

Green Diesel from Biomass via Fischer-Tropsch synthesis: New Insights in Gas Cleaning and Process Design

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ABSTRACT The interest in biomass is increasing in the light of the growing concern about global warming and the resulting climate change. The emission of the greenhouse gas CO₂ can be reduced when 'green' biomass-derived transportation fuels are used. One of the most promising routes to produce green fuels is the combination of biomass gasification (BG) and Fischer-Tropsch (FT) synthesis, wherein biomass is gasified and after cleaning the biosyngas is used for FT synthesis to produce long-chain hydrocarbons that are converted into 'green diesel'. To demonstrate this route, a small FT unit based on Shell technology was operated for in total 650 hours on biosyngas produced by gasification of willow. In the investigated system, tars were removed in a high-temperature tar cracker and other impurities, like NH₃ and H₂S were removed via wet scrubbing followed by active-carbon and ZnO filters. The experimental work and the supporting system analysis afforded important new insights on the desired gas cleaning and the optimal line-up for biomass gasification processes with a maximised conversion to FT liquids. Two approaches were considered: a front-end approach with reference to the (small) scale of existing CFB gasifiers (1-100 MW_{th}) and a back-end approach with reference to the desired (large) scale for FT synthesis (500-1000 MW_{th}). In general, the sum of H₂ and CO in the raw biosyngas is an important parameter, whereas the H₂/CO ratio is less relevant. BTX (*i.e.* benzene, toluene, and xylenes) are the design guideline for the gas cleaning and with this the tar issue is *de-facto* solved (as tars are easier to remove than BTX). To achieve high yields of FT products the presence of a tar cracker in the system is required. Oxygen gasification allows a further increase in yield of FT products as a N₂-free gas is required for off-gas recycling. The scale of the BG-FT installation determines the line-up of the gas cleaning and the integrated process. It is expected that the future of BG-FT systems will be large plants with pressurised oxygen blown gasifiers and maximised Fischer-Tropsch synthesis.

INTRODUCTION

Although biomass is the oldest energy source known to mankind, its current contribution to the primary energy consumption in the Western world is small. Biomass was gradually substituted after the discovery of huge amounts of cheap fossil fuels. Coal, crude oil, and natural gas were not only cheaper, but also more convenient to use. Furthermore, the 'new' fuels allowed applications that were not possible with biomass: liquid transportation fuels from crude oil and gas for cooking. Biomass appeared to have no future as energy source.

The insight that the fossil fuel reserves are limited, together with concerns over security of supply (*i.e.* the oil crises), initiated the first upraise of interest in biomass (and all other renewable energy forms) in the 1970s. However, continuously low fossil energy prices and the discovery of new fossil fuel reserves impeded the development of biomass technologies. In the 1980s the concern grew that global warming and the resulting climate change were enhanced (if not caused) by CO₂ emissions resulting from fossil fuel consumption. This concern resulted in the Kyoto protocol in which objectives to reduce the anthropogenic CO₂ emissions are

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documented. To achieve the Kyoto objectives, the share of renewable energy in the primary energy consumption has to increase significantly. The interest in biomass was renewed, as biomass is considered to be one of the most important renewable energy source for this century [1,2].

GREEN DIESEL

Biomass-based energy currently contributes to about 3% of the primary energy consumption in the European Union (EU). This share will have to be tripled within the next decade to meet the EU objective of 8.5% energy from biomass and residues in 2010. An important aspect of biomass is that liquid (bio) fuels can be produced from this renewable source [3]. The emission of the greenhouse gas CO₂ can be reduced when 'green' biomass-derived transportation fuels are used in cars, trucks, and buses. To illustrate this: in the Netherlands 390 PJ (1999) of transportation fuels are consumed annually [4] and replacement of only 5% fossil transportation fuels by renewable fuels would reduce the CO₂ emission by approx. 1.5 million tonnes per year. In addition to the EU objectives for primary energy (*i.e.* electricity and heat), the European Commission (EC) is preparing a directive for renewable transportation fuels. According the directive the target for the share of biofuels is 2% in 2005, increasing to 6% in 2010, and 8% in 2020 [5].

In the Netherlands, the government initiated the so-called GAVE programme to stimulate the demonstration of production chains for alternative renewable gaseous and liquid energy carriers. In the first study phase it was concluded that one of the most promising routes to produce 'green' fuels is the combination of biomass gasification (BG) and Fischer-Tropsch (FT) synthesis [6]. In this route biomass is gasified to yield a producer gas or biosyngas that is rich in H₂ and CO. After cleaning the biosyngas can be used as feed gas for a FT synthesis reactor where the H₂ and CO are converted into long-chain hydrocarbons that are subsequently converted into 'green diesel' in a post-processing step.¹

FISCHER-TROPSCH SYNTHESIS

In the catalytic Fischer-Tropsch (FT) synthesis one mole of CO reacts with two moles of H₂ to form mainly aliphatic straight-chain hydrocarbons (C_xH_y). Typical FT catalysts are based on iron or cobalt. About 20% of the chemical energy is released as heat in this exothermic reaction:



As follows from equation (1), the FT reaction consumes hydrogen and carbon monoxide in a ratio of H₂/CO = 2. When the ratio in the feed gas is lower, it can be adjusted with the water-gas shift (WGS) reaction.



Iron-based FT catalysts show considerable WGS activity and the H₂/CO ratio is adjusted in the synthesis reactor. In the case of cobalt-based catalysts the ratio needs to be adjusted prior to FT synthesis. Typical operation conditions for FT synthesis, when aiming for long-chain products, are temperatures of 200-250°C and pressures of 25-60 bar [7]. The polymerisation-like chain-growth reaction results in a range of products, comprising light hydrocarbons (C₁ and C₂), LPG

¹. In this paper "green diesel" refers to the high-quality ultra-clean diesel-like product produced with Fischer-Tropsch synthesis. This term is used to discriminate from "bio-diesel", which is a liquid product from esterification of vegetable oils (*e.g.* rapeseed oil and sunflower oil). Furthermore, "biosyngas" refers to a gas rich in H₂ and CO obtained by gasification of biomass. Biosyngas discriminates from "syngas", which is a comparable gas but from fossil origin, and from "biogas", which is gas produced by digestion of organic matter and consists mainly of CH₄ and CO₂.

(C₃-C₄), naphtha (C₅-C₁₁), diesel (C₉-C₂₀), and wax (>C₂₀) fractions. The distribution of the products depends on the catalyst and the process operation conditions. With respect to the production of green diesel, process conditions can be selected to produce maximum amounts of products in the diesel-range. However, an even higher yield of diesel can be achieved when the FT synthesis is optimised towards production of wax. The wax can be selectively cracked to yield predominantly diesel. For this hydro-cracking additional hydrogen is required, which can be produced from a syngas side-stream that is completely shifted to hydrogen via the WGS reaction (2).

BIOMASS GASIFICATION AND FISCHER-TROPSCH

In a joint research project, ECN and Shell are assessing options for an integrated BG-FT system. Biomass gasification technology has developed to the demonstration stage. Limiting to the most widely used circulating fluidised bed (CFB) gasifier, more than ten installations with a thermal input larger than 10 MW are currently in operation. In nearly all cases the raw product gas is used for firing of cement kilns or co-firing in coal power plants. Furthermore, a variety of smaller CFB installations are in operation as research facility or have the status of pilot-plant. Fischer-Tropsch synthesis is an established technology. Two companies have commercialised their FT technology, *i.e.* Shell (first plant in Malaysia) and Sasol (several plants in South Africa), using natural gas and coal as feedstock to produce the syngas, respectively. The integration of biomass gasification and Fischer-Tropsch synthesis, however, has not yet been demonstrated. The technically most critical and uncertain step in this route is the cleaning of the biosyngas.

The catalysts used in FT synthesis are intrinsically very sensitive to small amounts of poisons. For a number of important impurities in biosyngas, like the sulphur and nitrogen-containing compounds, the effects on the catalyst performance are known. Furthermore, for the removal of these compounds efficient techniques are (commercially) available, although designed for other processes and process conditions. For the removal of the specific biosyngas impurities (*i.e.* the "tars" present in syngas produced by CFB gasification) no technologically mature processes are available in biomass gasification research.

THIS PAPER

One of the targets of the joint ECN/Shell research is to develop the necessary gas cleaning to make biosyngas suitable as a feed gas for FT synthesis. Cleaning of biosyngas for application in gas engines has already been investigated and successfully demonstrated [8]. However, biosyngas cleaning for purpose of catalytic processes, like Fischer-Tropsch synthesis, is much more critical. This paper describes the results of experiments with a BG-FT system and provides new insights regarding the design of integrated BG-FT systems especially with respect to the scale of operation.

INTEGRATED BG-FT SYSTEM

The input of the studied biosyngas cleaning system is a typical biosyngas, while the output is determined by the syngas specifications set by the FT catalyst. The performance of the FT reactor and catalyst are only studied as far as the effect of impurities is concerned. As input for the study a biosyngas produced by a circulating fluidised bed (CFB) gasifier was used. The CFB technology is widely applied in biomass conversion (combustion as well as gasification) as this type of technology is robust, fuel-flexible, and suitable for scales ranging from one to several hundreds of megawatts. The current state-of-the art CFB gasifiers are generally operated at near atmospheric pressures and with air as gasification medium. For FT synthesis a cobalt-based catalyst is used, in view of its superior activity and selectivity relative to iron-based catalysts.

BIOSYNGAS

A typical composition of the raw biosyngas from an air-blown CFB gasifier is shown in Table 1. The syngas components H_2 and CO are present in a ratio of 0.9 and make up only 34 vol%, corresponding to 48.9% of the chemical energy (the LHV of the gas is 8.2 MJ/m_n^3). The remainder of the energy is mainly contained in CH_4 , C_2H_4 , and benzene (total of 44.4%). The major gas cleaning issue is the presence of 7 g/m_n^3 of tars in the gas. Tars are condensable organic compounds with boiling points between $80\text{--}350^\circ\text{C}$. When the temperature in the system decreases to below $\sim 350^\circ\text{C}$ tars start to condense resulting in fouling and ultimately in failure of the system. Typical inorganic biomass impurities are NH_3 , HCl, and H_2S , and in minor quantities COS, CS_2 , and HCN are present. Furthermore, 2 g/m_n^3 of solids are present in the raw biosyngas.

Table 1. Typical biosyngas composition for gasification of wood (15% moisture) at 850°C in an atmospheric air-blown CFB gasifier.²

Main Constituents	[vol%, dry]	[LHV%]	Impurities	[mg/m_n^3]
CO	18	27.8	NH_3	2200
H_2	16	21.1	HCl	130
CO_2	16	-	H_2S	150
H_2O (relative to dry gas)	13	-	all COS, CS_2 , HCN, HBr	< 25
N_2	42	-	dust, soot, ash	2000
CH_4	5.5	24.1		
C_2H_2 (acetylene)	0.05	0.4	Tar classes [9]	[mg/m_n^3]
C_2H_4 (ethene)	1.7	12.4	class 2 (hetero atoms)	350
C_2H_6 (ethane)	0.1	0.8	- <i>phenol</i>	160
benzene	0.42	7.9	class 3 (1-ring, excl. BTX)	370
toluene	0.07	1.6	class 4 (2,3-ring)	5300
xylenes	0.04	1.0	- <i>naphthalene</i>	2250
sum of tars	0.12	2.8	class 5 (≥ 4 -ring)	650
TOTAL	100	100	class 1 (unidentified)	330

FISCHER-TROPSCH FEED GAS

In commercial operation, catalysts are replaced or regenerated after a certain operational period. The definition of the gas cleaning is therefore based on economic considerations: investment in gas cleaning versus accepting decreasing production due to poisoning of the catalyst. Therefore, there are no 'hard' data on maximum levels for impurities in FT feed gas. For each plant the acceptable levels may be different. As rule-of-thumb a maximum value of 1 ppmV may be used for the sum of the nitrogen-containing and sulphur-containing compounds. For the halides and alkaline metals a lower level of 10 ppbV is assumed (Table 2).

With respect to the tars in general, there are no limits regarding poisoning of the catalyst. However, as the biosyngas needs to be compressed to 25–60 bar for FT synthesis, the concentration of the organic compounds must be below the dew point at FT pressure to prevent condensation and fouling in the system. Specifically, class 2 tars with S or N hetero atoms (e.g. thiophene and pyridine) need to be removed below ppmV level as they are intrinsically poisonous for the catalyst. Solids must be removed essentially completely, as they foul the system and may obstruct the fixed-bed.

². Calculated for a 5.5 MW_e installation, based on a large collection of experimental experience with the ECN 0.5 MW_{th} CFB gasifier BIVKIN. For information on the BIVKIN see: www.ecn.nl/biomass.

Table 2. Required removal levels for Fischer-Tropsch feed gas.

Impurity	Removal level
H ₂ S + COS + CS ₂	< 1 ppmV
NH ₃ + HCN	< 1 ppmV
HCl + HBr + HF	< 10 ppbV
alkaline metals	< 10 ppbV
solids (soot, dust, ash)	essentially completely
organic compounds (tars)	below dew point
- class 2 (hetero atoms)	< 1 ppmV

With respect to the other constituents of biosyngas, *i.e.* H₂, CO, CO₂, CH₄, N₂, paraffins (ethane and propane), and olefins (ethene and propene), there are no specifications. The gas is suitable as feed for Fischer-Tropsch synthesis assuming the biosyngas is free of tars and other impurities. This was demonstrated in our previous experimental work, in which FT runs were carried out with mixtures of the mentioned compounds to mimic (clean) biosyngases.

DESIGN APPROACH

In evaluating BG-FT systems, usually the gasifier is taken as starting point and the FT synthesis is considered as a consecutive operation. In this *front-end approach* the scale of the installation is determined by the scale of the gasifier, which is in the range of 10-100 MW_{th} for CFB gasifiers currently in operation. In the view of the ambition to replace a considerable fraction of the fossil-based transportation fuels by renewable transportation fuels, it seems logical to maximise the conversion of (bio)syngas to green diesel. Therefore, in the *back-end approach* the (desired) scale for the Fischer-Tropsch plant is taken as starting point. The relatively small FT plant of Shell in Malaysia (12,500 bbl/day) already corresponds to a thermal input of syngas of more than 1000 MW. For full-scale FT synthesis Shell studies plants with capacities of 75,000 bbl/day [10]. The latter scale would require a BG-FT plant with (several) gasifiers of 500-1000 MW_{th}. Both approaches require different process design and gas cleaning concepts.³

FRONT-END APPROACH

The principle idea in this approach is that *tri-generation* is the most economic configuration for scales of 1-100 MW_{th} [11]. In a tri-generation system the biosyngas is used for Fischer-Tropsch synthesis, with the off-gas being used to generate electricity and heat in a combined cycle (CC). The fundamental assumptions that rationalise this approach are:

- the gasifier is air-blown as the use of oxygen is not economic for these scales;
- the FT unit is operated in once-through mode to avoid build-up of inerts; this concerns especially N₂ which is present in about 40 vol% in the biosyngas,⁴ but also CO₂, CH₄, and gaseous FT products (C₁-C₄);
- no conditioning of the biosyngas (adjustment of H₂/CO ratio via the WGS reaction and CO₂ removal) prior to FT synthesis to reduce units and costs. Especially removal of CO₂ (present in 16 vol%) is an expensive operation that is not essential if the FT off-gas is not recycled.

³. In evaluating processes designs heat integration options and the plant's own electricity consumption are not considered. The net heat and electricity production is dependent of the power balance of the plant.

⁴. To produce a nitrogen-free biosyngas an indirect gasifier might be an option. However, as still no recycle can be incorporated due to the presence of other inerts (CO₂ and hydrocarbons) the basic design of the concept will not change.

Importance of H_2/CO ratio

As a consequence of the latter assumption (*i.e.* no syngas conditioning), the H_2 concentration is the limiting factor for the conversion in a once-through Fischer-Tropsch synthesis (*cf.* Table 1). In the case of 90% H_2 conversion, only 40% CO will be converted assuming a consumption ratio of $H_2/CO = 2$. The unconverted H_2 and CO together with the other gas compounds and the gaseous C_1 - C_4 hydrocarbons produced in the FT synthesis reaction are used for electricity generation. In Figure 1 an indicative energy balance for the tri-generation system is shown. These data are based on an assumed FT selectivity of 90% to C_5 + products (wax and liquids) versus 10% gaseous C_1 - C_4 products, and a CC with 50% electric efficiency. For simplicity it is assumed that the tars and BTX 'pass' the FT reactor as inerts and are converted in the CC.

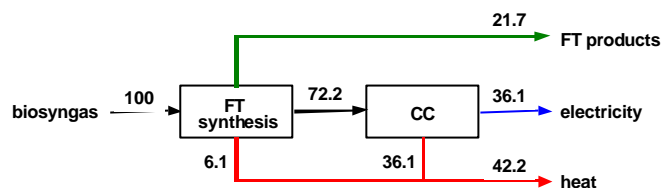


Figure 1. Indicative energy balance for tri-generation without shift.
Starting with biosyngas from a CFB (Table 1).

The yield of FT products is low due to the fact that H_2 and CO represent less than one half of the energy content of the syngas, in combination with the fact that the hydrogen deficiency limits the CO conversion to less than 50%. Therefore, in many studies on integrated BG-FT systems, the H_2/CO ratio in the biosyngas is used as an important gasifier selection criterion. The focus is on gasification technologies and operational conditions that afford biosyngases with higher H_2/CO ratios. In general, higher ratios are achieved by adding steam to the gasifier to shift to higher H_2 concentrations already in the gasifier. However, the use of steam is unfavourable for the overall gasification efficiency and results in a net decrease of the total efficiency and should therefore be avoided. Instead of compromising in the gasification efficiency to achieve a higher H_2/CO ratio, which nevertheless remains below the FT consumption ratio of 2, it is more reasonable to use a separate water-gas-shift step in the FT feed gas. When the gas is shifted to the consumption ratio prior to FT synthesis, the energy efficiency to FT wax and liquids is 41% higher (see Figure 2). Also the total energy efficiency to liquids products and power is higher, *viz.* 60.4 versus 57.8%.

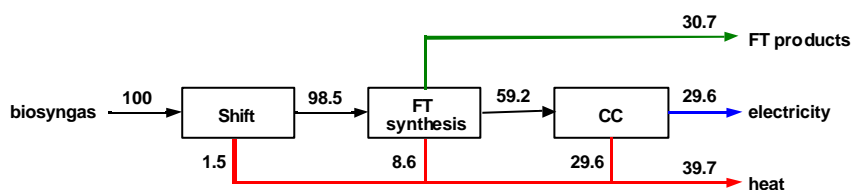


Figure 2. Indicative energy balance for tri-generation with shift to ratio of $H_2/CO = 2$,
starting with biosyngas from a CFB (Table 1).

When the purpose of a tri-generation plant is to maximise the production of FT products, a shift step will always be part of the system. Therefore, the H_2/CO ratio in the raw biosyngas is irrelevant as selection criterion. The total yield of H_2+CO in the gas is much more important with respect to the Fischer-Tropsch synthesis.

Tars are the issue in gas cleaning?

In the discussion in the previous section it was implicitly assumed that the gas was sufficiently clean for Fischer-Tropsch synthesis, however, in fact the raw CFB biosyngas does not meet the specifications (*cf.* Table 2). With the current state-of-the-art gas cleaning, biosyngas can be made suitable for application in gas engines [8]. This gas cleaning comprises dust removal by a cyclone, two wet scrubbers to cool the gas and remove tars by condensation and NH_3 and HCl by adsorption, and finally an electrostatic precipitator (ESP) for fine dust and tar aerosols. The 'clean' gas still contains approx. 2 g/m^3 tars (mainly class 4), but as the gas has a tar dew point of approx. 30°C , no condensation occurs if the gas is not further cooled. The NH_3 level was above 40 ppmV (removal efficiency is not optimal due to the presence of tars in the water), and the H_2S concentration was 100 ppmV, as this compound was not removed [8].

To meet the FT feed gas specifications the gas needs further cleaning. First of all, the organic compounds must be removed to a level at which no condensation occurs upon compression to FT synthesis pressure (25-60 bar). Taking naphthalene as reference, this would correspond to an allowable tar content of 2 ppmV, while for the BTX compounds this corresponds to 2500 ppmV (for 40 bar at 20°C).

ZnO and active carbon filters are considered suitable for removal of H_2S and remaining traces of other inorganic impurities (*e.g.* NH_3 , HCl , HCN , CS_2 , and COS), respectively. These two filters can be used as guard beds for the final protection of the catalyst and are considered a crucial part of the gas cleaning.

Although the active carbon is intended to remove traces of the inorganic impurities, it will also adsorb organic compounds in the gas. Therefore, the active carbon will effectively become a BTX removal step, as the concentration of BTX is still in large excess of the inorganic compounds. This would require frequent regeneration of the guard beds, which is not the preferred approach in the view of process reliability. This implies that it is preferred to remove the tars as well as BTX upstream of the guard beds. Thus, the removal of BTX, and not tars, from the biosyngas is the actual issue in gas cleaning for FT synthesis (as tars are readily removed under conditions for BTX removal).

Gas cleaning for tri-generation

So far no reported studies on BG-FT have considered BTX removal, as these compounds are inert in the FT synthesis. In the tri-generation approach, BTX are even desired for electricity generation in the CC considering the significant contribution to the caloric value of the gas. Conventional gas cleaning techniques used in biomass gasification are not capable of removing tars and BTX to ppmV level. However, recently ECN demonstrated a new powerful technology for tar removal [12]. With this so-called OLGA technology, tars are removed from the gas by an organic washing liquid. As the liquid has an affinity for the tars, the removal is based on absorption as well as liquid collection (the latter is the only mechanism in water scrubbers) [13]. Based on these mechanisms an OLGA unit can also be designed to remove tars as well as BTX to the required levels. Ideally, the tars and BTX are recycled to the gasifier where they are broken down.⁵

The basic process lay-out of the gas cleaning for the tri-generation system is shown in Figure 3. The tars and BTX are removed from the biosyngas with an OLGA unit and the inorganic impurities are removed by (conventional) wet gas cleaning techniques. H_2S and remaining trace impurities are removed with ZnO and active carbon filters, and then the gas is fed to the FT reactor (after compression at some point). The previous discussion on the H_2/CO

⁵. ECN has demonstrated that tars from the wet cleaning section can be recycled to the gasifier without accumulation of tars (*viz.* the tars are destructed). *Publication in preparation*.

ratio remains valid even after removal of BTX and the tars, and recycling to the gasifier, however, the numbers will change a little.

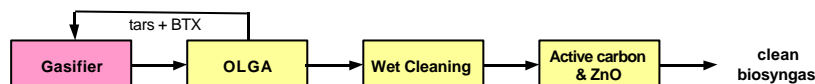


Figure 3. Process line-up of gas cleaning for tri-generation.

BACK-END APPROACH

To replace a significant part of the fossil diesel by its green equivalent, a large production capacity is required. Since FT facilities are relatively high capital intensive, the economy of scale is required to produce the green diesel competitively with other alternative renewable transportation fuels, *e.g.* bio-ethanol and bio-diesel (RME) [14]. This implies large-scale FT plants (of more than 1000 MW_{th}) that are dedicated to the production of FT liquids (*viz.* no tri-generation). Fundamental assumptions in this approach are:

- FT off-gas is recycled to the biomass gasifier to achieve maximum syngas conversion;
- electricity is only produced as 'by-product' from the relatively small recycle bleed stream;
- the yield of syngas (*i.e.* the sum of the H₂ and CO content) in the FT feed gas must be as high as possible;

Importance of maximum H₂+CO yield

The importance of a high yield of the syngas compounds H₂ and CO was already mentioned in the discussion of the tri-generation approach. When a maximum yield of FT products is aimed for, all the energy contained in compounds other than H₂ and CO is not available for the FT synthesis. Ideally, all CH₄ (24% of the energy), C₂H₄ (12%), and BTX (11%) should be converted into H₂ and CO. Considering both the demands for high CO+H₂ yield and the necessity to remove all tars and BTX from the FT feed gas, the most optimal process line-up contains a high-temperature tar cracker, in which all hydrocarbons are destructured to yield mainly H₂ and CO.⁶ In Figure 4 an indicative energy balance for a system with a thermal tar cracker is shown. For the oxygen-blown tar cracker and the shift (to H₂/CO = 2) together a 15% loss of chemical energy is estimated. As the FT off-gas is recycled (except for a relatively small bleed stream) a 95% overall syngas conversion to wax and liquids is assumed (with 20% heat production and 50% electric efficiency for the CC).

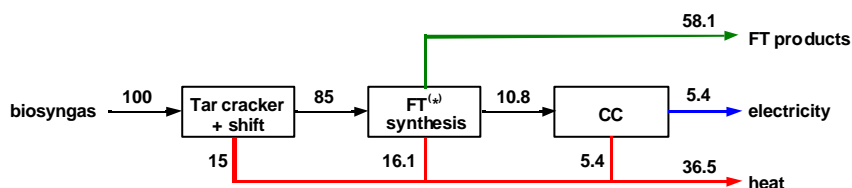


Figure 4. Indicative energy balance for maximum FT production. FT^(*) refers to the overall FT synthesis including recycle (for biosyngas from a CFB with a tar cracker).

⁶. Alternatively, a catalytic tar cracker or reformer may be used, which however introduces yet another step that is very sensitive to fouling.

The increase in the H_2+CO yield results in a much higher production of FT liquids and wax, and also in a higher overall efficiency of 63.5%. The small amount of electricity produced is sufficient to cover the own electricity consumption of the BG-FT plant. In contrast to the other cases described, about 10%-points of the heat is high temperature ($>1000^\circ C$) heat from the tar cracker and may be used to produce an additional 3 to 4%-points of electricity.

Oxygen gasification?

In the discussion in the previous section it was assumed that recycling of the FT off-gas is possible. To allow economically viable recycling, the concentration of inerts (*i.e.* N_2 and CO_2) in the gas should preferably be below 15 vol% [14]. With already 42 vol% N_2 in the raw biosyngas of an air-blown CFB gasifier this specification can never be met. Therefore, oxygen-blown gasification is required to prevent N_2 dilution of the gas. Although the costs of oxygen are high, they are justified (if optimum yield of FT products is pursued) at large scales by the enormous increase in FT yield.⁷ As part of the gas conditioning the system will also contain a CO_2 removal step to meet the inert specification.

Gas cleaning for maximised FT production

In Figure 5 the basic process lay-out for the gas cleaning for maximum FT yield is shown. All the tars, BTX, CH_4 , and other hydrocarbons are converted into mainly H_2 and CO in the tar cracker. For the tar-free gas the further cleaning is straightforward with wet gas cleaning techniques and ZnO and active carbon guard beds (*cf.* Figure 3).

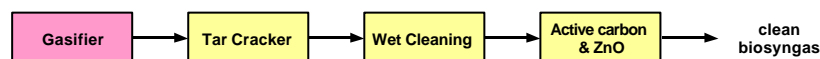


Figure 5. Process line-up of gas cleaning for maximized H_2+CO yield.

INTEGRATED TEST

To demonstrate the technical feasibility of using biosyngas for Fischer-Tropsch synthesis, in December 2001, a small FT unit based on Shell technology was operated for 150 hours on biosyngas produced by gasification of willow and gas cleaning as shown in Figure 5. This was the first demonstration of the production of Fischer-Tropsch wax from biomass [15].

PROCESS LINE-UP

For the integrated test a process line-up with tar cracker was used, to mimic an oxygen-blow gasifier, a low-temperature externally heated gasifier was used. The process line-up of the system used for the integral test is shown in Figure 6. The biomass (willow) is fed to low-temperature gasification (pyrolysis) reactor with a feed flow of 3 kg/h while argon is used for inertisation. The feed is converted mainly into a gas that is rich in tars and about 25 wt% of the feed (in the case of wood) is converted into char, which is separated. In the high-temperature oxygen-blow tar cracker (operated at $>1300^\circ C$) all tars in the gas are destructed, while also all BTX and almost all CH_4 are converted into syngas components.

The tar-free syngas is cooled and scrubbed with water in the aqueous scrubber to remove the inorganic impurities (mainly NH_3 and HCl). The clean gas is subsequently compressed to 60 bar in a two-stage compressor with intercooler, after which condensed water is separated. Under these conditions, approximately $8\text{ m}_n^3/\text{h}$ of wet raw biosyngas is produced. H_2S is removed from

⁷ A biosyngas with a low N_2 content can also be produced by indirect gasification. This option might be relevant to reduce operational costs, if the use of oxygen can be avoided in this way. However, oxygen is already required to operate the tar cracker.

the gas with ZnO filters and final polishing of the gas is achieved with active carbon filters. The compressed gas is stored in gas cylinders to provide a buffer for the Fischer-Tropsch experiments.

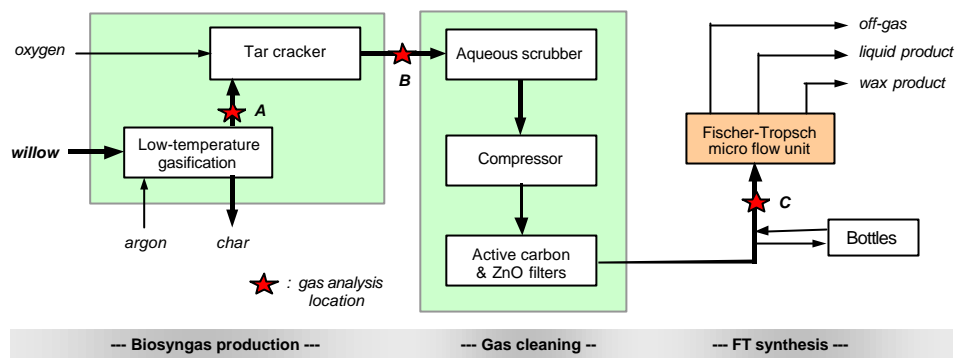


Figure 6. Flow sheet of the integrated system of the biosyngas production, gas cleaning and compression, and Fischer-Tropsch synthesis.

For Fischer-Tropsch synthesis a small micro-flow unit with an isothermal fixed-bed reactor is used with a proprietary Shell cobalt-based catalyst. Downstream of the FT reactor the product stream is separated into wax, liquid products, water, and off-gas. The FT off-gas with the lighter gaseous hydrocarbons and the unconverted CO and H_2 is flared in this test. In commercial applications it would be recycled to the gasifier or used for production of power or process heat. Reactor performance and catalyst degradation are monitored via the gas consumption rate, the off-gas composition, and the yield of wax and liquids.

EXPERIMENTAL RESULTS

The integrated test was carried out with willow (dried to 8% moisture) as feed material obtained from a Dutch energy farm [16]. As the micro flow FT unit consumes only $\sim 10 \text{ L}_n/\text{h}$ of gas, the gasifier was operated periodically to produce additional gas to fill the buffer. The compositions of the biosyngas up- and downstream of the tar cracker, and of the pressurised clean biosyngas are shown in Table 3. The tar cracker functions very well for the destruction of tars in the pyrolysis gas and conversion of CH_4 , C_2H_4 , C_2H_6 , and BTX into syngas components. In the scrubber all NH_3 is removed, while as expected, the ZnO filters remove H_2S quantitatively. The removal level of COS to $\sim 300 \text{ ppbV}$ is sufficient.

During the integrated test, the Fischer-Tropsch catalyst showed no loss of activity. The composition and quality of the wax and light product produced from willow were identical to products from fossil origin as followed from off-line analyses in the Shell laboratories. In January 2002 the test was repeated with an other catalyst sample with a test duration of 500 hours. Again the performance of the reactor was stable over the whole period and the catalyst showed no loss of activity. In Figure 7 samples of the willow and FT wax and light product are shown.

CONCLUSIONS

The emission of the greenhouse gas CO_2 can significantly be reduced by replacing fossil derived transportation fuels by renewable transportation fuels. An interesting route is the production of green diesel via biomass gasification and Fischer-Tropsch synthesis. The critical step is the necessary gas cleaning to make biosyngas suitable as a feed gas for FT synthesis. The

Table 3. Measured gas compositions (dry basis) during 150 hours test with integrated system of gasification, gas cleaning and compression, and FT synthesis.

Gas		Pyrolysis gas ^a	Biosyngas	FT feed gas
Analysis location		A	B	C
Temperature	[°C]	550	485	20
Pressure	[bar]	1	1	40
Moisture	[vol%, wet gas]	. ^a	42.4	0.05
CO	[vol%]	12.5	25.7	27.0
H ₂	[vol%]	6.3	28.9	29.4
CO ₂	[vol%]	13.1	31.1	28.8
N ₂	[vol%]	0.72	0.36	1.08
Ar	[vol%]	56.6	12.0	13.6
CH ₄	[vol%]	6.42	0.01	0.01
C ₂ H ₄	[ppmV]	5936	< 5 ^c	< 5 ^c
C ₂ H ₆	[ppmV]	7359	< 5 ^c	< 5 ^c
benzene	[ppmV]	736	< 5 ^c	< 5 ^c
toluene	[ppmV]	530	< 5 ^c	< 5 ^c
SPA tars ^b	[ppmV]	. ^a	< 10 ^c	< 10 ^c
NH ₃	[ppmV]	~	516	0.02
H ₂ S	[ppbV]	~	23789	< 10 ^c
COS	[ppbV]	~	47578	278
CS ₂	[ppbV]	~	207	< 10 ^c
TOTAL	[vol%]	100.0	100.0	100.0

^a. Composition on dry and tar-free basis; fraction of tars + moisture corresponds to 75 wt% of the pyrolysis gas. ^b. Concentration of tars measured by solid phase adsorption (SPA). ^c. Actual concentrations were below detection limit. The reported values are estimated maximum values.

experimental work and the supporting system analysis presented in this paper resulted in important new insights on the desired gas cleaning and the optimal line-up for biomass gasification processes with maximised yields of FT liquids. The major insights are:

- BTX are the design guideline for the gas cleaning and not the tars. Organic compounds in the gas will saturate the active carbon guard bed and have to be removed upstream of the guard beds. As BTX are harder to remove than the tars, the tar-issue is *de-facto* solved when the BTX are removed.
- The H₂/CO ratio in a raw biosyngas is irrelevant. To maximise the yield of FT products any process will contain a water-gas-shift step to adjust the H₂/CO ratio to the consumption ratio in the FT feed gas. Thus, it is the sum of H₂ and CO that is the more relevant parameter.
- A high FT yield requires the presence of a tar cracker in the system. The chemical energy contained in hydrocarbons present in biosyngas compounds is lost for FT synthesis unless these compounds are converted into H₂ and CO in a tar cracker.
- A high overall syngas conversion requires gasification with oxygen. Only FT off-gas with a low inert concentration can be recycled to the gasifier. Biosyngas obtained with air-gasification does not meet this specification.
- All inorganic biomass impurities can be removed sufficiently with conventional scrubbing and filtering techniques (when the gas is BTX and tar-free) as was shown in two independent test of 650 h in total.



Figure 7. Pictures of the willow used for the integrated test, Fischer-Tropsch wax, and the light product (viz. 'green diesel').

- The scale of the BG-FT installation determines the line-up of the gas cleaning and the integrated process. A tri-generation system is favourable for smaller scales as no air-separation, CO₂ removal, or FT off-gas recycle are required, however, the yield of FT products is limited. Optimisation of the production of FT liquids (on a large scale) requires oxygen-blow gasification, a tar cracker, CO₂ removal, and an FT off-gas recycle.

OUTLOOK

The technical feasibility of using biosyngas for Fischer-Tropsch synthesis was proven by two integrated test-runs of 650 hours in total. A good understanding was obtained of the essential issues in gas cleaning and process design. The challenge is now to improve the gasification and gas cleaning technologies to achieve higher energy efficiencies and reduce the costs. For example, oxygen-blown biomass gasification, required for high yield FT synthesis, is not yet well developed. Considering the system with an oxygen-blown gasifier and a consecutive tar cracker, one-step gasification at a high temperature in an entrained flow (EF) gasifier might prove to be more energy efficient.

A further issue is the gasification pressure. Pressurised gasification can result in large cost reductions, as higher throughputs are possible with same scale installations, and because compression of syngas from atmospheric pressure to FT synthesis pressure is extremely energy-intensive. Related to gasification at elevated pressure there are also important technical research questions, especially related to the biomass feeding and the use of inert gas, as well as the optimal pressure in view of electricity consumption.

Nevertheless, it is expected that the future of BG-FT systems will be large plants with pressurised oxygen blown gasifiers and maximised Fischer-Tropsch synthesis.

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