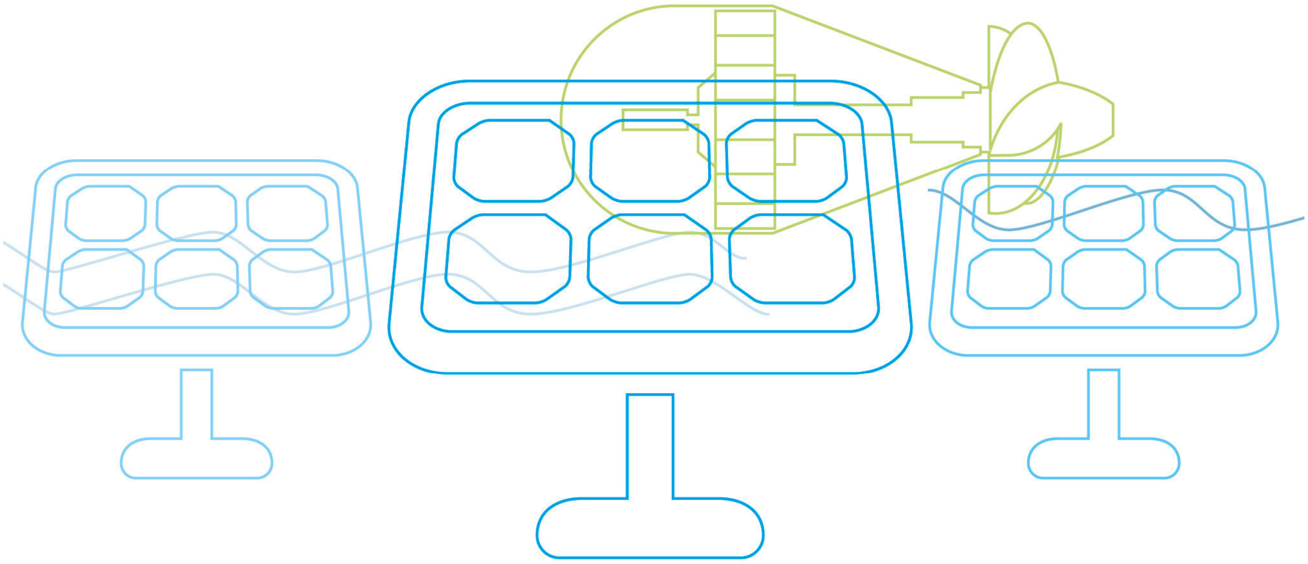
Blue Globe Report

Erneuerbare Energien #2/2009

Grundlagenuntersuchungen und Design einer Pilotanlage FT-Treibstoffe



Europäisches Zentrum für erneuerbare Energie Güssing GmbH

VORWORT

Die Publikationsreihe BLUE GLOBE REPORT macht die Kompetenz und Vielfalt, mit der die österreichische Industrie und Forschung für die Lösung der zentralen Zukunftsaufgaben arbeiten, sichtbar. Strategie des Klima- und Energiefonds ist, mit langfristig ausgerichteten Förderprogrammen gezielt Impulse zu setzen. Impulse, die heimischen Unternehmen und Institutionen im internationalen Wettbewerb eine ausgezeichnete Ausgangsposition verschaffen.

Jährlich stehen dem Klima- und Energiefonds bis zu 150 Mio. Euro für die Förderung von nachhaltigen Energie- und Verkehrsprojekten im Sinne des Klimaschutzes zur Verfügung. Mit diesem Geld unterstützt der Klima- und Energiefonds Ideen, Konzepte und Projekte in den Bereichen Forschung, Mobilität und Marktdurchdringung.

Mit dem BLUE GLOBE REPORT informiert der Klima- und Energiefonds über Projektergebnisse und unterstützt so die Anwendungen von Innovation in der Praxis. Neben technologischen Innovationen im Energie- und Verkehrsbereich werden gesellschaftliche Fragestellung und wissenschaftliche Grundlagen für politische Planungsprozesse präsentiert. Der BLUE GLOBE REPORT wird der interessierten Öffentlichkeit über die Homepage www.klimafonds.gv.at zugänglich gemacht und lädt zur kritischen Diskussion ein.

Der vorliegende Bericht dokumentiert die Ergebnisse eines Projekts aus dem Forschungs- und Technologieprogramm „Energie der Zukunft“. Mit diesem Programm verfolgt der Klima- und Energiefonds das Ziel, durch Innovationen und technischen Fortschritt den Übergang zu einem nachhaltigen Energiesystem voranzutreiben.

Wer die nachhaltige Zukunft mitgestalten will, ist bei uns richtig: Der Klima- und Energiefonds fördert innovative Lösungen für die Zukunft!

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Kurzfassung

Die Fischer-Tropsch-Synthese stellt ein interessantes Verfahren zur Produktion von Biotreibstoffen der 2.ten Generation aus Biomasse dar. In den letzten 5 Jahren wurde am Standort einer 8 MW Biomasse-Dampfvergasung eine Versuchsanlage errichtet, betrieben und kontinuierlich verbessert. Als Synthesegas wird reales Produktgas der Biomasse-Dampfvergasung eingesetzt, wobei ein kleiner Teilstrom (5-10 Nm^3/h) für die Synthese aufbereitet wird.

Ein noch nicht endgültig gelöstes Problem stellt die Wahl eines geeigneten Katalysators dar. Dies ist der erste Schwerpunkt in diesem Grundlagenprojekt. Die auf Universitäten (z.B. Univ. Strassburg, Prof. Kiennemann) hergestellten bisher getesteten Katalysatoren (Fe, Co) zeigen gute Ausbeuten und auch gute Aktivitäten, stehen aber nur in kleinen Mengen zur Verfügung. Daher ist es erforderlich, industriell hergestellte Katalysatoren zu testen und deren Eignung zu ermitteln.

Für dieses Projekt ist es gelungen, einen Kooperationsvertrag mit einem renommierten europäischen Hersteller von FT-Katalysatoren (sowohl Eisen, als auch Kobalt-Katalysatoren) abzuschließen, sodass im Rahmen dieses Projektes Testserien zur Ermittlung der Leistungsfähigkeit und der Langzeitstabilität durchgeführt werden konnten. Dabei wurde einerseits die Gasreinigung weiter optimiert und andererseits eine Anpassung der Katalysatoren an das eingesetzte Synthesegas durchgeführt. Dies ist unter Verwendung der vorhandenen Versuchsanlage erfolgt, wo unterschiedliche modifizierte Katalysatoren eingesetzt wurden.

Die folgenden Arbeitsschritte wurden durchgeführt:

- Test von derzeit verfügbaren Katalysator auf Kobalt-Basis
- Test von derzeit verfügbaren Katalysator auf Eisen-Basis
- Langzeittest mit dem optimierten Katalysator und der optimierten Gasaufbereitung

Nach Abschluss dieser Katalysatortests, wurde als zweiter wesentlicher Schwerpunkt im Rahmen dieses Projektes ein Design für eine Pilotanlage/Komponententestanlage entwickelt. Dabei wurde insbesondere auf eine Optimierung des Gesamtsystems Gasreinigung/Konditionierung/Synthese geachtet.

Abstract

The Fischer-Tropsch synthesis is an interesting process for the production of 2nd generation biofuels from biomass. During the last 4 years a research plant for the FT-synthesis has been constructed, operated, and continuously improved at the location of the 8 MW fuel biomass steam gasification plant. As synthesis gas a slip stream of the real producer gas (5-10 Nm^3/h) from the biomass steam gasification plant which has to be upgraded for this purpose has been used.

One still unsolved problem is the choice of a suitable catalyst for the Fischer-Tropsch synthesis. This is the first main part of this fundamental research project. At the University of Strassbourg (Prof. Kinnemann) several catalyst samples (Co based) were produced which showed good product yields and also good activities. The disadvantage of these catalysts is that only small amounts are available. Therefore, it is necessary to assess also industrially produced catalysts to find out the most suitable.

A co-operation agreement was signed with a well known European FT-catalyst manufacturer (Fe- and Co-catalysts). During this project several catalysts were tested to evaluate the performance and the long term stability. During these activities the gas purification and gas upgrading also was improved as well as an adaptation of the catalyst for the synthesis gas properties was aimed at. For this purpose the already existing research plant was used, where several modifications of the catalyst were tested.

The following working steps were carried out:

- Tests of the currently available catalyst based on cobalt as active element
- Tests of the currently available catalyst based on iron as active element
- Long term test of an optimized catalyst and the optimized gas treatment

After finalizing this catalyst testing a second main part of this project was carried out. This part was focussed on the development of a suitable design of a pilot plant / component testing plant. Special attention was paid on an optimized configuration of the overall system gas cleaning / gas conditioning / synthesis.

Summary

In the representational project basis research and design of a pilot plant for Fischer-Tropsch fuels is the object of investigation. The main focus is the selection of an adequate, industrial available catalyst for the FT-synthesis. Therefore two catalysts (iron- and cobalt-based) from a renowned producer were tested.

In Table 1 Table 1: Overview experiments – iron catalystand Table 2 an overview of the realised experiments for the iron and the cobalt catalyst is given.

Table 1: Overview experiments – iron catalyst

Number of experiment	Temperature [°C]	pressure [bar]	Gas flow [Nm³/h]	operating hours [h]
1	245-250	18	6.5	110
2	245-250	16	4.5	125
3	245-250	15	3.8	107
4	245-250	18	3.1	57
5	245-250	4	3.0	141
6	245-250	20	5.5	118
7	245-250	19	5.0	115
8	245-250	20	4.8	53

Table 2: Overview experiments – cobalt catalyst

Number of experiments	Temperature [°C]	Pressure [bars]	Gas flow [Nm³/h]	operating hours [h]
1	233	19.9	3.7	23
2	230	19.9	3.7	64
3	230	19.7	3.2	39
4	230	18.1	3.7	64
5	230	19.8	5.8	69
6	230	25	4.1	65
7	231	19.9	5.1	92
8	232	12.7	5.2	55
9	231	12.8	4.8	67
10	231	19.9	4.9	85

In this work, the hydrocarbon production rate, the hydrocarbon selectivity and syngas conversion over a iron- and cobalt-based catalyst have been investigated. As feed gas real product gas from the gasification plant in Güssing was used. The monitoring of the process showed that during the last experiments the catalyst lost activity. Analysis of the deactivation for the catalyst was done by the catalyst company and it showed, that there was a sulfur breakthrough in the gas cleaning. Nevertheless, the FT process was able to produce large amounts of FT product by a high conversion rate without condensing the full amount. The performance of the FT plant was excellent using the optimized parameters.

The implementation of the automation system has proven that the facility is also able to operate without any human support.

Analysis of the FT product showed that the hydrocarbon distribution was over the test series quite similar, but with differences between the iron and the cobalt based catalyst. Only a few experiments differ from the typical distribution. It can be assumed that at the first experiment starter waxes were transported out of the reactor. The product distribution of experiment no. 9 and 10 of the cobalt based catalyst might be related to the deactivation of the catalyst. The α-value was predominantly between 0.85 and 0.90 which was expected to the low temperature FT process. It was observed that at higher carbon numbers a second α-value occurs.

A complete mass balance could not be carried out due to that the flow of the off-gas could not be measured. Therefore, an integration of a gas flowmeter into the offgas line is for the calculation of the CO-conversion necessary. Instead of the CO-conversion the H2 ratio of the syngas was used for the 'possible maximal conversion' calculation. Furthermore, the gas analysis showed that the hydrogen to carbon monoxide ratio was almost about 1.8. However, by increasing the total amount of hydrogen and carbon monoxide, the steam reformer was able to raise the product yield.

The FT-diesel from the cobalt catalyst has a cetane number of above 70 which is fully at the same level as it is specified in literature. From the products of the iron catalyst no distillation was done, as here the pH value was to low and it was expected, that without any hydroprocessing the diesel cannot be used.

During the second part of the project the design of an up-scaled FT synthesis by a factor of 10 was done.

Further research and development will be done on this FT plant to improve this innovative biomass-based technology. In that sense a large scale biomass-based FT plant and thus the continuation of the sustainable development will be feasible in near future.

1 Introduction

1.1 Motivation

Fossil fuel resources are depletable and are mainly responsible for the increasing anthropogenic greenhouse gas emissions and consequently for global climate change. This is an incentive for the research and development of modern, efficient and sustainable technologies. Especially in the transport sector, renewable energy resources and technologies are a feasible solution to maintain reliability, and availability for a longer period. The utilization of biomass which is almost carbon dioxide neutral enables to produce several types of biofuels. Bio-synthetic fuel is produced via the Fischer-Tropsch synthesis using the synthesis gas of a biomass gasification process. To make this fuel cost-wise competitive with fossil fuel a lot of research and development has to be done in this field to form it ecologically and economically. In Güssing in a side stream of the existing biomass gasification plant the first biomass-based Fischer-Tropsch trial plant in Austria for bio-synthetic fuel production has been realized by the Technical University of Vienna. The plant gives the possibility to carry out advanced experiments for the sustainability of our resources.

1.2 Objectives

In cooperation with the biomass CHP in Guessing (BKG) the first biomass-based Fischer-Tropsch trial plant in Austria was realized in Guessing by Vienna University of Technology (TUV). TUV designed and installed a new Fischer-Tropsch-Reactor (slurry reactor) in a side stream of the existing allothermal fluidised bed gasifier at BKG. The new FT-synthesis plant operates in commercial environment and under permanent operation conditions. By this the long term performance and behaviour can be investigated. The catalysts used in the FT-slurry reactor at BKG are commercial FT-catalyst, but also research FT-catalysts are studied.

The 8 MW fuel biomass CHP plant based on a circulating fluidized bed steam blown gasifier producing heat and power (4.5 MWth, 2 MWel) with a gas engine went into operation in Guessing, Austria in the year 2002. At the middle of 2002 the gasifier and the gas cleaning system was coupled with the gas engine. Renet-Austria, a competence network on energy from biomass, consisting of experts from universities and industry started to develop this process further to a commercial stage. During the last years a lot of improvements could be reached. These improvements were connected on the one hand with changes in construction (e.g. feeding system, online particle separation) and on the other hand with advances in the operation performance.

Due to the excellent performance that was reached during the last years, several additional research projects could be started in Güssing. The producer gas from the circulating allothermal fluidized bed gasifier is nearly free of nitrogen and has got high hydrogen content. For this reason it is well suited for fuel cells as well as several synthesis products. Therefore, projects aiming at the development of processes for the production of synthetic natural gas and Fischer Tropsch liquids are currently carried out. In this project the production of Fischer Tropsch liquids is investigated.

1.3 Main focus

Main focus of work package 1 is to test industrial available FT catalysts in an existing trial plant with real synthesis gas and to find out, which catalyst is the most suitable one for further development.
Main focus of work package 2 is to design a pilot plant for producing FT fuels based on the results from the trial plant. The pilot plant should be described using flow sheets and drawings.

1.4 Classification to the program

The energy research program is geared to three basic directions: efficient use of energy, renewable energy sources and intelligent energy systems. Questions, which account to these directions, are of particular importance too.

The aim of the representational project with its work packages is therefore the optimisation and the enlargement of an energy centre for a multifunctional energy system, which make contribution to the basic focuses of the program. Thus systemic solution statements and involvement of solutions are of especial importance.

The project on hand fulfils a number of points, which the program “Energie der Zunkunft” is aimed. The project deals with the development of a regional, multifunctional energy centre, which has the ability to utilise a wide range of biogenous raw and residual materials. Moreover this centre should allocate a multiplicity of the required services (heat, electricity, liquid energy sources) in an efficient, low-priced and reliable way.

Exemplary the following issues could be named:

- By the exclusive use of regional renewable energy sources the principle of the program “Energiesystem der Zukunft” is significant supported.
- In the realisation of such regional energy centres new jobs were provided in the region and a high rate of adding value stay in the region.
- Greenhouse relevant emissions are considerable reduced through the use of regional available renewable raw and residual materials.
- The supply guarantee escalates by a multiplicity of local plants, which are using the fuel available in the region.
- The dependency of a region on fossil energy sources is significant reduced by such energy centres to the point of self-supply.
- The project on hand is characterized by high flexibility (both concerning the charge material and concerning the quantity and the nature of the product) and can therefore be conformed to particular local demand.
- This project is about a pilot project, which leads to a complete demonstration, as ranges like heat and electricity already exist in the present plant.
- Finally the R&D quality of the location increases as new, innovative methods should be developed respectively optimized and this advancement is of great importance for the future of the location.

Austria occupies a leading position in several sectors of a sustainable energy supply at this stage. Particularly the heating supply (biomass and solar), rudimental the power generation (CHP from biomass) and the supply of liquid energy sources (biodiesel) are concerned.

The project on hand could therefore expand the Austrian research and development expertise on further sectors of the sustainable energy supply from biomass as well (electricity, BioSNG, synthetic biofuel). So Austria could strike a constitutive role in this seminal technological sector.

1.5 Used methods

The first work package is primary of experimental character. For the estimation of the catalysts state-of-the-art research methods are used. The provided catalysts will be returned to the producer of the catalysts after use for detailed analysis. Based on the results from the trial plant (conversion, selectivity) and the detailed analysis on the catalyst the advancement of the catalysts will be carried out. For this reason it is ensured, that the know-how of the catalyst producer is integrated in the development and that they are involved in the development.

The second work package is engaged with the processing of the design based on the results of the trial plant. The formulation of the planning documents is carried out with today common instruments, e.g. flow-sheeting programs and CAD-programs for drawings.

1.6 Constitution of the work

Foremost the aims and content of the project as soon as the two work packages are illustrated. After this, the background of biofuels and the biofuels oft the first and the second generation are mentioned. Then the Fischer-Tropsch synthese is detailed described. Afterwards a description of the FT synthesis setup follows. Finally the experimental work on the iron- and cobalt-based catalysts as well as the results and conclusion on these experiments are descript.

2 Aims and contents of the project

The intention of this project is the test of industrial available FT catalysts in an existing trial plant with real synthesis gas to find out, which catalyst is the most applicable one for further development. In addition a pilot plant for producing FT fuels from biomass should be planned based on the results of the trial plant. This pilot plant should be represented by flow charts and engineering drawings for the most important appliances

The use of the synthesis gas from biomass gasification for FT synthesis has been basically determined for designing a pilot plant. For that purpose catalysts built on universities were primary used. Although these catalysts are available in small quantities, for further developments an industrial catalyst with steady quality and adequate availability is necessary. Therefore the only open point of this basic research is the availability of an adequate, industrial produced catalyst. Hence cooperation treaties were contracted with two famous European producers for FT catalysts for testing the currently available catalysts and to adapt these catalysts to the characteristic of the synthesis gas from biomass gasification. This should occur using the existing trial plant, where different modified catalysts can be established.

Moreover a pilot plant for producing FT fuels from synthesis gas from the biomass gasification should be planned. This pilot plant should contain all required components (precision cleaning, FT synthesis, fractional condensation). The size of this pilot plant should be selected that way, so that the production of FT fuels in bigger amounts is possible. These fuels should be used for PKW as soon as the development of further treatment processes like hydrogenation. The design of the plant should be performed as far as all important components are structural described.

The performance of the project is carried out according to the work packages, which are expressed in the project proposal (see Table 3).

Table 3: Overview of the work package for Projekt EZ-LP-IF

No	Titel	Status
AP 1	Selection of an applicable industrial available catalyst	completed
AP 2	Development of a design for a pilot plant (component testing plant)	completed

3 Biofuels

3.1 Background

Biofuel is a collective term for liquid and gaseous fuels which are mainly used in the transport sector and are predominantly produced from biomass. In view of the sustainable effect they are offering reduction of greenhouse gas emissions, regional development, social structure and agriculture, security of supply [1] and new income and employment opportunities in rural areas. Thus, the European Union (EU) determine in the adoption of a directive to support the utilization of biofuels and other renewable fuels. The directive 2003/30/EC requires the member states to maintain the indicative target for the share of biofuels to all petroleum-derived fuels for transport utility. This targets shall be 5.75 %, calculated on the basis of energy content, by the end of 2010 [2][3]. Moreover, an exception of the biofuels from the taxation works as a promotion, which is regulated by the directive 2003/96/EG [4]. Before the directive has been issued the EU set up the conception to substitute 20 % of conventional fuels in transport sector by alternative fuels such as biofuel, hydrogen and natural gas as well. The target shares of the alternative fuels in the transport sector until 2020 are given in Table 4 [5]. To achieve these European objectives a need for actions from short until long term are indispensable [6].

Table 4: Planned target share of alternative fuels in the EU [5]

	2005	2010	2015	2020
Biofuel	2 %	6 %	7 %	8 %
Natural Gas	0 %	2 %	5 %	10 %
Hydrogen	0 %	0 %	2 %	5 %
TOTAL	2 %	8 %	14 %	23 %

So far, the current biofuel supply is mainly based on so called “1st generation biofuels” [6] which are primarily produced from food crops such as grains, sugar beet and cane, and oil seeds. Due to the possible undue competition for land and water for food and fibre production the production of first generation biofuel is under review. An alternative to these biofuels are biofuels produced from non-food biomass. These “2nd generation biofuels” are using feedstock based on lignocellulosic materials such as straw, bagasse, forest residues, and purpose-grown energy crops including vegetative grasses and short rotation forests [7].

Table 5 and Table 6 represent the biofuels of the first and second generation and the feedstock used in their production [8].

The global production of biofuel increased from 4.8 billion gallons in 2000 to about 16.0 billion in 2007. This corresponds for less than 3 percent of the global transportation fuel supply. The United States, Brazil and EU are providing about 90 percent of the biofuel production [9].

Table 5: First generation biofuel and the feedstock used in their production [8]

Biofuel type	Specific names	Biomass feedstock
Bioethanol	Conventional bioethanol	Sugar beet, grains
Vegetable oil	Pure plant oil (PPO)	Oil crops (e.g. rape seed)
Biodiesel	Rapeseed methyl ester (RME), fatty acid methyl/ethyl ester (FAME/FAEE)	Oil crops (e.g. rape seed)
Biodiesel	Biodiesel from waste	e.g. frying and animal fat
Biogas	Upgraded biogas	(wet) biomass
Bio-ETBE		Ethanol

Table 6: Second generation biofuel and the feedstock used in their production [8]

Biofuel type	Specific names	Biomass feedstock
Bioethanol	Cellulosic bioethanol	Lignocellulosic
Synthetic biofuels	Biomass-to-liquids (BTL): Fischer-Tropsch (FT) diesel Biodimethylether (DME) Biomethanol SNG (Synthetic Natural Gas) Synthetic (bio)diesel Bio-Methyl-tert.-Butylether (MTBE)	Lignocellulosic
Biodiesel	Hydro-treated Biodiesel	Vegetable oils and animal fat
Biohydrogen		Lignocellulosic

3.2 First Generation

As already mentioned, there are several biofuels which are distinguished between their feedstocks and conversion processes. Currently, biofuels of the first generation, predominantly bioethanol and biodiesel, can be supplied in substantial amounts and they have mature commercial markets and progressive technologies [7][10]. **Fehler! Verweisquelle konnte nicht gefunden werden.** provides an overview about the conversion processes of biodiesel and bioethanol.

Biodiesel consists of fatty acid methyl ester (FAME) and is obtained via transesterification, a process where oil or fat reacts with methanol. An alternative to the fossil fuel derived methanol could be to use biomethanol or bioethanol for the production of Fatty Acid Ethyl Ester (FAEE) [11][8]. In comparison to the petroleum-derived diesel the biodiesel is superior in sulphur content, flash point, aromatic content and biodegradability [1]. In conventional diesel engine systems FAME biodiesel can be blended with petroleum diesel or used in pure form with only minor fuel system modification. Due to the solvent quality of FAME biodiesel, special adaptations in the fuel and engine system are necessary for long-term operation with biodiesel fuel. The higher the blend level, the higher the degradation [11]. It is feasible to undertake the transport, storage and retail system of conventional diesel as well for biodiesel [10].

The conventional diesel engine requires minor modifications to run on vegetable oils due to the relatively high viscosity. To reduce the viscosity of the oil it is converted to FAME or FAEE diesel via transesterification [12].

The production of bioethanol is based on the conversion of any biological feedstock that contains considerable amounts of sugar or materials such as starch or cellulose that can be converted into sugar. Basically, bioethanol is produced by enzymatic fermentation of the sugar. Depending on the utilization of the feedstock they may be separated into biofuel of first generation or as well second generation [11].

The fuels and car manufacturer communities postulate that almost all conventional gasoline engines are fully compatible with blends of 10 % bioethanol and 90 % gasoline. At higher addition of bioethanol some modifications of the engine are necessary and vary with local conditions such as climate, altitude and driver performance criteria. Flexible fuel vehicles enable to utilize any bioethanol blends. Bioethanol blends can be distributed through existing infrastructure system with relatively minor changes [11].

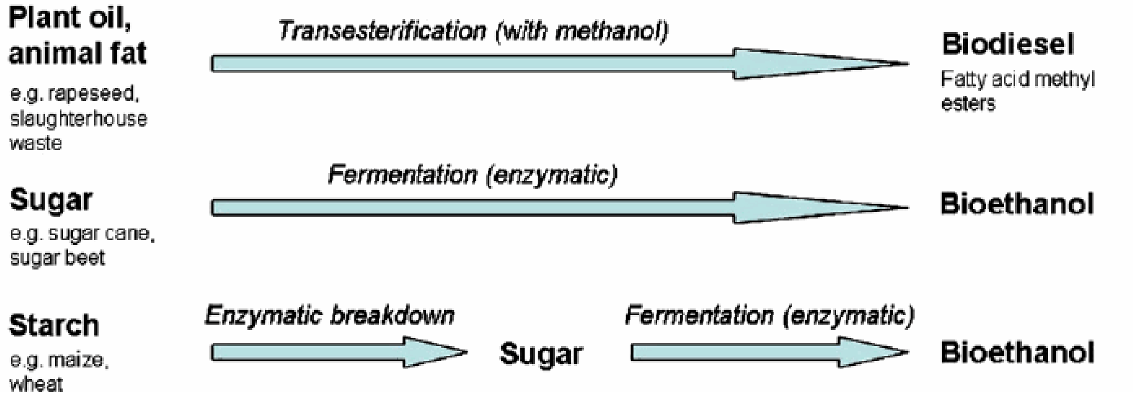


Figure 1: Conversion processes from biomass to biofuel [10]

In comparison to petroleum-derived fuels biodiesel and bioethanol have a lower energy density which is made up by a higher combustion efficiency [11]. Furthermore, the emissions of biodiesel and bioethanol are less polluting than petroleum-derived fuels. A positive well-to-wheel greenhouse gas balance of biofuels depends on the feedstock production, biofuel generation and biofuel distribution [10].

In order to prevent the limited land availability in Europe for energy crops, which are determining for the biofuel production, it is essential to promote sustainable investigations [10]. Therefore, to the further development for the efficiency of the biodiesel and bioethanol production, the development of the biofuels of the second generation is essential to make biofuels more competitive to fossil fuels.

3.3 Second Generation

In comparison to the first generation the second generation utilizes lignocellulosic biomass as feedstock which is non-edible and hence the competition to the food production are limited or avoided [14]. Lignocellulosic are originated from crop, forest or wood process residues, or long-lasting grasses and trees [7]. The processes used to convert the biomass to fuel are classified into biochemical and thermochemical. The biochemical process is adapted for ethanol and butanol production while the thermochemical process is the production pathway for synthetic fuels, including methanol, methane, Fischer-Tropsch liquid (FTL) and dimethyl ether (DME) [14].

Currently, the conversion technologies of the second generation biofuels are not technical proven at a commercial scale and the fuel production costs are estimated to be relatively higher than many of the first generation [7].

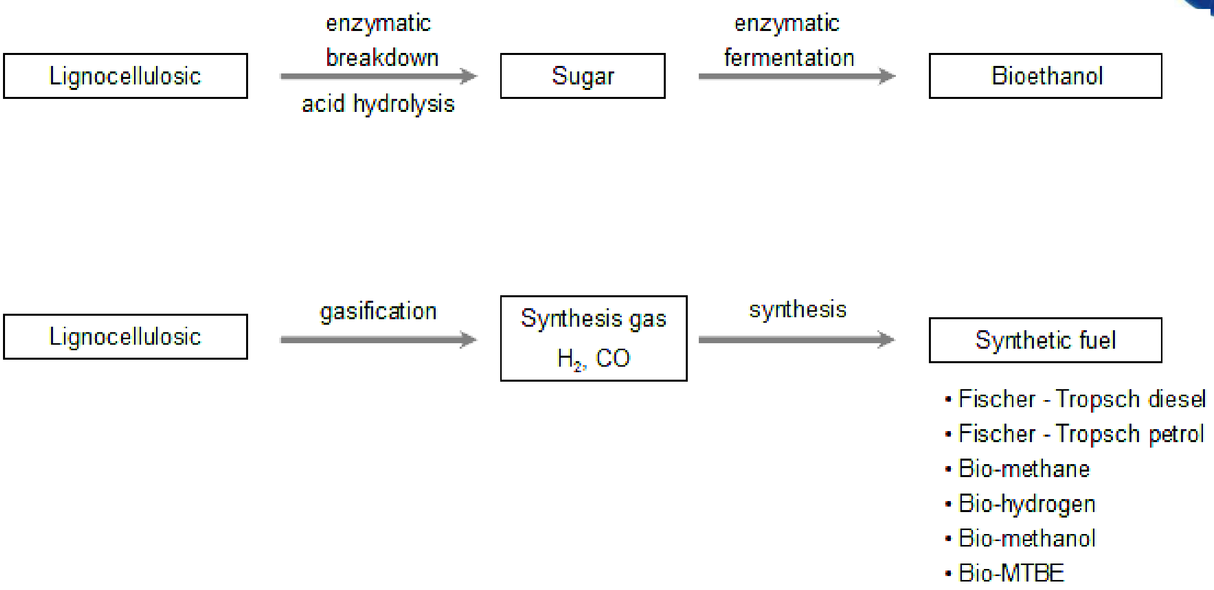


Figure 2: Second generation biofuel production and their conversion process [13]

The production of bioethanol of the second generation is made analog like the bioethanol production of the first generation whereby due to lignocellulosic as feedstock the compounds are broken down by an acid hydrolysis. In the thermochemical pathway, synthesis gas is generated through the gasification of residues or plant materials consisting of lignocellulosic. The yielded valuable gaseous product, including hydrogen and carbonmonoxide, can be used for several synthesis reactions to produce synthetic fuel [13].

Hydrogen can be attained with reforming the product of a gasification and pyrolysis that is on the one hand the synthesis gas and on the other hand the carbohydrate fraction of the bio-oil. The two equations, water-gas shift and steam methane reforming ((2.1)) are the main reactions for hydrogen production [1][15]. The water-gas shift equation is illustrated in chapter 4.3.

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad \Delta H_r^{\circ} = +251 \ kJ/mol \tag{1}$$

ΔH_r° ….. building enthalpy at standard conditions (25°C; 1bar)

For the extraction of methane the obtained synthesis gas is converted in a nickel based catalyst at a pressure of 5 – 10 bar and a temperature of 300 – 400 °C [13]. The methanation is described by following equation:

$$CO + 3H_2 \longrightarrow CH_4 + H_2O \qquad \Delta H_r^{\circ} = -206{,}0 \ kJ/mol \tag{2}$$

The use of different catalysts can lead to the conversion of methanol, including reduced NiO-based preparations, reduced Cu/ZnO shift preparations, Cu/SiO_2 and Pd/SiO_2, and Pd/ZnO [1]. The Cu/ZnO-Al2O3 catalyst works at a temperature of 220 – 275 °C and pressure of 50 – 100 bar [15]. The following equation illustrates the methanol synthesis:

$$CO + 2H_2 \longrightarrow CH_3OH \qquad \Delta H_r^{\circ} = -91 \ kJ/mol \tag{3}$$

For further utilization as a chemical intermediate methanol is used for the DME and methyl tert-butyl ether (MTBE) conversion. To produce MTBE methanol is reacting with isobutene in the presence of an acidic catalyst [15].

$$i - C_4H_8 + CH_3OH \longrightarrow (CH_3)_3COCH_3 \qquad \Delta H_r^\circ = -37 \ \ kJ/mol \tag{4}$$

After methanol is synthesized ((2.3)) it is dehydrated over an acid catalyst at methanol synthesis conditions whereby DME is yielded [15]. The methanol dehydration is given in equation (2.5).

$$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O \qquad \Delta H_r^\circ = -23 \ \ kJ/mol \tag{5}$$

Fischer-Tropsch liquids are formed in the Fischer-Tropsch synthesis where the synthesis gas is transformed into hydrocarbon products in highly exothermic reactions [15]. The theoretical background of the Fischer-Tropsch synthesis that is substantial within of this work is illustrated in the following section.

4 Fischer-Tropsch Synthesis

4.1 Introduction

The Fischer-Tropsch (FT) synthesis converts a gas mixture of carbon monoxide (CO) and hydrogen (H_2), also called syngas, into short and long chain hydrocarbons. Based on a chain-growth mechanism at the catalyst a specific product spectrum emerges. Depending on the temperature in the reactor it is distinguished between high temperature FT (HTFT, 300-350°C) and low temperature FT (LTFT, 200-240°C). The reaction carried out at an operating pressure of up to 40 bars. Principally, the basic steps for producing FT products are syngas generation, gas purification, FT synthesis, and product upgrading [15][16].

4.2 Development of the Fischer – Tropsch Synthesis

The origin of the FT synthesis goes back in the start of the 20th century. In 1902 the French inventors Sabatier and Senderens worked on a CO hydrogenation at high temperature of 200 to 280 °C and atmospheric pressure over Ni- and Co-catalysts to yield methane [17][18]. In 1908, Haber and Bosch established the ammonia synthesis and in 1913 Bergius developed the direct hydrogenation of coal [19]. But the main turn for the FT synthesis brought the patented process of the Badische Anilin- und Soda-Fabrik (BASF) in Ludwigshafen in 1913 [20]. According to the patent, hydrocarbons other than methane, alcohols, ketones and acids were produced via a catalytic hydrogenation of CO at high temperature and pressure, 300 – 400 °C and 120 atm. But BASF did not continue the work at this technological achievement and focused on the ammonia and methanol synthesis [21]. Based on the patented work by BASF, the German scientists Franz Fischer and Hans Tropsch continued the work on the synthesis of hydrocarbons at the 'Kaiser Wilhelm Institut für Kohlenforschung' (today Max-Planck-Institut), Germany. In 1920 and in 1925 their discoveries were patented [19][22]. At the first experiments with a gas mixture of carbon monoxide and hydrogen, called synthesis gas, Fischer and Tropsch reacted the gas in an alkali-iron catalyst, not into hydrocarbons but into a mixture of oxygen containing organic compounds that they called "synthol". In hope to produce liquid hydrocarbon motor fuels they continued this synthol - work and developed an iron-copper catalyst which enables to operate on lower temperatures and atmospheric pressure. Thereby, the oxygenated compounds are completely eliminated and only hydrocarbon gases and liquids are achieved [21].

In 1935 the industrialization of the FT process started with the first commercial facility by Ruhrchemie in Oberhausen, Germany. By the end of 1938, in Germany there were nine plants in operation and had a total production capacity of liquid fuels on FT synthesis basis of 660 ktons per year (kt/a) [19][23]. The syngas was exclusively produced from coal. During World War II, further FT complexes were built on Ruhrchemie licenses in Japan. After the war the interest in developing the FT process still existed. Therefore, Ruhrchemie and Lurgi advanced a fixed bed process with an iron catalyst, called ARGE reactor. In 1955, this reactor was installed the first time in Sasolburg, South Africa. The USA focused on the development of fluidized bed reactors for high temperature FT synthesis. Also this technology was commercially realized in South Africa. In the middle 1950s, FT synthesis and the plants became uneconomical due to the extremely low oil prices of that time. Because of political reasons, South Africa was obligated to continue the coal based FT fuel production. Until the first oil crisis the FT process was exclusively developed in South Africa. As a result several processes and reactor technologies have been developed and applied in South Africa. Nowadays, the most economic way to produce liquid fuel is to use natural gas for syngas generation (Gas To Liquid, GTL). Already existing and under construction large-scale industrial FT complexes will increase the worldwide capacity for fossil base FT fuels to about 30 Mt/a in 2010 [19].

Table 7: Existing and plants under construction for conventional FT synthesis **[19]**

Existing plants	Capacity [bpd (kt/a) *]	Raw material	Commissioning date
Sasolburg – South Africa	2500 (120)	Coal	1955
Secunda – South Africa	85000 (4000)	Coal	1980
Secunda – South Africa	85000 (4000)	Coal	1982
Mossel Bay – South Africa	30000 (1400)	Natural gas	1992
Bintulu – Malaysia	12500 (580)	Natural gas	1993
Qatar – Saudi Arabia	34000 (1600)	Natural gas	2006
Under construction			
Escravos – Nigeria	34000 (1600)	Natural gas	2007
Qatar – Saudi Arabia	140000 (6500)	Natural gas	2009

* barrels per day (values in kt/a calculated with assumed average product density of 800 kg/m³)

In addition to GTL the coal liquefaction (Coal To Liquid, CTL) via FT synthesis is becoming a significant technological alternative for fuel production especially in the USA and China due to their enormous coal reserves. However, CTL and GTL bring along additional CO_2 emissions during the entire fuel production which is a result of the deficient hydrogen content [19]. As already mentioned, an alternative to this unsustainable fuel production is the utilization of biomass as raw material for the syngas production. FT synthesis based on biomass is based on a new technology and therefore it requires progressing research and development.

4.3 Chemistry

The FT reactions stand for a catalytic polymerization reaction where components carbon monoxide and hydrogen react to hydrocarbons. The components carbon monoxide and hydrogen of the syngas can for instance be produced from the gasification of wood. Through the synthesis in highly exothermic reactions the carbon monoxide is hydrogenated to CH_2 units. Parallel to the FT reactions the CH_2 units are added into products of different chain lengths and function, depending on catalyst and synthesis conditions. These products are predominantly linear compounds such as paraffins, olefins and in inferior amounts oxygenated compounds [24][25][26]. The Figure 3 shows a simplified representation of the FT hydrocarbons production from the gasification to the final product.

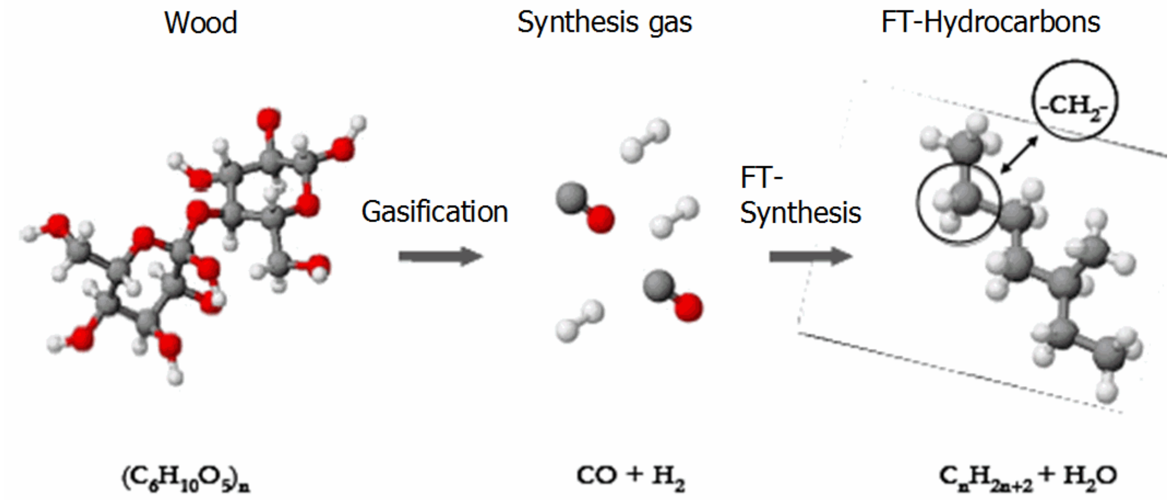


Figure 3: FT synthesis pathway to hydrocarbons (modified in [27])

The general equation of the FT synthesis and its reaction enthalpy is given in the following equation [28]:

$$CO + 2H_2 \longrightarrow (-CH_2-) + H_2O \qquad \Delta H_r^\circ = -152 \ kJ/mol \tag{6}$$

The exothermic water-gas shift reaction occurs in addition to the FT reaction when iron catalysts are used [28]:

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad \Delta H_r^\circ = -41 \ kJ/mol \tag{7}$$

Therefore, the net reaction for an iron catalyst is obtained by combining the equations (6) and (7) [28]:

$$2CO + H_2 \longrightarrow (-CH_2-) + CO_2 \qquad \Delta H_r^\circ = -193 \ kJ/mol \tag{8}$$

The following equations are representing the main reactions which can occur during synthesis. Besides to the reaction of paraffin, olefin, alcohol and aldehydes also the methanation ((2.2)) is counted to the FT reactions [15]:

$$nCO + (2n+1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O \qquad Paraffins \tag{9}$$

$$nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O \qquad Olefins \tag{10}$$

$$nCO + (2n+1)H_2 \longrightarrow C_nH_{2n+1}OH + (n-1)H_2O \qquad Alcohols \tag{11}$$

$$nCO + (2n+1)H_2 \longrightarrow C_{n-1}H_{2n+1}COH + (n-1)H_2O \qquad Aldehydes \tag{12}$$

The Boudouard reaction ((3.8)) is a further reaction which plays an important role in FT synthesis. Through the carbon deposition on the catalyst surface the catalyst is deactivated [15].

$$2CO \longrightarrow C + CO_2 \qquad \Delta H_r^\circ = -172 \ kJ/mol \tag{13}$$

During the FT synthesis the methanation and the Boudouard reaction are undesirable and have a reducing effect on the performance. They mainly depend on the reaction temperature. Increasing temperature promotes methane formation and carbon deposition that causes yield losses. To avoid this, appropriate choice of the operation parameters and adjustment of the syngas ratio are essential [30].

4.4 Reaction Mechanism

The general FT reaction (3.1) can be seen as a repeated reaction sequence in which hydrogen is added to carbon and oxygen while C-O bond is split and new C-C bond is formed. To form one CH2 unit at least the following reactions have to occur [29]:

- associative adsorption of CO
- splitting of the C/O-bond
- dissociative adsorption of 2H2
- transfer of 2H to the oxygen to yield H2O
- desorption of H2O
- transfer of 2H to the carbon to yield CH2
- formation of a new C/C-bond

Since the discovery of the FT synthesis various mechanisms have been proposed. The mechanism of the FT reaction on the catalyst surface is reviewed by Fischer, Anderson, Pichler and Schulz and by other. Fischer proposed surface carbides by the carbene mechanism. On the other hand this mechanism did not explain the formation of the large amounts of oxygenated products additionally to the paraffins and olefins. Therefore Anderson proposed a mechanism involving hydroxyl carbenes and Pichler and Schulz proposed the CO-insertion mechanism as explanation. Due to several variants for each mechanism only the important aspects of the reaction mechanisms are given here [31][32].

In the carbene mechanism the CO molecules are adsorbed and dissociated on the metal surface. By hydrogenation of the single carbon atoms the monomer CH_2 is formed. These methylene ($=CH_2$) units are the key intermediate and polymerize to surface alkyl species to form longer hydrocarbon chains [31][33]. The scheme of the hydrogenation of surface carbides to methylene groups is shown in Figure 4Figure 4: Schematic representation of initiation, chain growth and termination of the three main FT reaction mechanism [34].

In the hydroxycarbene mechanism, CO molecules are adsorbed but not dissociatively and are hydrogenated to hydroxycarbene units (CHOH-) which are the key intermediates. Two hydroxycarbene compounds are linked up by the elimination of water [31][33]. In Figure 4 the mechanism is given schematically. This mechanism provides a possible explanation for the formation of oxygenated compounds such as alcohols via hydrogenation and aldehydes via desorption. The hydrocarbons occur by the elimination of the OH units via hydrogen [33].

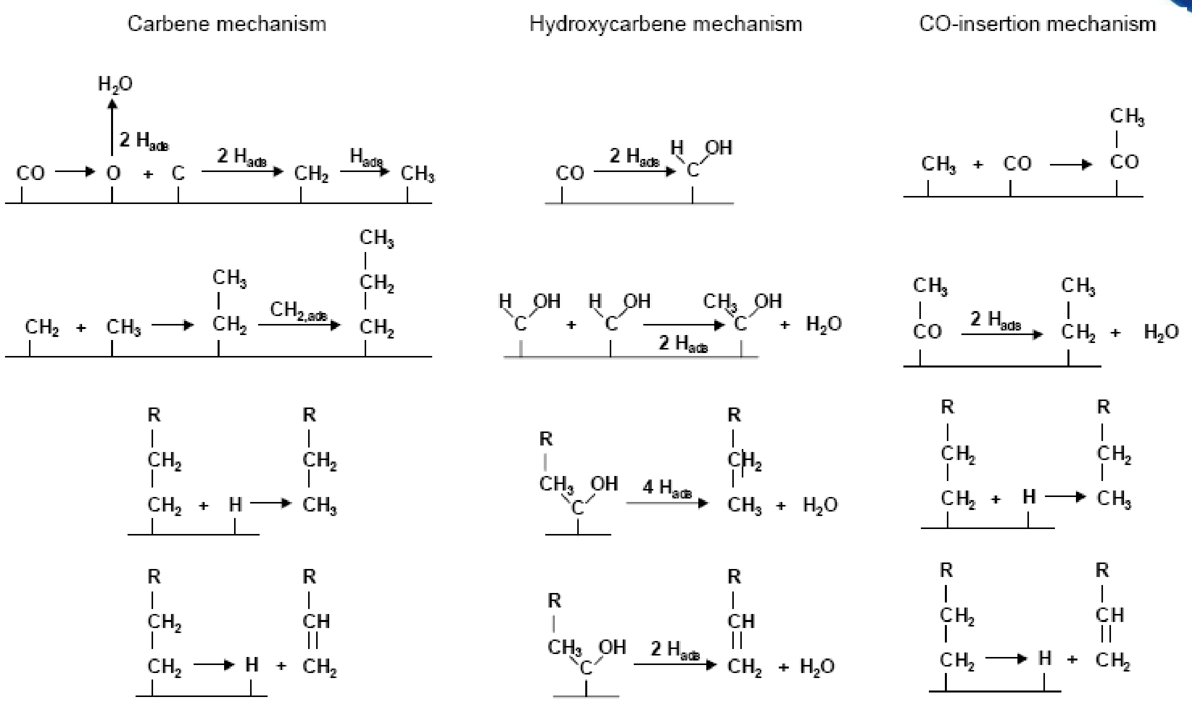


Figure 4: Schematic representation of initiation, chain growth and termination of the three main FT reaction mechanism [34]

The CO-insertion mechanism describes the chain growth via the insertion of a carbonyl intermediate (CO-) into the metal alkyl bond. The resulting compound is hydrogenated to an alkyl chain. Through the CO as monomer this mechanism explains the formation of alcohols, aldehydes, and hydrocarbons as well. The scheme of the CO-insertion mechanism is represented in the following [33].

After numerous examinations it is assumed that the combination CO-insertion mechanism and the carbene mechanism are the most probable [33]. Dry postulates that it can be assumed that chain growth is a stepwise process and the distribution of products is dependent only on the probability of chain growth (α) and thus the choice of reaction mechanism may be insignificant by changing the product spectrum. Dry further argues that the exact detail about the mechanism is not essential as long as process and catalyst parameters are well defined and manipulated accordingly [31].

4.5 Product selectivity

4.5.1 *Probability of chain growth*

The FT product selectivity is dependent on the ability of the catalyst to catalyze chain propagation against chain termination reactions. On the other side the produced products have no influence on the polymerization rate and furthermore, the probability of chain growth and chain termination are not affected by chain length. Assuming that chain growth is a stepwise process the entire product spectrum can be calculated. Therefore, a simple statistical distribution calculated from chain growth probability and carbon number can predict the selectivity of the various hydrocarbons [15][31]. This chain polymerization kinetics models, so called Anderson-Schulz-Flory (ASF) model, can be described by following equations:

$$\alpha = \frac{R_p}{R_p + R_t} \tag{14}$$

$$W_n = n(1-\alpha)^2 \cdot \alpha^{n-1} \tag{15}$$

R_p is the rate of chain propagation and R_t is the chain termination. W_n stands for the weight percent of the n carbon atoms held in the product whereby α is the chain growth probability [17][33]. The results of the ASF kinetics model are presented in Figure 5. The results from experimental determined product spectra and distribution are reflected, with only a few exceptions which are C_1 and/or C_2, in the curves of Figure 5Figure 5: Anderson-Schulz-Flory calculated product distribution [31]. The ASF model provides a correct overview about high yields which are only possible at the extreme ends of the spectrum, for instance CH_4 and waxes. For fractions in between only certain limits are possible for instance a maximum selectivity of 19 % for C3, 45 % for gasoline and around 25 % for diesel fuel [31].

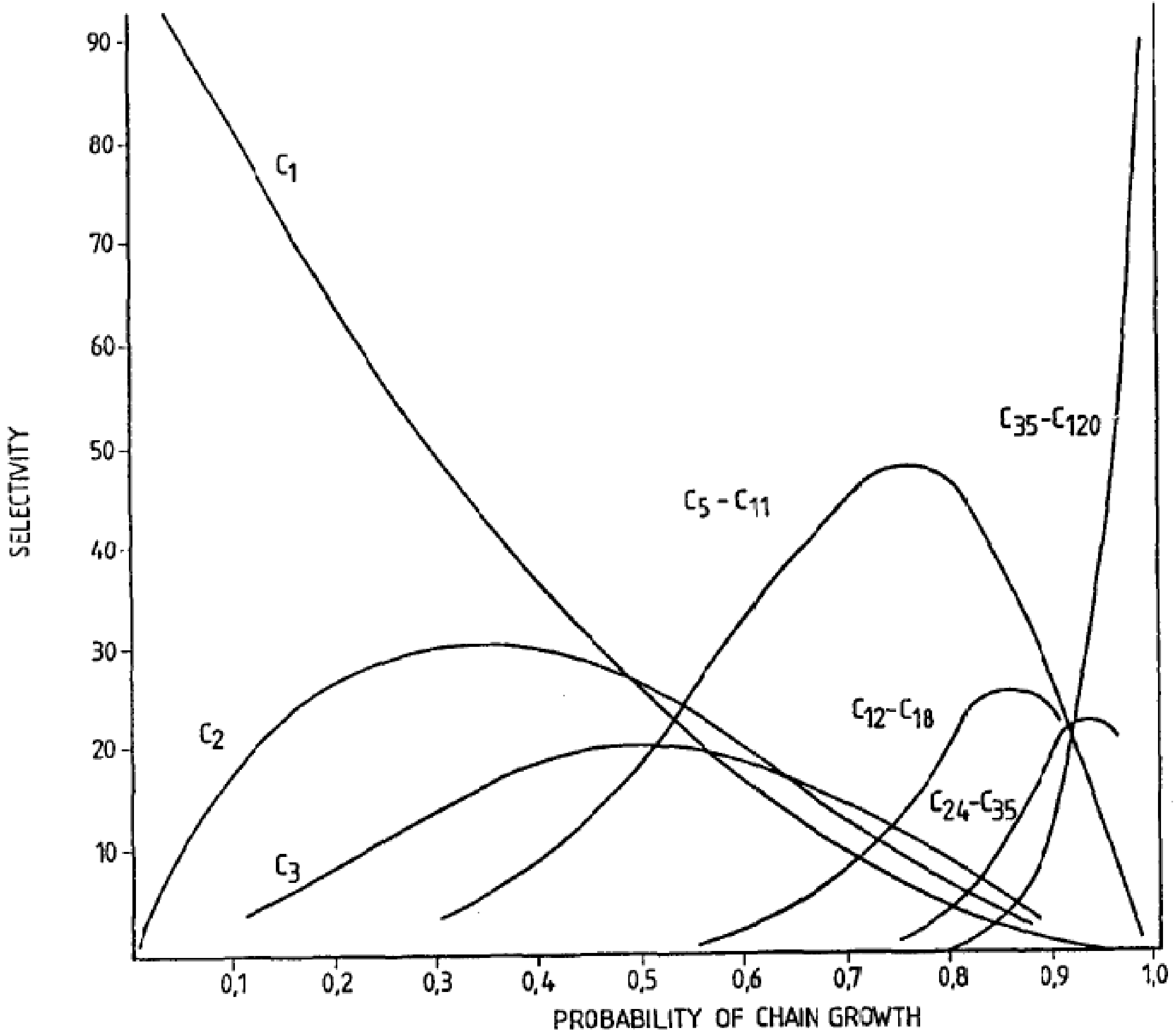


Figure 5: Anderson-Schulz-Flory calculated product distribution [31]

4.5.2 *Process effects*

As mentioned before the FT synthesis as polymerization-like chain growth reaction produces, irrespective of operating conditions, a wide range of hydrocarbons and oxygenated products. The operating parameters such as temperature, feed gas composition, pressure, catalyst type, and promoters influence the product distribution [23].

Temperature

The parameter temperature has independent of the feed gas composition at all FT catalyst always the same affect. With increasing operating temperature the selectivity moves towards lower carbon number products and to more hydrogenated products. In other words, the probability of chain growth decreases and CH_4 production increases. A probable explanation is the increased rate of hydrogenation of the CH_2 units to CH_4, which results in a decrease of the surface concentration of CH_2 units. This predicts the thermodynamic expectations that CH_4 formation is much more favoured than higher hydrocarbons [32][23].

Feed gas composition and pressure

Chemisorbed CO leads to the formation of CH_2 monomers and hydrogen to the chain growth termination. This mechanistic model proves the correlation between the H_2/CO ratio and the product distribution. The effect of the feed gas composition on the catalyst arises from the fact that CO (at iron catalyst also H_2O) chemisorbs strongly on the catalyst surface, while hydrogen is absorbed weekly. Under synthesis conditions the coating of the surface via hydrogen in comparison to CO (H_2O) is low. The cover with hydrogen is direct proportional to the partial pressure of hydrogen and inversely proportional to the partial pressure of CO and H_20. If the spread with hydrogen is increased by raising the hydrogen partial pressure then the probability will increase that the existing CH_2 species hydrogenates to methane and the long chain alkyl species do not continue to react but rather are hydrogenated to paraffins. That implies that the probability of chain growth is decreasing and the product spectrum moves to low carbon number products. Conversely, with increasing partial pressure of CO or H_2O high carbon number products are yielded. In this way the product distribution can be influenced by increasing or decreasing the hydrogen share. The process temperature has to be taken into account because in dependency of the temperature an altering affect of the feed gas composition on the catalyst exist [35].

For the cobalt based FT catalyst a H_2/CO usage ratio of about 2.15 is necessary, while when an iron based catalyst is used the water-gas shift reaction changes the overall usage ratio. Dependent on the temperature, the H_2/CO usage ratio lies at an iron based catalyst between 1.05 and 1.7 [23]. At the low temperature FT process for both iron and cobalt catalysts there is a relationship between the probability of chain growth and the H_2/CO usage ratio. The total pressure has for the iron catalyst only a little influence on α while for the cobalt catalyst α increases with increasing pressure up to 20 atm. A promoted iron catalyst is used for the high temperature FT process and α is influenced by the total pressure. But the gas factor that controlling α is a more complex one, involving the partial pressures of H_2, CO, CO_2 and H_2O [36].

The effects on the FT product selectivity by catalyst type and promoters are given in the following section.

4.6 Catalysts

4.6.1 *Generell*

For commercial application as catalyst material with a sufficient activity in the FT process only iron (Fe), cobalt (Co), nickel (Ni), and ruthenium (Ru) are suitable. Ruthenium is the most active one but it is very limited available and therefore it is very expensive. Nickel is also very active but it has two drawbacks: as powerful hydrogenating catalyst it produces too much CH_4 and with increasing pressure it forms volatile carbonyls and so it is continuously lost from the reactors. Consequently, iron- and cobalt-based catalysts are the only ones for practical use. The relative costs on metal basis of Fe:Co:Ni:Ru are 1:1000:250:50,000. The iron cobalt price difference is balanced by the higher activity and longer life time of Co [36].

4.6.2 *Deactivation*

Conversion of active metal site to an inactive oxide site, sintering, carbon deposition and poisoning are reasons for activity loss of FT catalysts. Some of these mechanisms are unavoidable and others can be prevented or minimized by ensuring that the used syngas obtains a cleanliness that is acceptable for the FT process [15].

Carbon and coke deposition is a deactivation mechanism that is largely unavoidable but it can be controlled by addition of promoters to catalysts, reaction temperature and pressure. The coke deposition can be removed via a high temperature hydrogen treatment wherewith the catalyst gets its activity back. Nevertheless, it is more economic to replace the catalyst than to lose production time due to hydrogen treatment. Cobalt-based catalysts have longer lifetimes based on the circumstance that coke deposition is higher for iron catalyst than cobalt catalyst.

Impurities in the syngas have a high poisoning potential to deactivate the catalyst whereas these components can be minimized to a harmless quota. For Fe, Co, and Ru sulfur-containing compounds, such as H_2S and organic sulfur compounds, have a permanent poisoning effect and thus the sulfur content must be lower than 0.1 mgS/Nm^3 syngas. This marginal value can be achieved for instance via “Rectisol” process (cold methanol scrubbing) which removes the sulfur content well. Chlorine also causes a deactivation of the catalyst because of its acidity. But the poisoning by chlorine has a lesser extent than sulfur [15][31].

4.7 Reactors

As mentioned before, there are two FT operation modes: The HTFT process at 300 °C to 350 °C with application of an iron-based catalyst and the LTFT process at 200 °C to 240 °C with application of either iron- or cobalt-based catalyst. Due to the fact that the FT reactions are highly exothermic it is substantial to remove the heat of the reactions from the catalyst particles to avoid overheating and 'hot spots'. Thereby, undesired formation of methane and also possible catalyst deactivation by coking and sintering and catalyst disintegration via Boudouard carbon deposition are avoided. Iron-base catalyst is easier infected by latter contamination as the cobalt-based catalyst [23][36].

There are two classes of reactors, the fixed bed and fluidized bed reactors. The fluidized bed reactor are divided into circulating fluidized bed, stationary fluidized bed and slurry reactor, whereby the circulating and the stationary fluidized bed reactors work at high temperatures. The application of the fixed bed and slurry reactor are at low temperature [32]. In this chapter are also new reactor concepts described including structured, microstructured and membrane reactors.

4.7.1 *Commercial Reactors*

Low-temperature operation

The principle of the multitubular fixed bed reactor (Figure 6) is that the catalyst particles are packed into narrow tubes in which the syngas is passed in a high flow to ensure rapid heat exchange. These tubes are surrounded on the outside by water that is converted to useful steam. The advantage of the narrow tubes is that the distance between the hot catalyst particles and the heat exchanger surface is low. Furthermore, the high syngas velocity causes a turbulent flow and that anon minimizes the settlings around the catalyst particles and at the heat exchanger walls. These conditions enable the rapid heat exchange and, thus, minimize exothermic temperature rises. The advantages of the multitubular fixed bed reactors are that they are easy to handle and to design, because the parallel tubes behave very similarly. The construction of the reactor enables simple separation of liquid products from the catalyst. The product trickles down through the bed and is separated by a vessel. Therefore, the fixed bed reactors are well suited for wax production. On the other hand the drawbacks are the relatively high capital costs and high gas compression costs caused by a high differential pressure over the packed fixed bed. Additionally, the removal and addition of the catalyst is a labor intensive process while the narrower the tubes the more difficult and time consuming the exchange.

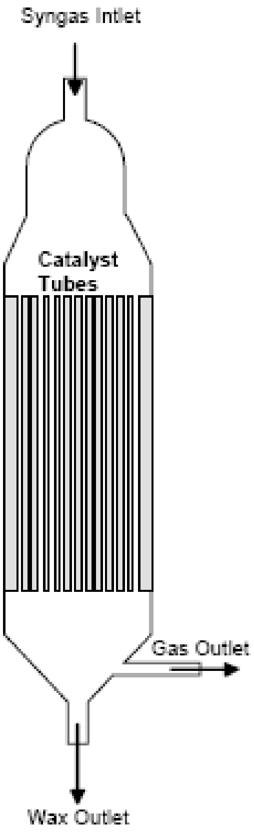


Figure 6: Multitubular fixed bed FT reactor [15]

The first commercialized fixed bed reactor was developed by Ruhrchemie and Lurgi in 1955. These so called and still used ARGE reactors operate at 25 bar and at a temperature at about 225 °C. The reactor consists of 2052 parallel tubes with diameters of 4 cm. The entire reactor is 12.8 m long and has a diameter of 2.95 m, filled with 40 m³ catalyst material. 50 % of the product is liquid wax. Based on the fixed bed reactor technology, Shell developed the Shell Middle Distillate Synthesis by using cobalt catalysts. The tubes have a diameter of 2.54 cm and a length of 12.2 m and this technology had successfully operated over several months [32][19].

A second reactor type that operates at low temperature is the slurry reactor (Figure 7), a version of the fluidized bed reactor. At this system the catalyst particles are suspended in a liquid, mainly FT wax product, through which the syngas is bubbled. The syngas streams from the bottom where it is dispersed via gas distributor to the top. Cooling coils ensure isothermal conditions in the reactor. The three-phases slurry system has temperature limitation, at a low temperature the liquid wax becomes very viscous while above about 280 °C the FT wax hydrocracks.

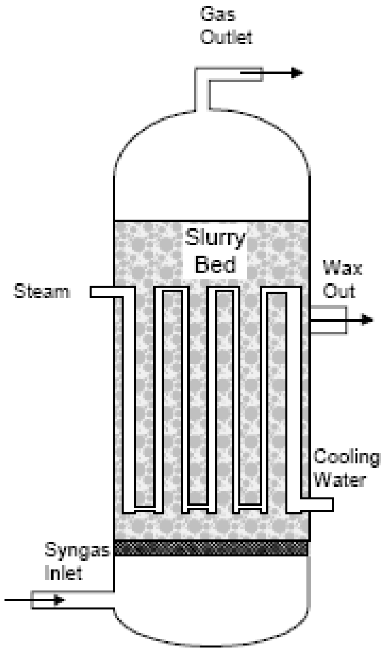


Figure 7: Slurry-phase bubbling-bed reactor [15]

The slurry reactor has many advantages over the fixed bed reactor, especially for FT wax production. The slurry reactor enables isothermal reaction conditions and thus no hot spots occur and a higher average temperature is possible. The catalyst particles are much smaller than in the fixed bed reactor and so the activity per unit mass of the catalyst is higher. The catalyst loading is lower and thus the catalyst consumption per unit product can be reduced up to 70 %. The removal and addition of the catalyst can ensue during operation which means much longer runs can be carried out. Compared to the multitubular fixed bed reactor the pressure drop over the slurry is significantly lower resulting in lower compression costs. Finally, the construction costs are also lower for the slurry reactor. A significant disadvantage of the slurry reactor in the wax producing mode is the separation of the net wax production from the suspended catalyst. There are several approaches from different companies to this problem and range from decantation to filtration [18][23][32][37].

The development of the slurry bed reactor is based on the invention of the Standard Oil Development Company in 1937. The objective of this invention was to control the temperature of catalytic gas reactions to maintain the reaction temperature within desired limits. Therefore, the catalyst was suspended in a liquid heat absorption medium and the suspension was passed through the reaction zone in direct contact with the reaction gas. It was patented in 1938 [38]. Kölbel developed in the 1950s the first commissioned slurry bed reactor for FT synthesis with 1.5 m inside diameter (i.d.) and 10 m³ volume. Sasol R&D started in the late 1970s to compare the performance of fixed and slurry bed systems with 5 cm i.d.. They found out that the two reactors gave similar conversions and selectivities. In 1993 a commercial unit with 5 m i.d. and 22 m height was built and has been operating successfully. Exxon successfully operated a cobalt-based catalyst in a 1.2 m i.d. slurry bed reactor for wax production [23][32].

High-temperature operation

A further alternative to the fixed bed reactor is the two-phase fluidized bed reactor. There are two types of two-phase reactors, the circulating fluidized bed (CFB) and the fixed fluidized bed (FFB) reactor which are depicted in Figure 8 (left figure). The CFB and FFB operate at high temperatures and thus only with iron-based catalysts. The yielded products under these conditions are linear α-olefins, gasoline and diesel fuel. The wax production is not possible with these reactors, because wax is liquid under FT conditions which results in agglomeration of the catalyst and hence de-fluidization [36].

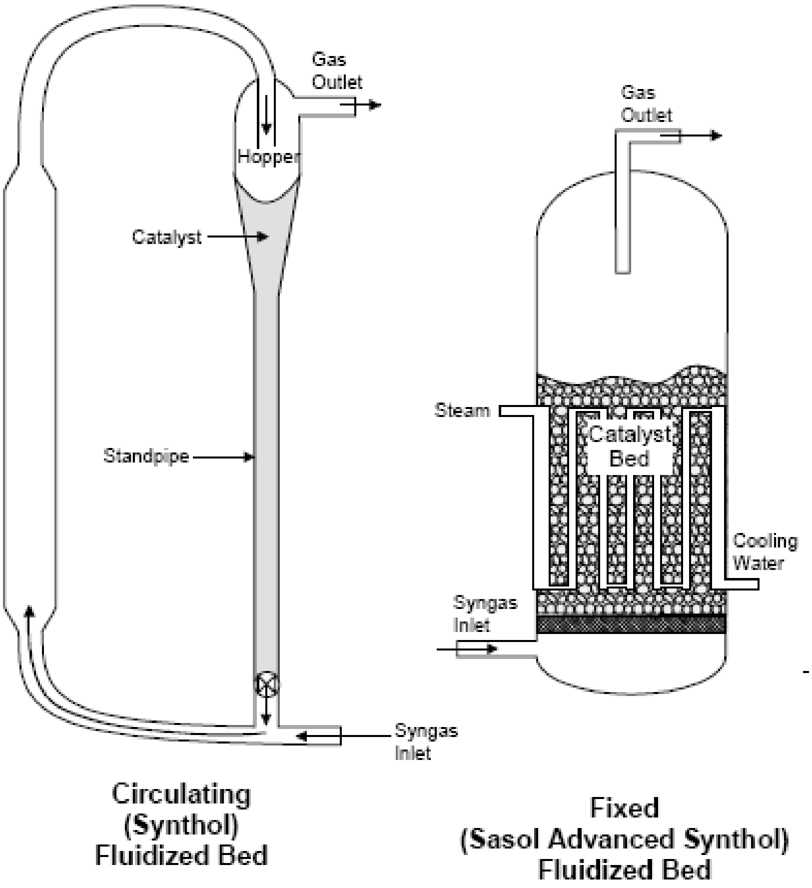


Figure 8: Fluidized bed FT reactors [15]

Sasol's first FT plant worked with the CFB reactor that was developed by Kellogg. The Sasol One plant consisted of a 2.3 m i.d. and 46 m high unit. The Sasol 2 and 3 CFB reactors, called Synthol reactors were improved and the capacities were increased threefold and have been operating successfully. The reactors work at about 350 °C and 25 bar with iron catalyst. The syngas enters with 200 °C into the reaction zone. At the bottom of the standpipe a slide valve adds catalyst to the syngas stream. In the reaction zone the heat exchangers remove about a third of the reaction heat. In the wide catalyst settling hopper section, the catalyst and gas are separated. The pressure drop over the stand pipe must always exceed that of the reaction zone else the syngas will stream through the standpipe instead.

A high catalyst loading in the reaction zone leads to a higher conversion. However, a problem is the carbon deposition on the catalyst at the high operating temperature which causes particle disintegration and a decrease in particle density. As a consequence, the activity of the catalyst is minimized and additionally the residence time and the catalyst loading in the reaction zone decreases.

Preventive, an online withdrawal of old catalyst and addition of fresh catalyst can avoid these problems [32].

The first commercial FFB reactor (Figure 8, right) operated, only for a short time, in the mid 1950s in the Brownsville, Texas, with about 20 bars and 300 °C. In the late 1970s, Sasol decided to continue the research and development of commercial size FFB units. In 1989 a 5 m i.d. and 22 m high unit came on stream. Until 1999, Sasol exchanged eight of their sixteen Synthol reactors by new FFB reactors [23]. In the FFB reactor the gas enters at the bottom through a gas distributor into the fluidized bed. Over cyclones gas and catalyst are separated [32]. The FFB reactor has many advantages over the CFB. For the same capacity the FFB reactor is in overall smaller and has 40 % lower construction costs. The wide construction of the reactor enables to install more cooling coils. The complete catalyst charge participates in the reaction, while in the CFB only a portion is included. The FFB has lower catalyst consumption. That is due to, the decreasing bulk density by carbon deposition has less significance in the FFB reactor and thus a lower rate of online catalyst changing can be accomplished. Compared to the CFB the FFB has lower gas and catalyst linear velocities and so only a slight abrasion and that allows longer on-stream times between maintenance inspections [23].

4.7.2 *New reactor concepts*

Structured Catalyst

The catalyst geometries are structured when the catalyst particles are ordered in a non-randomly fixed bed. Examples for these forms are catalytic packing, honeycomb or foam shaped catalysts. Honeycomb monolith channels are characterized by a large number of identical, parallel channels with a large geometric surface area. The honeycomb catalyst can be manufactured either completely from catalytically active material or an inert carrier is coated by a catalyst layer. Monolithic honeycombs have the property of high mass transfer and low pressure drop in gas-liquid reactions. On the one hand the mass transfer is optimized by the large surface area and on the other hand by choice of the optimal flow regime inside the capillaries. In order to achieve a high mass transfer coefficient and low pressure drop a slug flow regime is particularly advantageous. Currently, there are some honeycomb catalysts with cobalt coating in experimental stage. One problem is that the radial heat conductivity of ceramic honeycombs is very low. For this reason, to improve the temperature control the liquid product is circulating over an external heat exchanger [18][19].

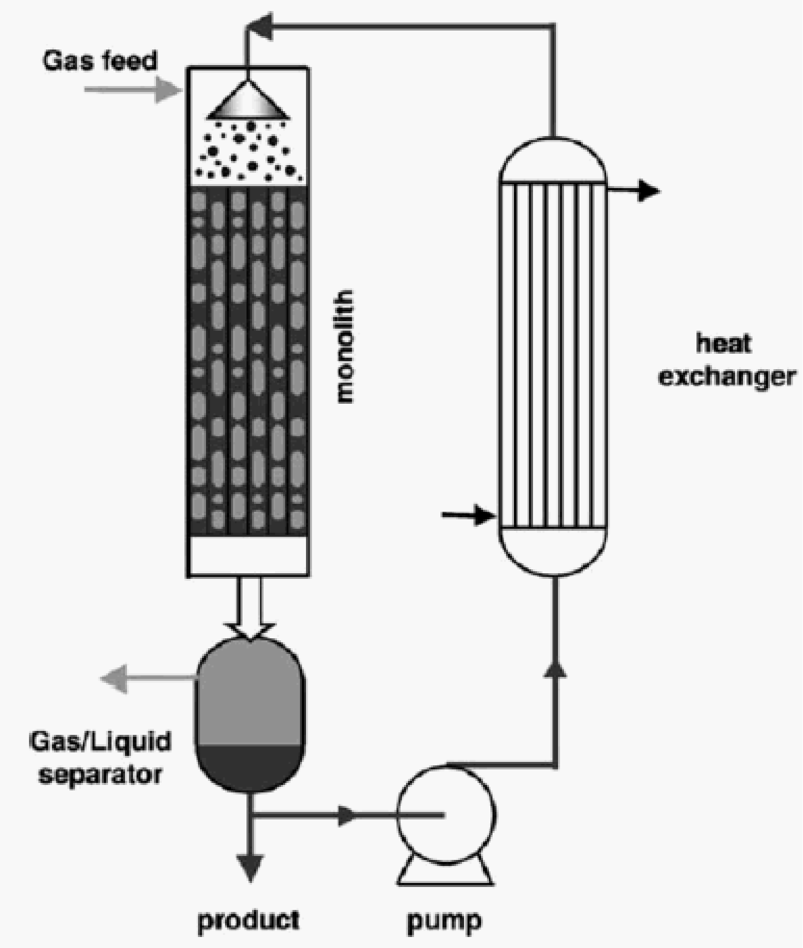


Figure 9: Honeycomb monolith reactor with external liquid recycle [19]

Microstructured reactors

Another reactor which is interesting especially for modern highly active catalyst is the microstructured reactor. The microstructured reactors use a large number of parallel small channels to improve the mass transfer characteristics. Consequently, the heat transfer is intensified which makes isothermal operation even for highly exothermic reactions possible. So far only a few results on the use of micro reactors have been reported. It is assumed that with the application of these micro reactors the capital cost can be reduced significantly and that by high conversion and low methane selectivity [19].

Membrane reactors

Membrane reactors are another innovative alternative to improve the FT syntheses. Membranes can be used in the FT synthesis in different ways:

- distributed feed of reactants
- in situ removal of water
- forced-through membrane contactor
- zeolite encapsulated catalysts

The distributed feed of reactants allows a better temperature control inside the reactor. Furthermore, with a controlled distribution of hydrogen into a CO stream the yield of heavy products increases. The in situ water removal can reduce the reoxidation of catalysts, increase WGS activity and the decrease the partial pressures of the educts. For an effective in situ removal of water without educt losses highly selective membranes are required. There are two different approaches for the application of forced through membrane contactors. Firstly, at the thermally conductive contactor module the syngas enters into the inner void space and streams through the membrane. The thermal conductivity of the membrane effects that at flat temperature profile a high space-time yield can be achieved. Secondly, one side of the forced through membrane is covered with a catalyst layer. The syngas is forced through the membrane to the catalyst. For the produced hydrocarbons the membrane has to be impermeable. The zeolite encapsulated catalysts is a combination of a FT catalys and an acidic zeolite membrane. The zeolitic membrane enables a diffusion of the educts to the catalyst where then the reaction occurs. Then the product also has to pass the membrane where hydrocracking and isomerization for a sharper chain length distribution takes place. Further research in the field of membrane reactors for FT synthesis is expected, especially one new membrane materials and reactor configuration [18][19].

4.8 Products

4.8.1 *Gasoline*

For the production of gasoline the HTFT is the most applicable by using FFB reactors with iron catalyst. In this way about 40 % straight run gasoline are produced. The produced propene and butane is oligomerized to gasoline which has high octane value due to the highly branched oligomers. On the other hand the straight run gasoline is highly linear with low aromatic content and has therefore a low octane value. To increase the octane value of the C_5/C_6 and C_7-C_{10} cut they have to be hydrogenated and isomerized, and respectively platinum reformed. The production of di-isopropyl ether by propene and water will also increase the octane number of the gasoline pool. However, gasoline production via FT synthesis is more complex and so the diesel fuel production is more attractive.

4.8.2 *Diesel*

LTFT is used to produce large quantities of high quality diesel fuel. According to the linearity of the hydrocarbons, the diesel cut has a cetane number (CN) of about 75 while the CN of the usual diesel varies from 40 to 50. On the other side the selectivity of the diesel is only about 18 %. About 45-50 % of the total is heavier than diesel (waxes) which can be hydrocracked to produce a large proportion of high quality diesel. This measure increase the final diesel to naphtha ratio to about 2.4:1 [23][39].

At the HTFT synthesis the hydrocarbons are more branched and consequently the CN of the FT diesel is about 55. The selectivity at the HTFT process tends to light alkenes. Via oligomerization the C_3-C_5 alkenes can be converted to a diesel with a CN of about 50. So the final diesel to naphtha ratio can be 1:1. Compared to the CN of the diesel and the diesel to naphtha ratio of the LTFT process, the HTFT process is for the high quality diesel production not suitable [39].

The FT diesel is not contaminated by substances such as sulfur compounds and consists solely of a low amount of aromatic compounds. This fuel is on the one hand applicable in areas where high quality diesel is required for appropriate applications and on the other for upgrading of lower quality diesel fuel via blending. The FT diesel can be used for instance as fuel for fuel cells driven car which is a very promising and energy-efficient alternative for the future [40].

4.8.3 *Chemicals*

The HTFT with iron catalyst is very suitable for the production of large amounts of linear α-olefins which are as petrochemicals more profitable than fuels. The olefin spectrum range from C_3, C_5-C_{12} to a C_{13}-C_{18} cut with a content of about 85, 70 and 60 % respectively. Ethylene and propylene are used for the production of monomers in the polymerindustry. The extracted and purified C_5-C_{12} cut can be used as comonomers. The longer chain olefins are converted via hydroformylation to linear alcohols which are used in the production of biodegradable detergents [23].

5 Description of the Fischer-Tropsch-Synthesis Setup

The experimental work is carried out in a side stream of the biomass combined heat and power plant (CHP) Güssing. At the biomass CHP Güssing about 2500 Nm³/h of product gas are produced and about 5 - 10 Nm³/h are taken for the laboratory scale FT plant.

5.1 Description of the biomass power plant in Güssing

To gain a high quality synthesis gas with a high heat value the Institute of Chemical Engineering of the Technical University of Vienna and AE Energietechnik developed in Güssing the FICFB-gasification system (Fast Internal Circulation Fluidized Bed). In this innovative system the process heat for the gasification is generated in a separate combustion section. The bed material transfers the heat from the combustion to the gasification zone and circulates steadily between these two zones (Figure 10). Generally, there are three possibilities to gasify the feedstock by either providing air, oxygen or steam. In this process the biomass in the gasification zone is gasified with steam in order to gain a nearly nitrogen free product gas. As biomass wood chips are used. They enter the fluidized bed gasification reactor, where the following process occurs: The wood chips are heated up, dried, devolatilised and converted mainly into CO, CO_2, CH_4, H_2, H_2O (gas) and C (char). Additionally, low amounts of byproducts like C_2H_4, and C_2H_6 and undesirable components e.g. tar, NH_3, and H_2S emerge. In the gasification process the following strongly endothermic reactions (2.1, 2.2) with water vapor take place [41][42][43]:

$$CO + H_2O \longrightarrow CO_2 + H_2 \tag{2.1}$$

$$C + H_2O \longrightarrow CO + H_2 \tag{2.2}$$

The FICFB-gasification system consists of two chambers: the gasifier as stationary fluidized bed reactor and the combustion chamber as circulating fluidized bed reactor [43]. These two chambers are connected via a chute, where bed material and any non-gasified carbon are transported into the combustion section. In the combustion chamber the remaining carbon is fully combusted, through which the bed material is heated up. Afterwards the heated bed material comes into a cyclone where it is separated from the gasflow and fed back into the gasifier. To reach the necessary heat for the gasification reactions additionally to the non-gasified carbon supplementary fuel like recirculated product gas, rapeseed methyl ester (RME) or wood can be used to modulate the temperature in the combustion section. Due to the separated sections each can be fluidized with the ideally suited medium. The gasification section is fluidized with steam and the combustion section with the essential air. This enables to separate the high quality product gas with a calorific value of 12 MJ/Nm³$_{(dry)}$ from the flue gas that comes out of the combustion section [43].

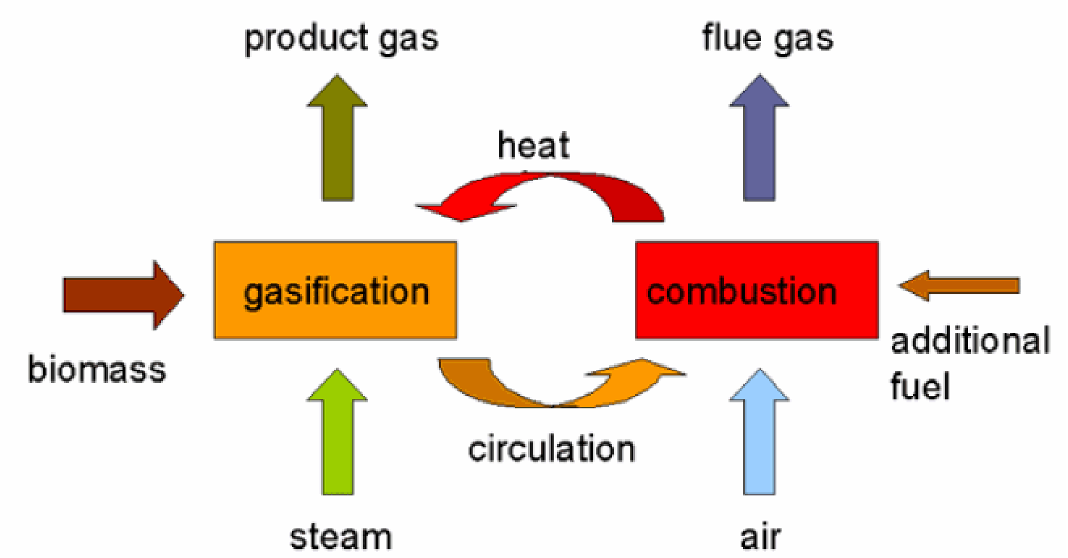


Figure 10: The innovative FICFB-gasification process [43]

Compared to gasifiers operating with air the FICFB-gasification system has the advantage that it generates a nearly nitrogen-free gas, which can be used after appropriate cleaning and treatment as a synthesis gas in the chemical industry, e.g. for the production of Fischer-Tropsch diesel or as an energy source for electricity and heat production via a gas engine [41][42].

At the combined heat and power (CHP) plant (Figure 11) in Güssing the synthesis gas is mainly utilized to produce heat and electricity. From a daily hopper the biomass are transported via a belt conveyor, a bucket conveyor, a metering bin and a metering screw conveyor to a system of screws and further into the gasifier. As mentioned above the gasification section is fluidized with steam, which is produced by the surplus of process heat. The combustion section is fluidized with air and the process heat for gasification is delivered via bed material circulation. After gasification the product gas is treated for final utilization. Firstly, the gas is cooled by a water cooled heat exchanger from 850 °C – 900 °C to about 160 °C – 180 °C. The next step of the gas treatment is a two stage cleaning system. At the first step a fabric filter separates the particles and some of the tar from the product gas. These particles are conveyed back to the combustion section. To remove the undesirable tar from the gas it flows through a gas scrubber with RME (Rapseed Methyl Esther) as solvent. The used scrubber liquid saturated with tar and condensate is vaporized and fed into the combustion section for thermal disposal of the solvent. In the gas scrubber the clean product gas is cooled down to approximately 40 °C which is at operation condition for the gas engine. Finally, the clean product gas is utilized in a gas engine to generate electricity and heat. During operation stop of the gas engine the gas can be used for combustion in a boiler to produce heat for the district heating system. To remove unburnt CO in the flue gas, it is catalytically oxidized. Additionally, an exhaust gas cooler gathers the sensible heat for district heating from the engine’s flue gas. The hot flue gas from the combustion section is used in an air preheater, steam superheater and a flue gas cooler to deliver heat to the district heating grid. Before it is released via a stack into the atmosphere together with the engine’s flue gas, a gas filter precipitates the particles [41][42].

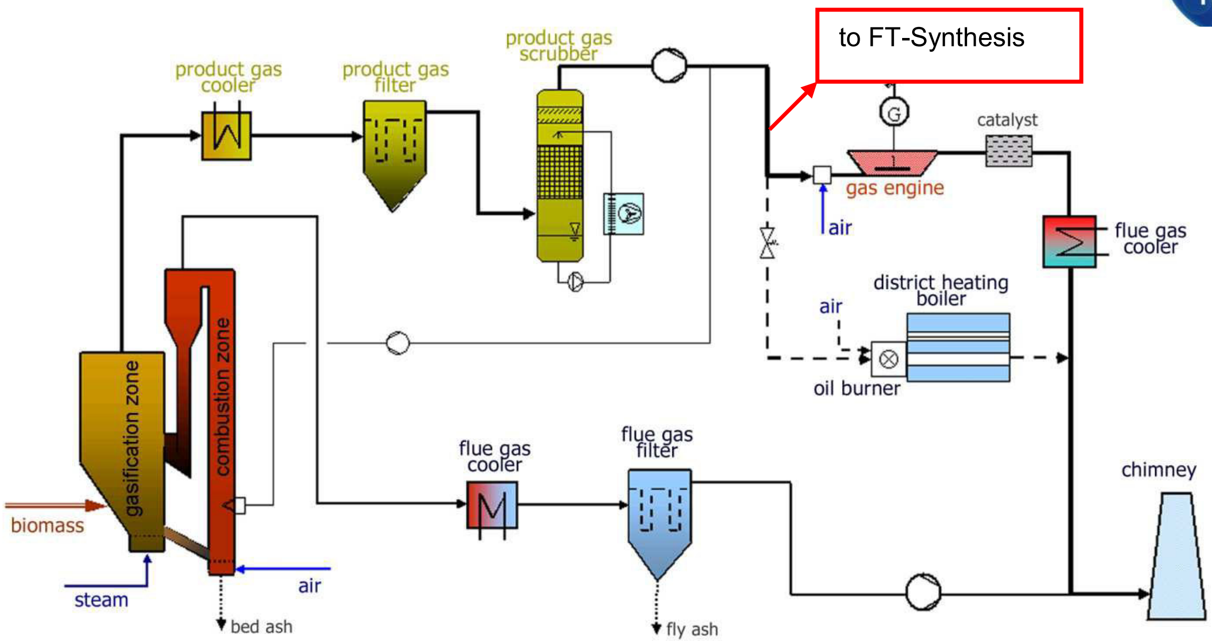


Figure 11: Flow chart of the CHP plant Güssing [41]

The significant characteristic data of the CHP plant in Güssing are illustrated in Table 8Table 8: Design data of the CHP plant Güssing [41]. As mentioned above the heat gained from product gas, flue gases, and engine's waste heat, but mainly from the product gas boiler, is fed into the district heating grid, which has a length of more than 30 km. Mainly industry, private houses, public offices, schools, and a hospital are connected to this grid. Furthermore, the generated electricity is sold to the electrical grid operator [41].

Table 8: Design data of the CHP plant Güssing [41]

Type of plant	Demonstration plant	
Fuel Power	8000	kW
Electrical output	2000	kW
Thermal output	4500	kW
Electrical efficiency	25.0	%
Thermal efficiency	56.3	%
Electrical/thermal output	0.44	-
Total efficiency	81.3	%

The gas composition of the cleaned product gas with a water content of about 10 Vol.% is presented in Table 9. The main gas components are hydrogen and carbon monoxide, which are most important for the FT synthesis. The nitrogen content results from its use as inert gas in the biomass feeding system and the particle filter [41].

Table 9: Gas composition of CHP plant Güssing (dry) [44]

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

Due to the FICFB-gasification process and gas cleaning the product gas reaches a high quality. Therefore, it can be used for different applications like CHP production with gas engines, gas turbines or fuel cells, hydrogen production and as synthesis gas for production of substitute natural gas (SNG), methanol and as well FT-diesel [41].

The biomass gasification demonstration plant in Güssing started the operation in 2001 and has in total, by the end of December 2009, about 43,000 hours of operation of the gas engine. The biomass CHP plant is in commercial operation and reaches approximately 6,500-7,000 hours of operation per year [44].

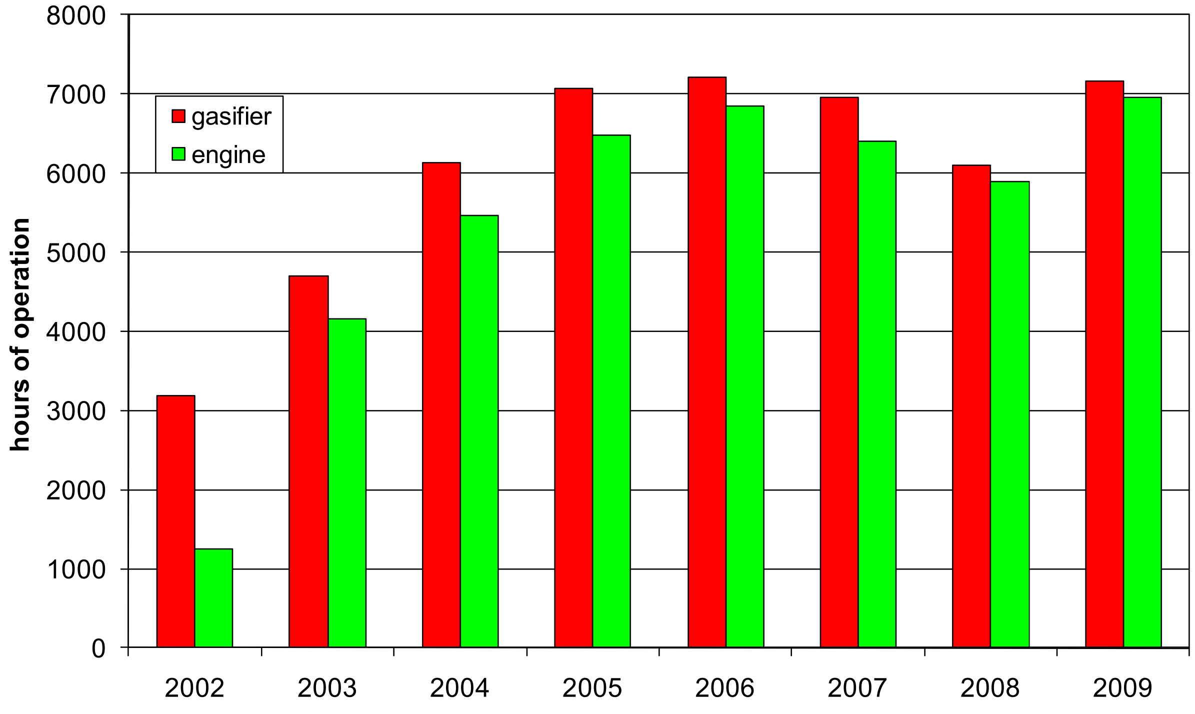


Figure 12: operation hours of biomass CHP Güssing

5.2 Description of the FT synthesis trial plant

The biomass-based FT trial plant was realized by the Technical University of Vienna (TUV) in cooperation with the biomass CHP plant in Güssing. TUV designed and installed a new FT reactor in form of a slurry reactor in a side stream of the existing allothermal fluidized bed gasifier at the biomass plant. The FT synthesis trial plant operates in commercial environment and under permanent operation conditions. By this the long term performance and behavior can be investigated. The catalysts used in the FT slurry reactor are commercial FT catalysts, but also research FT-catalysts are studied.

The flow chart in Figure 13Figure 13: Block diagram of the FT - plant [44] shows the test rig structure of the FT synthesis which consists of the following main parts [44]:

1. Steam reformer
2. Gas drying by biodiesel (RME) scrubber
3. Additional atmospheric gas cleaning by activated charcoal
4. Compression of the gas to 20-30 bar
5. Various fixed bed reactors (HDS, ZnO, CuO) for gas cleaning
6. Slurry FT reactor
7. Offgas scrubber to remove waxes from the offgas
8. Offgas cooler to remove liquid FT products from the offgas

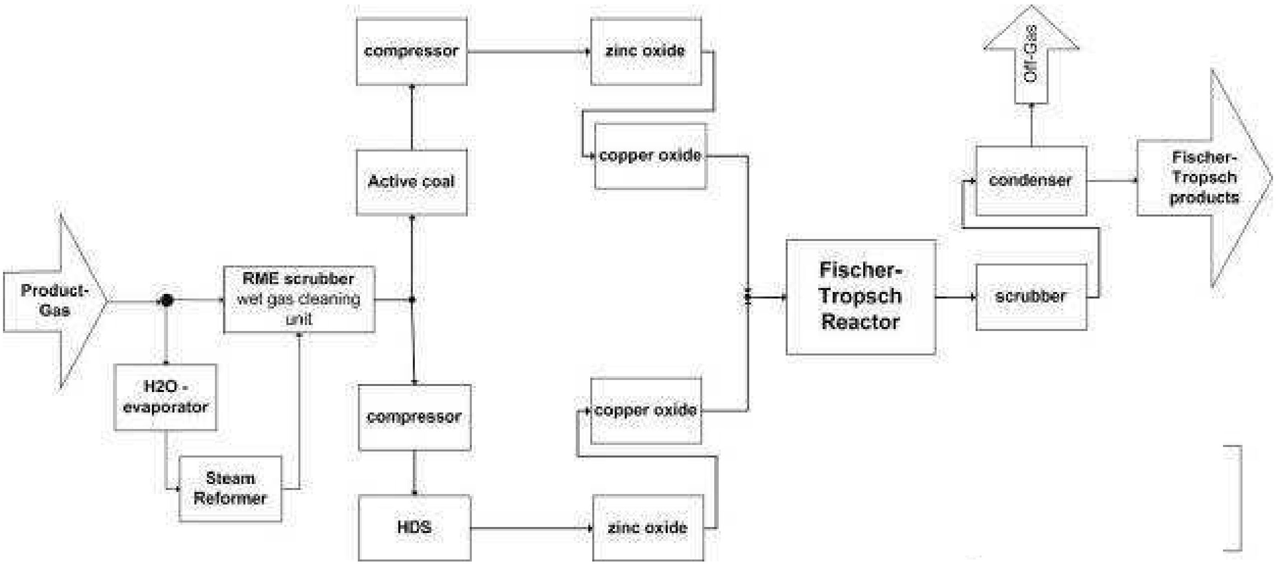


Figure 13: Block diagram of the FT - plant [44]

The product gas for the FT synthesis is withdrawn after the existing gas cleaning of the biomass plant which is shown in Figure 11**Fehler! Verweisquelle konnte nicht gefunden werden.**. The syngas with the gas composition given in **Fehler! Verweisquelle konnte nicht gefunden werden.** has at the point of withdrawal an excess pressure of about 80 mbar with a water content of ca. 10 vol%. It is conveyed over a 1 inch pipe with about 70 °C to a 2-way valve in the FT container. All automatic valves for the syngas circuit have a pneumatic actuator which is controlled by a magnetic valve. As it can be seen in the Figure 13, the syngas can get over a 3-way valve either directly to the wet gas cleaning unit or it enters the steam reformer before it comes to the gas drying and cleaning stage. That depends on the desired experimental conditions. In the steam reformer the hydrocarbons should be converted to H_2 and CO to increase the H_2:CO ratio. Subsequently it comes to the gas drying and cleaning section. This is essential due to the water content of about 10 % which would condense in the gas compression step. The scrubber cools the gas down to about 3 °C to remove the water and additionally it cleans the gas from aromatic components.

After the scrubber the gas quantity is measured with a gas meter. The removal of the organic sulfur compounds occurs either with the activated charcoal or the hydrodesulphurization (HDS) step. For these experiments in this project mainly the activated charcoal was used to remove catalyst poisons. This measure before the compression also has the advantage that the gas compressors are protected.

The gas compression is split into two steps. Firstly, the gas is compressed via two diaphragm pumps to about 5 bars. The pressure can be adjusted over the reduction valve. Secondly, a piston compressor, which is driven with compressed air, compresses the gas to 10 - 30 bars. To avoid any condensation of water and tars, all pipes 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 HDS reactor which converts organic sulfur compounds to H_2S, a ZnO adsorber and a CuO adsorber which remove the H_2S. When the activated charcoal is in operation then the gas gets after the gas compression directly into the ZnO adsorber and subsequent into the CuO adsorber.

After the gas treatment the gas flow is measured by a flow meter and over the 3-way valve the clean gas enters into the FT slurry reactor. The 3-way valve enables also to by-pass the FT-reactor. Before the gas is fed into the reactor it is heated up to about 230 °C. In the FT-reactor with a volume of 20 litres the FT reaction takes place. The FT products and the unreacted gases leave the reactor over sintered metal filters with a pore size below 5 µm.

Via two needle valves the gas is expanded from about 10-30 bars to about 100 mbars relative. Then the FT-products are separated from the gas stream. Therefore, the FT-product including the off-gas gets to the off-gas scrubber where water with about 80 °C is used to remove the heavy products (heavy diesel, waxes). After the scrubber the gas is cooled down in a heat exchanger to 5 °C to condensate the light fractions like naphtha and diesel. All the products are gathered in a glass receptacle and are withdrawn after the experiment. The non-reacted syngas is measured with the gas meter and is fed back to the CHP plant.

When the FT-plant is out of operation due to maintenance and revision work it is essential to rinse the whole plant with nitrogen. The nitrogen is taken from the storage tank of the CHP plant and is fed over a magnetic valve either before the RME scrubber or after the diaphragm pumps into the FT-plant. Two CO-detectors permanently control the air inside of the container on carbon monoxide emissions for personal protection and to shut down the plant at a critical value of 100 ppm.

The following sections describe every stage of the FT-plant, from the steam reformer to the off-gas cooler in more details.

5.2.1 *Gas upgrading*

Steam reforming

In the product gas of the biomass CHP plant consists of about 10 vol% of methane, which means that about one third of the chemical energy is bounded in the methane and cannot be utilized in the FT reaction. During the steam reforming step the hydrocarbons should be converted into hydrogen and carbon monoxide, which should increase the H_2/CO ratio and the conversion efficiency from biomass to FT fuels.

The development and dimensioning of the steam reforming reactor was done by DI Angela Potetz (TUV), who will write her doctoral thesis on this topic. So far different commercial catalysts were evaluated and the steam reforming reactor was integrated into the existing FT plant. In this section significant data of calculations and investigations to the steam reforming project are presented.

The steam reforming process is based on four main reactions. The steam methane reforming reactions (4.1) and (4.2) linked by WGS reaction (3.2) and the methane carbon dioxide reforming reaction (4.3):

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad \Delta H_r^\circ = +206 \ kJ/mol \tag{16}$$

$$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2 \qquad \Delta H_r^\circ = +165 \ kJ/mol \tag{17}$$

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2 \qquad \Delta H_r^\circ = +247 \ kJ/mol \tag{18}$$

The calculation of the thermodynamic equilibrium at 850 °C of the product gas is based on these reactions mechanisms. The results are given in Table 10.

In equilibrium the product gas does not contain any hydrocarbons. The aim is to react all hydrocarbons in the steam reformer to hydrogen and carbon monoxide. Additionally the H_2/CO ratio is influenced by this process. The H_2/CO ratio of the product gas from the CHP plant is normally 1.8:1, while by reforming of the hydrocarbons a H_2/CO ration of 2.1:1 can be achieved. Aforementioned, this H_2/CO ratio is an optimal value for the utilization of cobalt based FT catalysts. Due to this gas upgrading the steam reforming process is a good gas pretreatment for the FT synthesis.

Table 10: Results on thermodynamic equilibrium calculations at 850 °C

gas components	after gasifier	thermodynamic equilibrium	
H_2	40.0	57.0	vol% $_{dry}$
CO	22.0	27.4	vol% $_{dry}$
CO_2	23.0	14.6	vol% $_{dry}$
CH_4	10.0	0.0	vol% $_{dry}$
C_2H_4	2.5	0.0	vol% $_{dry}$
C_2H_6	0.5	0.0	vol% $_{dry}$
C_3H_6	0.5	0.0	vol% $_{dry}$
N_2	1.5	1.0	vol% $_{dry}$
H_2O	40.0	24.9	vol%

Another investigation that had to be done was the effect of sulfur poisoning of the catalyst. It was found that by increasing the temperature the H_2S poisoned catalysts can effectively be recovered. Therefore, the utilization of high reformer temperature of about 850 - 900 °C is the only effective measure to increase the sulfur resistance of nickel-based catalysts. This implies that allowing higher H_2S contents in the product gas although, operating at higher reformer temperatures, is economically disadvantageous.

The steam reforming reactor consists of the following main parts:

- Water dosing, to add the necessary amount of steam (adjustment of correct steam/carbon ratio)
- Heat exchanger to preheat the product gas to the desired temperature and to evaporate the water
- First reforming reactor
- Heat exchanger, to preheat the gas again to the desired temperature
- Second reforming reactor
- Heat exchanger to cool the gas for the inlet into the RME scrubber

The water dosing consists of a peristaltic pump which feeds water from a reverse osmosis into the first heat exchanger where it is vaporized. The heat exchangers are electrically heated by several tubular heating elements. Heating tapes are essential to reach the high temperatures, for the endothermal reactions and to prevent crystallization of naphthalene in the pipes. The last heat exchanger after the reactors cools down the gas via air blower above the boiling point to thwart water condensation. Subsequently it enters into to RME scrubber.

During the experiment the heating tapes were adjusted to keep the temperature on about 900 °C and the peristaltic pump fed the necessary steam into the steam reformer for a steam to carbon ratio of about 3.

Figure 14: Steam Reformer (left: without insulation; right: with insulation)

Gas drying and cleaning

The syngas drying and cleaning is divided into two sections. In the first section humidity, particles and tar contaminations are removed by the RME scrubber. In the next section fixed bed reactors with well-matched loadings, developed from TUV, remove contaminations such as H2S, organic sulfur as well as HCl to a certain value to avoid any poisoning of the FT catalyst.

RME scrubber

The concept of the scrubber was developed at the TUV and the plant-specific technical construction is described in detail in the diploma thesis of DI (FH) Stutterecker Werner [42]. Rapeseed methyl ester was chosen as solvent due to the good solvent characteristics and its availability at the rape mill in Güssing. The scrubber (Figure 15) consists of three parts, the glass receptacle, the glass column with the packing for the absorption and the droplet separator which is also made out of glass. All three parts are insulated. Systematically arranged packages are imbedded in the columns, which increase the contact area, turbulences and contact time of the syngas and solvent. The scrubber is operated in counter current flow which means that the solvent is circulating by a solvent pump from the top to the bottom whereas the syngas streams from bottom to the top. A small diaphragm pump extracts the solvent out of the storage tank of the biomass plant and conveys it to the scrubber. There it is blended with the circulating RME. In the receptacle the heavy condensate sediments to the bottom where it is removed by the pump. A level measurement actuates this pump to avoid that the level reaches either a certain maximum or minimum.

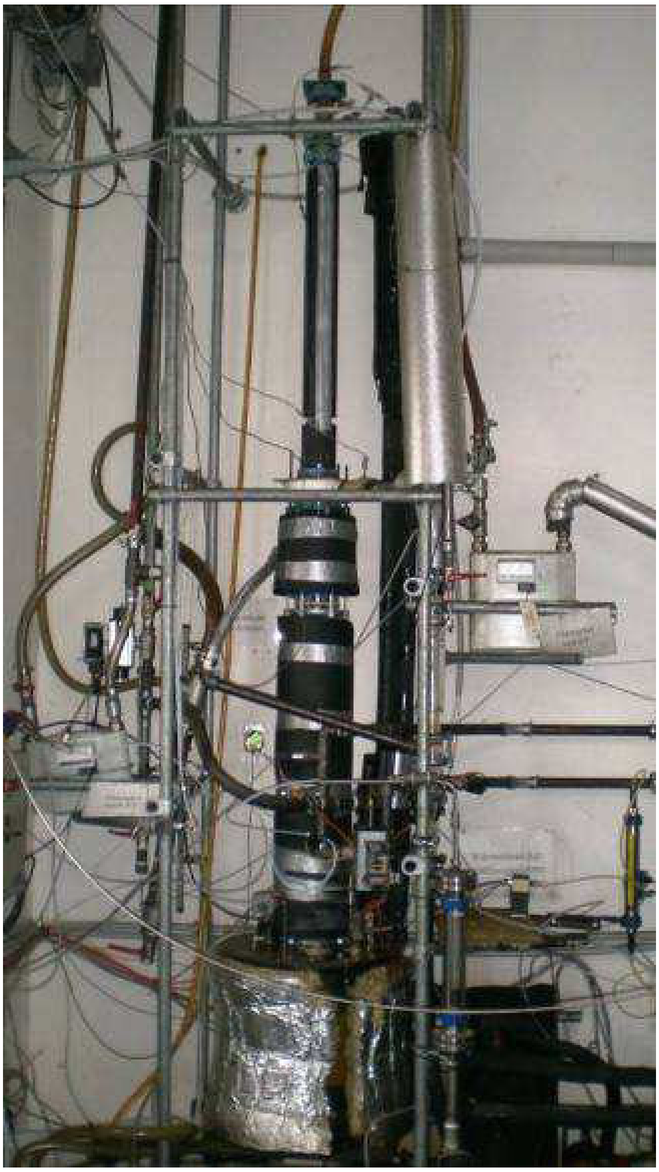


Figure 15: RME – Scrubber

The light solvent is exhausted via solvent pump and passes a heat exchanger where it is cooled down to less than 5 °C and subsequently it enters the column again at the top. Via a rotameter the flow rate can be adjusted manually. The temperature of the solvent is set by a cooling circuit. The cooling circuit consists of a water-glycol mixture that passes an electrical cooling system. The cooling temperature is controlled by a controller. All lines are insulated to reduce heat absorption.

As aforementioned the syngas enters the scrubber either directly or after the steam reforming process, depending on the chosen experiment conditions. From the scrubber it is released in the top of the receptacle and streams up throw the column where it is cooled and consequently dehumidified. At the top of the column the droplet separator achieves that the entrained water and solvent are intercepted. After this first gas treatment step the gas comes to a gas meter. After that it enters the activated charcoal filter for the removal of sulfur compounds.

Activated charcoal filter

As already mentioned in chapter 4.6.2, sulfur-containing compounds have a permanent poisoning effect and hence they deactivate the FT catalyst. The activated charcoal filter is responsible for the adsorption of the H_2S and organic sulfur compounds under almost atmospheric pressure. The active coal is coated with potassium iodide that acts as catalyst to convert H_2S to elementary sulfur. The dried syngas enters at the bottom and releases at the top of the filter. The activated charcoal filter is a simple gas treatment equipment and does not require any process controlling facilities such as pressure and temperature measurement.

Figure 16: Activated charcoal filter

HDS catalyst

The HDS catalyst converts the organic sulfur compounds into hydrogen sulfide with an organic residue. Organic sulfur compounds occur in form of mercaptanes, sulfides, disulfides and thiophenes. The following equation shows an example of the hydrogenation of a sulfur compound [46]:

$$R_1 - S - R_2 + 2H_2 \longrightarrow H_2S + H - R_1 + H - R_2 \tag{19}$$

R_2 = H or R (organic residue)

The reactor is wrapped into heating tapes which keep the temperature on a constant level. The HDS catalyst operates at a temperature of about 250 °C while the pressure varies depending on the experiment design. The reactor is electrically heated by tubular heating elements which are controlled by thermocouples. When the HDS catalyst was used then the gas is fed into the ZnO adsorber and the CuO adsorber where the converted sulfur compounds are adsorbed. However, the HDS catalyst was only used during one experiments. It was found that the HDS catalyst was not able to convert the organic sulfur compounds completely which resulting in a deactivation of the FT catalyst. Therefore, the activated charcoal filter was integrated in addition to the ZnO and CuO reactor into the gas cleaning setup.

ZnO and CuO Adsorber

The zinc oxide and copper oxide reactor adsorb the sulfur compounds. The desulphurization of the compressed syngas occurs between a reactive transition metal oxide and hydrogen sulfide resulting in metal sulfide and water (equation (4.5)).

$$M_yO_{x(s)} +_x H_2S_{(g)} \longrightarrow M_yS_{x(s)} +_x H_2O_{(g)} \tag{20}$$

M=Metal

Regeneration of the metal oxide can be done by oxidation. However, for further utilization it is desired that the adsorbent is re-transformed into a metal oxide and not into a metal sulfate (equation (4.6)) [46].

$$M_yS_{x(s)} + (3/2)xO_{2(g)} \longrightarrow M_yO_{x(s)} + xSO_{2(g)} \tag{21}$$

The ZnO reactor is used for the chemisorption of the H_2S and mercaptans but a certain residue remain in the gas flow. The following CuO reactor adsorbs these residues and additionally the thiophenes and chlorine compounds. The upgraded gas obtains a purity which is not poisoning the FT catalyst.

The ZnO and CuO reactors are electrically heated. The temperature and pressure are controlled by thermocouples and a pressure transmitter. The gas flows in both reactors from the bottom to the top through the fixed bed material.

Figure 17: Reactors for gas cleaning: left ZnO adsorber; right CuO adsorber [44]

Several experiments showed that the combination of activated charcoal under atmospheric pressure, the ZnO reactor and the CuO reactor under high temperature conditions lead to a gas composition with desired low impurities.

5.2.2 *Gas compression*

Diaphragm pumps

The two diaphragm pumps are connected parallel to achieve a certain volume flow. They obtain the syngas from and convey it into a special constructed duct system (see Figure 18). Additionally a magnetic valve and a pressure-reducing valve, which are connected parallel to the pumps, are integrated in this system. The magnetic valve is essential equipment for the start up of the pumps. Both pumps cannot start against pressure. Thus, the magnetic valve is automatically opened at each start and allows a pressure free run for about 10 seconds. The pressure-reducing valve has two functions. Firstly, via the valve the pre-pressure for the second compression step can be adjusted which directly influence the volume flow of the syngas through the FT-plant. Secondly, the valve avoids that the pumps are overburdened and opens to a certain pressure. The diaphragm pump can compress the syngas up to 6 bars. The compressed gas is stored for a constant flow rate in the buffer. A one-way valve avoids that the compressed gas flows back which would destroy the RME scrubber.

Figure 18: Two diaphragm pumps and the duct system [42]

Piston compressor

The piston compressor DLE 5-2-GG-C works to the principle of a pressure intensifier, to compress the gas up to about 30 bars. In the process a large pneumatic piston with low pressure transfers the energy to a small piston with high pressure. The pneumatic piston is moved by compressed air, provided from the screw compressor. The compressed air with 7 bars is fed into an air pressure tank. A magnetic valve and a pressure reducing valve control the compressed air supply. The produced outlet pressure of the piston compressor depends on the pressure of the compressed air which can be adjusted via the reducing valve. When the desired pressure is reached there is an equilibrium of forces between the pneumatic and the high pressure side. Thus, compressed air is utilized until the desired pressure is reached. The compressed syngas releases over a 6 mm stainless steel line to the gas cleaning stage. All lines are heated for the subsequent process and to avoid water condensation.

Figure 19: Piston compressor

5.2.3 *FT-slurry-reactor*

As FT reactor is a three-phase slurry reactor (Figure 20) in application which has been designed by TUV. The excess heat from the highly exothermic FT reactions is removed by cooling air. Thereby, a fan blows air through an outer shell, cools the reactor and releases over a foul-air duct. The fan and electrical heating tapes fixed outside keep the process temperature on a constant level. Additionally, the reactor is well insulated against heat loss. For a reliable temperature control there are ten thermocouples embedded in layers. The reactor has a volume of about 20 liters and is a tube which is 250 cm long with an inner diameter of 10 cm.

The compressed and clean syngas enters with a defined pressure and volume flow at the bottom into the slurry reactor. The gas streams through a nozzle floor to fluidize the catalyst. On the top of the reactor the produced FT-product as well as the not reacted syngas (=off-gas) are released over a filter. Immediately after the FT reactor two needle valves expand the compressed gas down to about 100 mbars relative for the product separation.

Figure 20: FT Slurry Reactor [44]

5.2.4 *Off-gas scrubber and cooler*

The product condensation is divided into two separation systems (Figure 21). Firstly, a scrubber separates the long chain hydrocarbons by the use of water. The scrubber consists of a glass receptacle and a glass column with systematically arranged packing. The gas mixture of FT product, water vapor and off-gas enters at the top of the receptacle, flows through the packing and emanates at the top of the column. The washing medium enters from the side at the top into the column and drains in counter current flow off into the receptacle. A pump circulates the water out of the heated receptacle, over an external and heated standpipe into the column. The temperature is kept at 80 °C to thwart that the packings are blocked by solid FT waxes. The temperatures are controlled by two controllers. The condensate product is gathered in the receptacle and floats on the water. After the experiments the separated product is manually withdrawn over a screw able opening.

Figure 21: left: Off-gas scrubber; right: Off-gas cooler

Secondly, short chain hydrocarbons are condensated in a cooler with two equal heat exchangers which operate alternating. The heat exchangers are positioned on a glass receptacle where the product is gathered. The gas flows from the top through a heat exchanger which is cooled down to about 5 °C by a water-glycol mixture. The cooling emulsion passes the same cooling system as the cooling circuit for the RME scrubber. In the tubes of the heat exchanger built-in components are embedded to increase the heat transfer. The products condensate and settle on the heat exchanger surface which causing a pressure drop over the heat exchanger. When the pressure loss reaches a certain value the gas flow is switched by a three-way valve to the second heat exchanger. Meanwhile, the clogged tubes are heated for about ten minutes to liquefy the product which drops into the receptacle. The temperature of both, the cooling and the heating circuit are controlled by two controllers. The off-gas and products which have a condensation temperature lower than the freezing point of water are emanated over a droplet separator to the gas meter and back to the CHP plant.

5.2.5 *Automation*

The FT plant operates with an automation system that is based on the hardware and software of the company National Instrument. The system uses as hardware so called ‘Fieldpoint’ modules and as software the program ‘LabView’. All thermocouples, digital and analogical inputs and outputs are connected to the Fieldpoint modules. Thereby, all valves, pressure transmitters, thermocouples, heaters, pumps and cooling systems are controlled by this automation system. The software LabView, which is connected to the FieldPoint modules, provides a clear visualization of the controlling. Additionally, the automation program is written in LabView. The controlling screen of the FT plant is represented in Figure 22. The automation system saves in an interval of two minutes all data of the operation conditions in a text file per day.

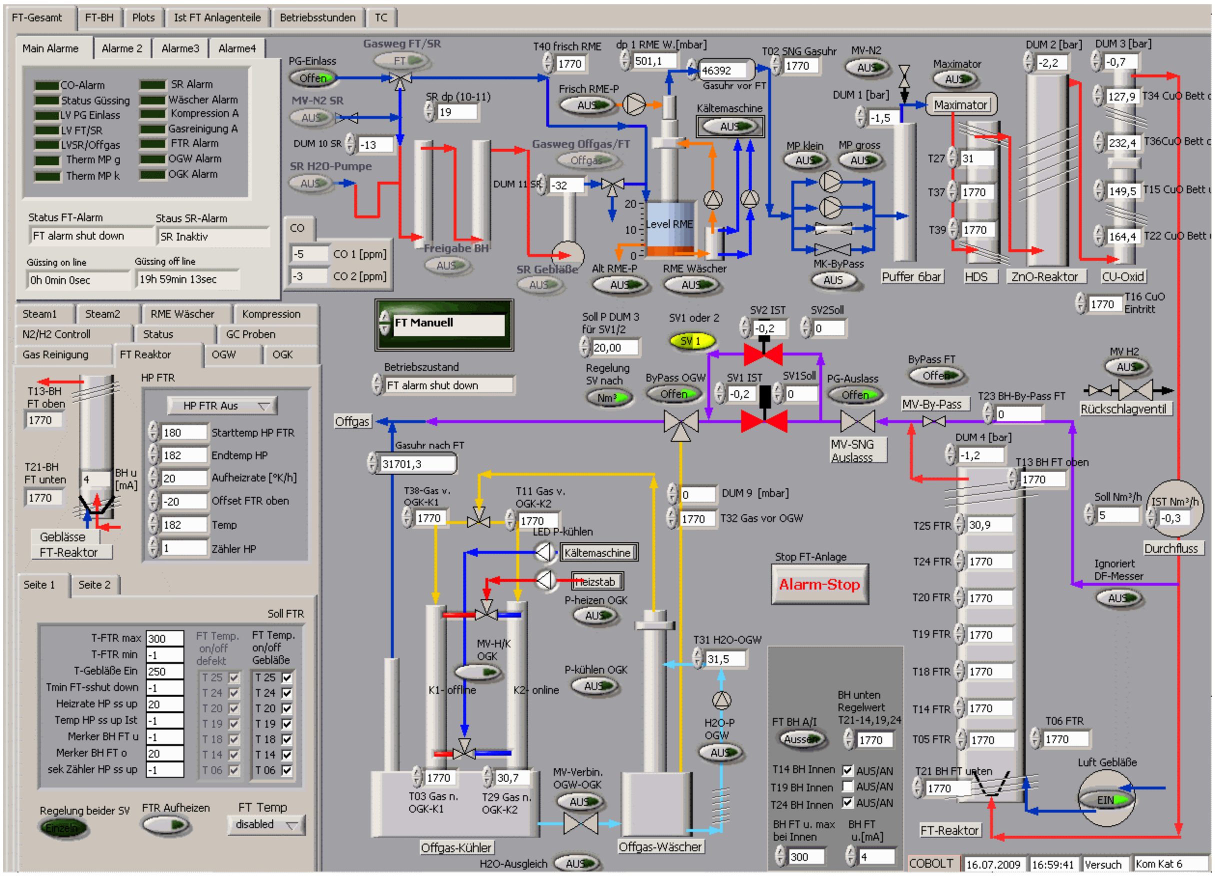


Figure 22: Screenshot of the automation system (plant out of order)

5.3 Analytics

5.3.1 *Gas flow and quantity*

Into the FT system are two gas meters integrated which measure the gas volume on the one hand that comes from and on the other hand that goes back to the CHP plant. After the gas cleaning section and before the FT reactor a flow meter indicates the gas flow through the plant.

5.3.2 *Gas analysis*

Permanent gas components and hydrocarbons

During the experiments semicontinuous online analysis of the gas compostion was accomplished. The concentration of gaseous hydrocarbons and the permanent gases in the syngas were measured online before the steam reformer, before and after the gas cleaning section and as well the off-gas from the FT-plant. As measuring instrument a gas chromatograph (GC) system Clarus 500 from Perkin Elmer has been installed. The gas is fed to the GC automatically by two small membrane pumps into an injection loop. After automatic opening of the magnetic valve at the desired gauge the injection loop is flushed by the cooled and dried gas for six minutes. Three different columns are in use to separate the components; they are connected with a 6-way and a 10-way fully automated valve. The GC is equipped with a thermal conductivity detector (TCD) connected in a series to a flame ionization detector (FID). All components except for Hydrogen are detected with the TCD, its signal is used to calculate the concentration of the permanent gases (O2, N2, CO, CO2). The gaseous hydrocarbons are also detected in the FID from which signal their concentration is derived. The hydrogen concentration is calculated as 100 minus the sum of the detected gas concentration in %.

The configuration of the GC is given in Table 11.

Table 11: Configuration of the gas chromatograph I

Gas chromatograph	
Type	Clarus 500
Company	Perkin Elmer
Detector	FID and TCD
Injection temperature FID	300°C
Injection temperature TCD	200°C
Injection mode	Splitless
Injection loop	500 µl
Column 1	6 feet Porapak Q 50/80 Mesh
Column 2	10 feet Molecular Sieve 5 A
Column 3	10 feet Porapak N 50/80 Mesh
Carrier 1	23 ml/min Helium 5.0
Carrier 2	30 ml/min Helium 5.0
Temperature program	45°C, hold 16min; 4°C/min from 45°C to 100°C, hold 5min; 15°C/min from 100°C to 180°C; hold 45 min

The GC has been calibrated with a defined gas which has almost the same composition as the product gas of the CHP plant.

Table 12: Calibration gas for gas analysis

Gas composition	Volume percent [Vol%]
C_2H_4	3.010
C_2H_6	0.497
C_3H_8	0.493
CH_4	10.010
CO	25.100
CO_2	19.920
N_2	2.007
H_2	rest

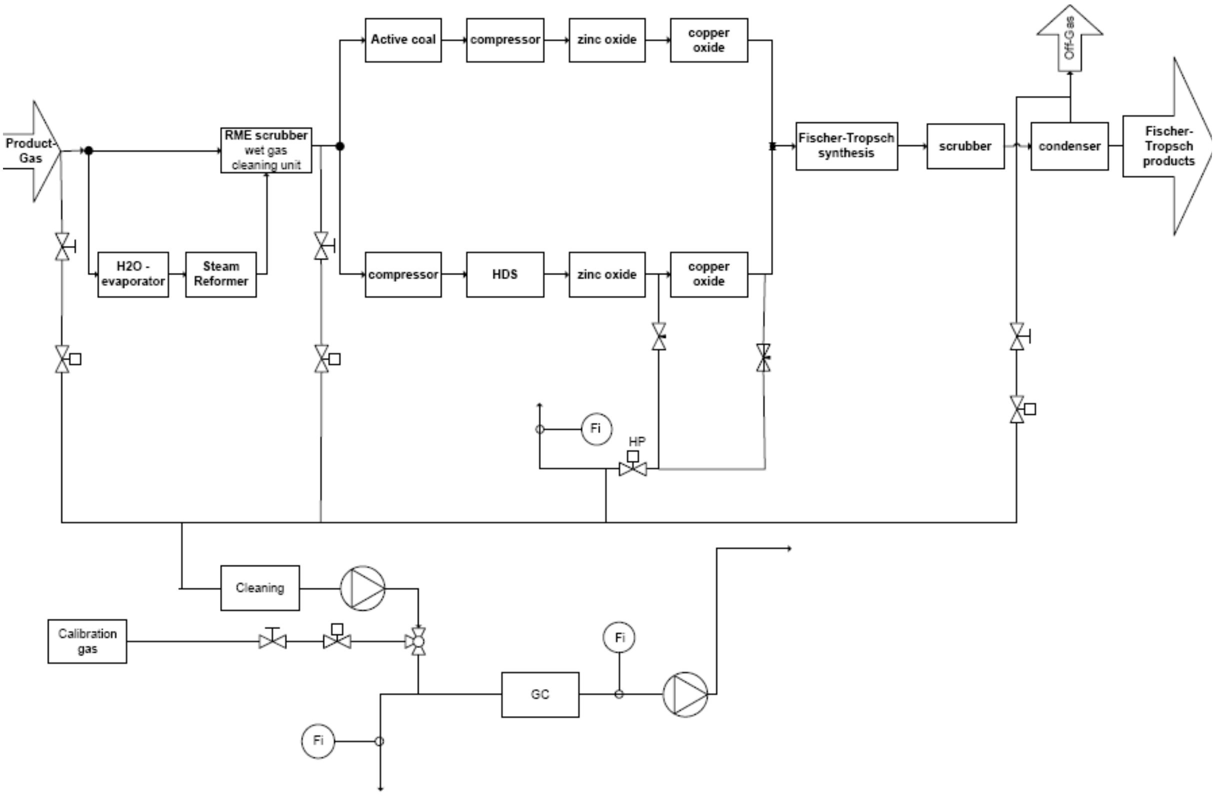


Figure 23: Scheme of the gas analytic

Sulfur and chlorine components

The sulfur and chlorine components are measured offline. As mentioned before, in the gas from the CHP plant are sulfur compounds in the form of H_2S, mercaptans and thiophens. H_2S and mercaptans are measured according to EN ISO 6326-3 where they are collected in KOH-solution and titrated with $AgNO_3$. Latter sulfur compounds are gathered in methanol and analyzed by gas chromatograph – mass spectroscopy (GC-MS). The GC-MS has a detection limit for sulfur components of 0.1 ppm.

Chlorine compound is in the form of HCl in the product gas. HCl is collected in distilled water and analyzed by ion chromatography.

5.3.3 *Analysis of the FT raw product*

The FT product which was withdrawn from the off-gas scrubber and off-gas cooler was analyzed in a GC Clarus 500 from the company Perkin Elmer by simulated distillation. The raw product was fed as a colloid suspension in CS_2 or C_6H_{14} to the GC by an autosampler using a syringe and separated in a capillary column under the use of a temperature program. As detector a FID has been installed. The configuration of the GC is given in Table 13.

Table 13: Configuration of the gas chromatograph II

Gas chromatograph	
Type	Clarus 500
Company	Perkin Elmer
Detector	FID
Injection temperature FID	350°C
Injection mode	Split 20:1
Column	Elite HT SimDist 6m x 0.53mm x 0.15µm
Carrier	5 ml/min Helium 5.0
Temperature program	35°C, hold 0min; 10°C/min from 35°C to 230°C, hold 0min; 5°C/min from 230°C to 390°C, hold 10min

5.3.4 *Distillation of the FT-Product*

The separated product in the off-gas scrubber and cooler has been distillated in a batch vacuum distillation apparatus (Figure 24). The apparatus mainly consists of a 20 liter glass flask, cowl heating, vacuum jacket column, distillation head, receiving flask, cooling trap, vacuum pump and cryostat. The 20 liter flask has a DN 100 flange to fill in the FT product and at the bottom a valve for emptying. The flask is heated by an electric cowl heating which is controlled by thermocouples. One thermocouple is placed at the cowl heating and another on at the top of the vacuum jacket column. The vacuum jacket column is used for a better separation and has a length of one meter. The distillation head consists of a jacketed coil condenser, reflux needle valve and a connection for a vacuum pump. The obtained product is gathered in a glass flask.

The yielded fractions are naphtha, diesel and waxes. At an absolute pressure of 1013 mbar the temperature range of naphtha ($\sim C_4 – C_9$) is from ambient temperature to 180 °C and of diesel ($C_{10} \sim C_{19}$) from 180 °C to 320 °C. The left product in the distillation flask is the wax fraction and is withdrawn over a valve at the bottom. The different fractions have been sent to different analysis.

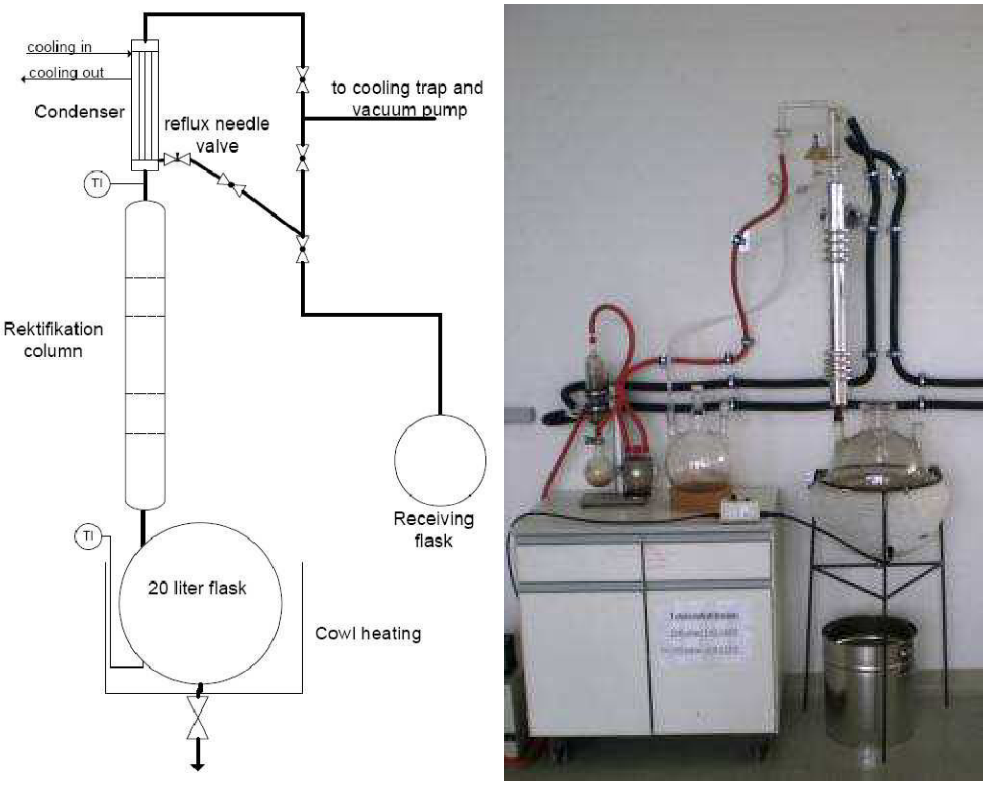


Figure 24: left: schematic distillation apparatus; right: laboratory vaccum distillation

5.3.5 *Fuel analysis*

The distillated FT product was send to an external company for the Fuel analysis according to EN 590:2004. The analyses of the physical properties are based on specific ISO standards. Table 14 provides an overview about the properties with the corresponding limits and test methods.

Table 14: EN 590:2004 diesel fuel requirements and test methods

Property	Units	Limits		Test-Method
		Min	Max	
Cetane number		51	-	EN ISO 5165
Density at 15°C	kg/m³	820	845	EN ISO 12185 EN ISO 3675
Polycyclic aromatic hydrocarbons	%(m/m)	-	11	EN ISO 12916
Sulfur content	mg/kg	-	10.0	EN ISO 20846 EN ISO 20884
Flash point	°C	> 55	-	EN ISO 2719
Carbon residue (on 10% distillation residue	% (m/m)	-	0.30	EN ISO 10370
Ash content	% (m/m)	-	0.01	EN ISO 6245
Water content	mg/kg	-	200	EN ISO 12937
Total contamination	mg/kg	-	24	EN ISO 12662
Copper strip corrosion (3 hours at 50°C)	rating	Class 1	Class 2	EN ISO 2160
Oxidation Stability	g/m³	-	25	EN ISO 12205
Lubricity, corrected wear scar diameter	µm	-	460	EN ISO 12156-1
Viscosity at 40°C	mm²/s	2.00	4.50	EN ISO 3104
Distillation recovered at 250°C	%(V/V)	-	< 65	EN ISO 3405
Distillation recovered at 350°C	%(V/V)	85		EN ISO 3405
Distillation: 95%(V/V) recovered at	°C	-	360	EN ISO 3405
Cold Filter Plugging Point (CFPP)	°C	-	-20	EN 116

6 Experimental Work

6.1 Iron catalyst

An overview of the experiments and the different conditions is given in the Table 15.

Table 15: Overview experiments – iron catalyst

Number of experiment	Type of catalyst	Temperature [°C]	pressure [bar]	flow [Nm³/h]	aktive hours [h]
1	Commercial Iron	245-250	18	6.5	110
2	Commercial Iron	245-250	16	4.5	125
3	Commercial Iron	245-250	15	3.8	107
4	Commercial Iron	245-250	18	3.1	57
5	Commercial Iron	245-250	4	3.0	141
6	Commercial Iron	245-250	20	5.5	118
7	Commercial Iron	245-250	19	5.0	115
8	Commercial Iron	245-250	20	4.8	53

The FT reactor was operated during all experiments between 245 and 250°C. The pressure and the flow of the gas were varied. Also one experiment was done at very low pressure, to see the influence of the pressure on the CO-conversion.

Typical operation data of the FT synthesis plant are shown in the following figures:

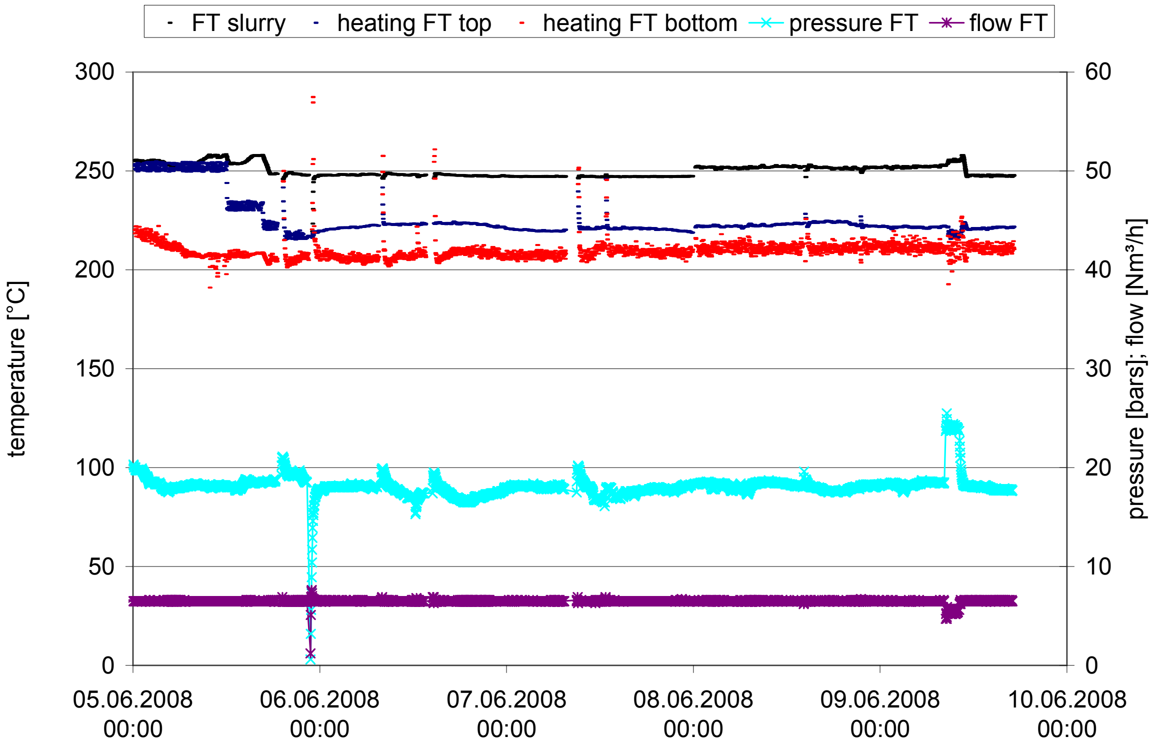


Figure 25: temperature, flow and pressure

As it can be seen from the above figures, the FT synthesis works very constant. There were short interruptions in the operation. These were mainly due to malfunctions in the biomass feeding system of the gasifier. During this time the temperature in the FT reactor was kept constant by electric heating and the whole FT plant was operated with nitrogen, to keep the fluidisation in the reactor and to avoid any settling of the catalyst.

The activity of the FT catalyst can be seen from the energy balance of the FT reactor. The FT-synthesis is an exothermic reaction. It was already observed in the first experiments, that the energy needed to keep the temperature of the FT reactor constant is direct proportional to the activity and CO-conversion of the reaction.

A deactivation of the FT catalyst is clearly pointed out by the lowering of the exothermy of the FT reaction. This results in a decreasing temperature difference between slurry and electrical heating.

During the experiments with the iron based FT catalyst no decrease of the temperature difference between slurry an electrical heating can be seen. This means that no deactivation of the FT catalyst took place.

The gas composition at different points of the FT plant is measured by a gas chromatograph and occasionally by an online system. The typical gas composition is given in **Fehler! Verweisquelle konnte nicht gefunden werden.**.

Table 16: gas composition

average	**CO**	**CO_2**	**CH_4**	**H_2**
after ZnO	21,4	21,3	7,6	42,8
after CuO	21,5	22,3	8,4	40,8
after FT	7,0	36,5	12,1	32,5

From the gas composition it can be clearly seen, that the iron based catalyst is active in CO-shift. During the experiments it was also observed, that almost no water was collected in the offgas treatment. It can be assumed, that the water produced during the FT reaction is immediately consumed by the CO-shift reaction.

The FT products, which were collected in the offgasscrubber (OGW) and in the offgascooler (OGK) were analysed by simulated distillation. Typical chromatograms are given in the following.

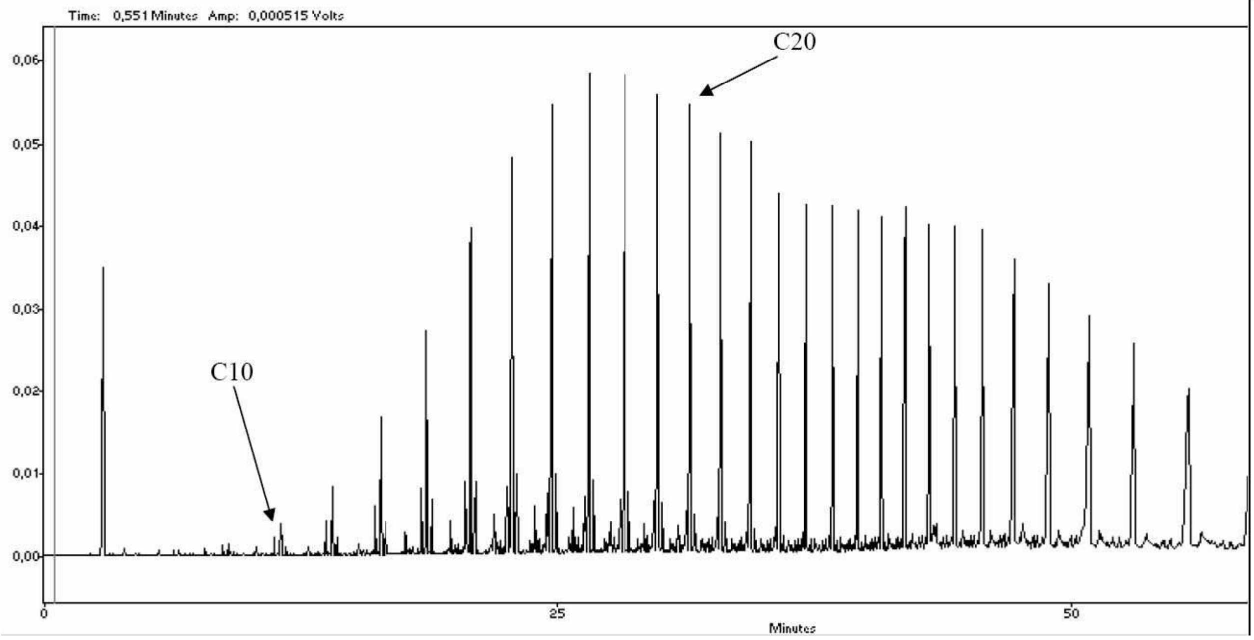


Figure 26: Chromatogram of Product from Offgasscrubber

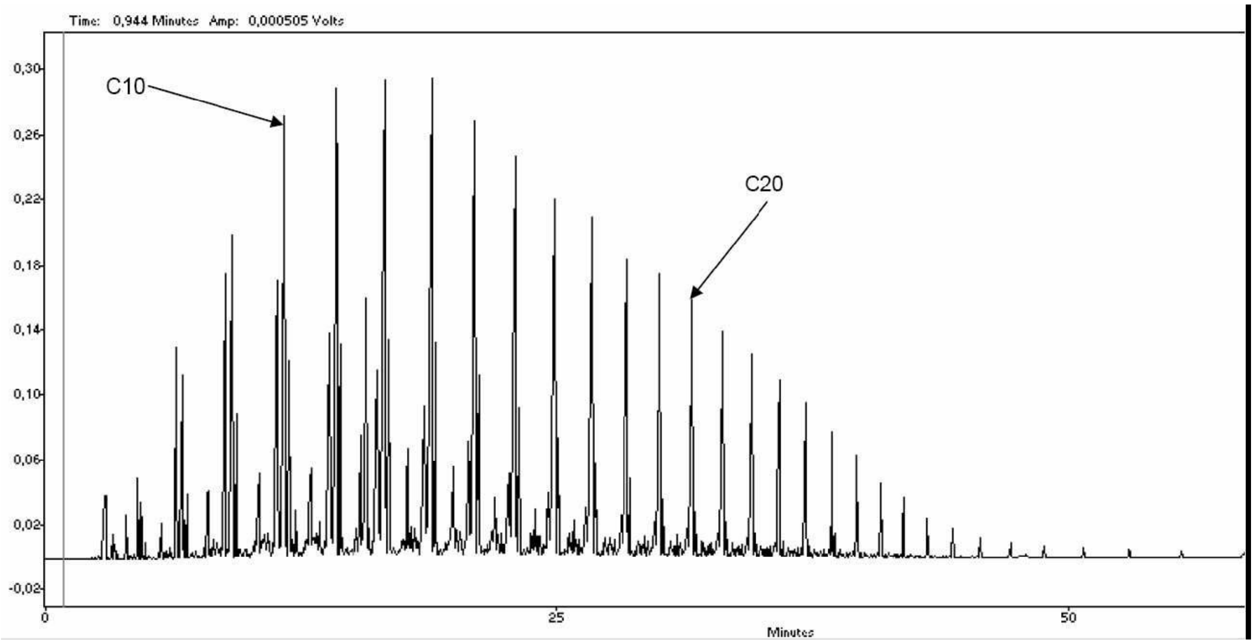


Figure 27: Chromatogramm of product from Offgascooler

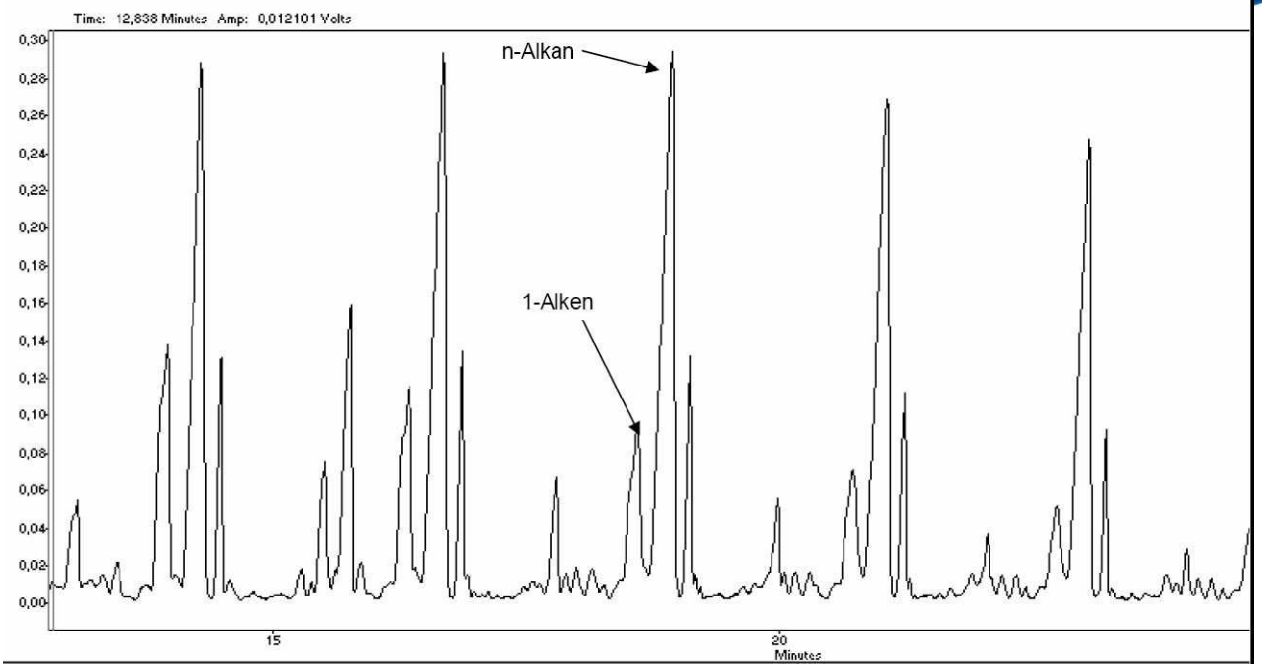


Figure 28: Detail from Chromatogramm of the product from Offgascooler

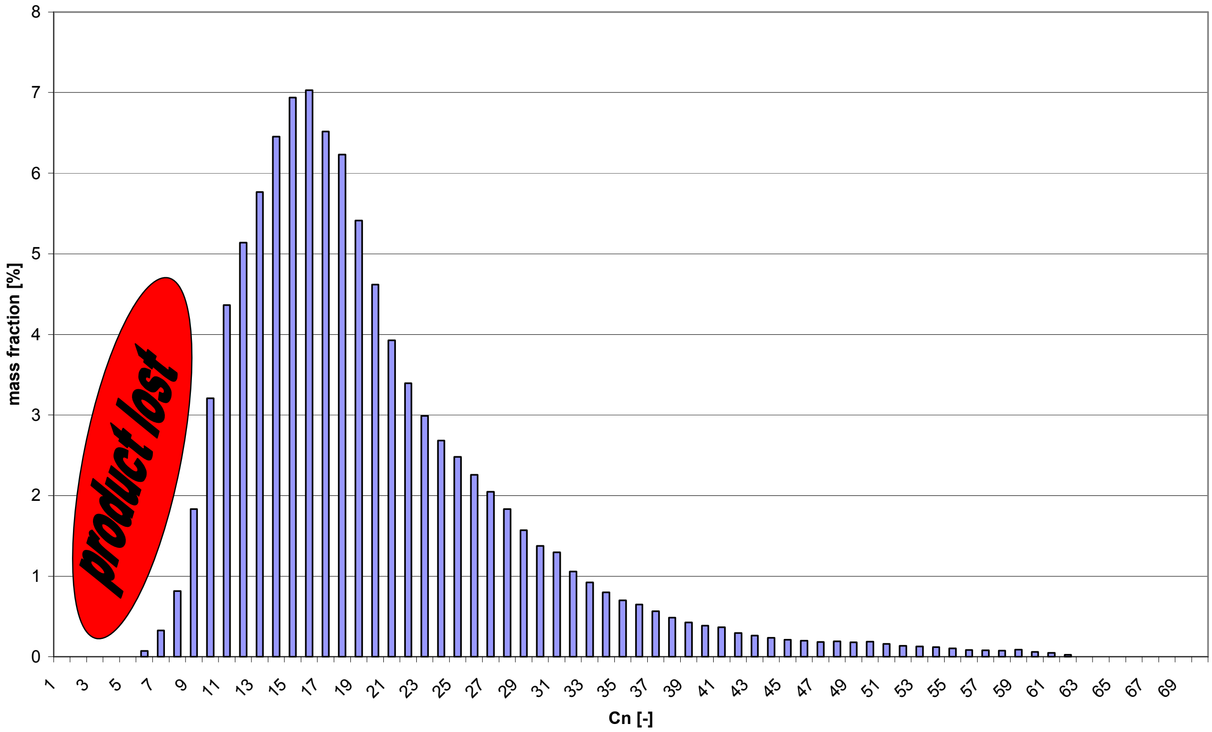
In Table 17 the main results of the experiments were summarised. In total the FT catalyst was for about 800 hours in operation and about 3700 m³ of product gas was used in the FT synthesis.

Table 17: Results of experiments

Experiment	pressure [bar]	flow[Nm³/h]	Amount of gas [m³]	Amount of condensed product [kg]	$g_{product}/Nm^3_{gas}$
1	18	6,5	712	19,8	27,8
2	16	4,5	560	12,0	21,5
3	15	3,8	403	10,2	25,2
4	18	3,1	177	1,7	n.a.
5	4	3,0	418	3,9	9,3
6	20	5,5	648	12,7	19,6
7	19	5,0	567	11,7	20,7
8	20	4,8	254	5,6	21,9
Sum:			**3738**	**77,6**	

n.a. here the amount of product was too low, to get reliable results

The CO-conversion to condensed products was quite low during all of the experiments. The theoretical amount at 100% conversions of CO is about $124 g_{product}/Nm^3_{gas}$. As the gaseous products are not condensed and liquid products below C_{15} are only partly condensed the carbon distribution was used together with the ASF plot to calculate the lost product. As an example the original Carbon distribution for experiment number 7 is given in Figure 29.



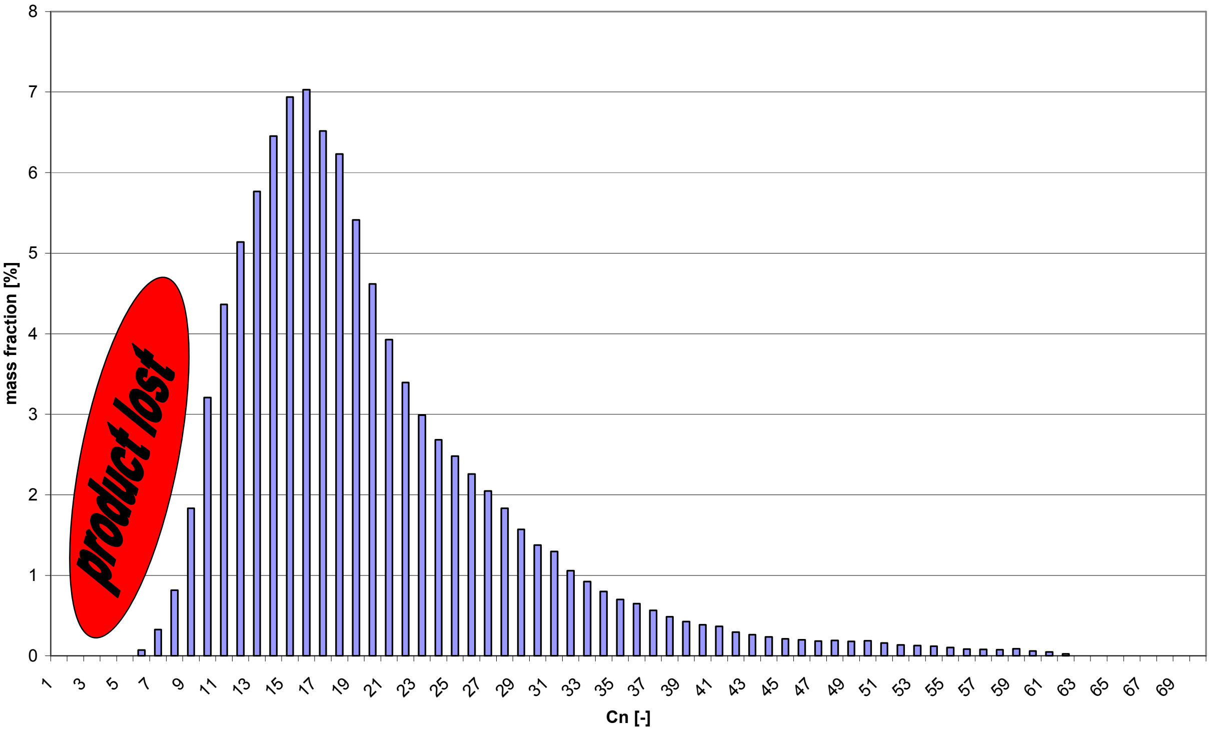


Figure 29: Carbon distribution of the condensed product

From this Carbon distribution the ASF distribution was plotted given in Figure 30.

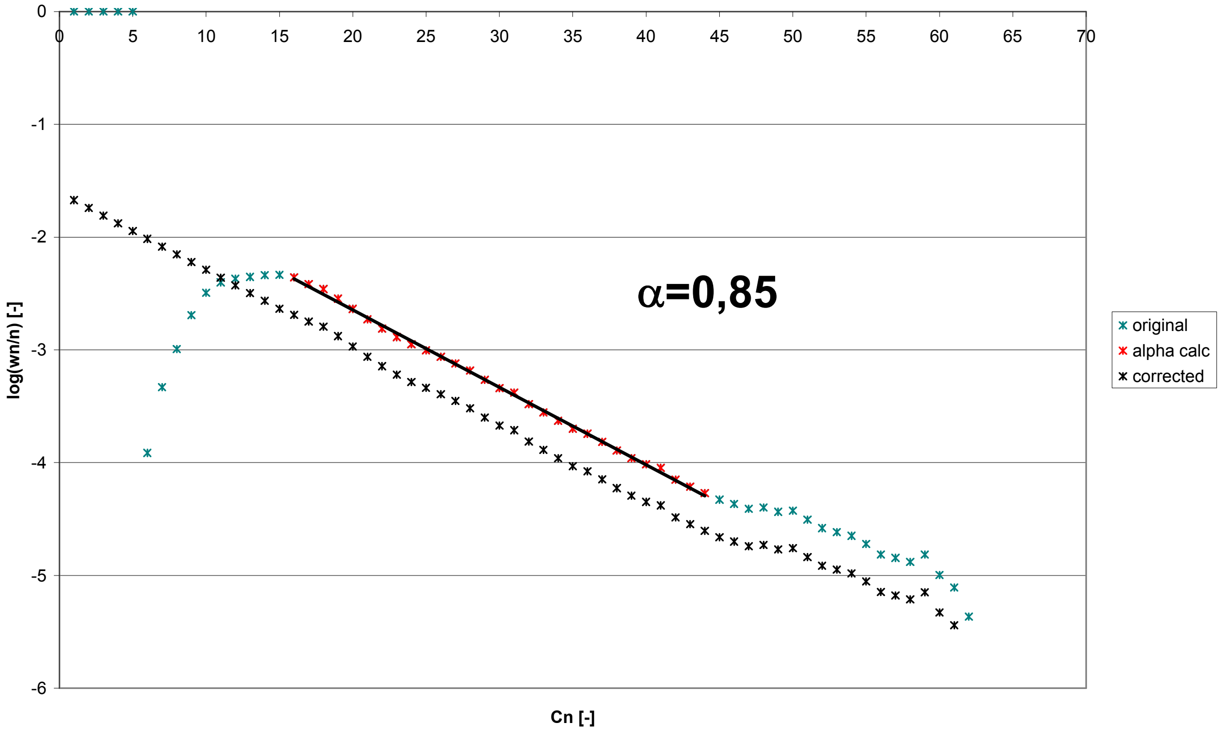


Figure 30: ASF plots

As it can be seen that the ASF plot of the original carbon distribution (blue) lacks in linearity for carbon numbers lower than 16 and a second alpha value for higher carbon numbers is observed. Therefore the first linear part (red) was used to derive the alpha value which was used for the calculation of the lost product with carbonnumbers lower than 16. The new and corrected ASF plot (black) was derived from the corrected carbon distribution given in Figure 31.

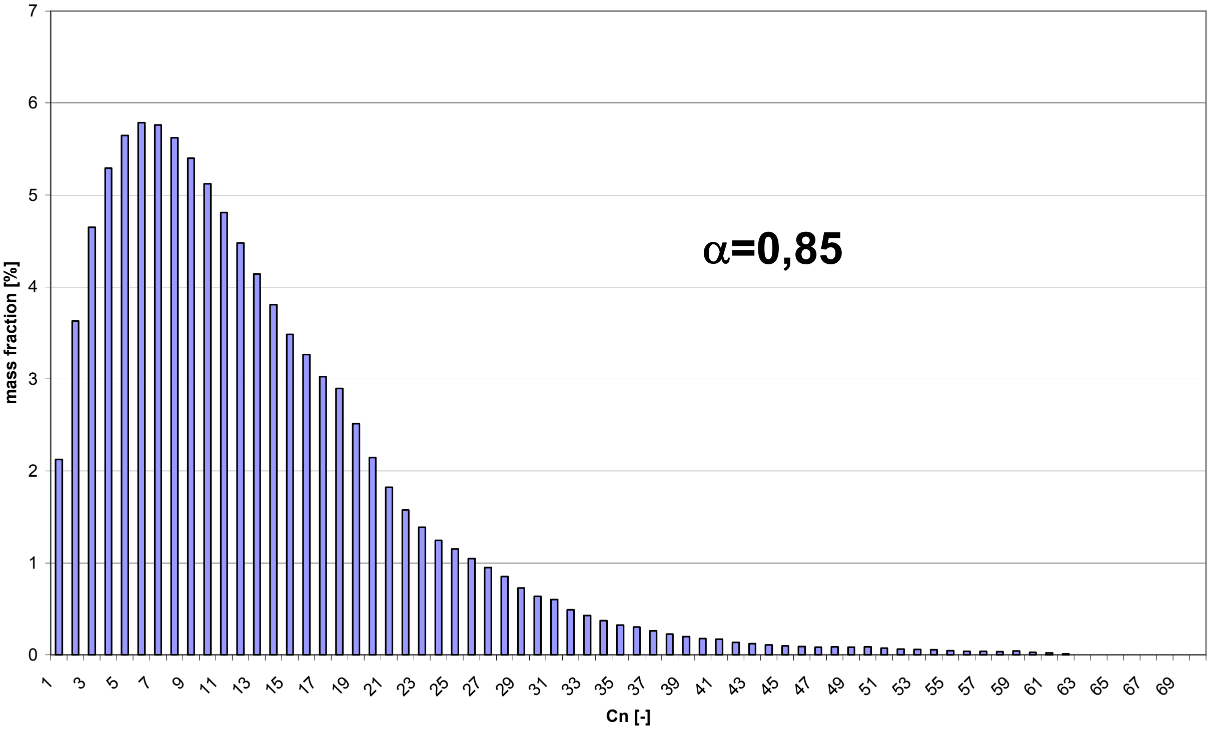


Figure 31: Corrected carbon distribution

As it can be seen the maximum of the mass fraction is found at C6, in contrast to the original carbon distribution, as it is expected for that alpha value.

The corrected carbon distribution makes it possible to calculate the lost product and therefore the CO conversion to the whole product and product with carbon numbers of 5 and higher both of which are given in Table 18.

Table 18: calculated results of experiments

Experiment	**SV [m^3/(kg h)]**	**alpha value [-]**	**CO conversion to C_n [%]**	**CO conversion to C_{5+} [%]**
1	2,59	0,81	68,0	52,2
2	1,79	0,83	37,5	30,0
3	1,50	0,84	46,0	37,8
4	1,25	0,81	n.a.	n.a.
5	1,18	0,87	14,6	12,7
6	2,20	0,81	44,6	34,2
7	1,98	0,85	33,1	27,9
8	1,91	0,87	29,5	25,6

n.a. here the amount of product was too low, to get reliable results

Conclusion of iron catalyst

An iron based FT catalyst was tested in the FT synthesis at the biomass CHP Güssing with real product gas from biomass steam gasification.

The catalyst was operated for about 800 hours and about 3700 Nm³ of product gas was lead over the catalyst. Stable operation without any deactivation of the catalyst could be achieved during all of the experiments.

The catalyst showed good activity in CO-conversion, but the amount of liquid products was lower than expected. For most of the experiments the CO conversion to hydrocarbons was in the area of 30-50%.

6.2 Cobalt catalyst

6.2.1 *Overview*

During the experiments solely a commercial cobalt based catalyst was used. To activate the cobalt catalyst it had to be reduced. For the reduction hydrogen diluted with nitrogen has been used. Into the FT-slurry reactor 2.5 kg of reduced cobalt catalyst were filled suspended in 10 kg 'starter' waxes from a Sasol plant.

Table 19 provides an overview of the experiments including the operation data mean temperature, mean pressure, mean gas flow in the slurry reactor and also when the steam reformer was used or not. For the parameter variation only pressure, the gas flow and the application of the steam reformer were varied. The catalyst company required operating at a temperature of 230 °C and therefore the temperature in the slurry reactor was not changed.

Table 19: Overview experiments – cobalt catalyst

Number of experiments	Temperature [°C]	Pressure [bars]	Gas flow [Nm³/h]	Steam reforming
1	233	19.9	3.7	yes
2	230	19.9	3.7	yes
3	230	19.7	3.2	yes
4	230	18.1	3.7	yes
5	230	19.8	5.8	yes
6	230	25	4.1	yes
7	231	19.9	5.1	yes
8	232	12.7	5.2	yes/no
9	231	12.8	4.8	no
10	231	19.9	4.9	no

The experiments are conducted on the following setup: Steam reformer – RME scrubber – Activated charcoal filter – Gas compression – ZnO absorber – CuO absorber – FT-slurry-reactor – Off-gas scrubber (OGW) – Off-gas cooler (OGK).

The test series started with the adjusted operation conditions of 230 °C, 20 bars and a gas flow of 5 Nm³/h. The adjusted gas flow could not be reached due to that the small diaphragm pump (Type N1200 E) has failed at the first day. Additionally, the automation system of the plant was enhanced by certain regulations which had to be controlled at the first experiment.

As it can be seen in the above table, at the first two experiments it was tried to stabilize the process by keeping the conditions on a constant value. The aim of the stabilization is to achieve an equilibrium in the slurry reactor between the starter waxes and the new product. Thus, it is possible that a certain amount of the starter waxes are transported out with the gas stream.

At interruptions during the experiments the temperature of the FT slurry reactor was kept on a constant value and the whole FT plant was operated with nitrogen to avoid any settling of the catalyst.

The plan was to continue after the test series with a final experiment in comparison to the first experiments. But after the tenth experiment the cryostat, as the cooling device for the RME scrubber and OGK, were damaged by lightning. Therefore further experiments were not carried out and it was decided to transfer the FT plant into the new building.

After each experiment the separated FT product in the OGW and OGK were withdrawn, weighted and marked with a sample number. Table 20 represents the experiment durations and the sample numbers of the withdrawn product of the OGW and OGK. The interruptions between the experiments were due to maintenance work at the FT plant and as well at the biomass CHP plant.

Table 20: Overview experiment duration and sample numbers

Number of experiments	Beginning	Ending	active hours [h]	Sample number OGW	Sample number OGK
1	16.04.2009 11:54	17.04.2009 13:32	23	FT 259	FT 260
2	17.04.2009 14:10	20.04.2009 15:02	63.8	FT 263	FT 261
3	05.05.2009 18:05	07.05.2009 16:38	39	FT 268	FT 265
4	07.05.2009 17:01	10.05.2009 17:09	64	FT 271	FT 270
5	26.05.2009 15:45	29.05.2009 13:03	69	FT 274	FT 273
6	29.05.2009 16:27	01.06.2009 17:53	64.6	FT 276	FT 275
7	08.06.2009 15:01	12.06.2009 14:07	92.3	FT 283	FT 282
8	12.06.2009 16:58	15.06.2009 14:52	55.3	FT 285	FT 284
9	15.06.2009 19:58	18.06.2009 15:32	67	FT 287	FT 286
10	18.06.2009 16:00	22.06.2009 20:02	84.6	FT 288	FT 289

6.2.2 *Activity of the cobalt-based catalyst*

6.2.2.1 Results of the experiments based on the catalysts activity

As it can be seen in the previous section, the FT process operated predominately constant with only few short interruptions. Aforementioned, these interruptions were mainly due to of maintenance work at the FT facility and as well at the CHP plant.

The FT synthesis is based on highly exothermic reaction and therefore the activity of the FT catalyst can be observed over the energy balance of the FT reactor. Therefore, the temperature difference between the FT slurry temperature and the electrical heating temperature is direct proportional to the activity of the FT catalyst.

The above represented graphs (significant graphs are given in this section again) with the operation data enable a visual examination of the catalyst activity. After the stabilization and the variation of several controlling parameters the conditions could be found to have a stable operation of the FT synthesis. As it can be seen in Figure 32, the temperature difference between the slurry reactor and the electrical heating was over the whole experiment constant. This means that no deactivation of the FT catalyst occurred.

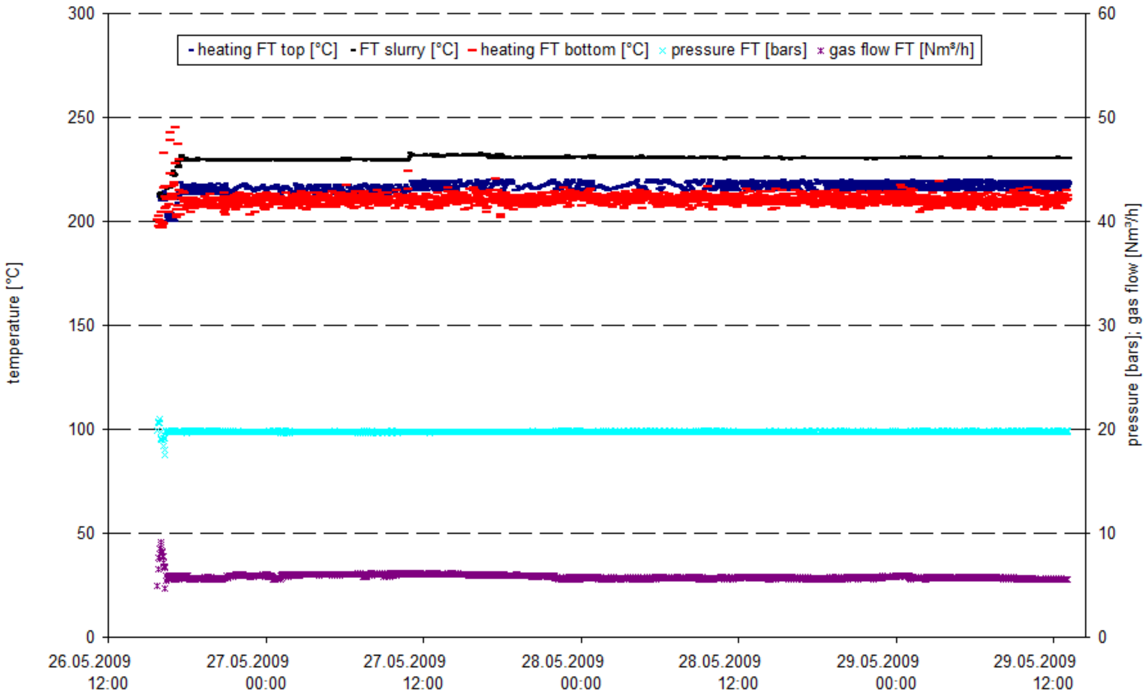


Figure 32: Operation data of experiment no. 5

Nevertheless, at the experiment no. 6, the temperature difference between the slurry and the electrical heating decreased this means that the exothermy of the FT reactions also decreased. Consequently, the FT catalyst was reduced with hydrogen. The monitoring showed that the temperature difference at experiment no. 7 was several degrees high. In Figure 33**Fehler! Verweisquelle konnte nicht gefunden werden.** to see that temperature difference over the time of the experiment was constant.

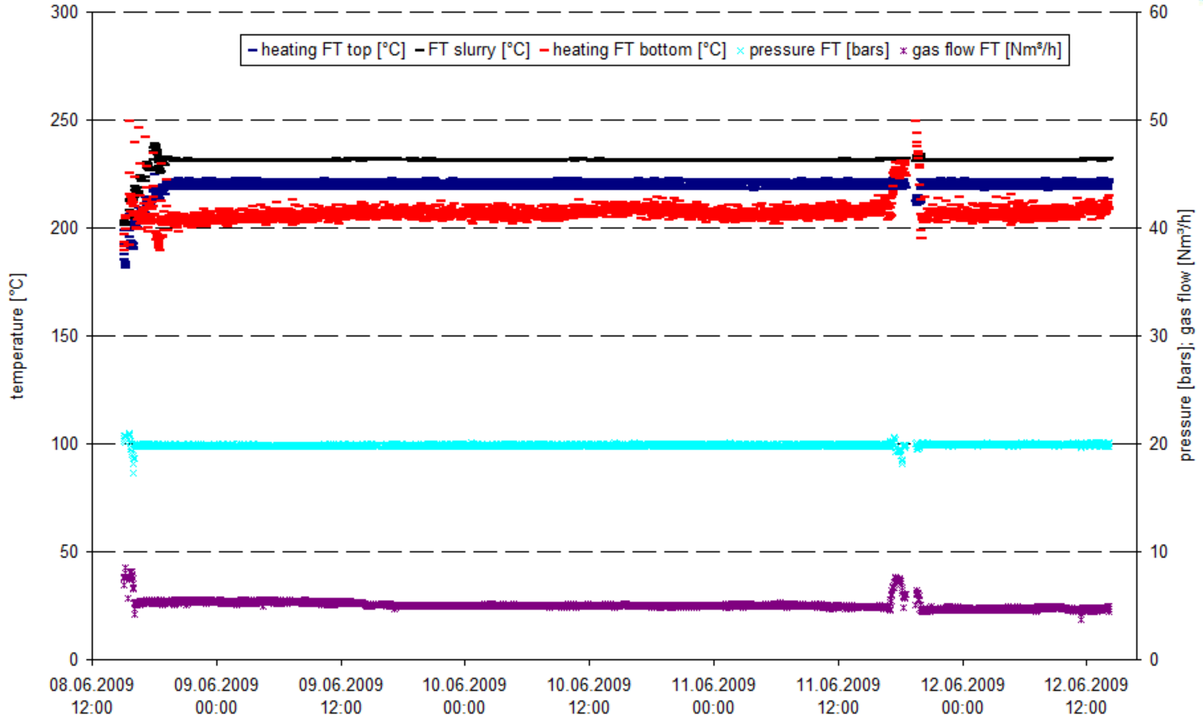


Figure 33: Operation data of experiment no. 7

After experiment no. 8 the slurry temperature and the electrical heating temperature came closer and so the catalyst lost activity. Finally, at the last experiment the temperature difference was minimal. This can be seen in the following graph with the operation date of the experiment no. 10.

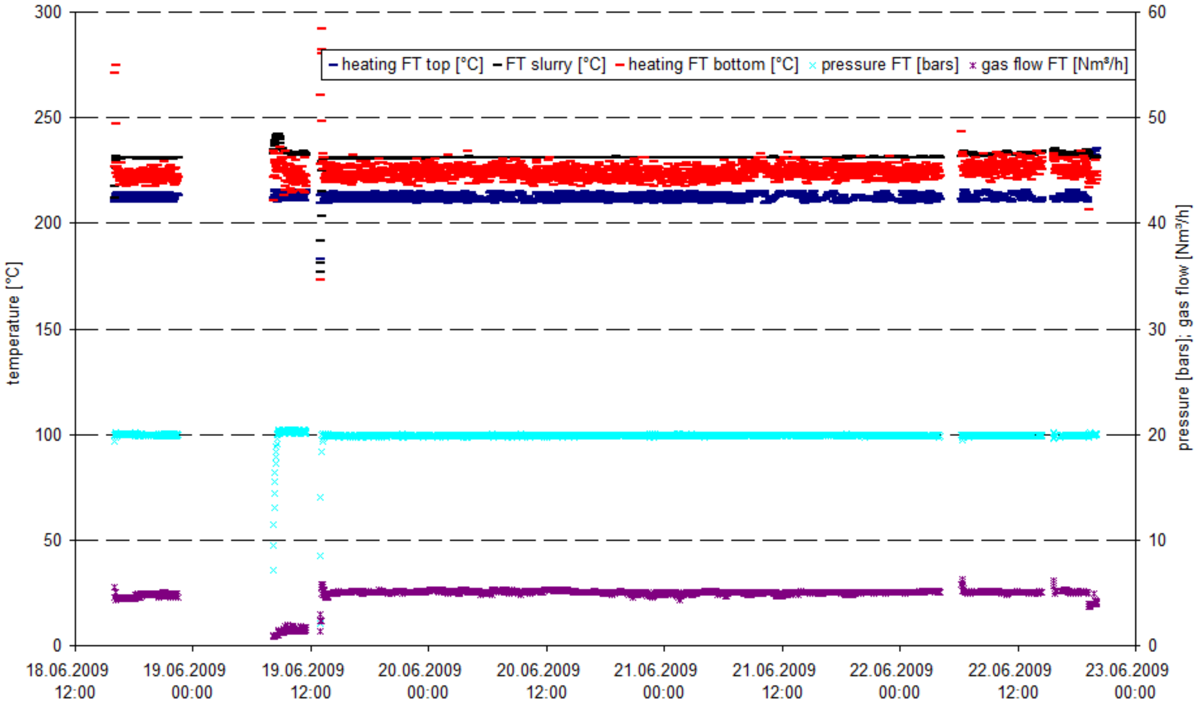


Figure 34: Operation data of experiment no. 10

6.2.2.2 *Conclusion to the catalyst activity*

At the beginning of the test series the cobalt-based catalyst operated very active. But over the time of the test series the temperature difference of the FT slurry and the electrical heating decreased continuously (Figure 35). The reduction with hydrogen after experiment no. 6 brought only a brief improvement. The reason for the decreasing activity of the catalyst was sulphur poisoning, due to a malfunction of the gas cleaning. The sulfur components in the syngas after the gas cleaning section were measured at the beginning of the experimental series but were under detection level at this time.

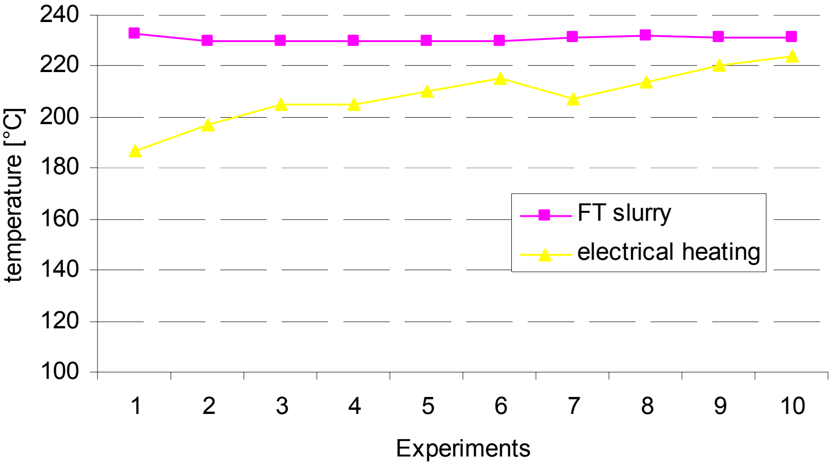


Figure 35: Mean temperature of FT slurry and electrical heating over the test series

6.2.3 **Produced FT product**

6.2.3.1 *Analysis of the produced FT product*

Figure 36: left: FT product of the OGW; right: FT product of the OGK

The gathered FT product from the OGW and OGK (Figure 36) were analyzed by simulated distillation. Thereby the mass fraction of the carbon number n has been determined by a GC-FID. The following chromatograms show the hydrocarbon distribution of the FT product separated in the OGW and OGK. The area of one peak is direct proportional to the mass of the hydrocarbon.

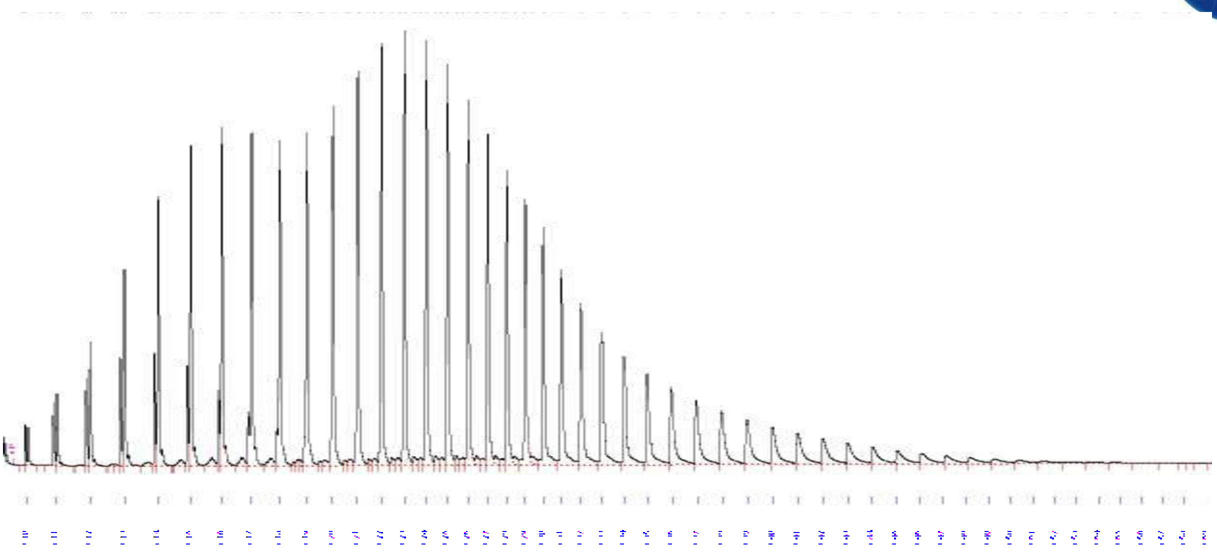


Figure 37: Chromatogram; Hydrocarbon distribution of FT product from the OGW; FT_274

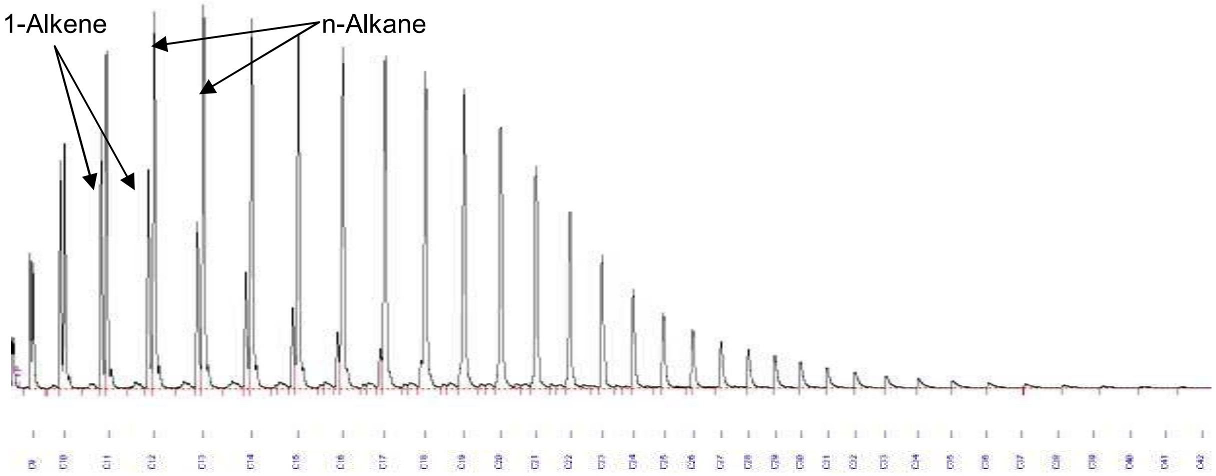


Figure 38: Chromatogram; Hydrocarbon distribution of FT product from the OGK; FT_273

The detected areas were transferred into an Excel file for the calculation of the total product distribution that was condensed. The following graphs with the product distribution correspond with the above chromatograms.

The total product distribution was used for the calculation of the chain growth probability. The FT product in the OGW and OGK are hydrocarbons with carbon number starting with 9 up to 60. The amount of product that was not condensed, including gaseous product and partly liquid product with carbon number up to 15, was calculated together with the Anderson-Schulz-Flory (ASF) plot.

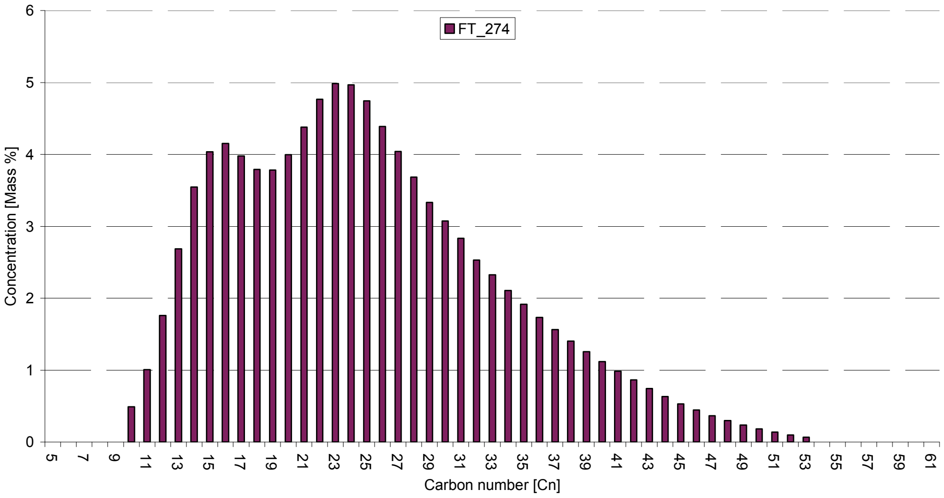


Figure 39: Product distribution in Off-gas scrubber; experiment no. 5

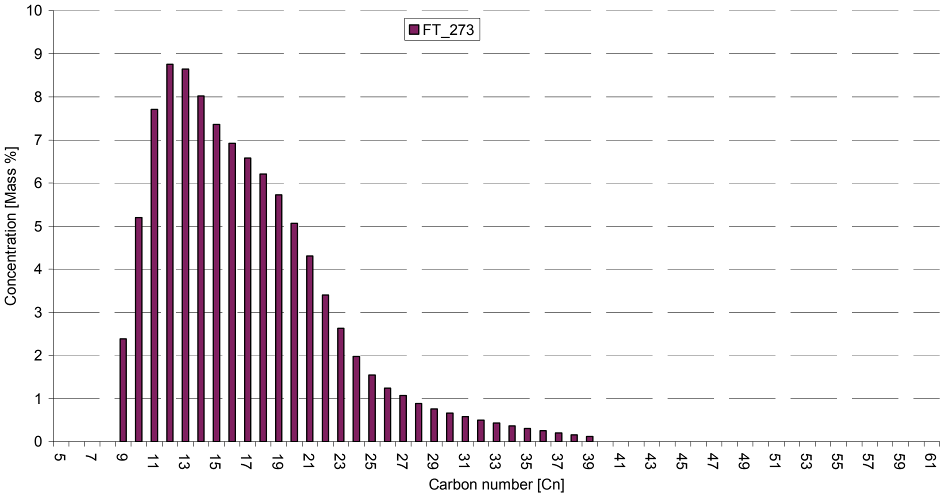


Figure 40: Product distribution in Off-gas cooler; experiment no. 5

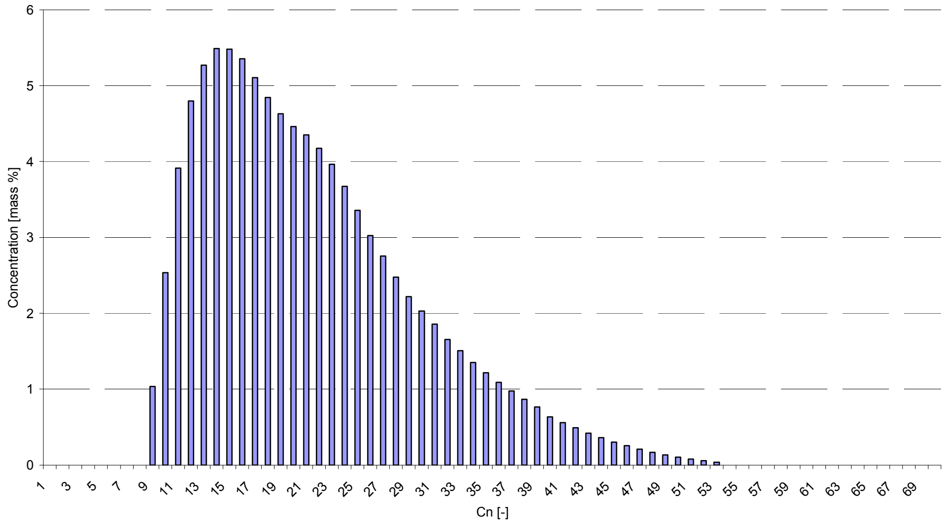


Figure 41: Total product distribution of experiment no. 5

For the calculation of the chain growth probability (α) of each experiment the decade logarithm of the mass fraction of the carbon number n divided per n is set against the carbon number n. By transforming equation (3.10) the following equation obtains which is used for the α calculation:

$$\log\frac{W_n}{n} = n\log(\alpha) + \log\frac{(1-\alpha)^2}{\alpha} \qquad (5.1)$$

$$\log\frac{(1-\alpha)^2}{\alpha} = const. \qquad (5.2)$$

In the following graph it can be seen that the linearity of the ASF plot of the 'original' product exist only over a short range. The range up to carbon number 16 shows that this fraction was only partly condensed and so in the ASF plot is a break. For the linear range a linear equation is determined and with the slope α value can be calculated.

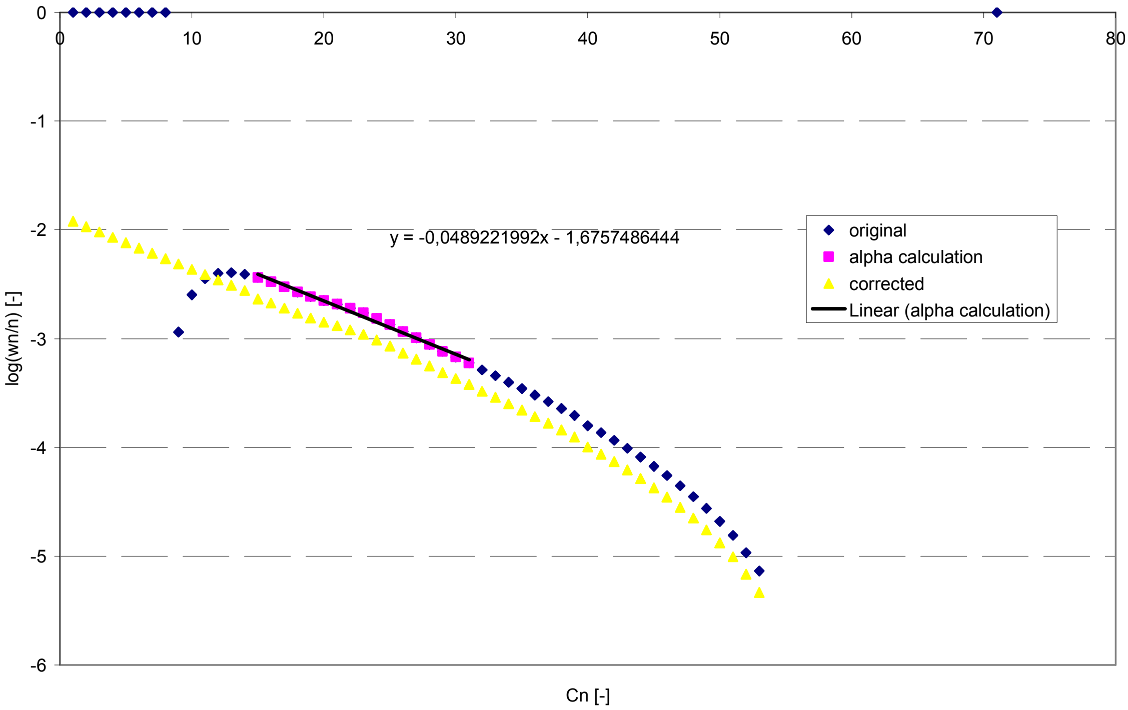


Figure 42: ASF plot; determination of alpha; experiment no. 5

In the following the original product distribution of each experiment is compared with the corrected product distribution according to the ASF plot. If the ASF plot has a different shape as in Figure 42 then it will be illustrated to the corresponding experiment. This shows which linear range of the ASF plot was used for the α calculation. All product distribution graphs of OGW and OGK and as well all ASF plots are to find in appendix.

6.2.3.2 Conclusion to the produced FT product--

The hydrocarbon distribution was almost similar only at the experiment no. 1, 9 and 10 were untypical distribution. The α was predominantly between 0.85 and 0.90 which was expected to the low temperature FT process. It was observed that at higher carbon numbers a second α occurs. The calculation of the lost product is slightly deficient due to that more α occur in the distribution.

The following table represents again all the results of the product analysis and the calculation of the corrected FT product based on the ASF plot.

Table 21: Results of the α calculation by the ASF plot

Number of experiments	active hours [h]	Sample number OGW	Sample number OGK	FT raw product [kg]	α	FT product by ASF [kg]
1	23	FT 259	FT 260	9.92	0.85	14.5
2	63.8	FT 263	FT 261	20.87	0.87	31.8
3	39	FT 268	FT 265	8.94	0.89	13.8
4	64	FT 271	FT 270	12.96	0.88	20.3
5	69	FT 274	FT 273	7.55	0.89	11.9
6	64.6	FT 276	FT 275	8.84	0.89	14.5
7	92.3	FT 283	FT 282	13.87	0.88	23.0
8	55.3	FT 285	FT 284	4.87	0.90	7.2
9	67	FT 287	FT 286	1.88	0.93	2.4
10	84.6	FT 288	FT 289	1.00	0.90	1.4
Sum				90.69		140.8

6.2.4 **Mass balance**

6.2.4.1 Results of the mass balance

Aforementioned, the gas is analyzed before and after the FT reactor by a GC-FID-TCD. The analyzed gas compounds are recorded and can be used to calculate the CO-conversion. Table 22 represents the analyzed gas composition while the H_2 and CO concentration are the most significant one.

Table 22: Syngas composition before FT reactor, in Vol%

Number of experiments	CH_4	C_2H_4	N_2	CO_2	CO	H_2
1	5.63	0.02	1.01	17.58	26.83	48.92
2	5.83	0.02	0.90	16.69	27.37	49.18
3	5.89	0.10	1.36	16.00	29.48	47.14
4	6.37	0.09	0.96	16.06	30.50	45.98
5	7.39	0.55	0.77	17.72	28.16	45.26
6	7.85	0.59	1.15	15.89	29.66	44.70
7	7.55	0.56	1.03	18.47	26.19	46.10
8	8.99	2.56	1.58	23.69	22.71	40.13
9	8.86	2.48	1.20	23.40	22.74	40.97
10	9.10	2.56	1.02	23.43	22.69	40.87

Table 23: Offgas composition after FT reactor, in Vol%

Number of experiments	CH_4	C_2H_4	N_2	CO_2	CO	H_2
1	11.81	0.02	2.37	33.68	20.33	31.49
2	10.75	0.02	2.24	27.99	23.69	35.04
4	9.81	0.00	1.10	19.72	29.60	39.43
6	1.25	0.02	1.34	31.57	18.10	31.50
7	10.04	0.18	1.19	23.20	24.88	39.90
8	11.95	0.39	1.48	29.34	20.32	33.62

9	10.36	0.93	1.29	25.41	22.25	37.84

The gas compounds C2H6, C3H6 and C3H8 are not included in this table because their concentration is under 1,00 Vol%. The offgas composition could not be carried out at the experiments no. 3, 5 and 10 due to a failure in the measuring section.

The CO-conversion is a possibility to calculate the theoretical amount of FT product that can be produced. On the other hand it enables to evaluate the activity of the FT catalyst. The following equation describes the CO-conversion (x_{CO}):

$$x_{CO} = \frac{c_{IN} \cdot \dot{V}_{IN} - c_{OUT} \cdot \dot{V}_{OUT}}{c_{IN} \cdot \dot{V}_{IN}} \tag{5.3}$$

c_{IN}..................CO part in syngas [V%]
c_{OUT}..................CO part in off-gas [V%]
V_{IN}..................gas flow into the FT reactor [Nm³/h]
V_{OUT}..................gas flow out of the FT reactor [Nm³/h]
x_{CO}..................CO-conversion []

Due to the fact that the gas flow out of the FT reactor is not measured this method for the CO-conversion calculation cannot be used. An other approach is to use the stoichiometry of the general FT reaction (3.1).

$$CO + 2H_2 \longrightarrow (-CH_2-) + H_2O$$

According to this equation an ideal H_2:CO ratio is 2. But the H_2:CO ratio obtain during the experiments a maximal value of 1.8. Thus, the hydrogen part is used as limiting component for the calculation of the theoretical maximal amount of product per Nm³ syngas.

$$v_{H_2} = \frac{c_{H_2}}{100} \qquad \left[\frac{m^3_{H_2}}{m^3_{SG}}\right] \tag{22}$$

v_{H_2}..................H_2 part in syngas
c_{H_2}..................H_2 concentration in syngas

$$n_{H_2} = \frac{v_{H_2}}{v_{mol}} \qquad \left[\frac{mol_{H_2}}{m^3_{SG}}\right] \tag{23}$$

n_{H_2}..................number of mol H_2 in m³ syngas
v_{mol}..................mol volume; 22.41 liter/mol

$$n_{CH_2} = 0.5 \cdot n_{H_2} \qquad \left[\frac{mol_{CH_2}}{m_{SG}^3}\right] \tag{24}$$

n_{CH_2} ....number of mol CH_2 based on m³ syngas

$$m_{CH_2} = n_{CH_2} \cdot M_{CH_2} \qquad \left[\frac{mol_{CH_2}}{m_{SG}^3}\right] \tag{25}$$

m_{CH_2} ....mass CH_2 based on m³ syngas

M_{CH_2} ....mol mass CH_2; 14 g/mol

In this way the theoretical amount of hydrocarbon that can be produced in the FT reactor is calculated. The next table includes the results of the calculation which is based on the above equations ((5.4)-(5.7)).

As it can be seen in the table, the possible product per gas volume is almost on the same level excluding the last three experiments without steam reforming. The 100 % conversion is based on the hydrogen content in the syngas before FT reactor. The relative value ($g_{Product}$/Nm³) was multiplied with the total gas amount used for the experiment to obtain the product amount by 100 % hydrogen conversion.

Table 24: Results of the calculation for 100% H_2 conversion

Number of experiments	Pressure [bars]	Gas flow [Nm³/h]	gas amount [Nm³]	$g_{Product}$/Nm³	at 100% conversion [kg]
1	19.9	3.7	86	0.153	13.1
2	19.9	3.7	233	0.154	35.8
3	19.7	3.2	126	0.147	18.6
4	18.1	3.7	234	0.144	33.6
5	19.8	5.8	402	0.141	56.8
6	25	4.1	268	0.140	37.4
7	19.9	5.1	469	0.144	67.5
8	12.7	5.2	288	0.125	36.1
9	12.8	4.8	322	0.128	41.2
10	19.9	4.9	413	0.128	52.7

6.2.4.2 *Conclusion to the mass balance*

Due to a missing gas flow measurement after the FT reactor the CO-conversion in the FT synthesis cannot be calculated. Therefore, the hydrogen content was taken, in refer to the general FT reaction, to calculate the maximal theoretical FT product that can be yielded.

In Table 25 the results are compared with the amount of the real produced FT product and the corrected product by ASF plot.

Table 25: 100% conversion in comparison to the amount of the real product and the product by ASF

Number of experiments	at 100% conversion [kg]	FT raw product [kg]	real conversion	FT product by ASF [kg]	Conversion by ASF
1	13.1	9.92	75	14.5	110
2	35.8	20.87	58	31.8	89
3	18.6	8.94	48	13.8	74
4	33.6	12.96	39	20.3	60
5	56.8	7.55	13	11.9	21
6	37.4	8.84	24	14.5	39
7	67.5	13.87	21	23.0	34
8	36.1	4.87	13	7.2	20
9	41.2	1.88	5	2.4	6
10	52.7	1.00	2	1.4	3
Sum	392.9	90.69	23	140.8	36

As it can be seen in the column “real conversion”, at the beginning of the test series the conversion was unexpected high which become temperate at the end of the test series. With the steam reformer the desired H_2:CO could not be achieved but the product yield was increased significantly. The ratios between the calculated FT products by the ASF plot to the 100 % conversion are at the first four experiments too high, especially at the first experiment. This might be due to the assumption that in the ASF plot more than one α is obtained.

6.2.5 *Distillation and FT-fuel analysis*

6.2.5.1 Result of the distillation and FT-fuel analysis

On completion of this work only the FT raw product of experiment no. 1 and 2 was distilled. The result of the distilled 30.79 kg product is represented in the following pie chart.

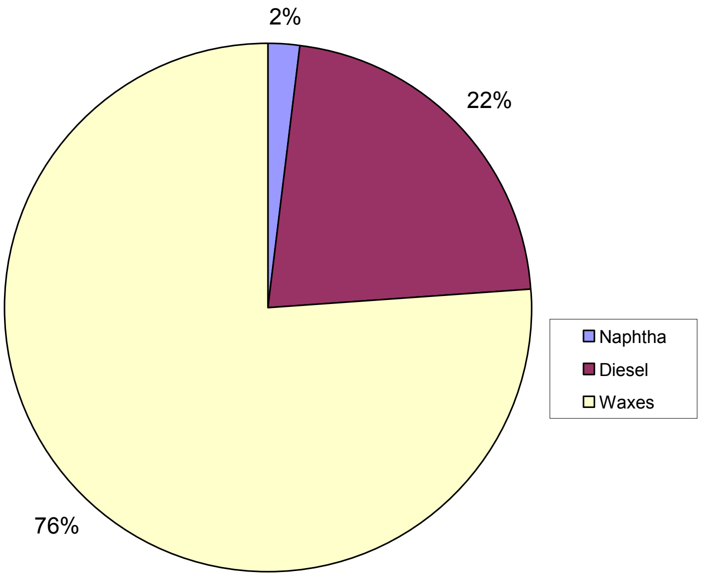


Figure 43: Product distribution of the distilled product

The fractions were sent to a company for fuel analysis according EN 590:2004 and the waxes are used to investigate an innovative hydrotreating process. As this work is still going on, at the moment no results are available.

6.2.5.2 Conclusion to the distillation and FT fuel analysis

The distillation is a simple and accurate approach to separate the FT product into the main fractions. The yielded fraction can so investigated of each other in different ways. The FT diesel has a cetane number of 71 that demonstrates the high quality of the produced FT diesel. The waxes fraction can be hydrotreated and so to increase the diesel ratio. With a small experiment it was proved that the FT diesel has a cleaner quality as the conventional diesel. Thereby, the FT diesel and the conventional diesel were burned in an oil lamp. At middle flame the conventional diesel started to emit soot while the flame of the FT diesel was ‘clean’.

7 Design of the Pilot Plant

In this chapter the description of a new pilot plant is given. Inside this project only the basic design of the pilot plant was done. The detailed engineering, construction and operation of such a plant will be done in future projects.

The pilot plant should be about 10 times larger than the lab scale plant. This is a good compromise between amount of FT product, which can be produced and risk of scaling up. So the pilot plant is designed for a gas flow of about **50-70 Nm³/h** to produce **5-10 kg/h** of raw product.

A pilot plant for FT synthesis consists of 3 main parts:

- Gas cleaning and compression
- FT reactor
- FT product separation from off gases

In the following these 3 parts of the pilot plant are described.

7.1 Gas cleaning and compression

The product gas from the gasifier consists mainly of hydrogen, carbon monoxide, carbon dioxide and methane, but there is also dust, particles, tar, and catalyst poisons like sulphur or chlorine in the product gas. In the pilot plant the product gas is taken before the gas engine, so dust and tars were already removed and only the catalyst poisons had to be removed.

For the design of a new gas cleaning there are 2 possibilities:

- Designing a complete new cleaning system, where the gas is taken from the freeboard of the gasifier
- Using the clean gas before the gas engine and only scaling up the existing gas cleaning from the lab scale FT plant

If the gas is taken from the freeboard, there is the advantage that from the pilot plant upscaling to a stand-alone demonstration plant is easier. If the gas is taken before the gas engine the gas treatment of the pilot plant will be much simpler and cheaper.

In the following figure the planed gas cleaning and treatment for the FT synthesis is given, if the product gas is taken from the freeboard:

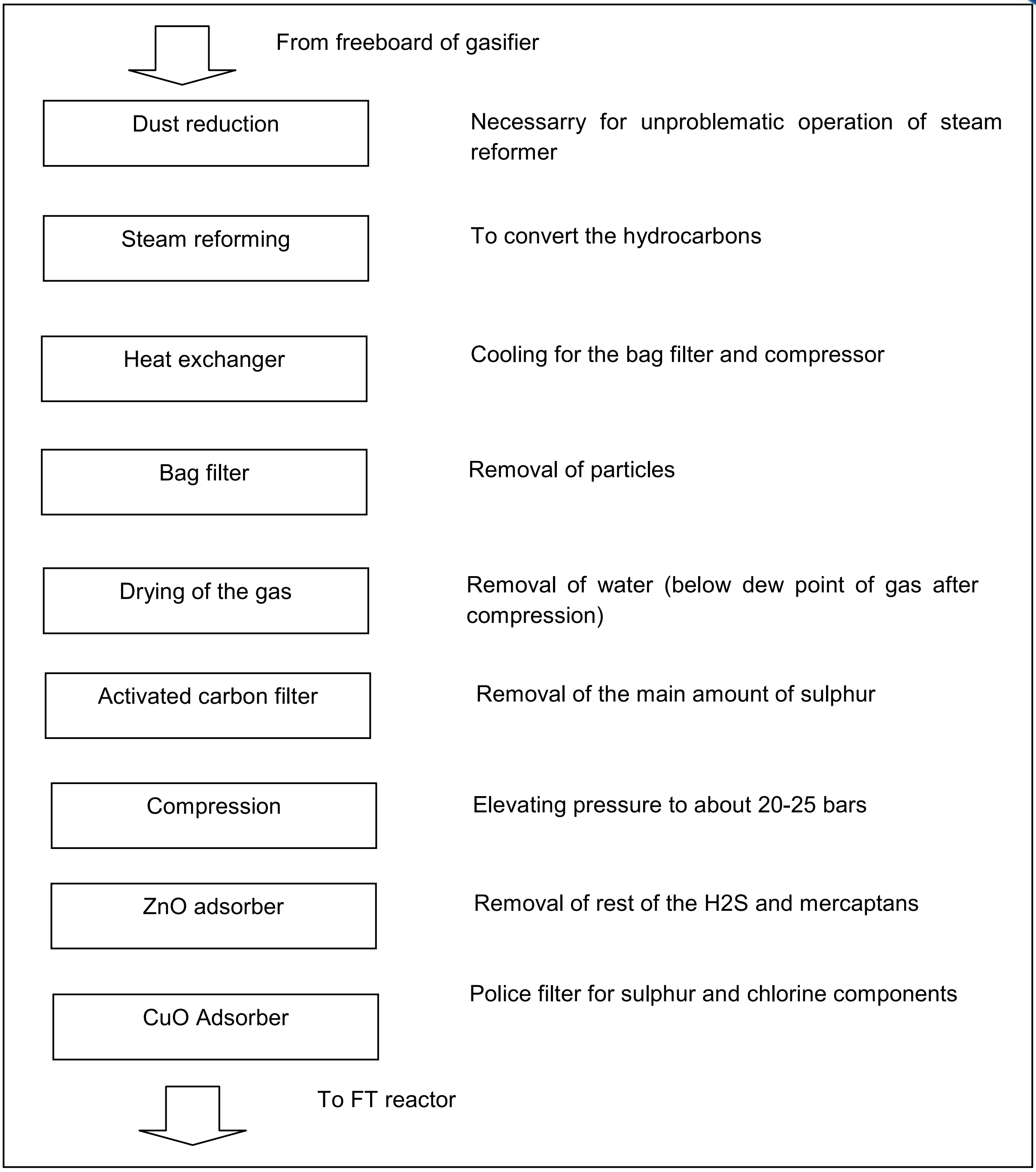


Figure 44: gas cleaning (gas from freeboard)

If the product gas is taken before the gas engine, the gas treatment is simpler, as no dust and tar removal has to be integrated. Also the operation of the steam reformer will be much more reliable with a dust free product gas.

The gas cleaning for product gas taken before the gas engine is given in the following figure.

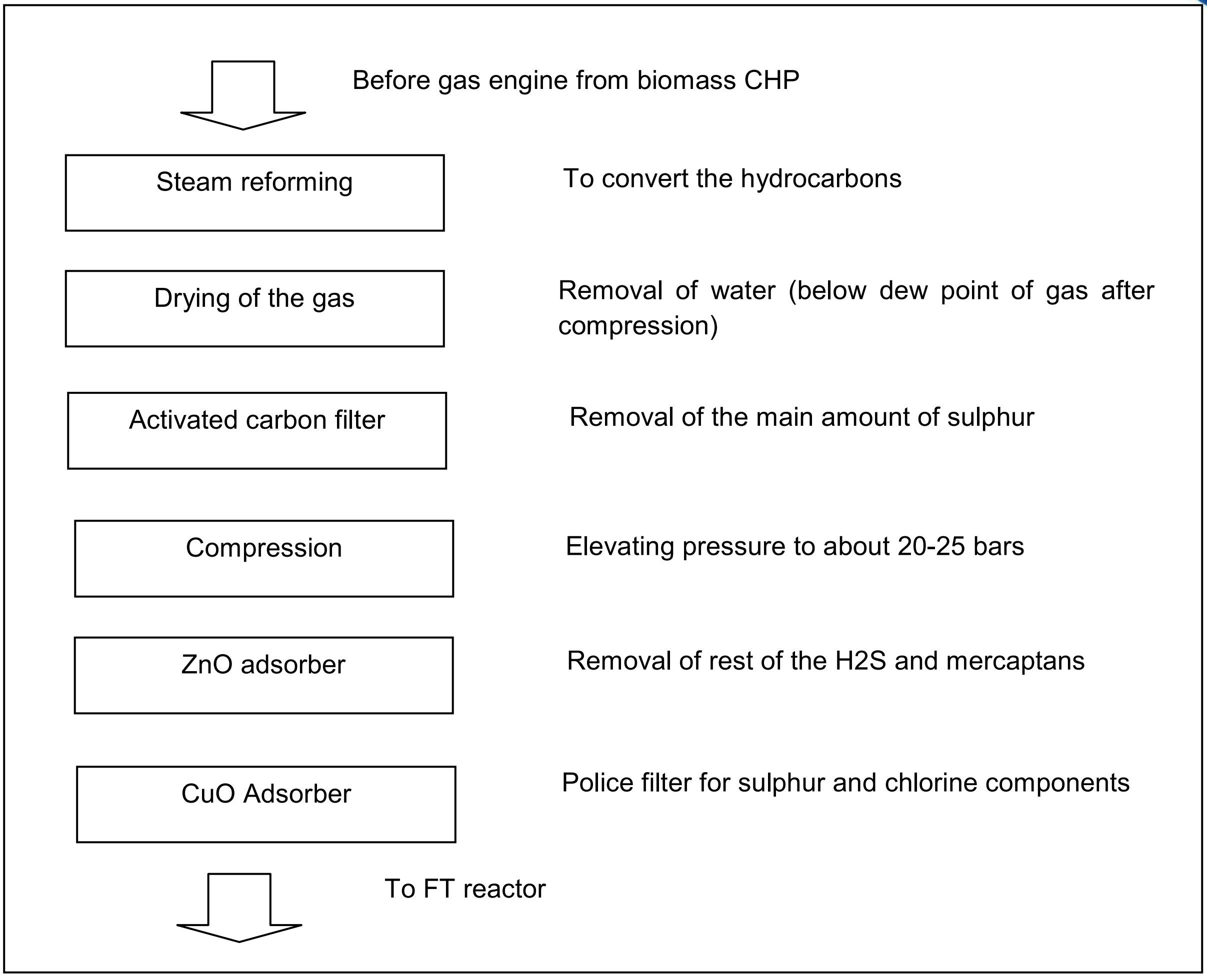


Figure 45: gas cleaning (gas before gas engine)

As the second system is much simpler, this gas cleaning concept was investigated in more detail. In the following the flow chart is given, where the main components and flows are shown.

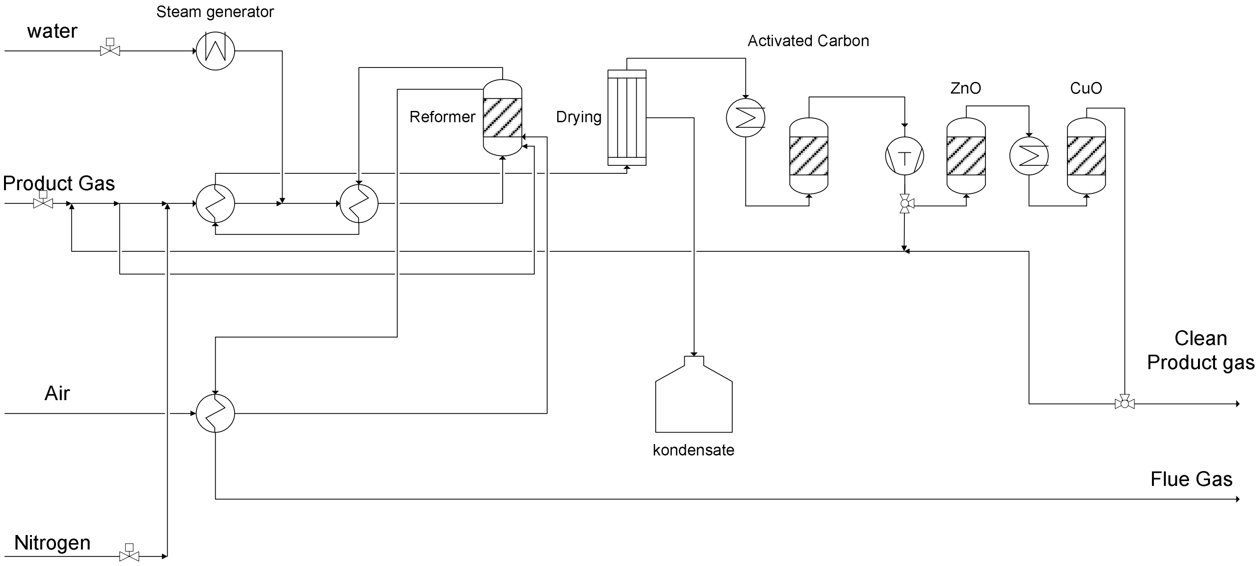


Figure 46: flow chart of gas cleaning

The gas cleaning consists of the following main components:

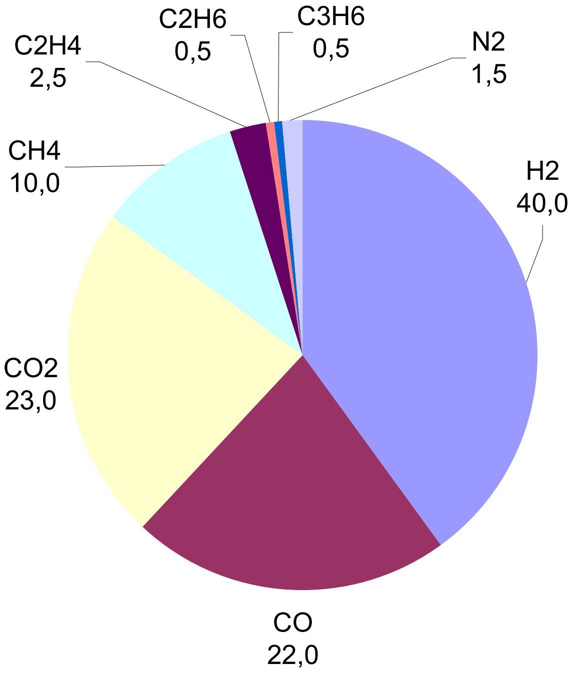
- Steam reformer incl. heat management and steam generation
- Drying of the gas
- Activated carbon filter
- Compression
- ZnO adsorber
- CuO adsorber
- Nitrogen supply for inertisation
- Product gas recycle for start up

The main components are described in the following chapters in more detail.

7.1.1 *Steam reforming*

The product gas of the FICFB gasification system has a remarkable amount of hydrocarbons. This is an advantage if BioSNG should be produced, but a disadvantage, if other synthesis reactions are done, likes FT or alcohol synthesis.

The dry gas composition is given in the following figures, based on volume and on energy content.



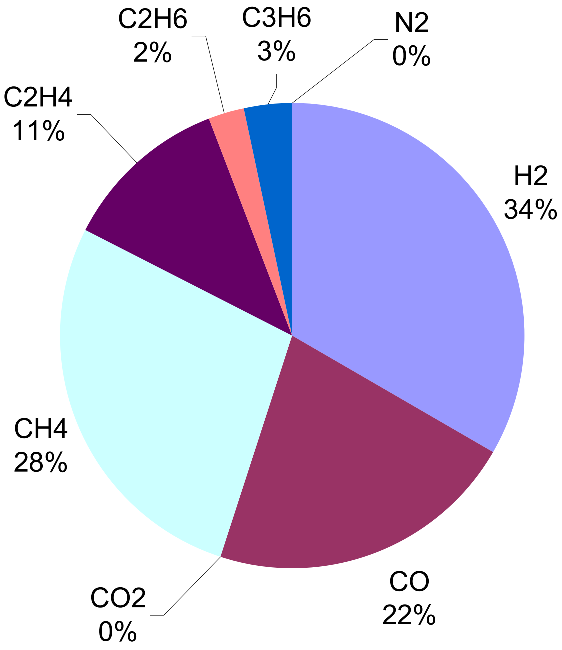


Figure 47: gas composition based on volume

Figure 48: Gas composition based on energy

As a very high energy content in the product gas (more than 40%) is in the form of hydrocarbons a steam reforming step is necessary to convert this hydrocarbons and to make them accessible for the FT reactions.

Based on thermodynamic equilibrium the gas composition at the exit of the steam reformer is given in the following table:

Table 26: gas composition

	Exit gasifier	After steam reformer	
H2	40,0	57,0	vol%$_{dry}$
CO	22,0	27,4	vol%$_{dry}$
CO2	23,0	14,6	vol%$_{dry}$
CH4	10,0	0,0	vol%$_{dry}$
C2H4	2,5	0,0	vol%$_{dry}$
C2H6	0,5	0,0	vol%$_{dry}$
C3H6	0,5	0,0	vol%$_{dry}$
N2	1,5	1,0	vol%$_{dry}$
H20	40,0	24,9	vol%

The steam reformer has the second advantage, that also the H_2:CO ratio is afterwards 2.1:1, which is optimal for the FT reaction.

The steam reformer was simulated in detail and the results are given in the following figure:

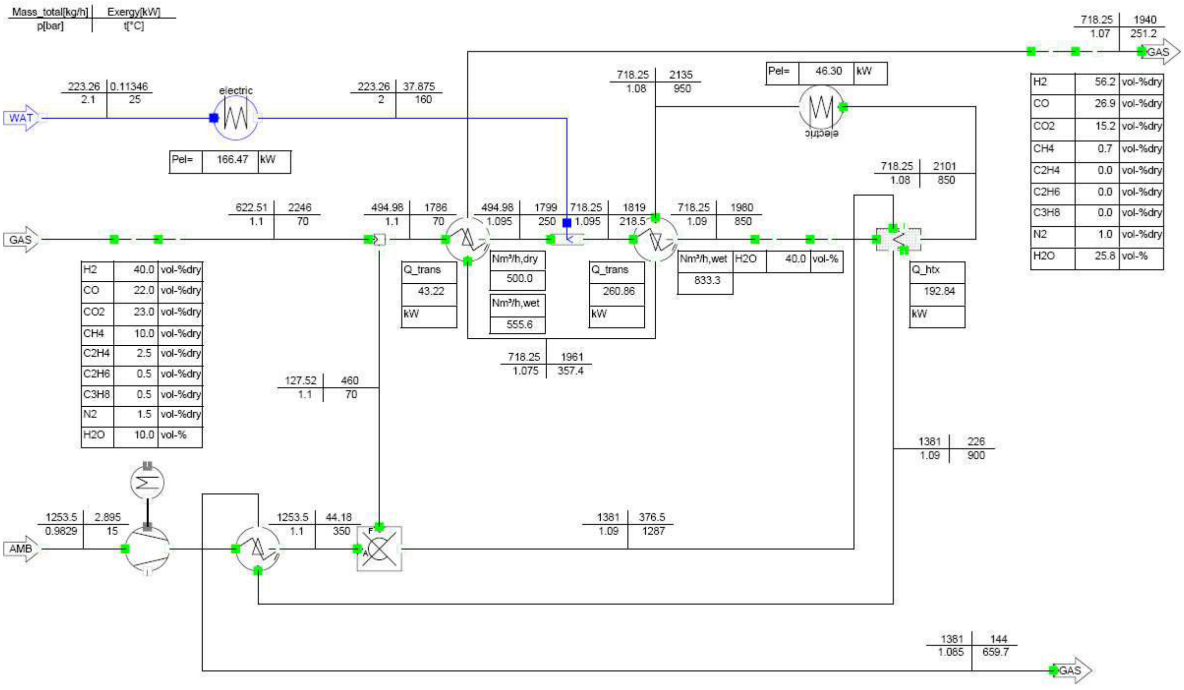


Figure 49: simulation results of steam reformer

In the steam reformer the conversion for methane was set to 90% and the conversion for the other hydrocarbons was set to 100%. These are typical values, which were reached with the laboratory scale steam reformer. The necessary water for the reforming is produced by an electric steam generator. The reformer is operated at 850°C and all the heat is produced by combustion of a slip stream of product gas.

After the reformer a drying step is necessary to remove the excess water from the steam reformer. Here only a condenser is included, which cools down the gas to about 5°C. After the condenser the gas has to heated up to about 50-70°C for the removal of the H_2S by the activated carbon.

7.1.2 *Sulphur and chlorine removal*

The second main gas treatment which is necessary is to remove the sulphur and chlorine components, as these are poisoning the FT catalyst. The removal of sulphur and chlorine components was already investigated by TUV extensively during their work on the FT synthesis and actually the gas can be cleaned to a level, that the FT synthesis can be operated without any deactivation for long periods. Till now the longest run on cobalt catalysts were about 600 hours and on ron catalyst about 700 hours, without any deactivation.

Another necessary step is the compression of the gas. As the biomass CHP Güssing is operated at atmospheric pressure, the gas has to be compressed to the level, which is necessary for the FT synthesis.

The compressor compresses the gas to about 20-30bars and also heats up the gas to about 230°C. With this temperature the gas goes over the ZnO-Adsorber and is cooled afterwards by a heat exchanger to about 100°C, which is the operation temperature of the CuO-Adsorber.

For starting up and cooling down and emergency shut downs nitrogen is used, which can be operated in a closed loop.

There is a second loop where the system can be operated with product gas. This is necessary if the biomass CHP does not produce gas for short periods (1-3 hours). This happens about once a week, due to malfunctions in the biomass feeding system. So during these short periods the gas cleaning section can be operated with product gas in a closed loop and no shut down of the system is necessary.

7.2 FT reactor

In the lab scale FT a slurry reactor is used. This type of the reactor has the advantage of excellent heat transfer and simple scale up. Therefore also in the pilot scale a slurry reactor will be used.

Slurry bubble columns, SBC's, are three phase chemical reactors of simple construction and operation and of wide applicability. They consist of a gas, solid and liquid phase, in which the solid is the catalyst and the gas is the reactant. The liquid is used to keep the solid in suspension and to act as a pathway for the chemical reaction between the reactant and the catalyst to take place.

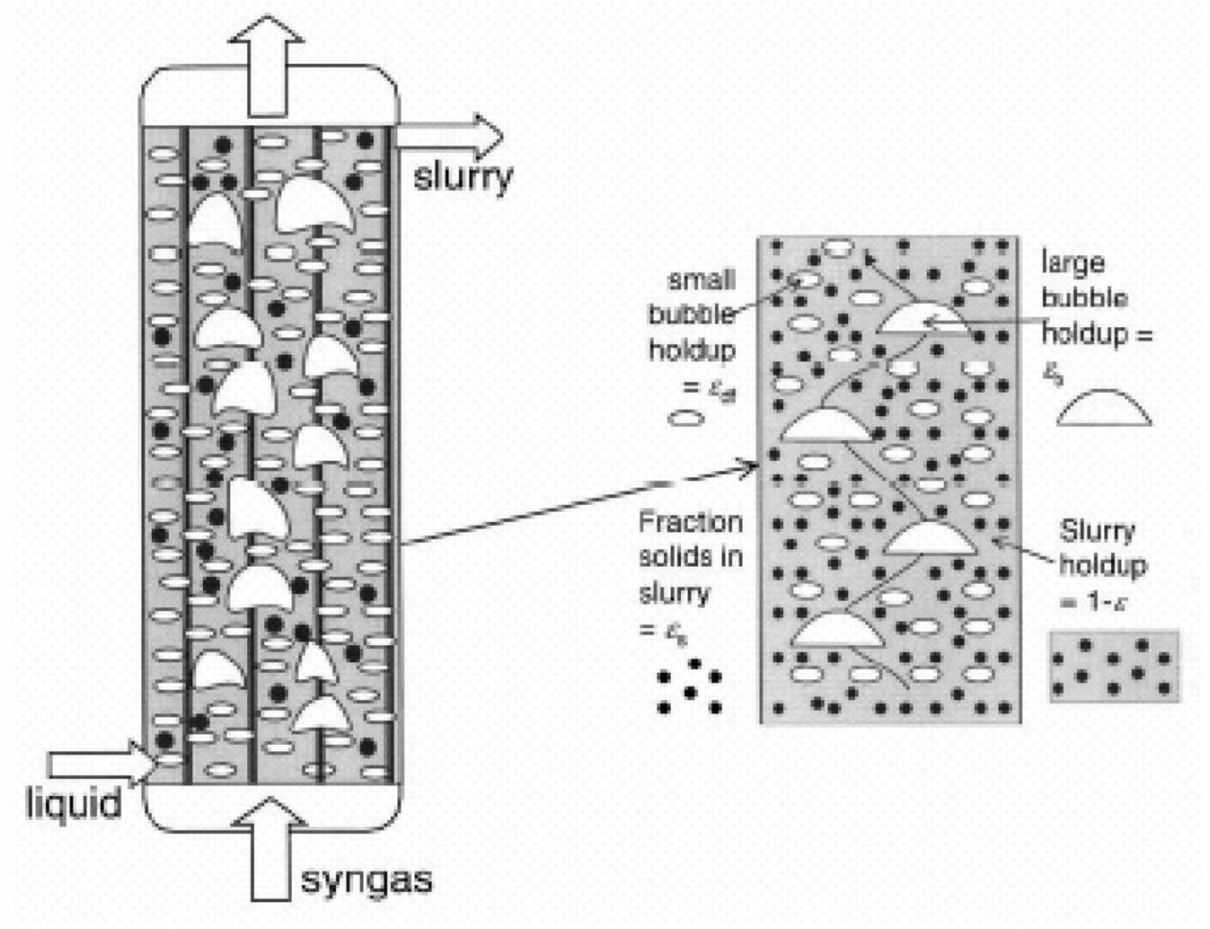


Figure 50: Slurry bubble column and phase description

7.2.1 *Gas Phase Dynamics*

The solid catalyst consists of small particles, typically less than 50µm, of relatively low sedimentation velocity, so they can be kept in suspension solely by bubbling the gas phase through the liquid. Industrially operated SBC's are cylindrical in shape with circular cross sections as it allows ease of gas sparger, the gas distribution system, design, as well as providing mechanical stability at the high operating pressures often encountered. The gas distribution needs to be uniform over the whole cross sectional area of the bubble column as it is crucial that there are no stagnant regions in the column where solids might be deposited. This problem has led to the design of many types of sparger from multiple configurations of various sized holes drilled on a plate, to single orifices, to plastic balls with micro-pores. In SBC's the velocity of this sparged gas plays an important part in the suspension of the solid catalyst particles as well as ensuring a homogeneous mixture of the liquid and solid phases to ensure a high rate of reaction. The minimum superficial gas velocity, U_{min}, needed to suspend the particles depends on many factors such as solids concentration in the column, particle size, liquid viscosity, gas pressure, gas density and particle density.

7.2.2 *Flow Regimes*

The homogeneous mixture of solid and liquid particles relies on the transition from a homogeneous flow regime to a heterogeneous, or churn-turbulent, flow regime in the column. In the homogeneous regime the superficial gas velocity, U, is below a certain value, U_{trans}, and in this regime bubble size distribution is narrow and a fairly uniform bubble size (1-7mm) is found. For a heterogeneous regime to exist, U must be above U_{trans}. In this flow regime, there is a wide distribution of bubble sizes and the environment in the column can be generalised as a two phase model, consisting of a dense phase; liquid, solid catalyst particles and small bubbles, and a dilute phase; large bubbles (20-70mm). These large bubbles have a high rise velocity and often traverse the column in a zigzag fashion, so plug flow conditions for the dilute phase exist. This high superficial gas velocity allows high throughputs of gas and improves heat transfer to cooling surfaces. The upward motion of the large bubbles churns up the dense phase, dragging fluid up in their wake, causing slurry backmixing and therefore dispersion of catalyst in the column.

7.2.3 ***Heat Transfer***

In SBC's heat transfer is usually via internal cooling coils, and unlike in other reactors, these coils do not interrupt the overall hydrodynamics of the system. The coils spacing and frequency is a factor of the conversion efficiency of the reactor. Steam at 10-20°C below the optimum reactor temperature is ran through these pipes to remove heat generated by the conversion reactions, while never adversely affecting the overall optimum temperature of the reactor. The slurry bed in the SBC acts as a heat sink thus the whole reactor is quite isothermal with no hot spots present, and so the reactor can be operated at high temperatures if so wished. High liquid rise and fall velocities in the axial and wall regions ensure high heat transfer coefficients, up to $1000 W/m^2.K$, can be obtained in SBC's. The heat transfer coefficient increases with increasing gas velocity and solids concentration.

7.2.4 ***Operation***

The SBC can be used in continuous operation for process such as methanol production and Fisher-Tropsch synthesis, due to the SBC's capability of on-line removal and addition of fresh catalyst. The system may be operated at high catalyst loading, 30-40% depending on the literature consulted. The increased catalyst concentration, ε_s, increases the gas conversion rate and the reactor capacity for further catalyst addition. This is due to the fact that increasing ε_s reduces the total gas hold-up which makes room for more catalyst. However, increasing ε_s also increases the number of cooling tubes required in the reactor, so the maximum catalyst concentration consistent with ease of handling is used in practice. The capacity of the SBC for high catalyst concentrations also allows economic deployment of low activity catalysts.

Increased ε_s corresponds to increased conversion rates, and low superficial gas velocity, U, also corresponds to increased conversion rates. However, with decreased U there is a loss in productivity. A compromise to this dilemma between conversion efficiency and productivity is to recycle the unconverted gas, mixing it with the input gas. This allows good productivity as well as good conversion rates.

Another way to improve conversion rates, while still operating at reasonably high U, is to introduce staging into the column. This consists of introducing sieve plates which encourage well mixed compartments of uniformly suspended catalyst and isothermal conditions optimised to the specific reaction required. However, there are no significant benefits to reactor conversion or productivity after a certain number of stages. This will vary depending on the specific reaction and configuration of the SBC. In many SBC processes, e.g. Fischer-Tropsch synthesis, the liquid phase used to suspend the catalyst particles is the desired product of the reaction. The problem of how to separate the newly formed liquid from the existing liquid suspending the catalyst was one which resulted in SBC's being disregarded as viable Fischer-Tropsch reactors for quite some time. However, filtration systems have been developed to separate the catalyst fines from the liquid product, although no information on these processes has been made public.

7.2.5 *Design of the slurry reactor for the pilot plant*

The design of the lab scale slurry reactor was done based on cold flow model experiments. In these experiments the optimal fluidisation conditions of the slurry reactor was investigated. Also the operation window of the slurry reactor was investigated in the cold flow model. Based on the results the hot slurry reactor was designed and installed at the biomass CHP Güssing. In the following figure the sketch of the lab scale reactor and of the pilot plant reactor are given.

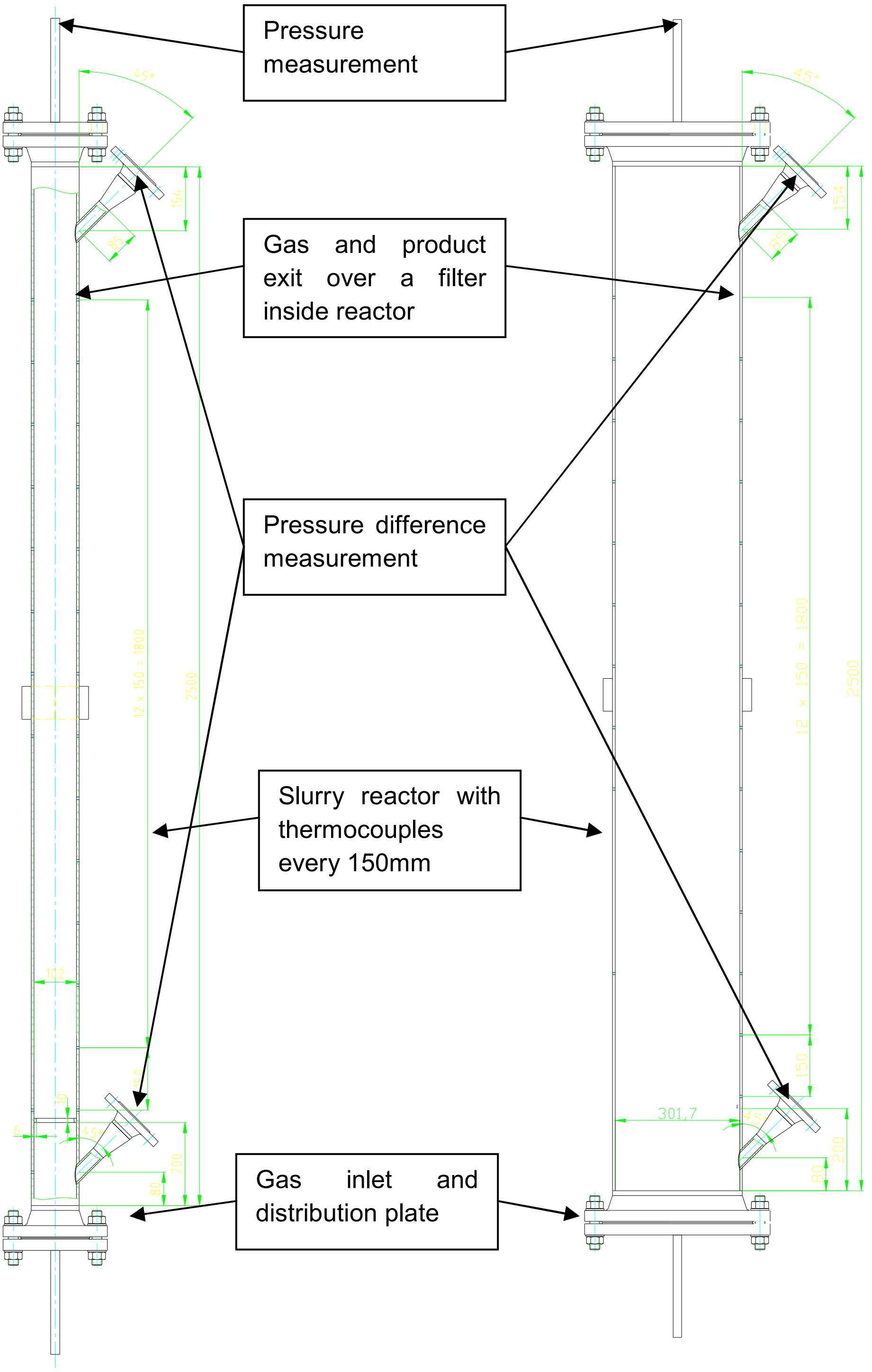


Figure 51: lab scale FT reactor

Figure 52: pilot plant FT reactor

The lab scale slurry reactor is a DN100 tube with a height of 2500mm. At the bottom there is the gas inlet with a distribution plate. The slurry inside the reactor has a height of about 2000mm and is controlled by the position of the filter. Over the filter the FT product and the un-reacted gases are taken out together and go to the product separation system.

The pilot plant FT reactor is similar to the lab scale reactor. The main difference is that the pilot plant reactor has an inner diameter of 300mm (DN300 tube). All other components like gas distribution, filter, measurements will be done similar to the lab scale reactor.

7.3 Product separation

As the FT product is taken together with the offgases (inerts like CH_4 or CO_2 and un-reacted H_2 and CO) out of the reactor a separation has to be done to collect the FT product. The offgases are sent back to the biomass CHP, so the separation is a important step to avoid any loss of FT product.

The FT product consists of hydrocarbons from C1 to C100, depending on the operation conditions. Beside also water is produced, which also has to be separated from the offgases. The separation cannot be done by simple condensation in a heat exchanger, as a part of the FT product becomes solid at temperatures below 100°C.

Therefore a fractioned condensation of the FT product is necessary, where in several steps the FT product is condensed, and removed from the gas stream. This fractioned condensation can be done either at the pressure of the FT synthesis, or after expanding the gases to atmospheric pressure.

In the lab scale FT plant the separation is done after expanding at atmospheric pressure. This has the advantage, that the equipment is much cheaper, as no pressure vessels are necessary. The product separation was originally developed during the EC-project Renew and further optimized in the national project EZ-P4 (energy centre for production of heat electricity and biofuels). It consists of a water scrubber, operated at about 80°C for separation of the heavy FT product (waxes) and a heat exchanger, where the gas is cooled to about 5°C for separation of the light FT products (gasoline diesel fraction). This system works well, although there is a loss of light products (C5-C10).

In Bioenergy 2020+ research is done at the moment for a high pressure separation of the FT products. Here the FT product is separated in a heat exchanger, operated at about 100°C) direct after the FT synthesis. This system has the advantage, that by the high pressure the dew points of the different components are higher and therefore the separation at a specific temperature is more efficient at high pressures compared to atmospheric pressure.

As at the moment there are no results available from the high pressure separation the design of the product separation of the pilot plant will be postponed, till first results are available.

8 References

[1] Demirbas, A. (2007): Progress and recent trends in biofuels, Progress in Energy and Combustion Science 33, Departement of Chemical Engineering, Selcuk University, Turkey, p. 2-5, 12,

[2] Di Lucia, L., Nilsson, L. J. (2007): Transport biofuels in the European Union: The state of play, Transport Policy 14, p. 533

[3] Directive 2003/30/EC (2003): Directive of the European Parliament and the Council on the Promotion of the use of Biofuels or other Renewable Fuels for Transport, 2003, Brussels, p. L123/44 – L123/45

[4] Richtlinie 2003/96/EG (2003): Richtlinie des Rates zur Restrukturierung der gemeinschaftlichen Rahmenvorschriften zur Besteuerung von Energieerzeugnissen und elektrischen Strom, p. L 283/57

[5] Kommission der Europäischen Gemeinschaft (2001): Mitteilung der Kommission – KOM(2001) 547, Brüssel, p. 2 and 14

[6] Fürnsinn, S., Hofbauer, H. (2007): Synthetische Kraftstoffe aus Biomasse: Technik, Entwicklung, Perspektiven, Chemie Ingenieur Technik 79, No. 5, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, p. 1

[7] International Energy Agency (IEA) (2008); From 1st- to 2nd- Generation Biofuel Technologies, France, p. 5 - 11

[8] BIOFRAC (Biofuels Research Advisory Council) (2006): Biofuels in the European Union: A Vision for 2030 and Beyond, European Communities, Report, p. 13.

[9] Coyle, W. (2007): The Future of Biofuels: A Global Perspective, Amber Waves, Issue 5, Vol. 5, p. 24

[10] Bomb, Ch., McCormick, K., Deurwaarder, E., Kåberger, T. (2007): Biofuels for transport in Europe: Lessons from Germany and the UK, Energy Policy 35, p. 2256 – 2259

[11] International Energy Agency (IEA) (2004): Biofuels for Transport, France, p. 33 – 36, 101 – 110,

[12] Demirbas, A. (2008): Biofuel sources, biofuel policy, biofuel economy and global biofuel projections, Energy conversion and management 49, p. 2109

[13] Bauer, G. (2008): Experimentelle Untersuchungen im Labor- und Technikumsmaßstab zur Fischer-Tropsch-Synthese bei atmosphärischem Druck, Dissertation, Institut für Verfahrenstechnik, Umwelttechnik und Technische Biowissenschaften, Technische Universität Wien, p. 5-6, 9-15, 30-33,

[14] United Nations (2008): Biofuel production technologies: status, prospects and implications for trade and development, United Nations Conference on Trade and Development, New York and Geneva, p. 9-15

[15] Spath, P.L., Dayton D.C. (2003): Preliminary Screening – Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas, National Renewable Energy Laboratory, Colorado, p. 5-8, 29, 31, 34, 41, 46, 90-106

[16] Prins, M.J., Ptasinski, K.J., Janssen, F.J.J.G., (2004): Exergetic optimization of a production process of Fischer-Tropsch fuels from biomass, Fuel Processing Technology 86, p. 377

[17] Opdal, O.A. (2006): Production of synthetic biodiesel via Fischer-Tropsch synthesis, Project report, Faculty of Engineering Science and Technology, Norwegian University of Science and Technology, p. 35-56

[18] Schiffermüller, L. (2008): Praktische und theoretische Untersuchung zur Fischer-Tropsch Normaldrucksynthese, Diplomarbeit, Technische Universität Wien, p. 9, 23-27,

[19] Guettel, R., Kunz, U., Turek, Th., (2008): Reactors for Fischer-Tropsch Synthesis, Chemical Engineering Technology 2008, 31, No. 5, p. 746-754

[20] BASF, (1913): Patent-Nr. 293787, Deutsches Reichspatentamt

[21] Stranges, A. N. (2003): Germany's Synthetic Fuel Industry 1927-45, Prepared for Presentation at the AIChE 2003 Spring National Meeting, Hystorical Development of the Fischer-Tropsch Synthesis Process – I, New Orleans, p. 2

[22] Fischer, F., and Tropsch, H., (1925): Patent-Nr. 484337 Verfahren zur Gewinnung mehrgliedriger Paraffinkohlenwasserstoffe aus Kohlenoxyden und Wasserstoff auf katalytischem Wege, Deutsches Reichspatentamt,

[23] Dry, M.E., (2002): The Fischer-Tropsch process: 1950-2000, Catalysis Today 71, p. 227 – 241

[24] Davis, B.H., (2001): Fischer-Tropsch synthesis: current mechanism and futuristic needs, Fuel Processing Technology, quoted in [13]

[25] Storsæter, D., Chen, D., Anderson, R.B. (2006): Microkinetik modelling fort he formation of C1 and C2 products in the Fischer-Tropsch synthesis over cobalt datalysts, Surface Science, quoted in [13]

[26] Fernandes, F.A.N., (2005): Polymerization Kinetics of Fischer-Tropsch Reaction on iron Based Catalysts and Product Grade Optimization, Chem. Eng. Technol., Nr. 8, quoted in [13]

[27] Fürnsinn, S. (2007): Outwitting the dilemma of scale: Cost and energy efficient scale-down of the Fischer-Tropsch fuel production from biomass, Dissertation, Technische Universität Wien,

[28] Kuntze, T., Hedden, K., Jess, A., (1995): Kinetics of the Fischer-Tropsch Synthesis using a Nitrogen-Rich Synthesis Gas, OIL GAS, p. 19-24, quoted in [13]

[29] Schulz, H. (1999): Short history and present trends of Fischer-Tropsch Synthesis, Applied Catalysis A: General 186, p. 4-11

[30] Linden, G. (1985): Zur Fischer-Tropsch-Synthese an multifunktionellen Cobalt/Zeolith-Katalysatioren, Bericht der Kernforschungsanlage Jülich, Nr. 2001, quoted in [13]

[31] Dry, M.E. (1990): The Fischer-Tropsch process – commercial aspects, Catal. Today, 6, p. 186-201

[32] Dry, M.E. (1996): Practical and theoretical aspects of the catalytic Fischer-Tropsch process, Applied Catalysis A: General 138, p. 323-343

[33] Van Dijk, H.A.J. (2001): The Fischer-Tropsch synthesis: A mechanistic study using transient isotopic tracing, Proefschrift, Technische University Eindhoven, p. 25-28

[34] Anderson R.B. (1984): The Fischer-Tropsch synthesis, Academic press Inc., Orlando, Florida, quoted in [31][33]

[35] Dry, M.E. (1989): Commercial conversion of carbon monoxide to fuels and chemicals, Journal of Organometallic Chemistry, quoted in [13]

[36] Dry, M.E. (2001): High quality diesel via the Fischer-Tropsch process – a review, Journal of Chemical Technology and Biotechnology, p. 45-47

[37] Espinoza, R.L., Steynberg, A.P., Jager, B., Vosloo, A.C. (1999): Low temperature Fischer-Topsch synthesis from a Sasol perspective, Applied Catalysis A: General 186, quoted in [18]

[38] Standard Oil Development Company (1938); Patent no. 496,159: An improved method of controlling exothermic catalytic reactions.

[39] Dry, M.E. (1999): Fischer-Tropsch reactions and the environment; Applied Catalysis A: General 189, p. 187-188

[40] Tijmensen, M.J.A., Faaij, A.P.C., Hamelinck, C.N., van Hardeveld, M.R.M., (2002): Exploration of the possibilities for production of Fischer-Tropschl liquids and power via biomass gasification, Biomass and Bioenergy 23, quoted in [18]

[41] Bolhàr-Nordenkamp, M., Rauch, R., Bosch, K., Aichernig, C., Hofbauer, H. (2002): Biomass CHP Plant Güssing – Using Gasification for Power Generation, Institute of Chemical Engineering, Technical University of Vienna, p. 1-6

[42] Stutterecker, W. (2005): Construction and start up of a slurry Fischer-Tropsch synthesis, Diplomarbeit; Energie- und Umweltmanagement, Fachhochschulstudiengänge Burgenland, p. 2-5

[43] Rauch, R., Hofbauer, H. (2003): Wirbelschicht-Wasserdampf-Vergasung in der Anlage Güssing, 9. Internationale Fachtagung "Energetische Nutzung nachwachsander Rohstoffe", p. 2-5

[44] Rauch, R. (2009): Results of the iron based FT catalyst at the biomass CHP Güssing, Report (confidential), Institute of Chemical Engineering, Technical University of Vienna, p. 4-6, 11-17

[45] Hofbauer, H., Rauch, R., Fürnsinn, S., Aichernig, Ch., (2005): Energiezentrale Güssing, Energiezentrale zur Umwandlung von biogenen Roh- und Reststoffen einer Region in Wärme, Strom, BioSNG und flüssige Kraftstoffe, BMVIT, Energie- und Umwelttechnologie, Wien, p. 50-64

[46] Kramreiter, R. (2004): Hochtemperaturadsorption von H_2S und HCl aus dem Produktgas einer Biomassevergasungsanlage für eine Brennstoffzelle, Diplomarbeit, TU Wien, quoted in [45][42]

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