DEVELOPMENT OF PROCESS ROUTES FOR SYNTHETIC BIOFUELS FROM BIOMASS (BTL)

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ABSTRACT: In Güssing a nearly nitrogen free product gas can be provided by the Fast Internal Circulating Fluidized Bed (FICFB) – gasification system. The main components of the product gas are hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4). A Fischer – Tropsch (FT-) trial plant uses the product gas components H_2 and CO in an exothermic, catalytic reaction to produce hydrocarbon chains. Catalysts based on iron and cobalt are used for the synthesis. In Güssing a slurry reactor is used for low temperature FT – synthesis. The main parts of the plant are the gas cleaning section, the gas compression section, the FT – slurry reactor and the product separation section. In the year 2008 eight experiments with a catalyst based on iron and from April to July 2009 ten experiments with a catalyst based on cobalt were done. Over 1400 operating hours were reached and approximately 170 kg of FT – raw product was produced. The product of the experiments with cobalt catalyst was split into the fractions naphtha, diesel and waxes by vacuum distillation. The long chain waxes of the distillation were used in a hydro – treater to convert them to diesel.

Keywords: biomass to liquid (BtL), Fischer Tropsch, gasification, polygeneration

1 INTRODUCTION

In Güssing the Fast Internal Circulating Fluidized Bed (FICFB) – gasification system is used to produce a high quality synthesis gas with a high calorific value. The principle of this process is an allothermic gasification with external heat input. In Figure 1 the principle of the FICFB – gasification process is shown.

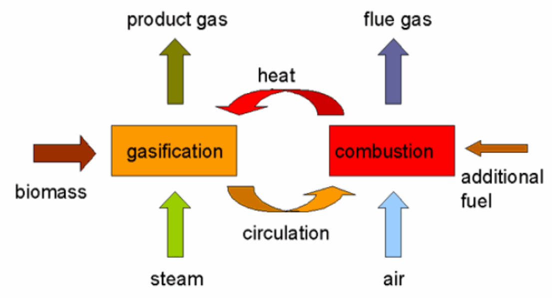

Figure 1: Mechanism of FICFB – process [6]

The FICFB – gasification process consists of two separated chambers. The gasifier is carried out as a stationary fluidized bed reactor and the combustion chamber as a circulating fluidized bed reactor. The gasification zone is fluidized with steam and the combustion zone with preheated air. The two chambers are connected over a chute, where the bed material and non – gasified carbon are transported into the combustion chamber. The used bed material is heated up in the combustion zone and is separated from the flue gas with a cyclone. The separated bed material takes the heat in the gasification zone. The bed material covers the energy demand for the strongly endothermic gasification process. In the gasification zone the wood chips are heated up, dried devolatilised and converted mainly into H_2, CO, CO_2, CH_4, H_2O (gas) and C (char). Low amounts of by-products like C_2H_4 and C_2H_6 and undesirable components like tar, NH_3 and H_2S are also produced.

The product gas is further treated for final utilization. The gas is cooled down from 850 °C – 900 °C to 160 °C – 180 °C with a water cooled heat exchanger. After that a fabric filter separates particles and some of the tar from the product gas. The undesirable tar is removed with a gas scrubber with RME (Rapeseed Methyl Esther) as solvent. In the gas scrubber the product gas is cooled down to approximately 40 °C. [6], [7], [8]

In Table 1 the gas composition of the cleaned product gas with a water content of about 10 Vol% is visible. The main components of the product gas are H_2 and CO, which are important for the FT – synthesis. [2]

Table 1: Gas composition of CHP plant Güssing (dry)

Main components		
Hydrogen	35 – 45	Vol.%
Carbon monoxide	19 – 32	Vol.%
Carbon dioxide	20 – 24	Vol.%
Methane	7 – 10	Vol.%
Minor components		
Ethene	2 – 3	Vol.%
C_3 - Fraction	0.5 – 1	Vol.%
Nitrogen	0.7 – 2.0	Vol.%
Possible poisons		
Ammonia	1000 – 2000	ppmV
Hydrogen sulfide	~ 150	ppmV
Organic sulfide	~ 30	ppmV
Hydrochloric acid	~ 5	ppmV
Benzene	5 – 8	g/Nm³
Naphthalene	1 – 2	g/Nm³
Tar (PAH[1] larger than Naphthalene)	0.02 – 0.05	g/Nm³
Particles	< 0.02	g/Nm³

[1] polycyclic aromatic hydrocarbons

The FICFB – process and the further gas cleaning steps provide a product gas with high quality. This enables the possibility for the utilization of this product gas for FT – synthesis. [6]

2 THE FISCHER – TROPSCH SYNTHESIS

2.1 Chemistry of Fischer – Tropsch synthesis

The FT – reaction is a catalytic polymerization reaction on the surface of a catalyst. The product gas components H_2 and CO react to hydrocarbon chains and water. During this highly exothermic synthesis the CO is hydrogenated to CH_2 - units. In dependence to the reaction parameters and the used catalyst the CH_2 – units are added into products of different chain lengths. The FT – product consists mainly of linear compounds such as paraffines, olefins and in slight amounts oxygenated compounds. In Figure 2 the principle reaction mechanism from wood chips to the FT – product is shown. [9], [10], [11]

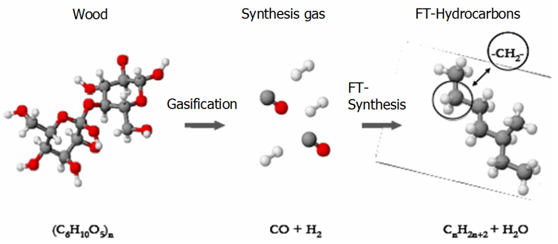

Figure 2: Reaction mechanism of FT – synthesis [4]

The general FT – reaction is a repeated reaction sequence. Hydrogen is added to carbon and oxygen while the C-O bond is split and a new C-C bond is formed. The following reactions have to occur to form one CH_2 – unit:

- Associative adsorption of CO – molecules
- Splitting of the C-O bond
- Dissociative adsorption of 2 H_2
- Transfer of 2H to the oxygen to yield H_2O
- Desorption of H_2O
- Transfer of 2H to the carbon to yield CH_2
- Formation of new C-C bond

[5]

2.2 High temperature Fischer – Tropsch synthesis

By the high temperature FT – synthesis the conversion takes place by temperatures between 300 and 350 °C and a pressure of 20 to 40 bars. The high temperature leads to products with lower carbon numbers and also to aromatic compounds. The high temperature synthesis is used to produce petrochemical primary materials like ethylene, propylene and also petrol. For this synthesis fluidized bed reactors are used. [3]

2.3 Low temperature Fischer – Tropsch synthesis

In comparison to the high temperature synthesis the low temperature FT – synthesis takes place by temperature between 200 and 250 °C and a pressure level of 20 to 30 bars. The low temperature is well suiting for the production of diesel and other high boiling hydrocarbons. For this type of synthesis fixed-bed reactors and slurry reactors are used. [3]

In Güssing a slurry reactor for low temperature FT – synthesis is used. A slurry reactor is a type of fluidized bed reactor. The catalyst particles are suspended in a liquid, mainly FT – wax product and the product gas bubbles through the reactor. The product gas streams from the bottom to the top and is dispersed at the bottom of the reactor via gas distributor. In the three – phase system between suspended catalyst particles, wax and product gas the reaction takes place. The reactor is cooled to ensure isothermal conditions. The slurry system has a temperature limitation. At low temperature the liquid wax becomes very viscous, while above 280 °C the FT – wax hydrocracks. [1]

2.4 Catalysts for Fischer – Tropsch synthesis

For the FT – synthesis catalysts based on iron, cobalt, nickel and ruthenium can be used. The catalyst choice has a major influence on the process control, product distribution as well as on economy of the synthesis. It is very important to use highly active and long-living catalysts.

Nickel catalysts have the characteristics that they produce mainly methane. This is not desired for the FT – synthesis.

Ruthenium has the highest activity of the named catalysts. Also the needed reaction temperature of 150 °C is good suitable for low temperature FT - synthesis, but the high price makes the usage of this catalyst type uneconomic.

The conventional used catalysts are based on iron and cobalt. Iron can be used for high- and low temperature FT – synthesis. Cobalt is only used for low temperature FT – synthesis. Iron based catalysts have a very low price, but they have the disadvantage to have a relative low lifetime. Cobalt based catalysts have a long durability, but the price is much higher.

Catalysts contain beside the catalytic active metal also different promoters, which increase the selectivity and durability of the catalyst. Typically cobalt based catalysts are used on oxidic, large-area carriers like SiO_2.

The FT – catalysts have a high sensitivity to sulphur components in the product gas and therefore gas cleaning is important. In terms of sulphur components a pureness of less than 0.1 ppm in the product gas is necessary. [3]

3 THE FISCHER – TROPSCH TRIAL PLANT

3.1 The Fischer – Tropsch Trial Plant

The biomass – based FT – trial plant in Güssing was realized by the Technical University of Vienna (TUV) in cooperation with the CHP plant. TUV designed and installed a new FT reactor in form of a slurry reactor.

The FT – trial plant is fed with product gas over a pipe bridge between research facility and CHP. The product gas is taken after the existing gas cleaning of the CHP plant. The excess pressure of the product gas lies by 80 mbar and the temperature at 70 °C. The plant operates in commercial environment and under permanent operation conditions. Commercial FT – catalysts as well as research FT – catalysts are studied during the experiments. In dependence to the used reaction parameters 5 to 10 Nm^3 product gas per hour are used for the experiments. The production capacity of the trial plant is about 2.5 kg FT – raw product per day. [1]

In Figure 3 the flow sheet of the FT – trial plant is visible.

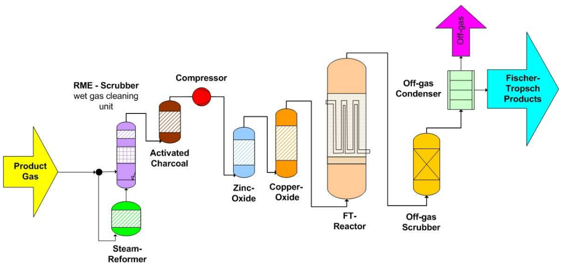

Figure 3: Flow sheet of FT – trial plant

3.2 Components of Fischer – Tropsch Trial Plant

The biomass – based FT – trial plant consists of following components:

- Steam – reforming unit to increase the H_2 and CO – content in the product gas
- RME – scrubber for gas drying
- Activated charcoal fixed-bed adsorber for desulphurization of the product gas

- Two – stage gas compression to 20 - 30 bars
- ZnO and CuO – fixed-bed adsorber for desulphurization of the product gas
- Slurry FT – reactor
- Off-gas – scrubber for separation of long chain hydrocarbons
- Off-gas – cooling unit for separation of short chain hydrocarbons

The product gas enters in dependence to the experimental setup conditions either the wet gas cleaning unit or the steam reforming unit. The steam reformer converts the hydrocarbons in the product gas to H_2 and CO to increase the H_2/CO – ratio. After that reforming step the gas comes in the gas drying and cleaning section of the trial plant. Very important is that the water content of about 10 Vol% in the product gas is removed before the compression step. The used RME – scrubber cools the gas to approximately 3 °C down to remove the water.

After the RME – scrubber the quantity of the gas is measured with a gas meter. An activated charcoal reactor is used under nearly atmospheric conditions to remove H_2S and also organic sulphur components. The reactor is placed before the compression step which has the advantage that the gas compressors are also protected.

The gas compression is realized with two compressors. At first the product gas enters a diaphragm pump and is compressed to approximately 1-5 bar. The pressure of 1-5 bar is necessary for the following piston compressor. A piston compressor is used to compress the gas to the desired end pressure level of 20 to 30 bars. The pipes after the compression step are heated by a trace heating to hold the temperature on a constant level.

The high pressure and high temperature gas cleaning section consists of a ZnO and a CuO – fixed-bed adsorbers to remove H_2S. The fixed-bed adsorbers are equipped with trace heating systems to reach the desired temperature for the reactions. After the gas cleaning section a flow meter is used to measure the gas flow.

After the gas cleaning sections the product gas is heated up to the desired reaction temperature. The cleaned and dried gas enters the slurry reactor at the bottom of the reactor over a nozzle floor to fluidize the suspended catalyst. The FT – reaction takes place in the slurry reactor with a volume of 20 liters. A fan and an electrical heating system fixed on the outside keep the process temperature on a constant level to reach isothermal conditions for the reaction. The gas is leaving the reactor over a sintered metal filter at the top.

The gas is expanded from the 20 – 30 bars to about 100 mbars relative. The separation of the FT – product from the off-gas stream is carried out in two steps. At first the off-gas is led to the off-gas scrubber where water with approximately 80 °C is used to remove the heavy products (heavy diesel and waxes). After the off-gas scrubber the gas is cooled down to about 5 °C by a heat exchanger to condensate the light fractions like naphtha and diesel. The product is collected in glass receptacles and taken out once per week. The non – reacted product gas is measured with a gas meter and is fed back to the CHP plant for further utilization.

The FT – Plant is equipped with an automation system, which allows the operation of the plant for longer periods unmanned. Field Point modules are used as automation hardware and LabView from the Company National Instruments (NI) is used as software. The plant can also be controlled and operated over the internet, which reduces the costs of traveling for longer experiments. [1], [2]

3.3 Further product treatment and analytics

During the experiments with the cobalt based FT – catalyst, the FT – raw product was split into the fractions naphtha, diesel and waxes by vacuum distillation. The vacuum distillation test rig was operated by a pressure level of 100 mbar absolute. The boiling range from naphtha was set from begin to 180 °C and diesel from 180 °C to 320 °C.

The liquid and solid FT – products were analyzed by simulated distillation. A gas chromatograph (GC) – system with Flame Ionization detector (FID) and capillary column for simulated distillation was used for this analysis.

Gas analyses were made online before and after the gas cleaning section as well as of the off-gas from the FT – plant. A GC – system is used from “Perkin Elmer” with TCD and FID detector for gas analysis. With this analysis system the concentration of the permanent gases (O_2, N_2, CO_2, CO; TCD – detector) and hydrocarbons (FID – detector) up to a carbon number of 4 can be analyzed. The H_2 – content was calculated over the difference between 100 % and the detected gas concentration. [1]

4 EXPERIMENTS WITH COBALT CATALYST

4.1 General information to the experiments

In the year 2009 from April to July 10 experiments with a commercial cobalt based catalyst were done. The catalyst had to be activated with hydrogen before usage. For the activation of the FT – catalyst a mixture of hydrogen with nitrogen was used. The reduced catalyst was suspended in “starter waxes”. Into the FT – slurry reactor the mixture of suspended catalyst particles and waxes were filled.

The experiments were accomplished on following experimental setup:

- Steam reformer
- RME - scrubber
- Activated charcoal filter
- Gas compression section
- ZnO - adsorber and CuO - adsorber
- FT-slurry-reactor
- Off-gas scrubber (OGW)
- Off-gas cooler (OGK)

4.2 Conditions of the experiments

In Table 2 an overview of the experiments with cobalt based catalyst is provided. For the experiments only the pressure and through put of the product gas was varied. The temperature was kept on a constant level of 230 °C by all experiments.

Table 2: Overview of the experiments

Number of experiments	Temperature [°C]	Pressure [bars]	Gas flow [Nm³/h]
1	233	19.9	3.7
2	230	19.9	3.7
3	230	19.7	3.2
4	230	18.1	3.7
5	230	19.8	5.8
6	230	25	4.1
7	231	19.9	5.1
8	232	12.7	5.2
9	231	12.8	4.8
10	231	19.9	4.9

The test series started with adjusted operation conditions of 230 °C, 20 bars and a product gas flow of 5 Nm³ per hour. During the first two experiments it was tried to stabilize the process by keeping conditions on a constant value. The aim of the stabilization process is to achieve equilibrium in the slurry reactor between the starter waxes and the new product. At interruptions during the experiments the temperature of the slurry reactor was kept on constant value and the FT – plant was operated with nitrogen to avoid any settling of the catalyst.

In Figure 4 the operation data of experiment No. 5 are illustrated. The time period of the experiment was 3 days. The product gas flow was adjusted to approximately 6 Nm³ per hour and the pressure level was by about 20 bars. During the experiment no malfunctions occur and the experimental conditions were kept on constant value.

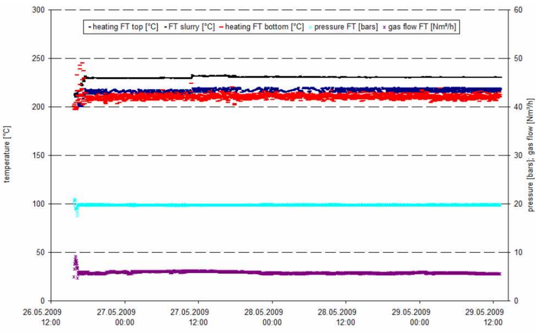

Figure 4: Test conditions of experiment No. 5

It can be seen in the figure that the temperature in the slurry reactor is lying over the temperature of the trace heating system of the reactor. This means that the reaction is exothermic.

The FT - synthesis is based on a highly exothermic reaction and therefore the activity of the catalyst can be observed over the energy balance of the FT - reactor. The temperature difference between the FT - slurry temperature and the temperature of the electrical heating system is direct proportional to the activity of the FT - catalyst. A deactivation of the FT – catalyst is pointed out by the lowering of the exothermy of the FT – reaction. This would result in a decreasing temperature difference between temperature in the slurry reactor and the temperature of the trace heating. [1], [2]

5 RESULTS OF EXPERIMENTS

During 10 experiments with the cobalt based catalyst 90.7 kg of FT – raw product was produced within 623 active hours. The taken samples of the product were analyzed by simulated distillation. Thereby the mass fraction of the carbon number n has been determined by a gas chromatograph with FID. In Figure 5 a chromatogram of the hydrocarbon distribution in the FT – raw product out of the off-gas cooling unit can be seen. The area of one peak is direct proportional to the mass of the hydrocarbon.

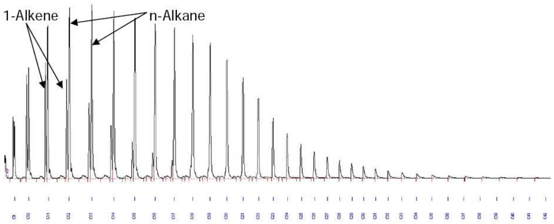

Figure 5: Chromatogram of hydrocarbon distribution

The total product distribution was used for the calculation of the chain growth probability α. The average product distribution over the experiments tends to a chain growth probability of 0.85 to 0.9, which is in the suitable range for a low temperature FT synthesis.

The total product distribution could be calculated out of the chromatograms of product probes of off-gas scrubber and off-gas cooler. The amount of product that was not condensed, this includes gaseous products and partly liquid products, was calculated with the Anderson – Schulz – Flory (ASF).

Figure 6 shows a corrected total product distribution. This figure includes also the FT – product, which was produced, but could not be condensed.

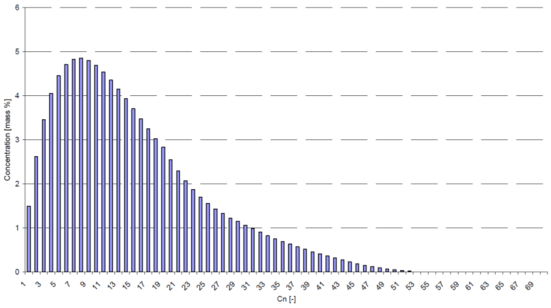

Figure 6: Corrected total product distribution

The calculation of the ASF plot resulted in a total amount of product of 140 kg. The average conversion rate over all experiments was consequent by over 64 percent.

The collected FT – product was split into the fractions naphtha, diesel and waxes by vacuum distillation. The vacuum distillation resulted in following distribution:

- 3 percent FT - naphtha
- 24 percent FT - diesel
- 73 percent FT - waxes

The distillated product was delivered to a project partner, which obtained the yielded amount of FT - fuel by cracking the longer hydrocarbon chains by hydro – treating.

Hydrogen is used together with a catalyst to break the hydrocarbon chains and also to isomerize the hydrocarbons to improve the quality of the product. The first results of the hydro – treating are very promising. The hydro – treating allows that 40 percent of the long chain FT – waxes can be transferred into diesel and so the yield of diesel can be improved to approximately 52 percent of the complete product.

The cetane number of the raw FT – diesel is by over 70, which is already a very good value. The diesel from hydroprocessing shows also a very good cold flow behavior and has a CFPP/CP of about – 60 °C. The raw FT – diesel consists to over 60 percent of n – paraffines and the hydroprocessed – diesel to over 90 percent of iso – paraffines. This is the explanation for the excellent cetane number of the FT – diesel and for the distinguished cold flow behavior of the hydroprocessed diesel.

6 CONCLUSION

The FT – synthesis enables the possibility to produce a Biofuel of the second generation with high quality, which is not in competition to food industry. The FT – product is free of aromatic components and incinerates without the formation of soot. It can help to replace the fossil derived transportation fuel and to reduce greenhouse gas emissions.

The FT trial plant at the biomass CHP Güssing was able to produce large amounts of FT – product from real biosyngas with a high conversion rate. The automation of the FT – trial plant showed that the facility is also able to operate without human support.

The analysis of the FT – raw product showed that the hydrocarbon distribution was quite similar over the test series. The chain growth probability was between 0.85 and 0.9. These values were expected for a low temperature FT – synthesis. The gas analysis showed that the H_2/CO – ratio was approximately 1.8. The steam – reforming unit was able to raise the product yield by increasing the total amount of H_2 and CO. [1]

A vacuum distillation test rig was used to split the FT – raw product into the fractions naphtha, diesel and long chain waxes. This separation process showed that the FT – raw product consists for the most part of long chain FT - waxes and FT – diesel.

Hydro – treating processes enable the possibility to enrich the amount of diesel by breaking the long chain waxes with H_2. FT – diesel and HPFT – diesel together amount in over 50 percent of the total FT – product and through further research the amount can be increased.

Screening and optimization of FT – catalysts and product improvements in quality and yield are the next work packages for the further fundamental research on the FT – trial plant.

Supplementary to the fundamental research the increase of the production capacity to pilot – plant scale, the upgrading to saleable products through hydro – treating and isomerisation and the test of FT – fuel in internal combustion engines are the next steps to make the biomass – based FT – synthesis state of the art.

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