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THE DIRECT CONVERSION OF SYNTHESIS GAS TO CHEMICALS

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DECLARATION

I declare that the work presented in this thesis is the result of my own endeavours, except where otherwise indicated. It has not been submitted before for any degree or examination at any other university.

Ernest Du Toit

December 2002

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ABSTRACT

The catalytic conversion of synthesis gas, obtainable from the processing of coal, biomass or natural gas, to a complex hydrocarbon product stream can be achieved via the Fischer-Tropsch process. The Fischer-Tropsch synthesis process has evolved from being mainly a fuel producing process in the early 1950's to that of a solvent and speciality wax production process towards the end of the 1970's. From the early 1980's there has been a clear shift towards the production of commodity chemicals in addition to fuel.

Advances in reactor technology, volatile crude oil markets and a world trend towards "clean" fuels may cause a shift towards coal and natural gas as the feedstock of choice for the chemical industry. Fischer-Tropsch plants are capital intensive ventures due to the complexity of the process. Viable returns on such projects can only be realised by adding value to the products obtained from such processes. The chemical industry places a high premium on certain chemicals such as olefins and higher alcohols. More selective production of such chemicals can contribute to increased profitability and thus more economically viable processes. The C_8+ alcohol and C_6+ olefin product range can be labelled as valuable chemicals. A major limitation in the traditional Fischer-Tropsch process is the low selectivity towards these valuable chemicals. The product distribution observed for a Fischer-Tropsch catalyst system conforms to the Schulz-Flory polymerisation mechanism, which is inherently non-selective.

This investigation deals with an iron-based catalyst that can best be described as a chemically selective Fischer-Tropsch catalyst. The product spectrum achieved with this so-called "ChemFT" catalyst can be seen as a breakthrough in terms of producing chemicals directly from syngas.

The investigation covers the following aspects:

- a review of the development of the ChemFT catalyst used in this investigation,
- the characterisation of the ChemFT catalyst,
- an experimental verification of the catalyst product spectrum with respect to alcohols and olefins, on both laboratory and pilot plant scale,
- the development of rate equations for Fischer-Tropsch and Water-Gas-Shift activity.

Experimental performance results of the ChemFT catalyst show high selectivity towards the desired alcohol product compared to traditional low temperature iron catalysts (8 – 14 C atom % vs. 2 – 4 C atom %). Similar olefin selectivity is obtainable with lower long chain paraffin selectivity (little or no wax formation). It is concluded that the ChemFT catalyst differs from conventional Fischer-Tropsch iron catalysts as far as selectivity and typical process conditions are concerned. Published reaction rate equations were evaluated for applicability to such a scenario. Known Fischer-Tropsch reaction rate equations described the catalyst kinetics fairly well. The theoretical base thereof was further improved by modifying the equations to include the effect of catalyst vacant sites. Published Water-Gas-Shift rate equations did not adequately describe the catalyst. It was shown that the accuracy of the Water-Gas-Shift equation could be improved by modifying it to account for CO_2 adsorption. Reaction rate equations for both the Fischer-Tropsch and Water-Gas-Shift reaction rates that are valid in the typical operating conditions are proposed.

OPSOMMING

Die Fischer-Tropsch proses kan gebruik word vir die katalitiese omsetting van sintese gas verkry vanaf die prosessering van steenkool, natuurlike gas of bio-massa, na 'n komplekse koolwaterstof produkstroom. Die Fischer-Tropsch sintese proses het ontwikkel vanaf 'n brandstof produserende proses in die vroeë 1950's tot een wat oplosmiddels en spesialiteits wasse produseer teen die einde van die jare 70's. Vanaf die vroeë 1980's was daar 'n duidelike beweging na die produksie van kommoditeits chemikalië addisioneel tot die produksie van brandstof.

Vooruitgang op die gebied van reaktor tegnologie, wisselvallige ru-olie markte en 'n wêreldwye tendens na "skoon" brandstowwe kan 'n dryfveer wees vir die gebruik van steenkool en natuurlike gas as grondstowwe vir die chemiese industrie. Fischer-Tropsch aanlegte is as gevolg van hul kompleksiteit groot kapitale ondernemings. Aanvaarbare opbrengste kan dus slegs verkry word vanaf die proses indien waarde toegevoeg kan word tot die produkte wat tydens die proses geproduseer word. Chemikalië soos olefiene en hoër alkohole haal hoë pryse in die chemiese industrie. Selektiewe produksie van hierdie chemikalië kan dus bydra tot verhoogde winsgrense en dus tot meer ekonomiese prosesse. Die C_8+ alkohol en C_6+ olefien produkfraksies kan gesien word as sogenaamde waardevolle chemikalië. Die produksie van hierdie waardevolle chemikalië is egter beperk in die tradisionele Fischer-Tropsch prosesse. Produk verspreidings van die Fischer-Tropsch katalitiese sisteme volg die Schulz-Flory polimerisasie meganisme wat inherent nie-selektief is.

Hierdie ondersoek handel oor 'n yster-basis katalisator wat beskryf kan word as 'n Fischer-Tropsch katalisator wat selektief is vir die produksie van chemikalië. Die produkspektrum verkry met behulp van hierdie "ChemFT" katalisator kan gesien word as 'n deurbraak in Fischer-Tropsch katalisator tegnologie in terme van die produksie van chemikalië direk vanaf sintese gas.

Die ondersoek dek die volgende aspekte:

- 'n oorsig van die ontwikkeling van die ChemFT katalisator,
- die karakterisering van die ChemFT katalisator,

- 'n eksperimentele verifikasie van die produkspektrum in terme van alkohol en olefien selektiwiteit op beide laboratorium en loodsaanleg skaal,
- die ontwikkeling van reaksie-tempo vergelykings vir beide die Fischer-Tropsch en Water-Gas-Skuif aktiwiteit van die ChemFT katalisator,

Eksperimentele resultate verkry met die ChemFT katalisator toon 'n produkspektrum met 'n hoë selektiwiteit tot die gewenste alkohol produkte in vergelyke met tradisionele lae temperatuur yster katalisatore (8 – 14 C atoom % vs. 2 – 4 C atoom %). Soortgelyke olefien selektiwiteite is verkry met minder langketting paraffien selektiwiteit. Daar is dus afgelei dat die ChemFT katalisator verskil van konvensionele Fischer-Tropsch Fe katalisatore betreffende die selektiwiteit en tipiese proseskondisies. Gepubliseerde kinetiese vergelykings is geëvalueer vir hul toepaslikheid. Gepubliseerde Fischer-Tropsch vergelykings kan die data redelik goed beskryf, hoewel die teoretiese grondslag daarvan verbeter kan word indien die effek van vakante katalisator oppervlaktes in berekening gebring word. Gepubliseerde Water-Gas-Skuif kinetiese vergelykings beskryf nie die katalisator voldoende nie. 'n Verbetering in die Water-Gas-Skuif vergelyking is gevind, indien die vergelyking aangepas is om voorsiening te maak vir CO_2 adsorpsie. Kinetiese vergelykings, wat geldig is in die ChemFT bedryfgebied, is vir beide die Fischer-Tropsch en Water-Gas-Skuif reaksies voorgestel.

RESUMÉ

The conversion of synthesis gas, which is a mixture of mainly CO and H_2, to a complex hydrocarbon product stream can be achieved via the Fischer-Tropsch (FT) process. Synthesis gas can be obtained from the processing of coal, natural gas or biomass. The following reactions can take place during the Fischer-Tropsch synthesis:

Prominent reactions	
• Paraffins	$(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$
• Olefins	$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O$
• Water-gas-shift reaction	$CO + H_2O \leftrightarrow CO_2 + H_2$
Less prominent reactions	
• Alcohol	$2nH_2 + nCO \rightarrow C_nH_{2n+2}O + (n-1)H_2O$
• Boudouard reaction	$2CO \rightarrow C + CO_2$
• Acids, ketones and aldehydes	Secondary reactions
Catalyst modifications	
• Catalyst oxidation/reduction	(a) $M_xO_y + yH_2 \leftrightarrow yH_2O + xM$
	(b) $M_xO_y + yCO \leftrightarrow yCO_2 + xM$
• Bulk carbide formation	$yC + xM \leftrightarrow M_xC_y$

FT synthesis was first practised on a commercial scale during World War 2 by Germany to provide for the fuel need. These plants were however shut down after the war due to unfavourable economics. Since then FT synthesis always came to the forefront when fears of crude oil shortages or high crude prices appeared. Earlier, plants such as that of Sasol constructed in the 1950's to produce fuel from coal reserves survived low crude prices by additionally producing high-priced FT waxes. The FT synthesis process evolved from a fuel supplying process to that of wax production in addition to fuel and towards the end of the 1970's, and early 1980's to a fuel production process with the additional production of commodity chemicals.

Towards the end of the 20 th century, FT technology had seen advances in the reactor technology used for slurry bed and fixed bed operation for low temperature and fluidised bed operation for high temperature FT. Examples of such development are the Sasol slurry phase and the Sasol advanced Synthol reactors. This together with volatility experienced in the crude oil markets and a world trend towards "clean" fuels could be a trigger for a shift towards coal and natural gas as the feedstock of the chemical industry.

Fuels derived from the FT process are low in sulphur and aromatic components. FT gas-to-liquid technology utilising natural gas has thus seen an upsurge of interest with a number of plants planned to be built in the very near future. FT plants are high capital ventures due to the complexity of the process. Viable returns on such projects can only be obtained by adding value to the products obtained from such processes. The chemical industry places a high premium on certain chemicals such as olefins and higher alcohols. More selective production of such chemicals can therefore contribute to increased profitability and thus more economically viable processes if prices of these products during 2000 are compared to that of fuel currently obtained from the same process (see Figure 1).

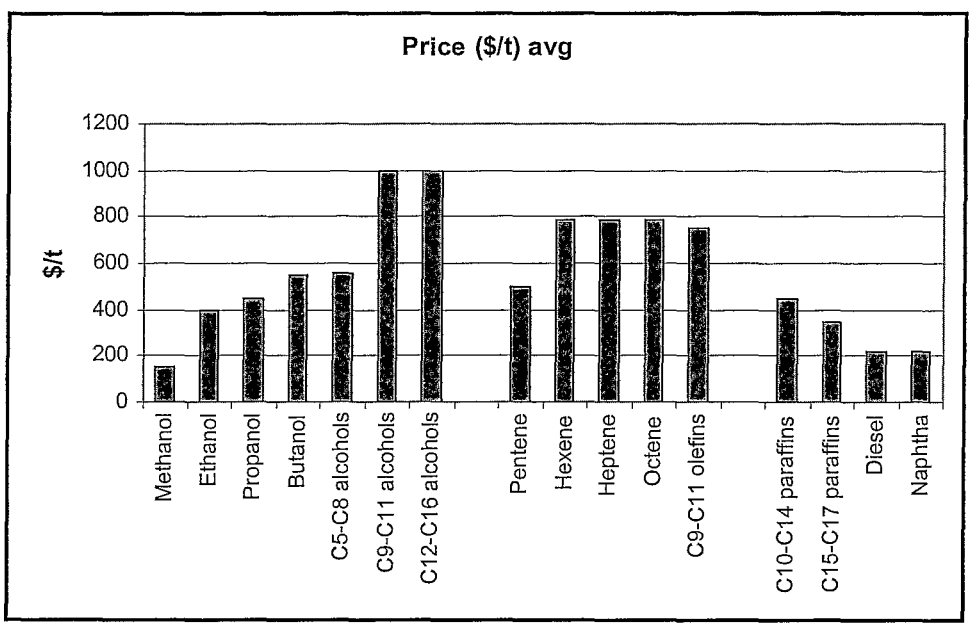

Figure 1: Product price comparison for the year 2000

From Figure 1 it can be seen that the C_8+ alcohol and C_6+ olefin product range can be labelled as valuable chemicals. However the FT product spectrum is a complex multi-component mixture of linear and branched hydrocarbons and oxygenated products such as alcohols and acids. Main products are linear paraffins and 1-olefins. A major limitation in the traditional FT process is the low selectivity towards the valuable chemicals. The product distribution observed for a variety of catalyst systems and under a variety of reaction conditions conforms to the Schulz-Flory polymerisation equation, which is inherently non-selective.

Innovative efforts are put into the development of FT catalysts to improve selectivity, the understanding and modelling of the kinetics involved, and improvement of the yields obtained. The development of a catalyst, which will be able to manipulate the products obtained from the FT process, in such a way that it will mainly produce valuable chemicals such as olefins and higher alcohols, will result in an enhancement of the product value.

The role of the alcohol formation reaction (normally seen as less prominent) will have to be seen as important relative to that of the olefin reaction, if one aims to produce alcohols in similar or greater quantities to that of the olefins. Currently used kinetic and selectivity equations might not fully describe a catalyst with the above-mentioned product spectrum.

This investigation therefore deals with an iron-based FT catalyst with the characteristics of being a valuable chemical selective catalyst. This catalyst is described as a "ChemFT" catalyst to differentiate it from traditional FT catalysts. The product spectrum achieved with this specific catalyst at selected operating conditions can be seen as a breakthrough in terms of producing valuable chemicals directly from synthesis gas.

An overview of the development of the new catalyst together with the characterisation of the ChemFT catalyst developed for the production of alcohols and olefins are given. An overview of some of the relevant literature and/or patents available on traditional Fischer-Tropsch catalysts and the product spectra associated with them is given, while the role of different promoters as found in literature is discussed in an effort to show that by understanding their role it should be possible to formulate a catalyst with desired activity and selectivity.

There are very few references to the simultaneous optimisation of the alcohol and olefin selectivity in the open literature. The overview was thus divided into catalysts with the aim of optimising the alcohol content and those aimed at optimising the olefin content of the synthesis product. Product selectivity is not only determined by the catalyst, but also the operating conditions such as temperature, pressure and space velocity. An experimental verification of the catalyst product spectrum is given at different operating conditions. The product selectivity is also verified on a pilot plant scale, where the effect of scale-up parameters on product selectivity is discussed.

The catalyst produces a product spectrum much narrower than normally associated with low temperature Fe based catalysts. The products are clean from the point of view that a high percentage of products are the linear 1-product with very little branching. For the $C_5 - C_{12}$ product fraction obtained at similar conversion levels the ChemFT catalyst has half the amount of internal olefin product and more than double the selectivity towards the desired alcohol product compared to traditional low temperature Fe catalysts (8-14 C atom % vs. 2 – 4 C atom %). Similar olefin selectivity is obtainable with much lower long chain paraffin selectivity (little or no wax formation), while the secondary olefinic products are mostly linear products.

It is shown that the catalyst possesses a degree of flexibility relating to operating conditions. By manipulating the operating temperature and pressure it is possible to increase the selectivity towards olefins and alcohols. The ChemFT process would fit in-between traditional high temperature and low temperature iron catalyst FT processes, taking into account the operating conditions (240°C and 20 – 65 bar(g)) and product selectivity.

It was concluded that the ChemFT catalyst differs from the conventional FT iron catalysts as far as selectivity and typical process conditions are concerned. It was thus anticipated that the known FT iron rate equations would not be adequate for this specific catalyst.

FT and Water-Gas-Shift (WGS) kinetics of the ChemFT catalyst developed for the production of alcohols and olefins are investigated. Literature considered to be relevant to the topic of Fe catalyst kinetics is reviewed. A large amount of literature is available on the topic of FT catalysts and their associated rate equations. Known rate equations have evolved from simple first order rate equations to complex equations which accommodates a wide range of operating conditions and catalyst behaviour.

Equations are either empirically formulated or derived by making use of the Langmuir-Hinshelwood-Hougen-Watson (LHHW) kind of equations. The formulation will normally start off from assuming one of the proposed mechanisms for the FT reaction, i.e. the carbide theory, enolic theory or the direct insertion theory. Further optimisation of the derived equations would depend on assumptions such as the degree in which the various reactants or products inhibit the observed reaction rate. It would appear throughout the literature that the researchers use an approximation for the FT synthesis of the combination of the simultaneous series-parallel reactions of the FT reaction and the WGS reaction. Generally the effect of small amounts of oxygenated products, primarily alcohols, and the CO_2 formed by the Boudouard reaction are neglected.

The application of the FT synthesis as a chemical production process with the primary aim of producing alcohols and olefins thus posed a situation where the now large amounts of oxygenated products are produced. It might not be possible to neglect these oxygenates any longer. Published rate equations are evaluated for their applicability to such a scenario. Rate equations for both the FT and WGS reaction rates that were valid in the typical operating conditions were proposed from modifying published equations to include the effect of catalyst vacant sites:

Fischer-Tropsch:

$$r_{FT} = \frac{k_o.e^{(-E_{FT}/RT)}.P_{H_2}{}^{\gamma}P_{CO}}{1+aP_{CO}}$$

$k_o = 58.84 \pm 2.94$ mol/gcat/s/bar^{A+1}

$a = 1.09 \pm 0.05$

$\gamma = 0.7$

Water-Gas-Shift:

$$r_{WGS} = \frac{k_o'.e^{(-E_{WGS}/RT)}.(P_{H_2O}P_{CO} - P_{CO_2}P_{H_2}/K_p)}{(1+a'P_{CO} + b'P_{H_2O} + c'P_{CO_2})^2}$$

$k_o' = 419.2 \pm 20.9$ kmol/gcat/s/bar^2

$a' = 0.98 \pm 0.05$

$b' = 1.19 \pm 0.06$

$c' = 0.54 \pm 0.03$

Activation energies calculated for both reactions (E_{FT} = 77 ± 4 kJ/mol and E_{WGS} = 101 ± 5 kJ/mol) agree well with those reported in literature, and show that the influence of mass transfer is minimal. Evaluation of the FT rate equations showed that the best-suited equations were all based on hydrogen dependency and can thus easily simplify to a first order equation for the dependence on hydrogen partial pressure. This observation is in line with literature reports of

hydrogen dependence at lower conversion levels. The final proposed rate equation does however include terms for CO and catalyst vacant site inhibition.

WGS reaction kinetics is a function of H_2O, CO and CO_2 inhibition. The proposed rate equation takes all of these into account. The presence of different terms and adsorption coefficient values in the FT and WGS rate equation denominators, give strong support towards proving that the two reactions occur on different catalytic sites.

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NOMENCLATURE

Abbreviations

APG	Arge Pure Gas
CFB	Circulating Fluidised Bed
ChemFT	Chemical selective FT catalyst
CSTR	Continuous Stirred Tank Reactor
FID	Flame Ionisation Detector
FT	Fischer-Tropsch
FTS	Fischer-Tropsch Synthesis
GC	Gas Chromatograph
GHSV	Gas Hourly Space Velocity (ml_n/gcat/h)
GRG	Generalised Reduced Gradient
HTFT	High Temperature Fischer-Tropsch
IPF	Institut Francais du Petrole
LHHW	Langmuir-Hinshelwood-Hougen-Watson
LTFT	Low Temperature Fischer-Tropsch
NAC	Non Acid Component
RMSE	Root Mean Square Error
SAS	Sasol Advanced Synthol
SSBR	Sasol Slurry Bed Reactor
TCD	Thermal Conductivity Detectors
TEM	Transmission Electron Microscopy
TFBR	Tubular Fixed Bed Reactor
TGA	Thermal Gravimetric Analysis
TPR	Temperature Programmed Reduction
WGS	Water Gas Shift

Symbols

a	Kinetic parameter for FT reaction rate equation	[-]
a'	Kinetic parameter for WGS reaction rate equation	[-]
A	pre-exponential factor of Arrhenius equation	[mol/(gcat.s.bar$^{(x')}$)]
A_i^{TCD}	Peak area count of component i in the TCD spectra	[-]
$A_i^{TCD,C}$	TCD peak area count of component i in the calibration gas	[-]
b	Kinetic parameter for FT reaction rate equation	[-]
b'	Kinetic parameter for WGS reaction rate equation	[-]
c	Kinetic parameter for FT reaction rate equation	[-]
c'	Kinetic parameter for WGS reaction rate equation	[-]
e	Number of optimised parameters	[-]
E_A	Activation energy	kJ/mol
E_{FT}	Fischer-Tropsch activation energy	kJ/mol
E_{WGS}	Water-gas-shift activation energy	kJ/mol
f	Number of data points included	[-]
k	Reaction rate constant	[mol/(gcat.s.bar$^{(x)}$)]
k_o	Rate constant in ideal state for FT reaction	[mol/(gcat.s.bar$^{(x)}$)]
k_o'	Rate constant in ideal state for WGS reaction	[mol/(gcat.s.bar$^{(x)}$)]
k_{FT}	Reaction rate constant of FT reaction	[mol/(gcat.s.bar$^{(x)}$)]
k_{WGS}	Reaction rate constant of WGS reaction	[mol/(gcat.s.bar$^{(x)}$)]
K_i	Equilibrium or adsorption constant	[-]
K_p	Equilibrium constant of the WGS reaction	[-]
m	Average number of hydrogen atoms per hydrocarbon molecule	[-]
M	Mass of unreduced catalyst	g
M_i	Metal i	[-]
n	Carbon number	[-]
n	Average carbon chain length for hydrocarbon products	[-]
n_i^T	Total molar flow rate of component i	mol/s.
$n_i^{T,IN}$	Total feed flow of component i	mol/s
$n_i^{T,OUT}$	Total out flow of component i	mol/s
P	Pressure	bar
P_i	Partial pressure of component i	bar

P_i^C	Quantity of i in the reference gas	mol %
r	Reaction rate	mol/gcat/s
r_{FT}	FT reaction rate	mol/gcat/s
r_k	Rate of the elementary reaction k	mol/gcat/s
r_{WGS}	Water gas shift reaction rate	mol/gcat/s
R	Gas constant	8.314 J/mol/K
S_{rel}	Relative variance	[-]
T	Temperature	K
W_n	Weight fraction of product containing *n* carbon atoms	[-]
x	average carbon chain length for alcohol products	[-]
y	Average number of hydrogen atoms per alcohol molecule	[-]

Greek letters

α	Chain growth parameter	[-]
ζ	Fraction of H_2O converted by the WGS reaction	[-]
θ_I	Surface fraction occupied by component i	[-]
Λ_i	mol of component i formed per second	mol/s
σ_i^2	Relative variance of the experimental selectivities	[-]
Φ	Catalytic site	[-]
Φ_1	Active site for FTcatalytic reaction	[-]
Φ_2	Active site for WGS catalytic reaction	[-]
$\acute{O}_i$	Mol of component i converted per second	mol/s
χ^2	Function to optimise	[-]

Superscripts and Subscripts

C	Reference / calibration gas
i	Component, data point index
k	Reaction index
o	Ideal state
T	Total
TCD	Relate to the TCD spectra

T,IN	Total relative to feed stream
T,OUT	Total relative to outlet stream
γ	Exponential constant
λ	Exponential constant
Φ_1	FTcatalytic site
Φ_2	WGS catalytic site
‘	Refer to the WGS reaction