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Title:	
GASIFICATION OF SOLID FUELS/SLURRY FOR PRODUCTION OF ADVANCED BIOFUELS	
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1. Introduction

The incentive for producing liquid fuels from biomass are both environmental and political. In the 2015 Paris agreement, it has been decided that global warming should be limited to a max. 2°C increase compared to pre-industrial temperatures. GHG emissions should therefore be lowered substantially by a switch from energy production via fossil fuel towards renewable fuels. Especially liquid biofuels are required as no such substitute is available or implemented for heavier transportation vehicles that still heavily depends on fossil fuel, e.g. diesel in trucks and kerosene in aviation. In the transportation sector, most delivered energy comes from, in decreasing order, gasoline, diesel, jet fuel, natural gas, other liquids and electricity (see Figure 1). Although the replacement of classic petrol cars to battery powered vehicles is promising, its total impact is small assuming the electricity required to charge the batteries is produced from fossil fuels. Bloomberg predicts that battery powered cars will be as cheap as gasoline powered cars by 2025, which leads to higher number of electric vehicles sold by 2038 [[1]].

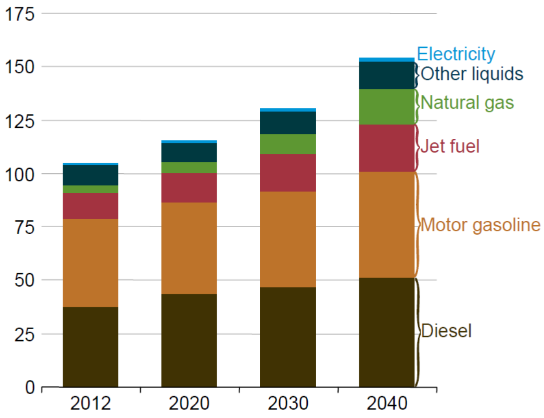

Figure 1: World transportation sector energy consumption by fuel (quadrillion Btu); projection 2012-2040 by the US Energy Information Administration (EIA) [[2]].

In 2009, the European Commission's Renewable Energy Directive was issued [[3]] to set national targets for the share of renewable energy in the final energy use of each EU country. That target was set at 20% renewable energy share in the EU by 2020 with a 10% target for liquid transportation fuels. An additional target has been set for at least 14% in 2030 for the transportation sector [[4]].

The new/revised renewable directive now includes slight alterations. It was revised in 2018 for the 2030 target stating 32% renewable, making the EU a global leader. Moreover, it states that the production of especially advanced biofuels should be promoted [[5]]. Advanced biofuels are defined as fuels derived from waste/biomass residues with lower greenhouse gas emissions without causing indirect land-use change, and do not compete

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[1] J. Shankleman, The Electric Car Revolution Is Accelerating, Bloomberg, 2017, https://www.bloomberg.com/news/articles/2017-07-06/the-electric-car-revolution-is-accelerating.

[2] EIA: International Energy Outlook 2016, U.S. Energy Information Administration, https://www.eia.gov/outlooks/ieo/pdf/0484(2016).pdf

[3] Directive 2009/28/EC of the European Parliament and of the Council, 23 April 2009.

[4] Directive (EU) 2018/2001 of the European Parliament and of the Council of 11 December 2018 on the promotion of the use of energy from renewable sources (Text with EEA relevance.)

[5] Directive (EU) 2015/1513, https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32015L1513.

directly for agricultural land for food and feed. Bringing non-agricultural land into production elsewhere, indirect land-use, can lead to increased greenhouse gas emissions and should be avoided.

Within the BECOOL project, complete value chains are investigated, from biomass to liquid fuel production in European south and Mediterranean countries. Different types of biomass/energy crops (annual, per annual, woody, herbaceous) are considered, including investigation of the most efficient ways to harvest and process these feedstocks as preparation for conversion to liquid fuels. These crops include eucalyptus, arondo donax and biomass sorghum. Competition of biomass growth and harvest with food and feed will be avoided by incorporating energy crops into current rotational cycles and/or use degraded land without increasing GHG emissions. This work, by expert groups in Europe, is part of project work packages 1 and 2. A second part of the value chains includes investigation of the most suited conversion of the harvested crops to produce liquid biofuels via thermochemical (work package 3) and biochemical conversion (work package 4). Technology of choice must be preferably demonstrated on at least TRL 6-7. Furthermore, kerosene, a fuel primarily used in aviation, has been chosen as desired biofuel in the thermochemical approach as no good renewable fuel alternatives exists as of yet.

Thermochemical processes such as gasification, can be used to convert biomass into bio-syngas (product gas), which gas can then be upgraded to transportation fuels and chemicals. In gasification, the production of synthesis gas from biomass is a key first step in the thermochemical route, where steam, and/or air are used as gasification agents to convert biomass into product gas. This product gas consists of a mixture of H_2, CO, CH_4, CO_2, hydrocarbons and impurities such as H_2S, which exact composition depends mostly on the gasification conditions such as temperature and pressure. Gasification of biomass can be done directly by using the primary solid biomass or indirectly using a pretreated intermediate such as bio-oil and char from a pyrolysis process. An advantage of using pretreated biomass streams such as pyrolysis oil and char can be found in feedstock energy density. Typical bulk densities of wood pellets and wood chips are 650 and 220 kg/m^3 with energy densities of respectively 12 and 3.0 GJ/m^3 (assuming HHVs of 19 and 15 MJ/kg). These values are significantly lower than typical energy densities of pyrolysis bio-oils, which have bulk densities in the order of 1200 kg/m^3 and energy densities in the range of 20 GJ/m^3 (assuming an HHVs 17 MJ/kg). Energy densities of bio-oil and char mixtures/slurries are even higher (> 22 GJ/m^3), because of the high energy density of char (25-30 MJ/kg LHV). Consequently, local pyrolysis close to the biomass source followed by centralized gasification can potentially reduce transportation costs and CO_2 emissions. Moreover, relatively simpler handling/logistic operations are expected when using the fuel in liquid form.

The value chains

In the BECOOL project, both the centralized conversion of biomass via gasification and the decentralized production of intermediate energy carriers, for subsequent gasification, are being investigated, with the aim of promoting the development of resilient and robust supply chains for advanced biofuels. Three value chains are considered for the thermochemical conversion, see Figure 2, namely:

1. Harvest, transport, decentralized chipping and drying along with fast pyrolysis to produce bio-oil, followed by centralized entrained flow gasification and FT upgrading. In this scenario, the delocalized pretreatment and energy densification using (fast) pyrolysis could reduce transportation costs thereby expanding the region of origin. Pyrolysis not only increases the energy density of the biomass, it also lowers the ash content and overall, it increases the uniformity of the biomass. Excess energy produced during pyrolysis can be used to dry the biomass at the delocalized (small) facilities.

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2. Harvest, transport, chipping drying and gasification of solid biomass in indirect gasification and upgrading to FT liquid fuel. In this concept, biomass is gasified in a central location, but transportation costs might be higher due to the absence of energy densification. Only harvest and chipping takes place delocalised, whereas drying takes place in the centralised conversion plant, where excess heat is readily available. Drying at a central location might not work for biomass high in cellulose with possible fermentation as consequence.

3. Harvest, transport, decentralized chipping and drying with fast and slow pyrolysis, followed by centralized gasification of mixtures/slurries and FT upgrading. Introduction of slow pyrolysis results in char as additional intermediate. Centralised entrained flow and/or indirect gasification could be applied for conversion of char/bio-oil mixtures. Alternatively, char could be used for soil enrichment for degraded land usage.

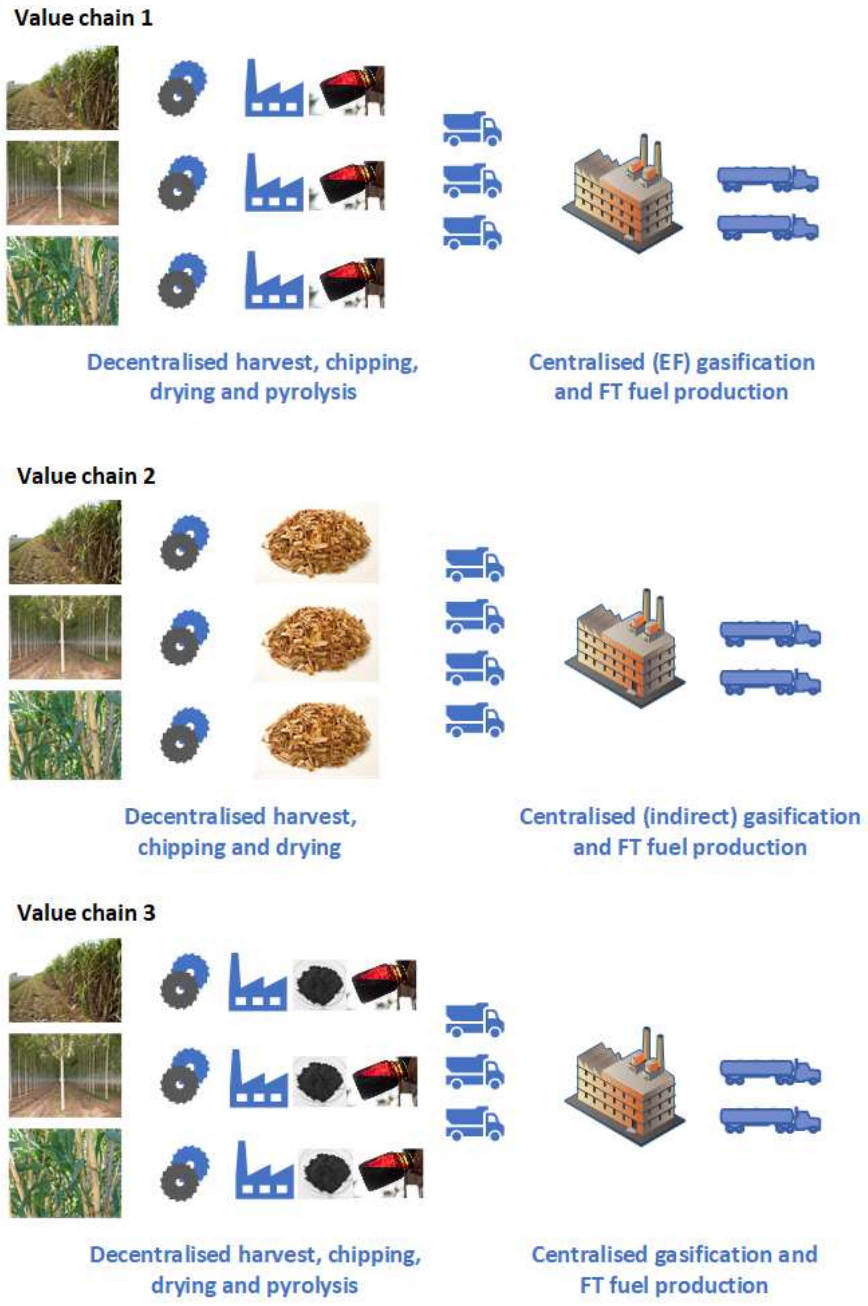

Figure 2: The three considered value chains for the thermochemical conversion of biomass.

In this work the focus is on the thermochemical conversion and technology. A first-of-a-kind (FOAK) conversion plant with a 100 MW thermal input capacity (into the gasifier) was chosen as a realistic scale for the value chains. This is a realistic scale when compared with known examples. Namely, in 2011, several projects were awarded with NER300 funding at a median scale of 160 MW synfuel [6]. These projects included Ajos BTL (Finland, biodiesel), GoBiGas phase 2 (Sweden, methane), UPM Stracel BTL (France, diesel), and Woodspirit (The Netherlands, methanol). An average of 144 M€ of funding was awarded, but none of the examples were realised. One of the largest realised gasification plants is the GoBiGas phase 1 in Gothenburg, Sweden with 30 MW biomass input and 20 MW methane output [7]. A larger scale results in lower production costs, but a lower total investment is easier to realize. For that reason, 100 MW thermal input to the gasifier was chosen with a corresponding synfuel output of approximately 50 MW.

Within the BECOOL project, actual experimental results will be generated and used to obtain accurate models of the value chains. For this reason, gasification experiments are performed to generate the required experience and data to establish valid value chains, using the energy crops chosen in this project. The solid-to-gas conversion results will be used to determine the best gas cleaning/upgrading strategy and can be used to determine the overall efficiency of the proposed thermochemical conversion.

<u>This work</u>

Results presented in this work, performed by ECN.TNO, are part of work package 3.2.1 and are divided into three sections. In Section 1, results of the indirect gasification of eucalyptus and biomass sorghum (supplied by UNIBO), part of value chain 1, are discussed. These gasification tests were performed in the lab scale 25 kW (Milena) gasifier, with a capacity of 5 kg/h. Several aspects were investigated in detail, such as the gasification behaviour of the feedstock in MILENA and the product gas composition. With this, the cold gas efficiency (CGE) and carbon conversion were determined.

In Section 2, the gasification of bio-oil and/or char (produced by RE-CORD) was studied using a direct fluidized bed gasifier as part of value chain concepts 2 and 3. This lab-based gasifier was used with a maximum feeding rate of 1 kg/h of bio-oil as well as char/bio-oil slurries. Tests will be carried out at larger scale than previously reported, in terms of process capacity with up to 1 kg/h for the gasification reactor and duration as up to 10 kg of intermediate energy carriers will be gasified. Gasification results include feedstock conversion and determination of the product gas composition.

In Section 3, the best upgrading strategy before FT synthesis will be discussed for the indirect gasification results as described in Section 1. Biomass gasification using different conversion technologies and conditions results in product gas with significantly different compositions. Each requires specific gas upgrading, including gas cleaning (including H_2S and tar removal) and conditioning (reforming and WGS) to obtain a syngas ready for FT synthesis.

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[6] NER3000. http://europa.eu/rapid/press-release_MEMO-12-999_en.htm

[7] A. Larsson, I. Gunnasrsson and F. Tengberg, The GoBiGas Project, Demonstration of the Production of Biomethane from Biomass via Gasification, 2018.

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2. Gasification of solid biomass

2.1 Experimental and methods

Eucalyptus and biomass sorghum were supplied by the University of Bologna and shipped from Italy to ECN.TNO late 2017 and were received as shown in respectively Figure 3 and Figure 4. Eucalyptus is a fast-growing tree, often grown for the wood industry. Eucalyptus is a perennial crop, which means it is planted and harvested every two years (short rotation coppice) or every 5 years (medium rotation coppice). After harvesting it contains about 50% moisture. Biomass sorghum is an herbaceous crop and is harvested yearly. In Italy Sorghum is harvested, dried directly on the field.

Figure 3: Biomass Sorghum as received.

Figure 4: Biomass Eucalyptus as received.

The moisture content and bulk density of the as-received material were determined and compared, as reported in Table 1.

Table 1:Moisture content and bulk density of the as received biomass.

	Unit	Eucalyptus	Sorghum
Moisture content (ar)	[%]	8.0	6.2

Bulk density (ar)	[g/L]	120	100

The low moisture content of 8.0% for eucalyptus and 6.2% for Sorghum indicates that they have been dried after chipping. Typically, from the field, Eucalyptus contains ~50% moisture after harvest and Sorghum contains ~70% or as low as 30% moisture after on-field drying depending on climate/weather conditions. The moisture content is more than suitable for indirect gasification where ~30% moisture or less is preferred. However, both materials are not yet suited for feeding into the lab-scale (Milena) gasifier, because of the very low bulk density and shape/size.

2.1.1. Eucalyptus pretreatment

It was decided to grind the as-received Eucalyptus, for which a Retsch SM300 grinder was used over 2, 4 ,6 and 8 mm screens. The 2 mm screen resulted in a fine powder, whereas the 4 mm screen gave the desired particle size. Unfortunately, the 4 mm material also proved difficult to feed due to the presence of long fibers and a low bulk density. For this reason, the decision was made to attempt to pelletize the grinded material which would then again be grinded. As the material contained about 8% moisture, additional water was added to increase the water content to 13%, which is optimal for producing pellets. A 60 L plastic drum was used to mix the material with water after which it was shaken thoroughly.

However, pelletizing the humidified Eucalyptus led to the formation of a grey dust. After addition of excess water, some pellets were made as shown in Figure 4. Changing the size of the pellet mould to a smaller one did not result in a reduction of the amount of powder. The powder could be turned into pellets only after the addition of 30% water. The produced pellets were successfully dried at 50°C and contained 38% moisture. These pellets were very hard and therefore easily grinded over the 4 mm screen with little dust and a material that could easily be fed (gravel like) with a transport screw. However, this process of pelletizing was discarded for Eucalyptus because the material was too different from the original in terms of colour and hardness.

Figure 5: Eucalyptus pellets from a 6 mm mould (left) and grinded pellets over a 4 mm screen (right).

Eventually, a different approach was chosen. The grinded (4 mm) as received material was fractioned by sieving over a 2 mm sieve to remove the particles that contained the loose fibers and fluffy material (that causes “bridging” in the feeding bunker and screw). The small <2 mm wood particles, about 85% of the material, could now be fed properly. The <2mm sieve fraction and the residue are shown in Figure 6. In total, 45 kg of this fraction was prepared.

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Figure 6: Eucalyptus <2mm sieve fraction (left) with the residue (right).

2.1.2. Sorghum pretreatment

Similarly to eucalyptus, biomass sorghum (simply referred to as sorghum) was first grinded to 4 mm and then humidified to 13%. The humidified Sorghum was pelletized using a 6x18.5 mm mould. Sorghum was fed into the pellet mill with a feeding screw at 16 kg/h where additional steam was added at a temperature of 120°C. The Sorghum/steam mixture reached a temperature of 70-75°C and the formed pellets came out with a shiny glow at 100-110°C. In total, 60 kg of pellets were produced. These pellets were then dried at 50°C after which they were grinded again over the 4 mm screen. Eventually, 45 out of 60 kg pellets were grinded, see Figure 7.

Figure 7: Sorghum pellets (left) with the grinded pellets (right).

2.1.3. Feedstock analysis

The proximate and ultimate analysis of both pretreated materials can be found in Table 2. Complementary, the elemental analysis can be found in the Appendix. Lower heating values (LHV) of both materials are similar at 16 MJ/kg. Sorghum contains a considerable amount of ash (5%), which might be expected from herbaceous biomass [8]. Part of this ash is soil, indicated by the high Si content of 11000 ppm. In the pretreated eucalyptus, only 150 ppm Si was present. Moreover, sorghum contains 1000 ppm sulphur, much more than the 340 ppm

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[8] Robert R. Bakker and H.W. Elbersen, 2005, Managing ash content and -quality in herbaceous biomass: An analysis from plant to product.

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in eucalyptus. Chlorine concentrations are high in both samples with respectively 0.13% and 0.15% in eucalyptus and sorghum. The nitrogen concentration in sorghum is high with 0.9% versus 0.4% in Eucalyptus. For comparison, beech wood contains 200-300 ppm sulphur, 0.0056% chlorine and 0.33% nitrogen [9].

Table 2: Proximate and ultimate analysis.

	Unit	**Eucalyptus**	**Sorghum**
LHV	[MJ/kg], ar	16.0	15.8
LHV	[MJ/kg], daf	17.8	17.4
Volatile content	[%], db	77.8	74.3
Ash content	[%], db	1.5	5.0
Moisture	[%], ar	7.9	3.8
C	[%], db	47.4	44.8
H	[%], db	6.1	5.9
O	[%], db	44.0	41.8
N	[%], db	0.4	0.9
S	[%], db	0.0340	0.100
Cl	[%], db	0.130	0.150

2.1.4. The MILENA gasifier

The gasification tests were done using the lab-scale indirect gasifier MILENA, which has a capacity of up to 5 kg/h solid biomass. A PFD and photo of Milena can be found in Figure 8. The BFB combustor has a diameter of 26.3 cm and the riser has an internal diameter of 3.6 cm. In Milena, gasification of biomass takes place in absence of air/oxygen, which results in a high calorific product gas [10]. The mild (700-900°C) gasification leaves char, which is transported to the combustion zone and burned in the presence of air. The heat supplied by char combustion is required for the endothermic gasification.

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[9] Phyllis2, database for biomass and waste, www.phyllis.nl

[10] C. van der Meijden, Development of the MILENA gasification technology for the production of Bio-SNG, PhD thesis, 2010

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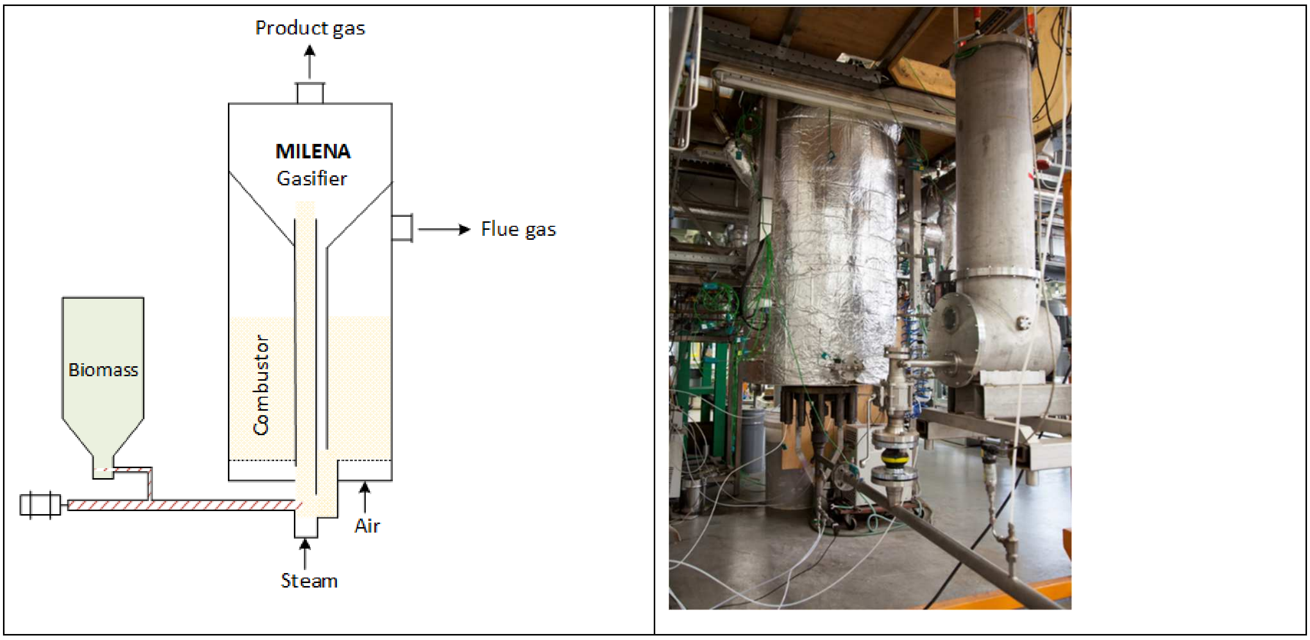

Figure 8: Schematic of the lab scale indirect gasifier Milena. Reactor is filled with sand that circulates through riser into settling, back into combustor. Add Milena 30kw lab-scale installation.

2.1.5. Gas analysis

To determine the gas composition, several different gas analyses were performed, see Table 3. These included continuously/online analysis with the gas analysis set (including a gas monitor set and µ-GC) and off-line analysis. Off-line analysis proceeds via extraction of the gas into a gas bag and subsequent gas analysis and/or via entrapment of the gas in cooled impinger bottles filled with an absorption liquid followed by wet chemical analysis.

To determine the concentration of tar, a wet chemical method is used, called the tar guideline. Here, isopropyl alcohol (IPA) placed in impinger bottles is used to trap tar through condensation. Consecutive cooling the raw gas to 40°C and -20°C enables the complete removal of both tar and tar aerosols, see also Figure 9. Naturally, also water is removed almost completely due to the traps at -20°C, which allows for determination of the water content in the product gas. Consecutively, GC analysis and Karl-Fischer titration of the IPA solution is performed to determine respectively the tar and water content in the liquid and therefore the gas.

Table 3: Applied gas analysis performed during the gasification experiments.

Sampling method	Components	Frequency	Measured components
Online Gas monitor set	Main gas	Continuous	CO, CO_2, CH_4, H_2, O_2
Online µ-GC analysis	Light gas	Every 5 minutes	CO, H_2, CH_4, C_2H_6, C_2H_4, C_2H_2,C_6H_6, C_7H_8, CO_2, N_2, H_2S, COS, Ne, Ar
Gas bags	Sulphur and trace carbon	As chosen	S-GC for Sulphur components and T-GC for trace hydrocarbons (up to toluene)
Tar guideline	Tar, H_2O	As chosen	Tar and condensables including water.

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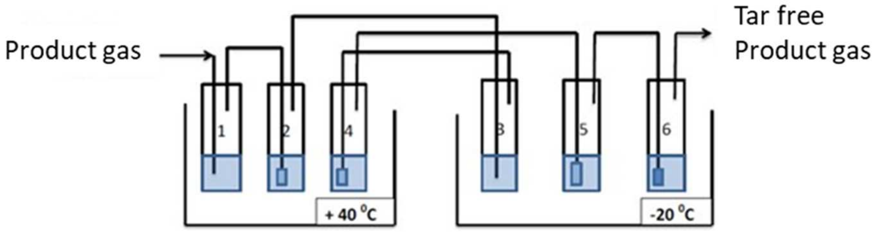

Figure 9: Tar guideline setup [11].

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[11] S.V.B. van Paasen et al. ECN-C--02-090, 2002, Guideline for Sampling and Analysis of Tar and Particles in Biomass Producer Gases.

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2.2. Results and discussion

In total 5 experiments were performed over 4 days, with a focus on gasification performance, including gasification stability, product gas composition and conversion efficiency. The aim was to both demonstrate the successful application and gasification of different types of biomass. Moreover, with the gas composition, the best upgrading strategy towards FT fuels can be determined and the conversion efficiency can be used to establish the overall process efficiency in the value chain models.

2.2.1. Experiment 1, eucalyptus.

Gasification settings

The experimental settings used during the gasification of Eucalyptus can be found in Figure 10 and Table 4. An average gasification temperature of 808°C was applied. CO_2 was used as a carrier gas for steam and in the transport screw. The total amount of steam was 1.2 kg/h which was chosen to simulate a moisture content of 20-30 wt% in the feedstock during gasification, which would be a realistic value at large scale. Both argon and neon were used as tracer gas to determine the product gas volume from the micro-GC data. Furthermore, 100 L/min of air was enough for full combustion of char leaving a slight excess of oxygen in the flue gas. Both argon and neon were used as tracing gas to determine the gas flows. As can be found in Table 4, only the averaged data between 9:07 and 9:47 was used as only in this period all parameters (incl. T, P, flow rates) were relatively constant. Gas analysis (offline and online) were performed at sampling point S1 (product gas) and S2 (flue gas).

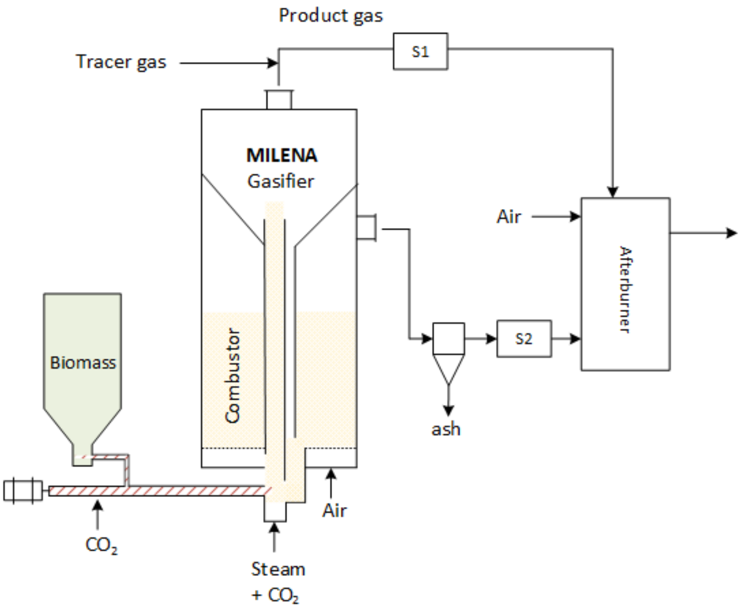

Figure 10: Schematic of the experiment setup including the experimental settings during Eucalyptus gasification. Both sampling points, S1 and S2 are included.

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Table 4: Eucalyptus indirect gasification conditions.

	Unit	
Time	[hh:mm]	9:07 – 9:47
Bed material		Olivine
T gasification in settling chamber	[°C]	808
T in bed combustor	[°C]	842
Fuel flow	[kg/h]	4.75
Feeding screw CO_2 flow	[NL/min]	3.0
Riser steam flow	[kg/h]	1.2
Riser steam carrier CO_2 flow	[NL/min]	1.0
Tracer gas Ne	[NmL/min]	20.0
Tracer gas Ar	[NL/min]	1.0
Combustion air	[NL/min]	100
Afterburner air	[NL/min]	397

<u>Experiment observations:</u>
A good impression of the (one-day) experiment can be found in the gasifier's temperature profile, see Figure 11. This plot includes the start-up of the gasification process, which occurred with beech wood. Beech wood is used for start-up as it is a relatively clean benchmark fuel, from which the gasification behaviour is known and works well. At 8:05, the switch from beech wood to Eucalyptus was made, which did not directly lead to major changes in temperature. As expected, the temperature in the combustor is about 35°C higher than the temperature in the riser (referred to as the gasification temperature, TI601). After the initial period, the tracing temperature of the reactor (in the reactor walls) was increased from 800°C to 850°C to ensure a gasification temperature of around 800°C. The dotted vertical lines mark the stable period running from 9:07 to 9:47. The actual monitored averaged values during this period of stable operation can be found in Table 4. A 42°C difference between the reactor walls (set temperature, 850°C) and the monitored temperature in the riser (TI601, 808°C) was obtained. Here, the trace heating supplies the additional energy that is required to maintain the gasification temperature. In a large-scale application, this heat can be supplied by an external fuel. Candidates for this supply include e.g. tar which is removed from the product gas in the OLGA gas scrubber, or purge gas available from downstream processing units.

All monitored temperatures, as shown in Figure 9 increase slightly after 8:05, until 9:47 when the experiment was ended. This is due to an increase of the temperature setting of the trace heating in MILENA.

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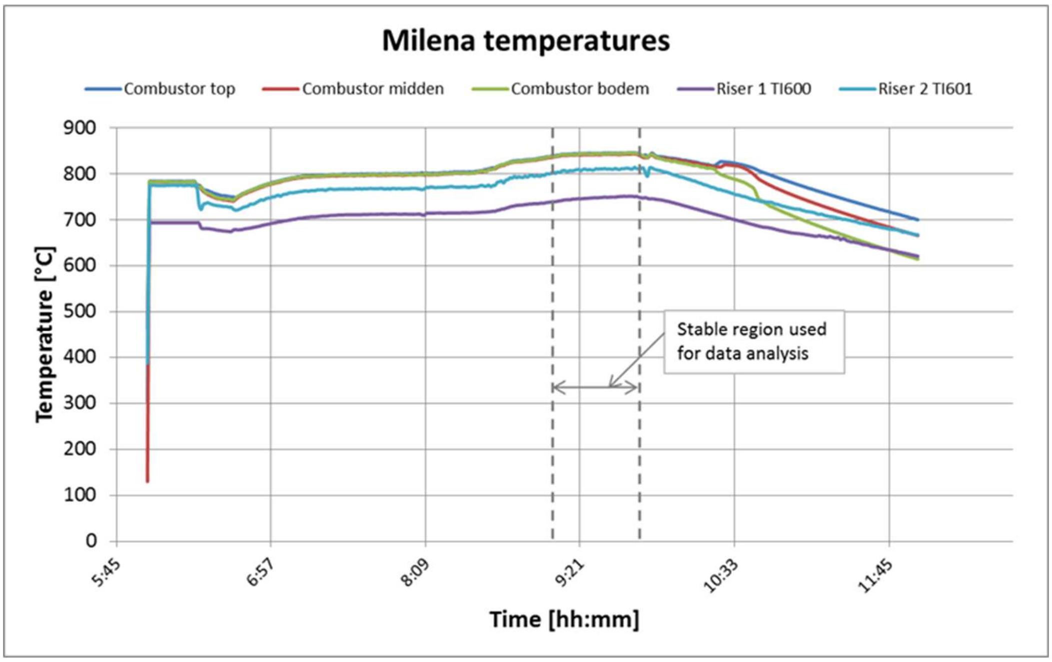

Figure 11: Temperature profile during the gasification of Eucalyptus.

Additionally, the monitored pressure during the gasification is plotted in Figure 12. It includes the pressure in the olivine bed (above bed plate), the freeboard (above the bed), the settling chamber (top of the riser), the pressure difference between the freeboard and the settling chamber and additionally, the pressure in the transport screw. In this plot, the start of the experiment at 8:05 is clearly registered by a dip disturb in the bed plate pressure. After this switch, the conditions stabilize somewhat. Overall, the pressure in the combustor was about 10 mbar higher than in the gasifier, indicated by the DP freeboard/settling chamber.

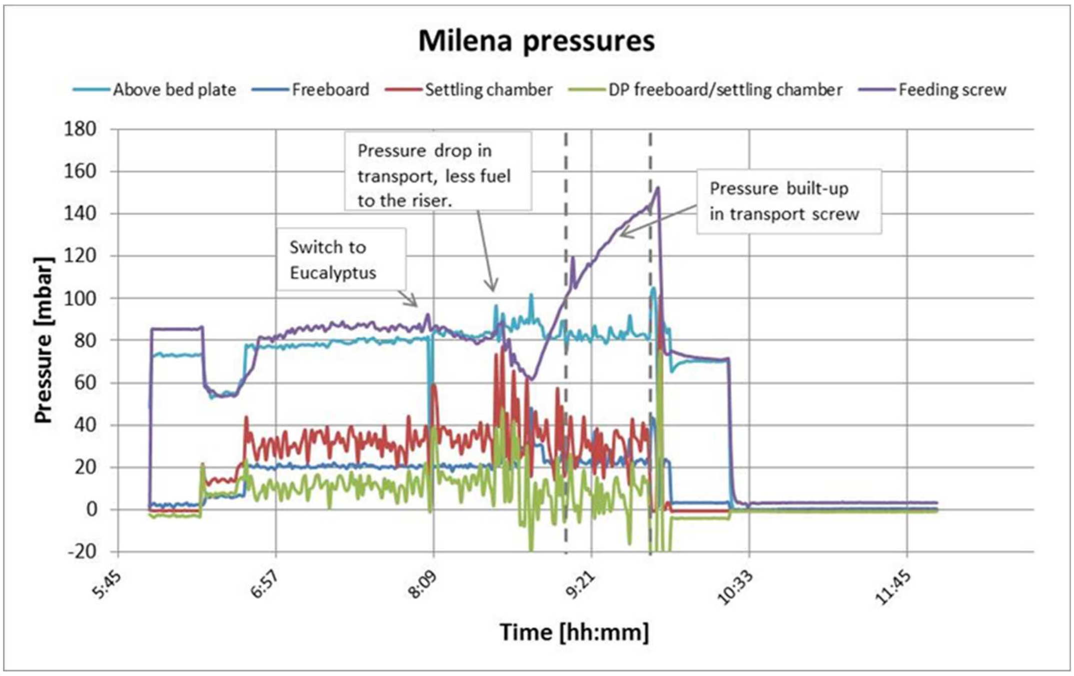

Figure 12: Pressure in MILENA during Eucalyptus gasification. The region between the dotted lines represents the stable region of operation.

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At around 8:40, the pressure in the transport screw decreases indicating that less fuel was fed to the riser. Nitrogen gas on the riser was used temporarily to overcome this lack of fuel and volatile matter and force start the bed solids circulation. This worked, but the pressure in the transport screw started to build up slowly. This eventually resulted in a shutdown of the system, because of a blockage in the transport screw (probably at the tip, just before the riser). This could be explained by the low bulk density of the feedstock and the large volume that needs to be transferred through the transport screw.

Product gas composition

In Figure 13, the product gas composition as determined by the online gas analyser is shown. It nicely shows why the stable region was chosen to obtain the reliable averaged data. During stable operation (highlighted in the figure by the dotted lines), the product gas contains 18-19 vol% H_2, 34-35 vol% CO, 11-12 vol% CH_4 and 22-24 vol% CO_2. A very similar composition was found before 8:05, during the gasification of beech wood. It should be stated that the CO_2 concentration is somewhat high at 22-24 vol%, because CO_2 was also fed to the gasifier as carrier gas. At around 8:40, a dip can be observed in the measured concentrations. This drop is caused by dilution of the product gas with nitrogen, which was used temporarily to secure circulation at that stage.

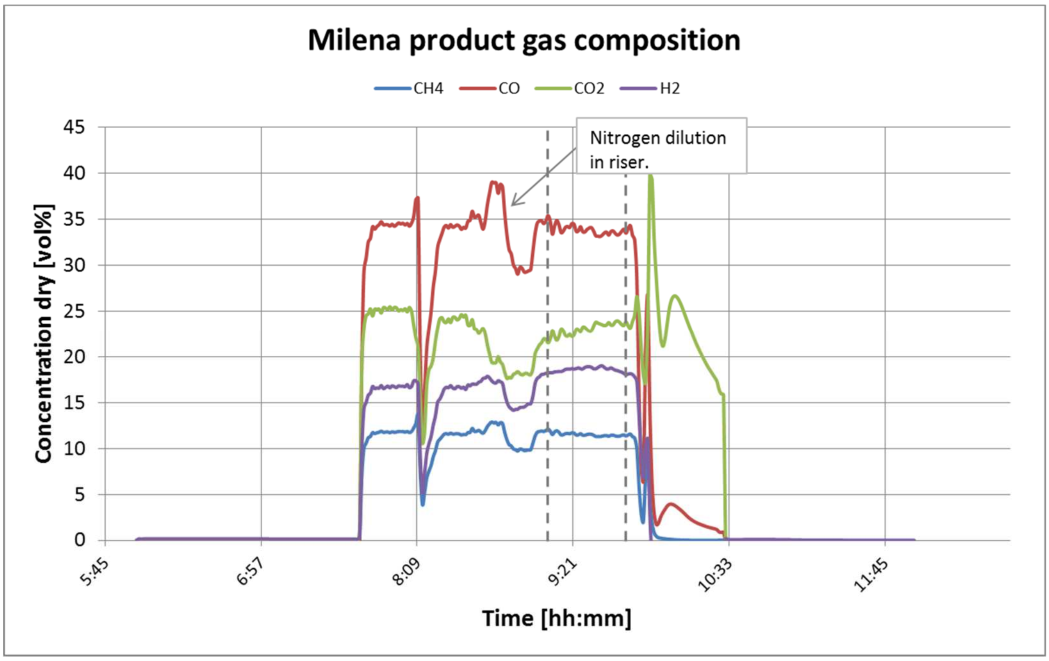

Figure 13: Product gas composition during the gasification of Eucalyptus.

The complete gas composition, as determined by the gas analyser, the micro-GC, GC and the tar guideline, is shown in Table 5. In this work, when referring to tar, it is considered without benzene and toluene, unless stated otherwise. This is done, because toluene and benzene can be determined separately by the µ-GC as well as via the tar guideline method. Both argon and neon were added as tracer gas from which the total gas volume and gas flow can be determined accurately. In this work, the neon number was used unless stated different.

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Table 5: Eucalyptus product gas composition on dry basis.

Gas component	**Method**	**Unit**	**Concentration, 808°C**
CO	µ-GC	Vol%	33.8
H_2	Gas monitor	Vol%	18.6
CO_2	µ-GC	Vol%	21.9
CH_4	µ-GC	Vol%	11.4
N_2	µ-GC	Vol%	3.5
C_2H_2	µ-GC	Vol%	0.3
C_2H_4	µ-GC	Vol%	4.2
C_2H_6	µ-GC	Vol%	0.4
Benzene	µ-GC	ppmV	7852
Toluene	µ-GC	ppmV	1689
Sum C3	C-GC	ppmV	3621
Sum C4	C-GC	ppmV	508
Sum C5	C-GC	ppmV	1005
Sum C6 (without benzene)	C-GC	ppmV	0
H_2S	µ-GC	ppmV	176
COS	µ-GC	ppmV	15
Thiophene	S-GC	ppmV	13
Methylmercaptane	S-GC	ppmV	7
Other S-organics	S-GC	ppmV	2
NH_3, HCN, HCl	--	--	n.d.
Tar total (excl. benzene and toluene)	Tar guideline	g/m3	39.7
Argon*	µ-GC	Vol%	2.3
Neon*	µ-GC	ppmV	416
Total		Vol%	98.6
Water content	Tar guideline	Vol%	43.2

As can be seen in Table 5, the H_2/CO ratio was somewhat low at 0.55. The concentration of benzene and toluene were respectively 0.8% and 0.2%. The concentration of all additional hydrocarbons was in line with prior experiments performed with woody biomass.

As for the sulphur components in the product gas, 15 ppmv COS and 176 ppmv H_2S were found. Also, the organic sulphur components are at acceptable levels with 13 ppmV thiophene and 7 ppmV methylmercaptane.

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A tar measurement was applied on the product gas using the tar guideline method in isopropyl alcohol (IPA). From the IPA, one sample was analysed on a non-polar GC-MS column using a standardized procedure to determine the concentration of each component. This provides an overview of most tar components that are present in the product gas. The total tar concentration in the product gas was 39.7 g/Nm^3, on a dry basis excluding benzene and toluene which are already identified by the μ-GC measurements. This includes unknown components that were detected in the GC but are not identified. For these components an average response factor is used to estimate their concentration. An overview of the known and unknown tar molecules is shown in Figure 14. The main component in tar is clearly naphthalene with 8308 mg/Nm^3, followed by xylene/styrene 3138 mg/Nm^3 and 3341 mg/Nm^3 o-cresol/indene.

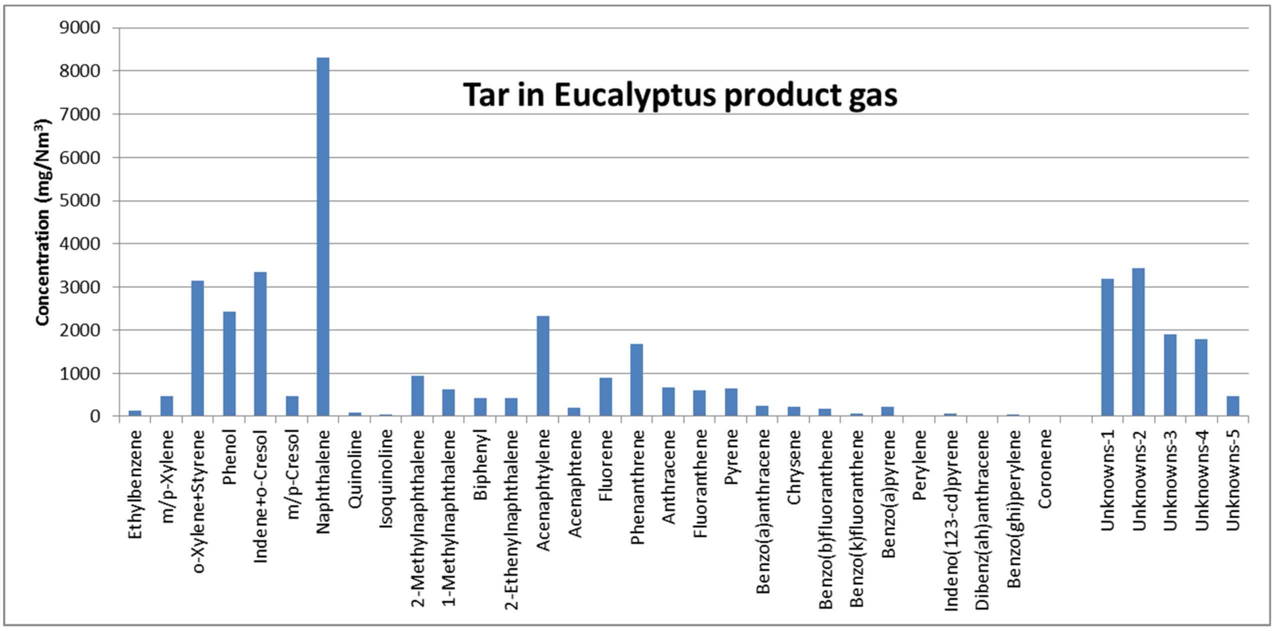

Figure 14: Eucalyptus product gas tar composition.

Additionally, to the product gas composition, the flue gas composition is reported in Table 6:

Table 6: Summary of the flue gas composition (eucalyptus).

Flue gas	Unit	Eucalyptus
CO_2	[vol%]	12.1
O_2	[vol%]	5.6
CO	[ppmV]	51.7
NO	[ppmV]	242.0
NO_2	[ppmV]	5.5
Total flow (based on N_2)	[NL/min]	97.7

In short, eucalyptus feeding of this fraction was troublesome as the eucalyptus feeding was blocked. Later it was found this had most likely to do with the feeding rate which cannot be kept at the normal feeding rate of

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up to 5 kg/h simply because the density of the material was extremely low with 220 g/L. In experiment 5, it was demonstrated that a lower feed rate resulted in stable gasification. The product gas composition was in line with what is expected for woody biomass.

2.2.2. Experiments 2 and 3, biomass sorghum.

Gasification settings

The gasification of Sorghum was performed at 717°C and 811°C. Therefore, the results of the run are divided into two (stable) regimes. Regime one from 7:45 to 9:10 at 717°C and regime 2 from 11:30 to 12:40 at 811°C. The additional parameters were however kept constant during the experiment, see **Errore. L'origine riferimento non è stata trovata.** and Table 7. Again, both argon and neon were used as tracer gas and CO_2 was used to flush the feed and steam carrier.

Table 7: Gasification conditions used during sorghum gasification.

	Unit	Regime 1	Regime 2
Time	[hh:mm]	7:45 – 9:10	11:30 – 12:40
Bed material		Olivine	Olivine
T gasification in settling chamber	[°C]	717	811
T in bed combustor	[°C]	750	845
Fuel flow	[kg/h]	4.43	4.43
Feeding screw CO_2 flow	[NL/min]	3.0	3.0
Riser steam flow	[kg/h]	1.2	1.2
Riser steam carrier CO_2 flow	[NL/min]	1.0	
Tracer gas Ne	[NmL/min]	20	20
Tracer gas Ar	[NL/min]	1.0	1.0
Combustion air	[NL/min]	115	115
Afterburner air	[NL/min]	397	397

Observations

In Figure 15, the temperature profile in the gasifier is shown illustrating the two temperature regimes at 717 °C (reactor set at 730°C) and a second at 811°C (reactor set at 837°C). This allowed comparison of the product gas composition, carbon conversion and conversion efficiency at different temperature. As can be observed, within the one-day experiment, the gasification proceeded smoothly without any interruption because of biomass feeding (successful pretreatment). Like the temperature, the pressures were stable during the experiment. The pressure difference between freeboard (combustor) and settling (gasification) was around 10 mbar, which prevents gas passing from combustor to gasifier and vice versa.

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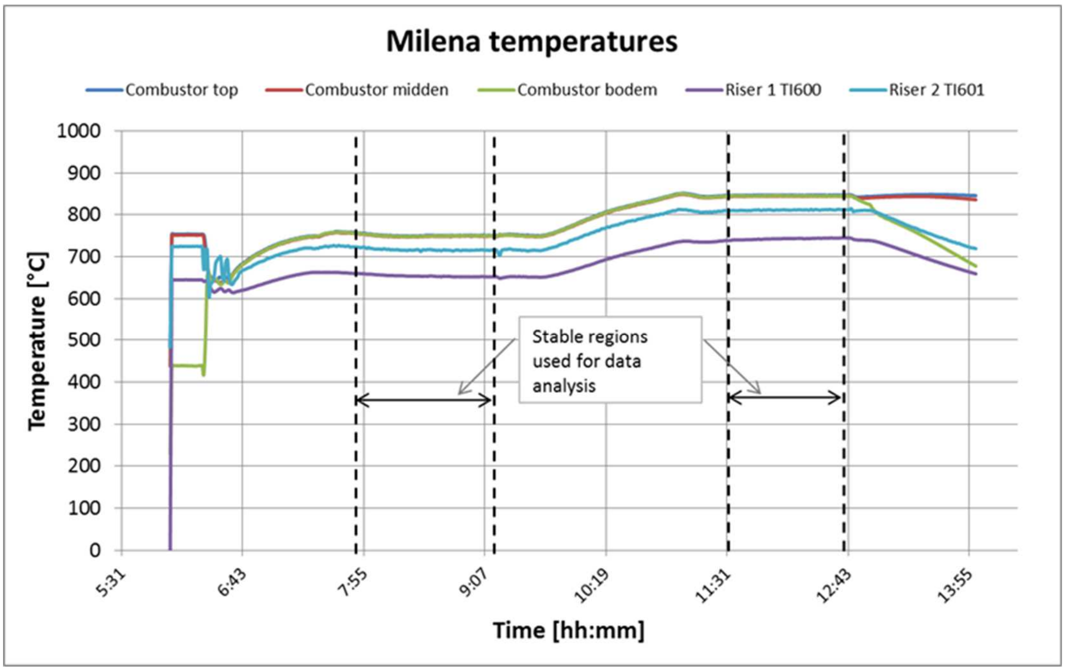

Figure 15: Temperature profile in Milena during sorghum gasification.

In Figure 16, the gas composition during the experiment are shown. When the temperature was increased from 717°C to 811°C, the relative concentration of the main gases changed only slightly. Most noticeable is the H_2 concentration that increases from 16.6 to 19.2% and CO that decreases from 27.9 vol% to 27.3 vol%. This indicates more water gas shift activity which might be a kinetic effect, with higher activity at higher temperature.

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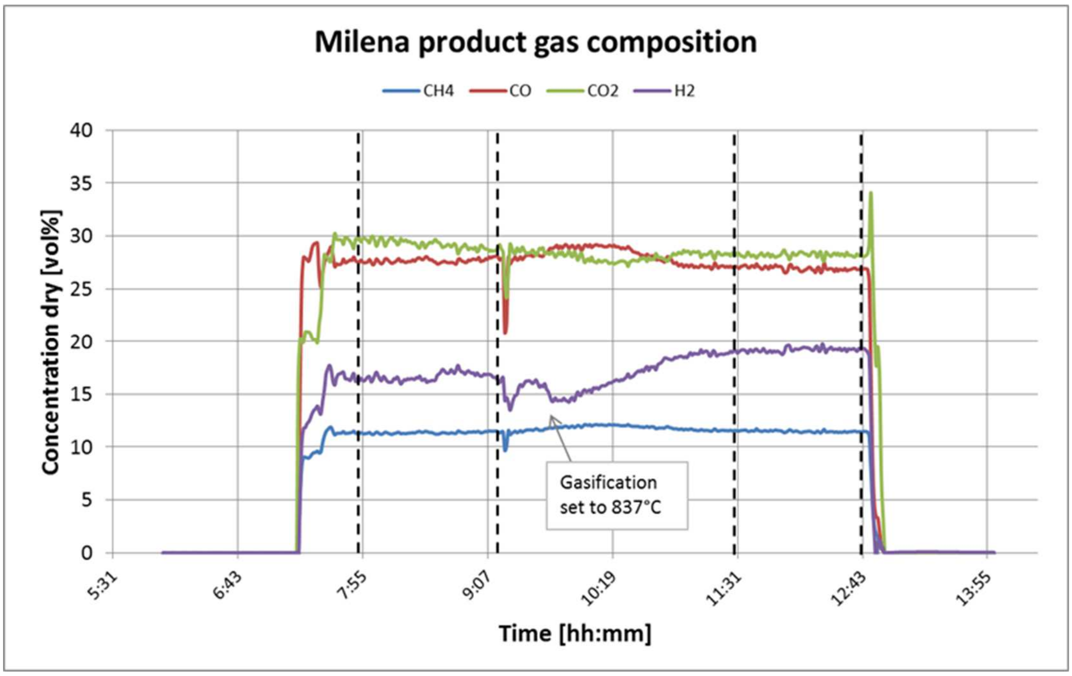

Figure 16: Product gas composition from the gas analyser during the gasification of sorghum.

Besides the higher H_2 concentration at 811°C, C_1 and C_2 hydrocarbon concentration remain constant and the concentration of C_3-C_6 hydrocarbons decreases, as shown in Table 8. However, the concentration of benzene increases from 4587 to 7448 ppmV. What directly stands out is the H_2S concentration between the low and high temperature conditions. The concentration profile of H_2S and COS, which are monitored by the µ-GC and therefore available for the entire run is highlighted in Figure 17. Under the initial low temperature conditions, the H_2S concentration in the product gas was 461 ppmv, which increased to 878 ppm at 811°C. This can be explained both by a higher conversion and by sulphur transport. Transport can occur, because olivine instead of silicon sand was used as bed material. Namely, the iron in olivine is capable of adsorbing H_2S, especially at low temperature [[12]]. This bound H_2S is then transported to the combustion zone of MILENA where it is oxidized to SO_2 and removed from the system. This continuous adsorption/desorption process can significantly diminish the amount of sulphur in the product gas. At high temperature, the amount of H_2S which is bound and therefore transferred to the combustor is much lower. A comparison with sand instead of olivine (see experiment 4) confirmed that indeed using sand resulted in a high H_2S content of 982 ppmV with 42 ppmV COS at 730°C. Surprisingly, the COS concentration decreased from 58 to 9 ppmV at 811°C, which was confirmed by both the micro-GC as the S-GC. For the organic sulphur components, thiophene and mercaptans, the concentrations vary. For methyl mercaptan, the concentration is significantly lower at high gasification temperature (19 vs 105 ppmv), possibly caused by more cracking/reforming activity. Thiophene is more stable and actually increased from 33 to 48 ppmV, possibly due to a similar transport effect as observed for H_2S.

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[12] J. Marinkovic, H. Thunman, P. Knutsson and M. Seemann, "Characteristics of olivine as a bed material in an indirect biomass gasifier", Chemical Engineering Journal, 2015, 279, 555-566.

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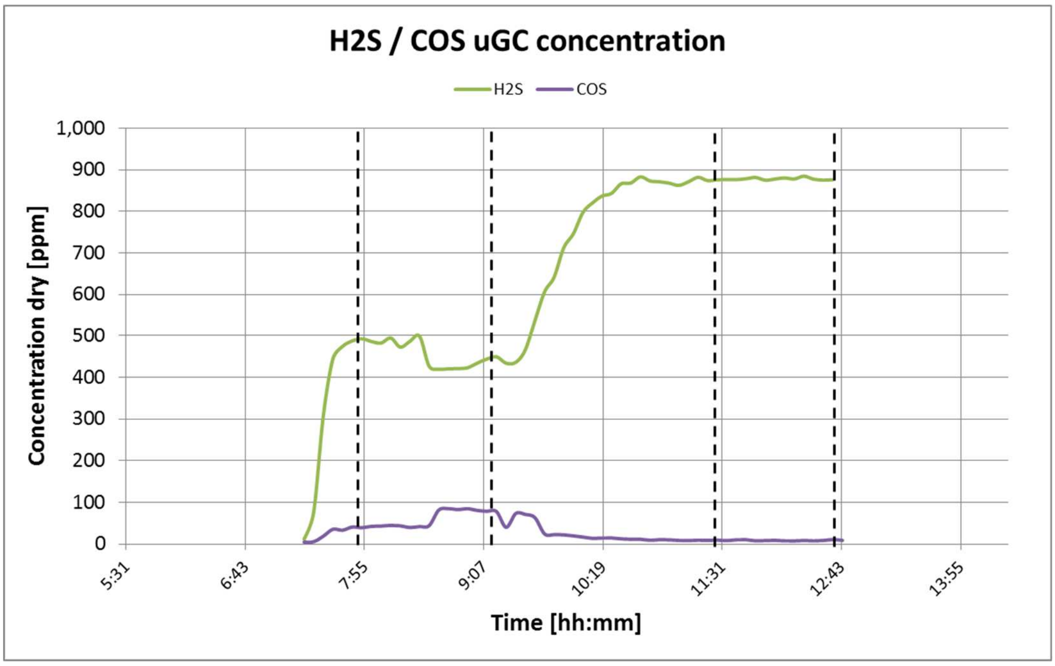

Figure 17: H_2S and COS in sorghum product gas.

Table 8: Average sorghum product gas composition.

Gas component	**Method**	**Unit**	**R1, 717°C**	**R2, 811°C**	***Eucalyptus***
CO	µ-GC	[vol%]	27.9	27.3	*33.8*
H_2	Gas monitor	[vol%]	16.6	19.2	*18.6*
CO_2	µ-GC	[vol%]	29.1	27.8	*21.9*
CH_4	µ-GC	[vol%]	11.2	11.4	*11.4*
N_2	µ-GC	[vol%]	2.5	3.3	*3.5*
C_2H_2	µ-GC	[vol%]	0.2	0.2	*0.3*
C_2H_4	µ-GC	[vol%]	3.8	4.3	*4.2*
C_2H_6	µ-GC	[vol%]	0.8	0.4	*0.4*
Benzene	µ-GC	[ppmV]	4587	7448	*7852*
Toluene	µ-GC	[ppmV]	1426	1328	*1689*
Sum C3	C-GC	[ppmV]	7788	1763	*3621*
Sum C4	C-GC	[ppmV]	1252	283	*508*
Sum C5	C-GC	[ppmV]	1431	665	*1005*
Sum C6 (excluding benzene)	C-GC	[ppmV]	9	0	*0.0*
H_2S	µ-GC	[ppmV]	461	878	*176*
COS	µ-GC	[ppmV]	58	9	*15.0*
Thiophene	S-GC	[ppmV]	33	48	*12.9*
Methylmercaptane	S-GC	[ppmV]	105	19	*6.5*
Other S-organics	S-GC	[ppmV]	9	11	*2.3*
NH_3, HCN, HCl	--	nd	nd	nd	*n.d.*

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Tar total (excl. benzene and toluene)	Tar guideline	[g/Nm^3]	42.7	nd	*39.7*
Argon*	µ-GC	[vol%]	2.8	2.2	*2.3*
Neon*	µ-GC	[ppmV]	546	427	*416*
Total		[vol%]	97.1	97.4	*98.6*
Water content	Tar guideline	[vol%]	51.0	nd	*43.2*

Nd = not determined.

A tar guideline measurement was done only during the initial gasification period at 717°C. The determined tar concentration in the product gas was 42.7 g/Nm^3, on a dry basis excluding benzene and toluene but including the unidentified tar components. An overview of the identified tar molecules is shown in Figure 18. The total tar concentration is somewhat higher than for Eucalyptus, which is to be expected at a lower gasification temperature. Moreover, the main tar component is phenol with 8395 mg/Nm^3 and not naphthalene which is an indication of a shift to lighter tar components as is the case with low temperature gasification (more tar, but lighter tar molecules).

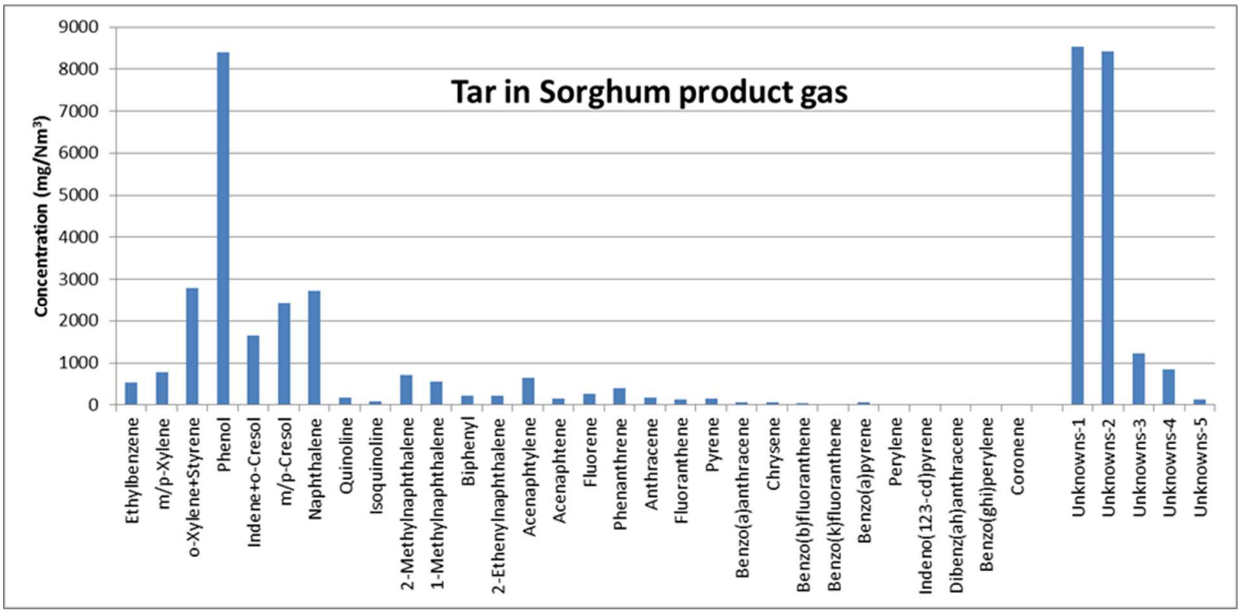

Figure 18: Tar composition in sorghum product gas.

The flue gas composition is shown in Table 9.

Table 9: Summary of the flue gas composition (sorghum).

Flue gas	**Unit**	**Sorghum**
CO2	[Vol%]	13.6
O2	[Vol%]	3.7
CO	[ppmV]	109
NO	[ppmV]	413
NO2	[ppmV]	14

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Total flow (based on N2)	[NL/min]	108.7

In short, the gasification of sorghum proceeded without substantial problems due to the proper pretreatment procedure, required at this small scale. Also, no bed agglomeration was observed, even at 811°C. Notably, only the H_2S concentration of 176 ppmv for eucalyptus and over 400 ppmv for sorghum varies significantly whereas all other components are remarkably similar between biomass types.

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2.2.3. Experiment 4, biomass sorghum.

Experiment settings

In experiment 4, the gasification of pretreated biomass sorghum was performed at 730°C (in between experiment 2 and 3) with sand as bed material. The average settings and conditions of the gasifier can be found in Table 10.

Table 10: Gasification settings sorghum.

Setting	**Unit**	
Overall experiment	[hh:mm]	09:00-15:30
Data averaged	[hh:mm]	11:30-13:00
Bed material		44 kg silica sand
T gasification in settling chamber	[°C]	730
T in bed combustor	[°C]	759
Fuel flow	[kg/h]	4.2
Feeding screw CO_2 flow	[NL/min]	3.0
Riser steam flow	[kg/h]	1.0
Riser steam carrier CO_2 flow	[NL/min]	1.0
Tracer gas Ne	[NmL/min]	10
Tracer gas Ar	[NL/min]	1.0
Combustion air	[NL/min]	109
Afterburner air	[NL/min]	347

Observations

In Figure 19, the pressure profile of the gasifier during the experiment is shown (temperatures were relatively stable). The gasifier was started with beech wood chips to achieve stable conditions before the feed was switched to the bunker containing sorghum. The gasification was relatively stable, till 13:30 when the regulator valve that controls the flow to the afterburner got blocked. This was probably caused by condensation due to the high tar concentration.

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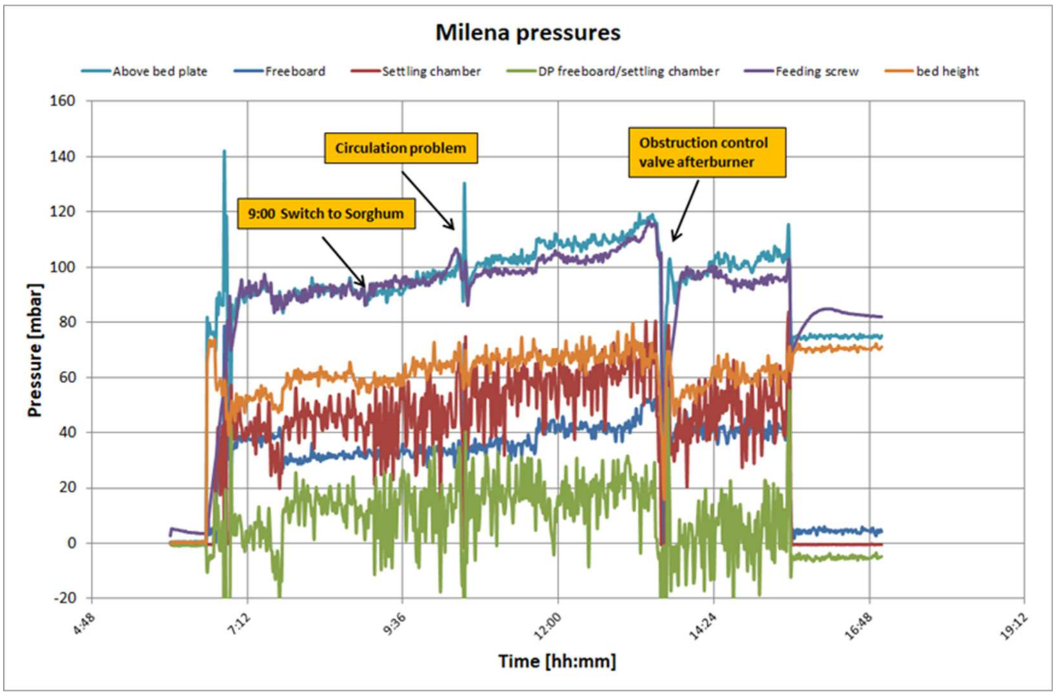

Figure 19: Monitored pressure within the MILENA gasifier during the gasification of sorghum.

Gas composition

The gas composition during the experiment can be found in Figure 20. The complete gas composition of the product gas, monitored at the absorber (after OLGA) i.e. the product gas after quantitative removal of tar, is shown in Table 11. Unfortunately, the gas composition downstream Milena was not determined, however, based on previous experience, it can be assumed that tar is removed in OLGA and approximately 20% of benzene and toluene are removed. The other components, permanent gases, light hydrocarbon vapours and H_2S/COS are not captured by OLGA. What stands out from the gas components is the level of sulphur. The H_2S concentration is very high with 982 ppmv. As sand was used in this experiment as bed material and not olivine, no sulphur transport to the combustor can take place and most sulphur ends up in the product gas end not in the flue gas as was the case in experiment 2 and 3 where olivine was used. Activated olivine can also lead to more shift activity, but also to more oxygen transfer from the combustor to the gasifier leading to more CO2 formation.

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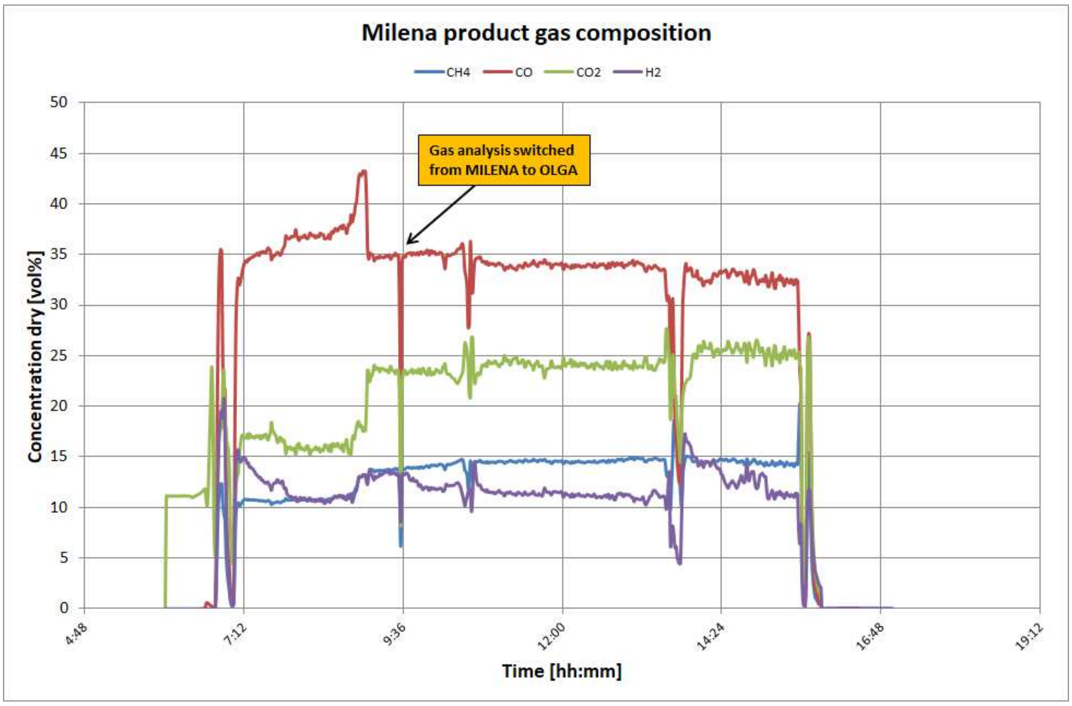

Figure 20: Sorghum product gas composition monitored by the gas analyser.

As mentioned above, the obtained tar concentration only serves as an indication. Namely, the tar sample was obtained after the tar removal unit (OLGA) and not directly at the gasifier outlet. Presumably, as with woody biomass gasification, much more tar will be present in the product gas, in the range of 40-60 g/Nm^3, when using sand as bed material.

Table 11: Average gas composition, sorghum gasification (730°C), downstream OLGA and Downstream ZnO bed.

Gas component	**Method**	**Unit**	Downstream OLGA, sand	**R1, 717°C**	**R2, 811°C**
Averaged			11:30-13:00		
CO	µ-GC	[vol%]	34.3	27.9	27.3
H_2	Gas monitor	[vol%]	11.3	16.6	19.2
CO_2	µ-GC	[vol%]	23.3	29.1	27.8
CH_4	µ-GC	[vol%]	14.5	11.2	11.4
N_2	µ-GC	[vol%]	3.5	2.5	3.3
C_2H_2	µ-GC	[vol%]	0.1	0.2	0.2
C_2H_4	µ-GC	[vol%]	4.6	3.8	4.3
C_2H_6	µ-GC	[vol%]	0.9	0.8	0.4
Benzene	µ-GC	[ppmV]	5264	4587	7448
Toluene	µ-GC	[ppmV]	1663	1426	1328
Sum C3	C-GC	[ppmV]	8344	7788	1763
Sum C4	C-GC	[ppmV]	1349	1252	283
Sum C5	C-GC	[ppmV]	1293	1431	665
Sum C6 (excluding benzene)	C-GC	[ppmV]	7	9	0

H_2S	µ-GC	[ppmV]	982	461	878
COS	µ-GC	[ppmV]	42	58	9
Thiophene	S-GC	[ppmV]	7	33	48
Methylmercaptane	S-GC	[ppmV]	107	105	19
Other S-organics	S-GC	[ppmV]	5	9	11
NH_3, HCN, HCl	--	--	n.d.	nd	nd
Tar total (excluding toluene)	Tar guideline	[g/Nm^3]	9.0 (94°C)	42.7	nd
Argon*	µ-GC	[vol%]	2.7	2.8	2.2
Neon*	µ-GC	[ppmV]	890	546	427
Total		[vol%]	97.3	97.1	97.4
Water content	Tar guideline	[vol%]	46.7	51.0	nd

*tracer gases, #measured by S-GC (below detection limit of micro-GC)

In short, in experiment 4, as in experiment 2 and 3, the feeding of the pretreated biomass sorghum proceeded without any issues such as blockage of the feeding tube. Only a minor interruption occurred due to the plugging of the outlet valve to the afterburner. Part of the product stream flows through this stream and part flows to the OLGA tar removal unit. As the valve was partially closed, and it provides a cold spot, the high tar concentration in the sorghum product gas can give tar/dust condensation. Much more H_2S was determined in product gas compared to experiment 2 and 3 due to absence of sulphur transport to the combustor. Also, the absence of an active bed material will result in a substantial increase in tar, although the tar concentration was not determined here.

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2.2.4. Experiment 5, eucalyptus in i-MILENA.

Gasification settings

In this one-day experiment, the gasifier was operated in reverse mode to increae the residence time, this reactor setup is referred to as i-Milena. The goal was to achieve a higher carbon conversion and CGE during the gasification of Eucalyptus in i-MILENA compared to the previous experimental results in "normal" MILENA. In i-MILENA, the feedstock is fed into the BFB where it is gasified in the presence of steam, and the combustion of the remaining carbon takes place in the riser. Because of the much larger reactor volume, the residence time of a wood particle to be gasified in the reactor is significantly higher. Assuming a 40x bed circulation and a 60 L BFB and 1.1 L riser volume. The residence time in Milena of the biomass is 20 seconds in the riser for gasification. In i-Milena BFB feeding, the residence time is approximately 18 minutes for gasification. Besides the different gasifier configuration, a difference from previous experiment was the much lower feeding rate which was applied as the bulk density is very low (no pellets like with sorghum) which can lead to plugging as in experiment 1. Furtermore, additional nitrogen was fed to the BFB to maintain fluidization in the bed. The overall experiment settings and conditions can be found in Table 12.

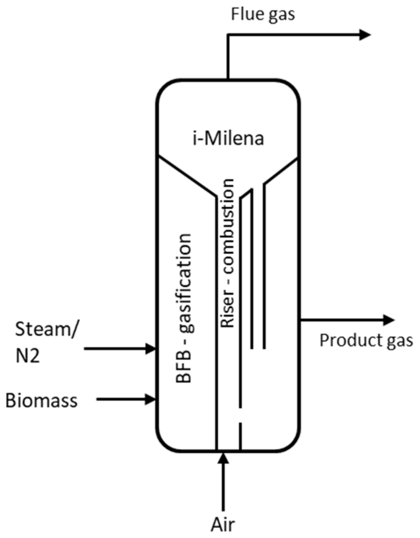

Figure 21: The i-Milena configuration in experiment 5.

Table 12: i-MILENA conditions and settings during the gasification of eucalyptus.

Setting	**Unit**	**Value**
Gasifier setting		i-MILENA
Complete run	[hh:mm]	8:31 – 12:24 (233 min)
Data averaged in period	[hh:mm]	10:30 – 11:30
Bed material		Olivine (<0.2 mm)
Reactor trace heating	[°C]	850
Fuel flow	[kg/h]	2.69
Gasification in BFB		
T gasification (average bed)	[°C]	815
Nitrogen	[NL/min]	25.0

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Carrier transport screw N_2	[NL/min]	1, 0.9
Steam	[kg/h]	1.3
Carrier steam N_2	[NL/min]	Set=2, actual=2.66 total
Tracer gas Ne	[NmL/min]	10.0
Tracer gas Ar	[NL/min]	1.0
Combustion in riser		
T in settling chamber	[°C]	819
Combustion air	[NL/min]	100
Afterburner air	[NL/min]	400

Observations

In Figure 22, a plot of the temperatures in i-Milena can be found. The gasification, now taking place in the BFB was found very stable during the experiment in the range of 810-820°C. No major temperature profiles in the bed were observed. Only the temperature at the flue gas exit was lower at approximately 740°C.

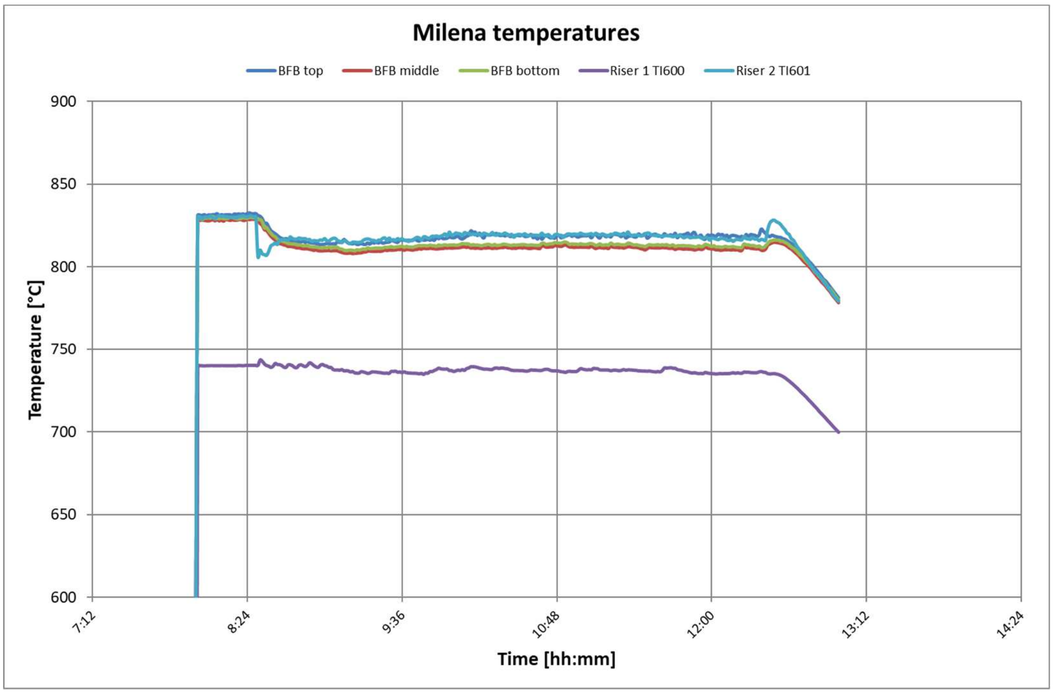

Figure 22: i-Milena temperature profile during the gasification of eucalyptus.

Gas composition

In Figure 23, the gas composition as determined by the gas analyser is plotted and in Table 13 the overall gas composition, including the tar and water content is summarized. The actual concentration are reported as well as the N_2-free results, which are added for comparison to the other gasification experiments. It should again be noted that the average values detected by the gas analyser and µ-GC were determined downstream OLGA. However, the tar guideline was naturally obtained directly in the product gas line after the gasifier. Benzene and toluene concentrations are therefore also taken from the tar guideline method and were indeed significantly higher than determined downstream OLGA. 24% benzene is removed by the OLGA and 31% toluene.

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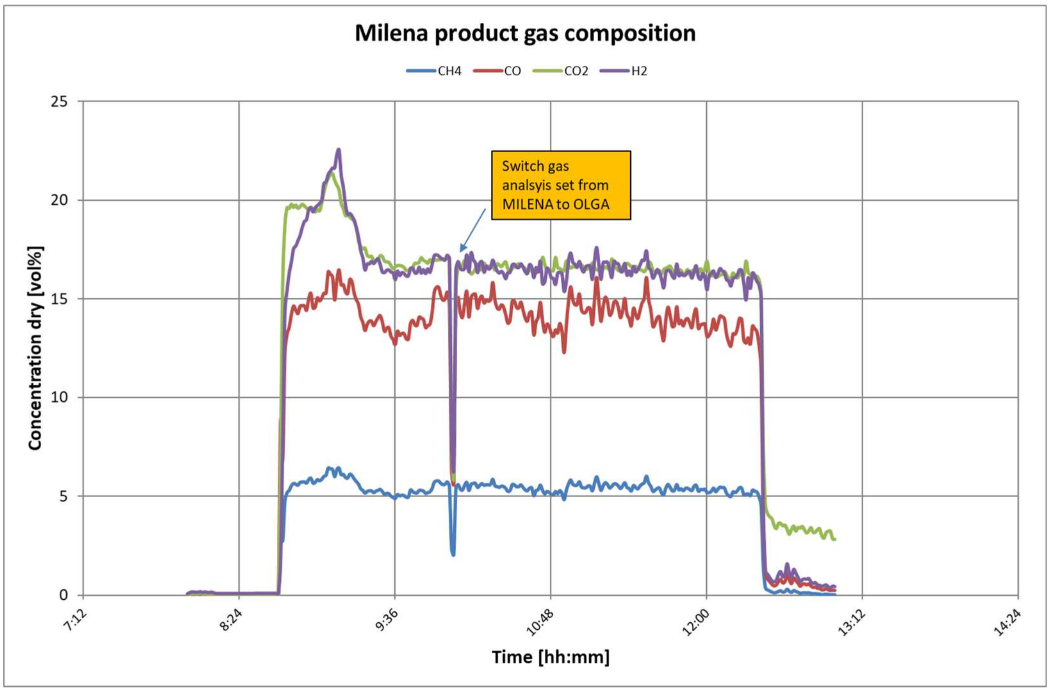

Figure 23: i-Milena eucalyptus product gas during experiment 5.

Table 13: Average product gas composition on dry basis and N_2-free basis for eucalyptus in i-Milena gasification.

Gas component	**Method**	**Unit**	**Eucalyptus i-Milena**	**Eucalyptus i-Milena (N_2-free)**	***EUCA***
CO	µ-GC	[vol%]	13.4	24.6	*33.8*
H2	Gas monitor	[vol%]	16.5	30.4	*18.6*
CO_2	µ-GC	[vol%]	14.9	27.4	*21.9*
CH_4	µ-GC	[vol%]	5.2	9.5	*11.4*
N_2	µ-GC	[vol%]	43.1	0.0	*3.5*
C_2H_2	µ-GC	[vol%]	0.1	0.2	*0.3*
C_2H_4	µ-GC	[vol%]	1.6	2.9	*4.2*
C_2H_6	µ-GC	[vol%]	0.1	0.1	*0.4*
Benzene	Tar guideline	[ppmV]	4142	7617	*7852*
Toluene	Tar guideline	[ppmV]	562	1033	*1689*
Sum C_3	C-GC	[ppmV]	178	327	*3621*
Sum C_4	C-GC	[ppmV]	17	31	*508*
Sum C_5	C-GC	[ppmV]	119	219	*1005*
Sum C_6 (excluding benzene)	C-GC	[ppmV]	8	15	*0.0*
H_2S	µ-GC	[ppmV]	141	260	*176*
COS	µ-GC	[ppmV]	10	18	*15.0*
Thiophene	S-GC	[ppmV]	6	11	*12.9*
Methylmercaptane	S-GC	[ppmV]	0	0.2	*6.5*
Other S-organics	S-GC	[ppmV]	1	0.9	*2.3*

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NH_3, HCN, HCl	--	nd	n.d.	n.d.	*n.d.*
Tar total (excluding toluene)	Tar guideline	[g/Nm^3]	13.8	25.4	*39.7*
Argon*	µ-GC	[vol%]	1.5	2.8	*2.3*
Neon*	µ-GC	[ppmV]	972	1787	*416*
Total		[vol%]	96.9	99.0	*98.6*
Water content	Tar guideline	[vol%]	31	57	*43.2*

The concentration of tar in i-Milena is considerably lower than in Milena with 25.4 g/Nm3 versus 39.7 g/Nm^3 at a similar ~800°C gasification temperature. However, the water content of the gas, on a N_2-free basis was relatively high (57 vol%) compared to the 43% in experiment 1. The higher water content of the gas results also in more WGS, illustrated by the much higher H_2 concentration of 30 vol%. This higher gasification activity and longer residence time resulted also in significantly less C_2-C_5 hydrocarbons. For example, the summed concentration of propane and propylene was 327 ppmv in i-Milena compared to 3261 ppmv in Milena product gas. This is also true for H_2S, which was also significantly higher in i-Milena (260 ppmv) compared to Milena product gas (176 ppmv) using the same bed material.

In short, no blockage of the transport screw were observed during eucalyptus feeding as the feeding rate was only 2.7 kg/h compared to 4.8 kg/h in experiment 1. In general, a much lower concentration of hydrocarbon components (C_2-C_5) as well as tar and H_2S were observed.

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2.3. Carbon conversion and cold gas efficiency

Carbon conversion

The carbon balances for the indirect gasification of eucalyptus and sorghum were calculated based on the product gas composition, the flue gas composition and the composition of the feedstock. The values were corrected for carbon (CO_2) introduced to the gasifier. The following equation was used to determine the carbon conversion:

$$\text{Carbon conversion (\%)} = \frac{\mathrm{C}_{\text{product gas}} - \mathrm{C}_{\mathrm{CO_2}}}{\mathrm{C}_{\text{feedstock}}} * 100\%$$

Where: $\mathrm{C}_{\text{product gas}}$ is the carbon contained in the product gas, in g/h.

$\mathrm{C}_{\mathrm{CO_2}}$ is the carbon added to the gasifier as CO_2, in g/h.

$\mathrm{C}_{\text{feedstock}}$ is the carbon contained in the lignin feedstock, in g/h.

The results can be found in Table 14. In experiment 1, the gasification of eucalyptus gave a carbon conversion (CC) to product gas of 57% excluding tar. An additional 18% of carbon was found in the flue gas of the combustor. The corresponding carbon mass balance adds up to 75% (excl. tar) and 81% (incl. tar) i.e. 19% of the carbon is not accounted for. A similar trend is observed with sorghum in experiments 2-4. With sorghum however, different gasification temperatures were applied, which resulted in improved carbon conversion to product gas. Conversions in experiments 2 and 3 of respectively 46% (717°C) and 59% (811°C) were achieved. However, the carbon in flue gas only decreased from 30% to 25%, relative to the feed, whereas 13% less carbon would be expected in the flue gas (244 g C more to product, 89 g C less to combustor). This is an indication of incomplete fuel conversion at these relatively low temperatures in the form of soot and char. Unconverted soot and char particles entrained in the product gas are not analysed by the gas detectors and go straight to the afterburner or are trapped and collected by the hot gas filter.

To determine the expected minimum carbon conversion, the feedstock's volatile content provides a good indication. This is only indicative as the volatile content may not have the same carbon composition as the feedstock itself. Nevertheless, looking at for instance eucalyptus, a volatility of 78% (on dry basis) is determined as part of the proximate analysis (see Table 2). This is much more than the 62% CC achieved in experiment 1. In experiment 5 a conversion of 79% was achieved in i-Milena, which is more in line with the volatile content of eucalyptus. Furthermore, for sorghum only a 59% CC was achieved in experiment 3, compared to a 74% volatile content.

Possible solutions to the low carbon conversion and carbon loss include:

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1. A higher gasification temperature (see experiment 2 and 3). Unfortunately, the possible temperature range is restricted as at high temperatures, ash starts to melt with accompanied bed agglomeration. This is especially true for high-ash herbaceous biomass.

2. A longer feedstock residence time in the reactor. This is partially confirmed by the i-Milena experiment where a much higher gasification residence time resulted in a total carbon conversion of 85% at 815°C.

3. A more reactive environment. This can be achieved by, for example, a catalytically active bed material and/or application of different (amounts of) gasification agents such as O_2, which is a strong gasification agent. This has not been investigated in the experiments within this work.

Table 14: Overview of the carbon conversions.

Exp.		**1**	**2**	**3**	**4**	**5**
In/out	**Unit**	**Eucalyptus**	**Sorghum**	**Sorghum**	**Sorghum**	**Eucalyptus i-MILENA**
Gasification temperature	**[°C]**	**808**	**717**	**811**	**730**	**815**
C in Fuel	[g C/h]	2074	1909	1909	1803	1145
C in Product gas (excl. tar)	[g C/h]	1309	873	1117	958	868
C in tar	[g C/h]	107	87	nd	nd	52
C in Flue gas	[g C/h]	378	564	475	517	71.9
			30%	25%		
Carbon conversion (excl. / incl. tar)	[wt%]	57 / 62	46 / 50	59 / nd	53 / nd	76 / 80
C balance (excl. / incl. tar)	[wt%]	75 / 81	75 / 80	83 / nd	82 / nd	82 / 86

Nd=not determined. All streams have been corrected for CO_2 added to the gasifier.

Cold gas efficiency

The cold gas efficiency (CGE) is defined as the energy of the product gas divided by the total energy introduced into the system, according to the following formula:

$$\mathrm{CGE}\ (\%) = \frac{\mathrm{E_{product\ gas}}}{\mathrm{E_{feedstock}}} * 100\%$$

Where $\mathrm{E_{product\ gas}}$: Total energy of the product gas, in kW (LHV basis).

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$E_{feedstock}$: Total energy content of the feedstock, in kW (LHV basis).

Here, the CGE does not include any additional energy supplied to the gasifier. On a small scale, heat supplied by combustion of char is not sufficient to maintain the required gasification temperature due to substantial heat loss. Trace heating is used for compensation and for system start-up. On a larger scale, naturally trace heating will not be used and additional heat is provided by combustion of tar that can be recycled from the tar scrubber.

The CGE results are shown in Table 15 where the energy output excluding and including tar are incorporated. As the CGEs are based on the fuel conversion to gas phase, the CGEs are highly related to the carbon conversion from feedstock to product gas.

For the gasification of eucalyptus in experiment 1, a product gas flow of 48.1 NL/min was determined with an output of 12.3 kW. A relatively low tar-free efficiency of 58% is thereby calculated. When considering tar, the energy output is 13.5 kW at a 64% efficiency i.e. 9% of to the total product heating value is tar. Additionally, in experiment 5, An extended gasification residence time was achieved in the i-Milena with eucalyptus as feedstock. A much improved CGE of 71% was achieved, due to the higher carbon conversion to product gas.

In the Sorghum gasification experiments, two different gasification temperatures were applied. At 717°C, a CGE of 45% was found excluding tar, which improved to 57% at 811°C. Clearly, in the gasification of sorghum, a higher temperature substantially improved both the carbon conversion and the CGE.

As the carbon conversion and CGE are related, possible options to improve the CGE are similar as those presented above for the CC (higher temperature, residence time and activation).

Table 15: Calculated lab-scale product gas flow and cold gas efficiency (CGE) for lignin gasification in Milena.

Exp.		**1**	**2**	**3**	**4**	**5**
In/out	**Unit**	**Eucalyptus**	**Sorghum**	**Sorghum**	**Sorghum**	**Eucalyptus i-MILENA**
Gasification temperature	**[°C]**	**808**	**717**	**811**	**730**	**815**
Feed flow	[Kg/h]	4.8	4.4	4.4	4.2	2.69
Input	[kW]	21.1	19.4	19.4	18.3	11.8
Product gas flow (excl. tar, dry basis)	[NL/min]	48.1	36.6	46.8	36.9	67.5
LHV	[MJ/Nm^3]	15.3	14.3	14.2	16.8	13.5[a]
Output	[kW]	12.3	8.7	11.1	10.1	8.0
Output (including tar)	[kW]	13.5	9.8	nd	nd	8.6

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CGE (excl. / incl. tar)	[%]	58 / 64	45 / 51	57 / --	55 / --	68 / 73

Nd=not determined. All streams have been corrected for CO2 added to gasifier. a) N_2 free

Intermediate conclusion

Compensation for the biomass input for the carbon conversion and CGE provides data for realistic values on a large scale. This implies a correction of 20% for experiment 1, assuming only 80% of the 4.8 kg/h was fed in experiment 1. This results in a total carbon conversion of 78% (incl. tar) and a CGE of 73% (excl. tar), more relevant as tar will be used in combustor to maintain temperature). For experiment 5, a 15% correction at a similar temperature reveals a 93% CC (incl. tar) and a 78% CGE (excl. tar).

As advice for further modelling of the value chain towards FT products is needed. Based on a correction, neglecting the unaccounted carbon, for **eucalyptus a 73% CC excl. tar** can be assumed with a **CGE of 73% excl. tar** at 810°C. The CGE is reported excluding tar as this is the “useful” fraction of the product gas which energy can eventually be processed into FT liquids. This has been verified by the Milena gasification model (based on wood) for large scale gasification assuming a 1% energy loss. The model predicts a gasification temperature of 810°C and 859°C flue gas. It practise, the tar could be send to the combustor providing more energy for combustion hereby increasing the temperature and carbon conversion. However, this assumption is not made here as it has not been demonstrated in these experiments. The additional energy could be used in combustion to supply additional heat required for e.g. biomass drying or district heating. This also accounts for the heat of the product gas and the flue gas. Operation at lower temperature is not desired due to the lower CC and CGE and the formation of more tar and higher hydrocarbon that can lead to fouling.

For **biomass sorghum**, respectively a **65% CC (excl. tar)** with a **CGE of 65% (excl. tar)** should be used at 800°C. Clearly 8% more useful gas (for FT production) can be obtained when gasifying eucalyptus. In theory, a lower carbon conversion to product gas implicates more char to the combustor and therefore a higher temperature and conversion (equilibrium is reached), however, due to the amount of ash (5%) in biomass sorghum as herbaceous crop, higher temperature is not advised. As for eucalyptus, also for sorghum, this excess heat could be applied elsewhere. On a large scale, excess heat production in the combustor could be compensated for by a different reactor design.

3. Gasification of bio-oil/char

The project partner RE-CORD has supplied ECN.TNO with a small batch sample of char (< 200 µm) and pyrolysis oil (from BTG) to be mixed at ECN.TNO with a char composition of 10 wt%. Both the bio-oil as the biochar were produced from the pyrolysis of a clean eucalyptus wood stream. The composition of bio-oil and the char are presented in appendix (Table 21).

The idea was to do a first characterization of the slurry properties to evaluate the possibility of feeding such mixture to the fluidized bed gasifier (WOB). Later RE-CORD has supplied ECN.TNO with a larger batch sample of about 8 kg of bio-oil and 1 kg of char with a particle size of < 100 µm. The final goal was to test this slurry mixture in a fluidized bed gasifier and characterize the product gas composition, gasification efficiency and gas heating value content, to identify and quantify possible benefits while comparing to direct solid biomass gasification.

3.1. Experimental and methods

Before the slurry spraying tests, the samples of the pyrolysis oil and the char were mixed in a 10 wt% char content slurry. Pictures of the samples are presented in Figure 24.

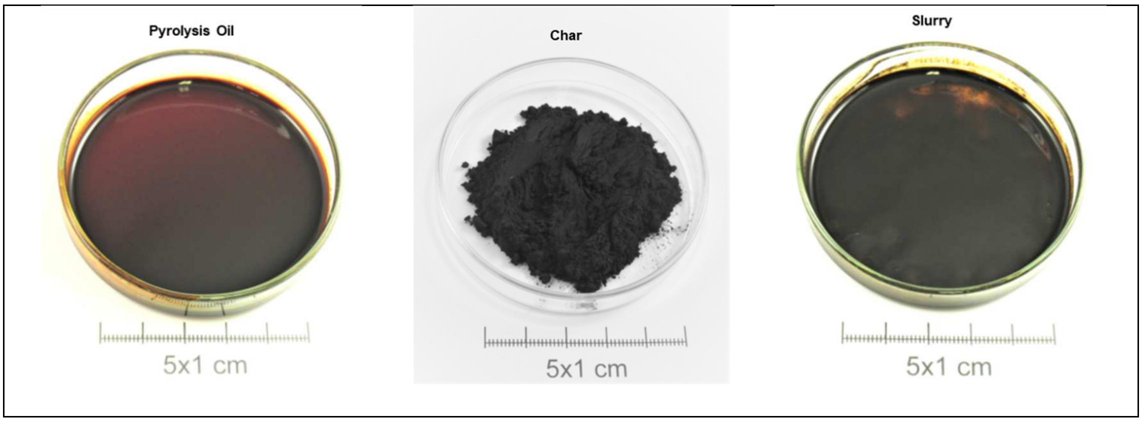

Figure 24. Pyrolysis oil and char samples used to make the slurry (10% wt in char).

In order to determine the moisture and ash contents of the slurry to be fed into the gasifier a thermogravimetric analysis (TGA) was done, under air, using a first set point of 105°C, a second of 550°C at a ramp temperature of 10°C/min. A plot of this TGA is given in Figure 25.

The determined moisture content was in the range of 25-30 wt% and the ash content was 0.5 wt% on dry basis. Due to the low ash content, it is not expected a major interaction of the ash with the bed material and therefore a normal silica-based sand was used in the gasifier, as bed material.

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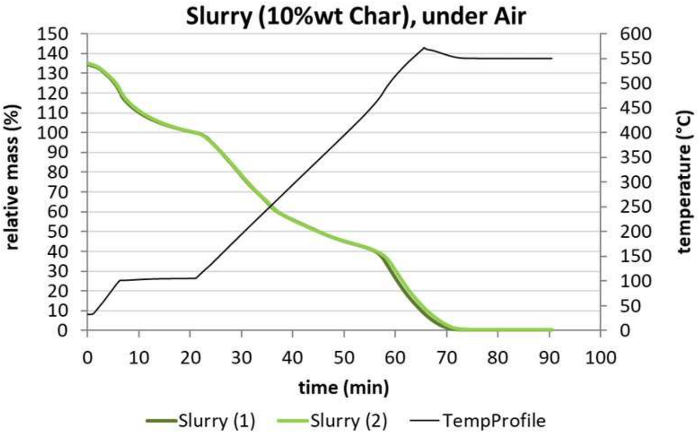

Figure 25. TGA results of the slurry (10% wt in char).

The dynamic viscosity of the slurry was determined in function of the temperature under heating (up to 90 °C) and cooling conditions (see Figure 26). If no major changes occur in the sample, it is expected that both lines overlap each other. However, this was not the case and a significant hysteresis was found between the heating and cooling curves, which means that most probably some evaporation occurred, and the sample became more viscous.

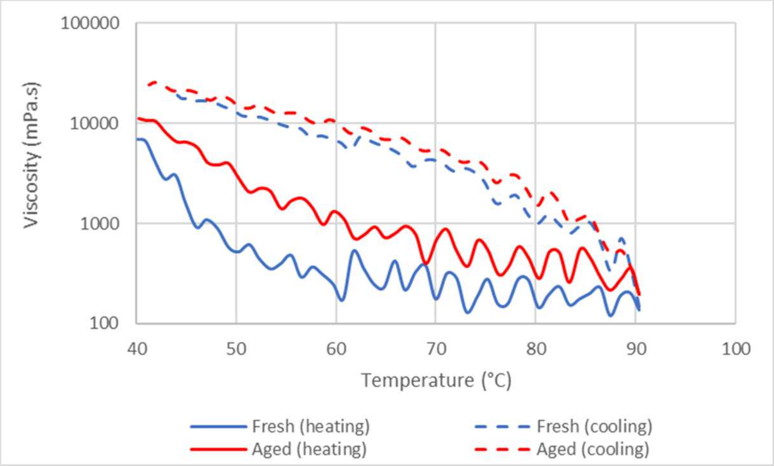

Figure 26. Viscosity results of the slurry (10 %wt in char) determined under a constant shear rate of 10 s^{-1}.

It is also probable that the heating promoted the viscosity increase due to typical oligomers and polymer precursors content of the bio-oil, which start to polymerize at temperatures higher than 70°C, and consequently, make bio-oil more viscous. In this case fouling in reactors, transport pipes and storage vessels could also be expected (Bridgwater, 1999). To evaluate the impact of long-time temperature exposition on the viscosity, the slurry was kept at 70-80 °C during two weeks in a closed container and the viscosity was measured again. As it can be seen in Figure 26, the viscosity increased slightly with aging at 70-80 °C but the impact of water loss (between heating and cooling cycles) is higher than the aging effect itself. However, it is not

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recommended long time temperature exposition (e.g. under storage) of the slurry, otherwise the viscosity can increase, and the material become more difficult to pump and to feed. Therefore, it was decided to prepare the slurry in the same day of the test.

The results of the viscosity tests showed that the slurry can be easily pumped at a temperature above 50 °C and can be sprayed at 60-70 °C. Higher temperatures can promote a fast evaporation and impact negatively on the atomization quality and therefore should be avoided.

To assess how the viscosity of the slurry sample react to a higher shear rate, which will be the case in the feeding probe tip due to the fast gas stream used to atomise the slurry, a shear rate sweep determination was also done and the results are presented in Figure 27. It can be observed that the viscosity decreases with the increment of the a shear rate. For a shear rate above 1000 s^{-1} the viscosity decreases to below 100 mPa.s, which assures a proper atomization of the slurry.

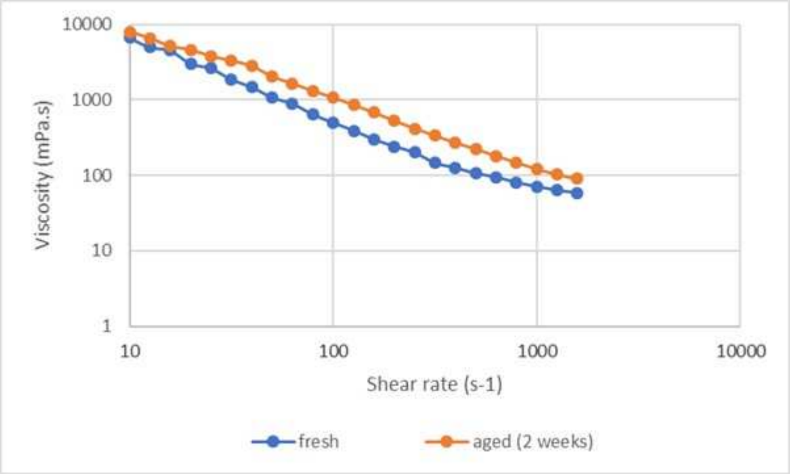

Figure 27. Viscosity results of the slurry (10% wt in char) determined under a constant temperature of 80 °C.

Viscosity and stability indicate that a pumping temperature between 50-60 °C and an injection at 70°C are ideal. Hence, the pump was calibrated under such conditions and the results of two samples of slurry are presented in Figure 28. As the two calibration curves are in good agreement, the calibration method is validated and were used to feed the desired amount of the slurry during the gasification tests. The total amount of slurry fed during each test were checked by mass differences, as well.

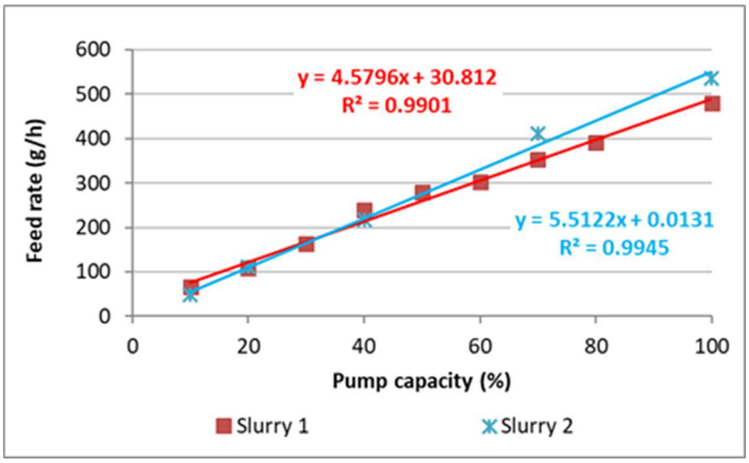

Figure 28. Pump calibration for the slurry (10% wt in char) feeding.

The tests were carried out in the WOB gasifier. It is a fluidized bed reactor with 7 cm ID, followed by a disengagement zone of 12 cm ID, a hot cyclone to recover the fine char/ash and a multiple sampling point lines for gas analysis. The layout of the gasification facility is shown in Figure 29.

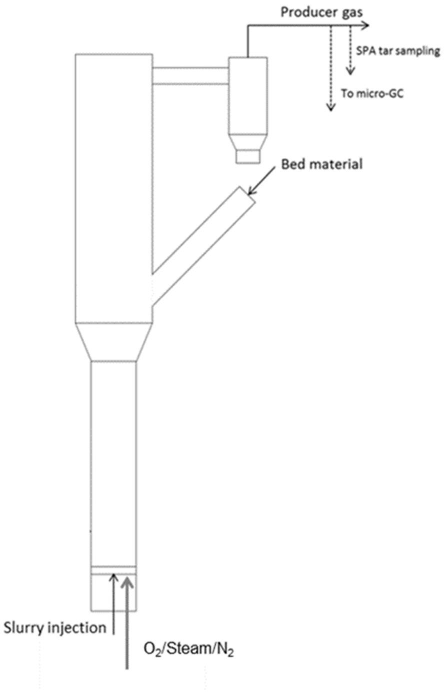

Figure 29. Layout of experimental setup in WOB gasifier.

The planned gasification conditions were planned, see Table 16, using a slurry feeding rate of 300 g/h and 1060 g of bed material.

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Table 16. Gasification test plan conditions.

Test #	T	Feed(1)	N_2 probe	Steam distributor	O_2 distributor (2)	N_2 distributor
	[°C]	[kg/h]	[NL/min]	[kg/h]	[NL/min]	[NL/min]
1	850	0.3	15/25	0.1 (~2.0 NL/min)	0.88	12.1
2	850	0.3	15/25	0.3 (6.0 NL/min)	0.88	8.1
3	850	0.3	15/25	0.0	0.88	14.1
4	900 (3)	0.3	15/25	0.1 (~2.0 NL/min)	0.88	12.1
5	900	0.3	15/25	0.3 (6.0 NL/min)	0.88	8.1
6	900	0.3	15/25	0.0	0.88	14.1

(1) fuel = 90% wt. pyrolysis oil + 10% wt. char. Pump set to 1.0 and 55(%) to get 0.3 kg/h (see Figure 5).

(2) To get ER ~ 0.3.

(3) If possible. If not, go to lower temperatures depending on the results of tests 1-3.

Approximately, 15 NL/min total flow (N_2) is required to spray the slurry through the injection probe. Additionally, the bed was fluidized with N_2 and the gasifying agent through the distributor plate at the minimum flow required. Ideally, the temperature in the probe should be below 70°C. Each test will have a duration of at least 2 hours, during which gas composition (with gas analyser for main gas components – O_2, CO_2, CO, CH_4 – and micro-GC were measured and a tracer gas (neon) was injected for molar balances. Furthermore, gas bags will be collected and analysed for trace GC and sulphur components. For tar content determination, SPA sampling will be applied.

3.2. Results and discussion

For the first test, the slurry was prepared 1h before starting the feeding. The char was gradually mixed with the pyrolysis oil till 10 wt% composition. The slurry was kept at 50 °C in a continuous stirred tank (see Figure 30). During feeding, the slurry is conveyed through a heated line to the pump and send to the injection probe through a second heated line, all working at 50 °C.

After the WOB gasifier was at stable temperature and at test #1 defined condition, the slurry feed was started. However, just after 1 min of feeding the pressure in the feeding line increased to over 3 bar indicating a blockage in the injection line. Several attempts were made to overcome this blockage, including increased pump settings and gas injection flow, but none succeeded. The installation was put to cooldown to be opened in the following day to inspect the feeding line.

After emptying and inspecting the stirred tank and linings, a significant layer of char particle clusters was found both on the wall and on the bottom of the tank (see Figure 31). This fouling layer seemed to be originated from a slow coking of the oil and the clustering of the 100 µm char particles, which were thought to be properly dispersed before. In fact, a check on the remaining slurry, which was not used and was kept at room temperature, didn't show this clustering behaviour. Moreover, while cleaning the linings and the pump, the same solid clusters were found in significant amount. It seems that stirring the slurry promoted the clustering

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and size increase of the char particles suspended in the oil. This contributes to a fast deposit build-up layer in the wall of the tank, as well, which promoted thermal wall resistance and consequent temperature wall increase and further escalation of the problem.

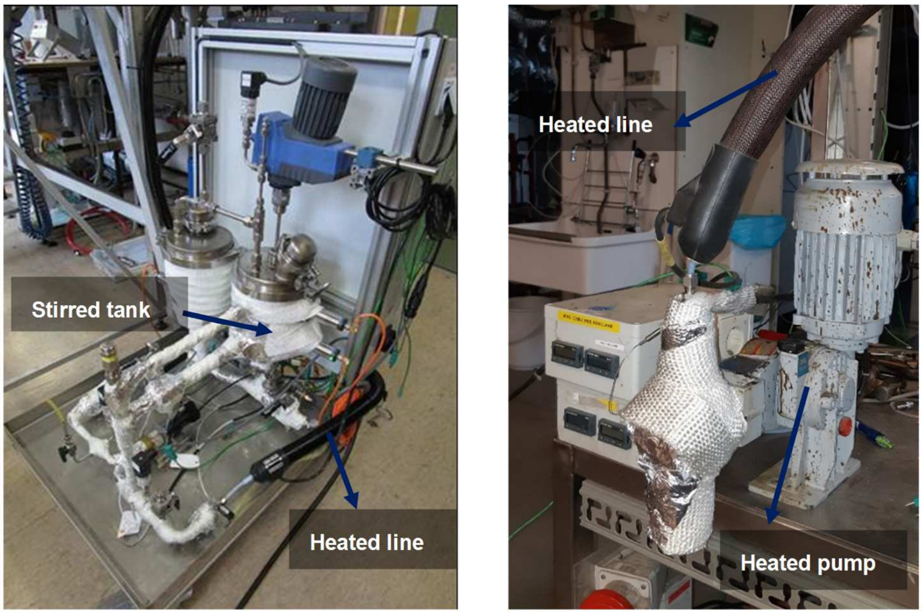

Figure 30. Slurry feeding experimental setup for the WOB gasifier.

Figure 31. Slurry fouling and char clusters developed in the feeding system.

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To overcome the probe blockage, the probe was placed a little bit less deep in the bed (0.5 cm instead 1.0 cm) and the spraying gas (N_2) was increased from 15 to 25 NL/min.

To prevent char particles build-up, a new heated slurry tank was constructed and stirring was avoided. The slurry was prepared and added to the tank 5 min before start feeding. A picture of the new feeding tank and of the WOB installation is given in Figure 32.

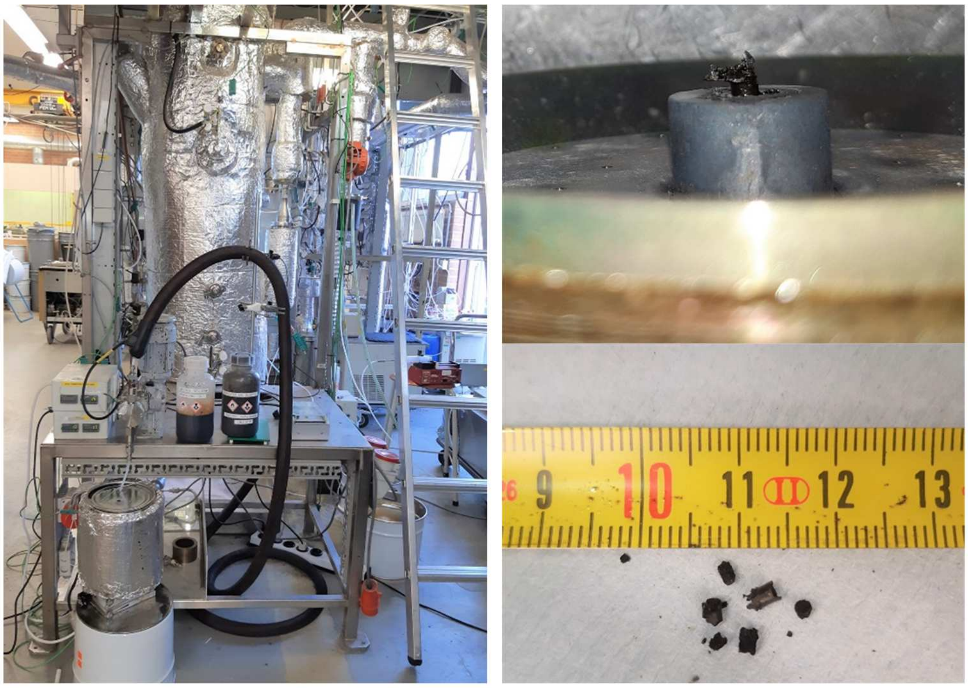

Figure 32. New feeding tank and the gasification installation - WOB. Detail on the injection probe tip, blocked with solidified slurry.

The new configuration allowed a total 10 min non-continuous feeding duration gasification test, followed by a new blockage of the probe tip, as can be observed in Figure 32. Unfortunately, there was not enough run time to achieve stable conditions and therefore no reliable gas composition could be retrieved from this test. The feeding system was opened and checked and some lumps of char/pyro-oil were found inside the pump, as can be observed in Figure 33.

This degree of lump formation was not observed previously during the first tests using the first sample of pyrolysis oils and the 200 µm char sent by RE-CORD in May 2018. Can be that the char smaller particle size contributed to the faster development of these lumps. To address this issue two small samples of slurry were prepared and tested at 60-70 °C for two days to access the lumps formation tendency. In Figure 34, it is possible to see that the sample prepared with the 100 µm char particle size (the current sample under testing) produced more lumps of “solid” slurry. These lumps can accumulate in the pump and in the probe causing irregular pumping and blockage of the probe as seen in Figure 32 and Figure 33. It seems that temperature and heavy stirring can promote the development of these lumps further.

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Figure 33. Lumps of slurry found inside the pump after inspection.

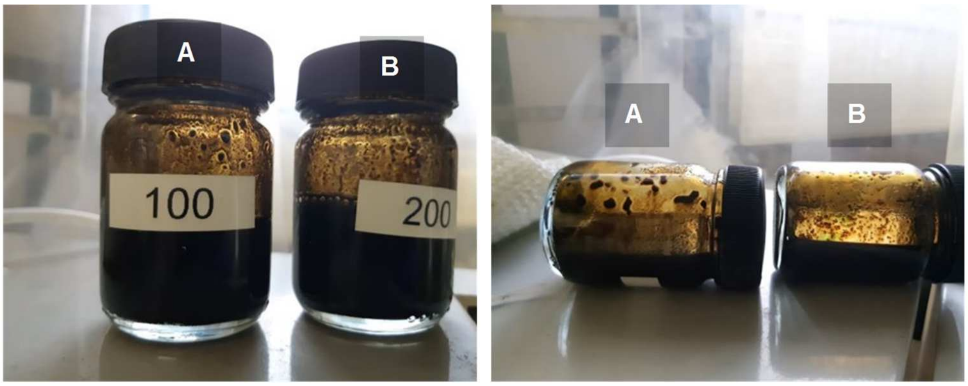

Figure 34. Lumps of slurry found in two different samples of slurry, produced with100 µm (A) and 200 µm (B) particles, tested at 60-70 °C.

In order to evaluate the performance of the pyrolysis oil in gasification, it was decided to start with the feeding of 100% pyrolysis oil and follow the first part of the tests proposed in Table 16 (the first 3 tests). The only differences were that a 25 NL/min stream of N_2 was used to spray the oil in the bed and the oil feeding system was operated at room temperature (25 °C).

The product gas composition obtained during the first test (#1) is presented in Figure 35. Steam ($H_2O/C = 0.85$) and O_2 (ER = 0.3) were used as gasification agents. The test proceeded at stable conditions, meaning that the feeding system works reliably with the pyrolysis oil, but the bed temperature (average of 770 °C) remained significantly below the chosen set point of 850 °C due to the high N_2 flow used to spray the oil and the water content of the bio-oil. Furthermore, the product gases were severely diluted, averaging on a volumetric basis 5.05% CO, 3.93% H_2, 2.45%CO_2 and 1.13% CH_4 (see Table 17). The product gas LHV was about 1.9 MJ/m^3, calculated based on the composition given in Table 17 and Table 18, where the trace gas constituents determined by GC are also presented. It is possible to observe the significant levels of trace components including benzene, toluene and tar. The tar is not included in the carbon conversion and cold gas efficiency calculations. Therefore, a high level of tar indicates that the fuel conversion is not complete. In fact, the calculated C conversion was 81.9 %, which limited the cold gas efficiency to a value of 80.6%. The sulphur components were also analysed but remained below the detection limit (also caused by the high dilution) of

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0.5 ppmV. The H_2:CO ratio was 0.78. The N_2-free gas composition is also given in Table 18, which was also normalized to 100%. The product gas LHV on a N_2 free basis was 14.5 MJ/m^3.

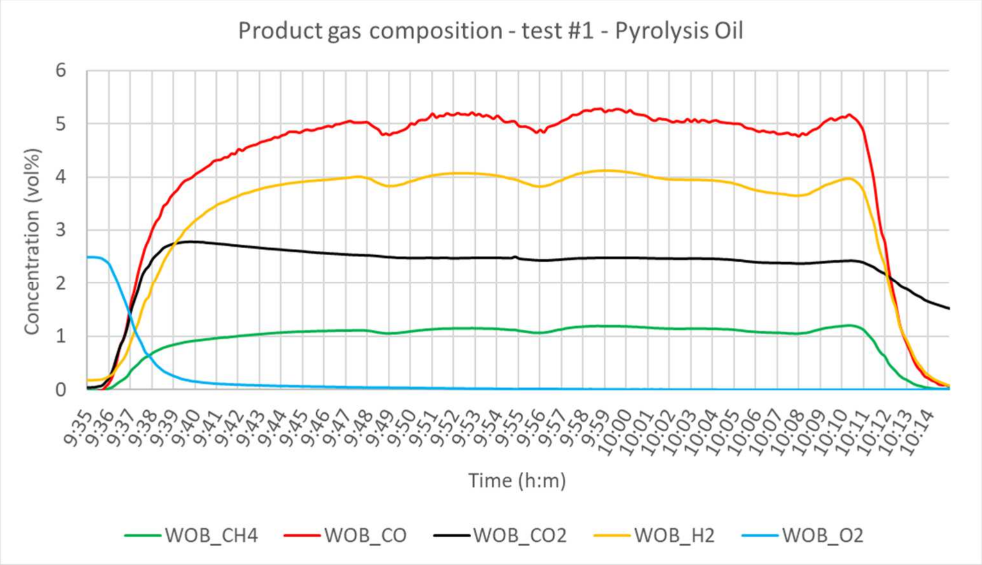

Figure 35. Product gas composition obtained during the gasification of pyrolysis oil under test #1 conditions (bed temperature = 770 °C).

Table 17. Product gas average composition obtained during the gasification tests of pyrolysis oil (bed temperature = 770 °C) on a dry basis.

test #	**Time h:m**	**Feed rate [g/h]**	**O_2 [vol%]**	**CO_2 [vol%]**	**CO [vol%]**	**H_2 [vol%]**	**CH_4 [vol%]**	**N_2 [vol%]**
1	9:50-10:10	380	0.01	2.45	5.05	3.93	1.13	87.43
2	10:40-11:00	353	0.02	2.67	4.97	4.00	1.10	87.24
3	11:30-11:45	311	0.06	2.18	4.07	3.02	0.81	89.86

test #	**C_2H_6 (ppmv)**	**C_2H_4 (ppmv)**	**C_3H_6 (ppmv)**	**C_2H_2 (ppmv)**	**Benzene (ppmv)**	**Toluene (ppmv)**	**tar (mg/Nm^3)**
1	158	4290	82	393	876	157	2412
2	114	3893	58	387	820	124	1857
3	94	2971	37	229	566	81	1704

Table 18. Product gas average composition obtained during the gasification tests of pyrolysis oil (bed temperature = 770 °C) on a dry basis and on a N_2 free and normalized composition.

Gas component	Method	Unit	Concentration*		
			test #1	test #2	test #3
CO	µ-GC	Vol%	38.4	37.4	38.9
H_2	Gas monitor	Vol%	29.9	30.1	28.8
CO_2	µ-GC	Vol%	18.7	20.1	20.8
CH_4	µ-GC	Vol%	8.6	8.3	7.8
N_2	µ-GC	Vol%	0	0	0
C_2H_2	µ-GC	Vol%	0.30	0.29	0.22
C_2H_4	µ-GC	Vol%	3.26	2.93	2.84
C_2H_6	µ-GC	Vol%	0.12	0.09	0.09
Benzene	µ-GC	ppmV	6661	6175	5406
Toluene	µ-GC	ppmV	1193	934	778
Sum C3	C-GC	ppmV	629	436	353
Sum C4	C-GC	ppmV	214	195	173
Sum C5	C-GC	ppmV	28	26	20
Sum C6 (without benzene)	C-GC	ppmV	15	28	18
H_2S	S-GC	ppmV	< 4	< 4	< 5
COS	S-GC	ppmV	< 4	< 4	< 5
Thiophene	S-GC	ppmV	< 4	< 4	< 5
Methylmercaptane	S-GC	ppmV	< 4	< 4	< 5
Other S-organics	S-GC	ppmV	< 4	< 4	< 5
NH_3, HCN, HCl	--	--	n.d.	n.d.	n.d.
Tar total (excl. benzene and toluene)	SPA	g/m^3	18.3	14.0	16.3

* N_2 free and normalized composition.

The second test (#2) was done using more steam ($H_2O/C = 1.64$) but the O_2 input was maintained. The gasification was fairly stable, but a slight pressure increase was detected in the pressure of the injection probe. Considering the composition of the product gas compared to test #1, there was a concentration increase in CO_2 and slightly in H_2 and a decrease in the CO, CH_4 and trace compounds in the product gas, with the increase of steam (Table 17 and Table 18). The online analysis of the product gas composition is presented in Figure 36. The LHV of the product gas was lower compared with test #1 reaching 1.8 MJ/m^3. Most probable this is because the fuel feed rate was also slightly lower, and the real ER was a bit higher than the set point of 0.3. Therefore, even when corrected to a N_2-free basis the LHV was 14.0 MJ/m^3, hence still lower when compared with test #1. In line with the product gas heating value, the C conversion and CGE were also lower (76.6 and 73.5% respectively).

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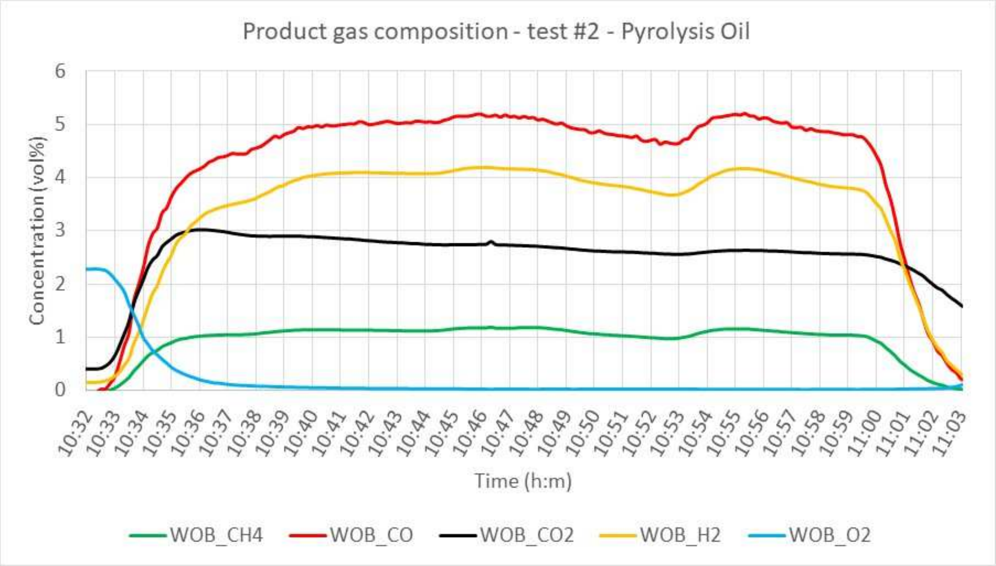

Figure 36. Product gas composition obtained during the gasification of pyrolysis oil under test #2 conditions (bed temperature = 770 °C).

The third test (#3) was done with no steam, using only O_2 as gasification agent. The test proceeded under stable conditions for about 25 min, after which a fast pressure increase in the feeding probe was observed and the flow through the probe decreased from 25 to 11 NL/min. This indicated that the probe was almost completely blocked, although the oil was still being fed. At this point the test was stopped. In Figure 37 it can be observed that in the final stage of the test the product gas concentration was increased in CO, CO_2, CH_4 and H_2 due to the lower flow of N_2. Probably due to the lower reactive atmosphere (no steam, although the oil moisture content assured a $H_2O/C = 0.45$) the pyrolysis oil reacted slower during this test and accumulated faster in the bottom part of the bed around the probe discharge point. Moreover, the relative low bed temperature contributed to the slow conversion of the pyrolysis oil. In fact, after cooling down, the installation was opened for inspection and a solid lump constituted by solidified pyrolysis oil and some sand particles was found attached to the probe tip and therefore was the cause of the blockage (see Figure 38). The oil inside the probe was still in liquid phase meaning that the oil could still be delivered if the lump was removed (consumed faster). In consequence, the product gas of the test #3 was poor in CO, CO_2, CH_4 and H_2, when compared to the first two tests (Table 17 and Table 18). The C conversion was significantly lower (73.6%), as well as the CGE (68.2%) and the LHV (1.4 MJ/m^3). Correcting to a N_2-free basis the LHV of the product gas was limited to 13.6 MJ/m^3.

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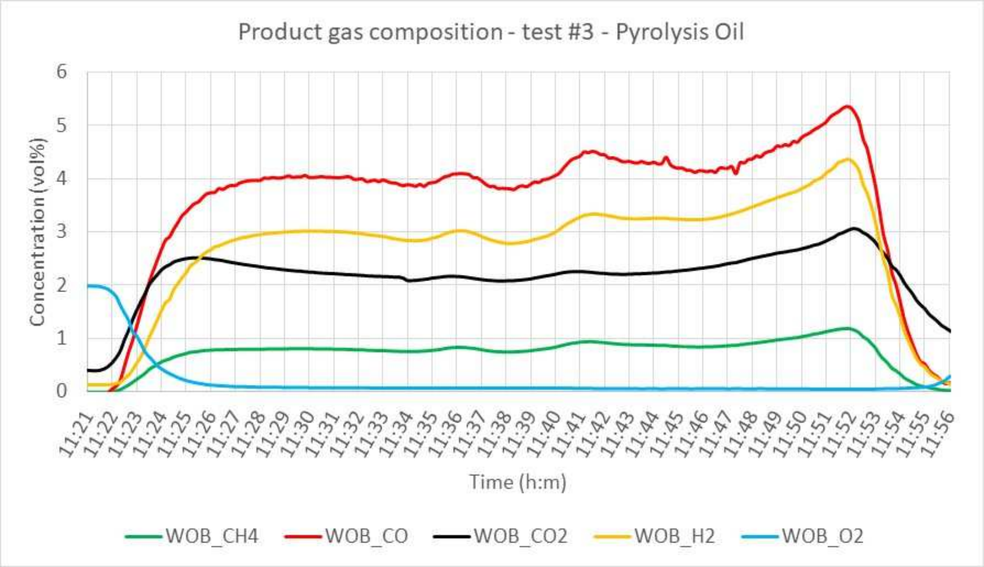

Figure 37. Product gas composition obtained during the gasification of pyrolysis oil under test #3 conditions (bed temperature = 770 °C).

Figure 38. Unconverted solidified biooil accumulated during the gasification test #3.

The gasification gas yields are presented in Figure 39, where it can be confirmed the significant lower fuel conversion obtained in test #3. The differences in carbon conversion, the LHV and the CGE are summarized in Figure 40. The lower yields obtained during test #2, when compared to test #1, already makes suspect that the fuel was accumulating in the reactor, making the bed temperature as the critical parameter in limiting the fuel conversion.

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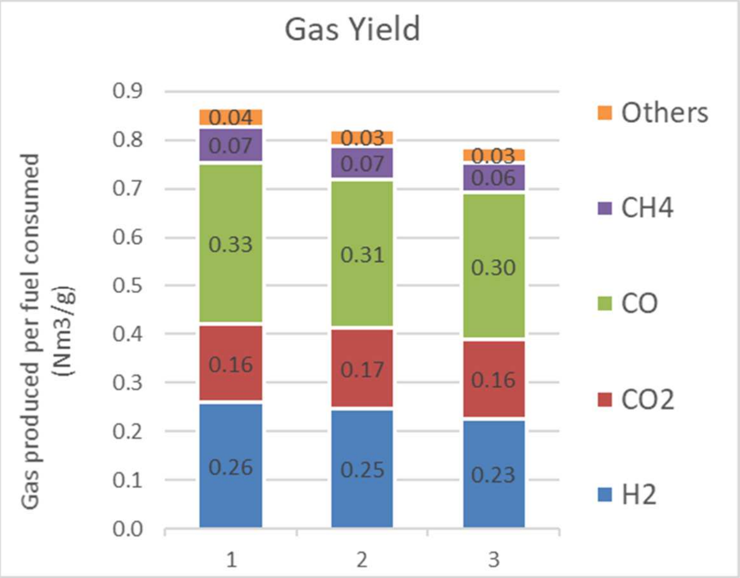

Figure 39. Comparison of the gasification gas yields between the three tests.

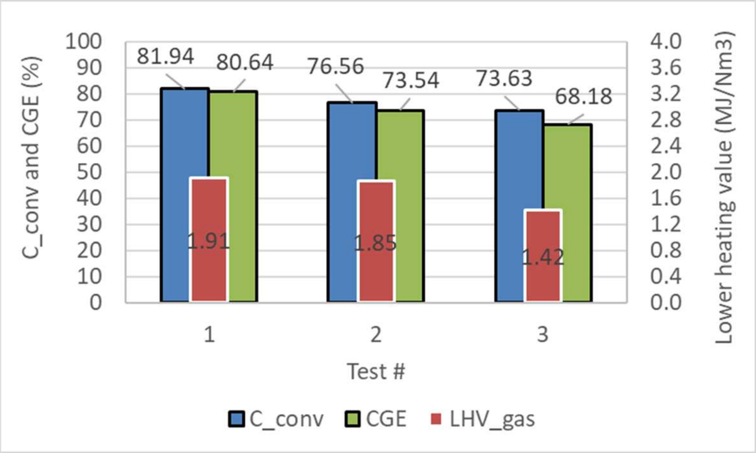

Figure 40. Comparison of the carbon conversion (CC), the LHV and the CGE between the three tests.

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4. Product gas upgrading for FT synthesis

This section deals with the required gas cleaning and conditioning (or upgrading) that is required prior to the catalytic Fischer-Tropsch synthesis. The Fischer-Tropsch synthesis is named after Prof. Franz Fischer and Dr. Hans Tropsch who reported on the preparation of hydrocarbons over an iron catalyst around 1924 [13]. In the Fischer-Tropsch synthesis, a mixture of H_2 and CO react in the presence of a transition metal catalyst. Mostly Fe and Co are industrially applied as catalyst. The Fischer-Tropsch reaction provides mainly linear hydrocarbons with a carbon number of C_1 to C_{20}+. A H_2/CO ratio of around 2.2 is required for the FT reaction, which is described by the following reaction:

$n\,CO + (2n+1)\,H_2 \rightarrow C_nH_{2n+2} + n\,H_2O$ FT alkanes ($\Delta H/n = -154.1$ kJ/mol)

Other (by-)products include olefins- and oxygen-containing compounds (oxygenates) via respectively the following reactions:

$n\,CO + 2n\,H_2 \rightarrow C_nH_{2n} + n\,H_2O$ FT alkenes

$n\,CO + 2n\,H_2 \rightarrow C_nH_{2n+1}OH + (n-1)\,H_2O$ FT alcohols (oxygenates) ($\Delta H/n = -147.0$ kJ/mol)

The Fischer-Tropsch process can be considered mature technology as most of the facilities run for more than 10 years. Two dominant players in the FT field are Shell and Sasol, with more than 50 years of experience in operating FT plants. Shell has i.a. plants in Malaysia (production of 14,700 bbl/d) and Qatar (140,000 bbl/d) using natural gas as feedstock. A flow scheme of the plant in Malaysia is shown in Figure 41. Shell uses fixed bed reactors loaded with supported Co catalysts at a temperature of 220°C and 25 bar. SASOL has i.a. plants in South Africa producing 5,000 bbl/day (SASOL 1) starting from coal gasification and in Qatar from methane producing 34,000 bbl/d. For the FT synthesis SASOL applies respectively precipitated Fe catalysts and supported Co catalysts.

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[13] F. Fischer and H. Tropsch, Preparation of synthetic oil mixtures (Synthol) from Carbon Monoxide and Hydrogen, Brennstoff-Chemie, 1923, 4, 276-285.

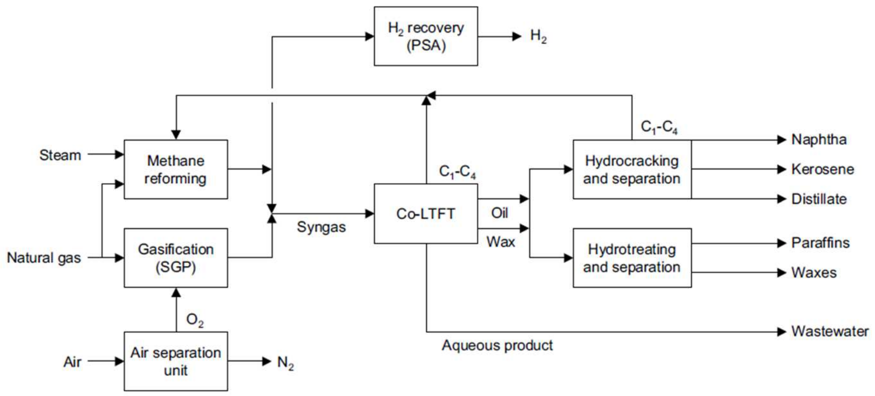

Figure 41: Flow scheme of the Shell Middle Distillate Synthesis (SMDS) at the Bintulu site [14].

Fischer-Tropsch production has also been combined with biomass gasification, but commercial processes do not exist. Examples of demonstration projects (maximum TRL 5) in Europe include the BioTfuel project in France and the FT pilot plant in Guessing, Austria [15].

Although the upstream preparation processes are different when comparing the gasification of biomass with that of coal and methane, the actual FT conditions remain the same. Product gas from biomass gasification contains, besides the required syngas (H_2/CO), methane, higher hydrocarbon (C_2-C_5), aromatic hydrocarbons (tar) and elemental S and N containing components. This needs to be upgraded to a gas containing predominantly H_2/CO preferably in a ratio of 2.2. Careful and extensive gas cleaning and upgrading is required to achieve this, much more than is the case for especially processes based on natural gas but also coal. The S/N containing products act as poison to the FT transition metal catalyst.

In Table 19, the gas components that are potentially poisons for the FT catalyst can be found including the required level of cleaning [16, 17]. The actual concentration in eucalyptus product gas as determined in experiment 1, Section 1 of this work is used as reference. In the last column of Table 19 some approaches are provided for their removal. As can be observed, most of the impurities must be removed down to extremely low levels. Good examples of catalyst deactivation upon dosing these impurities into syngas are hard to find. For HCN it has been reported that a concentration of 800 ppbv resulted in a catalyst (Co-Re) having a half-life of only 12 h [18].

Table 19: Typical impurities (excluding light hydrocarbons) expected in low temperature biomass gasification and allowed concentrations in FT synthesis

Gas component	**Eucalyptus product gas composition** (dry basis)	**Cleaning requirement for FT-S**	**Removal technology**
Particles (dust, soot and ash)	30 g/Nm^3 (a)	0	Cyclones, bag filter and scrubbers.
Tar	39.7 g/Nm^3	Removal to dew point below operational temperature of FTS.	Tar cracker or reformer. Alternatively, an oil scrubber.
Metals (Pb and Cu)	unknown	unknown	-

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[14] P. M. Maitlis and A. de Klerk (Editors), Greener Fischer-Tropsch Processes for fuels and feedstocks, Wiley-CVH, 2013.
[15] E.H. Boymans, E.T. Liakakou, ECN report ECN-E—17-057, Advanced liquid biofuels synthesis.
[16] M.J.A. Tijmensen, A.P.C. Faaij, C.N. Hamelinck and M.R.M. van Hardeveld, Biomass and Bioenergy, 2002, 23, 129-152.
[17] C.N. Hamelinck, A.P.C Faaij, H. den Uil and H. Boerrigter, Energy, 2004, 29, 1743-1771.
[18] Patent US006107353A, 1997, cyanide and ammonia removal from synthesis gas.

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Alkalis	unknown	10 ppb	-
Nitrogen (NH_3 + HCN)	3863 + 193 + organic N (b)	20 ppb	Aqueous acid/base scrubbers (NH_3 + HCN) and HDS (HCN).
HCl	194 ppmv (b)	10 ppb	Aqueous scrubber.
Sulphur (H_2S + COS + organic S)	176 + 15 + 22 ppmv	10 ppb	Liquid scrubbing using physical/chemical absorption. (HDS or reforming to convert organic sulfur to H2S).
CO_2	21.9 vol%	Variable	Adsorption on solid sorbents or liquid physical/chemical absorption.
C_1-C_7 hydrocarbons	18 vol%	Not necessarily poisonous to catalyst.	Conversion into syngas desired to maximize FT output. For instance, using a steam reformer.

(a) Average value for fluidized bed gasification based on wood gasification. (b) Based on indirect (wood) model calculations using eucalyptus as feed.

For the product gas compositions reported in this work, we foresee an upgrading strategy as found in Figure 42. Detailed description of gas upgrading can be found elsewhere [[19], [20]].

Crude product gas comes in at approximately 700-800°C where it should be cooled to 450°C in a heat exchanger producing steam. This can occur without fouling as the tar dew point is typically around 200°C. After gas cooling, the gas enters the OLGA columns including the Collector, ESP and absorber-stripper where the tar dew point is lowered to ~10-20°C followed by condensation of clean water. The condenser could be extended with an acid and/or caustic scrubber when required, although not foreseen here. It is assumed that most HCl is captures by the condensed water (in the form of NH_4Cl).

Then the gas is compressed to about 6 bar for conversion in the HDS. Here, organic sulphur and nitrogen components are converted towards respectively H_2S and NH_3. The H_2S/COS is then captured in a ZnO (or activated carbon) bed and the formed traces of NH_3 are captured downstream in the CO_2 removal unit. Cleaned product gas then enters a steam reformer to convert the additional hydrocarbons, which constitute a major part of the energy content, into syngas leaving maximum a few volume percent of CH_4. Naturally a higher CH_4 conversion is desired for the FT output but a higher heat demand is required (needs optimization). Part of the product gas will be required to fire the reformer. Before the second compression stage, the CO_2 should be removed using an amine scrubber. As Co-based FT catalyst is not WGS active, CO_2 up to ppmv levels is not required. CO_2 removal to below 1 vol% should be sufficient. In the second compression stage, the pressure is increased to 20-25 bar prior to conversion in the FT reactor.

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[19] A. Kohl, R. Nielsen, Gas purification, 1997, Gulf Publishing Company.

[20] P. J. Woolcock, R.C. Brown, Biomass and Bioenergy, 2013, 52, 54-84.

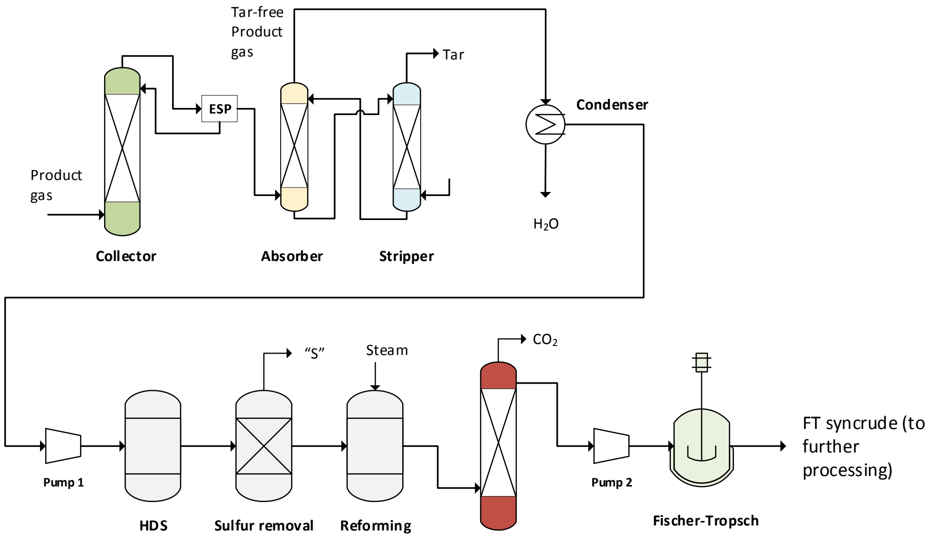

Figure 42: Possible system configuration for gas cleaning and conditioning upstream FT synthesis.

Naturally, many variations are possible and different choices will affect the required downstream processing. For instance, here a tar scrubber was selected leaving all the hydrocarbons (including BTX) intact, whereas a tar cracker/reformer would already provide a product gas rich in syngas and CO_2. An HDS unit would then be obsolete.

When comparing the gas cleaning and upgrading requirements of the solid biomass conversion (Section 1) compared to the bio-oil gas, the proposed gas treatment configuration could be applied for both. However, the concentration of e.g. tar was significantly lower in the bio-oil product gas. Moreover, as no sulphur was observed in the product gas, the catalytic conversion of organic sulphur component (e.g. thiophene) in a HDS reactor would not be required. At least smaller tar removal and/or HDS units would suffice, which would result in lower costs.

Verification of this system configuration are required both by modelling (Aspen plus, part of work package 3.2.3) and experimental work. Experimental verification will be done at ECN.TNO as part of the next stage of work package 3.2.1.

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5. Conclusions

Solid biomass conversion.

Eucalyptus:

- The raw as received chips were grinding and separated over a 2mm sieve to obtain <2mm particles without fibers/fluffy material. In experiment 1, feeding of this material led to a blockage in the transport screw, which was probably caused by the very low bulk density of the feedstock. In experiment 5, a lower feeding rate was used ~2.2 kg/h, which did not result in any blockage.
- The product gas composition from the indirect eucalyptus gasification was similar to that of other woody biomass, such as beech wood.
- At 808°C, 39.7 g/Nm^3 of tar was formed and 176 ppmv H_2S.
- The carbon mass balance did not fully close, 19% was unaccounted for. It is likely that part of the carbon leaves as unconverted soot/char with the product gas. This was partially confirmed in experiment 5 where a much longer residence time in i-Milena resulted in a better C closure of 86%.
- After correction of the carbon balance, a CGE and CC of 73% should be assumed at 800°C gasification using eucalyptus with a 20 wt% moisture content excluding tar for further value chain modelling.

Biomass sorghum:

- As received, chipped and dried, biomass sorghum was pelletized after grinding to <4 mm particles. These Sorghum particles were fed to Milena successfully with no bed agglomeration, which can be expected with a herbaceous biomass with a high (5%) ash content. This can be an issue due to the high concentration of alkalis and the accompanied ash melting temperature.
- Biomass sorghum gasification gave product gas with very high sulphur concentrations, because of the high sulphur concentration in the feed (1000 ppm). At 811°C, a H_2S concentration of 878 ppmv was found.
- Similar to eucalyptus gasification, the average overall carbon balans added up to ~80-85%.
- After correction of the carbon balance, a CGE and CC of 65% should be assumed excluding tar at 800°C for further value chain modelling, somewhat lower that

One of the major challenges in the lab-scale experiments was the carbon closure. The carbon closures for all experiments are in the range of 70-80%. Because of this, the actual determined CC and CGE are on the low side. Investigations into the source of the missing carbon is required. Possible extended residence time, better/more gasification agents and/or catalytic bed material will provide better conversion. Moreover, careful analysis of captured dust (ash + soot + char) is desired. The hypothesis here is that soot and/or char simply leave the reactor and can therefore not be analysed (and simply represent a loss).

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Conversion of bio-oils and bio-oil/char slurries.

The trials for gasification of the slurry revealed extensive feeding difficulties, which could not be overcome using the lab-scale BFB gasifier (WOB).

The bio-oil could be successfully fed to the gasifier having several advantages when compared to direct solid biomass gasification and the results showed that:

- The carbon conversion to product gas could be higher than with solid biomass gasification, up to 82% (excl. tar).
- The CGE was higher than with solid biomass gasification, up to 81% (excl. tar).
- The tar level was lower than with solid biomass gasification at 18 g/Nm^3 on a nitrogen free basis.
- The sulphur in the product gas was lower than with solid biomass gasification, remaining below < 4 ppmV on a nitrogen free basis.
- To accelerate the conversion rate and avoid accumulation of the bio-oil in the bed it is advised to use gasification temperatures over 800°C.

It is expected that the gasification of the char/bio-oil slurry will produce slightly lower values for carbon conversion and CGE. However, it is not expected that the gas composition will be much different from the gasification of the bio-oil, as long as the share of the char do not surpass 10 wt%.

Gasification experimental tests with the bio-oil and char are planned to be undertaken in the following months using another lab-scale experimental facility - Milena. Here it is planner to feed the bio-oil separately from the char to avoid spraying problems as verified in the BFB (WOB).

Gas upgrading for FT.

Finally, the best upgrading strategy was determined for upgrading the product gas before Fischer-Tropsch catalytic conversion. The product gas contains much tar due to the relatively mild gasification conditions in indirect gasification of solid biomass and slightly less for bio-oil gasification. Here, an Olga tar removal unit (an oil scrubbing process) was selected. Also much sulphur is present in the form of H_2S/COS, but more importantly, organic sulphur an HDS reactor is required in combination with a ZnO or activated carbon sorbent bed. A steam reformer is then placed to maximize the syngas content and to stear the H_2/CO ratio towards 2.2 desired in the FT reaction. Finally, an amine scrubber is placed to remove most CO_2, again to maximize the syngas output.

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Appendix A

Table 20: Proximate and ultimate analyses results of the pretreated eucalyptus and biomass sorghum.

	Unit	**Eucalyptus**	**Sorghum**
LHV	[MJ/kg], ar	16.0	15.8
LHV	[MJ/kg], daf	17.8	17.4
Volatile content	[%], db	77.8	74.3
Ash content	[%], db	1.5	5.0
Moisture	[%], ar	7.9	3.8
C	[%], db	47.4	44.8
H	[%], db	6.1	5.9
O	[%], db	44.0	41.8
N	[%], db	0.4	0.9
S	[%], db	0.0340	0.100
Cl	[%], db	0.130	0.150
Al	[mg/kg], db	42	210
As	[mg/kg], db	<1	<1
B	[mg/kg], db	6.1	6.6
Ba	[mg/kg], db	14	6.7
Ca	[mg/kg], db	6200	3700
Cd	[mg/kg], db	<0.1	0.21
Co	[mg/kg], db	140	8.4
Cr	[mg/kg], db	<0.9	2.2
Cu	[mg/kg], db	11	4.8
Fe	[mg/kg], db	46	240
K	[mg/kg], db	3100	12000
Li	[mg/kg], db	<0.3	<0.3
Mg	[mg/kg], db	740	3100
Mn	[mg/kg], db	12	25
Mo	[mg/kg], db	<0.8	<0.8
Na	[mg/kg], db	230	84
Ni	[mg/kg], db	3	1.4
P	[mg/kg], db	450	1200
Pb	[mg/kg], db	0.84	<0.6
Sb	[mg/kg], db	<3	<3
Se	[mg/kg], db	<1	<1
Si	[mg/kg], db	150	11000
Sn	[mg/kg], db	<0.9	<0.9
Sr	[mg/kg], db	35	24
Ti	[mg/kg], db	1.5	4.9
V	[mg/kg], db	<0.2	<0.2
W	[mg/kg], db	9.8	11
Zn	[mg/kg], db	20	37
	Db - dry basis, ar – as received, daf – dry as received.		

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Table 21: Proximate and ultimate analyses results of the eucalyptus pyrolysis bio-oil and char.

	Unit	**Pyrolysis Oil**	**Char**	**Slurry[#]**
Moisture	[%], ar	na	4.92	35.40
Volatile matter	[%], ar	na	14.18	83.16
Fixed carbon *	[%], ar	na	77.27	7.73
Ash (550 °C)	[%], ar	0.56	3.63	0.87
Ash (815 °C)	[%], ar	0.00	2.52	0.25
C	[%], ar	44.20	81.56	47.94
H	[%], ar	7.36	2.13	6.84
N	[%], ar	0.16	0.36	0.18
S	[%], ar	0.01	0.04	0.01
Cl	[%], ar	0.004	0.029	0.01
O	[%], ar	41.38	7.13	37.95
HHV	[MJ/kg], ar	17.2	30.5	18.53
LHV	[MJ/kg], ar	15.6	30.1	17.05
Al	[mg/kg], ar	4	644	68
As	[mg/kg], ar	< 1	< 1	< 1
B	[mg/kg], ar	< 0.7	16	2
Ba	[mg/kg], ar	0	70	7
Ca	[mg/kg], ar	33	11182	1148
Cd	[mg/kg], ar	< 0.1	< 0.1	< 0.1
Co	[mg/kg], ar	< 0.3	1	0.3
Cr	[mg/kg], ar	< 0.9	8	2
Cu	[mg/kg], ar	< 2	7	2
Fe	[mg/kg], ar	7	563	63
K	[mg/kg], ar	18	2588	275
Li	[mg/kg], ar	< 0.3	0	< 0.3
Mg	[mg/kg], ar	17	1265	142
Mn	[mg/kg], ar	3	102	13
Mo	[mg/kg], ar	< 0.8	1	1
Na	[mg/kg], ar	5	220	27
Ni	[mg/kg], ar	< 0.6	11	2
P	[mg/kg], ar	5	362	41
Pb	[mg/kg], ar	< 0.6	2	1
S	[mg/kg], ar	94	364	121
Sb	[mg/kg], ar	< 3	< 3	< 3
Se	[mg/kg], ar	< 1	< 1	< 1
Si	[mg/kg], ar	< 30	844	111
Sn	[mg/kg], ar	< 0.9	< 0.9	< 0.9
Sr	[mg/kg], ar	0.2	55	6
Ti	[mg/kg], ar	< 0.3	15	2
V	[mg/kg], ar	< 0.2	0.2	< 0.2
W	[mg/kg], ar	< 1	< 1	<1
Zn	[mg/kg], ar	4	13	5
Hg	[mg/kg], ar	<0.002	<0.002	<0.002
	ar - as received; * by difference; na - not applicable; [#]Calculated			

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