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# DISSERTATION

# Liquid Fuel Production from Biomass Gasification Product Gas of the Biomass Gasifier at Güssing/Austria – Catalyst Characterisation, Desing, Construction and Operation of a Fischer Tropsch Pilot Plant

ausgeführt zum Zwecke der Erlangung des akademischen Grades eines

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#### Vorwort und Danksagung

Die vorliegende Arbeit ist im Zuge meiner Tätigkeit als Forschungsassistent am Institut für Verfahrenstechnik, Umwelttechnik und Technische Biowissenschaften der Technischen Universität Wien entstanden.

In dieser Arbeit werden die bisherigen Entwicklungen für erneuerbare flüssige Kraftstoffe dargestellt. Mit Hilfe der durchgeführten Arbeiten soll ein möglicher neuer Weg zur Erlangung von flüssigen Kraftstoffen aus Biomasse gezeigt werden. Der zweite Teil der Arbeit, welcher in den Jahren 2004-2007 entstand, zeigt die praktische Umsetzung dieses Vorhabens. Im dritten Teil werden die Erkenntnisse zusammengefasst und soll die möglichen Potentiale der Fischer Tropsch Synthese in Kombination mit einer Biomassedampfvergasung aufzeigen.

Ich möchte allen danken, die am Entstehen dieser Arbeit mitgewirkt haben.

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## Kurzfassung

Ziel der Arbeit ist es, aus erneuerbarer Biomasse flüssige Kraftstoffe herzustellen. Um keine Konkurrenz zu konventionellen Agrarflächen darzustellen soll als Ausgangsstoff Holz dienen. Weiteres soll die Technologie in regionale Biomassekraftwerke integrierbar sein.

Eine Fischer Tropsch Versuchsanlage wurde geplant, errichtet und betrieben in Güssing (Österreich). Es wurden Langzeitversuche mit dem Produktgas des Biomassedampfvergasers durchgeführt. Verschiedene Katalysatoren für die Fischer Tropsch Synthese wurden charakterisiert und getestet. Die hergestellten Fischer Tropsch Produkte wurden analysiert, unter anderem auf den Einsatz in Verbrennungskraftmotoren. Begleitend zu der Versuchsanlage in Güssing wurde ein Kaltmodell zum 3-Phasen-Strömungsreactor (Slurry-Reactor) errichtet. Eine Analysenmethode wurde entwickelt um die Katalysatorverteilung im Slurryreaktor zu beurteilen.

Die Analysenergebnisse von den Fischer Tropsch Produkten, hergestellt von Kobalt basierenden Katalysatoren, ergeben einen qualitativ hochwertigen Kraftstoff. Die Eigenschaften des Kraftstoffes bei niedriger Temperatur müssen jedoch noch durch weitere Verfahrensschritte verändert werden um alle Anforderungen für Dieselkraftstoffe zu erfüllen. Eine weitere entscheidende Erkenntnis ist der Bedeutung von einer Produktgasreinigung um den Katalysator vor Vergiftung zu schützen. Es wurde erkannt dass die Konzentration an Schwefelverbindungen im Synthesegas unter 10 ppbv zu liegen hat um dauerhaft die Synthese zu betreiben.

Es konnte gezeigt werden, dass die Produktion von hoch qualitativen Kraftstoffen mit der Hilfe der Fischer Tropsch Synthese ausgehend von holzbasierender Biomasse möglich ist. Weiteres wurde erkannt, dass es der Kombination von verschiedenen Reinigungsschritten bedarf, um den Katalysator vor Inaktivierung bzw. Vergiftung zu schützen. Die Entfernung von Schwefelverbindungen wird nach wie vor eine entscheidende Rolle im Bereich der Fischer Tropsch Synthese mit Produktgas einer Biomassedampfvergasungspielen.

#### Abstract

Aim of this work is to synthesise renewable liquid fuel of high quality. The basic material should be woody biomass so that no competition to agricultural space arises. Further, the technology should be integrated into local biomass power plant.

A pilot plant for production of Fischer Tropsch fuel was designed, erected and continuously operated along the biomass stem gasification plant located at Güssing Austria. Different Fischer Tropsch catalysts have been characterised and tested in the pilot plant. The Fischer Tropsch products have been analysed, also with the focus on the applicability as automotive diesel fuel. Accompanying the pilot plant design phase, a cold model of the three phase slurry Fischer Tropsch reactor has been built. A method has been developed to measure catalyst distribution in the slurry phase.

The results are showing that the obtained Fischer Tropsch fuel from cobalt catalysts is of high quality and fulfils nearly all demands of diesel fuel. Some refining steps would be necessary to fulfil all demands like the low temperature parameters of the fuel. However the Fischer Tropsch fuel from the iron based catalyst would need more refining steps to fulfil all parameters. A further learning from the operation of the pilot plant is that the gas cleaning of the synthesis gas upstream of the Fischer Tropsch reactor is of crucial importance. Above all the separation of sulphur compounds from the syngas is necessary. The concentration of sulphur compounds should be less then 10 ppbv in the Fischer Tropsch feed stream.

It could be demonstrated that high quality fuel can be produced via Fischer Tropsch synthesis from the product gas of a biomass gasifier. The protection of the catalyst from poisoning is possible applying a combination of different gas cleaning steps. Sulphur removal will continue to be a challenge in Fischer Tropsch synthesis operated with product gas of a biomass gasification plant.

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# PART ONE

# INTRODUCTION & BACKGROUND

# **1** Introduction

# 1.1 Motivation

In order to do an assessment of the energy supply situation worldwide and in particular of the industrialized countries not only the different types of energy sources have to be taken into consideration. There are a lot of different issues which have to be discussed in respect of energy sources of the last decades. Nowadays the complex situation of energy supply is a construction of fossil oil exporting countries, oil exploring and processing companies, automotive and chemical industries and also the political constitution of each affected country. To sum up the complexity of that subject, catch phrases like "dependence on energy sources", "fossil fuels exploring countries and companies", "long term availability", "national and world wide social effects of imbalanced energy availability", "peace and war", "macroeconomic considerations like outflow of money", "jobs" and "new technologies for energy production" are often used in discussions about energy supply in our society.

Other omnipresent issues in the discussion about the fossil energy are the regional and global environmental effects. The limits of environmentally relevant emissions such as sulphur dioxide, nitrogen oxides, carbon monoxide, organic carbon, dust for fossil fuels driven devices like coal fired power plants and internal combustion engines have been reduced step by step during the last decades, but the total consumption of fossil fuels is increasing continuously. This means the emission of carbon dioxide is increasing with the consumption of fossil fuels. Until now no effective technology is in use in order to capture carbon dioxide sustainably from fossil fuels burning processes. Carbon dioxide from fossil fuels are responsible for the increasing anthropogenic greenhouse gas emissions and consequently for the global climate change.

Renewable energy sources are manifold but the share of renewable energy of the whole energy consumption of the European countries varies from 0% (Malta) to 39,8% (Sweden) [1]. Nearly all of the energy used in the EU transportation sector comes from fossil oil.

In our world it seems that fossil fuels energy is like the umbilical cord of industrial nations and no one is resolute enough to cut off this cord to stay on one's own feet.

To convince society that it's feasible to gain independency from fossil fuels is a big challenge and an incentive for the research and development of modern, efficient and sustainable technology. Especially in the transportation sector, renewable energy resources and technologies are a feasible solution for maintaining reliability and availability for a longer period. The utilization of biomass, which is almost carbon dioxide neutral, enables one to produce several types of biofuel.

However biofuels from the first generation like bioethanol and fuel made of vegetable oil are competing with agricultural products for nutritional purposes. With a world-wide view this competition entails ethical and social problems as long as the security of food for all countries is not given.

Alternatively biofuel production from biomass like wood and wood waste which does not compete with agricultural products might be a sustainable solution. A possible technical solution will convert biomass thermally into product gas. Then, via syntheses the product gas is transformed into a liquid fuel.

The motivation is to refine the Fischer Tropsch technology which could be implemented into power plants based on gasification technology. With that invention power plants might be

able to extend their spectrum of the energy portfolio. This means that it should be possible to also produce liquid fuels beside electricity and heat in biomass driven power plants.

# 1.2 Objectives

In the 6<sup>th</sup> frame work of the Program of the European Union one of the seven thematic priorities is "Sustainable Development, Global Change and Ecosystems". Within this topic one big issue is "Sustainable energy systems".

The University of Technology Vienna (TU-Vienna) participated in the project "RENEW". Within this project, in cooperation with the combined heat and power plant in Güssing (BKG) the implementation of a Fischer Tropsch trial plant was supposed to be realized. The Fischer Tropsch process was supposed to be installed in a side stream of the existing allothermal fluidized bed gasifier at BKG. A Fischer-Tropsch slurry reactor was designed and installed in a container at the site of BKG allowing for long term testing. Catalysts were tested in cooperation with the "Université Louis Pasteur" (Strasbourg).

Produced Fischer Tropsch products were characterized and prepared for standard fuel analyses. These fuel analyses were carried out at the "Instytut Technologii Nafty (ITN)" in Krakow (Poland).

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

The producer gas from the circulating allothermal fluidized bed gasifier is nearly free of nitrogen and has got a high hydrogen content. For this reason it is well suited for synthetic processes as well for fuel cell applications.

# **1.3** Formulation of the problem

In the run-up of that project subsequent points have been preliminarily decided:

- Syn-gas: Producer gas from biomass gasifier located in Güssing (Austria)
- Type of reactor: Bubble-slurry reactor

For the design of a Fischer Tropsch pilot plant following key issues have to be taken into consideration:

- Catalyst
- Composition of the syn-gas (product gas)
- Type of Fischer Tropsch reactor

It will be tested whether the producer gas from Güssing is suitable for FT-synthesis or not. The main components of the gas are hydrogen and carbon monoxide. Impurities in the producer gas like hydrogen sulfide can act as a catalyst poison. In experiments the impacts of the impurities on the FT-process were supposed to be demonstrated.

Long term experiments are supposed to demonstrate whether a stable process run can be estimated.

In order to run long term FT-synthesis experiments a slurry-bubble reactor along with all necessary adjoining units should be installed. Part of the pilot plant should be a coherent

analytical set up to monitor the process. It is scheduled to run continuous long term experiments with the pilot plant and the implemented analytics. The generated data should be saved and assessed for further developments of the whole process.

The set up of the pilot plant includes a section where the product gas is conditioned for the synthesis as well as a section where the off-gas is treated and the FT-products are separated.

Available catalysts are going to be tested in the project.

# **1.4** Structure of the work

The first part of the written work is a literature review. The content of that part starts with the classification of biofuels. Next is an overview of the historical development of Fischer Tropsch technologies. Subsequently a theoretical background of the FT-catalysis and catalysts is given, as well as an overview of developed FT-reactors. In that part a comparison on mass and heat transfer is given for different types of three phase reactors.

Within the first section a mind map with research questions is placed before the practical work is reviewed. Inside this design several key questions are formulated which are going to be treated at the end of the work.

The practical work on catalyst characterization is summed up in the following section. These works have been carried out at the "Université Louis Pasteur Strasbourg".

Design of the slurry reactor is done by cold flow model. Therefore, measurement methods of catalyst distribution in the slurry of a FT-reactor cold model are shown afterwards. Experiments with the cold flow model are described within this part.

Finally the implementation of the FT-pilot plant in Güssing is described.

For each section of practical work a discussion of the results of the experiments is added.

In the third part of the work a discussion on the research design questions is added.

# 2 Literature review

The analyses of the literature have been done before and accompanying the practical work. More or less with the year of 2008, this work has been practically finished. For personal reasons, it was not possible to publish the work in 2008. Now, in 2017, the literature review has been revised, especially the Chapters 2.1 to 2.5 have been updated.

## 2.1 Biofuels

## 2.1.1 Background

Biofuel is a collective term for liquid and gaseous fuels which are mainly used in the transportation sector and are predominantly produced from biomass. In terms of the sustainable effect they are offering reduction of greenhouse gas emissions, regional development, social structure and agriculture, security of supply [2], new income and employment opportunities in rural areas. The European Union (EU) determined 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 transportation utility. This target should have been 5.75 %, calculated on the basis of energy content, by the end of 2010 [3][4]. Moreover, an exception

of the biofuels from the taxation works as a promotion, which is regulated by the directive 2003/96/EG [5]. In reality, by 2010 a share of slightly less than 5% was attained [6]. Before the directive was issued, the EU set up the conception to substitute 20 % of conventional fuels in the transportation sector by alternative fuels such as biofuel, hydrogen as well as natural gas. These targets have been re-assessed and, currently, a share of 10% of fuels from renewable sources is the target for 2020. To achieve these European objectives, a need for actions from short until long term is indispensable.



Biodiesel Bioethanol Other biofuels Renewable electricity
Figure 1: Biofuel consumption in the EU 2006-2010 and projection to 2020 [6]

So far, the current biofuel supply is mainly based on so called "1st generation biofuels" [7] which are primarily produced from food crops such as grains, sugar beet, sugar cane and oil seeds. Due to the possible competition for land and water for food and feed 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 purposely grown energy crops including vegetative grasses and short rotation forests [8]. Table 1 and Table 2 represent the bio fuels of the first and second generation and the feedstock used in their production [9].

Bioluei type	Specific names	Diomass recusiock
Bioethanol	Conventional bioethanol	Sugar beet, grains
Vegetable oil	Pure plant oil (PPO)	Oil crops (e.g. rape seed)
Biodiesel	Rape seed 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 1: The	first generation bio fuel and the feedstoc	k used in their production [9]
Biofuel type	Specific names	Biomass feedst

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<b>U</b>		1 E 2
Biofuel type	Specific names	Biomass feedstock
Bioethanol	Cellulosic bioethanol	Lignocellulosic
Synthetic biofuels	Biomass-to-liquids (BTL): Fischer-	Lignocellulosic
	Tropsch (FT) diesel	
	Biodimethylether (DME)	
	Biomethanol	
	SNG (Synthetic Natural Gas)	
	Synthetic (bio)diesel	
	Bio-Methyl-tertButylether	
	(MTBE)	
Biodiesel	Hydro-treated Biodiesel	Vegetable oils and animal fat
Biohydrogen		Lignocellulosic

 Table 2: The second generation bio fuel and the feedstock used in their production [9]

The global production of biofuel increased from 4.8 billion gallons in 2000 to about 16.0 billion gallons in 2007. This corresponds with 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 [10].

## 2.1.2 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 [8][11]. Figure 2 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 fuels derived methanol could be to use biomethanol or bioethanol for the production of fatty acid ethyl ester (FAEE) [12][9]. In comparison to the petroleum-derived diesel the biodiesel is superior in sulphur content, flash point, aromatic content and biodegradability [2]. In conventional diesel engine systems FAME biodiesel can be blended with petroleum diesel or used in a pure form with only minor fuel system modification. Due to the solvent quality of FAME biodiesel, special adaptations in the fuel and engine systems are necessary for long-term operations with biodiesel fuel [12]. It is feasible to undertake the transportation, storage and retail system of conventional diesel as well as for biodiesel [11].

The conventional diesel engine requires minor modifications to run on vegetable oils due to its relatively high viscosity. To reduce the viscosity of the oil it is converted to FAME or FAEE diesel via transesterification [13].

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 sugar. Depending on the utilization of the feedstock they may be separated into biofuel of first generation as well as second generation [12].

The fuels and car manufacturer communities postulate that almost all conventional gasoline engines are fully compatible with blends of 10 % bioethanol in fossil 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 [12].



Figure 2: Conversion processes from biomass to biofuel [11]

In comparison to petroleum-derived fuels, biodiesel and bioethanol have a lower energy density which is made up by a higher combustion efficiency [12]. Furthermore, the emissions from 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 [11].

A relatively new development is the hydroconversion of triglycerides into liquid fuels. As in conventional biodiesel production, the feedstock is vegetable oil. In presence of  $H_2$  the process yields aliphatic hydrocarbons in the C<sub>15</sub>-C<sub>18</sub> range [109]. In this case, no reduced energy density is expected compared to fossil liquid hydrocarbons.

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 [11]. Therefore, for the further development of the efficiency of the biodiesel and bioethanol production, the development of biofuels of the second generation is essential to make biofuels more competitive to fossil fuels.

# 2.1.3 Second generation

In comparison to the first generation the second generation utilizes lignocellulosic biomass as feedstock which is non-edible and hence the competition for food production is limited or avoided [14]. Lignocellulosics are originated from crop, forest or wood process residues, or long-lasting grasses and trees [8]. 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 technically proven at a commercial scale and the fuel production costs are estimated to be higher than many of the first generation [8].

The production of bioethanol of the second generation is made analogous to the bioethanol production of the first generation whereby due to lignocellulosic as feedstock the compounds are broken down by a 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 carbon monoxide, can be used for several synthesis reactions to produce synthetic fuel [15].



Figure 3: The second generation biofuel production and their conversion process

Hydrogen can be attained with reforming the product of a gasification and pyrolysis that is the synthesis gas on the one hand and the carbohydrate fraction of the bio-oil on the other hand. The two equations, water-gas shift (2) and steam methane reforming (1) are the main reactions for hydrogen production [2][16].

$$CH_4 + H_2 O \rightarrow CO + 3H_2 \qquad \qquad \Delta H_r^\circ = +206 \frac{kJ}{mol} (1)$$

$$CO + H_2 O \rightarrow CO_2 + H_2 \qquad \qquad \Delta H_r^\circ = -41 \frac{kJ}{mol} (2)$$

 $\Delta H^{\circ}_{r}$  ......building enthalpy at standard conditions (25°C; 1 bar)

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 [15]. The methanation is described by the following equation:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$
  $\Delta H_r^\circ = -206 \frac{kJ}{mol}$  (3)

The use of different catalysts can lead to the conversion of methanol, including reduced NiObased preparations, reduced Cu/ZnO shift preparations, Cu/SiO2 and Pd/SiO2, and Pd/ZnO [2]. The Cu/ZnO-Al2O3 catalyst works at a temperature of 220 - 275 °C and pressure of 50 - 100 bar [16]. The following equation illustrates the methanol synthesis:

$$CO + 2H_2 \rightarrow CH_3OH$$
  $\Delta H_r^\circ = -91\frac{kJ}{mol}$  (4)

For further utilization as a chemical intermediate methanol is used for the DME and methyl tert-butyl ether (MTBE) conversion. To produce MTBE methanol reacts with isobutene in the presence of an acidic catalyst (5) [16].

$$i - C_4 H_8 + 2CH_3 OH \rightarrow (CH_3)_3 COCH_3 \qquad \Delta H_r^{\circ} = -37 \frac{kJ}{mol}$$
(5)

After methanol is synthesized (4) it is dehydrated over an acid catalyst under methanol synthesis conditions whereby DME is yielded [16]. The methanol dehydration is given in equation (6).

$$2CH_3OH \to CH_3OCH_3 + H_2O \qquad \qquad \Delta H_r^\circ = -23\frac{kJ}{mol} \qquad (6)$$

Fischer-Tropsch liquids are formed in the Fischer-Tropsch synthesis where the synthesis gas is transformed into hydrocarbon products in highly exothermic reactions (7) [16]. The theoretical background of the Fischer-Tropsch synthesis that is substantial within this work is illustrated in section 2.6 ff.

$$2H_2 + CO \rightarrow -CH_2 - + H_2O \qquad \qquad \Delta H_r^\circ = -165 \frac{kJ}{mol} \tag{7}$$

Pyrolysis of lignocellulosic biomass is an alternative thermal conversion process and could be a potential way to produce second generation biofuels. The pyrolysis is thermal degradation of biomass by heat in the absence of oxygen, which results in the production of charcoal (solid), bio-oil (liquid), and fuel gaseous products. The pyrolysis of biomass has been studied with the final objectives of recovering a biofuel with medium-low calorific power [35]. Depending on the operating conditions, the pyrolysis process can be divided into three subclasses: (a) Conventional pyrolysis, (b) Fast pyrolysis, and (c) Flash pyrolysis. Upgrading of the bio-oil is essential for further use as transport fuel. A drawback for pyrolysis-oil applications is the high content of partially oxidized hydrocarbons and the limited yield of liquid product compared to the char and gas fractions [107,108].

#### 2.2 Economic considerations

The drawback in producing synthetic fuels, via FT synthesis, is its cost compared to that of refining crude oil. It has been calculated that the production of synthetic fuels is only economically viable at crude oil prices above \$30 (US) per barrel [17]. On the next page is a graph showing crude oil price trends since 1960. Figure 4 shows the average price of each year in US \$ per Barrel crude oil. It can be seen that from 1986-1999 the oil price was below 20 \$ per barrel. Since 2001 the oil price has been rising permanently. In 2008 one barrel crude oil was traded for an average price for more than 90 US \$. After 2012, however, the prices dropped back to below 50 US \$ in 2016 for various reasons according to Figure 4.

Global economic expansion is the major reason for this recent rise in oil prices. The US economy has strengthened in recent years, and the Chinese economy is rapidly expanding, with annual oil demand increases up to 20 % before 2008, and with experts expecting this expansion to continue for some years to come, the demand of oil will also continue to increase further [19]. Oil companies have also tried to become more efficient in recent years, operating with lower stocks of oil. This results in less of a cushion in the market if supply interruptions occur, as with the war in the Middle East and ethnic tensions in Nigeria [19]. Supply interruptions may also be as a result of natural catastrophes, such as hurricane Katrina in the Gulf of Mexico causing the shut down of offshore terminals and refineries in late August 2005, and a \$5 increase in oil prices overnight. However, even if oil prices drop below \$30 again, the FT process can still be viable if some FT products can be sold as chemicals, such as linear alpha olefins, for double or more of the price. The development of more active catalysts and improvements in reactor design can also help in improving the processes cost-effectiveness [20].



Figure 4: Average crude oil prices \$ (US) per year 1970 – 2017 [18]

# 2.3 The history of Fischer Tropsch

The reaction to convert carbon monoxide and hydrogen to hydrocarbons was discovered in the early 1920s by Franz Fischer and Hans Tropsch. After the discovery of the reaction the process had a lively history. There are some literature overviews of the FT-process[21, 22].

Nowadays four different types of reactors are in use commercially. The reactor types can be divided into fixed bed reactors, slurry phase reactors, two phase fluidized bed reactors and microchannel reactor.

There has been increased interest in FT processing in the last 20 years due to the desire to exploit stranded or remotely located gas reserves [20]. The possibility of converting these reserves of gas into liquid via FT processing for ease of transportation is an attractive option. Environmental and political concerns into natural gas exploitation have had a bearing on the renewed interest in FT processing. Certain new oil fields are associated with high levels of natural gas, the flaring of which is prohibited, so the construction of FT plants to convert the methane into oil in order to access the crude oil is being considered [20].

# 2.4 Previous Fischer Tropsch developments

The first commercial FT plants to come into operation were in Germany, and by 1938 there were 9 fixed bed reactor based plants, using coal based syngas with a combined production of about 600x10<sup>3</sup> tonnes per annum [17]. However after WWII, these plants were shut down as they were uneconomical. In 1944 three FT plants were operating in Japan with a capacity of 110x10<sup>3</sup> tonnes per annum.

In 1950, in Brownsville, Texas, USA a fluidized bed plant using iron catalysts and methane based syngas came on stream with a capacity of 360x10<sup>3</sup> tonnes perannum. It shut down a short while later due to a sharp increase of the price of natural gas. In the 1940's, it was thought that the reserves of crude oil were running out and that the price of oil would rise sharply in the 50's as a result of this. This is why the Sasol One FT plant came on stream in 1955 in South Africa. It used both fixed and circulatory fluidized bed reactors and was coal

based with a capacity of 700x10<sup>3</sup> tonnes per anno. However, the discovery of huge deposits of oil in the Middle East meant that the price of oil did not rise as expected. The only reason that the Sasol One plant survived was that it also produced FT waxes which could be sold at high prices [17]. Because of the rising oil prices in the 70's, Sasol expanded and Sasol Two, 1980, and Three, 1982, were built with a combined capacity of 4200x10<sup>3</sup> tonnes per anno [17]. They employed circulating fluidized bed reactors and initially produced ethylene, gasoline and diesel fuel. Between 1995 and 1999, all 16 circulating fluidized bed reactors used at the Sasol plants were replaced with 8 fixed fluidized bed reactors. In 1992, the Mossgas FT plant came on stream in South Africa. It used circulating fluidized bed reactors and natural gas based syngas, with a capacity of 900x10<sup>3</sup> tonnes per annum. It currently produces gas and diesel fuels.

However, the limited reserves of natural gas in the area threaten the future of the plant [17].

In 1993 Shell opened a fixed bed FT plant in Malaysia which uses a cobalt catalyst and a methane based syngas, with a capacity of  $500 \times 10^3$  tonnes per annum. It produces high quality diesel fuels and waxes.

The Pearl GTL project from Shell and Qatar Petroleum was announced in July 2006 and has a design capacity of about 22000  $m^3$ /day of synthetic liquids. Since June 2011 commercial shipment from the Pearl GTL plant was made.

In 1993, Sasol brought a commercial scale slurry bed reactor FT plant on stream. It had a 5m inner diameter, used an iron-based catalyst and had a capacity of  $100x10^3$  tonnes per annum. This reactor came on stream 40 years after the first pioneering work on slurry bed reactors was undertaken [23].

To date the Sasol operation has been more successful than others. Plants two and three came on line when oil prices were peaking, while others came on line while prices were declining.

# 2.5 2<sup>nd</sup> generation of biomass to liquid plants

Second generation biomass to liquid fuels can contribute to green fuel policies without the problematic use of agricultural biomass crops as feedstock. Therefore, several 2<sup>nd</sup> generation BTL projects have recently been launched all over the world.

# 2.5.1 CHOREN (Freiberg, Germany)

CHOREN Industries developed the Carbo-V® gasifier technology after 1990. From 2001 onwards, a research and development project aimed at producing  $2^{nd}$  generation biofuel from the Carbo-V syngas. By the end of 2004, the FT plant had reached 22,500 operating hours. A first industrial-scale Carbo-V prototype plant ( $\beta$ -Plant) with a capacity of 45 MW<sub>th</sub> was subsequently built. The original plan was to produce 18,000 m<sup>3</sup> of FT fuel per year. However, CHOREN went into bankruptcy in 2011 and no successful operation of the industrial demonstration plant has ever been published [110].

# 2.5.2 BioTfueL

Figure 5 shows the concept of the BioTfueL project, which is put forward by Total and partners. The biomass is torrefied and then converted into syngas in a gasifier. Downstream, a gas cleaning and a conditioning device are installed. Via a FT-plant and a hydrotreating section, biofuel is obtained. In 2017 a demonstration plant is scheduled to come on stream. 2020 is the target date to demonstrate the technology in France [24]. The first industrial plant in 2020 will have a capacity of 5000 barrels (bbls)/day [110].



Figure 5: Concept of the BioTfuL project [111]

## 2.5.3 KAIDI

Kaidi Finland plans to build a 2<sup>nd</sup> generation biofuel plant in Kemi by 2019. Kaidi's technology is based on three process steps. Firstly, a plasma gasification of wood-based biomass should convert organic matter into syngas. Secondly, a syngas cleaning section scrubs and filters impurities. Finally, a FT-synthesis converts the syngas into bioifuel. The plant will produce 225.000 metric tons of FT products per year. [111]

## 2.5.4 Fulcrum

The Fulcrum process begins with the gasification of prepared municipal solid waste. A gas cleaning section consisting of a venturi scrubber, a packed gas cooler scrubber and an amine system remove entrained particulate as well as sulfur and carbon dioxide from the syngas. The FT-reaction takes place in a fixed-bed tubular reactor. The obtained products are upgraded in the last step. Hydrotreating, hydrocracking and hydroisomerisation converts the FT-products into jet fuel [112]. The Sierra BioFuels Plant located in Nevada, USA, has been designed to produce 10 million gallons per year of renewable FT-product, is set to begin commercial operations early 2019 [113].

## 2.5.5 Red Rock Biofuel

The technology of Red Rock Biofues is based on the gasification of woody biomass to produce syngas. The syngas is cleaned and sent to a FT-process. The obtained FT-products are hydroprocessed to produce jet diesel and naphta fuel Red Rock Biofuel is in cooperation with airline FeedEX Express and a refinery is developed to produce 16 million gallons per year of finished products [114].

# 2.6 Theoretical background of the Fischer Tropsch reaction

The starting materials of the Fischer Tropsch reaction are CO and H<sub>2</sub>. This gas mixture is called syngas, which is reacting on a catalyst surface to form -CH<sub>2</sub>-, the building blocks of FT products. The oxygen from the CO is released as water. The basic FT reaction (1) is:

$$\mathrm{CO} + 2\mathrm{H}_2 \rightarrow -\mathrm{CH}_2 - + \mathrm{H}_2\mathrm{O} \ (1)$$

 $\Delta H = -165 \text{ kJ/mol}$ 

The reaction is exothermic so heat is released.

For catalysts which have water gas shift (WGS) activity like iron-based catalysts the following reaction occurs where water produced in the FT reaction can react with CO to form additional H<sub>2</sub>:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$
 (2)

This reaction occurs both ways. For high temperature fluidized systems the WGS reaction for iron catalysts is rapid and near equilibrium throughout the reactor. This allows CO<sub>2</sub> to be converted to FT products via reverse WGS. The required ratio of H<sub>2</sub> to CO in the feed gas changes according to the process conditions and the catalyst type, but is typically around 2.

## 2.6.1 Possibilities of surface species on metallic catalysts

The FT-reaction takes place on a metallic surface. Metals which support the FT-reaction are from the eight B group of the periodic table. There are various possibilities of surface species on the catalyst surface at steady-state in the FT-reaction. The chemisorption of hydrogen plays an important role in the FT-reaction. Co and Ni [25] Ru [26] and Fe [27] support preferentially the chemisorption of hydrogen on threefold hollow sites.

The mobility of chemisorbed hydrogen is high [28]. This is a basis for the FT-reaction that hydrogen can react with other adsorbed species on the metallic surface. The formation of organic compounds does not necessarily take place at the same site and may even spill over to another metal crystallite [29]. Both associative and dissociative adsorption of CO occurs.

In literature reactions of dissociated CO as well as associated CO with hydrogen are reported. Dissociative adsorption of CO has been demonstrated by X-ray photoelectron spectroscopy (XPS) or pulse techniques for Ni, Co, Ru, and Fe at elevated temperatures (T > 350 K) [30]. An interaction between the metallic d-states and the CO  $2\pi^*$  and  $5\sigma$  states is well studied [31, 32]. Carbon monoxide adsorption takes place preferentially on the top-site of Co(0001) [33]. CO can dissociate to surface carbon and surface oxygen and has been investigated on planar and ridged Ru(0001) [34]. Direct CO dissociation seemed to be favoured on ridged surfaces, whereas dissociation by hydrogen insertion seemed to be favored on planar Ru(0001).

The reaction pathways in Fischer Tropsch might have a great variety but all together have the same steps if the FT-reaction is treated like a polymerisation reaction. The monomers are built in-situ from the gaseous reactants hydrogen and carbon monoxide.

The pathway can be divided into three sections:

- 1. The generation of a chain initator
- 2. The chain growth
- 3. The chain termination

A wide spectrum of products can be obtained by Fischer Tropsch and so numerous reaction pathways have been suggested to deal with that given fact. The four most common different mechanisms are the "alkyl, alkenyl, CO-insertion and enol" mechanisms.

## 2.6.2 The "alkyl" reaction pathway

Initiation:



Termination:

CH₂R I	<u>− H</u>	$CH_{2} = CHR$	a-olefin
, CH₂	+ H		n-naraffin
	+ OH	$CH_2OH - CH_2R$	n-alcohol

Figure 6: reaction pathway of the "alkyl" mechanism in Fischer Tropsch

In Figure 6 the reaction steps of the "alkyl" mechanism are demonstrated. The initiation starts with a dissociative CO-chemisorption where surface carbon and oxygen is formed.

Surface oxygen reacts with absorbed hydrogen to form water or with carbon monoxide to form carbon dioxide. The carbon on the metallic surface reacts with absorbed hydrogen stepwise to form CH, CH<sub>2</sub> and CH<sub>3</sub> surface species. The CH<sub>2</sub> species are the monomers for the chain growth reaction and the CH<sub>3</sub> species are the chain initiators for the Fischer Tropsch molecules. Chain growth is interrupted by the termination reaction. Figure 6 shows the three different termination reactions where  $\alpha$ -olefins, n-paraffins or n-alcohols are obtained.

The "alkyl" mechanism was developed from the so called "carbide"-mechanism from the early works in this field [35, 36].

Nowadays the "carbide"-mechanism does not have an importance in explaining the Fischer Tropsch reaction mechanism because iron forms stable carbides under Fischer Tropsch reaction conditions. Other Fischer Tropsch active metals like cobalt and ruthenium do not have a tendency to form carbides under typical Fischer Tropsch conditions.

Studies on the iron catalyst with radioactively labelled carbon have shown that the carbon in the Fischer Tropsch product does not have the origin from carbides carbon [37].

As a consequence the carbide-mechanism has been rejected. The formation of the C-C bounds takes place in the "alkyl"-mechanism over CH<sub>2</sub>-alkyl coupling reactions.

This reaction pathway is described theoretically by Zheng et al. [38]. The stability of the C<sub>1</sub>-fragments on metal surfaces is calculated and indicates a decrease of stability from CH<sub>3</sub>- to CH-fragments. When C<sub>1</sub>-fragments are coupling the C-C  $\sigma^*$  orbital's rise from below the Fermi level. It is initially filled and then empties as the reaction proceeds. Hence the lower the Fermi level the smaller the reaction barrier. Prior studies from Biloen et al. [39] support the "alkyl"-mechanism. They pre-doped Fischer Tropsch catalysts with <sup>13</sup>C-labeled carbon with a <sup>13</sup>CO/H<sub>2</sub> mixture. In the obtained products under Fischer Tropsch conditions they measured mainly <sup>13</sup>CH<sub>4</sub> and hydrocarbons containing several <sup>13</sup>C- atoms in the same molecule.

These results indicate that the carbidic species, once formed, can react with hydrogen to form  $CH_x$  intermediates. These intermediates are the monomers which polymerise to form hydrocarbons. There are several other studies which indicate that the reaction pathway might react over alkyl species.

For the formation of branched hydrocarbons Schulz et al. proposed a reaction pathway shown in Figure 7.



Figure 7: reaction pathway for branched hydrocarbons proposed by Schulz et al. [40]

The formation of oxygenates over the alkyl mechanism have not been experimentally demonstrated.

# 2.6.3 The "alkenyl" reaction pathway

The initial step for the activation of carbon monoxide is the same as the "alkyl" mechanism. Neurock et al. studied the formation of the first C-C binding over methylidene (CH) and methylene (CH<sub>2</sub>) to form vinyl (CHCH<sub>2</sub>) on Co and Ru surfaces.

The reaction is slightly exothermic on Co and endothermic on Ru. The reaction barriers have been determined for Co (55,9 kJ/mol) and Ru (119,5 kJ/mol) [42]. The polymerisation reaction involves the addition of a methylene species to a surface alkenyle species.

This is followed by an allyl-vinyl species [41]. Product desorption occurs over hydrogen addition where the products are  $\alpha$ -olefins.

This reaction pathway will explain the existence of  $\alpha$ -olefins in the Fischer Tropsch products, but not the formation of n-paraffins.

## 2.6.4 The "CO-insertion" and "enol" mechanism reaction pathway

To describe the reaction pathway for an oxygen containing compound in Fischer Tropsch, the so called "enol"-mechanism, according to Storch et al. is reported in literature [41]. The "enol"-mechanism might explain the formation of oxygen containing compounds as shown in Figure 9.

Initiator



 $\frac{HC = \overset{H}{C} - CH_2R + H}{\downarrow} \qquad H_2C = CHR \qquad \alpha \text{-olefin}$ Figure 8: The "alkenyl" mechanism [41]

Newer studies are showing that the reaction pathway over the CO-insertion is thermodynamically favored in comparison to the proposed reaction mechanisms, like the enol and the methylene mechanisms. Thermodynamic analysis from Welker et al. indicate that the CO-insertion mechanism is the thermodynamically favorable reaction pathway on diatomic Ru-clusters [43].

In Figure 10 the CO-insertion mechanism is outlined schematically. Absorbed carbon monoxide is the monomer in the CO-insertion mechanism. The chain initiator is a surface methyl species similar to the "alkyl"-mechanism but the reaction pathway is different in the CO-insertion mechanism theory. The elimination of the oxygen occurs via an alcohol intermediate.

The chain prolongation involves the insertion of CO into a metal–alkyl carbon bond which is then hydrogenated to produce an alcohol. The alcohol or alcohol precursor can also eliminate oxygen to produce an alkene product [45]. The CO insertion mechanism is well known in homogeneous catalysis [46]. Product elimination takes place through hydrogen addition or  $\beta$ -hydrogen elimination. Possible products are n-paraffins,  $\alpha$ -olefins, n-alcohols and aldehydes.

#### 2.6.5 Formation of carbon dioxide in Fischer Tropsch

In the Fischer Tropsch process the formation of carbon dioxide is a non desirable side reaction. This reaction primarily occurs when iron-based catalysts are used. Iron is active in the so called "water gas shift reaction" which is a slightly exothermic reaction shown in equation (1) below.

$$CO + H_2O \leftrightarrow CO_2 + H_2 + 42$$
kJ/mol (1)





Figure 9: "enol"-mechanism according to Storch et al. [44]

In the iron-catalyzed high temperature Fischer Tropsch the water gas shift reaction is close to the equilibrium. The formation of carbon dioxide in the low temperature Fischer Tropsch reaction over iron catalysts is less than in the high temperature Fischer Tropsch reaction. Studies from Botes show that the carbon dioxide formation is a first order kinetics in CO [47]. Hence the secondary reactions involve carbon dioxide formation and the kinetics are not clearly defined in low temperature Fischer Tropsch reactions. There are studies which suggest that the formation of carbon dioxide takes place in the magnetite phase, and the formation of hydrocarbons take place in the carbide phase. The formation of carbon dioxide is determined by the formation of a formate intermediate species from adsorbed carbon monoxide and dissociated hydrogen [48].

Up until now there is little literature on carbon monoxide formation on other catalysts.

Initiation



Figure 10: "CO-insertion" mechanism in Fischer Tropsch synthesis

# 2.7 Models of product distribution in Fischer Tropsch

## 2.7.1 Anderson Schulz Flory

To describe the product distribution in Fischer Tropsch the models from polymerisation reactions are used. One carbon atom is added at a time to the growing carbon chain. As a consequence chain termination can occur through hydrogen addition or through  $\alpha$ -hydrogen removal, followed by desorption from the catalyst surface. The product distribution can be predicted by the so called Schulz-Flory equation, when each carbon chain with the length of n carbons on the catalyst surface has the same probability of adding an additional carbon. The probability that no chain growth takes place is  $(1-\alpha)$ . The probability that a hydrocarbon chain contains n carbons is described below in the equation (1).

$$\mathbf{P}_{\mathbf{n}} = \boldsymbol{\alpha}^{(\mathbf{n}-1)}(1 \cdot \alpha) \tag{1}$$

 $P_n$  mole fraction of the *n*th oligomer

*n* carbon atoms in a hydrocarbon chain

 $\alpha$  Chain growth probability factor ( $0 \le \alpha \ge 1$ )

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

 $W_n$  mass fraction of the n<sup>th</sup> oligomer

Rearranging equation (2) and taking logarithm gives the Schulz-Flory equation:

$$\log \frac{W_n}{n} = n \log \alpha + \log \frac{(1-\alpha)^2}{\alpha}$$
(3)

When  $log \frac{W_n}{n}$  is plotted against *n* a straight line should by obtained where the slop is  $log \alpha$  if a Schulz Flory distribution is expected. With increasing  $\alpha$  values the product contains longer hydrocarbon chains [49]. In Figure 6  $\alpha$  is displayed against the selectivity. The expected product distribution for different  $\alpha$ -values can be easily estimated if the observed Fischer Tropsch system reacts like a Schulz Flory distribution.



Chain growth probability factor (Alpha)

Figure 11: Chain growth probability factor vs. selectivity (mass fraction) for different hydrocarbon fractions

The maximum yield for a middle distillate (C<sub>10-20</sub>) is about 40 wt% for a straight run when a reaction system in Fischer Tropsch synthesis is selected with an  $\alpha$  of about 0,8 - 0,9. At  $\alpha$ -values over 0,95 a high wax yield is achieved. Waxes can be transferred into the middle distillate via mild hydro cracking. In doing so a higher selectivity of middle distillates can be achieved.

Several abstracts report that in Fischer Tropsch deviations towards ideal Schulz Flory distribution have been observed. Schulz et al. has reported [50] a multitude of literature which is dealing with secondary olefin reactions.

Main secondary olefin reactions can be summarised in the following three reactions:

- Addition of hydrogen to the corresponding paraffin
- Double bonds shift of  $\alpha$ -olefins to olefins with internal double bonds
- Restarting of chain growing (re-incorporation of olefin)

#### 2.7.2 Deviations from ideal ASF-distributions in Fischer Tropsch

Iglesia et al. are report [51] a diffusion dependent model. Liquid filled catalyst pores reduce the mobility of long chain  $\alpha$ -olefins. Therefore their resistance time is prolonged and secondary reactions to form paraffinic products are enhanced. In Figure 12 two different

graphs of different contact times for the  $\alpha$ -olefin to paraffin ratio against the chain length (carbon number) are displayed. The longer the contact time the lower the  $\alpha$ -olefin content in the obtained product. A detailed explanation of the model is published in [51, 52].



Figure 12: Bed residence time and carbon number effects on α-olefin to n-paraffin ratio on Co/TiO2 (catalyst: 11.7% wt. Co, 0.015 dispersion; tubular packed-bed reactor; reaction conditions: 473K, 2000kPa, H2/CO=2.05) [52]

# 2.8 Catalysts

When selecting catalysts for commercial application of FT processes, only the metals Fe, Ni, Co and Ru have the required FT activity. In comparing the relative price of these metals, if the price of scrap iron is taken as 1.0, then the comparative prices of the others are Ni = 250, Co = 1000 and Ru = 50000 [23]. Ni produces excess CH<sub>4</sub> under practical FT conditions and Ru is too expensive, which leaves Fe and Co as viable FT catalysts [17]. Co is a lot more expensive than Fe, but it has a higher activity, which means less of it is required and it has a longer life time in the reactor.

## 2.8.1 Preparation - General

Before the metals are ready for use in a FT reactor, catalysts must be prepared through a number of chemical and physical techniques such as promotion, reduction and dispersion on a support material. The details of such processes will be discussed in a later section of this thesis for each individual catalyst. Chemical and structural promoters can influence the chain growth probability.

# 2.8.2 Operation Conditions in General

An increase in operating temperature results in a shift in catalyst selectivity towards lower carbon number products and to more hydrogenated products. This can be seen through a pronounced increase in CH<sub>4</sub> selectivity [17]. The degree of branching as well as the amount of secondary products formed such as ketones and aromatics increases [23]. In order to minimise reactor downtime and catalyst consumption, it is vital that catalysts remain at high activity for as long a time as possible. To ensure this it is vital that catalyst poisons do not enter the reactor. The incoming syngas should have a sulphur content of  $< 0.02 \text{ mg/m}^3$  [23]. In FT processing, the CO carbon-oxygen bond must be broken, which results in the carbon and oxygenated species being chemisorbed on the surface of the catalyst, creating carbided and oxidized metal sites [23]. This process involves rapid cycling, switching between carbided, oxidized and reduced states, which enhances sintering, where material flows into voids causing a decrease in overall size, and thus the loss of active surface area. The oxidized metal may also chemically interact with the support material forming inert aluminates, silicates etc. To avoid interaction with the oxidised metal the H<sub>2</sub>O/H<sub>2</sub> ratio must not be too high in the reactor. With recycling of tail gas after water and heavy product knock out, high conversions can be obtained [23].

## 2.8.3 Iron based catalyst

## Preparation

Iron catalysts for use in low temperature FT (LTFT) 200-240°C, are prepared by precipitation techniques, promoted with Cu and K<sub>2</sub>O and bound with SiO2. The composition of the prepared catalyst is usually 5g of K<sub>2</sub>O, 5g of Cu and 25g of SiO2 per 100g of Fe. These catalysts are usually also partially pre-reduced with H<sub>2</sub> or mixtures of H<sub>2</sub> and CO [23]. In high temperature FT (HTFT) 300-350°C, the catalysts are prepared by fusing magnate together with K<sub>2</sub>O and structural promoters like Al<sub>2</sub>O<sub>3</sub> or MgO. They are pre-reduced with H<sub>2</sub> at about 400°C [23]. For iron catalysts, the "basicity" of the surface is of vital importance. The probability of chain growth increases with chemical promotion through alkalis compounds in the order Li, Na, K and Rb [23]. The alkali metal salt enhances CO chemisorption and thus the rate of carbon deposition. The higher the surface concentration of surface atoms, the higher the coverage by -CH<sub>2</sub>- building blocks and thus a higher probability of chain growth.

## **Operating Conditions**

Bulk phase oxidation occurs on iron catalysts. At high temperatures, aromatics are formed which lead to fouling of the catalyst surface by aromatic coke. Large amounts of elemental carbon are formed which results in catalyst break up. It has been seen that if the syngas pressure is increased, the rate of carbon deposition is decreased, despite the higher FT production rates [23].

In LTFT processes, Fe catalysts can have high conversions, > 90%, but this requires a two stage operation together with gas recycling which increases both capital and running costs. For iron catalysts, the conversion profile does not change with an increase in total pressure if the residence time and other variables are constant [23]. Therefore, doubling the pressure and gas feed rates results in a doubling of the reactor production rate.

# 2.8.4 Cobalt based catalyst

## Preparation

Because of the high price of Co, the amount used needs to be minimized, while at the same time maximizing the available surface area for reaction. This is achieved by dispersing the Co on high area supports such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and TiO<sub>2</sub> [23]. The Co loadings are typically 10-30g per 100g of support material. Co catalysts are promoted with a small amount of noble metal such as Pt, Ru and Re, which enhance the reduction process and help keep the catalyst surface "clean" during the FT process [23]. Co catalysts are much less influenced by the presence of chemical or structural promoters than Fe catalysts. Noble metals enhance FT activity, but it is not clear whether the selectivity is affected [17].

## **Operating conditions**

Co catalysts are only used in LTFT processes. At higher temperatures excess methane is produced [17]. Fe is easier oxidised at lower H<sub>2</sub>O/H<sub>2</sub> ratios than Co. Under FT conditions oxygen atoms/ions will occupy more of the metals surface, resulting in a loss of activity of the FT reaction [23]. This gives Co catalysts a big advantage over iron catalysts. As Co is a more hydrogenating catalyst, the products in general are more hydrogenated and the CH<sub>4</sub> selectivity rises more rapidly with increasing temperature than it does with a Fe catalyst. Also as the reactor pressure rises, the wax selectivity rises. Co catalysts allow high conversions per pass without the need for recycling or two stage operations with knock out of water in between. However, very small Co particles could deactivate at high H<sub>2</sub>O/H<sub>2</sub> ratios, i.e. high conversions, and so it is advisable to run the two stage operation with water knock out in order to keep Co active [23].

# 2.9 FT products

The distribution of FT products is dependent on the catalyst used and the process operating conditions, i.e. temperature, pressure, residence time and composition of the gas. These factors determine the catalyst selectivity, and therefore the chain growth as described by the Anderson-Schultz-Flory equation discussed in the previous section. Table 3 shows the different products formed by extended chain growth.

Name Components	
Fuel Gas	C1 – C2
Liquid Petroleum Gas	C3 – C4
Gasoline	C5 – C12
Naphtha	C8 – C12
Kerosene	C11 – C13
Diesel	C13 – C17
Middle Distillates	C10 – C20
Soft Wax	C19 – C23
Medium Wax	C24 – C35
Hard Wax	C35+

Table 3: Conventions of fuel names and compositions [53]

To maximise gasoline production, the best option is to use a high capacity fixed fluidized bed reactor at an operating temperature of about 340°C, with an iron catalyst [23]. This produces about 40% straight run gasoline. This gasoline has a low octane value because of its high

linearity and low aromatic content. To boost this octane number and to oligomerize the low value by-products propane,  $C_3H_8$ , and butane,  $C_4H_{10}$ , into gasoline requires complex operations, such as platinum reforming [23].

To ensure maximum diesel fuel production, the best option is to use a high capacity slurry bed reactor with a cobalt catalyst operated to maximize wax production. Straight run diesel of high cetane value selectivity consists of about 20% of the total produced fuel. The fraction heavier than diesel products (C > 17) amounts to about 45-50%. Hydro-cracking of these products produces a high proportion of high quality diesel [23]. This diesel can be used in areas where there are very tight constraints on diesel quality or it can be used as blending stock to upgrade lower quality diesel. For example, FT derived sulphur-free diesel fuel is an attractive blending stock to use in order to meet the gas oil sulphur limits as set by the EU directive 1999/32/EC, of no more than 0.2 % by mass by July 2000, and 0.1 % by January 2008 [54]. Overall, the diesel fuel option is more attractive than the gasoline as the process as a whole is less complex. As the production of motor fuels via the FT process is not profitable when oil prices are at reasonable levels, i.e. \$ 20 a barrel, marketing linear paraffins, waxes and alpha olefins that are produced as by-products can help make the process more profitable. High melting FT waxes may be used in such applications as hot melt adhesives, inks and coatings, textiles, polymer processing and polishes [55]. Alpha olefins from high temperature FT (300-350 °C) can be sold as petrochemicals at a much higher price than fuels [23]. Ethylene, C<sub>2</sub>H<sub>4</sub>, can be used to produce polyethylene - the most widely used plastic in the world, polyvinylchloride, polystyrene etc. [56]. Propylene, C<sub>3</sub>H<sub>6</sub>, is used to produce polypropylene, acrylonitrile, propylene oxide etc. [57]. Purified C5 – C8 linear  $\alpha$ -olefins are used as co-monomers in polyethylene production. Longer chain olefins converted to linear alcohols are used in the production of biodegradable detergents. The low temperature (200-240 °C) FT processes produce predominantly longer chain linear paraffins. After mild hydrotreatment to convert olefins and oxygenates to paraffins, linear oils and various grades of linear waxes may be sold at high prices [23].

# 2.10 FT reactors

# 2.10.1 Pre WWII reactors

Early FT reactors developed before and during WWII, such as multi-tubular and fixed-bed reactors. They had very small capacities by current commercial standards and the relatively low velocities associated with once through flow of gas at relatively low temperatures and pressures meant that heat transfer rates from the bed to the cooling surface were low and therefore a very large cooling area would be required if these reactors were to be scaled up to the capacities associated with economically viable operations [58]. For the other early adiabatic bed reactors with external cooling, very large recycle streams were required to take up and transport the generated heat from the reaction. This would give rise to high pressure drops and very high energy consumption for the coolant recirculation if these systems were used for large scale FT synthesis [58].

# 2.10.2 Post WWII reactors

Reactors developed shortly after WWII had much more potential for large scale production of synfuels [58].

- Multi-tubular fixed bed reactor:
  - It operates with gas recycling, at moderate conversion per pass. It consists of double concentric tubes where the catalyst occupies the annular space surrounded by boiling

water. The production capacity is higher than those developed earlier because of the higher temperatures and pressures employed. A more uniform reaction rate profile over the reactor length and improved heat removal is a result of the higher gas velocities.

- Slurry reactors use syngas that is contacted in a bubble column with a slurry of fine catalyst particles suspended in liquid. Heat is removed by internal cooling pipes. Circulation of oil is used to attain high liquid velocities.
- The fluidized bed reactor operates in a bubbling regime, where reaction heat is removed via vertical bundles of cooling tubes.
- Circulating fluidized bed reactors use fine catalyst particles that are entrained by a high velocity (1-2 m/s) gas stream through a riser reactor. The catalyst is separated from the effluent by cyclones and is then returned to the reactor inlet. Two cooling zones in the riser remove reaction heat.

# 2.10.3 Commercial reactors

During the revival in interest in FT processing in the last 20 years, advanced reactors with large capacities have been commercialized or are considered ready for commercialisation. These are: Bubbling fluidized bed reactors, multi-tubular reactors and the internally cooled slurry bubble column reactors.

The first - the bubbling fluidized bed - can only produce light products of low  $\alpha_{ASF}$ , chain growth probability, and therefore cannot produce products heavier than gasoline [58]. This is due to the heavier tail of a high  $\alpha_{ASF}$  product condensing on the catalyst particles. Therefore, a liquid phase must be present in order to produce heavy products.

With the two remaining advanced reactors, multi-tubular (MT) and slurry bubble column (SBC) the slurry bubble column has many advantages over the multi-tubular. These include: The cost of construction of a SBC is only 25 % that of a MT; The differential pressure over the SBC reactor is about 4 times lower, resulting in lower gas compression costs; Lower catalyst loadings translate to four fold lower catalyst consumption per ton of product; The SBC bed is more isothermal and therefore can operate at a higher average temperature resulting in higher conversions; The on-line removal and addition of a catalyst in the SBC allows longer reactor runs [58].

A disadvantage of the SBC is that if a catalyst poison, such as  $H_2S$ , enters the reactor, all the catalyst in the reactor is deactivated. In a MT reactor the top layers of catalyst absorb all the  $H_2S$ , leaving the majority of the catalyst unscathed [58]. Another disadvantage of the SBC is catalyst attrition.

## 2.10.4 Jet loop slurry reactor

A liquid jet loop slurry reactor is a bubble column reactor equipped with a venturi-tube gas distributor and external slurry circulation. These jet loop reactors can be used in up-flow, as in conventional bubble columns, or down-flow (reversed-flow) modes for gas distribution, with the most recent focus on down-flow [59, 60]. Their basic principle is the external circulation of the slurry by means of a pump and the aspiration of the gas-slurry mixture through an ejector [61]. The ejector consists of a slurry ejector nozzle, a gas suction chamber, a mixing tube and a diffuser. The phases are brought into contact by pumping the slurry through the ejector nozzle, forming a fast jet which drags gas from the gas chamber into the mixing tube, then into the diffusion section and finally into the column. The slurry is pumped out of the bottom of the column and a circular baffle plate is placed a short distance above the outlet to prevent large gas bubbles from being pumped out along with the slurry. Furthermore to



prevent shortcircuiting of solid catalyst particles directly to the outlet, which would be detrimental to reaction rates.

Figure 13: (a) Jet loop slurry reactor (b) Ejector system [59]

#### **Solids suspension**

In systems with external circulation of slurry such as this, perfect mixing of the liquid and solid phases can be assumed [61], regardless of the superficial gas velocity as this is not the limiting factor. The main problem is keeping the solid particles in the suspension during the absence of a forced up-draft, except for the turbulence created when the slurry-gas, two-phase, jet reaches the bottom of the column and flow reversal takes place. The gas flow rate plays an important part in the suspension of solids. When the gas portion of the two-phase jet reaches the bottom, it rises due to buoyancy and creates a vertical velocity component which assists this suspension of solids.

#### Mass transfer

The liquid jet loop reactor produces very high gas-liquid interfacial areas. The high shear rates from the ejector which produces fine gas bubbles is the basis of the high volumetric gas-liquid mass transfer rates. However, during their stay in the column, these bubbles tend to coalesce and so reduce these benefits. For this reason, these reactors are best suited for fast reactions. It has been seen that an increase in gas jet flow rate and slurry flow rate has improved gas-liquid mass transfer rates. As far as solid catalyst particles are concerned, increasing particle density and size improves gas-liquid mass transfer rates as the larger particle size and density sheared and broke gas bubbles more easily, creating larger gas-liquid interfacial areas. Overall, gas-liquid mass transfer rates peak with low solids concentrations,  $\sim 2.5\%$ , and are highest in the axial component of the column [59].

#### Heat exchange

The external circulation of the slurry also facilitates the regulation of reactor temperature via a heat exchanger, which is a considerably easier task than that involved in a conventional bubble column.

#### Additional

An addition to the jet loop reactor is the introduction of a draft tube into the column, which can set up the circulating bed flow mode, where the liquid and solid particles circulate into the draft tube [62]. This mode of flow gives higher gas hold-ups and better contact between phases, thus higher reaction rates, than that of a conventional jet loop reactor.

## 2.10.5 Agitated tanks

Agitated tanks used as three phase reactors are essentially bubble columns with one or more impellers used to suspend the solid catalyst particles and mix the phases so as not to rely on a minimum superficial gas velocity and adequate distribution to achieve this. In fact, gas sparger design is not a major factor as the impellers may be designed to distribute the gas. To achieve this, an impeller must be designed and positioned near the bottom of the tank, as this reactor works in up-flow mode, to disperse the incoming gas, break up large bubbles and to keep the solids in suspension. A 45° pitched blade turbine [63] or a hydrofoil type impeller [64] are examples of impellers which can achieve this, and a curvature on the blades also aids in gas dispersion. Other impellers may be designed to give directional flow: up-draft, downdraft, radial or vortex. An upper impeller may be used to draw down gas from the bulk interface at the top of the column.



Figure 14: Agitated tank [64]

## **Impeller dynamics**

In tall, narrow agitated tanks, two or three impellers may be mounted on a single shaft. These impellers produce high local velocities so that large catalyst particles may be used. Catalyst sizes can vary from one type to another, but somewhere in the range 20-250µm is typical. Catalyst loadings are rarely above 5% in agitated tanks [64]. As the primary energy input is via the impeller and not the gas sparger, the solids are kept in suspension by the action of the impeller. Back-mixing is also achieved by this action. This means a minimum superficial gas velocity is not required and so low gas velocity inputs can be used, allowing high conversion rates. The gas-liquid mass transfer rate is also high because the impellers break up the bubbles, increasing the interfacial area, and because low solids concentrations are used, there is little coalescence of bubbles. The liquid-solid and overall mass transfer coefficients during reaction increase with increasing mixing intensity. This is because the amount of catalyst at

the gas-liquid interface increases with the mixing intensity, as there is an increase in the interfacial area as mentioned above.

If agitated tanks are used for particularly exothermic or endothermic reactions, heat exchanger coils will be required in the tank to keep the reactor at its optimum temperature. These coils interrupt natural flow patterns and have a negative impact on mixing [64]. Flow segregation baffles were used in agitated tanks to encourage, most commonly, an upward axial flow with down-flow in the annular, wall regions, to create circulation patterns and further aid mixing of the phases. Mixing in agitated tanks gets harder as the tank gets larger. The scale up of agitated tanks also has a negative effect on reaction selectivity and conversion rates, impacting on productivity [64]. The modelling of the internal hydrodynamics of an impeller introduced into a bubble column to ensure adequate mixing of the phases is a difficult job, especially if heat exchanger coils are present.

## 2.10.6 Micro-channel reactor

A Micro-Channel Reactor (MR) is a system with a large number of small, parallel channels of diameters below 1mm. This reactor provides effective heat removal and improved mass transfer characteristics for the exothermic reactions [66]. As shown in Figure 15 the catalyst is placed in the lower part of the channel so that the reactants are preheated in the channel to the desired reaction temperature. Temperature control is realized by two separate oil heating channels [65].



Figure 15: Reactor assembly of a single micro-channel testing unit [65].

The heat transfer is intensified to an extent, where isothermal operations even for highly exothermic reactions becomes possible. Results on the testing unit for Fischer Tropsch reactions show a temperature gradient in the microchannel reactor in a very narrow range ( $< 3^{\circ}$ C) [66].

Progress in MR for FTS is only likely to be achieved if the ratio of catalyst and reactor volume can be significantly increased [67].

## 2.10.7 Slurry bubble column reactors

#### Introduction

Slurry bubble column reactors (SBC) are classified as of multi phase reactors. Multi phase reactors can roughly be divided into fixed bed reactors, fluidized bed reactors and bubble column reactors. Bubble column reactors are basically constructed of a cylindrical vessel and a gas distributor at the bottom of the vessel. The gas phase is charged over the distributor at the bottom and into a liquid phase. If the liquid consists of solid particles like a catalyst it is called a slurry bubble column reactor. Bubble column reactors are widespread in the chemical-, biochemical-, petrochemical- and metallurgic industry. This type of reactor came into action for example for oxidation, chlorination, polymerization and hydrogenation processes. Very often aqueous systems are in use like in biochemical processes (fermentation, wastewater treatment). In this work the focus is on applications for use in Low Temperature Fischer Tropsch.

A significant book on the Fischer Tropsch slurry reactor as written by Professor W.-D. Deckwer [68]. The book is dealing with the experiences of the Rheinpreußen demonstration reactor that was 1,55 m in diameter and 8,6 m high. This reactor was run with coal derived synthesis gas with a H<sub>2</sub>/CO ratio of 0,67 and an iron catalyst at an intermediate temperature with the object of preferably producing gasoline. There is also a variety of patents which are dealing mainly with features like mixing, mass transfer, catalyst separation, gas distributor and cooling in slurry reactors. All these patents deal with reactors with a diameter of more than 1 m. There are several key parameters for the design of a slurry reactor. To summarize the literature the most important parameters are:

- Gas hold up
- Column dimension
- Maximum stable bubbles
- Flow regimes
- Solid concentration

## Gas hold up prediction

The earliest recorded formulation of a gas distribution theory is credited to Toomey and Johnstone [70] and is known as the two-phase theory of fluidization. This two-phase theory, developed to describe the gas distribution in conventional powder fluidized beds, can also be useful in describing the gas distribution in a slurry phase (also known as a slurry bubble column or slurry bed). Simply stated, the theory specified that all gas excess of that needed to bring a fluidized bed to minimum fluidization conditions passes through in the form of bubbles. This simple theory is modified slightly by defining a dense phase which consists of the aerated powder for gas - solid fluidization or the slurry aerated by small bubbles in the case of a slurry bubble column. Gas in excess of that required to maintain the dense phase passes through the bed in the form of bubbles that are referred to as the dilute phase. The gas hold up in the dense phase can be determined by means of a bed collapse experiment [71]. In the case of slurries, there is no minimum fluidization velocity, but there is a velocity at which a transition occurs between a homogeneous bubbly regime and the churn turbulent regime [72]. As the gas velocity increases above the transition velocity, the dense phase changes to a combination of dense and dilute phases, as defined by this modified two-phase theory. This approach was well described by Krishna et al. [73]. It is important to differentiate the dense phase gas hold up from the dilute phase gas hold up because the dense phase gas hold up is not affected by the column geometry, whereas for small diameter columns, the dilute phase gas hold up is determined mainly by the column geometry. For large diameter columns (larger than 1 m), the dilute phase gas hold up is surprisingly constant for all fluidized systems, while the dense phase gas hold up may vary widely depending on the gas, powder or slurry properties. In the case of slurries, prediction of the dense phase voidage (i.e. gas hold up) is usually unreliable because of the sensitivity of the liquid surface tension which is often affected by small amounts of impurities. Using the modified two-phase theory, the dilute phase voidage can be described using the equation:

$$\epsilon_b = \frac{(U - U_{df})}{U_b}$$

#### **Equation 1**

Using the correlation proposed by Werther [74] of  $U_b = \emptyset(g d_b)^{1/2}$  and substituting it into Equation 1 gives:

$$\epsilon_b = \frac{(U - U_{df})}{\emptyset(g \, d_b)^{1/2}}$$

#### **Equation 2**

Following the Darton et al. [75] approach, the diameter of a sphere having the same volume as the actual bubble, for dispersion heights exceeding  $h^*$  (where  $h^*$  is the height above the gas distributor where the bubbles reach an equilibrium size), is given by:

$$d_b = \alpha (U - U_{df})^{\frac{2}{5}} (h^* + h_0)^{4/5} g^{-1/5}$$
 for  $h^* \le h \le H$ 

#### **Equation 3**

Ellenberger and Krishna [73] derived the following equation for  $H \gg h^*$ :

$$\epsilon_{b} = \frac{(U - U_{df})^{4/5}}{\alpha^{1/2} \emptyset \ g^{\frac{2}{5}} (h^{*} + h_{0})^{2/5}}$$

#### **Equation 4**

Substituting for  $d_b$  from Equation 3 into Equation 2 gives Equation 4. This shows that the approach of Ellenberger and Krishna is consistent with the modified two-phase theory. It is also known that  $h^*$  is a function of (U -  $U_{df}$ ). Once this functional dependence has been determined, Equation 4 can be used to describe how the dilute phase gas hold-up,  $\varepsilon_b$ , varies with superficial gas velocity U (having also determined  $U_{df}$ ). Werther [74] proposed that, for columns with diameters smaller than 1m,  $\phi = \phi_0 (D_T)^{2/5}$  can be used with Equation 4 to quantify the dependence of dilute phase gas hold up on column diameter.

- $d_B$  average bubble diameter
- $D_{\rm T}$  column diameter (m)
- g acceleration due to gravity  $(9.81 \text{ ms}^{-2})$
- $h^*$  height above the gas distributor where the bubbles reach their equilibrium size (m)
- $h_0$  parameter determining the initial bubble size at the gas distributor (m)
- *H* height of the expanded bed (m)
- U superficial gas velocity (ms<sup>-1</sup>)
- $U_{\rm B}$  average bubble rise velocity (ms<sup>-1</sup>)
- $U_{df}$  superficial gas velocity through the dense phase (ms<sup>-1</sup>)
$\alpha$  constant in the bubble growth model of Darton et al.

 $\rho$  bed density (kg m<sup>-3</sup>)

 $\varepsilon_B$  gas hold-up in the 'dilute' phase, bubble fraction, fraction of the bed occupied by gas bubbles

Ø bubble rise coefficient

#### Column dimension and maximum stable bubble size

On the basis of studies on a mechanistic model and experiments at elevated pressure Luo et al. [76] show that the maximum stable bubble size is inversely proportional to the square root of the gas density.

$$D_{max} \approx 7,16\alpha^{\frac{2}{3}}E(\sqrt{1-\alpha^2})^{\frac{1}{2}}\sqrt{\frac{\alpha}{g\rho_g}}$$

**Equation 5** 

α	aspect ratio (height to width) of bubbles
D <sub>max</sub>	maximum stable bubble size (m)
$E\sqrt{1-\alpha^2}$	complete second kind elliptic integral
g	gravitational acceleration (m s <sup>-2</sup> )
$ ho_{g}$	density of gaseous phase (kg m <sup>-3</sup> )

The aspect ratio is hence about 0,21 for the large bubbles in liquids, and  $E(\sqrt{1-\alpha^2})^{\frac{1}{2}}$  is close to unity. For large bubbles rising in liquid-solids suspensions, the aspect ratio is approximated as 0,3 how Luo reported in [76] and  $E(\sqrt{1-\alpha^2})^{\frac{1}{2}}$  is 1,018. The simplified forms of Equation 5 are:

$$D_{max} \approx 2,53 \sqrt{\frac{\sigma}{g\rho_g}}$$
 (for  $\alpha = 0,21$ ; liquid)

**Equation 6** 

 $D_{max} \approx 3,27 \sqrt{\frac{\sigma}{g\rho_g}}$  (for  $\alpha = 0,3$ ; liquid-solids)

#### **Equation 7**

The effects of column dimension is well summarized by Kantarci et al. [77]. T. Shah et al. [78] reported that in bubble columns, the effect of column size on gas hold up is negligible when the column diameter is larger than 10–15 cm. Luo et al. [79] reported that the influence of the column height is insignificant if the height is above 1–3 m and the ratio of the column height to the diameter (aspect ratio) is larger than 5. Possible wall effects brought about by the use of small diameter columns ( $\leq 10$  cm) were also pointed out [80, 81]. It was reported that the gas hold up was not highly dependent on column diameter when the column diameter was larger than 10 cm, as long as mixing was well maintained. Daly et al. [82] found that the hold up is independent of the column height. Additionally, though not so significant, they obtained some differences in hold up with variation of the column diameter. It was observed that the hold up in small diameter column was slightly higher than that in larger diameter columns.

The effect of column dimensions on gas hold up in foaming systems has not received significant attention in literature. Pino et al. [83] observed no appreciable differences in the gas hold up of foaming systems between columns of 10 and 29 cm in diameter, in the semibatch mode of operation. It was also reported that the effect of column height was insignificant for height to diameter ratios between 3 and 12. At high gas velocities when foaming occurred, both column height and diameter had no effect on gas hold up, whereas, for non-foaming systems and for column diameters up to 15 cm, gas hold up was found to decrease with increasing column diameter. According to the two-phase model developed by Krishna et al. [84-86] the effect of column diameter on gas hold up should be separately analyzed for small and large bubble gas hold ups. It was found that the small bubble gas hold up is independent from the column diameter, while the large bubble gas hold up decreased with increasing column diameter. As a result the overall hold up is reported to decrease with increasing column diameter was described by the following relationship proposed by Krishna et al. [84]:

$$\varepsilon_{b,lg} = \alpha_2 \frac{1}{D_T^N} (V_g - V_{df})^{0.58}$$

#### **Equation 8**

 $\epsilon_{b,lg}$  gas hold up of large bubbles (dilute phase)

 $\alpha_2$  fit parameter ( $\alpha_2$  = 0.268 for gas liquid solids system solids < 16 %;  $\alpha_2$  = 0,3 for solids > 16 %)

N fit parameter (N = 0,18 for gas liquid solids system solids < 16 %; N = 0,18 for solids > 16 %)

D<sub>T</sub> column diameter

V<sub>g</sub> superficial gas velocity entering the column

V<sub>df</sub> superficial velocity of the dense-phase or superficial velocity of large bubbles

 $\sigma$  surface tension (Nm<sup>-1</sup>)

The critical column diameter for Fischer-Tropsch slurry reactors is discussed in [41]. It has been proposed that the critical column diameter above which the gas hold up is not influenced by the diameter is usually close to 15 cm and can be expected to decrease to some extent with increasing gas density and decreasing surface tension. Wall effects may be reduced on rising gas bubbles with decreasing bubble size. Equation 9 below shows gives a relationship to estimate the critical column diameter  $D_c$ :

$$D_{c} = 20 (\frac{\sigma^{2}}{g^{2}(\rho_{L} - \rho_{G})\rho_{G}})^{0,25}$$

#### **Equation 9**

- D<sub>c</sub> critical column diameter above which there is no effect of the column diameter on gas hold up any more (m)
- $\sigma$  surface tension (N m<sup>-1</sup>)
- g acceleration by gravity (m s<sup>-2</sup>)
- $\rho_{\rm G}$  gas density (kg m<sup>-3</sup>)
- $\rho_L$  liquid density (kg m<sup>-3</sup>)

Equation 9 gives a critical column diameter of 0,09-0,11m for gas densities of 6 and 10 kg m<sup>-3</sup> respectively.



Superficial gas velocity, U

Figure 16: Homogeneous and churn-turbulent regimes in a gas-liquid bubble column[87]

Krishna reports the behaviour of the gas hold up for different hydrodynamic regimes[87]. When a column filled with a liquid is sparged with gas, the bed of liquid begins to expand as soon as gas is introduced. As the gas velocity is increased the bed height increases almost linearly with the superficial gas velocity U, provided the value of U stays below a certain value  $U_{trans}$ . This regime of operation of a bubble column is called the homogeneous bubbly flow regime. The bubble size distribution is narrow and a roughly uniform bubble size, generally in the range 1-7 mm, is found. When the superficial gas velocity U reaches the value  $U_{trans}$ , coalescence of the bubbles takes place to produce the first fast-rising "large" bubble. The appearance of the first large bubble changes the hydrodynamic picture dramatically. The hydrodynamic picture in a gas-liquid system for velocities exceeding Utrans is commonly referred to as the heterogeneous or churn-turbulent flow regime. In the heterogeneous regime, small bubbles combine in clusters to form large bubbles in the size range 20-70 mm. These large bubbles travel up through the column at high velocities (in the range 1-2 m/s), in a more or less plug flow manner. These large bubbles have the effect of churning up the liquid phase. The large bubbles are mainly responsible for the throughput of gas through the reactor. Small bubbles, which co-exist with large bubbles in the churnturbulent regime, are "entrained" in the liquid phase and as a good approximation have the same backmixing characteristics of the liquid phase. The two regimes are portrayed in Figure 16 which also shows the variation of the gas hold up  $\varepsilon$  as a function of the superficial gas velocity U in a qualitative way. When the gas distribution is very good, the regime transition region is often characterized by a maximum in the gas hold up. The transition between homogeneous and churn-turbulent regimes is often difficult to characterize"[87].

In addition Krishna reports the problem of the prediction of the gas hold up. In Figure 17 the experimental data for three different systems are shown. Paraffin oil has a different gas hold up behaviour than the systems with water or Tellus oil.



Figure 17: Comparison of the total gas hold up measured in a column of 0.38 m internal diameter. Measurements with air-paraffin oil, air-water and air-Tellus oil. [87]

Physical data for the liquids in use for Figure 17:

air-paraffin oil	$(\rho_L = 795 \text{ kg/m}^3; \eta_L = 0,0029 \text{ Pa} \cdot \text{s}; \sigma = 0,029 \text{ N/m})$
air-water	$(\rho_L = 1000 \text{ kg/m}^3; \eta_L = 0,001 \text{ Pa s}; \sigma = 0,072 \text{ N/m})$
air-Tellus oil	$(\rho_L = 862 \text{ kg/m}^3; \eta_L = 0,075 \text{ Pa s}; \sigma = 0,028 \text{ N/m})$

Krishna compares different research results in [87] with the focus on the gas hold up and the column diameter. The results show a decline in the total gas hold up with increasing column diameter for water air systems. In addition Krishna summarizes results from preceding studies on single gas bubbles and swarm in liquids. Mainly he treats the system air water at normal pressure.

#### Solid catalysts impact on gas hold up and bubble size

The effect of solid particles in a flow regime of a paraffin - air - silica particles system has been analyzed by De Swart et al. and reported in [88]. He has collected data with an experimental set up consisting of a two dimensional glass column (cross section of 0,3m x 0,005m) and a video camera. Figure 18 demonstrates the influence of solid concentration in the slurry on the gas bubble behaviour. It shows that the higher the concentration on solids the lower the appearance of small bubbles. The effect of the total gas hold up in respect of the solid concentration is reported in [89]. In Figure 19 the gas hold up for different solid concentration is displayed. It is obvious that the gas hold up is decreasing, the higher the solid concentration is in the system. Likewise it can be observed that no maximum of the gas hold up appears at the transition zone between the homogenous and heterogeneous flow regimes at solid concentrations higher than 20 Vol.%. and this is indicated by the absence of small bubbles [89].



Figure 18: Influence of increased particle concentration: impression of three retraced video images obtained at 0.65 m above the distributor (air/paraffin oil slurries)[88].



Figure 19: Influence of increased particles concentration on the total gas hold up in a 0.38 m diameter column. (Air - paraffin oil (density,  $\rho L = 790 \text{ kg} \cdot \text{m}^{-3}$ ; viscosity,  $\eta L = 0.0029 \text{ Pa} \cdot \text{s}$ ; surface tension,  $\sigma = 0.028 \text{ N} \cdot \text{m}^{-1}$ )) The solid phase used consisted of porous silica particles (skeleton density = 2100 kg·m<sup>-3</sup>; pore volume = 1.05 mL·g<sup>-1</sup>; particle size distribution, dp: 10% < 27 µm; 50% < 38 µm; 90% < 47 µm).  $\epsilon_s$  is the volume fraction of solids in gas free slurry. The pore volume of the particles (liquid filled during operation) is counted as being part of the solid phase [89].

Other experimental data published in [89] by Krishna et al. is shown in Figure 20. In this experiment a bubble column system of paraffin oil – air without and with solids is operated under steady-state. At the time t = 0 the gas supply is shut-off and the dispersion level is monitored as a function of the time. A result of this experiment is that at a certain solid particle concentration the small bubbles disappear.



Figure 20: Dynamic gas disengagement experiments for air/paraffin oil and air/36 vol% paraffin oil slurry in a 0.38 m diameter column [89]. Physical properties are the same as described in Figure 19

#### Mass transfer from the bubble to the liquid

Calculation of conventional mass transfer rates based on the hold-up and size of large bubbles, yields relatively low rates. However, experimental data has shown actual rates to be 5-10 times higher than calculated [58]. It is quite difficult to determine gas-liquid mass transfer coefficients,  $k_{L}a$ , for slurry bubble columns, as the bubbles are continuously breaking up and coalescing. However it can be seen that with increased  $\varepsilon_s$ ,  $k_{L}a$  decreases due to the coalescence of bubbles generating a smaller interfacial area for mass transfer to occur. Larger and denser particles give rise to smaller bubbles as they have increased capacity for shearing bubbles, and this increases the  $k_{L}a$  because the interfacial area is increased. The design of the gas sparger is a major factor in  $k_{L}a$ , because if the bubbles formed are very fine, the  $k_{L}a$  is initially high, until the bubbles coalesce due to the presence of solids. Staging with sieve plates can improve  $k_{L}a$  as they break up large bubbles, improving the interfacial area [90].

The liquid-solid mass transfer coefficients are high due to the high concentrations of catalyst but are not as high as they could be, due to the slurry bubbles columns' limitations. Backmixing is used and the high U values are required to keep the solid particles in suspension and to mix the phases.

Overall, to achieve high mass transfer coefficients in one pass, > 90%, which is desirable to avoid recycling of un-reacted gas, requires high solid concentrations,  $\sim 30 - 40\%$ , low gas velocities and very often staging.

#### Heat transfer

In SBC's heat transfer works usually via internal cooling coils, and unlike in other reactors, these coils do not interrupt the overall hydrodynamics of the system [64]. 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 run 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 desired [23]. High liquid rise and fall velocities in the axial and wall regions ensure high heat transfer coefficients, up to 1000W/m<sup>2</sup>/K [91], can be obtained in SBC's. The heat transfer coefficient increases with increasing gas velocity and solids concentration.

#### Operation

The SBC can be used in a continuous operation for a process such as methanol production and Fischer-Tropsch synthesis, due to the SBC's capability of on-line removal and addition of a fresh catalyst [23]. The system may be operated at high catalyst loading, 30-40% depending on the literature consulted [23, 58]. The increased catalyst concentration,  $\varepsilon_s$ , increases the gas conversion rate and the reactor capacity for further catalyst addition. This is due to the fact that increasing  $\varepsilon_s$  reduces the total gas hold-up which makes room for more catalyst. However, increasing  $\varepsilon_s$  also increases the number of cooling tubes required in the reactor [58]. The capacity of the SBC for high catalyst concentrations also allows economic deployment of low activity catalysts [64].

Increased  $\varepsilon_s$  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 [90]. This consists of introducing sieve plates which encourage well mixed compartments of a uniformly suspended catalyst and isothermal conditions optimized to the specific reaction required. However, there are no significant benefits to the 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 formed liquid from the suspended catalyst was one which resulted in SBC's being disregarded as viable for 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.

# 2.10.8 Draft tube slurry bubble column

A draft tube slurry bubble column is essentially a bubble column with an inner tube to induce the circulation of the slurry. This type of slurry bubble column reactor is often used where it is desirable to increase contact between the phases throughout the bubble column relative to the original design, such as in waste water treatment and fermentation bioreactors [92]. The area inside the tube is known as the draft tube region and the area outside is known as the annular region. The draft tube channels the incoming gas at the inlet section of the column, which creates a zone of lower relative pressures at the bottom of the annular section. This difference in pressure between the two regions facilitates a re-circulating motion of the slurry, in which all phases rise in the draft tube and descend in the annular region. The geometry of this type of system determines its efficiency for mixing, suspension of solids and mass transfer.



Figure 21: Slurry bubble column with draft tube and spouted section [92]

#### **Gas Phase Dynamics**

In draft tube systems, a conical section may be used to enhance the solids and liquid circulation. This configuration is known as spouted bed. A small entrance section forms a jet with a high content of gas phase and a high velocity. Since the phases in the jet region move at a velocity that is higher than their superficial gas velocity, a downwards flow region is created near the wall of the conical section [92]. This circulating motion enhances interface mass transfer as well as contributing to suspension of the solids and mixing of the liquid phase. The draft tube bubble column can reach the circulating bed mode of operation, where the liquid and solid catalyst particles form homogeneous slurry at lower gas velocities than would be required in a conventional bubble column. It has been found that the superficial gas velocity required to reach the circulating bed mode was decreased by a factor of 4 when a draft tube was inserted into a conventional bubble column [92]. There was also found to be no difference in concentration of solids between the draft tube and annular regions.

#### Geometry

The effect of the ratio of draft tube to column diameter on the gas-liquid mass transfer coefficient, gas hold-up and liquid circulation velocities has been extensively investigated. Published results in literature have been surprisingly contradictory, due to slight differences in design pertaining to conical section design, draft tube clearance from conical section, apex

angle of conical section, etc [92]. This confirms that geometry of the system is crucial to all performance factors.

Once the gas reaches the top of the column, a large part of it disengages and the rest is drawn downward into the annular region. This means the superficial gas velocity and gas hold-up in the annular region is substantially lower than in the draft tube. The overall gas hold up per unit area is smaller than for a comparatively conventional bubble column. The position of the draft tube in the column, as mentioned earlier, has a major effect on the hydrodynamics of the bubble column. Lowering the position of the draft tube into the conical section increases the gas hold-up difference between the annular and draft tube. This also increases the pressure difference between the two regions and so circulation is improved [92].

#### Additions

Another addition that may be made to the draft tube bubble column is the introduction of a static mixer into the draft tube. A static mixer consists of right and left hand 90° angled corrugated stainless steel sheets. This type of mixer is intended to improve mixing and contact between the phases. The static mixers effect on gas-liquid mass transfer depends on the gas sparger used. Research by Goto has shown that for single nozzle gas spargers, which produce large bubbles, a static mixer disperses the bubbles and so the gas-liquid mass transfer coefficient rises as the interfacial area is improved [93]. For plastic ball type gas spargers, with fine pores and small bubbles, the mixer tends to encourage the coalescence of the bubbles and so the gas-liquid mass transfer coefficient becomes lower. The rate of liquid-solid mass transfer is increased by the presence of a mixer, though the mixer hinders liquid circulation as the circulation is mainly driven by the air lift action of the bubbles. The presence of a mixer also hinders the movement of solid particles in the draft tube [93].

# 2.11 Comparative discussion on three-phase slurry reactors

# 2.11.1 Catalyst Particle Loading

Table 5 shows an overview of the common solid particle sizes, solid concentration and minimum superficial gas velocity required to keep the solid particles in suspension for the five reactor options.

	SBC	Draft	Jet	Agitated
		<b>Tube SBC</b>	Loop	Tank
			SR	
Solids Size (µm)	<= 50	<= 50	<= 50	20 - 250
Solids Frac. (%)	<= 40	<= 40	~ 2.5	<= 5
Required Gas U for	High	Low	Highest	Lowest
suspension				

 Table 4: Comparison of solids parameters in different reactors [58-60, 64, 66, 92, 94]

# Slurry bubble column

The SBC allows very high rates of solid catalyst particle loading. Concentrations of up to 40% still allow manageable operation, too high concentrations result in excessive numbers of required heat exchanger coils. This high concentration of a catalyst is possible as increasing catalyst concentration,  $\varepsilon_s$ , reduces the total gas hold-up, which makes more room for additional catalysts. This potential for high  $\varepsilon_s$  allows the possibility for economic deployment

of low activity catalysts. The slurry bubble column requires small solid particles,  $< 50\mu m$  of low sedimentation velocity as they are to be kept in suspension solely by bubbling the gas phase through the liquid. Higher  $\epsilon_s$  requires higher superficial gas velocities, U, to keep the solids in suspension.

#### Draft tube SBC

The draft tube SBC has an increased capacity for a solid particle suspension compared to the conventional SBC. Similar sized particles and concentrations are used, but suspension can be achieved at lower U's, which will be discussed in the back-mixing section in more detail.

#### Jet Loop Slurry Reactor

Jet loop slurry reactors are normally operated at low  $\varepsilon_s \sim 2.5\%$ . Gas - liquid mass transfer rates peak at this concentration and higher concentrations may result in blockages in the ejector system. It is also necessary for the catalyst size to be small (< 50µm) in order to avoid these blockages.

#### **Agitated Tank**

The impellers in agitated tanks produce large local velocities capable of keeping large, dense catalyst particles in suspension, much larger than in a conventional SBC. A typical range of particle sizes that may be used is from 20 to  $250\mu m$ .  $\varepsilon_s$  is rarely above 5%.

#### 2.11.2 Back-mixing

#### Slurry bubble column

The primary energy input into a SBC is through the sparged gas and because of the system's simple design this is the only chance of achieving a homogenous mixture between the liquid and solid phases. To achieve this, the gas velocity needs to be above a certain U and U<sub>trans</sub>, so the column is in the heterogeneous flow mode. The value U<sub>trans</sub> is increased with increasing  $\varepsilon_s$ . It has been seen in tests that the SBC is not a particularly good mixer [95] with a well-defined bulk circulation of the liquid not developing and several circulation cells present, which are detrimental to the overall homogeniality of the slurry. With increasing U, the larger circulation cells break into smaller ones, or the size and location of these cells is altered. Staging with sieve plates helps to create well mixed compartments of a uniformly suspended catalyst.

#### Draft tube SBC

The draft tube SBC reaches the circulating bed mode of flow, where the phases are fully mixed at lower gas and liquid velocities than are required in a conventional bubble column. There is no difference in the solid concentration in the radial and axial positions in the draft tube and annular regions or between the two regions. An efficient longitudinal dispersion of solids is caused by the difference in the velocities of the gas and liquid phases. It has been found that the U required to reach the circulating mode of flow is decreased by a factor of up to four when a draft tube is introduced into a conventional bubble column [92]. It has also been found that as the draft tube diameter to column diameter ratio (DT/D) increases, so does the liquid circulation velocity [96]. This increase in DT/D also leads to an increase in the

minimum fluidization velocity [97]. The spouted bed section also enhances the solid-liquid circulation. It has been found that the inlet diameter to column diameter ratio must be less than 0.2 for the spouting action to be effective [92]. A small apex angle for the conical section leads to a good distribution of slurry in this section, avoiding stagnant regions and sedimentation of solids [92].

#### Jet loop slurry reactor

As the jet loop reactor has an external circulation, perfect mixing of the liquid and solid phases can be assumed. The main problems lie in keeping the solid particles in the column in the suspension. The critical liquid velocity (minimum liquid velocity required for complete circulation of the gas-liquid flow) and the minimum fluidization velocity (velocity required to suspend the solid particles completely) increase with increasing gas velocity and the loading of solids. The introduction of a draft tube allows even better mixing between the phases.

#### Agitated tank

The high local velocities produced by the impellers in an agitated tank also achieve adequate back-mixing of the phases, and uniform catalyst distribution can be assumed, although impeller design is crucial in ensuring no stagnant regions exist in the tank. Baffles may be used to create circulation patterns and further aid mixing. It has been found that as the tank gets larger, mixing gets harder [64] and so adequate back-mixing of the phases cannot be guaranteed for large diameters, such as 15-30m. Unlike in SBC's, internal heat exchanger coils interrupt the natural flow patterns and have an impact on mixing.

# 2.11.3 Mass transfer characteristics

#### Slurry bubble column

The calculation of conventional mass transfer rates based on the hold-up and the size of large bubbles yields relatively low rates. However, experimental data has shown actual rates to be 5 - 10 times higher than calculated [58]. It is quite difficult to determine gas-liquid mass transfer coefficients (k<sub>L</sub>a) for SBC's as the bubbles are continuously breaking up and coalescing. It can be seen though that with increased  $\varepsilon_s$ , k<sub>L</sub>a decreases due to the coalescence of bubbles generating a smaller interfacial area for mass transfer to occur. Larger and denser particles give rise to smaller bubbles as they have increased capacity for shearing bubbles, and this increases the k<sub>L</sub>a because the interfacial area is increased. The design of the gas sparger is a major factor in k<sub>L</sub>a, because if the bubbles formed are very fine, the k<sub>L</sub>a is initially high, until the bubbles coalesce due to the presence of solids. Staging with sieve plates can improve k<sub>L</sub>a as they break up large bubbles, improving the interfacial area [90].

The liquid-solid mass transfer coefficients are high due to the high concentrations of catalyst. However they are not as high as they could be, due to the SBC's limitations as far as backmixing is concerned and the high U values required to keep the solid particles in suspension and to mix the phases.

Overall, to achieve high mass transfer coefficients in one pass (> 90%) which is desirable to avoid the recycling of unreacted gas, requires high slurry concentrations ( $\sim$  30-40%) low gas velocities and very often staging.

#### Draft tube SBC

In draft tube SBC's spouting of the inlet gas enhances the gas-liquid mass transfer coefficient and the liquid-solid mass transfer coefficient. This section promotes circulation and contact between the phases if properly designed. Correct positioning of the draft tube can induce high circulation velocities of the slurry phase which improves both gas-liquid and liquid-solid mass transfer coefficients. The improved mixing, recirculation of a portion of the gas into the annular region and the lower superficial gas velocities that are possible mean that overall conversion rates are higher than in a conventional SBC. The geometry of the system is crucial in obtaining these high liquid velocities and circulation trends.

#### Jet loop slurry reactor

Initially the jet loop reactor produces a high gas-liquid mass transfer coefficient, but as explained in the previous part, this gets reduced over time in the reactor. The presence of solids in low concentration actually improves the gas-liquid interfacial area, and thus the gas-liquid mass transfer coefficient. The presence of a draft tube will improve both the gas-liquid and liquid-solid mass transfer coefficients due to improved mixing and enhanced suspension of solids. The overall conversion rates are not as high as for a conventional SBC due to the lower concentrations of the catalyst used.

#### Agitated tank

Higher gas-liquid interfacial areas are present in an agitated tank, as the impellers break up the incoming bubbles, and lower inlet gas velocities can be used than in a conventional SBC, so gas-liquid mass transfer coefficients are higher. Both the gas-liquid and liquid-solid mass transfer coefficients increase as the mixing intensity increases [64]. The agitated tank has a higher mass transfer efficiency than the conventional SBC, although overall conversion rates may be lower due to the low concentrations of catalyst used.

# 2.11.4 Conclusions

Taking into account the construction and operational factors of all the slurry reactor options, the reactor which offers the highest conversion efficiency, as well as relative ease of operation and construction, is the draft tube slurry bubble reactor. This is due to its good back-mixing and high liquid circulation rates, which allow good mass transfer rates, at low gas inlet velocities, with a just a simple alteration to the conventional slurry bubble column. However, to obtain the optimum draft tube to column diameter ratio, as well as the length and positioning of the draft tube and the dimensions of a spouted bed section, to generate the desired hydrodynamic conditions, requires further investigations.

A microchannel reactor offers a very high efficiency, since mass and heat transfer resistances are negligibly small. On the other hand, a microchannel reactor with only a thin layer of catalyst applied to the reactor walls does not provide enough productivity per unit of total reactor volume to become industrially attractive. Progress in the microchannel reactor for Fischer Tropsch synthesis will only be achieved if the ratio of catalyst and reactor volume can be significantly increased [67].

# **3** Research design / questions

Figure 22 illustrates the basic mind map of the project with the objective to obtain liquid fuel from biomass. From this map several questions of apparent importance are formulated. At the end of the work the idea is to attempt to answer all of these questions.

Catalysts:

- Which are appropriate catalysts in FT slurry reactors run by the producer gas of Güssing?
- What are the demands on catalysts for FT-synthesis?
- What influences will the producer gas of Güssing have on the catalyst?
- How can the process be controlled by the choice of catalyst?

Producer gas of Güssing:

- Is the usage of the producer gas appropriate with regard to the main compounds for FT-synthesis?
- What are the purity specifications for the producer gas from Güssing and how can these specifications be fulfilled?

FT-reactor design:

- How can a homogenous distribution be estimated for the catalyst in the slurry?
- What is the impact of the type of catalyst and catalyst loading?
- What dimensions/designs are required of the reactor for the pilot plant?
- How can the level in the Fischer Tropsch reactor be controlled?
- How can the temperature be controlled in the reactor?

#### Pilot plant:

- What impact has the producer gas on the different components of the FT-pilot plant?
- How can a continuous FT-product separation be realized?
- How can the process be controlled?

FT-product:

- What are the products from the FT-synthesis operated with the producer gas from Güssing?
- Is the obtained FT-product suitable for automotive purposes?



Figure 22: Basic mind-map for research design

# PART TWO

# PRACTICAL WORK

# 4 Catalyst characterization at the "Université Louis Pasteur Strasbourg"

The catalyst characterization was carried out in cooperation with Prof. Kienemann at the "Universté Louis Pasteur Strasbourg". All of the experimental work presented in Chapter 4 was collected and measured in the laboratory of Louis Pasteur University.

# 4.1 Introduction

For converting syngas (CO/H<sub>2</sub>) into hydrocarbons the use of suitable catalysts is necessary. For planning and designing of a Fischer Tropsch-slurry plant it is necessary to know about the catalytic and physical properties of the used catalyst.

In this work four different catalysts were tested with regard to the reducibility and activity of the catalysts.

Belows catalysts where tested:

- Type A (iron based Haber Bosch catalyst)\*
- Type B (iron based Haber Bosch catalyst)\*
- Co/Si (25% Cobalt on SiO<sub>2</sub>)\*\*
- Co/Ru/Si (25% Cobalt, 0,1%Ruthenium on SiO<sub>2</sub>)\*\*
- \* commercial Haber –Bosch catalyst
- \*\*developed and prepared at the Universite de Strasbourg

Following methods where used for the characterization:

- <u>Temperature programmed reduction (TPR)</u>: reductive performance of the catalysts under H<sub>2</sub>. Gives information about the reducibility of the catalyst.
- <u>Disproportionation of carbon monoxide on the catalyst</u>: Shows catalyst activity toward CO.
- <u>Activity tests:</u> Activity of the catalysts in the slurry-phase is tested at low temperature Fischer Tropsch reaction conditions.

# 4.2 Experimental set up

# 4.2.1 Temperature programmed reduction (TPR)

The TPR test rig is shown in Figure 23. The analysed catalysts (iron and cobalt) show only an activity for Fischer Tropsch-synthesis if they are in the metallic state. An important parameter for the catalyst is the temperature of reduction. High reduction temperatures may influence negatively the active surface of the catalyst. Sintering of the catalyst reduces the active surface. Additionally high reducing temperature requires special demands on the used equipment for reducing the catalyst. For the determination of the reduction performance the catalyst (oxide state) is weighted in and transferred to the reactor (fused silica U-tube). The catalyst is exposed to a constant flow of H<sub>2</sub> under a linear gradient of heat. The change in H<sub>2</sub> concentration of the reactor and the temperature is measured over the duration of the experiment.



Figure 23: TPR – rig

# 4.2.2 Experimental procedure of TPR:

The grounded and sieved catalyst is transferred to the reactor in a way that it is placed between fused silica wool. With the temperature controller a defined temperature gradient (5-15 °C/min) is adjusted. During the time of the experiment the degree of hydrogen (reducing agent) concentration is measured with the two TCD cells. The calibration of the system is carried out with four injections of a defined volume (0,4 ml) of hydrogen.

# 4.3 Carbon monoxide-disproportion test

The activity of the catalysts towards carbon monoxide is an indicator of the activity of the catalyst in Fischer Tropsch. The reduced catalysts are exposed several times ( $\sim 15x$ ) to a defined amount of carbon monoxide. The concentration of carbon monoxide and the formed carbon dioxide are measured. The disproportionation can be shown by the following equation:

$$2CO \to C + CO_2 \tag{1}$$

# 4.3.1 Description of the CO-disproportion rig

For reducing the catalyst the two flow meters are adjusted to produce a constant volume flow of hydrogen and helium. The temperature of the reactor can be controlled as well as the heating rate. For the disproportionation experiment the flow is set to 100% helium and with the six-directional injection valve (500  $\mu$ l) carbon monoxide is charged on the catalyst. The formed carbon dioxide and the concentration of the carbon monoxide are measured with the two TCD cells (reference and measuring cell). A chromatographic column (HYESEP R 2m) for separating carbon monoxide and carbon dioxide is placed before the TCD-cell. The data

storage and controlling of the six-directional injection valve occurs with the computer ENICA 31.

- Flowmeter BROOKS Instruments 5850 TR
- Reactor silica fused U-tube
- Column HEYSEP R (2m)
- Computer ENICA 31 (DELSI NERMAG Instruments)
- TCD-cells thermal-conductivity detector: GOW.NAC Thermiothor



Figure 24: Carbon monoxide - disproportion - rig

CO-Disproportion-rig

# 4.3.2 Performance of the experiment of CO-disproportionation

In the first part of the experiment the catalyst used is reduced. Initially the catalyst is weighed and transferred to the reactor. The reduction of the catalyst is than carried out with a constant volume flow of hydrogen and helium. The heating rate is set to one degree Celsius per minute. Once the desired temperature is reached the temperature level is kept constant until the end of the reducing part of the experiment. After the reduction of the catalyst the temperature is set to a defined level for the disproportionation reaction. The volume flow is switched to 100 % helium and the six-directional injection valve is purged with carbon monoxide. The valve is controlled in a way that fifteen injections of CO are carried out. Between each injection there is enough time for analysing the gas.

For calibrating the system, the reactor is cooled down to room temperature (no disproportionation takes place) and an additional three injections are carried out.

For the calibration of the system for carbon dioxide (for quantification of  $CO_2$ ) a defined amount of carbon dioxide is charged. A factor of 0,87 has been evaluated (CO is 1) which has been used for all test runs.

# 4.4 Activity tests of the catalysts in the stirred laboratory slurry reactor

For testing the performance of the catalyst, the catalyst is suspended in the slurry with a stirrer in the reactor, and the gases (CO, H<sub>2</sub>, N<sub>2</sub>) are passed into the solution. The Fischer Tropsch reaction is carried out under pressure (25-30bar) and a temperature ranging from  $240 - 280^{\circ}$ C.

# 4.4.1 Description of the experiment

For testing the catalyst the oxide form of the catalyst has to be reduced under hydrogen at a suitable temperature.

The catalyst is reduced in the CO-disproportionation rig. The tube (reactor) is fitted with a sintered disc. The catalyst is put into the reactor and it is reduced for several hours with hydrogen. The temperature gradient is kept at 1°C per minute until the desired temperature is reached.

After cooling down to ambient temperature the catalyst is transferred under nitrogen into the Fischer-Tropsch (FT) reactor directly into the slurry. The FT-reactor is installed into the rig and the pressure in the FT-reactor is increased with the help of the gas cylinders.

The flow of each gas is controlled by flow meters, and the pressure in the reactor is controlled by a pneumatic valve.

When the pressure and the temperature have been reached in the reactor, samples are taken from the leaving gas and are analysed with a GC-TCD.

At the end of the experiment the produced liquids in the reactor are analysed.



Part Two: Practical Work

# 4.5 Results of the catalyst characterisation experiments

#### 4.5.1 Results of temperature programmed reduction experiments

In Figure 26 and Figure 27 the temperature is displayed on the x axis and the response of the TCD-cells is displayed on the y axis. The blue line in Figure 26 indicates the time where the temperature was kept at the maximum value of 920°C while the experiment was continued. The higher the response the higher is the hydrogen consumption. This means that reduction of the catalyst takes place. See more at the discussion 4.6.1.



Figure 26: TPR of the catalysts Type A and Type B



Figure 27: TPR of the catalysts Co/Si, Co/Si\_calzined, Co/Ru/Si and Co/Ru/Si\_calziened

#### 4.5.2 Results for the carbon monoxide-disproportionation experiments

The catalysts Type A and Type B are reduced at different temperatures (500-750°C). The disproportionation is performed at 280°C.

Disproportionation tests with the catalysts Co/Si and Co/Ru/Si are carried out in the calzined and crude form after the preparation of the catalysts. The temperature of reduction is 400°C. Only the catalyst "Co/Ru/Si\_calzined" is reduced at 260 °C. The disproportionation tests took place at 240°C.

#### Results for the catalysts of the type Type A and Type B (iron oxide)

Figure 28 shows the carbon dioxide formation at different temperatures of reduction of the catalyst Type A. In Figure 29 we see the carbon-balance of the CO-disproportion test for the catalyst Type A. The same is shown for catalyst TypeB in Figure 30 and Figure 31.



Figure 28: Catalyst Type A; carbon dioxide formation at different temperatures of reduction [µmol/mg]



Figure 29: Catalyst Type A; carbon-balance [%] (charged carbon (100%) - measured carbon)



Figure 30: Catalyst Type B; carbon dioxide formation at different temperatures of reduction [µmol/mg]



Figure 31: Catalyst Type B; Carbon-balance [%] (charged carbon (100%) - measured carbon)

# Results for the catalystof the type Co/Si, Co/Ru/Si, Co/Si\_calzined and Co/Ru/Si\_calzined

The reduction temperature of the different catalysts is 400 °C. Only the catalyst "Co/Ru/Si\_calcined" is reduced at a temperature of 260°C.

As the catalyst contains a high amount of carbon the catalyst loses weight during reduction. The loss of weight could not be quantified within the run of one experiment. The reason is that the reactor cannot be weighed between the reduction and the disproportionation part of the experiment. Therefore the loss of weight is quantified by additional reduction runs and a factor (0,5 for the crude catalyst and 0,8 for the calcined catalyst) has been determined. Figure 32 - Figure 36 show the performance of the catalysts Co/Si, Co/Ru/Si, Co/Si\_calzined and Co/Ru/Si\_calzined.



Figure 32: Carbon monoxide consumption of the catalysts Co/Si, Co/Ru/Si, Co/Si\_calzined and Co/Ru/Si\_calcined (CO/catalyst [µmol/mg])



Figure 33: Carbon dioxide formation of the catalysts Co/Si, Co/Ru/Si, Co/Si\_calzined and Co/Ru/Si\_calzined (CO2/catalyst [µmol/mg])



Figure 34: Carbon consumption with the catalysts Co/Si, Co/Ru/Si, Co/Si\_calzined and Co/Ru/Si\_calzined [%]



Figure 35: Carbon dioxide formed with the catalysts Co/Si, Co/Ru/Si, Co/Si\_calzined and Co/Ru/Si\_calzined [%]



Figure 36: Carbon-balance of Co/Si, Co/Ru/Si, Co/Si\_calzined and Co/Ru/Si\_calzined [%] (Charged carbon (100%) - measured carbon)

# 4.6 Discussion of the results of the catalyst characterisation experiments

#### 4.6.1 Discussion of the TPR-results

The TPR of the catalysts of the type Type A and Type B show that the reduction starts at 500 to 600 °C and has its maximum hydrogen consumption at 800 °C.

For using those catalysts in Fischer-Tropsch slurry reactors the catalyst has to be reduced in an external reactor, because the slurry phase cannot be exposed to such high temperatures without undergoing decomposition.

For the cobalt catalysts the results from the TPR show that the temperature of reduction for the calzined catalysts starts at about 200°C. Both catalysts show a graph with two maxima. One maximum is at about  $250^{\circ}$ C /  $275^{\circ}$ C and the second is at about  $290^{\circ}$ C /  $325^{\circ}$ C. The reason therefore might be two different reducing steps. For the catalysts Co/Si and Co/Ru/Si only one maximum can be observed in Figure 27. Therefore the reducing temperature is at about  $350^{\circ}$ C for Co/Ru/Si-catalyst and  $400^{\circ}$ C for the catalyst without ruthenium.

#### 4.6.2 Discussion of the results of the CO disproportionation tests

#### Discussion of the results of the catalysts from the Type A and Type B

In Figure 28 and Figure 30 it can be seen that the conversion to carbon dioxide is decreasing with the increasing temperature of reduction. In the carbon balance (Figure 29 and Figure 31) it can be observed that at low reduction temperatures a negative balance is calculated. It can be explained that at a low reduction temperature the catalyst is not reduced completely and that carbon monoxide is reducing the catalyst and additional carbon dioxide is formed by the reducing reaction.

At high reduction temperatures the conversion of carbon monoxide is decreasing. It is assumed that melting processes on the surface of the catalyst are reducing the active surface. As a result the conversion of carbon monoxide is decreasing.

There is hardly any difference in the disproportionation behaviour between the catalyst "Type B" and "Type A". It seems that the pure iron catalyst "Type A" is showing a slightly higher disproportionation ability than the Type B catalyst.

#### Discussion of the results of the CO-disproportionation tests for the cobalt catalysts

At the carbon balance (Figure 36) it can be seen that the catalyst Co/Ru/Si\_calzined is showing a negative carbon balance. The reason might be the low reduction temperature, because the catalyst is not reduced completely. Reduction of the catalyst with carbon monoxide might influence the measurements. It can be seen that after each injection of carbon monoxide the disproportionation ability is decreasing constantly. This might be a result of carbon deposition on the surface of the catalyst. In this case each catalyst is behaving similarly. The ability of carbon monoxide consumption of the different catalysts stays in a range from 15 up to 30 %. The catalysts Co/Ru/Si, Co/Si\_calzined have similar values, as well as Co/Si and Co/Ru/Si\_calzined. The conclusion of this measurement is that there is not a direct relationship between the disproportionation ability of the catalyst in the calzined or non calzined form.

# 4.7 Results of the experiments of activity tests in the laboratory slurry reactor

The testing results for the catalyst Co/Si and Type B are summarized in Table 5. Figure 37 shows the CO consumption of both catalysts as a function of time and Figure 38 and Figure 39 show the respective product distribution.

Tuble of Summary of the test with the cuturyst constant Type D							
Catalyst(reduced):	Co/Si	Type B					
Catalyst reduction temp.:	400	550	[°C]				
Particle size:	below 100	80-100	[µm]				
Temperature of reaction:	240	280	[°C]				
Slurry weighed portion:	24,1593	24,71	[g]				
Catalyst weighed portion:	1,12	2,45	[g]				
N2	5,4	5,5	[ml/min]				
H2	11,3	11,3	[ml/min]				
СО	6,3	6,3	[ml/min]				
Reaction time:	65	72	[h]				
Squalene (internal standard):	0,2481	0,2426	[g]				
Sum of masses (before test):	25,7	27,4	[g]				
Sum of masses (after test):	28,7686	30,264	[g]				
Produced mass:	3,0686	2,864	[g]				
Aqueous phase:	2,4	2,3	[g]				
Organic phase	0,6686	0,564	[a]				

Table 5: Summary of the test with the catalyst Co/Si and Type B



Figure 37: Conversion (consumption of CO) over the time of the experiment of the catalyst Type B (30bar/280°C and Co/Si 30bar/240 °C)



Figure 38: Conversion of CO to the different gaseous product over the whole experiment time with two different catalysts (Type B (30bar/280°C) and CO/Si (30bar/240 °C))



Figure 39: Analysis of the liquid phase after the test run. CO-conversion to the different hydrocarbons over the whole time of the experiment

# 4.8 Discussion of the Results

# 4.8.1 Catalyst Co/Si

The experiment takes place at 30 bar and a temperature of  $240^{\circ}$ C. It can be seen in Figure 37 that in the first phase of the experiment the catalyst becomes more and more active. After the conversion reaches a maximum of about 60%, it decreases to a level of about 20 % where the conversion stays nearly constant at this level. This behaviour can be explained because in the beginning the catalyst becomes more active, since H<sub>2</sub> and CO are reducing the catalyst. Inactivation can be a reason for the forming of carbon compounds on the surface of the catalyst.

Figure 38 shows the amount of gaseous products over the whole experiment time. It can be seen that CO is converted to  $C_1$  and  $C_2$  ( $C_2H_4$  and  $C_2H_2$ ) compounds in the same amount. A higher conversion of CO is observed for hydrocarbons with a carbon number more than two. The less volatile the hydrocarbons are getting (increasing carbon number), the lower the concentrations are in the gaseous phase.

The analyses of the liquid phase (Figure 37) show that CO is transformed primarily to hydrocarbons with a carbon number between 14 and 30. The production of hydrocarbons with higher carbon numbers is decreasing continuously. The highest carbon numbers which are measured is around 60.

# 4.8.2 Catalyst Type B

The reaction conditions with the iron catalyst were 30 bar and 280 °C.

The iron catalyst is behaving different to the cobalt catalyst.

In Figure 37 it can be seen that the starting activity of the iron catalyst is very low and the activity is increasing continuously to the end of the experiment. At the end of the testing time

of approximately 72 hours, which was selected based on the typical behaviour of the Co/Si catalysts, the CO consumption activity had not yet reached a steady state.

To compare the two different catalysts in their activity towards the different products is difficult because the catalysts are showing a different behaviour in their development of their activity.

The iron catalyst shows a similar gaseous product distribution like the cobalt catalyst. The main liquid hydrocarbons have a carbon number between 12 and 20. The production of higher hydrocarbons is low and decreases more rapidly than with the cobalt catalyst.

There was only a short time for testing, so not every available type of catalyst could be tested. It was not possible to vary the parameters in order to optimize the processing parameters. Nevertheless we can assume that both types of catalysts are suitable for Fischer-Tropsch synthesis.

# 5 Cold model of the FT-reactor

# 5.1 Introduction

In this part of the work, an assessment of the dispersion of the solids in the slurry for different flow regimes is presented. The main aim is that the FT-catalyst should be suspended homogenously in the whole liquid. Previous works show the connection of the gas hold up in the slurry, solid concentration and reactor diameter of a FT-slurry reactor [98].

Here solutions have been found to build up a simple and narrow cold model close to defined physical parameters similar to the parameters in the hot reactor. For the cold model FT-reactor and for the FT-pilot plant in Güssing a slurry reactor of simple construction has been chosen. The liquid in the FT-reactor should be the produced product. For the start up commercial waxes have been used.

The gaseous phase is the producer gas of the gasifier in Güssing.

Reaction conditions in the FT-reactor are from 20-30 bar and a temperature of 200-280°C.

The cold model plant has been built up chronologically parallel to the FT-pilot plant. The cold model tests should give information about the distribution of the solid catalyst particles in the liquid phase.

The main parameters of interest which should be kept constant in comparison to the FT-plant are the viscosity and surface tension of the liquid. Other parameters are the properties of the solid particles namely the catalyst. For the reactor design of the cold model the same diameter of the hot reactor has been chosen.

To determine the relative solid concentration in the liquid a LCR-meter (inductance capacitance resistance-meter) has been brought into action.

In the project two different types of FT-catalysts were tested. One of them is an iron catalyst, which consists mainly of iron oxide in an unreduced state. The other catalyst is a cobalt catalyst supported on silica. One of the main physical differences between the two catalysts is the density. In the cold model the different behaviour should be analyzed in a spouted bed. It is assumed that a homogeneous distribution of the catalyst in the liquid phase enables a high efficiency of the reactor volume. If there are zones of a high catalyst concentration in a Fischer Tropsch reactor, the possibilities of hot spots in the reactor is definitely higher compared to a regular distribution of the catalyst in the reactor. Therefore a method has been developed to determine the relative concentration of a catalyst at different heights of the reactor column. A more detailed description on the measurement methods and about the cold model is given in the Diploma Thesis of Niall O Brien [99].

For the experiments on the cold model the following parameters have been taken into consideration:

- Viscosity of the liquid
- Density of the liquid
- Surface tension of the liquid?
- Density of the solid
- Diameter of the solid
- Linear gas velocity of the gas

# 5.2 Viscosity of the liquid

The viscosity of the liquid in Fischer Tropsch slurry reactors depends on two main factors: These are the temperature at which the Fischer Tropsch process is operating, and the product of the Fischer Tropsch reaction. The residual liquid in the Fischer Tropsch reactor depends on the vapour pressure of the produced liquids, the formation rate and the gas flow. For the design of the slurry reactor the physical properties of eicosane ( $C_{20}$ ) have been taken as a reference.



Figure 40: Vapour pressure v carbon number of n-Alkanes [100]

In Figure 40 the vapour pressure of n-alkane is displayed against the carbon number at 500°K (227°C) which is a typical temperature for "Low Temperature Fischer Tropsch" reaction conditions. It can be seen that the vapour pressure decreases rapidly to a carbon number of eighteen. For carbon numbers above 18 the vapour pressure decreases down to zero. This means that products in Fischer Tropsch with high carbon numbers mainly remain in the slurry phase, whereas the shorter n-alkanes tend toward leaving the Fischer Tropsch reactor in a gaseous state. Figure 41 illustrates the influence of the temperature on the viscosity of the slurry. Viscosity data on n-alkanes mixtures are rare. The properties of eicosane have been chosen for the reference properties in the cold model. Data above 300°C is not relevant because thermal decomposition of the organic compounds becomes more and more dominant. The impact of pressure on the viscosity of the liquid phase has been neglected.



Figure 41: Viscosity v temperature of eicosane; [101]

# 5.3 Density of the liquid

The density of the liquid hydrocarbons in Fischer Tropsch is within a range of 0,77-0,81 kg/l. N-alkanes with a higher number of carbon atoms have a higher density. Tetracosan (C<sub>24</sub>H<sub>50</sub>) has a density of 0,799 kg/l and decane (C<sub>10</sub>) 0,73 kg/l. To predict the composition of the liquid phase in a Fischer Tropsch reactor depends on various parameters like temperature, pressure, catalyst, syngas composition, etc. The dependence of the density of alkane is described in literature [102], but an exact calculation of the density of a multi component mixture at a certain temperature and pressure is complex and rather inaccurate. It has been assumed that the density of the liquid in the Fischer-Tropsch reactor in operation ranges between 0,75 and 0,80 kg/l.

# 5.4 Density and diameter of the solid particles

The density of the two different types of solid particles which have been used is very different. The basic material of the iron catalyst is iron oxide in an unreduced form. During reduction the properties of the particle density will change slightly. The pore volume of the catalyst has not been analysed. Data from literature has been used for the further calculations. The cobalt catalyst is supported on silica and has been developed at the "University of Strasbourg". The pore volume of the catalyst ranges between 0,4 and 0,6 cm<sup>3</sup>/g. It has been assumed that the pores of the particles are filled up with slurry. Further it is assumed that the particle density is a product of slurry filled pores and equals the true density of the catalyst. Hence the density of the catalyst is 2,6 g/ml.

The influence of the particle diameter of the settling velocity is described by Stokes' law:

$$\vec{F}_S = -6\pi\eta\vec{v}r$$
 (1) Stokes' frictional force  
 $F_G - F_A - F_S = 0$  (2) Equilibrium of forces

$$v_{St} = d^2 \rho g \frac{1 - \frac{\rho_f}{\rho}}{18\eta}$$
(3) Stokes' velocity

Fs	Stokes' frictional force [N]	n <sub>St</sub>	constant settling velocity [m/s]
F <sub>G</sub>	gravity [N]	ρ	density of the particle [kg/m <sup>3</sup> ]
FA	buoyant force [N]	$ ho_{ m f}$	density of the fluid [kg/m <sup>3</sup> ]
h	dynamic fluid viscosity [Pa s]	g	acceleration due to gravity [m/s <sup>2</sup> ]
n	velocity of the particle [m/s]	d	diameter of the particle [m]
r	radius of the particle [m]		

When the equilibrium of forces is reached the velocity does not increase anymore but becomes constant. From now on the particles have a constant velocity. The equilibrium or setting velocity  $v_s$  can be calculated from equation (3). Apart from that it can be seen in equation (3) that nst is proportional with d<sup>2</sup>. Equation (3) is valid under ideal conditions, such as a lot of fluid medium, a very smooth surface of the sphere and a small radius.

Usually particle concentrations of about 30 % (of mass) are used in slurry reactors for Fischer Tropsch. At such high concentrations of solid particles there are no ideal conditions. A swarm of particles like that, affects the settling behaviour of the particles. Different models with the use of empirical data are described in literature. A prediction for the influence of particles swarm for the settling behaviour could not be done without the studies on a model. A correction factor obtained by empirical experiments is created to make a correlation to ideal behaviour.

Two different types of particles have been used in the cold model experiment: (As mentioned before an iron catalyst and a supported cobalt catalyst came into action.) The crucial difference between the two catalysts for fluid dynamic properties lies in the density. As a consequence the particle diameter has to be adjusted accordingly.

# 5.5 Linear gas velocity

In a three phase slurry reactor the gas phase is responsible for keeping the solid particles in a suspension like a stirrer in an agitated tank. So on the one hand the gas phase is the reactant for the Fischer Tropsch reaction and on the other hand it has the function of mixing the liquid and the solid phase. As mentioned in the chapter 2.10.7 there are two different regimes of running a bubble column. They are divided into a homogeneous and into a heterogeneous regime: You can describe a homogeneous regime by the uniform bubble size. Usually the bubbles are of a small diameter (some mm) and all bubbles have more or less the same rising velocity. In a heterogeneous regime besides the small bubbles are also bigger bubbles with a completely different rising velocity. Big bubbles (diameter of some cm) are a lot faster in comparison to the small bubbles. The shape of the big bubbles are more elliptical, flat and very different from a spherical form. In the slipstream of these big bubbles solid particles are easily transported from way down to the top of a reactor column. The impact on mixing through big bubbles is large, but the mass transfer area is relatively small. For small bubbles the situation is vice versa.

During the experiments the focus has been on the dispersion of the catalyst in the reactor at different states.

# 5.6 Overview of solids concentration measurement

The literature shows that the standard method of solids concentration measurement in cold models is to take samples using a syringe from manometric taps located along the length of the column, and examine these samples to determine the local solids concentration. While it would be possible to introduce manometric taps into the cold model, this is not a viable option for the reactor, and also lacks an on-line aspect, as the samples need to be treated and examined in a laboratory.

#### 5.6.1 Commercial solids concentration measurement

There is very little information on solids concentration measurement in three-phase bubble columns available in literature. However there are measurement systems described for other two and three-phase systems.

#### 5.6.2 Optical measurement

This measurement technique uses laser diodes and photo diodes to measure the concentration of solids in a horizontal path [49]. However, these systems are generally non-intrusive to the system and so are usually used in conjunction with a glass or perspex column or transparent viewing window. The solids' concentrations that these systems usually work at are less than 5 %. The concentrations employed in Fischer-Tropsch reactors are about 30 - 35 %. So an optical system cannot possibly be expected to work accurately.

# 5.6.3 Computed tomography

This method is used for the measurement of the cross-sectional multiphase hold up; solid, liquid, gas. It consists of an array of detectors with an opposing  $\gamma$ -ray source, which rotates around the column to be scanned. The absorbance of an empty column, of a column with solids and gas, and of a column with a gas-liquid-solid slurry is measured. For each of these systems the intensity of absorbed radiation is different. Through the use of various algorithms the fractions of each phase in defined cells of the column can be calculated [43]. This method of solids concentration measurement requires a lot of analytical equipment and expertise in data analysis, not to mention the acquisition of a radioactive source, to be of use for the particular application in question.

# 5.6.4 Conductivity measurement

One method used in the industry to determine the solids concentration of a slurry is to measure its conductivity. Conductivity is a measurement of how well a material carries a current. The equipment used can operate on-line, may be non-intrusive, and can provide real time output of measurements. One such instrument measures local solids concentration around the pipe or column periphery and integrates these local values to obtain an area-average concentration [50]. Conductivity measurement may also be carried out using electrodes inserted into the slurry and measuring the local concentration of ions. Using a conductivity meter, different samples of gasoline with varying solids' concentrations were tested, but no readings were obtained for any of the samples. This indicated that conductivity measurement is not possible given the nature of the liquid. Highly sensitive measuring equipment will be required, which is not viable in this project.

# 5.7 Capacitance measurement development

Capacitance is a measurement of a materials capacitance to store electrical charge. This method has been used to determine solids concentration in gas-solid flows [51]. In this study, the capacitance measurement system consisted of a needle capacitance probe and a capacitance amplifier. The capacitance at the tip of the probe was directly linked to the solids concentration of the gas-solids flow. The amplifier converted the capacitance into a voltage, and the magnitude of the voltage was a measure of the solids concentration. In this case, the capacitance probe was purposely built to very high specifications so as to provide the highest possible sensitivity. To avoid lengthy and expensive research into designing a capacitance probe to fit our criteria, alternatively, ready made capacitance options were investigated. Capacitance probes are widely used in process operations to measure the level of liquids or solids in tanks, and are often used with hydrocarbon liquids, such as gasoline, with low dielectric constants. In this system the metal rod of the electrode acts as one plate of a capacitor and the tank wall acts as the other plate. As the level rises, the air or gas normally surrounding the electrode is displaced by material having a different dielectric constant. A change in the value of the capacitor takes place because the dielectric between the plates has changed. Capacitance instruments detect this change and convert it into a proportional voltage output signal.

#### 5.7.1 Capacitance theory

The basis in using this principle to measure solids' concentrations was that instead of the capacitance of the system around the probe changing due to a rise in liquid level, it would change due to an increase or decrease of the dielectric constant of the suspension surrounding it, as the solid particles have a substantially higher dielectric constant compared to gasoline. Even though this capacitance method had only been used previously in two phase flows this study investigated if it could be applied to three phase flows. In the cold model the air and gasoline phases had substantially lower dielectric constant of hydrocarbon fuels at reaction temperatures of around 230 °C is between 1.2 and 1.6 and the dielectric constant of the syngas is between 1 and 1.6. The measured difference of capacitance would, largely, only be due to the solids concentration differences. Using the Böttcher equation and the dielectric constants for iron, 14.2, and gasoline, 2.0, the theoretical dielectric constants of suspensions for a range of solids' concentrations were determined.

Böttcher Equation:

$$\frac{K_{\text{eff}} - K_h}{3K_{\text{eff}}} = \frac{(1 - \Phi)(K_p - K_h)}{K_p + 2K_{\text{eff}}}$$
(15)

Where;

K<sub>h</sub> Dielectric constant of fluid

- K<sub>p</sub> Dielectric constant of particles
- K<sub>eff</sub> Dielectric constant of suspension

 $\Phi$  Voidage of suspension (i.e. 5 % solids = 0.95 Voidage)



Figure 42: Dielectric constant v solids' concentration of ASC 100.29 iron powder in gasoline

#### 5.7.2 Probe selection

The area available in the column without significantly disturbing the hydrodynamics was very small, and so a probe of 50 mm length and 20 mm diameter and 10 mm guarding between the probe and tank wall was assumed in the calculations to determine the theoretical capacitance of the suspensions.

(4)

$$C = \frac{k.A.\varepsilon_0}{d}$$

Where;

- C Capacitance, [F]
- A Area of probe,  $[m^2]$
- d Distance between electrodes (guard distance), [m]
- k Dielectric constant
- εο Permitivity of a vacuum, [F/m]

This gives a capacitance of 6.15 pF for pure gasoline, 6.82 pF for 5 % solids and 28.12 pF for 70 % solids. This is a 0.67 pF difference between 0 % and 5 % solids. Therefore, to operate at the desired level required a probe of 0.1 - 0.2 pF sensitivity.

The probes available either had the desired sensitivity but not the required range, the required range but not the required sensitivity, or did not operate at reactor conditions of approximately 240 °C and 30 bar pressure.
## 5.7.3 Circuit construction

It was then decided to attempt to design and construct a simple circuit to measure the capacitance of the suspensions. The equations and values used for the selection of a probe were applied along with an equation for capacitive resistance to determine the resistance of a suspension to the flow of an AC (Alternating current) signal.

$$X_c = \frac{1}{2.\pi.f.C} \tag{17}$$

Where;

 $X_c$  Capacitive resistance,  $\Omega$ 

f Frequency of AC signal, Hz

C Capacitance, F

Taking the frequency of the AC signal to be 1 MHz, this gave a theoretical capacitive resistance of 25683  $\Omega$  for pure gasoline, 23417  $\Omega$  for 5 % solids and 5667  $\Omega$  for 70 % solids. If a voltage of 10 V is assumed for the circuit, this gives a current of 0.39 mA for pure gasoline, 0.43 mA for 5 % solids and 1.76 mA for 70 % solids.

As these are very small currents, with relatively little difference between that of pure gasoline and 5 % solids, an operational amplifier (op-amp) was employed to turn the small current into a readable voltage. An op-amp with a gain of 10 gives a voltage output of 3.9 V for pure gasoline, 4.3 V for 5 % solids and 17.6 V for 70 % solids.

While the theory of this method of capacitance measurement seemed sound, the practical implementation of the circuit did not prove to give adequate results. Noise in the signals, and the high tolerances of the components used meant that the small currents were not readable and were certainly not useable for the application that was required.

This circuit construction also left out an important measurement associated with the capacitance determination, the phase angle. The phase angle of a perfect capacitor is  $-90^{\circ}$ , and capacitance readings with a phase angle deviating significantly from this ideal have additional factors contributing to the signal and therefore cannot be used as a pure reading from which to determine capacitance.

# 5.8 Investigative impedance experiments

Collaboration with the Department for Chemical Technology and Analytics allowed access to an impedance meter. The absolute impedance of a substance can be related to the capacitance by the probe geometry and the following equation:

$$C = \frac{-j}{2\pi f Z} \tag{18}$$

Where;

- C Capacitance, F
- j Imaginary number
- f Frequency, Hz
- Z Impedance,  $\Omega$

Testing of pure gasoline showed that it has absolute impedance: its value is low but consistently above that of air and therefore a suitable liquid with which to measure capacitance. Further testing with various volume fractions of iron powder in gasoline at various frequencies followed. Those results are shown in the following graph, in which all results were observed to have a phase angle of between  $-89^{\circ}$  and  $-91^{\circ}$ .



Figure 43: Frequency v Impedance of different iron powder concentrations in gasoline

It can be seen that small differences in impedance are evident between the various solid volume fractions and that these differences are consistent over the various frequencies. This indicates that the differences are systematic and not statistical. This is a viable measurement method, once the required measurement sensitivity is achieved.

# 5.9 Description of the cold model

## 5.9.1 Methods and materials used in the cold model

#### Impedance meters

Hewlett Packard 4274A impedance meter operated at a frequency of 100 kHz and a voltage of 0.7 V.

## **Test Fixtures and Probes**

Several different designs of probe were used over the course of the experimentation. All these probes consisted of two lengths of coaxial cable, 2.5 m length, attached to two electrodes. These cables were attached to the HP 4274A and a self made test fixture with the following specifications.



Figure 44: Schematic of three-terminal configuration fixture [52]

Measurement range:  $100 \Omega$  to greater than  $10 M\Omega$ .

#### Probe

Two parallel pieces of tinplate, 20 mm square, approximately 0.5 mm thickness, 10 mm spacing.

These probes were attached to a plastic sleeve which were able to slide on a plastic bar, 6 mm in diameter, which was attached to the spouted bed sections, to allow ease of probe placement during experimentation.

## Liquid phase:

mix of aliphatics (viscosity 0,5 – 0,65 mPas at 20 °C)

#### Solid particles:

- iron powder  $1 10 \ \mu m$
- Unreduced cobalt catalyst supported on silica (< 100 μm)

#### Reactor (glas tube):

Material:glassHeight:1,5 mInner diameter:100mm

#### Gas phase:

Nitrogen at ambient pressure and temperature



Figure 45: Cold model

The test runs have been carried out with a circulating gas flow so that compounds with a high vapour pressure do not disappear in the liquid phase. This should avoid changing physical parameters like the viscosity of the liquid phase.

At all test runs the impedance has been measured at different probe positions of the column height.

# 5.10 Results from the cold flow model with the cobalt catalyst

The unreduced cobalt catalyst from the "Universite of Strasbourg" has been used for the measurements. Three kilograms of the catalyst were available for the test runs. The particle size was below 100 $\mu$ m. This was guaranteed by sieving the catalyst. The experiments demonstrate that the catalyst can be suspended homogenously in the slurry.

The output signal of the LCR-bridge reflects the relative concentration of the catalyst at different stages in the column.



Figure 46: 1/impedance v column height at a constant gas flow with different solids' concentrations of cobalt catalyst in fuel

In Figure 46 the different graphs for different catalyst concentrations in fuel can be seen. The concentration varies from 0 to 34 % (m/m). As described before, the solids' concentration is proportional to a function of 1/impedance. In all of the graphs it can be seen that the concentration of catalyst decreases slightly the higher the probe is placed in the column. A significant deviation of the particle loading over the column was not observed. The gas velocity for that experiment was 5 cm/s. A heterogeneous flow regime (small and big gas bubbles) is also observed.

These measurements have been carried out with different gas velocities (2-10 cm/s). The graphs for these experiments are very similar to Figure 46.

The experiments with the cobalt catalyst show that a supported catalyst with a diameter smaller than 100µm is nearly homogeneously spread over a bubble column.

# 5.11 Results with iron catalyst powder

For the tests on the cold model the iron catalyst of type B has been used. Therefore the catalyst was ground and classified. For the tests the catalyst was used in the unreduced state.

Iron catalyst particles fractions: $1 - 10 \mu m$ ,Gas velocity :6 cm/s



Figure 47: 1/impetance v column height at constant gas flow with different solid concentrations of iron catalyst Type B in fuel; gas inlet velocity: 6cm/s

Figure 47 shows that particle loadings less than 20% in the bubble column nearly have a homogeneous distribution of the particles over the column height. At higher particle loadings (more than 20%) a significant deviation from a homogeneous particle distribution in the column is observed. The higher the particle loading in the slurry the steeper is the negative gradient of the graph. This means that the concentration of particles in the lower part of the column is higher than in the upper part. Such an uneven distribution might cause hot-spots in running a slurry bubble Fischer Tropsch reactor.

# 5.12 Conclusion of the cold model experiments

A limit of the particle loading in a slurry bubble reactor for iron particles of  $1-10\mu m$  is found. Over the limit of 20 % the particles cannot be distributed homogenous in the liquid. Catalysts supported on silica are distributed homogeneous in the slurry bubble column. A limit is not detected in the range of a particle loading up to 34%. Based on these findings, the geometry of the FT pilot plant was chosen with the same diameter as the cold flow model but with an increased height. A reactor with an inner diameter of 0,1m and a height of 2,5m was installed.

# 6 Experimental set up of the Fischer Tropsch pilot plant operated with the producer gas of the Güssing biomass gasifier

# 6.1 Overall description of the biomass CHP Güssing

In Güssing/Austria an 8 MW (fuel power) demonstration plant shows the feasibility of the dual fluidized bed gasification process. The idea of this concept consists of two divided reaction zones: a gasification zone fluidized with steam and a combustion zone fluidized with air, which provides the energy for the gasification zone. There is a circulation loop of bed material between the two zones. Heat from the combustion zone is transferred with the bed material into the gasification zone. Product gas is kept separately from flue gas. The resulting product gas is nearly nitrogen-free and rich in hydrogen.

The product gas treatment at the biomass CHP consists of a heat exchanger, where the gas is cooled down to about 150°C, a bag filter, where particles are removed and a biodiesel scrubber, where the gas is cooled to about 40°C and the tars are removed.

The product gas for the FT-synthesis is taken from the gasification plant after the blower (see Figure 48).



Figure 48: Flow chart of CHP Güssing

The biomass CHP is in commercial operation and reaches about 7000 hours of operation per year at the moment.

The gas composition at the entrance to the gas engine is given in the following table. This gas is used for the experiments with the FT synthesis.

v. zas composition of the Chi C	Juessing	
Water content	V-%	~10
CH4	v-% (dry)	910
C <sub>2</sub> H <sub>4</sub>	v-% (dry)	23
C <sub>3</sub> -Fract.	v-% (dry)	0.51
СО	v-% (dry)	2226
CO <sub>2</sub>	v-% (dry)	2022
H <sub>2</sub>	v-% (dry)	3840
N2	v-% (dry)	1.22.0
H <sub>2</sub> S	v-ppm (dry)	~150
Organic S	v-ppm (dry)	~30
HCl	v-ppm (dry)	~5
NH <sub>3</sub>	v-ppm (dry)	10002000
Benzene	g/m <sup>3</sup> N (dry)	58
Napthalene	g/m <sup>3</sup> N (dry)	12
Tar (PAH larger than	g/m <sup>3</sup> N (dry)	0.020.05
Napthalene)		
Particulates (clean gas)	g/m <sup>3</sup> N (dry)	< 0.02
LHV	$MJ/m^{3}N$ (dry)	12.913.6

Table 6: gas composition of the CHP Guessing

# 6.2 Description of the FT test plant in Güssing

An overall description of the investigation FT-plant can be seen in Figure 49. The pilot plant is next to the biomass gasification plant in Güssing (Austria) in a 40 square meter sized building. The gas from the plant is taken after the RME-scrubber of the CHP-plant. The tube is heated up to 70°C so no condensation takes place in the 1 inch tube until the gas is entering the FT-container. The Fischer Tropsch plant can be divided into five parts:

- PG-cooling and pre-cleaning of the gas
- Compression of the product gas
- Gas cleaning unit
- The FT-reactor
- Off gas expansion, cooling and condensation

## 6.2.1 Product gas cooling and water separation

The first component of the FT pilot plant is a scrubber with a structured packing. The gas enters at the bottom, flows through the packing and leaves at the top of the scrubber. After the scrubber the gas is routed through a gas meter. In counter current the solvent circulates by the solvent pump. The scrubber consists of three parts, which are the receptacle, the column with the packing for the absorption and the droplet separator. All three are made out of glass by the company Schott Duran. At the bottom of the receptacle the solvent is drawn off by the solvent pump and flows through a plate heat exchanger, where it is cooled down. It then flows through a valve, where the flow rate of the solvent can be adjusted, followed by a rotameter, and finally passes via the solvent distributor into the scrubber. In the scrubber a liquid film builds up on the packing, on which surface the contact between the solvent and the gas rising from the receptacle takes place.



Figure 49: Overall description of the FT-plant in Güssing

The second circulation of the plate heat exchanger goes through an electrical cooling system in which a water-glycol mixture is pumped around. In Figure 50 the experimental set up of the scrubber tests is shown. The column with the packing for the absorption and the droplet separator both have a diameter of 100 mm. The length of the absorption stage is 1760 mm. The droplet separator is 460 mm long. The packing is a product of the company Sulzer Chemtech with the name Mellapak 250 X for the absorption stage and Mellapak 250 Y for the droplet separator. The type Mellapak shows a characteristic surface, which produces good separation results for low as well as for high liquid loads. The alternating placement of the individual diagonally toothed lamellae builds open crossing channels causing an optimal thorough mixture between the gas and the liquid. In Table 7 special parameters of the Mellapak packing are shown.



Figure 50: Flow chart of the scrubber for cooling the PG-gas

ble 7: Parameters of the Sulzer Chemtech Mella	pak packing	
Pressure difference per packing unit	0.3 - 1.0	mbar
(at $70 - 80$ % of the flood point about	2	mbar/m)
Lowest liquid load	0.2	m³/m²h
Highest liquid load	200	m³/m²h
Specific surface	250	$m^2/m^3$
Angle of the channels:		
X-Type	30	0
Y-Type	45	0
Free space	0.988	$m^3/m^3$
Material	stainless steel	

|--|

The plate heat exchanger is a product of the company GEA Ecoflex. Its system is called VARITHERM. The heat exchanger consists of a defined number of individual, profiled plates, which correspond to the required thermodynamic power. At each plate seals are responsible for a reliable sealing of the gaps between two plates and therefore determine the direction of the flow. In order to achieve the right contact of the plates every second plate has to be twisted 180°. Hence a lot of contact points, which support the stability of the gap between two plates, are created. The plates are embedded in a frame, which makes the whole heat exchanger stable.

The electrical cooling system, the cryostat, is made by the company Huber (polystat cc1/UCO15-1). A cooling liquid, which is a mixture of glycol and water in the ratio of 1:2, is being used. The cooling power of the cryostat was 1kW at a temperature of 0°C.

This cooling has been substituted with a 16 kW central cooling device during the project. The solvent pump is a simple radial centrifugal pump made by WEC World Electric Company, type KG115, and is throttled by a rotary valve, which is placed after the plate heat exchanger and before the rotameter which measures the flow rate of the solvent. The volume flow of the gas is measured with a gas meter (ELSTER BK-G6). The temperatures are being measured with thermocouples (type J).

# 6.2.2 Compression of the product gas

After the RME-scrubber the dried and pre-cleaned product gas is measured by a gas meter. After the gas meter the product gas is compressed in two steps.

In the first step the product gas is compressed by three diaphragm pumps which are connected in parallel. In this step the gas is compressed up to 4-5 bar. If diaphragm pumps are used, oil free compression of the gas can be ensured. For the compression a distributing device has been constructed. 1" and 2" diameter steel pipes have been used so that each pump is supplied with the same amount of gas (see Figure 51)



PG out / to buffer vessel

Figure 51: Diaphragm compressors and distribution system

At the start up of the diaphragm pumps a magnetic valve opens a bybass for 10 seconds. The bybass is placed on the gas distribution system so that the pumps are starting without any counter pressure. A pressure reducing valve is placed on the gas distribution system to control the maximum pressure in the first compression step. When the set pressure on the reducing valve is reached the valve opens and gas flows over a bypass back to the suction sides of the diaphragm pumps. A pressure vessel with 54 litres made for 7 bar is placed between the first and the second compression steps. A flow back valve is at the entrance of the 7 bar buffer to protect the RME-scrubber.

In the second compression step the product gas can be compressed up to 30 bar. For the compression a duplex compressor from "MAXIMATOR" is used. The system works as an amplifier pump. On the side with the bigger diameter cylinder there is the lower pressure (pressured air), and on the side with the smaller diameter the higher pressure is generated (product gas).

In Figure 52 the pressured air-driven compressor for the second compression step can be seen. The compressed air is produced by a screw compressor from the company "Atlas Copco". The amplifier is controlled by a magnetic valve in order to start and stop the compressor. A pressure reducing valve controls the pressure on the pressured air side of the pump. Usually a pressure of 5 to 7 bar is used.



Figure 52: Duplex compressor (pressured air-driven) for the second compression step up to 30 bar



Figure 53: Flow chart of the compression of the product gas

Used components: Diaphragms pumps: KNF Puffer: ID = 200 mm; V = 54 litres

## 6.2.3 Gas cleaning unit

The product gas from the biomass gasification contains several catalyst poisons. The crucial components are chlorine and sulphur compounds. The cleaning of the gas is done in fixed bed reactors. Wet gas cleaning solutions under pressure have been avoided because of the high investment costs. Two vessels with electrical heating systems have been installed.

The vessels are fitted with thermocouples to record the bed temperature in them.

The connection between the different vessels is made with stainless steel tubes. The tubes are isolated and electrically heated. The vessels are run at the pressure at which the FT-reaction takes place, this means that they are downstream of the compression zone. The two gas cleaning units are shown in Figure 55.

In Figure 53 the position of the activated carbon filter in the flow chart can be seen. The filter is run at ambient temperature and at a relative pressure of about 80 mbar.

During the project different materials of the  $1^{st}$  and  $2^{nd}$  gas cleansing units have been tested. In the  $2^{nd}$  gas cleansing unit zinc oxide has been used for H<sub>2</sub>S separation. In the  $1^{st}$  gas cleansing unit bed materials consisting of HDS-catalyst (hydrodesulfurization), aluminium sodium oxide or copper oxide have been tested.

Used components as displayed in Figure 55:

 $1^{st}$  gas cleansing unit: ID = 114 mm; V = 26 l  $2^{nd}$  gas cleansing unit: ID = 219 mm; V = 51 l

# 6.3 The Fischer Tropsch reactor

The FT-reactor is a 250 centimetres long tube with an inner diameter of 10 cm and a volume of 20 litres. On each end a flange is mounted. On the bottom where the gas is entering the reactor a sieve with a diameter of 2 cm is fixed. This sieve can be easily changed.



Figure 54: Gas entering facility fixed on the bottom flange of the FT-reactor (material: alumina)

At the top of the reactor the gas passes a metal filter with a pore size of  $5\mu m$ . Over the whole height of the reactor eight thermocouples are installed. The reactor is electrically heated. Furthermore the reactor can be cooled with air by a fan.



Figure 55: Flow chart of the sections gas cleaning, FT-reactor and product condensation

## 6.3.1 Off gas cooling and condensation

The off gas of the FT-reactor contains products which have been formed in the FT-reaction and not converted syngas. The FT-product consists of hydrocarbons with a carbon number up to sixty (C<sub>60</sub>), some alcohols and water. A two step separation system has been built up. In the first step a scrubber comes into action. With the scrubber long chain hydrocarbons are separated. The temperature is kept at 80°C to avoid solid decomposition in the scrubber. The washing medium in the scrubber is water and FT-products.

In the second step a gas heat exchanger device with a condenser is installed. Two equal systems are built up and operated alternately. When solid decompositions on the cooling surfaces cause an excess in the loss of pressure over the cooling device the gas flow is switched on to the second device. The solid decompositions are removed by heating.

# 6.3.2 Automation

For the automation of the plant a system from "National Instrument" is used. The so called "FieldPoints" are used for input and output of signals. With the software "LabView" the controlling has been programmed. A network is installed. Therefore the module FP-1000 is necessary which has the function of an interface between a computer and the "FieldPoint" elements. A schematic drawing of the setup can be seen in Figure 56. Thermocouples, digital in- and outputs, analogical in- and outputs cables are connected to the "FieldPoint" elements. All valves, flow meters, thermocouples, heaters, cooling facilities and pumps are controlled by this system. The "FieldPoint" elements are mounted in a separate distributor box. All other circuit breakers and power supply units are installed in another distributor box.



Figure 56: schematic illustration of the controlling system for the FT-plant

In Table 8 the FieldPoint elements, which are used at the FT-plant, are listed. In total 13 "FieldPoint" elements have been installed.

Name	Feature	#
TC 120	8 Channel thermocouple input module	5
AI 110	8 Channel, 16 Bit analog input module	1
AI 111	16 Channel, 16 Bit analog current input module	1
DI 301	16 Channel, digital input module	1
DO 410	8 Channel, 5-30V digital input module	3
DO 401	16 Channel, 5-30V digital output module	1
AO 200	8 Channel, 20mA current loop output module	1

 Table 8: Used Field Points elements from National Instrument for automation of the plant

The visualisation of the controlling is made with "LabView" software. Figure 57 shows the controlling panel of the FT-plant.



In the diploma theses [103] of Goritschnig M. the programming of the FT-control in "LabView" is described. The plant was constructed to run automatically for long term tests.

Figure 57: Control panel of the FT-investigation rig

# 6.4 Reduction of the catalyst

The catalysts used, are reduced for the experiments because the metals iron and cobalt are only active in the reduced state. The catalysts are stored in an oxide form.

For the reduction hydrogen has been used. A heated 6 litre reactor with three thermocouples to monitor the temperature in the reactor is used. Two heating circuits, one for the reactor and other one for the gas inlet supply are installed.

The temperatures are controlled by two controllers (JUMO iTron16). Quartz wool is placed at the bottom and at the top of the reactor. The hydrogen flow is controlled by a flow meter and can be diluted with nitrogen. The nitrogen flow is also controlled by a flow meter.

The off gas of the reducing reactor is cooled in a wash bottle where the produced water is condensed.

# $MO+H_2 \rightarrow M+H_2O$

Equation 10: (M: metal; H: hydrogen; O: oxygen) general equation for reducing metal oxide with hydrogen



Figure 58: Reduction apparatus for the FT-catalysts

The desired amount of catalyst for one experiment is poured into the reactor. The temperature for the heaters is controlled with a temperature ramp (°C/h). The gas flows for nitrogen and hydrogen are controlled by two needle valves. The flows are indicated by two flow meters and the total flow is between 7 and 10 l/min. The reductions are started with a hydrogen concentration of 10 to 15 % in nitrogen. During the last third of the reduction program the concentration of hydrogen in the gas flow is raised stepwise to a concentration of 80 to 100 %. After the reduction the catalyst is cooled down to ambient temperature with nitrogen. Next the catalyst is transferred under nitrogen into the liquid start waxes. The catalyst is transferred into the FT-reactor with the start waxes.



Figure 59: Temperature variation in the reducing reactor for a cobalt catalyst

# 6.5 Analysis

Different analytical devices are installed and used at the FT-plant in Güssing. Analysis of the FT-products took place at the "Vienna University of Technology" and at the

"Instituty Technology Naphty" in Kraków, Poland.

# 6.5.1 Gas Analysis of the producer gas

## GC-FID/TCD for permanent gas components and hydrocarbons

In order to measure the concentration of gaseous hydrocarbons and the permanent gases in the syngas and off-gas several gas sample valves are installed. A GC-system with a flame ionisation and thermal conductivity detector from Perkin Elmer has been installed. For automatic sampling a multi-way valve with a 500  $\mu$ l injection loop is used.

## **Used Equipment**

- GC-FID/TCD: Clarus 500 GC (Perkin Elmer)
- Packed columns: Column 1: 6 FT Porapak Q 50/80 Mesh

Column 2: 10 FT Molecular Sieve 5A

- Column 3: 10 FT Porapak N 50/80 Mesh
- 2 multi-way valves: one 6-way and one 10-way valve (fixed in the GC-oven)

Control of the multi-way valves:



Figure 60: Control of the multi-way valves and position of the GC-columns

In order to charge a gas sample the 6-way valve switches so that the helium transports the sample amount of  $500\mu$ I on the column 1. After the gases, nitrogen, oxygen, hydrogen, carbon monoxide and methane have passed the 10-way valve to get separated by column 2 (Mole Sieve 5A), the 10-way valve switches so that the carrier from the 6-way valve takes it place by column 1 and column 3 where carbon dioxide and hydrocarbons get separated.

The carrier from the 10-way valve passes column 2.

For purging the sample loop with syngas two pumps and a gas cooling device are installed.



Pump 1	NMP 830 KNE from KNF
Pump 2	NMP 05B from KNF
Both pumps are	e diaphragm pumps.

The device for taking samples is integrated into the controlling of the GC-system. The time of purging the loop has been about 5minutes and is a part of the GC-method.

Used GC-method:

Injector:	6-way valve with 500µl injection loop; (located in the GC-oven)
Carrier 1	23 ml/min helium
Carrier 2	30 ml/min helium
Temperature	70°C hold 16 min; 4°C/min 100°C; hold 5 min; 15°C/min 180°C hold
-	54 min
Valves:	6-way valve switches at 6,1 min; 10-way valve at 8,4 min (~5min
	sampling time for purging the injection loop)
FID:	300°C
TCD:	200°C

The system is calibrated with a defined gas mixture which has a similar composition to the product gas of the gasifier.

Calibration gas (Messer) composition in volume percent [%]:

-	CH <sub>4</sub> :	9,97	-	CO:	19,94
-	C <sub>2</sub> H <sub>6</sub> :	0,5	-	CO <sub>2</sub> :	20,05
-	C <sub>2</sub> H <sub>4</sub> :	9,97	-	N2:	3,0
-	C <sub>3</sub> H <sub>8</sub> :	0,499	-	H2:	43,01

Figure 62 (FID-detector) and Figure 63 (TCD-detector) show the chromatograms from one sample of the product gas of the Güssing gasifier. Above each peak the retention time is displayed. To identify and quantify the different gas compounds a gas mixture of a defined and similar composition is used. Below each peak the compound name is displayed. The FID is very sensitive to hydrocarbons, but other compounds (e.g. CO, CO<sub>2</sub>) cannot be detected. With the TCD all gas compounds can be detected except helium and hydrogen, because helium is used as the carrier and the difference of the thermal conductivity between hydrogen and helium is low. The concentration of hydrogen is calculated as the difference to 100%. Higher hydrocarbons can be detected with the FID when a gas sample from the gas stream after the FT condensation part is charged. These compounds have been loosely classified into three groups called C4, C5 and C6.



Figure 62: Chromatogram of the product gas of the Güssing gasifier. (Detector: FID; sample: 070702\_A017); Time [min] v Signal [mV]



Figure 63: Chromatogram of the product gas of the Güssing gasifier. (Detector: TCD; sample: 070702\_B017); Time [min] v Signal [mV]

# 6.5.2 Analysis of the liquid FT-product with the Gas-Chromatograph (GC)

For the analysis of the FT-product two different GC-columns are used. With the first GC-column it is possible to analyze hydrocarbons with a chain length up to a carbon number of 40.

With the second GC-column it is possible to analyze hydrocarbons up to a carbon number of 60.

## Used equipment and methods

GC	GC-17A SHIMADZU
Injector	Manual injection (325°C)
Detector	Flame ionisation detector (FID)
	(H <sub>2</sub> 5.0 (Air Liquid) / Synthetic Air (Air Liquid)) 325 °C
GC-column 1	HP-1 (Crosslinked Methyl Silicone Gum)
	60m x 0,25mm x 0,25µm film thickness
Method for GC-	
column 1	Column flow: (H <sub>2</sub> ) 2,3 ml/min; Split: 100:1;
	30°C, 7°C/min, 325°C 15min
GC-column 2	Varian Capillary Column; CP-SimDist
	10m x 0,32mm x 0,1µm #CP7521
Method for GC-	
column 2	Column flow: (He) 1 ml/min; Split 80:1;
	30°C, 7°C/min, 365°C, 70min

Liquid samples are applied directly. Solid samples are dissolved in carbon disulphide before they are added to the GC-system.

The injection volume is  $1\mu$ l for undiluted samples and  $5\mu$ l for the diluted samples with carbon disulphide. A  $10\mu$ l syringe (HAMILTON; #1701) is used to inject the samples.

## **Evaluation of the chromatograms**

The retention times of six different n-alkanes have been determined with external standards. A slight retention time shift of peaks has been observed from one run to another run, so an internal standard is applied with the sample. Usually tetracosane  $(n-C_{24}H_{50})$  is used for solid samples and pentadecane  $(n-C_{15}H_{32})$  for liquid samples to assign the peaks with the right carbon number.

For quantification the integrated area of the peaks was used. The integration was made with the program "CASS-VP Chromatography system, Version 4.2". It is assumed that the signal of the flame ionisation detector is proportional to the mass of the analyzed compound [105]. The relative concentration of the whole sample is calculated for each hydrocarbon number.

Diagrams (e.g. Figure 65) are displayed which shows the relative molar concentration of each hydrocarbon number. These diagrams are the "Product Distribution" of the FT-product.



Figure 64: Chromatogram of a FT-sample dissolved in CS<sub>2</sub>, (FT-product in the off gas; sample number FT\_141); Signal / Time; used column: column 2



Figure 65: Diagram of the evaluation for an FT-sample (FT\_141; FT-product in the off gas); Carbon number [C<sub>n</sub>] VS Concentration [Mol%]; GC-Column 2

# 6.5.3 Fuel analysis carried out by the "INSTYTUT TECHNOLOGII NAFTY"

The "INSTYTUT TECHNOLOGII NAFTY (ITN)" in Krakow (Poland) has analysed the crude FT-products and samples from the distillation.

Within the framework of the RENEW project, ITN is supposed to make the analysis according to EN590 and the World-Wide Fuel Charter.

Properties	Unit	EN 590:2004		World Wide Fuel Charter, category 4		Method	
	C IIII	Min	max	min	max	applied	
Cetane number	-	51,0	-	55	-	EN ISO 5165	
Density at 15oC	kg/m3	820	845	820	840	EN ISO 12185	
Polycyclic aromatic hydrocarbons	%(m/m)	-	11	-	2,0	EN 12916	
Total aromatics content	%(m/m)	-	-	-	15	EN 12916	
Sulphur content	mg/kg	-	50	-	sulphur free (5)	EN ISO 20884	
Flash point	oC	>55	-	>55	-	EN 2719	
Carbon residue	%(m/m)	-	0,30	-	0,20	EN ISO 10370	
Ash content	%(m/m)	-	0,01	-	0,01	EN ISO 6245	
Water content	mg/kg	-	200	-	200	EN ISO 12937	
Total contamination	mg/kg	-	24	-	10	EN 12662	
Copper strip corrosion (3h at 50 °C)	rating	class 1		class 1		EN ISO 2160	
Oxidation stability	g/m3	-	25	-	25	EN ISO 12205	
Lubricity, corrected wear scar diameter	mm	-	460	-	400	ISO 12156	
Viscosity at 40oC	mm2/s	2,00	4,50	2,00	4,00	EN ISO 3104	
Distillation % (V/V) recovered at 250 °C, (E)250	%(V/V)	-	< 65	-	-	EN ISO	
% (V/V) recovered at 350 °C, (E350)	%(V/V)	85	-	-	-	ASTM D	
95 % (V/V) recovered at, (T95)	°C	-	360	-	340		
Oxidation stability	g/m3	-	25	-	25	EN ISO 12205	
Cold Filter Plugging Point, (CFPP)	°C	-	-20	-	-20	EN 116	

Table 9: Generally applicable requirements and test methods for diesel fuel According to EN 590 and World-Wide Fuel Charter[106]

Parameter	Unit	World W Charter,	ide Fuel category 4	Test method	
		min	max		
90 % (V/V) recovered at, T90	°C	-	320	ASTM D 86	
Final boiling point, (FBP)	oC	-	350		
Total acid number	mg KOH/g	-	0,08	ASTM D947	
Ferrous corrosion	Rating	-	Light rusting	ASTM D 665	
Foaming tendency, foam vanishing time	S		15	NF M 07-075-97	
Foaming tendency, foam volume	ml		100	NF M 07-075-97	

## Table 10: Requirements specified exclusively by World-Wide Fuel Charter[106]

 Table 11: supplementary test methods [106]

Parameter	Unit	Method
Cloud point (CP)	°C	ISO 3015
Pour Point	°C	ISO 3016
High temperature stability of distillate fuels, % reflectance	Rating	ASTM D 6468
High temperature stability of distillate fuels, colour before/after	Rating	ASTM D 1500
Calorific value	kJ/kg	ASTM D 2384
Iodine number	gI/100g	IP 84
Water extract	pН	PN-84/C-04064
N-paraffin's content total	%(m/m)	In-house ITN met. no 1.96 (GC)

# 6.6 Distillation of the FT-product

The organic product of the FT-plant in the off-gas is distilled in a batch vacuum fractionated distillation apparatus. The pressure and the distillation temperature were selected in order to obtain the diesel fraction.

## Description of the distillation apparatus



Figure 66: Vacuum distillation apparatus

A ten litre glass flask with an opening for filling the flask and a valve for emptying the vessel is used. An electric cowl heating system with an integrated controller is installed. For separation a silvered vacuum jacketed Vigreux column with a length of one meter is installed. A thermocouple was placed at the top of the Vigreux column for monitoring the head temperature. A distillation head with a jacketed coil condenser, a needle valve and a device to connect the system to a vacuum pump are used. For the distillation product collection the receiving flask is installed.

The FT-product contains water which created a few problems at the beginning of each distillation run. The water gives rise to retardation of boiling. An attempt has been made to separate as much water as possible with the help of the bottom valve at the start phase of each run. During some runs it has been necessary to interrupt the distillation to drain off the water.

# 6.6.1 Parameters for the distillation

Pressure:	100 mbar (absolute), -900mbar (gauge)
<u>Fractions:</u> Gasoline: Diesel:	ambient temperature – 110°C 110°C – 213°C

The above parameters are selected in order to avoid too high temperatures at the bottom of the column. The obtained fractions are collected and sent for different analyses.

# 6.6.2 Experimental procedure

The catalysts are reduced with hydrogen before each experiment. After the reduction the catalysts are transferred under nitrogen into the start waxes. In the start up the FT-reactor is heated to 100-150°C. The temperature in the FT-reactor is raised with a ramp (°C/min) up to the desired temperature of the reaction.

Every experiment was interrupted several times. Reasons for this were an interruption in the syngas supply, leaking or other errors of any device of the FT-plant. During one break it was possible to purge the plant or parts of the plant with nitrogen or hydrogen. After an interruption of the syngas supply line the control automatically re-started the FT-rig.

Two different start waxes are used. The start waxes are analysed by a GC\_FID system. The results can be seen in chapter "Results of the start wax analyses with the GC-FID". In the experiments Nr. 1 to Nr. 7 the start wax\_01 and in the experiments Nr.8 to Nr.13 the start wax\_02 is used. The change of the wax was necessary because the wax\_01 is transported out of the reactor when the production of long chain hydrocarbons has been low. This causes a depletion of the slurry in the FT-reactor. With the start wax\_02 this phenomenon is not observed.

# 6.7 Overview and results of the Fischer Tropsch pilot plant experiments

Thirteen experiments were conducted using the biomass gasifier product gas as feed for the FT pilot plant. Different gas cleaning processes and various catalysts were used. The experimental procedure was improved from run to run based on the lessons learned with respect to sulphur deactivation of the catalyst. The experiments Nr. 1 to Nr. 12 were used for investigating different FT-catalysts, gas cleaning methods and parameter variations. After the variation of several parameters, the conditions are found to have stable operation of the FT-synthesis without any deactivation. In experiment Nr. 13, a long term test was possible.

The gas cleaning configurations used during the experiments is summarized in **Fehler! Verweisquelle konnte nicht gefunden werden.** The starting configuration was a sequence of a sodium aluminate bed followed by a HDS desulphurization step for conversion of any organic sulphur compounds to H<sub>2</sub>S, which is substantially removed in a ZnO adsorber bed. This configuration was maintained during Experiments 1-7. ZnO bed was used during all experiments. From Experiment 8 onwards, a CuO bed adsorber was added downstream of the ZnO bed. From Experiment 9 onwards, the sodium aluminate and the HDS catalyst were

omitted. In addition, during Experiments 11-13, an activated carbon adsorber was used upstream of the ZnO bed at the intermediate pressure level of 5 bar (gauge) (Experiments 11 and 12) and at atmospheric pressure upstream of the pre-compression step (Experiment 13). One reason, why the activated carbon adsorber was applied at low pressure was the water vapour condensation issue at increased pressure.

Number of experiment	Activated				
•	carbon	NaAlO	HDS	ZnO	CuO
1	no	yes	yes	Yes	No
2	no	yes	yes	Yes	No
3	no	yes	yes	Yes	No
4	no	yes	yes	Yes	No
5	no	yes	yes	Yes	No
6	no	yes	yes	Yes	No
7	no	yes	yes	Yes	No
8	no	yes	yes	Yes	yes
9	no	no	no	Yes	yes
10	no	no	no	Yes	yes
11	at 5bar	no	no	Yes	yes
12	at 5bar	no	no	Yes	yes
13	atmospheric	no	no	Yes	Yes, activated <sup>1</sup>

 Table 12: Gas cleansing used in experiments

<sup>1)</sup> a pre-treatment of the CuO was done according to the instructions of the catalyst company

An overview on the 13 experiments, the catalysts used and the operating conditions is reported in Table 13. About 5 kg of FT product were produced during Experiments 1 and 2 with an iron-based catalyst operated between 250 and 290°C. During these experiments, the main focus was on putting the pilot unit into operation and to test the accompanying analytical measurement procedures.

Number of experiment	Type of catalyst	catalyst [kg]	Temp. [°C]	pressure [bar]	flow [Nm3/h]	active hours [h]	FT raw product [kg]	Alpha
1	Iron	3	250-290	25-30	6	499	2	0,77
2	Iron	4	250-290	25-30	6	888	3	0,78
3	Cobalt	3	200-250	20-25	7	432	-	
4	Co/Ru	1	220-260	19,5-20,5	7,5	145	-	0,83
5	Co/Ru	2,6	230-240	22-25	7,3	610	27,6	0,90
6	Co/Ru	4	230	22-25	7,3	969	21,7	0,87
7	Co/Ru	6	230	17-20	5,5	417	16,6	0,83
8	pre- commercial	1	229-234	20-21	6,5	484	7,1	no value
9	Co/Ru	3	230	16-17	6,5	244	11,5	0,81
10	pre- commercial	2	230-240	18-20	7	225	24,6	0,87
11	pre- commercial	2	230	17-19	5,2	192	6,3	no value
12	pre- commercial	1,5	230	20-22	8,2	436	4,7	No value
13	pre- commercial	1,5	220°C 240°C 250°C	20-25	6,7	495	57,2	0,92 0,865C 0,855

 Table 13: Overview of the experiments

During Experiments 3-7, a cobalt-based catalyst developed and produced at the "Université de Starsbourg" by Prof. Kienemann was used. Only for Experiment 3, a catalyst sample with a too large particle size was used, causing hot spots in the bottom region, what indicated poor suspension properties. Following the experience from Experiment 3, a cobalt-ruthenium catalyst was developed by Prof. Kienemann. A particle size below 100µm is used both for the Co/Ru catalyst and for the pre-commercial catalyst used in Experiments 8 and 10-13. For these experiments, a homogeneous temperature distribution in the FT-reactor is observed. The temperature was the only measurement method in the hot FT-reactor to make decisions on the catalyst distribution in the FT-slurry.

The pre-commercial catalyst was produced by a catalyst company. Due to secrecy agreements no information is available from this catalyst. This catalyst is called "pre-commercial".

Table 15 lists the sample numbers taken after each experiment from FT-product. Most of the samples reflect the bulk product composition. Some samples refer to distilled fractions of the FT-product.

experiment #	Sample	experiment #	sample number
1	FT_10 - FT_014; FT_017; FT_019	8	FT_141 - FT_144
2	FT_020 - FT_022; FT_025; FT_029	9	FT_145 – FT_153; FT_155; FT_156
3		10	FT_154; FT_157 - FT_165; FT_167 - FT_171
4	FT_041 - FT_045	11	FT_172 - FT_174;FT_177
5	FT_046 - FT_084; FT_110	12	FT_180 - FT_190
6	FT_085 - FT_100; FT_101 - FT_106; FT_109; FT_111	13	FT_191 - FT_223
7	FT_112 – FT_115; FT_130 - FT_137; FT_140		

Table 14: Overview of experiments and sample numbers of products

The iron catalyst has been characterized in the chapter "Catalyst characterization at the "Université Louis Pasteur Strasbourg"

A continuous deactivation of the FT-catalyst is observed during the experiments Nr. 1 to Nr. 12. The monitoring of the deactivation in the FT-reactor occurs with the temperature difference between the slurry temperature and the heaters temperature of the FT-reactor. Figure 67 shows the deactivation of the FT-reaction monitored by the temperature difference over the time of the experiment (exemplarily shown for experiment Nr. 9). The deactivation might be a result of the catalyst poisoning by sulphur compounds. Knowledge on gas cleansing and running the plant have been collected during these experiments. The evaluation of the quality of the gas cleansing happens by the poisoning of the catalyst.

Different sulphur measurement methods are tested. The results of these measurements are not satisfying and are not suitable for this system.

Following systems have been tested:

a. An online Sulphur Chemiluminescence Detector (SCD) (in cooperation with the "Paul Scherer Institute (Switzerland)")

The minimum concentration of sulphur compounds in the syngas which are measured with this system is  $\sim$ 0,5 ppm. However for the FT-catalysts this concentration is too high to run stably for several days.

b. adsorption of sulphur compounds in wash bottles with Methanol at -20°C and added analyses with GC-MS

This method could be a very effective system but the following problems occurred:

- the long sampling time at low sulphur concentration causes blockage by solids in the adsorption apparatus
- handling, storage and transportation of the samples causes loss of dissolved compounds
- the available GC-MS system is not equipped with a cooled sampling system (constant loss of analytes over time when the samples are placed on the auto sampler)
- no online measurements are possible and analyses are time consuming

One challenge will be to develop an online sulphur measurement method which is sensitive and quick enough and can be integrated into the controlling of the FT-plant. This could protect the catalyst from unwanted poisoning.

A further evaluation of the gas cleansing device occurred during the analysis of the FTproduct and the used catalyst. These measurements have been carried out at the ITN, Poland.

The concentration in the product laid between 5 and 180 ppm sulphur for samples from the experiments from Nr. 1 to Nr. 12. The concentration of sulphur in catalyst samples (catalyst and slurry) had been up to 150 ppm.

Experimenet 13 was the most successful run in terms of FT-product yield and stability of catalyst activity. In comparison to the deactivation witnessed during experiment Nr. 3 - Nr. 12 (Figure 67), no significant change in the temperature difference between the electrical heater and the slurry was seen whole duration of the experiment of nearly 500 h. The observed CO conversion in the experiment Nr. 13 is about 50%. Furthermore, during experiment Nr. 13, no sulphur was detected on the catalyst and the concentration in the product was below 5 ppm.



Figure 67: Temperature difference between the electrical heater and slurry temperature over the time of experiment #9

## 6.8 Results of the start wax analyses with the GC-FID

Each FT-experiment is started with commercial waxes. In the test runs Nr. 1 to Nr. 8 the wax\_01 are used. At test runs with a higher number the wax\_02 has been used.

wax_01	Paraffin Type 5006
wax_02	Sasolwax H1 Pastillen

In the next two diagrams the product distribution of the start waxes is displayed.



Figure 68: Product distribution of the start wax\_01; carbon number  $[C_n]$  v concentration [Mol%]; GC-column 1



Figure 69: Product distribution of the start wax\_02; carbon number [Cn] VS concentration [Mol%]; GC-column 2

Figure 68 shows that the distribution of the start wax\_01 starts with a carbon number of about twenty and stops at thirty. The wax\_02 has a distribution mainly from thirty to sixty. At the first test runs it is observed that the waxes in the FT-reactor are transported out along with the gas stream. During experiments with a low activity the total amount of waxes is depleted in the reactor. In Figure 69 a wax\_02 with a higher melting point range is used. During experiments with the wax in the reactor was not observed.

# 6.9 Qualitative comparison: Results from the analyses by GC-FID of the FT-products produced with the iron catalyst and the cobalt catalyst

## 6.9.1 GC-FID analyses of products produced by the iron catalyst

The experiment Nr. 1 and Nr. 2 are carried out with an iron catalyst. The products are analysed with a GC-FID system. The analyses according the EN590 and the World-Wide Fuel Charter are done by "ITN".

Figure 70 and Figure 71 show the hydrocarbon distribution of the FT-product produced by the iron catalyst. The ratio between alkanes and alkenes can be read from the area of the peaks. The area of one peak is directly proportional to the mass of analyte. It can be seen directly from the chromatograms that the amount of alkenes is a lot higher than the alkanes. Figure 70 shows several peaks which have not been identified either as a n-alkane or as a n-alkene. These peaks could be other compounds which are produced by the iron catalyst or accumulated impurities from the syngas like benzene.



Figure 70: Chromatogram of sample FT\_029; FT-gasoline produced with an iron catalyst; time v signal (FID); GC-column 1



Figure 71: Chromatogram of sample FT\_015; FT-diesel fraction produced with an iron catalyst; time VS signal (FID); GC-column 1

# 6.9.2 GC-FID analyses of products produced by the cobalt catalyst

FT-products produced at experiments, where the cobalt catalyst is used, are analysed by GC-FID. The chromatograms from the products of the different experiments are very similar. Figure 72 and Figure 73 displays the chromatograms of the FT-product after the distillation.



Figure 72: Chromatogram (column 1) of a FT-gasoline fraction; sample FT\_058; experiment Nr. 5



Figure 73: Chromatogram (column 1) of the FT-diesel fraction by the cobalt catalyst; sample FT\_059; experiment Nr. 5

It can be clearly seen that the amount of n-alkanes is dominant. In comparison to the samples of the iron catalyst the amount of alkenes is very low. The comparison shows that the performance of the two different types of catalysts clearly differs.

Figure 74 and Figure 75 list the ratio between n-alkanes and n-alkenes from the diesel fraction of the two different catalysts. These two diagrams clearly show the big difference of the performances of the catalysts. It can be seen that the higher the carbon number is getting the lower is the relative concentration of alkenes.



Figure 74: Carbon number [Cn] vs mass [%]; diesel fraction (FT\_015); ratio between n-akanes and n-alkenes produced by an iron catalyst



Figure 75: Carbon number [Cn] vs mass [%]; diesel fraction (FT\_059); ratio between n-akanes and n-alkenes produced by a cobalt-ruthenium catalyst

# 6.10 Chain Growth Probability Factor – Anderson Schulz Flory Distribution

## 6.10.1 Chain Growth Probability Factor (α)

The chain growth probability factor  $\alpha$  describes the probability if a compound of  $C_n$  becomes a  $C_{n+1}$  compound. The value of  $\alpha$  is between 0 and 1. The higher the value of  $\alpha$  the higher the probability that the hydrocarbon chain is growing to higher carbon numbers. Equation:

$$Log(W_n / n) = n \log \alpha + const.$$
(1)
$$const. = \log \frac{(1 - \alpha)^2}{\alpha}$$
(2)

wn mass fraction of species with carbon number n
 n carbon number
 α probability of chain growth
 [49]

Figure 76 shows for different  $\alpha$ -values the carbon number distribution following the Anderson Schulz Flory equation. With an  $\alpha$  lower than 0,5 hardly any hydrocarbons with a carbon number higher than 10 are produced. With a value of 0,9 hydrocarbons over the whole range up to an carbon number of 50 are produced.



Figure 76: Sum functions for different Alpha values (mass % of hydrocarbons v carbon number)



Figure 77: Selectivity [%] v chain growth probability factor for different carbon numbers; calculated from equation (1) and equation (2).

Figure 77 shows that at an Alpha value from 0,9 nearly no C1-C3 compounds are formed. The main products have a chain length from C10 to C30. At an Alpha value of 0,7 mainly short hydrocarbon chains compounds from C1 to C10 are formed.

## 6.10.2 Evaluation of the chain growth probability factor

For the calculation of the Alpha value from the experiments the decade logarithm of the mass fraction of the carbon fraction n divided per n is plotted against the carbon number n. Equation (2) has been used for the determination of Alpha. The mass fraction of the carbon number n has been determined by analyses with the Gas Chromatography (SimDist).

The analyses are described in the chapter "Analysis". The chain growth probability factor is calculated for each experiment. The product in the condensation part of the FT-plant and the remaining slurry in the FT-reactor are analysed after one experiment. The start waxes are subtracted. The analyses of the gas phase are not used for the calculation. During experiments where the activity was decreasing rapidly the amount of the product was low. For these experiments it is not possible to use a whole spectrum of products because the amount of the start waxes is a lot higher than the products. So the carbon fractions which are overlapping between start waxes and the FT-product are not used for the determination of the chain growth probability factor in these experiments. For the calculation of Alpha the linear part of the ASF-plot is used.

During some experiments the operation parameters of the FT-plant were changing slightly. The reasons for this have been different performances of the FT-plant during one experiment. In Table 13 these effects has been taken into consideration by displaying the parameter in a range.



Figure 78: Carbon number [C<sub>n</sub>] v mass [%]; evaluated FT-product distribution of the experiment Nr. 9; condensed products minus the start wax\_02



Figure 79: Carbon number  $[C_n]$  v logX<sub>n</sub>/n; Anderson Schulz Flory plot; determination of  $\alpha$ ; (X<sub>n</sub>: mass fraction of the carbon fraction n; n = carbon number)
Figure 78 shows is the whole product distribution of the experiment Nr.9. All fractions are analysed by the GC-FID device and the carbon fractions are summarized separately. The start waxes are subtracted and the result is plotted in a diagram similar to that in Figure 78. It can be seen that in the zone where the start waxes have their carbon distribution the curve is showing some irregularities.

Figure 79 displays the linear part of the ASF-plot. The gradient of the graph is  $\alpha$ .

#### 6.10.3 Dependence of alpha on different temperatures of reaction

During the experiment Nr. 13 a variation of the temperature of the FT-reaction is made. The FT-reaction operates at three different temperatures. At each temperature the product is analysed separately and the coherence between  $\alpha$  and the temperature is plotted below.



Figure 80: Chain growth probability [a] vs temperature [°C] from the experiment Nr. 13

Figure 80 shows that the value of Alpha is decreasing with increasing temperature. That means that the higher the temperature the shorter the hydrocarbon chains are becoming. The pre-commercial catalyst is used and the pressure was kept at 20 to 25 bar.

### 6.11 Results of the fuel analyses carried out at the ITN

Table 16 and 17 show the fuel properties obtained with the iron-based and for the cobaltbased catalyst, respectively. Looking at the results for the diesel sample produced by the ironbased catalyst (Table 16), it can be observed that the sulphur content is at nearly 50 ppm. Also remarkable are the total acid number and the corrosive reaction towards iron and copper. To fulfil the specification of diesel fuel, the FT-product produced by an iron catalyst requires further upgrading such as hydroprocessing.

Parameter	Unit	FT_015	Method
Density at 15 °C	kg/m <sup>3</sup>	795,8	EN ISO 12185
Polycyclic aromatic hydrocarbons, total 1-ring aromatics 2-ring aromatics 3-ring aromatics	%(m/m)	9,0 6,3 1,2 1,5	EN 12916
Sulfur content	mg/kg	48,9	EN ISO 20884
Flash point	°C	72,5	EN 2719
Water content	mg/kg	-	EN ISO 12937
Total contamination	mg/kg	2,4	EN 12662
Copper strip corrosion (3h at 50 °C)	rating	1c	EN ISO 2160
Oxidation stability	g/m <sup>3</sup>	18,8	EN ISO 12205
Lubricity, corrected wear scar diameter (wsd 1,4, 60°C)	μm	299	ISO 12156
Kinematic viscosity at 40 °C	mm <sup>2</sup> /s	1,784	EN ISO 3104
Cloud Point (CP)	°C	-16	ISO 3015
Cold Filter Plugging Point (CFPP)	°C	-22	EN 116
High temperature stability of destillate fuels, % reflectance High temperature stability of destillate fuels, colour before	% rating rating	93,3 1,0 3,5	ASTM D 6468 ASTM D 1500 ASTM D 1500
High temperature stability of destillate fuels, colour after			
Foaming tendency, foam vanishing time Foaming tendency, foam volume	s ml	220 128	NF M 07-075-97
Total acid number	mgKOH/g	27,0	ASTM D 974
Ferrous corrosion	-	D strong	ASTM D 665

Table 15: Fuel analyses results from ITN for the diesel sample FT\_015; iron catalyst

#### Table 16: Results from ITN for the products of the cobalt-ruthenium catalyst

Parameter	Unit	Mean value	Min	Max
Cetane number	-	81,8	75,6	85
Density at 15 °C	kg/m <sup>3</sup>	776,2	773	787
Total aromatic hydrocarbon content	%(m/m)	2,2	1,0	3,1
1-ring aromatic hydrocarbons		1,4	0,4	2,3
2-ring aromatic hydrocarbons		0,5	0,2	0,8
3-ring aromatic hydrocarbons		0,9	<0,1	1,4
Aromatic hydrocarbon content	%(V/V)	0,2	0,0	0,9
Olefins content		10,2	6,6	13,1

		-	-	
Paraffins + Cycloparaffins content		89,5	86,9	93,4
Sulphur content	mg/kg	11,6	8,25	16,5
Sulphur mercaptan content	mg/kg	< 1	< 1	< 1
Flash point	°C	89	86,5	95,5
Carbon residue (on 10 % distillation residue) (on 10 % distillation residue)	%(m/m)	0,023	0,017	0,034
Ash content	%(m/m)	0,001	0,0008	0,0015
Water content	mg/kg	234,5	112	303
Total contamination	mg/kg	9,3	1,6	21,8
Copper strip corrosion (3h at 50°C) (3h at 50 °C)	rating	class 1a	class 1a	class 2c
Oxidation stability	g/m <sup>3</sup>	6,7	2	12
Lubricity, corrected wear scar diameter (wsd 1,4, at 60°C)	μm	341,7	327	356
Viscosity at 40°C	mm <sup>2</sup> /s	2,33	2,18	2,38
Cloud Point (CP)	°C	+2,7	0	+8
Cold Filter Plugging Point (CFPP)	°C	-3	-6	+5
Pour Point (PP)	°C	+1	-3	+4
High temperature stability of distillate fuels, % reflectance	%	97,7	93,7	99,7
High temperature stability of distillate fuels, colour before	rating	0	0	L 0,5
High temperature stability of distillate fuels, colour after	rating	L 0,5	L 0,5	0,5
Ferrous corrosion	rating	light (B <sup>++</sup> )	uncorrosive A	light (B <sup>++</sup> )
Foaming tendency, foam vanishing time	S	101,8	55,9	145,5
Foaming tendency, foam volume	ml	114,7	100	120
Calorific value	kJ/kg	43699,7	43627	43764
Iodine number	g I/100g	5,1	4,4	5,50
N-paraffin's content- total - GC	%(m/m)	82,4	77,68	84,52
Total acid number	mg KOH/g	0,6	0,44	0,95
Water extract	рН	7,3 (neutral)	6,8 (neutral)	7,4 (neutral)
Water reaction of aviation fuels				
- interface conditions	rating	1	1	1b
- separation	rating	3	3	3
- change in volume	cm <sup>3</sup>	-0,5	-1,0	0
Oxidation stability of aviation turbine				
Filter program differential	TT -	3	2	4
- Tube Deposit (Visual)	mm Hg rating	0	0	4
- uoo Doposit ( + isuur)				

Table 17 lists the results from the ITN for the samples produced by the pre-commercial catalyst. Sample FT\_179 is from experiment Nr. 11 where the first time activated carbon is used for gas cleaning. 5,1 ppm sulphur is found in this sample. In the sample FT\_215 from experiment Nr.13 2,7 ppm sulphur was detected. According to EN ISO 20884 oxygen compounds are limiting the validity of the measurement as a result of matrix effects. The range for the measurement is 5 to 500 ppm sulphur in fuel samples. The measured 2,7 ppm sulphur in the sample FT\_215 should be critically viewed with respect to the reliable measurement range, however, it can be safely stated that the value is smaller than 5 ppm.

Parameter	FT-179	FT-215
Cetane number	-	-
Density at 15 °C, kg/m3	770,5	774,0
Polycyclic aromatic hydrocarbons, %(V/V)	0,9	-
1-ring aromatic hydrocarbons	<0,1	-
2-ring aromatic hydrocarbons	<0,1	-
3-ring aromatic hydrocarbons	0,9	-
Sulphur content, mg/kg	5,1	2,7
Flash point, °C	-	100
Carbon residue (on 10 % distillation Residue), %(m/m)	-	-
Ash content, %(m/m)		-
Copper strip corrosion (3h at 50°C) (3h at 50 °C)	1a	-
Oxidation stability, g/m3		-
Lubricity, corrected wear scar diameter (wsd 1,4, at 60°C)	422	460
Viscosity at 40°C, mm2/s	2,016	2,477
% (V/V) recovered at 250 °C	65,0	-
Cold Filter Plugging Point (CFPP), °C	-9	-

Table 17: Fuel analyses from the pre-commercial catalyst

### 6.12 Conclusions and discussion of the results of the analyses of the FTproduct

#### 6.12.1 FT-product by the iron catalyst

The product from the iron catalyst was strongly smelling and had a brown colour. The distilled products had a yellow to brown colour. The odour of the distilled products (Gasoline and diesel) were the same as the crude FT-product. The pH value of the aqueous fraction of the condensation section of the FT-plant was around 2. Analyses by the ITN are showing a high acid value and a very corrosive behaviour. For automotive use the fuel had to be upgraded by an additional process step like hydro treatment. The GC-FID analyses are showing a higher amount of alkene than of alkane.

# 6.12.2 FT-Product by the cobalt-ruthenium catalyst and the pre-commercial catalyst

During the experiments with the cobalt-ruthenium catalyst and the pre-commercial catalyst, the product consisted mainly of paraffin. In general, the obtained diesel fraction was a clear

liquid with an undefined smell neither pleasant nor unpleasant. The amount of olefins varies between 5 to 15 percent in the products by the cobalt-ruthenium catalyst. Products from the pre-commercial catalyst contained up to 24,7 % of olefins. A corrosive behaviour was observed toward iron but toward copper the product was neutral.

The properties following EN 590:

- <u>Cetane number</u>: significant higher value which means a higher quality in comparison to conventional fossil fuel
- <u>Density</u>: The density is below the norm as a reason of the physical properties of n-alkanes.
- <u>Aromatic content:</u> the origin of aromatic compounds is the product gas; a correct mode of operation can avoid aromatic compounds
- <u>Sulphur content:</u> sulphur can be removed close to a concentration level of limit of detection; sulphur is a crucial catalyst poison and has to be removed to operate a FT-catalyst
- <u>Residuals and ash content</u>: if the post-treatments of the FT-product are carried out carefully this topic should not lead to any problems
- <u>Water content:</u> most samples fulfil the norm; some samples were beyond the norm. A reason might be a higher alcohol content in the sample.
- <u>Copper corrosion test:</u> usually the samples were within the norm
- <u>Oxidation stability:</u> all samples were within the norm
- <u>Lubricity and viscosity:</u> the samples fulfilled the norm, were able to be upgraded with additives
- <u>Cold filter plugging point:</u> all samples showed substandard behaviour; the reason is the chemical composition of the FT-product (n-alkane); Isomerisation of the FT-product can improve the low temperature behaviour; if the FT-diesel is used as a blending component it can be used directly.

It can be observed that, via FT-synthesis, a high quality fuel can be produced from biomass. The obtained diesel can be used directly as a valuable blending component for fossil diesel. If the FT-diesel is used undiluted isomerisation is necessary to fulfil the norm.

Besides diesel other products might be interesting from the FT-reaction. When the synthesis is operated with high alpha values the amount of long chain components will increase. The so called FT-wax might be interesting for the chemical industry as it is sulphur free and free from aromatic hydrocarbons. Of course the wax can be transformed into diesel and gasoline fractions for example through hydrocatalytic cracking.

# PART THREE

# **DISCUSSION & CONCLUSION**

### 7 Discussion

#### 7.1 Addressing of the research questions

In the following section there is an attempt to address the research questions which were formulated at the end of part one of this work.

#### 7.1.1 Questions about the catalyst

- Which are appropriate catalysts in FT slurry reactors run by the producer gas of Güssing?
- Are catalysts available for testing?
- What are the demands on catalysts for FT-catalysts in FT?
- What influences will the producer gas of Güssing have on the catalyst?
- How can the process be controlled by the choice of catalyst?

In the start of the project commercial Fischer Tropsch catalysts were not available. In cooperation with the Université Strasbourg it was possible to test typical low temperature catalysts based on cobalt supported on silica. The catalysts have been developed at the Universitè Strasbourg. Additionally commercial iron catalysts developed for the Haber-Bosch synthesis have been characterised. Catalyst characterisations show significant differences in the reducibility of the two different types of catalysts (Iron catalyst >500°C/cobalt catalyst ~280°C). Both types show a similar activity towards CO-disproportionation ( $2CO \rightarrow C+CO_2$ ) of about 0,05 µmol CO<sub>2</sub>/mg catalyst under the described conditions of the experiment. The main difference in the reaction conditions were the temperature of 280°C for the iron and 240°C for the cobalt catalyst.

Catalysts used in slurry bubble reactors have to fulfil certain physical properties. The main parameters are the particle diameter and the density of the catalyst. In the start-up phase, iron catalyst was tested in order to gain operating experience on Fischer Tropsch as well as to show possible alternatives to more expensive cobalt catalysts. A finding from the first experiment at the pilot plant in Güssing was that a homogeneous distribution of the catalyst in the SBC was essential. Inhomogeneous distribution of the catalyst causes the formation of hot spots in the SBC. Carbonization of the slurry takes place at temperatures above 300°C until the column is blocked totally. A crucial parameter for the catalyst in respect of a homogeneous distribution is the particle diameter in relation to the catalyst density.

Further knowledge from the experiments on the pilot plant in Güssing is the importance of an appropriate gas cleaning unit. Deactivation by sulphides of both types of catalysts has been observed.

To keep a SBC reactor running the produced liquid has to be appropriate for the system. In the case of the iron catalyst it could be observed, that the amount of the liquid phase is diminished over the time of experiment. Reasons for these observations are that the liquid phase is evaporated (even the start up waxes), and produced Fischer Tropsch products have a too low boiling point for the conditions of the reaction.

This phenomenon also has been observed with the cobalt catalyst at that point of time in the experiment when the activity of the catalyst was significantly decreased by catalyst poisons.

The choice of catalyst type has a deep impact on the product of Fischer Tropsch synthesis. Product analysis from the iron catalyst show an  $\alpha$ -value of 0,77 and corrosive behaviour toward ferrous material. The obtained fuel does not fulfil the demands for automotive use. Cobalt catalysts perform at an  $\alpha$  value around 0,9. After fractionated distillation the obtained product might be ready for use as diesel fuel.

#### 7.1.2 Questions about the FT-product

- What are the products from the FT-synthesis operated with the producer gas from Güssing?
- Is the obtained FT-product suitable for automotive purposes?

#### Iron catalyst:

Analyses of the gasoline and diesel fractions show that the main compounds are unsaturated alkenes. It can be noticed that the concentration of alkenes is twice that of alkanes (saturated). Analysis of the diesel fraction shows a high acid number (27 mgKOH/g) and a strong corrosive behaviour towards ferrous materials. Possible compounds might be carbon acids and alcohols which have not been analysed separately. To use this product for automotive purposes additional refinery steps are necessary. As seen in the analyses summed up in Table 15, several parameters do not fulfil the standards for diesel fuel. The project did not focus on the iron catalyst Fischer Tropsch synthesis, therefore, no additional investigation has been done on that topic.

#### Cobalt catalyst:

In comparison to the product from the iron catalyst the cobalt synthesised Fischer Tropsch product consists mainly of saturated n-alkanes. The concentration of unsaturated compounds is in total about 10%. In the GC-analyses it can be seen that the relative concentration of alkenes is decreasing the higher the hydrocarbon chain is becoming. The acid number is below 1mg KOH/g. The corrosive behaviour towards ferrous material is "light B++" to "not corrosive". The content of aromatic compounds is in a range from 0-3%. The fuel sample produced with the advanced syngas cleaning performance (activated carbon; ZnO; CuO<sub>activated</sub>) contains no aromatic compounds. This fact will give the conclusion that the aromatic compounds in the remaining samples are not produced by the Fischer Tropsch synthesis, but are part of the producer gas of the gasifier. The same conclusion is valid for the sulphur content in the Fischer Tropsch product.

The cold behaviour characteristics (cloud point, cold filter plugging point and pour point) of the diesel fractions show that at temperatures below  $\sim 10^{\circ}$ C the products are not applicable for automotive diesel fuel. As a consequence further refining steps are necessary. Isomerisation of the product will improve the cold behaviour characteristics.

#### 7.1.3 Questions about the producer gas of Güssing:

- Is the usage of the producer gas appropriate with regard to the main compounds for FT-synthesis?
- What are the purity specifications for the producer gas and how can these specifications be fulfilled?

It was shown that the producer gas of the Güssinger gasifier is appropriate for Fischer Tropsch synthesis. The ratio of hydrogen to carbon monoxide varies between 1,5 - 2. It was expected for application of the Fischer Tropsch synthesis that an advanced gas cleaning setup is necessary. Experiments showed a deactivation of the catalyst over the run time even when the measured sulphur concentration in the syngas after the gas cleaning unit was below 1ppm. At the experiment Nr. 13, a significantly lower deactivation of the catalyst could be monitored. On account of the sulphur concentration measured in the Fischer Tropsch product, the sulphur content in the syngas should be below 10ppb. A challenge will be a reliable deep desulphurisation process and an online gas analysis for the catalyst poison sulphur. In the project different combinations for the sulphur removal were tested. A combination of activated carbon and CuO<sub>activated</sub> demonstrated the best results. Further, different combinations of cleaning processes might be reducing the sulphur concentration to the desired limit.

Another process step for the producer gas are necessary for use in Fischer Tropsch synthesis. The water concentration in the gas has to be reduced below the dew point in the compressed state. From thermodynamic point of view, moisture in the syngas has a negative impact on the Fischer Tropsch reaction  $(2H_2 + CO \rightarrow -CH_{2-} + H_2O)$ . A rape seed oil metylester (RME) scrubber at low temperature was used to separate the water of the product gas. An additional benefit of that scrubber is that no decompositions of organic compounds (Naphtaline, PAH's, etc.) are blocking the gas cooling section. These entire organic compounds are soluble in RME under the prevailing conditions.

To remove chlorine from the producer gas, a fixed bed reactor with NaAlO was installed. It was assumed that no measurable chlorine could pass that process step. Therefore, no further actions were taken with respect to chlorine.

Ideally, the syngas could be conditioned in order to fulfil the desired specifications for the FT reaction in an optimized way. This would mean a sequence of a methane steam reforming step followed by a CO-shift stage in order to adjust the H<sub>2</sub>/CO ratio and, finally, to remove CO<sub>2</sub> and H<sub>2</sub>O from the syngas upstream of the synthesis step.

#### 7.1.4 Questions about the FT-reactor design

- How can a homogenous distribution be estimated for the catalyst in the slurry?
- What is the impact of the type of catalyst and catalyst loading?
- What dimensions/designs are required of the reactor for the pilot plant?
- How can the level in the Fischer Tropsch reactor be controlled?
- How can the temperature be controlled in the reactor?

In the start up of the project it was decided to install a Fischer Tropsch SBC of simple design and a cold model of similar parameters in parallel. One aim in the project was to operate as soon as possible the pilot plant to gain knowledge on gas cleaning, compression of the product gas, Fischer Tropsch product separation and analytics. In parallel, a cold model was installed to analyse the next parameters:

- Catalyst loading in the SBC
- Homogenous distribution of the catalyst
- Min. / max. nominal linear gas velocity

The cold model experiments show that the iron catalyst can be distributed homogeneously in a SBC up to a catalyst loading of about 20% (m/m). Higher loadings results in an inhomogeneous distribution of the catalyst in the SBC. This effect could also be observed in the pilot plant in Güssing by forming a hot spot in the SBC. This means that the Fischer Tropsch process cannot be controlled in a SBC with an inhomogeneous catalyst distribution.

Experiments with the cobalt catalyst supported on silica with the cold model are showing a homogeneous distribution of the catalyst up to 34% (m/m). Experiments with higher catalyst loadings were not done due to a limited amount of catalyst available for these tests. Consequently, no upper limit was detected. In literature a loading from 40% is given as reported in chapter 2.11.1 (Catalyst Particle Loading).

The boundary conditions for the design of the reactor have been a syngas flow of  $10 \text{ Nm}^3/\text{h}$  at 20 bar. Following the literature research (2.10.7) the minimum diameter of a SBC is about 10 cm so that wall effects are not dominant. Finally a SBC reactor with an inner diameter of 10 cm and a height of 2500 cm was installed.

#### Fischer Tropsch product separation

For the separation of the Fischer Tropsch product a sinter metal filter was installed in the upper part of the reactor. Off gas from synthesis as well Fischer Tropsch product passes the filter. Knowledge of that installation is that at long term operation catalyst decompositions might increase the pressure drop over the filter. The installation of larger filtration surfaces as well as in operation cleaning processes like washing or backwashing might compensate the observed pressure lost over the filter. Additionally a redundant installed filter will increase the reliability of the Fischer Tropsch reactor.

The level in the Fischer Tropsch reactor was controlled by the position of the filter. The filter was placed about 30 cm below the top of the reactor.

During the pilot plant the off gas from the Fischer Tropsch reactor was expanded to normal pressure. Therefore, an increase of the pressure lost over the filter up to 1-2 bar did not disturb the pilot plant operation.

#### Temperature controlling

The Fischer Tropsch reactor was equipped with an electrical heating system. Between the reactors outer wall with the electrical heating elements and the isolation a gap of a few centimetres was left so that a kind of pipe-in-pipe system was installed. The cooling of the reactor was made with the pipe-in-pipe system together with a blower. With these controls it was possible to adjust the demand temperature in the Fischer Tropsch reactor.

The temperature controlling system has indirectly monitoring the catalyst deactivation during the experiments. The more the electrical heater had been turned on, the less Fischer Tropsch activity (quantity of Fischer Tropsch product per time) could be detected.

The combination of the size of the pilot Fischer Tropsch reactor and the heat loss over the system resulted in that no additional cooling systems had to be installed. In the case of upscaling an additional heat exchanger should be installed. When the diameter of the reactor increases, the ratio of the reactor volume to reactor surface decreases. That means that the relative exchange surface for heat is decreasing. In the literature review the benefits of a draft tube are reported. In case of an upscale of the Fischer Tropsch reactor an installed draft tube might increase the mixing behaviour. Additionally the draft tube can be constructed as a heat exchanger.

#### 7.1.5 Questions about the pilot plant

- What impact has the producer gas on the different components of the FT-pilot plant?
- How can a continuous FT-product separation be realized?
- How can the process be controlled?

#### Gas pretreating and water removal:

The Fischer Tropsch pilot plant was built up step by step beside the gasifier in Güssing. It started with the construction of the container for the pilot plant. The first process steps was the gas cooling section. The fact that the "Vienna Institute of Chemical Engineering" had developed the rape methylester-scrubber for the biomass gasifier in Güssing, there were no problems to mention. In opposite was the operation of the cooling aggregate, especially in the warm summer months, where many breakdowns occured. A stop of the cooling devices causes problems in the compression section, as then the gas is too wet.

#### Gas compression:

On the basis of financial considerations a combination of a membrane pump and a doubleacting plunger pump was chosen. It was observed that the working life of the sealing of the plunger pump varied from 10-500 h. Additionally, corrosion was detected on the pressure plate of the pump. Reasons for these observed phenomena might be insufficient dewatering of the syngas as well condensation of organic compounds. These faults had effects on the experiments and the evaluation of them. Over the time of an experiment neither a constant gas flow nor a constant pressure could be achieved. In addition to that more and more syngas was lost at the leak of the plunger pump the more the sealing was damaged. That had the effect that several mass balances contained errors since the gas meter is placed before the compression section and had to be rejected.

During the experiments where an activated carbon gas cleaning unit was installed the working life of the plunger pump was increased significantly.

In the case of an upscaling of the pilot plant an alternative gas compression unit has to be used, to facilitate the operation of the plant.

#### Gas cleaning:

For all kinds of gas cleaning units fixed bed reactors were used. In the start up a system of NaAlO, HDS and ZnO was installed. At a later stage of the project further fixed bed gas cleaning material was tested. On the one hand activated carbon after the RME-scrubber was installed and on the other a CuO cleaning unit for deep desulphurisation was installed. In general the operation of the fix bed reactors ran without difficulties, only the CuO reactor was difficult to control.

The reduction of CuO with carbon monoxide and hydrogen are exothermic reactions. It was observed that with pure syngas the temperature control of the CuO-reactor involved a certain difficulty. An rise of temperature was monitored. The material of CuO or Cu respectively was sintered in the reactor so that no further operation was possible.

Sulphur is the compound of most interest in gas cleaning for Fischer Tropsch synthesis. The performance of the different experiments in respect to the different gas cleaning installations can be summed up as follows.

The initial installed system of NaAlO for chlorine removal and a combination of a HDScatalyst and a ZnO adsorbent are not sufficient to protect the Fischer Tropsch catalyst from poisoning. Analyses show rather high concentrations (~ 100 ppm) of sulphur in the Fischer Tropsch products as well as on the catalysts.

A significant change in the performance could be noticed by the implementation of a CuO gas cleaning unit. The specified "activation procedure" from the producer company for the CuO unit seemed to be essential for a deep desulphurisation performance.

The impact of the metal supported gas cleaning units (CuO reduced to Cu) on the global gas composition (hydrogen, carbon monoxide, carbon dioxide and methane) of the syngas was not significant.

Further investigations should be done on gas cleaning for Fischer Tropsch synthesis. The main point will be a reliable desulphurisation of the producer gas. A review on the whole process maybe a combination of different process steps which will fulfil that demand. During the last experiment a combination of activated carbon, ZnO and activated CuO showned a promising performance.

Another challenge will be an online supervision of the sulphur content in the syngas. Therefore the detection limit should be at 10ppb. With such an analytical installation it should be possible to monitor the sulphur concentration in the start up and down phases as well as in the stable state of the plant.

#### Off-gas treatment:

After the Fischer Tropsch reactor the off gas from the Fischer Tropsch synthesis was expanded to normal pressure. The formed organic Fischer Tropsch products as well as the aqueous phase should be condensed and separated in the down-stream process step. A scrubber operated at about 80°C to separate long chain hydrocarbons, and a condenser operated at about 2°C to condense light hydrocarbons.

Observations resulted in that heavy hydrocarbons were carried over to the sequent gas meter as well as deposits of solid hydrocarbons in the off gas tube back to the power plant. That gives rise to the speculation that stable aerosols are formed during the expansion of the off gas. The design of filters is challenging on the basis of the fact that the solutes to be separated are of a liquid, greasy and solid state. With regard to further development, the installation of a fractionated condensation system under pressure might avoid the formation of stable aerosols.

#### Automation

An automated pilot plant was installed so that long term experiments without work in shifts could be done.

The control system of the pilot plant switched off the aggregates in case of necessity (interruption of the product gas supply, limit of carbon monoxide in air, ...), and started up again automatically in case of positive readiness of all necessary signals and aggregates.

So up to now the influences caused by interruptions on key-areas (Fischer Tropsch catalyst, gas cleaning units) have not been analysed and it cannot be excluded that these interruptions might have negative impacts on these key areas. As a consequence everything possible should be done to diminish the number of interruptions. On the one hand the use of reliable aggregates might reduce shut downs and on the other hand the installation of a product gas buffer might tide over short interruptions of the product gas production.

## 8 Conclusion and Outlook

The executed Fischer Tropsch experiments in Güssing show that the process can be controlled and the obtained products are suitable for further applications.

The obtained diesel fuel synthesised from the producer gas of the Güssinger gasifier shows a product of high quality. For commercial use for automotive purposes additional processing steps like isomerisation of the n-alkane or blending are necessary to fulfil all aspects of the EN590 and the World Wide Fuel Charter. These processes are standard operations in today's crude oil refinery plants.

In this work only the products in the liquid organic phase have been analyzed. In further work more attention should be on the gaseous phase (C1 -  $\sim$  C6) and the soluble organic products in the aqueous phase like alcohols.

In the project it was found that the gas cleaning of the syngas is one of the most crucial steps in the process. This topic demands additional work to protect the catalyst from deactivation so that the whole process becomes more reliable. The developed combination of gas cleaning steps in this work forms a basis for further study. Linked to a reliable gas cleaning is an appropriate analysis. To develop an appropriate analysis down to 10 ppb of sulphur in the syngas will be a real challenge.

The pilot plant in Güssing was operated continuously. Nevertheless there were interruptions during the experiments. More work should be done to minimize these interruptions. Furthermore, the process in the different gas cleaning units should be analyzed in case of an interruption. It cannot be excluded that there is no negative impact on the catalyst during these periods.

During operation of the pilot plant in Güssing it was discovered that the condensation of the FT-product caused problems by blockage of tubes and different devices. Furthermore, the condensation of the product was not complete, even for products with a higher carbon number. An improvement of the separation of the Fischer Tropsch product might be produced by redesigning this section in a way that the products are separated under pressure and fractionated cooling.

The application of cobalt based catalysts result in products of high quality. The observed CO conversion in the best-performing experiment Nr. 13 was about 50%. With further experiments the conversion by changing the Fischer Tropsch reactor parameters should be optimized. Another approach to increase the conversion may be to change the gas composition of the syngas towards a higher  $H_2/CO$  ratio. Therefore, additional process steps such as a catalytic CO-shift stage will be necessary to increase the hydrogen concentration in the syngas.

# 9 Notation

## 9.1 Chemical elements / compounds

-CH2-	Alaiphatic hydrocarbon chain
Al <sub>2</sub> O <sub>3</sub>	Aluminium oxide
$C_2H_4$	Ethylene
C3H6	Propylene
C3H8	Propane
C4H10	Butane
CH <sub>3</sub> OCH <sub>3</sub>	Dimethyl Ester
CH <sub>3</sub> OH	Methanol
CH <sub>4</sub>	Methane
СО	Carbon monoxide
Corg	Organic carbon
Cu	Copper
Fe	Iron
$H_2$	Hydrogen
H <sub>2</sub> O	Water
$H_2S$	Di-hydrogen sulfide
Κ	Potassium
K <sub>2</sub> O	Potassium oxide
Li	Lithium
MgO	Magnesium oxide
Na	Sodium
NiO	Nickel oxide
Pd	Palladium
Pt	Platinum
R	Organic inactiv rest
Rb	Rubidium
Re	Rhenium
Ru	Ruthenium
SiO <sub>2</sub>	Silicon dioxide
TiO <sub>2</sub>	Titan oxide
ZnO	Zink oxide

## 9.2 Latin letters / symbols

А	Area of probe, [m <sup>2</sup> ]
AC	Alternating current

bar	10 <sup>5</sup> Pascal
С	Capacitance, [F]
°C	Celsius
d	Diameter / distance [m]
$d_B$	Average bubble diameter
Dc	Critical column diameter above which there is no effect of the column diameter on gas hold up any more (m)
$D_{max}$	Maximum stable bubble size (m)
$D_{\mathrm{T}}$	Column diameter (m)
f	Frequency, Hz
FA	Buoyant force [N]
FG	gravity [N]
Fs	Stokes' frictional force [N]
g	Acceleration by gravity (m $s^{-2}$ )
ь Н	Height of the expanded hed (m)
h	Dynamic fluid viscosity [Pa s]
h	Planck constant
h*	Height above the gas distributor where the hubbles reach their equilibrium size (m)
11	The first above the gas distributor where the bubbles reach then equilibrium size (iii)
$h_0$	Parameter determining the initial bubble size at the gas distributor (m)
i	Imaginary number
j K	Imaginary number Kelvin
j K k	Imaginary number Kelvin Dielectric constant
j K k K <sub>eff</sub>	Imaginary number Kelvin Dielectric constant Dielectric constant of suspension
j K k K <sub>eff</sub> Kh	Imaginary number Kelvin Dielectric constant Dielectric constant of suspension Dielectric constant of fluid
j K k K <sub>eff</sub> K <sub>h</sub> kJ	Imaginary number Kelvin Dielectric constant Dielectric constant of suspension Dielectric constant of fluid Kilo Joul
j K k Keff Kh kJ kLa	Imaginary number Kelvin Dielectric constant Dielectric constant of suspension Dielectric constant of fluid Kilo Joul Gas-liquid mass transfer coefficients
j K k Keff Kh kJ kLa Kp	Imaginary number Kelvin Dielectric constant Dielectric constant of suspension Dielectric constant of fluid Kilo Joul Gas-liquid mass transfer coefficients Dielectric constant of particles
j K k K <sub>eff</sub> K <sub>h</sub> kJ kLa K <sub>p</sub> kPa	Imaginary number Kelvin Dielectric constant Dielectric constant of suspension Dielectric constant of fluid Kilo Joul Gas-liquid mass transfer coefficients Dielectric constant of particles Kilo Pascal
j K k Keff Kh kJ kLa Kp kPa mg	Imaginary number Kelvin Dielectric constant Dielectric constant of suspension Dielectric constant of fluid Kilo Joul Gas-liquid mass transfer coefficients Dielectric constant of particles Kilo Pascal Miligramm
j K k Keff Kh kJ kLa Kp kPa mg mol	Imaginary number Kelvin Dielectric constant Dielectric constant of suspension Dielectric constant of fluid Kilo Joul Gas-liquid mass transfer coefficients Dielectric constant of particles Kilo Pascal Miligramm Mol
j K k Keff Kh kJ kLa Kp kPa mg mol MW	Imaginary number Kelvin Dielectric constant Dielectric constant of suspension Dielectric constant of fluid Kilo Joul Gas-liquid mass transfer coefficients Dielectric constant of particles Kilo Pascal Miligramm Mol Mega Watt
j K k Keff Kh kJ kLa Kp kPa mg mol MW MWel	Imaginary number Kelvin Dielectric constant Dielectric constant of suspension Dielectric constant of fluid Kilo Joul Gas-liquid mass transfer coefficients Dielectric constant of particles Kilo Pascal Miligramm Mol Mega Watt Mega Watt electric
j K k Keff Kh kJ kLa Kp kPa mg mol MW MWel MWth	Imaginary number Kelvin Dielectric constant Dielectric constant of suspension Dielectric constant of fluid Kilo Joul Gas-liquid mass transfer coefficients Dielectric constant of particles Kilo Pascal Miligramm Mol Mega Watt Mega Watt electric Mega Watt thermic
j K k Keff Kh kJ kLa Kp kPa mg mol MW MWel MWel MWth n	Imaginary number Kelvin Dielectric constant Dielectric constant of suspension Dielectric constant of fluid Kilo Joul Gas-liquid mass transfer coefficients Dielectric constant of particles Kilo Pascal Miligramm Mol Mega Watt Mega Watt electric Mega Watt thermic Carbon atoms in a hydrocarbon chain
j K k Keff Kh kJ kLa Kp kPa mg mol MW MWel MWel MWth n N	Imaginary number Kelvin Dielectric constant Dielectric constant of suspension Dielectric constant of fluid Kilo Joul Gas-liquid mass transfer coefficients Dielectric constant of particles Kilo Pascal Miligramm Mol Mega Watt Mega Watt Mega Watt electric Mega Watt thermic Carbon atoms in a hydrocarbon chain Fit parameter (N = 0,18 for gas liquid solids system solids < 16 %; N = 0,18 for solids > 16 %)
j K k Keff Kh kJ kLa Kp kPa mg mol MW MWel MWel MWth <i>n</i> N	Imaginary number Kelvin Dielectric constant Dielectric constant of suspension Dielectric constant of fluid Kilo Joul Gas-liquid mass transfer coefficients Dielectric constant of particles Kilo Pascal Miligramm Mol Mega Watt Mega Watt Mega Watt electric Mega Watt thermic Carbon atoms in a hydrocarbon chain Fit parameter (N = 0,18 for gas liquid solids system solids < 16 %; N = 0,18 for solids > 16 %)
j K k Keff Kh kJ kLa Kp kPa mg mol MW MWel MWel MWth <i>n</i> N	Imaginary number Kelvin Dielectric constant Dielectric constant of suspension Dielectric constant of fluid Kilo Joul Gas-liquid mass transfer coefficients Dielectric constant of particles Kilo Pascal Miligramm Mol Mega Watt Mega Watt electric Mega Watt thermic Carbon atoms in a hydrocarbon chain Fit parameter (N = 0,18 for gas liquid solids system solids < 16 %; N = 0,18 for solids > 16 %) Velocity of the particle [m/s] Constant settling velocity [m/s]
j K k Keff Kh kJ kLa Kp kPa mg mol MW MWel MWel MWth <i>n</i> N N	Imaginary number Kelvin Dielectric constant Dielectric constant of suspension Dielectric constant of fluid Kilo Joul Gas-liquid mass transfer coefficients Dielectric constant of particles Kilo Pascal Miligramm Mol Mega Watt Mega Watt Mega Watt electric Mega Watt thermic Carbon atoms in a hydrocarbon chain Fit parameter (N = 0,18 for gas liquid solids system solids < 16 %; N = 0,18 for solids > 16 %) Velocity of the particle [m/s] Constant settling velocity [m/s] Pascal

r U U <sub>B</sub>	Radius [m] Superficial gas velocity (ms-1) Average bubble rise velocity (ms-1)
$U_{df}$	Superficial gas velocity through the dense phase (ms <sup>-1</sup> )
Utrans	Transition superficial gas velocity (transition to coalescence of bubbels)
V V <sub>df</sub>	Volume Superficial velocity of the dense-phase or superficial velocity of large bubbles.
$V_g$	Superficial gas velocity entering the column
$W_n$	Mass fraction of the n <sup>th</sup> oligomer
Xc	Capacitive reactance, $\Omega$
Ζ	Impedance, $\Omega$

## 9.3 Greek letters / symbols

Ø	Bubble rise coefficient
Øo	Constant to determine column diameter dependence of the bubble rise coefficient
α	Constant in the bubble growth model of Darton et al. / or Aspect ratio (height to width) of bubbles
α2	Fit parameter ( $\alpha_2 = 0.268$ for gas liquid solids system solids < 16 %; $\alpha_2 = 0.3$ for solids > 16 %)
$\alpha_{ASF}$	Chain growth probability $(0 \le \alpha \ge 1)$
<b>E</b> 0	Permittivity of a vacuum, [F/m]
EB	Gas hold-up in the 'dilute' phase, bubble fraction, fraction of the bed occupied by gas bubbles
Eb,lg	Gas hold up of large bubbles (dilute phase)
ε <sub>s</sub>	Solid hold up (catalyst concentration)
$\eta_{\rm L}$	Dynamic viscosity of the liquid (Pa s)
π*	$\pi$ -Orbital activated
ρ	Density [kg/m <sup>3</sup> ]
$ ho_{\rm f}$	Density of the fluid [kg/m <sup>3</sup> ]
$ ho_g$	Density of gaseous phase (kg m <sup>-3</sup> )
ρl	Density of liquid phase (kg m <sup>-3</sup> )
σ	$\sigma$ -Orbital or surface tension (N m-1)
$\sigma^*$	σ-Orbital activated
Φ	Voidage of suspension

## 9.4 Abbreviations

ASF	Anderson Schulz Flory
BKG	Biomassekraftwerk Güssing (biomass power plant Güssing)
BTL	Biomass to liquid
CHP	Combiend het and power plant
DME	Dimethylester
ETBE	Ethyl-tert-butylether
EU	European Union
FAEE	Fatty acid ethyl ester
FAME	Fatty Acid Methyl Ester
FT	Fischer Tropsch
FTS	Fischer Tropsch synthesis
GC-TCD	Gas chromatograph - thermal-conductivity detector
HDS	Hydrodesulfurisation
HTFT	High temperature Fischer Tropsch
ITN	Instytut Technologii Nafty
LCR-	Inductance capacitance resistance meter
meter	
LTFT	Low Temperature Fischer Tropsch
MFM	Mass flow meter
MR	Micro-channel-reactor
MT	Multi tubular
MTBE	Methyl-tert-butylether
PG	Product gas
PPO	Pure Plant Oil
RME	Rape methylester
SBC	Slurry bubble column
SNG	Synthetic natural gas
TCD	Thermal conductivity detector
TPR	Temperature programmed reduction
TU	University of Technology
WGS	Water gas shift
WWII	World War Two

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vom 23. April 2009

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