance of 2 kg/cm^2.

- In function of the results obtained in the evolution with time of the mechanical properties, the Activity index of orujillo ash plus Portland cement Type I will be studied, according to standards (UNE 85-451-86. Additions for concrete. Fly ash), to better define the influence of the ash on the compressive strength of the mortars.

5. Application in Agriculture

These applications have been assessed for all the fly ashes characterised in this project. The main limitation for this route to be possible is that the ashes should fit some minimum requirements for considering good nutrients, i.e. concentration of K and P above some limits and also to be free of high concentration of heavy metals and organic derived components like PAH. This point is rather controversial since there are not specific regulations which control and establish these limits.

In this project it has been possible to establish some guidelines from different regulations found for specific uses, more specifically by comparing with regulations for valorisation of sewage sludges and compost in Spain, regulation for cultivation in Finland and Sweden, etc. With this information in mind, it has been possible to construct a picture which roughly establishes the requirements which should fit the ashes for being considered applicable in this utilisation.

For the ashes characterised in this project, none of them, except to those from orujillo fulfil the above requirements. In addition, if the application as fertiliser is assessed the ashes need to have a good portion of P and K in soluble way. The orujillo ashes have been analysed in this concern and showed very low soluble fraction of K and P in orujillo ashes (K and P contents measured in DIN and TCLP leachates: K soluble = 20-60%; P soluble < 1%).

To sum up, the agriculture utilisation is not a general route for biomass gasification ashes but merely a good candidate for some ashes, such as orujillo. In addition the use as fertiliser does not seem to be possible because of the very low soluble fraction of P and K in the ashes. Thus a reasonable route for these ashes could be the use as amendment. As example orujillo ash recycling to olive grove seems to be a good route for these ashes.

6. CONCLUSIONS

The work developed within the frame of GASASH project has allowed us to greatly expand the scenario about the specific utilisation routes for gasification ashes. From the technical point of view, different routes for biomass/wasted have been assessed. Some of them clearly show technical viability for further testing. Despite this, the definitive results of the project are far from being finished from the economical point of view.

Besides the technical aspects analyzed in this document other important aspects should be taken into account. For example, utilizations must be found close to the location of new gasification facilities, as the economics worsen rapidly with increased transportation costs. Also, one must be careful when considering utilisation routes that would mean transportation of the ashes into adjacent countries (more of an issue in the smaller EU States) as this would contravene cross-border restrictions on wastes. In addition, it is important to compare the results with country specific regulations. This will make it possible to predict whether gasification of a certain fuel will make sense without producing the ash themselves, e.g., when we know composition and leaching characteristics of orujillo-ash, we can see whether the ash matches regulation for the Dutch Building Materials Decree. All of these aspects should be studied and considering within the frame of WP4.

Appendix F Deliverable 17 Report on a detailed Characterisation of Different Gasification Ashes

DELIVERABLE REPORT No 17

CONTRACT N°: ENK5-CT-2002-00635

PROJECT N°: NNE5-2001-00598

ACRONYM: GASASH

PROJECT TITLE: Improvement of the economics of biomass/waste gasification by higher carbon conversion and advanced ash management

PROJECT CO-ORDINATOR: VTT Processes

PARTNERS :
VTT Processes (VTT)
Foster Wheeler Energia Oy (FWEOY)
Energy Research Centre of the Netherlands (ECN)
Asociación de Investigación y Cooperación Industrial de Andalucía (AICIA)
Pohjolan Voima Oy (PVO)
EMC Environment Engineering Limited (EMC)
Essent Energie Productie b.v. (EEP)

PROJECT START DATE : 1 November 2002

DURATION: 36 months

Date of issue of this report : November 2005

Project funded by the European Community under the 'EESD' Programme (1998-2002)

TABLE OF CONTENTS

1 Introduction and scope 3
2 Characterisation of ashes 3
2.1 Ashes characterised 3
2.2 Methods of characterisation 5
2.3 Standards applied 5
3 Detailed results on composition of ashes 6
3.1 Physical characterisation 6
3.2 Main elements 7
3.3 Metals 8
3.4 PAH 9
3.5 LHV of ashes 9
4 Leaching properties 10
4.1 DIN 38414 10
4.2 TCLP 12
4.3 Column tests 13
5 Conclusions 14

DELIVERABLE REPORT NUMBER 17

CONTRACT No: ENK5-CT-2002-00635
PROJECT No: NNE5- 2001-00598
ACRONYM: GASASH
DELIVERABLE TITLE: Report on a detailed characterisation of different gasification ashes

REPORT ON A DETAILED CHARACTERISATION OF DIFFERENT GASIFICATION ASHES

1 Introduction and scope

One of the earlier targets of the Gasash project has been to identify technical conditions for the most promising utilisation methods and to layout the ash treatment conditions needed for compliance with the relevant environmental and technical criteria. This has been accomplished by and extensive characterization work carried out on the raw ashes selected in this project. In particular, in the first stage of Gasash project the characterisation of ashes generated has permitted to assess the ability of these ashes to fulfil some constraints necessary for some well-known utilisation options. In general under the light of the characterization made on the raw ashes generated in this project, the existing methods can not be directly applied for gasification fly ashes. This is mainly due to the fact that the high carbon content of gasification fly and filter ashes limits the field of application. High chlorine and alkali are present in most of the ashes and heavy metals are also present in waste ashes. This makes even more difficult its plausible utilisation. Therefore, it has been concluded that physical or thermal treatments are most likely to be applied. These treatments included washing (for alkali and chlorine removal), low temperature combustion (carbon, LOI, PAH), and high temperature treatments (more persistent contaminants). Other options have also been investigated in this project.

The objective of this report is to summarise the characterisation work carried out during the course of Gasash project. This characterisation has been made on the ashes from optimised gasification processes (WP1) and advanced ash treatment processes (WP2). The aim of this report has been limited to the raw ashes generated from the gasification of the main fuels selected. However, there is a vast characterisation work on treated ashes or simply on products fabricated with the ashes. These data are not reported here and they are covered in relevant reports.

2 Characterisation of ashes

2.1 Ashes characterised

Nine main fuels have been selected for the investigation of the gasification fly ashes generated during its processing. **Table 1** covers these fuels together with the partner (VTT, AICIA, FWE, ECN and Amer) who has generated the ashes, and the gasifier that has processed the fuel and its scale.

Two especially relevant ashes are worth to note. Those from Lahti and Amer gasifiers. The first one, comes from the biggest atmospheric-operated CFB gasifiers in EU. Lahti ashes are fly ashes collected in a 50-80 MWth CFB gasifier at Lahti during 100% REF gasification in 2003. The REF (recovered fuel) is produced from origin-classified refuses, coming from households, offices, shops and construction sites nearby the city of Lahti. Typically the used REF contains 5-15% plastic, 20-40% paper, 10-30% cardboard and 30-60% wood. The second full-scale ashes is

batch of fly ash that has been taken from the 80 MW(th) Circulating Fluidised Bed Gasifier located at the AMER-9 Power Plant of Essent Energy (AMER-CFB). The ashes has been taken form the gasifier after about 5 days of operation in order to reach stable operation. The gasifier was at 900-920°C and the cyclone at 450°C or somewhat higher.

The other two ashes from FWE have been gasified in the 3 MWth atmospheric CFB pilot gasifier, at the Foster Wheeler Karhula R&D Center. They have been collected during straw gasification in 2000 and during RDF gasification in 2002. The RDF (refuse derived fuel) is produced from mixed municipal waste by removing the metal and glass by mechanical handling process. Composition of RDF is quite similar to REF, but it could contain higher amount of impurities like heavy metals and chlorine. The other ashes from ECN comes from the sewage sludge gasification of ECN's 500 kW circulating fluidised-bed gasifier (BIVKIN). This is an atmospheric circulating fluidized-bed gasifier of 500 kWth (max. fuel rate around 100 kg/hr). The riser is 6 m high and has a diameter of 20 cm. The sample has been taken from a second (hot) cyclone presented directly after the gasifier before a cooler.

Table 1. Ashes analysed in the project

Raw ashes characterised in Gasash-Project			
Fuel	**From**	**Gasifier**	**Scale(MW_{th})**
Orujillo	AICIA	BFB	0.15
MBM	AICIA	BFB	0.15
Wood Waste	VTT	BFB	1
SRF	VTT	CFB	0.3
RDF	FWE	CFB (Lahti)	50-65
Straw	FWE	CFB (Karhula)	3
RDF	FWE	CFB (Karhula)	3
Demolition wood	Essent/ECN	CFB (Amer)	85
Sewage Sludge	ECN	CFB (BIVKIN)	0.5

Other ashes have been gasified in smaller scale units of VTT and AICIA at pilot scale, i.e ≤ 1 MW_{th}. In particular, the ashes from VTT, have been collected in its two rigs. One has been collected during wood waste gasification in a 1 MW_{th} BFB plant. The ash was collected by hot gas filter at about 400^{o}C. The other ashes come from the gasification of SRF in a CFB gasification unit of 0.3 $MW_{th.}$ In both cases bed material of he gasifier was mixture of sand and limestone.

The ashes from the gasification of orujillo have been collected from the 150 kWth BFB AICIA's gasifier. The test trials were aimed at optimizing the operating conditions in order to reduce the volume and to improve the quality of the ashes generated. Therefore, the results are reported for several operating conditions, which are summarized as follows:

- RUN 9: ER=0,31 and T=820ºC.
- RUN 8: ER=0,29 and T=780ºC.
- RUN 7: ER=0,23 and T=790ºC.
- RUN 6: ER=0,24 and T=840ºC.
- RUN 5: ER=0,20 and T=700ºC.
- RUN 1: ER=0,46 and T=785ºC.

The MBM has also been gasified in AICIA´s rig. The role of bed material has also been investigated for this biomass and so, the results are present for various runs, using several bed materials together with different operating conditions:

- RUN 4: Inert: Ofite ER=0,35 and T=820ºC
- RUN 6: Inert: Ofite ER=0,25 and T=780ºC
- RUN 7: Inert: CaO ER=0,3 and T=790ºC
- RUN 8: Inert: Ofite + 30% CaO ER=0,3 and T=810ºC

In addition, the results from MBM and orujillo are presented for various samples, taken as different locations of the gasifier: first cyclone, second cyclone and overflow. The first and second cyclones are approximately at the same temperature. On the other hand, the overflow ashes give information about the conditions in the bed. From these it is possible to analyse the effect of elutriation on the gasification fly ashes.

The basic characterisation of the fuels is covered in the appendix of this report.

2.2 Methods of characterisation

The next itemised list summarise the methods that have been applied to characterise the ashes covered in Table 1.

- Physical characterisation (PSD)

- Elemental analysis (Standard for fuels): C, H, N (ASTM D-5373) and S (ASTM D-4239)

- Major components (XRD and chemical analyses): SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O and P_2O_5

- Trace elements (ASTM D-3683): As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, V , Zn, Hg, Sb, Se

- Ashes leachability and analysis of eluates according to:
  - DIN 38414
  - Compliance batch leaching test EN 12457/1-4 for L/S=10
  - TCLP (USEPA 1311)
  - Column test. Up-flow percolation test EN 14405

- Thermal analysis (TGA, DSC, DTA). This has been applied to further assess some applications and not to the raw ashes. Thus, this information is not dealt with in this report.

2.3 Standards applied

Depending of the ashes and the utilisation route selected for further analysis, a series of standards/regulations have been considered for comparing the characterisation data. These are well-known since are applied to other biomass and wastes gasification or combustion derived fly ashes. The most remarkable used are given as follows:

Construction:

- Dutch Building Material Decree (DBMD)
- Fly ash for concrete (EN 450)

- Fly ash for cement (EN 197)
- Valorisation of slags (OVS. Catalonia. Spain)

Agriculture:

- Metal limits in Compost (Spain)
- Heavy metal limits in Sewage-Sludge for Agriculture Applications (Spain)
- Metal Limit Values for Ash Utilisation in Cultivation (Finland)
- Recommended Minimum and Maximum Values for Components in Ash Products in Sweden

Together with these other standards have also been applied for testing the abilities of certain products made of ashes. For instance, for fire-resistances materials or bricks manufacture, the results of characterisation has been compared with the common practises found in the corresponding commercial products.

3 Detailed results on composition of ashes

3.1 Physical characterisation

The main size-distribution analysis of most ash samples is presented in **Table 2.** Also, it is included in this table some reference values for comparison purposes. In particular, it is included the size-distribution of a sample taken from a power plant burning orujillo (Las Lomas) and another from coal combustion (Los Barrios).

Table 2. Size characterisation of some ashes

				GRANULOMETRY		wt %			
PARTNER	**(µm)**	**> 300**	**300-150**	**150-75**	**< 75**	**> 90**	**90-75**	**75-45**	**< 45**
AICIA	**Orujillo**								
	9 Overflow	85.9	7.5	3.4	3.2				
	9 Cyclone 1					18	9	16	57
	9 Cyclone 2					1	7	22	70
	9 Orujillo					43	33	23	1
	8 Cyclone 1					20	11	17	52
	8 Cyclone 2					15	8	16	61
	8 Overflow	75	11.5	6	7.5				
	7 Overflow	86.5	9	2.5	2				
	7 Cyclone 1					15	11	20	54
	7 Cyclone 2					5	4	16	75
	6 Cyclone 1					28	16	21	35
	6 Cyclone 2					17	7	12	64
	6 Overflow	77.6	10.5	5.5	6.5				
VTT	**SRF**					0	2	10	88
FW	**RDF Lahti**					6	44	16	34
Other (as references)									
OFITE		96.5	1	0.5	2				
PP Combustion Orujillo		4	22	40	34				
Coal combustion ash		1	4	14.2	80.8				

3.2 Main elements

The main elements average values of orujillo and MBM ashes are displayed in **Table 3** (average of the two cyclones at different operating conditions). In **Tables 4 and 5** a detailed characterisation of the different gasification trials of orujillo and MBM is presented, respectively. **Table 6** includes the main elements contents of ofite and the original orujillo (fuel).

Table 3. Main elements in different ashes

						%w/w							
PART.	**ASH**	**Moisture**	**LOI**	**Fe_2O_3**	**CaO**	**MgO**	**SiO_2**	**Al_2O_3**	**Na_2O**	**K_2O**	**P_2O_5**	**Cl**	**S**
AICIA	Orujillo	1.75	20.26	5.32	26.08	8.64	41.02	8.03	1.29	8.26	1.50	0.64	0.11
	MBM	2.12	16.64	2.89	44.49	3.62	12.48	3.45	4.13	1.48	17.95	-	0.20
VTT	Waste wood	3.68	63.73	10.98	45.13	4.03	21.38	6.24	0.66	0.72	1.24	1.20	-
	SRF	1.47	23.80	2.95	38.96	3.30	27.93	21.49	1.46	0.65	-	2,8/4,6	-
FWE	RDF Lahti		33,18***	2.1	44.6	2.9	19.1	13.4	1.6	1.4	0,8 (0,69**)	4,3/2,1	0.34
	Straw		37,5***	0.3	14.4	1.2	32.3	0	0.2	6.1	0,4 (0,46**)	0.80	0.11
	RDF Karhula		20,9***	7.6	31.8	2.1	21	18.2	0.3	0.7	2,4 (2,52**)	8.90	0.25
ECN	AMER-CFB	0	-	0.97	6.8	0.94	17.75	1.42	0.63	0.87	0.32	1.07	-
	Sewage Sludge	-	-	15.79	10.54	1.73	32.1	9.61	0.75	1.71	16.74	0.06	1

* There are further components analysed for FWEoY ashes

** AICIA results

Table 4. Ash main elements from different orujillo tests

						%w/w							%w/w
RUN	**"Location"**	**Moisture**	**LOI**	**Fe2O3**	**CaO**	**MgO**	**SiO2**	**Al2O3**	**Na2O**	**K2O**	**P2O5**	**Cl**	**S**
9	Overflow	0.37	6.74	7.3	14.2	6.8	49.5	13.1	2.3	4.5	0.41	0.25	<0,05
9	Cyclone 1	0.91	13.91	5.1	24.7	8.0	41.4	8.8	1.4	7.4	1.53	0.91	0.14
9	Cyclone 2	2.21	19.22	5.5	27.1	9.2	35.5	9.0	1.3	8.6	2.20	0.99	0.12
8	Overflow	0.68	10.74	7.1	14.8	7.0	49.9	12.5	2.3	4.7	0.57	0.34	<0,05
8	Cyclone 1	1.23	18.36	6.0	20.8	8.2	44.0	9.9	1.7	5.8	1.17	0.50	0.06
8	Cyclone 2	0.92	16.75	5.5	26.0	8.5	38.3	9.0	1.3	7.8	1.47	0.71	0.1
7	Overflow	1	20.87	6.6	15.38	7.23	54.3	9.7	2.1	4.98	0.64	0.52	
7	Cyclone 1	1.08	18.16	5.4	23.19	8.38	43.6	7.54	1.3	7.85	1.21	0.40	
7	Cyclone 2	2.25	23.03	5.5	24.17	9.29	39.8	7.68	1.27	9.14	1.72	0.48	
6	Overflow	3.63	29.66	5.5	17.32	6.95	54.37	9.03	1.72	6.85	0.87	0.47	
6	Cyclone 1	1.96	23.4	5.7	26.94	8	42.8	8.25	1.42	7.18	1.10	0.57	
6	Cyclone 2	2.33	24.53	5	27.13	8.46	40.6	6.79	0.8	9.8	1.63	0.53	
6	Cyclone 1(B)	2.07	21.64	5.42	21.52	7.61	47.17	7.44	1.84	5.46			
1	Overflow	1.38	14.29	4.9	17.26	6.03	57.6	7.8	1.37	8.26			
1	Cyclone 1	1.07	15.57	4.37	31.6	8.55	41.38	6.36	0.92	10.3			
1	Cyclone 2	1.89	18.11	5.28	36.3	9.99	36.2	7.7	1.05	8.9			
5	Cyclone 2	3.11	30.49	5.1	23.47	9.53	41.6	7.9	1.15	10.9			

Table 5. Ash main elements from different MBM tests

						%w/w							
RUN	"Location"	Moisture	LOI	Fe2O3	CaO	MgO	SiO2	Al2O3	Na2O	K2O	P2O5	Cl	S
4	Cyclone 1	1.32	4.6	5.57	25.45	5.23	28.99	7.29	5.1	1.8	17.95		
6	Cyclone 1	1.16	8.14	2.53	41.71	3.62	10.03	3.19	4.66	1.24			0.22
6	Cyclone 2	6.13	24.84	4.06	31.98	4.68	15.60	4.85	5.94	2.56			0.36
7	Cyclone 1	0.89	11.53	0.78	61.10	2.14	3.60	0.70	3.35	1.06			<0,05
7	Cyclone 2	3.15	27.13	3.77	34.41	4.34	15.22	4.19	5.09	2.07			0.56
8	Cyclone 1	0.96	15.35	1.60	55.66	2.72	6.76	1.93	2.75	0.72			<0,05
8	Cyclone 2	1.25	24.89	1.93	61.11	2.60	7.18	2.02	2.01	0.98			<0,05

Table 6. Main elements in ofite and orujillo fuel

					%w/w							
Material	Moisture	LOI	Fe2O3	CaO	MgO	SiO2	Al2O3	Na2O	K2O	P2O5	Cl	S
OFITE	0.47	0.64	9.15	11.12	7.9	53.93	13.61	3.49	0.48	0.09	0.62	-
ORUJILLO	10.82	77.12	3.4	27.0	6.3	50.4	5.5	0.6	10.5	1.47	0.21	-

3.3 Metals

The metal concentrations in the ashes are reported in Tables 7 and 8. The values of orujillo and MBM displayed in **Table 7** are the average of the two cyclones for the different operating conditions tested. **Table 8** includes a detailed characterisation of ashes obtained in the different gasification trials carried out with orujillo.

Table 7. Metal concentrations in different ashes

							Metals in mg/kg									
SAMPLES	As	Hg	Se	Mo	Zn	Pb	Cd	Co	Ni	Cr	V	Cu	Ba	Sb	Mn	Sn
ORUJILLO ashes	<160	<100	<100	<100	210.5	<160	<16	<10	<100	761.5	83	145.75	288.75	<200	-	-
ORUJILLO Fuel	<160	<100	<100	<100	182	<160	<16	<10	<100	646	60	182	270	<200	-	-
MBM	<100	<100	<100	<20	398	100	<10	<10	864	636	<20	212	134	<20		
SRF	20				1500	920	14	19	96	530	41	2100		180	860	150
SRF	<100	<100	<100	<20	1660	426	<10	<10	122	786	<20	1474	1560	<20		
Waste wood	1430	<100	<100	<20	8412	1832	<10	<10	190	1212	<20	1436	2644	<20		
RDF Lahti	46.2	0.0077	<2	8.27	5340	722	5.88	21.1	47.9	83.3	15	1900	1345	362	766	-
AMER-CFB	99.2	-	4.2	3.8	4045.3	4735.6	8.0	21.0	26.9	496.9	12.1	422.8	3743.9	40.8	841.1	39.1
Sewage Sludge	9.26	0.02	1.44	21.06	1964.89	246.19	0.28	15.51	113.22	196.84	47.48	920.57	861.28	11.11	1362.71	43.26

Table 8. Metals concentration in different ashes

					Metals in mg/kg										
RUN	"Location"	As	Hg	Se	Mo	Zn	Pb	Cd	Co	Ni	Cr	V	Cu	Ba	Sb
9	Overflow	<160	<100	<100	<100	190	<160	<16	<10	<100	980	158	76	200	<200
9	Cyclone 1	<160	<100	<100	<100	234	<160	<16	<10	<100	734	74	186	296	<200
9	Cyclone 2	<160	<100	<100	<100	254	<160	<16	<10	<100	708	78	166	340	<200
8	Cyclone 1	<160	<100	<100	<100	188	<160	<16	<10	<100	760	92	134	276	<200
8	Cyclone 2	238	<100	<100	<100	176	<160	<16	<10	<100	726	84	164	276	<200
8	Overflow	<160	<100	<100	<100	142	<160	<16	<10	<100	812	136	88	144	<200
7	Overflow	246	<100	<100	<100	152	<160	<16	<10	<100	1154	122	72	144	<200
7	Cyclone 1	<160	<100	<100	<100	184	<160	<16	<10	<100	720	74	120	272	<200
7	Cyclone 2	<160	<100	<100	<100	240	<160	<16	<10	<100	722	74	156	298	<200
6	Cyclone 1	<160	<100	<100	<100	174	<160	<16	<10	<100	928	102	110	274	<200
6	Cyclone 2	<160	<100	<100	<100	234	<160	<16	<10	<100	794	86	130	278	<200

3.4 PAH

The PAH concentration values are presented in **Table 9**. These values have been analysed for some of the ashes produced after the orujillo gasification, because they turned out to be-- from a previous heavy metals screening--one of the main hopeful ashes to be applied in agriculture uses. Therefore, **Table 9** includes the PAH found in the ashes generated in different runs. The ashes from RDF collected in Lahti plant are also included in the table. Note that the PAH concentration in this latter is much higher than those found in orujillo ashes. However the orujillo content is relatively high for agriculture uses (<1 mg/kg).

Table 9. PAH values in some ashes

SAMPLES	RUN	"Location"	PAH(mg/kg)
ORUJILLO	1	Cyclone ½	67.5
	7	Overflow	<1,4
	7	Cyclone ½	10
	-	Cyclone 1 (mean)	18.8
	-	Cyclone 2 (mean)	86.8
MBM	6	Cyclone 1	165
RDF Lahti			350

3.5 LHV of ashes

In general, the carbon content of gasification fly ashes are much higher than that of combustion fly ashes. This is disadvantageous for most applications. However, for the possible use of the fly ashes as fuel this carbon content is very important. The calorific value of Lahti and Amer gasification fly ashes ranges from 14 to 25 MJ/kg. These values are comparable to the heating

values of peat and wood, despite the high ash content. For the ashes analysed in Gasash-project the loss-on-ignition (LOI), mainly carbon, ranges from 7 to 60 wt%. A great part of the effort of this project has been directed made towards the utilization as an alternative fuel. **Table 10** shows typical fuel analysis (Heating values, elemental and proximate analyses) made to the orujillo and MBM ashes in order to assess them as a fuel. While the orujillo ashes have an acceptable heating value, the MBM has very little energetic content. However, in both cases the heating values are much lower that those shown by industrial scale ashes (Amer and Lahti).

Table 10. Analysis of MBM and orujillo ashes to asses the fuel route

	(kcal/kg)	(wt %,w.b.)				(wt %,d.b.)				
	LHV d.b.	Moisture	Ash	Volatiles	Fixed C	C	H	N	S	O
ORUJILLO	1214	2.83	75.19	8.1	13.88	16.06	0.55	0.57	0.08	5.36
MBM	228	0.84	92.32	4.03	2.82	4.1	1.32	0.78	0.22	0.48

4 Leaching properties

4.1 DIN 38414

Average DIN 38414 leaching data from orujillo and MBM ashes are shown in **Table 11**. **Table 12** shows a detailed characterisation of the different gasification trials made on orujillo. **Table 13** contains the DIN leaching results of orujillo (fuel) as well as ofite. This could be of help for following key components. Finally the information provided in Tables 11 and 12 are re-calculated as mg/kg in order to directly assess the ashes with landfilling regulations.

Table 11. DIN 38414 leaching test results of some ashes

				Leachate DIN (mg/L)									
PARTNER	SAMPLES	pH	As (ppb)	Zn	Pb	Cd	Ni	Cr	V	Cu	Ba	K	P
AICIA	ORUJILLO	12.59	<1	0.1	0.1	< 0,03	0.1	<0,05	<1,9	0.09	1.83	27.35	0.02
	MBM	10.25		0.07	<0.1	<0.02	<0,05	<0.05	<1,9	<0.05		100.0	0.01
VTT	Waste wood	9.12	44	<0,02	<0,1	< 0,03	<0,05	<0,05	<1	<0,05	1.1		
	SRF	11.47	<1	0.03	0.13	0.03	0.12	<0,05	<1	<0,05	24.5		
FWE	RDF Lahti	12.17	1	0.04	0.1	< 0,03	0.08	<0,05	<1	<0,05	49.5		
	Straw	12.93	<1	0.17	0.14	< 0,03	0.11	<0,05	<1	0.05	2.7		
	RDF Karhula	10.10	<1	0.05	0.18	0.04	0.22	<0,05	<1	0.07	17.7		

Table 12. DIN leaching test results of orujillo ashes obtained at different test conditions

				Leachate DIN (mg/L)									
RUN	Location	pH	As (ppb)	Zn	Pb	Cd	Ni	Cr	V	Cu	Ba	K	P
9	Overflow	12.5	<1	<0,02	0.1	< 0,03	0.08	<0,05	<1,9	<0,05	1.4	15.00	0.03
9	Cyclone 1	12.68	<1	0.19	0.15	< 0,03	0.13	<0,05	<1,9	<0,05	3.1	25.28	0.02
9	Cyclone 2	12.66	<1	0.14	0.12	< 0,03	0.08	<0,05	<1,9	0.05	2.4	27.04	0.01
8	Cyclone 1	12.59	<1	0.07	0.12	< 0,03	0.14	<0,05	<1,9	0.12	2	26.79	0.02
8	Cyclone 2	12.63	<1	0.03	0.1	< 0,03	0.11	<0,05	<1,9	0.06	2.8	23.35	0.01
8	Overflow	12.34	<1	<0,02	<0,1	< 0,03	0.06	<0,05	<1,9	<0,05	1.2	21.93	0.02
7	Overflow	12.32	<1	0.04	<0,1	< 0,03	<0,05	<0,05	<1,9	<0,05	0.3	38.86	0.02
7	Cyclone 1	12.6	<1	0.13	<0,1	< 0,03	<0,05	<0,05	<1,9	0.06	0.9	22.81	0.05
7	Cyclone 2	12.55	<1	0.05	0.1	< 0,03	0.07	<0,05	<1,9	0.06	1.3	20.46	0.01
6	Cyclone 1	12.49	<1	<0,02	0.12	< 0,03	<0,05	<0,05	<1,9	0.05	0.7	44.11	0.01
6	Cyclone 2	12.48	<1	0.02	0.1	< 0,03	0.07	<0,05	<1,9	0.06	1.4	29.00	0.01
6	Overflow	12.59	<1	<0,03	<0,1	< 0,03	<0,05	<0,05	<1	<0,05	<0,5	32.83	0.02

Table 13. DIN leaching test results of ofite and orujillo (as original fuel)

			Leachate DIN (mg/L)									
SAMPLES	pH	As (ppb)	Zn	Pb	Cd	Ni	Cr	V	Cu	Ba	K	P
OFITE	8.51		0.03	<0,1	< 0,03	<0,05	<0,05	<1,9	0.05	<0,3	0.2	1.26
ORUJILLO	6.35	35	0.18	0.13	< 0,03	0.57	<0,05	<1,9	0.23	1.7	189.19	55.04

Table 14. DIN leaching test results expressed in mg/kg

				Leachate DIN (mg/kg)							
SAMPLES	RUN	Location	As	Zn	Pb	Cd	Ni	Cr	V	Cu	Ba
ORUJILLO	9	Overflow	<0,01	<0,2	1	<0,3	0.8	<0,5	<19	<0,5	14
	9	Cyclone 1	<0,01	1.9	1.5	<0,3	1.3	<0,5	<19	<0,5	31
	9	Cyclone 2	<0,01	1.4	1.2	<0,3	0.8	<0,5	<19	0.5	24
	8	Cyclone 1	<0,01	0.7	1.2	<0,3	1.4	<0,5	<19	1.2	20
	8	Cyclone 2	<0,01	0.3	1	<0,3	1.1	<0,5	<19	0.6	28
	8	Overflow	<0,01	<0,2	<1	<0,3	0.6	<0,5	<19	<0,5	12
	7	Overflow	<0,01	0.4	<1	<0,3	<0,5	<0,5	<19	<0,5	3
	7	Cyclone 1	<0,01	1.3	<1	<0,3	<0,5	<0,5	<19	0.6	9
	7	Cyclone 2	<0,01	0.5	1	<0,3	0.7	<0,5	<19	0.6	13
	6	Cyclone 1	<0,01	<0,2	1.2	<0,3	<0,5	<0,5	<19	0.5	7
	6	Cyclone 2	<0,01	0.2	1	<0,3	0.7	<0,5	<19	0.6	14
	6	Overflow	<0,01	<0,2	<1	<0,3	<0,5	<0,5	<10	<0,5	<5
MBM	4	Ashtray		<0,2	<1	<0,2	21	<0,5	<19	<0,5	
	4	Cyclone 1		0.7	<1	<0,2	<0,5	<0,5	<19	<0,5	
Waste wood	-	-	0.44	0.2	1	0.3	<0,5	<0,5	<10	<0,5	11
SRF	-	-	<0,01	0.3	1.3	0.3	1.2	<0,5	<10	<0,5	245
RDF Lahti	AICIA	-	0.01	0.4	1	<0,3	0.8	<0,5	<10	<0,5	495
RDF Lahti	FW		0.24	0.66	0.46	0.016	0.08	0.08	0.08	0.04	140
Straw	-	-	<0,01	1.7	1.4	<0,3	1.1	<0,5	<10	0.5	27
RDF Karhula	-	-	<0,01	0.5	1.8	0.4	2.2	<0,5	<10	0.7	177

4.2 TCLP

The same information presented above for DIN leaching test is also presented for USEPA TCLP test in **Tables 15-17**. In particular, in **Table 15**, the data of orujillo and MBM displayed are the average values of the two cyclones at different operating conditions. A detailed characterisation of the different trials carried out with orujillo is presented in **Table 16**. Finally, **Table 17** displays the results from leaching tests done directly to the orujillo-fuel as well as to the ofite.

Table 15. TCLP leaching test results of some ashes

			TCLP leachates (mg/L)									
SAMPLES	**pH**	**As (ppb)**	**Zn**	**Pb**	**Cd**	**Ni**	**Cr**	**V**	**Cu**	**Ba**	**K**	**P**
ORUJILLO	10.29	5.00	0.03	0.20	0.04	0.28	<0,05	<1,9	<0,05	3.45	38.39	0.04
MBM	5.07		0.67	0.21	0.03	4.4	<0.05	<1,9	0.05			21.56
Waste wood	6.47	204	35.9	0.64	0.22	0.57	<0,05	<1	0.25	5		
SRF	10.47	8	0.03	0.23	0.05	0.29	<0,05	<1	0.08	11.5		
RDF Lahti	10.23	<1	0.06	0.16	0.04	0.26	<0,05	<1	0.06	18.2		
Straw	10.53	<1	0.03	0.15	0.04	0.19	0.05	<1	0.08	4.5		
RDF Karhula	6.24	2.5	106.8	1.53	2.9	3.35	<0,05	<1	0.32	9.6		

Table 16. TCLP leaching test results of orujillo ashes at different test conditions

			TCLP leachates (mg/L)									
RUN	**Location**	**pH**	**As (ppb)**	**Zn**	**Pb**	**Cd**	**Ni**	**Cr**	**V**	**Cu**	**Ba**	**K**	**P**
9	Overflow	6.64	4	0.12	0.92	0.1	0.82	<0,05	<1,9	<0,05	3.3	21.1	0.89
9	Cyclone 1	11.44	<1	0.03	0.23	0.04	0.29	<0,05	<1,9	0.05	4.3	29.9	0.02
9	Cyclone 2	11.13	<1	0.03	0.22	0.04	0.28	<0,05	<1,9	0.05	4	33.0	0.01
8	Cyclone 1	9	9	0.02	0.17	0.03	0.28	<0,05	<1,9	0.05	3.3	39.8	0.06
8	Cyclone 2	11.65	<1	0.02	0.23	0.04	0.29	<0,05	<1,9	*<0,05*	4.1	29.1	0.02
8	Overflow	7.18	5	0.05	0.18	0.04	0.64	<0,05	<1,9	*<0,05*	3.3	30.3	1.47
7	Overflow	6.91	1.5	0.12	0.17	0.04	0.52	<0,05	<1,9	*<0,05*	3	62.5	0.57
7	Cyclone 1	10.25	<1	0.04	0.19	0.04	0.25	<0,05	<1,9	*<0,05*	3.4	33.8	0.01
7	Cyclone 2	10.16	<1	0.03	0.19	0.04	0.25	<0,05	<1,9	*<0,05*	3.2	32.6	0.02
6	Cyclone 1	8.56	6	0.03	0.14	0.03	0.3	<0,05	<1,9	<0,05	2.4	66.2	0.16
6	Cyclone 2	10.16	<1	0.02	0.19	0.03	0.26	<0,05	<1,9	<0,05	2.9	42.7	0.02
6	Overflow	7.24	3	0.1	0.2	0.03	0.38	<0,05	<1	*<0,05*	2.3	58.8	0.04

Table 17. TCLP leaching test results of ofite and orujillo (as original fuel)

			TCLP leachates (mg/L)									
SAMPLES	**pH**	**As (ppb)**	**Zn**	**Pb**	**Cd**	**Ni**	**Cr**	**V**	**Cu**	**Ba**	**K**	**P**
OFITE	4.83	<1	0.08	<0,1	< 0,03	0.05	<0,05	<1,9	<0,05	0.7	1.3	0.32
ORUJILLO	4.96	25	0.3	0.16	0.03	0.43	*<0,05*	<1,9	0.15	3.2	100.0	100.00

4.3 Column tests

In some applications, the information provided by the column test EN 14405 is one of the references for the assessment of the plausible ash utilisation (DBMD). Thus, in this project, some of the ashes has been analysed under this approach. In particular, sewage sludge, demolition wood and orujillo ashes are included in **Table 18**. In addition, the fourth column of Table 18 displays the results from the column test of the orujillo fly-ashes used to make bricks.

Table 18. Column test results of some ashes

Leachate Column test (mg/kg)				
PARTNER	ECN	ECN	AICIA	AICIA
SAMPLES	AMER-CFB	Sewage sludge	Orujillo	Ash for bricks
pH	11.2	11.66	12.17	10.73
Al	14.3	171.24		
As	0.02	0	0.49	0.54
B	0.5	3.01		
Ba	127	1.26	6.05	1.1
Ca	5921	2875.82		
Cd	0	0	0.05	0.05
Cl	9713	305.32		
Co	0	0	0.28	0.06
Cr	0	0.04	0.05	0.26
Cu	0.05	0.65	1.61	1.17
Fe	0.02	0.16		
Hg			0.49	0.49
K	3100	69.49		
Li	0.25	0.17		
Mg	0.25	0.16		
Mn	0	0		
Mo	0.52	3.05	0.81	0.4
Na	1481	45.3		
Ni	0	0.01	1.34	0.1
P	0.08	0.12		
Pb	708.8	0.07	0.49	0.49
S	1096	8111.4		
Sb	0.25	0.14	0.1	0.1
Se	0.1	0.94	0.49	0.49
Si	37.5	270.8		
Sn	0	0	0.49	0.49
Sr	35.6	4.23		
Ti	0	0		
V	0.01	0	0.1	3.13
Zn	11.7	0.0465	3.52	8.16

5 Conclusions

In this report a thorough work focussed on the detailed characterisation on the ashes generated in the Gasash project has been presented. This has permitted to assist in selecting and further testing of the most promising utilisation routes and treatment options. From the results presented in this report the following can be concluded:

- Fly ashes from gasification of biomass and waste are very diverse in composition and behaviour resulting from the large variety in fuels and specific operational parameters
- Gasification fly and filter ashes show in general very high carbon content compared with combustion ashes.
- High chlorine and alkali contents are present in most ashes
- Heavy metals are present in high concentrations in waste-derived ashes (RDF, demolition wood and SRF).
- The existing utilization methods for coal combustion ashes can not be directly applied for gasification fly ashes.
- Gasification bottom ashes are similar to combustion bottom ashes so in principle, they should not present problems for their utilisation.

These results have allowed us to preliminary screen the existing utilisation options for combustion ashes (mainly from coal). The characterisation work presented in this report is based on raw ashes. Further results can be found in relevant reports, where a thorough characterisation work has been carried out on the ashes combined with other materials (clay in bricks, a binder such as lime in fire-resistance materials, etc), or after the original ashes have been submitted to a previous treatment (combustion, washing, etc).

Appendix G Deliverable 20 Report on the Influence of Optimised Ash Management of the Economy of the Gasification Process

DELIVERABLE REPORT No 20

CONTRACT N°:	ENK5-CT-2002-00635
PROJECT N°:	NNE5-2001-00598
ACRONYM:	GASASH
PROJECT TITLE:	Improvement of the economics of biomass/waste gasification by higher carbon conversion and advanced ash management
PROJECT CO-ORDINATOR:	VTT Processes
PARTNERS :	VTT Processes (VTT) Foster Wheeler Energia Oy (FWEOY) Energy Research Centre of the Netherlands (ECN) Asociación de Investigación y Cooperación Industrial de Andalucía (AICIA) Pohjolan Voima Oy (PVO) EMC Environment Engineering Limited (EMC) Essent Energie Productie b.v. (EEP)
PROJECT START DATE :	1 November 2002
DURATION:	36 months
Date of issue of this report :	November 2005

Project funded by the European Community under the 'EESD' Programme (1998-2002)

Executive summary

The cost of ash management is one of the largest cost items in the operation economy of a gasification plant if the ashes have to be landfilled. There is a considerable economical potential if a reliable and economically feasible method can be introduced for the ash management. Utilisation of the ashes offers at the same time also environmental benefits in replacing primary materials from the nature and by avoidance of landfilling.

Several potential methods were identified and developed for the management of gasification ashes at the Gasash-project. The most promising methods were tested and demonstrated in a laboratory or in a pilot scale and the designs of the best ones were up-scaled to an industrial scale. Those methods and ash management routes which fulfilled the operational and environmental criteria in up-scaled size were evaluated economically.

The properties of gasification ashes vary to a large degree depending on the gasification fuel and gasification conditions. Thus alternative ash management options are needed and the most suitable ones should be selected for each case. The complexity and operational cost of the methods vary widely. The simplest method is to burn the ash with the gasification gas if it is technically and environmentally possible. The other end of the scale is represented by oxygen flame smelting of ash containing chlorides and heavy metals. Several methods are available between these two for different ash qualities. The best method for each case is the one which fulfils the environmental and technical requirements at that case with the lowest cost. Usually the same method is the least demanding in operational features for the case. In general the basic selection of the method depends on the contaminants of the ash so that if the ash contains soluble chlorides and heavy metals a more complex method must be used whereas if the ash is relatively clean with high carbon content only the simple methods can be used.

The methods identified and developed for **relatively clean fly ashes** are in order of increasing cost and complexity:

- Use of the ash as fuel without treatment
- Use of the ash as fuel after granulation
- Combustion of the ash in an integrated fluid bed combustor and use of the product as secondary construction material
- Combustion of the ash in an integrated fluid bed combustor followed by granulation and use of the product as forest fertiliser
- Sintering of the ash to produce aggregate for construction purposes

The developed methods for **fly ashes with heavy metals and soluble contaminants** are in an increasing cost and complexity order:

- Washing out of the chlorides and use of the washed ash as fuel in a suitable furnace or incinerator
- Washing out of the chlorides and combustion of the ash in an integrated fluid bed combustor and use of the product as secondary construction material
- Washing out of the chlorides followed by sintering and use of the product as aggregate in construction

- Smelting of the ash in oxygen smelter and use of the product as aggregate in construction

Gasification bottom ashes can be utilised in most cases as secondary construction materials. Bottom ash from the gasification of solid recovered fuel contains a considerable amount of metals in metallic form. These metals can be recovered from the ash with relatively simple unit operations in such quantities that the operation is expected to have a positive cash flow.

The work done at the Gasash-project showed that there are alternatives for landfilling of gasification ashes. The majority of the technically feasible alternatives are economically more attractive than landfilling. The cost of landfilling is expected to increase within the EU-area and this is likely to improve the economical performance of the ash processing in the future. The results of the economical evaluation show that only smelting and combined washing and sintering of very contaminated ashes are expected to exceed landfilling cost of the same ashes at present. The increasing cost and limitations of landfilling are however likely to turn also these methods interesting in the future.

The work showed that ash management improvements can have a considerable effect on the economy of a gasification plant. In some cases a new environmentally and economically feasible ash management route is a prerequisite for construction of a gasification plant as special landfilling capacity may not be available.

Table of contents

1 Introduction and description of the project 4

2 Potential methods for the gasification ash treatment 6

2.1 Utilisation of the carbon containing fly ash as fuel in boilers and industrial furnaces 6

2.2 Production of secondary construction material by fluid bed combustion 7

2.3 Production of secondary construction material by combined washing and fluid bed combustion 10

2.4 Utilisation of oxidised biomass ash as fertiliser and soil improver 11

2.5 Production of aggregates by oxidising sintering 13

2.6 Production of aggregates by oxygen smelting 14

2.7 Metal recovery from SRF gasification bottom ash 17

3 The influence of optimised ash management methods on the economy of the gasification process 19

4 Conclusions 27

DELIVERABLE REPORT NUMBER 20

CONTRACT No: ENK5-CT-2002-00635
PROJECT No: NNE5- 2001-00598
ACRONYM: GASASH
DELIVERABLE TITLE: Report on the influence of optimised ash management on the economy of the gasification process

REPORT ON THE INFLUENCE OF OPTIMISED ASH MANAGEMENT ON THE ECONOMY OF THE GASIFICATION PROCESS

1 Introduction and description of the project

The overall objective of the Gasash-project has been to improve the economy of gasification of biomass and waste by developing sustainable and economical methods for utilisation and management of ashes. The project covers the ashes from atmospheric fluid bed gasification. Reduction of the ash volume and ash quality improvement was selected as the main targets of the project. Utilisation of the ashes was clearly preferred over landfilling as management option.

The development work of the Gasash-project has been concentrating on the following main topics:

- Development and optimisation of gasification and gas cleaning processes to reduce the ash volumes and to improve the ash quality
- Development of process improvements and new components that would reduce the ash volumes and/or improve the ash quality
- Development of ash utilisation methods and routes

Fluid bed gasification produces two types of ashes, fly ash and bottom ash. The management of fly ash is a challenging task because that ash type contains carbon and carbon compounds and in case of waste gasification also chlorides and heavy metals. The bottom ash is usually well oxidised fairly inert ash that contains only low amount of residual carbon. The chemical composition of the bottom ash is typically very close to the combustion ash of the similar fuel.

The work concentrated mainly on the fly ashes because the cost of the fly ash management is an important factor in the gasification plant economy. Gasification bottom ashes can normally be managed in the same way as combustion ashes. A method to recover metal material was also developed for bottom ash management.

The project composed of the following main tasks which were grouped into work packages and were elaborated by the project partners in co-operation.

- Selection of fuels and review of existing ash utilisation methods
- Optimisation of operation parameters

- Characterisation of ashes from different fuels
- Development of ash treatment methods
- Development of technical components
- Development of ash utilisation routes
- Technical and environmental evaluation and up-scaling of the methods and utilisation routes
- Economical evaluation of the methods and utilisation routes

The work consisted of:

- Compiling and evaluation of the existing data on the possible ash management and treatment methods and utilisation routes
- Development of possible alternatives for new utilisation routes and treatment methods
- Laboratory tests of the developed methods:
  - Granulation
  - Solidification
  - Fluid bed combustion
  - Oxidising sintering of ashes
  - Oxidising smelting of ashes
  - Ash washing
  - Bottom ash metal recovery
- Development of new technical components for the new treatment processes
- Testing of the new components and application of existing components and unit operations in a pilot scale for the following processes:
  - Cooling arrangements and ash separation
  - Bubbling fluid bed combustion (BFB) equipment
  - Circulating fluid bed combustion (CFB) equipment
  - Auxiliary components for fluid bed combustion (feeding, control and ash separation components)
  - Integration of fluid bed combustion into gasification process
  - Granulation
  - Ash washing
- Characterisation of the ashes and utilisation products from the various tests with the developed processes
- Evaluation of the methods and selection of the technically and environmentally acceptable ones for further work
- Up-scaling of the designs of the technically and environmentally feasible methods into an industrial scale
- Technical and environmental evaluation of the up-scaled methods
- Economical evaluation of the technically and environmentally feasible methods
- Evaluation of the impact of optimised ash management on the economy of gasification process and energy production utilising gasification of biomass and waste

This report presents the estimated impacts of the developed methods and management routes on the economy of gasification process. The technical solutions and management routes are described briefly in this report only to introduce them. The detailed results of the development work, analysis, tests and evaluations have been described in the relevant reports.

2 Potential methods for the gasification ash treatment

Based on the evaluations the following ash management methods were considered to be technically and environmentally feasible:

2.1 Utilisation of the carbon containing fly ash as fuel in boilers and industrial furnaces

The carbon content of the gasification fly ashes is at most cases high enough to provide heating values of the same range as the heating values of dry wood or forest residues. In many cases the carbon content of biomass gasification fly ash is in the area of 40 to 60 % resulting in the heat values (LHV) of 13 to 18 MJ/kg. The waste gasification fly ashes contain somewhat lower amounts of carbon, but can still well be considered to be fuels in respect of heat values.

The simplest way to utilise the energy content of the fly as is to leave it in the gas and burn it with the gas. This method is technically possible when the ash is derived from fuels that produce relatively clean ashes and the gas is burned in a coal or biomass boiler. This method is not possible if the gas-ash mixture contains considerable amounts of chlorides or heavy metals because of corrosion risk and environmental reasons.

If the ash is separated, as the case is in many applications, it can be utilised by firing in a separate boiler or by co-firing with some other fuel. In case of normal boilers the co-firing is also restricted from technical and environmental point of view to ashes from relatively clean fuels only. However, waste gasification ashes could be fired in the similar way at waste incinerators or process furnaces equipped and licensed for contaminated fuels. Handling of carbon containing dry ashes requires special technique and skill because these ashes are of very fine particle size and can easily mix with air to form explosive mixtures. Therefore it is in some applications beneficial to granulate the ash for easier handing and feeding.

When gasification fly ash is used as fuel the inorganic content of the ash is oxidised and carbon and organic compounds are burned off with the efficiency provided by the boiler. According to the present interpretation ashes are considered in the EU-legislation as waste and ashes from waste incineration and waste gasification are considered to be hazardous waste. This means that boilers and furnaces utilising ashes must be licensed for firing of waste or hazardous waste. The basic assumption in legislation is that the ashes from the utilisation of ashes are hazardous waste. This leads to a need to prove the utilisation of these ashes safe case by case. These interpretations and requirements work strongly against the use of the gasification ashes as fuels in boilers in general. At present the implementation and national interpretation of the directives governing the utilisation

of by-products and waste derived materials vary from country to country. The same is valid also for national implementation of the waste incineration directive and requirements for co-firing of waste materials.

Combustion of gasification ashes is an interesting alternative to utilise the energy content of the ashes and to improve the ash quality for further applications. In principle all techniques, grate, pulverised or fluid bed firing are possible for combustion of high carbon ashes. Grate firing however requires always an additional step of granulation prior the firing. In the Gasash-project the work concentrated on fluid bed firing as the other methods were not expected to offer advantages over it.

As mentioned the licensing requirements for ash firing units are tight and set very strict requirements for the flue gas cleaning and firing conditions. These become easily the key design parameters for the possible firing units.

Good quality gasification ashes can be used as fuel in cement kilns, smelters and other process furnaces. However also this is covered tightly in licensing.

Ashes from waste gasification contain typically too high amounts of chlorides and heavy metals and can be fired only at properly designed incinerators. Washing out of the chlorides from the ash before firing is considered to be a technically and environmentally feasible method to improve the properties of the ash so that it can be utilised as co-firing fuel at suitable kilns, furnaces and boilers.

It was shown at the tests performed in the Gasash-project that a water wash at right conditions can effectively lower the amount of chlorides of the ash with only a minimum leaching of heavy metals and organic material into the water. This is very important for the management of the washing liquid. The firing of washed ash, although it contains heavy metals is technically and environmentally possible in some kilns or smelter applications where large amounts of chlorides cannot be accepted. Also fluid bed firing and especially integration of fluid bed firing into a gasification– gas cleaning process is easier when the chloride content of the ash is first lowered.

2.2 Production of secondary construction material by fluid bed combustion

Secondary construction material means in this context a material that can be utilised in the secondary structures of roads, embankments and landscaping. Examples of these structures are noise abatement banks, side support embankments of junctions, light traffic pathways and landscaping of reclaimed areas for parks and parking places. These are structures where the good load bearing capacity of aggregate is not absolutely necessary and lower grade stable material produced from ash could be used in large scale. Environmental safety of the material is of prime importance also at these applications and it must be secured at most cases with pre-treatment of the ash.

At present the acceptance of recovered materials for construction is based on specific regulations only in Denmark[1] and in The Netherlands[2]. In the other EU-countries the acceptance criteria are based in general environmental and safety legislation[3]. There is legislation work ongoing at finalisation phase in Finland for a binding regulation concerning utilisation of recovered materials in the ground construction. The final text version of the proposed regulation[4] was published in June 2005 for discussion. The proposed criteria in the draft regulation are based on the criteria for inert waste as stipulated in the directive 1999/31/EY on the acceptance of waste material to landfill. The structure of the proposed regulation is such that it determinates the general procedures and general property criteria for acceptance of waste to be used in ground construction work. Individual criteria for specific waste types (like crushed concrete or PC boiler fly ash) are set through testing and acceptance procedures including environmental safety assessment as described in the regulations. At present there are ready criteria for the use of the following waste materials in ground construction:

- Crushed concrete
- Coal ashes
- Peat ashes
- Ashes from the combustion of clean wood and biomass

The acceptance criteria are in general in line with the criteria for inert waste in the directive 1999/31/EY with tighter values for cadmium and vanadium. The criteria are also generally in line with the present Dutch Building Material Decree but are tighter at the leaching of some heavy metals. The Finnish draft sets the criteria for total organic carbon content at 3 % and a tight LS 10 chloride leaching limit of 800 mg/kg in general and 2 400 mg/kg for structures protected from rainfall.

In case of gasification ashes the criteria requirements can only be met if organic compounds and carbon are removed from the ash and chlorides as well as other easily soluble components are stabilised or removed.

According to the view based on the work done in the Gasash-project the criteria can be fulfilled by the following ways:

- For fly ash from clean biomass gasification
  → **Oxidising** to burn off the residual carbon and organic compounds.
- For fly ash from gasification of contaminated biomass
  → **Oxidising** to burn off the residual carbon and organic compounds and to evaporate chlorine and low boiling metal compounds.

At oxidising the carbon and carbon containing compounds of the ashes are burned and the solubility of the ash is lowered at the same time as possible chloride salts are

[1] Regulation 655/2000 (Denmark)
[2] Building Material Decree 1999 (The Netherlands)
[3] Background memorandum for bill (proposed legislation) concerning the utilisation of certain waste materials in ground construction, Ministry of Environment of Finland 7.7.2005
[4] A draft proposal for regulations concerning the utilisation of certain waste materials in ground construction work, Ministry of Environment of Finland, 7.7.2005

decomposed and chlorine evaporates from the ash. The chemical state of the ash is turned at the process from reduced to oxidised.

The technical feasibility of fluid bed combustion for oxidising of gasification ashes was tested at the Gasash-project and the results indicate that this route could offer a very potential alternative for ash management. According to the results oxidising can be done very efficiently in a fluid bed reactor. The technical feasibility of a bubbling fluid bed reactor (BFB) and circulating fluid bed reactor (CFB) was demonstrated in pilot scale in the Gasash-project. Both methods performed well with all tested gasification fly ashes. CFB design results in smaller size equipment that BFB. The general principle of fluid bed combustion of gasification ashes is shown in the figure 1.

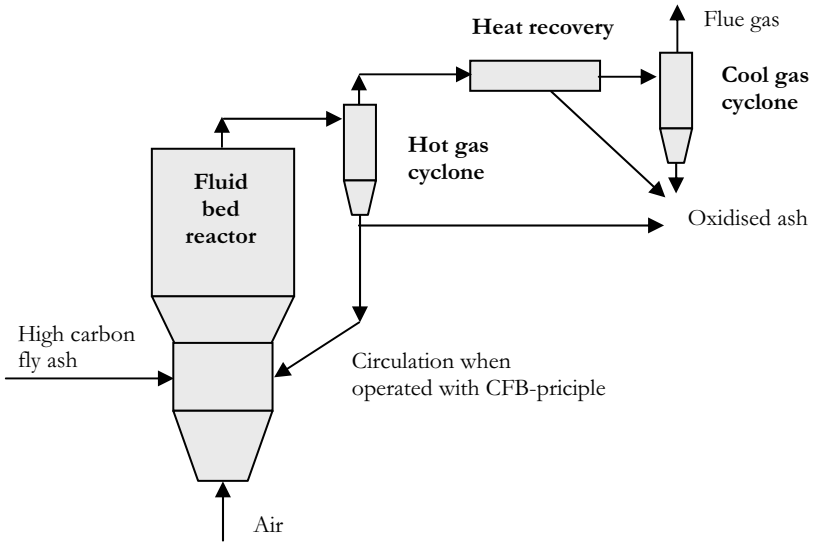


Figure 1. General principle of fluid bed combustion of gasification ashes.

Typical carbons contents of gasification ashes are high enough for stable operation of the process without support fuels. The feeding of the ash into the reactor needs to be designed carefully to enable good control of the feed because the ash is very light and of fine particle size.

Both designs need ash separation and flue gas cleaning systems that depend on the composition of the feed ash. In case of chlorine and heavy metal containing feed a full dry flue gas treatment process with fabric filter and injection of sorbent and activated carbon is anticipated to meet the emission limits.

Oxidising process could be integrated into a gasification plant so that the flue gases from the oxidiser are fed into the gasifier after ash separation. This provides a compact solution where a separate flue gas cleaning unit is eliminated as the oxidiser flue gases are used as one feed stream of the gasifier and the gasifier gas cleaning process handles also the oxidiser flue gases. The technical operation of this principle was demonstrated in pilot scale in the Gasash-project.

The combustion ash is expected to meet the requirements for secondary construction materials provided that the ash separation is done in a temperature zone where possible chlorides are in vapour phase. This must however be confirmed by testing for each type of gasification ash because the compositions of ashes vary to a large degree depending on the original fuel.

2.3 Production of secondary construction material by combined washing and fluid bed combustion

Production of secondary construction material from gasification ashes with oxidising fluid bed combustion is considered to be a technically feasible method for management of gasification fly ashes. If the ash contains large amounts of chlorides the cleaning of the combustion flue gases becomes however a major issue and the amount of flue gas cleaning product increases. This lowers the environmental feasibility of the process as there will be a need for further treatment of a relatively large amount of chlorine containing material. The integration of ash combustion process into a gasification process is also a challenge in case of high chloride ash because of a risk of chlorides concentrating into the integrated gasification – gas cleaning – ash combustion loop.

Possibilities to remove the chlorides from the gasification ash or lower the chloride content considerably before combustion were studied in the Gasash-project to find a solution to these questions. Based on this an ash washing method was developed and tested with good results first in a laboratory scale and then at pilot-scale test runs.

Chlorine present in the waste gasification fly ashes originate usually from a variety of materials in the gasification feed. Typical sources of chlorine are PVC-plastics and common salt NaCl in the waste derived fuel. Chlorine is present in the gasification ashes mostly in the form of chlorides of alkaline or alkaline-earth metals, for example $CaCl_2$, KCl and NaCl. These are very soluble in water and cause high solubility of the ash. The solubility of these compounds can actively be utilised in ash management and large amount of chlorides can be removed from the ash with water wash. At an optimum pH and temperature and with short washing time the solubilities of other components are relatively low.

Based on the results achieved at the Gasash-project and related studies an industrial ash washing process was designed. It could consist of a slurry preparation followed by a cascade washing in filtering unit where the liquid is separated from the solid material.

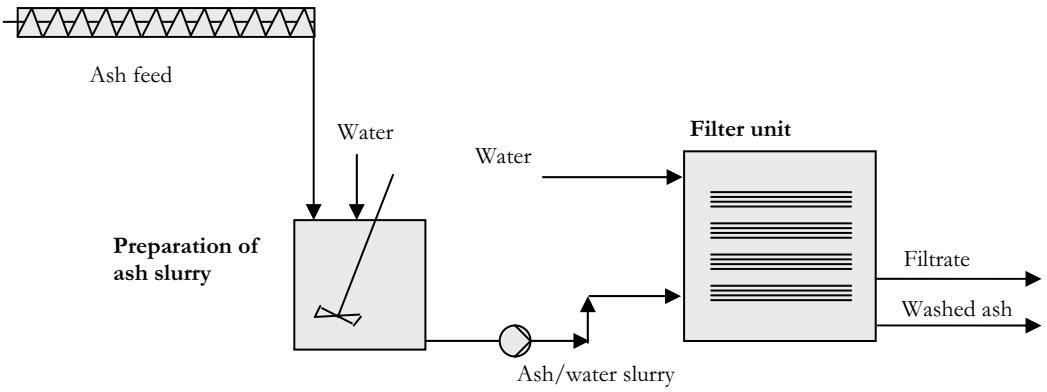


Figure 2. A general diagram of an ash washing process.

The main chemical composition of the filtrate is close to saline water and its disposal is not expected to be a major issue. One potential utilisation application for washing filtrate is a power plant flue gas desulphurising process where it could be used as process water and as a source of chlorides.

Washing is a technically potential treatment method to reduce chloride content and solubility of fly ashes from the gasification of contaminated biomass and waste derived fuels. It's estimated to provide main benefit at preparation of fuel from a high carbon ash containing chlorides.

Washed ash can be oxidised in a fluid bed combustor to produce inert construction material that can be utilised in the secondary structures of roads, embankments and landscaping as described earlier. The technical feasibility of this method was preliminary demonstrated at the tests performed in the Gasash-project.

2.4 Utilisation of oxidised biomass ash as fertiliser and soil improver

Ashes from the combustion of biomass contain minerals in relatively good proportion for forest cultivation. There is enough phosphor and potassium in wood ash for a fertiliser effect although the solubility of phosphor is low. Nitrogen content of any ash is usually negligible for fertilising purposes. The soil pH can be increased with biomass ash through the liming effect caused mainly by Ca- and K-oxides. This improves the availability of nutrients to plants. Many important trace elements like Mg, Co and B are also present in biomass ashes. Direct application of biomass gasification ashes as fertilisers is however not a feasible option because of the high carbon and PAH content. However many gasification ashes with low heavy metal content could be processed for forest cultivation. This can be done by oxidising the ash to minimise the carbon content and to destroy the PAH-compounds. This oxidises the minerals and there is also some indication that the solubility of potassium increases at oxidisation.

Utilisation of oxidised clean biomass gasification ashes as fertilisers and soil improvers in forest and parkland areas is considered to be a feasible ash management option. The ash

can be oxidised in a fluid bed combustion process as described earlier. In practice there is usually a need to granulate the ashes for easier handling. Granulation also restricts the quick first phase fertiliser and alkalisation effect that takes place if the ash is spread in powder form. Granulated ash has a smooth long term fertilisation effect with less leaching of nutrients into the natural waters than form powder ash. Granulation is necessary in many cases also for practical appearance of fertilising. If that large amount of ash would be used in powder form it would turn the fertilised area grey and "dirty looking" for some time. The amount of ash needed for a real fertiliser effect is 5 to 10 times of the amount of present commercial fertilisers.

Oxidised biomass gasification ashes are considered to suit best for marshland forests where the soil contains only sparsely potassium and low pH results in low phosphor availability.

The contents of nutrients and heavy metals in the fertilisers used in the food production chain in farming and gardening are tightly controlled by legislation in most EU-countries. The low nutrient values of the ashes make the nutrient/contaminant relation of the ashes low and the possibilities to meet the requirements with gasification ash based fertilisers are considered minimal.

Some biomasses contain cadmium is such high level that its concentration in the ash and oxidised ash may cause concern also in forest fertiliser use. Fir bark, willow and straw from some regions are examples of this type of biomasses. Ash fertilising of forest however raises the soil pH and this lowers the solubility of cadmium as shown in a study made by Pasanen et.al.[5].

Ashes from gasification of contaminated biomass and waste are not feasible for fertiliser use because of the heavy metals that are present in the ash even after washing and oxidisation.

Fly ash from gasification of animal waste like meat and bone meal (MBM) contain large amount of phosphor and this makes the fertiliser use of this special material an attractive option.

At present the regulations for fertilisers and possible acceptance of ash fertilising vary between the EU-countries. The requirements are however likely to be harmonised but still there is a clear need to take the local conditions and soil properties into account when ash fertilising is considered.

[5] Cadmium in Wood Ash Used as Fertiliser in Forestry: Risks to Environment and Human Health; J. Pasanen, K. Louekari, J. Malm, Ministry of Agriculture and Forestry, Finland, Publications 5/2001

2.5 Production of aggregates by oxidising sintering

Use of ashes to substitute natural aggregates would offer an utilisation route for large volumes of ash. This would be desirable from economical and ecological point of view as it could reduce excavation of large amounts of natural gravel, sand and rock.

Oxidising sintering is used commercially to sinter carbon containing coal fly ash. The process produces good quality aggregate for construction use. This is a well established industrial method used in England. The same principle could be applied for gasification fly ash provided that variation of the ash composition is not too large. The carbon content of the ash should be quite constant to keep the sintering temperature in the right range. Ash must be granulated prior sintering and if needed the carbon content could be controlled at the granulation to a desired level by addition of low carbon ash into the mix when needed.

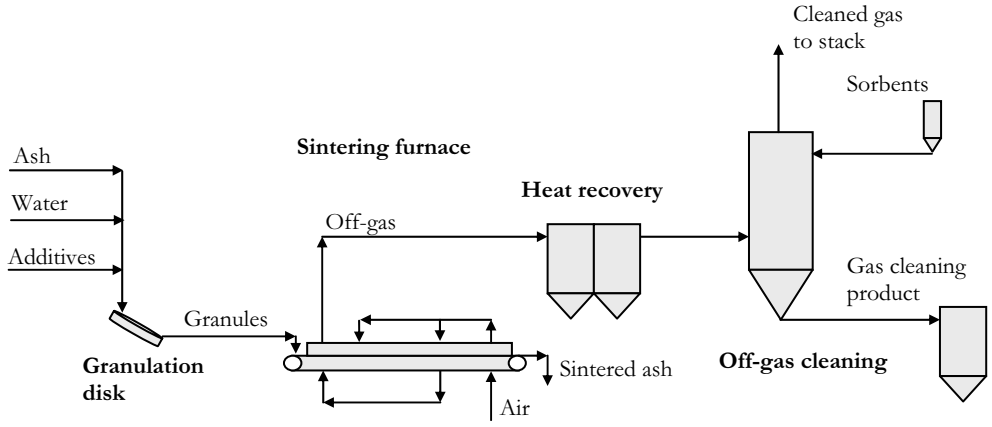


Figure 3. General diagram of oxidising sintering of gasification fly ash.

At industrial scale the sintering unit would be a long conveyor type gate furnace on which the ash is fed as a layer. The gate transfers the material into an ignition section of the furnace where it is heated by auxiliary burners to ignition temperature. After that the grate movement transfers the ash into a sintering section where the carbon of the ash burns and heats the material to sintering temperature. As mentioned the ash must be granulated before feeding into the furnace so that a porous stable layer can be formed on the grate.

Sintering of the gasification fly ashes was tested at the Gasash-project at a laboratory scale. At one test series the ash was granulated prior sintering and active oxidising by light air blow through the granulate layer was used. The ash was not granulated at the other test and it was sintered in a bowl at a laboratory oven. The leachability of harmful compounds from the sintrate samples was tested and found to be low enough to fulfil the Dutch criteria for construction materials at the both test cases.

The handling of the process off-gases is a demanding task at this method, especially if the gasification ash contains chlorine compounds. Waste gasification fly ashes need to be washed prior sintering to reduce the chloride content. A likely flue gas handling method is a dry gas cleaning with fabric filter and sorbent injection. This needs however confirmation by further testing.

2.6 Production of aggregates by oxygen smelting

Many types of smelting processes have been developed in the steel industry to manage the metal containing dusts from blast furnaces, converters and electric arch smelters. The temperatures reached at these processes are high enough to smelt the metal/metal oxide ashes into liquid state. Some metal compounds end into the process off-gases and can be recovered at the gas cooling. In some cases metals are recovered also from the molten liquid. Oil, gases, coal, coke or waste plastics are used as fuels at these processes. Many processes use oxygen instead of air.

Several of these methods could be used for smelting gasification ashes. Gasification ashes contain enough unburned carbon to provide the energy needed to smelt the ash with a need of additional fuel only at ignition phase. In many cases the amount of carbon and carbon compounds in the gasification ash is so high that the ash can be diluted with some lower heating value material especially if the process uses oxygen. According to the tests done at the Gasash-project the melting points of waste gasification ashes vary from 1150 °C to 1400 °C. The large variation is caused by the differences in the composition of gasification fuels and bed materials. This clearly emphases the necessity of individual adaptation of the method for each case.

The organic compounds are effectively decomposed and oxidised at ash melting temperatures in the presence of oxygen. Also Cl- and F-compounds decompose in practice well at these temperatures.

Oxidising smelting could offer a route to produce aggregates from gasification ashes. It could be mainly considered as an option to manage fly ashes from the gasification of contaminated biomass and waste. Technical complexity and high cost make it unlikely for treatment of clean ashes.

The smelting could be done at lower temperature if the ash is mixed with a suitable lower melting point material like crushed waste glass. In this case some components of the ash form lower melting eutectic compounds with glass material and some are encapsulated within the molten mass.

The flue gas treatment of ash smelting processes requires special designs because the flue gases contain dust and partly molten droplets. The surface of these droplets could be solid and covered with dust while the inside is still molten. When a droplet collides on a surface of a duct or heat exchanger pipe it breaks and the molten material solidifies on the cooler surface forming deposits. Also chemical reactions take place on the cooling

phases of the gas-dust mixture and cause some materials to solidify on the equipment surfaces.

The smelting was tested in the Gasash-project both in a laboratory and in a pilot scale. A complete melting of fly ash from the gasification of contaminated biomass was achieved at the pilot scale tests and basalt type solid material was produced. The leachability of heavy metals from that material was low and complied to the Dutch regulations for utilisation of secondary construction products. Detailed results are described in the relevant reports.

At smelting the volatile metal compounds and chlorides end up into the smelter off-gas. The emission limit requirements for ash smelter off-gas are expected to be according to the waste incineration directive 2006/76/EY. A dry gas cleaning process with sorbents is likely to meet the requirements this but needs confirmation by further testing.

At present there are several techniques for smelting. The following two were selected as examples of potential industrial scale techniques for oxidising smelting of the ashes:

- A slagging cyclone combustor[6]
- A slagging bowl-type oxygen flame combustor[7]

They both are oxidising methods and developed to smelt metallurgical dusts. The temperatures reached at these processes are high enough to smelt gasification ash completely and both are likely to offer good burn-out of the carbon and an effective evaporation of the chlorine compounds.

[6] Kawasaki horizontal swirl combustion-process, Kawasaki Heavy Industries and Commercialisation of MSW Incineration System with Direct Ash Melting by Thermal Cracking for High Efficient Generation of Electricity, Terasava et.al., Mitsubishi Heavy Industries, Ltd. Technical Review Vol. 38 No. 2 (June 2001)

[7] Daido DSM-process, Daido Steel Co., Japan

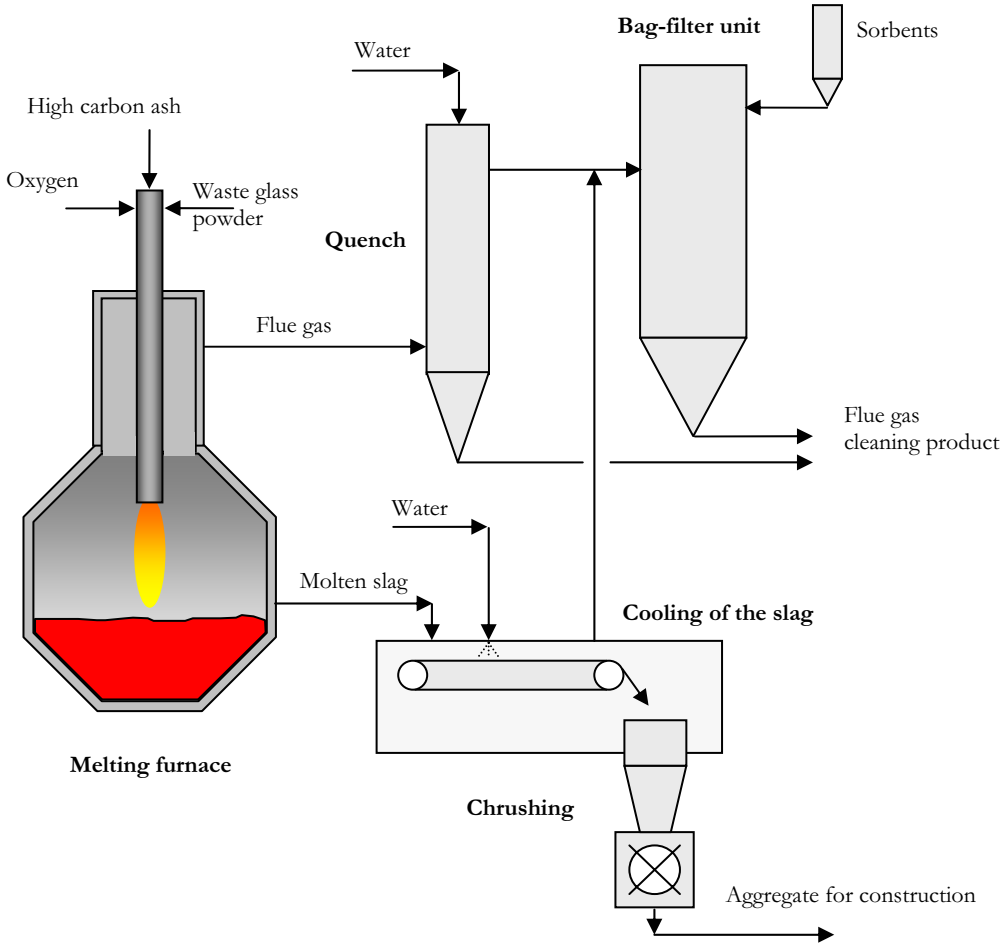


Figure 4. Conceptual process design of an oxygen flame smelting of gasification fly ash.

The bowl-type oxygen flame smelting process is considered to suit better for waste gasification fly ashes than swirling flow smelting because the ash stays longer in molten phase and this ensures more complete decomposition and evaporation of chlorine compounds. The importance of slag delay time for chlorine evaporation has also been reported by Kesselring[8] for salt containing ashes in connection of the tests with Deglor-process.

Based on the above the oxygen flame smelting process was selected to be the basis for up-scaling and further evaluations.

A bowl type oxygen flame smelter-process consists of an arrangement where dust and fuel is fed pneumatically into an oxygen burner and the slag is collected in a bowl or ladle under the burner. The smelting takes place mainly in the burner flame but continues also in the bath of molten slag in the bowl heated by the flame radiation. Japanese Daido

[8] Thermische Rückstandsbehandlung zur Überfürung in glasartige Rest- und Wertstoffe; Kesselring Paul, Short project descriptions of the Swiss Priority Programme Environment 1992-1995, www.sppe.ch/kurzfassungen/pdf/waste_p1/kesselring_6_16.pdf (30.6.2005)

Steel Co.[9] has developed this type of a process for smelting metallurgical dusts and it is in commercial use in Japan to smelt metallurgical dusts.

Based on the tests and up-scaling the oxidising smelting of high carbon gasification fly ash together with waste glass in an oxygen flame smelter is one technically potential alternative to produce synthetic aggregate for construction use. It must however be noted that the operation and maintenance of smelting processes is demanding and not typical for power or gasification plants.

2.7 Metal recovery from SRF gasification bottom ash

The bottom ashes from the gasification of solid recovered fuels contain considerable amount of metals in metal form. These metals originate from the items and metal scrap in the waste from which the SRF is produced. The typical SRF production processes include metal recovery operations like magnetic separation of ferrous metals and eddy current and gravity separation units for non-ferrous metals. These units remove and recover bulky scrap metal and also most part of the smaller metal items. Careful removal of metals is essential for SRF production so that the fuel can be handled properly in conveyors and feeders. It is also very important that there are no large metal particles in the fuel that would block the ash removal systems of boilers or gasifiers. In spite of metal removal and recovery at the solid recovered fuel production facilities there is quite some amount of small metal items and particles left in typical SRF.

The metal material concentrates at the gasification process into the bottom ash mostly in non-oxidised metal form. The amounts and distribution of metallic metals in the SRF gasification bottom ash were analysed in connection with the Gasash-project. The ash samples analysed in connection with the Gasash-project were from the gasification of SRF produced from domestic dry waste collected in Southern Finland.

The analysis made showed that there where the following average amounts of metals in metallic form in the coarse fraction (> 1,5 mm) of the SRF gasification bottom ash:

- Ferrous metals 5 – 10 %
- Copper and copper alloys 5 – 10 %
- Stainless steels 3 – 8 %

The samples contained also some smaller, but very much varying amounts of aluminium in metal form. The total amount of coarse fraction of bottom ash is estimated to be in the range of 1 to 2 % of the amount of SRF feed of the gasifier.

At an industrial application the bottom ash flow could be split into coarse and fine fractions by sieving and the fine fraction could be recycled back to the gasifier as part of the bed material feed.

[9] Daido Steel co.; http://www.daido.co.jp/english/products/engineering/engineering_dsm.html (30.6.2005)

The process could consist of a magnetic separation unit followed by a density-gravity-classifier. A possible general arrangement of metal recovery is shown in the figure 5.

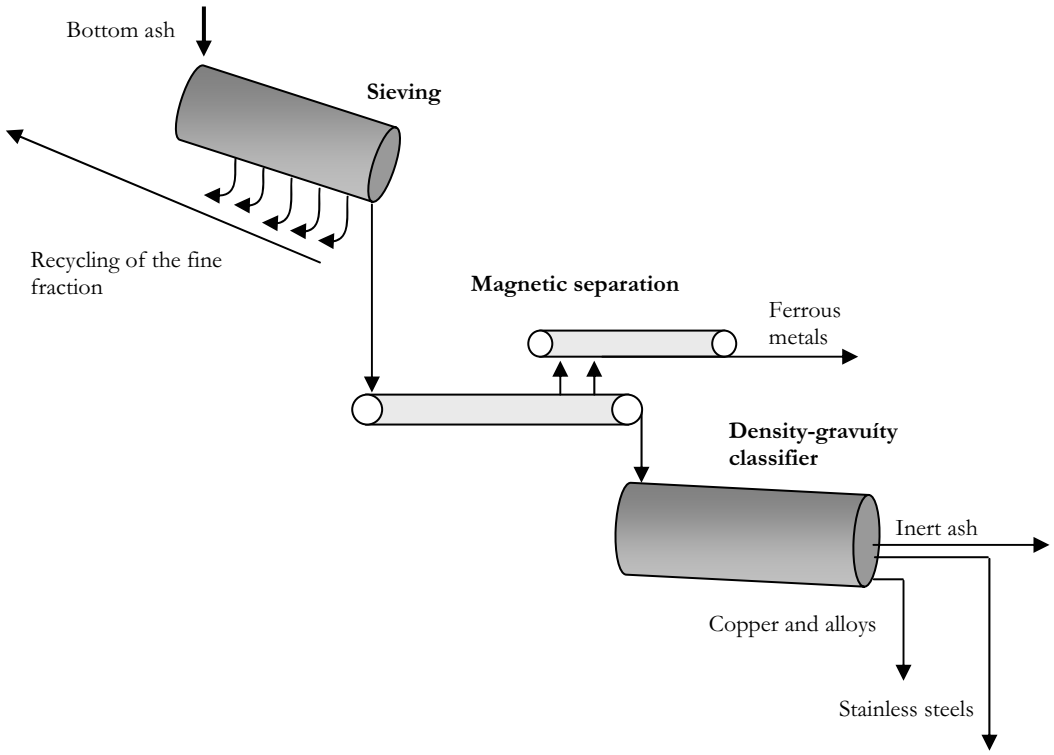


Figure 5. Main process steps in the recovery of metals from the SRF gasification bottom ash.

The recovery of metals from SRF gasification bottom ash is considered to be a technically feasible method which has the following benefits:

- Valuable resources are recovered
- The process is considered to be relatively straightforward and it utilises commercial unit operations
- It both reduces the amount of ash and improves its properties at the same time
- The process has no effluents or emissions

The properties of the residual ash fraction of the metal recovery need to be confirmed case by case because of the large variation according to the SRF type and quality. It is likely that in some cases the residual fraction can be utilised as secondary construction material.

3 The influence of optimised ash management methods on the economy of the gasification process

The methods and ash management routes which were found to be feasible at the technical, operational and environmental analysis were selected for economical analysis. The purpose of this analysis was to compare the economical performance of the methods and especially evaluate their impact on the overall production economy of gasification plants and power production utilising atmospheric fluid bed gasification.

Combinations of the methods were also evaluated as in many cases they are likely to provide desired feasible routes to manage gasification ashes.

The basic criteria of the selection were the operational feasibility of the methods. It means in this context functionality and scalability of the methods as well as the environmental performance. The methods which were evaluated to convert the gasification ash into an acceptable product or raw material or utilise the energy content of the ash were considered to meet the required functionality. The possibility to utilise the method technically in an industrial scale was used as the criteria for scalability. The present and known future regulations for emissions and safety were used when evaluating the environmental performance. These regulations contained the directives for waste incineration and landfilling and the regulations for occupational health and safety as well as present and anticipated future building material requirements.

The following ash management methods and routes were selected for economical analysis:

- **Use of fly ash as fuel** in boilers and process furnaces
- **Granulation** to improve the ash properties for further processing or utilisation as fuel
- **Washing** to improve the ash properties for further processing or utilisation as fuel
- **Fluid bed combustion** to recover the energy content of ash and to improve the ash properties
- **Integrated fluid bed oxidation** to recover the energy content of ash and to improve the ash properties
- Production of aggregate with **oxidising sintering process**
- Production of aggregate with **oxygen smelting process**
- **Fertiliser and soil improvement** use of clean ash
- **Metal recovery** from bottom ash of SRF gasification

The ash production amounts of 1 500 t/hour for fly ash and 250 t/hour for bottom ash (after 75 % internal circulation) were selected as the basis of economical evaluations. These capacities were estimated to be relevant for an anticipated industrial gasification

plant with fuel capacity of 80 MW. Smaller scale methods can offer feasible solutions at individual cases but in general a quite large capacity is needed for economical operation.

The process designs, flow diagrams and principles presented in the earlier chapters of this report were used as the technical basis of the economical evaluations. In many cases the design phase included discussions with manufacturers of the similar type of equipment and adaptation of the present designs for the specific purposes. Based on this the cost estimates were made for the equipment, structures and buildings as well as for automation, instrumentation, electrification and for other systems, engineering and management. Budget quotes were asked for the key components. Estimates for equipment and systems were then compiled into total investment cost estimates.

Estimates for variable operational and fixed operational costs were also prepared.

Budgetary quotes were asked for special cost items like sodium bicarbonate, granulation additives etc. to confirm the cost level. Power consumption estimates are based on the preliminary design and yearly operation time. Manpower cost estimate was based on the average manpower cost at power stations in Finland.

Variable operation cost includes also the management of the flue gas treatment products and other residues in the cases where such are unavoidable. At the cases where there is a positive cash flow from the sale of the product the expected product price was estimated by a comparison with equivalent product manufactured of primary raw materials. All cost estimates and prices are in 2005 cost level without future inflatory escalations.

The yearly operation time of the ash production and the relevant ash management capacity was assumed to be 5 500 hours. This yields with the previous assumptions to a yearly capacity of 8 250 tonnes of fly ash and 1 375 tonnes of bottom ash. The unit cost of ash management was based on these capacities.

The effect of the alternative ash management methods on the production cost of gasification gas was calculated assuming a 15 year operation and lifetime for gasification and ash management. The effect of the potential methods on the production cost of electricity was also calculated using a 15 year period of operation.

The accuracy of the process values and cost estimates vary as is natural at this phase of technology development. There is also some variation of the technical basis of the methods. At the most advanced cases the technological solutions are based on successful pilot scale tests. Because of the uncertainty the estimated production costs figures represent expected mean values rather than exact figures and must be used with caution. To describe this most figures are presented with a ± 25 % range.

The following table summarises the estimated ash handling costs of different methods. The table should be read to show the relative differences of the methods for evaluation of the usefulness of different method rather than giving exact economical performance figures.

Table 1. Estimates of the ash management cost levels with alternative methods and routes for fly ash.

Treatment method/route **Fly ashes**	**Ash management cost; eur/t** Low – Mean – High	**Products of the method**
Landfilling at a special site, 0-case	150	None
Use as fuel without treatment	0	Low grade fuel
Granulation and use as fuel	17....24....31	Low grade fuel
Washing and use as fuel	14....20....29	Low grade fuel
Combustion of clean ash in integrated CFB, use as construction material	21....29....39	Secondary construction material + energy
Combustion of clean ash in integrated CFB + granulation, use as forest fertiliser	38…53…70	Low grade fertiliser + energy
Combustion of clean ash in integrated BFB, use as construction material	28....40....55	Secondary construction material + energy
Washing + combustion in integrated CFB, use as construction material	35…49…68	Secondary construction material + energy
Combustion of clean ash in stand-alone CFB, use as construction material	22....31....42	Secondary construction material + energy
Combustion of contaminated ash in stand-alone CFB, use as construction material	38....54....72	Secondary construction material + energy
Combustion of clean ash in stand-alone BFB, use as construction material	29....43....58	Secondary construction material + energy
Combustion of contaminated ash in stand-alone BFB, use as construction material	45....65....89	Secondary construction material + energy
Oxidising sintering of clean ash, use as aggregate	34....61....94	Aggregate
Oxidising sintering of contaminated low chloride ash, use as aggregate	79....130....179	Aggregate
Washing + oxidising sintering of contaminated ash, use as aggregate	93…150…208	Aggregate

Oxidising smelting, use as aggregate	203....274....351	Aggregate

Table 2. Estimates of the ash management cost levels with alternative methods and routes for bottom ash

Treatment method/route **SRF gasification bottom ash**	**Ash management cost; eur/t** Low – Mean – High	**Products of the method**
Basic case, landfilling	50	None
Use as construction material without treatment	0	Low grade construction material
Metal recovery + landfilling	-175…-93...-8 (profit per ton of ash)	Metals

The methods are estimated to have the effects shown in the tables 3 and 4 on the production cost of gasification gas. The mean values of the estimated ash handling costs of different methods and routes have been used as calculation bases.

It should be noted that the ash handling cost is a relatively large cost item if the ash has to be landfilled in a special landfil. The ash management cost of an industrial scale gasifier is with the assumed landfilling cost levels of 150 eur/t for fly ash and 50 eur/t for bottom ash about 1,3 Meur/year. This is clearly a major cost item for a gasifier plant. However it is not always only a cost question, but in some cases there is no possibility to deposit large amount of ash in special landfills as there may not be landfill capacity available.

The estimated effect of the improvement of carbon conversion has also been shown in the table 3. It has been assumed that the improvement could be achieved through optimisation of the gasifier operating parameters with no additional cost. This may not be fully realistic but shows the magnitude of cost benefit related with that item.

Table 3. Estimates of the economical impact of different fly ash management methods on the cost of gas.

Ash management route	**Ash management cost**	**Economical impact on production cost of gas**	
		Clean fuel	Contaminated fuel
Alternatives for fly ash	eur/t (ash)	eur/MWh(gas)	eur/MWh (gas)
Basic case, special landfill	150	0,0	0
Use as fuel	0	-3,0	not relevant
Granulation + use as fuel	24	-2,5	not relevant
Washing + use as fuel	20	not relevant	-2,7
Combustion in integrated CFB	29	-2,4	not relevant
Combustion in integrated CFB + granulation + use as fertiliser	53	-1,9	not relevant
Combustion in integrated BFB + use in construction	40	-2,2	not relevant
Washing+integrated CFB + use in construction	49	not relevant	-2,1
Combustion of relatively clean ash in a stand alone CFB + use in construction	31	-2,3	not relevant
Combustion of Cl-containing ash in a stand alone CFB + use in construction	54	not relevant	-2,0
Combustion of relatively clean ash in a stand alone BFB + use in construction	43	-2,1	not relevant
Combustion of Cl-containing ash in a stand alone BFB + use in construction	65	not relevant	-1,8
Sintering of biomass ash + using as aggregate	61	-1,8	not relevant
Sintering of low chloride SRF ash + use as aggregate	130	not relevant	-0,4
Washing + sintering of high chloride SRF ash + use as aggregate	150	not relevant	0,0
Oxygen smelting of ash + use as aggregate	274	not relevant	+2,6
Improvement of carbon conversion without additional cost (optimisation of oper. Parameters)			
- ash C-content 50 % → 30 %	150	-0,8	-0,9
- ash C-content 50 % → 20 %	150	-1,1	-1,2
- ash C-content 50 % → 5 %	150	-1,4	-1,5

Table 4. Estimates of the economical impact of different bottom ash management methods on the cost of gas.

Ash management route	**Ash management cost**	**Economical impact on production cost of gas**	
		Clean fuel	**Contaminated fuel**
Alternatives for bottom ash	eur/t (ash)	eur/MWh(gas)	eur/MWh (gas)
Basic case, landfill	50	0,0	0
Use of relatively clean ash in construction without treatment	0	-0,2	not relevant
Metal recovery from SRF ash + landfilling	-93	not relevant	-0,5

The tables 5 and 6 show the estimated effect of different ash management alternatives on the production cost of electricity produced using the gasification gas. An efficiency of 35 % from gas to electricity has been assumed.

Table 5. Estimates of the economical impact of different fly ash management methods on the cost of electricity.

Ash management route	**Ash management cost**	**Economical impact on production cost of electricity**	
		Clean fuel	Contaminated fuel
Alternatives for fly ash	eur/t (ash)	eur/MWh(e)	eur/MWh (e)
Basic case, special landfill	150	0,0	0
Use as fuel	0	-8,5	not relevant
Granulation + use as fuel	24	-7,1	not relevant
Washing + use as fuel	20	not relevant	-7,8
Combustion in integrated CFB	29	-6,8	not relevant
Combustion in integrated CFB + granulation + use as fertiliser	53	-5,5	not relevant
Combustion in integrated BFB + use in construction	40	-6,2	not relevant
Washing+integrated CFB + use in construction	49	not relevant	-6,1
Combustion of relatively clean ash in a stand alone CFB + use in construction	31	-6,7	not relevant
Combustion of Cl-containing ash in a stand alone CFB + use in construction	54	not relevant	-5,8
Combustion of relatively clean ash in a stand alone BFB + use in construction	43	-6,0	not relevant
Combustion of Cl-containing ash in a stand alone BFB + use in construction	65	not relevant	-5,1
Sintering of biomass ash + using as aggregate	61	-5,0	not relevant
Sintering of low chloride SRF ash + use as aggregate	130	not relevant	-1,2
Washing + sintering of high chloride SRF ash + use as aggregate	150	not relevant	0,0
Oxygen smelting of ash + use as aggregate	274	not relevant	+7,5
Improvement of carbon conversion without additional cost (optimisation of oper. Parameters)			
- ash C-content 50 % → 30 %	150	-2,4	-2,6
- ash C-content 50 % → 20 %	150	-3,2	-3,4
- ash C-content 50 % → 5 %	150	-4,0	-4,3

Table 6. Estimates of the economical impact of different bottom ash management methods on the cost of electricity.

Ash management route	**Ash management cost**	**Economical impact on production cost of electricity**	
		Clean fuel	Contaminated fuel
Alternatives for bottom ash	eur/t (ash)	eur/MWh(e)	eur/MWh (e)
Basic case, landfill	50	0,0	0
Use of relatively clean ash in construction without treatment	0	-0,5	not relevant
Metal recovery from SRF ash + landfilling	-93	not relevant	-1,4

4 Conclusions

The cost of ash management is one of the largest cost items in the operation economy of a gasification plant if the ashes have to be landfilled. There is a considerable economical potential if a reliable and economically feasible method can be introduced for the ash management. Utilisation of the ashes offers at the same time also environmental benefits in replacing primary materials from the nature and by avoidance of landfilling.

Several potential methods were identified and developed for the management of gasification ashes at the Gasash-project.

The properties of gasification ashes vary to a large degree depending on the gasification fuel and gasification conditions. Thus alternative ash management options are needed and the most suitable ones should be selected for each case. The complexity and operational cost of the methods vary widely. The simplest method is to burn the ash with the gasification gas if it is technically and environmentally possible. The other end of the scale is represented by oxygen flame smelting of ash containing chlorides and heavy metals. Several methods are available between these two for different ash qualities.

The methods identified and developed for **relatively clean fly ashes** are in order of increasing cost and complexity:

- Use of the ash as fuel without treatment
- Use of the ash as fuel after granulation
- Combustion of the ash in an integrated fluid bed combustor and use of the product as secondary construction material
- Combustion of the ash in an integrated fluid bed combustor followed by granulation and use of the product as forest fertiliser
- Sintering of the ash to produce aggregate for construction purposes

The developed methods for **fly ashes with heavy metals and soluble contaminants** are in an increasing cost and complexity order:

- Washing out of the chlorides and use of the washed ash as fuel in a suitable furnace or incinerator
- Washing out of the chlorides and combustion of the ash in an integrated fluid bed combustor and use of the product as secondary construction material
- Washing out of the chlorides followed by sintering and use of the product as aggregate in construction
- Smelting of the ash in oxygen smelter and use of the product as aggregate in construction

Gasification bottom ashes can be utilised in most cases as secondary construction materials. Bottom ash from the gasification of solid recovered fuel contains a considerable amount of metals in metallic form. These metals can be recovered from the

ash with relatively simple unit operations in such quantities that the operation is expected to have a positive cash flow.

The work done at the Gasash-project showed that there are alternatives for landfilling of gasification ashes. The majority of the technically feasible alternatives are economically more attractive than landfilling. The cost of landfilling is expected to increase within the EU-area and this is likely to improve the economical performance of the ash processing in the future. The results of the economical evaluation show that only smelting and combined washing and sintering of very contaminated ashes are expected to exceed landfilling cost of the same ashes at present. The increasing cost and limitations of landfilling are however likely to turn also these methods interesting in the future.

The work showed that ash management improvements can have a considerable effect on the economy of a gasification plant. In some cases a new environmentally and economically feasible ash management route is a prerequisite for the construction of a gasification plant as special landfilling capacity may not be available.

The future work in the development of gasification ash management could be divided in two main areas which however interact much with each other. First of these is the securing of the basis for the use of the ash management products in construction and forest fertilising from legal and scientific points of view. The second area is the demonstration of the following most feasible methods in industrial or semi-industrial scale:

- Granulation
- Washing
- Fluid bed combustion alternatives
- Bottom ash metal recovery

Many features and intellectual rights of the developed designs are owned or patented by the project partners or equipment manufacturing companies with whom the partners have co-operated during the project. The partners of the Gasash-project are interested in developing the methods further to reach commercial operation level and welcome contacts in case of interest for co-operation or need for further information.

Appendix H Deliverable 23 Comparison of the Results from Different Ash Treatment Methods

DELIVERABLE REPORT NUMBER 23

CONTRACT N° : ENK5-CT-2002-00635

PROJECT N° : NNE5-2001-00598

ACRONYM : GASASH

PROJECT TITLE : Improvement of the economics of biomass/waste gasification by higher carbon conversion and advanced ash management

PROJECT CO-ORDINATOR : VTT Processes

PARTNERS : VTT Processes (VTT)
Foster Wheeler Energia Oy (FWEOY)
Energy Research Centre of the Netherlands (ECN)
Asociación de Investigación y Cooperación Industrial de Andalucía (AICIA)
Pohjolan Voima Oy (PVO)
EMC Environment Engineering Limited (EMC)
Essent Energie Productie b.v. (EEP)

PROJECT START DATE: 1 November 2002 **DURATION : 36 months**

Date of issue of this report : October 2005

Project funded by the European Community under the 'EESD' Programme (1998-2002)

DELIVERABLE REPORT NUMBER 23

CONTRACT No: ENK5-CT-2002-00635
PROJECT No: NNE5- 2001-00598
ACRONYM: GASASH
DELIVERABLE TITLE: COMPARISON OF ASH TREATMENT METHODS DEVELOPED IN WP2

Comparison of ash treatment methods developed in WP2

1 Introduction

The aim of this report is to compare process developments developed in WP2 (WP2 Process developments related to gasification and gas cleaning). Main focus was in gasification process developments in order to improve ash quality already in gasification and gas cleaning process. Original plan of WP2 was to develop three to four different methods. However, during the project implementation one of those methods was identified to be not suitable to be applied for upgrading of gasification derived fly ash and work plan was revised. Revised program was focused on ash treatment methods, which can be applied after taking ash out from the process. After this revision four different process developments were included into work plan. However, only one of these methods can be seen as a further developed of gasification and gas cleaning process when other methods were more after treatment methods of filter dust.

2 Developed methods

2.1 CFB combustion of filter dust followed by ash treatment

Developed process was not one single step process but series of steps as following:

1. CFB combustion of filter dust
2. Solidification of oxidised ash

Process chain was based on separate CFB combustion, not directly integrated to the gasification process. Solidification can be based on use of water or some chemicals to increase strenght of solidified ash granules.

2.2 Sintering of granulated filter ash

Developed process was based on granulation of carbon containing filter dust and sintering of these granules.

2.3 Integrated oxidation of filter dust

Method is based on complete oxidation of filter dust in fluidised bed reactor, which is integrated to the gasifier. Flue gases of integrated oxidiser are fed to the main gasifier as a secondary air in order to avoid the need of additional gas cleaning equipments of flue gases. Products of integrated filter dust oxidiser are oxidised carbon free ash and hot air to be utilised in gasifier.

2.4 Other methods (revised work plan)

Six forms of after-treatment methods were tested using explorative tests:

1. *Dry screening* was found to be capable of producing a small ash fraction with relatively high carbon content and a lower content of contaminants. However, the bulk of the material remains more or less as it is. Techno-economic assessment should determine whether screening out this fraction is attractive for using it as a fuel.

2. *Pelletisation* of the fly ash was found to be possible and produces fuel pellets, which have improved characteristics for logistics and storage. The composition is not changed. Success depends on finding a buyer for the fuel and then deciding whether turning the ash into pellets is useful.

3. *Immobilisation* in a carbonaceous material like C-fix was found to produce building material that can be used in unlimited amounts. It is a technically a viable form of after-treatment, that is expected to be applicable to all utilisation options where a water repelling binder is used. Competition from other waste materials is expected.

4. *Low-temperature combustion* was found to be a possible form of after-treatment converting carbon-rich fly ash into a low-carbon fly ash that is nearly identical to fly ash from fluidised-bed combustion with improved potential for utilisation in cement products and with lower costs when land filled.

5. *High-temperature combustion* was found to be a technically acceptable way to convert carbon-rich biomass into building material, either by producing a fly ash similar to coal fly ash or by vitrification.

6. *Controlled leaching* was found to be a promising after-treatment technique, suitable for removing salts. When the pH is controlled, heavy metals are precipitated and the washing liquid can be disposed at low cost, in particular when discharged to the sea.

Based on the results of the explorative tests, it was decided to concentrate further research on *vitrification of the ashes* with special attention to co-incineration with other waste streams.

3 Comparison of developed methods

Developed methods can be compared based on several different criterions. Overall comparison should take account technical, environmental and economic impacts. This report is focused mainly on technical issues because overall evaluation is done in other WP's of GASASH project.

Only one of the developed methods was directly further development of gasification and gas cleaning process when the other methods can be seen as after treatment methods. Integrated oxidiser is directly connected to the gasifier in order to feed oxygen containing flue gases to the gasifier as a hot secondary air. This integration enables significant advantage by avoiding additional flue gas cleaning of exhaust gases of the oxidiser. In addition, no additional heat recovery is needed to utilise sensitive heat of flue gases.

Filter dust quality can be improved significantly by integrated oxidiser. Carbon content can be reduced from 15...60 % to below 1 % and most of metals can be oxidised. Quality of oxidised ash can be compared to fly ash of combustion process. Composition of oxidised ash depends on the original fuel of the gasifier as it the case in combustion process.

Environmental impacts of integrated oxidation are limited to further use of oxidised ash. Gaseous emissions are not increased by the use of integrated oxidiser.

Separate CFB combustion followed by solidification of fly ash has many similarities to integrated oxidation but combustor is not integrated to the gasifier. Technically filter ash treatment in CFB combustor is more or less equal to integrated oxidiser but flue gases are not fed to the gasifier and some other ways to clean the flu gases are required. If stand-alone plant is applied, a separate complete flue gas cleaning system is required. Technically this can be done, but investment and preparation cost will have negative impact on overall feasibility.

After CFB combustion quality of fly ash is very similar to quality of fly ash after integrated oxidiser. Solidification (with water or some chemicals) upgrades physical form of ash but does not have significant positive impact on leaching properties of ash.

Sintering of granulated filter dust was based on direct granulation of carbon containing filter dust without any additional oxidation before granulation. The aim was to oxidise carbon during sintering phase. Sintering was done in air atmosphere at 1000-1350^{o}C.

Stable granules can be from gasification fly ashes by the pelletizing method only with water addition. Sintering of the granulated gasification fly ash requires high temperature, over 1300°C. In the ash sintering methods the most part of problematic inorganic impurities vaporize, especially chlorine. Unburned carbon oxidizes very effectively. Additionally, a sintering decreases the leaching of some heavy metals.

High temperature sintering was proved to be technically suitable method to produce high quality products from filter dust. Disadvantages of this method are related to need of efficient exhaust gas cleaning systems and energy consuming high temperature sintering. The results of chemical analyses indicate that sintered ashes are environmentally acceptable products.

High temperature vitrification is capable to produce high quality product for construction purposes. However, this method has more or less same disadvantages that sintering of granules but even higher energy consumption during vitrification processing.

4 Conclusions

Methods developed and studied in WP2 are not directly comparable because technical targets of different methods are not the same. Some methods are focusing on improvement of quality of filter dust when some other methods are purely after treatment methods in order to produce products, which could be applied in construction or some other applications. All methods have some positive but also negative impacts on technical performance, emissions or economy. The overall evaluation and comparison of these methods has to include, which is done in details in WP4 and reported separately.