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Gas Cleaning for Integrated Biomass Gasification (BG) and Fischer-Tropsch (FT) Systems

Experimental demonstration of two BG-FT systems ("Proof-of-Principle")

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PREFACE

The work described in this report was carried out within the framework of the project "*Gas Cleaning for Integrated Biomass Gasification Fischer-Tropsch Systems*" and was co-financed by the Agency for Research in Sustainable Energy (SDE) under project number P2000-015. Account manager for SDE was prof. ir. C. Daey Ouwens. Partners in the project were the unit ECN Biomass of the Energy research Centre of the Netherlands (ECN), Shell Global Solutions International, and Utrecht University (Copernicus Institute). Applicable ECN project number was 7.2222 (and 7.2271 for the extension).

The results of the system assessment activity of the project have been published separately. In the underlying report only the summarised results are included (Appendix A); the complete results can be found in: Hamelinck, C.N.; Faaij, A.P.C.; Uil, H. den; Boerrigter, H.: *Production of Fischer-Tropsch transportation fuels from biomass; technical options, process analysis and optimisation, and development potential*, Utrecht University, Copernicus Institute, report NWS-E-2003-08, March 2003.

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KEYWORDS

Biomass, gasification, gas cleaning, tar, Fischer-Tropsch synthesis, cobalt catalyst, green diesel, renewable energy, transportation fuels, tri-generation, circulating fluidised bed (CFB), tar cracker, entrained flow.

ABSTRACT

This report 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 syngas production for FT synthesis.

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EXECUTIVE SUMMARY

Introduction

Biomass is considered to be an important renewable energy source for this century. An important aspect of biomass is that liquid (bio) fuels can be produced from this renewable source. One of the most promising routes to produce ‘green’ fuels is the combination of biomass gasification (BG) and Fischer-Tropsch (FT) synthesis. In this route biomass is gasified to yield a product gas or biosyngas that is rich in H_2 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.

Fischer-Tropsch Synthesis

The Fischer-Tropsch reaction results in a range of products, comprising light hydrocarbons (C_1 and C_2), LPG (C_3-C_4), naphtha (C_5-C_{11}), diesel (C_{12}-C_{20}), and wax ($>C_{20}$) fractions. The maximum amount of liquid products (“fuels”) that can be produced from a (cleaned and properly conditioned) syngas is approx. 70% (overall syngas-to-fuel energy efficiency) and approximately 25% of the energy is released as heat. The remaining 5% of the energy contained in the FT off-gas (*i.e.* unconverted syngas and C_1-C_4 products) can be used to generate electricity.

The catalysts used in FT synthesis are intrinsically very sensitive to small amounts of impurities. Rule-of-thumb specifications for impurities that might be present in biomass-derived syngases are less than 1 ppmV for both the total sulphur (H_2S, COS, and CS_2) and nitrogen containing impurities (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 the concentration of inert gases (*i.e.* CO_2, N_2, CH_4, and larger hydrocarbons) a ‘soft’ maximum of 15 vol% is defined.

System definition

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_{th}) that are dedicated to the production of FT liquids from biosyngas, as was concluded in a 2002 study assessing the techno-economic aspects of large-scale biosyngas manufacturing (for FT diesel synthesis) from imported biomass.

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 BG-FT system the gasifier is preferably oxygen-blown to prevent N_2 dilution of the gas. In a typical CFB product gas, the syngas components 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 CH_4, larger hydrocarbons, BTX, and the tars. Typical inorganic biomass impurities are NH_3, HCl, and H_2S, and in minor quantities COS, CS_2, and HCN are present. 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 H_2 and CO.

Three system concepts were defined suitable for the biosyngas production:

(1) 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 H_2 and CO. The biosyngas is cleaned with standard techniques as used for fossil syngas: dust filters, wet-scrubbing techniques (for NH_3 and HCl), ZnO filters for H_2S, and active carbon police filters. After conditioning (H_2/CO adjustment and CO_2 removal) the gas is compressed to the FT synthesis pressure (25-60 bar).

(2) Entrained Flow 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 (EF) gasifier is used (already at FT synthesis pressure). 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 necessary, 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.

(3) CFB gasifier, OLGA, plus reformer

In the third concept another approach towards tar removal and hydrocarbon conversion is followed. After the gasifier, the tars (and BTX) are removed with the OLGA tar removal technology 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 conditioning and compression is similar as in the first concept.

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 at the ECN laboratories. 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.

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 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 NH_3 and 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. H_2S was removed with 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 FT 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 [7,8]. 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. The (theoretical) ASF chain-growth parameter was determined from the analysis of the products and was found to be consistent with the C_5+ selectivity of 0.93 determined from the mass balance.

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.

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. 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 was confirmed by off-line analyses in the Shell laboratories. Furthermore, the biomass origin was confirmed by carbon-14 dating of the product samples.

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).

Conclusions

This report 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. A downstream reforming step to convert the hydrocarbons in the product gas into a syngas was not included in the study.

<u>Tar cracking</u>. In a tar cracker all organic compounds in the product gas (*i.e.* tars, BTX, CH_4, and C_2-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.

<u>Gas cleaning for inorganic impurities</u>. 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.

<u>Gas cleaning for organic impurities</u>. 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.

<u>Fischer-Tropsch synthesis</u>. With the appropriate cobalt-based catalyst applied in this study, C_5+ selectivities around 90% were obtained for H_2/CO ratios in the range of 0.8-2.1. This implies that the catalyst is very suitable for once-through Fischer-Tropsch synthesis systems. 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.

<u>Summarising</u>. 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.

Outlook

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". 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 and FT biofuel would depend on support mechanisms to make it viable. Nevertheless, there is an incentive to develop these BG-FT systems, as the positive environmental impact of the current biofuels is limited (*i.e.* biodiesel and bio-ethanol).

Although on the long term dedicated large-scale Fischer-Tropsch production plants are required to optimise the energetic utilisation of biomass, on the short and medium term other system concepts can be selected to demonstrate (parts of) the technology and facilitate implementation. In the view of ECN, *trigeneration* concepts are very suitable for this purpose.

In the underlying study the gas cleaning systems have been developed for fluidised bed gasification of biomass. However, for the production of biosyngas, gasification of biomass in a slagging entrained flow (EF) gasifier has been identified as the preferable production route, considering the apparent simplicity of the system and the relatively high net biomass-to-biosyngas efficiency. The tar cracker as discussed in this report is conceptually similar to such an EF gasifier and the defined and demonstrated gas cleaning for inorganic impurities is similar.

1. 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 CO_2 emissions resulting from fossil fuel consumption. This concern resulted in the Kyoto protocol in which objectives to reduce the anthropogenic CO_2 emissions are 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 sources for this century [1,2].

1.1. Background

An important aspect of biomass is that liquid (bio) fuels can be produced from this renewable source [3]. The life-cycle emission of the greenhouse gas CO_2 can be reduced when 'green' biomass-derived transportation fuels are used in cars, trucks, and buses. In 2003 the European Commission (EC) has issued a directive for sustainable 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 to even higher shares in 2020 (*i.e.* more than 10% is suggested).

In the Netherlands, in the late 1990s a governmental study was carried out towards the potential of replacing gaseous and liquid energy carriers (GAVE[1]) in the context of the reduction of CO_2 emissions and sustainable energy management. This GAVE study identified cellulose ethanol and Fischer-Tropsch diesel as most suitable green transportation fuels for the Netherlands situation, with application as gasoline blending fuel and diesel substitute, respectively [4]. The promising results formed an important argument for starting the second phase of the GAVE programme[2] aimed at demonstrating complete integrated GAVE chains, *viz.* from biomass production, 'green' fuel production, to application and fleet tests. It was projected that consortia would be formed for demonstration of the technology and the integrated chains. Although, several initiatives and consortia were started with financial support from GAVE, almost all consortia decided not to continue into a demonstration project because of the high technical risks (due to the absence of mature and proven technologies) and the absence of sufficient financial governmental support to compensate for the high economical risks.

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[1]. GAVE is the Dutch acronym for "Gaseous and Liquid Energy Carriers".

[2]. The GAVE programme is managed by the Netherlands Agency for Energy and the Environment (Novem).

In the system assessments carried out in the first phase GAVE study, successful technology development was assumed to overcome barriers and uncertainties or to realise the optimisations required to reduce costs. At time of the study commercial ethanol production plants exist (*e.g*. based on corn and sugar cane), however, the production of Fischer-Tropsch diesel from biomass had not yet been performed, let alone been demonstrated on a reasonable scale.

Therefore, parallel to the GAVE activities, in 1999 a project was started to assess the technical and first-order economic feasibility of producing FT products from biomass. Partners were Shell Global Solutions, ECN Biomass, and Utrecht University, and the project was sponsored by the Agency for Research in Sustainable Energy (SDE). In the Fischer-Tropsch route, biomass is gasified to yield a product gas or biosyngas that is rich in H_2 and CO. After cleaning and conditioning the gas can be used as feed gas for a FT synthesis reactor where the H_2 and CO are converted into long-chain hydrocarbons that are subsequently converted into ‘green diesel’ in a post-processing step.

The study concluded that typical product gases from biomass gasification are suitable as feed for FT synthesis assuming the gas was free of impurities and that the long-term economic perspectives were positive compared to alternative renewable transportation fuels [5]. The project results motivated the project partners to continue the development of integrated biomass gasification Fischer-Tropsch (BG-FT) systems. The technically most critical and uncertain step in this route is the cleaning of the FT feed gas. As this topic had been not been addressed in the previous study, the new R&D project had to focus on solving this issue.

1.2. Scope & Objective

At the start of the project (late 2000), atmospheric air-blown technologies were the state-of-the art for biomass gasification. Typically, the product gases were used for co-firing (without or after limited cleaning) or for the combined production of heat and power (CHP) with gas engines. The scale of gasifiers in semi-commercial plants was typically a few megawatts for CHP and several tens of megawatts for co-firing applications. The state-of-the-art gas cleaning for CHP applications generally comprised dust filtering or removal and wet scrubbers to remove tars and ammonia (NH_3). The quality of these ‘cleaned’ gases is insufficient to meet the specifications for FT synthesis and extensive additional work-up of the gases is required.

Based on the state-of-the-art of the key biomass gasification and gas cleaning technologies, the original scope of the project was resultantly narrowed to BG-FT systems based on atmospheric air-blown gasification with gas cleaning to meet CHP specifications. In the course of the project, important developments in biomass gasification and gas cleaning technologies were made and new insights were generated both within the project as in parallel (inter)national projects. This allowed the scope of the project to be widened and develop new concepts for integrated biomass gasification and Fischer-Tropsch synthesis systems. The process that has resulted in the development of these new system concepts is described in Chapter 3.

Within the scope, the overall objectives of the project were defined as:

1. Development of additional gas cleaning downstream an existing gasifier to meet the Fischer-Tropsch specifications, and
2. to demonstrate the suitability of the developed gas cleaning by using the cleaned gas in a downstream FT synthesis reactor to produce FT liquids from biomass (“***Product in a bottle***”).

1.3. This report

This reports describes the results of the development of gas cleaning options for integrated biomass gasification Fischer-Tropsch systems. The main results are discussed in the body of the report, while all detailed and specific results are included in appendices.

The chemistry of Fischer-Tropsch synthesis is briefly introduced in Chapter 2 and the specifications for FT feed gases are defined. In Chapter 3 the scope of the project is discussed in detail in perspective of the process to develop optimum BG-FT systems.

In the project two main approaches towards BG-FT systems are defined for which gas cleaning has been developed. In Chapter 4 the results for the system with high-temperature tar destruction are discussed, while in Chapter 5 the results of the system based on tar removal with the OLGA technology are discussed. The Fischer-Tropsch results of the integrated experiments are presented in Chapter 6. The conclusions of the project results are presented in Chapter 7.

Definitions

The following definitions are used throughout this report, or are included for reference, as they relate to the topic of this report:

Syngas	or synthesis gas, mainly containing H_2 and CO (and some N_2, CO_2), from fossil origin (*i.e.* coal or natural gas);
Product gas	Gas obtained by (low temperature) gasification of biomass containing H_2 and CO, as well as CO_2, CH_4, BTX, and other light hydrocarbons;
Biosyngas	Chemically similar to syngas, but produced from biomass directly by high temperature gasification, or by reforming or cracking of product gas;
Biogas	Gas produced by digestion of organic matter and consisting mainly of CH_4 and CO_2;
SNG	Substitute Natural Gas or “Green Gas”, mainly consisting of CH_4, produced by methanation of product gas or biosyngas, or alternatively by CO_2 removal from biogas;
Green diesel	high-quality ultra-clean diesel-like product produced with Fischer-Tropsch synthesis from biosyngas or product gas;
Bio-diesel	Liquid product from trans-esterfication of vegetable oils (*e.g*. rapeseed oil and sunflower oil).

2. FISCHER-TROPSCH SYNTHESIS

2.1. Introduction

The Fischer-Tropsch (FT) synthesis was discovered in 1923 by the German scientists F. Fischer and H. Tropsch at the Kaiser Wilhelm Institute for Coal Research in Mülheim, Germany. In the synthesis hydrocarbons are produced from syngas, *viz.* a mixture of the gases CO and H_2. Historically, Fischer-Tropsch processes have been operated on large industrial scale to produce synthetic fuels as alternative for non-available fossil fuels (*i.e.* in Germany in the 1930s and 1940s and in South Africa during the oil boycott). To date, the FT process receives much attention because the hydrocarbon products are "ultra-clean" due to the nature of the synthesis process, *i.e.* they are essentially free of sulphur or aromatics. In Thailand and Greece Shell GTL blended with fossil diesel is available to reduce local soot and SO_2 emissions.

2.2. Chemistry

2.2.1. Synthesis

In the catalytic FT synthesis one mole of CO reacts with two moles of H_2 to form mainly parafin straight-chain hydrocarbons (C_xH_{2x}) with minor amounts of branched and unsaturated hydrocarbons (*i.e.* 2-methyl paraffins and α-olefins), and primary alcohols. Typical operation conditions for FT synthesis are temperatures of 200-250°C and pressures between 25 and 60 bar [6]. In the exothermic FT reaction about 20% of the chemical energy is released as heat:

$$CO + 2H_2 \Rightarrow -(CH_2)- + H_2O \qquad (2.1)$$

2.2.2. Catalysts

Several types of catalysts can be used for the Fischer-Tropsch synthesis - the most important are based on iron (Fe) or cobalt (Co). Cobalt catalysts have the advantage of a higher conversion rate and a longer life (over five years). The Co catalysts are in general more reactive for hydrogenation and produce therefore less unsaturated hydrocarbons (olefins) and alcohols compared to iron catalysts. Iron catalysts have a higher tolerance for sulphur, are cheaper, and produce more olefin products and alcohols. The lifetime of the Fe catalysts is short and in commercial installations generally limited to eight weeks.

As follows from equation (2.1), the FT reaction consumes hydrogen and carbon monoxide in a molar ratio of $H_2/CO = 2$. When the ratio in the feed gas is lower, it can be adjusted with the water-gas shift (WGS) reaction (2.2):

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad (2.2)$$

Iron-based FT catalysts show considerable WGS activity and the H_2/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.

2.2.3. Product distribution

The polymerisation-like Fischer-Tropsch chain-growth reaction results in a range of products, comprising light hydrocarbons (C_1 and C_2), LPG (C_3-C_4), naphtha (C_5-C_{11}), diesel (C_{12}-C_{20}), and wax (>C_{20}) fractions. The theoretical chain length distribution can be described by means of the Anderson-Schulz-Flory (ASF) equation, which is represented as:

$$\log\frac{W_n}{n} = n \cdot \log\alpha + \log\frac{(1-\alpha)^2}{\alpha} \tag{2.3}$$

where W_n is the weight fraction of a product consisting of n carbon atoms and α the chain growth probability factor. Higher α values give more high molecular weight products as can be seen in Figure 2.1. The value of α is characteristic of the particular catalyst employed in the Fischer-Tropsch process and, depending on the needs of a particular production process, catalysts and process operation conditions can be tailored towards the production of predominantly low or higher molecular weight hydrocarbons.

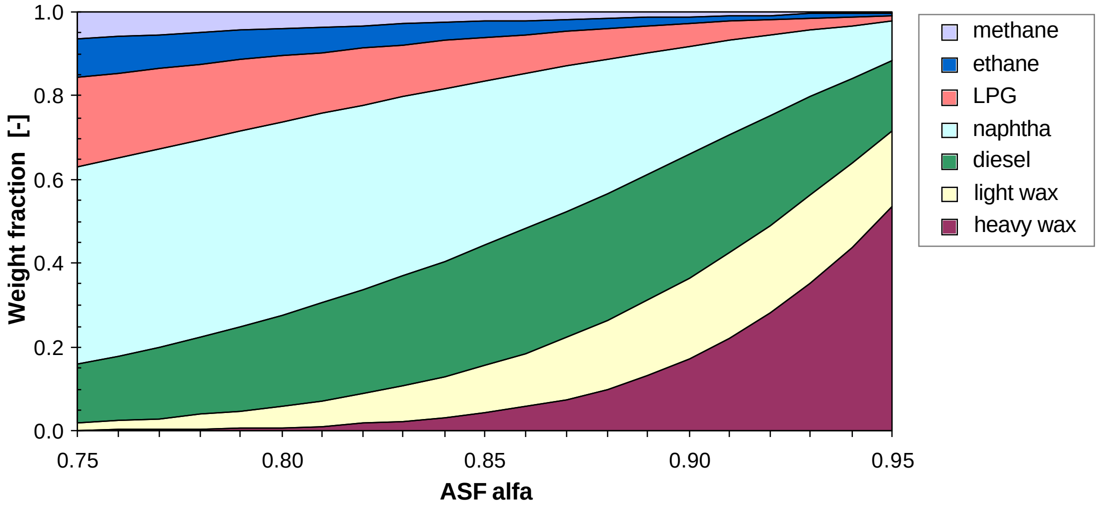

***Figure 2.1**. Theoretical Anderson-Schulz-Flory (ASF) product distribution for Fischer-Tropsch synthesis, with LPG (C_3-C_4), naphtha (C_5-C_{11}), diesel (C_{12}-C_{20}), light wax (C_{21}-C_{30}), and heavy wax (>C_{30}).*

In practice, there is often a deviation from the ideal ASF distribution especially with regards to the lower hydrocarbon yields. C_1 yields are usually higher than predicted, whereas C_2 (as well as C_3 and C_4) yields are lower. To incorporate the deviation from the ideal ASF distribution with regard to the yields of the C_1-C_4 hydrocarbon, as "rule-of-thumb" these values can be re-calculated according to equations (2.4) and (2.5).

$$W_1 = \frac{1}{2} \times \left(1 - \sum_{i=5}^{\infty} W_i\right) \tag{2.4}$$

$$W_{2,3,4} = \frac{1}{6} \times \left(1 - \sum_{i=5}^{\infty} W_i\right) \tag{2.5}$$

2.2.4. Green diesel yield

With respect to the production of green diesel, process conditions can be selected to produce maximum amounts of products in the diesel-range. However, the diesel yield is in that case limited to approximately 30 wt%, as can be seen in Figure 2.1. A much higher yield of diesel can be achieved when the FT synthesis is optimised towards production of wax. 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 via the WGS reaction (2.2).

The maximum amount of liquid products ("fuels") that can be produced from a (cleaned and properly conditioned) syngas is approximately 71% (overall syngas-to-fuel energy efficiency; $\eta_{G\text{-}t\text{-}F}$), as follows from:

Syngas conversion (η_{CO+H2})		FT products (η_{FT})		FT C_5+ products (η_{C5+})		hydrocracking to fuel (η_{hydro})		Gas-to-Fuel ($\eta_{G\text{-}t\text{-}F}$)
0.95	×	0.80	×	0.95	×	0.98	=	0.71

The syngas (η_{CO+H2}) conversion in the Fischer-Tropsch synthesis reactor is 95%. Only 80% of the energy in the gas is retained in the paraffin FT product (η_{FT}); the remainder is released as reaction heat. The selectivity of the FT process to C_5+ products (liquid and wax) is 95% (η_{C5+}), the other 5% are gaseous C_1-C_4 products. The heavier FT products can be selectively converted into fuels in the hydrocracking step with 98% efficiency (η_{hydro}). The energy contained in the FT off-gas (*i.e.* unconverted syngas and C_1-C_4 products) can be used to generate electricity.

2.3. Feed gas specifications

The catalysts used in FT synthesis are intrinsically very sensitive to small amounts of impurities. 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. Rule-of-thumb specifications are presented in Table 2.1 for known impurities and for impurities that might be present in biomass-derived gases [7,8].

***Table 2.1**. Fischer-Tropsch feed gas specifications.*

Impurity	Removal level
H_2S + 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[a] (tars)	below dew point
- class 2[b] (hetero atoms)	*< 1 ppmV*

[a] Organic compounds include also BTX. [b] Class 2 tars comprise phenol, pyridine, and thiophene.

A maximum value of less than 1 ppmV is defined for both the sum of the nitrogen-containing and sulphur-containing compounds. For the halides and alkaline metals a lower level of less than 10 ppbV is assumed. With respect to the organic constituents that are present in biomass product gases (*i.e.* tars and BTX), tars in general, there are no limits regarding poisoning of the catalyst. However, as the gas 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 fixed-bed reactors.

With respect to the other possible constituents (depending on the gasification concept) of the FT feed, *i.e.* CO_2, N_2, 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 (but the lower, the better). The presence of inerts requires larger reactors and higher total gas pressures. CO_2 can readily be removed with standard techniques, but 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.

2.4. Commercial processes

2.4.1. Fischer-Tropsch synthesis

Today, Fischer-Tropsch synthesis is an established technology [9,10,11] and two companies have already 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. Sasol uses iron catalysts and operates several types of reactors, of which the slurry bubble column reactor is the most versatile (*i.e.* applied in the Sasol Slurry Phase Distillate; SSPD). Shell operates the SMDS (Shell Middle Distillate Synthesis) process in Bintulu, Malaysia, which produces heavy waxes with a cobalt-based catalyst in multi-tubular fixed bed reactors. In 2003 Shell has started the engineering for a 75,000 bbpd SMDS plant in Qatar, while Sasol has a 30,000 bbpd cobalt-based SSPD plant under construction in Qatar.

2.4.2. Syngas cleaning

Syngas is a versatile building block in chemical industry. The total global annual use of fossil-derived syngas is approximately 5800 PJ_{th}, which corresponds to 2% of the total primary energy consumption. The largest part of the syngas is used for the synthesis of ammonia for fertiliser production (~55%), the second largest share is the amount of hydrogen from syngas consumed in oil refining processes (~24%), and smaller amounts are used for methanol production (12%). The two large Fischer-Tropsch processes mentioned annually consume 484 PJ_{th} of syngas, which corresponds to approximately 8% of the total amount [12,13,14].

Most syngas is produced by partial oxidation of natural gas (84%); the rest is produced by gasification of coal, while some additional small amounts are generated in refinery processes. The cleaning of the raw syngas from partial oxidation is a well-known and commercially available process (Figure 2.2) [15]. The general approach is to quench the raw hot gas with water to cool the gas and removed solid particles (*viz.* dust, soot, and ash) and the volatile alkaline metals. Upon syngas production, H_2S, NH_3, COS (and CS_2), and HCN are formed from sulphur and nitrogen in the fuel. The NH_3 is removed downstream together with the halides (*viz*. HCl, HBr, and HF) with a water washer and H_2S is removed either by absorption or after conversion to elementary sulphur (*i.e*. the Claus process) - the adsorption removal is preferred (cheaper) when relatively small amounts of H_2S are present. Similar is valid for the presence of COS and HCN. These impurities are hardly removed in the gas cleaning and are captured in the guard beds. When a syngas contains higher loads of these compounds it is economically more attractive to install a hydrolysis step to convert the compounds to H_2S and NH_3, respectively, that are readily removed in the gas cleaning. With this cleaning process the syngas specifications are met (*cf*. Table 2.1).

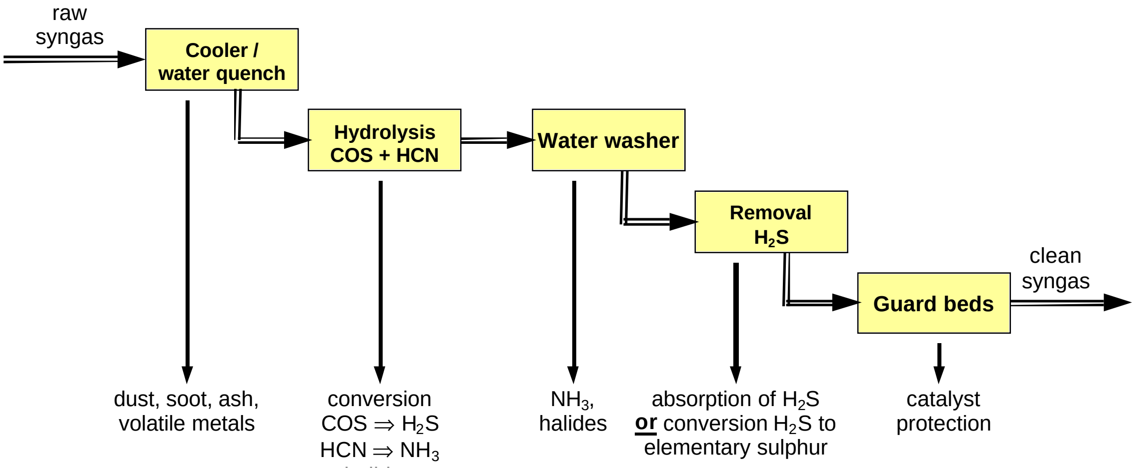

***Figure 2.2**. Schematic representation of general industrial approach towards cleaning of syngas from partial oxidation of natural gas based on commercially available technologies [15].*

3. SYSTEM DEVELOPMENT PROCESS

The boundaries of the original scope of the project were set by the state-of-the-art of the biomass gasification and gas cleaning technologies at time of writing of the project proposal (late 2000). In the course of the project new insights were generated and continuous progress was made in technology developments in biomass gasification and gas cleaning. In this chapter the process is described that resulted in the development of optimum integrated biomass gasification and Fischer-Tropsch systems.

3.1. Technology selection

3.1.1. Gasifier

The circulating fluidised bed (CFB) gasifier was identified as suitable type of biomass gasifier because of its flexibility with respect to feedstocks, high throughput, and the operational experience obtained in various commercial and demo projects. Of the most widely used CFB gasifier more than ten installations with a thermal input larger than 10 MW are currently in (semi) commercial operation. Furthermore, a variety of smaller CFB installations are in operation as research facility or have the status of pilot-plant. In nearly all cases the raw product gas of the commercial installations is used for firing of cement kilns or co-firing in coal power plants. All gasifiers use air as oxidising medium and most installations are operated at near atmospheric pressure (except for the Värnamo plant in Sweden, which operated at 16 bar). Therefore, as starting point for the project a product gas from an atmospheric air-blown CFB gasifier was used as reference - a typical composition is shown in Table 3.1 [7]. Additional motivation for using this type of gasifier was the availability of a 0.5 MW_{th} CFB gasifier “BIVKIN” at ECN that could be used for the project.[3]

The syngas components H_2 and CO are present in a ratio of 0.9 and make up only 34 vol% of the gas, 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 contained in CH_4, larger hydrocarbons, BTX, and the tars (present in 0.12 vol% or 7 g/m_n^3). “Tars” comprises a wide spectrum of organic components, which generally contain a high degree of aromatic rings. Tars are condensable organic compounds with boiling points between 80-350°C. When the temperature in the system decreases to below ~350°C tars start to condense resulting in fouling and ultimately in failure of the system. For understanding, tar components are organised in classes based on their chemical, condensation and solubility behaviour [16]. 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 product gas (after the cyclone).

3.1.2. Gas cleaning

Most applications of the CFB are found in co-firing and in most cases the work-up only comprises limited gas cooling and in some cases de-dusting with a cyclone, if any work-up is installed. For the application of the product gas in an engine for the combined production of heat and power (CHP) extensive gas cleaning is required. The major gas cleaning issue is the

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[3]. For information on the BIVKIN see: www.ecn.nl/biomassa/products/experiments/bivkin.

presence of 7 g/m_n^3 of tars in the gas. The state-of-the-art gas cleaning for CHP applications generally comprised de-dusting with cyclones, aqueous scrubbers to quench the gas and remove the remaining dust, NH_3, HCl and condense a large amount of the tars, and a wet electrostatic precipitator (ESP) to remove the tar aerosols and dust fines [17]. Typical removal efficiencies are: well above 99% for NH_3 (and HCl), approximately 60% for the tars, while H_2S and COS are not removed. The remaining concentration of NH_3 in the clean gas is about 10 ppmV. After the cleaning, the product gas is saturated with tars, *i.e.* the tar concentration is determined by the tar dew point at the given temperature. Typically, this temperature is 20-40°C, which results in tar concentrations of 1-3 g/m_n^3 (!!). Although, the tar load is still very high in the gas, it can be applied in a gas engine where the tars will be burned, if the gas temperature is maintained above the tar dew point.[4] Otherwise, tars start to condense resulting in fouling and contamination of the system.

***Table 3.1**. Typical product gas composition (dry basis, normalised) for gasification of wood (15% moisture) at 850°C in an atmospheric air-blown CFB gasifier [7].*

Main Constituents[a]	[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	[mg/m_n^3]
C_2H_4 (ethylene)	1.7	12.4	class 2 (hetero atoms)	350
C_2H_6 (ethane)	0.1	0.8	*- phenol*	*160*
benzene (BTX)	0.42	7.9	class 3 (1-ring, excl. BTX)	370
toluene (BTX)	0.07	1.6	class 4 (2,3-ring)	5300
xylenes (BTX)	0.04	1.0	*- naphthalene*	*2250*
sum of tars	0.12	2.8	class 5 (≥ 4-ring)	650
TOTAL	100	100	class 1 (unidentified)	330

[a]. 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.

3.1.3. Additional gas cleaning requirements

It is obvious that the ‘cleaned’ product gas of an atmospheric air-blown CFB does not meet the FT feed gas specifications defined in Section 2.3, especially with respect to the presence of the tars. To meet the 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).

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[4]. The tar dew point is an important parameter to determine if tar related problems, like fouling, could occur; the absolute amount of tars present in a gas is much less relevant. More information on tar dewpoints and a calculation tool can be found on: www.thersites.nl (site operated by ECN Biomass).

ZnO filters are considered suitable for removal of H_2S to meet the specification. Remaining traces of the inorganic impurities (*e.g*. NH_3, HCl, HCN, CS_2, and COS) can be removed with active carbon filters that are also applied as guard beds for the final protection of the catalyst. The presence of these two filters is 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 essentially all organic compounds upstream of the guard beds, in spite of the fact that this is not a requirement set by the Fischer-Tropsch synthesis specifications. Thus, the removal of BTX, and not the tars, should be the design criterion for the gas cleaning, as tars are readily removed under conditions for BTX removal.

Parallel to the underlying Fischer-Tropsch project, ECN Biomass developed the OLGA tar removal technology to solve the tar-related ‘problems’ in integrated biomass gasification CHP plants. This development was started as the lack of reliable and cost-effective technologies hampered the break-through and the wide implementation of biomass CHP plants. With the OLGA technology tars are removed very efficiently and even specification for FT synthesis can be met.

3.1.4. OLGA tar removal technology

The fundaments for the OLGA development were laid in 2001 with a first conceptual design, which was patented by ECN. In essence an OLGA unit comprises a scrubber to wash the tars from the gas and a stripper to regenerate the washing liquid (Figure 3.1). The characteristic features are the use of a special organic washing liquid (‘oil’) and the temperature operating range. The gas inlet temperature of OLGA has to be higher than the tar dew point (typically >300°C) to prevent tar fouling upstream the OLGA. The gas outlet temperature is kept above the water dew point to avoid mixing of condensed water and scrubbing liquid (loaded with tars) [18,19].

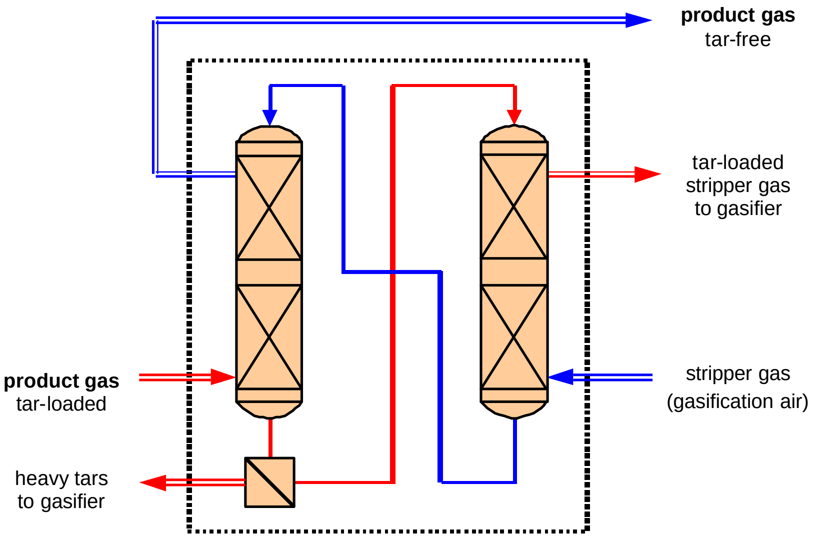
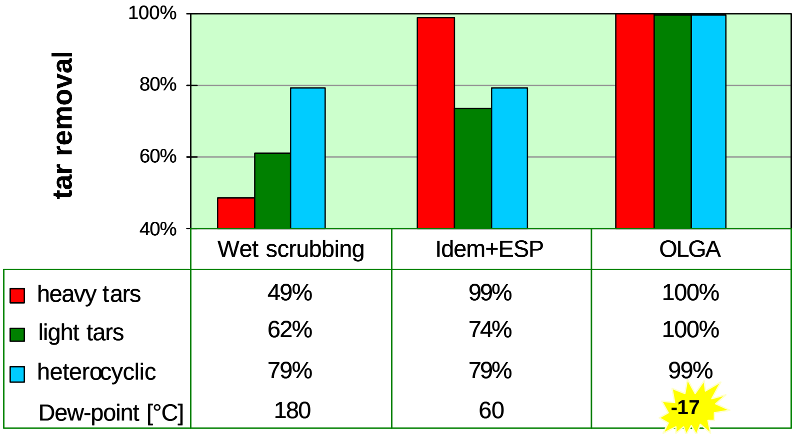


Figure 3.1. *Schematic process layout of an OLGA tar removal unit.*

The product gas is cleaned from tars in the OLGA scrubber after upstream cooling and solids removal. Heavy tars are separated from the washing oil, which is further regenerated in the stripper. Both the heavy tars and the stripper gas loaded with tars are recycled to the gasifier where the tars are destructed. By this integrated approach, there are no tar waste streams that need treatment.

In Figure 3.2 the typical performance of the OLGA technology is compared to the state-of-the-art wet scrubbing techniques. In these experiments the OLGA was designed and operated optimally for CHP application (*i.e.* to remove 99% of the phenol), whereas most of the BTX was allowed to remain in the gas, as this enhances the stability and efficiency of the gas engine. Due the tar dew point well below -10°C, a CHP plant can be operated safely without the risk of tar fouling.



	Wet scrubbing	Idem+ESP	OLGA
🟥 heavy tars	49%	99%	100%
🟩 light tars	62%	74%	100%
🟦 heterocyclic	79%	79%	99%
Dew-point [°C]	180	60	-17

***Figure 3.2**. Typical performance of the OLGA technology compared to state-of-the-art wet scrubbing gas cleaning techniques, with and without an ESP. Data for atmospheric air-blown gasification of wood; tar concentrations in raw product gas were approx. 8-10 g/m_n^3.*

The OLGA performance can be enhanced to also remove BTX to meet Fischer-Tropsch process specifications. Due to the availability of the OLGA technology the tar and BTX removal issue in the gas cleaning was overcome.

3.2. System definition

3.2.1. Trigeneration

Initially, the projected scale of BG-FT plants was determined by the scale of the CFB gasifier sthat were in operation, *i.e.* typically in the range of 10-100 MW_{th}. Furthermore, the principle idea was that *“trigeneration”* is the most economic and hence the most attractive configuration for these scales [20]. In a tri-generation system the cleaned product gas is used for Fischer-Tropsch synthesis, with the off-gas being used to generate electricity and heat in a combined cycle (CC); see Figure 3.3.

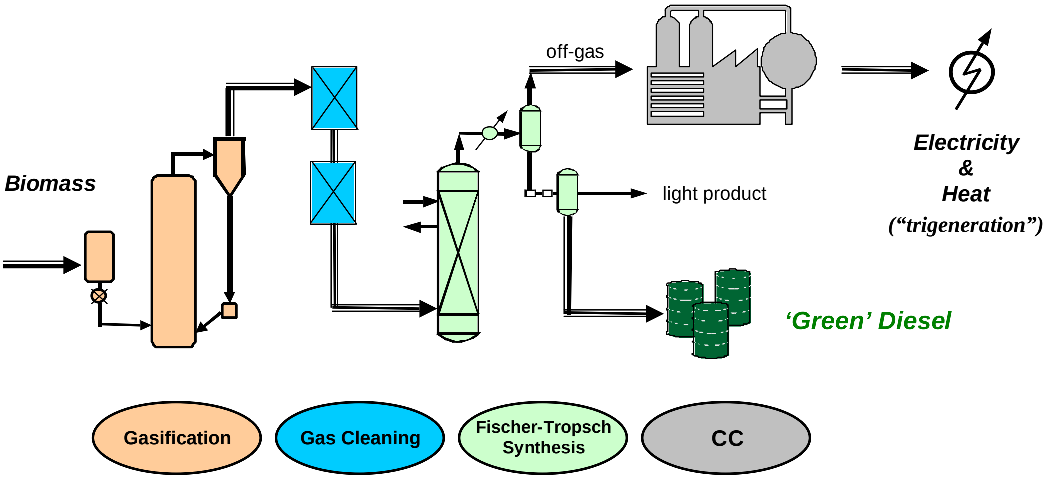


***Figure 3.3**. Co-production of green diesel, electricity and heat ("trigeneration").*

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 N_2 which is present in about 40 vol% in the product gas,[5] but also CO_2, CH_4, and gaseous FT products (C_1-C_4);
- no CO_2 removal (present in 16 vol%) prior to FT synthesis to reduce units and costs; CO_2 removal is not essential if the FT off-gas is not recycled.

The disadvantage of this approach is that the potential yield of FT products is limited due to the fact that H_2 and CO only represent less than one half of the energy content of the product gas. In Figure 3.4 an indicative energy balance is shown for a Trigeneration system. It is assumed that the H_2/CO ratio is adjusted by water-gas-shift to the consumption ratio (H_2/CO= 2) prior to FT synthesis. Furthermore, a FT selectivity is assumed of 90% (no recycle) to C_5+ wax and liquid products versus 10% gaseous C_1-C_4 products, and a combined cycle (CC) with 50% electric efficiency.

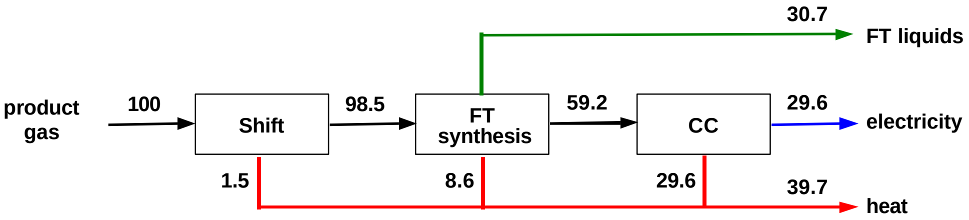


***Figure 3.4**. Indicative energy balance for tri-generation with shift to ratio of H_2/CO = 2, starting with product gas as in Table 3.1.*

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[5]. To produce a nitrogen-free product gas an indirect gasifier is also an option. However, as still no recycle can be incorporated due to the presence of other inerts (*i.e.* CO_2 and hydrocarbons) the basic design of the concept will not change.

The energy efficiency of FT (C_5+) liquids production is 30.7%; almost an equal amount of electricity is produced. The yield of FT liquids can only be increased when the CH_4 and C_2-hydrocarbons are converted into syngas to allow their energy content to be used for FT synthesis.

3.2.2. Maximum Green Diesel production

The "trigeneration" approach was developed from an essentially technical point of view. However, the thinking about BG-FT systems changed dramatically due to new insights in the economics of Fischer-Tropsch installations and the definition of targets by the EU for alternative fuel substitution. To reach these ambitious targets, large amounts of alternative renewable fuels have to be produced and large production facilities are 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); see next section. This implies large-scale FT plants (of more than 1000 MW_{th}) that are dedicated to the production of FT liquids (*viz.* no trigeneration). 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 off-gas and from steam generated by cooling of the hot product gas. Alternatively, heat can be produced to generate process steam;
- the yield of syngas (*i.e.* the sum of the H_2 and CO content) in the FT feed gas must be as high as possible.

These requirements have a major impact on the demands for suitable gasification and gas cleaning technologies. 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% [21]. 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 (see below). Furthermore, the system will also contain a CO_2 removal step as part of the gas conditioning to meet the inert specification.

Secondly, when a maximum yield of FT products is aimed for, all the energy contained in compounds other than H_2 and CO is not available for the FT synthesis. Ideally, all CH_4 (24% of the energy), C_2H_4 (12%), and BTX (11%) should be converted into H_2 and CO. Considering both the demands for high CO+H_2 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 destructed to yield a *syngas* mainly containing H_2 and CO. Alternatively, a catalytic reformer might be used, however, a separate removal step (*i.e.* OLGA) is then still required.

In Figure 3.5 an indicative energy balance for a system with a higher-temperature thermal tar cracker is shown. For the oxygen-blown tar cracker and the shift (to $H_2/CO = 2$) 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).

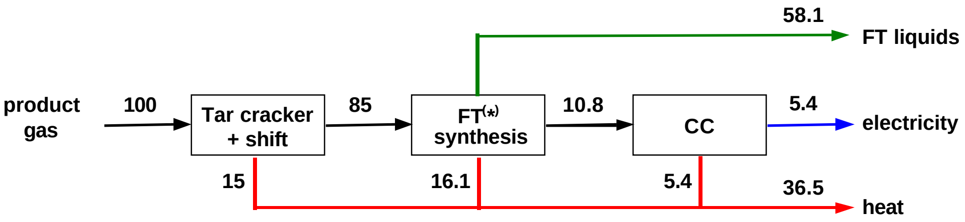

***Figure 3.5**. Indicative energy balance for maximum FT production. FT(*) refers to FT synthesis including recycle (for product gas from a CFB with a tar cracker).*

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 trigeneration case, about 10%-points of the heat is high temperature (>1000°C) heat from the tar cracker and may be used to produce an additional 3 to 4%-points of electricity or steam for the air separation unit (ASU).

3.2.3. Entrained flow gasification

In the previous section it was concluded that for maximum FT liquids production a high-temperature tar cracker is required downstream the CFB gasifier to convert all hydrocarbons in the product gas into H_2 and CO, *i.e. to convert the product gas into a real syngas*. To produce a syngas, alternatively, the biomass may be directly gasified at a high temperature instead of the staged approach with a low-temperature (~900°C) CFB gasifier and a high-temperature tar cracker (~1300°C). At these temperatures (~1300°C), fluidised bed gasifiers cannot be used. Therefore, an entrained flow (EF) gasifier has to be applied. EF gasification is a well-established technology for coal and heavy oil residues, however, no examples exist of EF gasification of pure biomass.

However, the potential of entrained flow gasification for biosyngas production gave ground for further and detailed investigation. In 2003 a parallel study on this topic was carried out by ECN and Shell. The results of this study are reported in references 22 and 23.

3.3. Large-scale production systems

In the previous section it was stated that maximum Fischer-Tropsch fuel production is required to produce the green diesel cost effectively. This was the conclusion from 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 [21]. In this study, a production of 8,000 MW of cleaned and conditioned biosyngas was assumed, as the resulting amount of green diesel produced is approximately equivalent with the current Dutch fossil diesel consumption (~240 PJ). Biomass is imported, as in the Netherlands insufficient biomass is available within a range that allows cost effective truck transport. Resultantly, 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. In Figure 3.6 the line-up of the overall production system is shown.

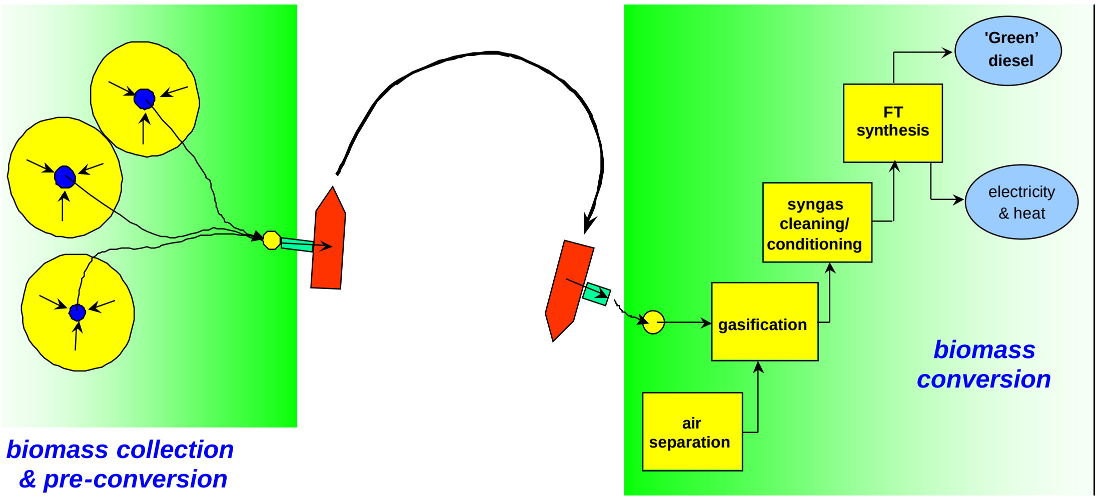

***Figure 3.6**. Overall line-up of production system for large-scale biosyngas and Fischer-Tropsch synthesis from imported biomass.*

In the system, biomass is collected in forestry areas in the Baltic republics and delivered as logs to the biomass collection facility (bcf). At the bcf gate a biomass price of 4 €/GJ was assumed; this price is realistic for the future large-scale biomass market. After intermediate storage the logs are transported by truck to the harbour (hub), shipped to Rotterdam, transhipped, and gasified after pre-treatment (chipping and drying) to produce 8,000 MW of biosyngas for Fischer-Tropsch synthesis. Both the syngas production with an oxygen-blown CFB gasifier and a downstream high temperature tar cracker and with an oxygen-blown entrained-flow gasifier were considered.

In Figure 3.7 the cumulative cost build-up for biosyngas production is shown for three overall system biomass-to-fuel efficiencies. From the figure can be seen that the biomass price already makes up approximately 50% of the biosyngas price. The impact of overall biomass-to-biosyngas efficiency is evident: the lower the efficiency, the more (expensive) biomass is required to produce the targeted 8,000 MW of biosyngas. Furthermore, the cost of transport, transhipment, and pre-treatment increase correspondingly. For the efficiency range of 55-70-85% (*i.e.* pessimistic, realistic, and optimistic), the biosyngas production price ranges from 8.6 to 13.1 €/GJ. If cheaper biomass can be obtained the biosyngas price may decease to 7.1 or even 5.3 €/GJ (based on biomass prices of 2 and 0.5 €/GJ, respectively) [21]. The results were similar for the system based on entrained-flow gasification of pulverised biomass, within the uncertainty ranges of the study.

3.4. System requirements

In this chapter the new insights and continuous technology developments in the field of biomass gasification and biosyngas production have been discussed. With respect to the original scope of the project, these insights and developments resulted in additional requirements for BG-FT systems:

- To replace a significant part of the fossil diesel by its green equivalent, a large production capacity is required.
- The biomass costs are the determinant parameter in the green diesel production cost. Therefore, a high biomass-to-fuel efficiency is required.

- To achieve high FT liquid yields, all the chemical energy in the gasification gas should be present in the syngas components H_2 and CO. The gasifier must produce a biosyngas instead of a product gas.
- Similarly, the off-gas from the FT synthesis reactor must be recycled to achieve maximum H_2 and CO conversion. Therefore, an oxygen-blown gasifier must be used and the gas conditioning has to comprise CO_2 removal, as only limited amounts of inert are allowed in the syngas.
- Although, since the development of the OLGA tar removal technology a trigeneration system is technical feasible with respect to the gas cleaning, trigeneration is undesirable due to the limited yield of FT liquid.

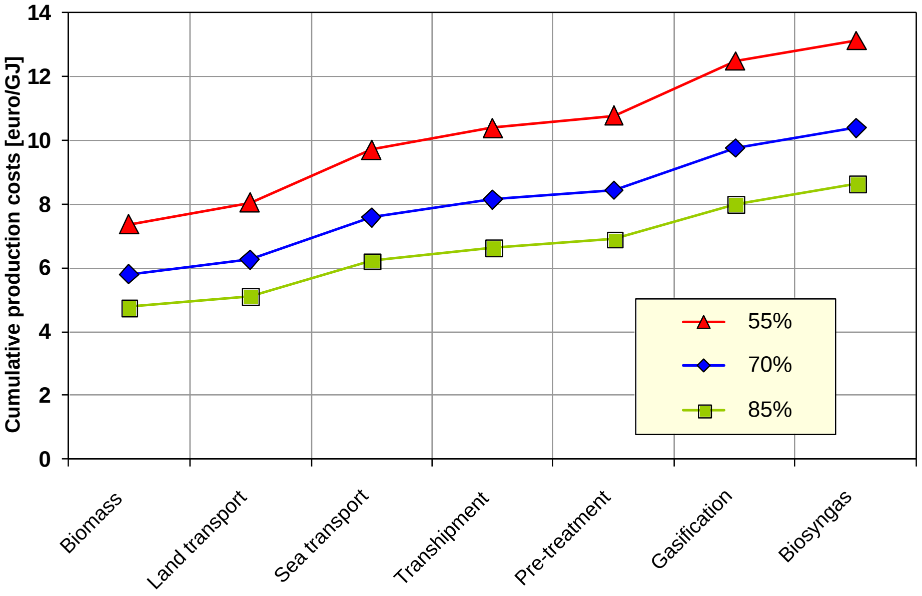

***Figure 3.7**. Cumulative biosyngas production costs as function of the overall biomass-to-biosyngas efficiency. Based on system with pressurized (20 bar) oxygen-blown CFB gasifier with tar cracker. Biomass price is 4 €/GJ at bcf.*

3.5. Developed systems

Considering the system requirements defined in the previous section, in the ECN concepts large integrated and centralised plants are assumed to benefit optimally from energy integration options and additionally from the economy-of-scale of FT synthesis and product upgrading. Furthermore, the developments focus on production of a clean and conditioned *biosyngas.* Product gas is only considered as an intermediate product. Additionally, the required syngas H_2/CO ratio was set equal to the FT consumption ratio (*i.e.* $H_2/CO = 2$) and the required pressure was set to 40 bar [24].

Three systems concepts were defined suitable for the biosyngas production (discussed in the next sections):

1. CFB gasification plus tar cracker;
2. EF gasification of pre-treated biomass;
3. CFB gasification, OLGA tar removal, plus reformer.

3.5.1. 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 at 1300°C all the tars, BTX and the hydrocarbons are cracked and converted into mainly H_2 and CO. The biosyngas is cleaned with standard techniques as used for fossil syngas (*cf.* Section 2.4.2): dust filters, wet-scrubbing techniques (for NH_3 and HCl), and ZnO filters for H_2S. After conditioning (H_2/CO adjustment and CO_2 removal) the gas is compressed to the FT synthesis pressure (40 bar). The concept is schematically depicted in Figure 3.8.

***Figure 3.8**. Concept with CFB gasifier plus tar cracker.*

3.5.2. EF gasification of pre-treated biomass

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 3.9. Downstream the gasifier the cleaning and conditioning is similar to the previous concept (except that additional compression is not required). However, upstream pre-treatment of the biomass is required, as smaller particles (100 µm to 1 mm) are required to allow stable feeding and to ensure complete conversion in the EF gasifier due to the short residence times. The biomass chips (~5 cm), which are normally used to feed a CFB gasifier, need to be pulverised, either directly or after a mild thermal pre-treatment (*viz.* torrefaction) [22].

***Figure 3.9**. Concept with EF gasification of pre-treated biomass.*

3.5.3. CFB gasifier, OLGA, plus reformer

In the third concept another approach towards tar removal and hydrocarbon conversion is followed (Figure 3.10). Downstream the gasifier, the tars (and BTX) are removed with the OLGA tar removal technology and subsequently returned to the gasifier ("recirculation to extinction'). Hydrocarbons are not removed with OLGA, therefore, after the wet cleaning these compounds are converted in a catalytic reformer. The disadvantage of this step is the required temperature 'swing' from ambient temperature downstream the gas cleaning, to ~800°C in the reformer, and subsequent to ~200°C for FT synthesis. The conditioning and compression is similar as in the first concept.

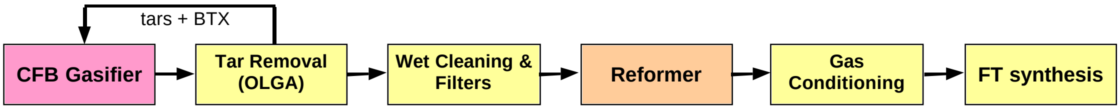

***Figure 3.10**.Concept with CFB gasifier, OLGA tar removal, plus reformer.*

3.6. Specified objective

Considering the discussion in this chapter, the specific objective of the project has converged to be:

Delivering the Proof-of-Principle of integrated systems of biomass gasification, gas cleaning, and Fischer-Tropsch synthesis of both CFB concepts (with tar cracker and OLGA) to demonstrate the suitability of the gas cleaning to meet Fischer-Tropsch specifications.

The gas conditioning (water-gas-shift and CO_2 removal) was not included in the systems as gas conditioning of clean gas is conventional technology. Similarly, catalytic reforming of biomass product gas was not included in the study.

Research on the entrained flow system was not carried out as the critical issues for this concept relate to the feeding and gasification and not to the gas cleaning. The issues related to entrained flow gasification of biomass were addressed in a parallel project (reported in reference 22).

4. CFB GASIFIER PLUS TAR CRACKER

A system based on an oxygen-blown circulating fluidised bed (CFB) gasifier with a downstream oxygen-blown tar cracker at 1300°C is suitable to produce a nitrogen-free biosyngas. In this chapter, results are described of integrated biomass gasification, gascleaning, and lab-scale Fischer-Tropsch synthesis experiments to demonstrate this system.

4.1. System line-up

The line-up of the lab-scale most representative for the system to be demonstrated is shown in Figure 4.1. In this system, biomass is gasified in the ECN atmospheric bubbling fluidised bed gasifier “WOB” (Dutch acronym for Fluidised Bed Installation for Biomass) [25].[6] Oxygen is used as gasifying medium to produce an essentially nitrogen-free product gas, while steam is added to moderate the temperature in the bed of the gasifier. The product gas of approx. 850°C is fed to a high-temperature tar cracker where the temperature is raised to 1300°C by the addition of oxygen and combustion of part of the gas. Ideally, al the tars, BTX, CH_4, and C_2-hydrocarbons are destructed and converted into syngas components. The tar cracker is externally heated to compensate for the relatively high heat losses in this lab-scale set-up. The gas leaving the tar cracker is cooled, and dust, soot, and ash are removed in a high temperature ceramic gas filter operated at 400°C. The gas is further cooled and cleaned from NH_3, HCl, and other inorganic impurities in a water scrubber at room temperature.

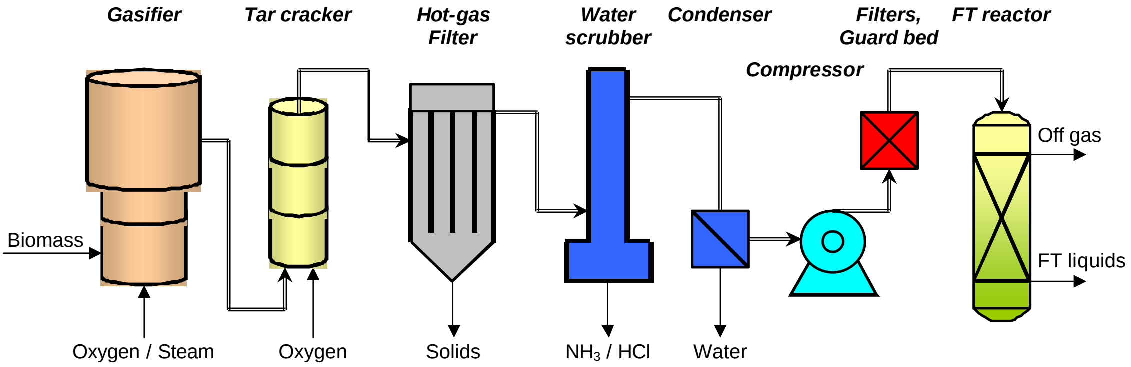

***Figure 4.1**. System line-up of integrated biomass gasification Fischer-Tropsch synthesis system based on oxygen-blown fluidised bed gasification and tar cracker. See text for detailed description of the system.*

Water is condensed from the clean gas and subsequently the gas is compressed to the desired pressure in a two-stage compressor with intercooler. The compressed gases are passed through a ZnO filter to remove the H_2S and for final polishing through an active-carbon guard bed to remove all remaining trace impurities. Typically, the product gases are compressed up to 60 bar. The compressed gas is stored in gas cylinders to provide a buffer for the Fischer-Tropsch

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[6]. For information on the WOB see: www.ecn.nl/biomassa/products/experiments/wob.

experiments; with gas buffering capacity of 300 L available at ECN this is equivalent to 18,000 L_n^3 of product gas.

In the experiments, however, it appeared that thermal tar cracking is less efficient than expected. The light tar fraction disappeared to a significant extent, the heavy fraction diminished substantially, but the intermediate fraction grew considerably. After two seconds residence time at 1400°C the total tar content still amounted to 35% of the original value. Gaseous hydrocarbons were broken down effectively at 1300°C to 1400°C, although CH_4 requires several seconds residence time because of its relatively high stability. The addition of O_2 seems to reduce the stability of CH_4 and C_2H_4 significantly, but high H_2O and CO_2 concentrations may be relevant too. Breakdown of tar and gaseous hydrocarbons produces a lot of soot. The formation of soot could be suppressed by the addition of steam and O_2, which resulted in higher H_2O and CO_2 concentrations in the gas. Additional experiments are required to determine optimum conditions that reduce soot and promote cracking of intermediate tar compounds.

Considering that fact that the tar destruction was insufficient to meet the FT feed gas specifications and excessive soot formation resulted in clogging of the downstream gas filter, it was decided to use a 'derived' system for the integrated test including the ECN staged gasification installation "Pyromaat".[7] The Pyromaat consists of an externally heated low-temperature (pyrolysis) reactor and a high-temperature tar cracker. In this line-up the tar cracker performance was sufficient due to higher temperature, longer residence times, and lesser soot formation that could be established. The process line-up of the complete system is shown in Figure 4.2. In the low-temperature reactor 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°C) the tars in the gas are destructed.

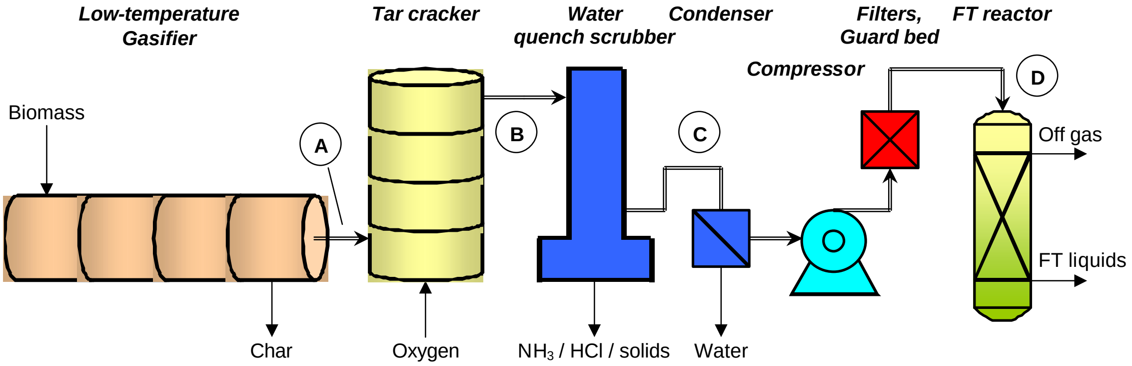

***Figure 4.2**. System line-up of integrated biomass gasification Fischer-Tropsch synthesis system used to mimic a system based on oxygen-blown fluidised bed gasification and tar cracker. See text for detailed description of the system.*

The tar-free biosyngas is quenched to cool the gas and scrubbed with water in the aqueous scrubber to remove the inorganic impurities (mainly NH_3 and HCl) and all the solids. In the tar cracker significant amounts of soot were formed but the soot was removed in the scrubber

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[7] . For information on the Pyromaat see: www.ecn.nl/_files/bio/leaflets%20en/B-00-018.pdf.

without operational problems. The system downstream of the water scrubber is similar as in the set-up described above.

4.2. Experimental results

4.2.1. Gasification

Willow (dried to 8% moisture) obtained from a Dutch energy farm was used as biomass feed material [26]. A feed flow of 3 kg/h was applied, while a small flow of argon was used for inertisation. The pyrolysis gas consists for approximately 75% of tars and moisture and in addition contains large concentrations of CH_4, C2-hydrocarbons, and BTX (Table 4.1). In the tar cracker all tars, and almost all CH_4 are converted into syngas components. Under these conditions, approximately 8 m_n^3/h of wet raw biosyngas is produced.

***Table 4.1**. Measured gas compositions (dry basis) during 150 hours integrated test with system of pyrolysis, methane-fired tar cracker, water scrubber, compression, gas polishing, and FT synthesis. See Figure 4.2 for line-up and gas analysis location.*

Gas		**Pyrolysis gas[a]**	**Cracker gas**	**Scrubber gas**	**FT feed gas**
Analysis location		**A**	**B**	**C**	**D**
Temperature	[°C]	550	485	60	20
Pressure	[bar]	1	1	1	40
Moisture	[vol%, wet gas]	.[a]	42.4	5.2	0.05
CO	[vol%]	12.5	25.7	26.8	27.0
H_2	[vol%]	6.3	28.9	30.3	29.4
CO_2	[vol%]	13.1	31.1	31.1	28.8
N_2	[vol%]	0.72	0.36	0.62	1.08
Ar	[vol%]	56.6	12.0	11.1	13.6
CH_4	[vol%]	6.42	0.01	0.01	0.01
C_2H_4	[ppmV]	5936	< 5[c]	< 5[c]	< 5[c]
C_2H_6	[ppmV]	7359	< 5[c]	< 5[c]	< 5[c]
benzene	[ppmV]	736	< 5[c]	< 5[c]	< 5[c]
toluene	[ppmV]	530	< 5[c]	< 5[c]	< 5[c]
SPA tars[b]	[ppmV]	.[a]	< 10[c]	< 10[c]	< 10[c]
NH_3	[ppmV]	~	516	1.1	0.02
HCl	[ppmV]	~	49	2.1	< 0.3[c]
H_2S	[ppbV]	~	23789	19985	< 10[c]
COS	[ppbV]	~	47578	39970	278
CS_2	[ppbV]	~	207	< 10[c]	< 10[c]
TOTAL	[vol%]	100.0	100.0	100.0	100.0

[a]. Composition on dry and tar-free basis; fraction of tars + moisture corresponds to approx. 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.

4.2.2. Gas cleaning

The biosyngas from the tar cracker is free of tars, BTX, C_2-hydrocarbons, while only a negligible amount of CH_4 is present in the gas (Table 4.1). The remaining impurities in the gas are the inorganic compounds. Compared to low temperature gasification (*i.e.* product gas composition in Table 5.1), the NH_3 concentration in the cracker gas is relatively low, while the COS is present in a very high concentration; typically in fluidised bed gasification only a few percent of the sulphur is present as COS and the major part as H_2S. Due to the high-temperature approximately 50% of the NH_3 is destructed and converted into N_2, while due to the additional presence of a large concentration of CO_2 a significant part of the H_2S reacts to COS.

In the water scrubber >99% of the NH_3 and most of the HCl are removed. As the lab-scale experimental set-up was not designed and optimised to meet FT specification the remaining concentrations are slightly above the limits. However, after the active carbon guard bed filters the specifications are met.

H_2S and COS are removed only for a small part in the scrubber due to the poor water solubility of these compounds. After compression, H_2S is completely removed by the ZnO filters (below 10 ppbV). COS is removed for ~99% in the active carbon guard bed to an acceptable level of ~300 ppbV, while the small amount of CS_2 is removed completely. The successful FT synthesis test performed with this gas (see below), clearly proves the validity of the defined COS specifications (*cf.* Table 2.1). Although the COS removal is sufficient to meet the FT specifications, considering the COS load of the gas, probably a COS hydrolysis step would be included in the gas cleaning of a commercial installation (*cf.* Section 2.4.2).

4.2.3. Fischer-Tropsch synthesis

For Fischer-Tropsch synthesis a small micro-flow unit with an isothermal fixed-bed reactor was used with a proprietary Shell cobalt-based catalyst. Downstream the FT reactor, the product stream was separated into wax, liquid products, water, and off-gas. Reactor performance and catalyst activity and selectivity were monitored via the gas consumption rate, the off-gas composition, and the yield of wax and liquids. Detailed description of the FT set-up is given in Section 6.1.

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 integrated 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 [7,8]. 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. The results of the integrated FT experiments are discussed in Chapter 6, including more details on synthesis conditions and product characteristics.

4.3. Discussion

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. When product or pyrolysis gas from low-temperature gasification is cracked at a high temperature all organic compounds are destructed and converted into mainly syngas. 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 impurities that require a total different gas cleaning approach.

Upon high-temperature tar cracking of product or pyrolysis gas significant amounts of soot are formed. This soot is a gas cleaning issue as large amounts of solid material needs to be removed, but also represents a significant loss of efficiency (*i.e.* the energy content of the soot carbon). Further development of the BG-FT system based on oxygen-blown gasification and tar cracking should focus on optimisation of the tar cracker.

5. CFB GASIFIER PLUS OLGA TAR REMOVAL

In the previous chapter was discussed that a system based on an oxygen-blown circulating fluidised bed (CFB) gasifier with a down-stream oxygen-blown tar cracker at 1300°C is suitable to produce a nitrogen-free *biosyngas*. In this chapter results are described of the system in which the tars are physically removed from the product gas using the OLGA technology and where the product gas after cleaning from the inorganic impurities, is used for Fischer-Tropsch synthesis. This gas cleaning approach is followed in a system with a catalytic reformer; the reforming step was not included in the experimental study, as this reforming is a commercial technology (*cf.* project objective in Section 3.6).

5.1. System line-up

The line-up of the integrated biomass gasification Fischer-Tropsch synthesis system is shown in Figure 5.1. Biomass is gasified in the ECN lab-scale atmospheric bubbling fluidised bed gasifier “WOB”. Oxygen is used as gasifying medium to produce an essentially nitrogen-free product gas and steam or CO_2 is added to moderate the temperature in the bed of the gasifier. The gasifier is typically operated at 830-900°C. The raw product gas passes a high-temperature gas filter (ceramic candle) operated at 350°C to remove essentially all the solids.

The lab-scale OLGA unit is operated to remove all the tars and a maximum amount of the BTX. The OLGA applies a special organic washing liquid with a high affinity for the tars [18,19]. The gas leaving OLGA at a temperature of 60-100°C (determined by the water dewpoint of the gas) is further cooled and cleaned from NH_3, HCl, and other inorganic impurities in a water scrubber at room temperature. Both the OLGA and the water scrubber are equipped with a stripper to regenerate the washing oil and water, respectively. In the lab-scale line-up these stripper gases are flared, whereas in full-scale installations the stripper tars and NH_3 would be recycled to the gasifier. 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.

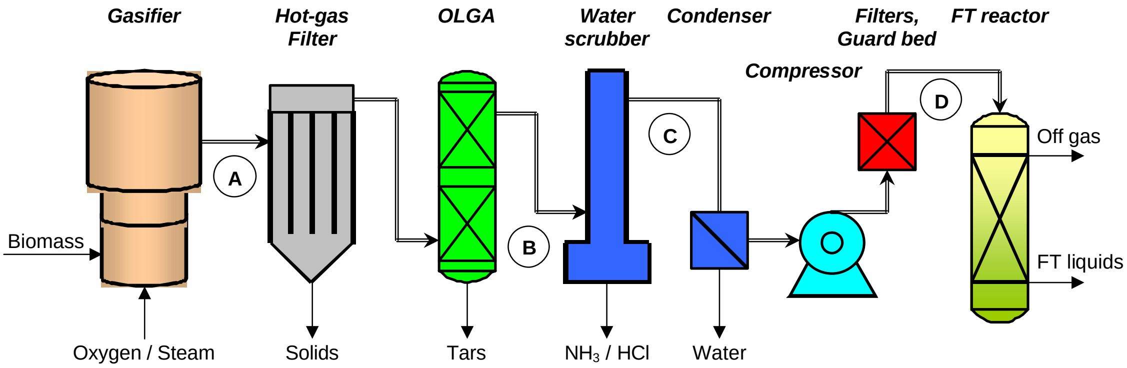

***Figure 5.1**. Simplified system line-up of integrated biomass gasification Fischer-Tropsch synthesis system based on oxygen-blown fluidised bed gasification and OLGA tar removal. Locations of gas analysis are indicated. See text for detailed description of the system.*

5.2. Experimental results

5.2.1. Gasification

Beech was used as biomass feed material [26]. Several gasification tests have been carried with oxygen/steam and oxygen/CO_2 mixtures to determined a minimum amount steam or CO_2 at which the gasifier could still be operated stably without temperature peaks while maintaining sufficient fluidisation velocity. 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). At a gasification temperature of 850°C, approximately 1.3 m_n^3 of wet product gas was produced with a feed rate of 1.2 kg/h of beech. The product gas contained approximately 23 g/m_n^3 of tars, almost 1.5 vol% of BTX, and more than 10 vol% of CH_4 and C_2-hydrocarbons (Table 5.1).

Table 5.1. *Measured gas compositions (normalised, dry basis) during 500 hours integrated test with system of oxygen/steam gasification in WOB, OLGA tar removal, water scrubber, compression and gas polishing, and FT synthesis. See Figure 5.1 for line-up and gas analysis locations.*

Gas		***Product gas***	***OLGA gas***	***Scrubber gas***	***Clean gas***
Analysis location		***A***	***B***	***C***	***D***
Temperature	[°C]	850	60-100	20	20
Pressure	[bar]	1	1	1	40
Moisture	[vol%, wet gas]				0.05
CO	[vol%]	28.0	28.1	28.2	30.0
H_2	[vol%]	23.0	22.0	21.9	22.8
CO_2	[vol%]	28.2	29.6	29.6	26.7
N_2	[vol%]	2.24	2.11	2.16	2.47
Ar	[vol%]	4.82	4.86	5.01	5.17
CH_4	[vol%]	9.11	9.06	9.05	9.42
C_2H_4	[vol%]	3.08	3.21	3.21	3.00
C_2H_6	[vol%]	0.25	0.25	0.21	0.25
C_2H_2	[vol%]	0.16	0.17	0.17	0.15
benzene	[ppmV]	6813	5018	4507	101
toluene	[ppmV]	710	377	282	19
SPA tars[a]	[ppmV]	4114	< 10[b]	< 10[b]	< 10[b]
NH_3	[ppmV]	~	1304	8.5	0.06
HCN	[ppmV]	~	~	~	< 6[b]
HCl	[ppmV]	~	0.67	< 0.3[b]	< 0.3[b]
H_2S	[ppbV]	~	~	116496	< 10[b]
COS	[ppbV]	~	~	4030	50
CS_2	[ppbV]	~	~	940	30
TOTAL	[vol%]	100.0	100.0	100.0	100.0

[a]. Concentration of tars measured by solid phase adsorption (SPA). [b]. Actual concentrations were below detection limit. The reported values are estimated maximum values.

5.2.2. Gas cleaning

Solids are removed from the raw product gas by the hot gas filter. In the downstream OLGA unit essentially all the tars were removed from the product gas, while benzene and toluene were removed for approx. 25 and 50%, respectively. Removal of the inorganic impurities from the tar-free gas was similar to the cleaning of the biosyngas (*cf*. Section 4.2.2). In the water scrubber most of the NH_3 and HCl was removed; in the scrubber also an additional 10 and 25% was removed of the benzene and toluene, respectively. Typically, this benzene and toluene is stripped together with the NH_3 from the water in the stripper and recycled to the gasifier. After the active-carbon guard bed the dew point specification for these organic compounds is easily met. In a larger installation the OLGA unit will bed designed to remove BTX to lower levels to meet the FT feed specifications directly and decreased the BTX loading of the filters.

Due to the lower gasification temperature compared to the system with a tar cracker, most of the sulphur is present as H_2S with only a few percent COS. H_2S is removed by the ZnO filters and removal of COS (and CS_2) was established by the active-carbon guard beds.

As additional protection of the FT catalyst in the integrated test, an “oxygen-trap” was installed immediately upstream of the FT reactor to capture possible trace concentrations of oxygen present in the gas from the gasifier.[8] As the material applied exhibited hydrogenation activity, the unsaturated compounds ethylene and acetylene reacted with hydrogen to ethane, *e.g*. for ethylene shown by reaction (5.1). Under the conditions applied almost 90% of the ethylene was converted into ethane, whereas all acetylene was converted.

$$C_2H_4 + H_2 \quad \Rightarrow \quad C_2H_6 \tag{5.1}$$

5.2.3. Fischer-Tropsch synthesis

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 smaller amount of ethylene (after the partial hydrogenation). The hydrogenation reactions in the oxygen-trap consumed hydrogen resulting in an even lower effective H_2/CO ratio of 0.65 in the FT feed gas. Therefore, additional hydrogen was added to the FT feed gas to compensate for the consumed hydrogen and re-establish the H_2/CO ratio of 0.76 in the FT feed gas.

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 of the FT products was confirmed by carbon-14 dating of the product samples. The results of the integrated FT experiments are discussed in Chapter 6, including more details on synthesis conditions and product characteristics.

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[8]. The material used was an ICI Cu-Zn based low-temperature shift (LTS) catalyst operated at 60°C.

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). Considering the low concentration of ethylene in the feed gas of this experiment, the impact on the results will not be very significant.

5.3. Discussion

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. After removal of tars and other organic compounds from the product gas with the OLGA technology, 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.

For larger installations, the performance of the OLGA unit must be optimised for maximum removal of the BTX compounds to reduce the loading of the active-carbon filters. This optimisation could not be carried out in the existing laboratory line-up, however, this is readily achieved in the design of a new unit.

Product gases from typical biomass gasifiers contain several percentages of ethylene and other olefin hydrocarbons. The behaviour of these compounds in Fischer-Tropsch synthesis and the effect on the product formation is not well known. In further development of integrated BG-FT systems based on oxygen-blown gasification and tar removal this topic should be further investigated.

6. FISCHER-TROPSCH EXPERIMENTS

In this chapter, selected Fischer-Tropsch results are presented of the integrated biomass gasification (BG) Fischer-Tropsch (FT) experiments. In preparation of these experiments parametric Fischer-Tropsch studies were performed.

6.1. System line-up

The Fischer-Tropsch synthesis experiments were carried out in the fixed-bed micro-flow synthesis reactor "POTTOR" (the line-up is shown in Figure 6.1). The feed gas was pre-heated and fed to the externally heated reactor. CO, H_2, He, and N_2 are available to pre-mix gases to the desired syngas composition and inert concentration. The reactor was also coupled to gasification and gas cleaning infrastructure to allow integrated experiments with biosyngas or product gas as feed. The reactor is typically operated at temperatures of 200-250°C and pressures of 15-60 bar.

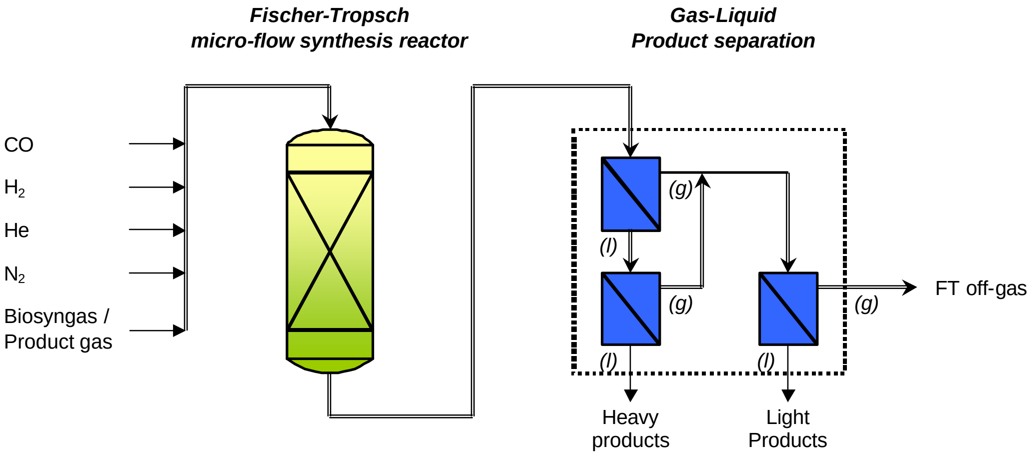

***Figure 6.1**. System line-up of Fischer-micro-flow synthesis reactor and product separation. See text for detailed description of the system.*

In the reactor part of the syngas is converted into hydrocarbons. In the product separation the waxes (or heavy product; HP) are collected in a heated vessel. The gaseous stream is cooled to condense the liquid (or light) FT products (LP). Most of the product water formed during FT synthesis is also condensed with the liquid product. The remaining gaseous products and the unconverted feed (*i.e.* the off-gas) pass a gas volume measurement device and the off-gas composition is analysed online with a GC. The gas is not recycled but flared. The wax and liquid product collection vessels are emptied with regular intervals to check the mass balances.

6.2. Parametric study H_2/CO

The focus of the parametric Fischer-Tropsch studies was mainly on cases comprising once-through FT synthesis with product gases of biomass gasifiers. This means gases with relatively low concentrations (*i.e.* partial pressures) of H_2 and CO and variable H_2/CO ratios between 0.8 and 2.0 depending on the specific gasifier. With the appropriate cobalt-based catalyst used in the experiments, C_5+ selectivities around 90% were achieved in experiments with H_2/CO ratios between 1.0 and 2.1. This implies that the catalyst is very suitable for once-through Fischer-Tropsch synthesis systems.

For once-through Fischer-Tropsch synthesis a H_2/CO feed ratio of 1.7 is chosen as this is expected to give a good compromise between CO conversion and C_5+ selectivity, *i.e.* the CO conversion is limited at lower ratios, while the C_5+ selectivity decreases at higher ratios. To achieve the optimum FT performance the H_2/CO ratio in the feed gas will preferably be shifted to 1.7 for once-through operation.

The inlet H_2+CO partial pressure in combination with the concentration inert is an important parameter in FT synthesis to achieve maximum syngas conversion. Typically, an inert percentage of 15% is used as a ‘soft’ rule-of-thumb maximum for optimised FT synthesis.

6.3. Integrated BG-FT experiment

In December 2001, for the first time in the world, Fischer-Tropsch products were synthesised from biomass (willow). Figure 6.2 shows a picture of the willow wood used as feed material, and the Fischer-Tropsch wax and liquids as produced in the integrated test. This unique and successful experiment received a lot of attention, both from the scientific community as from the (national) media.

***Figure 6.2**. Pictures of the willow used for the integrated test in December 2001, Fischer-Tropsch wax, and the light product (viz. 'green diesel').*

6.3.1. Experimental

The Fischer-Tropsch test run was carried out with the biosyngas produced by low-temperature gasification and cracking of the tars (see Section 4.2). The FT synthesis was carried out at a pressure of 30 bar and at a temperature of 227°C. The off-gas was analysed online while the wax (HP) and liquid (LP) products were analysed after the experiment for mass balance purposes and to determine the product distribution and composition.

6.3.2. Product distribution

In Figure 6.3 a plot is shown for the chain-length product distribution of the hydrocarbons in the Fischer-Tropsch synthesis experiment. The plot is constructed by combining the analysis of the off-gas, HP, and LP. The plot is not very reliable for the ranges where the analytical data overlap. Except for roughly the $<C_{10}$ products, the decreasing trend in the formation of higher carbon number products is clear. For the (theoretical) ASF chain-growth parameter, a value of $\alpha = 0.92$ was determined from the slope for C_{30}-C_{60} of the plot. This apparent high selectivity for higher hydrocarbons is consistent with the C_5+ selectivity of 0.93 determined from the mass balance.

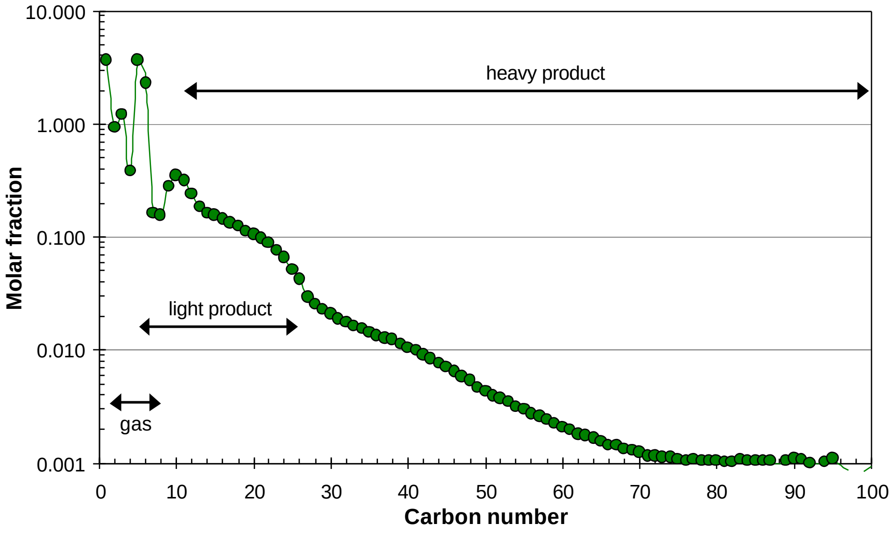

***Figure 6.3**. Hydrocarbons product distribution (molar basis). The plot is composed based on processed (partly overlapping) analysis data from the off-gas, light product (LP), and the heavy product (HP), as indicated.*

6.3.3. Product composition

In Fischer-Tropsch synthesis mainly paraffin straight-chain hydrocarbons (C_xH_{2x}) are produced. However, in addition also minor amounts are formed of branched and unsaturated hydrocarbons, and primary alcohols. In Figure 6.4 the hydrocarbon composition of the liquid products is shown. It is obvious that the formation of by-products is significant for products with a carbon number below fifteen; at higher carbon numbers >80% of the products are paraffin levelling of to ~95% for carbon number above twenty. The alcohols products are the major product for C_8 but the concentration decreased quickly and stabilises in the $>C_{10}$ range to amounts below 10%. The 1-olefins (or α-olefins) have a significant contribution in the lighter product range, while the 2-olefins(cis) form only a few percent of the product spectrum. Both olefin products are not formed at higher carbon numbers. Formation of other by-products (*e.g.* branched and trans-olefins) is negligible and not separately included in the plot.

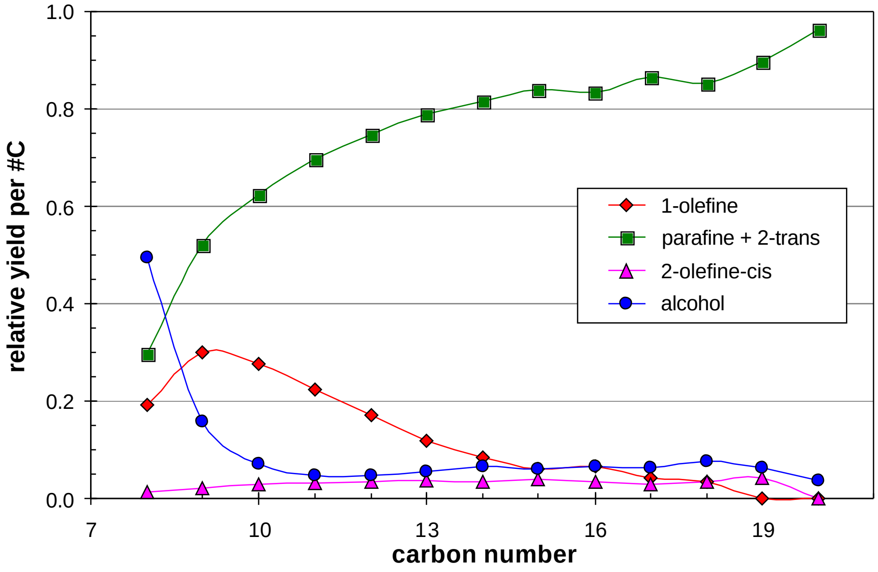

***Figure 6.4**. Relative product formation in Fischer-Tropsch synthesis for each carbon number. Data from analysis of light fraction (LP).*

These by-products are not ‘useless’ with respect to the production green diesel. In the hydro-treatment upgrading of the wax and liquid Fischer-Tropsch products to produce green diesel, these alcohol and olefin by-products are converted into paraffins.

7. CONCLUSIONS & OUTLOOK

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

7.1. Conclusions

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.

Objective
Two integrated systems of biomass gasification, gas cleaning, and Fischer-Tropsch synthesis were assessed to demonstrate the suitability 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_4, and C_2-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 system 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. 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 the parametric studies, high C_5+ selectivities can be obtained for H_2/CO ratios in this range. This implies that the catalyst is very suitable for once-through Fischer-Tropsch synthesis systems.

Proof-of-Principle

After gas cleaning, biosyngas and product gas meet the specifications for Fischer-Tropsch synthesis, as was shown in the three successful integrated test-runs with two different systems. There are no biomass-specific impurities that require a totally different gas cleaning approach. 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 development of the biomass gasification Fischer-Tropsch route to produce renewable transportation fuels, and the start of a Proof-of-Concept project to demonstrate the route on pilot-scale.

7.2. Outlook

Technology selection

In the underlying study the gas cleaning systems have been developed for fluidised bed gasification of biomass. In a parallel study, direct gasification[9] of biomass in a slagging entrained flow (EF) gasifier has been identified as optimum biosyngas production route, considering the apparent simplicity of the system and the relatively high net biomass-to-biosyngas efficiency [22].[10] 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 [27]. In a recently started ECN project the system will be optimised and operated to deliver the Proof-of-Concept, resulting in a conceptual design for a BG-SNG pilot plant.

Large-scale BG-FT implementation?

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

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[9]. “Direct” EF gasification of biomass refers to the use of solid biomass as feed material without pre-conversion into bio-oil or bio-slurry. The biomass may be pre-treated by torrefaction to homogenise the material and allow pneumatic feeding.

[10]. A system with a comparable high efficiency is the combination of an EF gasifier with a preceding CFB gasifier. In the CFB gasifier the inhomogeneous solid biomass is converted at relative low temperature in gas and char, which are combined fired on the EF gasifier (of the same type). In this system energy-intensive pre-treatment steps (*i.e.* milling) or inefficient pre-conversion steps are avoided. The difference of this system with the CFB + tar cracker system is that in the latter, the solids are separated and not fired on the EF gasifier.

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.

Current biosyngas and renewable fuel developments

Although on the long term dedicated large-scale Fischer-Tropsch production plants are required to optimise the energetic utilisation of biomass, on the short and medium term other system concepts can be selected to demonstrate (parts of) the technology and facilitate implementation. In the view of ECN, *trigeneration* concepts are very suitable for this purpose. In these demonstration tri-generation plants not the whole chain from biomass to liquid fuel has to be demonstrated. In case of a BG-FT plant, the synthesis can be limited to the production of the FT crude (*i.e.* wax and liquids) that is upgraded to green diesel in a centralised facility to benefit from economy of scale for this part of the process.

Internationally, within the framework of European Integrated Project “RENEW” (co-ordinated by Volkswagen) pilot systems are being developed for liquid fuel synthesis (methanol as well as FT liquids). Also in the Netherlands initiatives for the production of renewable syngas (*i.e.* biosyngas) are started. Biosyngas is a key-topic in the governmental programme to define the desired role of biomass in the ‘transition’ to a more sustainable society (*i.e.* “Biomass Transitie”). In several ongoing Transitie projects the aim is the realisation of pilot and demonstration plants for biosyngas and/or renewable fuel production.

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APPENDIX A. SUMMARY SYSTEM ASSESSMENT

The text in this appendix is based on the Executive Summary from the report below that was prepared as sub-activity of the project:

Title	Production of FT transportation fuels from biomass; technical options, process analysis and optimisation, and development potential
Authors:	Carlo N. Hamelinck, André P.C. Faaij, Herman den Uil, Harold Boerrigter
Institute	Utrecht University>Copernicus Institute >Science Technology Society
Publication Date	March 2003
ISBN	90-393-3342-4
Number	NWS-E-2003-08

A.1. Introduction

Fischer-Tropsch (FT) diesel derived from biomass via gasification is an attractive clean and carbon neutral transportation fuel, and directly usable in the present transport sector. Previous research indicated that FT diesel could be produced at 9.1-16.7 €$_{2002}$/GJ (long and short term). Thus, without exemption of excise duty and vat (11.6 and 3.5 €/GJ in the Netherlands), it cannot compete with fossil diesel (Rotterdam product price over past five years was 2.6-7.0 €/GJ, BP 2002). These studies were still of a strong explorative nature, bearing rough assumptions on process equipment performance, ignoring the influence of process conditions on conversion and selectivity in the FT reactor, and rough in the economic analysis. Furthermore these studies listed improvement options to bring the production costs of bio FT diesel to a competitive level. Various essential system components are not commercially available and require development over time.

The underlying study incorporates these improvements and refines the technical and economic analysis. The main system efficiency improvements reside in combined production of FT liquids with power, application of pressurised gasifiers, and in combining high selectivity with high conversion in the FT reactor. Since about 75% of the investment costs are in the pre-treatment, gasification and gas cleaning section, the influence of the gasification pressure and medium (air, oxygen enriched air, or pure oxygen) on economies of both gasifier and down-stream equipment are studied more closely. The scale of the conversion system is expected to be an important factor in the overall economic performance, but at the same time the perspectives for large throughput biomass gasifiers are (heavily) disputed. Therefore, special attention is given to the technical perspectives for large-scale pressurised biomass gasification. Furthermore, insight is gained in the sensitivity of Fischer-Tropsch catalysts to contamination in the biomass-derived synthesis gas, in necessary gas cleaning equipment to avoid catalyst poisoning and ageing, and in reactor design.

A.2. System concepts

System components necessary for FT production from biomass are analysed and combined to a limited set of promising conversion concepts (Figure A.1). The main variations are in gasification pressure, the oxygen or air medium, and in optimisation towards liquid fuels only, or towards the product mix of liquid fuels and electricity. The technical and economic performance is analysed. For this purpose a dynamic model was built in Aspen Plus, allowing for direct evaluation of the influence of each parameter or device, on investment costs, FT and electricity efficiency and resulting FT diesel costs.

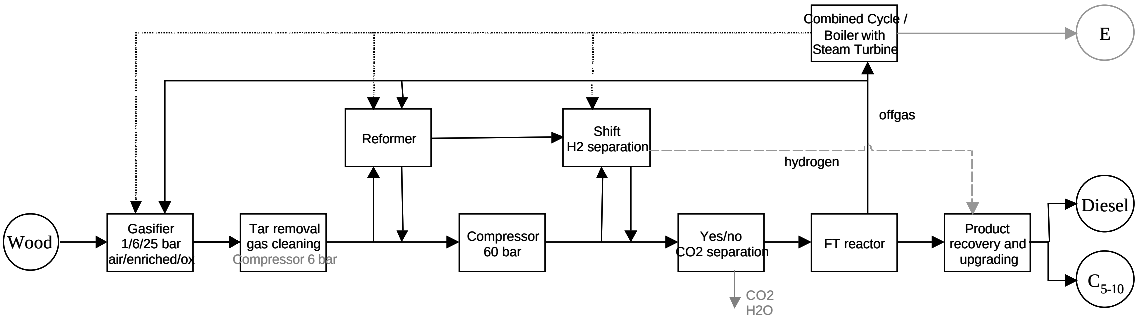

***Figure A.1**. Summary of possible process configurations for FT production.*

A 400 MW_{th} input plant (or 168 $MW_{FT,HHV}$) applying conventional technologies is taken as the *key concept* for further analysis. It consists of a 25 bar oxygen fired gasifier, followed by a tar cracker and wet gas cleaning and a solid bed FT reactor with 70% once through conversion. The Total Capital Investment or TCI for this concept is 286 M€, this complies with literature values found for grass roots natural gas fed FT plants. A high conversion (90% of $CO+H_2$) can be realised in once through mode by application of a large reactor. Of course this results in higher capital costs, but since the capital costs of the FT reactor are not crucial for the total capital investment, in total a higher conversion leads to lower FT diesel production costs. Overall efficiencies for the best performing systems are 40-45% on HHV basis. With such systems FT liquids can be produced at 16 €/GJ.

A.3. System comparison

System variations to the above named *key concept* give the following insights (see Figure A.2):

- Removing the 30 vol% CO_2 fraction prior to the FT reactor improves both selectivity and efficiency, but due to the accompanying increase in investment this does not result in lower product costs.
- The efficiency for the dry gas cleaned concepts is slightly higher than wet cleaned concepts, because the ceramic membrane more effectively shifts (since product is taken away) than the traditional shift reactor, hence less steam is needed. This is outweighed by a slightly higher capital investment, such that the resulting fuel price is the same.
- The oil scrubber effectively returns BTX and tars to the gasifier where they are cracked, but much energy remains in methane, ethane and ethane, resulting in lower FT yields. The performance of concepts with oil scrubber improves when adding a reformer, however, this turns out to be a more expensive combination than a single tar cracker.
- Application of a recycle loop instead of once through does not improve the production costs: The continuous temperature leaps and product leaps (syngas partly to C_{1-4} product, and than back to syngas) lead to both a low selectivity and a low overall efficiency. Furthermore, the capital costs are high.

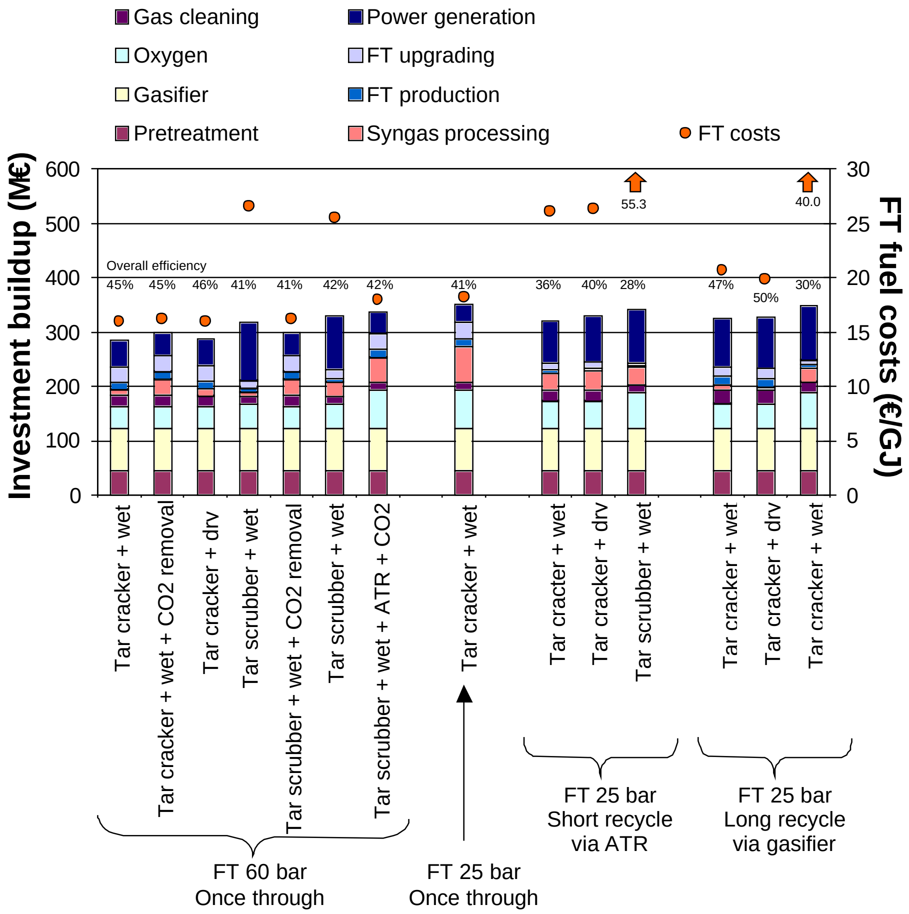

***Figure A.2**. Variations on the key concept (25 bar oxygen gasification and 90% CO+H_2 conversion), applying other gas cleaning trains, reforming and/or CO_2 removal, once through or recycle mode. The overall (fuel+electrical) HHV efficiency is indicated.*

A.4. Production costs

The FT liquids production costs for the short term are still about two to four times the production costs for Fossil diesel. Fossil diesel costs strongly depend on the oil price, and could go up. Green diesel could be exempted from excise duty and VAT (11.6 €/GJ and 3.5 €/GJ in the Netherlands) to value the environmental benefits of green FT diesel. The combined effect possibly makes FT diesel from biomass competitive with fossil diesel.

On the longer term (~15 years), more cost improvements are foreseen. The combined effects of larger production scale (2000 MW_{th}) and cheaper biomass (2 €/GJ) may bring the FT fuel production costs to 11.5 €/GJ. The technical and economical performance may be improved by for example developments in oxygen production and gasification, application of catalytic tar cracking instead of thermal, increased selectivity towards the desired product in FT synthesis. These technical developments combined with technological learning (capital costs reduce with 15% for the third generation plant) bring the FT diesel costs to 9 €/GJ.