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Kinetics, selectivity and scale up of the Fischer-Tropsch synthesis

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Introduction

1.1 Fischer-Tropsch (FT) Process

Coal and natural gas can be utilized as feedstock of the chemical industry and the transportation fuels market. The conversion of natural gas to hydrocarbons (Gas-To-Liquids route) is currently one of the most promising topics in the energy industry due to economic utilization of remote natural gas to environmentally clean fuels, specialty chemicals and waxes. Alternatively, coal or heavy residues can be used on sites where these are available at low costs. The resources of coal and natural gas are very large, see Table 1.1. Coal and natural gas can be converted into synthesis gas, a mixture of predominantly CO and H₂, by either partial oxidation or steam reforming processes. Possible reactions of synthesis gas are shown in Figure 1.1.

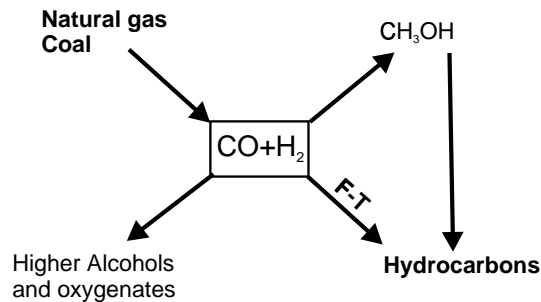


Figure 1.1 Possible reactions from synthesis gas.

Table 1.1 World fossil fuel reserves and consumption (EJ,10¹⁸J) [1].

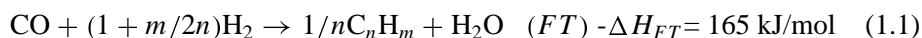
	Reserves	Consumption (1991)
Coal (1991)	27,185	69.91
Crude oil (1992)	6,054	143.67
Natural gas (1992)	4,512	79.44

Table 1.2 Major overall reactions in the Fischer-Tropsch synthesis.

Main reactions	
1. Paraffins	$(2n + 1)\text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$
2. Olefins	$2n\text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{2n} + n\text{H}_2\text{O}$
3. Water gas shift reaction	$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$
Side reactions	
4. Alcohols	$2n\text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{2n+2}\text{O} + (n - 1)\text{H}_2\text{O}$
5. Boudouard reaction	$2\text{CO} \rightarrow \text{C} + \text{CO}_2$
Catalyst modifications	
6. Catalyst oxidation/reduction	a. $\text{M}_x\text{O}_y + y\text{H}_2 \rightleftharpoons y\text{H}_2\text{O} + x\text{M}$
	b. $\text{M}_x\text{O}_y + y\text{CO} \rightleftharpoons y\text{CO}_2 + x\text{M}$
7. Bulk carbide formation	$y\text{C} + x\text{M} \rightleftharpoons \text{M}_x\text{C}_y$

The conversion of the synthesis gas to aliphatic hydrocarbons over metal catalysts was discovered by Franz Fischer and Hans Tropsch at the Kaiser Wilhelm Institute for Coal Research in Müllheim in 1923 [2, 3]. They proved that CO hydrogenation over iron, cobalt or nickel catalysts at 180-250 °C and atmospheric pressure results in a product mixture of linear hydrocarbons. The Fischer-Tropsch product spectrum consists of a complex multicomponent mixture of linear and branched hydrocarbons and oxygenated products. Main products are linear paraffins and α -olefins. The overall reactions of the Fischer-Tropsch synthesis are summarized in Table 1.2. The hydrocarbon synthesis is catalyzed by metals such as cobalt, iron, and ruthenium. Both iron and cobalt are used commercially these days at a temperature of 200 to 300 °C and at 10 to 60 bar pressure [4, 5].

The reactions of the FT synthesis on iron catalysts can be simplified as a combination of the FT reaction and the water gas shift (WGS) reaction:



where n is the average carbon number and m is the average number of hydrogen atoms of the hydrocarbon products. Water is a primary product of the FT reaction, and CO_2 can be produced by the WGS reaction. The WGS activity can be high over potassium-promoted iron catalysts and is negligible over cobalt or ruthenium catalysts.

Figure 1.2 shows a block diagram of the overall Fischer-Tropsch process configuration. The commercial process involves three main sections, namely: synthesis gas production and purification, Fischer-Tropsch synthesis, and product grade-up. These subjects are described in more detail below. Choi et al. [6] gives a capital cost breakdown of these three individual process sections for a 45,000 bbl/day FT plant. The synthesis gas preparation (that is air separation plant, partial oxidation, steam reforming of natural gas, and syngas cooling) is about 66 % of the total on-site capital costs. The FT synthesis section consisting of FT slurry reactors, CO₂ removal, synthesis gas compression and recycle, and recovery of hydrogen and hydrocarbons is 22 % of the total costs. Finally, the upgrading and refining section of hydrocarbons is about 12 %. Consequently, cost reduction of synthesis gas production is the most beneficial. Note, however, that at a fixed production rate the selectivity of the FT process directly affects the size of the syngas generation section. A high selectivity of the FT process to desired products is of utmost importance to the overall economics.

1.1.1 Synthesis Gas Production

Synthesis gas can be obtained by steam reforming or (catalytic) partial oxidation of fossil fuels: coal, natural gas, refinery residues, biomass or industrial off-gases. The composition of syngas from the various feedstocks and processes is given in Table 1.3 [7, 8]. Synthesis gas can be obtained from reforming of natural gas with either steam or carbon dioxide, or by partial oxidation. The most important reactions are:



Usually, a combination of synthesis gas production processes is used to obtain synthesis gas with a stoichiometric ratio of hydrogen and carbon monoxide.

Synthesis gas produced in modern coal gasifiers (Shell/Koppers or Texaco gasifiers) and from heavy oil residues has a high CO content in comparison to synthesis gas from natural gas. If synthesis gas with a H₂/CO ratio below 2 is used, the composition is not stoichiometric for the Fischer-Tropsch reactions (see Table 1.2). Then the water gas shift reaction is important to change the H₂/CO ratio to 2. Figure 1.3 shows the application ranges for iron (high WGS-activity) and cobalt catalysts (no WGS activity) [10]. Inexpensive iron catalysts in comparison to cobalt can directly convert

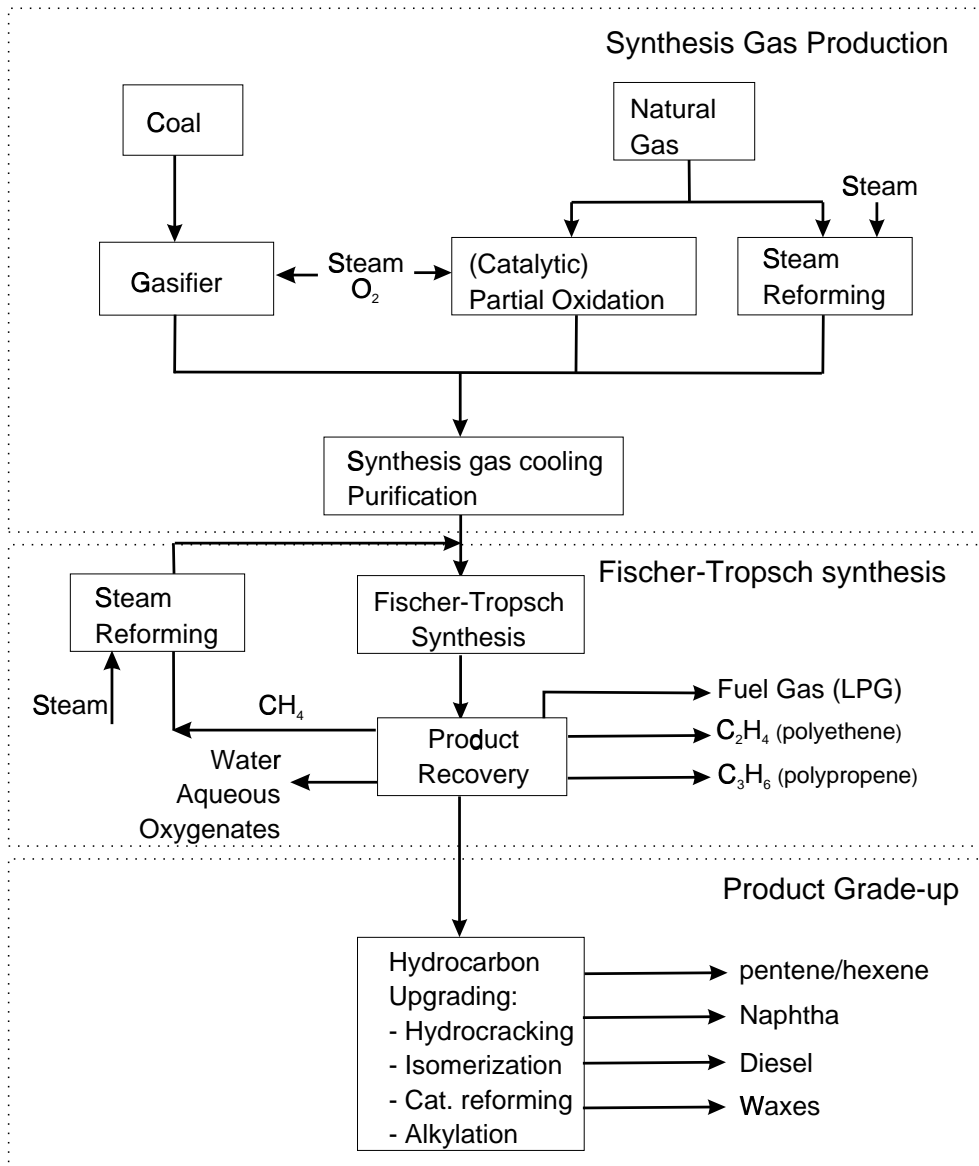


Figure 1.2 Overall process scheme Fischer-Tropsch.

Table 1.3 Synthesis gas compositions.

Feedstock	Process	Component (vol%)			
		H ₂	CO	CO ₂	Other
Natural gas, steam	SR ¹	73.8	15.5	6.6	4.1
Natural gas, steam, CO ₂	CO ₂ - SR ²	52.3	26.1	8.5	13.1
Natural gas, O ₂ , steam, CO ₂	ATR ²	60.2	30.2	7.5	2.0
Coal/heavy oil, steam	Gasification ¹	67.8	28.7	2.9	0.6
Coal, steam, oxygen	Texaco gasifier ¹	35.1	51.8	10.6	2.5
Coal, steam, oxygen	Shell/Koppers gasifier ¹	30.1	66.1	2.5	1.3
Coal, steam, oxygen	Lurgi gasifier ³	39.1	18.9	29.7	12.3

SR= steam reforming, CPO= catalytic partial oxidation, ATR= autothermal reforming

¹ Data from Cybulski et al. [7]

² Data from Basini and Piovesan [9]

³ Data from Perry and Green [8]

low H₂/CO ratio synthesis gas without an external shift reaction [11–13].

New ceramic membranes might become interesting for significant cost reduction of synthesis gas production by 30-50 % [14]. Reduction of the synthesis gas costs could also be accomplished by a decrease of steam/carbon and oxygen/carbon ratios in the feedstock [9]. Basini and Piovesan [9] compared economical evaluations of steam-CO₂ reforming, autothermal reforming, and combined reforming processes. They concluded that combined reforming has the lowest production and investment costs at a H₂/CO ratio of 2.

Although the capital costs predominate, the cost price of natural gas is also an important factor in the overall process economics of GTL (Gas-To-Liquids) Fischer-Tropsch plants. Remote gas fields or natural gas associated with crude oil production has a low cost or a negative value as an undesired by-product. Reduction of flaring of associated natural gas and the unfavorable economics of gas reinjection make the Fischer-Tropsch process economically viable. FT derived fuels are easily transported in standard vessels or pipelines relative to natural gas and LNG.

1.1.2 Fischer-Tropsch Synthesis

The Fischer-Tropsch synthesis section consists of: FT reactors, recycle and compression of unconverted synthesis gas, removal of hydrogen and carbon dioxide, reforming of methane produced and separation of the FT products. The most important aspects

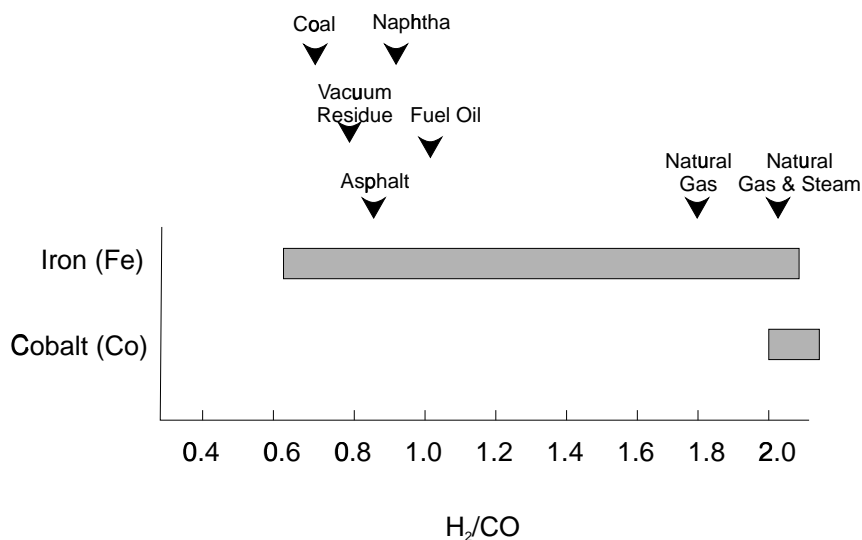


Figure 1.3 Feedstocks and catalysts [10].

for development of commercial Fischer-Tropsch reactors are the high reaction heats and the large number of products with varying vapor pressures (gas, liquid, and solid hydrocarbons). The main reactor types which have been proposed and developed after 1950 are [5, 15, 16]:

1. Three-phase fluidized (ebulliating) bed reactors or slurry bubble column reactors with internal cooling tubes (SSPD: Sasol; GasCat: Energy International, AGC-21: Exxon, see Figure 1.4a)
2. Multitubular fixed bed reactor with internal cooling (Arge: Sasol; SMDS: Shell, see Figure 1.4b)
3. Circulating fluidized bed reactor with circulating solids, gas recycle and cooling in the gas/solid recirculation loop (Synthol: Sasol) (Figure 1.4c)
4. Fluidized bed reactors with internal cooling (SAS: Sasol) (Figure 1.4d)

Sie [5] compared the advantages and disadvantages of the two most favorite reactor systems for the Fischer-Tropsch synthesis of high molecular weight products: that is the multitubular trickle bed reactor and the slurry bubble column reactor. Major drawbacks of the bubble column are requirements for continuous separation between

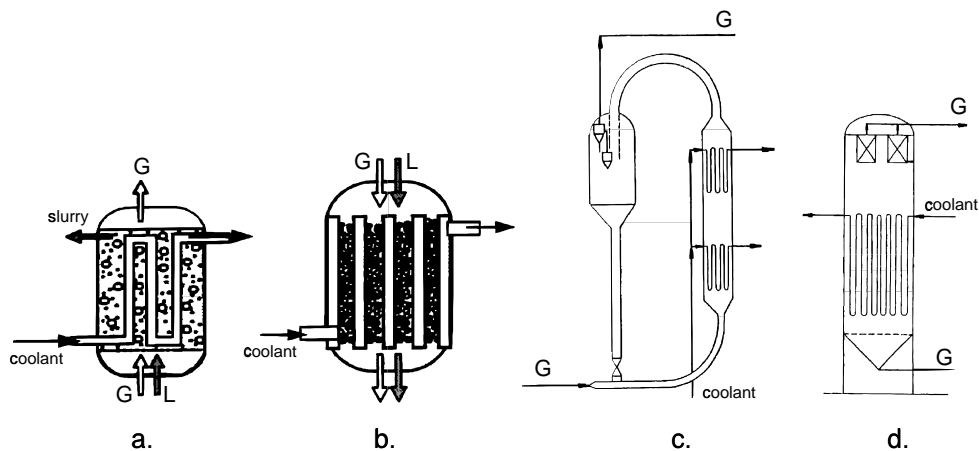


Figure 1.4 Possible reactors for Fischer-Tropsch synthesis [5, 16]. a. Slurry bubble column reactor; b. Multitubular trickle bed reactor; c. Circulating fluidized bed reactor; d. Fluidized bed reactor.

catalyst and liquid products, a smaller scaling-up factor (500) in comparison to the multitubular reactor (max. 10,000), and possible attrition of the catalyst particles. The advantages are [17]: 1) Low pressure drop over the reactor. 2) Excellent heat transfer characteristics resulting in stable reactor temperatures. 3) No diffusion limitations. 4) Possibility of continuous refreshment of catalyst particles. Disadvantages of the multitubular reactor are the larger catalyst particles, the required equal distribution of gas and liquid streams over all tubes, and the large reactor weight due to a large number of tubes for effective heat transfer area. However, the most important disadvantage of the multitubular reactor probably is in the high costs of 10 to 100,000 tubes, typical for commercial scale.

De Swart [18] modeled a cobalt-based FT process both in trickle bed reactors and in slurry bubble column reactors. The major conclusion was that 10 multitubular trickle bed reactors (6 m diameter, 20 m height) or 4 slurry reactors (7.5 m diameter, 30 m height) can produce 5000 tonnes of middle distillates (C_{5+}) per day. Mainly due to the high heat transfer rates occurring in the slurry system, the capital costs of this system reportedly can be 60 % lower than that of the multitubular system [18]. Jager [19] stated that the costs of a single 10,000 bbl/day slurry reactor system is about 25 % of that of a tubular fixed bed reactor. Although these capital cost figures look impressive, it is emphasized again that the C_{5+} selectivity is crucial to overall economics. In other words, if a cheaper reactor delivers a lower C_{5+} selectivity, the larger syngas section needed may off-set the initial advantages.

1.1.3 Product Upgrading and Separation

Conventional refinery processes can be used for upgrading of Fischer-Tropsch liquid and wax products. A number of possible processes for FT products are: wax hydrocracking, distillate hydrotreating, catalytic reforming, naphtha hydrotreating, alkylation and isomerization [6, 20]. Fuels produced with the FT synthesis are of a high quality due to a very low aromaticity and zero sulfur content. The product stream consists of various fuel types: LPG, gasoline, diesel fuel, jet fuel. The definitions and conventions for the composition and names of the different fuel types are obtained from crude oil refinery processes and are given in Table 1.4.

Table 1.4 Conventions of fuel names and composition [1].

Name	Synonyms	Components
Fuel gas		C ₁ - C ₂
LPG		C ₃ - C ₄
Gasoline		C ₅ - C ₁₂
Naphtha		C ₈ -C ₁₂
Kerosene	Jet fuel	C ₁₁ -C ₁₃
Diesel	Fuel oil	C ₁₃ -C ₁₇
Middle distillates	Light gas oil	C ₁₀ -C ₂₀
Soft wax		C ₁₉ - C ₂₃
Medium wax		C ₂₄ - C ₃₅
Hard wax		C ₃₅ +

The diesel fraction has a high cetane number resulting in superior combustion properties and reduced emissions (see Table 1.5). New and stringent regulations may promote replacement or blending of conventional fuels by sulfur and aromatic free FT products [21, 22]. Also, other products besides fuels can be manufactured with Fischer-Tropsch in combination with upgrading processes, for example, ethene, propene, α -olefins, alcohols, ketones, solvents, specialty waxes, and so forth. These valuable by-products of the FT process have higher added values, resulting in an economically more attractive process economy. The value of Fischer-Tropsch products used as blending stocks for transportation fuels (kerosene and diesel) is higher than crude oil derived fuels due to their excellent properties (see Table 1.5). Choi et al. [6] assumed the FT gasoline and FT diesel to be 10.07 \$/bbl (0.24 \$/gallon) and 7.19 \$/bbl (0.17 \$/gallon) more expensive than transportation fuels derived from crude oil.

Table 1.5 Product quality, adapted from Sie [5] and Gregor [22].

Product	Property	SMDS products	Hydrocracked Arge FT-wax	Specification
Diesel	Cetane number	70	> 74	min. 40
	Cloud point, °C	-10	-7	-20 to +20
Kerosene	Smoke point, mm	> 100	> 50	min. 19-25
	Freezing point, °C	-47	-43	max. -47 to -40

1.2 Industrial Fischer-Tropsch Processes

Below, the major industrial Fischer-Tropsch processes are discussed briefly. The emphasis is on processes developed after 1980. Table 1.6 gives an overview of the major companies and their patents divided in the following sections: 1. FT catalyst development; 2. process design and development; 3. upgrading of specific FT products. A comparison of the several industrial Fischer-Tropsch companies is presented in Table 1.7.

Table 1.6 Estimate of patents of the major companies active in Fischer-Tropsch (April 1998).

Company	Catalyst development	Process development	Separation and product grade-up
BP	13	4	0
Exxon	71	15	5
Rentech	1	8	0
Sasol	2	3	3
Shell	45	27	13
Statoil	5	3	1
Syntroleum	0	1	0

Energy International

Energy International (Pittsburgh) is owned by Williams International Corp. (formerly owned by Gulf Oil Corp.) which is promoting slurry bubble column reactors for the FT process. They claim the major advantage of their process to be low capital costs in comparison to other processes. Highly active cobalt catalyst on alumina carriers

Table 1.7 Comparison of the major companies active in Fischer-Tropsch (October 1998).

Company	Synthesis gas preparation ¹	FT reactor	Capacity (bbl/day)	Catalyst
Energy Int.	PO with O ₂	slurry	-	Co
Exxon	CPO (O ₂)	slurry	200	Co
Rentech	PO with O ₂ , SR, ATR	slurry	235	Fe
Sasol	PO with O ₂ , SR, coal gasification	slurry fluidized	2,500 110,000	Fe, Co
Shell ²	PO with O ₂	fixed	12,500	Co
Syntroleum	ATR with air	fixed	2	Co

¹ (C)PO= (Catalytic) Partial Oxidation, SR= Steam Reforming, ATR= Autothermal Reforming

² Capacity until December 1997

(GasCat catalyst) produce a high liquid fuel yield relative to other cobalt catalysts [23]. Energy International performs a US Department of Energy funded study for the concept of a 25,000 bbl/day floating Fischer-Tropsch plant for the deep waters of the Gulf of Mexico (Remote Gas Strategies, October 1997).

Exxon

The Exxon's process is known as AGC 21 (Advanced Gas Conversion 21st Century) [24]. The process consists of the following steps: 1. Fluidized bed synthesis gas production; 2. Slurry phase FT reactor; 3. Hydro-isomerization process. Exxon has a 200 bbl/day GTL pilot plant in Baton-Rouge, USA, that has been operating until 1996. The AGC-process can be scaled up to commercial plants producing 50,000-100,00 bbl/day at a location in Qatar [25]. A significant number of patents (about 70) between 1980-1993 of Exxon deal with the development of new formulations of catalysts. Main emphasis is on cobalt and ruthenium-based catalysts. Recent licenses (after 1993) are also dealing with slurry-phase processes [26, 27].

Rentech Inc.

Rentech licenses an iron based catalyst [28] and a slurry phase process [29–31] for the production of high quality FT diesel. Rentech built 0.038 m and 0.15 m diameter slurry reactors on laboratory scale. A 1.8 m diameter and 16.7 m high slurry reactor producing 235 bbl/day was built in Pueblo, Colorado, U.S in 1992. Recently, this plant

was dismantled and transported to Arunachal, India where it is expected to produce 350 bbl/day of waxes in 1999 in cooperation with the Indian company Donyi Polo Petrochemicals Ltd.

Sasol

Sasol has operated commercial Fischer-Tropsch plants since 1955. A detailed review of Sasol's commercial plants from 1950 to 1979 is given by Dry [32]. A commercial plant in Sasolburg (South Africa) (Sasol 1) uses multitubular (2050 tubes, 50 mm ID) fixed bed and entrained bed Kellogg reactors. Synthesis gas is predominantly produced with Lurgi coal gasifiers. Sasol 2 and Sasol 3 plants in Secunda went on stream in the beginning of the eighties. These plants use circulating fluidized bed reactors (Synthol, Figure 1.4c) for the production of fuels and low molecular weight olefins. Currently, Sasol has two new processes for the Fischer-Tropsch synthesis. A process at high temperatures (HTFT: 330-350 °C) for the production of gasoline and light olefins and a process for wax production at lower temperatures (LTFT: 220-250 °C). The HTFT is performed in Synthol circulating fluidized bed (CFB) reactors, but a more efficient Sasol Advanced Synthol (SAS) reactor with gas-solid fluidization was developed recently [16]. The Synthol reactors will be replaced by the new SAS reactors. Conventionally, ARGE tubular fixed bed reactors were used for the LTFT process. In 1990, a slurry bubble column reactor (Sasol Slurry Phase Distillate; SSPD) with a diameter of 1 m was commissioned [15]. A commercial-scale slurry reactor is in operation since 1993 and has a diameter of 5 m and a height of 22 m with a capacity of about 2,500 bbl/day. Table 1.8 shows an overview of different Sasol reactors [15, 19]. Further scale up of the SSPD reactor is planned to 20,000 bbl/day per reactor.

Table 1.8 Sasol Fischer-Tropsch commercial reactors (bbl/day), adapted from Jager [19].

	CFB	SAS	ARGE	SSPD
Total installed capacity	110,000	11,000	3,200	2,500
Capacity per reactor	6,500	11,000	500-700	2,500
Potential per reactor	7,500	20,000	3,000	20,000

Phillips Petroleum, Sasol, and Qatar General Petroleum Corp. signed a memorandum of understanding to build a 20,000 bbl/day GTL plant at Ras Laffan, Qatar. The new complex will use Sasol's Slurry Phase Distillate Process. Start-up is planned for 2002 (Remote Gas Strategies, August 1998). Sasol and Chevron announced plans (May 1998) to build a 20,000 bbl/day GTL (Gas-To-Liquids) plant based on the SSPD

technology in Nigeria. The estimated cost price of this complex is \$ 500-600 million (Remote Gas Strategies, May 1998). Most patents of Sasol (see Table 1.6) concern the development of a slurry reactor with continuous in-situ wax-solid separation [33] and grade-up of olefins by hydroformulation [34].

Shell

In 1993, Shell started up a \$ 850 million FT synthesis plant in Bintulu, Malaysia. The Shell Middle Distillate Synthesis (SMDS) process [5, 35] produces heavy paraffins on a cobalt catalyst in multitubular trickle bed reactors. Part of these products are sold as wax specialties; another part is hydro-cracked over a noble metal catalyst into clean transportation fuels (see Table 1.5). The plant converts 100 million cubic feet/day of natural gas from off-shore fields by non-catalytic partial oxidation into 12,500 bbl/day hydrocarbons. The air separation plant of the SMDS plant in Bintulu exploded in December 1997. Shell Oil wants to reopen the SMDS plant in 1999 (Remote Gas Strategies, April 1998). Most Shell patents focus on either catalyst development or on the way the SMDS process is preferably carried out, for example, see patents [36, 37]. Some patents for improving a slurry process have been filed as well [38–40].

Statoil

Patents of Statoil involve slurry reactor design and continuous catalyst-wax separations with the use of filtration [41]. Recent patents with respect to Fischer-Tropsch catalysis concern the development of cobalt catalysts promoted with Rh, Pt, Ir, or Re on alumina (for example, [42]). Statoil formed an alliance with Sasol for the development of floating Fischer-Tropsch plants on ships or floating production systems. These floating off-shore plants can be used to utilize natural gas associated with oil production [43].

Syntroleum

Syntroleum is a small research firm in Tulsa, Oklahoma, USA, which has signed licensing agreements with Texaco, ARCO, Kerr-McGee, and Enron. A laboratory pilot plant (2 bbl/day) is used to demonstrate their FT process. They claim that their process eliminates a costly air separation unit, since their Autothermal Reformer (ATR) produces nitrogen-diluted synthesis gas from natural gas [44]. Nitrogen can be used to remove some of the generated heat during the FT reaction. The Syntroleum process is the basis of an agreement between Texaco, Brown & Root and Syntroleum to develop

a 2,500 bbl/day GTL plant, starting end 1999 (Remote Gas Strategies, January 1998). Recently, Syntroleum and Enron announced final agreement to build a 8,000 bbl/day GTL plant in Wyoming, USA. The plant is expected to operate in 2001 [45].

1.3 Research on the Fischer-Tropsch Synthesis

An optimal design with respect to product yield and selectivity of a large scale reactor requires a deep understanding of hydrodynamics, reaction kinetics, catalytic system and FT chemistry (see Figure 1.5). Research on the various aspects of the FT process will be discussed briefly. A detailed review on kinetics and selectivity of the Fischer-Tropsch process is given in Chapter 2.

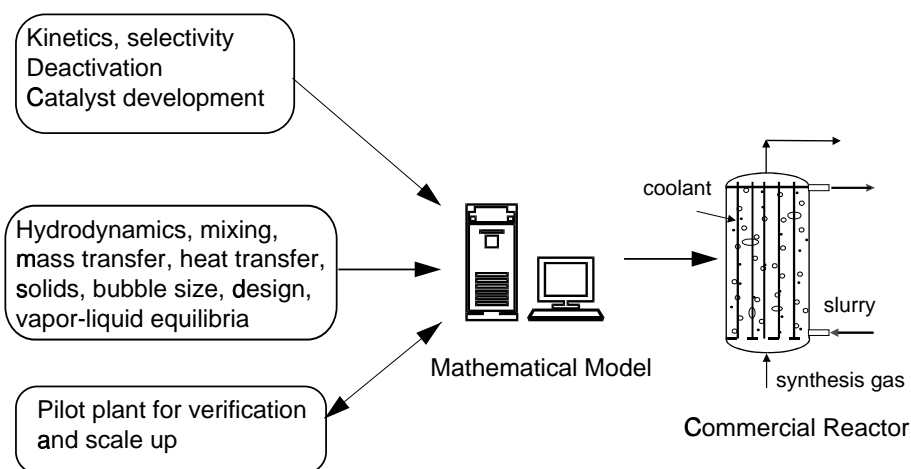


Figure 1.5 Modeling of a large scale Fischer-Tropsch reactor.

Reaction Kinetics

The complexity of the FT reaction mechanism and the large number of species involved is the major problem for development of reliable kinetic expressions. Most catalyst studies aim at catalyst improvement and postulate empirical power law kinetics for both the carbon monoxide conversions and the carbon dioxide formation rate [46, 47]. Langmuir-Hinshelwood-Hougen-Watson (LHHW) type of rate equations have been applied in literature (see Chapter 2.8). The water gas shift reaction can play a dominant role on iron catalysts. Only a few studies report on WGS kinetics on

iron catalysts under FT conditions. A thorough comparison of the available literature models is presented in Chapter 2.

Product Selectivity

The products from the Fischer-Tropsch synthesis form a complex multicomponent mixture with substantial variation in carbon number and product type. Main products are linear paraffins and α -olefins. According to Anderson [48], the product distribution of hydrocarbons can be described by the Anderson-Schulz-Flory (ASF) equation: $m_n = (1 - \alpha)\alpha^{n-1}$ with m_n the mole fraction of a hydrocarbon with chain length n and the growth probability factor α independent of n . α determines the total carbon number distribution of the FT products. The range of α depends on reaction conditions and catalyst type. Dry [49] reported typical ranges of α on Ru, Co, and Fe of: 0.85-0.95, 0.70-0.80, and 0.50-0.70, respectively. More recent references report Co catalysts with chain growth factors between 0.85-0.95 [5]. Significant deviations from the ASF distribution are reported in literature: i) Relatively high yield of methane. ii) Relatively low yield of ethene. iii) Change in chain growth parameter α and exponential decrease of the olefin to paraffin ratio with increasing carbon number. These deviations are predominantly caused by secondary reactions of α -olefins, which may readsorb on growth sites of the catalyst surface and continue to grow via propagation with monomer or terminate as hydrocarbon product. Details on the characteristics of the product selectivity and on modeling of the selectivity are discussed in Chapter 2.

Reactor Engineering Model

Mathematical modeling of FT slurry bubble columns was reviewed by Saxena et al. [17] and more recently by Saxena [50]. He showed that none of the available models is accurate enough for a reliable reactor design. The bottleneck appears to be the lack of reliable kinetic equations for all products and reactants based on realistic reaction mechanisms. Until now, none of the available literature models obtain enough details to describe the complete product distribution of the Fischer-Tropsch synthesis at industrial conditions (high temperature and pressure) as a function of overall consumption of synthesis gas components and operating conditions. Either the product distribution model (ASF behavior) or the kinetic scheme (no WGS and rates equations with first order in hydrogen) is oversimplified, or the hydrodynamic situation is unrealistic under industrial (churn-turbulent or heterogeneous flow regime) operating conditions. The features of the models available will be compared in Chapter 7.

1.4 Aims and Outline of this Thesis

The problem to be dealt with in this thesis is the lack of accurate models for product distributions and reaction kinetics, necessary for reliable design and scale up of industrial Fischer-Tropsch processes.

Therefore, the major aim of this thesis is the development of a product distribution model and a kinetic model both in gas-slurry as well as in gas-solid reactors over a commercial precipitated iron catalyst based on own experimental work. The product distribution model should be able to explain the deviations from the ASF distribution observed experimentally. It should include a mechanistic model of olefin readsorption and kinetics of chain growth and termination on the same catalytic sites. Accurate intrinsic rate expressions for the CO conversion to Fischer-Tropsch products and for the water gas shift (WGS) reaction over a precipitated iron catalyst on the basis of reliable mechanisms are another aim. A detailed multicomponent mathematical model for a large scale slurry bubble column reactor with use of our detailed models is the final aim of this thesis.

Chapter 2 presents a literature review on the kinetics and selectivity of the Fischer-Tropsch synthesis. The focus is on the reaction mechanisms and kinetic models of the water gas shift and Fischer-Tropsch reactions. Literature product selectivity models are reviewed as well. Here the areas which require further research will be defined.

Chapter 3 describes the experimental setup of the kinetic experiments both in a gas-solid and gas-slurry laboratory kinetic reactor and the catalyst applied. The analytical section and the experimental procedures are described as well.

The development of a new α -Olefin Readsorption Product Distribution Model (ORPDM) based on own experiments for the gas-solid FT synthesis, over a precipitated iron catalyst is presented in Chapter 4. The effect of variation of process conditions on the selectivity is described as well.

Chapter 5 presents the kinetic experiments and kinetic modeling of the CO hydrogenation and the water gas shift reaction of gas-solid Fischer-Tropsch synthesis over the precipitated iron catalyst.

The influence of the slurry liquid on the product selectivity and the reaction kinetics is presented in Chapter 6. The product selectivity model developed for the gas-solid system will be applied for the description of the product selectivity at industrially relevant conditions over a precipitated iron catalyst suspended in the slurry phase. Furthermore, Chapter 6 describes kinetic modeling of the gas-slurry Fischer-Tropsch synthesis based on a methodology derived in Chapter 5.

The models obtained in Chapters 4-6 and literature data on hydrodynamics and mass transfer in the heterogeneous flow regime are incorporated in a multicomponent reaction engineering model for a large scale Fischer-Tropsch slurry bubble column reactor in Chapter 7. The main novel aspect of this model is that, for the first time, multicomponent vapor-liquid equilibria with detailed kinetic expressions for all reactants and products (based on original experimental work) are combined to predict the compositions of the gaseous and liquid streams and the performance of a slurry bubble column reactor.

References

- [1] Kroschwitz, I.; Howe-Grant, M., *Kirk-Othmer encyclopedia of chemical technology*, Wiley & Sons, New York, fourth edn. **1996**.
- [2] Fischer, F.; Tropsch, H., Über die Herstellung synthetischer ölgemische (Synthol) durch Aufbau aus Kohlenoxyd und Wasserstoff, *Brennst. Chem.* **1923**, *4*, 276–285.
- [3] Fischer, F.; Tropsch, H., *German Patent 484337* **1925**.
- [4] Jager, B.; Espinoza, R., Advances in low-temperature Fischer-Tropsch synthesis, *Catal. Today* **1995**, *23*, 17–28.
- [5] Sie, S.T., Process development and scale up: IV Case history of the development of a Fischer-Tropsch synthesis process, *Rev. Chem. Eng.* **1998**, *14*, 109–157.
- [6] Choi, G.N.; Kramer, S.J.; Tam, S.T.; Fox, J.M., Design/economics of a natural gas based Fischer-Tropsch plant, in *Spring National Meeting*, American Institute of Chemical Engineers, Houston, 1996 .
- [7] Cybulski, A.; Edvinsson, R.; Irandoust, S.; Andersson, B., Liquid-phase methanol synthesis: modelling of a monolithic reactor, *Chem. Eng. Sci.* **1993**, *48*, 3463–3478.
- [8] Perry, R.H.; Green, D., *Perry's chemical engineers' handbook*, McGraw-Hill, New York, 6th edn. **1984**.
- [9] Basini, L.; Piovesan, L., Reduction on synthesis gas costs by decrease of steam/carbon and oxygen/carbon ratios in the feedstock, *Ind. Eng. Chem. Res.* **1998**, *37*, 258–266.
- [10] Rentech, Gas to liquids home page, <http://www.gastoliquids.com/tech2.htm> (accessed December 1998).
- [11] Rao, V.U.S.; Stiegel, G.J.; Cinquegrane, G.J.; Srivastave, R.D., Iron-based cat-

- alysts for slurry-phase Fischer-Tropsch process: Technology review, *Fuel Process. Technol.* **1992**, *30*, 83–107.
- [12] Xu, L.; Bao, S.; R.J., O'Brien; Raje, A.; Davis, B.H., Don't rule out iron catalysts for Fischer-Tropsch synthesis, *CHEMTECH* **1998**, *8*, 47–53.
- [13] Raje, A.P.; Davis, B.H., Fischer-Tropsch synthesis: process considerations based on performance of iron-based catalysts, *Fuel* **1997**, *76*, 273–280.
- [14] Udovich, C.A., Ceramic membrane reactors for the conversion of natural gas to syngas, *Stud. Surf. Sci. Catal.* **1998**, *119*, 417–422.
- [15] Jager, B., Developments in Fischer-Tropsch technology, *Stud. Surf. Sci. Catal.* **1997**, *107*, 219–224.
- [16] Jager, B.; Dry, M.E.; Shingles, T.; Steynberg, A.P., Experience with a new type of reactor for Fischer-Tropsch synthesis, *Catal. Lett.* **1990**, *7*, 293–302.
- [17] Saxena, S.C.; Rosen, M.; Smith, D.N.; Ruether, J.A., Mathematical modeling of Fischer-Tropsch slurry bubble column reactors, *Chem. Eng. Commun.* **1986**, *40*, 97–151.
- [18] De Swart, J.W.A., *Scale-up of a Fischer-Tropsch reactor*, Ph.D. thesis, University of Amsterdam, Amsterdam, The Netherlands **1996**.
- [19] Jager, B., Developments in Fischer-Tropsch technology, *Stud. Surf. Sci. Catal.* **1998**, *119*, 25–34.
- [20] Choi, G.N.; Kramer, S.J.; Tam, S.T.; Fox, J.M.; Carr, N.L.; Wilson, G.R., Design/economics of a once-through natural gas based Fischer-Tropsch plant with power co-production, in *Coal liquefaction and solid fuels*, Pittsburgh, 1997 .
- [21] Fox, III, J.M., The different catalytic routes for methane valorization: an assessment of processes for liquid fuels, *Catal. Rev.-Sci. Eng.* **1993**, *35*, 169–212.
- [22] Gregor, J.H., Fischer-Tropsch products as liquid fuels or chemicals. An economical evaluation, *Catal. Lett.* **1990**, *7*, 317–332.
- [23] Singleton, A.H., Advances make gas-to-liquids process competitive for remote locations, *Oil Gas J.* **1997**, 68–72.
- [24] Eisenberg, B.; Fiato, R.A.; Mauldin, C.H.; Say, G.R.; Soled, S.L., Exxon's advanced gas-to-liquids technology, *Stud. Surf. Sci. Catal.* **1998**, *119*, 943–948.
- [25] Davis, B.H., Fischer-Tropsch conversion of gas to liquid, *Appl. Catal. A* **1997**, *155*, N4–N7.
- [26] Behrmann, W.C.; Mauldin, C.H.; Pedrick, L.E., Patent WO 9414735 **1994**, Exxon.
- [27] Koros, R.B., US Patent 5384336 **1995**, Exxon.
- [28] Benham, C.B.; Bohn, M.S.; Yakobson, D.L., US Patent 5504118 **1996**, Rentech.

- [29] Benham, C.B.; Bohn, M.S.; Yakobson, D.L., US Patent 5620670 **1997**, Rentech.
- [30] Benham, C.B.; Bohn, M.S.; Yakobson, D.L., US patent 5621155 **1997**, Rentech.
- [31] Benham, C.B.; Bohn, M.S.; Yakobson, D.L., US Patent 5534437 **1996**, Rentech.
- [32] Dry, M.E., The Fischer-Tropsch synthesis, in J.R. Anderson; M. Boudart, eds., *Catalysis-Science and technology*, vol. 1, Springer-Verlag, New York, 1981 pp. 160–255.
- [33] Inga, J.R.; Jager, B.; Kelfkens, R.C.; Malherbe, F.E.J.; Smith, M.A.; Steynberg, A.P., Eur. Patent 609079, US patent 5599849 **1994**, Sasol.
- [34] Betts, M.J. Dry, M.E.; Geertsema, A.; Rall, G.J.H., Patent WO 9701521 **1997**, Sasol.
- [35] Sie, S.T.; Senden, M.M.G.; Van Wechum, H.M.H., Conversion of natural gas to transportation fuels via the Shell Middle Destillate Synthesis process (SMDS), *Catal. Today* **1991**, 8, 371–394.
- [36] Bode, D.; Sie, S.T., Eur. Patent 188304 **1986**, Shell.
- [37] Post, M.F.M.; Sie, S.T., Eur. Patent 167215 **1984**, Shell.
- [38] Engel, D.C.; Van der Honing, G., Patent WO 9731693 **1997**, Shell.
- [39] Wijn, E.F.; Danckaerts, A.M., Eur. Patent 694325 **1996**, Shell.
- [40] McEwan, M.W.; Teekens, M.B., US Patent 694325 **1978**, Shell.
- [41] Lorentzen, G.B.; Myrstad, T.; Westvik, A., US Patent 5520890 **1995**, Statoil.
- [42] Eri, S.; Goodwin, J.G.; Marcelin, G.; Riis, T., US Patent 4801573 **1989**, Statoil.
- [43] Statoil, Press release April 14, **1997**.
- [44] Agee, K.L.; Willingham, F.Y., WO Patent 9733847 **1997**, Syntroleum.
- [45] Syntroleum, Press release February 24, **1998**.
- [46] Bub, G.; Baerns, M., Prediction of the performance of catalytic fixed bed reactors for Fischer-Tropsch synthesis, *Chem. Eng. Sci.* **1980**, 35, 348–355.
- [47] Newsome, D.S., The water-gas shift reaction, *Catal. Rev.-Sci. Eng.* **1980**, 21, 275–318.
- [48] Anderson, R.B., *Catalysts for the Fischer-Tropsch synthesis*, vol. 4, Van Nostrand Reinhold, New York **1956**.
- [49] Dry, M.E., Catalytic aspects of industrial Fischer-Tropsch synthesis, *J. Mol. Catal.* **1982**, 17, 133–144.
- [50] Saxena, S.C., Bubble column reactors and Fischer-Tropsch synthesis, *Catal. Rev.-Sci. Eng.* **1995**, 37, 227–309.