



Project acronym: BECOOL

Project full title: Brazil-EU Cooperation for Development of Advanced Lignocellulosic Biofuels

Grant Agreement Number: 744821

Project start date: 01.06.2017

Deliverable 3.14

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| Title: | |
| OVERALL REPORT ON GASIFICATION EXPERIMENTS AND RESULTS | |
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| Date: | March 2022 |

Dissemination Level: Public

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Abbreviations

| | |
|------|---------------------------------|
| BW | Beech wood |
| BAG | Bagasse from sugarcane |
| ar | as received |
| nd | not determined/measured |
| db | dry basis |
| daf | dry ash-free basis |
| PG | Product gas |
| SMR | Steam methane reforming |
| FTS | Fischer-Tropsch synthesis |
| HDS | Hydrodesulphurisation |
| CO2R | CO ₂ absorption unit |
| LHV | Lower heating value |

Introduction

In the BECOOL project, entire value chains including biomass harvest, collection, upgrading and conversion to transportation fuels are studied. With the aim of promoting the development of resilient and robust supply chains for advanced biofuels. For the biomass conversion, both the centralized conversion of (solid) biomass via gasification and the decentralized production of intermediate energy carriers, for subsequent gasification, are included.

Biomass and residual biomass considered in BECOOL include eucalyptus (EUC), giant reed (GR), biomass sorghum (SO), bagasse (BA) and a lignin-rich residue (RL) from a biomass refinery plant. More information on the considered value chains can be found in D2.1 [1]. A short overview of the different BECOOL feedstocks, including properties relevant for the thermochemical conversion, can be found in Table 1.

Table 1: Relevant properties of BECOOL feedstocks for thermochemical conversion [1].

| Biomass type | Type/Harvest | Average moisture at harvest | Ash content and ash melting point (MP) | Cellulose/hemicellulose /lignin [%] |
|---------------------|-------------------------------------|-----------------------------|--|-------------------------------------|
| Eucalyptus | Short (2-3y) medium (4-5y) rotation | 50% | 2%, MP depends on fertilization and harvest time | 43/25/23 (BW: 48/22/24) |
| Giant Reed | Perennial grass | 50-70% (~30% on field) | 5%-6%, 954°C | 33/27/18 |
| Biomass Sorghum | Annual energy crop | 70%-80% | 4%-9%, 953°C | 40/25/9 |
| Bagasse | From sugar cane | 40%-50% | 1%-15% [2], 1237°C | 39/27/18 |
| Lignin rich residue | From bioethanol plant | 50%-60% | 5%-15% | 50-60% lignin |
| Lignin rich residue | Fabiola fractionation [3] | 50%-60% | 0.5-25% | >95% lignin |

For the conversion plants, an integral part of the entire value chain, two types of gasification plants are considered [4]. These are;

- Entrained flow (EF) gasification at high temperature (>1000°C) for which (decentralized) biomass pretreatment is required. Fast pyrolysis is one of the pretreatment options that provides a bio-oil for EF gasification.
- Low temperature steam gasification, in a fast circulating fluidized bed gasifier (MILENA [5]) at 700-900°C. This low temperature gasification can be followed by tar reforming at high temperature, or tar

[1] D. Chiamonti et al., 2018, BECOOL Deliverable D2.1, "Description of full biomass supply chains".

[2] Phyllis biomass database, <https://phyllis.nl/>.

[3] K. Damen, A.T. Smit, W.J.J. Huijgen, J.W. van Hal, RRB 13 Conference, 2017, Fabiola: fractionation of biomass using low-temperature acetone.

[4] I. Hannula, V. Nikkanen, E. Boymans, M. Saric, 2020, BECOOL Deliverable D3.6, "Models for biomass to liquid fuels".

[5] <https://synovatech.com/our-technology-platform/>

absorption at low temperature. A graphical representation of the gasification route using tar absorption, which is the focus in this work, can be found in Figure 1. It includes the required gas cleaning (tar removal, water wash), gas upgrading (HDS, SMR, CO₂ absorption) and Fischer-Tropsch (FT) synthesis.

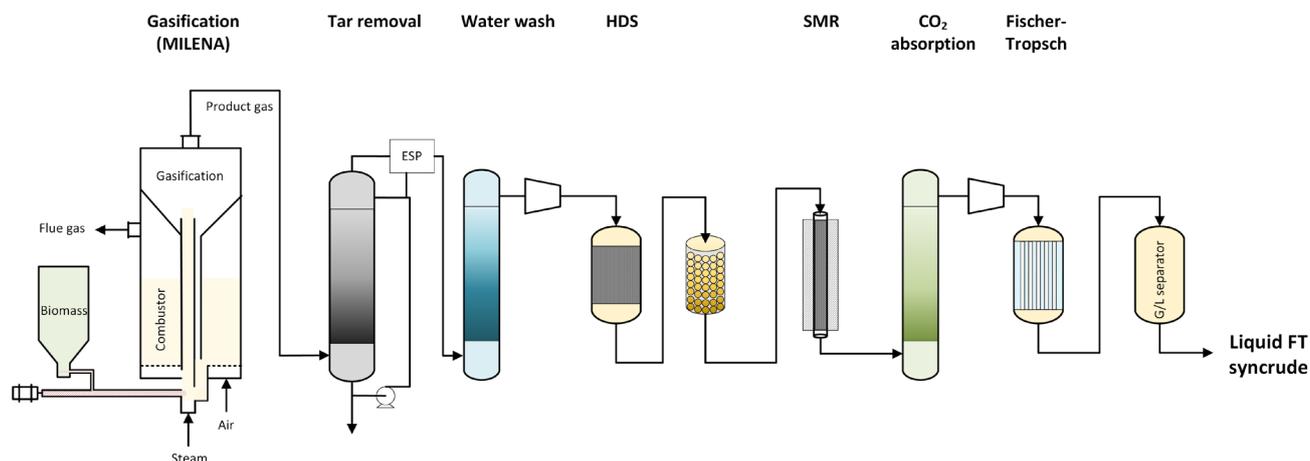


Figure 1: Simplified PFD of the low temperature steam gasification followed by PG cleaning, upgrading and FT synthesis.; one of the BECOOL conversion processes.

This work focuses on the experimental validation and demonstration of the biofuel production process as depicted in Figure 1. It includes biomass gasification (25 kW) and gas cleaning, gas upgrading and finally the FT synthesis. Woody biomass (beech wood chips) and bagasse were used as feedstock in this 10-day campaign. The experimental results will be discussed and compared with the Aspen Plus model calculations with special attention to the process chemical efficiency.

Experimental

Experiment setup

The layout of the experiment is shown in the process flow scheme in Figure 2. For reporting purposes, a division into three sections was made, also shown in Figure 2;

Section 1: Gasification + gas cleaning,

Section 2: Gas upgrading

Section 3: Fischer-Tropsch synthesis.

This test included 10 individual days of testing, involving start-up in the morning and shutdown at the end of the day i.e., no overnight sessions were included. An overview of the experimental program can be found in Table 2. Day 1 to 4 were used to perform the analysis around the gasification and gas upgrading and in parallel start-up of the FT pilot unit (stand-alone) using synthetic gas from gas cylinders. From Day 5 the entire process is running, except Day 8 where the FTS booster required maintenance.

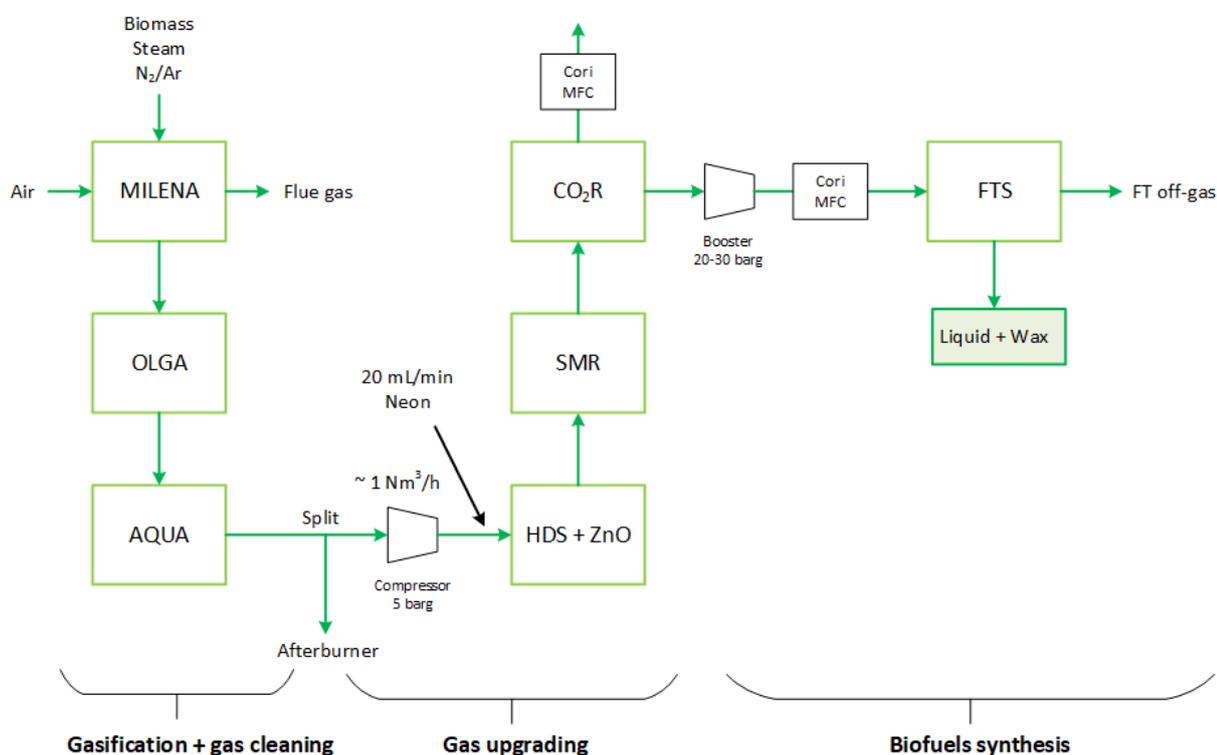


Figure 2: Experimental layout

Table 2: Overview of the experimental days

| | Gasification | Upgrading | Synthesis |
|------------|--------------|-----------|-----------|
| Day 1 | | | |
| Day 2 | | | |
| Day 3 | | | |
| Day 4 | | | |
| Day 5 | | | |
| Day 6 | | | |
| Day 7 | | | |
| Day 8 | | | |
| Day 9, BAG | | | |
| Day 10 | | | |

Feedstock

Beech wood chips were used as main feedstock, because it is the benchmark feedstock for the MILENA gasifier, and it is available in the large quantities required for all the operational hours in this campaign. To also include a BECOOL feedstock, bagasse (BAG) was used as feedstock on Day 9, see Figure 3. Ground bagasse pellets were used, as described in Deliverable 3.9 [6].

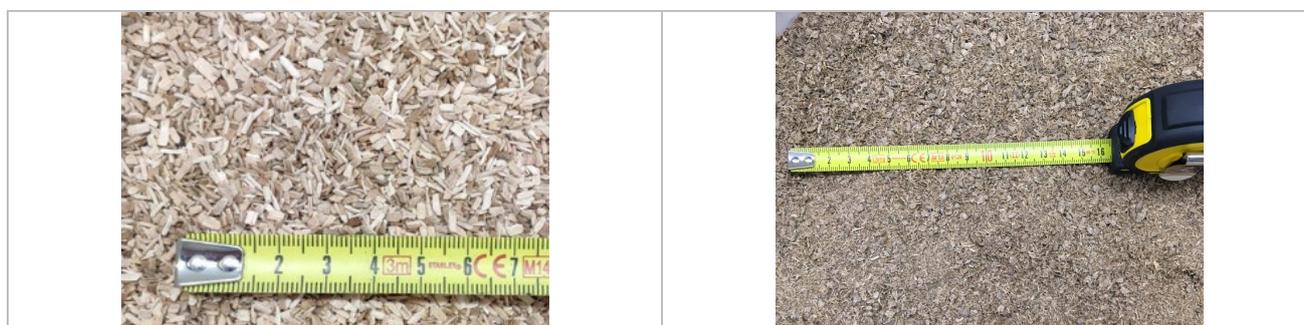


Figure 3: Beech wood chips (left) and bagasse ground pellets (right) used as feedstock.

The physicochemical properties of both materials, as fed to gasifier, can be found in Table 3. Methods used: B.N035; chloride, nitrate, sulphate and bromide via ion chromatography, B.N202; gravimetric determination of moisture, volatiles and ash, B.N203; calorific value, B.N211; CHN analysis, B.N213; O analysis, B.S231; ICP-AES, O.N203 and O-SB08 (ash composition).

⁶ E.H. Boymans, B.J. Vreugdenhil, Deliverable 3.9 (the BECOOL project): Gasification of solid fuels for production of advanced biofuels: update, 2021, 1-18.

Table 3: Physicochemical properties on dry basis (db), unless stated as received (ar) or dry ash free (daf).

| Analyse | Unit | BW chips | BAG pellets |
|------------------|-------------|----------|-----------------|
| LHV | [MJ/kg], db | 17.8 | 17.8 |
| Volatile content | [%] | 80.9 | 82.3 (85.2 daf) |
| Ash content | [%] | 1.3 | 3.4 |
| Moisture | [%], ar | 8.9 | 5.0* |
| C | [%] | 47.5 | 47.5 |
| H | [%] | 6.4 | 5.4 |
| O | [%] | 48.8 | 45.8 |
| N | [%] | 0.17 | 0.24 |
| S | [%] | 0.024 | 0.027 |
| Cl | [%] | 0.0056 | 0.024 |

Settings

Following the conversion blocks as depicted in Figure 2, the average settings of each unit can be found in Table 4 and Table 5. The first step of the process involved the biomass gasification in the MILENA gasifier. The product gas (PG) was then sent through the tar removal unit (OLGA) followed by water condensation (AQUA). More detailed specifications of these units can be found in deliverables 3.5 and 3.9.

Table 4: Average settings of the individual units.

| MILENA Gasifier | | |
|-------------------------------------|----------|------------------------|
| Feedstock | | Beech wood or bagasse |
| Feedstock input | [kg/h] | 5.0 |
| Bed material | | 44 kg Olivine (0.3 mm) |
| T gasification in settling chamber | [°C] | 820 |
| T in bed combustor | [°C] | 855 |
| Steam riser | [kg/h] | 1.1 |
| Transport screw N ₂ flow | [NL/min] | 1.0 |
| Tracer gas Ar | [NL/min] | 1.0 |
| Combustion air | [NL/min] | 100 |
| OLGA tar removal | | |
| Collector | [°C] | 80 |
| ESP | [°C] | 90 |
| Absorber | [°C] | 80 |

| | | |
|--------------------|------|-----|
| Stripper | [°C] | 160 |
| AQUA | | |
| Outlet temperature | [°C] | 17 |

Part of the gas (~23%) was then compressed and sent through the gas upgrading units, while the remaining gas was directly sent to the afterburner. Neon gas was added, as a tracer gas, to the PG after the split in order to quantify the gas flow at each sampling point. Sampling points were located downstream of each unit. Downstream of the CO₂ absorption unit, a mass-flow meter was placed to allow for determination of the absolute flow from the upgrading section. Alternatively, the gas passes through a booster (pressure increase to 20-30 barg), followed by a mass-flow meter to enter the Fischer-Tropsch synthesis (FTS) reactor. From the CO₂R unit, the bio-syngas can thus be sent either to the afterburner or the FTS reactor. This allowed for start-up of the FTS reactor in parallel with synthetic gas mixtures (not shown in Figure 2). Finally, a FTS off-gas meter (Ritter) downstream of the FTS reactor measured the volumetric flow which was used to determine the syngas conversion. Average settings of both the upgrading and fuel synthesis sections can be found in Table 5.

Table 5: Settings upgrading and synthesis units

| | | |
|---|----------|-------------------------------|
| Compressor | [barg] | 0 → 5 |
| Pressure, all | [barg] | 5 |
| HDS – ZnO – AC | | |
| Neon (tracer gas) | [mL/min] | 20 |
| HDS catalyst (CoMo/Al ₂ O ₃) | [g] | 1500 |
| HDS set temperature | [°C] | 250, 300, 400 |
| HDS gas inlet temperature | [°C] | 300 (TC4 before entering bed) |
| HDS average temperature | [°C] | 340-470 |
| Reactor 11 (ZnO) | [g] | 1500 |
| Reactor 11 temperature | [°C] | 250 |
| Reactor 12 (AC) | [g] | 1000 |
| Reactor 12 temperature | [°C] | 150 |
| SMR, steam reformer | | |
| SMR catalyst (Ni/α-Al ₂ O ₃) | [g] | 816 |
| Steam | [g/h] | 710 |
| Temperature gas outlet | [°C] | 850 |
| CO₂R | | |
| Absorption liquid | | Amine solution |
| Absorber | [°C] | 40 |

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|--|--------|-----------|
| Stripper | [°C] | 110 |
| | | |
| Booster | [barg] | 5 → 20 |
| FTS unit | | |
| Catalyst pellets (Co/Al ₂ O ₃ + SiC) | [g] | 350 + 486 |
| Reactor inner diameter/length | [mm] | 26/2500 |
| Temperature set | [°C] | 200 |
| Average temperature | [°C] | 200-220 |

Gas and liquid analysis

The flue gas composition (from the gasifier's combustion zone) was monitored by a dedicated gas monitor set. To determine the PG composition at the various sampling points, a variety of gas sampling methods were performed, see Table 6. These included continuous online analysis with gas analysis sets (including a gas monitor set and μ -GC) and offline analysis. Offline analysis proceeded 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 [7]. The tar and water determination measurements were performed according to the CEN/TS 15439 tar guideline [8]. Additionally, the permanent gases and vapours in the FTS gas were measured online with a multichannel GC, whereas the product liquids were measured with a GC-MS for identification of the hydrocarbons plus GC-FID for quantification.

Table 6: Gas/liquid analysis methods used to determine the PG composition.

| Sampling | Instrumentation | Measured components |
|---------------------------|---|--|
| Online gas monitor set | ABB Advanced Optima analyser. | CO, CO ₂ , CH ₄ (NDIR) H ₂ (TCD) O ₂ (Paramagnetic) |
| Online μ -GC analysis | Varian CP4900 4-channel micro-GC with TCD. | CO, H ₂ , CH ₄ , C ₂ H ₆ , C ₂ H ₄ , C ₂ H ₂ , C ₆ H ₆ , C ₇ H ₈ , CO ₂ , N ₂ , H ₂ S, COS, Ne, Ar. |
| Gas bags | Sulphur components using Shimadzu GC17A with FPD detector and trace carbon using the TRACE GC-FID. Dräger tubes with color indication for HCN. | All reported sulphur components and C1-C6 hydrocarbons. HCN. |
| Tar guideline | Thermo Scientific Trace 1310 GC with FID for liquid analysis. KF titration. | Respectively all tar components and PG moisture content. |
| Impinger bottles | Liquid analysis [7]. | NH ₃ , HCN, HCl. |
| FTS gas, online | GC equipped with separate channels with HS-N column with TCD detector, Molsieve 5A column with TCD detector and PlotQ column with FID detector. | N ₂ , Ar, CO ₂ , CH ₄ , CO, H ₂ , C ₁ -C ₄ . |
| FTS condensates | Agilent 7890A 5975C GC-MS and a Thermo Trace 1310 GC-FID both equipped with a J&W VF-5ms (30 m, 0.25 mm, 0.25 μ m) capillary column. | Condensates from the hot (C10+) and cold (C5+) separators to determine carbon number distribution. |

[7] G. Aranda Almansa *et al.*, IEA Bioenergy Task 33, Gas analysis in gasification of biomass and waste, ISBN 978-1-910154-43-4.

[8] 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.

Results and discussion

For clarity, the results will be discussed following the sections as stated in the experimental section, namely gasification + gas cleaning, gas upgrading and biofuels synthesis. Starting Day 4, the sand bed material in the gasifier was changed for Olivine, and from this day most upgrading units were online. Hence, the reporting will only include results starting Day 4.

Section 1: Gasification + gas cleaning

Major trends in the overall gasification results of Day 4 to 10 will be briefly highlighted followed by a closer look at two specific experimental days. Even though the gasifier was started up every day, the gasification temperatures were very constant at around 820°C with the combustion zone approximately 35°C higher, as can be observed in Figure 4. Similarly, the concentration of the main gas components in the PG were relatively constant. CO, the gas present at the highest concentration decreases from 43 to 37 vol%. Conversely, CO₂ increases throughout the campaign from 10 to 15 vol%. This could be the result of increased shift activity by the bed material, although the hydrogen concentration increases less than would be expected from 17 to 19 vol%.

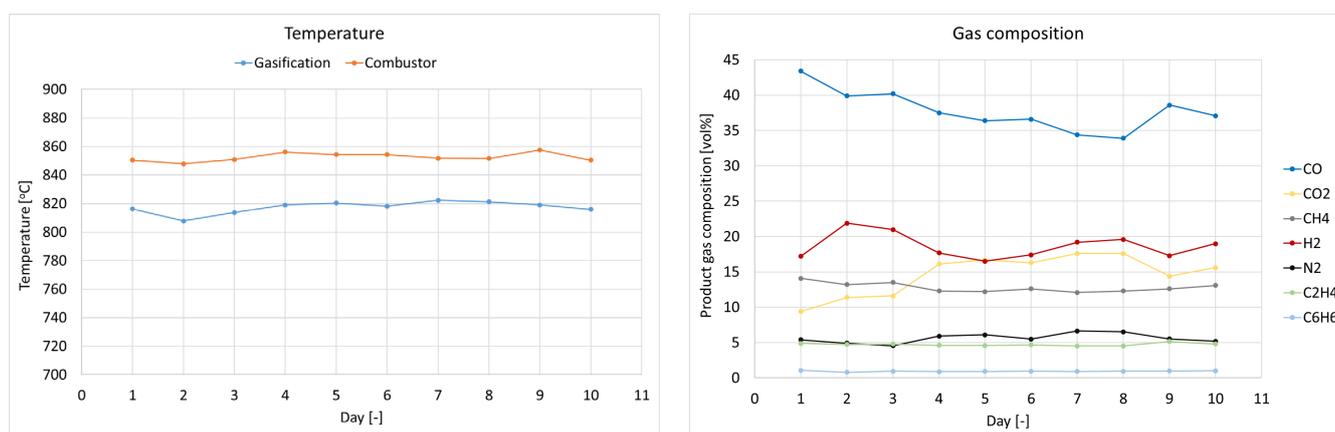


Figure 4: Average temperatures (left) and PG composition (right) of the MILENA gasifier throughout the campaign.

For Day 4 (beech wood) and Day 9 (bagasse), the complete PG compositions can be found in Table 7. For Day 4, measurements were performed both at MILENA and AQUA outlet whereas during Day 9 only downstream AQUA. This AQUA sampling point is positioned downstream of the condenser and therefore represents a tar- and water-free gas. As not all wet chemical analysis were done on the same day, some values within brackets () are taken from another day.

In general, the PG composition for bagasse was found to be remarkably similar to that of beech wood. Only minor differences can be found such as the higher sulphur content as seen in the chemical composition of the feedstock.

Table 7: Averaged PG composition downstream MILENA and OLGA-AQUA on dry basis.

| | | Day 4 MILENA | Day 4 AQUA | Day 9 AQUA |
|------------------------------------|----------------------|--------------|------------|------------|
| Feedstock | | BW | BW | BAG |
| CO | [vol%] | 36.1 | 37.5 | 38.6 |
| H ₂ | [vol%] | 18.4 | 17.7 | 17.3 |
| CO ₂ | [vol%] | 16.7 | 16.1 | 14.4 |
| CH ₄ | [vol%] | 12.2 | 12.3 | 12.6 |
| N ₂ | [vol%] | 4.9 | 5.9 | 5.5 |
| C ₂ H ₂ | [vol%] | 0.3 | 0.3 | 0.3 |
| C ₂ H ₄ | [vol%] | 4.5 | 4.6 | 5.2 |
| C ₂ H ₆ | [vol%] | 0.3 | 0.4 | 0.4 |
| Benzene | [ppmv] | 8488 | 9049 | 9920 |
| Toluene | [ppmv] | 1205 | 1293 | 1290 |
| Sum C ₃ | [ppmv] | 1599 | 1594 | 1135 |
| Sum C ₄ | [ppmv] | 1221 | 1201 | 1026 |
| Sum C ₅ | [ppmv] | 101 | 101 | 76 |
| Sum C ₆ (excl. benzene) | [ppmv] | 5 | 5 | 4 |
| H ₂ S | [ppmv] | 105 | 126 | 199 |
| COS | [ppmv] | 13 | 9 | 13 |
| Thiophene | [ppmv] | 9 | 5 | 13 |
| Methylmercaptane | [ppmv] | 1 | 2 | 1 |
| Other S-organics | [ppmv] | 0 | 0 | 0 |
| NH ₃ | [ppmv] | nd | 9 | nd |
| HCN | [ppmv] | nd | 89 | nd |
| HCl | [ppmv] | nd | 0 | nd |
| Tar total (excl. toluene) | [g/Nm ³] | (51.4) | 3.4 | (3.4) |
| Argon | [vol%] | 1.9 | 1.9 | 1.91 |
| Neon | [ppmv] | 0 | 0 | 0.0 |
| Sum (excl. tar) | [vol%] | 96.5 | 98.0 | 97.5 |
| Water content | [vol%] | 52.9 | 2.1 | (2.1) |
| Flow excl. tar (based on Ar) | [NL/h] | 3331 | 3390 | 3315 |
| CGE excl. tar, LHV basis | [%] | | 67.2 | 68.2 |
| CGE model | [%] | | 78 | 78 |
| CC PG tar free / flue | [%] | | 71/20 | 70/21 |

| | | | | |
|----------------------------|-----|--|-------|-------|
| CC (gasification model)[9] | [%] | | 74/18 | 74/18 |
|----------------------------|-----|--|-------|-------|

Values between brackets were extrapolated from another measurement day. Nd = not determined. Gasification temperature was 819°C, at a feeding rate of 5 kg/h biomass and 1.1 kg/h steam.

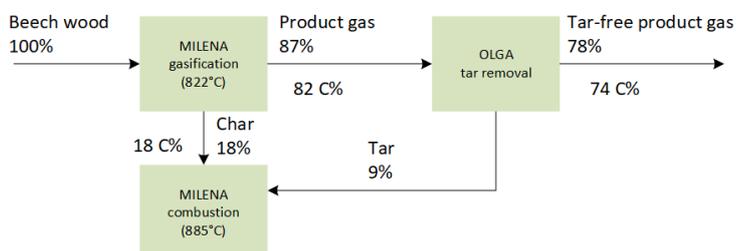


Figure 5: MILENA-OLGA CGE and CC as determined by the gasification model [9].

During Day 4, the carbon conversion to PG is somewhat low at 71% on a tar-free basis, but close to the expected value from the gasification model (74%). This can partially be explained by the 20% of carbon that was measured in the flue gas, slightly higher than the predicted 18%. The much lower efficiency on LHV basis (67% vs 78%) can only partially be explained by the missing conversion of feedstock to PG. Another reason was oxygen transfer from the combustor to the riser resulting in a product gas with a lower heating value as part of the PG is combusted, as observed by the higher CO₂ concentration in the PG with olivine. Overall, the differences between experimental results and model can be explained by the olivine used in the gasifier instead of sand. Sand is the basis of the model, which does not include oxygen transfer nor the lower carbon conversion, thereby producing higher conversions. The expected benefits of olivine (better tar conversion and more hydrogen through WGS) were not obtained as the olivine was not activated yet. With bagasse as feedstock, very similar gasification results were found in terms of the PG composition.

For Day 4, the pressure and temperature profiles during gasification are presented in Figure 6. Very stable trends in temperature and pressure can be observed.

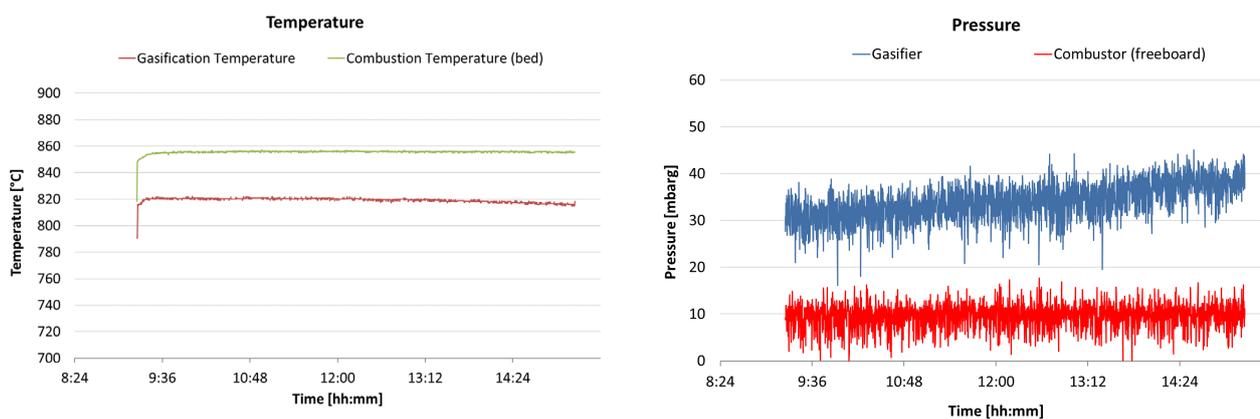


Figure 6: Temperature (left) and pressure (right) profile in the gasification and combustion areas of MILENA during Day 4.

Moreover, in Figure 7, the gas composition profiles of the product gas downstream MILENA and AQUA are presented. As can be seen in the left graph, the CO value presented an increasing trend throughout the

[9] V. Nikkanen, E. Boymans, 2022, BECOOL deliverable D3.12, Benchmarking of gasification and fast pyrolysis models: update.

experiment, from roughly 35 to almost 38 vol%, while CO₂ values dropped by approximately 2 vol% at the same interval. A rather slow increase was also noted for CH₄, but it was less than 1 vol%.

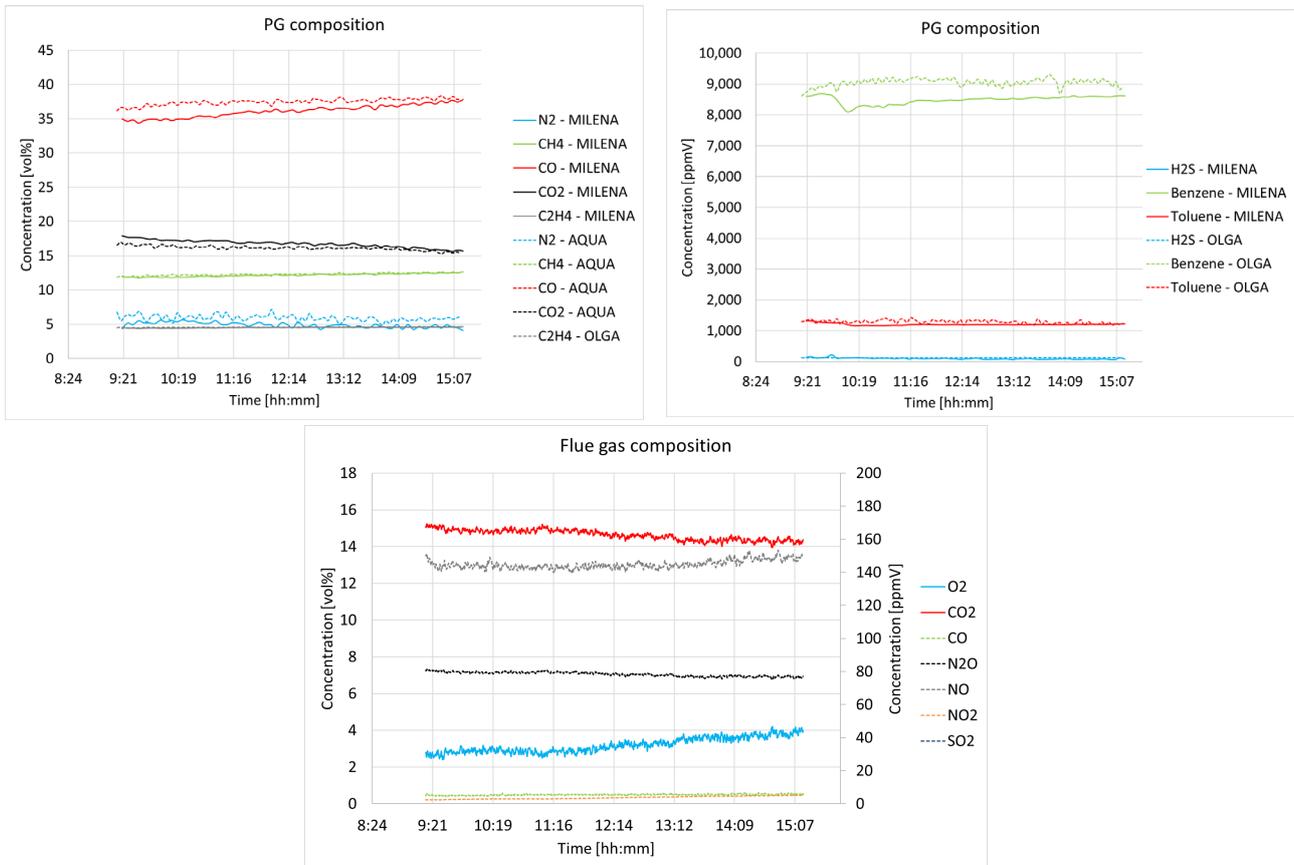


Figure 7: Gas composition profile as measured after MILENA and OLGA (top) and composition of combustion flue gases (bottom) during Day 4 on dry basis.

During Day 9, bagasse was used as gasification feedstock. The temperature and pressure profiles that were observed at the combustion and gasification areas of MILENA, are presented in Figure 8.

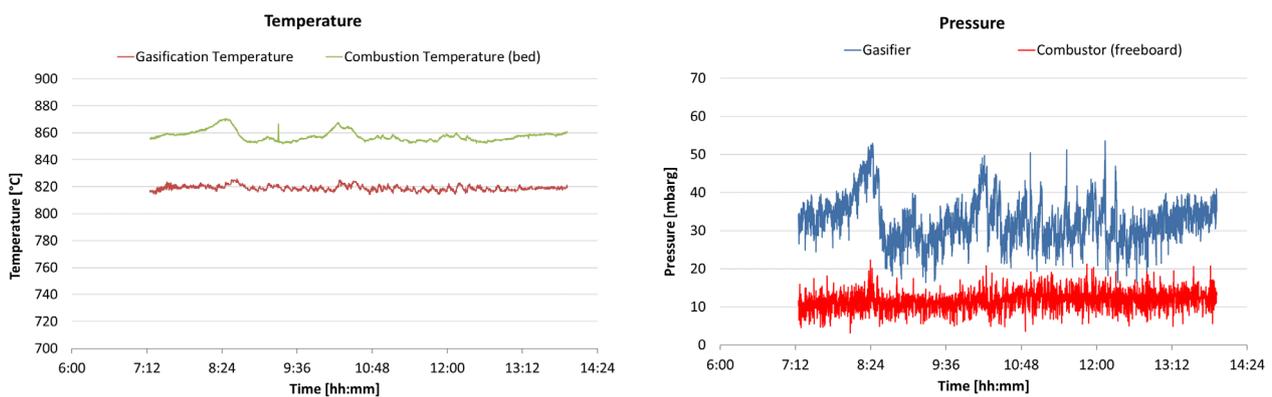


Figure 8: Temperature (left) and pressure (right) profile in the gasification and combustion areas of MILENA during Day 9 (bagasse).

From the temperature profile in Figure 8, it can be observed that despite the gasification temperature being relatively stable, its value was oscillating more compared to the case of beech wood experiments. A more unstable profile was obtained for the combustion temperature, where the main peaks (deviations) noticed

around 08:30 and 10:17, corresponding to the major pressure peaks noticeable in the pressure profile. These pressure peaks (and its consequences) were caused by a blockage in the line to the afterburner.

The gas composition profile as measured using a μ GC downstream AQUA (condenser), is presented in Figure 9. Overall, the individual gaseous product concentration profiles were relatively stable throughout the experiment, with the oscillations presented following, as expected, the patterns of the product gas pressure profile. The oscillations were mostly observable for the benzene production profile.

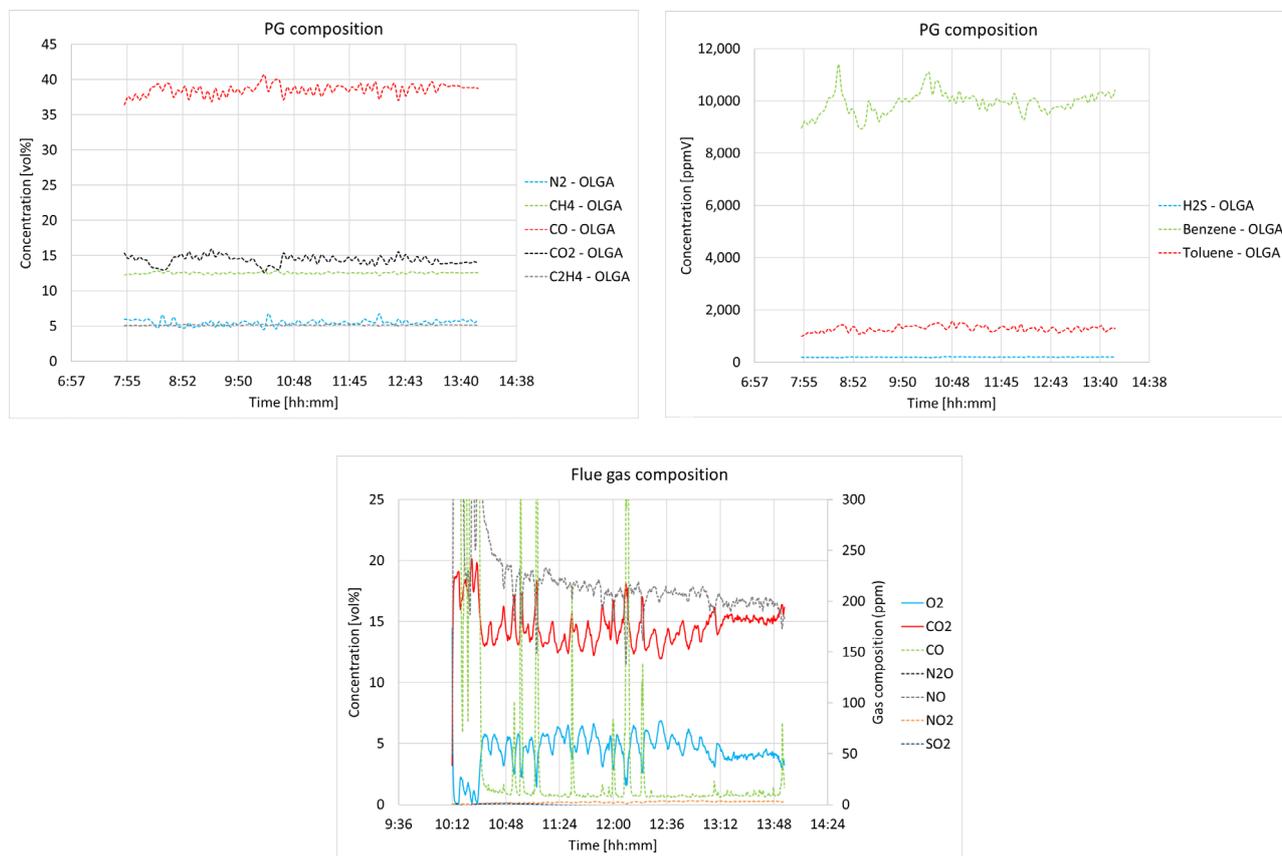


Figure 9: Gas composition profile as measured downstream MILENA and AQUA (top) and composition of combustion flue gases (bottom) during Day 9 (bagasse).

Section 2: Gas upgrading

Downstream of the AQUA, in the gas upgrading section, the PG firstly passed through the HDS reactor to convert organic-S into H_2S and COS . This was followed by sorbent beds R11 and R12, which were filled with ZnO and AC , respectively, for the adsorption of H_2S , COS and remaining nitrogen components. Removal of sulphur- and nitrogen-containing components to ppb level was required for the catalytic conversions downstream. With the analytical tools applied here, this implied staying below the detection limits. In Table 8, which summarizes the PG compositions at the different stages for Day 4, 7 and 9, it can be observed under “R12” that this was indeed the case for all days. Table 8: Average product gas compositions on dry basis at different stages in the gas upgrading section during Day 4, 7 and 9.

| | | Day 4 31-01 | Day 4 | Day 4 | | Day 7 07-02 | Day 7 | Day 7 | Day 7 | | Day 9 10-02 | Day 9 | Day 9 |
|--|-------------------------|----------------|-------------|-------------|--|----------------|-------------|-------------|-------------|--|----------------|-------------|-------------|
| Sampling position, downstream | | AQUA | R12 | CO2R | | AQUA | R12 | SMR | CO2R | | AQUA | R12 | CO2R |
| CO | [vol%] | 37.5 | 40.8 | 29.7 | | 34.4 | 36.0 | 23.1 | 30.8 | | 38.6 | 39.8 | 31.2 |
| H ₂ | [vol%] | 17.7 | 13.3 | 64.1 | | 19.2 | 13.4 | 51.4 | 62.7 | | 17.3 | 11.7 | 63.3 |
| CO ₂ | [vol%] | 16.1 | 15.6 | 0.1 | | 17.6 | 21.0 | 18.2 | 0.4 | | 14.4 | 18.3 | 0.1 |
| CH ₄ | [vol%] | 12.3 | 15.2 | 0.3 | | 12.1 | 13.9 | 0.2 | 0.4 | | 12.6 | 14.5 | 0.4 |
| N ₂ | [vol%] | 5.9 | 7.0 | 3.9 | | 6.6 | 7.0 | 3.3 | 4.1 | | 5.5 | 6.2 | 3.4 |
| C ₂ H ₂ | [vol%] | 0.3 | 0.0 | 0 | | 0.3 | 0.0 | 0.0 | 0.0 | | 0.3 | 0.0 | 0.0 |
| C ₂ H ₄ | [vol%] | 4.6 | 0.0 | 0 | | 4.5 | 0.0 | 0.0 | 0.0 | | 5.2 | 0.0 | 0.0 |
| C ₂ H ₆ | [vol%] | 0.4 | 6.0 | 0 | | 0.4 | 5.5 | 0.0 | 0.0 | | 0.4 | 6.2 | 0.0 |
| Benzene | [ppmv] | 9049 | 112 | 0 | | 9273 | 10813 | 0 | 0 | | 9920 | 9171 | 0 |
| Toluene | [ppmv] | 1293 | 90 | 0 | | 1360 | 1548 | 0 | 0 | | 1290 | 1529 | 0 |
| Sum C ₃ | [ppmv] | 1594 | 2979 | 1 | | 1320 | 2277 | 0 | 0 | | 1135 | 2202 | 10 |
| Sum C ₄ | [ppmv] | 1201 | 302 | 0 | | 1020 | 1251 | 0 | 0 | | 1026 | 1199 | 7 |
| Sum C ₅ | [ppmv] | 101 | 1 | 0 | | 4 | 2188 | 2 | 0 | | 76 | 604 | 3 |
| Sum C ₆ (excl. benzene) | [ppmv] | 5 | 0 | 0 | | 76 | 6 | 0 | 0 | | 4 | 2 | 0 |
| H ₂ S | [ppmv] | 126 | 0 | 0 | | 129 | 0.1 | 0 | 0 | | 199 | 0 | 0 |
| COS | [ppmv] | 9 | 0 | 0 | | 4 | 0 | 0 | 0 | | 13 | 0.1 | 0 |
| Thiophene | [ppmv] | 5 | 0 | 0 | | (5) | 0 | 0 | 0 | | 13 | 0 | 0 |
| Methylmercaptan e | [ppmv] | 2 | 0 | 0 | | (2) | 0 | 0 | 0 | | 1 | 0 | 0 |
| Other S-organics | [ppmv] | 0 | 0 | 0 | | (0) | 0 | 0 | 0 | | 0 | 0 | 0 |
| NH ₃ | [ppmv] | 9 | 51 | nd | | (9) | nd | nd | nd | | nd | nd | nd |
| HCN | [ppmv] | 89 | nd | nd | | (89) | 0.3 | 0 | 0 | | nd | 0.7 | 0 |
| HCl | [ppmv] | 0 | nd | nd | | 0 | nd | nd | nd | | nd | nd | nd |
| Tar total (excl. toluene) | [g/Nm ³] | 3.4 | nd | nd | | (3.4) | nd | nd | nd | | (3.4) | nd | nd |
| Argon | [vol%] | 1.9 | 2.1 | 1.3 | | 1.8 | 1.9 | 0.9 | 1.2 | | 1.91 | 2.1 | 1.2 |
| Neon | [ppmv] | 0 | 0.16 | 0.12 | | 0 | 0.17 | 0.08 | 0.10 | | 0.0 | 0.16 | 0.09 |
| Sum (excl. tar) | [vol%] | 98.0 | 100.3 | 99.4 | | 98.2 | 100.6 | 97.1 | 99.5 | | 97.5 | 100.4 | 99.5 |
| Flow excl. tar (based on Ar) | [NL/h] | 3390 | 3043 | 5136 | | 3468 | 3307 | 7360 | 5636 | | 3315 | 3029 | 5569 |
| Efficiency* | [%] | 67.2 | 61.2 | 68.3 | | 67.2 | 69.6 | 77.6 | 75.1 | | 68.2 | 65.7 | 75.1 |
| <i>Aspen plus model efficiency</i> | [%] | <i>77.8</i> | <i>76.0</i> | <i>87.8</i> | | <i>77.8</i> | <i>76.0</i> | <i>87.8</i> | <i>87.8</i> | | <i>77.8</i> | <i>76.0</i> | <i>87.8</i> |

Values between brackets were extrapolated from another measurement day. Nd = not determined. * PG/biomass input, LHV (excl. tar). Downstream AQUA the gas was split and only the split stream (23%) passed through the other units, which is not accounted for in the Table for efficiency comparison reasons.

Subsequently, steam reforming in the SMR converted the remaining hydrocarbon into primarily syngas. Objectives to be achieved in the SMR included full methane conversion as well as obtaining a H₂/CO ratio of ~2 required for FTS. Some initial tuning of the conditions was required to find the optimal settings at 720 g/h steam (steam to CO+CH₄ ratio of 2.5) and 850°C (gas outlet). Methane in the PG was lowered from around 15 vol% to 0.2-0.3 vol% achieving a conversion of 98-99%, as reported in Table 8 for e.g., Day 7. As a result of the reforming reactions, the gas volume doubles due to the formation of much (low density) hydrogen with a significant amount of CO₂ formed. This CO₂ was then removed to below 0.5 vol% using an amine absorption process in the CO₂R unit. The final syngas has the desired H₂/CO ratio of 2.0-2.2 and contained less than 5 vol% of inerts including N₂.

Besides the gas compositions, also the conversion efficiencies were determined by dividing the PG total LHV by the biomass input. As can be observed in Table 8, an efficiency of 68.3% was achieved after CO₂R, whereas 75.1% was achieved on Day 7 and Day 9. This had to do with the sorption of mostly benzene and toluene on the activated carbon bed in the first days, which resulted in a lower calorific gas entering the SMR and CO₂R units. After breakthrough of these components higher efficiencies were obtained. Moreover, as can be expected, the total LHV increases through SMR (mostly due to an increased gas volume through hydrogen production) as this is an endothermic process.

In general, not accounting for the adsorption, the experimental efficiencies were about 10% lower compared to the Aspen plus calculated values. This difference was almost completely caused by the lower efficiency in the gasifier as explained in section 1.

Section 3: Fischer-Tropsch synthesis

In the gas upgrading section, a clean product gas was produced containing on average 31 vol% CO, 63 vol% H₂, 4 vol% N₂ and minor amounts of CO₂ and CH₄. These are the specifications desired for the Co-catalysed Fischer-Tropsch synthesis (FTS), which operates at relatively low temperature in the range of 220-250°C. The FTS reactor is a 2.5 m long fixed-bed reactor filled with catalyst pellets. One of the major challenges in the FTS reaction is the high exothermicity of $\Delta H_r = -165 \text{ kJ/mol}_{\text{CO}}$. For this reason, the reactor tube has an inner diameter of only 26 mm to allow a minimum radial spacing between the cooled reactor wall and the reactor axes. On the shell side, thermal oil is used to heat/cool the reactor. However, even with this reactor design, it is required to slowly ramp up the reaction conditions to achieve the desired conditions of WHSV = 2 g_{gas}/g_{cat}/h, T=230°C and 20 barg. Temperature, syngas concentration and absolute pressure are all parameters that can be used to control the reactivity and therefore the CO conversion. If for example the temperature is raised too quickly, a runaway could occur at the top of the catalyst bed. Because the reaction heat at this elevated temperature might not dissipate in time and the increased temperature results in an increased reactivity. This self-reinforcing process causes a local temperature runaway.

Here, it was aimed to achieve a CO conversion of 30-50%, which is typical for a fixed bed FTS process. In Figure 10, a profile of the reactor's temperature and pressure during Day 6 is shown. As can be observed,

pressure was used as the controlling parameter to bring the reaction to the desired CO conversion and a period of relative stability was achieved before a short runaway occurs, which was quickly controlled again. Due to the duration of the day experiments it was not easy to achieve multiple hours of steady conversion. Already a few hours were typically required to bring the reactor to FTS conditions while avoiding runaway reactivity. The average pseudo steady-state conditions and results can be found in Table 9. In total, more than 3.5 L of liquid/wax hydrocarbon products were obtained throughout the experimental campaign, see Figure 11.

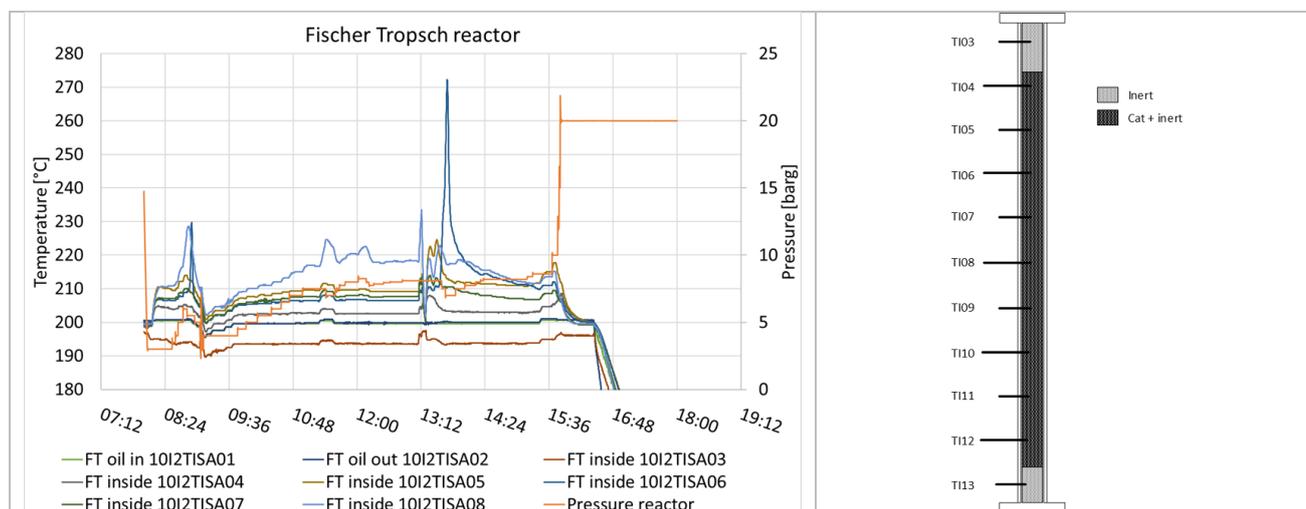


Figure 10: Temperature-pressure profile of the FTS reactor during Day 6 (left) and a cross section of the reactor (right).

Table 9: FTS conditions and achieved averaged conversion and selectivity.

| Conditions | | | Results | | |
|------------|--------|-----|-----------------------------|------|----|
| T set | [°C] | 200 | CO conversion | [%] | 34 |
| P | [barg] | 8 | Selectivity C ₅₊ | [%C] | 80 |
| Flow | [g/h] | 600 | Selectivity CH ₄ | [%C] | 11 |

No FTS off-gas was recycled in this experiment, and for this reason it was not possible to determine the overall efficiency directly from the experimental results. In the actual process the FTS off-gas would be recycled back to the FTS reactor inlet, or to the steam reformer. Alternatively, a once-through FTS process would be applied by using slurry or micro reactors, such as in the Aspen Plus modelling where a microreactor concept was assumed. It is important to note that part of the off-gas, consisting of unconverted syngas and lower hydrocarbon by-products (mostly methane), is required to provide the high temperature heat in the SMR.

However, conversion factors can be used to determine the overall process efficiency based on the experimental results. Assuming a total CO conversion of 90%, a conversion efficiency of 75% (exothermicity) and a liquids selectivity of 80% (S C₅₊), this would provide a final efficiency for the biomass to liquids process of 40% on LHV basis [10]. This is lower than the 48% calculated in the process Aspen Plus model [9].

[10] Calculation of efficiency: 75.1% (upgraded gas) * 0.9 (CO conv.) * 0.75 (exothermicity) * 0.8 (selectivity) = 40%.

However, when correcting for the lower gasification efficiency, the demonstrated efficiency would be equal to the process efficiency obtained in the model.



Figure 11: FTS condensable products collected from the hot (wax) and cold separators (light hydrocarbons).

Conclusions and outlook

In short, the following conclusions were drawn for this experimental campaign:

Both beech wood and bagasse were successfully converted into liquid FTS products via the BECOOL process including gasification + gas cleaning, gas upgrading and Fischer-Tropsch synthesis. For a total of 10 days.

In total more than 3.5 L of liquid/wax hydrocarbon products were obtained throughout the experimental campaign.

Only minor differences in gas composition between wood and bagasse were observed. The gasification of bagasse was slightly less steady due to the nature of the feedstock (chips vs ground pellets).

An overall efficiency was determined from the experimental work at 40% on LHV basis, for the FTS liquid product over the biomass input. This was 8 percent points lower than calculated in the Aspen Plus model, which can be explained completely by the lower gasification efficiency.

Olivine was used as bed material instead of sand from Day 4 to 10. As a result, the cold gas efficiency was approximately 10% lower than predicted by the model (sand based), because a higher amount of carbon/char was transferred to the combustor (20% vs 18%). Secondly, oxygen transfer from the combustor to the gasification zone lowered the calorific value of the gas by partial combustion as evidenced by the higher CO₂ concentration in the PG. A lower formation of tar or more WGS, expected with olivine, were not observed.

The gas cleaning and upgrading strategy followed in this process successfully lowered the concentration of the main impurities (H₂S and HCN) to below detection limit. The steam reformer as part of the upgrading section provided almost full conversion of all hydrocarbons (98+% CH₄) while providing the syngas at the desired H₂/CO ratio of 2.0–2.2. Furthermore, the CO₂R unit allowed for the removal of CO₂ to below 0.5 vol%

Duration tests (continuous day and night) are required to provide real steady-state results without start-up effects. This would allow the monitoring of catalyst deactivation with time, for additional catalyst characterization.