EOS-LT Consortium
Biomass Gasification and Gas Cleaning

Final Report 2007-2011

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Preface

The Energy research Centre of the Netherlands (ECN), Eindhoven University of Technology (TU/e), University Twente (UT), Delft Technical University (TUD) and Biomass Technology Group (BTG) have formed a consortium, with ECN as co-ordinator, to conduct R&D on biomass gasification and gas cleaning in the framework of the Energie Onderzoek Subsidie Lange Termijn (EOS-LT) subsidy programme, managed by AgentschapNL on behalf of the Dutch Ministry of Economic Affairs, Agriculture and Innovation. This report summarizes the consortium activities during the period 1 April 2007 until 31 December 2011.

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Abstract

From 2007 to 2011 the company BTG and the universities of Eindhoven, Twente and Delft performed research related to biomass gasification and ensuing gas cleaning. The work was co-ordinated by ECN and funded by grants from the Dutch EOS-LT programme. Research was performed by 5 PhD students and staff of the parties involved. Subjects covered were bed materials in fluidised-bed gasifiers, fouling in gas heat exchangers, tar removal by plasma, flame-generated radicals or catalysts, gasification and reforming of pyrolysis oil to syngas, and self gasification of biomass at high temperature and pressure. Results have been reported in progress reports covering periods of one year each and in many contributions to symposia, conferences and scientific journals. The present report covers the whole period with emphasis on the final results.

Keywords

Biomass, gasification, fouling, gas cleaning, tar, syngas, pyrolysis, catalytic reforming.

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Introduction
The Energy research Centre of the Netherlands (ECN), Eindhoven University of Technology (TU/e), University of Twente (UT), Delft Technical University (TUD) and Biomass Technology Group (BTG) have formed a consortium, with ECN as co-ordinator, to conduct R&D on biomass gasification and gas cleaning in the framework of the Energie Onderzoek Subsidie Lange Termijn (EOS-LT) subsidy programme, managed by AgentschapNL on behalf of the Dutch Ministry of Economic Affairs, Agriculture and Innovation. This report summarizes the consortium activities during the period 1 April 2007 until 31 December 2011.

Research was divided over 7 tasks. Tasks 1, 2 and 3 were executed by TU/e, task 4 and 5 by UT, task 6 by TUD and task 7 by BTG. The EOS consortium partners perform additional and more fundamental research, on subjects not covered by ECN or supportive to subjects which are included in the ECN programme. In general, research by the partners is meant to broaden and deepen the understanding of fundamental issues, while ECN research should be more market oriented. Each of the 7 tasks and results obtained are described separately.

Task 1: Bed materials
The conversion of tars is considered the major technical barrier for the successful development of commercial biomass gasification. Catalysts, used as bed material inside the gasifier, may have the ability to overcome this problem. They can increase the yield of gas at the expense of tars and char and they can tailor the composition of the gas to the specific desired product. 'Naturally occurring' minerals are abundant, relatively inexpensive and disposable which makes them attractive to use in the gasifier as bed material.

Dolomite ($MgCO_3 \cdot CaCO_3$) and related compounds like magnesite ($MgCO_3$) and calcite ($CaCO_3$) promote the water gas shift reaction (production of H_2 at the expense of CO) and reduce the tar content of the gas. The amount of H_2 doubles and naphthalene is reduced more than 50%. These bed additives need to be calcined in order to become active. Calcination occurs due to the release of CO_2 bound to the material upon the increase of temperature. This process changes the chemical composition on the surface of the mineral and increases its porosity. This increase of surface area is crucial for the activity of dolomite and related compounds. Tar is adsorbed in the pores of the materials making them function as tar holders. Depending on the surrounding environment the adsorbed tar may be subjected to different cracking reactions. Inert environment promotes thermal cracking which leads to a gas rich in CO and H_2. Oxygen promotes oxidation reactions leading to an increase of CO_2. Water promotes steam reforming producing a gas rich in H_2 and CO_2. Results with inert alumina show that the adsorption of tar is a physically controlled process.

Olivine ($[Mg,Fe]_2SiO_4$) is considered as an interesting alternative to dolomite, though it seems to work in a distinct way. Regardless of the pre-treatment that the olivine is subjected to it always remains a non-porous material. However the applied pre-treatment is crucial to the behaviour of olivine. Oxidation drives the iron of the mineral into the iron oxide form. When placed in the gasifier the oxidized olivine promotes the formation of CO_2 at the expense of CO. In reducing conditions, the iron of the mineral is driven to its metallic form. When used in the gasifier H_2 is promoted at the expense of H_2O. The reduced olivine has a higher performance concerning tar cracking. It is four times more effective than the oxidized olivine in the conversion of naphthalene and converts more than 80% of the naphthalene produced in inert conditions. However the influence of the reduced olivine in the Boudouard reaction (production of solid carbon) should be studied in more detail.

Task 2: Fouling in heat exchangers

The unwanted deposition of extraneous particulate matter on a heat-exchange surface is a major cause of concern in energy intensive heat recovery systems like biomass gasifiers, coal fired boiler and waste incinerators. The thermal energy is extracted from the flue gas using a system of heat exchangers. The flue gas is however contaminated with particulate matter, tar, nitrogen, sulphur and alkali compounds which can eventually form insulating layers. The deposit layers have very low thermal conductivity and may lead to drastic loss in thermal efficiency apart from maintenance problems and capital losses. The focus of task 2 is to understand the process of particulate fouling from a fundamental view point based on particle surface interactions and the global effects associated with process conditions by experiments. A numerical model to capture the deposition and removal of particles over heat exchanger surfaces is aimed at.

Particles which arrive at the heat exchanger surface and undergo inertial impaction can stick to the surface, rebound and might remove other previously deposited particles. In order to model the process, a sticking criterion is necessary. The interaction of a particle with other particles on the heat exchanger surface can be either in a dry state or in the presence of a thin liquid film due to condensation of alkali compounds. Detailed experiments were performed to evaluate the sticking criterion for particle impaction over a liquid coated surface under elastic and elastic-plastic deformation conditions. An empirical relation in terms of Stokes number was evaluated to determine the energy loss in the thin interstitial liquid film. A critical Stokes number range between 2 and 5 was observed below which particles do not rebound from the surface. In the Stokes number range of 5 to 20, the particles were observed to rebound but do not overcome the viscous effects of the liquid layer.

A high-temperature closed-loop vertical wind tunnel was designed and constructed to perform fouling experiments under controlled conditions. The effect of gas velocity, particle concentration, particle size distribution, gas temperature, heat exchanger tube orientation and geometry was studied. A measurement technique that allowed the evaluation of temporal evolution of the fouling layer thickness was used. The experimental investigations revealed that the shear induced by the gas flowing around the tube has a major effect on the overall deposit growth dynamics. The geometry and orientation of the tube indicated that deposition and removal of particles is strongly coupled to the flow dynamics and particle surface interactions.

A numerical model was implemented in a commercial software package to capture the deposition and removal of particles. The deposition model was based on particle-surface interactions including elastic-plastic deformations and the removal model was based on the rolling moment induced by the flow and on the energy transferred by other impacting particles. The fundamental impaction experiments along with the controlled experiments have provided better insight into the process of particulate fouling and resulted in the development of a numerical model, which can be used to develop strategies to minimize particulate fouling.

Task 3: Tar removal by radicals or plasma

During the process of biomass gasification, tars are formed which exit the gasifier in vapour phase. On, or in cold pipes, e.g. sampling pipes of biomass pyrolysis or gasification plants, tars tend to condense, and then gradually carbonize or polymerize. Tar condensation creates problems like fouling and plugging of after-treatment, conversion and end-use equipment. Tar formation during the thermal decomposition of biomass is not avoidable. For the wide-spread application of biomass gasification it is of great importance to convert or remove the tars at high temperature before condensation takes place.

The research focuses on an after-treatment technique which is known as partial combustion or partial oxidation. During partial combustion producer gas is partially combusted at a low air factor, reducing the tar content by tar cracking. Former research has demonstrated the possibilities and difficulties of tar conversion by partial combustion. Some questions remained unanswered, e.g. what is the role of radicals formed as intermediates during combustion. The

current status of technology and the promising advantages led to the inspiration to uncover more of the fundamentals of tar conversion in a partial combustion reactor. A modelling approach has been chosen as the main research tool.

Modelling of combustion applications very often requires the use of detailed chemistry models in two or even three dimensional geometry. To account for tar conversion, complex reaction mechanisms involving many chemical species and reactions have to be used. The use of such detailed mechanisms results in high computational costs. Reduction methods, such as chemical reduction techniques, decrease the computational burden. The reduction technique regarded here is the flamelet-generated manifold (FGM) approach.

The purpose of this research is twofold. Firstly, to gather additional knowledge of the physical and chemical mechanisms behind tar conversion by partial combustion. Secondly, to implement this knowledge into the existing FGM technique. The FGM development, which took a lot of effort, is also relevant to other multi-dimensional combustion systems. For example, it is now possible to calculate concentrations of species like NO_x using complex reaction mechanisms in 3D geometry with a limited computational effort.

Research was performed along the following steps:

1. Study of tar chemistry and the effect of residence time in a homogeneous reactor (0D).
2. Extensive validation of some well-known 2D diffusion flames (without tars).
3. Complex experimental validation (using laser diagnostics in cooperation with Lund University in Sweden) of a single 2D diffusion flame, with addition of tar chemistry.
4. Modelling of the 3D partial combustion reactor.

The research has provided a modelling tool that can be used to study tar chemistry in 3D geometry accurately but with modest computational effort. The results show that it is unlikely that naphthalene (tar modelling component) can be converted up to the experimental value of 95%. The numerical results showed a decrease in naphthalene concentration of only 5%. So, based on the observations in this thesis work, it appears that applying a partial combustion reactor to convert tars in producer gas, is able to convert only a very small part of the tars. The remaining tar will most likely lead to soot formation.

Pulsed corona tar conversion

Reducing tars is one of the major items that need to be solved when biomass gasification is applied. This task focuses on a new method where radicals are generated to attack the relatively weak tar molecules in a hot producer gas. Radicals are efficiently generated by non-thermal plasma, particularly pulsed corona plasma. *Objective* - to map the influence of radicals on tar conversion at high temperature (immediately after the gasifier unit) and to develop a novel technology that combines the benefits of existing technologies. *Approach* - we focus on finding the leading reaction mechanisms for tar removal by corona plasma using the numerical model RADICAL, as developed by Filimonova from the Institute for High Temperatures (IVTAN), Moscow, Russia. Sensitivity analysis is used to identify the more important reactions. The following data is obtained and analyzed:

- Yields of radicals and reactive species as generated by the corona plasma.
- Naphthalene decomposition on specific input energy at different gas compositions.
- Dependency of naphthalene concentration on time during the pulse for different pulses.
- Leading reactions for several components in dependency on time during the pulse for different pulses.

Conclusions from kinetic modelling:

- The results of simulation on naphthalene removal in biogas, pure N_2 and mixtures of N_2 with CO, CO_2 and H_2 are in good agreement with the experimental data. Plasma-

- chemical processes in discharge and post discharge stages were taken into consideration.
- It has been found that the reaction of naphthalene with excited nitrogen molecules plays a key role in the removal process. The influence of N_2* towards naphthalene removal is much lower when CO molecules are added, because of quenching. In this case, O- and H-radicals are dominating the process. The contribution of N_2* towards naphthalene removal in producer gas is much lower because of relatively low N_2 concentrations (as compared to the other gas mixtures). O-radicals are produced by reactions of CO_2 with N atoms. When moisture is present naphthalene removal occurs via combination of H, N_2* and OH radicals respectively.
- Reactions of naphthalene with excited species occur a short time after the pulse (10^{-6} s). During the removal process the balance of naphthalene in a streamer trace is mainly determined by the diffusion of naphthalene from outside of the trace in each cycle.
- The simulated results for mixtures with H_2 and CO do not give good agreements with the experimental observation, with exception of the syngas mixture.

Conclusions from experiments: the higher diffusiveness of radicals at higher gas temperatures contribute to the higher radical yields. The estimated yields are in fact a global value and a measure of the radical utilization, rather than the actual radical production value by means of the plasma itself. The diffusion effect with the favourable oxidation kinetics thus contributes to the observed decrease in energy requirements.

Task 4: Gasification and reforming of pyrolysis oil
Presently, biomass based fuels and chemicals are starting to become more popular due to the rising cost of fossil fuels. These fuels/chemicals will reduce global dependence on crude oil, natural gas etc to a certain extent, and also support rural economies. One such fuel intermediate from solid biomass is pyrolysis oil, which provides a platform to produce fuels/chemicals that would have been produced from fossil fuels. Synthesis gas (syngas; CO + H_2) is an essential intermediate in a refinery to produce valuable chemicals such as methanol, di-methyl ether, hydrogen, Fischer-Tropsch fuels etc. Syngas can be produced via steam reforming from a variety of feedstocks, which can range from naphtha, natural gas to coal and include any carbon feedstocks.

The research described in this report focused on the production of syngas from renewable biomass-based feedstocks; via catalytic steam reforming of pyrolysis oil and glycerol. Pyrolysis oil is produced by the thermal cracking of solid biomass such as forest, agricultural waste residues. This liquid has potential to be a feedstock in a reformer, steam/hydro-cracker, boiler etc. Crude glycerol is a by-product from the bio-diesel production and an interesting feedstock for syngas production.

At first, gasification of pyrolysis oil was investigated by changing the temperature, droplet sizes and concentration. It was observed that temperature ranging from ~500 C to 850°C has no effect on char production from pyrolysis oil. Vapour cracking reactions to gas were found to be dominant over the temperature range studied. In order to reduce the char production, the pyrolysis oil droplet size has to be reduced from millimetres to microns. In other words, high heating has to be applied. The concentration of pyrolysis oil has no effect on char production at high heating rate (~10^6 °C/min), whereas at low heating rate (~100°C/min), the production of char increases with the concentration. It was concluded that a certain fraction present in the pyrolysis oil was responsible for char formation with a reaction order higher than one.

Next, the influence of steam to carbon ratio (S/C), residence time of gases and pressure was studied on product distribution (gas, vapour and char) of pyrolysis oil. Steam has a very low influence in controlling the char production at the experimental conditions studied. However, gas composition was largely affected by adding steam to the gasification of pyrolysis oil.

Increasing the residence time of the gas/vapours, produces more gases with no change in the char yield. Effect of pressure (1 -15 bar) is currently investigated in the high pressure gasifier.

A comprehensive examination of commercial Ni/Alumina catalysts was made on steam reforming of bio-liquids such as pyrolysis oil and glycerol. It is concluded that it is possible to reform these bio-liquids at steam reforming conditions (~800°C, S/C = 3). Nevertheless, the activity and stability of the catalyst was poor and not comparable with methane steam reforming. The presence of potassium in the catalyst affects the hydrocarbon reforming activity to a large extent. Magnesium was considered to be a better promoter than potassium for bio-liquids steam reforming. Also, the presence of alkali-hydroxides in glycerol leads to more char during gasification. For glycerol, organic impurities such as FAMEs, di and tri glycerides affect the reforming activity. We also studied reforming of a mix of methane and bio-liquids (i.e. co-reforming or hybrid steam methane reforming). The activity and stability was improved, however, a regeneration step was required for long and stable operation. To tackle this problem, a fluid/flexi coking concept was proposed.

Finally, a detailed techno-economic evaluation was made of hybrid steam reforming of methane with bio-liquids. A detailed mass and energy balance was performed using UNISIM. The economic evaluation suggests that ~50% of bio-liquids with 50% natural gas reforming is possible and this concept will attract refineries when natural gas price increases to above 0.5 €/Nm^3 while bio-liquids are available at 100 €/tonne.

The results of this research namely 1) a thorough understanding of evaporation/gasification of bio-liquids such as pyrolysis oil, crude glycerol 2) comprehensive knowledge on behaviour of Ni/Alumina catalysts on pyrolysis oil/crude glycerol reforming 3) a detailed economic analysis of hybrid steam reforming process, provides scope for the development of a reforming process for efficient conversion of biomass to syngas, which was the ultimate target of this study.

Task 5: Self gasification of biomass
Biomass self-gasification focuses on the production of bio-methane via the gasification route by using the alkali metals already contained in the biomass as gasification and methanation catalysts. Process modelling focused on the possibility of obtaining an autothermal gasifier without the addition of O_2/air (at gasifier temperature of 700 - 800°C and at gasifier pressure of 1 - 35 bar). The option for an overall autothermal process was investigated as well under these conditions. Experimental work focused on the role of alkali metals in the gasification and methanation reactions.

Results on process simulations pointed out that it is possible to obtain an autothermal gasifier under certain operating conditions. Overall (HHV) efficiencies to methane obtained were 48 - 66%. An overall autothermal process was not possible, unless improved or new CO_2 separation technologies are utilized with low energy requirements ($\leq$ 2 MJ/kg CO_2). Experimental results showed that biomass ash drastically enhances gasification rate when impregnated into the biomass. The role of biomass ash on the methanation reaction and the mechanism of its catalytic activity are currently under investigation.

Task 6: Catalytic tar removal
At TUD, in the first project year an extensive literature study was carried out concerning novel catalytic tar reduction techniques for (fluidized bed based) biomass gasification. The results have been published in a.o. a review article. This lead to a 'Go' concerning the associated task. Due to the reduced time left after this first year, no full-time PhD student could be appointed and the study was performed with help of part-time PhD and master students. A plan for experiments was made together with ECN in which catalytic filtration and selective catalytic destruction of heavy tars were found to be most interesting. The first aspect could unfortunately not be carried out in the framework of this project due to IPR issues with the German company involved (Pall Filter Systems). Thus in close cooperation with ECN and partly at their premises

experiments were carried out with a focus on cheap bed materials that in potential could be used to reduce the content of heavy tar species. Therefore, experiments were performed with real dedusted gas from the MILENA gasifier and catalytic conversion tests were performed in a fixed bed of iron silicate. Significant conversion of heavy tars was obtained. In general, it can be concluded that the iron silicate is suitable for tar reduction treatment because of its performance during the experiments which is effective at high temperature (total Class V tars reduction rate was up to 50%) and raw gas flow circumstances. Tar conversion was higher at the highest temperature 850ºC, and the conversion rates of Class II, IV and V tars were 79%, 15% and 49%, respectively.

Kinetic data were derived from these experiments and applied in an Aspen Plus^{TM} model to simulate tar conversion. The modelling results were in agreement with the prediction from theory on the aspects of the trends of conversion rate with different parameters and the reduction rates of different classes of tars. However, the tar conversion rates from the simulation were higher than from tests, probably because of the hypothesis and simplifications from the real experiments and reactions. The Class II tars (represented by phenol C_6H_6O) in the model reacts about 15% more, 10% and 20% for Class V (represented as naphthalene $C_{10}H_8$) and Class IV tars (represented by fluoranthene and pyrene $C_{16}H_{10}$). The simulated main product gas trend was almost identical except for the H_2O content due to its associated known practical measuring inaccuracy.

With the Delft HTGCU test rig CH_4 blank testing of a gas similar to MILENA gas has been performed with interesting results obtained. The CH_4 was found to be reduced under all conditions. Varying gas residence time at one certain temperature, the CH_4 decomposes increasingly from 0.5 s to 1.5 s. The effect of iron silicate on the conversion of naphthalene under different temperatures and different residences were also examined using the Delft HTGCU set up. However, the results were remarkable, since the inlet and outlet naphthalene analysed from SPA results were generally below the detection limit (<30μg per sample). This could be due to several reasons: the leakage of naphthalene at the top of tar evaporator, the partial blockage of naphthalene at the sampling point and the analysis accuracy. On the other hand, it was observed that –after prolonged time- serious sintering had taken place, leading to the conclusion that under reducing conditions with typical MILENA gas, 850°C is a too high temperature to use for this bed material. It is recommended in the light of this result to perform extensive thermodynamic equilibrium calculations using FACTSAGE^{TM} to obtain confirmation whether liquid phases are expected to an appreciable extent given relevant process conditions. This was outside the scope of the current contract.

Task 7: Conversion of biomass pyrolysis oil
A gasifier was developed in which clean (syn)gas can be produced from pyrolysis-oil and/or pyrolysis vapours at relatively low temperatures. Throughout the project, a number of technical issues were resolved, and a small scale (1 – 3 kg/hr) gasifier suitable for both process options was developed. Important research items were the fuel-air mixing behaviour, the energetic efficiency of the process and the influence of catalysts on the process performance. The catalytic research included both the type of catalyst (fixed bed versus monolithic) as well as the active component (Ni versus Pt/Rh).

For both the pyrolysis-oil gasification, as well as the pyrolysis-vapour reforming, encouraging results are obtained. Clean product gas can be obtained at temperatures between 800 and 900°C. For both processes, cold gas efficiencies above 70% can be obtained. For the vapour-reforming option, it is expected this value can increase by another 10%, the improvement for the oil-gasification is expected to be limited to a few percent.

During the course of the project, some advantages and disadvantages of both processes were encountered. The vapour reforming process seems especially suitable for the local production of

heat and electricity from biomass residue streams. The oil gasification process seems better suitable for the large scale, centralized production of clean syngas.

With the above mentioned results, BTG's primary targets set in the project were obtained. The activities regarding both gasification processes will be continued in the form of a PhD research program. This research program should generate a positive boost to both the process development and implementation, as well as to the knowledge transfer in the form of (scientific) publications.

Samenvatting

Inleiding

Het Energieonderzoek Centrum Nederland (ECN), de Technische Universiteit Eindhoven (TU/e), de Universiteit Twente (UT), de Technische Universiteit Delft (TUD) en Biomass Technology Group (BTG) hebben een consortium gevormd, met ECN als coördinator, voor het uitvoeren van onderzoek in het kader van het Energie Onderzoek Subsidie Lange Termijn (EOS LT) programma, dat door AgentschapNL wordt beheerd namens het Nederlandse Ministerie van Economische Zaken, Landbouw en Innovatie. Dit rapport vat de consortium activiteiten samen over de periode 1 april 2007 tot 31 december 2011.

Onderzoek was verdeeld over 7 taken. Taak 1, 2 en 3 werden uitgevoerd door TU/e, taak 4 en 5 door UT, taak 6 door TUD en taak 7 door BTG. De partners in het EOS consortium voeren aanvullend en meer fundamenteel onderzoek uit, op onderwerpen buiten het ECN programma of ondersteunend onderzoek aan onderwerpen binnen het ECN programma. In het algemeen dient het onderzoek door de partners te leiden tot breder en diepgaander begrip van fundamentele aspecten, terwijl ECN onderzoek meer marktgericht dient te zijn. Elk van de 7 taken en daarbij behaalde resultaten worden apart beschreven.

Taak 1: Bed materialen

De conversie van teren wordt beschouwd als de belangrijkste technische hindernis voor de succesvolle ontwikkeling van commerciële biomassa vergassing. Katalysatoren, gebruikt als bed materiaal in de vergasser, kunnen mogelijk dit probleem oplossen. Ze kunnen de opbrengst van gas ten koste van de teer en char verhogen en ze kunnen de samenstelling van het gas op het specifieke gewenste product aanpassen. "Natuurlijk voorkomende" mineralen zijn er in overvloed, relatief goedkoop en "disposable" waardoor ze aantrekkelijk zijn om te gebruiken in de vergasser als bedmateriaal.

Dolomiet ($MgCO_3 \cdot CaCO_3$) en verwante stoffen als magnesiet ($MgCO_3$) en calciet ($CaCO_3$) bevorderen de watergasshiftreactie (de productie van H_2 ten koste van CO) en verminderen het teergehalte van het gas. De hoeveelheid H_2 is twee keer zo groot en de hoeveelheid naftaleen neemt met meer dan 50% af. Deze bed additieven moeten gecalcineerd worden om actief te worden. Calcineren doet CO_2, die is gebonden in het materiaal, vrijkomen bij stijgen van de temperatuur. Het proces verandert de chemische samenstelling aan het oppervlak van het mineraal en verhoogt de porositeit. Dit is van cruciaal belang voor de activiteit van dolomiet en verwante verbindingen. Teer wordt geadsorbeerd in de poriën van het materiaal waardoor die functioneren als teerhouders. Verschillende omgevingen bevorderen verschillende kraak-reacties. Een inerte omgeving bevordert thermisch kraken, wat leidt tot een gas rijk aan CO en H_2. Zuurstof bevordert oxidatiereacties die leiden tot een toename van CO_2. Water bevordert "steam reforming" en het produceren van een gas rijk aan H_2 en CO_2. Resultaten met een inert aluminiumoxide tonen aan dat de adsorptie van teer een fysiek gecontroleerd proces is.

Olivijn ($[Mg,Fe]_2SiO_4$) wordt beschouwd als een interessant alternatief voor dolomiet, al lijkt het te werken in een andere manier. Ongeacht de voorbehandeling, blijft olivijn altijd niet-poreus. De toegepaste voorbehandeling is cruciaal voor het gedrag van olivijn. Oxidatie drijft ijzer in het mineraal naar de ijzeroxide vorm. In een vergasser bevordert geoxideerd olivijn de vorming van CO_2 ten koste van CO. Reductie drijft het ijzer in het mineraal naar zijn metallische vorm. In een vergasser bevordert gereduceerd olivijn H_2 ten koste van H_2O. Gereduceerd olivijn is ook actiever bij het kraken van teer. Het is vier keer effectiever dan geoxideerd olivijn bij de omzetting van naftaleen en zet meer dan 80% van de naftaleen om die onder inerte condities gevormd wordt. De invloed van gereduceerd olivijn op de Boudouard reactie (productie van vaste koolstof) moet nog in meer detail bestudeerd worden.

Taak 2: Vervuiling van warmtewisselaars

Het ongewenst neerslaan van deeltjes op een warmtewisselend oppervlak, ofwel particulate fouling, vermindert de prestaties van energieconversie systemen zoals biomassavergassers, kolengestookte boilers en afvalverbrandingsinstallaties. In deze installaties wordt de thermische energie aan de rookgassen onttrokken door een warmtewisselaar. De rookgassen bevatten echter deeltjes die bestaan uit teer, stikstof-, zwavel- en alkaliverbindingen die kunnen neerslaan en een isolerende laag kunnen vormen. Deze isolerende laag veroorzaakt een verminderd thermisch rendement, en verhoogt de onderhoudskosten.

Het doel van taak 2 is tweeledig. Enerzijds wordt door middel van experimenten het effect van procescondities op het ongewenst neerslaan van deeltjes onderzocht. Anderzijds worden de plak- en verwijderingsmechanismen van deeltjes op droge en natte oppervlakken in detail bestudeerd.

Deeltjes die tegen een warmtewisselend oppervlak botsen, kunnen zich hechten aan het oppervlak, kunnen terugkaatsen of kunnen eerder gedeponeerde deeltjes verwijderen. Om dit proces te modelleren is een hechtcriterium gedefinieerd. De interactie van een deeltje met andere deeltjes op het warmtewisselend oppervlak vindt plaats in droge toestand of in de aanwezigheid van een dunne vloeibare film als gevolg van bijvoorbeeld de condensatie van alkaliverbindingen. Gedetailleerde experimenten werden uitgevoerd om het hechtcriterium te evalueren voor een met een vloeistof gecoat oppervlak onder elastische en elastisch-plastische vervormingsomstandigheden. Een empirische relatie op basis van het Stokes getal is opgesteld om het energieverlies te bepalen in de dunne interstitiële vloeistoffilm. Een kritisch Stokes getal tussen 2 en 5 werd waargenomen waaronder deeltjes niet terugstuiten van het oppervlak. Voor Stokes getallen van 5 tot 20 werd waargenomen dat de deeltjes in eerste instantie terugstuiten, maar niet de viskeuze effecten van de vloeistoflaag kunnen overwinnen.

Een hoge temperatuur closed-loop verticale windtunnel is ontworpen en gebouwd om vervuilingsexperimenten uit te voeren onder gecontroleerde omstandigheden. Het effect van gassnelheid, deeltjesconcentratie, deeltjesgrootteverdeling, gastemperatuur, warmtewisselaar oriëntatie en geometrie is bestudeerd. Hierbij werd een meetmethode toegepast waarmee de ontwikkeling in de tijd van de aangroei van de vervuilingslaag gemeten kon worden. Uit de experimenten is gebleken dat de afschuiving veroorzaakt door het rookgas dat rondom de buis stroomt, een grote invloed heeft op de dynamiek van de depositie aangroei. Uit de experimenten met een verschillende geometrie en oriëntatie van de buis bleek dat het neerslaan en verwijderen van deeltjes sterk gekoppeld is aan de stromingsconfiguratie en de interactie van de deeltjes met het oppervlak.

Het neerslaan en verwijderen van deeltjes is in een commercieel softwarepakket gemodelleerd. In het model zijn de relaties voor het neerslaan van deeltjes gebaseerd op deeltjesoppervlakte interacties en elastisch-plastische vervormingen. De relaties voor het verwijderen van deeltjes zijn gebaseerd op het rolmoment dat veroorzaakt wordt door de kracht van de stroming uitgeoefend op de deeltjes.

Zowel de fundamentele als de gecontroleerde deeltjesdepositie experimenten hebben beter inzicht gegeven in het proces van deeltjesvervuiling. De resultaten zijn geïmplementeerd in een numeriek model dat gebruikt kan worden om strategieën te ontwikkelen om de nadelige effecten van depositie van deeltjes te verminderen.

Taak 3: Teerverwijdering door radicalen of plasma

Tijdens de vergassing van biomassa worden er teren gevormd die de vergasser in gasvorm verlaten. Deze teren condenseren op en in koudere leidingen, waar ze vervolgens geleidelijk inkolen of polymeriseren. Teercondensatie veroorzaakt grote problemen zoals vervuiling en de verstopping van nabehandelings- en eindgebruiksapparatuur. Teervorming, tijdens thermische ontleding van biomassa, kan niet voorkomen worden. Voor de grootschalige inzet van biomassa

vergassing is het van groot belang om de gevormde teren om te zetten of te verwijderen op een hoge temperatuur (voordat de teren condenseren).

Het onderzoek richt zich op een nabehandelingmethode die bekend staat als partiële verbranding of partiële oxidatie. Daarbij wordt een deel van het gas verbrand en het teergehalte gereduceerd door de teren te kraken. Eerder onderzoek heeft aangetoond wat de mogelijkheden en moeilijkheden zijn van teeromzetting met behulp van partiële verbranding. Verscheidene vragen zijn nog onbeantwoord, zoals de vraag welke rol radicalen spelen die als tussenproduct bij verbranding ontstaan. De huidige status van beschikbare technologieën en de veelbelovende voordelen hebben geleid tot de inspiratie om de fundamentele werkingsprincipes achter teerconversie middels partiële verbranding te onderzoeken. In dit onderzoek is gekozen om modellering te gebruiken als voornaamste gereedschap.

Het modelleren van verbrandingstoepassingen vergt het gebruik van gedetailleerde chemische modellen in een twee- of driedimensionale (2D of 3D) geometrie. Bij teerconversie, is het gebruik van complexe reactiemechanismen met veel chemische componenten en reacties noodzakelijk. Dat leidt tot hoge rekentijden, waarmee hoge kosten gepaard gaan. Door het gebruik van reductiemethoden wordt de rekentijd aanzienlijk verminderd. In dit onderzoek is er gebruik gemaakt van de flamelet-generated-manifold (FGM) aanpak.

Het doel van het onderzoek is tweeledig. Ten eerste het vergaren van kennis van het proces van teerconversie door partiële verbranding. Ten tweede het verwerken van deze kennis in de FGM methode. De ontwikkeling van FGM, waaraan het meeste werk is besteed, is ook van belang voor andere verbrandingstoepassingen. Het is, als voorbeeld, mogelijk om binnen een geringe rekentijd de concentratie van verscheidene emissies (zoals NO_x) in een complexe 3D geometrie te bepalen met het gebruik van complexe reactie mechanismen.

De opbouw van het onderzoek is stapsgewijs doorlopen:

1. Een homogene reactor studie (0D) waarin de chemie van teren is bestudeerd en de rol van verblijftijd.
2. Een uitgebreide validatie van een enkele, bekende 2D diffusievlam (zonder teren).
3. Een complexe experimentele validatie (met gebruik van laserdiagnostiek in samenwerking met de Universiteit Lund in Zweden) van een enkele 2D diffusievlam, met de toevoeging van teerchemie.
4. Het modelleren van de 3D partiële verbrandingsreactor.

Het onderzoek heeft geleid tot een modelleringsgereedschap waarmee nauwkeurig, met een acceptabele rekentijd, teerchemie in een 3D geometrie kan worden bestudeerd. De resultaten voor de partiële verbrandingsreactor laten echter zien dat maar 5% van de hoeveelheid naftaleen wordt omgezet. Dit wijkt sterk af van de gemeten 95% omzetting tijdens experimenten in het verleden. Op basis van deze eerste resultaten zou men kunnen concluderen dat partiële verbranding enkel een klein deel van de teren kan omzetten. Het is zeer waarschijnlijk dat het overige deel van de teren zal doorgroeien tot roet.

Teer conversie met behulp van gepulste corona technologie
Reductie van teren is een van de cruciale aandachtspunten van biomassa vergassing. Deze taak richt zich op een nieuwe methode, waarbij radicalen in-situ geproduceerd worden om in een heet biomassa productgas de (relatief zwakke) teermoleculen oxidatief te degraderen. Radicalen worden op efficiënte wijze gegenereerd door een niet-thermisch plasma, specifiek een gepulst corona plasma. Doelstellingen: de invloed in kaart brengen van radicalen op de conversie van teer bij hoge temperaturen (direct na de vergassingsinstallatie), en een nieuwe technologie ontwerpen, die de voordelen van bestaande technologieën combineert. Benadering: we richten ons op het vinden van de primaire reactiemechanismen van teerverwijdering door gepulste corona technologie, met behulp van het numerieke RADICAL model, ontwikkeld door dr. E. Filimonova, verbonden aan het Instituut voor Hoge Temperaturen (IVTAN) in Moskou.

Gevoeligheidsanalyse is toegepast om de belangrijkste reactiepaden te identificeren. De volgende gegevens zijn verkregen:

- Opbrengsten van radicalen en andere reactieve deeltjes, die door het corona plasma geproduceerd worden.
- De ontleding van naftaleen als functie van de specifieke energie input en gassamenstelling.
- Pulstijdafhankelijke concentratie van naftaleen, onderzocht voor verschillende pulstypen.
- Primaire reacties en hun afhankelijkheid van de pulstijd en pulsvorm

Conclusies uit kinetische modellering:

- De simulatieresultaten van naftaleenverwijdering uit biogas, zuivere stikstof of synthetische mengsels van stikstof met CO, CO_2 en H_2 zijn in goede overeenstemming met experimentele gegevens. Plasmachemische processen in de ontladingsfase en post-ontladingsfase zijn in de berekeningen meegenomen.
- Er is geconstateerd, dat de reactie van naftaleen met aangeslagen stikstofmoleculen (N_2*) een belangrijke rol in het verwijderingsmechanisme speelt. De invloed van N_2* op de naftaleenverwijdering is veel geringer wanneer CO moleculen aanwezig zijn, ten gevolge van quenching. In deze situatie zijn O en H atomen dominant. De bijdrage van N_2* tot naftaleenverwijdering in productgas is veel minder vanwege de relatief lage N_2 concentraties, vergeleken met de andere bestudeerde gasmengsels. O atomen worden geproduceerd door reacties van CO_2 met N atomen. Indien vocht aanwezig is, vindt de verwijdering van naftaleen plaats via de gecombineerde reacties van respectievelijk H atomen, N_2* moleculen en OH radicalen.
- Reacties van naftaleen met aangeslagen deeltjes vinden plaats kort na de puls (10^{-6} s). Gedurende het verwijderingsproces wordt de massabalans van naftaleen in een ontladingskanaal voornamelijk bepaald door de diffusie van naftaleen vanuit de gasfase, bij iedere pulscyclus.
- De gesimuleerde resultaten voor mengsels van H_2 en CO geven geen goede overeenstemming met de experimenten, met uitzondering van het syngas mengsel.

Conclusies uit experimenten: de hogere diffusiesnelheden van radicalen bij hogere gastemperaturen dragen bij aan de hogere radicaalopbrengsten. De geschatte opbrengsten zijn in feite globale waarden en een maat voor radicaalconsumptie, in plaats van een actuele plasma-intrinsieke radicaalproductieterm. Het diffusie effect met de hieraan gerelateerde gunstige oxidatiekinetiek draagt aldus bij aan de geobserveerde reductie van energie behoefte.

Taak 4: Vergassing en reforming van pyrolyse olie
Biobrandstoffen en bio chemicaliën worden steeds populairder door de stijgende kosten van fossiele brandstoffen. Deze brandstoffen/chemicaliën verminderen 's werelds ruwe olie afhankelijkheid en helpen daarnaast met de ontwikkeling van landelijke economieën. Eén interessante route voor de productie van biobrandstoffen/chemicaliën maakt gebruik van het tussenproduct pyrolyseolie dat vervolgens via vergassing/stoom reformen omgezet kan worden in het platform bouwblok synthese gas (CO + H_2) dat al grootschalig wordt gebruikt in de fossiele petrochemische industrie voor de productie van bijvoorbeeld, waterstof, methanol, DME en Fischer Tropsch brandstoffen.

Het onderzoek in deze taak betreft het omzetten van bio-vloeistoffen naar synthese gas via katalytisch stoom reformen en vergassing. Twee bio-vloeistoffen zijn in dit project onderzocht, namelijk pyrolyseolie (afkomstig van ligno-cellulose bijproducten van hout/landbouw) en glycerol (bijproduct van transesterificatie van plantaardige oliën). De speerpunten van dit onderzoek waren: verdampen en vergassen, katalysator ontwikkeling, procesontwikkeling en integratie met fossiele industrie.

Taak 5: Zelfvergassing van biomassa

Zelf-vergassing van biomassa richt zich op de productie van bio-methaan via de vergassingsroute. Hierbij worden the alkali metalen die de biomassa bevat ingezet als vergassings- en methaniseringskatalysatoren. De nadruk bij de uitgevoerde processimulaties was niet alleen de mogelijkheid om een autothermale vergasser te verkrijgen zonder toevoer van O_2/lucht, maar ook een netto autothermaal proces (onder condities van: vergasser temperatuur 700 - 800°C en vergasser druk 1 - 35 bar). Het experimentele werk was gericht op de activiteit van alkali metalen op de vergassings- en methaniseringsreacties.

De resultaten uit de processimulaties gaven aan dat de mogelijkheid bestaat om een autothermale vergasser te bedrijven onder specifieke condities. Totaal (HHV) methaan rendementen waren in een regime van 48 - 66%. Het bedrijven van een netto autothermaal proces was niet mogelijk onder de gesimuleerde condities, tenzij verbeterde of nieuwe CO_2 scheidingstechnologieën zouden worden ingezet met een lager energieverbruik ($\leq$ 2 MJ/kg CO_2). De reeks experimentele resultaten liet zien dat biomassa as de vergassingssnelheid verhoogt wanneer die in de biomassa is geïmpregneerd. De katalytische werking van biomassa as op de methaniseringsreactie wordt momenteel onderzocht.

Taak 6: Katalytische teerverwijdering

In het eerste projectjaar heeft TUD een uitgebreide literatuurstudie uitgevoerd naar nieuwe, state-of-the-art technieken voor teerreductie voor (op wervelbed gebaseerde) vergassing van biomassa. De resultaten zijn gepubliceerd in o.a. een uitgebreid overzichtsartikel. Dit heeft geleid tot een "Go" voor de hieraan gerelateerde taak.

Vanwege de gereduceerde tijd die overbleef na dit eerste jaar kon geen voltijds promovendus worden aangesteld en is het vervolgwerk uitgevoerd met behulp van een in deeltijd werkende promovendus en een master student. Een plan voor de uitvoering van de experimenten werd opgesteld in samenwerking met ECN. Daarin is het accent gelegd op "katalytische heet gas filtratie" en "selectieve katalytische reductie van zware teren", als meest interessante onderwerpen van onderzoek.

Het eerstgenoemde onderwerp kon niet worden uitgevoerd in dit projectkader vanwege IPR issues met de betrokken Duitse firma (Pall Filter Systems). Daarom is besloten om in nauwe samenwerking met ECN experimenten uit te voeren, deels bij ECN, met de focus op relatief goedkope bed materialen die potentieel geschikt werden geacht voor de reductie van zware teer componenten.

In dit kader werden experimenten uitgevoerd met reëel ontstoft gas afkomstig van de MILENA vergasser. Deze katalytische conversieproeven werden uitgevoerd in een vast bed van ijzersilicaat. Significante conversies van zware teren werden behaald. Uit dit experimentele werk kan worden geconcludeerd, dat ijzersilicaat geschikt lijkt als teerreductietechniek die effectief is bij hogere temperatuur (totale teerklasse V teerreductiegraad bedroeg tot ~50%) op basis van ruw product gas. Teerconversie was het hoogst bij de hoogst toegepaste temperatuur van 850ºC en de conversie waarden van klasse II, IV en V teren bedroegen respectievelijk 79%, 15% en 49%.

Verder werden kinetiek gegevens afgeleid uit deze experimenten en geïmplementeerd in een eenvoudig Aspen Plus[TM] model voor simulatie van teerconversie. De resultaten van dit model waren in overeenkomst met de theoretisch voorspelde waarden voor de trends van de conversiegraad met verschillende procesparameters en de reductiegraden van de verschillende teerklassen. Echter, de absolute teerconversiewaarden van de simulaties lagen hoger dan die van de experimenten. Waarschijnlijk is dat het gevolg van de aangenomen vereenvoudigingen van de teercomponenten. Klasse II teer (vertegenwoordigd door fenol, C_6H_6O) wordt in het model tot 15% meer omgezet. Voor klasse V teer (gerepresenteerd door naftaleen, $C_{10}H_8$) voorspelt het model 10% meer en voor klasse IV teren (vertegenwoordigd door fluorantheen en pyreen,

$C_{16}H_{10}$) 20% meer. De gesimuleerde trends voor de belangrijkste productgassen was praktisch identiek aan de experimenten, met uitzondering van het watergehalte, dat in de praktijk relatief onnauwkeurig experimenteel bepaald wordt.

Met de Delftse HTGCU (hoge temperatuur gasreinigingseenheid) testopstelling is een testserie (blanco) CH_4 "reforming" uitgevoerd met een gas dat overeenkwam met MILENA gas. Hierbij zijn interessante resultaten verkregen. CH_4 bleek onder alle onderzochte condities verlaagd te worden in concentratie. Door de gas verblijftijd te variëren bij een temperatuur, vertoonde CH_4 een toenemende conversie bij verblijftijden van 0.5 s tot 1.5 s.

Het effect van ijzersilicaat als bed materiaal op de conversie van naftaleen bij verschillende temperaturen en verblijftijden is in dezelfde opstelling onderzocht. De resultaten waren opmerkelijk: de inlaat- en uitlaat naftaleenconcentraties, geanalyseerd met behulp van de SPA techniek, lagen onder de detectielimiet (<30μg per monster). Dit kan worden herleid naar verschillende mogelijke omstandigheden: naftaleen verlies aan de top van de teerverdamper, een partiële blokkade van gecondenseerd naftaleen bij het bemonsteringspunt, alsmede analyse nauwkeurigheid. Verder is waargenomen, dat – na langere tijd op verhoogde temperatuur - (harde) sintering was opgetreden. Dat leidt tot de conclusie dat bij reducerende omstandigheden zoals met typisch MILENA productgas, een temperatuur van 850°C te hoog lijkt voor dit bedmateriaal. In het licht van dit resultaat wordt aanbevolen om meer gedetailleerde thermodynamische (fase)evenwichtsberekeningen uit te voeren met behulp van FACTSAGE™ software, om aan te tonen of significante hoeveelheden vloeibare fase(s) te verwachten zijn bij de genoemde procescondities. Dit viel echter buiten de scope van het huidige project.

Taak 7: Conversie van biomassa pyrolyseolie
BTG heeft de productie van syngas via pyrolyse onderzocht. Een drietal procesvariaties zijn voorgesteld, waarbij er twee gebruik maken van katalytische vergassing van respectievelijk pyrolyseolie, en pyrolysedampen. De derde variatie betrof de productie van syngas via entrained flow vergassing van pyrolyseolie. Voor de katalytische processen is gedurende het vierjarige project uitgebreid experimenteel onderzoek uitgevoerd. De entrained flow vergassing van pyrolyseolie is als papieren studie uitgevoerd in het eerste jaar van het project. In het onderzoek is een aantal commercieel beschikbare technologieën (Texaco, Shell, Lurgi) vergeleken. Met name het asgehalte van de pyrolyseolie bepaalt de exacte configuratie van de vergasser. Ondanks de lage asconcentratie (< 0.1 gew.%) in pyrolyseolie blijkt de as samenstelling en hoeveelheid cruciaal in het ontwerp van de vergasser. Additionele complicatie voor de route ontstaat wanneer pyrolyseoliën van verschillende biomassa soorten worden gebruikt, aangezien elk type biomassa andere as (combinaties) bevat. Uit de studie bleek de Lurgi technologie het meest flexibel ten aanzien van de voeding.

Voor de andere procesvariaties is een vergasser ontwikkeld waarmee op lage temperatuur een schoon (syn)gas geproduceerd kan worden uit pyrolyseolie en/of pyrolysedampen. Voor beide procesvariaties bestaat het proces uit twee verschillende onderdelen, die achtereenvolgens in de vergasser plaatsvinden. Allereerst wordt de temperatuur van de voeding middels partiële oxidatie verhoogd tot 800-1000°C. Belangrijke aspecten van de partiële oxidatie zijn het minimaliseren van vaste koolstof en het leveren van voldoende energie voor de katalytische reforming stap.

Het experimentele onderzoek is begonnen met het optimaliseren van de partiële oxidatie stap. Voor de dampvergassing bleek een statische mixer met "swirl body" de beste oplossing. Voor de olievergassing gaf een lucht atomizer met stoomspiraal de beste partiële oxidatie. Oorspronkelijk is voor beide procesvariaties een separate experimentele opstelling gebruikt. Gedurende het project is de olievergasser in de dampvergasser geïntegreerd. Het onderzoek aan de monoliet katalysatoren is hierdoor vereenvoudigd. Belangrijke onderzoek items na optimalisatie van de partiële oxidatie waren de brandstof-lucht verhouding, de energetische efficiëntie van het proces en de invloed van de katalysator op de procesvoering. Het katalysator

onderzoek had betrekking op zowel het type katalysator (vast bed versus monoliet) als op de actieve component (Ni versus Pt/Rh).

Voor beide proces varianten zijn bemoedigende resultaten geboekt. Schoon productgas kan worden geproduceerd bij temperaturen tussen de 800 en 900°C. Voor beide processen werd een "cold gas efficiency" behaald boven de 70%. Voor de dampvergassing wordt verwacht dat deze waarde nog ca. 10% kan toenemen, voor de olievergassing zal de potentiële verbetering minder zijn.

Tijdens het onderzoek is een aantal voor- en nadelen van beide processen aan het licht gekomen, waardoor het toekomstperspectief van de processen verschilt. De dampvergassing lijkt met name geschikt voor lokale productie van warmte en elektriciteit uit reststromen, terwijl de olievergassingr beter toegepast kan worden voor centrale productie van schoon syngas.

Met bovenstaande resultaten is de primaire doelstelling van het project voor BTG behaald. Na dit project zal de procesontwikkeling worden voortgezet in de vorm van een promotie- onderzoek. Het promotieonderzoek zal een positieve invloed hebben op de kennisoverdracht in de vorm van toekomstige wetenschappelijke publicaties.

1. Introduction

The EOS-LT research programme as defined in 2004 [1] is based on the vision formulated by the Biomass Transition project, according to which in 2040 bio-energy will make up 30% of the total energy consumption in the Netherlands. On behalf of the Platform Bio-based Materials, ECN and Wageningen University analysed whether and how the 30% target could be met in 2030 [2]. The analysis showed that the target is ambitious and quantified the contributions to be expected from the three focal points selected in the EOS-LT research programme:

- Biomass gasification and gas conditioning (including syngas production from gas fuel)
- Biorefineries
- Biomass conversion, co- and auxiliary incineration in E-plants

ECN, TU/e, UT, TUD and BTG[1] have formed a consortium to execute a project which relates to the first of these three focal points. The consortium was formed with the intention to cooperate for a period of at least four years, in which PhD students at the university could perform research and report their results in a thesis. Because of the limits of the EOS-LT budget, subsidy was granted only for periods of one year at a time.[2] That is why this final report covers not just one but four EOS projects: EOSLT06007, EOSLT07007, EOSLT08007 and EOSLT09002.

According to the EOS-LT research programme the consortium research area is relevant for three energy market segments:

- Gaseous fuels (SNG [3], H_2)
- Electricity and heat
- Transportation fuels (and chemicals)

The project focuses on gasification as the principal biomass conversion process. Gasification concepts often are considered promising because of reasons like improved environmental performance, fuel flexibility, output flexibility, emissions, and efficiency. It is envisaged that biomass gasification in the Netherlands *ultimately* should take place at large scale. This not only results in relatively high efficiencies, low specific costs, low emissions and less non-technical problems (permits, locations). It also reduces logistic costs as in the Netherlands a significant amount of biomass must be imported to reach the 2020 and 2040 renewable goals [2]. Small-scale gasification however, will play a crucial role for (1) the cheap conversion of local biomass, and (2) the smooth transition to large-scale systems. Hence, options both for small-scale and large-scale systems are taken into account.

The next chapter describes the consortium research programme. The work was divided over seven tasks. Results are presented in chapter 3, in separate sections for each task. Chapter 4 gives details about the project execution. Chapter 5 discusses the contributions of the research performed to the EOS long term objectives. Chapter 6 presents the results in terms of outcome indicators.

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[1] ECN = Energy Research Centre of the Netherlands, TU/e = Eindhoven University of Technology, UT = University of Twente, TUD = Delft University of Technology, BTG = Biomass Technology Group.
[2] Actually, the last period was extended to a duration of 21 months.
[3] SNG = substitute (or synthetic) natural gas, essentially a methane-rich product similar to natural gas.

2. Consortium research programme

2.1 Research goals

The consortium partners perform research on biomass gasification and gas conditioning relevant for the three market segments identified in the EOS LT programme: gaseous fuels, electricity and heat, and the production of liquid fuels and chemicals. However, the focus is on technology to be used in the production of gaseous and liquid fuels. Research goals are:

- Development of technology for gasification of solid biomass, more specifically indirect (allothermal) gasification and self-gasification.
- Optimization of the methane content in biomass producer gas, obtained by gasification, by the use of catalytically active bed materials in the gasifier.
- Development of technology for the production of syngas ($\approx CO + H_2$) by gasification of solid biomass or by gasification of pyrolysis oil produced from solid biomass.
- Better understanding of fouling issues in gas heat exchangers.
- Development of technology for removal of tar from biomass producer gas.
- Development of gas cleaning for removal of contaminants which can poison catalysts needed to convert producer gas or syngas to SNG ($\approx CH_4$), liquid fuels or chemicals.

2.2 Research tasks and cooperation

The ECN long-term research programme on biomass gasification as described in [3] forms the backbone of the consortium research programme. The EOS consortium partners perform additional and more fundamental research, on subjects not covered by ECN or supportive to subjects which are included in the ECN programme. In general, research by the partners is meant to broaden and deepen the understanding of fundamental issues, while ECN research should be more market oriented.

ECN
Research on biomass gasification and gas conditioning at ECN aims mainly at the production of gaseous fuels, viz. SNG and syngas. SNG can replace natural gas in all its applications. Syngas can be used to produce electricity and heat, and is important as intermediate for the production of liquid fuels and chemicals. ECN focuses on technologies needed for bio-SNG production, i.e. the MILENA gasification technology, OLGA tar removal technology, and catalytic gas cleaning.

ECN acts as co-ordinator of the present project. ECN research and the co-ordinator task are not financed from the project budget, but from separate EOS funds allocated to ECN for long-term energy research.

TU/e
Research at TU/e within this project covers three subjects related mainly to gaseous fuels and electricity and heat. Research is performed by three PhD students and scientific staff. The three subjects correspond to the following tasks:

Task 1. The role of bed material in fluidised-bed gasifiers, especially the effect of bed material on the composition of the gas produced.
Task 2. Fouling in gas heat exchangers.
Task 3. Removal of tar from biomass producer gas by plasma or flame-generated radicals.

UT

Research at UT within this project covers two subjects aimed mainly at the production of gaseous fuels and transportation fuels and chemicals. Research is performed by two PhD students under guidance of scientific staff. The two subjects correspond to the following tasks:

Task 4. Gasification and reforming of pyrolysis oil to syngas which can be used to produce gaseous fuels like CH_4 and H_2, liquid fuels and chemicals, or electricity and heat.

Task 5. Self gasification, i.e. the production of CH_4 from biomass by decomposition at high temperature and pressure, assisted by the catalytic activity of elements present in biomass ash.

TUD

Task 6 is performed by TUD. It involves conditioning of biomass producer gas, and more specifically catalytic tar removal. It is mainly relevant for the production of gaseous fuels and electricity and heat. Research is performed by a post-doc and scientific staff.

BTG

Task 7 is performed by BTG. It concerns the conversion of biomass pyrolysis oil to syngas which can be used for the production of gaseous or liquid fuels, chemicals, and electricity and heat. Research is performed by scientific staff.

3. Results

Most of the work at ECN was directed to the development of technology for bio-SNG production. In 2008, an 800 kW_{th} 'pilot' MILENA gasifier was officially taken into operation by minister Cramer. In 2009, the gasifier was coupled to the existing OLGA tar removal system. Tests showed that both the gasifier and tar removal needed some design changes. These have been implemented and tested in 2010 and 2011.

Research at ECN on producer gas cleaning downstream the OLGA tar removal concentrated on removal of organic sulphur compounds and hydrogenation and reforming of unsaturated and aromatic hydrocarbons.

The HVC company has got involved in the SNG development process. In November 2010, HVC and ECN organised a 'green gas day' (www.groengasinzicht.nl) in Alkmaar to increase public awareness and present plans to build a 10 MW bio-CHP demonstration plant as a first step to a bio-SNG plant. Unfortunately, a project proposal submitted by HVC and ECN in 2010 to build the bio-CHP plant did not get a grant from the TERM programme for administrative reasons. HVC and ECN are now planning to build a bio-SNG demonstration plant in cooperation with other companies within the 'Green Deal' framework.

Research on syngas production at ECN focused on catalytic reforming of producer gas from the MILENA gasifier. A cooperation agreement was signed with NREL (USA), but confidentiality issues delayed experimental work. Instead, experiments were performed in co-operation with TUD. Results are reported under task 6.

Work performed by ECN and financed by EOS-LT and other sources has resulted in numerous articles in journals and books [4-10], reports [11-15] and contributions to conferences and symposia [16-59] on biomass gasification, product gas cleaning and production of SNG or liquid fuels. As can be seen from the references, much effort has been spent on promoting bio-SNG for heat production and as second generation transport fuel. As mentioned above, the HVC company has shown serious commitment to bring ECN MILENA gasification technology to the market and several other parties have declared their interest in participating in a 10 MW SNG demonstration facility to be built in Alkmaar. It is expected that an investment decision will be taken in 2012.

Results of work performed by the partners in the project are discussed below. Results are presented in separate sections devoted to the tasks defined in Section 2.2.

3.1 Task 1: Bed materials

Author: C.F. Mourao Vilela (TU/e)

Gasification is a thermo-chemical process that can convert the solid biomass into a product gas through partial oxidation at high temperatures. The product gas contains H_2, CO, CO_2, CH_4, other hydrocarbons (e.g. C_2H_4, C_2H_6) and H_2O, but also some contaminants like hydrogen sulphide (H_2S), ammonia (NH_3), hydrogen chloride (HCl) and tars (condensable organics). The product gas can be further conditioned with the removal of contaminants and adjustment of its composition for the production of electricity, chemicals or transportation fuels. Tar is a lump word that defines the organic contaminants. Their conversion or destruction is seen as one of the greatest technical challenges to overcome for the successful development of commercial gasification technologies. Tars are problematic because they can condense at low temperatures (already at 400°C) blocking and clogging process equipment downstream the gasifier. Besides this they are poisonous for catalytic reactors.

Catalysts are one type of treatment that can be used. Known as hot gas cleaning the application of catalysts will serve two purposes: to increase the yield of gas at the expense of tars and char and to tailor the composition of the gas to the specific desired product. They can be applied in the gasifier itself as bed material (primary catalysts) or in a secondary reactor, downstream the process (secondary catalysts).

To study the influence of bed additives in the process of biomass gasification a small scale fluidized bed gasifier was designed and built. This is a flexible and rather simple system that allows online measurements through a mass spectrometer. The experimental procedure can be divided into three steps. In the first one the bed is placed inside the reactor, the flow and type of carrier gas are chosen and the desired temperature settled. The second step concerns the introduction of the biomass particle when the temperature of the reactor stabilizes at the set point. When the gasification process is finished oxygen is allowed to enter, burning the solid carbon present in the bed. This will be the third step. As soon as the combustion is finished a new experiment can be performed without the necessity to cool down the reactor.

Pyrolysis, a thermo-chemical process by itself, is the first step of gasification. It is held responsible for the conversion of the solid biomass into three different types of products: a solid (char), liquid (tars that condense at room temperature) and gas. To understand the gasification process it is crucial to understand pyrolysis. To test the reliability and reproducibility of our experimental set-up the role of temperature and gas phase residence time under inert conditions (pyrolysis) was studied. The bed material used was sand and cellulose was the chosen biomass model compound. Each experiment was repeated at least three times, and the results presented here are average values. Also the standard deviation is presented even though it cannot always be seen in the figures. This happens because the symbols are just larger than the standard deviation values.

Figure 3.1a shows the influence of temperature on the material balance of the carbon from the original biomass. $C_{conversion}$ is the fraction of carbon from the original biomass present in the permanent gases, $C_{combustion}$ is the solid carbon that remains in the bed after pyrolysis and $C_{undetected}$ is the fraction of carbon that could not be traced and is assumed as tar. Figure 3.1b shows the energy content of the gas. The variable α_{energy} informs the amount of energy present in the original feedstock that will be converted into the permanent gases. The gas phase residence time of these experiments was 5 s.
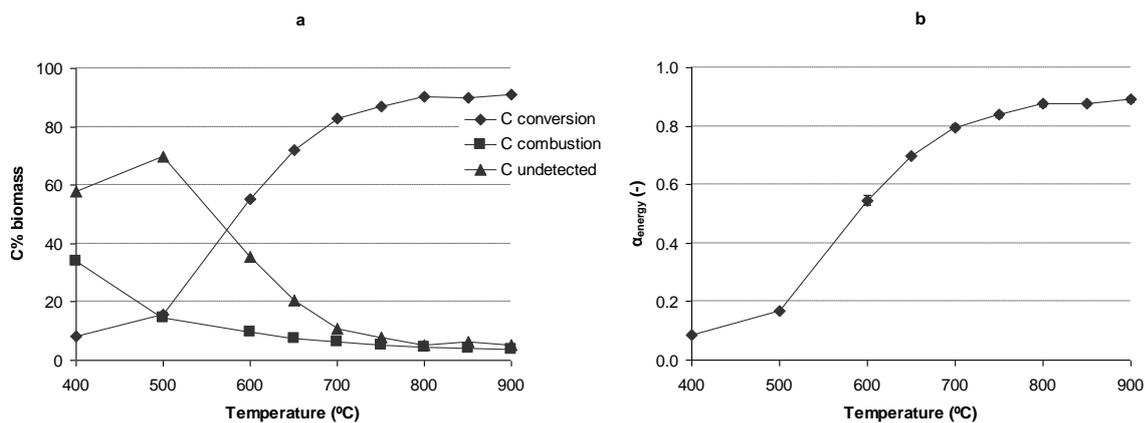
Figure 3.1   (a) Carbon from the original biomass distributed over permanent gases ($C_{conversion}$), char ($C_{combustion}$) and tars ($C_{undetected}$) and (b) energy content of the product gas as function of temperature.

Temperature plays a crucial role in pyrolysis. In the range studied there are crucial shifts between the patterns of the different product yields. Low temperatures favour char formation and high temperatures favour gas production. Above 600°C the gases are always the main product and above 800°C the cellulose conversion into gas is almost complete. The gas yield for cellulose is essentially the inverse of the tar yield, with negligible char yield except at the lowest temperatures. Tars reached a maximum at 500°C. Above this temperature, tar yield decreases with the increase of temperature indicating the start of cracking reactions. Above this temperature the gas yield is the inverse of the tar yield. This shows evidence of the role played by tar cracking reactions in the production of gas.

The trend of the energy content follows the pattern of $C_{conversion}$. If more gas is being produced with the increase of temperature, due to tar cracking reactions, then the energy content of the gas is also increasing. Of course, this can only happen if the main gases formed with the increase of temperature have high calorific value. This is what occurs since it is shown in figure 2 that CO, H_2 and CH_4 are favoured with the increase of temperature. If CO_2 and H_2O were main products from secondary tar reactions, in our experiments, then the values from Figure 3.1b should be lower because these gases have no calorific value. With the increase of temperature the energy bounded to tars is transferred to the non condensable gases. Above 800°C around 90% of the energy present in the parent cellulose is transferred to the permanent gases.
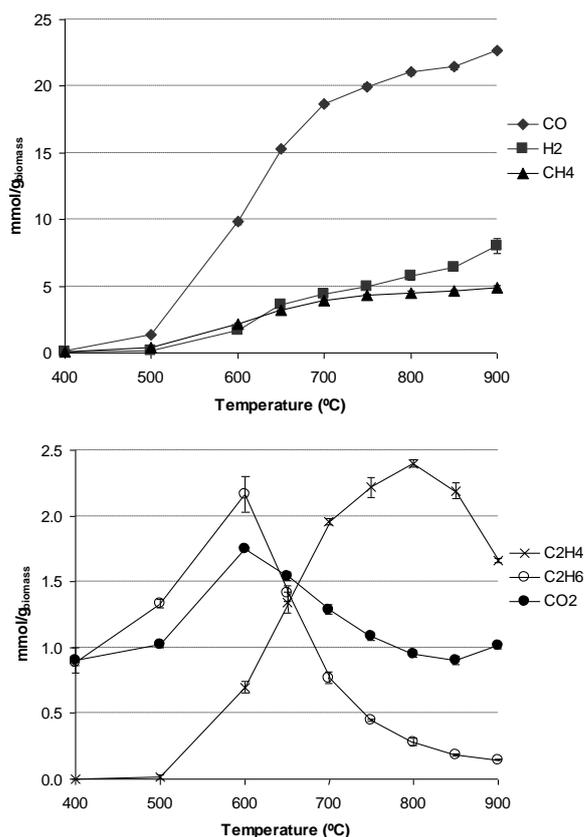
Figure 3.2   Gas composition of the permanent gases as function of temperature.

Figure 3.2 shows the behaviour of the analyzed permanent gases with temperature. It should be pointed out that the results are normalized with the weight of the biomass 'as received'. Above 500°C all the gases increase with special focus on CO which increases sharply. It is also above this temperature that C_2H_4 starts being formed. These results show the role played by tar cracking in the gas production. CO is the main product of tar cracking but also C_2H_4, CH_4, H_2 and CO_2 are formed. This suggests that the dominant contribution to the yield of these products comes from secondary decomposition of the tar rather than from primary degradation of cellulose.

It is interesting to outline the behaviour of the analysed hydrocarbons. C_2H_6, the heaviest, starts to crack at lower temperatures followed by C_2H_4. The amount of CH_4, the lightest molecule, increases through all ranges of temperatures studied, though very slowly at higher temperatures. The reactivity of these hydrocarbons shows evidence of a chain cracking sequence that progressively reduces the molecular weight of the products.

Tar is a lump word that agglomerates several different compounds. The nature of tar depends on the conditions of the system, among which the temperature plays crucial role. The first type of tars generated are mixed oxygenates, very reactive, and known as primary tars. If the conditions are suitable these primary tars will crack, producing non permanent gases and other type of tars known as secondary tars. These tars can be further cracked and tertiary tars will be formed among which the polynuclear aromatics (PNAs) represent a great deal. With the increase of severity conditions the oxygen tar content reduces as does the hydrogen to carbon ratio. Based on this information there was an attempt to identify and analyse some tar compounds assigned as model for the different groups. Acetol ($C_3H_6O_2$) is assumed as representative for primary tar. Toluene (C_7H_8) considered as an intermediate though not always classified as secondary tar. Naphthalene ($C_{10}H_8$) considered as model for PNAs. Though benzene (C_6H_6) is not considered as tar by several researchers its presence is important and also analysed.
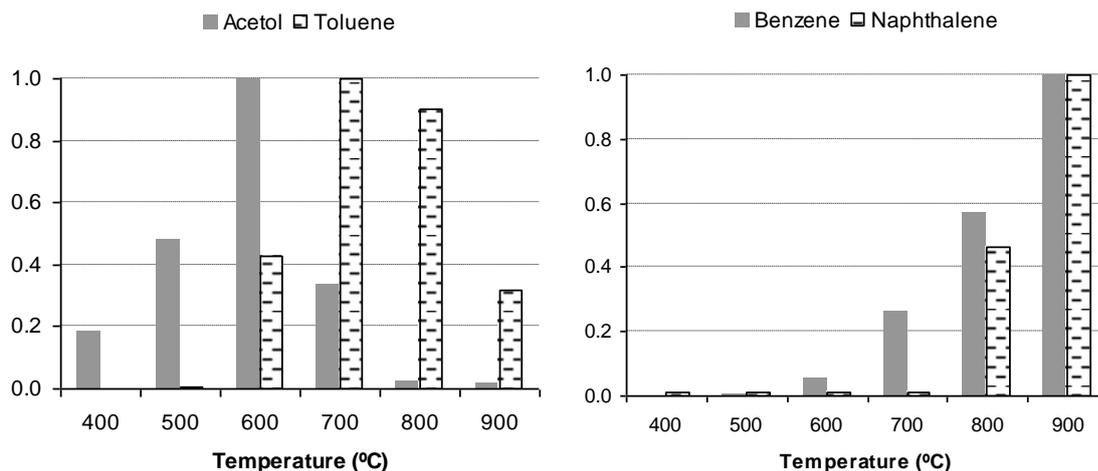
Figure 3.3   Tar compounds as function of temperature.

Figure 3.3 shows the influence of temperature over the above mentioned compounds. The results show a dynamic system under the influence of temperature. Acetol behaves as a typical primary tar compound. Its content reaches a maximum at 600°C, and at 800°C (and above) it gets almost completely converted. Toluene behaves as an intermediate, being converted at very high temperatures (800°C) and its presence is only noticed at 600°C and above. Naphthalene as model for polynuclear aromatics starts being produced at high temperatures (800°C) and reaches its maximum at the highest temperature studied, 900°C. Benzene behaves similarly to naphthalene, increasing with temperature though its presence is already noticed at temperatures as low as 600°C. These results clearly show the effect of temperature on the nature of tars. Low temperatures favour primary tars rich in oxygen while high temperatures decrease the total amount of tars but favour the formation of polynuclear aromatics which are more difficult to crack.

The effect of the gas phase residence time over biomass pyrolysis was also studied. Figure 3.4 shows this effect in the gas composition as well as in the overall carbon balance. The temperature of the process was 800°C; sand was the bed material and cellulose the feedstock.
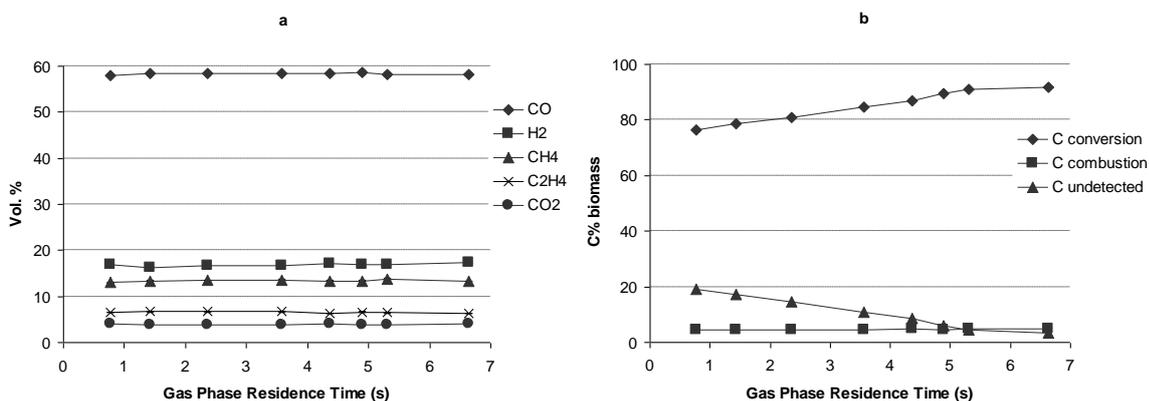
Figure 3.4   (a) Product gas composition (inert and water free) and (b) overall balance of carbon as function of gas phase residence time.

CO is the most dominant gas species when expressed on a volume percent basis (inert and water free), and represents more than 50% of the product gas. The volume fraction of H_2 is also important and constitutes approximately 17% of the product gas. CH_4, C_2H_4 and CO_2 are also present in substantial amounts. Comparing Figure 3.4a with Figure 3.4b we see that, although the product composition remains constant through the residence time, the $C_{conversion}$ is increasing and reaches a maximum at the highest residence times. This means that the volume of non-condensable gas is increasing with higher residence times though its composition remains the

same. Because the value for $C_{combustion}$ remains constant, around 4 - 5% of the original carbon, the increase of gas released is due to tar cracking reactions. Since the composition does not change we can conclude that CO is the main product of the cracking of tars but also CH_4, C_2H_4, H_2 and CO_2 are formed. Similar conclusion was reached when analysing the influence of temperature.

$C_{combustion}$ remains constant through the residence time. This is an expected result since the temperature and heating rate do not change with the residence time of the gas phase. This result proves the reproducibility of our system.
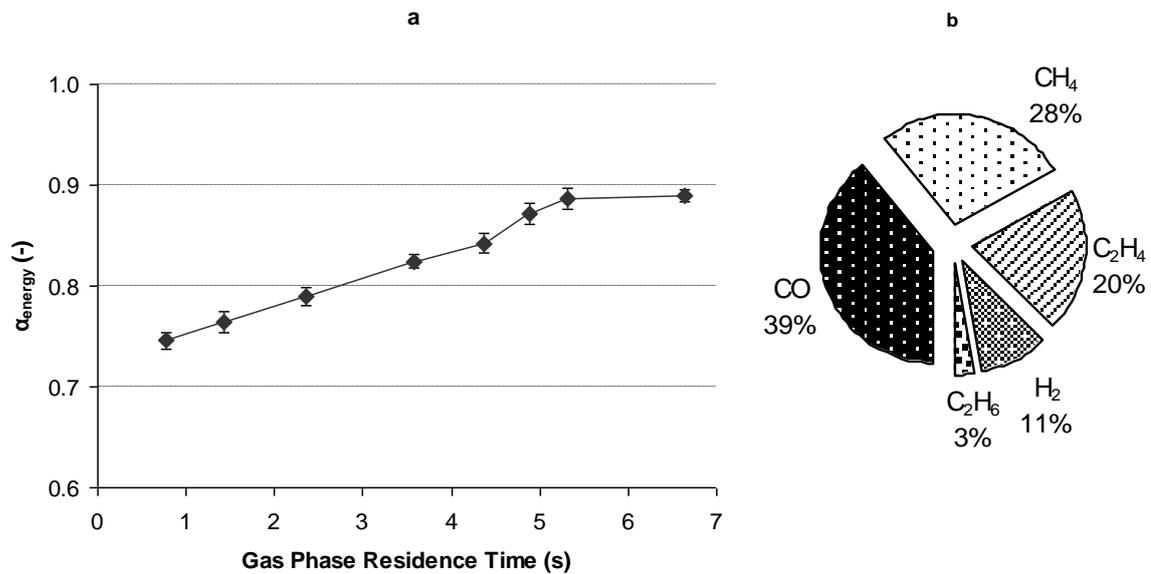
Figure 3.5   (a) Energy content of the product gas as function of the gas phase residence time and (b) share of energy of each component.

Figure 3.5 shows the energy content of the product gas and the share of energy of each component. As expected, if more gas is being produced, its energy content increases as well. The energy bound in tars is transferred to the non condensable gases. It is interesting to notice that this trend follows exactly the trend of $C_{conversion}$. This happens because the main products formed from the tar cracking (e.g. CO, H_2, CH_4 and C_2H_4) have high calorific value. If CO_2 and H_2O were main products from secondary tar reactions, in our experiments, then the values from this figure should be lower because these gases have no calorific value. At the highest residence time almost 90% of the energy present in the cellulose is transferred to the product gas.

CO, the dominant gas, has the highest share of energy. H_2 is the second most dominant gas in terms of volume but because it is lighter, when compared to the others, its share in energy is only 11%. It should be stressed that CH_4 and C_2H_4 account for almost 50% of the energy content in the gas produced.
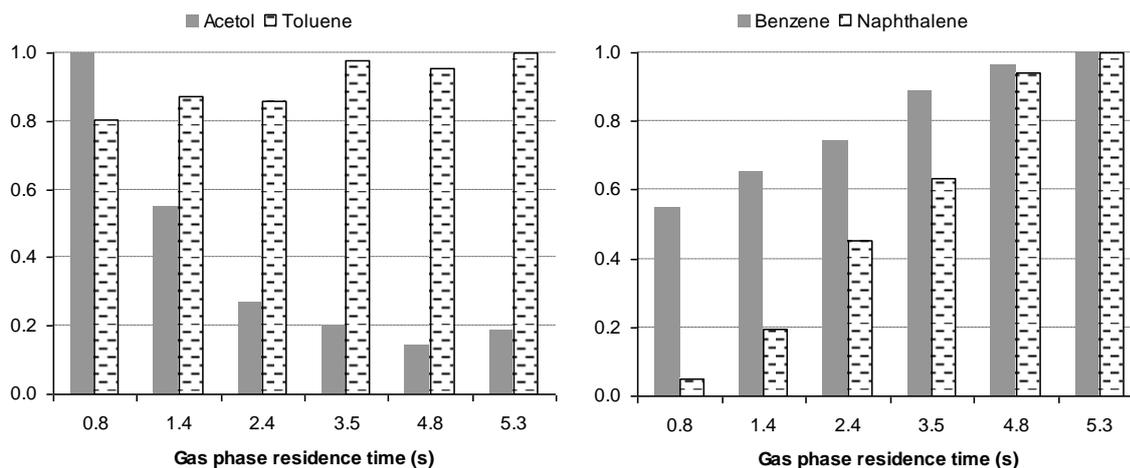
Figure 3.6   Tar compounds in function of gas phase residence time.

Figure 3.6 shows the influence of the gas phase residence time in the different tar compounds that were analysed. Attending to the conclusions reached with the influence of temperature it is expected that due to the increase of the gas phase residence time primary tars should be converted and tertiary tars should be formed. Figure 3.6 sustains this assumption. With the increase of residence time acetol is converted while naphthalene and benzene are formed. This shows that during the range of gas phase residence time studied tars are being converted and rearranged leading to less amount of tar but to more aromatics. There is no clear trend concerning toluene though it seems to be formed with the increase of the gas phase residence time.

The study of influence of temperature and gas phase residence time clearly shows that the pyrolysis process is very dynamic and the role played by the cracking of tars in the production of the permanent gases is crucial. CO accounts as the main product from tar conversion but also CH_4, C_2H_4 and H_2 are products. Naphthalene stands as an important compound representing polynuclear aromatics. Increasing the severity of pyrolysis (temperature and residence time) the tertiary compounds became important part of tar. These sets of experiments also show the reliability and reproducibility of our system.

Having characterized the system under inert conditions the influence of certain bed materials was studied. The primary goal is to apply bed additives inside the gasifier. 'Naturally occurring' minerals are abundant, relatively inexpensive and disposable which makes them attractive to use in the gasifier as bed material. Dolomite, a calcium magnesium ore ($MgCO_3 \cdot CaCO_3$), has been extensively investigated as biomass gasifier tar destruction catalyst. Olivine, a magnesium aluminosilicate ($[Mg,Fe]_2SiO_4$), is considered as an interesting alternative to dolomite.

Figure 3.7 shows the influence of dolomite and related compounds (magnesite [$MgCO_3$] and calcite [$CaCO_3$]) in the gas composition from biomass pyrolysis and in the distribution of carbon from the original biomass. These materials were calcined in situ. Upon calcination (release of CO_2 adsorbed in the material) they become porous materials. These experiments were performed at 800°C with cellulose as feedstock. Argon was the carrier agent and the gas phase residence time was 5 s. Also the results with sand are presented as basis of comparison.
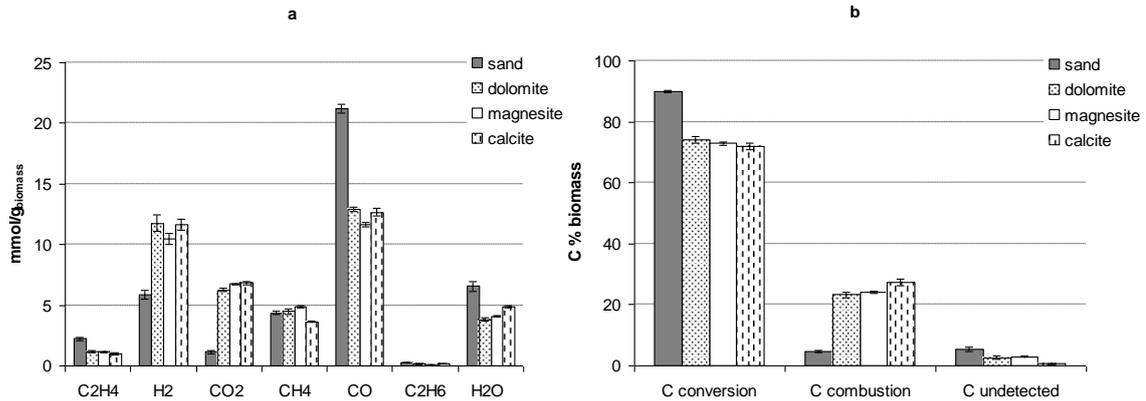
Figure 3.7   (a) Product gas composition and (b) overall balance of carbon in function of bed material.

From a general overview the three materials behave very similarly. When compared with sand they seem to promote the water gas shift reaction. H_2 and CO_2 increase at the expense of CO and H_2O. Also C_2H_4 seems somehow to be reformed while CH_4 remains unchanged (except in the case of calcite). The interesting results arise when comparing the values from the overall balance of carbon. Less carbon is present in the product gas and more carbon remains in the bed. Also fewer tars seem to be present in the overall process since less carbon was undetected. These results lead to the postulation that tars are adsorbed in the pores of the material. In this way tars do not flow freely through the freeboard and are not converted into permanent gases. This explains why the value of $C_{conversion}$ is lower than in the case of sand. It can be assumed then that if fewer tars are cracked less energy is transferred from them into the permanent gases. This can be assessed through Figure 3.8a.
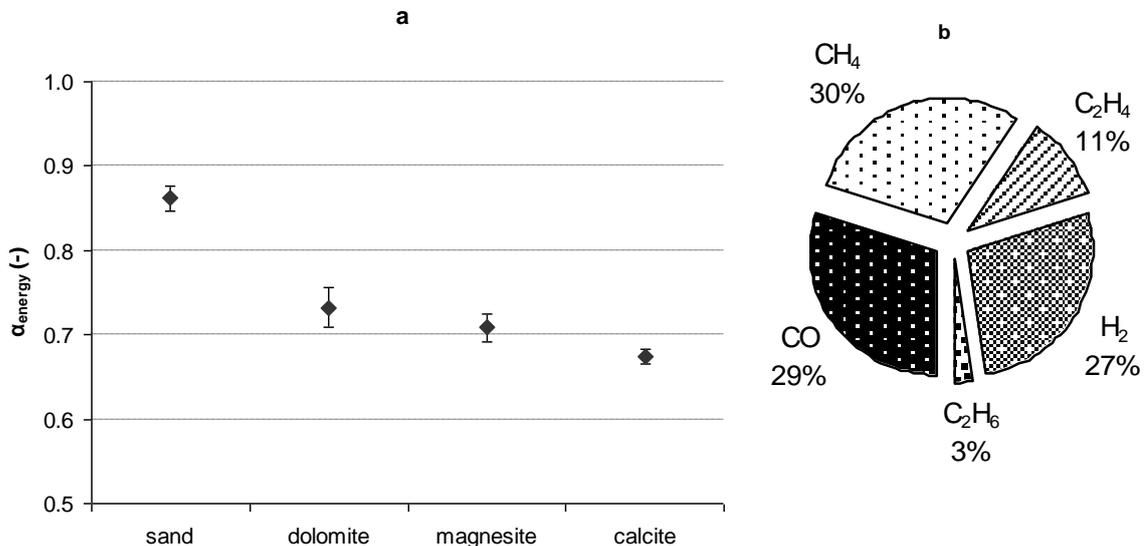
Figure 3.8   (a) Energy content of the product gas as function of the bed material and (b) share of energy of each component with dolomite as bed material.

Comparing Figure 3.8b with Figure 3.5b one can see the shift in the share of energy by each compound when changing sand for dolomite. Since H_2 increases with dolomite its share of energy also increases from 11 to 27%. CO and C_2H_4 decrease while CH_4 remains the same. These results are the expected ones attending to the values of Figure 3.7.

From Figure 3.7b it was concluded that the presence of the catalytic materials leads to a decrease in the tar content. Figure 3.9 shows the influence of these bed materials in the analysed

tar compounds. Again all the materials behave very similarly. The use of these catalysts leads to a decrease of naphthalene and benzene. Once again toluene does not show a clear trend. Acetol increases which leads to the postulation that this compound results also from the cracking of the stored tars in the dolomite and related compounds.
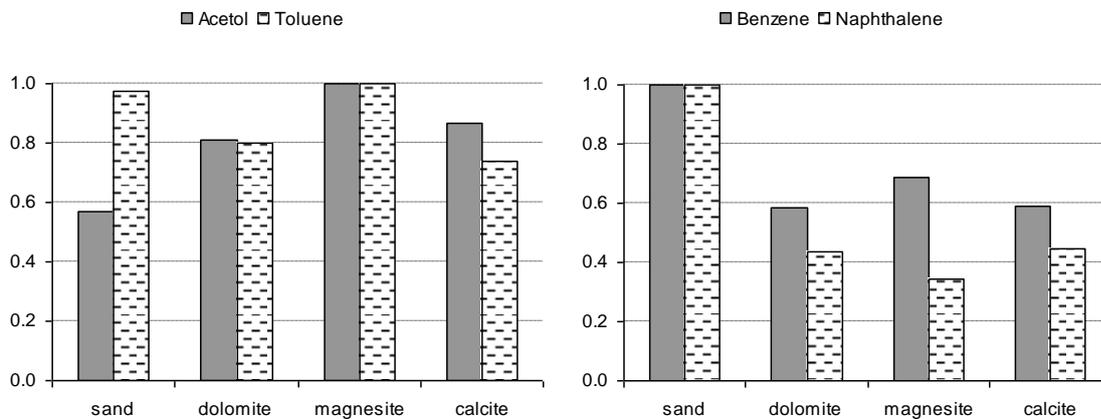
Figure 3.9   Tar compounds in function of bed material.

Other tests were done with three different types (acidic, neutral and basic) of porous alumina (Al_2O_3) as bed material. There was no difference in the results between the different types of alumina. It was noticed that even a higher amount of tar was adsorbed on alumina, compared with dolomite, which may be explained with the higher surface area as well as wider pores of this material. The content of naphthalene and benzene increased as well when compared with dolomite and even sand. Assuming that tars are stored in the alumina they have enough time to be converted into tertiary tars which may explain the increase of naphthalene and benzene. It was also noticed a very high value of solid carbon that remains in the bed after the process is finished, which may be due to soot formation. These results also lead to the conclusion that dolomite and related compounds exert a catalytic effect over the tars adsorbed on the material.

Assuming then that tars are adsorbed in the material it is expected that depending on the surrounding environment different types of reactions will occur. If the environment is inert only thermal cracking will occur with the release of CO and H_2. If steam is present in the system steam reforming followed immediately by water gas shift will promote the release of H_2 and CO_2. If oxygen is present then CO_2 will be the main product. These conclusions can be asserted in Figure 3.10a which shows the influence of the environment in the cracking of the tars stored in the bed material. It has to be pointed out that these values are not accounted in the results of gas composition presented in Figure 3.7a. Consequently they are not taken into account for $C_{conversion}$ from Figure 3.7b. They are enclosed in the result of $C_{combustion}$. Based on this information Figure 3.10b shows the fraction of $C_{combustion}$ that will be converted into gas (C_{gas}) and that will remain in bed as solid carbon (C_{char}). Figure 10b shows that steam produces the least amount of solid carbon while argon (thermal cracking) gives rise to the highest amount of soot. It should be pointed out that the environment from these figures was not pure steam or pure oxygen but rather a small fraction, around 2.5%.

Other tests were performed changing the gas phase residence time with dolomite as bed material. These results allowed us to conclude that some tars still flow freely through the freeboard and are still converted into permanent gases.
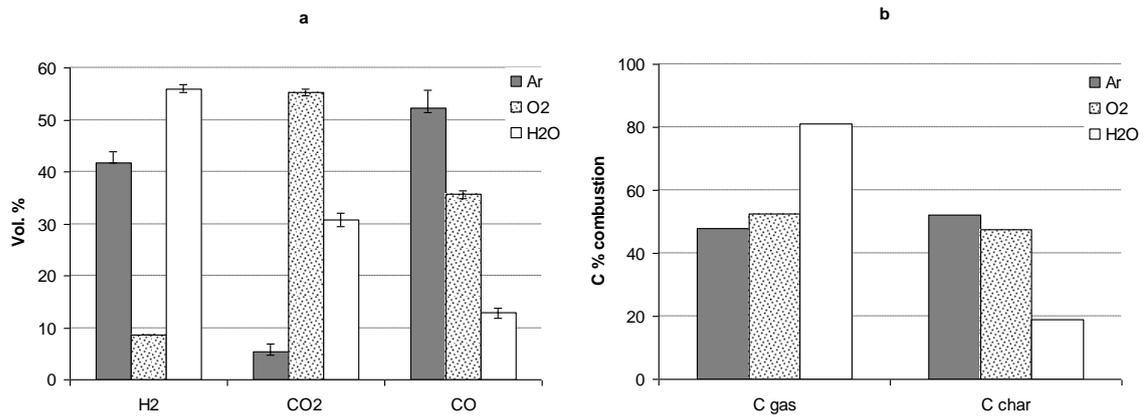
Figure 3.10 a) Cracking of tars stored in the dolomite under different environments and b) fraction of carbon present in the tars adsorbed in the dolomite that is converted into gas (C_{gas}) and remains as solid carbon (C_{char}).

Based on all the performed tests we conclude that the tar is physically adsorbed on the material though part of it still flows with the permanent gases. Depending on the environment the material stored will suffer different reactions. Besides these points dolomite and related compounds exert a catalytic effect over tars and over the composition of the product gas. Dolomite, magnesite and calcite behaved very similarly.

Olivine was also a material tested. Figure 3.11 shows the influence of olivine in the gas composition from biomass pyrolysis (results normalized with the weight of biomass 'as received') and in the distribution of carbon from the original biomass. The temperature of the process was 800°C and cellulose the feedstock. The carrier gas was argon and the gas phase residence time around 5 s. The olivine was subjected to two in situ pre-treatments. The olivine was oxidized at 800°C in 20% O_2 in Ar during 30 min (Oxi Olivine). The olivine was oxidized at 800°C during 30 min in 20% O_2 in Ar followed by a reduction, at the same temperature, in 5% H_2 in Ar during 30 min (Red Olivine). Also the results with sand and dolomite are shown as basis of comparison.
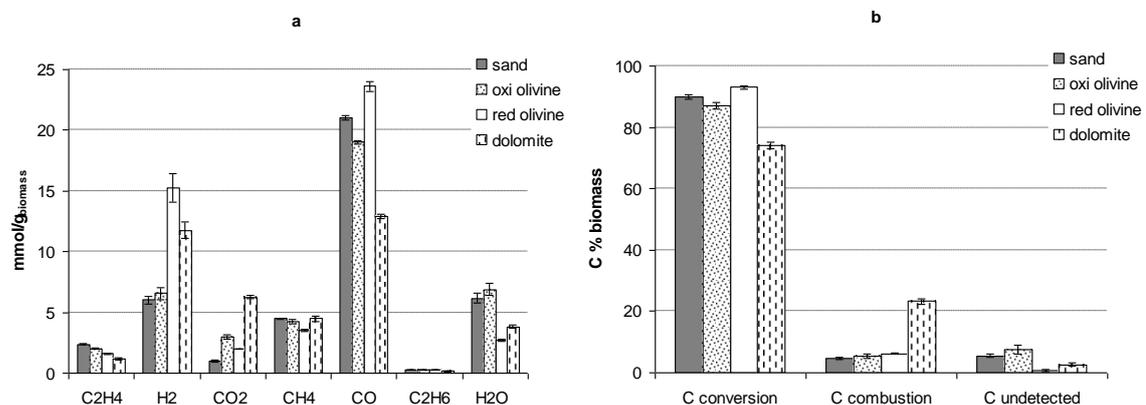
Figure 3.11 (a) Product gas composition and (b) overall balance of carbon in function of bed material.

It is clear from Figure 3.11 that different pre-treatments on the olivine lead to different effects. When compared with sand the oxidized olivine promotes CO_2 at the expense of CO while the reduced olivine promotes H_2 at the expense of H_2O. To understand these results we should have in mind the different states of iron that may be present in the olivine (see Figure 3.12).

Hematite		Magnetite		Wustite		Iron
Fe_2O_3	$\xleftarrow{\text{Oxidation}}$ $\xrightarrow{\text{Reduction}}$	Fe_3O_4	$\xleftarrow{\text{Oxidation}}$ $\xrightarrow{\text{Reduction}}$	$Fe_{(1-v)}O$	$\xleftarrow{\text{Oxidation}}$ $\xrightarrow{\text{Reduction}}$	Fe

Figure 3.12 Different forms of iron oxide.

Hematite is the most oxidized form while iron is the most reduced form. When olivine is placed in an oxidizing environment as pre-treatment, its iron content will be driven towards the hematite state. When in contact with the produced gas the oxidized iron present in the olivine will be reduced. In this way the oxygen present in the iron oxide will be transferred into the product gas. CO reduces the olivine releasing CO_2. This explains why comparing the results with sand the oxidized olivine generates more CO_2 at the expense of CO. A similar approach can be taken in the case of the reduced olivine. In contact with the syngas the reduced iron will be oxidized by H_2O releasing H_2. That is why the reduced olivine produces the highest amount of H_2 at the expense of H_2O. Attending to these results one may assume that CO is a better reducer than H_2 and that H_2O is better than CO_2 as an oxidant

The increase of CO when the olivine was reduced can not be explained with the redox reactions of the iron. Compared with sand more CO but also more CO_2 are generated. Since there is some reduction in C_2H_4 and CH_4 one may already expect an influence of the reduced material in the tar cracking. Figure 3.11b shows the overall carbon material balance. The differences between sand and the oxidized olivine are not substantial, though they suggest that less carbon is present in the condensable gases with a slight increase in the solid carbon that remains in the bed. The $C_{undetected}$ somehow remains higher in the case of the oxidized olivine. In the case of reduced olivine the results are more striking. More carbon is present in the gas, more remains in the bed and the overall that could not be traced is almost meaningless. The reduced iron exerts influence in the path of tar cracking leading to CO instead of CH_4 and C_2H_4. These results suggest a catalytic effect by the reduced iron in tar cracking. The increase of CO_2, compared with sand, may be explained by the Boudouard reaction known to be catalyzed by metallic iron. This assumption is supported by a slight increase in $C_{combustion}$. CO_2 may be formed from the reduction of the iron by CO as well. It may be that not all the iron is in its metallic form and can still be reduced by the CO present in the produced gas and so releasing CO_2. Or some of the oxidized iron by water is reduced again with the CO present in the produced gas.

The differences between the influence of olivine and dolomite are clearly shown in Figure 3.11. Dolomite promotes strongly water gas shift towards the production of H_2. Concerning tars it seems that first they are adsorbed on the porous of dolomite and then subjected to catalytic reactions promoted by the dolomite. The pre-treatment has a clear influence in the effect of olivine which is related to redox reactions of the iron. It seems that reduced olivine has the best performance, more H_2 and CO released and less tar present in the product gas. But this effect has to be studied in detail since it seems that the Boudouard reaction is promoted by the reduced olivine which leads to the formation of soot and as consequence may create runaway conditions.

Figure 3.13a shows the energy content of the product gas in function of the bed material. Figure 3.13b shows the share of energy of each component with reduced olivine as bed material. Dolomite produces the gas with least energy content which was already explained before. The oxidized olivine produces a gas with less energy content than sand which is explained by the fact that CO_2 (no calorific value) is produced at the expense of CO (high calorific value). Reduced olivine has the best performance. It promotes formation of H_2 at the expense of H_2O but also CO is promoted due to tar cracking. Reduced olivine favours the transfer of the energy bounded to tars into the permanent gases. We should have in mind that this may not a fair comparison to dolomite. In these results the potential gas generated by cracking of tars stored in the dolomite is not accounted.

Figure 3.13 (a) Energy content of the product gas as function of the bed material and (b) share of energy of each component with reduced olivine as bed material.

Figure 3.14 Tar compounds in function of bed material.

Comparing the overall balance the results point out that the reduced olivine produces less tar when compared with dolomite and the oxidized olivine is the one that presents the least effect. The results analysing the single tar compounds point to the same direction (see Figure 3.14). Dolomite always behaves better than the oxidized olivine. Less benzene, toluene and naphthalene are produced which leads to the conclusion that less tars are present in the produced gas. The reduced olivine seems to produce even less tars than dolomite and that can be visualised clearly with naphthalene. The amount of benzene that is reduced is similar. Also less toluene is present. It is evident that the reduced olivine always behaves better than the oxidized olivine. It produces a gas richer in energy content and with fewer tars.

Conclusions
- Cracking of tars plays a crucial role in the production of permanent gases. Increasing the severity of the process (higher temperatures and higher gas phase residence times) leads to conversion of tars into permanent gases. But a process too severe leads to the formation of PNAs which are very difficult to destroy and due to that very problematic.
- Dolomite exerts a clear catalytic effect on the process. Water gas shift reaction is promoted towards the production of H_2 and fewer tars are present in the product gas. In our experiments there was no clear difference between dolomite and related compounds (magnesite and calcite).
- The pre-treatment that is subjected to olivine has a clear influence on the behaviour of this material. Oxidized olivine promotes production of CO_2 at expense of CO and reduced olivine promotes H_2 at the expense of H_2O. The reduced olivine seems to promote tar cracking reactions which is not seen with oxidize oxidized.

3.2 Task 2: Fouling in heat exchangers

Authors: K. Kumar and C.C.M. Rindt (TU/e)

Introduction

The product gas from biomass gasification is usually contaminated with particulates, alkali compounds and tar components. The deposition of particulate matter on heat exchanger surfaces is known as particulate fouling. The layer formed by such deposition has a very low thermal conductivity and eventually reduces the efficiency of the system. This also leads to higher maintenance costs. In order to design new and efficient systems, and to understand the prevailing systems, predictive numerical models are indispensable.

Particles in the gas stream can deposit over the heat exchanger surface owing to different mechanisms like thermophoresis, electrophoresis, Brownian diffusion, inertial impaction and vapour condensation. Among these mechanisms, inertial impaction and vapour condensation play a major role. To numerically describe the process of fouling, the individual mechanisms of deposition and removal of particles must be treated properly. Further, process conditions like gas phase velocity, temperature, tube geometry and arrangement, particle concentration affect the overall fouling process. It is very difficult to understand the effect of each individual parameter using input from industrial-scale experiments. To discriminate between the influence of the various parameters, controlled fouling experiments are needed.

Objectives

The objective of this study was diversified in to 4 focus areas.

A. Sticking conditions for particle impaction to dry and liquid-coated surfaces
   When a particle reaches a heat exchanger surface, it can interact with a dry surface or a surface coated with a thin liquid film formed due to condensation of tar or alkali species present in the gas stream. Particle drop experiments were carried out to compare and evaluate the available models for a particle impacting a dry or a liquid-coated surface. A new methodology is developed to evaluate the amount of energy lost in the liquid film.
B. Design and construction of a setup to perform controlled fouling experiments
   An experimental setup was designed, constructed and tested to evaluate the effects of various process conditions on the fouling behaviour in a controlled way. Fouling layer growth experiments can be performed under controlled conditions for longer times (up to days) and at elevated temperatures (up to 500°C) using the experimental facility.
C. Evaluation of the effects of various process conditions on fouling
   Several experiments were performed under controlled conditions to evaluate the effect of process parameters.
D. Development of a numerical model to capture the fouling process
   The information gained from the impaction experiments and a model accounting for particle removal due to shear was implemented in commercial CFD software (FLUENT^{TM}) to simulate particle deposition under dry and wet conditions

Results

Part A: Sticking conditions for particle impaction to dry and liquid-coated surfaces. The parameter used to quantify whether or not a particle adheres to a surface is termed as 'sticking probability'. The impaction of a dry particle with a surface devoid of any liquid is termed as dry impaction and the impaction in presence of a liquid layer between the incoming particle and the surface is termed as wet impaction. The dry and wet impaction processes were studied to gain better understanding and to provide input to the numerical deposition models.

For a dry impaction, the outcome of an impact can be determined using the principles of contact mechanics. A critical velocity can be defined and a particle will stick to the surface if its impact velocity is less than the critical velocity, else it will rebound off the surface. The momentum

loss of a particle impacting a surface is generally quantified by the ratio of the rebound velocity to that of the impact velocity and is termed as restitution coefficient. Thus,

$$e = \frac{V_{rebound}}{V_{impact}} \tag{3.1}$$

$Stk = \frac{mV_{impact}}{6\mu\pi r^2}$ For a particle impacting a liquid coated surface, the sticking and rebound criteria can be defined based on the non-dimensional Stokes number defined by the relation:

$$\tag{3.2}$$

where m is the mass of the particle, v the impact velocity, r the particle radius, and μ the dynamic viscosity of liquid layer.

An experimental facility was built to study the impaction of particles over dry and liquid coated surfaces. The facility and an example of images it produces are shown in Figure 3.15. An analytical model for dry impaction was validated with the experiments and is used in the numerical modelling.

(a)   (b)
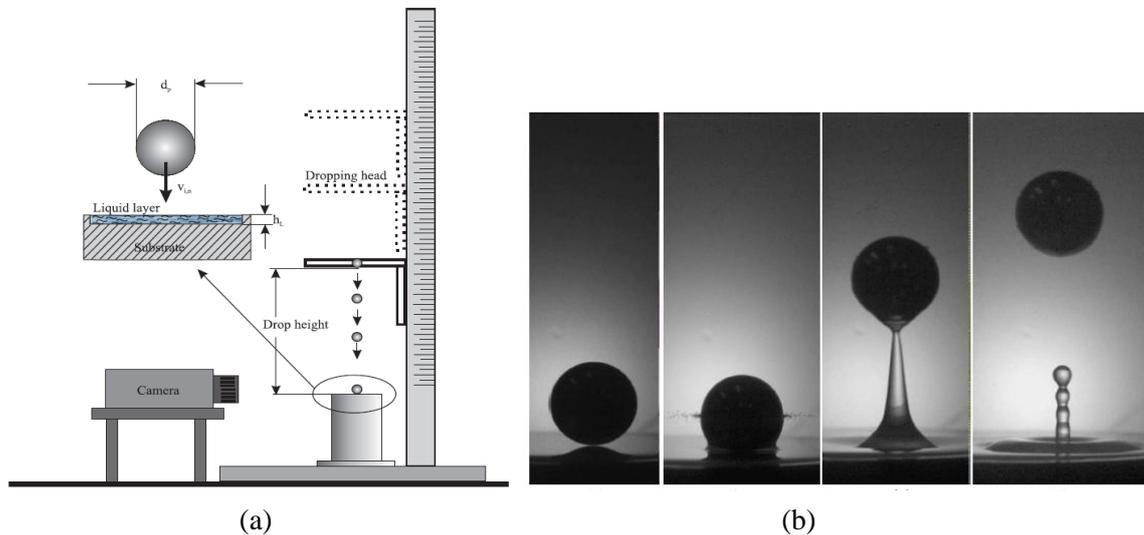
Figure 3.15 (a) Schematic representation of the experimental setup for drop experiments used to evaluate sticking criteria for particle impaction over dry and liquid coated surfaces; (b) A sequence of images from a high speed recording showing the impact and rebound of a particle over a liquid coated substrate.

The impaction and deposition mechanism under wet conditions is considerably different owing to the viscous losses in the liquid phase. During a particle impaction over a liquid coated surface, a major portion of the particle kinetic energy is dissipated in the liquid layer and this enhances the sticking probability. It is important to evaluate the energy lost by the particle during such an impact in order to describe the sticking condition. A detailed literature survey was conducted to find suitable models. Basically, two models were found in the literature and experiments were performed for a wide range of Stokes numbers in order to evaluate the models.

Figure 3.16 (a) and (b) show the comparison of the numerical models and the experimental data for particles impacting a liquid coated surface for varying Stokes numbers. Different particles, substrates and liquids were used in the experiments. It was observed that the models had limited applicability. In order to setup a model which can describe the sticking behaviour under wet

conditions and can be used in numerical calculations, detailed experiments were carried out to evaluate the energy balance for the wet impaction process.

(a)

(b)
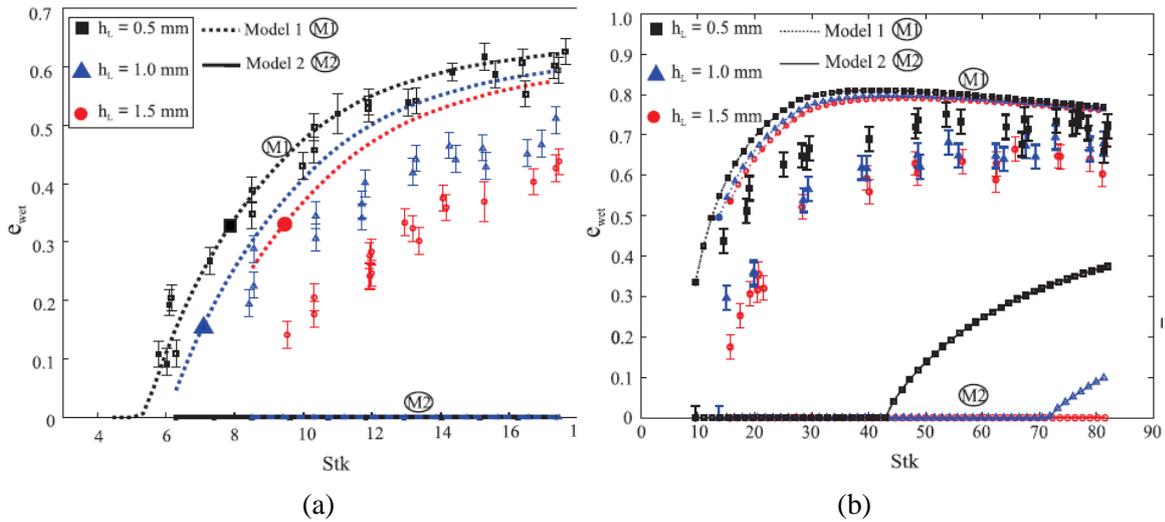
Figure 3.16 Restitution coefficient for wet impaction in the Stokes number range of (a) 0 to 18 and (b) 10 to 80.

The detailed experiments indicate that the particle impaction behaviour can be visualized in three distinct regions based on the Stokes number. In most of the cases, a critical Stokes number (Stk_{cr}) was observed beyond which the particle begins to rebound and was found to be between 2 to 5. Thus, a perfect sticking range can be described where the particle loses all of its kinetic energy and does not rebound $0 < Stk < Stk_{cr}$. A second region can be observed ($Stk_{cr} < Stk < 100$) for which the particle loses significant amount of energy in the viscous layer and the rebound velocity is very low. A third region beyond $Stk = 100$ exists where almost 50% of the particle kinetic energy is lost in the liquid layer. For drastically higher Stokes numbers > 5000, the rebound characteristics of the particle are similar to dry impacts indicating minimal energy losses in the liquid layer.
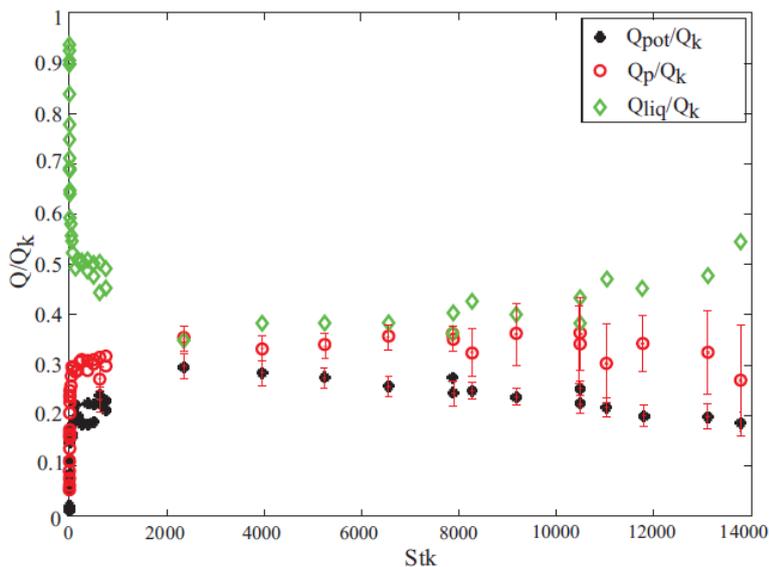
Figure 3.17 Measured energy balances for particles impacting a liquid coated surface and undergoing elastic-plastic deformation.

A particle striking a liquid coated surface will initially loose a certain part of its kinetic energy in the liquid layer and then comes in contact with the substrate during which it can undergo deformation. After impaction, based on the elastic stored energy the particle will rebound to a certain height. Figure 3.17 shows the energy dissipated in the liquid layer (Q_{liq}), the potential energy of the particle (Q_{pot}) at the maximum height when the particle rebounds and the energy dissipated in the elastic-plastic deformation (Q_p). The energies are normalized with the incoming particle kinetic energy (Q_k). An empirical equation was formulated to evaluate the energy loss in the liquid layer which can be implemented in the numerical model to determine the particle sticking probability.

If the particle and substrate properties are known, the present work provides a means to evaluate whether a particle will stick to the surface and also if the impaction will cause dents and erosion of the substrate in the presence of a liquid layer.

Part B: Design and construction of a setup to perform controlled fouling experiments.
Figure 3.18 shows the controlled fouling experimental facility which was conceptualized and built. The experimental facility is basically a closed loop vertical wind tunnel which can deliver air at velocities ranging from 1 m/s up to 5 m/s and a temperature in the range of ambient to 500°C. Particle concentration in the flow can be controlled by injecting the required quantity into the air using a screw feeder. Three windows are provided at the test section in order to observe and measure the evolution and growth of the fouling layer.
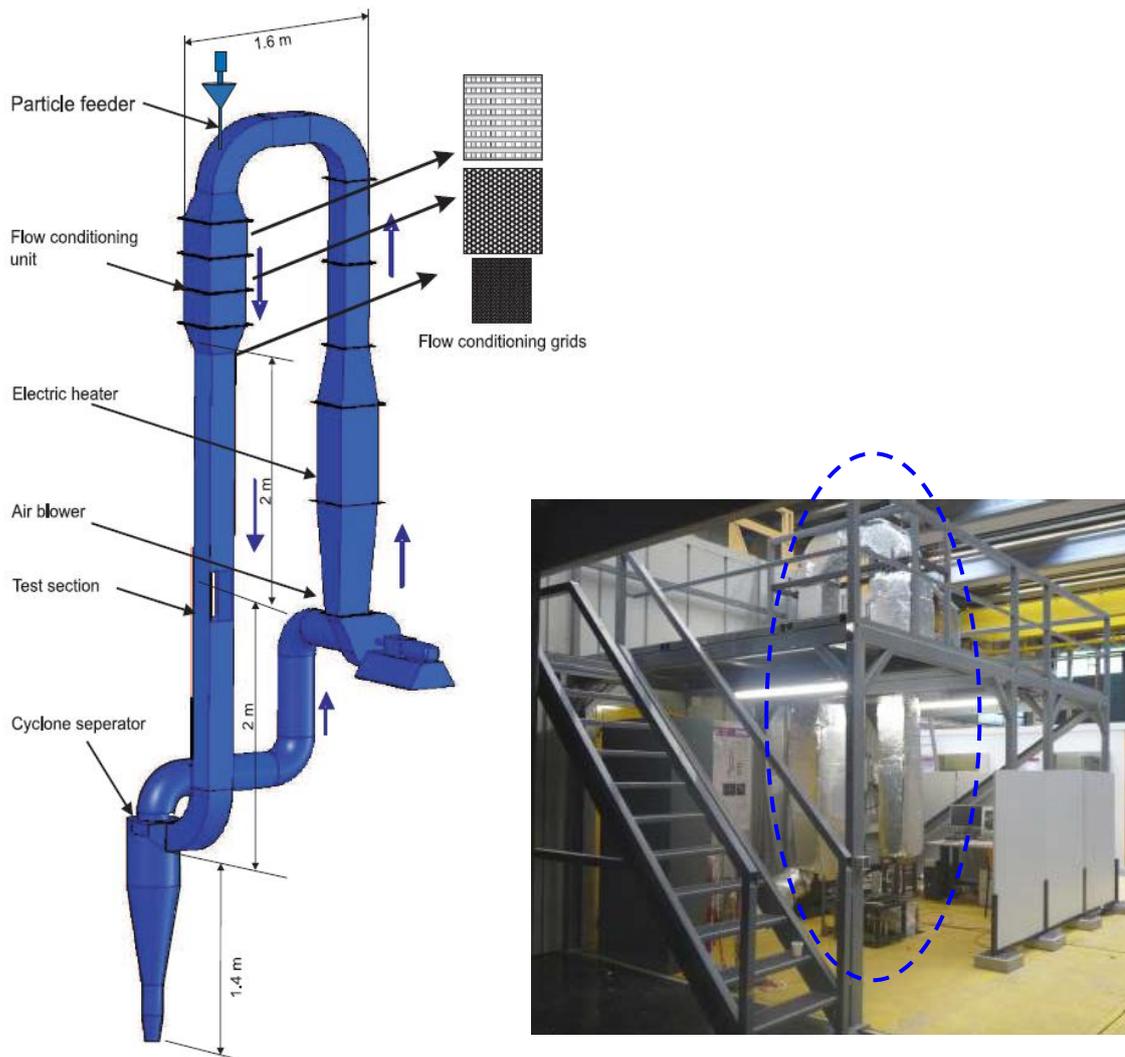
Figure 3.18 The controlled fouling setup showing all elementary parts: air blower, electric
heater, particle feeder, flow conditioning unit, test section and cyclone separator.

The flow parameters chosen to investigate in the present work include: carrier phase velocity, temperature, and humidity. Particle parameters include: particle concentration in the flow, particle type and particle size distribution (PSD). Target parameters that influence deposition include: target size, shape, material, orientation to the flow, liquid coating on the surface of the target etc. In most of the cases, changing one variable inadvertently changes another variable. For example, changing the orientation of the target geometry changes the wall shear, flow field and the interaction of particles with the surface. This exactly defines a need for a controlled experimental facility which reduces the number of unknown parameters that affect the end result as much as possible.

Figure 3.19 shows a typical measurement of the development of the fouling layer thickness as function of time. The raw images indicate the clean tube at the start of the experiment and the fouled tube.
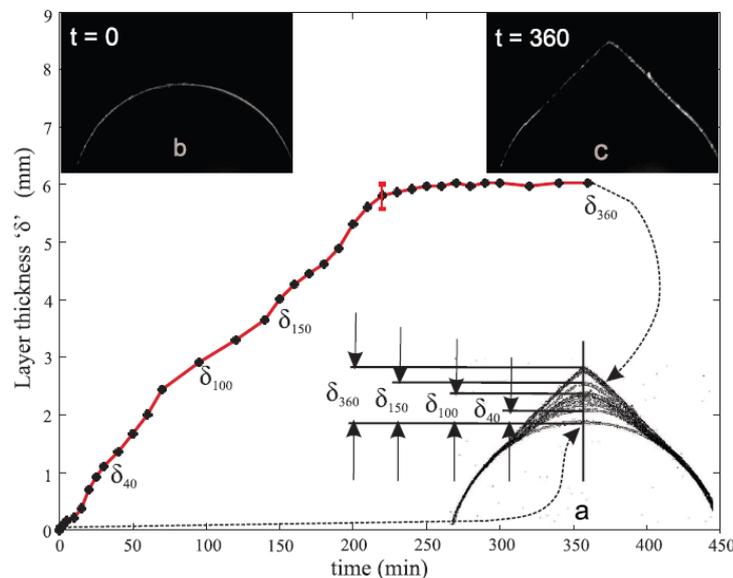
Figure 3.19 (a) Processed image depicting the evolution of the fouling layer, (b) raw image of
the tube taken before the experiments and (c) raw image of the fouled tube at the
end of the experiments.

Part C: Evaluation of the effects of various process conditions on fouling. Table 3.1 shows the matrix of all experiments performed. Various parameter classes were defined: particle (type, concentration and distribution), velocity, temperature and tube (geometry, orientation and material). In each experiment only one parameter was changed with respect to a reference fouling experiment: 2.0 g/m^3 of 20 μm glass particles in an air flow of 1.5 m/s and 20°C around a stainless steel circular tube with an outer diameter of 30 mm.

The following conclusions were drawn from the experimental observations.

- The gas velocity was found to have a very strong influence on the overall deposition process for both dry and wet conditions. For dry deposition, the asymptotic fouling thickness was found to be inversely proportional to the square of the velocity.
- Experiments performed at higher temperatures indicated the importance of particle properties on the deposition process.
- The geometry of the tube is an important parameter which influences deposition to a large extent by reducing the critical sticking velocity for the particles Thus, as the particle deposits on a surface and forms a layer, the geometry changes, which in turn

changes the flow field. As the layer geometry changes, the critical sticking velocity changes and lowers the number of particles that deposit.

- The presence of a liquid layer enhances particle deposition. The difference in mass of particles collected for wet deposition after 1 minute indicated an increase of 92% as compared to the dry deposition mass collected after the same time. Based on the Stokes number, the sticking probability and the erosion characteristics can be determined.
- By altering the tube orientation, it was observed that the limiting velocity for fouling reduced drastically. It is also seen that the particle collision dynamics governs the deposition mechanism to a large extent. A detailed numerical model which captures the particle collision and removal dynamics will aid in better design procedures to minimize fouling.

Table 3.1 Parameter settings for all experiments performed and nomenclature

Particle	$C_p (g/m^3)$	V_g (m/s)	T_g(°C)	Tube
1) $G(20)$	2.0	1, 1.55, 1.8, 2, 2.25, 2.5	22	SS D30
2) $Ca(40)$	2.0	1.5, 3, 5	22	SS D30
1) $G(20)$	0.2, 0.8, 2.0	1.5	22	SS D30
2) $Ca(40)$	2.0, 6.0, 8.0	1.5	23	SS D30
1) $G(20)$	2.0	1.5	22, 200, 500	SS D30
2) $Ca(40)$	2.0	1.5	23, 500	SS D30
3) UHMWPE	0.25	1.5	20, 70, 100	SS D30
$G(20)$	2.0	1.5	25	Glass, Brass, Steel, Copper, Aluminum, PVC
$G(20)$	2.0	1.5	23	SS D21,D30 D38,D51
$G(20)$ $Ca(40)$ Ash	2.0	1.5	25	
$G(20, 55, 80, 143)$	2.0			
Mixture 1,2,3,4	2.0	1.5	23	SS D30
$UHMWPE$	0.38			
Ash	0.3			
(Influence of liquid layer)				
$G(20), G(143), Ca(40), Ash, Glycerol$	2	1.5, 3.0	23	SS D30, PVC,Sq(45°)
$G(20), G(143), Oil 1(\mu = 0.049\ Pas)$	2	1.5		SS D30
$G(20), G(143), Oil 2(\mu = 0.156\ Pas)$	0.25	1.5		SS D30
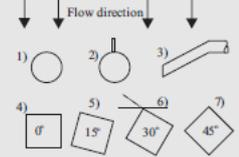
V_g	Gas phase velocity 100 mm above the tube axis
C_p	Particle concentration in the flow
T_g	Gas phase temperature
SS Dx	Stainless steel circular tube of outer diameter x = 21, 30, 38 and 51 mm
Sq	Square tube of 40 mm side
G(y)	Glass particles with mean diameter of y = 20, 55, 80 and 143 μm
$Ca(40)$	Calcium carbonate particle with mean diameter of 40 μm
UHMWPE	Ultra high molecular weight poly ethylene
Ash	Ash particles procured from a Dutch biomass gasifier
PVC	Poly Vinyl Chloride
Mix 1	Mixture of G(20) and Ca(40) 50:50 by weight
Mix 2	Mixture of G(20) and Ca(40) 75:25 by weight
Mix 3	Mixture of G(20) and G(55) 50:50 by weight
Mix 4	Mixture of G(20) and G(80) 50:50 by weight

Part D: Development of a numerical model to capture the fouling process. The numerical models developed for particle deposition under dry and wet conditions were implemented in a commercial computational fluid dynamics package (FLUENT[TM]). Further, the removal of particles due to a shear flow was also implemented in the numerical model. A 2-dimensional circular cylinder subjected to a cross-flow was considered and the influence of gas phase

velocity, geometry and presence of a liquid film were demonstrated. As a preliminary step, the flow field and the particle transport and deposition models were validated with experimental data. Figure 3.20 shows the domain and grid used in the calculations. Figure 3.21 shows validation results of the flow model using the non-dimensional friction coefficient around the cylinder, and of the deposition model using the collection efficiency. A satisfactory agreement was found between the numerical and literature values.
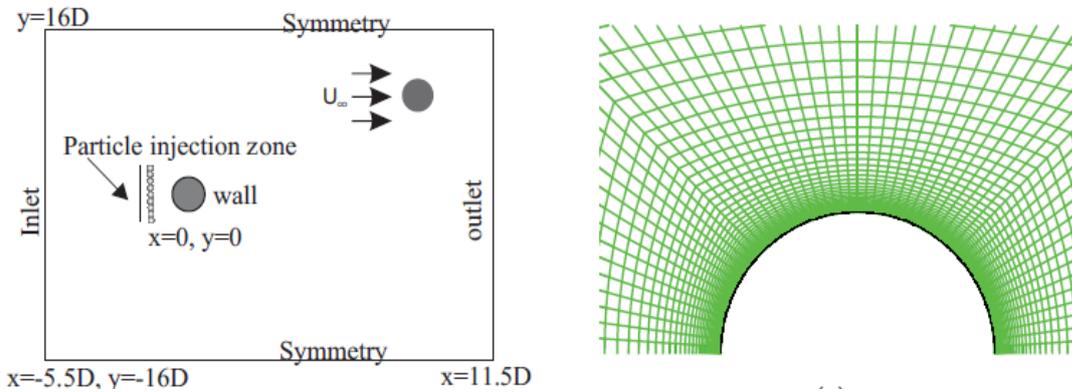
Figure 3.20 Domain (left, not to scale) and grid around the cylinder (right) used in the flow calculations.
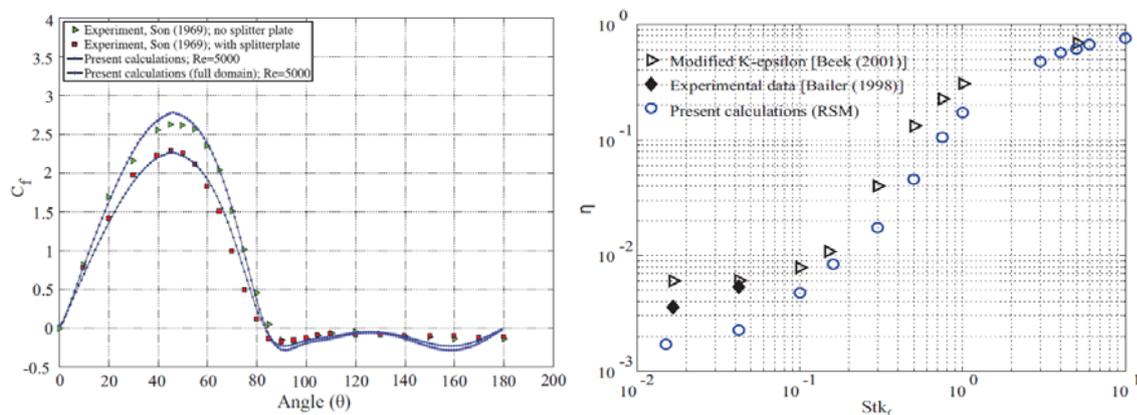
Figure 3.21 Validation of flow field (left) and of deposition model (right).

In Figure 3.22 the results are presented of particle deposition calculations for the different stages of a fouling experiment ranging from the clean tube configuration at the start of the experiment up to the final asymptotic layer configuration. It is demonstrated that the largest deposition rate is calculated for the clean tube and that this deposition rate slowly decreases as the fouling layer thickness increases indicating that the model is capable to capture an asymptotic layer growth.

The study was further extended to square cylinders at different orientations to the flow and a qualitative comparison was made to the experimental observations as shown in Figure 3.23. It is concluded that the numerical model is capable of capturing the effects of gas velocity, particle concentration, heat exchanger tube geometry and the growth of the fouling layer in time because the results were consistent with the experimental observations. Figure 3.23 shows the prediction of the numerical model for particle deposition over a square tube oriented at different angles to the flow direction and the comparison with the experimental observations.

It can be concluded that the numerical model developed is capable in capturing the fouling characteristics under various circumstances and can be used to predict particulate fouling in several sections of a heat exchanger system and can, therefore, serve as a vital tool in designing optimal systems which are less prone to particulate fouling.
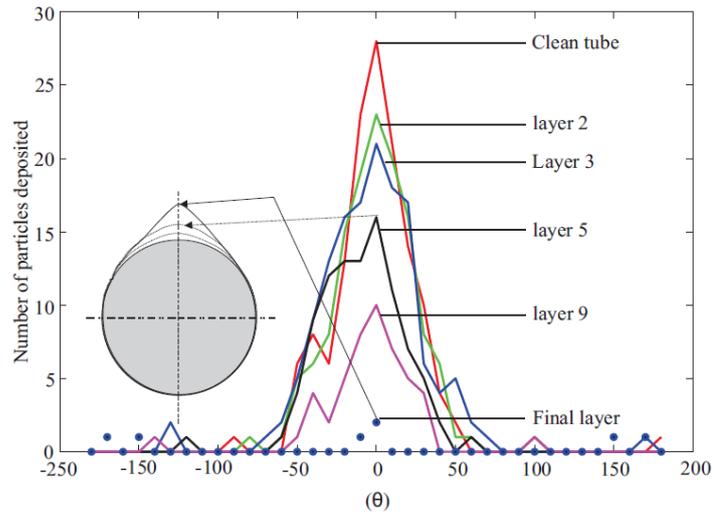
Figure 3.22 Numerical results capturing the evolution of fouling layer thickness
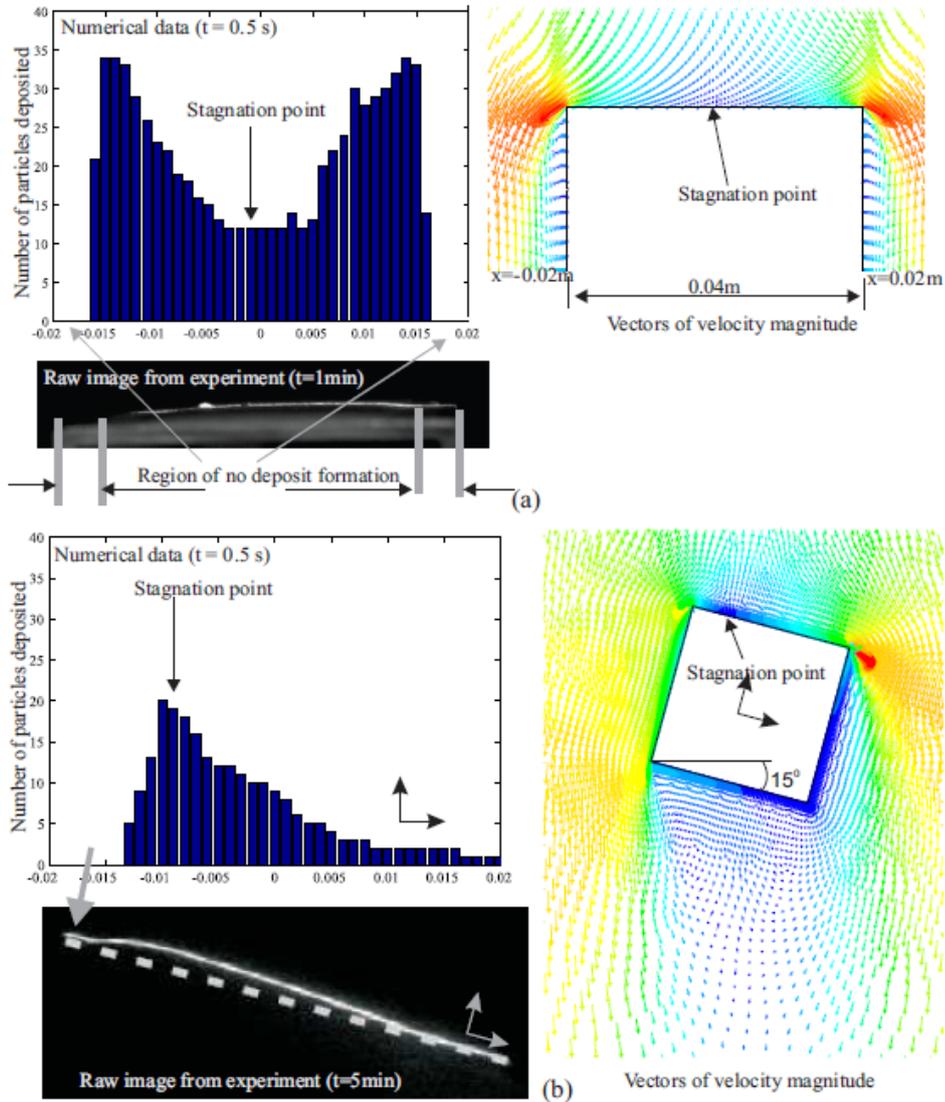
Figure 3.23 Calculated particle deposition profiles for a square cylinder for 2 orientations of the cylinder to the flow. As a comparison also the experimental results are shown.

3.3 Task 3: Tar removal

3.3.1 Tar removal by flame-generated radicals

Authors: L.M. Verhoeven and J.A. van Oijen (TU/e)

Purpose of the study

Former research at TU/e has shown the possibilities and difficulties of tar conversion by partial combustion, leaving questions unanswered. The current status of technology and the promising advantages led to the inspiration to uncover more of the fundamentals of tar conversion in a partial combustion reactor. Since knowledge is required of the complex interplay between chemical kinetics and fluid flow in a multi-dimensional environment, a modelling approach has been chosen as the main research tool. Laser-diagnostic measurements have been performed in an idealized lab-scale burner for validation of the newly developed numerical model.

Modelling of tar conversion by partial oxidation requires the use of detailed chemistry models in two or even three-dimensional simulations. To account for tar conversion, complex reaction mechanisms involving many chemical species and reactions have to be used. It is well-known that the use of such detailed mechanisms results in extremely high computational costs and that efficient methods are needed to decrease the computational burden. Chemical reduction techniques have been introduced to treat this problem. The reduction technique regarded here is the flamelet-generated manifold (FGM) approach [60]. This method was extensively studied in premixed flames, both laminar and turbulent. At the same time, the extension of FGM to non-premixed flames has been investigated as well. Applying FGM for the numerical simulation of multidimensional flames leads to a gain in computational cost of approximately two orders of magnitude.

The purpose of the executed research is twofold. The bigger picture concerns gathering additional knowledge of the physical and chemical mechanism behind tar conversion by partial combustion. To achieve this, a large investment was made in the available reduction technique FGM. This investment will result in the application of FGM to more complex combustion applications, including phenomena like soot formation.

Homogeneous reactor study

As a first step, partial combustion of tar-contaminated producer gas has been modelled by using detailed reaction mechanisms in simulations of homogeneous reactors. Tar is described by a collection of Polycyclic Aromatic Hydrocarbons (PAHs). The analysis tool applied is the CHEMKIN II simulation package.

$$\lambda = \frac{\frac{m_{ox}}{m_{fu}}}{\left(\frac{m_{ox}}{m_{fu}}\right)st}$$ Two different biogas mixtures have been examined. The first mixture is taken from the experiments executed by Houben, which have demonstrated the principle of tar removal by partial oxidation and form the basis behind the executed research as a whole [61]. The experiments were executed to investigate if tars can be converted into lighter components for small values of the air factor λ, which is described by:

(3.3)

where m_{ox} and m_{fu} represent the mass of oxidant and fuel. The subscript *st* indicates that the conditions between the brackets are stoichiometric.

During past experiments different synthetic gas mixtures, resembling producer gas, were saturated with naphthalene (which resembles the tar content found in producer gas). These mixtures did not contain any CO, due to health safety issues. The mixture was kept at 473 K, to prevent condensation of the naphthalene, and was fed to a partial combustor where air was added through seven small nozzles (see Figure 3.24). The mixture consisted of H_2, CH_4 and N_2. The second mixture examined in the calculations is the producer gas of the indirect gasification technology MILENA, developed by ECN. The purpose of including MILENA producer gas in this work can be found in the additional value of examining the effect of tar conversion by partial combustion on genuine producer gas.
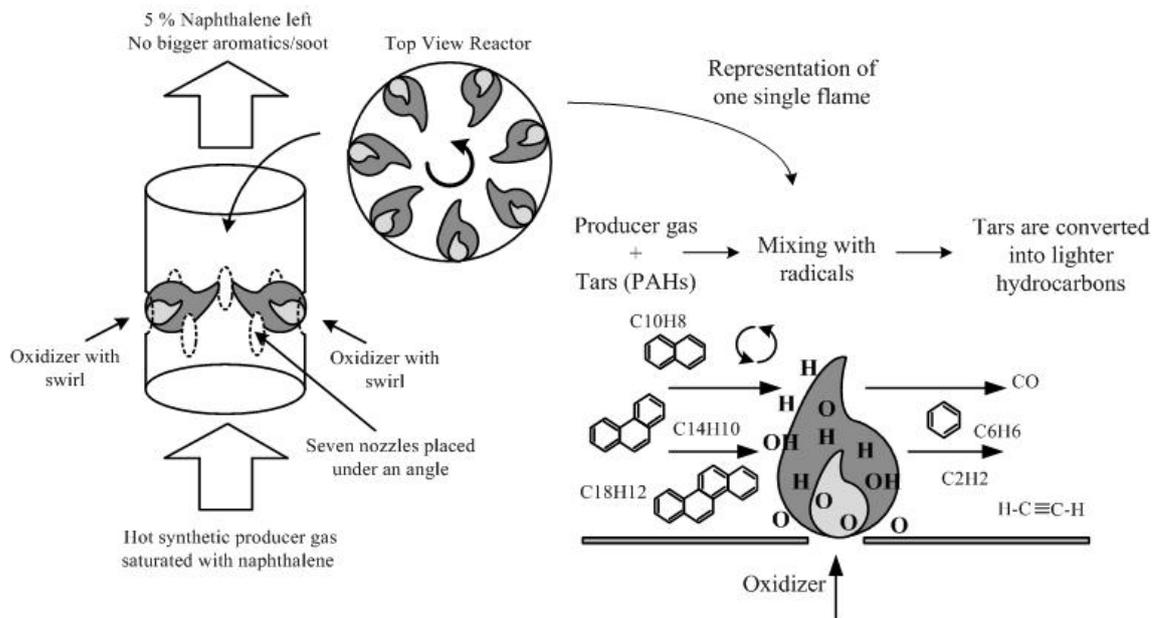
Figure 3.24 Working principle of tar conversion by partial combustion

The two examined mixtures are very different when it comes to composition, amount of tar, temperature, and caloric value. Yet the results show the same trends for both cases, when it comes to naphthalene conversion and the formation of soot precursors as function of λ and the residence time τ. And although three different chemical mechanisms were employed with different sub-mechanisms for Polycyclic Aromatic Hydrocarbon (PAH) ring growth, no large qualitative differences could be observed in the results.

According to the experimental data of Houben, λ = 0.20 corresponds to the most suitable environment for tar conversion. Experiments demonstrated that the biggest part of the added naphthalene was removed and that only 7.5 wt% was converted to aromatic species that contain more than two rings (analysis was made of one- to five-ring PAHs). For larger values of λ the concentration of PAHs with more than two rings increased. The fact that no PAHs with more than five rings could be measured can mean that they are simply not present or that the measurement technique was not able to detect them. This implies that the possibility of polymerization of PAHs with more than five rings to subsequently form soot cannot be ruled out.

When chemical equilibrium calculations are considered, naphthalene is fully converted and soot appears to be formed in the form of solid carbon (graphite). The formation of solid carbon is strongly influenced by temperature. An increase in temperature or methane concentration results in an increased solid carbon concentration. The PSR simulations show that, for all values of λ, which were considered here, soot precursors (defined here as species with a molar mass larger

than that of naphthalene $C_{10}H_8$) are formed. A transition point, where soot precursors are not formed, at $\lambda = 0.20$ or smaller values of λ, could not be observed. At realistic values of the residence time τ and the air factor λ, 10 to 50 % of the initial naphthalene concentrations remain unconverted. The results also show that the process is strongly influenced by temperature and residence time.

It is interesting to see that in a nearly carbon-free producer gas, naphthalene is converted to smaller hydrocarbons (at $\lambda = 0.20$), which agrees with the experimental observations. Polymerization does not occur, even after the formation of methane and acetylene. However, when methane is present in the producer gas (5 vol%) larger PAH species are formed. Roesler et al. [62] studied the role of methane on the growth of aromatic hydrocarbons and soot in several fundamental combustion processes. They concluded that the effect of the methane content on the formation of PAH and soot production in a non-aromatic fuel mixture changes significantly depending on the combustion system used. For a diffusion flame containing a small amount of aromatic hydrocarbons, it holds that increasing the methane fraction of the fuel results in a conversion of carbon into soot via a synergistic chemical mechanism. They stated that the synergy of methane with other hydrocarbons to produce PAH can be attributed to the ability of methane to produce methyl radicals, that will then promote the production of aromatic species that rely on odd-carbon numbered species. According to Roesler, benzene, naphthalene, and pyrene show the strongest sensitivity to the presence of methane: this synergy trickles down to soot via enhanced inception and surface growth. They observed these results strongest under fuel rich environments (premixed) and in diffusion flames. These conditions resemble the conditions used in the experiments of Houben. Houben also executed experiments without the addition of naphthalene, which showed that no soot was formed. It is interesting to see that with the addition of such a small amount of naphthalene this strong tendency to polymerization is observed (in calculations presented here and in the past experiments). The conversion of naphthalene is in line with experiments executed by Houben. However, a different trend was witnessed during experiments regarding polymerization. Experimentally, polymerization was only observed for values of $\lambda > 0.20$, while in the numerical analysis polymerization always takes place.

Connecting two Perfectly Stirred Reactors (PSR) to approach the process of partial combustion in a more realistic manner, does not improve the similarity between the experimental observations and the simulations. Although this approach shows an increase in radical production by a factor 100, their corresponding lifetimes seem too short to contribute to the conversion of naphthalene, which occurs at larger values of τ. The results, when compared to the application of a single PSR, show that a decrease in naphthalene coincides with an increase in temperature. Since the radicals do not exist very long, the results indicate that the conversion of naphthalene is mainly caused by an increase of temperature.

Based on these executed simulations, it seems that polymerization does occur when partial combustion is applied to convert the tar model component naphthalene, in contrast to the experimental results. In practice, this would make partial combustion less suitable for most biomass gasification installations. However, the experimental results of Houben demonstrated that tar conversion at $\lambda = 0.20$ is possible without the formation of soot. The difference between experimental and numerical results may be attributed to spatial inhomogeneous distributions of species (and temperature) in the reactor.

Modelling diffusion flames
From the first modelling study it seems that tar conversion by partial combustion cannot be fully described by homogeneous reactor models. The inclusion of spatial effects, like diffusive and convective transport, in the model is investigated in the following sections. To include detailed chemical information in a multi-dimensional combustion system, without the occurrence of extremely high computational costs, a chemical reduction technique is required. The technique considered in this work is the Flamelet-Generated Manifolds (FGM) method. The basic

assumption of FGM is that a multi-dimensional flame can be considered as a collection of one-dimensional flames, called flamelets. To demonstrate the potential of FGM in non-premixed combustion, a well-documented diffusion flame is modelled. The solution of FGM is compared to the solution of the full set of transport equations with a detailed chemistry model. PAH chemistry is not taken into account at this stage, due to the limitation of the number of species that can be involved in solving the full set of transport equations.

Modelling of combustion applications very often requires the use of detailed chemistry models. If, for instance, accurate predictions of NO or soot formation are required, complex reaction mechanisms involving many chemical species and reactions have to be used. It is well-known that the use of such detailed mechanisms results in extremely high computational costs and that efficient methods are needed to decrease the computational burden. The modelling efficiency could be increased enormously, if it would be possible to decouple the chemical kinetic processes in the flame from the main flow and mixing processes. This approach is implemented by chemical reduction techniques which are based on the observation that a typical combustion system contains many chemical processes with a much smaller time scale than the flow time scales. Based on this observation the total number of differential equations which has to be solved, can be reduced by assuming the fast processes in steady state. Multiple methods, referred to as reduction techniques, have been developed. Each of these methods identifies the fast chemical processes in a different manner.

A reduction technique which decouples chemical kinetic processes from the main flow and mixing processes by solving a set of one-dimensional flamelet equations describing the internal structure of the reaction front, separately from the flow is the flamelet-generated manifold (FGM) approach. This method has been extensively studied in premixed flames, both laminar and turbulent. In the FGM approach, a low-dimensional manifold is created in composition space from solutions of flamelet equations (describing one-dimensional flame behaviour). In mathematics a manifold is defined as a mathematical space that on a small enough scale resembles the Euclidean space of a specific dimension, called the dimension of the manifold. Thus, a line and a circle are one-dimensional manifolds, a plane and sphere (the surface of a ball) are two-dimensional manifolds, and so on into high-dimensional space.

$\varphi = \varphi(CV1, CV2) = \varphi(Z, \Upsilon)$,It is assumed that a multi-dimensional flame can be regarded as a collection of one-dimensional flamelets. Flamelet simulations are performed in a pre-processing step. In this work, a series of flamelet solutions are used to create a 2D manifold parameterized by two controlling variables. The dimension of the manifold is defined by the number of used controlling variables. Although any choice of controlling variables that results in a single valued function is possible, a natural selection of the controlling variables is the mixture fraction Z and a reaction progress variable Y, viz.

$$(3.4)$$

in which φ can denote any thermochemical variable like a species mass fraction Y_i or the temperature T. So, it is assumed that the species mass fractions and other parameters, like temperature, can be described by a function which only depends on the controlling variables Z and Y. Since the pioneering work of Peters, non-premixed flamelet tables have been used in many turbulent flame studies, both using the original parametrization in terms of mixture fraction and scalar dissipation (Z, χ) and a parametrization in terms of progress variables (Z, Y) as in FGM methods. In order to understand and improve flamelet modelling it is believed crucial to validate the application of flamelet based methods with the solution of the full chemistry model in a laminar flame, where accurate validation is possible. Figure 3.25 shows the calculated temperature in a laminar co-flow diffusion flame using FGM or the full chemistry model.

Results for unity Lewis numbers demonstrate that it is still difficult to capture differential diffusion effects to a satisfactory level. Using non-unity Lewis numbers in solving the one-dimensional flamelets leads to a significant improvement of the results. Incorporating an

estimated Lewis number for Y also leads to further improvements. With the current definition, the Lewis number of Y ranges from $Le_{H2} = 0.317$ to $Le_{CO2} = 1.414$. This artificial cut-off of Le_Y, which was necessary due to the maximum value of Y near the stoichiometric mixture fraction, could lead to numerical instabilities. Significant deviations are observed near the axis because of enhanced radial diffusion effects due to the fact that the flame is strongly curved. These effects are not accounted for in the laminar flamelets, which are used to span up the applied manifold. This is underlined by the results of the one-dimensional flamelet calculations. The results show the capability of FGM to reproduce planar chemical flame structures with the inclusion of preferential diffusion. The improvements found by implementing a varying Lewis number for Y are significant. The use of curved flamelets could lead to further improvements of the results of the multi-dimensional calculations. This has been investigated for premixed turbulent flames. It is also possible to include a model for the tangential diffusion terms Q_i in the flamelet calculations. Solving the flamelet equations for different amounts of tangential diffusion then results in an extra dimension to the manifold. These two options can be investigated in further research.
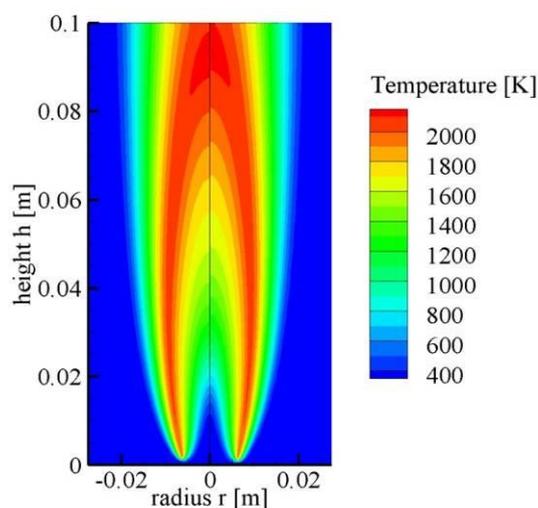
Figure 3.25 Contour plot of the temperature in a laminar co-flow diffusion flame. FGM results on the left and the results of the full chemistry model on the right.

Keeping further understanding and improvement of the preferential diffusion terms in mind, it can be concluded that FGM is an efficient dimension reduction technique that has great potential for accurate simulations of non-premixed flames. The results emphasize that modelling multi-dimensional non-premixed laminar flames which include differential diffusion with laminar flamelet models is still a challenging task. The results of this section have been published in the journal of Combustion and Flame [63].

Modelling diffusion flames with the addition of PAHs
A laminar non-premixed flame, with a tar model component (an aromatic hydrocarbon) added to the fuel stream, has been modelled with FGM. To investigate if Polycyclic Aromatic Hydrocarbon (PAH) chemistry can be considered to be 'slow' chemistry, as was indicated by the homogeneous reactor calculations, an a priori study has been executed to investigate the applicability of FGM when PAH chemistry is involved. Several studies have been executed. One study focuses on the effect of tabulating steady or unsteady flamelets on the performance of a FGM in one-dimensional diffusion flames. To validate the performance of FGM in multi-dimensional environments, a numerical validation is almost impossible. The cause is the limitation of the number of species that can be involved in solving the full set of transport equations in a multi-dimensional geometry. Therefore, a comparison has also been made of FGM results with measurements.

Since a two-dimensional numerical validation is not possible due to the limitation of the amount of species involved in solving the full set of transport equations, several efforts have been made to compare FGM against experiments. To measure the qualitative distribution of OH and PAHs on a planar cross-section of the flame, Laser Induced Fluorescence (LIF) has been applied. The experimental data from the LIF measurements has been compared to the FGM solution. The measurements and calculations of a flame doped with benzene can be seen in Figure 3.26. It can be concluded that the qualitative OH profiles found by the experiments and the FGM model are in good agreement. The PAH profiles of both the experiments and the calculations showed agreement in the lower region of the flame. The location of maximum PAH concentration did not agree, but a ring analysis showed that with increasing height an increase in aromatic rings is involved. This may indicate that a large part of the PAH species, which have been excited by the laser sheet, can be considered to be large aromatic species which are not accounted for in the applied reaction mechanisms which is limited to four-ring aromatics. A growth in PAH concentration, with increasing dopant concentration, has been visible for both computational as experimental results. Although no quantitative comparison could be made, the results show that the model is able to capture several flame characteristics which can be considered to be typical for PAH formation in a multi-dimensional laminar non-premixed flame.
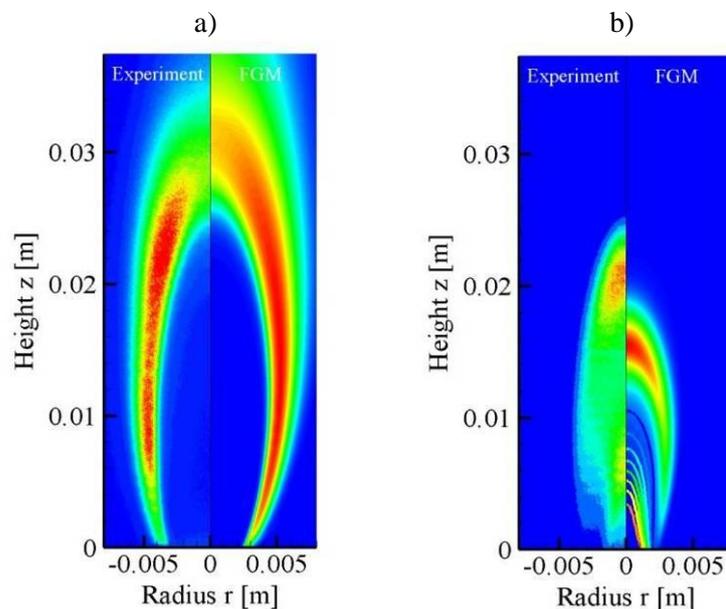
Figure 3.26 Laminar co-flow methane-air diffusion flame doped with Benzene - 2667 ppm
a) Comparison of OH LIF signal (left) and OH concentration calculated by FGM (right). b) Comparison of PAH LIF signal (left) and PAH concentration calculated by FGM (right). The concentration of the dopant benzene has been made visible by coloured iso-lines. The colour scheme is based on the normalization of both the signal strength (experiment) and the species mass fractions (FGM model).

Modelling the partial combustion reactor in 3D
The multiple (inverse) diffusion flames create local radical pools and a rise in temperature. The experimental work performed by Houben [61] and Van der Hoeven [64] led to the believe that due to the mixing of these radicals with the remaining producer gas, the naphthalene is converted into smaller hydrocarbons. The conditions of the most successful experiment have been used to construct a manifold of laminar steady counter-flow diffusion flamelets, which has been employed in a 3D simulation of tar conversion in the reactor designed by Houben.

To reduce the computational cost, one-seventh of the entire reactor geometry has been modelled. To study the fate of the tar model component naphthalene, a contour plot is created showing the mass fraction of naphthalene (left hand side of Figure 3.27) at different levels in the reactor. There appear no regions (other than the flame front), which can indicate that the tar

model component is converted by subsequent mixing with radicals, like OH. The results show that at the exit of the reactor naphthalene is still present. A mass balance of all ingoing and outgoing flows shows that at the exit 95 % of the initially added tar model component remains unconverted. The velocity profile (right hand side of Figure 3.27) shows that there is no homogeneous flow pattern at the exit, but that there are two rings with a slightly higher velocity magnitude. The velocity can be considered to be the lowest in the middle of the reactor, and on the walls (due to the no-slip boundary conditions which have been applied on the walls).
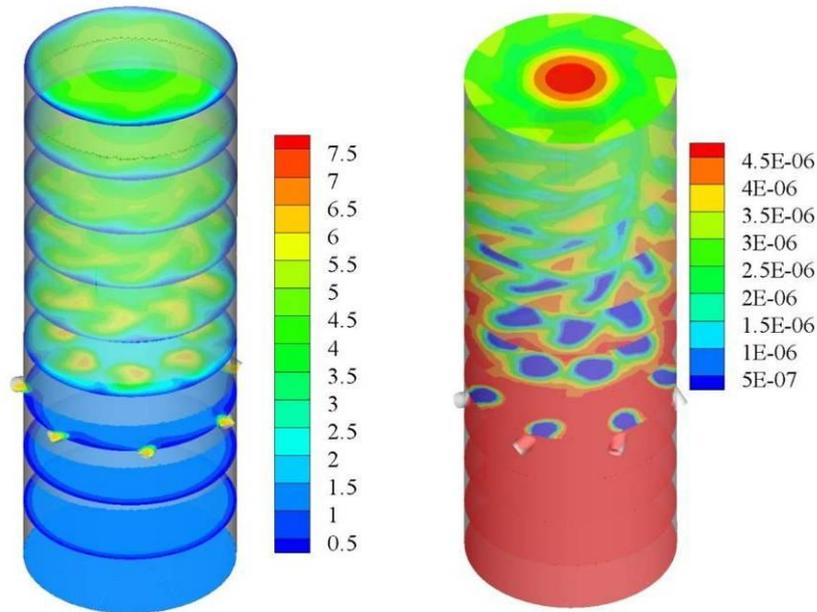
Figure 3.27 Contour plot of the mass fraction of naphthalene (left) and the velocity magnitude [m s^{-1}] (right) at different heights of the reactor.

Figure 3.28 shows the distribution of the mass fraction of OH. Three iso-surface values have been plotted. The swirling shape of the inverse diffusion flames is clearly visible. The radical species OH is, as can be expected, only present close to the flame front. The homogeneous reactor calculations indicated that OH radicals do not exist long ($\tau = 10^{-5} - 10^{-4}$ s), which makes the subsequent mixing with naphthalene, higher up in the reactor, unlikely.

The results have demonstrated the capability of FGM to model complex flow structures with the inclusion of detailed chemistry. The results show that in the middle of the reactor the composition of the initial fuel mixture (producer gas) is unaltered. This would suggest that the mixing in the reactor can be improved. When the reactor is scaled up to a size which would be required for an industrial gasifier the involved Reynolds numbers increase as well. This would most probably lead to a turbulent flow which would enhance the mixing in the reactor.

Figure 3.28 Contour plot of 3 iso-values of the mass fraction of OH being 1e-3, 2e-3, and 3e-3 (max. Y_{OH} = 3.5e-3). The shape of the swirling flames is clearly visible.

An analysis of the incoming and outgoing mass flows of the reactor has shown that a large fraction of the initial concentration of naphthalene exits the reactor. Only a small part of naphthalene is converted, mainly into combustion reaction products but also a small fraction into larger PAH species. Although no strong proof has been found that polymerization is favoured over cracking, the presented results indicate that partial combustion, in the examined reactor design, is not able to convert tars into smaller hydrocarbons. The numerical tool developed in this project can be used to further investigate tar conversion by partial oxidation and it can assist in the design process of new and improved reactors.

3.3.2 Tar removal by plasma

Authors: A.J.M. Pemen and W.F.L.M. Hoeben (TU/e)

Background

Reducing tars is one of the major items that need to be solved when biomass gasification is applied. This task focuses on a new method where radicals are generated to attack the relatively weak tar molecules in a hot producer gas. Radicals are efficiently generated by non-thermal plasma, particularly pulsed corona plasma. This technique, if successful, could enable combined tar, dust and particulate removal in single equipment.

In a previous study by TU/e [65, 66], proof of concept studies were done on a real gasifier to verify this idea. Results from field tests on a real wood gasifier indicate that tar molecules can be broken down and simultaneously dust particles can be removed from the gas stream. Also experiments were performed: (i) to identify chemical mechanisms and (ii) to determine energy requirements for decomposition of naphthalene at various temperatures.

Objective

The objective of this joined research project is to map the influence of radicals on tar conversion at high temperature (immediately after the gasifier unit) and to develop a novel technology that combines the benefits of existing technologies.

Approach

We focus on finding the leading reaction mechanisms for tar removal by corona plasma using the numerical model RADICAL, as developed by Filimonova from the Institute for High Temperatures (IVTAN), Moscow, Russia [67, 68]. The most stable tar molecule, naphthalene, is

used as a model compound in this study. A chemical data base governing the process is developed. Sensitivity analysis is used to identify the more important reactions. The following data is obtained and analyzed:

- Yields of radicals and reactive species as generated by the corona plasma.
- Naphthalene decomposition on specific input energy at different gas compositions.
- Dependency of naphthalene concentration on time during the pulse for different pulses.
- Leading reactions for several components in dependency on time during the pulse for different pulses.

Item 1 – kinetic modelling of corona tar removal
Simulation of reactive species as generated by pulsed corona discharges. The problem of simulation of the cleaning process includes description of two stages. The first, fast stage is generation of primary active species during streamer propagation. The second, slow stage is the chain of chemical transformations triggered by these species. The input parameters for the modelling of the second stage are G-values for generation of radicals, ions, excited molecules and atoms.

Streamer parameters are governed by the kinetic and transport properties of electrons and by the rate of photo-ionization: production of precursor electrons ahead of the streamer front at absorption of ionizing radiation emitted by the streamer head. Calculation of kinetic and transport coefficients in various mixtures of nitrogen with H_2, CO, CO_2 and H_2O (at high content of N_2), including biogas, shows that their values are close (in the range of electric fields relevant to streamer propagation) to those in air and in pure nitrogen. In our calculations of the electron energy distribution function (EEDF) the BOLSIG+ code [69] has been used.

As for the photo-ionization efficiency, in pure nitrogen it is about two orders of magnitude lower than in air; and the dependence on the distance from the source of radiation in N_2 being rather close to that in air [70]. A mechanism of photo-ionization in pure nitrogen and in its mixtures with gases other than oxygen (such as biogas) is not clear. In our simulations the value of photo-ionization efficiency in the considered mixtures is taken the same as in pure nitrogen. Additionally the absorption of ionizing photons by CO_2 molecules has been taken into account. The absorption coefficient was taken from [71]. Such approach results in the identity of streamer parameters in all the considered mixtures.

It follows that the value G_j for the production of active particles of sort j at a given mixture composition may be evaluated by weighting of partial G-values as $G_j = \Sigma X_i G_{ij}$, where X_i is the molar fraction of species of sort i, G_{ij} is the partial G-value for production of species j in the reaction of electrons with particles of sort i (normalized to the relative density of species i equal to unity). Note that in this approach the values G_{ij} are independent of mixture composition. They are governed by the reduced electric field in the streamer head, the latter being relatively weakly dependent on the external conditions (gas pressure and temperature, the applied voltage, the geometry of the discharge gap) [68]. The estimates for G_{ij} in mixtures of N_2 with H_2, CO, CO_2, CH_4 and H_2O obtained on the basis of streamer simulations and analytical consideration are as follows:

$$G_{CH3,H} = 6, \quad G_H = 2.6, \quad G_{CO,O} = 0.5,$$
$$G_{OH} = 0.02, \quad G_{C,O} = 0.6, \quad G_N = 0.25,$$
$$G_{N(2D)} = 0.25, \quad G_{N2(A3\Sigma)} = 2.2, \quad G_e = 0.7.$$

Note that the G-value for $N_2(A^3\Sigma)$ is evaluated with account of cascade transitions both from both higher triplet and from singlet states. It is assumed that the dominating channel of nitrogen dissociation is $N_2 + e \rightarrow N(^4S) + N(^2D)$ [72]. Primary positive ions in a chain of fast ion-molecule reactions transform into more stable positive ions, reaction time of $\sim10^{-9}$ s. The latter recombine with electrons, resulting in an additional (to direct dissociation) production of active particles. Detailed ion kinetics is not included in the presented model; it is assumed that the

dominating stable ion is N_4^+ (in pure N_2 and its mixtures with H_2), H_2O^+ (in mixtures including H_2O) or CO_2^+ (in mixtures including CO_2). The dominating channels of dissociative recombination of these ions are assumed to be $N_4^+ + e \rightarrow N_2 + N_2(A^3\Sigma)$ [73] and $CO_2^+ + e \rightarrow CO + O(^1D)$, $H_2O^+ + e + M \rightarrow OH + H + M$, reaction time is $\sim10^{-8}$-10^{-7} s.

In Table 3.2 the G-values are given in pure nitrogen, in the mixture $10\%CO_2+90\%N_2$ and in biogas, estimated according the above relations. These G-values are used at the modelling of the second stage of the cleaning process.

Table 3.2   Calculated G-values (number of particles produced per 100 eV of input energy) in three productgas mixtures, at a gas temperature of 200°C.

	Gas: pure N_2	Gas: 90% N_2 + 10% CO_2	Gas: 50% N_2 + 20% CO + 12% CO_2 + 17% H_2 + 1% CH_4
H	-	-	0.5
C	-	-	0.12
N_2^*	2.9	2.0	1.1
N	0.25	0.22	0.12
$N(^2D)$	0.25	0.22	0.12
O	-	0.05	0.18
$O(^1D)$	-	0.7	0.7
CH_3	-	-	0.06

Chemical kinetical modelling of naphthalene conversion. Simulation of tar conversion in the reactor has been carried out using the approach and software RADICAL [74]. The model takes into account the specifics of energy input: the energy is released in narrow streamers channels, the species are distributed non-uniformly in space, and energy is deposited discretely during many pulses. The chemical transformations are simulated in the streamer trace spreading due to diffusion, with account of the change of the background-gas composition caused by preceding discharge pulses. The set of chemical kinetic processes included 350 elementary reactions involving 77 components. The reaction data were taken from many sources, indicated in [75, 76]. The temperature effect on the removal process was considered similar to one in the work of [75]. A peculiarity of the reactor system [65, 66], consisting of an active (discharge) zone and a 'dead' zone, is taken into account [67]. Gas is circulated in and out of the active zone in a recycle loop driven by a high-temperature fan.

For the modelling of chemical conversion in the mixture after streamer propagation, the knowledge of the number densities of active species in the streamer trail is required. As the number densities are proportional to the G-values, they can be easily estimated by comparison of corresponding G-values with the G-value for generation of electrons, $G_e \approx 0.7$, taking into account that the number density of electrons n_e in streamer channels in the considered gas mixtures is about $5\times10^{14}\ \delta^2\ cm^{-3}$, where δ is the ratio of the gas density to its normal value (corresponding to atmospheric pressure and room temperature).
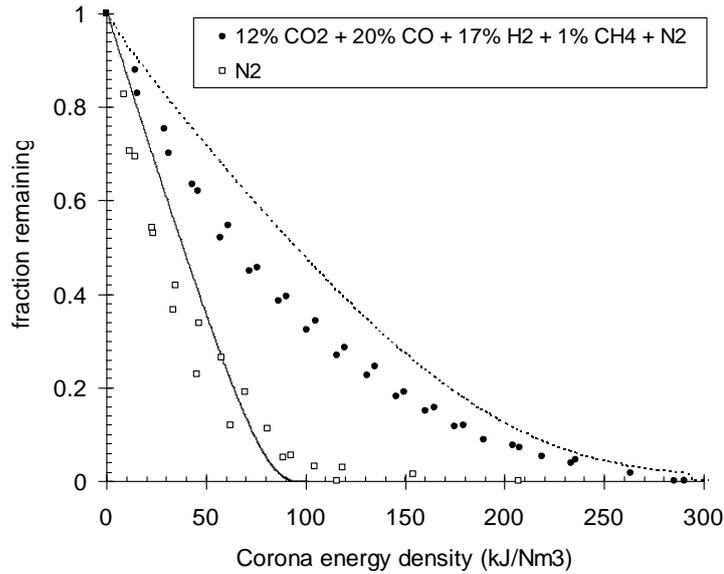
Figure 3.29 Remaining fraction of naphthalene in synthetic product gas and in nitrogen. Gas temperature 200°C. Solid line: calculations, points: experimental data.

Results of calculations. Figure 3.29 shows the results of naphthalene removal depending on the specific energy input in pure N_2, and in biogas $50\%N_2+20\%CO+12\%CO_2+17\%H_2+1\%CH_4$. The experimental data [65] are also shown (various sets of symbols correspond to various sets of experimental data obtained in similar conditions). The best removal is observed in pure N_2, where the leading reactions are:

$$N_2(A^3\Sigma) + C_{10}H_8 \rightarrow \text{products}, k=1.6\cdot10^{-10} \text{ cm}^3 \text{ s}^{-1} \qquad (3.5)$$
$$N(^2D) + C_{10}H \rightarrow \text{products}, k=3\cdot10^{-11} \text{ cm}^3 \text{ s}^{-1} \qquad (3.6)$$
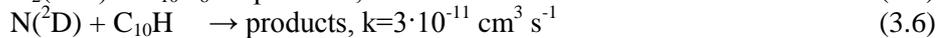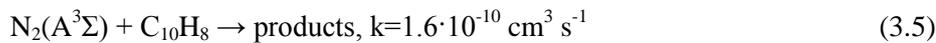
The rate constants for processes (3.5) and (3.6) were taken according to the data [77] for reaction of C_6H_6 with $N_2(A^3\Sigma)$, and for reactions of different hydrocarbons with $N(^2D)$, respectively (as the data for naphthalene are not available). In the reaction (3.6) atom H may be released [77]. Competitive process for $N_2(A3\Sigma)$ removal is self-quenching:

$$N_2(A^3\Sigma) + N_2(A^3\Sigma) \rightarrow N_2 + N_2(A^3\Sigma) \text{ , } k = 4\cdot10^{-10} \text{ cm}^3 \text{ s}^{-1} \qquad (3.7)$$
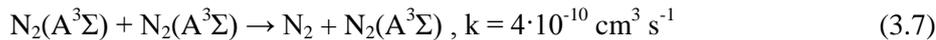
With decreasing naphthalene concentration due to processes (3.5) and (3.6) the contribution of reaction (3.7) in the removal of $N_2(A^3\Sigma)$ increases.

When CO_2 is added to N_2, the G-value for $N_2(A^3\Sigma)$ becomes lower (see Table 3.2), so that the contribution of reaction (3.5) in the removal process diminishes, however the additional naphthalene removal becomes noticeable (though less effective), in reactions with O and H atoms [76, 78]:

$$O + C_{10}H_8 \rightarrow H + C_{10}H_7O, k=2.32\cdot10^{-11}\exp(-902/T) \text{ cm}^3 \text{ s}^{-1} \qquad (3.8)$$
$$H + C_{10}H_8 \rightarrow \text{products}, k= 1.41\cdot10^{-9}\exp(-2570/T) \text{ cm}^3 \text{ s}^{-1} \qquad (3.9)$$
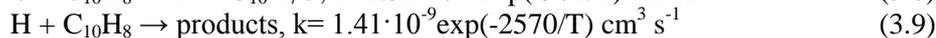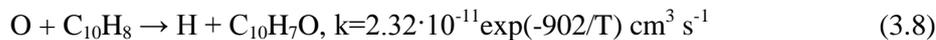
Atoms O appear both at the streamer stage and as the product of quenching of $O(^1D)$ and of the reactions with NO and $N_2(A^3\Sigma)$:

$$N_2 + O(^1D) \rightarrow O + N_2 \text{ , } k= 1.8\cdot10^{-11}\exp(110/T) \text{ cm}^3 \text{ s}^{-1}, [74, 75] \qquad (3.10)$$
$$CO_2 + O(^1D) \rightarrow O + CO_2, k= 7.4\cdot10^{-11}\exp(120/T) \text{ cm}^3 \text{ s}^{-1}, [74, 75] \qquad (3.11)$$
$$NO + N \rightarrow O + N_2, k= 2.2\cdot10^{-11}\exp(160/T) \text{ cm}^3 \text{ s}^{-1}, [74, 75] \qquad (3.12)$$
$$CO_2 + N_2(A^3\Sigma) \rightarrow O + CO + N_2, k= 2\cdot10^{-14}\text{cm}^3 \text{ s}^{-1}, [75, 77] \qquad (3.13)$$
$$CO_2 + N \rightarrow CO + NO, k= 3.2\cdot10^{-13}\exp(-1710/T) \text{ cm}^3 \text{ s}^{-1}, [74, 75] \qquad (3.14)$$
$$CO_2 + N(^2D) \rightarrow CO + NO, k= 3.6\cdot10^{-13} \text{ cm}^3 \text{ s}^{-1}, [77] \qquad (3.15)$$
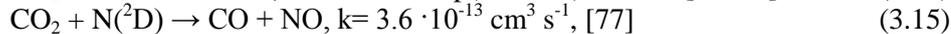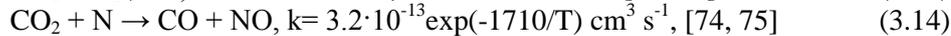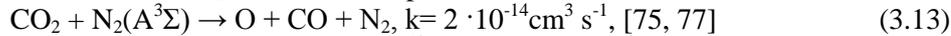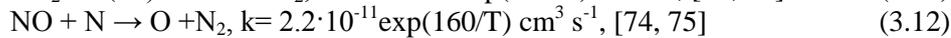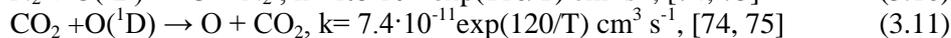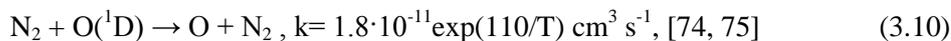
At the biogas treatment, due to the presence of H_2 molecules in the incident mixture, the concentration of atoms H is higher than in the case of $CO_2:N_2$ mixture, and that the main process of naphthalene removal is reaction (3.9). The role of reaction (3.5) is decreasing also due to the fast quenching of $N_2(A^3\Sigma)$ by CO [77]:

$$CO + N_2(A^3\Sigma) \rightarrow N_2 + CO, \ k=3.8\cdot10^{-11} \exp(-940/T) \ cm^3 \ s^{-1}. \qquad (3.16)$$
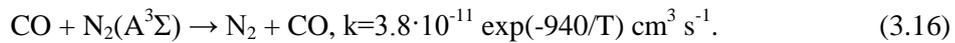
Because in the biogas the concentration of atoms H grows in comparison with the $CO_2:N_2$ mixture, the consumption of H in the reactions with CO, CHO, $C_{10}H_7O$ and other species increases without an advantage for naphthalene removal. On the other hand, NO reacts with NH producing O, OH and H radicals, so that the total number of these produced radicals is higher than the number of O atoms formed in reaction (3.12). Naphthalene removal by OH radical is important in the presence of H_2O in the gas primordially or at the end of removal process (last cycles), with production of water in the reactor.

In such a complex mixture as biogas there are many processes competitive to useful reaction (3.5). For this reason, naphthalene removal is notably worse than in pure N_2. During the removal process, the balance of $C_{10}H_8$ in a streamer trace is mainly determined by the diffusion of $C_{10}H_8$ from outside of the trace in each pulse.

Conclusions from kinetic modelling
- The results of simulation on naphthalene removal in biogas, pure nitrogen and mixtures of N_2 with CO, CO_2 and H_2 are in good agreement with the experimental data [65, 66]. Plasma-chemical processes in discharge and post discharge stages were taken into consideration.
- The reaction of naphthalene with exited N_2 molecules plays a key role in the removal process. The influence of N_2* towards naphthalene removal is much lower when CO molecules are added, because of quenching. In this case, O and H radicals are dominating the process. The contribution of N_2* towards naphthalene removal in biogas is much lower because of relatively low N_2 concentrations (as compared to the other gas mixtures). O radicals are produced by reactions of CO_2 with N atoms. When moisture is present naphthalene removal occurs via combination of H, N_2* and OH radicals.
- Reactions of naphthalene with excited species occur a short time after the pulse (10^{-6} s). During the removal process the balance of naphthalene in a streamer trace is mainly determined by the diffusion of naphthalene from outside of the trace in each cycle.
- The simulated results for mixtures with H_2 and CO do not give good agreements with the experimental observation, with exception of the syngas mixture.

Figure 3.30 Picture of the experimental setup at TU/e-E for corona induced tar removal.

Item 2 – lab experiments on corona induced tar removal

Experimental setup. A dedicated corona tar reactor setup has been designed and successfully installed in the EES high voltage laboratory (see Figure 3.30). The setup features a compact continuous flow corona reactor, for versatile and enhanced scanning of corona-induced conversion parameters. The gas flow system allows experiments of gas mixtures up to 4 components at flow rates of 0.6 to 30 sLm plus dosage of water vapour. The tar injection system features a temperature controlled vessel with molten model tar, which is continuously nitrogen gas-purged. The gas circuit is fully temperature traced and the maximum reactor operating temperature is 800°C. The hybrid design allows combination of the corona process with a subsequent catalytic bed reactor treatment. Extra system features are process parameter history backup and gas leakage monitoring. The pulsed power system comprises a high voltage DC power supply, capacitor bank, triggered spark gap and a transmission-line-transformer. The system delivers fast high voltage pulses (typical values are voltage 25 kV, pulse energy 200 mJoule, pulse risetime 20 ns) at repetition rates up to 1 kHz. The electrode geometry is a wire-cylinder one.

Diagnostics. A Shimadzu QP2010 Plus gas chromatograph-mass spectrometer has been installed for identification of the complex corona-induced tar degradation product spectrum. The instrument facilitates separation of polycyclic aromatic hydrocarbons via a dedicated WCOT GC column (type 5%-diphenyl 95%-dimethyl polysiloxane, length=30 m), whereafter detection by both a quadrupole mass filter (m/z up to 1090) and a flame ionization detector occurs. Tar sampling from the corona reactor occurs via a peristaltic pump driven heated gas line, loading the GC sample valve. Semi-quantification of tar and product flows is established by calibrating the FID detector with methane. Energy requirements at observed tar conversion levels are determined from the applied corona pulse energy via voltage & current probe measurements.

Additionally, the high temperature corona batch reactor [65, 66] has been modified for fast CCD imaging (with a sub-ns shutter time 4Picos camera) of streamer discharge channels. In this way, the influence of gas composition & - temperature on the plasma can be studied via streamer dimensions, velocity and spectral emission characteristics. The bottom flange has been equipped with a set of 50 mm diameter quartz window mounts, that can be translated along the reactor azimuth. The pulse power source of the corona biomass batch reactor has been adapted for fast streamer. The transmission line transformer has been extended for camera synchronization.

Experimental results on removal of organic compounds. For testing the performance of the pulsed corona reactor, the degradation of simple volatile organic compounds has been studied. Toluene and limonene oxidative degradation has been measured as a function of the energy density with gas chromatography - mass spectrometry. A typical example is shown in Figure 3.31. Obtained data are compatible with literature references.
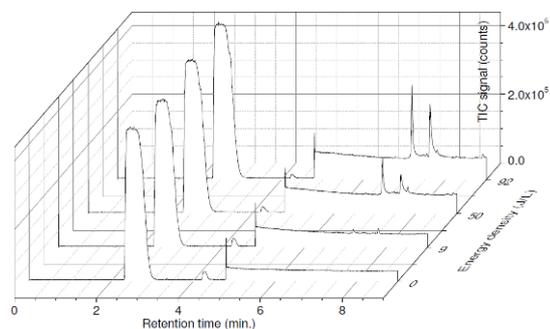
a. Toluene oxidation, GC-TIC overall chromatogram
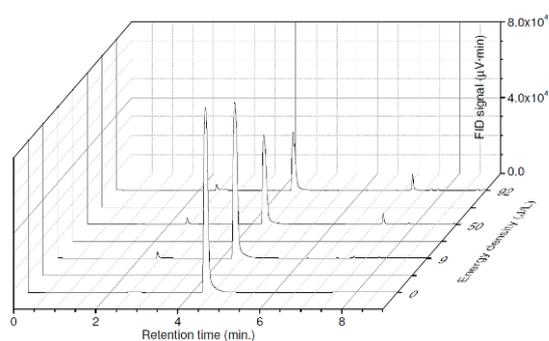
b. Toluene oxidation, GC-FID overall chromatogram
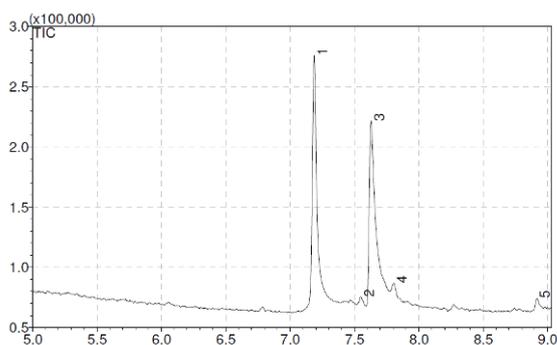
Peak #	Compound name
1	Acetic acid
2	Ethanediol diformate
3	Formic acid
4	Benzaldehyde
5	3-Methyl-2,5-furandione

c. Detail GC-TIC spectrum of the toluene oxidation products at 92 J/L with identified peaks

Figure 3.31 GC-TIC and FID chromatograms and spectrum of the toluene oxidation products at 92 J/L with identified peaks.

The oxidation product range, resolved with a FFAP GC column, features an energy density-dependent spectrum of oxygen-functional hydrocarbons, which has been explained on basis of literature studies. The toluene degradation product spectrum is simple and exhibits acetic and formic acid formation with increasing energy density, together with a limited number of other intermediate oxidation products. Regarding the latter, hydroxylated toluenes typically have not been identified. The limonene degradation product spectrum is complex, featuring ketones, esters, epoxides and carboxylic acids. Again, energy density dependent formation of acetic and formic acid formation has been observed. The observation of epoxide functional intermediate oxidation products at high limonene conversion level -but at the same time low energy density typically underwrites the importance of resolving the degradation product spectrum of a priority compound in advanced oxidation technology.

Referring to the applied diagnostics, following items can be summarized. The FFAP column has appeared to be very suitable for separation of complex mixtures of corona-induced oxidative degradation products of non-polar (and polar) priority compounds. One clear prerequisite is that the target compound should be separable from the unretained species, in order to be able to determine the conversion level. The standalone (integral carbon) FID analyzer is a simple and robust instrument for determination of lower limit conversion levels of hydrocarbon target compounds, especially suitable for environments where a GC-MS cannot operate or is not available.

Radical dependence on streamer diffusiveness. Pulsed corona, when applied to fuel gas, creates radicals, ions and other excited species. For the destruction of tar by corona discharges, the following mechanisms play a role: (i) production of radicals; (ii) utilization of radicals for tar removal; and (iii) radical termination. If there are no significant radical termination reactions, the removed amount of the pollutant linearly depends on the corona energy density. It is obvious that radical destruction processes, either via linear or nonlinear termination reactions, reduce the total energy efficiency. At higher gas temperatures, we expect the corona discharges to be much more diffuse. Consequently, radical termination is likely to be less (as compared to lower temperatures) due to easier and faster diffusion of the radicals out of the streamer channel.
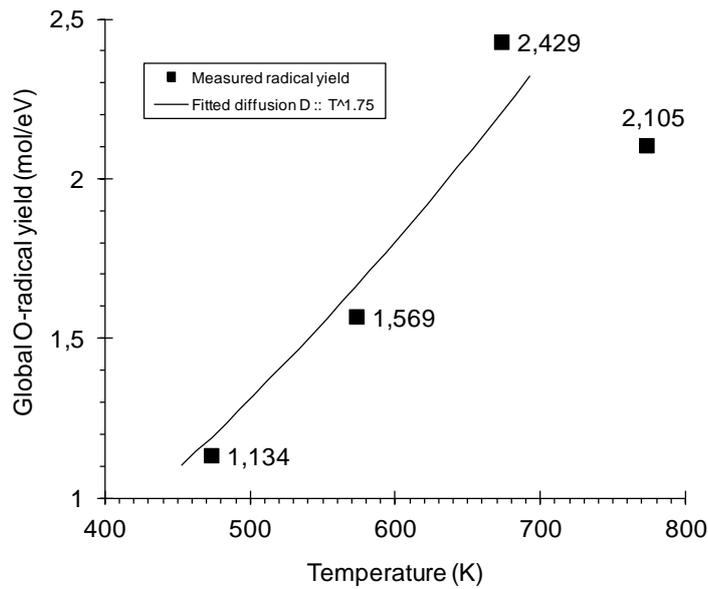
Figure 3.32 Estimated O-radical yields at different temperatures.
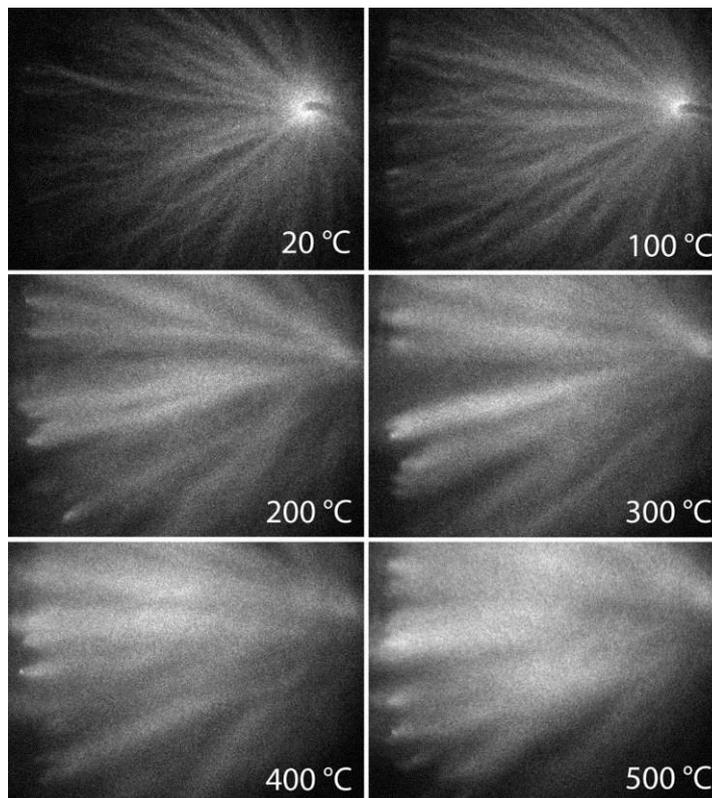
Figure 3.33 Spatial development of the pulsed corona plasma at various temperatures.

In order to analyze this effect, radical yields and spatial development of the corona discharges have been evaluated at various temperatures. The estimated O-radical yields (in mol/100 eV) are listed in Figure 3.32. As expected, the fast radical-radical reactions that occur within the local areas of streamer channels decrease due to higher diffusion coefficient with increase in temperature ($D \approx T^{1.75}$). The spatial development of the corona discharges is shown in Figure 3.33. The images confirm that the corona discharges become more diffuse at higher temperatures, which apparently leads to a reduced termination of radicals.

Conclusions from the experiments. The higher diffusiveness of radicals at higher gas temperatures contribute to the higher radical yields. The estimated yields are in fact a global value and a measure of the radical utilization, rather than the actual radical production value by means of the plasma itself. The diffusion effect with the favourable oxidation kinetics thus contributes to the observed decrease in energy requirements.

3.4 Task 4: Gasification and reforming of pyrolysis oil

Authors: R.P. Balegedde Ramachandran and G. van Rossum/S.R.A. Kersten (UT)

Introduction

Catalytic steam reforming consists of two stages: In the first stage, pyrolysis oil is atomized into fine droplets in a gasifier where the oil droplets are converted to gases, vapours and char. After separating the char, vapour-gas mixture is reformed to synthesis gas using a steam reforming catalyst. There are several advantages of this process. They are:

1) Pyrolysis liquid has higher volumetric energy density than solid biomass

2) Pyrolysis liquid is easily compressible and transportable.

3) This process opens up opportunities to reform other bio based liquids such as crude glycerol from trans-esterification process.

4) To take advantage of the existing natural gas steam reformers and considering the availability of biomass for large scale steam reforming process, there is a possibility to replace natural gas by a fraction of bio-liquids such as pyrolysis oil or crude glycerol (from trans-esterification process), nevertheless without sacrificing the carbon in the mixed feed stock. This concept is proposed as 'Hybrid steam reforming' (HSR). A simple scheme of HSR is presented in the Figure 3.34.
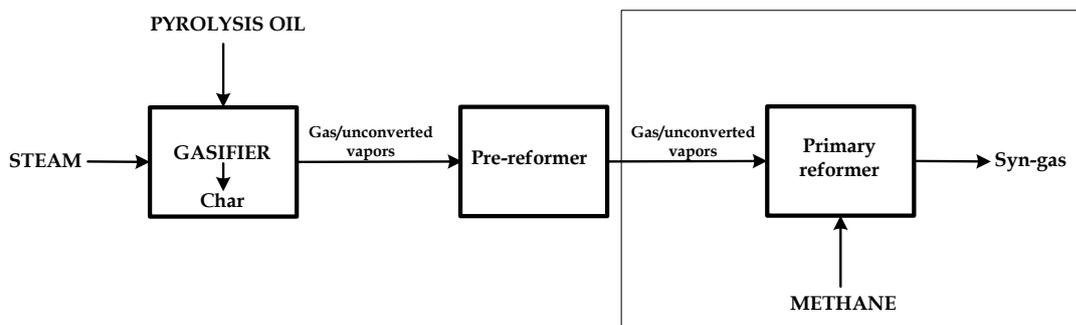
Figure 3.34 Schematic representation of synthesis gas production via hybrid steam reforming of pyrolysis oil and methane

However, there are many research questions to be answered. They are as follows:

Atomization/Gasification of pyrolysis oil:
- How is carbon distributed from pyrolysis oil to vapour, gas and char?
- Do heating rate and droplet size have effect on product distribution?
- Does pressure have any effect on gasification of pyrolysis oil?

Catalytic reforming of pyrolysis oil
- How behaves a traditional steam reforming catalyst (nickel on alumina) in terms of activity?
- How to do this process in existing reforming units?

Some of the highlights of research work are presented below.

Gasification of pyrolysis oil [79, 80]

The evaporation of pyrolysis oil was studied at varying heating rates ($1–10^6$ °C/min) with surrounding temperatures up to 850°C. A total product distribution (gas, vapour, and char) was measured using two atomizers with different droplet sizes (~100 micron and ~2000 micron). Figure 3.35 shows the effect of temperature between 500 and 850°C on product distribution. It was shown that with very high heating rates (~10^6 °C/min) the amount of char was significantly lowered (~8%, carbon basis) compared to the maximum amount, which was produced at low heating rates using a TGA (~30%, carbon basis; heating rate 1°C/min). The char formation takes

place in the 100 – 350°C liquid temperature range due to polymerization reactions of compounds in the pyrolysis oil. All pyrolysis oil fractions (whole oil, pyrolytic lignin, glucose and aqueous rich/lean phase) showed charring behaviour. The pyrolysis oil chars age when subjected to elevated temperatures (~700°C), show similar reactivity toward combustion and steam gasification compared with chars produced during fast pyrolysis of solid biomass. However, the structure is totally different where the pyrolysis oil char is very light and fluffy. To use the produced char in conversion processes (energy or syngas production), it will have to be fixed to a carrier.
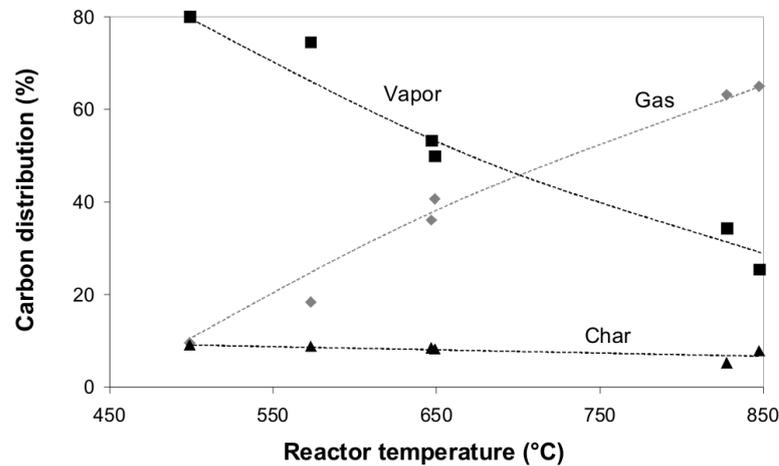
Figure 3.35 Product distribution during the gasification of pyrolysis oil using an ultrasonic atomizer (droplet size ~100 micron)
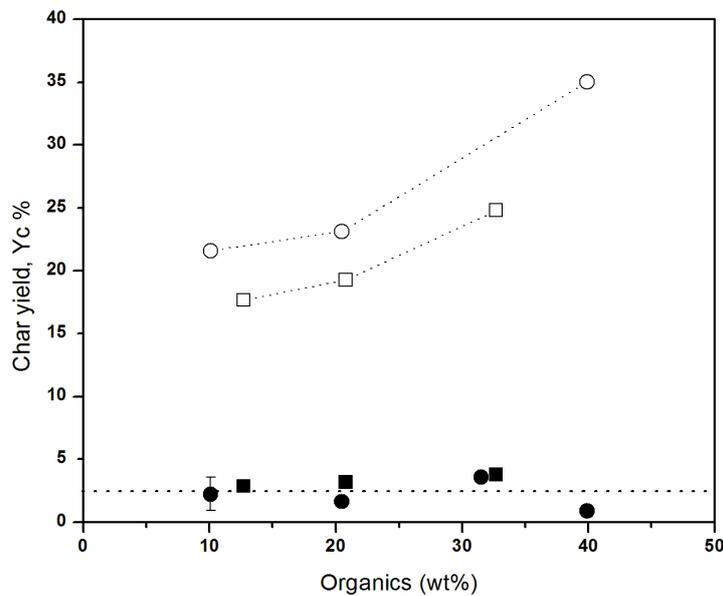
Figure 3.36 Effect of organic concentration on char yield by different heating rates. Reactor temperature 510 ± 10 °C, ● – glucose atomization, ■ - aqueous fraction of pyrolysis oil atomization, ○ – glucose (heating rate 100°C/min), □ – aqueous fraction of pyrolysis oil (heating rate 100°C/min)

The results obtained from the gasification of pyrolysis oil reveals that not a single lumped components class in pyrolysis oil can be identified that is primarily responsible for the char formation. At low heating rate, higher concentrations of organics in the bio-liquids result in higher char yields, which reveals that a certain fraction in the oil produce char with a reaction order higher than one (polymerization reactions). The effect of organic concentration on char yield is shown in the Figure 3.36. The measured trends in char yield can be described by a

model in which certain fraction of oil is converted by two parallel reactions to char and gas/vapour.

Gasification of glycerol [81]

With the ever-increasing production of bio-diesel, a surplus of crude glycerol, which is a by-product from trans-esterification process, is available in the global market. The crude by-product stream typically comprises of a mixture of glycerol, methanol, inorganic salts (mainly catalyst residue), free fatty acids and fatty acid methyl esters in varying quantities. Purification is required to transform the crude glycerol to usable state for food and pharmaceutical applications. As a first step in purification, excess methanol is distilled and re-used for the trans-esterification process. A neutralization step is required to purify crude glycerol further, to convert alkali catalyst into its salts, typically around 5% present in the crude. To find the gasification behaviour, several crude glycerol feed stocks were investigated. A tie-up has been made with BioMCN, Delfzijl, Netherlands.

Some of the crude glycerols investigated are:

1. Direct crude obtained from trans-esterification process (in house crude). This crude contains glycerol with low purity. It also contains fatty acids methyl esters, di and tri glycerides and potassium hydroxide (catalyst used for trans-esterification process)
2. Neutralized crude from BioMCN (contains ~82% glycerol, ~3% organic impurities and 1-2% salts (NaCl – this is because alkali hydroxide was neutralized using an acid)
3. High quality glycerol from BioMCN (~99%, ~<0.5% organic impurities)
4. Super high quality glycerol (99.999%)
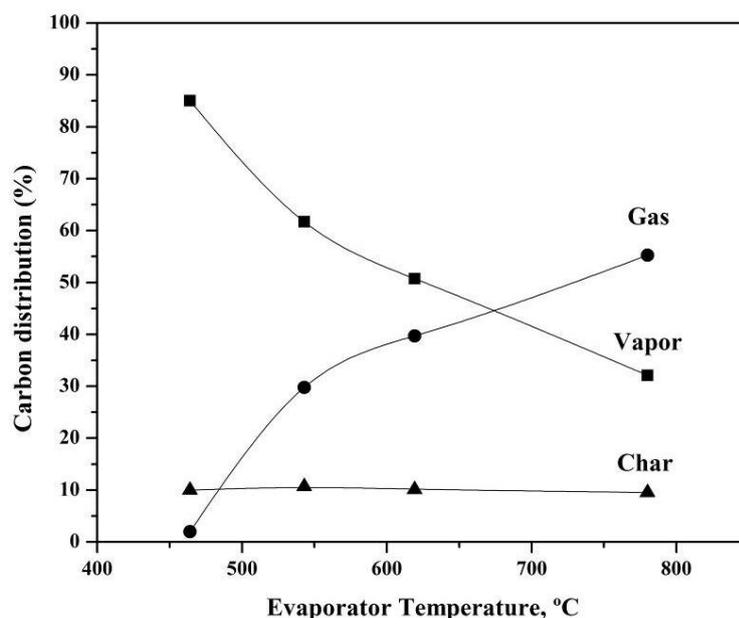
Figure 3.37 Carbon distribution over the gas, vapour and char during the gasification of glycerol in the presence of KOH.

Pure glycerol with KOH and direct crude glycerol formed considerable amount of char on carbon basis (~10%), whereas no carbon loss as char was observed for neutralized, high quality, super high quality and pure glycerol. Figure 3.37 shows the effect of glycerol doped with KOH during gasification. Neutralized glycerol formed considerable amount of salts in the evaporator. The results obtained show that alkali present in the glycerol was responsible for polymerizing higher molecular components formed during evaporation. Therefore, to make reforming process a flexible one, solid handling (char in the case of pyrolysis oil) or salts in the case of crude glycerol) becomes mandatory.

Catalytic steam reforming of pyrolysis oil [82]

Steam reforming of pyrolysis oil (T = 800°C, S/C = 1 & ~9) was studied using two commercial Ni on alumina catalysts (commercial naphtha reforming catalyst - one with different promoters such as K, Mg and the other one unpromoted, which is commercial natural gas steam reforming catalyst) and a research catalyst (promoted using Mg alone). The principal objective of this work is to elucidate the reasons for catalyst deactivation during pyrolysis oil and glycerol steam reforming by characterizing the aforementioned catalysts for their activities, surface area, pore size, chemical composition, hydrogen chemisorption, temperature programmed oxidation, reduction and scanning electron microscopic pictures.
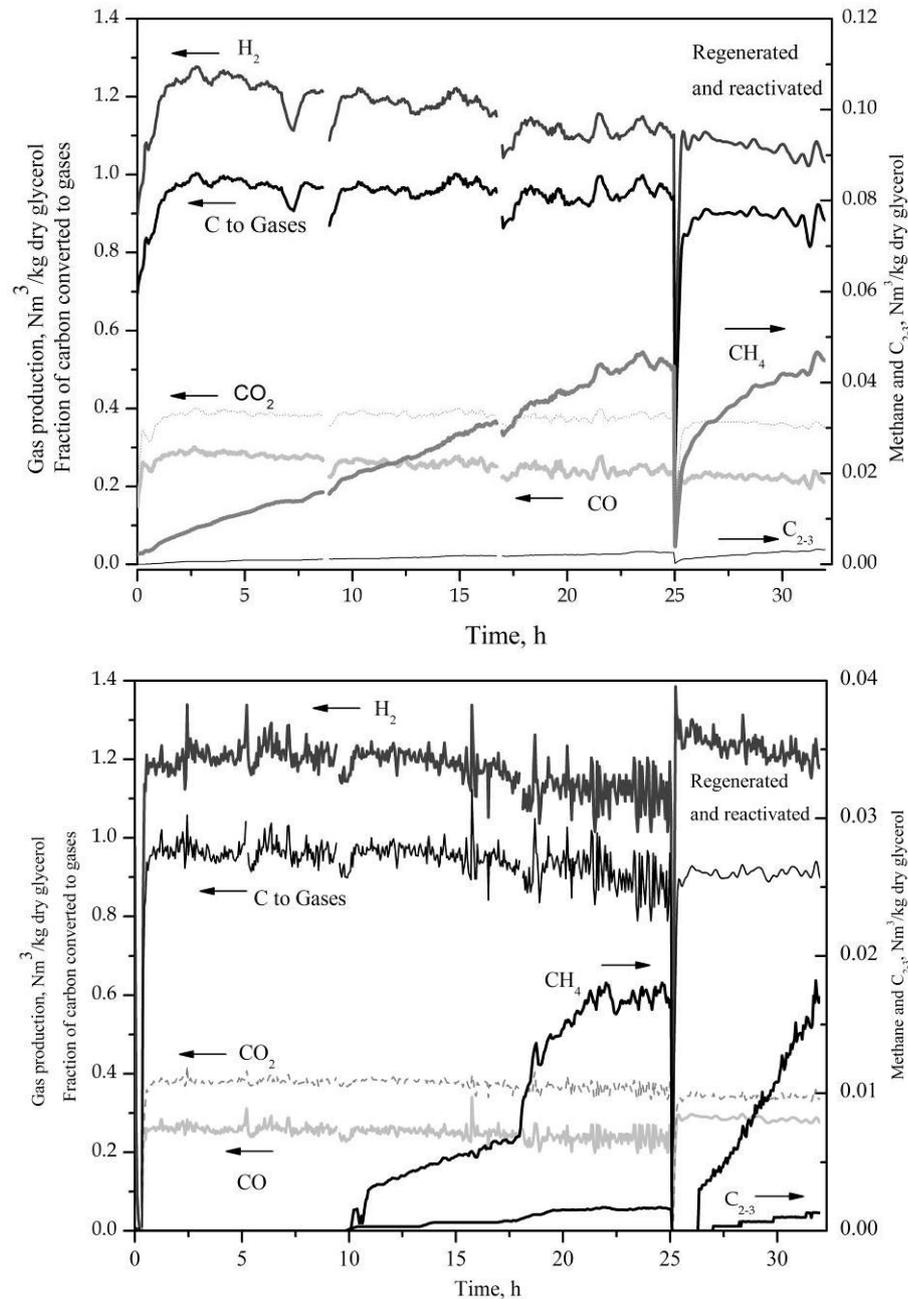
Figure 3.38 Steam reforming of crude glycerol 2: catalyst A (top), *S/C* = 3, *T*$_{cat}$ = 804°C; catalyst B (bottom) *S/C* = 3, *T*$_{cat}$ = 795°C. *S/C* = 3, *T*$_{cat}$ = 803°C. For all cases GC$_1$HSV = 600 h^{-1}.

High K amount deteriorates the CH$_4$ reforming activity (CH$_4$ produced during gasification) during steam reforming of glycerol and pyrolysis oil. K-promoted catalyst loses its initial

activity and never retained it when reforming was carried out after regeneration. Unpromoted and Mg promoted catalysts were able to retain their respective activities after regeneration. Surface area of the catalysts, pore volume, metal surface area and amount of H_2 adsorbed were found to be decreased after catalytic steam reforming. K was released during steam reforming, however major portion of K was found within the catalyst itself. The amount of the coke deposited on the K-promoted catalyst was found to be higher than on the unpromoted catalyst. This is quite unusual because K is a well known promoter to suppress coke formation. In the case of bio-liquids, there may be a side reaction between oxygenated vapours and K- present on the catalyst surface. It is also known from the gasification experiments that presence of KOH polymerizes glycerol in the liquid phase. Coke deposition on catalysts was found to be the major reason for deactivation of the catalyst, whereas the irreversible loss in the activity was due to K present in the catalyst. To facilitate stable bio-liquids reforming operation in a fixed bed, frequent regenerating steps are required.

Catalytic steam reforming of crude glycerol [81]
Steam reforming of crude glycerol (~83% purity at T = 800°C, S/C = 3) was studied using commercial naphtha reforming catalyst (catalyst A - Ni-K-Mg-Al_2O_3) and commercial natural gas reforming catalyst (catalyst B – Ni/Al_2O_3). The results revealed that loss in activity of Ni/Al_2O_3 steam reforming catalyst, the main reason for loss in initial activity was due to the presence of organic impurities such as FAMEs, di and tri glycerides. For unpromoted Ni/Al_2O_3 the catalyst, similar to pyrolysis oil reforming, activity is retained after regeneration, whereas for promoted catalyst the initial activity was never retained. Results are shown in Figure 3.38.
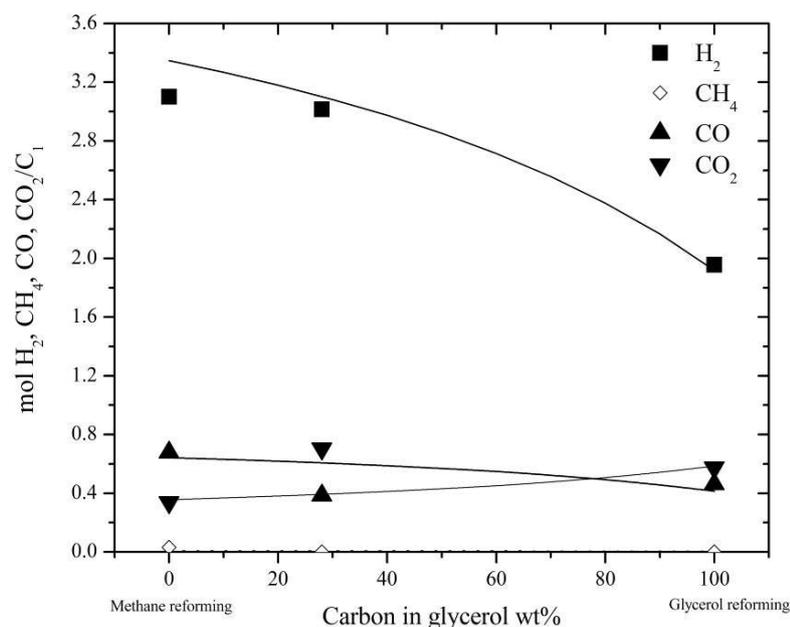
Figure 3.39 Hybrid reforming of methane with pure glycerol, Glycerol 28%, Methane 72%, Pre-reformer – S/C ~ 15, T = 590°C, GC_1HSV = 516 hr^{-1}, Primary reformer – S/C ~ 3, T = 791°C, GC_1HSV = 958 hr^{-1}. Comparison of methane, hybrid and glycerol steam reforming experiments (points) with thermodynamic equilibrium (line).

Hybrid steam reforming of methane and bio-liquids [81, 83]
In the hybrid steam reforming experiment, a 0.28 weight fraction of carbon in glycerol was co-reformed with 0.72 weight fraction of methane on C_1 basis. The test was carried out for 4 h. Figure 3.39 shows the gas production obtained from three cases. 1) Methane steam reforming 2) Hybrid reforming and 3) glycerol steam reforming. The line indicates the equilibrium gas production obtained at 800°C and S/C =3. The gas production was almost constant over the period of 4 h. An average carbon recovery of ~ 97% was obtained. The gas production is

expressed in mol of gas produced per carbon atom. For all the cases, the experimental value almost reached the equilibrium values. This concept requires clean feedstock such as pure glycerol or neutralized crude.

A detailed techno-economic evaluation was made of hybrid steam reforming of methane with bio-liquids. A detailed mass and energy balance was performed using UNISIM. The economic evaluation suggests that ~50% of bio-liquids with 50% natural gas reforming is possible and this concept will attract refineries when natural gas price increases to above 0.5 €/Nm^3 while bio-liquids are available at 100 €/tonne.

Future work
1) Hybrid steam reforming of methane and pyrolysis oil is studied in the lab scale set-up. The catalyst behaviour during hybrid steam reforming will be investigated.
2) A high pressure gasification of pyrolysis oil (up to 20 bar) was built. The carbon distribution from pyrolysis oil to gases, vapour and char will be investigated.

3.5 Task 5: Self gasification

Authors: P. Nanou and G. van Rossum/S.R.A. Kersten (UT)

Introduction
Biomass self-gasification focuses on the production of bio-methane via the gasification route by using the alkali metals already contained in the biomass as gasification and methanation catalysts. The research questions that arise for this work can be divided in two main groups:

- From the coal gasification research of the 1980's it was claimed that a similar process running on coal entailed an autothermal gasifier without the addition of air/O_2 to the system (results are presented below under the heading 'Process performance analysis')
    - Is this also the case if biomass would be used instead?
    - When looking into the process as a whole, is it possible to obtain a net autothermal process also by feeding biomass?
    - If not, where does the bottleneck lie?
- The concept utilizes alkali metals contained in the biomass itself as gasification and methanation catalysts (results are presented below under the heading "Effect of alkali metals/ash on gasification and methanation").
    - Do alkali salts catalyse gasification?
    - If yes, how should these salts be put into contact with the biomass in order to work catalytically?
    - Do these salts also catalyse methanation?
    - What is the mechanism of catalysis by salts?

Process Performance Analysis
The route to methane via gasification of a dry biomass was investigated by modelling different possible process configurations with Aspen Plus. Three possible configurations were identified and were compared with respect to their HHV efficiency to methane and the process energy demand with varying gasifier temperature (700-800°C) and pressure (1-35 bar).

Conventional proposed biomass gasification processes for methane production from dry biomass are usually two-step process configurations. This type is referred to as 'once-through' configuration and is given in Figure 3.40A. The second possible configuration is the 'full (syngas) recycle' mode which is proven to work for pressurized coal gasification (Exxon) and is presented in Figure 3.40B. Another alternative is the combination of the two aforementioned configurations, termed 'partial (syngas) recycle' mode and is depicted in Figure 3.40C. The process conditions applied in the models are given in Table 3.3.

Table 3.3 Process conditions used in the models.

Biomass Moisture Content	6 wt%
Biomass Input	25°C, 1 bar
Water Input	25°C, 1 bar
Steam/Carbon (mol/mol) (Gasifier)	1.50 – 2.43
Compressors (also cryogenic unit)	Multistage (with intercooling)
Recycle split (only in partial recycle mode)	50%
Methanation reactor	350-500°C, 35 bar
S_1 separator (water condenser)	43°C
S_2 separator (CO_2 separation unit)	35°C
S_3 separator (only in full recycle mode-cryogenic separation)	-147 to -138°C, 35 bar
CH_4 product	25°C, 35 bar
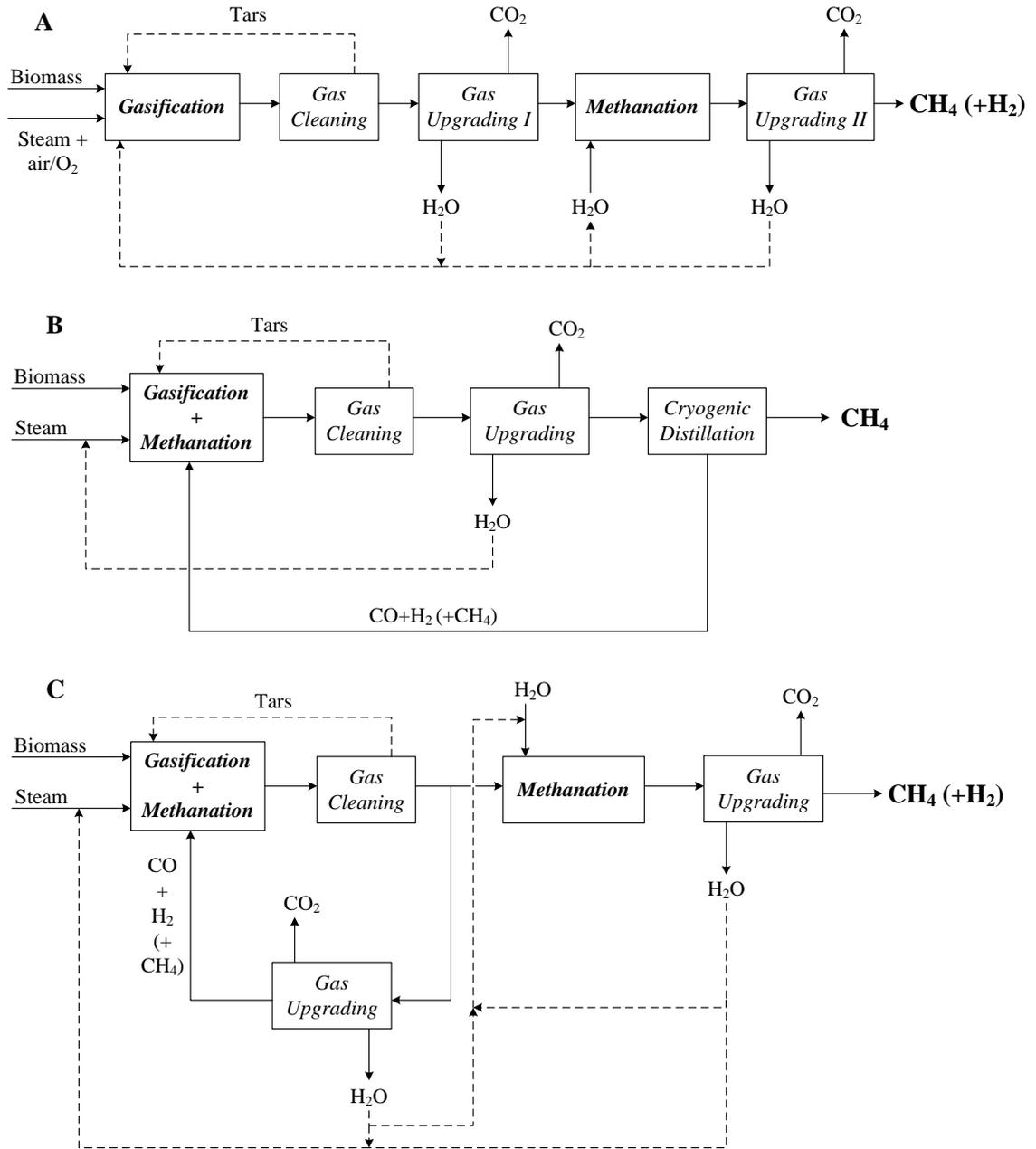
Figure 3.40 Block diagrams of the (A) once through, (B) full recycle and (C) partial recycle configurations.

The HHV efficiency to methane is expressed on primary energy input and is calculated by:

$$\eta_{CH_4} = \frac{HHV_{CH_4}\Phi_{m_{CH_4}} + HHV_{H_2}\Phi_{m_{H_2}}}{(HHV_{biomass} + \sum Q + \sum W)\Phi_{m_{biomass}}} \times 100\% \qquad (3.17)$$

where $\quad \sum Q = Q_{\text{hot utility}} + Q_{S2}$ $\qquad\qquad\qquad\qquad\qquad (3.18)$

$\qquad \sum W = 3W_{\text{compressor(/turbine)}} + 3W_{\text{recycle compressor}} + 3W_{\text{pumps}} + 3W_{\text{solid}} + 3W_{S3} \qquad (3.19)$

and where all units are expressed in MJ/kg dry biomass feed, unless otherwise stated.

The number '3' is preceding each work expression 'W', because it is assumed that electricity is produced with an efficiency of $\eta=1/3$ from an energy source. The efficiency expression also includes H_2 which can be present in the product gas (max. 6 mol%) for the case of the methanation and the combined configurations, because in these cases it is considered as part of the final product. $Q_{hot\ utility}$ is the process energy demand in hot utility, after heat integration analysis and is read from the cold-hot composite diagrams constructed for each case and Q_{S2} is the energy demand of the CO_2 separation unit (set at 4 MJ/kg CO_2).

No energy input is included in eq.(3.17) for separator S_1, because this is taken into account indirectly through system coolers in the hot-composite curve and is therefore incorporated in the $Q_{hot\ utility}$ expression. $W_{compressor(/turbine)}$ is the net work required for the compressor(/turbine) system, $W_{recycle\ compressor}$ is the work required for compression of the recycle stream to overcome the assumed pressure drop of $\Delta P = 1$ bar (only in the case of the recycle and the combined configuration), W_{pumps} is the sum of work required for the pumps of the gasifier and methanation reactor water feeds, W_{solid} is the energy required for feeding the solid biomass into the gasifier. The last parameter is added because the model uses a liquid biomass feed, underestimating the actual energy demand. The assumption is made that the solid biomass is pressurized in lock hoppers and a screw feeder is used for biomass injection in the form of 0.5 mm particles. The energy requirement varies from 0.62 to 1.05 MJ$_e$/kg dry biomass. This includes electricity consumption for compression of the inert gas and the power consumption for size reduction (milling) of the wood to 0.5 mm particle size. In the case of the recycle and combined configurations, the recycle stream (already compressed) can be used for pressurizing the lock hoppers, therefore the minimum energy requirement is calculated for those cases, which is only the milling of the wood (energy requirement of 0.62 MJ$_e$/kg dry biomass). W_{S3} (included only in the case of the recycle configuration) is the energy requirement for the cryogenic separation unit S_3. This includes only work expressions for the compressors of the system.

According to this efficiency definition, the maximum efficiency to CH_4 obtained from reaction stoichiometry:

$$C_6H_8O_6 + 2H_2O \rightarrow 3CH_4 + 3CO_2 \qquad\qquad (3.20)$$

can be calculated as

$$\frac{3MW_{CH_4}}{MW_{biomass}} \frac{HHV_{CH_4}}{HHV_{biomass}} \times 100\% . \qquad\qquad (3.21)$$

This gives a maximum efficiency to methane of 89%.

Results. Table 3.4 presents the overall results of this study. Overall efficiencies to CH_4 obtained were in the range of 48 - 66%. This corresponds to 54 - 74% of the theoretical maximum (89%). The partial (syngas) recycle configurations give the highest overall efficiencies to methane (55 - 66%), the once-through give lower overall efficiencies to CH_4 (49 - 63%), and the full (syngas) recycle give the lowest overall efficiencies to CH_4 (48 - 58%).

Table 3.4   Overall results for the three studied process configurations.

Process configuration	η_{CH4}, % (HHV basis)	Autothermal Gasifier	Autothermal Process, only if:	Required CO_2 separation technology
Once-through	49-63	700°C (20-35 bar)	< 1 MJ/kg CO_2	Membranes CO_2 sorbents
Full (syngas) recycle	48-58	700°C (20-35 bar)	2 MJ/kg CO_2	Scrubber
		700°C (10-15 bar)	< 1 MJ/kg CO_2	Membranes CO_2 sorbents
		800°C (10-35 bar)		
Partial (syngas) recycle	55-66	700°C (10-35 bar)	2 MJ/kg CO_2	Scrubber

The gasifier can operate autothermally without the addition of O_2/air under certain conditions, included in Table 3.4. As far as the process is concerned, it appears that heat always has to be supplied to the process, either at gasifier temperature level (800 - 900°C) or at CO_2 separation unit temperature level (100°C). There is the possibility to obtain an overall autothermal process, but only in the cases where low-temperature hot utility is needed (100°C). Therefore, the bottleneck for obtaining an overall autothermal process lies in the energy demand of the CO_2 separation unit. None of the three studied configurations can operate without extra heat added, unless a CO_2 separation unit with low-energy requirements can be employed (≤ 2 MJ/kg CO_2) by means of an improved or new CO_2 separation technology.

Effect of alkali metals/ash on gasification and methanation
A high ash content in the gasifier / biomass particles can be achieved by recycling ashes via impregnation of the biomass or by creating a high ash holdup in the gasifier. In biomass gasification, direct production of gases via the pyrolysis vapours is very fast. Char remains in this process and normally reacts slowly to gas. In this work we investigate the catalysis of char steam gasification by various minerals with the focus on catalysis by wood ash.

$$\text{Biomass} \begin{cases} \text{Vapors} \longrightarrow \text{Gas} \\ \text{Char} + H_2O/CO_2 \longrightarrow \text{Gas} \end{cases}$$
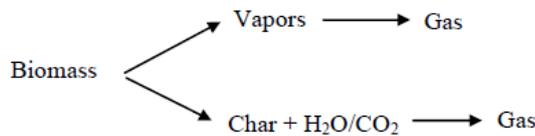
Results. Biomass-derived char conversion in steam was studied in a TGA system. Minerals/salts that are most present in biomass are potassium (K), sodium (Na) and calcium (Ca). These compounds were individually tested in their carbonate and hydroxide forms. Actual biomass ash was also tested. The results are presented in Figure 3.41 and Figure 3.42.

These results show that potassium, sodium, calcium and ash enhance steam gasification rates of char, with an apparent zero order dependency in char. The latter is not yet fully understood (in terms of catalysis and possible reaction mechanism) and is currently being investigated. Biomass ash works as well in catalyzing the steam gasification of char, but only when impregnated in the wood. Just mixing the ashes with char results in much lower gasification rates for X > 0.2 (see Figure 3.42B). Also, the results point out that the gasification reactivity of char in steam does not depend on the 'initial' mode of occurrence of the mineral/salt as noted from the similar reactivity profiles of KOH and K_2CO_3. Most reported mechanisms assume that oxides, hydroxides and carbonates for a certain amount of char matrix, 'built in' carbonate which is the actual active compound. SEM images of the chars (Figure 3.43) reveal that KOH causes a drastic change in char structure and surface area, whereas with K_2CO_3 the char maintains its original structure.

Therefore, as the rates of these chars are equal we can conclude that the catalytic reactivity does not depend on surface area. Figure 3.44 shows the reactivity differences when the salts are removed from a char + KOH sample by water washing prior to gasification. The high surface area char without KOH has the same reactivity as untreated char (Figure 3.44). Clearly, the potassium is most important in enhancing the rate.

As far as the overall process in concerned it becomes clear that the ash has to be recycled to the gasifier by impregnating the biomass feed (Figure 3.45). The main water-soluble compounds of the ash include (after reaction in water): KOH, NaOH and $Ca(OH)_2$. The main water-insoluble compounds that are purged from the system are: Al_2O_3, SiO_2 and Fe_2O_3.

The effect of the minerals/ash on the methanation reaction is currently still under investigation.
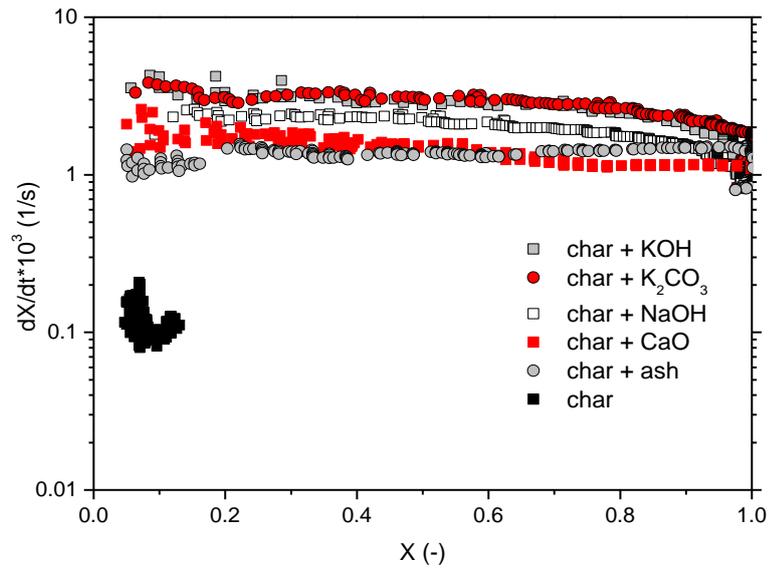
Figure 3.41 Char conversion rate in steam vs. conversion for the tested minerals/salts. T = 700°C, P_{H2O} = 1 bar, Metal/Carbon (mol/mol) = 0.046.
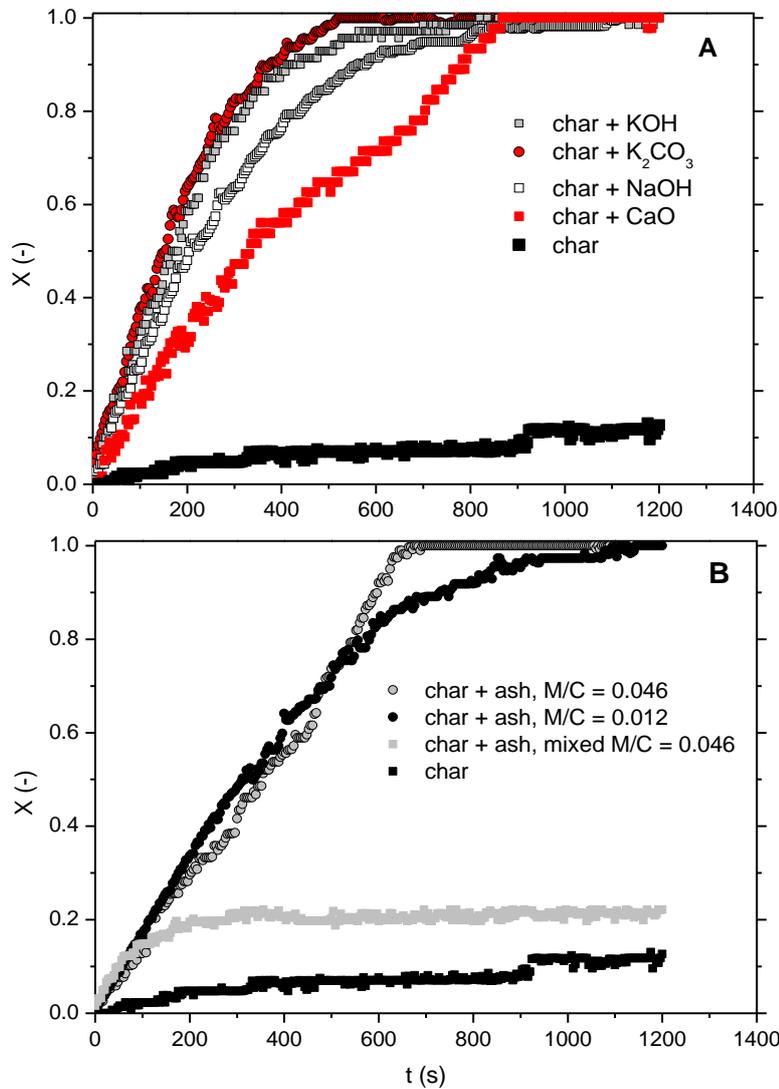
Figure 3.42 (A) Effect of different minerals/salts on wood char conversion. Metal/Carbon (mol/mol) = 0.046. (B) Effect of ash concentration and addition method on wood char conversion. Char conversion in steam at T=700°C and P_{H2O}= 1 bar.
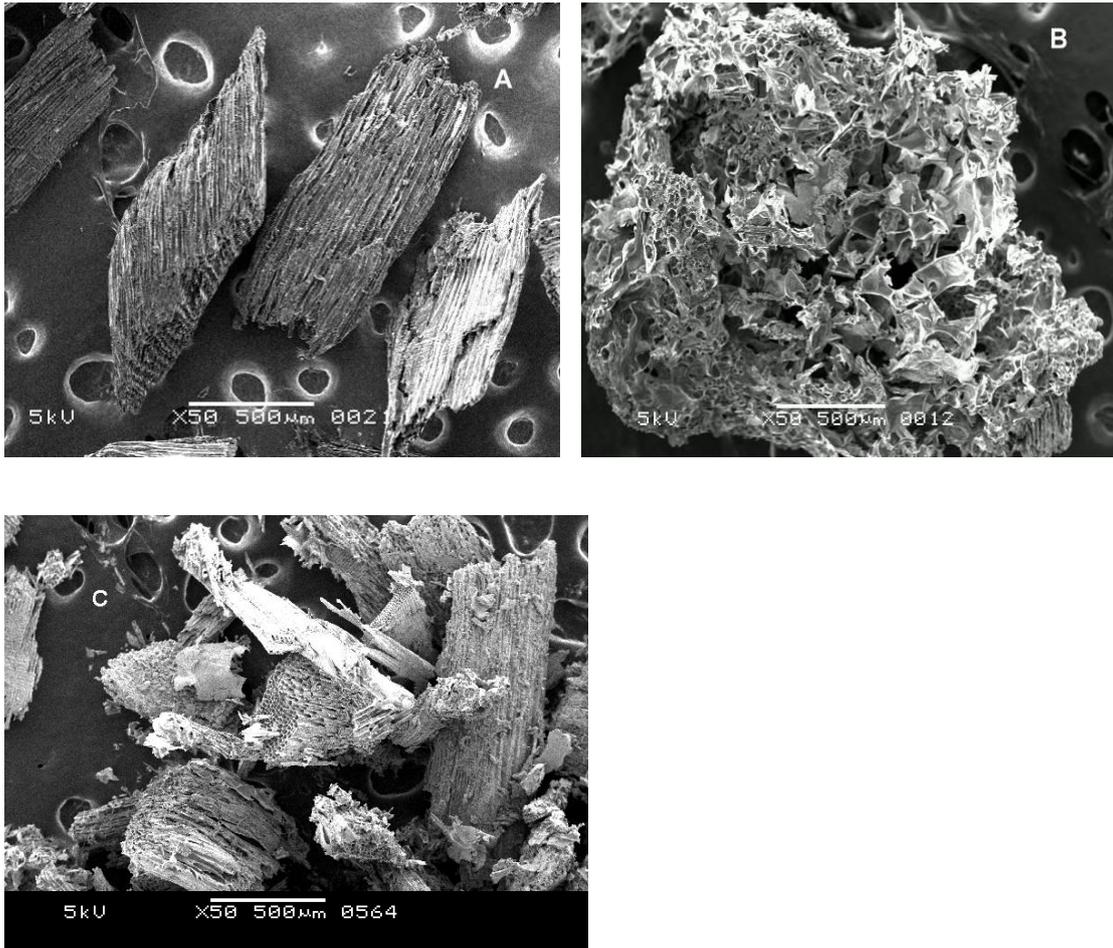
Figure 3.43 SEM images of chars prior to gasification. (A) char, (B) char + KOH, M/C (mol/mol) = 0.046 and (C) char + K_2CO_3, M/C (mol/mol) = 0.046.
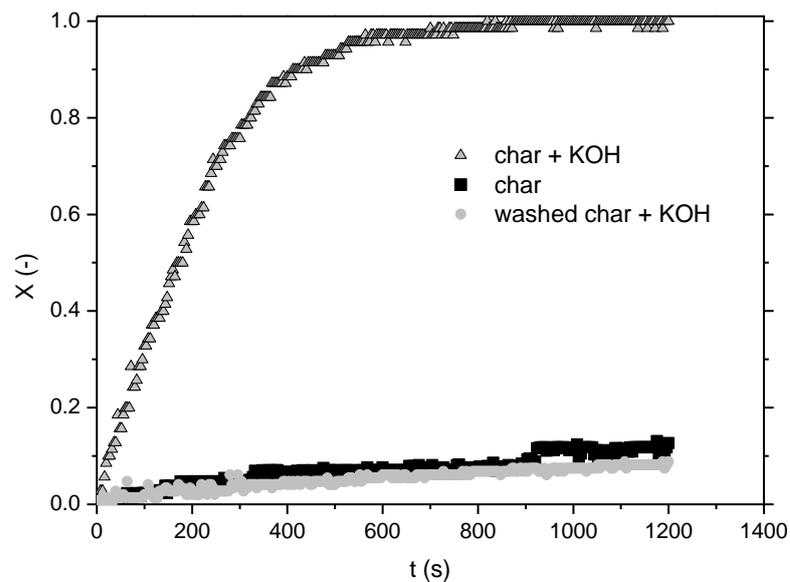
Figure 3.44 Effect of catalyst vs. char surface area on wood char conversion. Char conversion in steam at T = 700°C and P_{H2O} = 1 bar. ["washed char+KOH" is char produced from wood impregnated with KOH after which the salt is removed again].
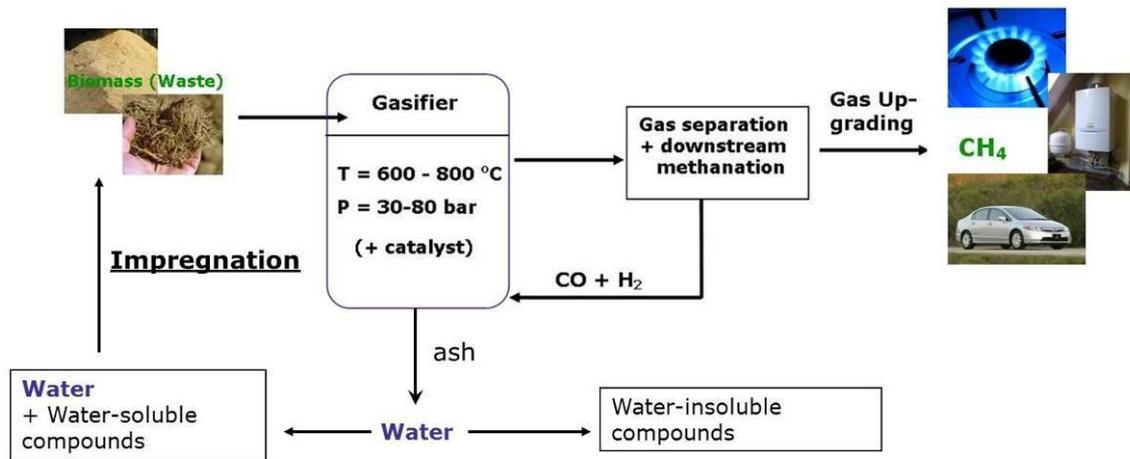
Figure 3.45 Steam gasification concept for methane production from lignocellulosic biomass. Steam for the reactions enters the gasifier together with the impregnated biomass.

3.6 Task 6: Catalytic tar removal

Author: W. de Jong (TUD)

Introduction

Syngas produced from biomass gasification is an economically and technologically feasible alternative to traditional fossil fuel for heat and electric generation as well as transportation fuel production [1]. However, contaminants contained in product gas such as organic components (e.g., tar), inorganic components (e.g., H_2S, HCl) and particles largely limit the applications of syngas produced from biomass gasification. As one of the most problematic compound classes, tar can result in various problems associated with condensation, aerosol formation and polymerization to form more complex deposits. The MILENA process is primarily aimed at the production of SNG for injection in the existing natural gas infrastructure. Although using the gas scrubbing process OLGA has solved the downstream tar problem, still upstream of the scrubbing step tars are present in the gas that impact the gas cooling step situated before the scrubber section. Therefore, TU Delft had in a joint effort together with ECN a look into ways to cheaply solve these issues.

Aim

The aim of the work was to investigate the possibility of selectively converting heavy tar compounds into lower molecular weight species (and –partly- removing particles as well), thus keeping the CH_4 content in the raw gas virtually unchanged. This study therefore aimed at enhancing the cooling step with respect to fouling before the gas produced using MILENA technology is further cleaned from tars based on OLGA scrubbing. Finally, one or two catalytic materials which are potentially able to reduce heavy tars and thus reduce tar dew point were to be investigated. Moreover, optimum operation conditions were to be determined.

Methods and setups

The following steps have been applied in this research project:

1) To facilitate determining experimental conditions, a comprehensive literature survey towards catalytic tar reduction by focusing on various cheap catalytic materials, gas composition as well as process conditions (reaction temperature and residence time) was carried out (first project year). Gas composition selection for testing at TUD was based on MILENA syngas which consisted of main gases namely CO, H_2, CO_2, CH_4, H_2O, all types of tars, other gases like HCl, NH_3, H_2S etc. and solid particles. To focus on tar reduction reactions, H_2S, COS, HCl and NH_3 were not taken into account.

2) To perform catalytic tar reduction experiments, two setups were used: a tube furnace reactor at ECN and an existing high temperature gas cleaning unit (HTGCU) at TUD.

   - The tube furnace reactor at ECN was used to investigate how tar components contained in the real raw product gas produced from MILENA gasifier could be reduced under different process conditions. A simplified scheme of the experimental setup at ECN is shown Figure 3.46. The reactor has an inside diameter of 30 mm and is 480 mm long, made of steel which could withstand the high temperatures. Catalysts were filled to half tube and some inert materials (glass beads) were put at the top of the reactor to achieve an evenly distributed temperature profile. A slip of the gas produced from MILENA gasifier was cooled down to around 400°C before entering the reactor.

   - The HTGCU at TUD was used to investigate how methane and tar model components reduced under different process conditions. This setup mainly consists of gas supply lines, tar evaporator, fixed bed quartz glass reactor and online gas analyzer. The produced gases (e.g., CO, CO_2, H_2, CH_4) were analyzed directly by the online gas analyzer. Since the quartz glass reactor was found easily broken and not well sealed at the flanges, a metal reactor (see Figure 3.47) was designed and built to overcome the issues. The new reactor was made of stainless steel (Grade 310) that could stand high temperature and the tensions or forces due to thermal expansions. Due to the failure of

furnace heating wire, a new heating system has been designed for HTGCU by using another type of heating shell which is also used for 100 kW$_{th}$ steam/oxygen blown CFBG unit at TUD. For both setups, the Solid Phase Adsorption (SPA) method was used to analyze tar components. All samples were taken before and after the reactor.

3) Finally, the kinetic parameters, i.e. apparent activation energy (Ea) and apparent pre-exponential factor (k$_0$) for the decomposition of tar components produced from MILENA, CH$_4$ of blank test on HTGCU were determined. Tar reduction behaviour was simulated using Aspen Plus Software by using the determined kinetic parameters and then compared with the experimental results. The reduction of tar model components (e.g., naphthalene) was performed on HTGCU.
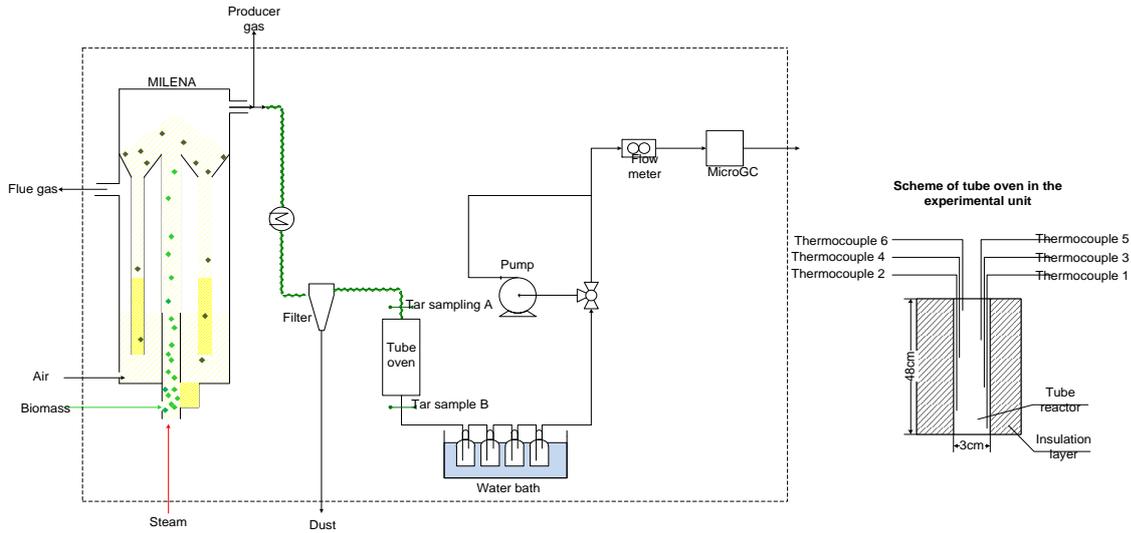
Figure 3.46 Scheme of the experimental setup at ECN
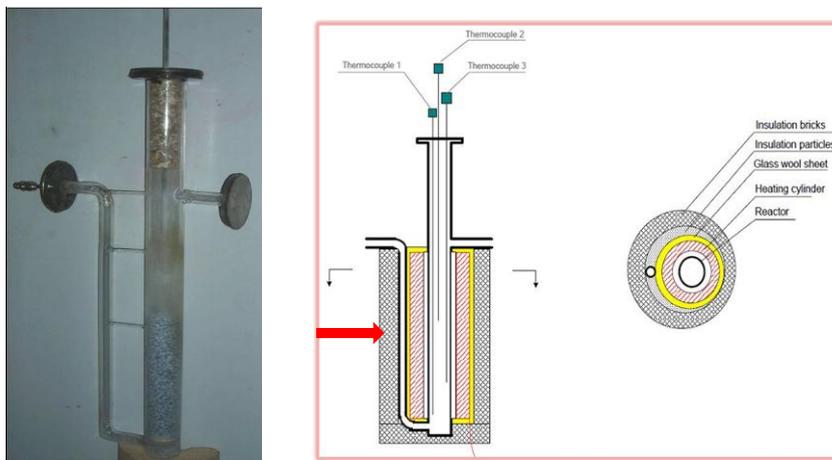
Figure 3.47 A schematic of the new heating system for the Delft fixed bed test reactor (HTGCU).

Results and discussion [84, 85]

Bed materials selection: From the literature overview [84], it was found that various catalysts are used for tar reduction. Based on the catalyst production method, they can be classified into two major groups and shown in Figure 3.48. Both classes of catalysts have been largely used and have pros and cons. According to the project requirements, several criteria (e.g., hardness, reactivity, disposal problems, price) were taken into account for catalyst selection. Based on the requirements, two catalysts were selected for the experiments which were Austrian olivine and iron silicate.
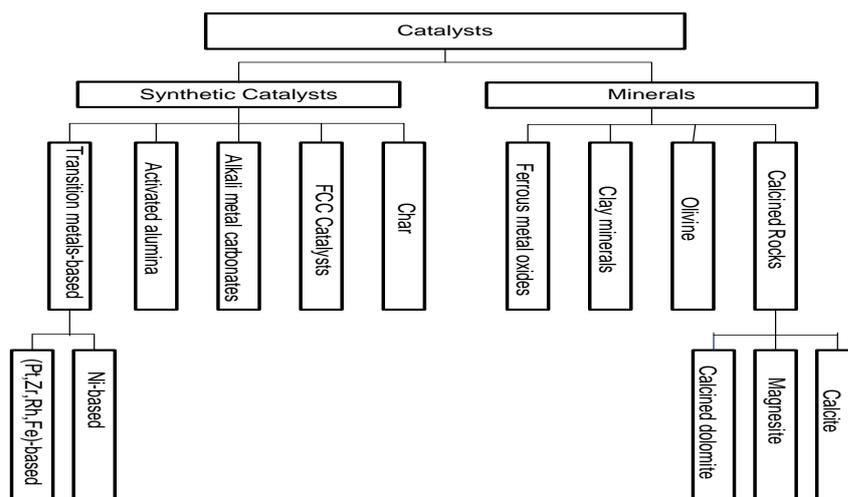
Figure 3.48 Classification and types of catalysts used for tar reduction

Real tar components reduction: The catalytic effect of the iron silicate as bed material on each type of quantified tars in the product gas produced from MILENA gasifier at ECN was investigated. The mass balance calculation is shown in Table 3.5.

Table 3.5   Mass balance results of syngas tests using iron silicate

Condition	850°C, 1.5s		850°C, 1.0s		850°C, 0.5s		800°C, 1.5s		750°C, 1.5s	
[g/min]	inlet	outlet	inlet	outlet	inlet	outlet	inlet	outlet	inlet	outlet
CO	0.408	0.343	0.612	0.490	1.067	0.781	0.412	0.373	0.352	0.368
H_2	0.021	0.022	0.032	0.031	0.051	0.041	0.020	0.021	0.019	0.019
CO_2	0.477	0.507	0.715	0.717	1.170	0.963	0.511	0.516	0.483	0.495
CH4	0.084	0.079	0.126	0.110	0.223	0.159	0.084	0.077	0.073	0.074
H_2O	0.094	0.111	0.314	0.390	N/A	0.314	0.438	0.459	0.420	0.399
Tar ($>C_{10}$)	0.017	0.013	0.028	0.017	0.044	0.033	0.024	0.020	0.024	0.019
Total tar	0.021	0.016	0.033	0.022	0.055	0.053	0.029	0.027	0.029	0.027
Flow	1.179	1.138	1.942	1.851	5.303	4.756	1.565	1.537	1.444	1.456
Dew point [°C]	239.3	222.3	239.0	218.4	241.8	231.4	237.6	228.0	239.6	229.0

From Table 3.5 one can observe that mass balance closure is significantly deviating from 100% in some of the experiments since the measured water contents at the outlet are not accurate enough, probably due to measuring inaccuracies during the experiments. The inlet water content in Table 3.5 is calculated from an element balance, which is different from the actual moisture in syngas (30%~35%). The trends of the main gases under different reaction conditions are not identical and dissimilar to blank tests. The increase of CO_2 and decrease of CO show the direction of WGS reaction

$$CO + H_2O \leftrightarrow H_2 + CO_2 \qquad\qquad (3.22)$$

is from left to right (more severe to less severe conditions). Both CH_4 and tar content are reduced, as well as the dew point of the gases.

Tar conversion at different temperatures: The tar conversion rate X is defined as $X = (C_{in} - C_{out})/C_{in}$ x 100%. Generally a higher reaction temperature leads to improved tar reduction which can be caused by thermal and/or catalytic conversion. The reactions are reversible, so that the concentrations of the reactants and products, and reaction conditions (mainly temperature) have impact on the results, such as reaction direction, kinetic parameters, and conversion rate, etc. On the other hand, the catalytic activity depends on the temperature, and consequently changes the reaction results. Because of the differences of catalyst structure and compositions, the activity differs. If there were different experimental results for olivine, the

difference in activity can be explained as different compositions from iron silicate, because none of the catalysts is porous, the surface areas of them are comparable for similar particle sizes.
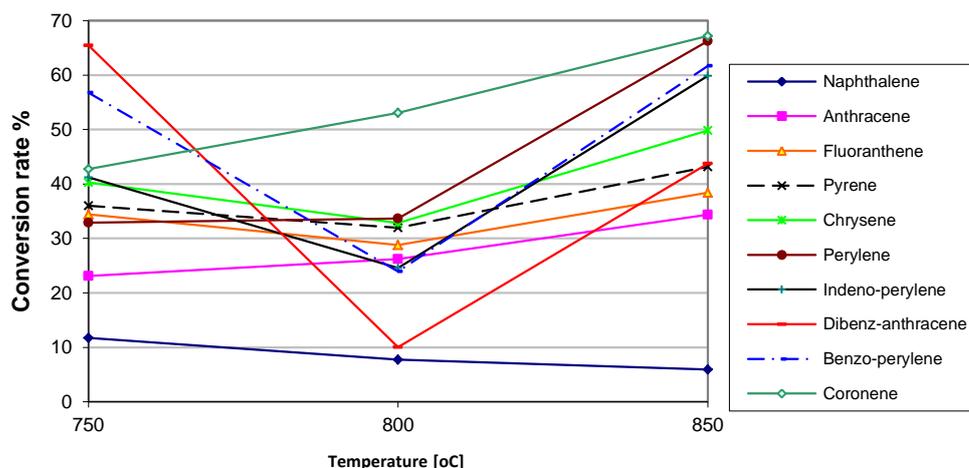
Figure 3.49 Heavy tar component conversion rate with temperatures. Gas residence time: 1.5s, catalyst: iron silicate.

According to literature study, the tar conversion is increased by a higher temperature. However, the experimental results of heavy tars were not following the expected trend, as shown for some of them in Figure 3.49. An increase in reaction temperature had a positive influence on the decomposition of anthracene, pyrene and corone, but also lead to a higher naphthalene concentration in the product gas. With an increase in temperature from 750°C to 850°C, the conversion rates of other tar components like fluoranthene, chrysene etc. fluctuated, instead of showing a continuously increasing trend. Generally, the conversion rate increased with molecular weight (MW), for example $X_{naphthalene} < X_{anthracene} < X_{coronene}$ as the $MW_{naphthalene} < MW_{anthracene} < MW_{coronene}$.

The conversion rates of fluoranthene, pyrene, chrysene, indeno-perylene, dibenz-anthracene and benzo-perylene showed the lowest values at 800°C, rather than at 750°C. Even with such an observation, high temperature results in good tar conversion performance if a moderate temperature range was applied, 850°C rather than 800°C. From Figure 3.49, it can be seen that 850°C gave the optimal conversion rate with the reaction conditions.

Table 3.6   Apparent activation energy for tar decomposition (real gas conversion conditions).

Tar	Kinetic parameters		Tar	Kinetic parameters	
	E_{app} (kJ/mol)	$k_{0,app}$ (s^{-1})		E_{app} (kJ/mol)	$k_{0,app}$ (s^{-1})
Coronene $C_{24}H_{12}$	65	751	Benzo(ghi)-perylene $C_{22}H_{12}$	11	1.3
Dibenz(a)-anthracene $C_{22}H_{14}$	N/A	N/A	Benzo(e)-pyrene $C_{20}H_{12}$	N/A	N/A
Indeno(123-cd)-perylene $C_{22}H_{12}$	49	84	Benzo(a)-pyrene $C_{20}H_{12}$	91	9.7E3
Benzo(b)-fluoranthene $C_{20}H_{12}$	82	3.2E3	Benzo(k)-fluoranthene $C_{20}H_{12}$	93	1.2E4
Perylene $C_{20}H_{12}$	93	1.3E4	Anthracene $C_{14}H_{10}$	44	30
Naphtalene $C_{10}H_8$	N/A	N/A	Class V	35	16
Class IV	40	7.1	Class II	251	3.9E11

Agent: $H_2O + CO + CO_2 + H_2$ Catalyst: iron silicate Temperature: 750 - 850°C

Kinetic parameters for some tar components: Based on the results analysed, the apparent activation energy and apparent pre-exponential factor for tar kinetic decomposition were calculated and the results are shown in Table 3.6. For the calculation, the estimated apparent

activation energy of iron silicate was assumed to be constant in the studied temperature range. The apparent rate constant was varied with temperature by an Arrhenius-type relationship.

From Table 3.6 it can be seen that the reactions of Class II were the fastest, showing the largest kinetic parameters and these were followed by Class V. Class II tars reacted very easily on iron silicate and the heaviest tars tended to convert to more stable forms. Reactions of Class IV tars of which more than 50% was naphthalene were the slowest because of the stable properties of such Class IV tars. Unfortunately, the amount of Class III tars increased rather than decreased, thus its activation energy and apparent rate constant cannot be calculated using simple Arrhenius Law.

Modelling of tar conversion in Aspen Plus: Because of the limitations of the Aspen Plus databank, some types of tars were not included, thus phenol (C_6H_6O) was chosen to represent the whole Class II tars for it formed $80\%_{wt}$ among Class II tars. Naphthalene ($C_{10}H_8$) is well known as a typical Class IV tar which weighted more than 50% in Class IV tars. $C_{16}H_{10}$ referring to fluoranthene and pyrene were chosen as model compounds for Class V tars, which in sum are more than 60% of Class V tars. The gas was composed of the main gases with approximately the same compositions in MILENA syngas which are listed in Table 3.7 and N_2 represented all other gases in the syngas. There were three total inlet volume flows resulting in gas residence times τ from 0.5 s to 1.5 s.

Table 3.7   Aspen Plus real tar conversion simulation input

Component	Mole-fraction [%]	Temperature [°C]	Pressure [bar]
CO	22	400	1
H_2	16	*Gas flow [L/min]*	*Residence time τ [s]*
CO_2	17	3.9	1.5
CH_4	8	5.7	1.0
H_2O	32	11.6	0.5
N_2	4.675	*Model*	*Diameter x Length [mm]*
C_6H_6O	0.02	RPlug	30 x 480
$C_{10}H_8$	0.25	*Catalyst voidage*	*Catalyst weight [kg]*
$C_{16}H_{10}$	0.025	0.486	0.6
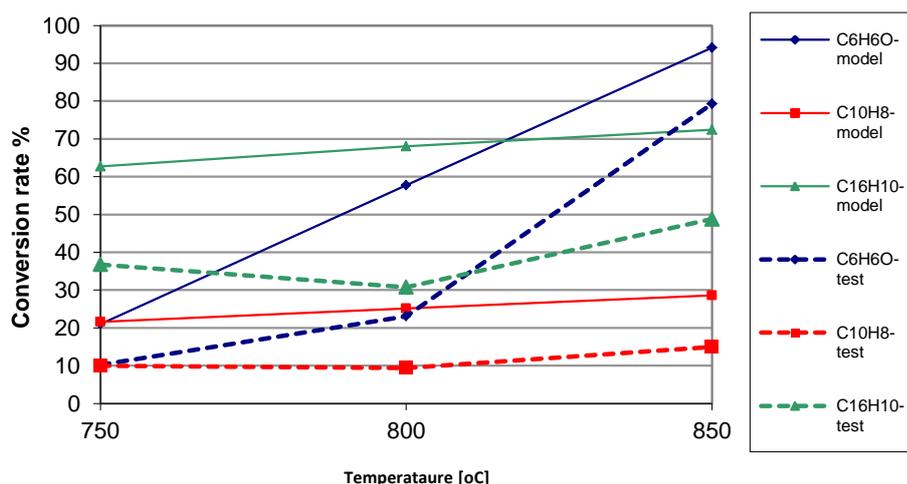
Figure 3.50 Tar conversion modelling and test results with varying temperatures ($\tau = 1.5$ s)

Figure 3.50 compares the modelling and experimental results of tar conversion at different temperatures. For all three tar classes modelling shows the same tendency as the experimental results. The conversion rate at 850°C was higher than at lower temperatures. But the rates from modelling were higher than the ones obtained from experiments. One reason is that the three

compounds had their own properties that were used to represent the entire class, which would definitely cause differences. Another reason is that in a real process, the tars may not only convert to CO and H_2O. They can reform to lighter or heavier tars, be cracked to CO_2 or even carbon. The modelling conditions were hypothetic that also affected the modelling results. The model gas and calculation method in Aspen Plus were assumed to be an idealized case. However, in the tests, there were more compounds and particulates which may influence the contact to the catalysts that reduced the direct contact with the catalytic support. To summarize, the model was simplified from the real situation which overestimated the results from the model reactions that were considered but neglected the consequences from others that were taken out.

Blank test - CH_4 conversion: In order to compare with experimental results obtained from the ECN rig and investigate effects of operating conditions on tar conversion, two stages of experiments have been carried out on the HTGCU set up using artificially made-up gases based on the composition of MILENA syngas at TU Delft.

Since CH_4 is one of the most common hydrocarbons in product gas obtained from biomass gasification, the effect of the catalyst (iron silicate) on CH_4 conversation under different temperatures (750°C, 800°C, 850°C) and residence times (0.5 s, 1.0 s, 1.5 s) were examined.

Table 3.8   Mass balance of CH_4 concentration variation tests at 850°C

Residence time [s]	0.5		1.0		1.5	
Gas flow [g/min]	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
CO	1.000	0.973	0.400	0.467	0.246	0.271
CO_2	1.572	1.183	0.785	0.539	0.484	0.359
CH_4	0.246	0.236	0.123	0.104	0.076	0.067
H_2	0.084	0.077	0.042	0.036	0.026	0.022
H_2O	0.189	0.303	0.110	0.208	0.050	0.155
Mass balance [g/min]						
C-balance	1.041	0.916	0.478	0.426	0.294	0.265
H-balance	0.166	0.170	0.085	0.085	0.050	0.056
O-balance	1.883	1.686	0.898	0.844	0.538	0.554

Table 3.9   Mass balance of CH_4 concentration variation tests at 750°C

Residence time [s]	0.5		1.0		1.5	
Gas flow [g/min]	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
CO	0.866	0.925	0.448	0.477	0.278	0.324
CO_2	1.701	1.417	0.880	0.661	0.546	0.409
CH_4	0.266	0.259	0.138	0.126	0.085	0.078
H_2	0.091	0.085	0.047	0.042	0.029	0.026
H_2O	0.191	0.311	0.066	0.131	-	0.054
Mass balance [g/min]						
C-balance	1.034	0.977	0.535	0.479	0.332	0.309
H-balance	0.178	0.184	0.089	0.088	0.050	0.052
O-balance	1.902	1.836	0.955	0.870	0.556	0.530

Mass balance calculation: The experimental data obtained from CH_4 conversion at 850 and 750°C is listed in Table 3.8 and Table 3.9. It can be seen that the concentration of CH_4 decreased under all the operational conditions with a varying reduction degree from 0 to 21%, which is probably due to dry and steam reforming reactions

$$CH_4 + CO \leftrightarrow 2CO + 2\,H_2 \tag{3.23}$$

and

$$CH_4 + H_2O \leftrightarrow CO + 3\,H_2 \tag{3.24}$$

The water gas shift (WGS) reaction (3.22) seemed to go reversely due to less H_2O addition to the reaction, which led to an increase in the concentration of CO accompanied with a decrease in the concentrations of CO_2 and H_2. The inlet water content was unknown thus the mass balances were calculated based on optimal C, H and O balances.

CH_4 conversion with temperatures: The effect of different temperatures on CH_4 conversion is shown in Figure 3.51. It can be seen that generally a higher temperature led to a higher conversion rate of CH_4. At a temperature of 850°C, the conversion rate of CH_4 obtained at residence time of 0.5 s, 1.0 s and 1.5 s was around 5%, 12% and 21%, respectively. However, an increase in the temperature form 750 to 800°C caused a decrease in the conversion rate of CH_4 at lower residence times. This observation did not totally agree with the results obtained from ECN testing using real gasification product gas. The results obtained from ECN testing showed that a higher conversion rate of CH_4 was obtained at a temperature of 800°C instead of 850°C, which could be due to more complicated steam reforming reactions occurring in real product gas such as light hydrocarbon and tar reforming (leading to methane formation).
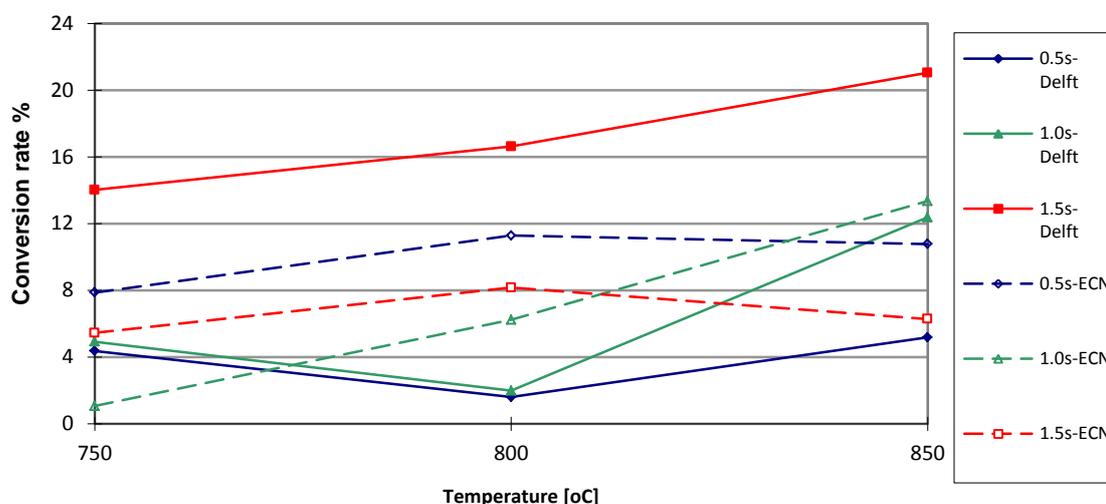
Figure 3.51 CH_4 conversion rate in made up syngas experiments (Delft HTGCU) with varying temperatures by comparison with CH_4 behavior in real MILENA syngas.

Tar model components conversion: Naphthalene and anthracene have initially been selected as tar model components. The effect of the catalyst (iron silicate) on the conversion of naphthalene at different temperatures and different residence times were examined. Regarding the variation of gas composition at different operational conditions, a representative case at a temperature of 850°C is presented in Table 3.10.

Table 3.10   Variation of gas composition at 850°C with $C_{10}H_8$ in the gas

Residence time [s]	-	0.5	1.0	1.5
Gas composition [vol% dry]	Inlet	Outlet	Outlet	Outlet
CO	21.78	28.93	29.53	29.19
CO_2	27.23	23.51	23.99	25.14
CH_4	11.70	10.43	10.62	10.67
H_2	31.99	28.49	29.78	29.34
N_2	7.31	8.62	6.09	5.67

The concentration of $C_{10}H_8$ in simulated gas was about 0.15 vol% on a wet basis and thus it could be neglected during the analysis of the main gas constituents. The inlet gas composition of each gas was assumed to be constant. From Table 3.10, it can be seen that the concentration of CO in the gas increased with increasing residence time. When the residence time was increased from 0.5 to 1.5 s, the concentration of CO increased from 22% to 29%. However, a reduction in the concentrations of CO_2, H_2 and CH_4 was also observed simultaneously under all cases and

the variations were smaller with longer residence times. These observations showed that a reverse water gas shift reaction (WGS), and methane reforming occurred during these experiments.

All SPA samples have been sent to ECN for analysis. However, the results were remarkable, since the inlet and outlet naphthalene analysed from SPA results were generally below the detection limit (<30μg per sample). This could be due to several reasons: the leakage of naphthalene at the top of tar evaporator, the partial blockage of naphthalene at the sampling point and the analysis accuracy. After this measurement series was performed, the reactor contents were studied and it appeared that sintering had taken place. This may have been contributing to the remarkable tar measurements; anyhow this feature is of industrial application relevance, as thus under reducing conditions with a prolonged exposure time at 850°C iron silicate is not recommended to be used.

Conclusions and recommendations
Experiments were performed with real dedusted gas from the MILENA gasifier and catalytic conversion tests were performed in a fixed bed of iron silicate. Significant conversion of heavy tars was obtained. In general, it can be concluded that the iron silicate is suitable for tar reduction treatment because of its performance during the experiments which is effective at high temperature (total Class V tars reduction rate was up to 50%) and raw gas flow circumstances. Tar conversion was higher at the highest temperature 850°C, and the conversion rates of Class II, IV and V tars were 79%, 15% and 49%, respectively.

Moreover, kinetic data were derived from these experiments and applied in Aspen Plus model to simulate tar conversion. The modelling results were in agreement with the prediction from theory on the aspects of the trends of conversion rate with different parameters and the reduction rates of different classes of tars. However, the tar conversion rates from the simulation were higher than from tests, probably because of the hypothesis and simplifications from the real experiments and reactions. The Class II tars (represented by phenol C_6H_6O) in the model reacts about 15% more, 10% and 20% for Class V (represented as naphthalene $C_{10}H_8$) and Class IV tars (represented by fluoranthene and pyrene $C_{16}H_{10}$). The simulated main product gas changing trend was almost identical except the H_2O content due to the practical measuring inaccuracy.

With the Delft HTGCU test rig CH_4 blank testing of a gas similar to MILENA gas has been performed with promising results obtained. The CH_4 was found to be reduced under all conditions. Varying gas residence time at one certain temperature, the CH_4 decomposes increasingly from 0.5 s to 1.5 s.

The effect of iron silicate on the conversion of naphthalene under different temperatures and different residences were also examined using the Delft HTGCU set up. However, the results were not satisfying, since the inlet and outlet naphthalene analysed from SPA results were generally below the detection limit (<30μg). This could be due to several reasons: the leakage of naphthalene at the top of tar evaporator, the partial blockage of naphthalene at the sampling point and the analysis accuracy. On the other hand, it was observed that serious sintering had taken place, leading to the conclusion that under reducing conditions with typical MILENA gas, 850°C is a too high temperature to use for this bed material. It is recommended in the light of this result to perform extensive thermodynamic equilibrium calculations using FACTSAGE[TM] to see whether liquid phases are expected to an appreciable extent given relevant process conditions. This was outside the scope of the current contract.

3.7   Task 7: Conversion of biomass pyrolysis oil

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Objectives

In task 7, the production of syngas through pyrolysis has been studied. Three process variations were proposed at the start of the project. Two variations included the catalytic gasification of respectively pyrolysis-oil and pyrolysis vapours. The third option concerned the high temperature entrained flow gasification of pyrolysis oil. For both catalytic gasification processes, an extensive experimental study has been performed throughout the project. For the entrained flow gasifier, a paper study has been performed on the suitability of pyrolysis-oil conversion in existing entrained flow gasifiers.

Three commercial available entrained flow technologies (Texaco, Shell, Lurgi) were compared. The ash fraction of pyrolysis oil is the main factor determining the configuration of the gasifier. Despite the low ash content (<0.1 wt%) in pyrolysis oil, the ash composition and amount are crucial in the gasifier design. Another complicating factor for the entrained flow route is the option to use pyrolysis oils from different types of biomass, as each kind of biomass has its own ash content and composition. According to our study, Lurgi technology is the most flexible one with respect to biomass input.

For the other process options, a gasifier was developed to produce clean (syn)gas at low temperature from pyrolysis oil or vapours. In both cases, the process comprises two consecutive steps. The first step is heating to 800 - 1000°C by partial oxidation. Important aspects to be considered are minimization of carbon formation and the production of sufficient energy for the catalytic reforming step. The experimental research started with optimization of the partial oxidation step. In case of vapour gasification, a static mixer with 'swirl body' proved to be the best solution. In case of oil gasification, an air atomizer with steam spiral gave the best results. At first, separate experimental installations were used for both process options. In the course of the project, the oil gasifier was integrated with the vapour gasifier. This simplified research on catalyst monoliths. After optimization of the partial oxidation step, further research items were the air-fuel ratio, energy efficiency of the process and the role of the catalyst. The latter concerned both the physical form (fixed bed versus monolith) and the active ingredient (Ni versus Pt/Rh).

In the fourth year of the project, research on catalytic gasification of pyrolysis oil and pyrolysis vapours over monolithic catalyst has been continued. In the previous experimental campaign, the majority of the work was concerned with the 'vapour reforming' process. Also, relatively low amounts of catalyst, i.e. high space velocities, were used to measure tar conversion properties of the different catalysts.

As observed in detail in task 4, evaporation of pyrolysis oil unavoidably leads to the formation of a char residue. In this task, the philosophy to avoid operational difficulties regarding char formation is by application of the open structured monolith catalysts. Blockage of the catalytic bed can thus be avoided. The objective of the current work is to determine the performance of the monolith catalysts. The performance is judged on the gas composition and the tar content in the product gas. The carbon to gas ratio (CtG), which can be regarded as the opposite of the char formation, is also measured.

Materials & Methods

For a detailed description of the setup, the reader is referred to the report of the previous period; a short description is added below.

A commercially available nozzle, liquid cap type 2050-SS and air cap type 70-SS, obtained from *Spraying Systems Co.* is used to atomize pyrolysis oil with air (oxidizing agent) and N_2 (as balance to prevent variation of air amount to influence atomizing behaviour) at ambient temperature. The spray is introduced at the top of the hot gasifier, where it is mixed with steam, preheated to 600°C. At the top-part of the gasifier, the partial oxidation reactions generate the heat required for the overall process. The hot gaseous mixture is then catalytically reformed over one or more monolith catalysts. In the current experimental campaign, two monoliths were used, the first one nickel based, the second containing a platinum and rhodium (Pt/Rh) mixture, both on a ceramic support. Both monoliths are available in two lengths, thus enabling the variation of catalytic space velocity in the setup. After the gasifier, the product is cooled down in a water scrubber, after which a number of gas quality measurements are performed. The tar concentration is determined before the gas cooling section, to prevent tar condensation prior to sampling.

In contrast with the vapour reforming process, the catalytic gasification of pyrolysis oil requires a relatively high Equivalence Ratio (ER or λ, see eq.3.3) to obtain the temperature desired (> 800°C) for adequate hydrocarbon conversion. This higher ER is a direct result of two characteristics of pyrolysis oil:

  i.   The reactivity of pyrolysis oil excludes the option to pre-heat the feedstock & air.
  ii.   The relatively low energy density, ~ 16 MJ/kg (a.r. basis) of pyrolysis oil.

To determine if autothermal operation is approached, the power consumed by the electrical ovens placed around the reactor is monitored during the experiments. The power consumption by the electrical ovens was very limited, typically < 0.2 kW, which is below 3% for the 6 kW$_{th}$ process. Therefore the conditions were considered sufficiently autothermal for this research.

Performance parameters:
For two catalyst amounts (GHSV ~ 5000 hr^{-1} and ~ 2500 hr^{-1}), the influence of ER and S/C on the process performance was studied. The main performance indicators are:

  •   Gas composition
  •   Tar concentration
  •   Carbon to gas ratio

The gas composition measured at different positions in the gasifier, is compared to the theoretically derived equilibrium conditions of the gaseous components. In a system with adequate feedstock conversion, the process is dominated by two gas-phase equilibrium equations, the Water Gas Shift (WGS) reaction (3.22), and the Methane Steam Reforming (MSR) reaction (3.24).

Using thermodynamics, the equilibrium constants for reversible gas-phase reactions can be derived as function of temperature. Many good literature sources are available on this subject, in this study, work of Rostrup-Nielsen and Christiansen [86] is followed. Here, the equation to determine equilibrium constant K$_{eq}$ is derived using the assumption the ideal gas law is applicable. At atmospheric pressure, and these temperatures, this is acceptable. When the equilibrium constants for the WGS and MSR reactions are plotted as function of temperature, Figure 3.52 can be derived.

Results – experimental validation
Since some (minor) modifications were made compared to the previous experimental setup, the steady-state behaviour and reproducibility of the experimental setup were validated. In Figure 3.53, the actual gas composition for the experiment with longest runtime is presented. A small fluctuation in the product gas composition is visible for the 3 hours on-stream. The H_2 production decreases somewhat, while the CH_4 concentration increases slightly. The last points in the H_2 and CO measurements suffered from an error in the GC measurement, and are omitted from plotted trend line.
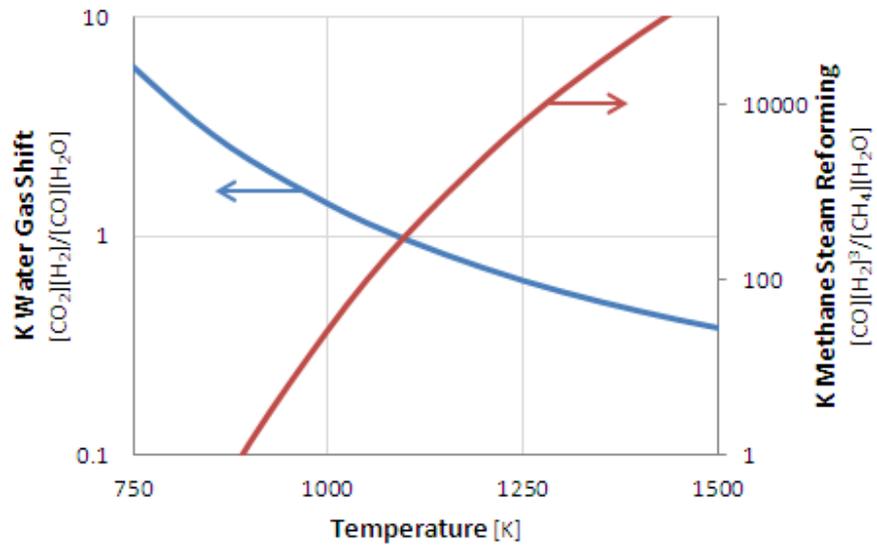
Figure 3.52 Equilibrium constants for the Water gas Shift and Methane Steam Reforming reactions.
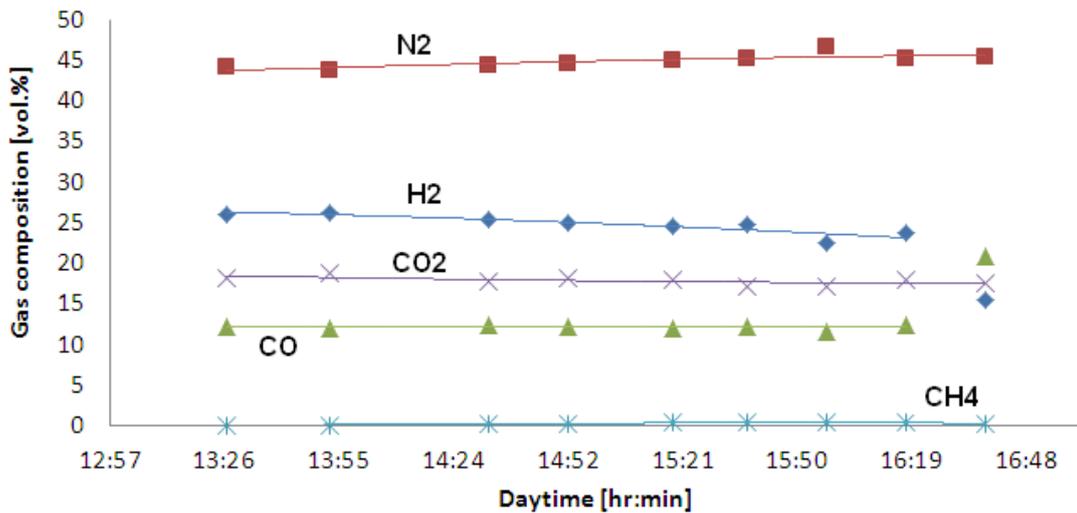
Figure 3.53 Gas composition for a single experiment; lines just indicate the trends.
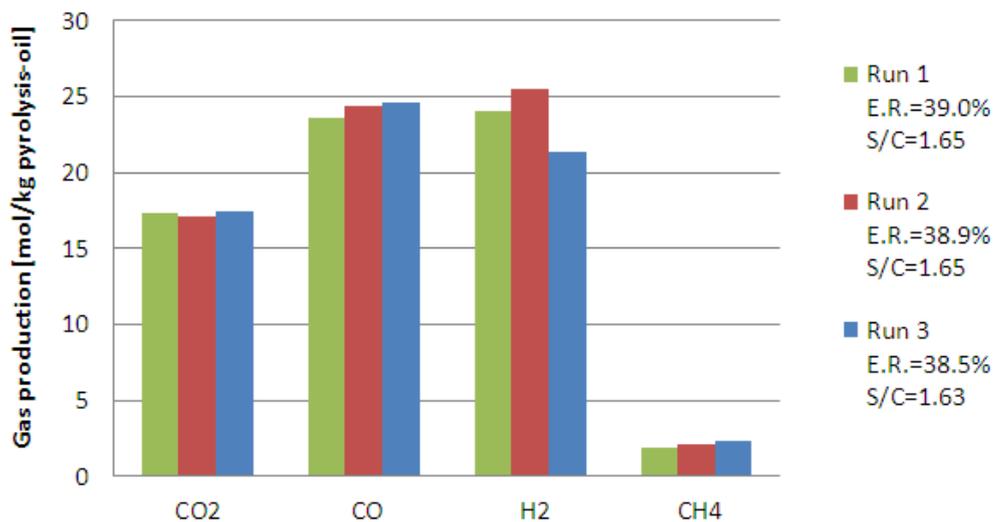
Figure 3.54 Gas composition reproducibility tests.

To determine the reproducibility, three experiments were performed under the same conditions. Figure 3.54 presents the results. The first two measurements were in fact the first and second experiment from the experimental campaign, the third measurement was the 7th experiment from the campaign. To correct for the small variation in pyrolysis oil feedrate (typically 1 - 2%), results are presented in mole per kg of pyrolysis oil fed to the system. Since the amount of air and steam are set to fixed values, the fluctuation in pyrolysis oil feedrate results in a small variation in ER and S/C. As can be seen from Figure 3.54, there is a small difference, mainly in the H_2 and CH_4 production for the three experiments. The difference is however quite small, and could very well be the result of decreased catalytic activity due to char/coke deposition on the catalyst. From these results, it is concluded the reproducibility of the experiments is sufficient.

Results – Carbon to Gas ratio

Figure 3.55 shows the carbon to gas (CtG) ratio as function of the ER, while Figure 3.56 presents CtG as function of S/C. The blue lines in Figure 3.55 and Figure 3.56 present the temperature after the catalyst bed. Obviously there is a relation between the temperature and the carbon to gas conversion. Since it was chosen to vary ER and SC, the temperature is not constant in the system. For increasing ER, the temperature increases. The increase in CtG ratio is therefore amplified in Figure 3.55. For the graph, points from both catalyst configurations are included, mainly because it is expected the majority of the carbon to gas conversion is dominated in the partial oxidation zone, and not by the catalyst. If this is in fact true cannot be confirmed with the currently available experimental data. One point clearly deviates from the trend, in this test the system might have suffered from less good atomisation of the pyrolysis oil.
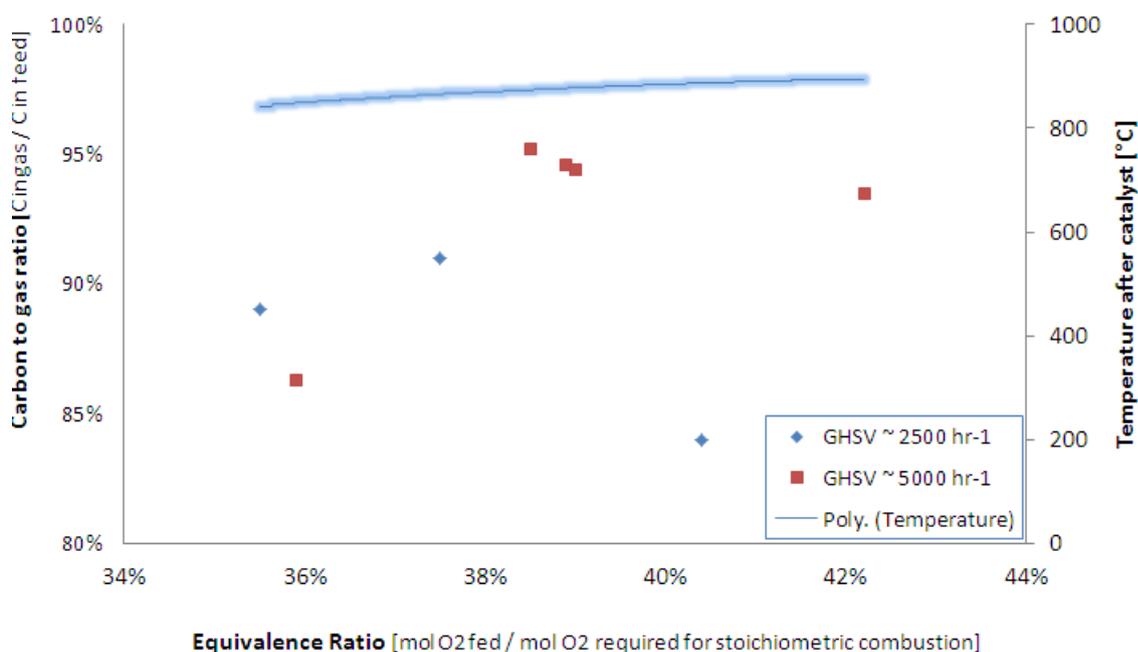
Figure 3.55 Carbon to gas ratio as function of ER (S/C = 1.6)

The effect of an increasing S/C on the CtG ratio, shown in Figure 3.56 is limited. Normally, one would expect a distinct increase of CtG with increasing S/C. However, this effect is suppressed here by the effect of a simultaneously decreasing temperature.

Results – Gas composition

Figure 3.57 and Figure 3.58 show the gas production as a function of the ER for two different space velocities. Closed symbols represent measured data points, open symbols the calculated equilibrium composition. The equilibrium composition is calculated based on the measured temperature and the molar ratio of the elements present in the gas. In this way, the 'loss' of elements, mainly carbon due to char/soot formation, is not taken into account.
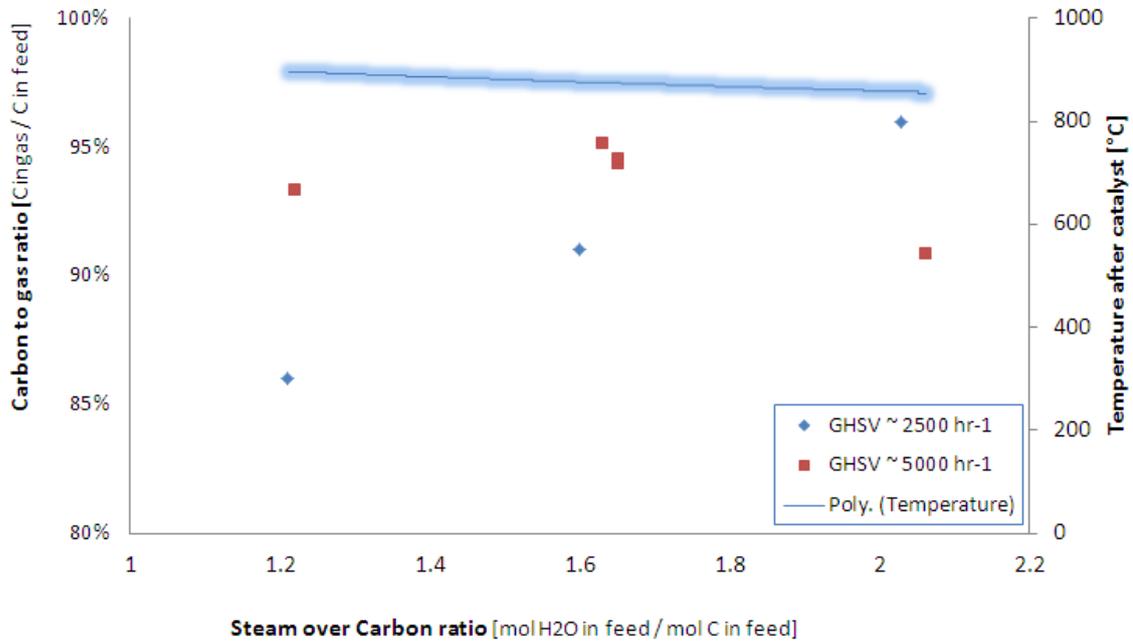
Figure 3.56 Carbon to Gas ratio as function of S/C (ER ~ 38%).

Clearly, the experiments with the large amount of catalyst produce a gas close to the expected equilibrium composition. For the lower amount of catalyst (GHSV ~ 5000 hr^{-1}) the equilibrium is not reached. The measured concentrations of both H_2O and CO are above the equilibrium, while H_2 and CO_2 are below the expected concentrations. This implies the residence time and/or activity of the catalyst is not sufficient to reach the WGS equilibrium.

As can be seen from Figure 3.57, the influence of ER on the gas composition is limited for the measured range.
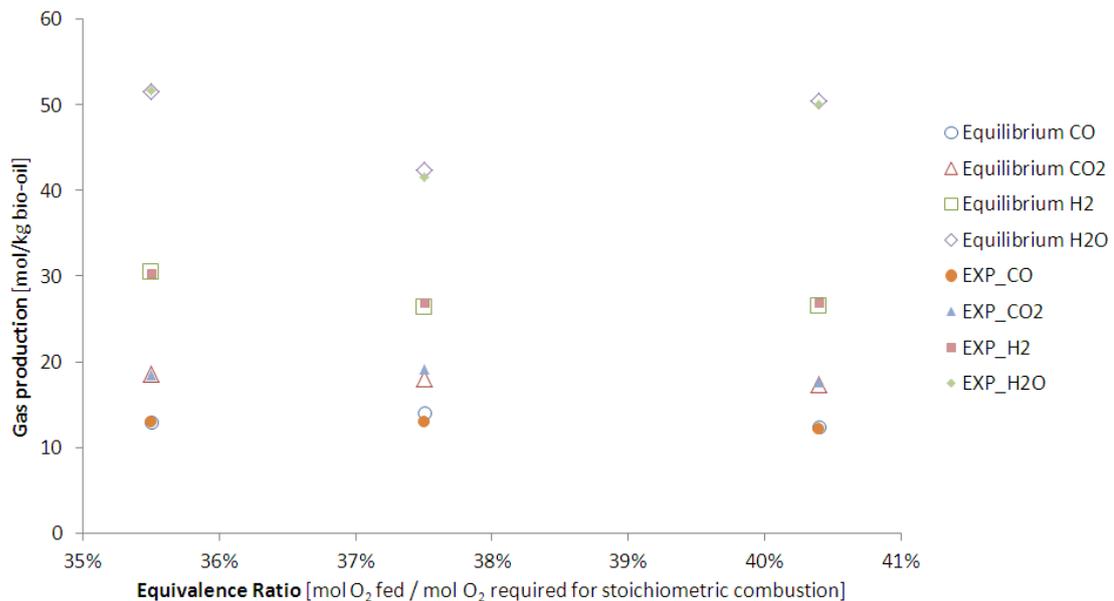
Figure 3.57 Gas composition as function of ER for GHSV ~ 2500 hr^{-1} at S/C~1.61mol/mol.
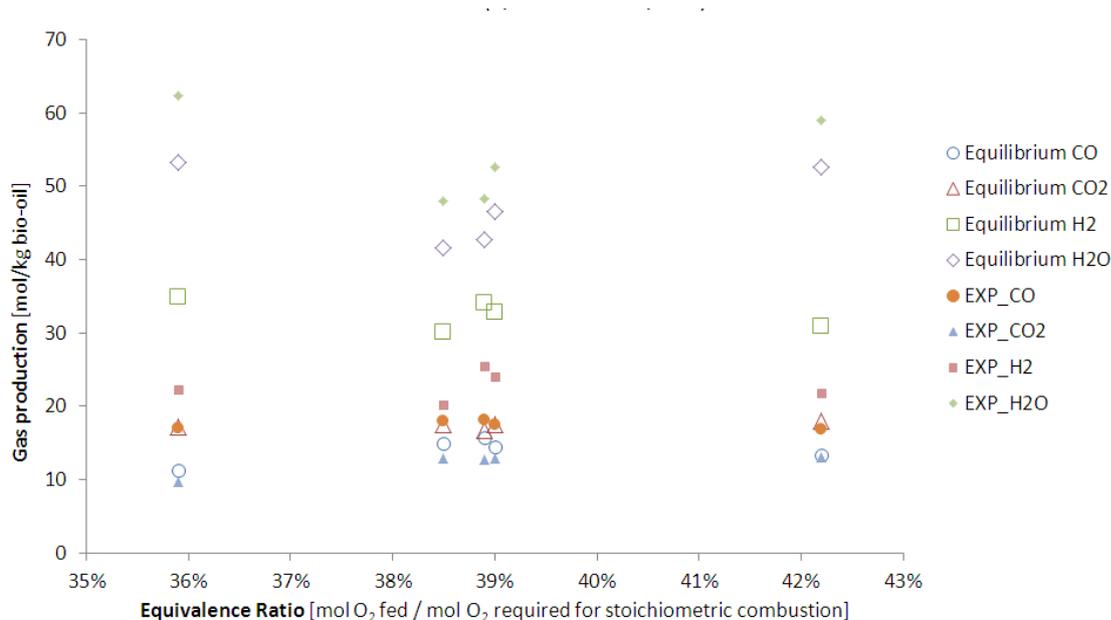
Figure 3.58 Gas composition as function of ER for GHSV ~ 5000 hr^{-1} at S/C~1.64 mol/mol.

When similar graphs are plotted, this time with the gas production as function of the S/C ratio, similar results are obtained. At a GHSV of 2500 hr^{-1}, the equilibrium is reached quite well. At a GHSV of 5000 hr^{-1}, again the measured H_2O and CO concentrations are above the equilibrium values, while the H_2 and CO_2 concentrations are below the equilibrium values (see Figure 3.59 and Figure 3.60). Here, again the influence of the S/C ratio is somewhat limited over the measured range.
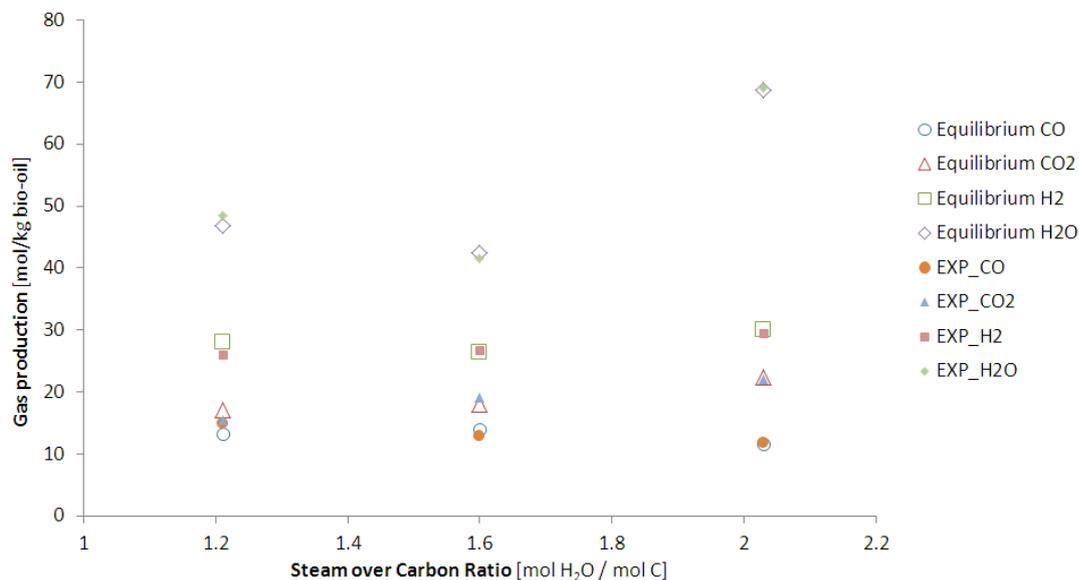
Figure 3.59 Gas composition as function of the S/C ratio for GHSV ~ 2500 hr^{-1} and ER~38%.
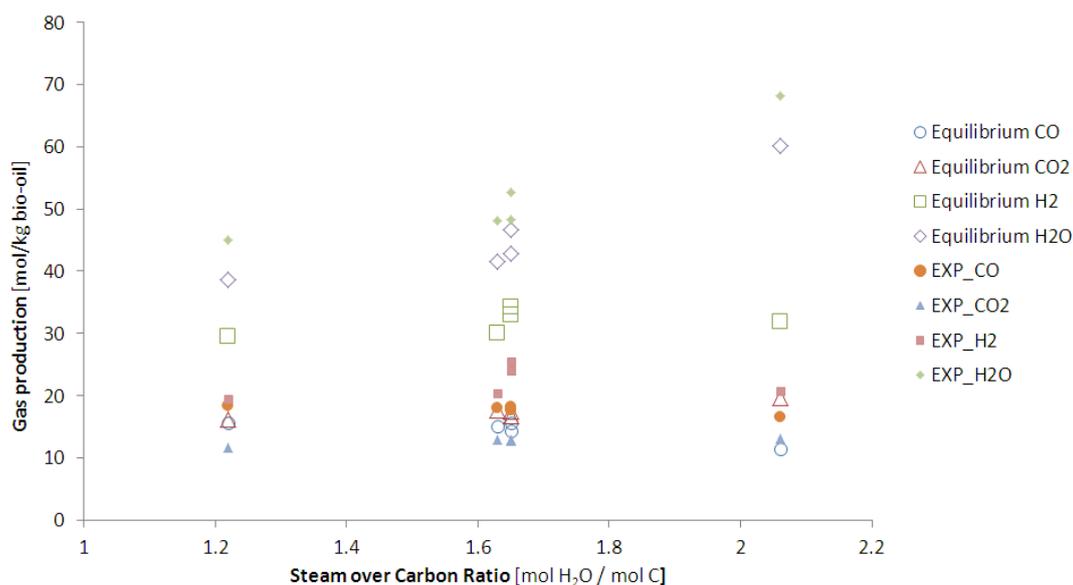
Figure 3.60 Gas composition as function of the S/C ratio for GHSV ~ 5000 hr^{-1} and ER~39%.

Results – Tar concentration

While in previous work, the tar concentration was deliberately kept quite high by using a low ER and a small amount of catalyst, in this part both the ER and catalyst amounts were increased, to obtain a clean product gas. Figure 3.61 gives the tar concentration in the product gas as function of the ER for both catalyst configurations. The tar concentration in the product gas decreases with increasing ER for the experiment with a high Space Velocity, which is according to the expectations. For the experiments with low Space Velocity the tar concentration in the product gas is very low for all experiments.
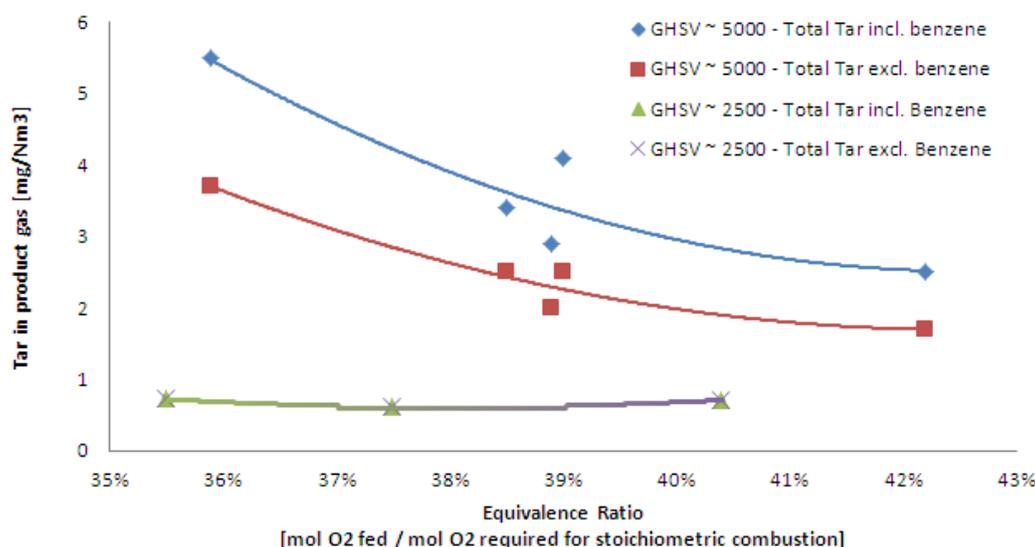
Figure 3.61 Tar concentration in the product gas as function of ER for two catalyst configurations.

Even when benzene is included as tar component, the highest tar concentration measured was still below 10 mg/Nm^3, which is considered suitable for most applications [87]. For the experiments with a large amount of catalyst, the tar concentration was always below 1 mg/Nm^3, which is close to the detection limit of the analysis method used. The product gas can be considered virtually tar-free at these conditions.

Conclusions

The main conclusions and achievements of the experimental study on the catalytic gasifiers are the development of an experimental setup that allowed the stable, reproducible and autothermal catalytic gasification of pyrolysis oil. The monolithic catalysts proved to be very suitable in the catalytic gasification of pyrolysis oil. The conversion of hydro(oxygenated)carbons is very high, and the char formation did not result in operational problems in the system.

Regarding the entrained flow gasifier study, especially the ash content of the pyrolysis oil seemed crucial. Even though the ash content is < 0.1 wt.%, this amount and the ash composition dictate the exact configuration of the gasifier. Additional complications arise when the gasifier is fed with pyrolysis oil obtained from several biomass sources. Based on the technology comparison, the Lurgi technology seems the most flexible with respect to the feedstock properties. Important recommendations for further development of the entrained flow gasification of pyrolysis oil are:

1. Further reduction of the ash content in pyrolysis oil.
2. Perform an experimental study on the behaviour of ashes from several different pyrolysis oils, where specific focus is on the extreme conditions present in the entrained flow gasifier.
3. Research on the possible pollution in heat exchangers, required for heat integration in the gasifier.

Discussion

Production of syngas through autothermal catalytic gasification of pyrolysis oil seems promising. To produce actual syngas, pure O_2 must be used as oxidising agent instead of air. This will be part of future research. Also, it is desired to test the catalytic stability for longer times. For commercial operation, the char which is currently entrained from the gasifier and captured in the gas scrubber must also be recovered in a continuous manner.

In the fourth year of the project, some vapour-gasification experiments were performed as well. These experiments showed promising results, however a thorough experimental campaign could not be performed. It was chosen therefore to omit the experimental results from this report.

4.   Execution of the project

General

The original plan assumed that funding would be granted for a period of four years, consistent with the usual contract term for PhD students. However, due to budget constraints, funding was granted only for one year and consecutive proposals had to be submitted in following years. The first contract period started in April 2007, but only one of the five PhD positions involved was actually occupied at that date. The other four followed with an average delay of five months. As a result, only 70% of the budget available for the first term was spent. During the second and third period, expenditures were equal to and above the available budget. The government decision to end the EOS-LT programme in 2010 threatened to leave the universities without funding for most of the final year of the PhD contracts. A practical solution was found in which funding for work at TUD, TU/e and BTG not performed by PhD students was reduced and funding for the PhD positions made proportional to the remaining contract periods.

According to the original plan, TU/e and UT would get grants of 90 k€ per year for each of the PhD positions, to cover the salary of the PhD students, material and travel costs and additional costs for support and guidance. TUD and BTG would get similar grants but not employ PhD students. When TU/e, and later TUD and UT too, changed their methods for the calculation of hourly tariffs, expenditures rose above 90 k€ per year per PhD. However, the grants did not change and the universities bore the excess costs.

The delayed start of most PhD contracts, individual circumstances and experimental problems or setbacks all contributed to the fact that at the end of the fourth EOS LT contract still some work remains to be done. One PhD thesis was defended successfully in November 2011. A second one is ready for defence in February 2012. The remaining three will be finished at a later date in 2012. Work at TUD and BTG was executed according to plan, albeit that the scope of their research was redirected after the first year.

Details about each of the tasks are given below.

Task 1: Bed materials

As compared to the original project plan, there have been no major changes in research subject or budget expenditures.

At TU/e an intermediate size gasifier was available at the start of the project, but some of its components didn't work properly. The instrumentation was insufficient to allow the planned mapping of the chemical conversion in the gasification process. Consequently, it was decided not to use the existing equipment but to build a dedicated small laboratory installation. Unfortunately, this led to an unforeseen delay of one year in the progress of the research. However, the choice for a small-scale approach kept cost and delay within acceptable limits.

The newly built experimental facility has proven itself very useful for research on the chemistry of the gasification process and especially for research on the time dependence of process steps. As research on gasification at the chemistry department of TU/e will soon come to an end, the equipment will be transferred to the department of mechanical engineering for use in future research.

Task 2: Fouling in heat exchangers

The design, construction and testing of the controlled fouling experimental facility took more time than anticipated, partly due to delay by part suppliers and partly by unexpected problems like malfunctioning of the particle feeder and the flow conditioning unit.

An initial effort was made to implement the occurrence of condensation in the controlled fouling experimental facility, but due to budget and time constraints, the complete implementation could not be achieved. However, in order to capture the influence of condensation of alkali species and tar components on heat exchanger tubes, deposition experiments were conducted with tubes which were coated with different liquid layers.

Task 3A: Tar removal by radicals
The majority of the problems occurred during the execution of the required experimental validation of the FGM model with the inclusion of tar chemistry. After the construction of the experimental setup the available diagnostic methods were not applicable. Multiple efforts were made to measure tar components with a technique known as laser absorption. The outcome of these measurements showed that it was not possible to apply laser absorption to execute the required measurements. This could not have been foreseen by means of a literature study, which was executed on forehand as well. By cooperating with a colleague PhD student parts of both our setups were combined and with help of the University of Lund (Sweden) we managed to execute the measurements which were necessary to validate the FGM model. This led to a considerable setback in the time schedule which made it impossible to do a full parameter study of the partial combustion reactor which would have led to designing an optimal reactor geometry. In addition, the majority of analyses indicated that partial combustion is most likely not suitable to convert tars into smaller hydrocarbons. This could not have been foreseen, based on the experimental data which served as a starting point of the executed research.

Task 3B: Tar removal by pulsed corona discharges
On the modelling part we focussed on identifying the major mechanisms for radical production and radical based tar removal at one single temperature of 200°C. We were able to find a full set of relevant chemical reactions and their reaction constants at this temperature. However, no reliable data on the temperature dependence of these reactions was found, and thus the modelling work was restricted to 200°C only.

We needed more time than foreseen to get the experimental setup running: (i) we changed the corona reactor type from wire-plate to wire-cylinder configuration in order to generate a more homogeneous corona plasma, and (ii) the temperature tracing of gas lines was difficult. But finally in the last year of the project the setup run smoothly. Another problem was the method to inject model tars (naphthalene) into the setup, by vaporizing the tar, and injecting it via a pre-heated carrier gas. We were not able to solve the problem with clogging, and also a good control over the amount of injected tar (thus the concentration) was not possible. Therefore we decided to perform experiments on more easily to inject hydrocarbons, such as toluene.

Task 4: Gasification and reforming of pyrolysis oil
Two new set-ups were used in the research which had to be designed, constructed and de-bottle-necked. This is a time consuming process and involves high costs in especially the second and third years of the PhD project.

Since the PhD started a bit later than the EOS project itself, costs in the first project year were relatively low compared to the costs in consecutive years.

Task 5: Self gasification of biomass
Initially, a high pressure set-up was built for experiments to simultaneously check gasification, cracking, water-gas shift and methanation activity of the proposed biomass self-gasification process. Due to the different orders of magnitude of the rates of the various reactions this approach did not results in directly usable data. The process steps were then decoupled and measured separately using capillary, thermo gravimetric analysis and high pressure fixed bed techniques. This approach gave satisfactory results and on this basis, new design rules were obtained for the overall process.

Since the PhD started a bit later than the EOS project itself, costs in the first project year were relatively low compared to the costs in consecutive years.

Task 6: Catalytic tar removal

Experimental work, performed after the first project's year (in which an extensive literature study was made) with a 'Go-No Go' moment resulting in a 'Go' has been hampered by technical issues with the Delft HTGCU set up. Joint experiments performed with real gas at ECN done by TUD were successfully carried out though. Initially, it was considered that for the Delft HTGCU rig quartz glass should be used as reactor wall material as this is catalytically inert. This, however, turned out to be not successful at all due to repeated breaking of the glass. Thus a new reactor was made (AISI 310 steel). In the end comparatively little time for experiments was left due to the abovementioned material issue and also issues with heating and what later appeared, sintering of the iron silicate bed material (which is on the other hand an interesting, non expected result).

Table 4.1   Budget and expenditures at TUD in the last contract period (2010-2011).

Description	Category	Budget [€]	Expenditures [€]
Salaries	A1	51552	64169
Equipment	A2	7519	-
Materials/Consumables	A3	9000	771
Third party costs	A4	-	9514
Total		68071	74454

Table 4.1 shows the budgeted and actual costs at TUD for the last contract period. Salaries were higher than expected. More hours were dedicated to the project as a consequence of the reported technical issues with the set up that had to be solved. Moreover, more time has been spent on kinetic modelling aspects that were not initially foreseen. Equipment costs were planned for the use of a special GC which could measure sulphur species. However, it was not used as we concentrated on main components and tars. Accordingly, no equipment costs are reported.

Actual costs of Materials/Consumables were lower than originally planned due to the reported set up issues, but also result from the fact that tar analyses have been performed by ECN and associated costs became 'third party costs'. The 'third party costs' also include costs made for the appointment as a third party of the student assistant who performed part of the research work.

Task 7: Conversion of biomass pyrolysis oil

In the first year the entrained flow gasifier study has resulted in a 'No-Go' for further research on entrained flow gasification of pyrolysis oil. The emphasis was put on catalytic gasification for the production of syngas. No specific problems were encountered in the experimental work, although in the middle of the project the integration of the oil gasification setup and the vapour gasification setup required quite a lot of resources. This investment has paid off in the last part of the project, where the experimental work could be performed much more efficiently. Also, this enables the comparison of both processes on equal grounds. This way, some uncertainties can be ruled out, which otherwise might have influenced the conclusions drawn from the research.

5. Contribution to EOS long term objectives

5.1 Contribution to a sustainable energy supply

5.1.1 Contribution to the goals of the EOS-LT programme

The EOS-LT research programme selected three focal points:

- Biomass gasification and gas conditioning (including syngas production from gas fuel)
- Biorefineries
- Biomass conversion, co- and auxiliary incineration in E-plants

The consortium formed by ECN, TU/e, UT, TUD and BTG has performed research related to the first of these three focal points. According to the EOS-LT programme, the consortium research area is relevant to three energy market segments: gaseous fuels, electricity and heat, and transportation fuels and chemicals.

Gasification research at ECN focuses on the development of technology for SNG production from biomass. It involves MILENA gasification and OLGA tar removal technologies, followed by thorough gas cleaning to protect methanation catalysts.

Research performed at TU/e in task 1 and at UT in task 5 has provided valuable information on the role of gasifier bed materials on the composition of the gas produced. Tar absorption by bed materials, as observed at TU/e, is important for the MILENA gasifier technology developed by ECN, as it determines the energy balance and efficiency of the gasification process.

Important practical problems related to biomass gasification are fouling of gas coolers and downstream equipment by deposition of particles and tar. Research at TU/e in task 2 has given more understanding of the processes involved in particle deposition. Research at TU/e in task 3 and at TUD in task 6 has given new insights in the usefulness of several options to reduce tar problems by cracking of tar components.

Research by UT in task 4 and by BTG in task 7 focused on the production of syngas for the production of liquid fuels and chemicals. Good progress was made in the conversion of liquid feedstock (pyrolysis oil and glycerol) to syngas. Information obtained on char and carbon formation is relevant too for catalytic tar cracking, studied by TUD in task 6.

5.1.2 Contribution to a technological breakthrough or innovation

Task 1: Bed materials
The project has delivered a deeper understanding of fundamental processes that occur during gasification of biomass and of conditions required to obtain the gas composition most suited to the applications mentioned above. The product gas has the required high calorific value and minimum of unwanted components which hamper downstream synthesis processes or conversion equipment. More specifically, in this task we have studied chemical conversion reactions of biomass on heating in the gasification process. The research has provided valuable information on the evolution of gaseous components like H_2, CO, CO_2, CH_4 and higher hydrocarbons. The higher hydrocarbons which may condense on cooling are indicated collectively as 'tars'.

Bed materials in a fluidised-bed gasifier can have catalytic properties. Dolomite and olivine are well-known examples. The effect of these materials on fundamental gasification reactions has been studied. The ECN MILENA gasification technology promises superior performance for bio-SNG production. Knowledge of fundamental gasification processes, and of how to tune the

product gas composition, is paramount for the optimization of the technology towards bio-SNG production. The MILENA development concerns leading-edge technology in the Dutch R&D on biomass conversion. Tar absorption by bed materials, as observed at TU/e, is important for the MILENA gasifier technology developed by ECN, as it determines the energy balance and efficiency of the gasification process.

Task 2: Fouling in heat exchangers
Before the fuel gas from the gasification process is transported for external use, it is cooled in a gas-cooler. Fine particles, ashes, alkalis, metal compounds and nitrogenous compounds are produced during biomass gasification. These contaminants deposit on the heat exchangers of the gas-cooler forming an insulating layer, which reduces the overall heat transfer coefficient and can result in operation failure. Deposit formation on heat transfer surfaces, namely slagging or particulate fouling, is one of the main problems in biomass gasification and leads to extra capital expenditure, increased fuel costs associated with fouling, production loss and maintenance problems.

The development of an experimental setup for fouling tests under controlled and realistic conditions is world-wide unique. A numerical model was implemented in a commercial software package to capture the deposition and removal of particles. The fundamental impaction experiments along with the controlled experiments have provided better insight into the process of particulate fouling and resulted in the development of a numerical model, which can be used to develop strategies to minimize particulate fouling.

Task 3: Tar removal by radicals or plasma
The further development of FGM has led to a modelling tool which can be used to other complex combustion systems (for instance to determine harmful emissions).

With regard to pulsed corona tar removal:
1. A complete set of chemical reactions and their reaction rates for corona based tar removal has been established, and implemented in the simulation tool RADICAL. This enhancement of the reaction database, and experience we gained with it, allow us to use RADICAL for other pulsed corona applications, such as air purification (VOC removal, NO_x abatement, odour control).
2. The results of this project will be applied in a new project on waste gasification, together with KU Leuven and a group of EU companies. The results will be used to develop an engineering model for pulsed corona based tar conversion, with the purpose of process analysis of an entire waste gasification process.

Task 4: Gasification and reforming of pyrolysis oil
Gasification/steam reforming of pyrolysis oil was experimentally evaluated and both stand alone and hybrid (integration with fossil feed) modes were investigated. It was shown that current commercial catalysts cannot be used directly but that a 'guard' pre-reforming catalyst is necessary next to an initial pyrolysis vapour conversion. The work done in this task has attracted the interest of BioMCN, a company in Delfzijl which produces second generation bio-methanol. Currently, a valorisation research proposal is being set-up where this conversion route will be further explored.

Task 5: Self gasification of biomass
The results obtained in this work show that it is in principle possible to produce second generation bio-methane from biomass at high pressure using its own minerals as a catalyst without the addition of air/oxygen. However, the integrated process still has to be tested.

Next to biomass gasification, initial tests also showed promising results that synergy is possible between task 4 (pyrolysis oil gasification) and task 5 (self gasification) with the usage of bio-slurries (char in pyrolysis oil). This could be a good alternative to the biomass to DME process,

currently tested on pilot scale (Bioliq, Germany), which consists of pyrolysis, slurry preparation, entrained flow gasification, gas clean-up and DME synthesis.

Task 6: Catalytic tar removal
In close cooperation with ECN, TUD has generated knowledge in the field of reforming of (higher) hydrocarbon species using relatively cheap bed materials (olivine, iron silicate); this has not yet led to a breakthrough, however, more insight has been obtained into the conditions under which reduction of heavy tars – preventing excessive methane conversion- occurs. ECN can continue to implement the concept, making use of the TREC process unit, scaling up the quantity of bed material.

Task 7: Conversion of biomass pyrolysis oil
The work performed in the project has contributed to the goal of syngas production from biomass. Three specific routes were studied, all involving pyrolysis as initial process. Conversion of biomass through pyrolysis yields specific logistic advantages. It also creates the opportunity to use a dedicated catalyst in the gasification process, since compounds potentially poisonous for the catalyst are removed to a large extent in the primary pyrolysis process.

The contribution of the research on the implementation of the route from biomass to energy is twofold. Applications of pyrolysis oil on commercial scale are currently limited, but there is a very large potential market. On the other hand, the limited production of pyrolysis oil has a negative impact on the development of pyrolysis oil applications. In this research project, an application for the conversion of pyrolysis oil is developed, thus stimulating the implementation of commercial scale pyrolysis oil production plants. The implementation of BTG's fast pyrolysis process is the main goal for the future, and is thought to potentially deliver a major contribution to the long term goals of producing renewable energy and materials from biomass.

5.1.3 Implementation of results and future research

For several years already, the HVC company has shown interest and active participation in the technology development at ECN. Plans to build a 10 MW demonstration CHP plant in Alkmaar have been stalled by lack of funding. However, several other parties have now also committed themselves to participation in a 'Green Deal' project to build an SNG demonstration plant at the same site.

The fundamental research on bed materials, self gasification, tar removal and heat exchanger fouling provide vital support and knowledge for the more technologically oriented development at ECN. Unfortunately, financing future research is hampered by the discontinuing of the EOS-LT programme and by the reduced funding of ECN. Part of the work will probably continue within the 'top sector energy'.

Several companies are interested in the work performed in task 2:
1) MAHLE Behr Industry GmbH & Co. KG offers expertise in engine cooling and air conditioning for off-highway vehicles. Agricultural and construction vehicles as well as their engine cooling system (i.e. radiators, charge air coolers) are exposed to contamination by organic and inorganic pollutants. The fouling layer (e.g. sand) on the aluminum surface of the heat exchanger increases the heat transfer coefficient and drastically reduces its cooling performance. The components have to be cleaned periodically – related with a downtime and loss in productivity of the vehicle. To overcome this problem, various coatings of the finned heat exchanger surface have been defined and shall be investigated with respect to their fouling behavior in the controlled fouling setup.
2) Innospec Specialty Chemicals is the largest dedicated fuel treatment company in the world, developing and marketing additives for different types of fuel. The additives can increase fuel efficiency and reduce harmful emissions. Besides, they are also interested in the development of coatings to reduce fouling. In that perspective the company was interested in controlled fouling experiments at elevated temperatures up to 500°C.

Results obtained within task 3 of this project will be applied in a new project on waste gasification, together with KU Leuven and a group of EU companies. The results will be used to develop an engineering model for pulsed corona based tar conversion, with the purpose of process analysis of an entire waste gasification process.

TUD research on gas cleaning (including tars) for biomass gasification will be continued in a new EU project (BRISK), which started 1 October 2011. It has been granted within the framework of the FP7 INFRASTRUCTURES.

The fundamental research on gasification and reforming of pyrolysis oil has already proven its value to commercial applications by the involvement of BTG and the interest shown by BioMCN. BTG intends to continue this research.

5.2 Expansion of the knowledge position of the Netherlands

5.2.1 Expansion of knowledge and research facilities

If the SNG demonstration plant in Alkmaar can be realised according to present plans, it will be a direct competitor to a 20 MW installation in Sweden which is expected to become operational in 2013 and which will use gasifier technology developed several years ago in Austria. However, ECN is confident that its technology can yield higher efficiency and become leading when proven. Even apart from the SNG development, several foreign parties have shown serious interest in the ECN MILENA gasification and OLGA tar removal technology.

Several new research facilities have been realized by the consortium partners. At TU/e, a new facility was built to study the gas evolution from biomass and subsequent reactions in the gas phase. Another new facility was built in which controlled deposition experiments can be carried out. The pulsed corona research facility was extended and improved. Computer models were developed to study deposition processes and reactions involved in plasmas and tar cracking. UT and BTG realized new facilities for the production of syngas from liquid feedstocks.

5.2.2 Dissemination of knowledge and results of research

The consortium partners have organized several meetings to present their work to a broader public. These include:

- The official opening of the pilot MILENA gasifier by minister Cramer in September 2008.
- Groen Gas dag organised by ECN and HVC in November 2010.
- Biomassa onderzoeksdag at TU/e in February 2009.
- Kivi Niria onderzoeksdag, at UT, 19 May 2011.
- IEA Roadshow – Bioenergy, at TU Delft, faculty 3mE, 11 November 2011.

The consortium partners also presented their work in posters and oral contributions at conferences and symposia, and published articles in reports, scientific journals and conference proceedings.

Work performed by ECN and financed by EOS-LT and other sources was presented in articles in journals and books [4-10], reports [11-15] and contributions to conferences and symposia [16-59].

Task 1
Results of the work have been presented as poster [88-92] and oral presentations [93-95] at conferences and symposia.
Task 2

The work performed has resulted in a PhD thesis [96], articles in refereed proceedings of conferences [97-99], poster contributions [100-104] and oral presentations [105-109] at conferences and symposia.

Task 3
The work performed has resulted in a PhD thesis [110]. Results of the work have been presented as poster [111-117] and oral presentations [118-121] at conferences and in publications [63, 122].

Task 4
Some results of the work have already been published in refereed journals [79-81], other results will be included in future articles [82, 83]. The work has also been presented at a number of conferences and symposia [123-126].

Task 5
Results of the work have been presented as poster [127-128] and oral presentations [129-130] at symposia and conferences or have been published in refereed journals [131-133], while another has been submitted [134].

Task 6
TUD has produced a number of articles and reports on the subject of biosyngas cleaning and tar reduction, based on work performed within the EOS LT projects [84, 85, 135-138]. The work was also presented at several meetings [139, 140].

Task 7
BTG has produced two articles presented on conferences [141, 142]. Follow-up of the research activities is planned in the form of a PhD research program, covering both the catalytic pyrolysis oil gasification as well as the vapour 'gasification' process.

6. Outcome indicators

A PhD thesis was written and defended in November 2011 [110]. Another one has been written and will be defended in February 2012 [96]. Work on three more PhD theses is in progress. At the University of Twente, one PhD defence (task 4) is expected to take place in June 2012 and the second one (task 5) in the final quarter of 2012.

The research of task 4 has drawn attention of commercial parties and this conversion route will be further valorised (pyrolysis oil hybrid reforming for the production of chemicals/fuels)

An MSc thesis [85] was written and defended successfully in December 2010 concerning the conversion of model tar species on natural rock materials. It describes the experimental work performed in the past year(s) within task 6.

Based on a.o. this project at TUD further research will be performed on gas cleaning (including tars) for biomass gasification. A new EU project, called BRISK, has been granted within the framework of the FP7 INFRASTRUCTURES and has started 1 October 2011.

A new book – agreed with publisher Wiley-Blackwell - covering a.o. the topics biomass gasification and gas cleaning for syngas production will be written with co-authoring of researchers of the majority of the cooperating partners, edited by TUD (W. de Jong).

BTG plans to continue, and even intensify, the research on both processes. The gasification of pyrolysis oil is believed to be a major potential application for pyrolysis oil. This development stimulates the development of a pyrolysis oil market, as well as the development of the pyrolysis-oil gasification technology as such.

The implementation of the fast pyrolysis technology is done through a specialized daughter company of BTG; BTG Bioliquids B.V. BTG Bioliquids B.V. has plans for the construction of a fast pyrolysis plant converting 5 ton/hour of waste wood into pyrolysis oil in Hengelo (NL) which are already in an advanced stadium. One of the major obstacles in the actual realisation of the plant is the limited amount of options to sell the pyrolysis oil at a realistic price. The research concerning the development of technology enabling the production of syngas from pyrolysis oil results in an increased value product compared to the utilisation of pyrolysis oil for heat and electricity production.

The strategy regarding the development of the gasification technology is to co-operate with a partner specialized in gasification technology.

Regarding the development of the vapour reforming technology, a new potential application for fast pyrolysis is developed. The conversion of biomass residues with high ash (and moisture) content by fast pyrolysis often results in poor pyrolysis oil yields and lower oil quality. For these residue streams, the vapour reforming process is ideally suitable.

The RTD on both the production of fuel gas and syngas is continued through the European project 'SupraBio'. In cooperation with Ghent University, a PhD project has been started on the subject.

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