

**GAS CLEANING FOR INTEGRATED BIOMASS  
GASIFICATION (BG) AND FISCHER-TROPSCH (FT)  
SYSTEMS; EXPERIMENTAL DEMONSTRATION OF  
TWO BG-FT SYSTEMS**

**Presented at “The 2<sup>nd</sup> World Conference and Technology Exhibition  
on Biomass for Energy, Industry and Climate Protection”  
in Rome, Italy, 10-14 May 2004**

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# GAS CLEANING FOR INTEGRATED BIOMASS GASIFICATION (BG) AND FISCHER-TROPSCH (FT) SYSTEMS; EXPERIMENTAL DEMONSTRATION OF TWO BG-FT SYSTEMS

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**ABSTRACT:** This paper describes the results of a study towards the development of gas cleaning technology for two integrated biomass gasification (BG) and Fischer-Tropsch (FT) synthesis systems. The first system involves tar destruction with a thermal tar cracker to produce a biosyngas, followed by wet gas cleaning to remove the (inorganic) impurities. The second system involves the removal of the organic impurities (*viz.* tars) from the gasifier product gas in an OLGA unit, followed by wet gas cleaning to remove the inorganic impurities. The technical feasibility of producing Fischer-Tropsch liquids from biomass via both systems was demonstrated by integrated BG-FT experiments of more than 500 run-hours. The results of this study show that there are no biomass-specific impurities in biomass-derived syngas that require a totally different gas cleaning approach compared to state-of-the-art coal or natural gas based FT synthesis.

**Keywords:** biomass conversion, gas cleaning, Fischer-Tropsch.

## 1 INTRODUCTION

Biomass is considered to be an important renewable energy source for this century [1]. An important aspect of biomass is that liquid (bio) fuels can be produced from this renewable source. In 2003 the European Commission has issued a directive for alternative transportation fuels in addition to the EU objectives for primary energy (*i.e.* electricity and heat). According to the directive the target for the share of biofuels is 2% in 2005, increasing to 5.75% in 2010, and possibly even to 8% in 2020.

One of the most promising routes to produce 'green' fuels is the combination of biomass gasification (BG) and Fischer-Tropsch (FT) synthesis [2]. In this route biomass is gasified to yield a product gas or biosyngas that is rich in H<sub>2</sub> and CO. After cleaning and conditioning the biosyngas can be used to synthesise FT 'green' diesel. FT diesel is an ultra-clean high quality fuel as it contains no sulphur and aromatics and the fuel is directly applicable in the current infrastructure and diesel engines.

## 2 FISCHER-TROPSCH SYNTHESIS

### 2.1 Green diesel yield

The Fischer-Tropsch reaction results in a range of products, comprising light hydrocarbons (C<sub>1</sub> and C<sub>2</sub>), LPG (C<sub>3</sub>-C<sub>4</sub>), naphtha (C<sub>5</sub>-C<sub>11</sub>), diesel (C<sub>12</sub>-C<sub>20</sub>), and wax (>C<sub>20</sub>) fractions. Typically, process

conditions are optimised for maximum wax production. The wax can be selectively hydrocracked to yield predominantly diesel. For this hydrocracking additional hydrogen is required, which can be produced from a syngas side-stream that is completely shifted to hydrogen. The maximum amount of liquid products ("fuels") that can be produced from a (cleaned and properly conditioned) syngas is approx. 65% (overall syngas-to-fuel energy efficiency). This follows from: 95% syngas conversion in the Fischer-Tropsch synthesis; 78% of the energy in CO+2H<sub>2</sub> is retained in the paraffin product (the remainder is released as reaction heat); 95% selectivity to C<sub>5</sub>+ products (liquid and wax - the other 5% are gaseous C<sub>1</sub>-C<sub>4</sub> products); and 98% hydrocracking selectivity of the heavier FT products to fuels. The energy contained in the FT off-gas (*i.e.* unconverted syngas and C<sub>1</sub>-C<sub>4</sub> products) can be used to generate electricity.

### 2.2 Feed gas specifications

The catalysts used in FT synthesis are intrinsically very sensitive to small amounts of poisons. 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. Rule-of-thumb specifications for impurities that might be present in biomass-derived syngases are less than 1 ppmV for both the total sulphur ( $\text{H}_2\text{S}$ , COS, and  $\text{CS}_2$ ) and nitrogen containing impurities ( $\text{NH}_3$  and HCN), and less than 10 ppbV for both the total halides and alkaline metals. Organic compounds (tars) must be removed to a level at which no condensation occurs upon compression to FT synthesis pressure (25-60 bar). For naphthalene this corresponds to an allowable content of 2 ppmV, while for the benzene compounds this corresponds to 2500 ppmV (for 40 bar at 20°C) [3, 4].

With respect to the other possible constituents (depending on the gasification concept) of the FT feed, *i.e.*  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$ , and larger hydrocarbons, there are no ‘hard’ specifications. However, similar to the gas cleaning, specifications are set by economic considerations. For the concentration of these gases, which are inert in the FT synthesis, a ‘soft maximum’ of 15 vol% is defined (the lower, the better). The presence of inerts requires larger reactors and higher total gas pressures.  $\text{CO}_2$  can readily be removed with standard techniques, but  $\text{N}_2$  and the light-end hydrocarbons cannot be removed at reasonable costs. Therefore, in the production of the FT feed gas the presence of significant concentrations of the latter compounds should be avoided.

### 3 SYSTEM DEFINITION

#### 3.1 Large-scale production

Since Fischer-Tropsch facilities are relatively highly capital intensive, large fuel production capacities are required to produce the green diesel competitively with other alternative renewable transportation fuels, *e.g.* bio-ethanol and bio-diesel (RME). This implies FT plants (of more than 1000 MW<sub>th</sub>) that are dedicated to the production of FT liquids, as was concluded in a 2002 study with ECN, Shell Global Solutions, and BTG as main partners assessing the techno-economic aspects of large-scale biosyngas manufacturing (for FT diesel synthesis) from imported biomass [5]. A production of 8,000 MW of cleaned and conditioned biosyngas was assumed (approximately equivalent with the current Dutch fossil diesel consumption of ~240 PJ).

The Rotterdam Harbour area (*i.e.* the ‘Maasvlakte’) was selected as location for the hypothetical BG-FT plant and the biomass was assumed to be delivered from different production sites by sea transport. A biomass production price of 4 €/GJ was assumed; this price is realistic for the future large-scale markets. The calculated biosyngas production prices for this large-scale system ranged from 6 to 13 €/GJ (with a large dependence on the biomass price) [5]. Resultantly, biomass-based FT diesel will be two to three times as expensive as diesel from fossil origin.

#### 3.2 Gasification

The circulating fluidised bed (CFB) gasifier was identified as potentially suitable type of gasifier because of its fuel flexibility, high throughput, and the operational experience. In a typical CFB product gas, the syngas components  $\text{H}_2$  and CO are present in a ratio of ~1.0 and make up only ~50% of the chemical energy of the gas. The remainder of the energy is contained in  $\text{CH}_4$ , larger hydrocarbons, BTX, and the tars. Typical inorganic biomass impurities are  $\text{NH}_3$ , HCl, and  $\text{H}_2\text{S}$ , and in minor quantities COS,  $\text{CS}_2$ , and HCN are present.

In a BG-FT system the gasifier is preferably oxygen-blown to prevent  $\text{N}_2$  dilution of the gas, which is a prerequisite to allow economically viable recycling of the FT off-gas (to optimize the yield of liquid FT products). The potential yield of FT products is limited when (cleaned) CFB *product gas* is used for FT synthesis. To maximise the yield of FT products, all hydrocarbons in the CFB *product gas* should be converted to yield a *syngas* containing mainly  $\text{H}_2$  and CO. Three systems concepts were defined suitable for the biosyngas production:

1. CFB gasification plus tar cracker;
2. Entrained-flow (EF) gasification;
3. CFB gasification, OLGA tar removal, plus reformer.

#### 3.3 CFB gasifier plus tar cracker

An oxygen-blown CFB gasifier is used to obtain a nitrogen-free gas. In a downstream (oxygen-blown) tar cracker operated at 1300°C all the tars, BTX and the hydrocarbons are cracked and converted into mainly  $\text{H}_2$  and CO. The biosyngas is cleaned

with standard techniques as used for fossil syngas: dust filters, wet-scrubbing techniques (for  $\text{NH}_3$  and  $\text{HCl}$ ), and  $\text{ZnO}$  filters for  $\text{H}_2\text{S}$ . After conditioning ( $\text{H}_2/\text{CO}$  adjustment and  $\text{CO}_2$  removal) the gas is compressed to the FT synthesis pressure (40 bar). The concept is schematically depicted in Figure 1.



**Figure 1:** Concept with CFB gasifier plus tar cracker.

### 3.4 EF gasification

In the CFB plus tar cracker concept the biomass is gasified and subsequently brought to a high temperature to destruct the tars and hydrocarbons. Alternatively, the high temperature may be established directly in the gasifier. In that concept an entrained flow gasifier is used (already at 40 bar); see Figure 2. Downstream the gasifier the cleaning and conditioning is similar to the previous concept (except that additional compression is not required). However, upstream pre-treatment (*i.e.* milling) of the biomass chips (~5 cm), which are normally used to feed a CFB gasifier, is required, as smaller particles (<1 mm) are required to allow stable feeding and to ensure complete conversion in the EF gasifier due to the short residence times.



**Figure 2:** Concept with EF gasification.

### 3.5 CFB gasifier, OLGA, plus reformer

In the third concept another approach towards tar removal and hydrocarbon conversion is followed (Figure 3). After the gasifier, the tars (and BTX) are removed with the OLGA tar removal technology [6,7] and subsequently returned to the gasifier (*viz.* ‘recirculation to extinction’). Hydrocarbons are not removed with OLGA, therefore, after the wet cleaning these compounds are converted in a catalytic reformer. The EF conditioning and compression is similar as in the first concept.



**Figure 3:** Concept with CFB gasifier, OLGA tar removal, plus reformer.

## 4 PROOF-OF-PRINCIPLE DEMONSTRATION

The proof-of-principle of the gas cleaning approaches of both CFB concepts has been delivered in integrated gasification, cleaning, and Fischer-Tropsch synthesis tests in the ECN laboratories [3]. A test of the entrained flow concept was not carried out as the critical issues for this concept relate to feeding and ash behaviour and not to the gas cleaning [8].

### 4.1 Gasifier plus tar cracker

To mimic this system on lab-scale, the biomass (willow) was gasified in a low-temperature externally heated gasifier. The gas was fed into the high-temperature (1300°C) oxygen-blow tar cracker where all tars, BTX, and almost all  $\text{CH}_4$  were destructed and converted into syngas components. The tar-free biosyngas was quenched to cool the gas and scrubbed with water in the aqueous scrubber to remove the inorganic impurities (mainly  $\text{NH}_3$  and  $\text{HCl}$ ) and all the solids. Significant amounts of soot were formed but the soot was removed in the scrubber without operational problems. The clean gas was subsequently compressed to 60 bar.  $\text{H}_2\text{S}$  was removed with  $\text{ZnO}$  filters (below 10 ppbV) and final polishing of the gas was achieved with active carbon filters.

The technical feasibility (“*proof-of-principle*”) of using biomass-derived syngas for Fischer-Tropsch synthesis was proven by two integrated test-runs of 650 hours in total. For Fischer-Tropsch synthesis a small micro-flow unit with an isothermal fixed-bed reactor was used with a proprietary Shell cobalt-based catalyst.

***In December 2001, for the first time in the world, Fischer-Tropsch products were synthesised from biomass in a 150 hours test with this system.***

During the test, the Fischer-Tropsch catalyst showed no loss of activity or selectivity. In January 2002, the test was

successfully repeated in a 500 hours experiment [3,4]. The composition and quality of the wax and light products produced from willow were in all cases identical to products from fossil origin, as followed from off-line analyses in the Shell laboratories. For the (theoretical) ASF chain-growth parameter, a value of  $\alpha = 0.92$  was determined from the analysis of the products. This apparent high selectivity for higher hydrocarbons is consistent with the  $C_{5+}$  selectivity of 0.93 determined from the mass balance.

#### 4.2 CFB gasifier plus OLGA tar removal

This gas cleaning approach is followed in a system with a catalytic reformer; the actual reforming step was not included in the experimental system line-up. Biomass (beech) was gasified at 850°C in the ECN lab-scale atmospheric bubbling fluidised bed gasifier with oxygen as gasifying medium to produce an essentially nitrogen-free product gas and with added steam or  $CO_2$  to moderate the temperature in the bed of the gasifier. In comparison with air ( $O_2$  concentration is 21 vol%) the concentration  $O_2$  in the gasification medium could be increased to as high as 63 vol% (in steam).

The raw product gas passes a high-temperature gas filter to remove essentially all the solids. The tars and BTX are removed in the OLGA unit. The OLGA applies a special organic washing liquid with a high affinity for the tars [6,7]. The gas leaving OLGA is further cooled and cleaned from  $NH_3$ , HCl, and other inorganic impurities in a water scrubber. Both the OLGA and the water scrubber are equipped with a stripper to regenerate the washing oil and water, respectively. Further processing of the gas is similar to the other system.

Water is condensed from the clean gas and subsequently the gas is compressed to the desired pressure. The compressed gases are passed through a ZnO filter to remove the  $H_2S$  and an active-carbon guard bed to remove all remaining trace impurities.

In contrast to the system containing a tar cracker and producing a *syngas*, the Fischer-Tropsch feed gas was a *product gas* containing  $CH_4$ , ethane, and a small amount of ethylene. The technical feasibility (“*proof-of-principle*”) of using a biomass-derived product gas for Fischer-Tropsch

synthesis was proven by the integrated 500 hours test-run.

***In March 2003, Fischer-Tropsch products were synthesised from a biomass-derived product gas in a 500 hours test with this system.***

During the integrated test, the catalyst showed no loss of activity or selectivity, and the composition and quality of the wax and light products produced from beech were identical to products from fossil origin, as followed from off-line analyses in the Shell laboratories. Furthermore, the biomass origin was confirmed by carbon-14 dating of the product samples.

#### 4.3 Fischer-Tropsch synthesis

The  $H_2/CO$  ratio of typical product gases is in the range of 0.8-2.1. With the appropriate cobalt-based catalyst applied in this study,  $C_{5+}$  selectivities around 90% were obtained for  $H_2/CO$  ratios in this range. This implies that the catalyst is very suitable for once-through Fischer-Tropsch synthesis systems.

Saturated (paraffin) hydrocarbons in the Fischer-Tropsch feed gas behave as inerts in the synthesis; this is not the case for the unsaturated (olefin) hydrocarbons of which especially ethylene might be present in significant concentrations. Under FT synthesis conditions ethylene is a ‘very reactive’ compound; it may be hydrogenated or re-inserted on the catalyst surface to react further in the FT chain-growth reaction, which will result in slightly different results with respect to product distribution and hydrogen consumption (compared to syngases typically used for FT synthesis).

## 5 CONCLUSIONS

This paper describes the results of a study towards the development of gas cleaning technology for integrated biomass gasification (BG) and Fischer-Tropsch (FT) synthesis systems.

The scope of the project was set to systems for dedicated production of FT liquids with maximum biomass-to-fuel efficiencies to benefit from the economy of scale and to produce the FT diesel

competitively with other alternative renewable transportation fuels. This implied that tri-generation concepts were not considered and that in gasification a *biosyngas* instead of a *product gas* must be produced.

Two integrated systems of biomass gasification, gas cleaning, and Fischer-Tropsch synthesis were assessed and demonstrated to deliver the Proof-of-Principle of two systems with different gas cleaning approaches to meet Fischer-Tropsch specifications, *i.e.*:

(1) Oxygen-blown CFB gasifier plus oxygen-blown tar cracker to produce a biosyngas, with wet gas cleaning to remove the (inorganic) impurities;

(2) Oxygen-blown CFB gasifier to produce a product gas, plus OLGA unit to remove the organic impurities (*viz.* tars), and a similar wet gas cleaning to remove the inorganic impurities. The reforming step to convert the hydrocarbons in the product gas into a syngas was not included in the study.

Tar cracking. In a tar cracker all organic compounds in the product gas (*i.e.* tars, BTX, CH<sub>4</sub>, and C<sub>2</sub>-hydrocarbons) are destructed to produce a biosyngas. Upon high-temperature tar cracking of product gas or pyrolysis gas significant amounts of soot are formed, representing an efficiency loss and creating a gas treatment issue. Optimisation of the tar cracking process conditions is the major development topic in optimisation of BG-FT systems with a high temperature step.

Gas cleaning for inorganic impurities. The produced biosyngas can be further cleaned from inorganic impurities with the same technologies that are used for cleaning of syngas from fossil origin. There are no biomass-specific inorganic impurities that require a totally different gas cleaning approach. The technical feasibility (“*proof-of-principle*”) of using a cleaned *biosyngas* for Fischer-Tropsch synthesis was proven by two integrated test-runs of 650 hours in total.

Gas cleaning for organic impurities. With an OLGA unit tars and other organic compounds are removed from the product gas. After the removal of the organic impurities, the gas can be further cleaned from the inorganic impurities with conventional technologies. There are no

biomass-specific organic impurities that require a high temperature removal step in the system. The technical feasibility (“*proof-of-principle*”) of using a cleaned *product gas* for Fischer-Tropsch synthesis was proven by an integrated 500 hours test-run.

Fischer-Tropsch synthesis. Product gases from biomass gasification contain several percents of olefin hydrocarbons (in particular ethylene). These components may participate in the FT reaction or sequential reactions, hence the prediction of product formation in the reactor becomes somewhat more difficult.

Summarising. The results of this study have unambiguously proven the *technical* feasibility of producing Fischer-Tropsch liquids from biomass. These positive results justify, from a technical perspective, a further technology development of the route of biomass gasification and Fischer-Tropsch for the production of renewable transportation fuels.

## 6 OUTLOOK

In underlying study gas cleaning has been developed for systems based on fluidised bed gasification of biomass. Results from a parallel study indicate that direct gasification of biomass in a slagging entrained flow (EF) gasifier is probably more attractive to produce biosyngas, considering the higher net biomass-to-biosyngas efficiency [8]. However, the tar cracker as discussed in this report is conceptually similar to an EF gasifier (*i.e.* in the systems assessed just the input differs: product gas versus solid biomass, respectively). Therefore, the defined and demonstrated gas cleaning for inorganic impurities is also applicable downstream an EF gasifier.

Although systems based on fluidised bed gasification are not the first candidates for green diesel production, the assessed system with fluidised bed gasification and OLGA tar removal is very promising for the production of Substitute Natural Gas (SNG) or “green gas”. In December 2003 ECN has demonstrated the first production of SNG with this system. In a recently started ECN project the system will be optimised and

operated to deliver the Proof-of-Concept and make a design for a BG-SNG pilot plant.

In spite of the positive technical results of underlying and parallel projects, it seems too early to implement BG-FT technology on a commercial scale. First of all, the very large required capital investment poses a “capital hurdle”– meeting the EU biofuel directive in 2010 via BG-FT alone would require an investment of some 25 billion euros. Secondly, as the resulting product is between two to three times more expensive than mineral diesel, the *economic sustainability* of this route is (under the current economic conditions) insufficient. Similar to the current “first generation” biofuels (ethanol from starch and sugar, and fatty acid methyl esters like RME) the more advanced BG-FT biofuel would depend on market disrupting support mechanisms to make it viable.

Nevertheless, as the positive environmental impact of the current “first generation” of biofuels is limited and their costs are as well several times higher than those of mineral diesel, there still is an incentive to develop more advanced systems for the ‘second generation’ biofuels, like the biomass-based Fischer-Tropsch fuels. In the latter case, work should be focused on reducing the cost of biomass as well as improving the conversion technology, in order to drive down both the capital hurdle and the excess manufacturing costs relative to mineral diesel.

## 7 ACKNOWLEDGEMENT

Financial support from the Dutch Agency for Research in Sustainable Energy (SDE) is acknowledged.

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