



IEA Bioenergy
Technology Collaboration Programme

Gasification of Liquids derived from Direct Thermochemical Liquefaction

IEA Bioenergy Task 34

December 2023





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Gasification of Liquids derived from Direct Thermochemical Liquefaction

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Summary

Gasification of DTL-oils and by-products for the production of renewable fuels, chemicals and materials through the syngas intermediate platform allows the utilization of biomass residues in current (refinery) processes. While a lot of combinations of liquefaction and gasification technologies can be considered, only the use of FPBO (slurry) in entrained flow gasifiers has been tested on MW scale.

Based on the results published in open literature the technical feasibility of the route can be considered as a rather low-risk option. Fuels from various resources can be converted by gasification. The syngas product composition depends on the fuel and applied gasification technology, but generally the dry gas contains 25-50% H₂, 25-45% CO and 20-30% CO₂, which is similar to the gas obtained by direct biomass gasification. The energy efficiency of the DTL-oil gasification is comparable to direct biomass gasification. To establish a viable business case, the potential advantages of DTL-oil gasification (improved logistics allow a better economy of scale, easier pressurization, up front removal of inorganic elements) should outweigh the costs of the added liquefaction step.

Gasification as such is a technology that is widely implemented in refinery operations worldwide and DTL-oils are not considered technologically challenging to be applied as feedstock. The main hurdles which need to be taken is to establish the commercial viability of the route and to increase the availability of DTL-oil (market size).

Combining the gasification process with water electrolysis to form a hybrid process, in which oxygen from electrolysis is used as oxidant in the gasifier and hydrogen is added to the syngas before product synthesis, could provide an optimal synergy between the simultaneous production of advanced biofuels and e-fuels.

Currently there is no fuel standard for DTL-oils to be used as feedstock for gasifiers. Based on the experience with DTL oil gasification an indicative list of quality parameters is suggested as input for future standardization activities. Specific attention needs to be paid to the suitability of analysis standards in combination with the complex nature of DTL-oils.

Glossary / abbreviations

BL	Black Liquor
BtL	Biomass to Liquid
CFD	Computational Fluid Dynamics
DME	Dymethyl Ether
DTL	Direct Thermochemical Liquefaction
EF	Entrained Flow
ETC	Energy Technology Center (now RISE)
FCC	Fluid Catalytic Cracking
FPBO	Fast Pyrolysis Bio Oil
FT	Fischer Tropsch
GHG	GreenHouse Gas
GE	General Electric
HTL	HydroThermal Liquefaction
IEA	International Energy Agency
KIT	Karlsruhe Institute of Technology
NREL	National Renewable Energy Laboratory
PEM	Proton Exchange Membrane
PtL	Power to Liquid
RED	Renewable Energy Directive
TRL	Technology Readiness Level

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Introduction

Biomass residues and waste streams can be used as feedstock for direct thermochemical liquefaction (DTL) technologies to produce a renewable energy carrier in liquid form. DTL techniques include Fast Pyrolysis to produce Fast Pyrolysis Bio-Oil (FPBO) and hydrothermal (or solvent) liquefaction for the production of bio-crudes. FPBO is currently produced on commercial scale with various installations in operation worldwide. The FPBO is used for heat generation as well as co-feeding in a FCC cracker to produce renewable transportation fuels¹. Biocrude production is in a pre-commercial development stage, with several pilot/demonstration activities pushing for commercial implementation. An overview of the commercial status of DTL technologies was published recently².

The use of DTL-oils as feedstock to produce renewable synthesis gas (syngas), i.e. a mixture of hydrogen, carbon monoxide and carbon dioxide³ was investigated by several consortia worldwide from gram to ton scale. Use of DTL-oils as feedstock for gasification is a way to introduce biomass residues and waste streams in existing (refinery) processes replacing (part of) the fossil-derived products in existing markets. While direct gasification of biomass residues and waste streams to syngas is also intensively investigated and implemented on commercial scale, the gasification of DTL-oils can have some distinct advantages from a logistic, economic, and technical point of view.

For gasification processes the scale of operation is a very important factor in the economic feasibility, large scale installations of several hundred MW input are desired to minimize the production costs. The feedstock quantity required at a single location however is challenging to secure. In particular, this holds for low-energy-density biomass residues and waste streams. Decentralized conversion of the low-energy-density feedstocks in DTL-oils is a way to improve the logistics of the value chain, improving the economic feasibility as well as limiting the GHG emission during transport. From a technical point of view, the initial conversion by DTL is advantageous as the liquid can be fed more-easily in a pressurized gasifier compared to a solid fuel. Depending on the process details, the inorganic contaminants (ash) present in biomass residues and waste streams can be separated during DTL as well, avoiding expensive technical solutions to deal with these components in the gasifier (slag formation) and gas cleaning systems. Furthermore, DTL-oils are much more uniform compared to the original biomass residues and wastes, allowing a single gasifier unit to operate on various feedstocks at the same time.

In this report, an overview is presented on the status of DTL-oil gasification on pilot- and demo-scale (TRL ≥ 5). Moreover, potential alternatives such as the gasification of DTL by-products and hybrid gasification systems are briefly discussed. Finally, the requirements for standards and analysis methods are shortly assessed and an outlook for the future potential of DTL-oil gasification is given.

Overview of (large) pilot activities

The gasification of DTL oil focusses on the production of synthesis gas, to be used for a variety of end products. Typical products of interest include synthesis of methanol, ethanol, dimethyl ether (DME), diesel and gasoline (Fischer Tropsch), and hydrogen. When capturing CO₂ from the gas, production of 'carbon-negative' products is possible as well. Gasification of DTL oil to produce a fuel gas for heat and power applications is not pursued as DTL oils can be used for heat and power generation directly.

The gasification of DTL oil has been the subject of research and development work for several decades, however no commercial scale installations are or have been in operation so far. Furthermore, notable DTL oil gasification activities at TRL ≥ 5 are all based on FPBO, there is no information publicly available on the gasification of biocrudes from hydrothermal liquefaction. In this chapter an overview is given on the various initiatives where DTL oil gasification was investigated at pilot or demonstration scale. The initiatives are grouped based on the gasification technology applied, which is shortly introduced as well.

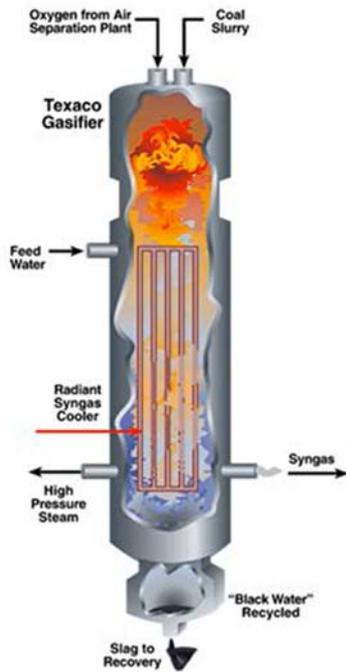
ENTRAINED FLOW GASIFICATION

Entrained flow gasifiers operate at very high temperatures (often > 1400 °C). These temperatures are realized by mixing the fuel with a sub-stoichiometric amount of pure oxygen. Steam can be added to the gasifier as well, as moderator for improved temperature control and to increase the steam reforming reaction of (hydro)carbons. The high temperatures ensure a rapid reaction of the fuel, which is needed (in combination with small fuel particles/droplets) to achieve high conversion efficiencies without requiring high residence times. One of the main challenges in designing entrained flow gasifiers is to ensure the gasifier construction material can withstand the high temperatures. Depending on the gasifier fuel, additional requirements may apply. Coal fed entrained flow gasifiers must deal with the inorganic elements (ash) present in the fuel. At the operating conditions of entrained flow gasifiers, (part of) the ash will melt, which must be taken into account in the design. This melt fraction is used within the gasifier in so called 'slagging' gasifiers as a way to protect the gasifier material. Entrained flow gasifiers designed to be operated on natural gas don't have to deal with ash in the feedstock and can be operated as 'non-slugging' entrained flow gasifiers. Both systems, and the specific experience with DTL oils in them, is discussed in more detail below. For more details on entrained flow gasifiers see Higman and van der Burgt⁴.

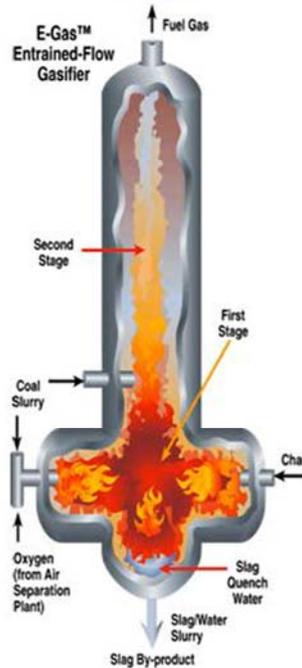
Slagging gasifiers

Several slagging gasifiers have been designed, constructed and operated to gasify coal. The most common types are those developed by General Electric (GE), ConocoPhillips and Shell (Fig. 1). The GE design applies a downflow of reactants, where the refractory material of the reactor wall is protected by the slag. Syngas is cooled by a water quench and removed from the side of the gasifier, while the slag is removed from the bottom of the gasifier. In the ConocoPhillips gasifier (originally designed by Dow Chemical) consists of two stages, in the first stage the coal/water slurry is fed from two opposite injection points near the bottom of the gasifier, where it reacts in the high temperature zone. Syngas flows upwards in the gasifier, where a second coal slurry injection point is added. Slag and quench water is removed from the bottom of the gasifier. The Shell gasifier feeds the coal and oxygen near the bottom end of the gasifier, with upflow of syngas. The reactor wall is indirectly cooled with water to produce high pressure steam and the slag is removed from the bottom of the gasifier.

GEE Texaco Gasifier



ConocoPhillips E-Gas



Shell SCGP

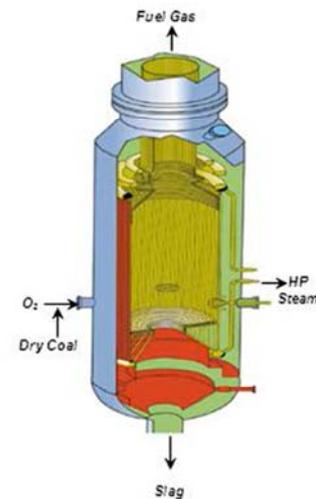


Fig. 1: Slagging gasifier designs by General Electrics (left), ConocoPhillips (middle) and Shell (right).

Several consortia investigated the gasification of DTL oil (slurry) in a slagging gasifier, these activities are discussed in more detail below:

bioliq® (Germany)

The bioliq® process developed at Karlsruhe Institute of Technology (KIT) aims at the production of synthetic fuels and chemicals from residual biomass. The energy density of the widely distributed growing biomass is increased by de-centralized pre-treatment of the biomass. The intermediate product, the so called biosyncrude®, can be transported economically meaningful over long distances to centralized industrial plants for synthetic fuel production⁵. The complete process chain (see Fig. 1) from pyrolysis over high-pressure entrained flow gasification, gas cleaning and conditioning to fuel synthesis was built up and commissioned in a collaboration between institutes of the Research Center Karlsruhe / Karlsruhe Institute of Technology, industrial partners and public funding agencies between 2005 and 2014. At first, the biomass is converted into pyrolysis oil and coke at approximately 500 °C applying fast pyrolysis. Sand is used as heat carrier in the twin-screw mixing reactor. The product consists of about 34 % organic condensate (pyrolysis oil), 25 % aqueous condensate, 20 % pyrolysis coke with the balance to 100 % being non-condensable pyrolysis gas, which is suitable for heating the sand or drying and preheating the feedstock. A suspension of pyrolysis coke and oil, referred to as biosyncrude®, is fed to the high-pressure entrained flow gasifier, where it is converted to a tar free synthesis gas at pressures up to 80 bar and temperatures above 1200 °C. After gas cleaning and conditioning, gasoline-grade fuel is produced in two stages via dimethyl ether as intermediate product⁶.

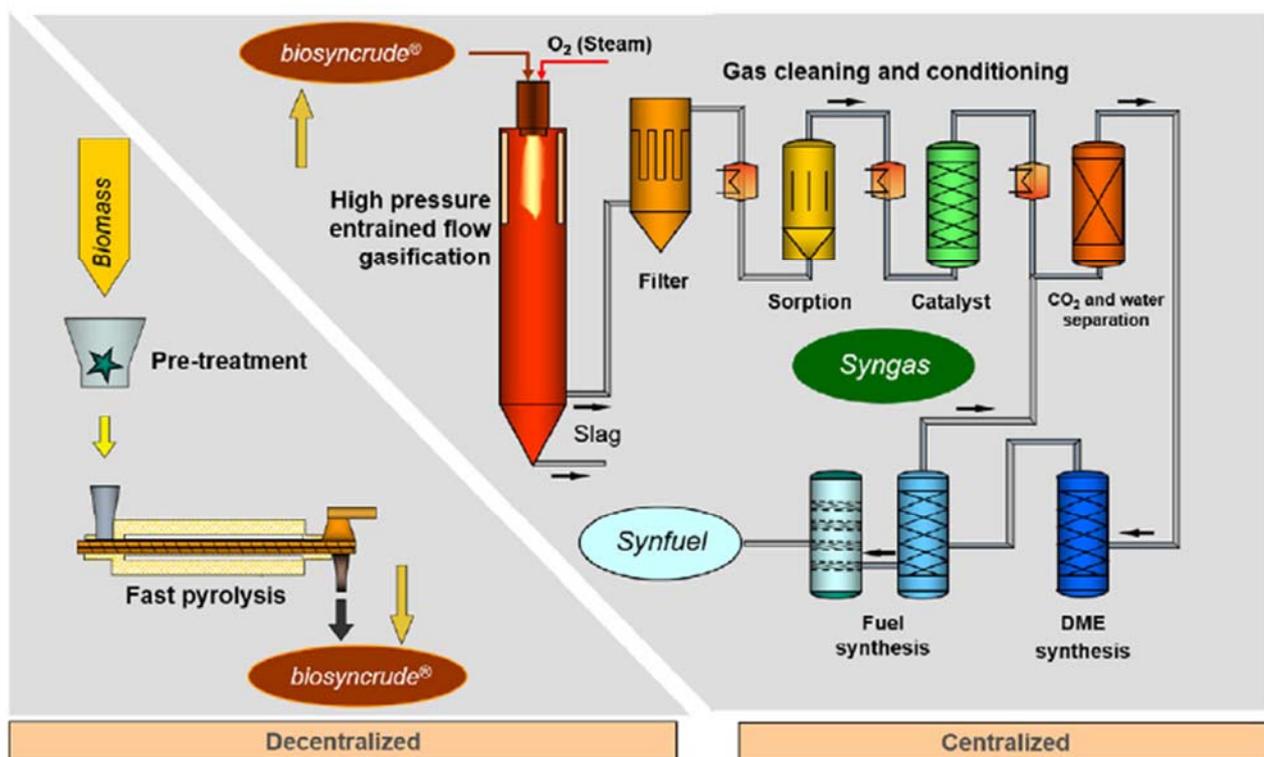


Fig. 2: bioliq® process flowsheet

The design of the bioliq® high-pressure entrained flow gasifier is based on the Lurgi-MPG Technology (multi-purpose gasification) of Air Liquide Global E&C Solution Germany GmbH, Frankfurt. It can be operated at pressures of 40 and 80 bar with a capacity of 5 MW (P_{th}) corresponding to a fuel throughput of 1 t/h for a fuel with a calorific value of 18 MJ/kg. Applying steam and oxygen as atomization and gasification medium, the biosyncrude® is converted to synthesis gas at temperatures above 1200 °C. The reactor is equipped with a segmented cooling screen covered with refractory material, where a firmly adhering coat of slag prevents abrasion of the refractory and corrosion of the cooling screen. The liquid slag melt leaves the reactor via a water quench and a slag locker. The high pressure entrained flow gasifier is in operation since 2012, operated in 24/7 continuous mode for individual measurement campaigns. During 2300 h of operation synthesis gas was produced from model and technical fuels like mono ethylene glycol and beechwood pyrolysis oil/coke suspensions, respectively⁶.

The gasifier is equipped with extensive measurement devices enabling complete mass, species and energy balances. Thus detailed characterisation and simulation of the gasification process allows to develop robust tools based on ASPEN plus and CFD for the industrial design and scale up. Depending on the operating conditions and feedstock, synthesis gas with H_2/CO ratios between 0.75:1 and 1:1 is produced. The composition of the dry synthesis gas lies in the range of 26 to 35 vol% for hydrogen, 27 to 39 vol% for carbon monoxide and 14 to 28 vol% for carbon dioxide. Very low methane concentrations under 0.1 vol% are reached. The difference to 100 vol% is nitrogen used for flushing. Balancing errors typically are in the order of approximately 5 %, which is very small for a technical system. At high temperatures nearly complete carbon conversion as well as equilibrium composition and temperature of the synthesis gas are reached⁶. Fuel type specific data is derived from the experiments carried out with a broad range of fuel specifications. Resulting k-values, reactor temperature and carbon conversion are the basis for scale up to 100 and 500 MW high pressure entrained flow gasifiers. Fig. 4 shows the results for a low and a medium calorific pyrolysis oil.

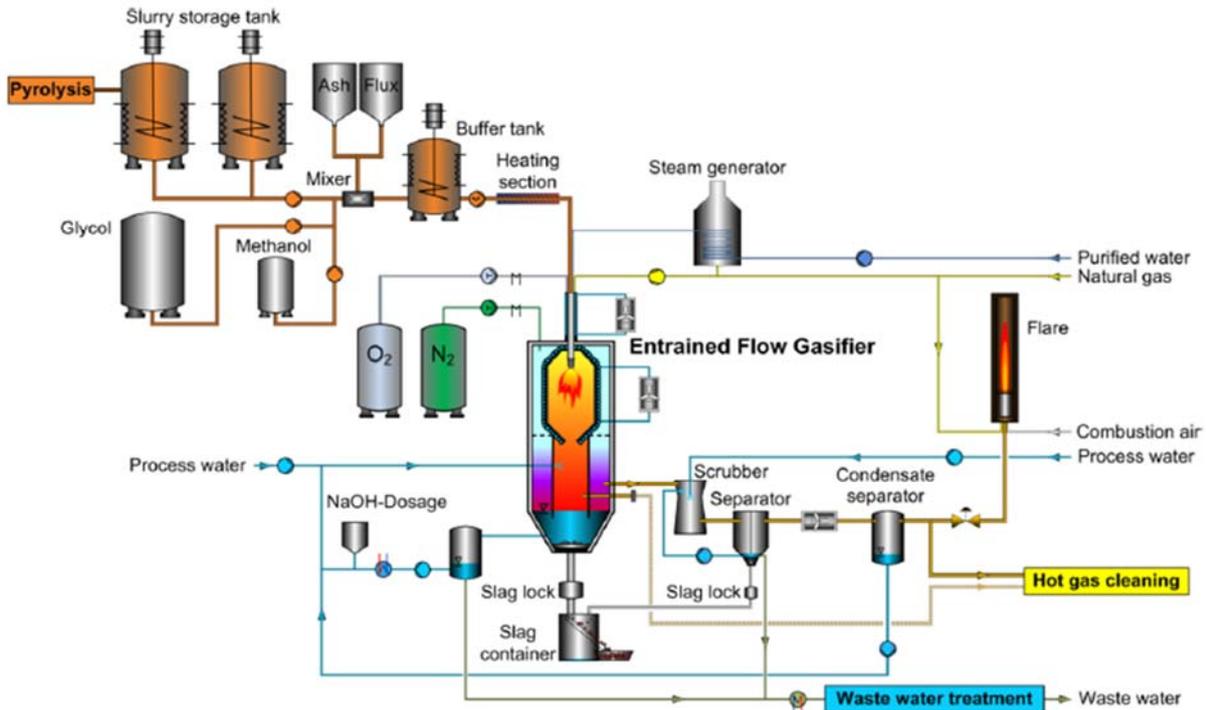


Fig. 3: Process flowsheet of the high-pressure entrained flow gasifier.

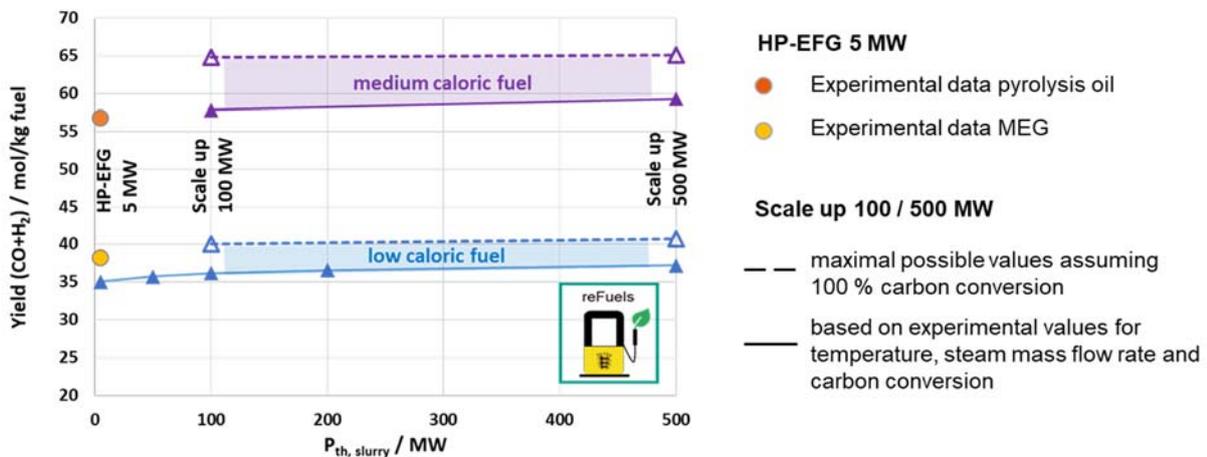


Fig. 4: Scale up based on experimental data from a 5 MW, high-pressure entrained flow gasifier for two types of fuels (low and medium calorific value).

Chemrec (Sweden)

The Swedish company Chemrec was established with the specific aim to convert the black liquor (BL) by-product from paper mills through entrained flow gasification. In Piteå (Sweden) a pressurized, oxygen-blown development plant called DP1 was erected in 2005, which is based on an existing atmospheric black liquor gasifier in operation at Weyerhaeuser's New Bern mill (US)⁷. The core unit of the DP1 plant is the entrained flow reactor with capacity of approximately 3 MW and integrated quench cooler. The temperature in the reactor is normally kept slightly above 1000 °C, which is a relatively low temperature for entrained flow gasifiers. This low temperature can be applied because the BL contains a high concentration of inorganic elements (up to 30%) which increase the reactivity of the fuel. The product mixture of melted inorganic salts (slag) and gas is quenched in a water spray at the reactor outlet, after separating the gas the liquid is called 'green liquor', which is recycled back to the paper mill to re-use the salts. The quality of green liquor is very important in the overall process operation. A schematic drawing of the Chemrec unit is given in Fig. 5.

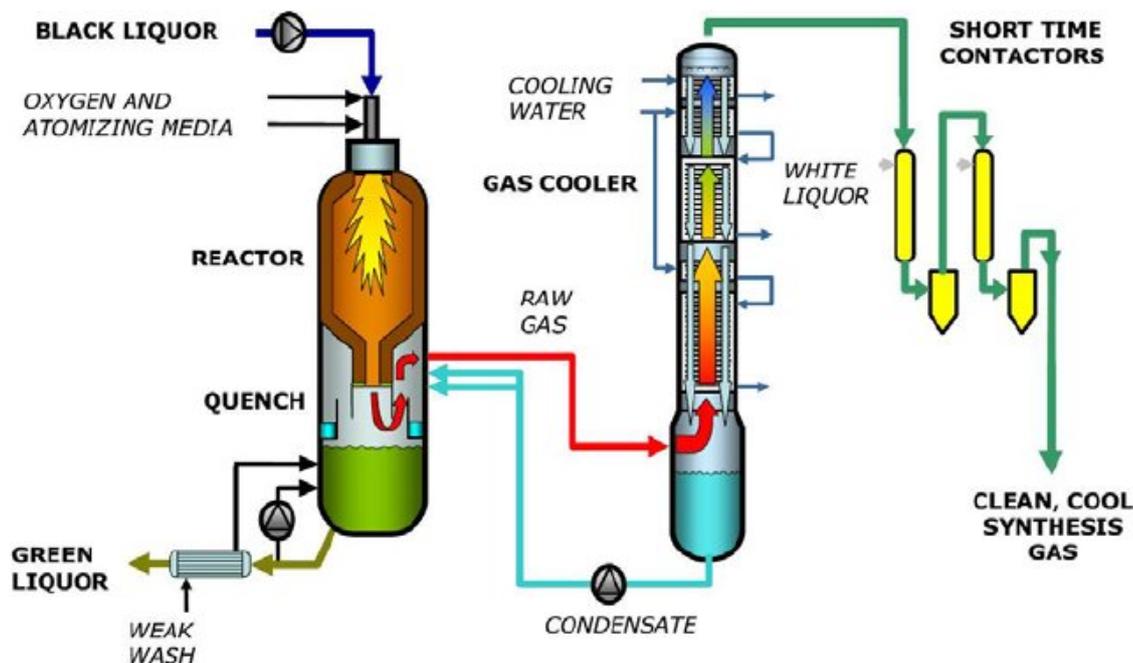


Fig. 5: Chemrec - Black liquor entrained flow gasification process⁸

The DP1 plant was extensively used to test various aspects of the gasification process. Within the European research project BioDME (FP7, #218923) the production of DME and usage as transportation fuel in trucks was demonstrated. In total 10 Volvo BioDME trucks drove over 720.000 km on the BioDME. After the BioDME project the DP1 plant was taken over by the Lulea technical university under the 'LTU Biosyngas program'. In total 1000 ton of methanol and DME was produced in the DP1 plant till May 2016⁹.

After extensive laboratory testing, the co-gasification of BL with FPBO was investigated in the DP1 plant in 2016. The BL and FPBO were mixed prior to gasification. BL/FPBO ratio's consisting of 100/0, 90/10, 85/15 and 80/20 were tested. In total 130 ton of black liquor and 5 ton of FPBO was gasified in a period of 5 days, operating at a load of approximately 3 MW. The results of the study show that a pilot plant designed for BL needs only minor modifications to gasify BL/FPBO blends. Blending FPBO with the BL had a notably positive impact on the performance of the gasification process. After the initial testing the co-gasification concept was further validated, achieving in total 1100 hours of operation in which approximately 170 ton of FPBO was converted. The syngas produced during this campaign was used for 900 hours with methanol/DME synthesis, showing robust operation and no difference in green liquor quality compared to BL only gasification. The dry syngas composition for the 80/20 blend ratio consisted of 37 vol.% H₂, 30 vol.% CO, 29 vol.% CO₂ and minor quantities of CH₄ and N₂, reaching a cold gas efficiency of 70%¹⁰.

Non-slugging gasifiers

Non-slugging entrained flow gasifiers operate in the same temperature region as slugging gasifiers. The designation 'non-slugging' is obtained by the feedstock which should be (almost) ash free, rather than the technology. Non-slugging entrained flow gasifiers are mainly used to convert oil residues from refinery operation and natural gas, often to generate the hydrogen required in the refinery. Technologies for gasification of oil and natural gas (partial oxidation of natural gas) were developed at the end of the 1940s by Texaco and early 1950s by Shell, these two technologies have continued to dominate this segment of the market since that time¹¹. The non-slugging gasifiers consists of a burner mounted on top of a refractory lined reactor vessel, operated in down-flow. When operated on liquid feed, the processes produce a small amount of residual carbon, which is necessary to sequester the small content of ash that enters the reactor.

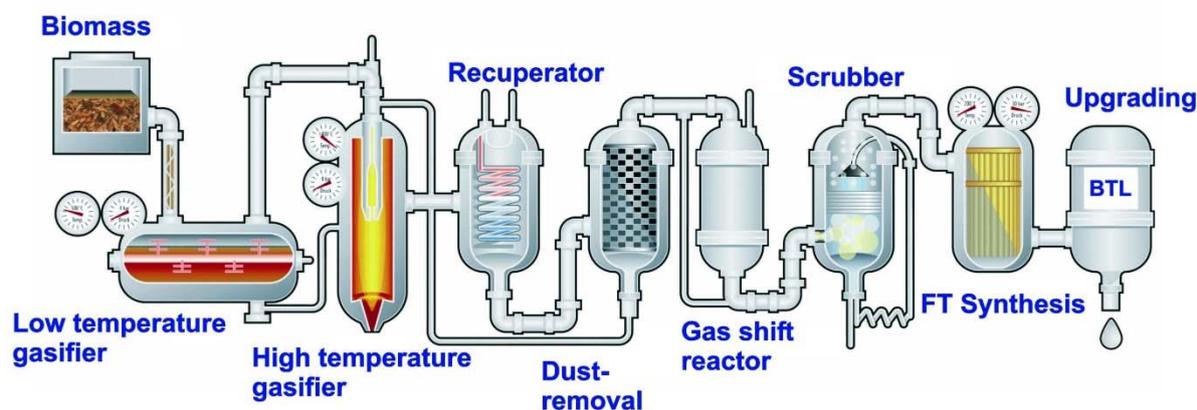


Fig. 6: Carbo-V process flow diagram¹²

UET - Freiberg / Carbo-V (Germany)

In principle, the Carbo-V concerns a slagging gasifier, but was operated with pyrolysis oil in non-slagging mode and therefore presented here. The Carbo-V gasifier type was originally developed by CHOREN and currently owned by Linde Engineering¹³. This gasifier is developed for solid feedstocks, where the feed is first devolatilized in a low temperature gasifier (pyrolysis reactor). The produced gases/vapours are then mixed with oxygen at the top of the high temperature gasifier to achieve the desired temperature, the solid (char) from the low temperature gasifier is injected at a lower part in the high temperature gasifier, where slag is removed from the bottom (see Fig. 6).

In 2002 about 1.5 ton of FPBO was gasified in the 1 MW entrained flow gasifier from UET located in Freiberg¹⁴. The experiments with FPBO were carried out by injection of the FPBO directly in the high temperature gasifier, for which a separate FPBO pump was installed on-site. Clean wood derived FPBO was gasified at a capacity of around 140 kg/h for over 10 hours until all the FPBO was consumed. Because of the low ash content in the FPBO, there was no slag removal from the bottom of the gasifier. The temperature in the gasifier was maintained at around 1200 °C, the syngas composition consisted of approximately 30 vol.% CO, 25 vol.% CO₂ and 20 vol.% H₂. The CH₄ concentration was around 2.5 vol.%, which is a factor 10 higher than predicted by the thermodynamic equilibrium. The remainder of the gas consisted primarily of N₂, which was used as purge stream in the process. Analysis of the test results showed that discrepancies with the thermodynamic equilibrium could be attributed to¹⁵:

1. The low temperatures of the gasification process, due to the relatively low flow of FPBO;
2. The rather unsteady character of the run;
3. Significant heat losses, calculated to be around 15-20% (f.i. no gas preheating);
4. The addition of quite significant amounts of (cold) purge gases such as air and nitrogen.

On basis of the overall elemental balance the amount of soot produced was calculated, approximately 10 wt.% of FPBO ended up as soot, which is high compared to experiments published by amongst others Chitti¹⁶.

PEBG - ETC/Rise (Sweden)

The former Energy Technology Centre (ETC), now part of RISE, developed a pressurized entrained flow gasifier to gasify solid biomass. The gasifier is a non-slagging gasifier where biomass powder is reacted with pure oxygen to form synthesis gas. The gas is cooled in a water quench at the bottom of the gasifier (see Fig. 7).

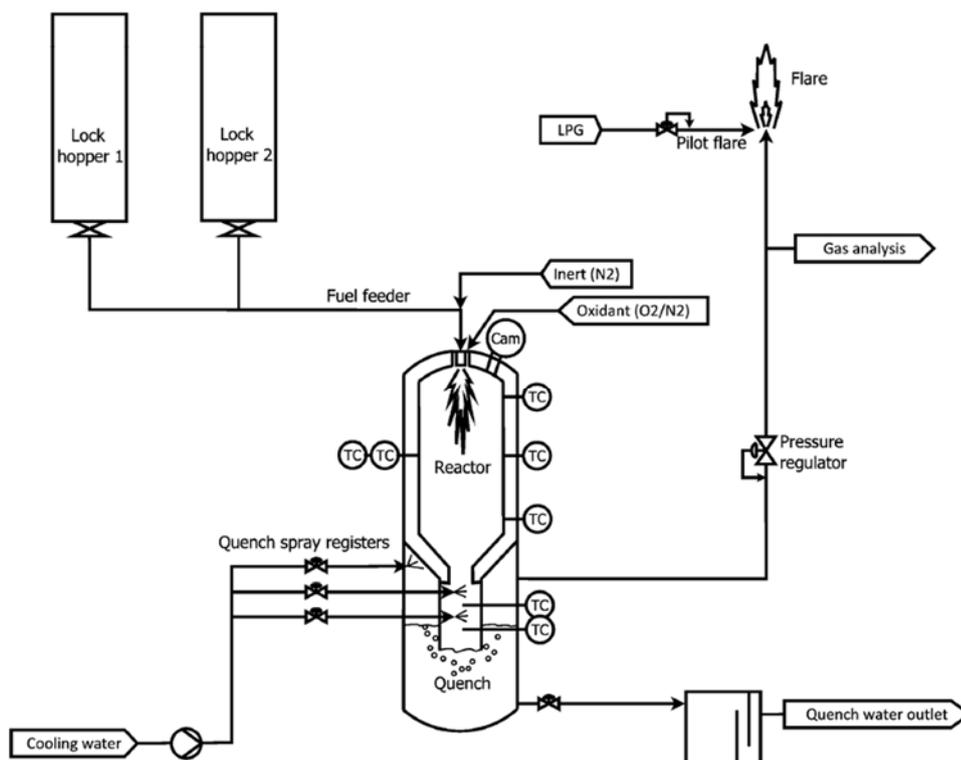


Fig. 7: Schematic representation of the pressurized entrained flow biomass gasifier (PEBG) by ETC (RISE).

In the European project Suprabio (FP7 # 241640) the solid fuel burner was replaced with a liquid spray nozzle to perform gasification experiments with FPBO. Both wood- and straw-derived FPBO were gasified at a thermal load of 0.4 MW (~80 kg FPBO/h) at a pressure of 4 bar and a temperature around 1250 °C. Wood derived FPBO was gasified in a 50-hour run showing stable operating conditions could be achieved over a 2-day period. A power failure in the oxygen generation plant triggered an emergency stop halfway through the run but the gasifier could be re-started without problems. Straw derived FPBO was used as well to investigate feedstock flexibility of the system. Average syngas volume fractions of 46% CO, 30% H₂ and 23% CO₂ were obtained for both pyrolysis oils¹⁷; the gas composition during the 50-hour run on wood derived FPBO is presented in Fig. 8. About 2 vol.% CH₄ remained in the product gas, along with 0.1 vol.% of C₂H₂ and C₂H₄. Minor quantities of H₂S (3 and 23 ppmv), COS (22 and 94 ppmv) and benzene (310 and 532 ppmv) were found for wood and straw derived FPBO respectively. The experimental results show that pyrolysis oils from different biomass feedstocks can be processed in the same gasifier, and issues with the variable ash composition and potential melting behaviour can be avoided by applying the fast pyrolysis as pre-treatment before gasification.

The carbon to gas conversion for these tests was around 90%, similar to those observed in the UET tests described above. Approximately 10 wt.% of the carbon present in FPBO ended up as soot. The atomization behaviour of the nozzle was found to have a direct impact on the carbon to gas conversion, which is supported by observations previously published by Van Rossum¹⁸ and Chhiti¹⁹. Both Van Rossum and Chhiti show that a lower heating rate (obtained with larger droplets / worse atomisation) increases the formation of a solid residue (char).

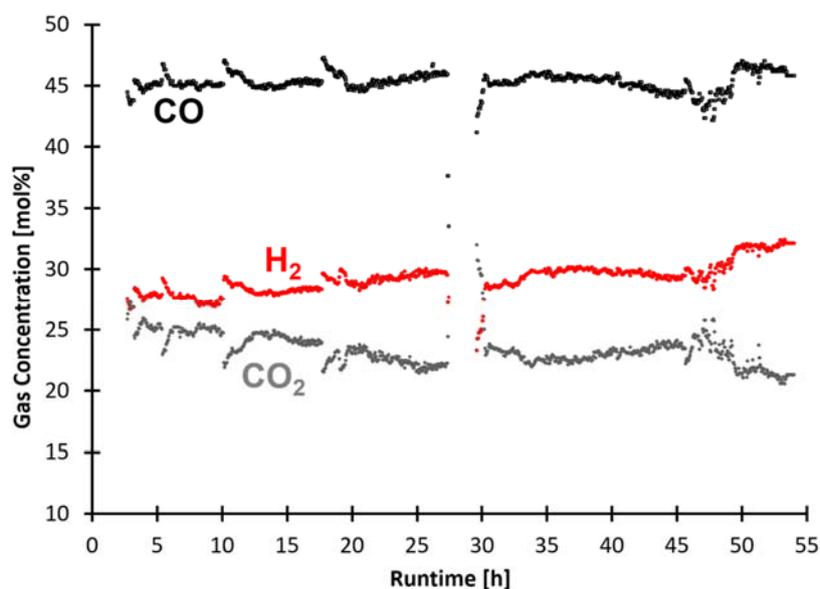


Fig. 8: Syngas composition for wood-derived FPBO gasification

SUMMARY

An overview of the DTL oil gasification results in (large) pilot scale is presented in Table 1.

Table 1: Overview of DTL oil gasification results from pilot and demonstration plants

Gasifier Name	Bioliq	DP1		Carbo-V	PEBG
Gasifier type	EF-Slagging	EF-Slagging		EF-Slagging*	EF-Non Slagging
Fuel type	FPBO slurry	Black-Liquor/ FPBO (80/20)	BL (100%)	FPBO	FPBO
Capacity [kg/h]	1,000	1,000	1,000	140	80
Capacity [MW]	5	3	3	1	0.4
Pressure [bar]	40 - 80	30	30	1	4
Total amount of DTL-oil converted [ton]	1050	170	-	1.5	7
Typical gas composition (on N ₂ free basis)					
H ₂ [vol.%]	26-35	37	36	25	30
CO [vol.%]	27-39	30	26	37	46
CO ₂ [vol.%]	14-28	27	34	31	23
CH ₄ [vol.%]	< 0.1	1	1.5	3	2

* = operated in non-slugging mode during the FPBO gasification run.

was utilized for evaporation and gasification, after which a fixed catalytic bed was placed for steam reforming. This system allowed the production of a clean syngas for over 11 hours without activity loss of the catalyst. The syngas contained 61% H₂, 25% CO and 14% CO₂, however it must be noted external energy was supplied to the system and these results do not represent autothermal operation.

Autothermal catalytic reforming

Another example of a gasifier containing a catalyst to improve fuel conversion is the so called autothermal catalytic reformer developed by BTG. This gasifier consists of a partial oxidation zone similar to those encountered in entrained flow gasifiers, followed by a catalytic reforming section (see Fig. 10). Steam is added as reactant to the gasifier as well, both as moderator to control the temperature and as reactant. These kinds of gasifiers are typically used for natural gas / naphtha reforming and usually operate at smaller scale than entrained flow gasifiers. The design allows the operation at lower temperatures (typically ~900 °C) which requires less stringent material properties/design and potentially increases the overall efficiency because a lower equivalence ratio can be applied.

A 10 kW oxygen blown autothermal catalytic reformer was constructed and tested for the gasification of various FPBOs at BTG. In the research and development work commercially available naphtha and methane steam reforming catalysts are applied in a fixed bed operating mode. Previous work with an air-blown gasifier also investigated the use of monolith type structured catalysts²¹.

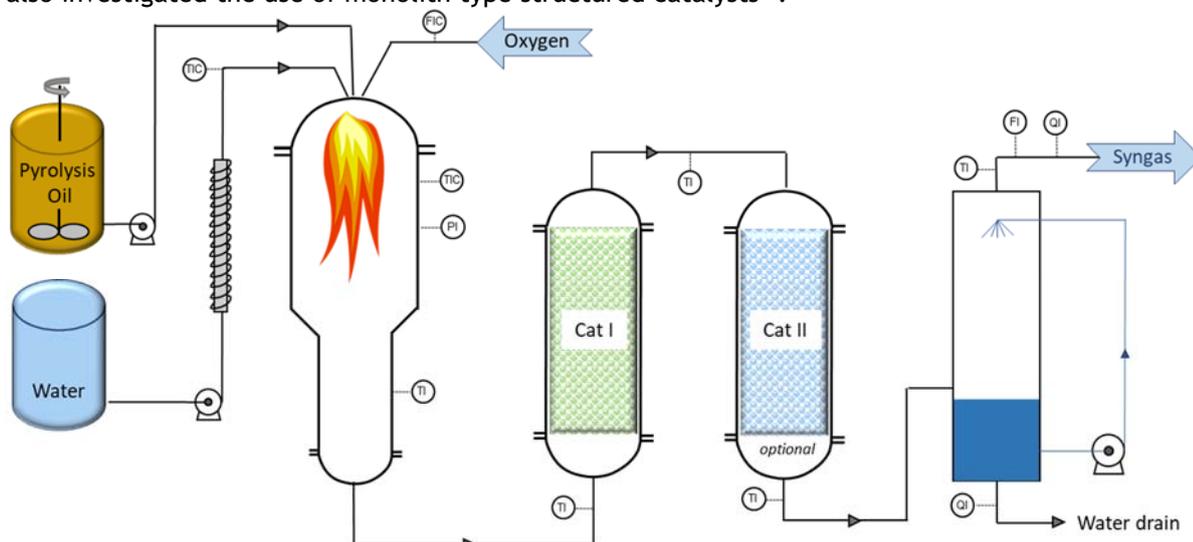


Fig. 10: Autothermal catalytic reformer pilot plant from BTG²²

The gasifier was operated on FPBOs from various feedstocks (eucalyptus, arundo, sorghum, sugarcane bagasse and pine wood) to investigate the feedstock flexibility of the value chain. The syngas composition and yield were quite constant for each of these feedstocks. Typically, 1.7 Nm³ syngas is produced for each kg of FPBO, with 50 vol.% H₂, 20-25 vol.% CO and 25-30 vol.% CO₂. The H₂/CO/CO₂/H₂O concentrations were close to the thermodynamic equilibrium of the water-gas shift reaction. Methane reforming did not achieve the thermodynamic equilibrium for most cases, with CH₄ concentrations ranging from 1.1 to 2.8 vol.% for the residual feedstocks²³. Optimization of the gasifier using wood-derived FPBO, with proper atomisation and a sufficient amount of catalyst, CH₄ concentrations below 0.1 vol.% were obtained. The formation of char/coke/soot in the partial oxidation zone is troublesome when fixed bed catalysts are applied in the reforming zone, leading to an increased pressure drop over the catalyst bed. In a previous system, where air was used as oxidant, monolithic catalysts were successfully applied to avoid these operational issues²⁴.

GASIFICATION OF BY-PRODUCTS

An alternative route to consider is the utilization of the by-products from the DTL processes. In particular, the steam reforming of aqueous fractions for hydrogen production can be of interest for process integration purposes.

Steam reforming of the aqueous fraction from HTL processing

The steam reforming of the aqueous fraction from HTL processing is proposed (by for example the Heat-to-Fuel project²⁵) as a way to generate the hydrogen required in further upgrading of the biocrude oils from HTL processing to obtain hydrocarbon products. The overall scheme is presented in Fig 11.

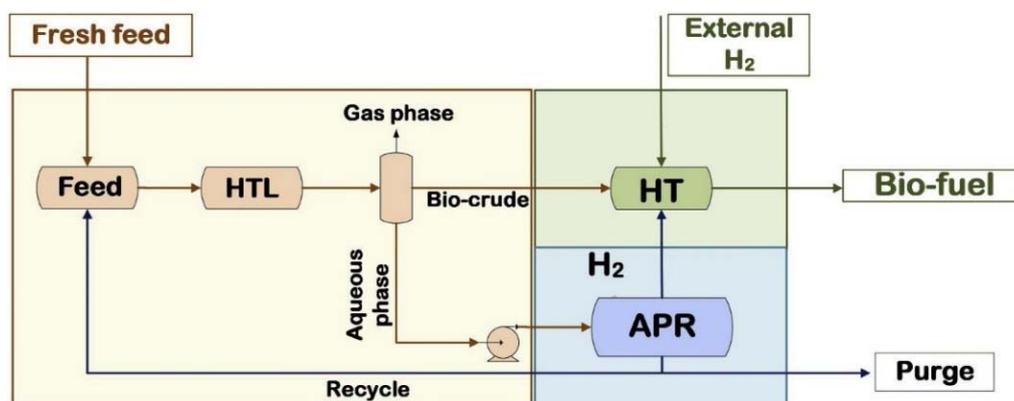


Fig. 11: Integration of aqueous phase reforming (APR) with a hydrothermal liquefaction and hydrotreatment process²⁶.

Tests of the aqueous phase reforming were performed at the Politecnico di Torino. In a batch-wise reactor setup with typically 75 ml of aqueous phase and 0.375 gram of Pt (5%)/C catalyst. At a final temperature of 270 °C, gas with approximately 50 vol.% H₂ could be produced. Carbon to gas ratio's were relatively low and varied from 15 to 30%. Preliminary calculations show that approximately half of the H₂ required for hydrotreating of the bio-crude can be supplied via APR.

Steam reforming of the aqueous fraction from FPBO

At the National Renewable Energy Laboratory (NREL) the steam reforming of FPBO for hydrogen production was investigated. While initial results seemed promising, rapid deactivation of the catalysts by carbon deposits was identified as critical issue in the process. Various technical solutions were proposed, including the use of a catalytic fluidized bed, however the commercially available steam reforming catalysts were designed for fixed bed operation and lacked mechanical strength needed in the fluidized bed mode. As alternative the steam reforming of the aqueous fraction was studied in more detail as carbon deposits were much less pronounced with the aqueous fraction. By applying this technique, syngas with ~70 vol.% H₂, 20 vol.% CO₂ and 10 vol.% CO could be produced for a period of 10 hours²⁷. It must be noted that this system was not operated autothermal, external energy was supplied to the process. In later work²⁸, the combination of partial oxidation and steam reforming was investigated by the same group. Even though 11-30% of the carbon present in the pyrolysis oil formed deposits in the evaporator, 9-11 wt.% of hydrogen could be produced, which corresponds to 70-83% of the stoichiometric potential. Under autothermal conditions a syngas with 60% H₂, 34% CO₂ and 6% CO could be produced from the aqueous fraction of oak derived pyrolysis oil.

HYBRID CONCEPTS

Recently, hybrid concepts were proposed in which gasification is combined with water electrolysis. The oxygen required for gasification can be obtained from the electrolyser while the hydrogen is added to the syngas to improve the syngas composition as illustrated in Fig. 12.

The hybrid concept is a way to significantly increase the overall product yield for any biomass-based system including DTL liquids. Typically, the raw syngas composition from biomass gasification is not ideal for synthesis of products like methanol and FT hydrocarbons, which is a direct result of the elemental composition and heating value of the biomass feedstock. The H₂/CO ratio in the syngas is lower than desired, and normally this ratio is adapted by including a water-gas shift reaction. It leads to an increase in CO₂ and consequently a reduction in carbon efficiency (e.g. C in the targeted end products). By adding the hydrogen from electrolysis to the syngas the water-gas-shift can be largely avoided, and the product yield can be

roughly doubled which also means doubling the carbon efficiency. However, the effect on the overall energy efficiency is less pronounced as the energy input to the electrolyzer should also be taken into account. The products from the hybrid concept can be seen as a combination of advanced Biofuels end eFuels (i.e a combination of BtL & PTL).

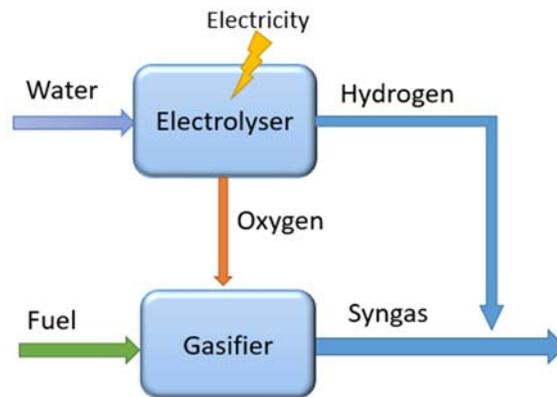


Fig. 12: Electrolysis - gasification hybrid concept.

Hybrid concepts have also been considered for DTL gasification systems. A detailed evaluation of a hybrid system is made by Landalv et al²⁹. Here black liquor and pyrolysis oil co-gasification is combined with water electrolysis to provide syngas for methanol synthesis. The hybrid option allows for a 55% increase in methanol production capacity, where 88% of the energy from the electricity is converted to methanol.

In 2021, Shell proposed³⁰ a hybrid system for the production of sustainable aviation fuels (SAF) from a combination of FBPO gasification and water electrolysis. This project (SATURN) proposed to combine the existing gasifier with their new activities on hydrogen production in the Rheinland refinery (Refhyne I, a 10 MW PEM electrolyser) and Refhyne II (a 100 MW PEM electrolyser, to be build)³¹. Hydrogen from the electrolyser is combined with syngas from the existing partial oxidation unit for synthesis of heavy paraffins. The CO₂ from the syngas is also utilized through a reversed water gas shift reaction with hydrogen from electrolysis for additional CO (see Fig. 7). The current status of this initiative is unknown.

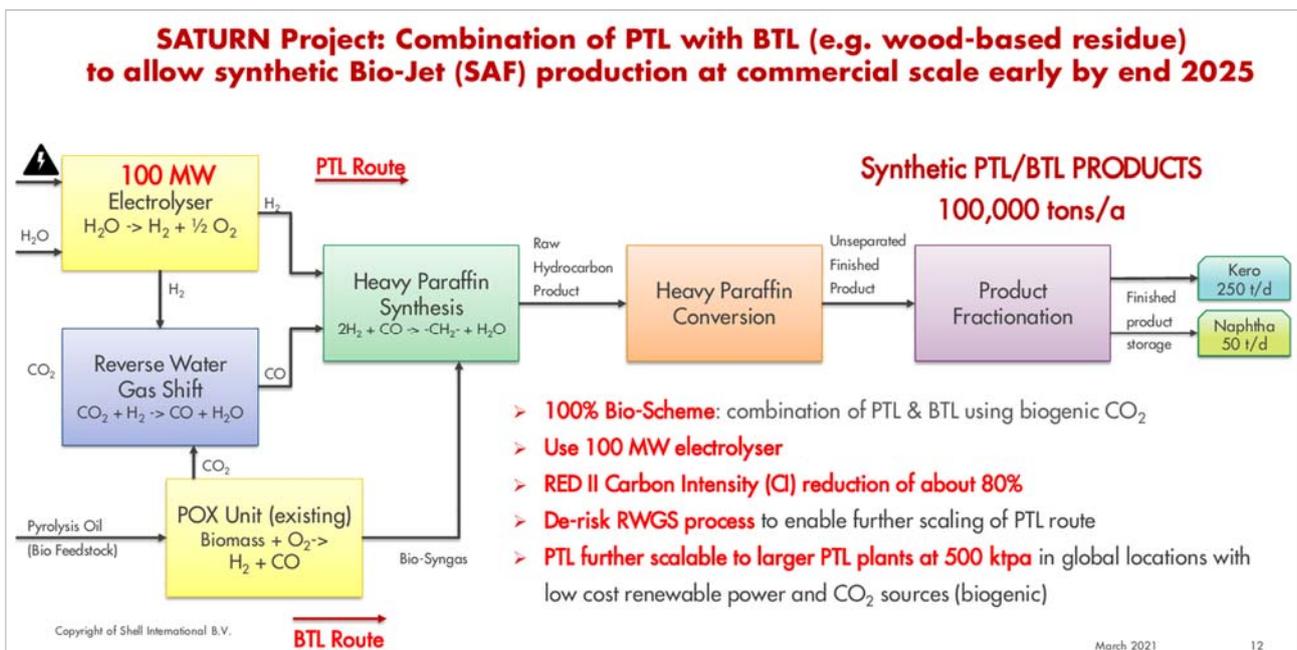


Fig 13: Schematic representation of the Saturn project scheme for a hybrid gasification plant.³⁰

Quality parameters and analysis methods

Already in 2013 CEN (European Standardization organization) received a mandate to develop standards for pyrolysis oil quality for a number of applications including “A Technical Specification for a quality specification for pyrolysis oil suitable for gasification feedstock for production of syngas and synthetic biofuels”. Within CEN standardization different reports are possible depending on actual state-of-the-art:

- European Standard (EN): leading to full implementation, as national standard, Europe-wide, which may also serve the European regulatory purposes of the New Approach;
- Technical Specification (CEN/TS): serves as normative document in areas where the actual state of the art is not yet sufficiently stable for a European Standard;
- The Technical Report (CEN/TR): for information and transfer of knowledge;

A European Standard was developed for the use of FPBO in boilers (EN 16900:2017), and a Technical Report was provided for the use of FPBO in internal combustion engines (CEN/TR 17103:2017). Eventually however, the Technical Specification was not developed for gasification due to lack of data and industrial interest. A Technical Report was probably also more suitable for FPBO gasification and a better reflection of actual State-of-the-Art in this field.

QUALITY PARAMETERS & ANALYSIS METHODS

In all cases, information is required on physical-chemical properties of the FPBO relevant for the specific application, proposed ranges as well as the suitable analysis methods to determine the selected properties. In this chapter an initial assessment of relevant properties for FPBO gasification is given to provide information and transfer knowledge. Specifications or property ranges may differ depending on the actual gasification system (i.e. slagging, non-slagging, catalytic).

Viscosity

The viscosity of FPBO is important aspect for the atomization of the liquid. Generating a very fine droplet (mist) is crucial to achieve high heating rates in the gasifier and minimize formation of solid carbon. The viscosity is a function of the liquid temperature, and increasing the temperature leads to a strong reduction of the viscosity. However, to avoid excessive repolymerisation, pre-heating of FPBO is limited to around 80-90 °C without risking blockage of the feeding line/nozzle. Density and surface tension are also relevant for atomization, but the viscosity is the major factor. Adding 10-20 wt% of ethanol (or other alcohol) does also improve the atomization as it leads to a reduction in all three properties (viscosity, density and surface tension). ASTM D445 is a suitable method viscosity can be measured.

Heating value

The heating value (LHV) has a major impact on the relation between the equivalence ratio and temperature in the gasifier. Fuels with a higher heating values require less oxygen to achieve the desired operating temperatures, which in turn result in higher (energetic) efficiencies. Producing FPBO with a higher heating value is a way to improve the efficiency, however this is usually accompanied by an increased viscosity. There is no general minimum value for the heating value, however low heating value fuels may not be commercially and energetically efficient. The heating value can be measured (ASTM D4809:2018) or calculated from its composition (CHNOS, water and ash).

Homogeneity

FPBOs are known to exhibit phase-separation behaviour in case either the moisture content and/or the extractives content exceeds a certain threshold. For the gasifier it is important that a stable fuel composition is used to prevent unstable (partial) combustion and wide temperature fluctuations. Separation of phases may also cause problems in the fuel pipes and in the burner, e.g. if water separates from the oil phase or volatiles evaporating from the oil. Unfortunately, no standard qualitative method is available to determine homogeneity of FPBO. An approach is measure other parameters like moisture content at different locations in the liquid to investigate the homogeneity.

Mineral/ash content

The presence of minerals in the FPBO can affect the gasification process in multiple ways. For a slagging gasifier the ash content and composition need to be appropriate to obtain a flowing liquid slag in the system, i.e. the slag viscosity should be in the right range or additives will be required. For non-slagging gasifiers a low ash content is required to avoid fouling. Downstream syngas cleaning and product synthesis units also need to be considered when the mineral content is evaluated. In case of catalytic gasification (reforming), likely the acceptable ash level is even lower as poisoning of the catalyst must be considered. On the other hand, minerals may have a catalytic effect, enabling lower temperatures to reach high conversion efficiency as demonstrated for example in the co-gasification of black liquor and FPBO. The determination of minerals present in FPBO is quite complex as reported in a recent Round Robin study initiated by IEA³².

In addition to the properties in the previous paragraph some other chemical-physical properties of FPBO should be determined/reported to enable the assessment of FPBO gasification.

Elemental analysis

In order to assess resulting product gas quality and the required amount of gasifying agent it is important to know the carbon, hydrogen, nitrogen, and oxygen content of the FPBO. A suitable method is ASTM D5291. The elemental composition can also be used to calculate the heating value of the fuel. Moreover, sulphur and chlorine are two elements that should be reported since they significantly affect downstream syngas use/ cleaning. A Round Robin study on measuring Cl and S in FPBO was conducted by IEA³²

Water Content

It is important to know the water content of FPBO since excessive amount of water can lead to phase separation, and moreover it has a negative impact on the energetic efficiency. It is likely that gasifier operators rely on a variety of FPBO sources and blend material on site, which makes this an important quality parameter. It also directly affects the heating value and the viscosity. Water content in FPBO can be measured by the Karl-Fischer method (ASTM E203).

Stability

FPBO is a product that may undergo ageing, especially at elevated temperatures. This ageing might lead to an increase in water content and hence affect phase stability. Obviously, for the operation of the gasifier the actual properties are relevant, and therefore properties should be determined at the time of use. Stability should be considered when oil needs to be stored over longer times (i.e. > few months). Methods have been developed to determine stability based on a fast-ageing test followed by measuring the changes in water content, viscosity or carbonyl content (ASTM E3146-20). Further information on stability testing can be found in the IEA Round-Robin study on this topic³³

Solids content

Depending on the type of gasifier it is possible to tolerate a comparably high level of solid particles (char) in the FPBO. Solids content must be reported as well as an indication of maximum particle size to be expected. A high solids content will have a significant impact on the properties of the FPBO (e.g. viscosity, mineral content, heating value etc). For non-slagging and catalytic gasification the solids content should be as low as possible. A suitable method for the determination of solid sin FPBO is ASTM D7579.

Ash melting temperature

Slagging gasifiers operate with a molten slag layer to protect reactor walls and act as heat screen simultaneously. To ensure reliable operation of slagging gasifiers, ash melting temperature is important which may vary significantly for the minerals content of different biogenic feedstocks. The ash melting point can be determined by e.g. the Seger Cone method (ASTM D1857). For non-slagging gasifiers and catalytic

gasification this property is not considered to be of high relevance.

Soot building substances

It is known that certain substances in the feed oil may lead to undesired soot formation in the gasifier (e.g. naphthalenes, benzenes, acetylene). The presence of these components in FPBO have been subject of an IEA study³⁴, and it was shown that these substances are typically not present in biogenic FPBO or in very low amounts (ppm range).

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