Energy
Westerduinweg 3
1755 LE Petten
P.O. Box 15
1755 ZG Petten
The Netherlands

www.tno.nl

T +31 88 866 50 65

TNO report

TNO 2018 R11007 | Final report

Gasification of plastics-containing residue streams: product gas composition and economics of biochemicals/monomers retrieval/co-production

Date	28 November 2018
Author(s)	A.J. Grootjes, B.J. Vreugdenhil, G. Aranda Almansa, P. Kroon
Number of pages	29 (incl. appendices)
Number of appendices	1
Project number	5.2816 (ECN)

Management summary

Title :	Gasification of plastics-containing residue streams: product gas composition and economics of biochemicals/monomers retrieval/co-production
Author(s) :	A.J. Grootjes, B.J. Vreugdenhil, G. Aranda Almansa, P. Kroon
Date :	28 November 2018
Project nr. :	5.2816 (ECN)
Report nr. :	TNO 2018 R11007

Gasification is a thermochemical process which converts solid fuels into a gas with a useful heating value that can be further processed into a variety of products (heat, power, fuels and chemicals), thus creating smart market opportunities for the valorisation of low-value solid feedstock. As part of the work for development and commercialization of the MILENA and OLGA technologies at industrial scale, this report compiles results of gasification tests performed at pilot scale using waste. The results from the measurement campaign carried out in the pilot MILENA/OLGA show that the product gas is a medium calorific value gas, rich in base chemicals/monomers like ethylene, propylene, styrene and benzene.

The comparison of waste incineration to Waste-to-Energy via gasification shows that gasification is preferred from both the economical as well as circularity point of view. Gasification of waste produces a gas with considerable value, suitable for power production though allows for further valorisation as well. Co-production of BTX (Benzene, Toluene, Xylene) adds value to Waste-to-Energy processes, but also to other processes such as the production of Renewable Natural Gas (RNG). Finally, removing BTX from product gas is a new way of recycling plastics, thermo-chemical recycling (second generation recycling).

Summary

In densely populated countries, like in Western-Europe, waste recycling is one of the cycles that contribute to the circular economy. The remaining solid residue after recycling still contains plastics as well as organic matter and gasification is a suitable option for the valorization of these waste streams. Gasification is a thermochemical process which converts solid fuels into a gas with a useful heating value that can be further processed into a variety of products (heat, power, fuels and chemicals), thus creating smart market opportunities for the valorization of low-value solid feedstock. Some of the outcomes of this work include the MILENA indirect gasification process, the OLGA tar removal. As part of the work for development and commercialization of the MILENA and OLGA technologies at industrial scale, this paper/presentation reports and compiles results of gasification tests performed at pilot scale using ICOPOWER® pellets (made of specifically collected commercial waste). The results are based on the gasification of the ICOPOWER® shredded pellets and are compared to available data for gasification of wood and a plastic waste consisting of essentially only plastic ('Plastic waste') in the pilot installation.

Product gas composition from MILENA pilot –scale experiments with wood, ICOPOWER® and plastic waste.

Product gas	Pine wood	ICOPOWER®	Plastic waste	
CH_4	15.2	19.4	26.5	[vol.%, d.b.]
CO	42.7	20.3	7.0	[vol.%, d.b.]
CO_2	11.8	16.9	7.3	[vol.%, d.b.]
H_2	23.2	19.5	11.7	[vol.%, d.b.]
Sum C_3	n.m.	2.6	9.5	[vol.%, d.b.]
Sum C_4	n.m.	1.0	4.0	[vol.%, d.b.]
Sum C_5	n.m.	0.03	0.17	[vol.%, d.b.]
Benzene	0.9	2.4	4.0	[vol.%, d.b.]
Toluene	0.1	0.4	0.7	[vol.%, d.b.]
Tar	46	81	109	[g/Nm^3]
LHV (excl. tar)	18.7	28.8	48.4	[MJ/Nm^3]

As the results show, gasifying waste streams that contain plastics, like ICOPOWER® and plastic waste, results in a gas with higher concentrations of hydrocarbons like ethylene, propylene, benzene, toluene, resulting in a significantly higher calorific value of the product gas. These hydrocarbons not only contain a lot of energy, they also have economic value as partially biogenic chemicals/monomers recovered from the product gas.

The comparison of waste incineration with Waste-to-Energy via gasification shows that gasification with co-production of BTX is preferred from both the economical as well as circularity point of view.

In conclusion, gasification of waste produces a product gas with components of considerable value, which is not valorized when turned into flue gas directly. Co-production of BTX adds additional value to Waste-to-Energy and Waste-to-Renewable Natural Gas (RNG) processes. Finally, removing BTX from product gas is a new way of recycling plastics, i.e. thermo(chemical) recycling.

Contents

1 Introduction

In densely populated countries, like in Western-Europe, waste recycling is one of the cycles that contribute to the circular economy. In a so-called Materials Recovery Facility (MRF) materials like metals, glass, PET and HDPE are reclaimed from the waste. The remaining solid residue from the MRF still contains plastics as well as organic matter and can be processed into Refuse Derived Fuel (RDF) or Solid Recovered Fuel (SRF), as pellets or fluff. A product made from RDF is the ICOPOWER® energy pellet of ICOVA. The feedstock for the production of ICOPOWER® is waste from trade, services and authorities, and other waste products. Through a mechanical separation of the high-heating value fraction from the waste fraction, a secondary energy carrier with precise combustion properties is produced. The ICOPOWER® energy pellet, supplied as a homogeneous product, can be used to replace fossil fuel such as coal in industrial applications (e.g. cement production). Gasification is a suitable option for the valorisation of these RDF streams by converting them into a valuable product gas, from which the constituents (benzene, ethylene and propylene) can be recovered.

Gasification is a thermochemical process in which a solid carbonaceous fuel (e.g. coal, biomass, or waste) is converted into a combustible gas called product gas or syngas (depending on the gas composition) under sub-stoichiometric conditions and medium-high temperatures (700-1200°C). The key feature of the gasification process is that 70-80% of the chemical energy initially contained in the initial solid fuel is kept in the product gas. The product gas, in turn, is a versatile energy carrier which, after proper cleaning, can be used in a number of applications: production of heat/power/mechanical energy, or feedstock for synthesis/recovery of fuels and chemicals.

Gasification is thus a suitable option for the energy valorisation of low-value solid feedstock such as waste or agricultural residues by converting them into a flexible gaseous energy carrier which can be cleaned and transported more easily than the initial solid feedstock, and which can be efficiently converted into a range of products. Added benefits of waste gasification are e.g. a substantial reduction in the quantity of waste, a significant reduction in environmental pollution, a reduction in the demand for land for waste disposal.

An important factor that has to be considered in the design of a gasification plant is the feedstock. The physical and chemical properties relevant for thermochemical conversion processes (summarized in Figure 2) will influence the design of the fuel pre-treatment system, the conversion process and the required gas cleaning train. Woody biomass has in general high moisture content, low bulk density, high volatile content, higher H/C and O/C ratios (thus, lower heating value), low N, S, and Cl content, and a low ash content with a low concentration of alkaline metals (Na, K). In comparison with woody biomass, herbaceous biomass (e.g. straw, miscanthus) has lower density, higher Cl and S content, and lower ash melting point. This makes herbaceous biomass more challenging in terms of conversion. The properties of lower-value fuels, such as waste-derived feedstock (e.g. RDF, SRF), pose even higher technical challenges on the process, including fouling, deposition and corrosion in the gas cooling sections of the plant, as well as bed agglomeration in fluidized-bed gasifiers/combustors. But there is a great opportunity for waste

gasification with respect to the possibility of the separation of valuable co-products from product gas.

ECN developed CFB gasification technology for approximately 12 years. The experience gained with modifying and operating a 500 kW pilot plant was used to develop the indirect MILENA gasifier. The gasifier contains separate sections for gasification and combustion, see Figure 1.

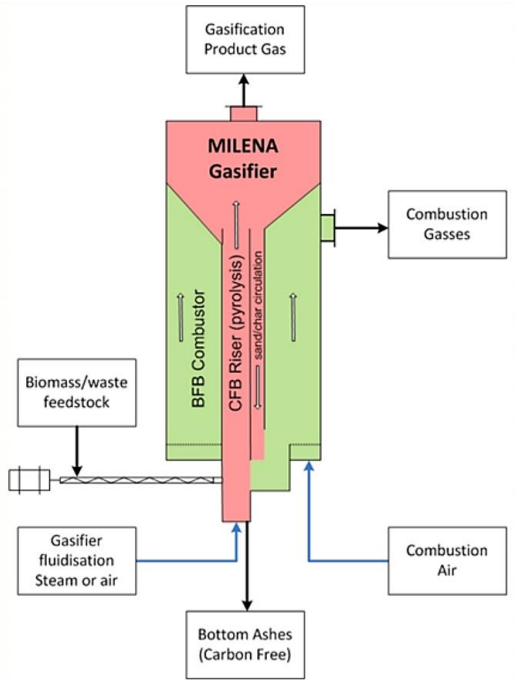

Figure 1 Overview of the MILENA gasifier.

The MILENA gasification process converts biomass into a combustible product gas with high efficiency. After cleaning, this gas can be used to generate power with gas engines or gas turbines. The gas produced by the MILENA gasifier is very suitable for application in a gas engine or gas turbine because of the higher calorific value of the gas (typical up to 20 MJ/mn^3 dry, compared to 4 – 7 MJ/mn^3 for a conventional air blown gasifier) and the complete conversion of the fuel (typical fuel conversion for downdraft or fluidized bed gasifiers is 85 - 95%).

One of the compounds formed during gasification is tar. Heavy tar in the product gas has a high dew point of around 450°C. Tar condensation can initiate fouling in a gasification process that ultimately result in the malfunctioning or plugging of equipment. The high maintenance costs and reduction in the yearly operating time due to stand stills leads to an increase in the operating costs. In order to remove tar above the water dew point ECN developed the OLGA technology. OLGA is a patented ECN invention and an acronym for oil-gas scrubber. OLGA is a series of two oil scrubbers where tars are removed from the gas, see Figure 2.

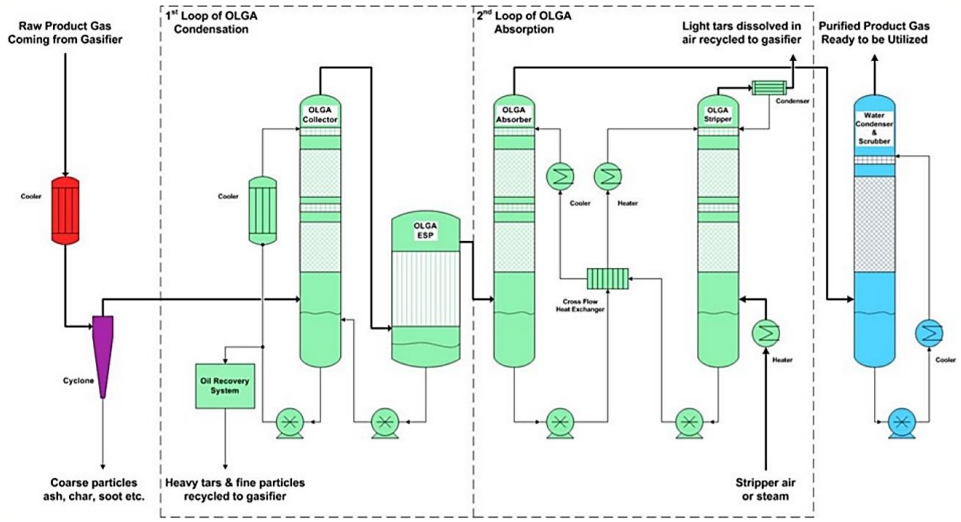

Figure 2 Overview of the OLGA system.

The first (collector) scrubber removes fine dust and heavy tars, whereas the second scrubber (absorber) removes light tars (e.g. phenol, naphthalene) [1]. The liquid used in the absorber loop is regenerated in the stripper, using air as stripping medium. The pilot OLGA also includes a wet electrostatic precipitator (ESP) for the removal of fine dust and oil aerosols from the gas between the first and second scrubber. Both heavy tars removed in the collector and tar-loaded stripping air can be recirculated back to the combustor side of the MILENA gasifier, thus using the energy contained in the heavy tars in the gasification reactor. OLGA operates above the water dew point. When the gas is further cooled the water that condenses does not contain tars. This makes the treatment of waste water easier.

ECN and partner Dahlman Renewable Technology (DRT) cooperate in the development of MILENA and OLGA. MOJI (Milena Olga Joint Innovation B.V.) is a joint venture formed around the gasification technology MILENA and the tar removal process OLGA.

Waste gasification, due to the content of plastics of the solid waste fuel, boosts the yield of benzene, toluene, xylene (BTX) and unsaturated hydrocarbons, which are a potential source of revenues. Therefore, co-production cannot only help decrease the costs of gasification processes, but it also creates new opportunities for a circular economy.

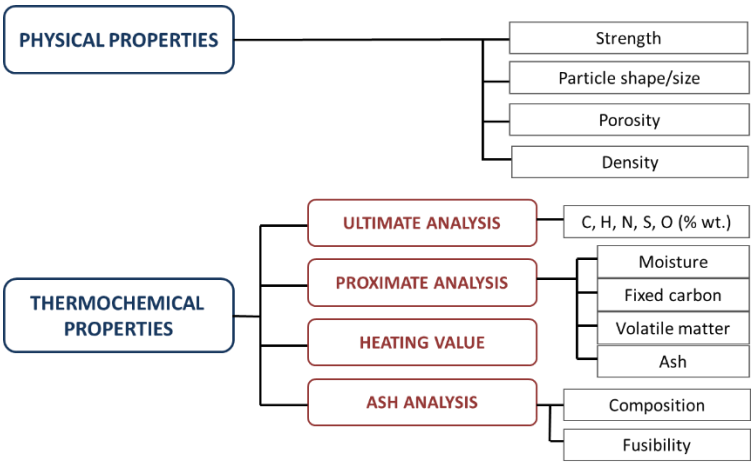

Figure 3 Overview of feedstock properties influencing the design of the gasification process.

The gasifier operating conditions influence both the quality of the product gas (composition, tar content/composition, contaminants) and the process performance (cold gas efficiency, carbon conversion). Among the operating conditions, the operating temperature is one of the most influential, particularly during the gasification of low-value, troublesome waste feedstock. Temperature control can effectively contribute to the mitigation of ash-related problems, such as agglomeration, fouling and corrosion. In previous work of ECN and Royal Dahlman where several waste feedstock (paper rejects, RDF, and meat and bone meal) were tested, it was found that gasification at temperatures of ~ 750°C leads to a trade-off between fuel conversion and release of contaminants to the gas phase, thus improving plant availability [2]. There is an increase of the retention of troublesome compounds in the bed material and the cyclone ash, and a decrease of the release into the gas phase. However, in an indirect gasifier the overall carbon conversion remains 100%, as remaining carbon will generate additional latent heat in the form of flue gas.

With this background, this paper reports and compiles results of waste gasification performed at ECN at pilot scale (800 kW_{th}, HHV), with different types of feedstock: biomass (wood) and plastic waste (industrial waste, plastic waste). The data set includes the results from the most recent measurement campaign carried out at the pilot MILENA/OLGA using shredded ICOPOWER® waste pellets as feedstock. The feedstock for the production of ICOPOWER® is waste from trade, services and authorities, and other waste products. Through a mechanical separation of the high-heating value fraction from the waste fraction, a secondary energy carrier with precise combustion properties is produced. The ICOPOWER® energy pellet, supplied as a homogeneous product, can be used to replace fossil fuel such as coal in industrial applications (e.g. cement production). This extensive work has been carried out in the last years as part of the development of the MILENA, OLGA and ESME technologies [3][4][5]. These results will be put into perspective to analyse the effect of the biomass/waste feedstock on the quality of the resulting product gas, and thus on the possibilities for the final application, gas cleaning/upgrading and economics of building blocks/monomers from indirect gasification of waste.

2 Objectives

The main objectives of the work carried out for this report are the following:

- Obtain performance data from MILENA and OLGA pilot experiments when operated on 100% waste feedstock and wood;
- Produce mass and energy balances;
- Perform a techno economic study focused on the concept of a circular economy of recyclable materials in RDF by comparing a waste incineration plant to a MILENA waste gasification plant with BTX and ethylene recovery.

3 Material and methods

3.1 Experimental facility

The 800 kW_{th} pilot plant is composed of the MILENA gasifier, gas cooling system, OLGA tar removal and water scrubber. The clean product gas is then directed to a burner. A schematic layout is displayed in Figure 4, showing the set-up which has been used for the test.

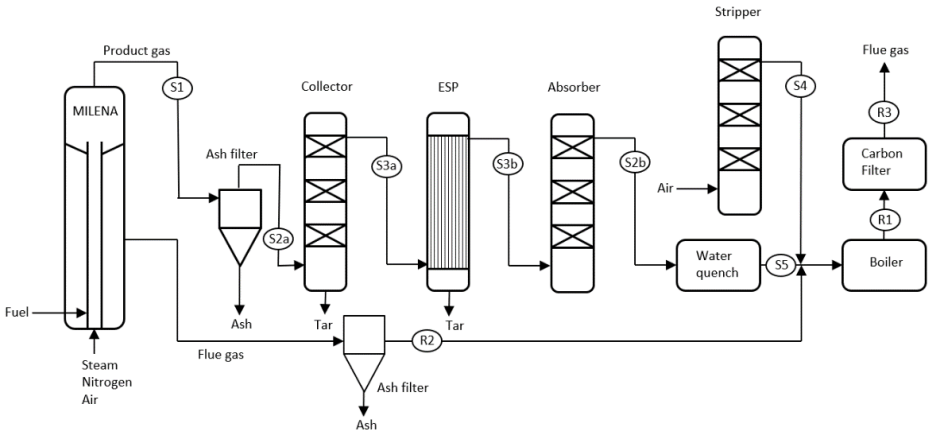

Figure 4 Schematic layout of pilot MILENA/OLGA.

Extensive measurements were carried out on product gas after MILENA and OLGA. Besides product gas composition and flue gas composition, other compounds such as tar, sulphur, nitrogen and chlorine compounds were analyzed in order to map the distribution of these components during waste gasification.

3.2 Feedstock preparation

The feedstock used for the gasification experiment was ICOPOWER® energy pellets, a commercial product from industrial waste produced and supplied by ICOVA. The characterization of the waste-derived ICOPOWER® feedstock used in the test is presented in Appendix A.

Prior to the gasification tests in the pilot plant, the pellets were shredded to a screen size of approximately 15 mm to account for the limitations set by the pilot plant feeding system and design. Furthermore, shredding is necessary in order to prevent large dense fuel particles being transported to the combustor, leading to too much carbon in the combustor. The downside of shredding the pellets is that the shredded material contains more fines, which can lead to a higher dust concentration in the product gas. See Figure 5 for the pellets before and after shredding.

Figure 5 ICOPOWER® energy pellets, before and after shredding.

4 Experimental procedure

The bed material used in the test was quartz sand (particle size 0.3 – 0.5 mm). During the test online monitoring of product gas (H_2, CO, CO_2, CH_4) and flue gas (O_2, CO_2, CO, C_xH_y, NO, NO_2) was carried out. Complementary, online micro-GC analysis (CO, CO_2, CH_4, O_2/Ar, C_2H_4, C_2H_6, C_6H_6, C_7H_8, H_2S, COS, N_2) of product gas was carried out. Moreover, wet chemical analysis was performed for the determination of HCl, NH_3, HCN, and SO_2 (flue gas). SPA (Solid Phase Adsorption [6]) analysis was carried out to determine the content and composition of tar at different locations of the gas line to track the performance of the OLGA tar removal system. Additionally, the tar guideline method [7] was used to complement the SPA method.

The settings of the MILENA gasifier are summarized in Table 1. The pilot plant experiment was started using natural gas and wood pellets. Once the set point of the temperature was reached the fuel was switched to the ICOPOWER® feedstock. Compared to wood, ICOPOWER® has a higher calorific value meaning that the capacity of the installation is reached at a lower ICOPOWER® feeding rate. Furthermore, it contains plastic, resulting in a denser product gas, richer in hydrocarbons. The reduction of feedstock mass flow, operation at a lower temperature and the increase of hydrocarbons in the product gas reduce the gas velocity in the riser, which was compensated by adding N_2 (for this experiment approximately 30 Nm^3/h) to the riser to be able to use ICOPOWER® in the existing facility. In order to compare results of different pilot scale experiments on an equal basis, nitrogen-free data is presented in Chapter 6. During the test, measurements and analyses were carried out over the process.

Table 1 MILENA gasifier settings during pilot plant measurement campaign.

Experiment	100% shredded ICOPOWER® pellets
Fuel flow (kg/h)	96
Steam flow (kg/h)	28
Fluidization N_2 (Nm^3/h)	30
T of gasification (°C)	750
T of combustor bed (°C)	810
Combustion air (Nm^3/h)	140

Tar was removed from the product gas using the OLGA tar removal technology.

5 Results

In April, 2016, shredded ICOPOWER® pellets were gasified in the pilot scale MILENA gasifier and are compared to available data for wood and plastic waste gasification in the pilot installation. The ICOPOWER® pellets and wood feedstocks were gasified at a temperature of 750°C. When gasifying the plastic waste, it was decided to lower the temperature further to 700°C, in order to avoid ash and tar related problems. The product gas was subsequently cleaned by the OLGA tar and dust removal system, followed by a water scrubber to remove water, HCl and NH_3. The cleaned product gas was burned in a boiler. In total, 53 hours of gasifying ICOPOWER® at an average rate of 96 kg/h was achieved, resulting in a thermal input of the gasifier of on average 630 kW_{th} (HHV). There were two unforeseen shutdown events, the first was caused by a software problem, shutting down cooling fans and the second was caused by a faulty flame sensor of the boiler. The MILENA gasifier and OLGA tar and dust removal system operated flawless.

5.1 Observations

Figure 6 shows that the riser-gasifier temperature of MILENA stabilized at approximately 750°C, whereas the combustor temperature was about 80°C higher. The gasification temperature was intentionally kept at 750°C based on previous waste gasification experiments at ECN on lab and pilot scale, and DRT and RWE Essent on 4 and 80 MW_{th} industrial scale in Tondela (Portugal) and Geertruidenberg (The Netherlands) in order to mitigate ash related problems such as downstream condensation of evaporated salts, while maintaining sufficient fuel conversion [8]. No additives were used.

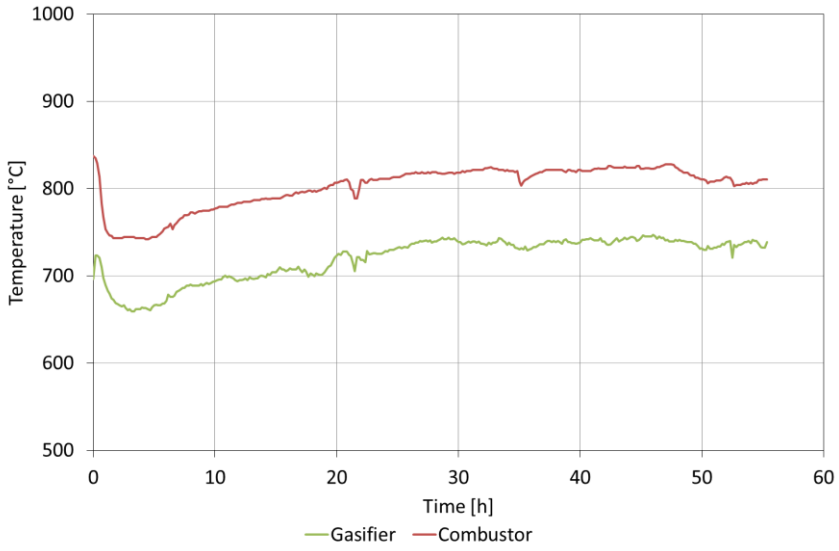

Figure 6 MILENA temperatures in the gasifier and combustor sections.

5.2 Gas composition (product gas and flue gas)

Table 2 compares the product gas composition during ICOPOWER® gasification (on nitrogen-free basis) after MILENA, before OLGA, with the compositions obtained in earlier pilot scale experiments with wood and plastic waste. For the

ICOPOWER® test the presented data is based on µ-GC and SPA tar measurements. As can be seen, with increasing plastic content in the fuel, the gas contains more hydrocarbons such as methane, ethane, ethylene, C_3 to C_5, and BTX, resulting in less CO and H_2. The effect of the product gas composition on the calorific value of the gas can be seen clearly by an increase of 18.5 MJ/Nm^3 to 48 MJ/Nm^3. The product gas in particular is suitable for catalysis and co-production, as well as for heat and power applications. Apart from heat and power, co-production of chemicals like BTX and ethylene with Renewable Natural Gas (RNG) production can be an attractive option since hydrogenating and reforming these unsaturated hydrocarbons and BTX (precursors of coke in the methanation catalyst) comes at the expense of a hydrogenation and pre-reformer reactor. Additional hydrogen and/or steam is needed for this reforming step and result in a loss of efficiency. It would make more sense to extract these hydrocarbons from the gas prior to hydrogenation and methanation. Furthermore, the increasing amounts of higher hydrocarbons, compared to the wood case show the potential of these compounds as a source of income.

Table 2 Summary of product gas composition, N_2-free.

Product gas	Pine wood	ICOPOWER®	Plastic waste	
CH_4	15.2	19.4	26.5	[vol.%, d.b.]
CO	42.7	20.3	7.0	[vol.%, d.b.]
CO_2	11.8	16.9	7.3	[vol.%, d.b.]
H_2	23.2	19.5	11.7	[vol.%, d.b.]
O_2	0	0	0	[vol.%, d.b.]
Ar	0.0	0.2	0.2	[vol.%, d.b.]
C_2H_4	4.9	14.7	24.7	[vol.%, d.b.]
C_2H_6	0.5	1.8	3.7	[vol.%, d.b.]
Sum C_3	n.m.	2.6	9.5	[vol.%, d.b.]
Sum C_4	n.m.	1.0	4.0	[vol.%, d.b.]
Sum C_5	n.m.	0.03	0.17	[vol.%, d.b.]
H_2S	148	1,633	575	[ppmV, d.b.]
COS	11	48	12	[ppmV, d.b.]
Thiophene	n.m.	58	16	[ppmV, d.b.]
Benzene	0.9	2.4	4.0	[vol.%, d.b.]
Toluene	0.1	0.4	0.7	[vol.%, d.b.]
NH_3	46	3,778	1,806	[ppmV, d.b.]
HCN	n.m.	2,975	2,550	[ppmV, d.b.]
HCl	9	301	n.m.	[ppmV, d.b.]
Tar	46	81	109	[g/Nm^3]
LHV (excl. tar)	18.7	28.8	48.4	[MJ/Nm^3]

Table 3 displays the flue gas composition and the higher levels of CO and NO_x when gasifying ICOPOWER® and plastic waste can be attributed to a lower overall secondary combustion temperature as a result of the secondary air injectors at relatively small scale and a higher amount of nitrogen in these fuels. At large scale, the secondary combustion temperature will be higher, lowering the CO level in the flue gas. No emission mitigating actions (operational nor chemicals dosing) were applied to lower these emissions during the test.

Table 3 Summary of flue gas composition.

Flue gas	Pine wood	ICOPOWER®	Plastic waste	
CO_2	12.3	10.8	9.7	[vol.%, d.b.]
O_2	5.9	6.5	5.3	[vol.%, d.b.]
CO	0	153	149	[ppmV, d.b.]
NO	10.5	273	94	[ppmV, d.b.]
NO_2	0.7	18	4.6	[ppmV, d.b.]

5.3 Tar measurements

Tars have been plotted according to the ECN tar classification system[1] , based on tar solubility:

Class 1: GC undetectable (heavy tar fraction (roughly ≥7-ring PAHs), thus represent the gravimetric tars, not measured by GC analysis)
Class 2: Heterocyclic components (phenol, cresol)
Class 3: Aromatic components 1 ring: xylene, styrene. Benzene and toluene not included
Class 4: Aromatic components (2, 3 rings)
Class 5: Aromatic components (>3 rings)
Unknowns: Tar compounds that are sampled and measured (a peak is found in the chromatogram), but it is unknown what the individual components are. In principle components in this class belong to the other classes and are classified according to the volatility of the compounds:

Unknowns-1 Benzene t/m Naphthalene
Unknowns-2 Naphthalene t/m Phenanthrene
Unknowns-3 Phenanthrene t/m Pyrene
Unknowns-4 Pyrene t/m Benzo(e)pyrene
Unknowns-5 Benzo(e)pyrene t/m Coronene

Gasifying high ash, plastic waste feedstock may result in fouling downstream of the gasifier due to large, heavy tars and condensation of salts. In order to avoid fouling, and mitigate ash related issues, a gasification temperature of maximum 750°C was used, based on results from previous experiments. Furthermore, when gasifying the plastic waste, it was decided to lower the temperature further to 700°C.

The tar analysis results are summarized in Table 4. Class 1 tar was not determined and is therefore not presented in Table 4. Classes 2 to 5, Unknowns and a total, consisting of tar from classes 2 to 5 and the unknowns are given in the table. Tars were measured by the Solid Phase Adsorption (SPA) method and by using the tar guideline. The difference between both methods is that the tar guideline can capture light components such as benzene, toluene, xylene, styrene better, but the SPA method is faster, cheaper and well suited for experiments with high gasification temperatures (>750°C). Note that benzene normally is not considered a tar by definition.

[1] H. Boerrigter, S.V.B. van Paasen, P.C.A. Bergman, J.W. Könemann, R. Emmen, A. Wijnands. "OLGA" tar removal technology. ECN-C--05-009 (ftp://ftp.ecn.nl/pub/www/library/report/2005/c05009.pdf)

Table 4 Summary of tar measurements, reported nitrogen free and dry gas basis

Exp nr	Gasification temp [°C]	Location	Method	Class 2 [g/Nm^3]	Class 3 [g/Nm^3]	Class 4 [g/Nm^3]	Class 5 [g/Nm^3]	Unknowns [g/Nm^3]	Total tar (excl. class 1) [g/Nm^3]
Pine wood	750	After MILENA	SPA	4.8	4.5	22.5	1.5	13.1	46.4
Pine wood	750	After absorber	SPA	0.0	0.7	0.4	0.0	1.0	2.1
Pine wood	750	After quench	SPA	0.1	0.7	0.4	0.0	1.2	2.4
ICOPOWER®	752	After MILENA	SPA	5.2	9.9	33.5	2.6	30.2	81.4
ICOPOWER®	752	After absorber	SPA	0.0	4.3	0.4	0.0	2.4	7.1
ICOPOWER®	752	After quench	SPA	0.0	3.9	0.3	0.0	2.1	6.2
ICOPOWER®	752	After MILENA	Guideline	6.8	29.4	34.0	2.1	41.3	113.7
ICOPOWER®	752	After absorber	Guideline	0.1	5.3	1.0	0.0	10.1	16.5
Plastic waste	693	After MILENA	SPA	2.7	25.4	37.9	3.1	40.5	109.4
Plastic waste	693	After absorber	SPA	0.1	6.5	0.7	0.0	5.4	12.8
Plastic waste	693	After quench	SPA	0.0	2.3	0.6	0.0	4.0	7.0

As can be seen, comparing the SPA data and the guideline data of the ICOPOWER® experiment, the guideline measures about 40% more tar than by the SPA method. The difference is mainly in the Class 3 tars and the Unknowns (containing Unknown Class 1 components). Class 3 is only the sum of two components xylene and styrene. This shows that the SPA method alone is not sufficient when gasifying waste at low temperature, because more Class 3 type of tars are produced. Furthermore it shows that low temperature waste gasification results in a significant amount of tar that may have a large impact on the heat balance of MILENA, when it is fed to the combustor. Tar represents almost 20% of the energy in the fuel and this suggests that instead of using it for energy, other outlets e.g. chemicals may become interesting as well.

The total amount of SPA tar of the plastic containing feedstocks is higher, compared to wood. However, the concentration of class 5 tars (mainly influencing the tar dew point), is lower than for the pilot experiment using wood. Typically, class 5 tars condense at relatively high temperature at low concentrations thus can cause tar related fouling issues.

When gasifying waste at a temperature of less than 750°C, the tar distribution shifts from class 5 towards class 2, 3 and 4 tars. These tars are less problematic in terms of fouling issues and can be removed easily by OLGA. The operation of OLGA can be seen clearly when comparing 'After MILENA' samples with 'After absorber'. The total amount of tar after OLGA is about 8% of the amount produced by MILENA. Most importantly, the class 5 tars have been reduced to zero. About 95% of all the tars measured by the SPA method were removed from the product gas. Overall, the tar removal efficiency of the OLGA system is in accordance with the design specifications of this pilot-scale OLGA system. It is noted that this OLGA system was initially designed for tar removal downstream a direct air blown gasifier operated on clean biomass (±5 g/Nm^3 tar), not an indirect gasifier operated on waste (±80 g/Nm^3 tar).

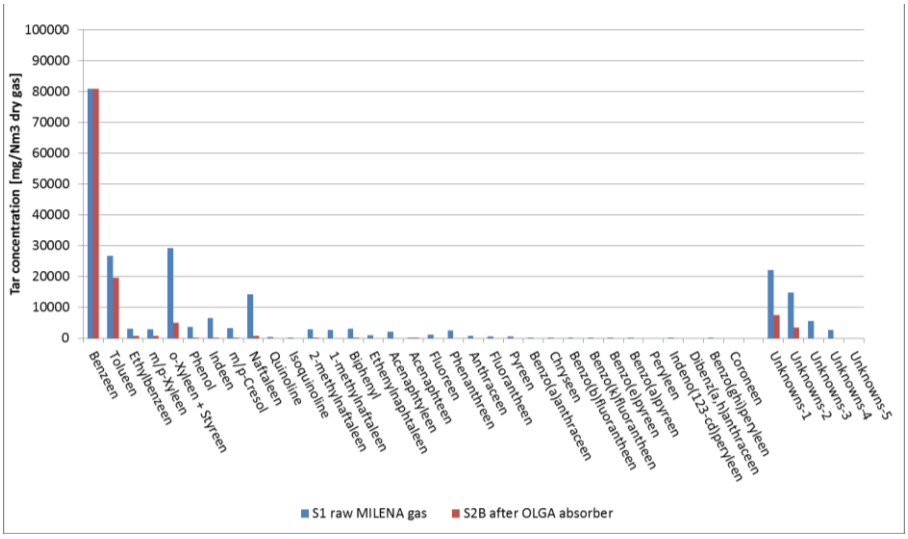

Figure 7 Detailed composition of guideline tar in product gas (N_2-free basis).

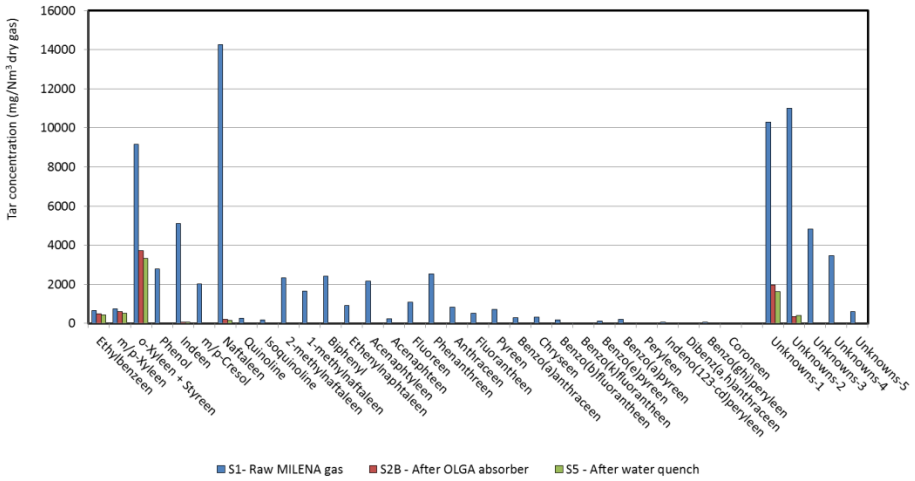

Figure 8 Detailed composition of SPA tar in product gas from ICOPOWER® (N_2-free basis).

Figure 7 and Figure 8 show the detailed composition of the quantified tars in the product gas of the experiment using shredded ICOPOWER® pellets as feedstock, expressed on a N_2-free basis. As can be seen, the tar distribution is towards the aromatic 1-, 2- and 3-ring compounds like indene, naphthalene and phenanthrene. The tar guideline method measures benzene and toluene accurately and as can be seen, OLGA practically removes no benzene, 20% toluene, and up to 80% of ethylbenzene, xylenes and styrene.

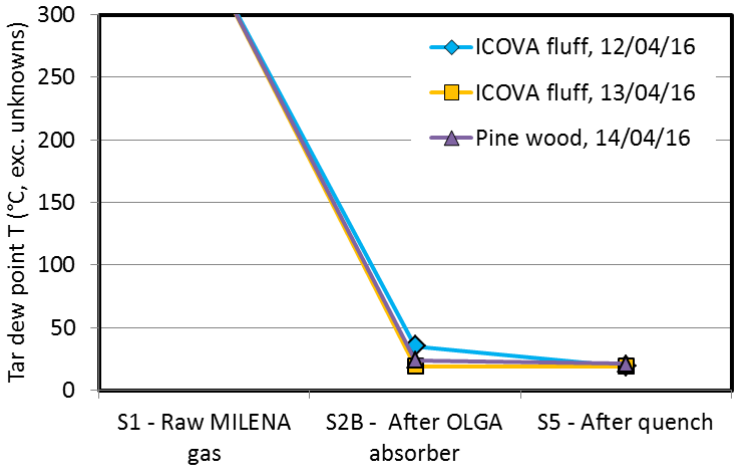

Figure 9 Evolution of the tar dew point along the process: MILENA, OLGA and water quench.

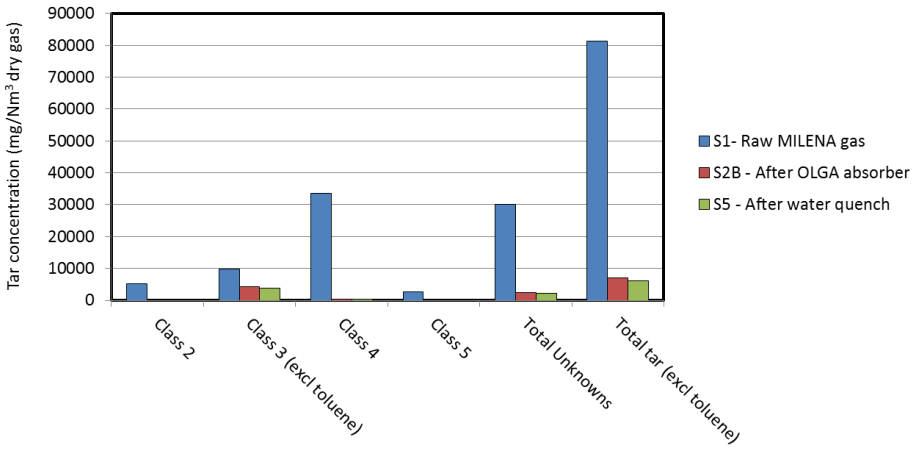

Figure 10 Tar composition according to ECN classification along the system: MILENA, OLGA and water quench. Values expressed in N_2-free basis.

Figure 9 and Figure 10 plot the evolution of the tar along the MILENA/OLGA/water quench system. As can be seen, the pilot OLGA is able to remove class 2, 4 and 5 tars completely. More than 90% of the total tar is removed in OLGA, the tar dew point being reduced from well above 300°C to ~20°C.

5.4 Ash analysis, dust loads and cyclone efficiency

Table 5 shows the averaged ash flows, gas flows and dust load for the flue gas bag house filter and the product gas cyclone, during the analyzed period 12 April 16:40 to 13 April 02:40.

Table 5 Ash flow.

	Product gas cyclone	Flue gas
Ash flow [kg/h]	6.8	5.4
Gas flow [Nm^3/h]	79	153
Dust load product gas total [g/Nm^3]	107	35

Table 6 shows the most important results of the proximate, ultimate analysis of the ashes.

Table 6 Ash analysis.

	Product Gas Cyclone ash[1]	Flue Gas Bag house filter ash[1]
Sample date	13 April 05:28 – 08:35	13 April 01:12 – 07:18
Moisture content (% wt., ar)	n.m. [2]	
Ultimate analysis (% wt., dry basis)		
C (550°C)[3]	29.9	<0.1
H	n.m.	n.m.
N	n.m.	n.m.
S	0.06	0.02
O	n.m.	n.m.
Cl	5.1	2.7
Proximate analysis (% wt., dry basis)		
Volatile matter	n.m.	n.m.
Ash (815°C)[3]	64.0	97.8
HHV (MJ/kg, dry)	n.m.	n.m.
ICP analysis (mg/kg, 10 highest concentrations, dry basis)		
Al	71,617	90,103
Ca	118,764	74,497
Fe	18,484	12,060
K	13,063	10,716
Mg	8,986	6,523
Na	20,455	12,993
P	4,450	3,227
S	7,344	1,106
Si	113,778	291,246
Ti	7,524	4,978

[1]ECN analysis report 18371, [2]n.m. = not measured, [3]Based on TGA result

As can be seen from the data, the chlorine content of the ashes is high. Metals, known to form chlorides (like $AlCl_3$, Al_2Cl_6, KCl, NaCl, $MgCl_2$, $FeCl_3$, $PbCl_2$, etc.) and with the potential risk of forming low melting point eutectics, are found in high concentrations in the cyclone ash. This can be explained by the low gasification temperature, preventing the salts from entering the gaseous phase thus the salts remain as solids in the cyclone ash. This is a positive result, since gaseous salts can cause fouling upon condensation and high temperature corrosion in MILENA and downstream product gas equipment like gas coolers. The bag house filter ash contains less of these compounds, with about 2%. Furthermore, it can be seen that the bag house filter ash is free of carbon, indicating complete combustion in the BFB of MILENA.

5.5 Chlorine balance

Given the importance of chlorine in waste gasification, it is necessary to determine the fate of chlorine during the process. For this, the distribution of chlorine among the solid, liquid and gaseous streams during the ICOPOWER® test has been determined. The concentration and flows of gases have been averaged over the period of 12 April 16:40 until 13 April 02:40. The flow rates of product gas and flue gas have been estimated using a nitrogen balance over the riser and the combustor, respectively (it has been assumed that the gas recirculation between riser and combustor is negligible). The inlet and outlet chlorine mass flows are summarized in Table 7 to Table 9.

Table 7 Chlorine in ICOPOWER® feedstock liquid and gaseous streams.

	Fuel flow [kg/h]	Moisture content [wt.%, as received]	Cl [wt.%, dry basis]	Mass flow Cl [kg/h]
Chlorine in ICOPOWER®	94	2.3	1.16	1.07

Table 8 Chlorine in ashes.

	Flow [kg/h]	Cl [wt.%]	Mass flow Cl [kg/h]
Baghouse filter	5.4	2.7	0.15
Cyclone ash	6.8	5.1	0.34
Bed material	n.m.	n.m.	n.m.

Table 9 Chlorine in MILENA product- and flue gas.

	Flow [Nm^3/h, dry]	Cl [mg/Nm^3]	Mass flow Cl [g/h]
MILENA product gas	78.6	249	19.6
MILENA flue gas	169.0	314	51.0

As can be checked, approximately 6.6wt.% of the chlorine initially contained in the fuel ends up in the gaseous streams, either product gas or flue gas. 1.8 wt.% of the Cl appears in the MILENA product gas, and 4.8 wt.% ends up in the flue gas. On the other hand, 46 wt.% of the initial Cl ends up as cyclone ash and filter ash. The chlorine balance does not close well which can be explained by not having measured chlorine in the bed material and as methyl chloride (both not measured).

5.6 Carbon balance

Based on the data of the test, using µ-GC and SPA/guideline tar results, the carbon balance of MILENA has been calculated, along with the carbon conversion and cold gas efficiency (CGE). It shows where the carbon from the feedstock is going. These numbers are corrected for carbon which is introduced via other sources, such as methane. The overall closure of the balance is 87%. The missing 13% can be related to class 1 tars as well as to soot and char that was not removed by the product gas cyclone.

The carbon balance shows that OLGA will recycle > 15% of the carbon to the combustor (as tar or char), which will lead to a surplus of energy. Investigating means of valorizing the tars from OLGA starts to make sense when gasifying waste.

Overall conclusions of the experiments are that the ICOPOWER® is a high energy fuel that results in a product gas rich in hydrocarbons and showed no problems in terms of gasifier hydrodynamics, temperatures, pressures and fouling behavior. Stable gasification conditions do depend largely on the fuel quality. Pretreatment of the very inhomogeneous fuel showed the capabilities of MILENA in converting the fuel. For a full scale application, feeding fluff RDF waste, it is expected that MILENA will operate in a similar stable manner as when feeding the shredded pellets at pilot scale.

OLGA performed well from a control point of view. The collector, absorber and stripper columns were operating according to expectation.

6 Techno-economic comparison of waste incineration and waste gasification

The results have shown that gasification of plastic containing waste (e.g. derived from Municipal Solid Waste (MSW)) results in a high calorific value product gas that is suitable for heat and power generation, synthesis and harvesting of valuable co-products from product gas. Therefore, a great opportunity for waste gasification with respect to the harvesting of valuable co-products from product gas is present. Waste gasification, due to the content of plastics in the solid waste fuel, boosts the yield of Benzene, Toluene, Xylene (BTX) and unsaturated hydrocarbons, which are a potential source of income. Therefore, co-production cannot only help decrease the costs of gasification processes, but it also opens the way to concepts such as circular economy.

In this chapter a comparison is made between (1) a waste-to-electricity plant that generates energy from a steam turbine cycle, driven by incinerating waste, (2) a MILENA gasification plant, generating electricity and (3) a MILENA gasification plant generating electricity and co-producing BTX.

First a comparison of price scenarios is shown in Figure 11 and Figure 12 for gasification of wood and wastes. The assumptions for the scenarios are given in price data, based on market information, see Table 10. It is clear that the input cost of waste is lower compared to wood. At the same time, the product gas of gasified waste represents a higher value due to the higher amount of C_{2+} hydrocarbons, especially the unsaturated hydrocarbons. Furthermore, the ratio of the accumulative value of CO/H_2 and CH_4 to C_{2+} hydrocarbons shifts more to the C_{2+} hydrocarbons side for the waste feedstocks.

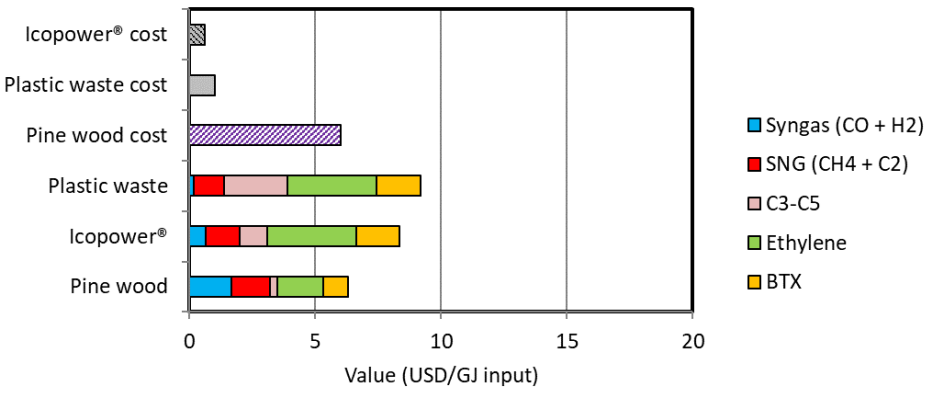

Figure 11 Price scenarios for product gas components for the low price scenario.

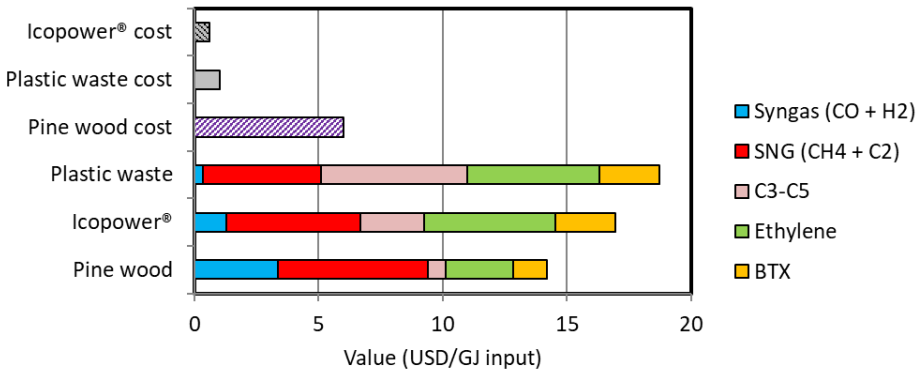

Figure 12 Price scenarios for product gas components for the high price scenario.

Table 10 Price data for the scenarios [9][10][11].

	Low-price scenario	High-price scenario
Syngas (CO + H_2) ($\$_{2016}$/GJ)	5	10
RNG (CH_4 + C_2H_6) ($\$_{2016}$/GJ)	6	24
C_3-C_5 ($\$_{2016}$/GJ)	12	28
Ethylene ($\$_{2016}$/GJ)	15	22
BTX ($\$_{2016}$/GJ)	16	21

For the economic comparison between a waste incineration plant and the MILENA gasification plant with and without BTX recovery, Return on Investment (ROI) is calculated. For the conversion of $\$_{2016}$ to €$_{2016}$ an average of 0.89 €/$ is used. The assumptions for the calculations are the following:

- ROI of 6% for incineration
- Electricity at 6 €ct/kWh
- MSW at -60 €/ton
- RDF production facility included for the gasification process, excluding revenues for recyclable streams from this facility, ICOPOWER® RDF is used as feedstock
- Gasification based on ETI data (source: Identifying Likely Late-stage WTE Gasification Candidates, Chris Cothran, Gasification Analyst at Stratas Advisors, Presented at TCBiomass 2015)
- Scaled to 90 MW_{th} input
- BTX case based on lab/pilot data
- BTX separation adds 2% CAPEX
- Power island capacity is reduced with 15% for BTX case

In Table 11 the ROI is given. For the MILENA gasification plant with BTX recovery, the low and high price scenarios for BTX are used.

Table 11 Economic comparison of waste incineration vs gasification

Cases	Waste incineration	MILENA GT	MILENA GT BTX
Feedstock input (MW_{th})	174	90	90
Output electricity (MW_e)	38	31.5	27.1
Output heat (MW_{th})		0	0
Output BTX (MW_{LHV})		0	12.7
Waste/feedstock cost (M€/y)		-13.0	-13.0
Electricity revenues (M€/y)		15.1	13
BTX revenues low (M€/y)		0	5.4
BTX revenues high (M€/y)		0	7.4
ROI (%)	6	16	-
ROI low price BTX (%)	-	-	21
ROI high price BTX (%)	-	-	23

Gasification of waste produces a product gas with considerable value, suitable for power production though can allow further valorization as well. Co-production of BTX adds value to Waste-to-Energy processes, but also to other processes such as the production of Renewable Natural Gas (RNG). Finally, removing BTX from product gas is a new way of recycling plastics, second generation recycling.

7 Conclusions and recommendations

Gasification is an essential technology for valorization of plastic containing wastes, for which the only alternative is landfill or incineration. The pilot scale testing on a commercially available feedstock ICOPOWER®, showed the technical possibility of the MILENA and OLGA for valorizing these feedstocks. The subsequent analyses of the results show that there is a very positive future business case when the valuable gas components are recovered.

When comparing incineration to gasification, in all electricity price scenarios the Return On Investment (ROI) of the Waste-to-Energy option by gasification is better than for the incineration case. Furthermore, at low electricity prices recovery of Benzene, Toluene and Xylene (BTX) is economically more viable than leaving it in the gas and making electricity.

In conclusion, gasification of waste produces a product gas with considerable value, which is a waste if turned into flue gas directly. Co-production of BTX adds value to Waste-to-Energy processes, (Return on Investment increases 5 to 7% points), but also to other processes such as the production of Renewable Natural Gas (RNG). Finally, removing BTX from product gas is a new way of recycling plastics, second generation recycling.

The experiment, where for a period of 53 hours an RDF in the form of ICOPOWER® pellets was gasified, resulted in valuable results ranging from the gas composition, chlorine balance to the post test inspection. The gas composition shows enrichment in hydrocarbons, as a result of low temperature waste gasification. Another good result of low temperature gasification is that, despite the high chlorine content of the fuel, only 6% of the chlorine in the fuel ended up in the product- and flue gas. During low temperature gasification significantly more tar is produced, in the order of 2 to 3 times more than for wood gasification. This calls for a reconsideration of utilizing tar obtained through OLGA as a heat source in MILENA. It might well become a separate product, due to the quantity and the reduced need in MILENA. Also significantly more cyclone ash was produced, which results in a higher fine dust loading to OLGA. The carbon balance was made to account for 87% of the carbon in the waste. 13% of the carbon in the feedstock was not measured and assumed to be class 1 tars and fine particulate carbon.

The effort put in analyzing the tars using guideline tar analysis and in analyzing the larger hydrocarbons C_3 up to C_5 resulted in an improved mass balance, but also clearly shows the added value of removing these components from the gas.

From an OLGA stand point, the results are interesting since on one side the OLGA did not capture any benzene. Secondly, the amount of ethylbenzene and styrene are much higher than the naphthalene concentrations, but the design of OLGA is still based on the premises that naphthalene is the major component. Recovery of light tars seems a good solution for the surplus of energy that will end up in the MILENA and with the BTX scrubbing technology developed at ECN part of TNO, these learning might be applied to the recovery of styrene by the OLGA system.

8 References

[1] http://www.royaldahlman.com/renewable/assets/Uploads/DAHLMAN-INFO-OLGA.pdf

[2] Grootjes, A.J.; Aranda Almansa, G.; Meijden, C.M. van der; Willeboer, W.; Spanjers, M.; Kant, H.F. de; Spit, R. Gasification of low-value feedstock (paper rejects, RDF and MBM) at laboratory (5 kWth) and commercial (80 MWth) scale. ECN-M--15-025 (2015). Presented at the 23rd European Biomass Conference and Exhibition. Vienna (Austria), 2-6 June 2015 https://www.ecn.nl/publications/ECN-M--15-025

[3] Rabou, L.P.L.M.; Aranda Almansa, G. 500 hours producing bio-SNG from MILENA gasification using the ESME system ECN System for MEthanation (ESME): a novel technology successfully proven. ECN-E--15-008 (2015) https://www.ecn.nl/publications/ECN-E--15-008

[4] Dahlman Renewable Technology. OLGA technology http://www.royaldahlman.com/renewable/home/tar-removal/olga-technology/

[5] ECN. MILENA biomass gasification process http://www.milenatechnology.com/

[6] Claes Brage, Qizhuang Yu, Guanxing Chen and Krister Sjostrom. Use of amino phase adsorbent for biomass tar sampling and separation. Fuel Vol. 76, No. 2, pp. 137-142, 1997

[7] W. van de Kamp, P. de Wild, U. Zielke, M. Suomalainen, H. Knoef, J. Good, T. Liliedahl, C. Unger, M. Whitehouse, J. Neeft, H. van de Hoek1 and J. Kiel. TAR MEASUREMENT STANDARD FOR SAMPLING AND ANALYSIS OF TARS AND PARTICLES IN BIOMASS GASIFICATION PRODUCT GAS. 14th European Biomass Conference, 17-21 October 2005, Paris, France.

[8] Grootjes, A.J.; Aranda Almansa, G.; Willeboer, W.; Spanjers, M. Waste gasification improvements. ECN-L--15-072 (2015). Presented at the ACI Biomass to Power, Berlin, Germany, 16 - 17 September, 2015. https://www.ecn.nl/publications/ECN-L--15-072

[9] ICIS Chemical Business, 7-13 March 2016 | 39

[10] http://www.globalpetrolprices.com/lpg_prices/

[11] http://www.platts.com/news-feature/2015/petrochemicals/pgpi/index

9 Signature

Petten, 28 November 2018 TNO

M.H.F. Overwijk
Head of department

A.J. Grootjes
Author

A Feedstock analysis

Feedstock	Pine wood	ICOPOWER®	Plastic waste
Moisture content 105°C (wt. %, ar)	11.0	2.3	0.2
Proximate analysis (dry basis)			
Ash content 550°C (wt.%)	0.6	13.8	10.8
Ash content 815°C (wt.%)	0.5	12.8	9.8
Volatile matter (wt.%)	83.0	76.9	85.2
Higher Heating Value, HHV (MJ/kg, dry basis)	20	24	33
Ultimate analysis (dry basis)			
C (wt.%)	50	52.4	65
H (wt.%)	6.4	7.3	9.8
N (wt.%)	<0.1	0.9	0.8
O (wt.%)	45	27.30	14.4
Br (mg/kg)	<10	58	52
Cl (mg/kg)	84	11583	15830
F (mg/kg)	<10	92	48
Ash composition (mg/kg, dry basis)			
Al	51	9737	11724
As	<6.7	2	7
B	4	38	34
Ba	15	254	203
Ca	1397	22616	12352
Cd	<0.5	2	7
Co	51	4	11
Cr	< 4.4	170	160
Cu	< 8.2	305	356
Fe	258	3500	3265
K	388	2139	2140
Li	< 1.5	3	4
Mg	354	1518	1160
Mn	122	145	74
Mo	< 4.2	4	10
Na	71	3352	4554
Ni	< 2.8	68	99
P	35	931	513
Pb	< 3	98	85
S	212	1844	764
Sb	< 16.6	82	2
Se	< 6.8	< 1.4	< 6.8
Si	193	19966	n.m.
Sn	< 4.4	57	26
Sr	8.0	72	52
Ti	4	1545	n.m.
V	< 1.2	4	3
W	112	2	8
Zn	7	286	603

[1]ECN analysis Rap17648, 18202 and 18148

From the fuel composition it can be seen that the ICOPOWER® energy pellets contain more carbon and less oxygen. This in combination with a higher heating value, compared to wood, indicates a significant amount of plastic in the fuel. The chlorine content in the fuel is relatively high, at around 1.2wt.%, which is typical for plastics. Furthermore, the fuel contains low to moderate levels of aluminum, calcium, iron, potassium, magnesium, silica, lead and sodium.