



STUDY OF THE SELECTIVITY TO LIGHT HYDROCARBONS IN FISCHER-TROPSCH SYNTHESIS

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DECLARATION

I declare that this thesis is my own unaided work. It is being submitted for the Degree of Doctor of Philosophy to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

_____ on this ____ day of _____

(Candidate)

ABSTRACT

Many reports in the open literature have focused on Fischer-Tropsch (FT) kinetics, yet none of them appear to be able to explain FTS completely. Few of the FT models consider the production of olefins and paraffins separately. To study whether the selectivity to olefins and paraffins follows similar trends and if kinetics alone suffices to explain FT phenomena, a series of FT experiments were conducted in a fixed bed reactor loaded with 10% Co/TiO₂. FT feeds were periodically switched from syngas to syngas + N₂ by adjusting the total reactor pressure so that the reactant partial pressures (P_{CO} and P_{H_2}) remained constant.

During the initial deactivation (the first 1200 hours), it was found that the formation rates of olefins remained fairly constant (in some cases they increased) while those of paraffins decreased. This indicates the deactivation is mainly caused by the decrease in the paraffin formation rate. Currently, none of the published kinetic models can explain the phenomenon that the decay of the reaction rates of olefins and paraffins were not the same during the deactivation. At steady state (1055 to 2700 hours, overall reaction rate fairly constant), adding extra N₂ decreased the selectivity to the light hydrocarbons. These results suggest that by feeding the extra N₂ there could be an increase in selectivity and formation rates to long chain hydrocarbons (C₅₊).

Plotting molar ratios of paraffin to olefin (P/O) with carbon number $n+1$ versus the ratio with carbon number n revealed linear relationships which are independent of feed gases, catalyst activity and reaction temperature. These results imply that product distributions might be determined by some sort of equilibrium. Another plot of normalised mole fractions of C_{*n*}H_{2*n*}, C_{*n*+1}H_{2*n*+2}, and C_{*n*}H_{2*n*+2} in ternary diagrams showed that after disturbances these product distributions tended to stable points. It is suggested that this could be due to slow changes in the liquid composition after the disturbances.

Although not all the results are explained, the researcher emphasises that normal kinetics alone cannot explain these results completely. There might be factors,

including vapour-liquid equilibrium or reactive distillation, which are worthy of consideration to explain FTS.

DEDICATION

To my family, future wife and children

To my late mother Muleka wa Mukena mwana Lusa

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PRESENTATIONS AND PUBLICATIONS

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LIST OF ABBREVIATIONS, NOMENCLATURES AND SYMBOLS

abs	Absolute
Afrox	African Oxygen Limited
AIChE	American Institute of Chemical Engineers
ASF	Anderson–Schultz–Flory
bbl/day	barrels per day
BET	Brunauer–Emmett–Teller
BRICS	Brazil Russia India China South Africa
BTL	Biomass to liquid
CFB	Circulating fluidised bed reactor
Co	Cobalt
CO	Carbon monoxide
CSTR	Continuous stirred-tank reactor
CTL	Coal to liquid
EDS	Energy dispersive X-ray spectroscopy
EDTA	Ethylenediaminetetraacetic acid
EELS	Electron energy loss spectroscopy
EXAFS	Extended X-ray absorption fine structure
FBR	Fixed bed reactor
Fe	Iron
FFD	Fixed fluidized bed reactor
FID	Flame ionisation detector
FR	Flow rate
FT	Fischer-Tropsch
FTIR	Fourier transform infra-red
FTS	Fischer-Tropsch synthesis
GC	Gas chromatograph
GTL	Gas to liquid
H ₂	Hydrogen
HTFT	High temperature Fischer-Tropsch
ICCT	International Conference on Chemical Thermodynamics

ICP	Inductively coupled plasma
ID	Internal diameter
LPG	liquefied petroleum gas
mL/min	Millilitre per minute
mol/min	Mole per minute
n	Carbon number
N ₂	Nitrogen
NMF	Normalised mole fractions
NTP	Normal temperature and pressure
OD	Outside diameter
P	Pressure
P&ID	Piping and instrumentation diagram
PetroSA	The Petroleum Oil And Gas Corporation of South Africa
RHS	Right hand side
S	Syngas
S+N ₂	Syngas + nitrogen
SA	Surface area
SAIChE	South African Institution of Chemical Engineers
SASOL	South African Coal, Oil and Gas Corporation
SEM	Scanning electron microscopy
T	Temperature
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
TGA	Thermo gravimetric analysis
TOS	Time on stream
TPR	Temperature-programmed reduction
UHP	Ultra high purity
VLE	Vapour-liquid equilibrium
WCST	World Congress on Sustainable Technologies
WGS	Water-gas shift
W _n	Mass fraction of the species with carbon number n
XPS	X-ray photoelectron spectroscopy

XRD	X-ray diffraction
α	Chain growth probability
β	Variation of the vapour pressure coefficient
μm	Micrometre

CHAPTER 1

INTRODUCTION

1.1 Problem statement and justification of the study

Transportation fuel is a valuable and indispensable commodity in the modern world. Fuels for sea, air and land transportation are produced from hydrocarbons. These hydrocarbon sources include crude oil and Fischer-Tropsch (FT) syncrude. Fischer-Tropsch synthesis (FTS) is a process used for the production of synthetic fuels from synthesis gas (syngas) through a metal catalyst. Syngas, a mixture of carbon monoxide and hydrogen, can be obtained from several sources like coal, natural gas or recently even biomass. In comparison, FT syncrude is environmentally more friendly than crude oil for the production of transportation fuels [1,2].

For the past decade increased interest in synthetic fuels (synfuels) has been caused by a number of factors [1-6] including: syncrude has inherently better properties than crude oil for the production of transportation fuel; increasing world demand for fuels (seeking an alternative fuel route for energy security); the clean burning nature of synfuels due to the absence of impurities and in particular sulphur (new environmental constraints for low sulphur, clean fuels); increasing desire to monetize stranded gas reserves as energy prices rise; the growing interest in producing renewable, environmentally sustainable fuel from the gasification of nonedible biomass and co-production of electricity and fuels in FutureGen. The conversion of syngas to hydrocarbon products represents a potentially attractive alternative to petroleum-derived fuels and chemicals.

FT products depend on the type of catalyst, feed composition, reactor and operating conditions used. The catalyst is crucial in FT processes and once the catalyst is deactivated there is a strong possibility that the activity and selectivity to the FT products will be affected. Previous work is discussed in Chapter 2 of this

thesis. These studies have reported on the overall catalytic activity before, during and after deactivation. Only limited results have been published on the formation rate and selectivity to olefins and paraffins during catalyst deactivation.

Furthermore, the FT products rely on the feed content in the reactor. One of the factors that needs to be addressed is to better understand the FT products after other molecules (organic and inorganic) have been co-fed with the syngas during the FT process. These are addressed in the survey presented in Chapter 2 of this thesis. Researchers [7-12] have carried out FT investigations on syngas diluted with nitrogen with much of the work done by Jess and co-workers [13-15]. They have shown that FTS with nitrogen-rich syngas could be an alternative to classical processes because the investment costs are probably lower. The majority of these experiments have been conducted with constant total pressure, which resulted in the reactant partial pressures (P_{CO} and P_{H_2}) varying. Now the question is: if nitrogen is co-fed to syngas while keeping P_{CO} and P_{H_2} unchanged by adjusting the total pressure and flow rate, how will the overall FT activity, the formation rate and selectivity to light olefins and paraffins be affected?

Although FTS products are useful, it is usually more profitable to obtain less light hydrocarbons such as methane and oxygenate products, which are often undesirable. It has been reported that the commercialization of the FT technology suffers from two of the major limitations. These are limited selectivity for the main products and catalyst deactivation [16]. Cobalt-based catalysts are only used in the low temperature Fischer-Tropsch (LTFT) process as at the higher temperatures excess CH_4 is produced [17]. LTFT was originally performed in tubular fixed bed reactors (FBR) [18]. In this investigation both cobalt-based catalyst and FBR will be used with LTFT. It is evident that the formation and distribution of the FT products are very sensitive to the types of catalysts used as well as the feed content. Methane can be used as a source of fuels production and chemicals [19] via the FT process but as mentioned before such FTS processes are generally not profitable. Thus methane is usually considered an undesirable product in the FT process. An interesting question is whether co-feeding nitrogen to syngas during FT processes can reduce the amount of methane produce.

In addition, data from the literature reveal that the FT product formation and distributions are often analysed as a function of time on stream, carbon number, olefin to paraffin ratio and CO conversion, to mention just a few. Interesting novel correlations have been published [20,21] where firstly, the molar ratio of paraffin to olefin of length $n+1$ are plotted as a function molar ratio of paraffin to olefin of length n , and secondly, ternary plots of normalised mole fractions of 3 paraffins and olefins of similar lengths. Considering the FT features such as reactant conversions and selectivity, and FT reaction conditions, e.g. temperature, pressure, flow rate and feed content the present author wanted to compare his results with those of the previous authors, and to see whether their results are more generally applicable.

From the literature it is known that the environment in which FTS operates renders the mechanism and thermodynamic studies of the FT reaction very complicated. The FT reaction is usually regarded as kinetically controlled, as opposed to thermodynamically controlled, due to simulations having shown that thermodynamically methanation is preferred to heavy product formation [22]. This researcher intended to expand on previous results from his research group, which indicated that the overall product distribution is possibly thermodynamically affected [22,23]; the product distribution might be determined by considering reaction equilibrium [21,22]; and finally the olefin distribution in the FTS reaction might be determined by thermodynamics [22,24]. The application of FT technology involves a number of compromises and optimizations [25] it is therefore evident that further investigations on FT processes are still warranted, particularly on the above mentioned FT features. For the purpose of this study, the researcher set three main objectives.

1.2 Objectives of the study

The three main objectives of this study are:

- To investigate the effect of catalyst deactivation on the formation rate of light olefins and paraffins, also on the selectivity to light paraffins and olefins.

- To investigate the effect of co-feeding nitrogen into a fixed bed FT reactor on the catalytic activity, formation rate and selectivity to the light paraffins and olefins by adding extra nitrogen and changing the total pressure in proportion in order to keep the partial pressures of the reactants (CO and H₂) as well as the molar flow rates of reactants at the reaction conditions fairly constant.
- To analyse the results using different kinds of plots to find out if the products only follow fundamental reaction behaviour, or whether there are other factors which play an important role in determining the apparent kinetics.

1.3 Thesis outline

The thesis outline gives a brief description of what will be discussed in the chapters that follow.

Chapter 2 (Literature review): This chapter gives background information on the literature on FTS, which includes history and development, catalysts, reactors, reaction processes, co-feeding, kinetics and mechanism, product distributions and vapour-liquid equilibrium (VLE) in FTS.

Chapter 3 (Experimental methodology): This chapter describes the method for the preparation of the catalyst, the experimental procedures and techniques used in this study. The methods used to analyse and calculate the experimental results are also stated and explained.

Chapter 4 (Fischer-Tropsch synthesis: a study on the deactivation of a titania based cobalt catalyst): This chapter investigates the effect of catalyst deactivation on the formation rate and selectivity of olefin and paraffin products separately during FTS when using 10% Co/TiO₂ catalyst in a fixed bed reactor. The changes of catalytic activity, product formation rate and selectivity, olefin to paraffin ratio before, during and after the catalyst deactivation will be compared and discussed.

Chapter 5 (Effect of feeding extra nitrogen into a fixed bed Fischer-Tropsch reactor while keeping the partial pressures of reactants the same): This chapter concerns the effect on the catalytic performance of feeding extra nitrogen into the Fischer-Tropsch reactor. In order to keep the 'reaction kinetics' the same in all runs, the molar flow rate of H_2 and CO as well partial pressures of the reactants (CO and H_2) were kept fairly constant while varying the molar flow rate of N_2 and the reactor pressure. The experiments were continued until the FT catalytic activity had reached an approximately steady state with low conversions. The overall activity, formation rate and selectivity to the light paraffins and olefins with different reaction conditions are calculated, compared and discussed.

Chapter 6 (A study of the short chain hydrocarbon product distribution in Fischer-Tropsch synthesis over a cobalt catalyst): This chapter focuses on the light hydrocarbon (C_1 - C_6) product distributions which were analysed at different stages of the FT process as the activity of the catalyst declined. The chain growth probabilities of olefin and paraffins for each reaction run will be calculated and compared. The effect of other aspects, such as the selectivity, reactant conversion and reaction quasi-equilibrium, on the short chain product selectivity are also discussed.

Chapter 7 (A study of Fischer-Tropsch synthesis: does product distribution follow thermodynamics?): In this chapter, a ternary diagram is used to plot the relationships between the amounts of three kinds of hydrocarbons (C_nH_{2n} , $C_{n+1}H_{2n+2}$ and C_nH_{2n+2}) produced in the research experiments. The author also looks at the relationship between the ratios of paraffin (P) to olefin (O) namely P_{n+1}/O_{n+1} against P_n/O_n where n is carbon number from 2 to 5, as has been done in previous papers by his research group, and he discusses the significance of the results.

Chapter 8 (Conclusion and recommendations): This chapter gives a summary of the conclusions drawn from the results obtained in each chapter and also presents perspectives for future research.

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CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter examines the Fischer-Tropsch synthesis (FTS) literature. The literature review includes history and development, catalysts, reactors, reaction processes, co-feeding, kinetics and mechanism, products distribution and vapour-liquid equilibrium (VLE) in FTS. With the exception of the history and development of FTS and syngas production, the researcher has discussed separately some of the FTS features mentioned above in the introduction to each chapter. Redundant details are therefore not provided in this review.

2.2 Fischer-Tropsch synthesis

2.2.1 History and development

The history and development of Fischer-Tropsch synthesis (FTS) spans periods including the synthesis of methane in 1902; the formation of ethylene in 1908 and the manufacture of a liquid 'oil' from synthesis gas in 1913 to the discovering of high hydrocarbon productivity and selectivity in the conversion of coal derived synthesis gas (syngas) in 1923 [1,2]. Commercial developments in Germany and other countries, with coal derived syngas using cobalt catalyst, were achieved from 1929 to 1949. From 1950 to 1990, the application of an iron catalyst in the Sasol commercial plants in South Africa using syngas from coal was carried out. The initiation of Fischer-Tropsch gas to liquid (FT GTL) based on both iron and cobalt catalysts at commercial capacity started with two plants at PetroSA (Mossel Bay, South Africa) and Shell GTL (Bintulu, Malaysia). Further commercial developments expanded with two large projects confirmed at ORYX GTL (Sasol) and Pearl GTL (Shell) in Qatar. Many more concepts such as Sasol Chevron (six), ExxonMobil, Syntroleum and Statoil/PetroSA were proposed [1–5].

On the other hand, industrialised nations realised that petroleum was essential to their economies in the 1920s. The large production of automobiles, the introduction of aircraft and petroleum-powered ships, and the recognition of petroleum's high energy content compared to wood and coal, required a shift from solid to liquid fuels as a major energy source [5]. Stranges reported that industrialised nations concluded that synthetic fuel could contribute to their growing liquid fuel requirements based on four factors: (i) the shift from solid to liquid fuel as a major energy source, (ii) the invention of the Bergius and F-T coal-to-petroleum conversion or synthetic fuel processes, (iii) recognition that global petroleum reserves were finite and much less than global coal reserves and that petroleum's days as a plentiful energy source were limited, and (iv) the desire for energy independence [5].

In brief, FTS is a chemical reaction which converts syngas into synthetic fuels and other waxy products from carbon based material using a metal catalyst. The process was discovered in 1923 by Franz Fischer and Hans Tropsch while working on the production of hydrocarbon from coal over metal catalysts at the Kaiser Wilhelm Institute for Coal Research in Mülheim, Germany. At commercial level, the first FT plants to produce synthetic fuel was the Steinkohlen-Bergwerk Rheinpreussen plant located in Mörs-Meerbeck (Homberg, Ruhr) near the Rheinpreussen coal mine [1–6]. Currently SASOL in South Africa is one of the biggest producers of synthetic fuel from FT processes.

2.2.2 Synthesis gas production

Syngas is often produced from any carbon based feedstocks such as natural gas, coal and biomass. In the first step of the overall process, the carbonaceous feed is converted to syngas (a mixture of carbon monoxide and hydrogen) via reaction with steam and optionally oxygen. Solid feeds (coal and biomass) are typically converted in a gasifier, of which different varieties are known [7,8]. The most common feeds used to prepare syngas for FTS are coal (rich in carbon) and natural gas (rich in methane). Three basic methods of converting a carbon based material into syngas exist, i.e. reforming, partial oxidation, and catalytic partial

oxidation. Coal conversion is more expensive than natural gas conversion. However, it may be worthwhile if the coal price is low enough and if both electricity and higher value hydrocarbon products are co-produced with liquid fuels on a large scale [9,10]. The partial oxidation of coal is often referred to as gasification. Coal and solid dry biomass (wood and straw) are converted to syngas by thermo-chemical processes which include gasification, gas cleaning, conditioning, methanation of the producer gas and subsequent gas upgrading [7]. The most important reactions in the coal gasification process are shown in equations (1) to (4) [11]:



The conversion of natural gas takes place in a reformer, for example partial oxidation (POX), autothermal reforming (ATR) or steam methane reforming (SMR) [8]. The syngas from industrial partial oxidation has a low H_2/CO ratio, i.e. $\text{H}_2/\text{CO} = 0.5 - 2$ and $\text{CO}/\text{CO}_2 = 5 - 15$. In all cases, a near-to-equilibrium syngas mixture is obtained of which the H_2/CO ratio can be adjusted via the water-gas shift (WGS) reaction [6] which is shown in equation (5):



From the POX technique, natural gas is converted into syngas of H_2/CO ratio close to 2 as displayed in equation (6).



Basically, POX mixes natural gas and oxygen and reacts them via an exothermic non-catalytic reaction. The operation is carried out at high temperature as opposed

to steam reforming. In catalytic partial oxidation, a catalyst replaces the flame in the POX. The advantages of the catalytic partial oxidation of methane over steam reforming of methane are the low exothermicity of the process and the high reaction rates [6,12].

From SMR, natural gas and steam are often catalytically and endothermically converted to syngas that consists of H₂/CO ratio of 3 as shown in equation (7).



This is a catalytic process operated at 850 °C and due to the water gas shift reaction, CO reacts with H₂ resulting in even more H₂ produced. Hence, the actual H₂/CO ratio is in the range of 5–7 [6,12].

From ATR, the technique combines SMR and POX in one reactor to produce syngas. This process provides the desired H₂/CO ratio of 2:1 and it has a high thermal efficiency. This process provides an inherent thermal efficiency and economy of scale advantages as compared to partial oxidation reactors or the multitude of parallel tubes in the steam reformers. There is a wide range of operating temperatures to produce a H₂/CO ratio of 2:1 which is required for FTS [12].

Nowadays, FT synthetic fuels facilities rely on the utilisation of coal (coal to liquids: CTL) and stranded natural gas (gas to liquids: GTL). But applications such as biomass to liquids (BTL) and waste to liquids call for smaller scale plants that leverage the benefits of the FT technology in conjunction with localised and smaller feed sources for example municipal waste [13]. The economic and ecological importance of 'green' FTS derived transportation fuels is based on generation of syngas by biomass conversion (renewable energy source). This route has the advantage that almost all biomass materials are suitable for gasification to produce syngas for the FTS process [14]. Further discussion on the BTL FT process can be found in the literature [7,15,16]. The production of purified syngas is the most expensive section in a full range FT plant. Thus it is desirable that the syngas composition should match the overall usage ratio of the FT

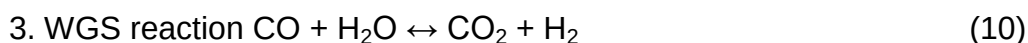
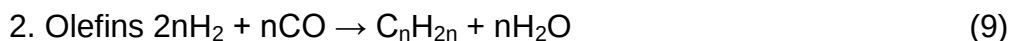
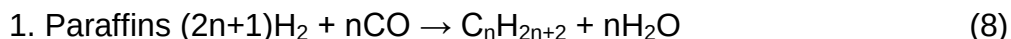
reactions, which in turn depends on the product selectivity and side reactions i.e. WGS [17]. Thus regardless of the source, syngas that has a 2:1 H_2/CO ratio will be used throughout the experiments in this project.

2.2.3 FT process: reactions

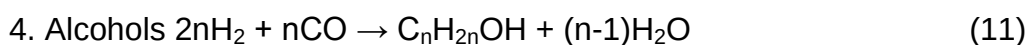
FTS is a polymerisation process which converts syngas to hydrocarbons over metal catalysts. The FT product spectrum consists of a complex multi component mixture of linear and branched hydrocarbons and oxygenated products. Main products are linear paraffins and olefins. The hydrocarbon synthesis is catalysed by metals such as cobalt, iron, and ruthenium. Both Fe and Co are used commercially these days at 200–300 °C and at 10–60 bar. FTS on iron catalysts can be easily said to be a combination of the FT reaction and the WGS reaction. Water is a primary product of the FT reaction, and CO_2 can be produced by the WGS reaction [18].

The commercial process of a FT plant involves three main sections namely: syngas production and purification, FTS, and product upgrading. To repeat what was mentioned, the syngas production is the most costly section. For instance, a report gives a capital cost breakdown of these three individual process sections for a 45,000 bbl/day FT plant [19]. The syngas preparation is about 66% of the total on-site capital costs. The FTS section consisting of FT slurry reactors, CO_2 removal, syngas compression and recycling, 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 syngas production is the most beneficial. Yet, it is noteworthy that at a fixed production rate the selectivity of the FT process directly affects the size of the syngas generation section [19]. A high selectivity of the FT process to desired products is of the utmost importance to the overall economics [18]. Summaries of major reactions with the carbon number $n \geq 1$ in the FTS [11,20] are displayed in the equations (8) to (12):

Main reactions



Side reactions



FT processes are also categorised based on the temperature at which the operation is being carried out and the products obtained differ. For example, the syncrude produced during high temperature (300–350 °C) Fischer-Tropsch (HTFT) synthesis is gaseous at reaction conditions; more than one product phase is formed on cooling. Low temperature (200–260 °C) Fischer-Tropsch (LTFT) syncrude is a two phase mixture at reaction conditions, but at ambient conditions the syncrude from LTFT synthesis consists of four different product phases: gaseous, organic liquid, organic solid (wax) and aqueous [21]. Medium temperature Fischer-Tropsch (MTFT) ranges from 270 to 300 °C, the product phases are similar to those of LTFT. A summary of FT processes including the type of catalyst, type of reactor, technology and operator is depicted in **Table 2.1**.

Table 2.1: FT processes currently in industrial operation [21]

Process	Catalyst	Reactor	Technology	Operator
HTFT	Fused Fe	Circulating fluidised bed	Sasol Synthol	PetroSA
HTFT	Fused Fe	Fixed fluidised bed	Sasol Advanced Synthol (SAS)	Sasol
LTFT	Precipitated Fe	Fixed bed	ARGE ^a	Sasol
LTFT	Precipitated Fe	Slurry bubble column	Sasol Slurry Bed Process (SSBP)	Sasol
LTFT	Co-SiO ₂	Fixed bed	Shell Middle Distillate Synthesis (SMDS)	Shell
LTFT	Co-Al ₂ O ₃	Slurry bubble column	Sasol Slurry Bed Process (SSBP)	Sasol

2.2.4 FT product upgrading

It is known that one of the key technologies for gas to liquid (GTL), coal-to-liquid (CTL) and biomass-to-liquid (BTL) conversion, referred to as XTL, is FTS. The product from FTS is a synthetic crude oil often labelled syncrude. Similarly as for crude oil, the syncrude has to be further refined to produce transportation fuels [21]. The last major step in an XTL process is the work-up of hydrocarbons to final products including transportation fuels. The production of fuels typically involves a hydroprocessing step, while sophisticated separation techniques are often required to produce chemicals or chemical intermediates of required purity [8]. The standard product upgrading techniques that are used in refineries are also suitable for the upgrading of the FT wax [13]. Conventional refinery processes can be used for upgrading FT liquid and wax products. The conversion technologies considered are: double bond isomerisation, dimerisation/oligomerisation, skeletal isomerisation, etherification, aliphatic alkylation, aromatic alkylation, metathesis, hydrogenation/hydrotreating, hydroisomerisation, hydrocracking, catalytic cracking, coking, thermal cracking, catalytic reforming, aromatisation, alcohol dehydration and olefin hydration [18,21]. The syncrude from HTFT synthesis is more olefinic, rich in oxygenates (mainly alcohols, carboxylic acids and ketones) and contains aromatics, while syncrude from LTFT synthesis contains mainly

straight chain paraffins, olefins and alcohols [21]. FT wax consists mainly of linear hydrocarbon chains over a large boiling range and has a virtually zero-level of S- or N-contaminants and aromatics [9]. Fuels produced with the FTS are of a high quality due to a very low aromaticity and very low sulfur content [18]. The transportation fuel classes that are generally produced during fuels refining are: motor-gasoline, jet fuel (aviation turbine fuel) and diesel fuel [21]. In general product streams from all processes consist of various fuel types: liquefied petroleum gas (LPG), gasoline, diesel fuel, and 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 2.2**.

Table 2.2: Conventions of fuel names and composition [9,11]

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 was		C ₂₄ –C ₃₅
Hard wax		C ₃₅ +

The FTS is operated in three modes namely high-temperature (300–350 °C), MTFT (270–300 °C) and low-temperature (200–260 °C) processes. High-temperature processes with iron-based catalysts produce gasoline and linear low molecular mass olefins, whereas low-temperature processes with either iron or cobalt catalysts produce significant quantities of high molecular mass linear waxes [17].

2.3 FT catalysts

The primary goal of any cobalt catalyst preparation for FT synthesis is to produce a significant concentration of stable cobalt metal surface sites. The goal of catalyst preparation is also to avoid loss of cobalt atoms in the support matrix during catalyst preparation, pretreatments and FT reaction [22]. FT catalysts can be prepared by means of incipient wetness impregnation (IW), precipitation (PR) and spreading (SP) techniques [22,23]. Optimum catalysts with high cobalt concentration and site density can be prepared by controlled reduction of nitrate precursors introduced via melt or aqueous impregnation methods [24].

Several authors have reported that the most active metals for the FTS are ruthenium, cobalt, iron and nickel [25–28] among the group VIII transition metals. Iron, cobalt, nickel, and ruthenium display intermediate behaviour and are excellent FT catalysts. These metals possess the capacity to dissociate CO. The major disadvantage of nickel is that it readily forms volatile metal-carbonyls, limiting the reaction pressure and thus the FT productivity. A further drawback of nickel is the production of methane at industrial conditions [9]. Three of these metals based catalysts are discussed as follows:

- Iron catalysts for the FTS generally consist of precipitated iron. The precipitated iron is promoted with K and Cu resulting in high activity and selectivity. Al_2O_3 and SiO_2 are added as structural stabilisers. Usually, Fe-based catalysts are relatively cheap with Fe-carbide the active phase for FT. Fe-oxides are also formed and are active for the WGS reaction. The WGS activity of the catalyst results in a low carbon efficiency of the GTL process. The application of Fe-based catalysts in the production of heavy wax is limited, though they are selective for light olefins at high temperature. Moreover, water has an inhibiting effect on the activity, resulting in low conversions per pass. The latter effect results in large recycle streams after water removal [9].
- Cobalt catalysts are usually supported on metal oxides due to the higher cobalt price and better catalyst stability. The active phase is metallic cobalt; the tendency

of cobalt to form carbides at 200–300 °C and 25–40 bar is low. The WGS activity of Co-based catalysts is low and water is the main oxygen-containing reaction product. The cobalt generally has strong interaction with metal oxide supports. Hence promoters such as Ru, Re, or Pt are applied to facilitate reduction of cobalt oxides. Compared to Fe-based catalysts, olefins tend to re-enter the chain growth process by readsorption on Co-based catalysts, increasing the selectivity towards heavy hydrocarbons. Co-based catalysts are very suitable for wax formation in slurry bubble columns and can operate at high conversions per pass [9].

- Ruthenium catalysts are the most active FT catalysts. A high molecular weight wax is obtained at reaction temperatures as low as 150 °C. The catalyst is active in its metallic form and no promoters are required to stabilise its activity. However, the high price of ruthenium excludes its application on industrial scale and the use of Ru-based catalysts for the FTS is limited to academic studies [9].

The performance of cobalt catalysts depends on various aspects including: cobalt particle size, cobalt reduction and cobalt phase composition, which are generally associated with catalyst support, promoters as well as process conditions. These parameters which also control the catalyst structure are essential for adequate catalytic performance in FT synthesis [22]. The dependence of the activity of cobalt-based catalysts for Fischer-Tropsch synthesis on the type of cobalt precursor and support material has been studied. The activity relative to the support material changed in the following order: $\text{ZrO}_2 < \text{TiO}_2 < \text{CeO}_2$ [23]. Other researchers have investigated and found that Catalyst Co/SiC provided good catalytic results at temperatures higher than 235 °C whereas Co/bentonite showed high catalytic activity at low temperatures. However, Co/bentonite was found to enhance the formation of oxygenated compounds. Hydrocarbon distribution was also influenced by the support. Co/ Al_2O_3 shifted to lighter hydrocarbon than Co/ TiO_2 and Co/bentonite. Co/SiC gave rise to higher molecular weight hydrocarbons products as compared with Co/alumina catalyst [29]. Zhu et al. [30] used SiO_2 , TiO_2 , and SiC as supports for cobalt catalysts. The results differed considerably in intrinsic bed thermal conductivity and revealed that SiC has better properties. The promoters used in the FT catalysts include a variety of promoters,

including noble metals (Ru, Pt and Re) and non-reducible metal oxides such as B, La, Zr, and K [31]. While Re and the above-noted three common oxide supports do not affect the Fischer-Tropsch activity and selectivity of the relatively large cobalt crystallites, some modifications of SiO_2 and Al_2O_3 supports (with MgO, Y_2O_3 , ZnO, and Ce_2O_3 , by coating and coprecipitation) reduce site activity by up to an order of magnitude [32].

Jacobs et al. [31] observed significant support interactions on the reduction of cobalt oxide species in the order $\text{Al}_2\text{O}_3 > \text{TiO}_2 > \text{SiO}_2$. Promoters Ru and Pt exhibited a similar catalytic effect by decreasing the reduction temperature of cobalt oxide species, while Re impacted mainly on the reduction of Co species interacting with the support. Promoters' non-reducible metal oxides such as B, La, Zr, and K were found to cause the reduction temperature of Co species to shift to higher temperatures, resulting in a decrease in the percentage reduction. For both Al_2O_3 and SiO_2 , modifying the support with Zr was found to enhance the dispersion. A slurry phase impregnation method led to improvements in the reduction profile of Co/ Al_2O_3 [31]. Promotion with Ru or Pt allowed for the reduction of cobalt species interacting with the support, yielding a greater number of active sites and, therefore, a higher initial catalyst activity on a per gram catalyst basis [31]. TPR results showed that Co/ TiO_2 and Co/bentonite were easier to reduce than Co/ Al_2O_3 and Co/SiC based catalyst [31]. On the other hand, the precursors of the metal used in the catalyst including using cobalt EDTA and ammonium cobalt citrate precursors resulted initially in very small cobalt oxide particles. The catalysts prepared with cobalt nitrate had larger particles that could be easily reduced to metallic cobalt as determined by X-ray photoelectron spectroscopy (XPS) [32]. The low loading (2.5 wt%) and high-loaded catalyst (5.0 wt%) exhibited a reasonable activity and, in addition, an interesting and remarkably high selectivity toward higher hydrocarbons, and also a very high Schultz-Flory parameter [32].

Cobalt catalysts used in the FTS are relatively expensive (as compared to iron) and need to have a high metal dispersion and long life to be able to offer a good balance between cost and performance [33]. The main conclusions of the

comparison between cobalt and iron catalysts for slurry phase FT application are as follows:

- Cobalt catalysts are more active than iron catalysts on a weight basis.
- The selectivity of cobalt catalysts is very sensitive to changes in process conditions, with lower methane selectivities achieved at higher syngas and water partial pressures.
- Deactivation of iron catalysts is more severe than for cobalt catalysts, which translates to a useful catalyst life of months versus years respectively.
- Cobalt can tolerate much higher water partial pressures than iron and this has significant implications for the single reactor capacity that can be achieved [8].

Cobalt and iron based FT catalysts are the most used catalysts industrially. Cobalt and iron are the only viable industrial choices of FT catalysts [34]. Productivity and selectivity to C_{5+} are critical in the design of an FT catalyst and reactor. Cobalt-based catalysts appear to provide the best compromise between performance and cost for the synthesis of hydrocarbons from the natural gas or biomass derived CO/H_2 mixtures [24]. For the experiment in this study the researcher used cobalt based FT catalysts.

2.3.1 Catalyst deactivation

Catalyst deactivation is a very important topic for commercial cobalt-FT operation due to the high catalyst cost. Fundamental understanding of the deactivation mechanisms at play during FTS is key to extending catalyst lifetime [35]. Catalyst deactivation in the Fischer-Tropsch reaction has been a topic of industrial as well as academic interest for many years. To trace the origin of catalyst deactivation is in many cases difficult. It is usually a complex problem where several mechanisms contribute to the loss of activity/selectivity [36]. This is because the chemical environment in the FTS reactor encompasses a large number of interacting species which may negatively affect catalytic activity [36].

The main causes of catalyst deactivation in cobalt based FTS as they appear in the literature are poisoning, re-oxidation of cobalt active sites, formation of surface carbon species, carburisation, surface reconstruction, sintering of cobalt crystallites, metal-support solid state reactions and attrition [36]. Researchers have proposed various deactivation mechanisms for cobalt FT based catalysts [35–37].

For example, following a comprehensive study into the deactivation of a cobalt catalyst under realistic FTS conditions the following intrinsic deactivation mechanisms were identified: (1) sintering of Co active phase, (2) carbon deposition and (3) surface reconstruction [35]. Although many research teams [35,37,38] have identified carbon deposition as a leading cause of catalyst deactivation, additional deactivation causes available in the literature include poisoning by sulphur [39], nitrogen containing poisons [40], oxidation of metallic Co and support-compound formation [41,42] and oxidation by water [37]. However, Loosdrecht et al. [35,37] showed that oxidation is not a deactivation mechanism during FTS for supported Co catalysts with crystallite size in excess of 2 nm as the FT environment was found to be strongly reducing. Furthermore, according to these authors [35,37] the oxidation of cobalt can be actually prevented by selecting the correct combination of the reactor partial pressures of hydrogen and water ($P_{H_2O}=P_{H_2}$) and the cobalt crystallite size. In short, oxidation is not a major deactivation mechanism for industrial Co/Al₂O₃ [37].

On the other hand, the effects of CO and H₂ partial pressures on the deactivation by carbon, in the absence of other deactivation forms, of a CoPt/AlSi Fischer-Tropsch catalyst revealed that (a) decreasing H₂/CO ratio at constant P_{CO} and (b) increasing H₂/CO ratio at constant P_{H_2} increase deactivation rate, possibly due to (a) formation of less hydrogenated and (b) more hydrogenated polymeric carbon forms [41]. By changing pretreatments, experimental conditions, catalyst micro- and macroscopic properties and instrumentation may facilitate different deactivation mechanisms. Although the effect of water is well documented [35,37], it is still unidentified if the effect is kinetic, diffusional or oxidative [36].

In addition to these suggested mechanistic pathways that are based on theoretical and experimental studies for the deactivation of Co-FTS catalysts [44], many other mechanisms may lead to loss in catalyst activity [40]. In FTS, for instance, inherent catalyst deactivation and operational catalyst deactivation will occur. Inherent catalyst deactivation occurs due to the exposure of the catalyst to realistic (clean) FT conditions (i.e. temperature, partial pressures of H₂, CO, CO₂, and H₂O, and possible product compounds), whereas additional deactivation routes may play a

role in the operation of the catalyst [45]. During FTS temperature increases could lead to catalyst deactivation. Furthermore, the type of reactor affects the deactivation: slow catalyst deactivation takes place in very small fixed bed reactors (1% per day), while deactivation was much more significant in the slurry reactor. After the initial start-up period, the carbon monoxide conversion remains unchanged for several days in larger fixed bed reactors [46]. Researchers have shown that the catalyst deactivation sometimes behaves differently depending on the support of the catalyst [47–49].

2.3.2 Characterisation techniques

There is always a need to know the catalyst composition before, during and after the FT processes. For a better FT activity, cobalt, nickel, and ruthenium have to remain in the metallic state under FT conditions [50]. For instance, the metallic properties of Co have been proven with in situ extended X-ray absorption fine structure by Ernst et al. [51]. On the other hand, the composition of iron-based catalysts changes during FTS. Characterisation of the several phases with in situ laser Raman spectroscopy [52], in situ magnetic measurements [53], or Mössbauer spectroscopy [53,54] may give evidence of the reactivity of the several active species [54].

Some of these techniques are described in the Appendix section. Numerous characterisation techniques used for the chemical and physical analysis of catalysts are available in the literature [48,55–61]. The mostly used include X-ray diffraction (XRD), temperature programmed reduction (TPR), Brunauer–Emmett–Teller (BET), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), Inductively coupled plasma (ICP), Extended X-ray absorption fine structure (EXAFS), Electron microscopy and spectroscopy such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy are also employed.

2.4 FT reactors

The most important aspects for development of commercial FT reactors are the high reaction heats and the large number of products with varying vapour pressures (gas, liquid, and solid hydrocarbons). The main reactor types which have been proposed and developed after 1950 are:

- Three-phase fluidised bed reactors or slurry bubble column reactors with internal cooling tubes (SSPD: Sasol; GasCat: Energy International, AGC-21: Exxon),
- Multi-tubular fixed bed reactors with internal cooling (Arge: Sasol; SMDS: Shell),
- Circulating fluidised bed reactors with circulating solids, gas recycle and cooling in the gas/solid recirculation loop (Synthol: Sasol), and
- Fluidised bed reactors with internal cooling (SAS: Sasol) [20].

From the more recent developments of Fischer-Tropsch reactors, it has been reported that the more advanced reactors with potential for large-scale conversion of natural gas to liquid hydrocarbons belong to the classes of fluidised bed, multi-tubular fixed bed, and slurry reactors [62,63].

These three main types of reactors used for FT reaction are briefly discussed as follows [63,64] and described below.

a) Fixed bed reactors which are used by Sasol to produce high value linear waxes at low temperatures (225 °C). The catalyst is loaded in 5 cm i.d. tubes. Heat removal is achieved by converting water circulating outside of the tubes into steam [62,65];

b) Fluidised bed reactors with either a fixed or a circulating bed. The main difference between the two types of reactors is that in the fixed fluidised bed reactor (FFD) the catalyst bed remains stationary and the gases pass upward through the bed while in the circulating fluidised bed reactor (CFB) the catalyst is

entrained in the fast moving stream. The main advantages of FFB over CFB reactors include low construction cost, increase in cooling capacity, low overall catalyst consumption because of a lower rate of on-line catalyst removal and replacement with fresh catalyst to maintain high conversions [62,63].

c) Slurry bed reactors in which gas is bubbled through a suspension of finely divided catalyst in a liquid which has a low vapour pressure at the temperature of operation. The advantages of slurry over multi-tubular reactors are low cost of reactor train, lower gas compression costs, lower catalyst consumption per tonne of product, ability to operate at a higher average temperature resulting in higher conversions and on-line removal/addition of catalyst allows longer reactor runs. The disadvantage of this type of reactor is that in the case of catalyst poisoning, all the catalyst is deactivated whereas in the case of a fixed bed reactor the poisoning substance is adsorbed by the top layers of catalyst, leaving the balance of the bed essentially untouched [17,62]. Laboratory scale size fixed bed reactors (FBR) were set up to achieve the objectives of this research.

Possible reactors for FTS are: (a) slurry bubble column reactor; (b) multi-tubular trickle bed reactor; (c) circulating; (d) fluidised-bed reactor [64]. Reactor types that have commercial relevance for the FT synthesis can broadly be classified into two types, namely two-phase (High-temperature FT; HTFT) or three-phase (Low-temperature FT; LTFT), and moving or stationary catalyst bed reactors [8]. Each of these reactors presents some advantages and disadvantages as summarised in **Table 2.3**.

Table 2.3: Advantages and disadvantages of some selected FT reactors [15,64]

Feature	Fixed bed	Fluid bed (circulating)	Slurry
Temperature control	Poor	Good	Good
CH ₄ formation	Low	High	As fixed bed or lower
Flexibility	Intermediate	Little	High
Product	Full range	Low molecular weight	Full range
Catalyst affectivity	Lowest	Highest	Intermediate

Further information on the development and characteristics of these reactors can be found in the scientific literature [8,63–67].

2.5 FTS co-feeding

Syngas is the feed to the FT process. As the feed in FTS is central to the process numerous studies have been conducted on the feed composition and co-feeding of different molecules with the syngas for the FT reactions [68–70]. In terms of co-feeding, rigorous studies have been conducted and some of the molecules that have been co-fed so far include water [70–76], gases like CO₂ [77–82] and hydrocarbons like olefins [83–88] just to mention a few. Although researchers [89–92] have published findings on nitrogen containing compounds including ammonia, inorganic compounds such as nitrogen gas have not been reported on intensively. But to show the importance of co-feeding in FT reaction, already in the 1950s scientists had investigated FT processes with both inorganic and organic compounds to be exact CO₂, CH₄ and N₂ and they have shown that the addition of these diluents decreased the rate of FT reaction [93].

On the other hand, it has been shown that additives such as small 1-alkenes, alcohols, or CO₂, act as chain initiators for the FTS, and both additive initiated and conventional FTS proceed simultaneously, with their respective products overlapping. The majority of work in this area has shown that additive molecules do not contribute to chain growth, although added olefins and alcohols have been

shown to be incorporated into FTS products, usually through chain initiation [94]. However, to date, the effects and influences of the additives (i.e. N_2) discussed in this paper on the overall product distributions and on the catalysts activity have not been thoroughly investigated. As co-feeding experiments have shown, olefins adsorb on the catalyst surface and influence the overall FTS product distribution. It could therefore be envisaged that additives such as olefins could be used in the FTS to modify the catalyst surface, e.g. by selectively binding to and/or inhibiting certain active sites such as those promoting chain growth of higher hydrocarbons, or secondary hydrogenation, in order to improve the overall efficiency and selectivity of the process [94].

The addition of n-hexane to the feed of the FTS at realistic conditions will not result in supercritical FT conditions. Thus, an increase in the effectiveness factor has been observed, if the FTS is performed under internal mass transport limiting conditions [95]. Patzlaff et al. [96] conducted experiments based on 1-alkene and ethane co-feeding with cobalt and iron catalysts and showed that superimposed distributions with different chain growth probabilities are the result of different chain growth mechanisms. When co-feeding alcohols, the dependence of the ratio of the two distributions on the pressure of hydrogen and carbon monoxide and the promoter effect of alkali on iron catalysts also serve to support the hypothesis of the two mechanisms. They also point to the carbon monoxide insertion mechanism as the second mechanism that is characterised by the higher growth probability of the resulting Anderson–Schulz–Flory (ASF) distribution [97].

The effects of water on FTS are quite complex and depends on the support and its nature, Co metal loading, its promotion with noble metals, and preparation procedure [70–76]. Dalai and Davis [71] have summarised the effects of water in FTS with three scenarios, based on different results reported in the literature: (1) the effect of water on supported cobalt catalyst can be viewed as an oxidation process. The extent of oxidation is a function of cobalt crystallite size and the ratio of reactor partial pressures of hydrogen and water (P_{H_2O}/P_{H_2}). (2) The effect of water is related to the average support pore diameter. (3) Water can have kinetic effects. For example, water can lower the barriers to CO dissociation by direct

interaction with co-adsorbed CO and inhibit the secondary hydrogenation of olefin products as a result of competitive adsorption of water [71].

Fairly recently, Yan et al. have demonstrated that Fe-Pd/ZSM-5 catalyst (a bi-functional catalyst) yields relatively high activity and selectivity in producing liquid hydrocarbons when running FT with nitrogen-rich syngas [98]. Conversely Visconti and Mascellaro [99] co-fed nitrogen to the reactor increasing the nitrogen content (23.5 to 45.1%) while keeping the total pressure unchanged and found that the CO conversion dropped. It is most likely that the CO conversion decreased due to the drop in the reactant partial pressures as the total pressure was kept constant while increasing the nitrogen content. Nevertheless, most researchers who investigated FT with nitrogen-rich syngas have indicated that the process is feasible because of the possibility to reduce costs [59,69,100–102]. The addition to the FTS of molecules like olefins, alcohols, carbon dioxide, water, and isotope markers has improved the understanding of the reaction mechanism. These same molecules were also used in an attempt to explain the deviations observed from the ASF distribution [94]. In the current investigation, the researcher co-fed nitrogen to the FTS reactor while keeping the partial pressures of reactants the same, and he analysed the results on the activity, selectivity and product distribution. Thus, the true N₂ effect on the FTS activity and selectivity are obtained.

2.6 FTS mechanism and kinetics

FTS is a surface catalysed polymerisation process that is thought to use CH_x monomers, formed by hydrogenation of adsorbed CO, in order to produce hydrocarbons with a broad range of chain length and functionality. Chain growth is thought to occur by the addition of surface methylene species to adsorbed alkyl groups; these alkyl groups can undergo β -hydrogen abstraction to form linear α -olefins or hydrogen addition to form *n*-paraffins on Co catalysts [22,103,104]. Suggested mechanisms of the hydrocarbon and oxygenate formation in the FTS and water gas shift reaction have been reported in the literature [11,18,20]. As already mentioned, FTS is a polymerisation reaction with the following steps [26]: (1) reactant adsorption; (2) chain initiation; (3) chain growth; (4) chain termination;

(5) product desorption; (6) readsorption and further reaction. A variety of surface species were proposed to describe chain initiation and chain growth. Several compounds are possible monomers for chain growth. The most important growth mechanism for the hydrocarbon formation on cobalt, iron, and ruthenium catalysts is the surface carbide mechanism by CH_2 insertion. It is uncertain if the monomer formation proceeds via hydrogenation of dissociated or un-dissociated CO. Secondary reactions occur when primary products desorb from a site and interact with another catalytic site before leaving the reactor. Novak et al. [105] reported possible secondary reactions of olefins: (i) hydrogenation to give n-paraffins, (ii) isomerisation, (iii) cracking and hydrogenolysis, (iv) insertion into growing chains, mostly effective for C_2H_4 and C_3H_6 , and (v) readsorption and initiation of hydrocarbon chains. Secondary reactions can influence the type and molecular weight of the hydrocarbon products.

Pour and Housaindkht [106] have suggested the following mechanism steps: 1) chain termination occurs with beta hydrogen elimination and 1-alkenes primary products 2) Following reactions: re-adsorbed 1-alkenes hydrogenate to form intermediates for surface chain growth with C_1 : CO, HCO, HCOH, CH and CH_2 . These C_1 species have various hydrogenation degrees which are as follows: CO, HCO, HCOH, CH, and CH_2 . If chain termination occurs with C_1 monomers that exhibited higher degree of hydrogenation (like CH_2 species), the produced hydrocarbons becomes lighter than other C_1 species [106]. Furthermore, the readsorption of alkenes is considered as a reverse step of alkenes desorption reaction in the comprehensive kinetics model. The formation rate expressions of products including alkanes, alkenes and alcohols are derived on the basis of CO insertion mechanism. The comprehensive kinetics incorporating the effect of alkenes readsorption and the following secondary reaction is developed on the basis of CO insertion mechanism [107]. On the other hand, two dominant conflicting mechanistic proposals of the FT reaction are the carbide mechanism and the CO insertion mechanism, which involve cleavage of the C–O bond of CO before incorporation of a CH_x species into the growing hydrocarbon chain (the carbide mechanism) or after incorporation into the growing hydrocarbon chain (the

CO insertion mechanism). The choice of a particular mechanism has important kinetic consequences [108].

Amongst several mechanisms reported in the literature, the most accepted mechanism is CH₂ insertion of the carbide theory of FT [20,106]. Furthermore, the dependencies of hydrocarbon product distributions of iron and cobalt catalysed FTS on partial pressures of reactants (P_{H2} and P_{CO}) have suggested that products with lower growth probability are formed by the well accepted CH₂ insertion mechanism. Chain length distributions of products obtained on cobalt catalysts are slightly modified by secondary chain growth of re-adsorbed alkenes but also by hydrogenolysis of hydrocarbons [96]. In a case where there are low H surface concentrations, mostly at high CO pressures, decomposition of CHOH following CH hydrogenation is dominating for methane formation. In addition, the methane formation and the first C–C bond formation go through an identical carbon pool, namely CH_x whereas at high H surface concentration, they could go through different carbon pools [109].

On the other hand, CO dissociation is considered to be the crucial step in the FTS to produce ‘clean’ fuel from syngas [110]. Nijis and Jacobs agreed that CO disproportionation initiates the FT reaction. But they pointed out that polar conditions (acidic catalysts and addition of water) stimulate chain growth in FTS [111]. For Co catalysts, Ojeda et al. have found by theoretical analysis that unassisted CO activation is not competitive with the H-assisted route, leading to oxygen rejection pathways via H₂O exclusively, consistent with previous reports. Monomer formation via the H-assisted CO activation route would completely dominate on Co catalysts [112]. Various other researchers [11,18,20] have proposed mechanisms of the hydrocarbon synthesis from CO and H₂ which can be seen below from equation (14) to equation (25):

Adsorption





Surface reactions

Water formation



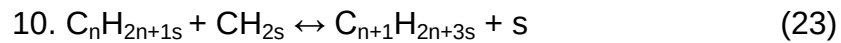
Chain initiation



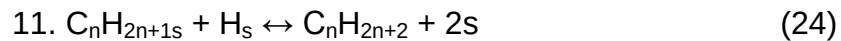
Methanation



Chain growth



Hydrogenation to paraffins



β -dehydrogenation to olefins

The FTS mechanism is still not fully understood and the product distribution does not generally follow a typical Anderson–Schulz–Flory (ASF) distribution [94]. The major problem in describing the FT reaction kinetics is the complexity of its reaction mechanism and the large number of species involved [113]. The mechanistic proposals for the FTS used a variety of surface species and different elementary reaction steps, resulting in empirical power law expressions for the kinetics. In most cases the rate determining step was assumed to be the formation of the monomer. These rate expressions for the consumption of syngas mainly differ in the nature of the monomer and of the adsorption of CO, H₂ and products (H₂O and CO₂) on the catalyst surface. Ideally, the development of kinetic rate expressions should be based on each possible rate determining process in a well-defined mechanistic scheme in the hydrocarbon-forming reactions [18,20]. Discussions on the kinetics of iron and cobalt catalysts follow:

- Iron Based Catalysts: in general for iron catalysts, the FT reaction rate increases with H₂ partial pressure and decreases with partial pressure of water. The mechanistic kinetic rate expressions for iron catalysts are all based on the formation of the monomer species as the rate determining step in the consumption of syngas. Several theories for the formation of the monomer species are postulated in the literature: i) carbide mechanism [105] and ii) combined enol/carbide mechanism [114].

- Cobalt Based Catalysts: remarkably, nearly all kinetic expressions developed for cobalt based catalysts have a different form from that for iron based catalysts. Generally, these kinetic equations are based on a rate determining step which involves a dual-site surface reaction, resulting in a quadratic denominator in the rate expression. Furthermore, inhibition terms of H₂O on cobalt catalysts are not reported in literature. Because the WGS reaction hardly plays a role on cobalt, hardly any CO₂ is formed. In comparison to the iron catalyst, the kinetic research

on cobalt catalysts is more comprehensive. The situation on cobalt catalysts is easier due to the absence of the water gas shift reaction and less different catalytic sites [18,20].

The most significant difference between the iron and cobalt equations is the absence of a water vapour pressure term in the latter equation (cobalt equation). This potentially gives cobalt a big activity advantage over iron catalysts [17]. The kinetic expressions for n-paraffin and olefin formation are developed on the basis of combining alkyl and alkenyl mechanisms without taking into account the readsorption and secondary reactions of olefins [115]. In addition, based on the fact that olefin can be hydrogenated to paraffin while paraffin can undergo hydrogenolysis, it has been shown that C_{2+} olefins and paraffins are formed from a common precursor, and that, in the absence of further olefin hydrogenation, the olefin to paraffin ratio in the products depends only on the H_2 partial pressure [116]. FTS rate expressions for Co catalysts from the literature that are commonly used were selected and these are presented in **Table 2.4**.

Table 2.4: Summary of selected kinetics FTS models for Co catalysts from the literature [117–119]

Kinetic models	Parameters	Refs
$r_{FT} = kP_{CO}^a P_{H_2}^b$	k, mol/g-cat/h/MPa ^(a+b) 0.0137 a b -0.35 0.81	[120]
$r_{FT} = \frac{kP_{CO}P_{H_2}^{0.74}}{(1 + K_1P_{CO})^2}$	k, mol/g-cat/h/MPa 0.3080 K ₁ , MPa ^{-1.0} 3.90	[121]
$r_{FT} = \frac{kP_{CO}^{0.5}P_{H_2}^{0.5}}{(1 + K_1P_{CO}^{0.5} + K_2P_{H_2}^{0.5})^2}$	k, mol/g-cat/h/MPa 0.0976 K ₁ , MPa ^{-0.5} K ₂ , MPa ^{-0.5} 2.36 -0.67	[122]
$r_{FT} = \frac{kP_{CO}P_{H_2}^{0.5}}{(1 + K_1P_{CO} + K_2P_{H_2}^{0.5})^2}$	k, mol/g-cat/h/MPa ^{1.5} 0.0782 K ₁ , MPa ^{-1.0} K ₂ , MPa ^{-0.5} 1.95 -0.48	[122]
$r_{FT} = \frac{kP_{CO}P_{H_2}}{(1 + K_1P_{CO})^2}$	k, mol/g-cat/h/MPa ² 0.2696 K ₁ , MPa ^{-1.0} 3.61	[123]
$r_{FT} = \frac{kP_{CO}^{0.5}P_{H_2}}{(1 + K_1P_{CO}^{0.5})^3}$	k, mol/g-cat/h/MPa ^{1.5} 0.2460 K ₁ , MPa ^{-0.5} 1.65	[124]
$r_{FT} = \frac{k\left(\frac{P_{CO}P_{H_2}^{1.5}}{P_{H_2O}}\right)}{\left(1 + K_1P_{CO}P_{H_2}/P_{H_2O}\right)^2}$	k, mol/g-cat/h/MPa ^{2.0} 0.01470 K ₁ , MPa ^{-1.0} 0.19	[125]
$r_{FT} = \frac{kP_{CO}P_{H_2}^{0.5}}{(1 + K_1P_{CO} + K_2P_{H_2}^{0.5} + mP_{H_2O})^2}$	k, mol/g-cat/h/MPa ^{1.5} 0.0560 K ₁ , MPa ^{-1.0} K ₂ , MPa ^{-0.5} m, MPa ^{-1.0} 1.61 -0.51 -0.17	[126]
$r_{FT} = \frac{kP_{CO}^{0.65}P_{H_2}^{0.75}}{1 + K_1P_{CO}^{0.5}}$	k, mol/g-cat/h/MPa ^{1.25} 1.136 K ₁ , MPa ^{-0.5} 8.16	[127]

Based on the kinetic studies in the literature and particularly in **Table 2.4**, it is evident that there is a variety of rate expressions as well as a wide range of activation energies for FT catalysts. Glasser et al. [113] have reported that this raises questions about which of these data, kinetic parameters and rate expressions can be relied on for estimating reaction rates and/or conducting preliminary reactor design. As a result, this strongly suggests that the complex FT reaction behaviour may not be described efficiently by kinetics alone [113].

2.6.1 FTS selectivity

The process conditions as well as the catalyst influence the product selectivity. The influence of the syngas conversion on the product selectivity is strongly related to the influence of the process conditions. The process conditions that influence the product selectivity include:

- Temperature: Increase of temperature results in a shift towards products with a lower carbon number on iron, ruthenium, and cobalt catalysts. Various studies observed an increase of the olefin to paraffin ratio on potassium-promoted precipitated iron catalysts with increasing temperature [18,20].
- Partial pressure of H_2 and CO: most studies show that the product selectivity shifts to heavier products and to more oxygenates with increasing total pressure. Increasing H_2/CO ratios in the reactor gives lighter hydrocarbons and a lower olefin content [18, 20].
- Time on stream: deactivation of catalysts during the FTS may affect the activity and selectivity to hydrocarbon products. An increase of the selectivity to oxygenates is reported in the literature, after a period of 1300 hours on stream with a precipitated promoted iron catalyst. An increase of the methane selectivity and low-molecular products is also observed on iron catalysts [18,20].
- Reduction of the catalyst: the hydrocarbon selectivity appeared to relate strongly to the pre-treatment procedure. Olefin selectivities are reported to decrease after hydrogen reduction in comparison to reduction with CO or synthesis gas [18,20].

The products from the FTS on Co, Fe, and Ru show several characteristics including:

- The carbon-number distributions for hydrocarbons gives the highest concentration for C_1 and decreases monotonically for higher carbon numbers, though around C_3 - C_4 often a local maximum is observed [18,20].

- Olefins from iron catalysts exceed 50% of the hydrocarbon products at low carbon numbers, and more than 60% of these are α -olefins. The ethene selectivity is low in comparison to propene. The olefin content decreases asymptotically to zero with increasing carbon number on Co, Ru, and Fe catalysts. For cobalt catalysts both the fraction of total olefins and α -olefins are smaller, and both decrease with carbon number [18,20].
- A change in chain growth parameter in the distribution is only observed for linear paraffins and not for olefins [18,20].
- Yields of alcohols are maximum at C_2 and decrease with carbon number. Low yields of methanol are probably the result of thermodynamic limitations [18,20].

Moreover, the effects of operating conditions on catalytic performance revealed that CO conversion, methane and light olefin selectivity increased as operating pressure increased. The higher H_2/CO molar ratio leads to higher methane and lower olefin selectivity, but CO conversion decreased with ratios from 1 to 2 and then increased from a 2 to 3 molar ratio. By increasing temperature, selectivity to the lighter products increased and it was also apparent that CO conversion increased with temperature [128]. The underlying reasons for selectivity and activity changes with increasing partial pressure of water are not fully understood, and are probably the result of a complex interplay of transport processes, cobalt particle size and the effect of water on the formation of active carbon species and/or the removal of inactive carbon species from the catalyst surface [129]. The product distribution for the FTS is normally described using the kinetically derived ASF model [130].

2.6.2 Models of the product selectivity

Various models of the FTS products selectivity exist including: ASF distribution, deviations from ASF distribution and comprehensive product distribution models. Significant deviations from the ASF distribution reported in the literature are sometimes assigned to analytical difficulties and non-steady-state conditions of the reactor system [18,20]. ASF distribution models will be discussed in detail in the

next section. It has been previously proposed that deviation from ASF is due to readsorption and incorporation of 1-alkenes followed by subsequent chain growth. Patzlaff et al. disagreed and suggested that based on the kinetics model, Co catalyst incorporation of 1-alkenes cannot be the main reason of ASF deviation [131]. Many models for describing the FTS over supported cobalt catalysts have been postulated but there is still much debate over its mechanisms and governing physico-chemical phenomena, particularly those relating to secondary reactions of olefins [132].

Some other models have been developed based on the effect of the product accumulation leading to deviations from ASF behaviour in FTS [132] and these models postulated that the accumulated products enhance the readsorption by diffusion and vapour-liquid equilibrium [99,133]. Furthermore some of these models were unable to predict all the salient features of non-ASF distribution [134,135], while models that could predict non-ASF behaviour were either based on simplified mechanisms [136] and/or empirical constants [137]. On the other hand, Kuipers et al. [84] have attributed non-Flory distributions to the higher solubility of larger alpha olefins within intrapellet and interpellet liquids in three phase reactors. But according to Iglesia [24] it is correct to assume that VLE favours the presence of larger olefins in FTS liquids, but it is incorrect to conclude that such higher concentrations lead to faster readsorption rates. Visconti argued that his model is the only model that describes a comprehensive kinetics model that incorporates both VLE and product yields as a function of process conditions. The most relevant variable is the one in which pressure affects both product distribution and vapour liquid split [138].

Kruit et al. explained for the selectivity of the Fischer-Tropsch process, the deviations from single alpha product distribution can be explained by gradients in process conditions [139]. On the other hand, Stenger, Jr. and Askonas [140] have reported that thermodynamics can predict olefin formation and selectivity of some hydrocarbons. But the solubility-enhanced olefin readsorption, even if it were consistent with thermodynamics, cannot account for the observed effects of site

density and pellet size on selectivity, because neither catalyst property can in any way influence VLE [24].

2.7 FT product distributions and Vapour-liquid equilibrium

Chemical reactions are driven by the chemical potential of reactants. For a given reactant species, its chemical potential is identical in two or more phases, as long as these phases co-exist in thermodynamic equilibrium. Transport limitations could however prevent attainment of thermodynamic equilibrium between phases [24]. For any species, a diffusion limitation is based on a comparison of its generation rate (products) or disappearance rate (reactants) with its diffusion rate, and the latter is a function of its surface composition which depends on vapour–liquid separation [141]. The product accumulation qualitatively explains the experimental results for FTS. The effect of accumulation of products on VLE in the reactor shows that VLE is reached inside the FT reactor for components up to carbon C_{17} [142]. There are at least two ways that product accumulation can impact the product distribution: (1) diffusion limitations within the catalyst pore system which could increase the extent of olefin readsorption and reincorporation by chain initiation and (2) holdup in the liquid phase due to VLE [143]. The design and the performances of reactors for the low-temperature Fischer-Tropsch synthesis (LTFT) may be strongly affected by the presence of a liquid phase creating a boundary layer around the catalyst pellets and filling their pores. At LTFT conditions with cobalt catalyst: more than 99 mol. % of HCs products are vapour phase in particular C_{20-} species are entirely in the vapour phase, C_{31+} species are almost entirely liquid, $C_{21-}C_{30}$ species are split between the two phases [138].

VLE plays an important role in modelling the behaviour of an FT reactor [142]. Caldwell and van Vuuren [144] were the first to realise the importance of VLE considerations in the FTS modelling. They used Raoult's law to describe VLE. Recently, a variety of VLE thermodynamic models have been used to model FT products [145]. The results obtained also suggest that Raoult's law sufficiently describes VLE in a FT reactor. The preferential holdup of heavier products in the reactor affects the VLE modelling. Thus, some of the complexities in the FTS can

be caused by a combination of simple phenomena such as product holdup and VLE. The interactions of these phenomena cause quite complex behaviour [142]. In a continuous stirred-tank reactor (CSTR) the reaction product is separated into liquid and vapour, which are assumed to be in thermodynamic equilibrium according to Raoult's law under the reaction conditions [141]. The interaction among three phenomena such as VLE, partial reaction equilibrium and kinetics can lead to quite complex behaviour and may help to explain the apparently conflicting behaviour found by many researchers in trying to model the system [113].

The thermodynamically expected distributions of the products of FTS in terms of molecular weight distribution and olefin formation are close to distributions which have been observed experimentally. The product distributions include C_2 to C_{15} primary olefins, C_1 to C_{15} normal paraffins, C_1 to C_8 normal alcohols, carbon dioxide, and water [140]. Moreover olefin readsorption rates depend only on the olefin thermodynamic activity (not its concentration), which at VLE is identical in the liquid and gas phases and independent of solubility at steady state. In three-phase reactors, the residence time of any products removed predominantly in the gas phase (C_1 - C_{20}) is controlled exclusively by gas phase residence time and the reactor gas hold-up as long as VLE is maintained [24]. Thermodynamics and experimental results are consistent in many ways such as in predicting value of the chain growth probability. Thermodynamic alpha values equal experimental alpha values when temperature and pressure are changed. For example, the alpha value increases with increasing pressure and decreases with increasing temperature [140].

It has been reported from the literature [60] that the distribution for n-paraffins can be described by the ASF equation as shown in equation (26):

$$m_n = (1 - \alpha)\alpha^{n-1} \quad (26)$$

where the growth probability factor α is independent of n and m_n is the mole fraction of a hydrocarbon with chain length n . α is defined by:

$$\alpha = \frac{R_p}{R_p + R_t} \quad (27)$$

where R_p and R_t are the rate of propagation and termination, respectively. α determines the total carbon number distribution of the FT products as shown in **Figure 2.1**.

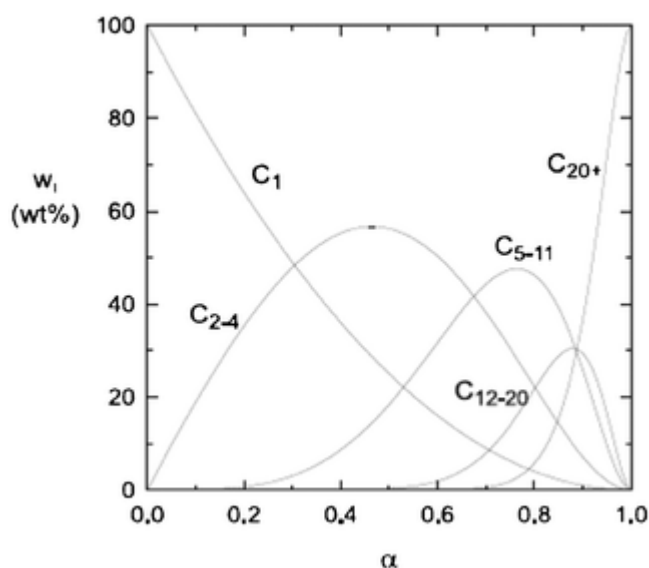


Figure 2.1: Hydrocarbon selectivity as function of the chain growth probability factor α , calculated using equation (26) [20].

The range of α is dependent on the reaction conditions and catalyst type. For instance, Dry 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 [17]. It has been reported that the chain growth probability, α , decreases with an increase of the reactor temperature [18,20]. The hydrocarbon product distributions depend on partial pressures of reactants. For cobalt: modification of distributions by secondary chain growth of re-adsorbed 1-alkenes is possible whereas for iron the secondary chain growth has been proved as negligible [96].

Friedel and Anderson [146] used thermodynamic equilibrium arguments to suggest that alpha olefins were primary FT products. The literature [105] showed that this suggestion was later substantiated experimentally, proving that paraffins

and internal olefins were secondary FT products formed from the primary alpha olefins. The FT process is best considered as multiple subsystems each working to achieve a partial equilibrium. The hydrocarbon homologous series are the first partial equilibrium [130]. Bell [147] concluded that the FT system is an example of thermodynamically controlled catalysis. While Schultz [148] noted that a dynamic thermodynamically controlled equilibrium of surface segregation is attained. On the other hand, Raje and Davis [149] used VLE to account for negative deviations in slurry reactor systems. Finally, Norval has reported that equilibrium theory explains far more observations in FT chemistry than has previously been thought [130].

2.8 Conclusion

This literature survey makes it clear that after 90 years the FTS process is very far from understood. While it is agreed that it is primarily a polymerisation process giving rise to a distribution of mainly olefins and paraffins the mechanism by which this occurs on catalysts is still the subject of much debate. Many of the FT features such as deactivation; product distributions; kinetics and mechanism and equilibrium aspects of the FT processes are still subjects of controversy regardless of the progress that has been made so far. This thesis will look at some of these areas and try to throw some light on some of the aspects of FTS.

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CHAPTER 3

EXPERIMENTAL METHODOLOGY

3.1 Introduction

In this chapter, each step of the experimental procedure used for the preparation of the supported cobalt catalyst is described.

It is well known that Fischer-Tropsch synthesis (FTS) is a complex reaction. Among the factors that contribute to this complexity are the large number of products FTS yields, and the rigorous requirements of the experimental setup. Furthermore, good practice in FTS experimentation includes calibrating the instruments and devices used to carry out the processes. In order to avoid systemic error and to achieve a good mass balance, the researcher has to exercise scrupulous efficiency when building the FT rig and analysing the experimental results.

The experimental setup procedures applied for the FTS, the chemicals used, and the techniques applied for the analysis of the products are illustrated in the sections that follow.

3.2 Chemicals and materials

All of the chemicals used in this study were analytical grade. Anhydrous solvents of high purity were used as received from the suppliers (Afrox, Sigma Aldrich and Merck), unless otherwise specified. Catalysts were prepared from the chemicals stocked in the laboratory where the research was done, as described in **section 3.3**.

3.3 Catalyst preparation

A supported cobalt catalyst (10% Co/TiO₂) by mass was used in this investigation. The catalyst was prepared by incipient wetness impregnation from cobalt nitrate - Co(NO₃)₂·6H₂O - (Sigma-Aldrich) and Titanium di-oxide TiO₂ (Degussa Titania, TiO₂,

P25, Surface area = $50 \text{ m}^2\text{g}^{-1}$), as previously reported [1,2]. Typically, titanium dioxide was mixed with distilled water, in a mass ratio of 1:1, to form a paste, which was then dried at 120°C for two hours and calcined in a Muffle oven at 400°C (increasing the temperature at a rate of $5^\circ\text{C}/\text{min}$) for six hours. It was then left in the oven overnight to cool to ambient temperature. The dried and calcined paste was crushed, and the particles sieved to separate out those with a diameter between 500 and $1000 \mu\text{m}$. These were collected to form the support used in the next stage of catalyst preparation.

The amount of cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) required was calculated on a cobalt metal loading of 10% of the mass of the support. Thereafter, the appropriate amount was dissolved in distilled water; the volume required having been measured according to the pore volume per gram of the support. The support and the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution were then mixed, dried (at 120°C for two hours), and calcined in a sequence similar to that described above, to create the cobalt catalyst.

Apart from its use in the FT experiments, the surplus cobalt catalyst obtained was kept for further experiments, including characterisation. The cobalt-based FT catalyst was characterised by various techniques, which also involved the use of microscopic and spectroscopic instruments. This was followed by elemental and surface analysis. More specific details of the instrumentation employed for characterisation of the chemical and physical properties of 10% Co/TiO₂ catalyst are given in **Appendix A**.

3.4 Experimental setup and procedure

The researcher constructed a rig based on the piping and instrumentation diagram (P&ID) depicted in **Figure 3.1**. The experimental setup consisted of the following: a tubular fixed bed reactor (FBR); hot and cold trap; tubing; pressure gauges; mass flow controller boxes; a programmable temperature controller box; and transformers. In addition, he used electrical wiring, heating tapes, a thermal blanket, thermocouples and quartz wool. After the rig-building had been completed, the author flushed the system with pressurised nitrogen, and used soapy water to test for leaks. Then he heated the stainless steel tube lines ($1/8$ inch OD, Swagelok) from the reactor's exits

and the hot trap to the gas chromatograph (GC) inlet to 150 °C. This temperature was maintained throughout the period of the experiment to prevent condensation of the products and the un-reacted feeds.

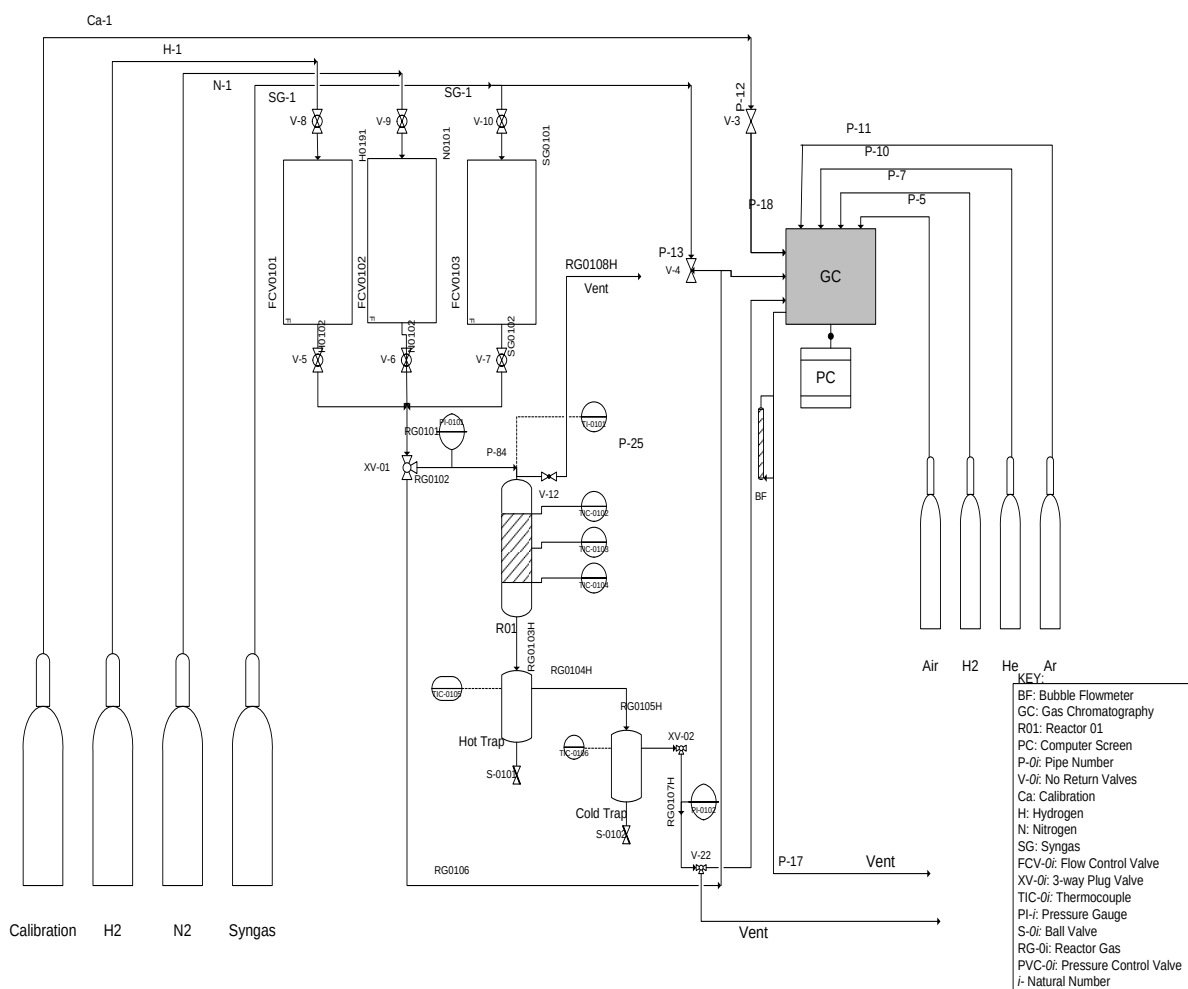


Figure 3.1: Piping and instrumentation diagram of the experimental setup used, including the reactor, hot and cold traps, pressure gauges, valves, bubble flow meter and gas cylinders, and the connections to the GC and computer.

3.4.1 FTS reactors

Of the many types of FT reactor available, three of the best-known are the fluidised bed, the fixed bed and the slurry phase reactors. The fixed bed reactor (FBR) offers the greatest technical and economic advantages when the engineer is working on a small scale. These include *i)* the capacity to scale up the process in a straightforward way; *ii)* the possibility of 90% and more selectivity to the higher hydrocarbons; and *iii)* the ease and cost-effectiveness with which wax can be separated from the catalyst [3]. FBR is used for low-temperature (180–250 °C) FTS with either iron or cobalt catalysts to produce high molecular mass linear waxes, which in turn can be hydro-cracked to produce diesel of an exceptionally high quality [4,5]. In the research described in this thesis, the writer used an FBR to carry out his experiments. The setup comprised one reactor, made of stainless steel and obtained from Autoclave Engineers, mounted vertically in the rig. The dimensions of the reactor are: a free volume of 10 mL, an internal diameter (ID) of 8 mm, and a tube length of 204 mm. A thermal blanket was used to cover the reactor and the heated tubing regions to minimise heat loss.

A schematic representation of the reactor is depicted in **Figure 3.2**. The feed gas flows downward through the catalyst bed in a profile approximating that of a plug flow.

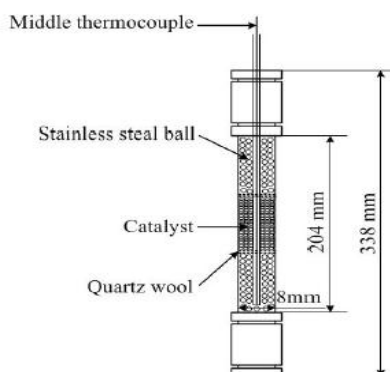


Figure 3.2: Schematic representation of the fixed bed reactor used in this study [6].

3.4.1.1 Fixed bed reactor: temperature profile

The FT reaction is known to be a highly exothermic process, which means that there is a risk that the temperature in the catalyst bed will overshoot the desired value during the FT reaction. In order to avoid temperature runaway, it is necessary to use small ID FBR. The catalyst bed was operated at an isothermal temperature, since non-isothermal operation could make the results difficult to interpret and thus make the correlation of the results with the operational conditions difficult (erroneous) [7].

Consequently, in this research, the writer took precautions to ensure that the FTS was operated isothermally within the catalyst bed. These precautions included: a) wrapping the heating tapes around the top and bottom of the reactor; b) using the reactor heating element passed through the middle of the tube to control the temperature of the main catalyst bed; and c) insulating the whole reactor from top to bottom with a sufficient amount of cotton wool.

The temperature profile at the axis of the reactor tube was measured to confirm that the temperature was maintained at a constant level. A thermocouple (1/16 inches, ANATECH), which was connected to the programmable temperature controller box, enabled the researcher to monitor the temperature of the central bed. This made it possible to achieve a temperature profile with a temperature difference of ± 0.1 °C between the top and bottom of the catalyst bed region (30 mm in length in the middle of the tube). **Figure 3.3** illustrates an example of the temperature profiles obtained.

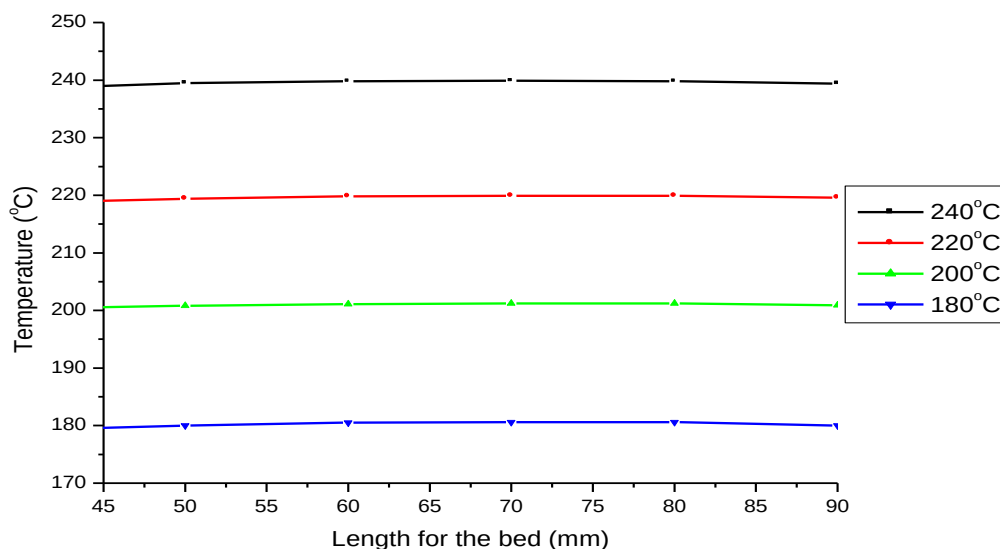


Figure 3.3: Temperature profile in the FBR catalyst bed for different temperatures, from 180–240 °C.

3.4.2 Loading the FTS catalyst into the reactor

Having prepared the cobalt-based catalyst, the researcher loaded one gram (500-1000 μm) into the middle of the tube of the reactor. He placed thin layers of quartz wool above and below the catalyst, followed by stainless steel balls at both top and bottom (see **Figure 3.2**). The function of the balls was to preheat the inlet gas and support the catalyst bed.

3.4.3 Catalyst drying and reduction

The metals used in FTS, work as catalysts after they have been reduced by means of a process that converts the cobalt oxide particles into cobalt metal. Prior to the FTS experiments, the writer activated the cobalt catalyst by drying it under a flow of pure N_2 (UHP, Afrox, South Africa) at a rate of 60 mL(NTP)/min. The temperature was ramped at a rate of 10 °C/min and held at 120 °C for an hour. The drying process swept away moisture in the reactor tube and catalyst. Then he switched the gas from nitrogen to hydrogen, maintaining a constant flow rate of 60 mL(NTP)/min to reduce the cobalt catalyst. The temperature was raised at a heating rate of 10 °C/min, and

kept at 350 °C at atmospheric pressure for 24 hours. Thereafter, the reactor was allowed to cool down to a temperature below 100 °C. The hydrogen was then purged to allow the gradual introduction of synthetic gas (syngas), a mixture of carbon monoxide and hydrogen (H_2 :CO ratio 2 with 10% N_2 for mass balance), which was used as a feed for the subsequent FTS reaction.

3.5 Fischer-Tropsch synthesis (FTS) experiments

3.5.1 FT reactions

A number of FTS reactions were carried out under various conditions in one FBR. In some of the experiments, the syngas feed was periodically switched to syngas with extra nitrogen to investigate the effect of nitrogen co-feeding in FTS. The syngas feeds were introduced into the reactors at various flow rates monitored by the mass flow controllers (Brooks Instrument 5850). The pressure in the reactor and the two knockout pots (vapour–liquid separators) was maintained using a back pressure regulator (Swagelok), which was located next to the cold trap. This reduced the gaseous stream containing the gas phase products and un-reacted feed to atmospheric pressure.

After the cold trap the tail gas passed through the sampling loops of the online gas chromatograph (GC) DANI GC 1000 for analysis and the flow rate was measured using a bubble flow meter at the end of the vent. The online GC was coupled with two thermal conductive detectors (TCD), labelled TCD A and B, and a flame ionisation detector (FID). These were used for inorganic (including methane) and organic products respectively. The temperature of the hot trap was maintained at 150 °C and reactor pressure, whereas the cold trap was kept at room temperature and reactor pressure. Condensed wax was collected from the hot trap. Products from cold trap were separated into an oil and aqueous phase, while the condensed wax was liquefied before being analysed by the off-line GC (DANI Master GC), which was equipped with an FID only.

The analyses of the activity and selectivity of the FT products were carried out and then presented as a function of various parameters, such as time on stream, CO

conversion, and carbon number. These were followed by more focused investigations of the selectivity to light hydrocarbons, kinetics; catalyst deactivation; chain growth probability; and product distribution of the FT processes. Details of each of these aspects of the FTS reactions are given separately in the chapters that follow.

3.5.2 FTS sample collection

Unless otherwise stated, liquid products from both the hot and cold traps were collected at least every 72 hours of time on stream, in sample vials for the wax and the mixed oil and aqueous phase. The knockout pots were maintained at room temperature for the cold stream and at 150 °C for the hot effluent streams throughout the experiments. The gas phase products was automatically sampled and monitored by an online GC every 83 minutes from the tail gas line, which was set at 150 °C. (The GC connection to the FT rig can be seen in **Figure 3.1.**) The gas phase sampling and analysis included both the hydrocarbon and inorganic compounds. The experimental setup had been designed to allow catalyst activity (CO and H₂ conversions), rates of formation, and selectivity to the hydrocarbons to be monitored constantly.

3.5.3 FTS product analysis

As mentioned above, the gas phase products of the FT reaction were directly analysed online with a GC instrument, while the liquid and solid phase products collected from the cold and hot traps were analysed by means of an offline GC. The online GC was equipped with a TCD and a FID, whereas only the latter was required for the offline GC. Prior the product analysis, the syngas feed containing 10% nitrogen and that with diluted with a range of higher amounts of nitrogen (up to 28%) was screened. This was done because the nitrogen in the feed was used as an internal standard for the calculation of both the reaction conversion and rate, and the product selectivity. The online and offline GCs were connected to computers equipped with Clarity software.

3.5.3.1 Setup of the online GC

The gas products created by the reaction were sent to the GC sampling loop through the tail gas line, which was heated to 150 °C, as were the three multiple sampling valves in the GC to which the gas was then sent. The TCD and FID detectors were maintained at 220 °C.

The configuration of the DANI GC system is displayed in **Figure 3.4**.

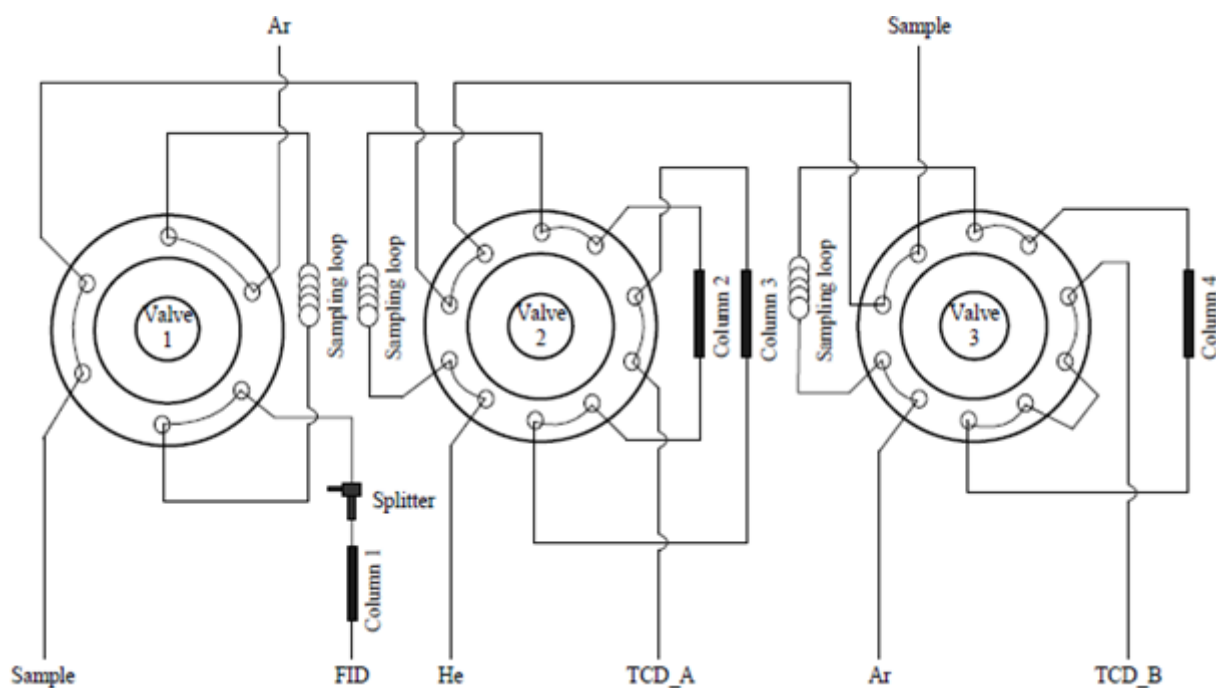


Figure 3.4: Schematic representation of the online GC configuration [6].

A summary of the characterisation of the columns and carrier gases of the DANI GC is given in **Table 3.1**.

Table 3.1: Specifications of the GCs employed in this study and the gases analysed

On-line GC	DANI GC 1000
Detector 1	FID, T=220 °C
Column 1	Varian capillary column (Cp-Poraplot Q-HT), 12.5m*0.53mm*20µm
Sample valve temperature	150 °C
Carrier gas	Ar Baseline with flow rate of 30 mL(NTP)/min
Oven temperature programme	Hold at 50 °C for 8 min, heat to 200 °C at 8 °C/min, hold at 200 °C for 45 min
Product analysis	C ₁ -C ₉
Detector 2	TCD-A, T=220 °C
Column 2	Teknokroma, porapack Q (Tmax: 250 °C), 80/100 mesh, 2m*1/8"*2.1mm
Column 3	Teknokroma, molecular sieve 13X (Tmax: 400 °C), 80/100 mesh, 2m*1/8"
Sample valve temperature	150 °C
Carrier gas	Ar Baseline with flow rate of 30 mL(NTP)/min
Oven temperature programme	Hold at 50 °C for 8 min, heat to 200 °C at 8 °C/min, hold at 200 °C for 45 min
Product analysis	CH ₄ , CO ₂ , N ₂ , CO
Detector 3	TCD-B, T=220 °C
Column 4	Teknokroma, molecular sieve 5A (Tmax: 400 °C), 80/100 mesh, 1.5m*1/8"
Sample valve temperature	150 °C
Flame gas	Air Instrument Grade with flow rate of 20 mL(NTP)/min and H ₂ Baseline with flow rate of 200 mL(NTP)/min
Carrier gas	He Baseline, 30 mL(NTP)/min
Oven temperature programme	Hold at 50 °C for 8 min, heat to 200 °C at 8 °C/min, hold at 200 °C for 45 min
Product analysis	H ₂
Off-line GC	
Detector	FID, T=350 °C
Column	Capillary Column MegaWax
Sample valve temperature	320 °C
Flame gas	Air, Instrument Grade, with flow rate of 30 mL(NTP)/min and H ₂ Baseline with flow rate of 300 mL(NTP)/min
Carrier gas	Ar Baseline with flow rate of 30 mL(NTP)/min
Oven temperature programme	Oil: heat to 300 °C at 3 °C/min, hold at 300 °C for 60 min Wax: heat to 300 °C at 5 °C/min, hold at 300 °C for 120 min
Product analysis	C ₅ -C ₄₀

Feed analysis and measurement of the calibration gases

The online analysis of the gas phase products can be described briefly, as follows. The FID detector in the online GC was connected to an amplifier. Varian capillary columns (see **Table 3.1**) using argon gas as the carrier gas were utilised to analyse the gaseous olefin and paraffin products from C₁–C₉. The computer, which was connected to the online GC, employed Clarity software to record the GC signal. The TCD A used a helium carrier gas to identify CH₄, CO₂, N₂ and CO, whereas TCD B measured H₂ with argon as the carrier gas. A dual filament-type detector, connected to an electrometer amplifier, was fitted to each of the TCDs. Both the detectors and the amplifiers provided excellent sensitivity to the concentrations of inorganic components and methane in the range used in this series of experiments.

In order to obtain accurate data on the molar composition of the feeds, both syngas and diluted syngas were directed to the GC through a 1/8-inch stainless steel tube that bypassed the reactor. The feed composition was measured four times each taking 15 minutes using two detectors TCD A and TCD B. In a similar method, the GC was calibrated with a gas made of hydrocarbons CH₄, C₂H₄, C₂H₆ and inorganic gases H₂, CO₂, N₂ and CO. The areas of the gas compositions of three of the four chromatographs, that had compositions within one percentage point, were calculated and the average used. Both feed and calibration gases were measured at 60 mL(NTP)/min and 75 mL(NTP)/min at FT reaction operational conditions, for reasons that will be given in Chapters 4 and 5.

The chromatographs resulting from the feed analyses and GC calibration are shown in **Figure 3.5** and **Figure 3.6** respectively. Typical chromatographs of the gas phase products are depicted in **Figure 3.7**.

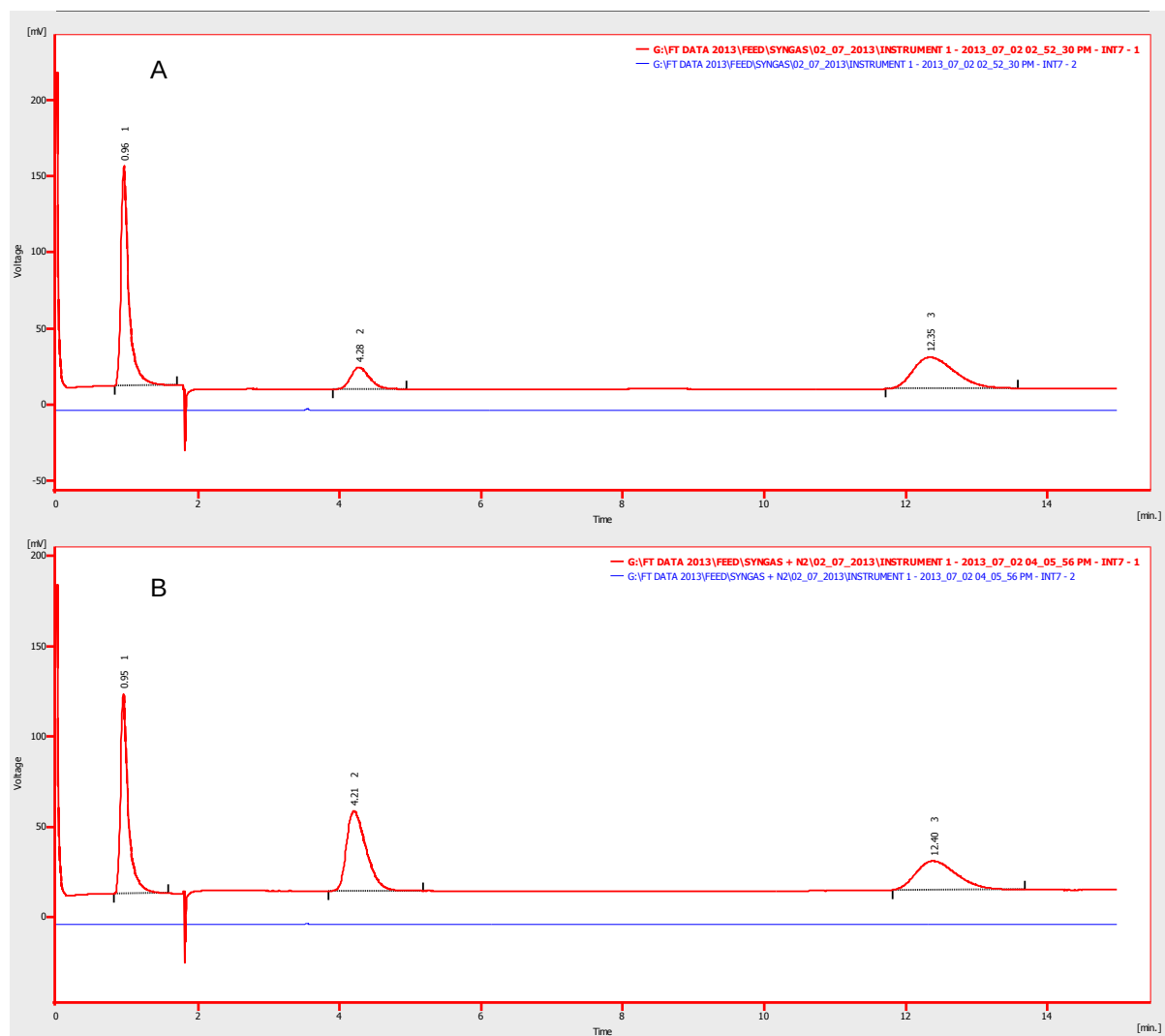


Figure 3.5: Chromatographs representing the feed analysis at 60 mL(NTP)/min (A) and 75 mL(NTP)/min (B).

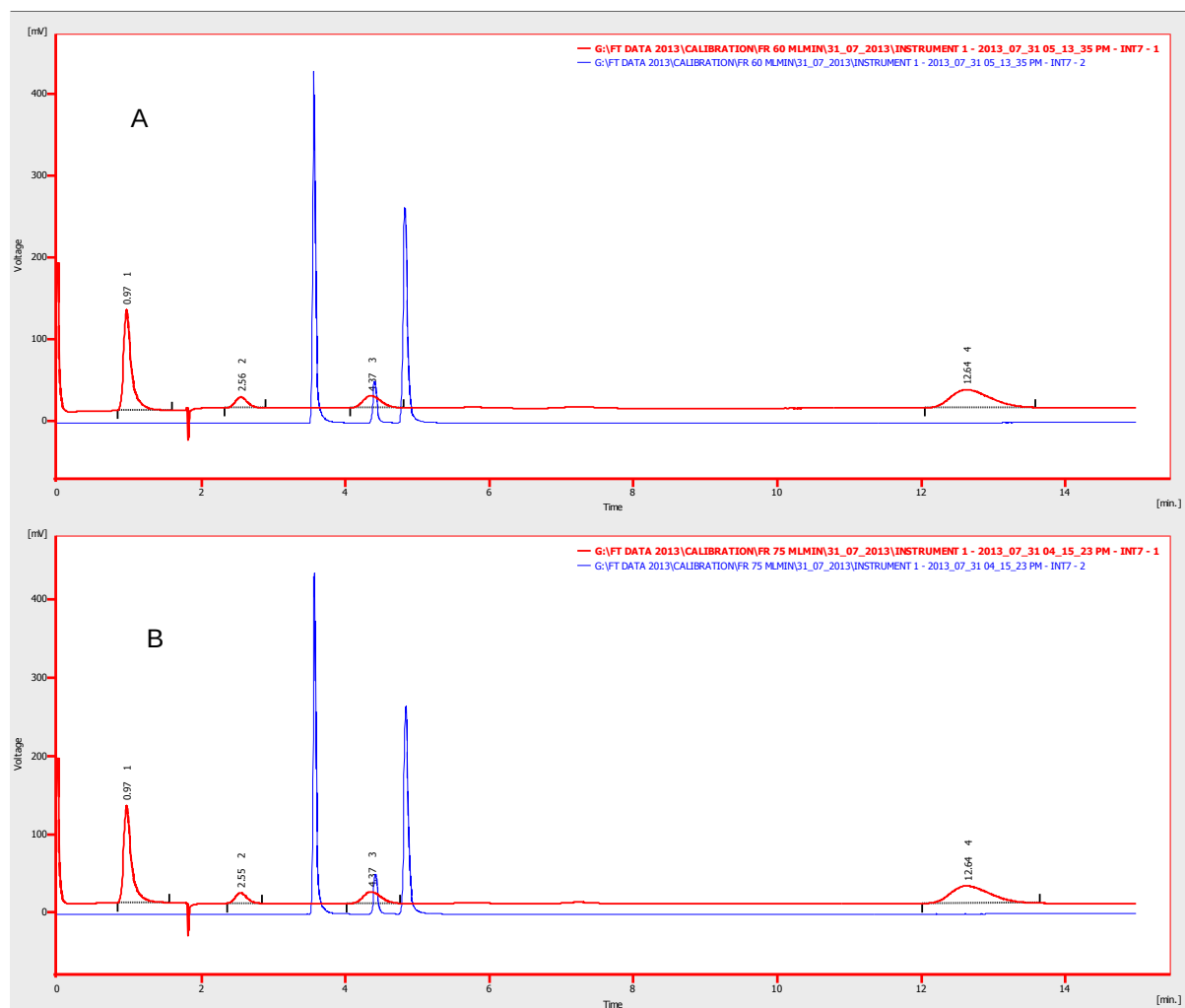


Figure 3.6: Chromatographs for the calibration gas measurement 60 mL(NTP)/min (A) and 75 mL(NTP)/min (B).

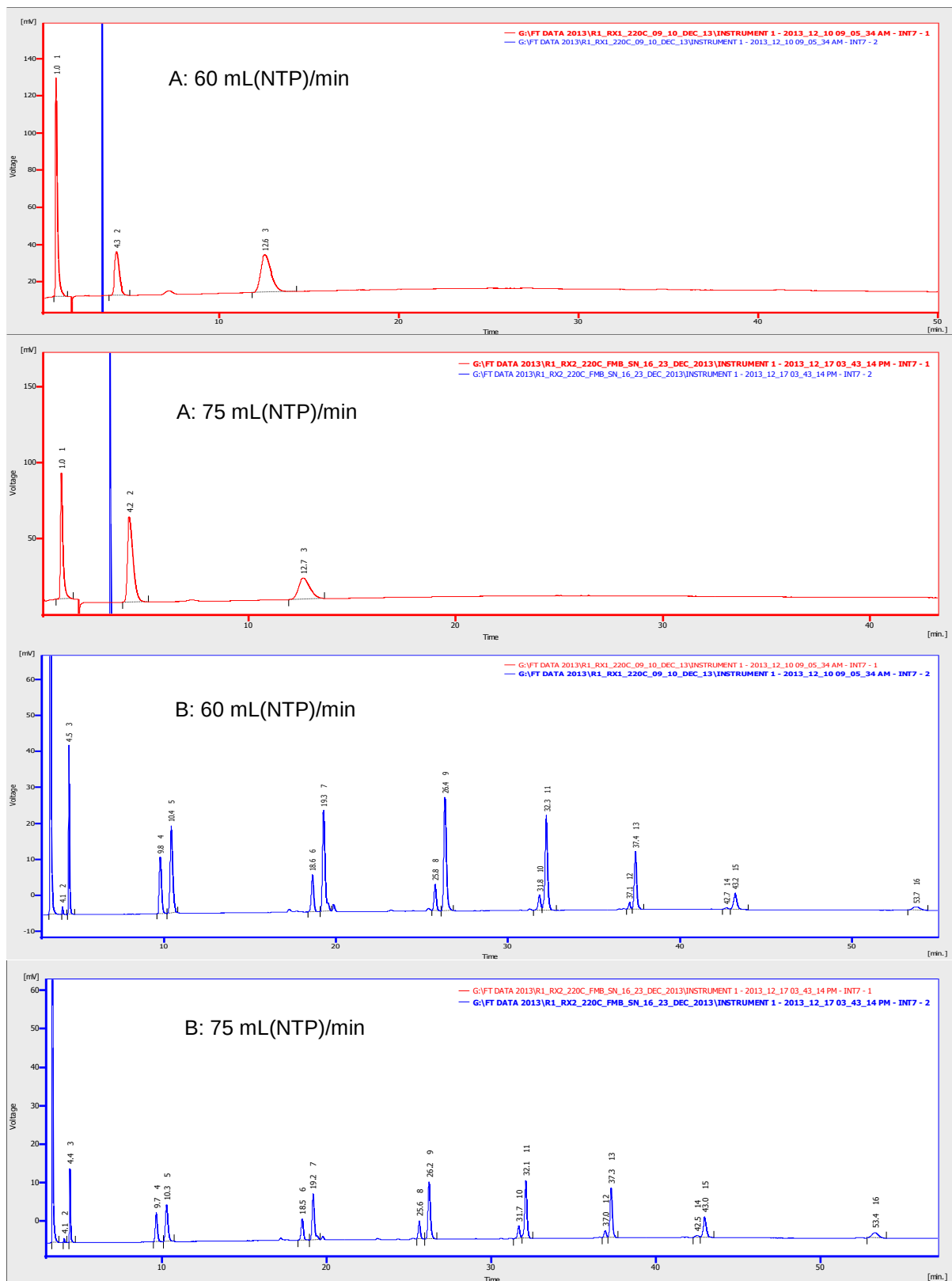


Figure 3.7: Typical TCD (A) and FID (B) online chromatographs for the gas phase products analysed at 60 mL(NTP)/min (syngas) and 75 mL(NTP)/min (syngas with extra nitrogen).

3.5.3.2 Setup of the offline GC

The analysis of the long chain hydrocarbons, oil and wax products, was carried out using an offline GC with a FID on a capillary column MegaWax TR21. The measurements of these products were performed with a DANI Master GC instrument. The GC was connected to a computer that recorded the amplified signal from the detector. Argon gas was used as a carrier gas for the 0.1 µl samples of each of the oil and wax products, which were injected into the GC by syringe. The temperature programmes used for the GC were ramped to prevent the accumulation of long chain hydrocarbons in the column. Cyclohexane (C_6H_{14}) was employed as the reference component to identify peaks in the chromatographs. The analysis of the condensed phase products indicated that the mass response factors were around one. Consequently, it was possible to acquire a mass composition straightforwardly from the GC peak area percentages.

The chromatographs of the reference component (C_6H_{14}), oil and wax samples are shown in **Figure 3.8**.

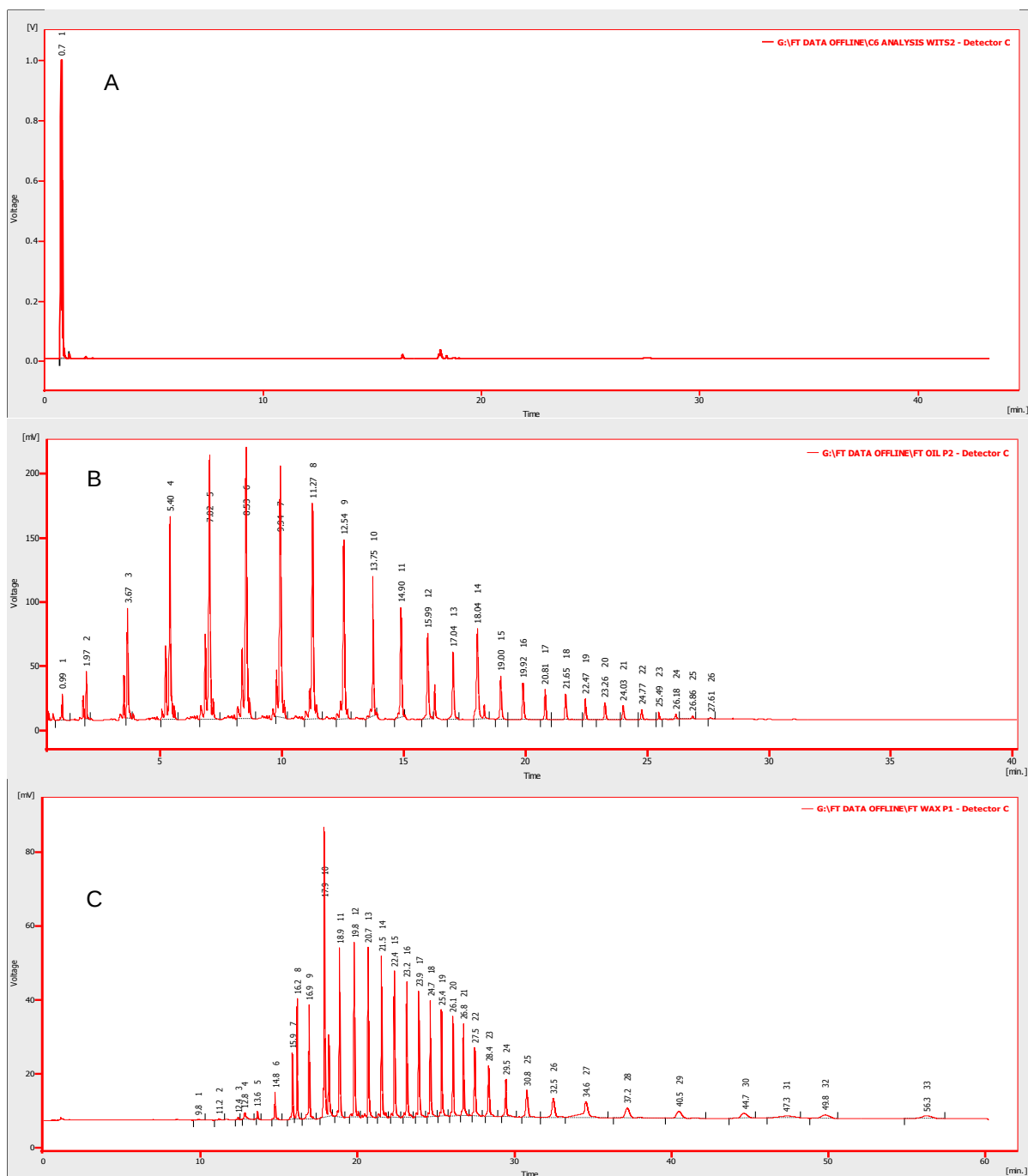


Figure 3.8: Typical FID offline chromatographs (A) for reference component; long chain hydrocarbon products (B) for the oil and (C) for wax samples.

The identification of peaks from the chromatographs obtained from the online and offline GCs analysis are summarised in **Table 3.2**.

Table 3.2: Summary of the components analysed by online and offline GCs

Peak number	On-line TCD Gas	On-line FID Gas	Off-line FID Oil	Off-line FID Wax
1	H ₂	P ₁	C ₆	C ₈
2	N ₂	O ₂	C ₇	C ₉
3	CO	P ₂	C ₈	C ₁₀
4		O ₃	C ₉	C ₁₁
5		P ₃	C ₁₀	C ₁₂
6		O ₄	C ₁₁	C ₁₃
7		P ₄	C ₁₂	C ₁₄
8		O ₅	C ₁₃	C ₁₅
9		P ₅	C ₁₄	C ₁₆
10		O ₆	C ₁₅	C ₁₇
11		P ₆	C ₁₆	C ₁₈
12		O ₇	C ₁₇	C ₁₉
13		P ₇	C ₁₈	C ₂₀
14		O ₈	C ₁₉	C ₂₁
15		P ₈	C ₂₀	C ₂₂
16		O ₉	C ₂₁	C ₂₃
17			C ₂₂	C ₂₄
18			C ₂₃	C ₂₅
19			C ₂₄	C ₂₆
20			C ₂₅	C ₂₇
21			C ₂₆	C ₂₈
22			C ₂₇	C ₂₉
23			C ₂₈	C ₃₀
24			C ₂₉	C ₃₁
25			C ₃₀	C ₃₂
26			C ₃₁	C ₃₃
27				C ₃₄
28				C ₃₅
29				C ₃₆
30				C ₃₇
31				C ₃₈
32				C ₃₉
33				C ₄₀

P = paraffin; O = olefin; and C = hydrocarbon (olefin+paraffin)

Furthermore, the peak areas in the chromatographs of the feeds and calibration gas were later used to calculate the flow rate, the CO and H₂ conversions, the selectivity to the products, and the rate of formation of the products as demonstrated in the mathematical expressions depicted in equations (3.1) to (3.14), which represent each species of the FT reactions.

3.6 Mass balance calculations

The calculations used to determine the mass balance are similar to those used by various researchers [6-11], and are given below. Samples of the feeds gas were analysed in order to establish the amount of reactant entering the reactor. The actual molar composition of the feed gas was determined by using calibration data and relative response factors. The calibration gas used contained molar percentages of 2.5% CH₄; 0.2% C₂H₄; 0.5% C₂H₆; 10% CO; 5% CO₂; and the remainder, N₂.

The molar percentage of a compound θ in the gas was calculated as:

$$\% \theta_{gas} = \left(\frac{A_{\theta,gas}}{A_{\theta,cal}} \right) \cdot \% \theta_{cal} \quad (3.1)$$

where:

$\% \theta_{cal}$ = the molar percentage of compound θ in the analysed gas;

$A_{\theta,gas}$ = the integrated area of the GC peak corresponding to the compound θ in the analysed gas;

$A_{\theta,cal}$ = the integrated area of the GC peak corresponding to the compound θ in the calibration mixture;

$\% \theta_{cal}$ = the molar percentage of compound θ in the calibration mixture.

For compounds for which calibration data could not be obtained directly from the calibration mixture, that of a reference compound and relative molar response factor was used, and expressed as:

$$\% \theta_{gas} = \left(\frac{A_{\theta,gas}}{A_{\theta,cal}} \right) \cdot \% A \alpha_{cal} \cdot RF_{\theta,\alpha} \quad (3.2)$$

where:

$\%A_{\alpha_{cal}}$ = the molar percentage of the reference compound α in the calibration mixture;

$A_{\alpha_{cal}}$ = the integrated area of the GC peak corresponding to the reference compound α in the calibration mixture; and

$RF_{\theta,\alpha}$ = the relative response factor of the compound θ with respect to the reference compound α .

C₂H₄ was used as the reference for olefins, and C₂H₆ as the reference for paraffins.

Molar response factors for hydrocarbon products are presented in **Table 3.3**.

Table 3.3: Molar response factors for hydrocarbon products

Carbon Number	Olefin	Paraffin
2	1	1
3	0.70	0.74
4	0.78	0.55
5	0.47	0.47
6	0.40	0.40
7	0.35	0.35
8	0.32	0.32
9	0.28	0.28
10	0.24	0.24
11	0.21	0.21
12	0.19	0.19
13	0.18	0.18
14	0.17	0.17
15	0.15	0.15

The experimental setup (shown in **Figure 3.1**) used in this research was configured in such a way that the outlet flow rate could be calculated from the inlet volumetric flow rate. To repeat what has already been mentioned, N₂ in the syngas was fed to serve as an internal standard as well as a co-feeding agent for extra nitrogen. N₂ is an inert gas; as such the amount of N₂ is expected to be the same at the inlet with feed as at the exit with products. The N₂ balance across the reactor is therefore expressed as:

$$F_{in} \cdot X_{N_2,in} = F_{out} \cdot X_{N_2,out} \quad (3.3)$$

where:

F_{in} = the total molar flow rate [mol/min] of the reactor feed;

F_{out} = the total molar flow rate [mol/min] of the reactor outlet gas stream;

$X_{N_2,in}$ = the molar fraction of nitrogen in the reactor feed; and

$X_{N_2,out}$ = the molar fraction of nitrogen in the reactor outlet gas.

The rate of CO conversion can be calculated as shown below:

$$-r_{CO} = \frac{F_{CO,in} - F_{CO,out}}{m_{cat}} \quad (3.4)$$

where:

$F_{CO,in}$ = the molar flow rate [mol/min] of CO in the reactor feed;

$F_{CO,out}$ = the molar flow rate [mol/min] of CO in the reactor outlet gas;

m_{cat} = the mass [grams] of catalyst; and

r_{CO} = the rate of CO conversion [mol/min/g_{cat}].

In equation 3.4, when negative values have been obtained, the rate of CO conversion is multiplied by -1 to report positive values of r_{CO} :

$$F_{CO,in} = F_{in} \cdot X_{CO,in} \quad (3.5)$$

$$F_{CO,out} = F_{out} \cdot X_{CO,out} \quad (3.6)$$

where $X_{CO,in}$ and $X_{CO,out}$ are the CO mole fractions in the reactor feed and outlet gas respectively.

After introducing equations (3.5) and (3.6) into expression (3.4), and after showing F_{in} as a function of F_{out} in equation 3.3, the rate of CO consumption can be set out as:

$$-r_{CO} = \frac{F_{out} \cdot \left[X_{CO,in} \cdot \left(\frac{X_{N_2,out}}{X_{N_2,in}} \right) - X_{CO,out} \right]}{m_{cat}} \quad (3.7)$$

The mathematical formula shown in equation (3.8) was used to determine the rate of CO conversion directly, as $X_{CO,in}$ and $X_{N_2,in}$ were known from the premixed gas cylinder and $X_{CO,out}$ and $X_{N_2,out}$ had been derived from the reactor outlet gas analysis. F_{out} was also calculated from the total gas volumetric flow rate at the reactor outlet by assuming the ideal gas law.

The CO conversion was calculated as follows:

$$\%CO_{conv} = \frac{\left[X_{CO,in} - X_{CO,out} \cdot \left(\frac{X_{N_2,in}}{X_{N_2,out}} \right) \right] \cdot 100}{X_{CO,in}} \quad (3.8)$$

The rate of formation of a gas product θ_i was calculated as follows:

$$r_{\theta_i} = \frac{F_{out} \cdot X_{\theta_i,in}}{m_{cat}} \quad (3.9)$$

where:

r_{θ_i} = the rate in mole/min/g_{cat} ; and

$X_{\theta_i,in}$ = the mole fraction of product θ_i in the reactor outlet gas.

The carbon balance was checked as follows:

$$[nC]_{gas,product} + [nC]_{liquid,product} + [nC]_{wax,product} = -r_{CO} \cdot t \cdot m_{cat} \quad (3.10)$$

where nC represents the total number of moles of carbon contained in a product fraction (gas, liquid or wax) at the end of the mass balance period, t .

The error on the carbon balance was calculated as:

$$\%error = \frac{\{-r_{CO} \cdot t \cdot m_{cat} - [nC]_{gas,product} + [nC]_{liquid,product} + [nC]_{wax,product}\}}{-r_{CO} \cdot t \cdot m_{cat}} \cdot 100 \quad (3.11)$$

The carbon balance was considered satisfactory when the % error was < 5.

The product selectivity was calculated on a moles of carbon basis, as follows:

$$Sel(\theta) = \frac{[nC]_{\theta}}{-r_{CO} \cdot t \cdot m_{cat}} \quad (3.12)$$

where $Sel(\theta)$ represents the selectivity of product θ and $[nC]_{\theta}$ the moles of carbon contained in the product θ .

Olefin/paraffin ratio

Olefin/paraffin (O/P) ratio considered the relative molar amount for the same carbon number in the outlet stream, which was calculated as follows:

$$\frac{O_n}{P_n} = \frac{N_{C_nH_{2n}}}{N_{C_nH_{2n+2}}} \quad (3.13)$$

Olefin/olefin ratio

The olefin/olefin (O_n/O_{n-1}) ratio showed the relative molar amount of neighbouring olefins in the outlet stream, and was calculated as follows:

$$\frac{O_n}{O_{n-1}} = \frac{N_{C_nH_{2n}}}{N_{C_{n-1}H_{2(n-1)}}} \quad (3.14)$$

Normalised mole fractions for C_nH_{2n} , C_nH_{2n+2} , and $C_{n+1}H_{2(n+1)}$

The normalised mole fractions (NMF) represented the relative mole fractions for C_nH_{2n} , C_nH_{2n+2} , and $C_{n+1}H_{2(n+1)}$, which was expressed by:

$$NMF = \frac{N_i}{\sum N_i} \quad (3.15)$$

where N_i represents the molar amount of C_nH_{2n} , C_nH_{2n+2} , and $C_{n+1}H_{2(n+1)}$.

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CHAPTER 4

FISCHER-TROPSCH SYNTHESIS: A STUDY ON THE DEACTIVATION OF A TITANIA BASED COBALT CATALYST

The material in this chapter has been written in a paper format and is ready for submission. Some of the data are accepted for a poster presentation at AIChE annual meeting 2015.

Abstract

The catalyst is crucial in Fischer-Tropsch synthesis (FTS) and once the catalyst is deactivating both the activity and selectivity to the FT products could be affected. With the aim of understanding the effect of catalyst deactivation on the formation rate and selectivity to the light olefin and paraffin products separately during FTS, a group of FT experiments were conducted using 10% Co/TiO₂ catalyst in a fixed bed reactor.

A catalyst deactivation, 'CO conversion dropped from 46.1% to 12.8%', was observed during the time on stream (TOS) from 110 to 1200 hours. The results showed that selectivity to olefins increased with a drop in the CO conversion whereas the selectivity to paraffin did not change much. By comparing the product formation rates before, during and after deactivation, it was shown that the olefin formation rate was fairly constant, and in some case the rate increased, while the paraffin formation rate dropped. This indicates that the deactivation is mainly caused by the change in the paraffin formation rate. The results imply that the design of a cobalt based FTS should consider the formation rates of olefin and paraffin separately.

4.1 Introduction

The Fischer-Tropsch (FT) process is used for the production of synthetic fuels and other waxy products from origins such as natural gas, coal and biomass using a metal catalyst. The conversion of CO and H₂ into products, hydrocarbons and oxygenates, through FTS depends on various parameters [1]. Iron and cobalt are the most used metals as FT based catalysts. In comparison between iron and cobalt based FT catalysts, cobalt catalysts have high activity and selectivity to linear alkanes, less water gas shift reaction and it is believed that the cobalt based FT catalysts deactivate less rapidly. But the cobalt FT catalysts aren't immune to disadvantages which include the high cost of the cobalt [2–4].

Indeed, the catalyst is crucial in FT processes and once the catalyst is deactivated there is a strong possibility for the activity and selectivity of the FT products to be affected. How to trace the source of catalyst deactivation is difficult in many cases because it is usually a complex problem where several mechanisms contribute to the loss of activity and/or selectivity [5]. As a result, the deactivation of catalysts has raised many debates amongst academics and industrialists about its origin. For instance, some authors [2,4,6–8] have reported that oxidation causes the deactivation of Co catalyst in FT. But Saib et al. disagreed and reported that under realistic FT conditions, sintering of a cobalt (Co) active site, carbon deposition and surface reconstruction are the reasons for the deactivation of the cobalt catalyst [3]. Tsakoumis et al. have added more reasons for the deactivation of Co catalyst including carbidisation and attrition [5]. Therefore, not knowing for sure the causes of deactivation, catalyst deactivation is a major challenge in cobalt based Fischer-Tropsch synthesis. Issues such as the change in deactivation rate with time on stream imply that the actual cause of deactivation is the result of a combination of several phenomena and not just one aspect. To add to the complexity of the topic, although catalytic systems show different behaviour deactivation is an inevitable phenomenon in FTS [5].

Product formation in FT processes has been discussed in the literature. In particular, Todici et al. have developed a schematic representation of FT which

shows that the product formation follows: 1) chain propagation, hydrogenation to n-paraffins and desorption to 1-olefins and 2) the secondary reactions of 1-olefin through hydrogenation, isomerisation and readsorption of olefins. The readsorption of olefin mechanism is further supported by the exponential increase in the 1-olefin to n-paraffin ratio [9]. Moreover, van Der Laan and Beenackers [10] have reported that for certain catalytic systems, secondary hydrogenation of olefins may take place. On the other hand, van Der Laan and Beenackers [10] have reported in their review, citing Sarup and Wojciechowski who made several assumptions but managed to derive expressions for the methanation and a mechanistic formulation for the paraffin formation based on the optimised model for the rate of CO consumption. There is definitely a link between the CO consumption rate and the formation of paraffin as will be demonstrated here. However, at low carbon numbers secondary reactions hardly affect the product distribution, which is reflected by the observed *n*-independence of the paraffin/olefin selectivity at low carbon numbers [11]. Zhou et al. reported that the deactivation rate of the catalyst increased with increasing feed (reactants) ratios while the olefins to alkanes ratio (C_{2-40}) decreased with increasing deactivation rate [12]. Yao et al. have also reported findings on the products formation rate and selectivity during the catalyst deactivation in FTS [13].

Furthermore, it is generally agreed by researchers that FTS is influenced by parameters including the syngas composition, the type of catalyst and its deactivation, the type of reactor and the operating conditions. As demonstrated above, studies in the literature have focused on decreasing the deactivation rates of these catalysts [6,8,14–17]. Several other researchers focused attention on employing different catalyst particle sizes, promoted and unpromoted catalysts while investigating the catalyst deactivation [17–22]. Other scientists while studying the catalyst deactivation have shown much interest on the characterisation of catalyst before the FT experiment starts, *in situ* characterisation and characterisation of used catalyst [5,23–25]. Moreover, most of the papers reported the catalytic activity before, during deactivation and after the FT processes. But only a few of them [12,13] have mentioned the product formation and selectivity during the catalyst deactivation whereas only one [13] has reported

on the formation rate and selectivity of olefin and paraffin separately. So, regardless of some details about the effects of these parameters being available in the literature, the attempts to improve the understanding of the formation and selectivity of the olefins and paraffins in FTS is still warranted. Therefore, in this investigation, the researcher reports on how the catalytic activity, deactivation of catalyst, product formation rates and selectivity of the products are affected when using Co/TiO₂ in fixed bed reactor during FT processes.

4.2 Fischer-Tropsch experiment: catalyst testing

In this study, a supported cobalt catalyst (10% Co/TiO₂ by mass) was used for the FT experiments. The catalyst was prepared by incipient wetness impregnation from cobalt nitrate - Co(NO₃)₂.6H₂O - (Sigma-Aldrich) and Titanium di-oxide TiO₂ (Degussa Titania, TiO₂, P25, Surface area = 50 m²g⁻¹), as previously detailed [26,27].

The researcher placed one gram of 10% Co/TiO₂ into the middle of the fixed bed FT reactor, dried at 120 °C for an hour under nitrogen atmosphere flowing at 60 (NTP)mL/min, and reduced it *in situ* with pure hydrogen at a flow rate of 60 (NTP)mL/min and temperature set at 350 °C for 24 hours all at atmospheric pressure. When the catalyst was reduced, the temperature of the reactor was cooled down to the ambient temperature. Then the FT experiments began with syngas. The syngas, 30%CO/60%H₂/10%N₂ by volume, was introduced into the reactor with a flow rate of 60 (NTP)mL/(min.gcat) at atmospheric pressure. Then, the reactor pressure was gradually increased to 20 bar (gauge) which was followed by a progressive increase of the reactor temperature to 200 °C. Once the temperature reached 200 °C, the reactor was kept at these conditions and the FT reaction conducted for 48 hours.

Thereafter, the reaction temperature was gradually increased to 220 °C while keeping the other reaction conditions the same as at 200 °C. After about 250 hours at these conditions another set of FT experiments with syngas was carried also for more than 250 hours at 220 °C. For these experiments the feed gas was switched

from syngas (S), '60% H_2 /30% CO /10% N_2 by volume', to syngas with an extra N_2 ($\text{S}+\text{N}_2$), '48% H_2 /24% CO /28% N_2 by volume' with a constant partial pressure of H_2 at 12.5 bar (abs) and CO at 6.20 bar (abs) by adjusting the total flow rate and pressure for a new FT reaction with $\text{S}+\text{N}_2$. After the FT reaction with $\text{S}+\text{N}_2$, the feed gas was switched back to syngas feed with the same reaction conditions as for the previous FT reaction with syngas.

The FT experiments were conducted by periodically switching the feed from 'syngas' to 'syngas + N_2 ' while keeping the reactants (H_2/CO) partial pressures the same. Each of the feed gases was interchanged more than seven times, with time on stream increment to 2668 hours. The temperature of the reactor was maintained at 220 °C throughout the experiments for both FT runs with syngas and syngas + N_2 . After a time on stream of 667 hours, when the researcher was switching the feed gas of the reactor from syngas to syngas + N_2 , suddenly one of the mass flow controllers malfunctioned. Hence, the flow of feed gas (syngas and syngas + N_2) to the reactor was stopped while 15 (NTP)mL/min of N_2 only was fed into the reactor.

While the FT rig was fixed by replacing the malfunctioned MFC, the nitrogen alone flow into the reactor was carried out for 193 hours (eight days) while the new MFC was being calibrated and installed. Then, the syngas was used to purge the new MFC system by sending the syngas into the connections while the direction of the pipe lines was oriented to vent for about 5 minutes to avoid oxygen contamination into the FT system. Thereafter, the connections were directed towards the reactor and the FT reactions continued. The current work focuses on the group of experiments conducted from 110 to 1200 hours. The reaction and feed conditions for the FTS experiments over the cobalt based catalyst are listed in **Table 4.1**.

During these reactions, the researcher monitored the tail-gas composition with an online DANI GC 1000 gas chromatometer, equipped with flame ionisation detector (FID) and thermal conductivity detectors (TCD A and TCD B), to analyse the different gas phases—(C_1 – C_9), (CH_4 , CO_2 , N_2 , CO) and H_2 respectively. He also used Clarity software to process chromatographs. Each detector was connected to

a Varian capillary column: (CP-PoraPLOT Q-H) for FID; Teknokroma, porapak Q and Teknokroma molecular sieve 13X for TCD A; and a Teknokroma, molecular sieve 5A for TCD B.

Table 4.1: Reaction and feed conditions for the FTS experiments over a cobalt based catalyst

Case	Syngas (S)	Syngas + N ₂ (S+N ₂)
Catalyst	10% Co/TiO ₂	10% Co/TiO ₂
Mass (gram)	1	1
Temperature (°C)	220	220
Reactants partial molar flow rate (mol/min) for: FR _{H2} FR _{CO}	0.075 0.038	0.075 0.037
Reactants partial pressure (bar abs) for: P _{H2} P _{CO}	12.51 6.26	12.41 6.20

4.3 Results and discussion

4.3.1 Catalytic activity and product formation rate

The reactants (CO and H₂) consumption rates and the product formation rates of light hydrocarbons as a function of time on stream were measured. The results are shown in **Figure 4.1 (A)** for the reactant consumption rates; **(B)** for the methane, **(C)** for olefins (O₂–O₅) and **(D)** paraffins (P₂–P₅) formation rates. The first two days of the FT reaction start-up point are not reported in these graphs. Although, the FT experiment started at 200 °C (for two days), the results in this Chapter

focus on the data obtained when the temperature was set at 220 °C only. It is important to note that the dashed lines in **Figure 4.1** represent the starting points of switching the two kind of feed gases: syngas to syngas with extra N₂.

From this **Figure 4.1 (A)**, the activity of the catalyst declined gradually with time on stream TOS from 110 to 1200 hours. The catalytic activity decreased even more after the nitrogen alone flow during the time zone from 667 to 859 hours. Thereafter the consumption rates of the reactants remained fairly constant with time. During the same period of TOS (110 to 1200 hours), the methane formation rate decreased similarly with the decline of the catalytic activity of the reaction. Previous authors reported similar trends for methane formation rate and CO conversion [28]. Additionally, it is evident from this data that the catalytic activity for the reactants consumption rate is comparable to the light paraffin (P₂–P₅) formation rates, see **Figure 4.1 (A)** and **(D)**, whereas the olefin formation rates (**Figure 4.1 (C)**) did not follow the trends as displayed in **Figure 4.1 (A)**. The interesting points are in the trend of the paraffin and olefin during the catalyst deactivation periods. On one hand, **Figure 4.1 (A)** and **(C)** reveal that when the catalytic activity decreased, the formation rate of the light olefins (O₂–O₅) did not decrease. In fact they tend to increase slightly with TOS, and there is a noticeable increase after the nitrogen alone flow in the reactor. On the other hand, the formation rates of light paraffins (P₁–P₅) decreased with the catalyst deactivation in the zone of 110 to 1200 hours. Previous researchers have reported similar findings [13]. Thus the overall catalytic activity appears to be affected by the formation rates of the paraffins only. The results obtained at steady state when the catalytic activity seemed stable are presented in Chapter 5.

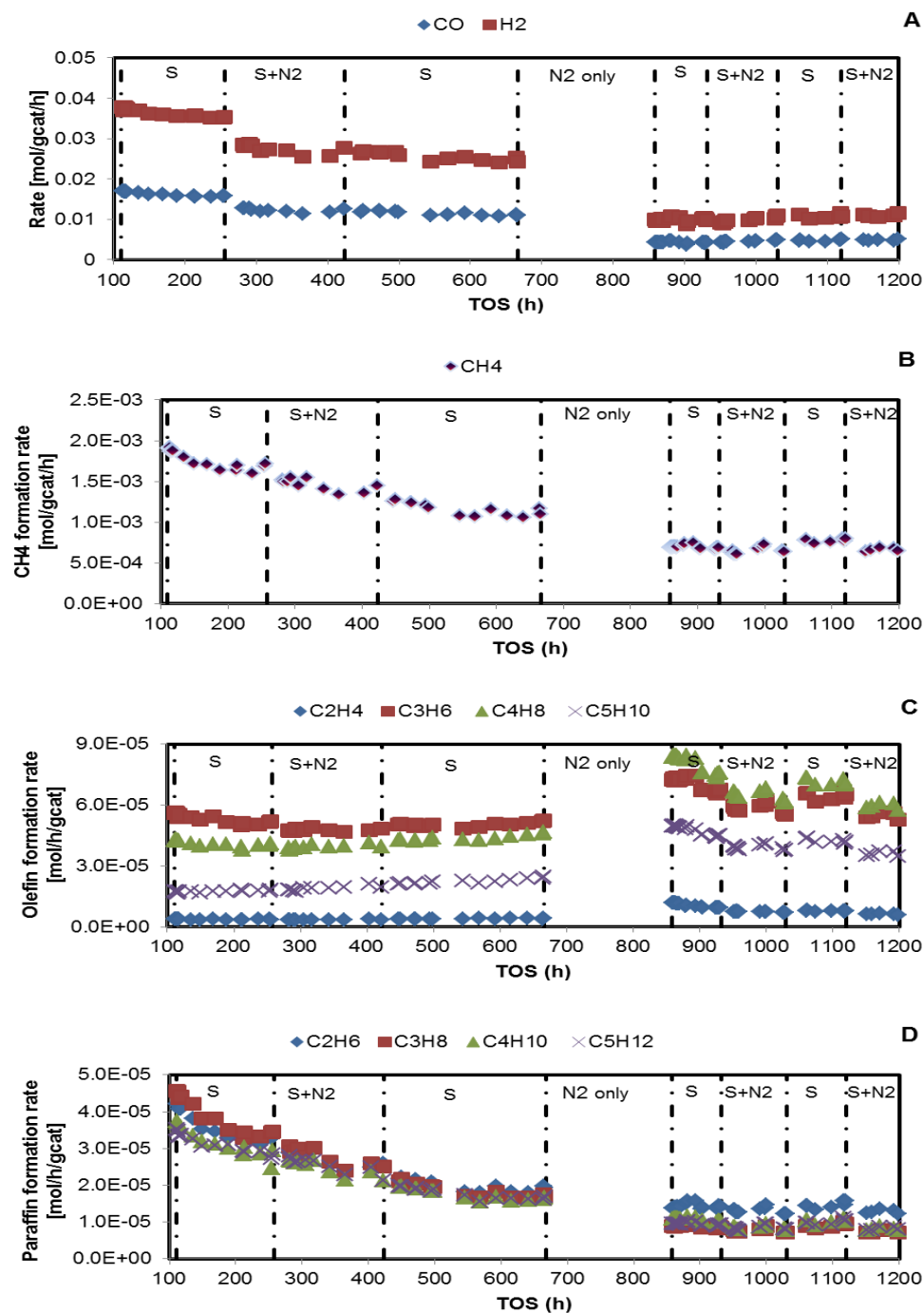


Figure 4.1: Reactant consumption rates (A); formation rates of (B) methane; (C) light olefin; and (D) light paraffin as a function of time on stream (TOS) during FT runs with 10% Co/TiO₂ in a fixed bed reactor at 220 °C while keeping the reactants partial pressure and volumetric flow rate the same (see **Table 4.1**). There was nitrogen only flow during TOS between 667 and 859 hours.

4.3.2 Reaction conversion and selectivity of the products

The conversions of the reactants (CO and H₂) and the selectivity of light hydrocarbons as a function of time on stream were plotted. The results are displayed in **Figure 4.2** as follows (A) for CO conversion, (B) for methane selectivity, (C) for olefins (O₂–O₅) and (D) for the light paraffins (P₂–P₅) selectivities. The data show that the CO conversion decreased from 46% to 30% with time on stream (TOS) from 110 to 667 hours. Thereafter the nitrogen alone was introduced to the reactor for 8 days and the CO conversion dropped from 30% to 13% between TOS 667 to 859 hours. The observation of **Figure 4.1 (A)** and **Figure 4.2 (A)** reveals two stages of the catalyst deactivation; the first deactivation appeared with TOS increment 110 to 667 hours and the second deactivation from 859 to 1200 hours after the nitrogen alone flow to the reactor was stopped. Subsequently the conversions remain fairly constant for a long period of TOS and those results are detailed in chapter 5. The decrease in the CO conversions with time on stream agrees with previous publications. For instance, Raje and Davis [29] have found that the reactants conversion decreased rapidly from 72% to 40% in the first 100 hours of time on stream. Subsequently, the deactivation rate decreased with synthesis gas conversion decreasing from 40% to 20% in the next 650 hours. Once again, it is important to note that the dashed lines in **Figure 4.2** represent the starting points of each FT experiment with the reaction conditions listed in **Table 4.1**.

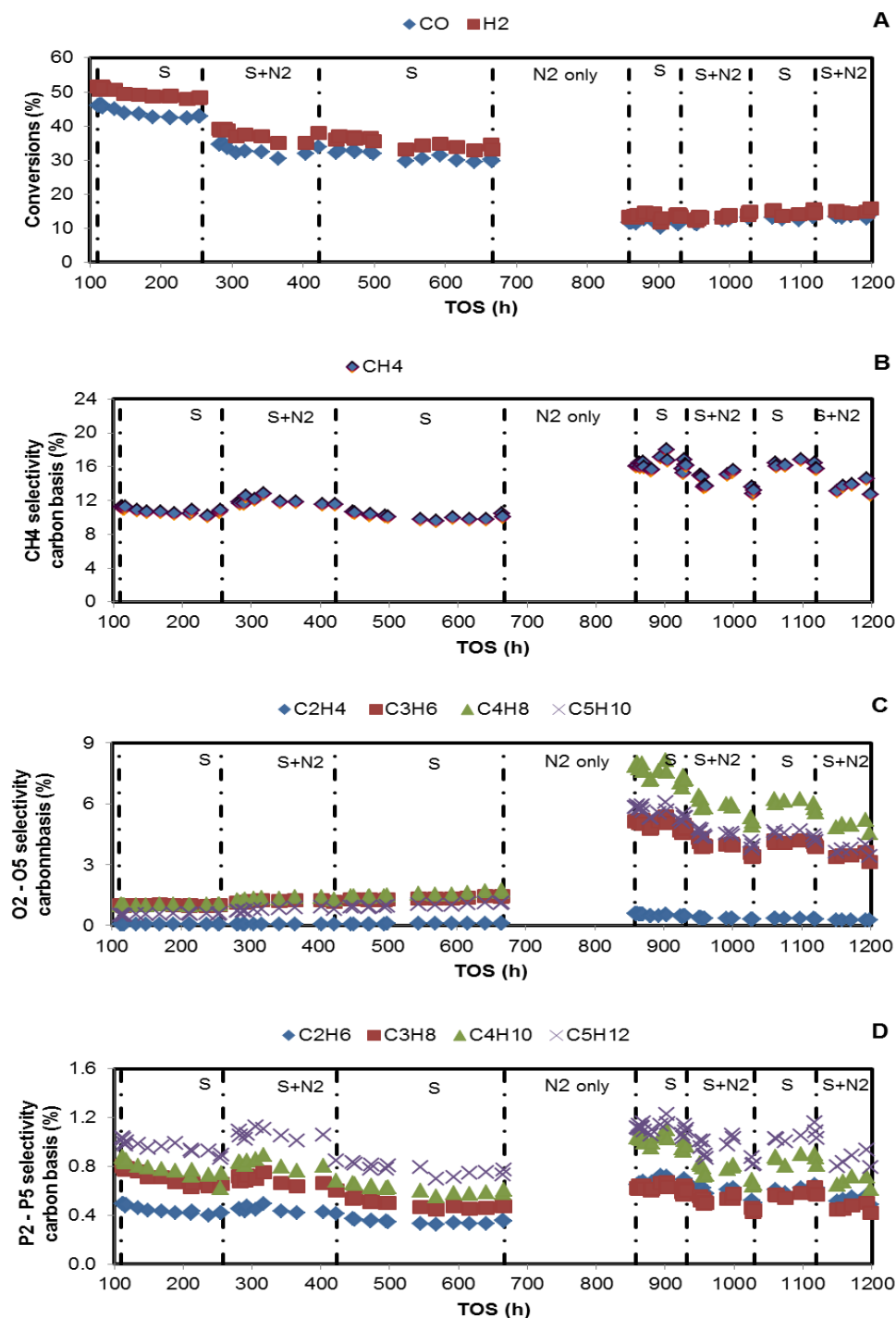


Figure 4.2: Reactant conversions (A); selectivity to (B) methane; (C) light olefin; and (D) light paraffin as a function of time on stream (TOS) during FT runs with 10% Co/TiO₂ in a fixed bed reactor at 220 °C while keeping the reactants partial pressure and volumetric flow rate the same (see **Table 4.1**). There was nitrogen flow only during TOS between 667 and 859 hours.

The results in **Figure 4.2 (B)** show that the methane selectivity remained fairly constant with TOS ranging from 110 to 667 hours. Thereafter the selectivity to methane increased from 10 to 16% when the CO conversion dropped (30% to 13%) at TOS 667 to 859 hours. Lastly, the methane selectivity declined again in the zone ranging from TOS of 859 to 1200 hours. These data indicate that the methane selectivity also changed with time on stream as the catalyst deactivates. The present results are consistent with previous reports [30–32] of an increase in the methane selectivity when the CO conversions dropped. Furthermore, the manner in which the methane selectivity changes with CO conversion relies on the type of catalyst and operating conditions [32].

The selectivity to light olefin (O_2 – O_5) increased when the CO conversion dropped during FT runs with 10% Co/TiO₂ in a fixed bed reactor at 220 °C between 110 to 1200 hours. Although the conversions of the reactants were decreasing with time on stream, the selectivity to light olefins tend to increase as illustrated in **Figure 4.2 (C)** for the TOS from 110 to 667 hours. Among all the light olefins O_2 – O_5 , the selectivity to olefin O_2 is very low when compared to the other light olefins. Previous reports revealed similar findings [33]. Further observation of the data in **Figure 4.2 (A)** and **(C)** revealed something important to note namely a significant increase in the selectivity to all light olefins O_2 – O_5 after the nitrogen flow only period during the time from 667 to 859 hours. The data achieved in the present research laboratory are in agreement with the previous report [34] which also found that when the CO conversion decreased the selectivity to olefins increased.

On the other hand, for the light paraffins the selectivity remained rather constant (with a few small changes) in the zone 110 to 1200 hours when the CO conversion decreased as depicted in **Figure 4.2 (A)** and **(D)**. It is interesting to note that the selectivity to light paraffins (P_2 – P_5) did not change much even after the time on stream of 667 to 859 hours. This is interesting because the selectivity to light paraffins (P_2 – P_5) did not change much regardless of the drastic decline obtained for the conversions of the reactants during the same period of time 110 to 1200 hours.

In brief, during the catalyst deactivation in the zone 110 to 1200 hours while the reactor was kept at 220 °C with the reactants partial pressure and volumetric flow rate the same (see **Table 4.1**) the conversions of the reactants decreased, the selectivity to the olefins increased whereas the selectivity to the paraffins did not change. But in general there are a smaller ups and downs in terms of the selectivity of both olefins and paraffins with time on stream.

4.3.3 Reactant conversions and the ratio of olefin to paraffin

The reactant conversions and the ratio of olefins to paraffins (O/P) as a function of time on stream (TOS) were analysed. The results are shown in **Figure 4.3 (A)** for the reactant conversions and **(B)** for the O/P. The data show that during the catalyst deactivation which is proven by the decrease in the reactant conversions, the O/P ratio increased with TOS in the zone 110 to 1200 hours. The O/P ratio jumped significantly when the CO conversions decreased further after the researcher stopped the nitrogen flow alone in the reactor and fed the syngas again. The results suggest that the O/P ratio is a function of reactant conversion, the higher O/P ratio would be obtained with a lower reactant conversion for cobalt catalyst FTS. Additionally, the researcher's data discussed in this thesis revealed that the increase of the olefin to paraffin with decreasing the conversions also accord with previous publications [13,35]. Moreover, Rane et al. reported that the relationship between the O/P ratio and the C₅₊ selectivity is due to the changes in hydrogenation activity on the catalyst [36].

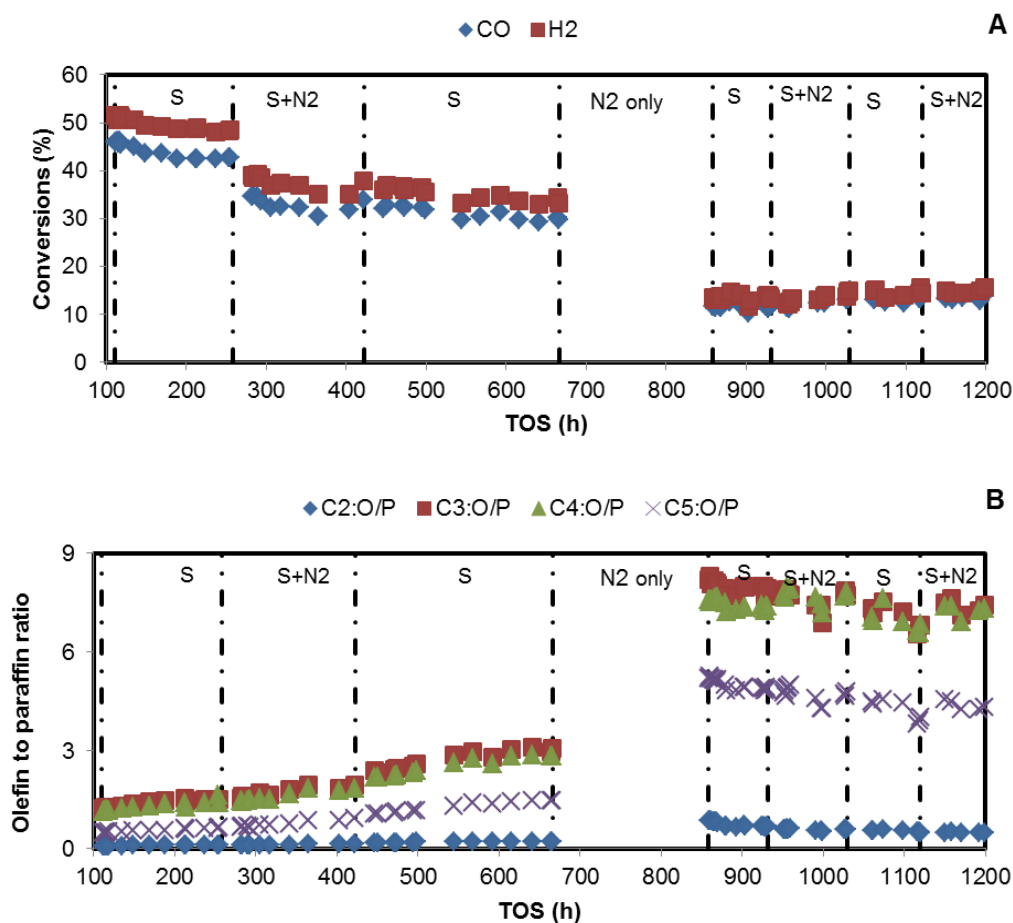
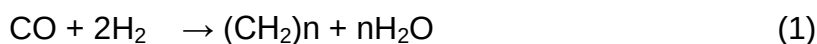


Figure 4.3: The reactant conversions (A) and olefin to paraffin ratio (B) as a function of time on stream during FT runs with 10% Co/TiO₂ in a fixed bed reactor at 220 °C while keeping the reactants partial pressure and volumetric flow rate the same (see **Table 4.1**). There was nitrogen only flow during TOS between 667 and 859 hours.

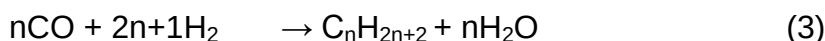
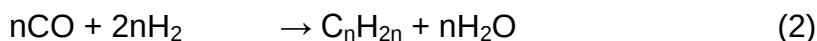
In summary, the results showed a decrease in the catalytic activity which could be due to various factors affecting the deactivation of the catalyst. There are two sections of catalyst deactivation noticed from the experimental data. The findings obtained indicate that the catalytic activity decreased first with time on stream with a further decrease after the nitrogen alone flow in the reactor. The deactivation of cobalt catalyst is often attributed to one or various phenomena. For example, Jacobs et al. found that in FTS when the CO conversions are higher the water partial pressure (P_{H_2O}) increased resulting in a higher catalyst deactivation rate [2]. Moreover in the case of high pressure of CO and H₂O, the reinsertion of olefins

appears to be the most important secondary reaction. Yet the deactivation of catalysts during the FTS may affect the activity and selectivity to hydrocarbon products [10]. For instance it has been reported that FT reaction rates and hydrocarbon selectivities on cobalt supported catalysts could significantly evolve during the reaction [30]. Oxidation is one of the reported causes of deactivation. But other researchers [4] have concluded that the oxidation of cobalt catalyst can be prevented by things such as the correct combination of the reactor partial pressures of hydrogen and water. The effect of water in FT process has been found to be controversial with some scientists suggesting an improvement in the catalytic activity and others believing that the presence of water degrades the activity [37]. The liquid build up in the reactor and changes in the properties of the catalyst might be one of the reasons for catalyst deactivation [38]. Although several explanations are given in the literature [2,3,7] for the deactivation of cobalt based FT catalyst, the researcher's findings indicate that in addition to the reasons available there is something more fundamental which is linked to the paraffin formation rates.

For example, it is generally accepted that overall FTS can be approximately represented by equation (1):

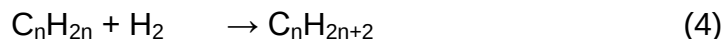


However the main products of the FT reaction are shown in equations (2) and (3):



The researcher's results revealed that when the CO conversions decreased the selectivity to the olefin increased, see **Figure 4.2**. Bukur et al. also reported that the olefin selectivity decreased with increasing in the CO conversion [39]. Similar findings were furthermore reported [40] and the authors suggested that the decrease could be due to the hydrogenation of primary olefins and the secondary reactions of primary olefins through isomerisation and readsorption. Secondary

reaction is a well known and accepted step in FT reaction. Yao et al. [13] have suggested that the liquid phase may promote a secondary reaction of the primary reaction olefins, especially in the case of olefin hydrogenation as represented in equation (4):



From the literature [27, 38], it has been reported that the liquid product deposition in the catalyst can change the catalyst activity and product selectivity. Furthermore, Yao et al. [13] have stated that secondary olefin hydrogenation can be fostered by the liquid phase and that any of the factors that alter the amount of liquid accumulated on the catalyst surface or in the catalyst pores will affect the FT product composition as well. For instance, the researcher's data (**Figure 4.1**) show that the CO consumption rate and paraffin formation rates decreased while that of olefin did not change much with time on stream from 110 to 667 hours. During the present experiment, at this time 667 hours, nitrogen alone was allowed to flow into the reactor which could purge out some of the liquid products that might have been deposited on the pores and/or surface of the catalyst hence leaving less amount of liquid on the catalyst surface. Then at 859 hours, the flow of nitrogen was stopped and syngas re-introduced into the reactor, the researcher noticed a catalyst deactivation (CO conversion declined from 30% to 13%) and the paraffin formation rate also dropped whereas that the olefin formation had increased as depicted in **Figures 4.1** to **4.2**. As explained above, it is possible to attribute the rate degradation to the diminution or termination of the liquid build up in the catalyst which could be another part of reason to suppress the olefin secondary hydrogenation. Catalyst deactivation may be the main reason to decrease the extent of secondary hydrogenation of olefins.

To further support this view, consider the Todici et al. [9] schematic representation of FTS based on the FTS active sites to attempt an explanation of the olefin and paraffin formation trends with the following scenario: 1) the hydrogenation of the intermediate complex to paraffin and the chain growth propagation take place, whereas 2) the secondary hydrogenation of 1-olefin is suppressed in favour of 1-

olefins desorption/readsorption and secondary isomerisation of the complex to 2-olefins. These two possible mechanisms might justify why olefin production remained almost the same, see TOS 110 to 667 hours of **Figure 4.1 (C)**, and/or in some cases increased, e.g. 859 to 1200 hours of **Figure 4.1 (C)**, during the researcher's experiment with 10% Co/TiO₂ while paraffin yields decreased. Other researchers [41], Dictor and Bell, have already reported the suppression of olefin hydrogenation and isomerisation which enhanced the formation of aldehydes and branched hydrocarbons on iron based catalysts. In addition, a concept has been reported from the literature [9,42] that the secondary readsorption of olefins, followed by continued chain growth, causes the shift toward heavier products. Furthermore, in a case where the majority of olefins readsorbed and did not hydrogenate or isomerise, the result would be a non-ASF distribution [42]. According to the present findings, one can suggest that there could be more than one formation pathways for olefins and paraffins during FTS. Although it is not yet proven, the researcher suggests the possibility of having two parallel formation pathways, one for the olefin and the other for the paraffin during FTS. Thus there is discrimination between olefin and paraffin during the 10% Co/TiO₂ catalyst deactivation in FTS. Finally, nitrogen is known to be an inert gas. Although, the researcher used ultra-pure grade nitrogen, there might be traces of oxygen in the cylinder which could oxidise the cobalt catalyst slowly and this might explain the decline in the CO conversion from 30% to 13% after N₂ alone passed through the reactor system for 8 days (**Figure 4.2**). This effect is unlikely under the FT reaction conditions which are strongly reducing [3,4].

4.4 Conclusion

In this investigation, a series of FT experiments were conducted in a fixed bed reactor loaded with one gram of 10% Co/TiO₂ at 220 °C. The reactor total pressure and molar flow rates were adjusted so that the reactants partial pressures (P_{CO} and P_{H₂}) and volumetric flow rates remained constant. The effect of the catalyst deactivation on the molar selectivity and formation rates of light olefins (O₂–O₅) and paraffins (P₂–P₅) were analysed and compared.

From the laboratory data obtained from 110 to 1200 hours, two stages of catalyst deactivation were observed. First from 110 to 667 hours, the results showed that: (1) the CO conversion dropped from 46% to 30%; (2) the selectivity to olefin increased slightly whereas the selectivity to paraffin did not change much; (3) olefin formation rate remained fairly constant, while the paraffin formation rate dropped; (4) the O/P ratio increased with time on stream up to 667 hours. At TOS between 667 to 859 hours, nitrogen alone flow was passed in the reactor due to a malfunctioning mass flow controller which was replaced. The second catalyst deactivation stage was at TOS from 859 to 1200 hours. And the following results were obtained: (1) the CO conversion dropped from 30% to 12.8%; (2) the selectivity to olefin increased significantly whereas the selectivity to paraffin did not change much; (3) olefin formation rates also increased while the paraffin formation rates dropped; (4) the O/P ratio increased considerably. In brief, the trends of the selectivities and formation rates of olefin and paraffin products are not the same during the catalyst deactivation. The data indicate that the catalyst deactivation is mainly caused by the decrease in the paraffin formation rate but not by the one of olefin. Furthermore, the reading of the data could be that the different paraffin formation rate is a result from the catalyst deactivation mechanism, meaning that the spent catalyst appears to have weaker hydrogenation activity.

Currently, none of the published models can solely explain fully the phenomenon that the decays of the reaction rates of olefin and paraffin were not the same during the catalyst deactivation. The results suggest the possibility of having two active sites on the 10% Co/TiO₂ catalyst, one mainly responsible for olefin production and the other for paraffin formation during the researcher's FT experiments. And the liquid phase covering the catalyst surface or filled in the catalyst pores may affect the secondary olefin hydrogenation reaction. These findings could make a valuable contribution to the understanding of the mechanism of the product formation during FTS.

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CHAPTER 5

EFFECT OF FEEDING EXTRA NITROGEN INTO A FIXED BED FISCHER-TROPSCH REACTOR WHILE KEEPING THE PARTIAL PRESSURES OF REACTANTS THE SAME

The data contained in this chapter are written in a paper format and the manuscript is with editor at the Chemical Engineering Journal.

Some of the data were presented at conferences namely SAChE 2014 and AIChE 2014 national and international respectively.

Abstract

The effect of nitrogen co-feeding in Fischer-Tropsch synthesis (FTS) in a fixed bed reactor with 10% Co/TiO₂ catalyst was investigated while keeping the partial pressure of the reactants the same. The comparison results were obtained from more than four different switches FT runs between syngas and syngas + N₂. The results indicated that although almost no effect for catalyst activity for the overall reaction rate was observed, a significant positive effect on the catalytic performance of 10% Co/TiO₂ catalyst under the reaction condition with N₂ co-feeding was revealed. This included the lower selectivity to the undesired light hydrocarbons especially methane, and a decrease on the formation rates of light hydrocarbons for both paraffin and olefin products. Such results cannot be explained by classic kinetics alone as the partial pressures of CO and H₂ were held constant. The present laboratory data indicated that there might be a possibility to increase the selectivity and formation rate of long chain hydrocarbons (C₅₊) by feeding extra amount of N₂ for FTS.

5.1 Introduction

Fischer-Tropsch (FT) synthesis is a well-known chemical reaction in which synthesis gas is converted to liquid fuels over a metal catalyst. Several transition metals including cobalt, iron, nickel and ruthenium can be used in FT. However, cobalt and iron are the most applied in commercial FT for various economical and technical reasons [1]. Among the reported commercial catalysts, cobalt based catalysts have high activity for hydrogenation and tend to produce linear alkanes [2]. FT reaction yields a large range of products including the main wanted paraffins, olefins as well as a small amount oxygenates. Despite being studied for over many decades the FT reaction is still not that well understood. The reaction results are often complex and contradictory. Perhaps the complexity is not just due to the reaction mechanism? The complexity might be caused by a combination of simple phenomena such as reaction kinetics, vapour-liquid equilibrium, and product accumulation inside the reactor or preferential stripping of lighter products and reactants. The individual phenomena are quite simple; however, the interaction of these phenomena could cause quite complex behaviour.

Several FT kinetic models reported in the literatures have been used to predict the reaction activity, and most of them show that FT reaction rate depends strongly on the reactants partial pressures which indicate that constant FT reaction rates should be obtained with constant reactant partial pressures. However, some experimental results revealed that when the feed flow rate was increased with fairly similar partial pressures of the reactants in the reactor, there was a positive effect on the FT activity and product selectivity [3]. Such results appear not to be in agreement with the results obtained from the usual kinetic models for example one of the kinetic models reported by Zennaro et al. [4]. In addition, researchers [3, 5, 6] attributed the improvement of the FTS activity to a higher rate of removing of the liquid hydrocarbon film (liquid phase) formed on the catalyst surface which led to the reduction of the diffusion length of the reactant to the active site.

Due to the importance of feed in FTS, numerous studies have been conducted on the feed composition and co-feeding of different molecules to syngas for FT

reactions [7-9]. In terms of co-feeding, rigorous studies have been conducted and some of the molecules that have been co-fed so far include water [10-15], gases like CO_2 [16-21] and hydrocarbons like olefins [22-27] just to mention a few. However, inorganic compounds such as nitrogen gas have not been reported on intensively yet. But to show the importance of co-feeding in FT reaction, already in the 1950s scientists have investigated FT process with both inorganic and organic compounds to be exact CO_2 , CH_4 and N_2 and they have revealed that addition of these diluents decreased the rate of FT reaction [28]. Fairly recently, Yan et al. have demonstrated that Fe-Pd/ZSM-5 catalyst (a bi-functional catalyst) yields relatively high activity and selectivity in producing liquid hydrocarbons when running FT with nitrogen-rich syngas [29]. Furthermore, most researchers who investigated FT with nitrogen-rich syngas have indicated that the process is feasible because of the possibility to reduce cost [8,30-33]. Jess et co-workers have studied FTS with nitrogen rich syngas and found that extra nitrogen in syngas doesn't affect the kinetics of FT process [30, 31].

The addition of each of these components to the FT reaction has their advantages and drawbacks depending on the angle of enhancement researchers are looking for by adding them. Nevertheless, in most cases, while scientists might use the same co-feeding agent the data sometimes revealed contradictory findings. Now, an important question is whether kinetics is sufficient to explain FTS. Based on previous reports [3,28,30] it is obvious that more studies are needed, including: laboratory experiments with Co catalyst. This is in order to try to ascertain both whether kinetics alone is enough to explain FTS and whether the FT process with co-feeding nitrogen is profitable as compared to FT technology with nitrogen free syngas.

Therefore in this work, the effect of feeding extra nitrogen into a fixed bed Fischer-Tropsch reactor, while keeping the partial pressures of reactants the same by adjusting the flow rate of N_2 and the total pressure in the reactor, on the catalytic performance of a cobalt based catalyst has been investigated. In order to keep similar 'reaction kinetics' experiments were done until FT catalytic activity had reached steady state with low conversions. This was to ensure the partial

pressures of the reactants were fairly constant during all the runs. More details about the experimental work are described in the next section.

5.2 Experimental procedure

A supported cobalt catalyst (10% Co/TiO₂) by mass was used in this investigation. The catalyst was prepared by incipient wetness impregnation from cobalt nitrate - Co(NO₃)₂·6H₂O -(Sigma-Aldrich) and Titanium di-oxide TiO₂ (Degussa Titania, TiO₂, P25, Surface area = 50 m²g⁻¹) as previously reported [16]. Typically, the support was made first. Titanium di-oxide was mixed with distilled water to form a paste. The paste was then dried at 120 °C for two hours and calcined in a Muffle oven at 400 °C (ramping rate of 5 °C/min) for six hours. The calcined paste was left overnight to allow the oven to cool down to ambient temperature. The dried and calcined paste was crushed, and the particles sieved to separate out those with a diameter between 500-1000 µm. The TiO₂ and the Co(NO₃)₂·6H₂O solution were then mixed, dried (at 120 °C for two hours) and calcined leading to the cobalt catalyst.

Briefly, one gram of the cobalt catalyst was loaded in the centre of a fixed bed FT reactor, dried, reduced with H₂, and kept in the reactor. The researcher then introduced syngas to replace the pure H₂ from the system. The FT experiments were conducted as explained in Chapter 4 with time on stream up to 1029 hours. Before the feeds for each FT run was changed to a different feed composition, the traps were emptied. The reaction was kept for a day to allow for stability in order to commence a new FT run in a similar manner to that previously done. Hence, the traps were emptied of the wax, oil and water at 1029 hours for the experimental data which were described in Chapter 4. From 1055 hours a new set of FT runs was started. The new set of FT runs consisted of switching periodically between two kinds of syngas: H₂ 60% by volume, CO 30% and 10% N₂ and syngas + N₂: H₂ 48% by volume, CO 24% and 28% N₂ and fed them into the reactor with a constant partial pressure of H₂ at 12.5 bar (abs) and CO at 6.20 bar (abs) by adjusting the total flow rate and pressure. This was done periodically with total time on stream up to 2668 hours. The temperature of the reactor was maintained

at 220 °C throughout the experiments for both FT runs with syngas and syngas + N₂. The FT process produced gas and liquid hydrocarbons products. The gas phase products were monitored with an online DANI GC 1000 gas chromatography, equipped with flame ionisation detector (FID) and thermal conductivity detectors (TCD A and TCD B). The FT operating conditions are summarised in **Table 5.1**.

Table 5.1: Reaction and feed conditions for the FTS experiments on a cobalt based catalyst

Case	S	S+N ₂
Catalyst	10% Co/TiO ₂	10% Co/TiO ₂
Mass (gram)	1	1
Temperature (°C)	220	220
Reactants partial molar flow rate (mol/min) for: FR _{H2} FR _{CO}	0.075 0.038	0.075 0.037
Reactants partial pressure (bar abs) for: P _{H2} P _{CO}	12.51 6.26	12.41 6.20

Note: S - syngas; S+N₂ syngas + N₂, FR - flow rate; and abs - absolute.

5.3 Results and discussion

5.3.1 Reaction conversion and product selectivity

The conversions of the reactants as a function of Time on Stream (TOS) were determined and the results are presented graphically in **Figure 5.1 (A)**. From this figure, it seems like the addition of nitrogen to the syngas did not affect the conversions of the reactants very much. In order to clearly show the changes of the FT reaction conversions between the conditions with syngas and syngas + N₂, the average values of the reactants conversions operating at a stable state for each FT run are plotted in bar charts for the nine FT runs depicted in **Figure 5.1 (B)**. These results show tiny changes in the values with changing of the feeds from syngas (S) to syngas + N₂ (S+N₂). For example, the conversions for both CO and H₂ are 13.94% and 15.48% respectively for the FT run with syngas and 13.41% - and 15.33% respectively for the FT run with syngas + N₂ (S+N₂), for switch one shown in **Figure 5.1 (A)**. The data plotted in both **Figure 5.1 (A)** and **Figure 5.1 (B)** showed that similar FT reaction conversions were achieved for using syngas only and syngas + N₂. Because both the CO conversions and H₂ conversions are fairly constant and below 16% for all the runs listed in **Table 5.2**, the partial pressures of the reactants in the reactor at a stable state were similar for FTS with syngas and FTS with syngas + N₂.

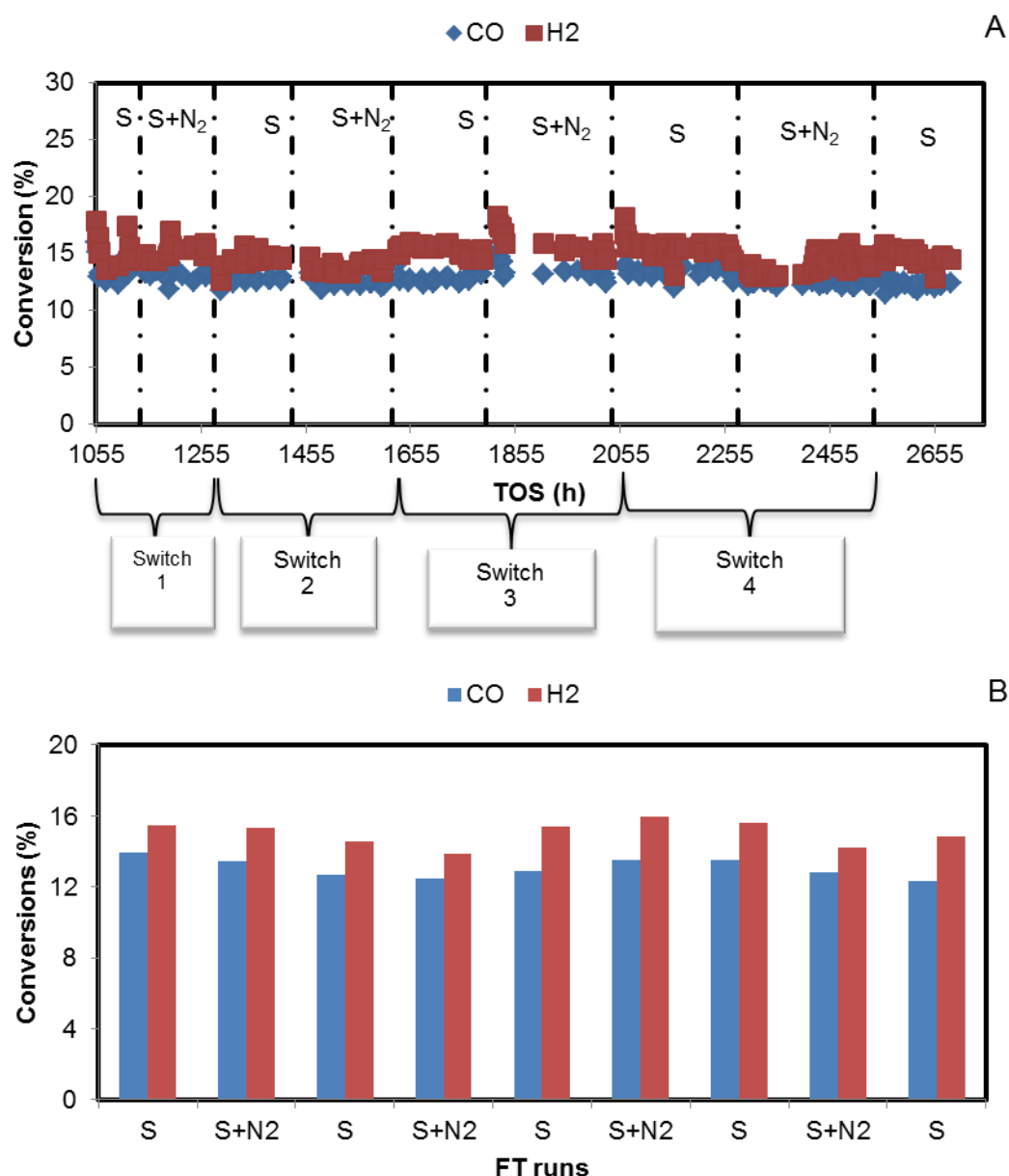


Figure 5.1: Effect of feeding extra nitrogen into the reactor while keeping the reactant partial pressures the same on: (A) the reactants CO and H₂ conversions as a function of TOS under the reaction conditions listed in **Table 5.1** and (B) average data of the CO and H₂ conversions for the eight FT runs on syngas (S) and syngas + nitrogen (S+N₂) representing four switches as shown in **Table 5.2**.

The summary of the conditions for each switch of the FT runs exhibited in **Figure 5.1** is listed in **Table 5.2**.

Table 5.2: Summary of the reaction and feed conditions for the FT experiments over a cobalt based catalyst

Switching number	FT runs	Starting time on Stream	Reaction conditions (see Table 5.1)
First	1	At 1055.76 hours	S
	2	At 1150.74 hours	S+N ₂
Second	3	At 1292.75 hours	S
	4	At 1462.86 hours	S+N ₂
Third	5	At 1631.06 hours	S
	6	At 1822.08 hours	S+N ₂
Fourth	7	At 2063.60 hours	S
	8	At 2299.69 hours	S+N ₂

Furthermore the effect of nitrogen co-feeding in the fixed bed FT reactor on the methane selectivity was also measured. The results are presented in **Figure 5.2 (A)** for the selectivity of methane as a function of TOS and **Figure 5.2 (B)** depicts the average values of the methane selectivity for the four switches of the FT experiments listed in **Table 5.2**. From this data, it is obvious that the experiments with syngas + N₂ had a lower methane selectivity than the runs for syngas only, which means co-feeding nitrogen in FTS has a positive effect on the selectivity of methane. This is because methane is usually one of the undesired products in FTS. That it is a positive development is confirmed as other researchers have also indicated that methane is an unwanted product [8] and limited selectivity for the main products is one of the challenges for commercial FT technology [29]. This is

therefore an important finding as the reduction in the selectivity to methane would be of great importance in a commercial FT process.

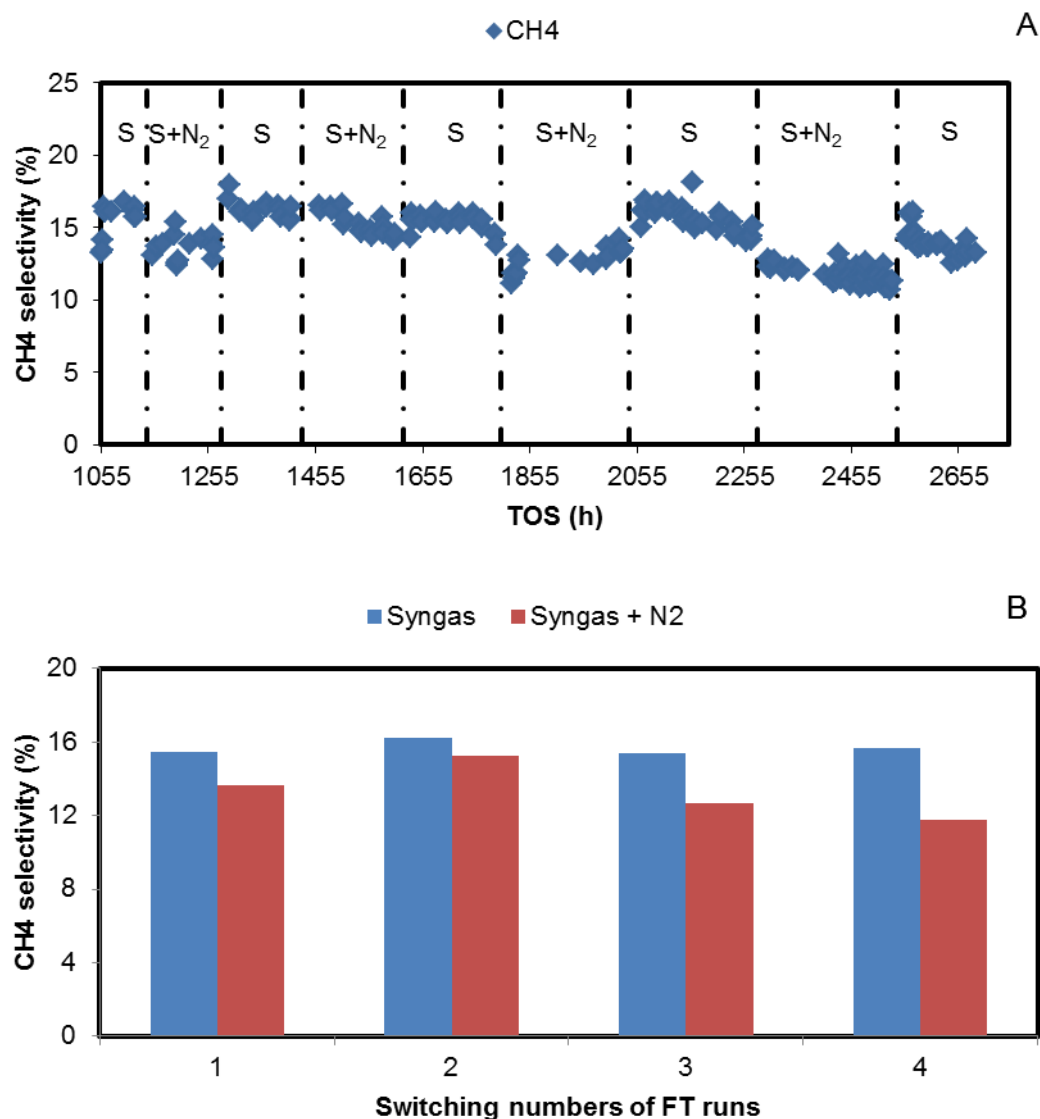


Figure 5.2: Effect of feeding extra nitrogen into the reactor while keeping the reactant partial pressures the same on: (A) CH₄ selectivity as a function of TOS under the reaction conditions listed in **Table 5.1** and (B) for the average data of CH₄ selectivity for the four switches representing eight FT runs on syngas (S) and syngas + nitrogen (S+N₂) as shown in **Table 5.2**.

The results for the selectivity to total light hydrocarbons (olefins plus paraffins) from C₂ to C₅ are presented graphically as a function of TOS in **Figure 5.3 (A)** and the average data values of the selectivity are plotted for the FT runs in bar charts as shown **Figure 5.3 (B)**. **Figure 5.3 (B)** clearly shows a decline in the products selectivity when the feed of the FT experiments was periodically switched from syngas to syngas with extra nitrogen.

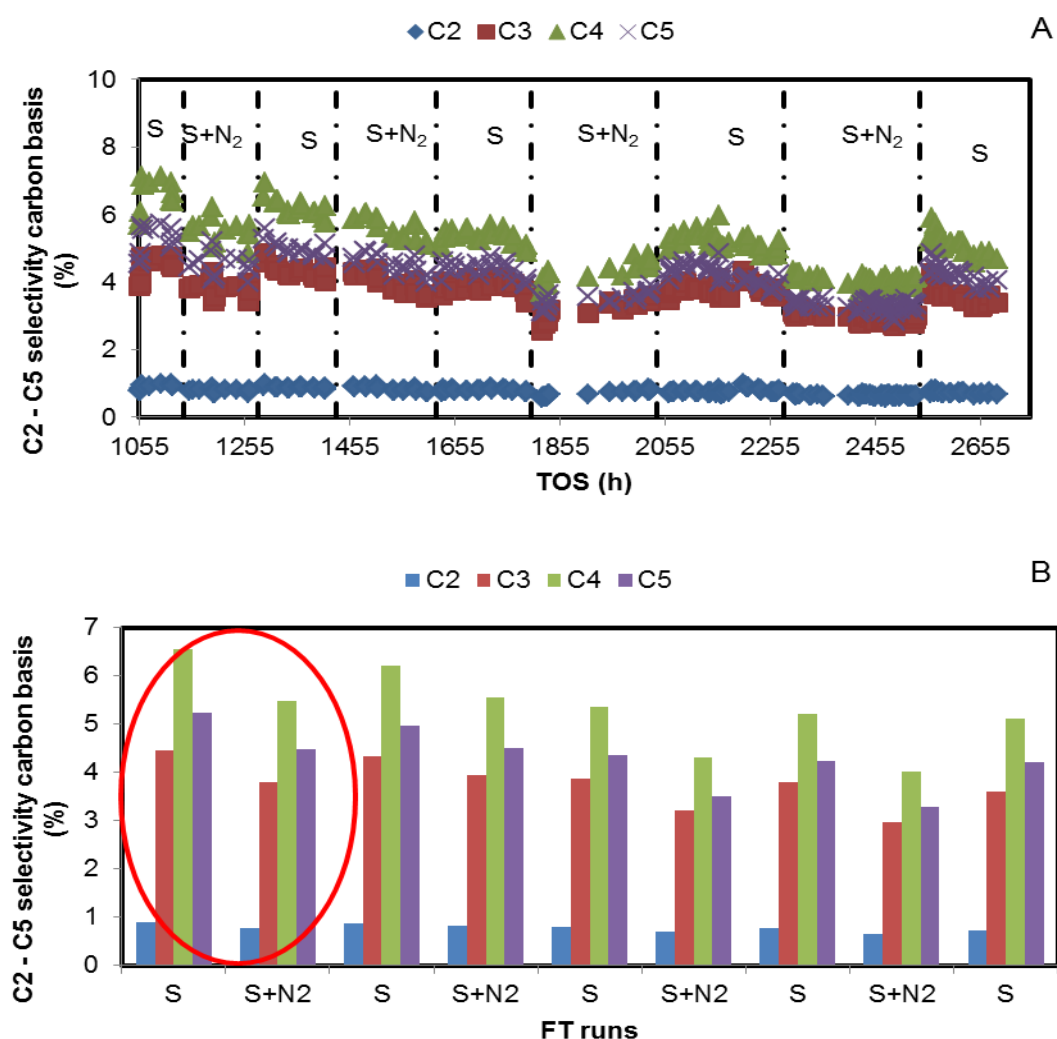


Figure 5.3: Effect of feeding extra nitrogen into the reactor while keeping the reactant partial pressures the same on: (A) the selectivity to total light hydrocarbons (C₂-C₅) as a function of TOS under the reaction conditions listed in **Table 5.1** and (B) for the average data of total light hydrocarbons (C₂-C₅) selectivity for eight FT runs of syngas (S) and syngas + nitrogen (S+N₂) representing four switches as shown in **Table 5.2**.

The effect of adding extra nitrogen into the reactor on the selectivity of light olefins (O₂-O₅) and paraffins (P₂-P₅) was also determined similarly as for the total light hydrocarbons in **Figure 5.3**. The results are presented in **Figure 5.4** and **Figure**

5.5 for the light olefin and paraffin respectively. In both **Figures 5.4 (B)** and **5.5 (B)**, the selectivity decreased when FT runs were carried out with syngas + N₂.

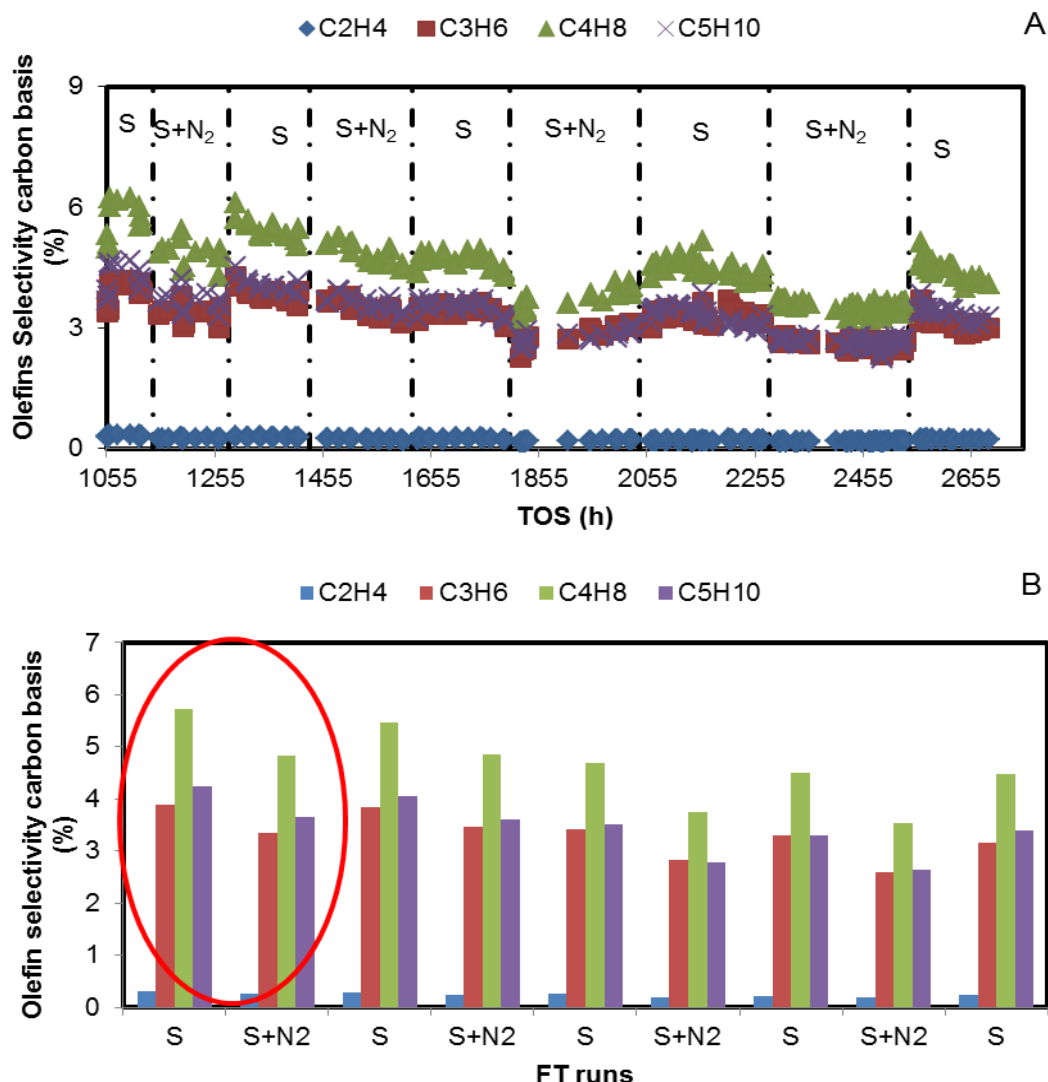


Figure 5.4: Effect of feeding extra nitrogen into the reactor while keeping the reactant partial pressures the same on: (A) the selectivity to light olefins (O₂-O₅) as a function of TOS under the reaction conditions listed in **Table 5.1** and (B) for the average data for light olefins (O₂-O₅) selectivity for the eight FT runs on syngas (S) and syngas + nitrogen (S+N₂) representing four switches as shown in **Table 5.2**.

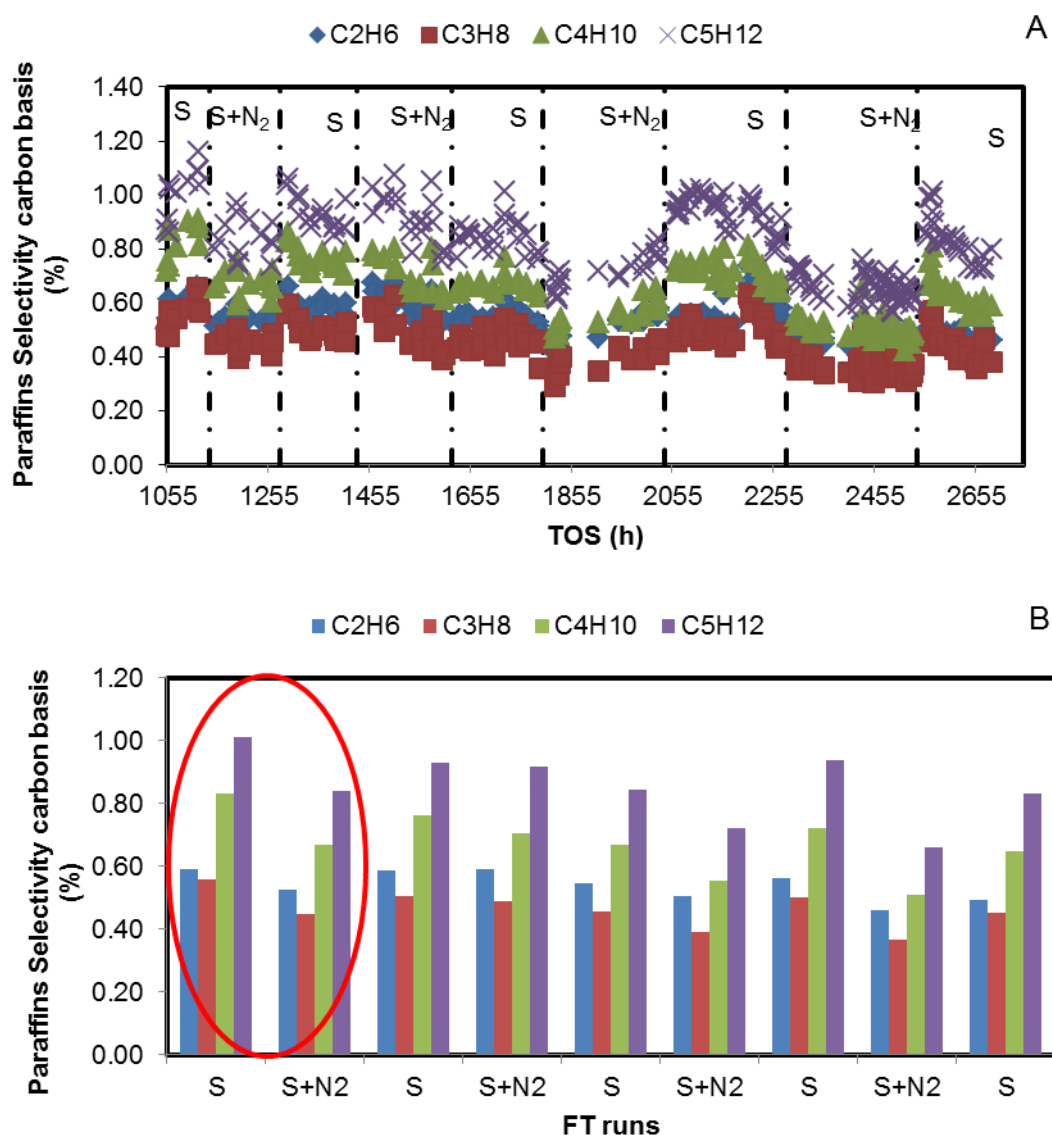


Figure 5.5: Effect of feeding extra nitrogen into the reactor while keeping the reactant partial pressures the same on: (A) the selectivity to light paraffins (P₂-P₅) as a function of TOS under the reaction conditions listed in **Table 5.1** and (B) for the average data of light paraffins (P₂-P₅) selectivity for the eight FT runs on syngas (S) and syngas + nitrogen (S+N₂) representing four switches as shown in **Table 5.2**.

In order to do a comparison study between the FT runs from syngas (S) to syngas + N₂ (S+N₂), the researcher has plotted the selectivity (average data) from two FT runs (switch one shown in **Table 5.2**) namely from syngas (S) to syngas with extra nitrogen (S+N₂) for total light hydrocarbons (C₂ to C₅), olefins (O₂-O₅) and

paraffins (P_2 – P_5) in **Figure 5.6 (A), (B) and (C)**, respectively. These data show that co-feeding extra nitrogen into the fixed bed reactor exhibits a decline in the selectivity to all light hydrocarbons C_2 to C_5 including olefins and paraffins. This is regarded as an improvement commercially when one is trying to make liquid fuels.

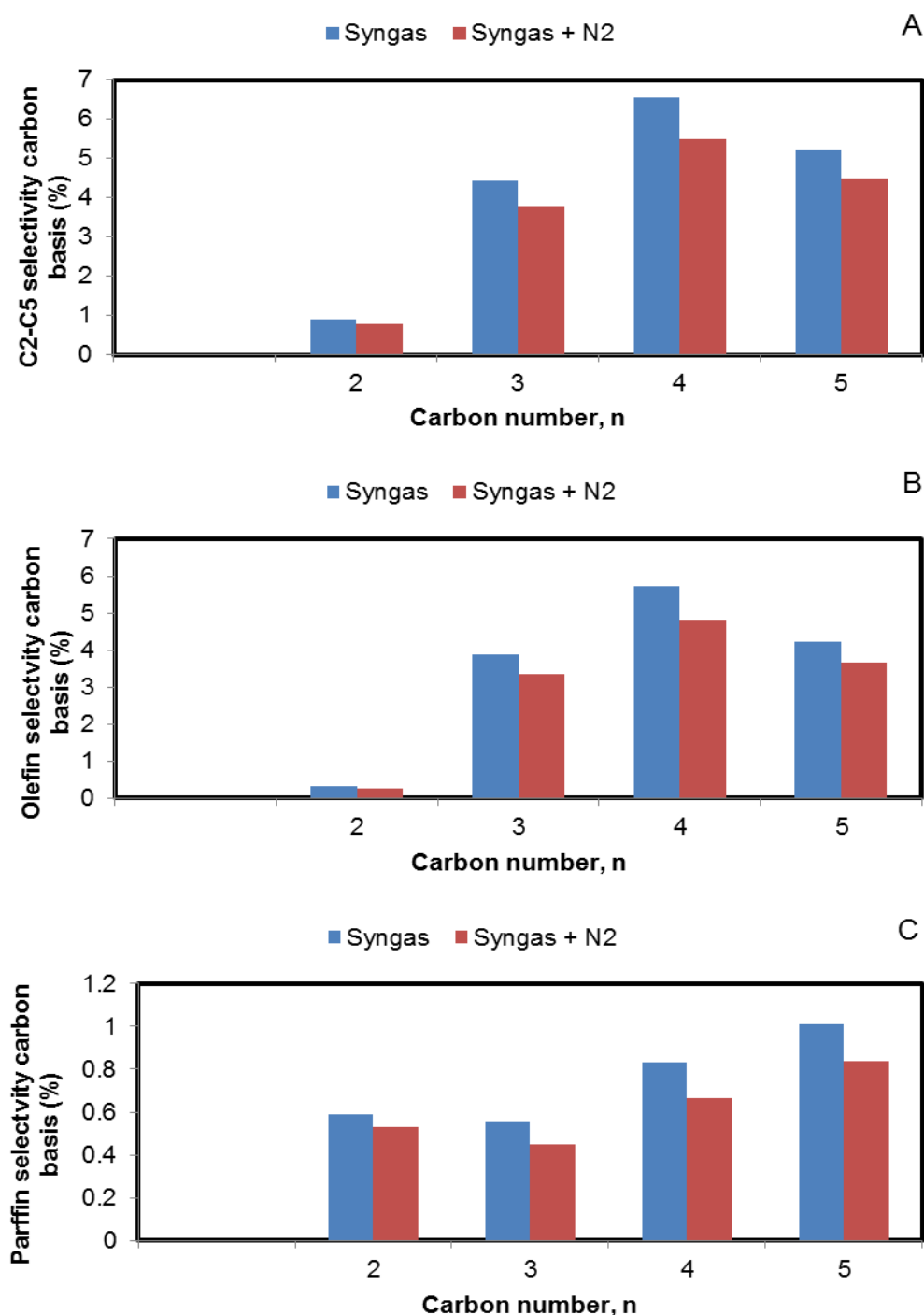


Figure 5.6: Effect of feeding extra nitrogen into the reactor, while keeping the reactant partial pressures the same, on the selectivity (average data): (A) to total light hydrocarbons; (B) for olefins and (C) paraffins as a function of carbon number under the reaction conditions listed in **Table 5.1** for the first switch of the FT runs as shown by the red oval shapes in **Figures 5.3 to 5.5**.

The product selectivity of C_1 to C_{5+} including paraffin and olefin for two sets of the experiments (Switching 4 under the reaction condition shown in **Table 5.2**) are listed in **Table 5.3**. The data reported in **Table 5.3** is the average value at steady state for each runs. The crucial information to be found in **Table 5.3** is that when extra nitrogen was added to syngas, the selectivity to the undesired light hydrocarbons (C_1 - C_4) shows a decrease. On the contrary, calculated using the carbon balance, the selectivity to the long chain hydrocarbons of C_{5+} is increased.

Firstly there is the significant drop (3.92 difference, 33% decrease) recorded for the methane when extra nitrogen was added to the syngas. For the other light hydrocarbons (C_2 - C_4) including olefins and paraffins, the amount of decrease is quite different and climbed with the hydrocarbon chain length as shown in **Table 5.3**. One can see that the addition of the extra nitrogen decreased the amount of each of the light hydrocarbons by 20-30%. This effect can also be seen in the table with the increased selectivity to C_{5+} .

These are important findings and strange too at the same time because under the same operating conditions, see **Table 5.1**, almost the same CO conversions approximately 13% was obtained, while the selectivity to the light hydrocarbons (C_1 - C_4) with syngas + N_2 declined which suggests the C_{5+} products are increased. Another important point is that more olefins were produced than paraffins except for the paraffin with carbon number 2 (P_2).

Table 5.3: Summary of the product molar selectivity for the short chain hydrocarbons for the fourth switch experiment for the two FT runs of syngas (S) and syngas + N₂ (S+N₂) in Table 5.2 obtained under the reaction conditions listed in Table 5.1. C-Hydrocarbon (Paraffin + Olefin); P-paraffin; and O-olefin

Selectivity (Carbon basis %)	S	S+N ₂
C ₁ (CH ₄)	15.66	11.74
C ₂	0.78	0.65
• P ₂	0.56	0.46
• O ₂	0.21	0.19
C ₃	3.80	2.97
• P ₃	0.50	0.37
• O ₃	3.30	2.60
C ₄	5.22	4.03
• P ₄	0.72	0.51
• O ₄	4.50	3.53
C ₅₊ (balance)	74.54	80.61

5.3.2 Reactant consumption rates and product formation rates

One can easily convert the selectivity results to rates of formation. However the rate data do not seem to provide any extra insights. As such it is not necessary to present the detailed rate findings here. However, in summary with regard to the rates, the researcher's nitrogen co-feeding for FTS had a minimal effect on the CO consumption rate, decreased the methane reaction rate, dropped the light olefin reaction rates and slightly reduced the light paraffin rates. For more details, please refer to **Appendix B**.

5.3.3 Ratio: olefin to paraffin ratio (O/P)

The olefin to paraffin ratio for the light hydrocarbons data were plotted against the time on stream. The results are shown in **Figure 5.7 (A)**. From this graph it is difficult to make out any significant trends. In an effort to better understand the results, the researcher plotted the average data of the O/P ratio for all light

hydrocarbons 2 to 5) for the eight FT runs switching between S and S+N₂. The results presented in a bar chart are shown in **Figure 5.7 (B)**. The graphs show that there were no significant differences when the feed was switched from syngas to the run with syngas + N₂.

In conclusion, it is clear that while the addition of the extra nitrogen did not affect the overall activity of the catalyst, it did decrease the rates of formation (or selectivity) to the lower hydrocarbons, both olefins and paraffins, by about 20-30%, while the olefin to paraffin ratio showed no discernible trend.

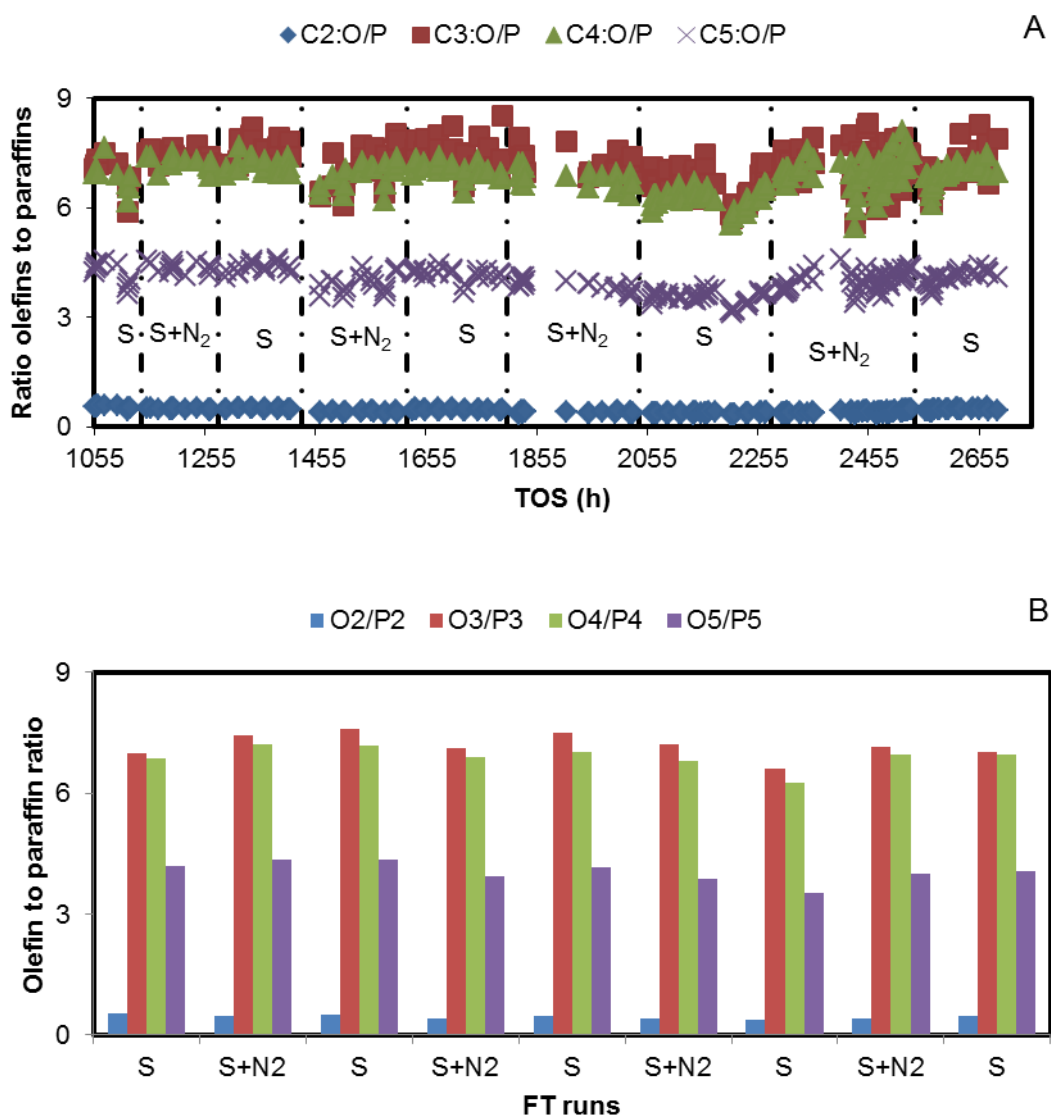


Figure 5.7: Effect of feeding extra nitrogen into the reactor while keeping the reactant partial pressures the same on: (A) the olefin to paraffin ratio of light hydrocarbons (2 to 5) as a function of TOS under the reaction conditions listed in **Table 5.1** and (B) for the average data of light hydrocarbons (2 to 5) of the olefin to paraffin ratio for the eight FT runs of syngas (S) and syngas + nitrogen (S+N₂) representing four switches as shown in **Table 5.2**.

In comparison with some previous results: Snel [7] co-fed an oxygenate (diethyl ether) while keeping unchanged the total pressure and total volumetric flow rate and showed this caused an increase in the reaction activity. Dai and Yu [33] found

that the total pressure and gas hourly space velocity (GHSV) had a significant effect on the catalytic performance of $\text{CeO}_2\text{-Co/SiO}_2$ catalyst when using of nitrogen-rich syngas as feedstock to the fixed bed reactor. On the other hand, a study by Visconti and Mascellaro [34] revealed that both the CO conversion and chain growth probability dropped when the nitrogen co-feeding content was increased (23.5 to 45.1%) to the reactor while keeping the total pressure constant. This difference in the reaction rates and selectivity to products is thus also seen in these findings. The question is why is the difference noticed?

In particular, the researcher designed his experiments in such a way that he tried to keep the partial pressures of the reactants the same, whether the extra nitrogen was added or not. This was done by changing both the flow rate and the total pressure in proportion when the extra nitrogen was added. Furthermore the fact that after these changes were made the conversions were very similar strengthens the case for suggesting that any phenomenon depending on the partial pressures alone cannot adequately explain the changes in the production rates or selectivity to the lower hydrocarbons. Something other than normal reaction kinetics or stripping (vapour-liquid equilibrium (VLE)) must be causing this. This is because the dependences on *partial* pressures are the same for both cases and should not depend on the *total* pressure.

The researcher has only been able to come up with one possible explanation when changes depend on total pressure but not on partial pressures. This suggests that the phenomenon that is involved here is boiling. As the formation of bubbles (boiling) depends on a mechanical property, namely the vapour pressure inside the bubble must be marginally greater than the total pressure, this could perhaps explain the results presented in this Chapter. Building a simple model may show the effect of bubbling. It is known that if the system is ideal, it can be written for each component i:

$$x_i P_i^* = y_i P$$

and in total $\sum x_i P_i^* = \sum y_i P = P$

where x_i is the mole fraction of component in the liquid, P_i^* is the vapour pressure of the pure component i at the temperature of the reactor, y_i is the mole fraction of component i in the gas phase and P is a pressure, the value of which will be discussed below.

Now, examine the meaning of P for two different cases, namely VLE and Boiling.

VLE: in this case $P = P^{\text{Total}} - \sum P_i^{\text{inerts}}$

Where P^{Total} is the total pressure of the system

And P_i^{inerts} are the partial pressures of the virtually insoluble gases i

Boiling: In this case $P = P^{\text{Total}}$

Now the two scenarios can be compared:

Firstly, for VLE when extra nitrogen is added relative to the case without, $P^{\text{Total}} - \sum P_i^{\text{inerts}}$ remains the same in both cases as the extra total pressure is due to the extra nitrogen partial pressure and this has been taken into account by increasing the total pressure accordingly. Thus in these circumstances the right hand side (RHS's) remain the same.

However, for boiling the RHS's are different in the two cases. In order for this to be true as the values of P_i^* remain the same in the two cases (same temperature), the only way for this to be true is that there must be more of the lighter components in the liquid at the higher total pressure. Thus in the two cases the liquid composition on the surface of the catalyst must be different. As the catalyst surface is covered in liquid this could affect the nature of the reaction. This is particularly likely to be the case as the olefin to paraffin ratio of these lighter hydrocarbons has been shown to be much greater than one, and it is well known that the addition of olefins to FTS can affect the reaction. The effect of boiling in the pores has not really been studied previously and further study is needed to confirm the presumption.

5.4 Conclusion

The effect of feeding extra nitrogen into the Fischer-Tropsch reactor on the catalytic performance of a cobalt based catalyst has been investigated here by comparing the results between two switches of FT runs, labelled reaction with syngas (S) and reaction with diluted syngas (S+N₂) in which an extra amount of N₂ was co-fed into the reactor while increasing the total pressure in order to keep the partial pressures of the reactants the same.

Comparing the results between syngas and syngas + N₂ while keeping the partial pressures (P_{CO} and P_{H_2}) the same, similar CO conversions (relatively low on average 13%) were obtained, the light hydrocarbons selectivity was decreased with syngas + N₂ which implied the C₅₊ selectivity was increased. With regard to the rates based on these results, the nitrogen co-feeding for FTS had a minimal effect on the CO rate, decreased the methane reaction rate, dropped light olefin reaction rates and reduced the light paraffin rates.

At present, the existing kinetics models and simple VLE cannot be used to explain this experimental phenomenon, which suggests that the complexity of FT system is not only due to the reaction mechanism, but might be due to other factors as well. A model based on boiling (bubbling) is suggested as a possible way in which the results could be explained. However, these results indicate that co-feeding N₂ into FTS might produce more long chain hydrocarbons. This could have positive implications for the design of XTL systems (Coal/Biomass/Natural gas/ Waste to Liquid Fuels).

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CHAPTER 6

A STUDY OF THE SHORT CHAIN HYDROCARBON PRODUCT DISTRIBUTION IN FISCHER-TROPSCH SYNTHESIS OVER A COBALT CATALYST

The material in this chapter has been written in a paper format for submission to the Journal of Catalysis.

Abstract

The light hydrocarbon (C_1 - C_6) product distributions from a fixed bed Fischer-Tropsch reactor with a 10% Co/TiO₂ catalyst were analysed over an extended period of time as the activity of the catalyst changed. These short chain hydrocarbon product distributions were studied starting at 200 °C with syngas for 48 hours and then increasing the temperature to 220 °C. The feed was then switched back and forth from syngas to syngas + extra N₂ with increased total pressure in such a way as to keep the reactant partial pressures the same in both cases.

The results showed that at the higher temperature (220 °C), more short chain paraffins were obtained than short chain olefin products. The chain growth probability (α) values for the olefins (O_3 - O_6) were smaller than those for the paraffins (P_3 - P_6) under all the FT reaction conditions studied. The results showed that the co-feeding of N₂ to the syngas during FT runs slightly increased the α values for most of the FT runs. At low reaction conversion the olefin selectivity was higher than that of the selectivity to paraffin. The light paraffin α values were high reaching 1. The data also showed that light olefins α values increased with increasing selectivity to the olefins asymptotically reaching a value of approximately 0.79 whereas the values for the paraffins weren't affected by these changes in conditions. This asymptotic behaviour might be indicative of an approach to reaction equilibrium amongst the olefin species.

Overall, these results show that the change operating conditions caused by loss of activity with time affects olefin and paraffin product distributions differently. This suggests that olefin and paraffin product distributions should be considered separately in the development of models for FT processes.

6.1 Introduction

Fischer-Tropsch synthesis (FTS) has been reported as a surface polymerisation type reaction since the early days of FT [1-4]. This reaction entails a chain growth mechanism in which a monomer is inserted into the growing chain of carbon atoms in a molecule [4]. It appears that FT processes are controlled by several phenomena including reaction mechanism and kinetic factors. However, there are many contradictions in terms of the mechanism and kinetics for FTS. Although the controversy exists, researchers mostly agree that the methylene (CH_2) insertion mechanism is the primary mechanism in FTS [3,5-9]. This accepted model of FTS has been used to define the product distribution and predict the selectivity trends of hydrocarbons as a function of carbon number [4]. This mechanism leads to the product distribution resulting from the chain propagation rate relative to the chain termination rate, which is often referred to as chain growth probability α [5]. The Anderson-Schulz-Flory (ASF) distribution describes the chain growth probability and is given by the equation (1) below [10,11]:

$$\log \frac{W_n}{n} = n \log \alpha + \text{const.} \quad (1)$$

where W_n is the mass fraction of the species with carbon number n . α values are obtained from the slope of the plot of $\log \frac{W_n}{n}$ against the carbon number n . A higher α value means a higher selectivity to heavy hydrocarbons.

The majority of the reported ASF plots showed a nearly straight line only in the C_4 – C_{12} region [10,12]. However, for most catalysts, including the most commonly used iron and cobalt catalysts, clear deviations from this ideal distribution are observed [5,13]. It is generally accepted that deviations from the classical ASF distribution are unavoidable and are prominent for C_1 (methane), C_2 (especially ethylene) and heavy hydrocarbons [14]. The relative amounts of olefins, paraffins and total hydrocarbons with carbon number are important in determining how well the ASF model fits the results. For example, Todić et al. have shown that when the slope

for the olefin is much steeper than that of paraffin it causes the non-ASF features of the total hydrocarbon distribution [4].

On the other hand, it is known that the ASF product distribution changes with the occurrence of secondary reactions in FTS. At high conversions (high H_2O partial pressures) at FTS conditions, reinsertion of olefins appear to be the most important secondary reaction [13]. Yet, at low carbon numbers secondary reactions hardly affect the product distribution [15]. Although the growth probability factors and the formation rates of the products depend on the partial pressure of CO and H_2 they appear to be independent of the carbon number [13]. For example, Patzlaff et al. reported the dependence of hydrocarbon product distributions on partial pressures of reactants for both iron and cobalt FT catalysts [9]. Moreover, it should be mentioned that temperatures and CO conversion are variables that affect the product distribution [16]. Due to the polymerisation-like growth mechanism of FTS, the selectivity to a certain product or product range will always be limited [17]. For example, Wang et al. found it difficult to selectively produce some olefins (C_2 and C_3) and concluded that the challenge is to break through the ASF distribution function for the sake of selectivity [18]. Thus the yield of light olefins ($\text{C}_2\text{--C}_4$) cannot be made to reach some desired levels. This is because of the limitation imposed by the ASF distribution of FTS and this remains a huge challenge to be overcome [18].

As mentioned before, FT is reported to be a stepwise chain growth reaction. Hence, we believe that further understanding of the product chain growth starting from the light hydrocarbons under different conditions would bring extra clarity into the understanding of the FTS reaction. Because of the economic value of the heavy hydrocarbons, numerous FTS reports in the literature consist of investigations on the product distributions of middle distillate to heavy hydrocarbons obviously in some cases starting from methane [3,4,9,10,19-22]. Although some authors have published α values in the zone $\text{C}_1\text{--C}_7$ [10,23], not many studies have focused on the ASF distribution of light hydrocarbons ($\text{C}_1\text{--C}_6$) in particular including olefins and paraffins separately.

In order to try to understand how important kinetics was in the production of light hydrocarbons via the FTS reaction, a set of novel experiments were done. These consisted of alternating the flow rates to the reactor between two different situations. These two situations consisted in keeping the partial pressures of the reactants the same while in the second case extra inert gas (nitrogen) was added. This was achieved by increasing the overall pressure when the extra nitrogen was added in such a way as to keep the reactant partial pressures the same.

6.2 Fischer-Tropsch synthesis: experimental procedure

The experimental results presented in this chapter are the sum of those previously presented in Chapters 4 and 5. The experimental method is again briefly described. A supported cobalt catalyst (10% cobalt metal /TiO₂ by mass) was used in the current work. One gram of this cobalt catalyst was loaded into the fixed bed FT reactor, dried under the nitrogen atmosphere and reduced *in situ* with pure hydrogen. Once the catalyst was reduced, the temperature at the reactor was gradually increased to 200 °C. At the same time the researcher fed firstly syngas (H₂ 60%, CO 30% and 10% N₂ by volume) into the reactor to replace the pure H₂ and carried out the FT process for two days. Thereafter, the temperature of the reactor was increased to 220 °C for the remainder of the experiments. The second kind of feed (syngas + N₂) was composed of H₂ 48%, CO 24% and 28% N₂ by volume was fed into the reactor while increasing the total pressure from 20 to 25 bar. Overall the FTS was carried out by switching alternatively between these two types of feeds (syngas and syngas + N₂) with a constant partial pressure of H₂ at 12.5 bar (abs) and CO at 6.20 bar (abs) while adjusting the total flow rate and pressure. The reaction conditions for the FTS experiments which consisted of switching feeds from syngas (S) to syngas with extra N₂ (S+N₂) and vice versa are displayed in **Table 6.1**.

Table 6.1: Reaction and feed conditions for the FTS experiments over a cobalt based catalyst

Case	Syngas (S)	Syngas + N ₂ (S+N ₂)
Catalyst	10% Co/TiO ₂	10% Co/TiO ₂
Mass (gram)	1	1
Temperature (°C)	200-220	220
Reactants partial molar flow rate (mol/min) for: FR _{H2} FR _{CO}	0.075 0.038	0.075 0.037
Reactants partial pressure (bar abs) for: P _{H2} P _{CO}	12.51 6.26	12.41 6.20

Wax was collected from the hot trap that was kept at 150 °C, and water and oil were collected from the cold knockout pot maintained at room temperature. The knockout pots were emptied prior to each set of FT experiments when the feeds were switched from syngas (S) to syngas + N₂ (S+N₂) or in the reverse direction. In between changes, the reactor was kept for a day to achieve stability before the new FT run was started.

However, after 667 hours, an unexpected event occurred, namely a mass controller malfunction. As a result N₂ alone flowed into the reactor and for a duration of about eight days (193 hours). Afterward the nitrogen flow was stopped and syngas was again fed to the reactor and switching was resumed. This was allowed to continue for a substantial time, up to 2700 hours. Throughout the FT runs the tail gas from the rig was monitored with a DANI GC fitted with a flame ionisation detector (FID) and two thermal conductivity detectors (TCD A and TCD

B). This was for the analysis of both inorganic and hydrocarbons in the gas phase. The data acquired are presented and discussed in the next section.

6.3 Results and discussion

6.3.1 CO conversion and product selectivity

The CO conversion and product selectivity of the short chain hydrocarbons were measured and the results are displayed in **Figure 6.1 (A)** for CO conversion, **(B)** for methane selectivity, **(C)** for selectivity to light olefins and **(D)** for selectivity to light paraffins. In this case the author defines selectivity to a certain product (olefin or paraffin) as the percentage of carbon in that material in the product relative to the amount of carbon monoxide converted. From this figure (**Figure 6.1**) three different major stages are noticeable, which include the period from 0 to 48 hours (FT run with syngas at 200 °C), deactivation with time on stream from 110 to 667 hours (FT runs with S and S+N₂ at 220 °C) and 1000 to 2700 hours (FT runs with S and S+N₂ at 220 °C) when the FT reaction reached steady state after nitrogen alone was passed through between 667 and 859 hours. Each of these stages has revealed different behaviour as depicted in **Figure 6.1** and has been explained in Chapters 4 and 5 of this thesis. Briefly, the changes noticed include the deactivation with time on stream and that obtained after the period of nitrogen alone flow in the reactor. The selectivity to olefins and paraffins was affected by these catalytic variations. In addition changes are obtained relating to the co-feeding of nitrogen to the reactor. The main reason for plotting **Figure 6.1** is to enable one to see the short chain product distribution with regard to these changes.

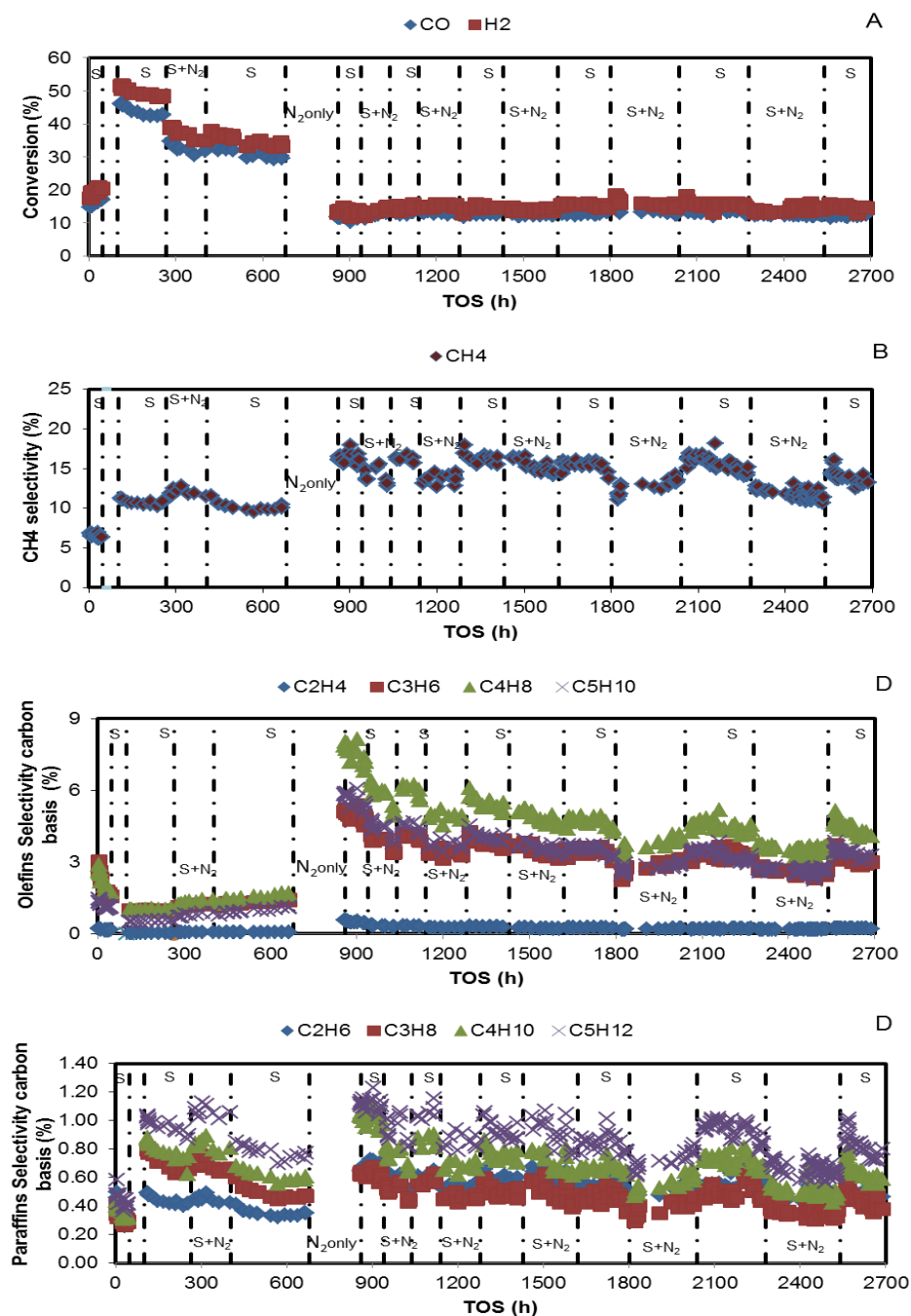


Figure 6.1: Reactant conversions (A); selectivity to (B) methane; (C) light olefin; and (D) light paraffin as a function of time on stream (TOS) during FT runs with 10% Co/TiO₂ in a fixed bed reactor at 200 °C for 48 hours and 220 °C while keeping the reactant partial pressures and volumetric flow rate the same (see **Table 6.1**) for the remainder of the experiment. There was nitrogen flow only during TOS between 667 and 859 hours.

6.3.2 Product distributions for the light hydrocarbons

As described above, the product distributions for the light hydrocarbons in the fixed bed reactor loaded with 10% Co/TiO₂ catalyst at different FT reaction conditions (see **Table 6.1**) were measured. The researcher first considered the long time data (after 951 hours) when a steady state had been reasonably well achieved, see **Figure 6.1 (A)**, and plotted the logarithmic mass fraction of the products against the carbon number (C₁ to C₆). The graphs obtained are displayed in **Figure 6.2** and **Figure 6.3** for the experiments conducted with syngas and syngas + N₂ respectively. Interestingly, at steady state the results show that the data are almost superimposed for each carbon number for both **Figures 6.2** and **6.3 (A)** for olefins, **(B)** for paraffins and **(C)** for overall hydrocarbons displaying nearly straight lines from C₃ to C₆. The slopes from these linear functions as depicted in both **Figures 6.2** and **6.3 (A), (B) and (C)** were used in the calculation of the product growth probability (α). As is usual the results for the carbon numbers C₁ and C₂ were omitted. The graphs appear almost identical, the data revealed that alpha values increased quite insignificantly (0.01) from FT runs with syngas to FT runs with syngas + N₂ e.g. for olefin 0.78 to 0.79; 0.97 to 0.98 for paraffin and 0.81 to 0.82 for the overall hydrocarbon. The chain growth probability (α) values are often determined for the carbon number C₁ to C₆₊ from graph known as Anderson-Schulz-Flory (ASF) plot. However, the focus of this study is on the light hydrocarbons (C₁ to C₆), and as such the researcher embraced the term chain growth probability by default. He next asked, how is the product distribution affected at what he termed the unstable conditions of the FT reactions where the CO conversion is different at different times on stream?

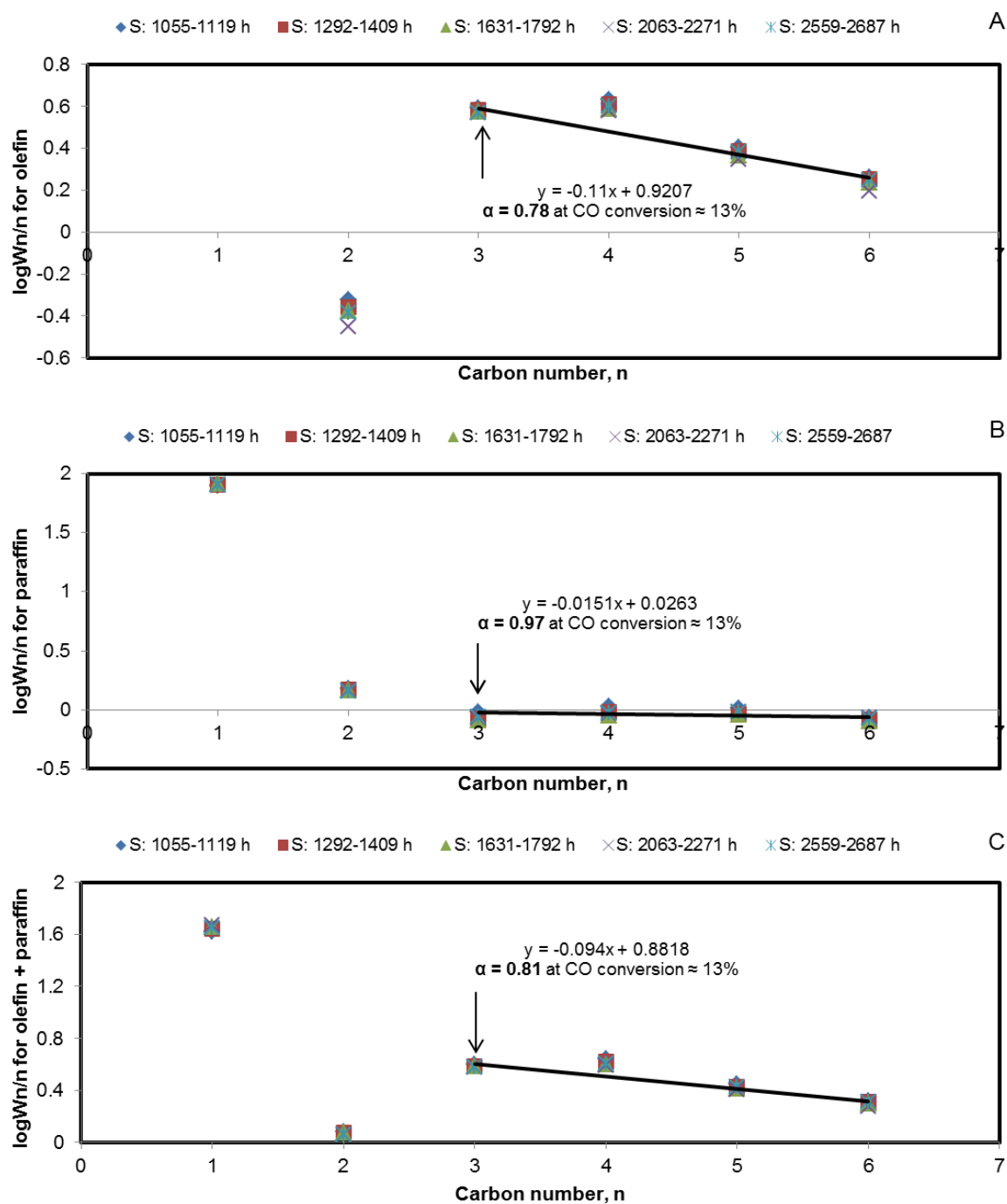


Figure 6.2: The chain growth probability as a function of carbon number (A) for olefins, (B) for paraffins and (C) for overall hydrocarbons during FT runs with 10% Co/TiO₂ in a fixed bed reactor when the FT reaction had reached steady state. These results are for FT runs with syngas only at different TOS.

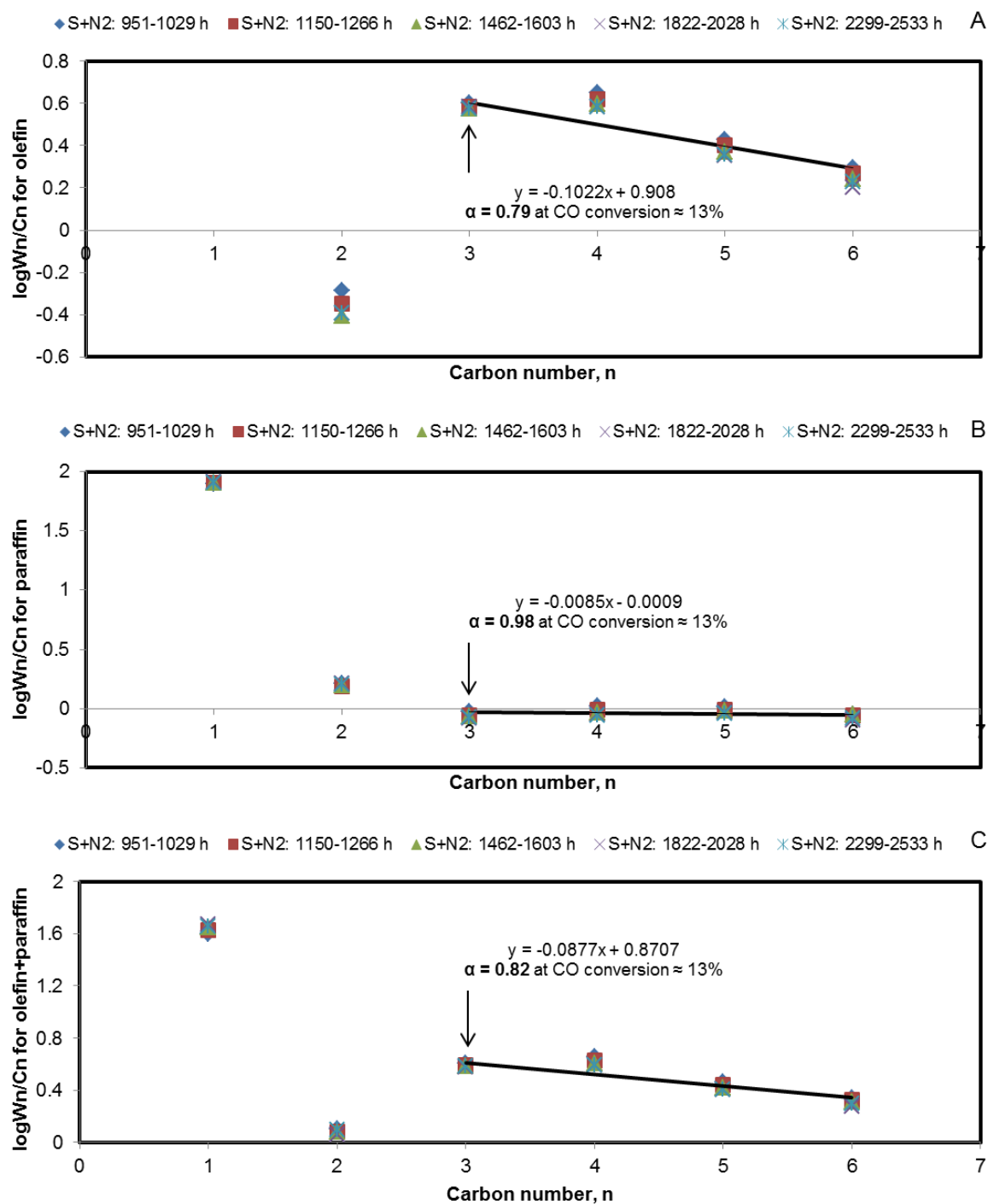


Figure 6.3: The chain growth probability as a function of carbon number (A) for olefins, (B) for paraffins and (C) for overall hydrocarbons during FT runs with 10% Co/TiO₂ in a fixed bed reactor when the FT reaction had reached steady state for FT runs with syngas + N₂ only at different TOS while keeping the reactant partial pressures and volumetric flow rate the same as for syngas alone.

The researcher similarly plotted the ASF graphs for the logarithmic mass fraction of the products as a function of the carbon number (C_1 to C_6) at different TOS (4-931 h) when the activity was changing (see **Figure 6.1**). These are presented in **Figure 6.4 (A)** for light olefins (O_2 – O_6), **(B)** for paraffins (P_1 – P_6) and **(C)** for the light hydrocarbons (C_1 – C_6). **Figure 6.4 (A)** shows a much steeper slope for the olefin mass fraction with carbon number than the paraffin mass fractions with the same carbon number in **Figure 6.4 (B)**. The addition of olefin and paraffin gave the plot for the overall hydrocarbon as can be seen **Figure 6.4 (C)**. These findings are in strong agreement with experimental data from previous publications [4,13]. The graphs in **Figure 6.4** show that for the light hydrocarbons reasonably straight lines can be obtained in the range of chain lengths 3 to 6. In the region of carbon numbers 3 to 6 considered here, the present research findings essentially agreed with the literature although the literature reported a nearly straight line for the hydrocarbons in the range 4 to 12 [10,12]. This is in line with other researchers [24,25]. This investigation examined only the results for the light hydrocarbons in the gas phase. As these are the gas-phase hydrocarbons leaving the last condenser at room temperature it is possible that some of these might be dissolved in the liquid phase. However, the researcher estimates only about 1% of the C_6 comes out in the liquid phase. As this study is merely using the results to compare different situations using the same experimental method, this should not affect the validity of the arguments.

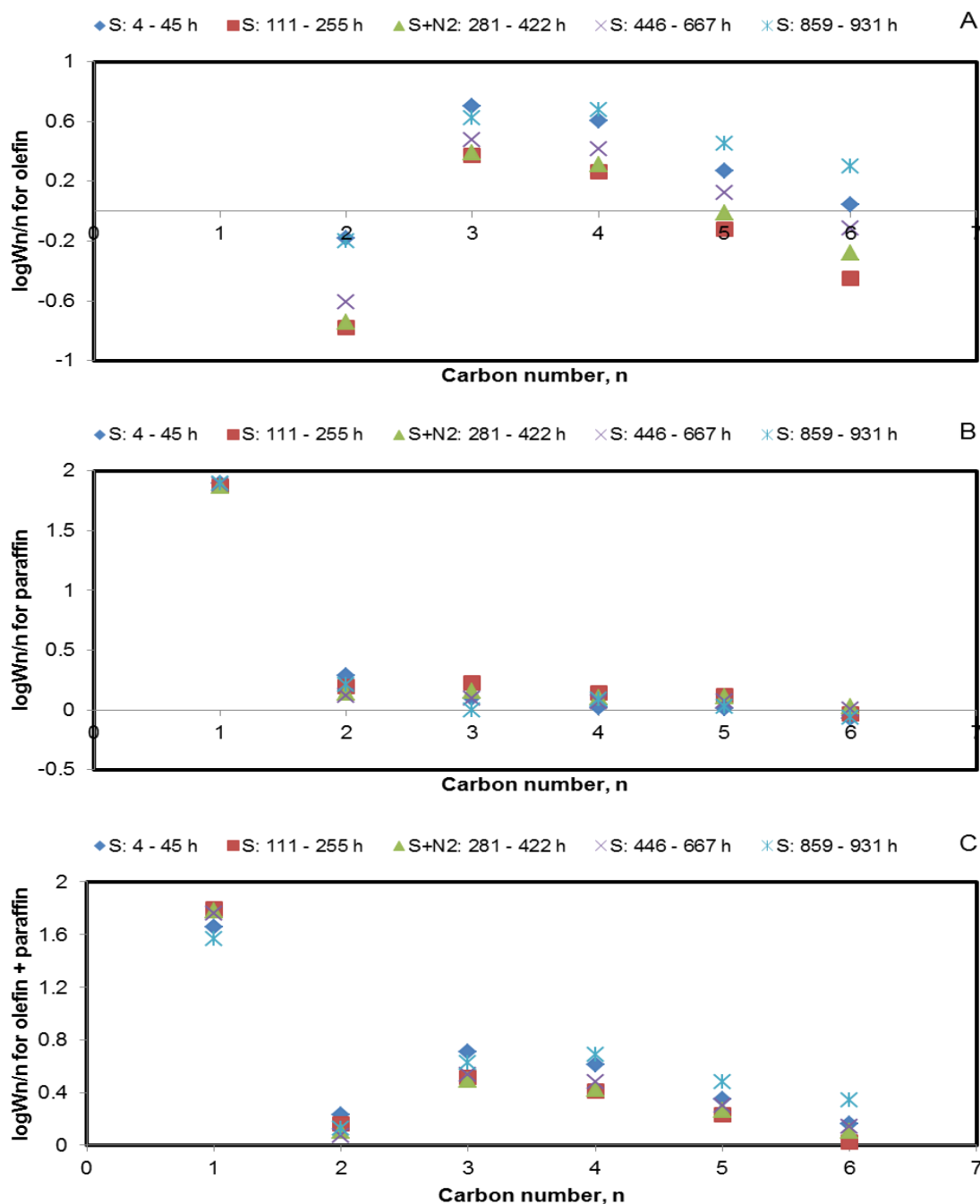


Figure 6.4: The product distribution as a function of carbon number during FT runs with 10% Co/TiO₂ in a fixed bed reactor (A) for olefins, (B) for paraffins and (C) for overall hydrocarbons while keeping the reactant partial pressures and volumetric flow rate the same. The average CO conversions for the FT runs were: 16% (4 to 45 h); 45% (111 to 255 h); 33% (281 to 422 h); 31% (446 to 667 h) and 13% (859 to 931 h). S: syngas; S+N₂: syngas with extra N₂ and h: hours.

The slopes from **Figure 6.4 (A), (B) and (C)** were once again used in the calculation of the product growth probability (α) whereas before the carbon numbers 1 and 2 were omitted. The α values obtained are summarised in **Table 6.2** according to the specific FT runs and time on stream. The α values of olefins O_3 – O_6 decreased from 0.59 to 0.52 when the FT reaction temperature was increased to 220 °C from 200 °C. The chain growth probability values of the light paraffin (P_3 – P_6) also dropped from 0.89 to 0.83 from 200 °C to 220 °C. Thus the α values of olefin and paraffin declined when increasing the reactor temperature by 20 °C. For the overall hydrocarbons, in the region of carbon numbers 3 to 6, the α values were increased from 0.65 to 0.68 when the reactor temperature was increased from 200 °C to 220 °C. This is in line with Fletcher's work [26] whose finding showed that the chain growth probability in the range C_3 to C_7 was increased from 0.63 at 220 °C to 0.75 at 270 °C. However, the results do not accord with well documented findings which numerous other researchers have observed [13,23,27,28]. It is most likely that the overall α value for C_3 – C_6 is higher at higher temperature because at this temperature (220 °C) relatively more paraffin products than olefins were obtained (see **Figure 6.1**). This is probably because, as is generally known, paraffin hydrocarbons have a higher α value than olefins, hence the overall α value is near to the one for paraffin at higher temperature. Moreover, from **Table 6.2**, the α values increased from 0.52 to 0.62 for olefin, 0.83 to 0.94 for paraffin and 0.68 to 0.73 for light hydrocarbons with a time on stream increment from 111.88 to 667.00 hours as the catalyst deactivated at (see **Figure 6.1**). Further rises of olefin α values were obtained after the reactor was purged with N_2 (this is the period where N_2 alone was fed to the reactor) from 667 to 895 hours. The olefin chain growth probability values changed from 0.62 to 0.76 while the CO conversion dropped from 30% to 13% (see **Figure 6.1**), whereas the light paraffin values were not affected by the previous nitrogen alone flow in the reactor at TOS 667 to 895 hours

Table 6.2: Summary of the growth probability values for light olefin, paraffin and light hydrocarbon and olefin to paraffin ratios obtained during FT runs with 10% Co/TiO₂ in a fixed bed reactor while keeping the reactant partial pressures and volumetric flow rate the same

Region	FT runs	TOS (hours)		α values			Ratios			
	Feed switch	From	To	O ₃ –O ₆	P ₃ –P ₆	C ₃ –C ₆	O ₂ /P ₂	O ₃ /P ₃	O ₄ /P ₄	O ₅ /P ₆
Region R1	{ S ^a : 200°C	4.63	44.52	0.59	0.89	0.65	0.515	6.071	5.774	2.721
Region R2	{ S: 220°C	111.88	255.37	0.52	0.83	0.68	0.104	1.379	1.293	0.562
	{ S+N ₂ ^b : 220°C	281.86	422.33	0.58	0.92	0.74	0.130	1.727	1.607	0.754
Region R3	{ S: 220°C	446.98	667.00	0.62	0.94	0.73	0.209	2.723	2.522	1.277
	{ N ₂ only: 220°C									
Region R4	{ S: 220°C	859.06	931.02	0.76	0.95	0.78	0.754	7.989	7.461	5.008
	{ S+N ₂ : 220°C	951.32	1029.49	0.77	0.98	0.80	0.579	7.666	7.721	4.692
	{ S: 220°C	1055.76	1119.89	0.76	0.97	0.79	0.535	6.951	6.860	4.182
	{ S+N ₂ : 220°C	1150.74	1266.25	0.77	1.00	0.80	0.492	7.427	7.227	4.356
	{ S: 220°C	1292.75	1409.66	0.76	0.99	0.79	0.497	7.597	7.170	4.350
	{ S+N ₂ : 220°C	1462.86	1603.94	0.75	1.01	0.79	0.407	7.038	6.862	3.919
	{ S: 220°C	1631.05	1792.34	0.75	1.00	0.79	0.471	7.472	7.029	4.155
	{ S+N ₂ : 220°C	1822.08	2028.67	0.73	0.99	0.77	0.397	7.198	6.790	3.859
	{ S: 220°C	2063.6	2271.12	0.73	1.01	0.78	0.376	6.588	6.237	3.520
	{ S+N ₂ : 220°C	2299.69	2533.24	0.75	1.00	0.78	0.404	7.089	6.929	3.981
	{ S: 220°C	2559.6	2687.4	0.76	1.00	0.80	0.474	6.986	6.922	4.057

^a S: syngas; ^b S+N₂: syngas with N₂

The FT reaction achieved a CO conversion of approximately 13% at steady state (see **Figure 6.1**); at the same time the variations of the chain growth probability α values for O_3 – O_6 , P_3 – P_6 and C_3 – C_6 are quite small, see **Table 6.2**. FT with syngas + N_2 had negligibly different α values from those from syngas alone for the experimental runs as displayed in **Figure 6.2** and **Figure 6.3**.

In this study α values of up to 1.01 for light paraffin (P_3 – P_6) have been reported for some reaction conditions, especially in the reaction time zone from 1150 to 2687 hours, as shown in **Table 6.1**. In the open literature, reports on α values equal to one or more are not well documented. **Figure 6.5** is an example of the short chain paraffin product distribution as a function of carbon number. Based on **Figure 6.5**, it is easy to see that the values of $\frac{W_n}{n}$ with carbon number 3 to 6 for paraffin products are quite similar, which indicates that the α value under this reaction condition is near to 1. **Figure 6.6** shows the formation rate of light paraffin hydrocarbons as a function of time on stream until 2700 hour. This shows that there was initially a reasonably rapid drop in rate getting close to the final steady state value prior to the nitrogen flushing period.

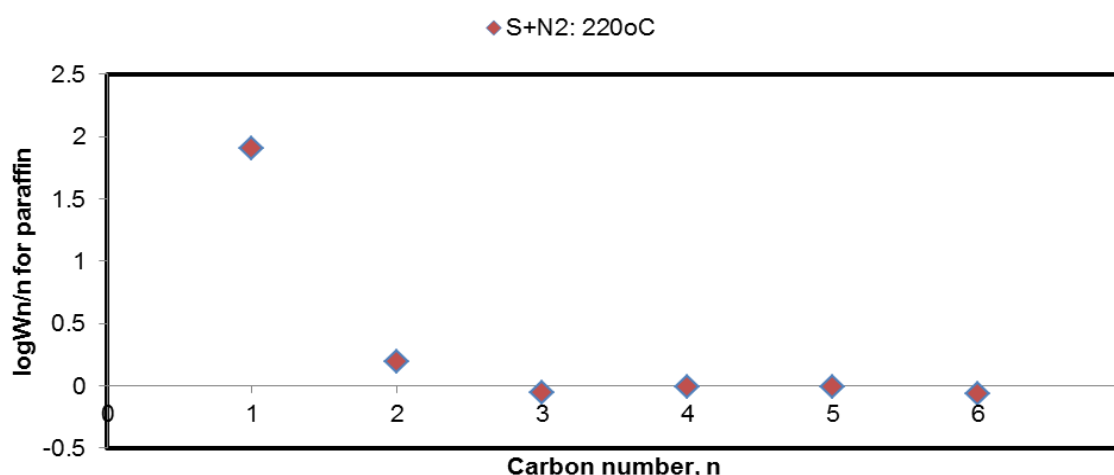


Figure 6.5: The chain growth probability for the light paraffins as a function of carbon number during FT runs with 10% Co/TiO₂ in a fixed bed reactor under an FT run of syngas with extra nitrogen (S+N₂) and time on stream 1150.74 to 1266.25 hours (see **Table 6.1**).

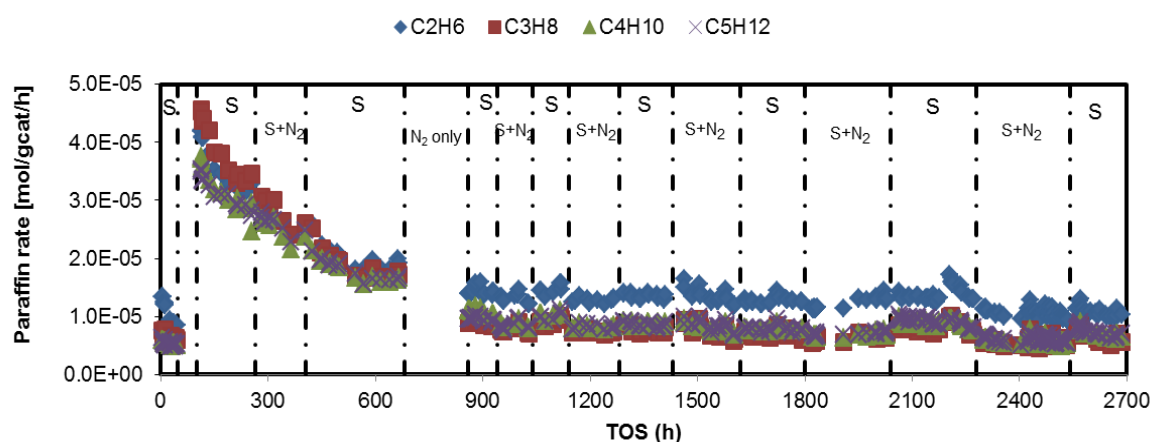


Figure 6.6: The formation rate of light paraffins as a function of time on stream (TOS) during FT runs with 10% Co/TiO₂ in a fixed bed reactor at 200 °C for 48 hours and 220 °C (for the remainder of the experiments) while keeping the reactants' partial pressure and volumetric flow rate the same (see **Table 6.1**). There was nitrogen flow only during TOS between 667 and 859 hours.

Based on these findings shown in **Table 6.1** and **Figures 6.1** to **6.6** the researcher would say that there is indeed more than one factor impacting on the product distribution in FTS. This is consistent with the literature that many factors have an effect on the chain growth probability during FT experiments including the temperature, which in turn also affects the CO conversion [27]. The next section will deal with the effect of CO conversion on the chain growth probability.

6.3.3 CO conversion and short chain hydrocarbon growth probability

The effect of CO conversion on the products' chain growth probability (α) was examined for the unsteady state and part of the FT run at the stable state of the experiments, as per **Figure 6.4**. When the data of **Table 6.2** and of **Figure 6.1 (A)** were compared, the researcher realised that the short chain product distribution changed with the catalyst deactivation. Therefore he thought it might be worthwhile to plot the chain growth probability values versus the CO conversions. The results are shown in **Figure 6.7**: blue dots for olefins, red dots for paraffins

and green dots for overall hydrocarbons with carbon number n . This graph shows α values decrease with increase in CO conversion. This also shows deactivation resulted in relatively more light hydrocarbons (high α (C_3 – C_6)) selectivity.

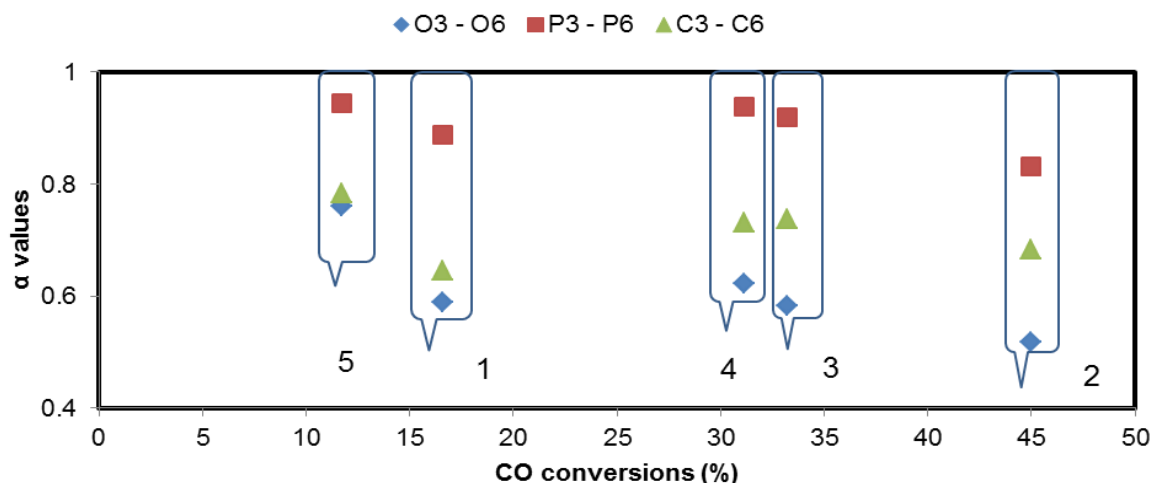


Figure 6.7: The chain growth probability as a function of CO conversions during FT runs with syngas (S) and syngas with extra nitrogen (S+N₂) with 10% Co/TiO₂ as the catalyst in a fixed bed reactor while keeping the reactant partial pressures and volumetric flow rate the same. The sequential FT runs TOS (hours) were: 1) S: 200 °C (4.63 h to 44.52 h); 2) S: 220 °C (111.88 h to 255.37 h); 3) S+N₂: 220 °C (281.86 h to 422.33 h); 4) S: 220 °C (446.98 h to 667.00 h) and 5) S: 220 °C (859.06 h to 931.02 h).

Other researchers [17,29] have also pointed out the complexity of CO conversion on the chain growth probability. The relationship between the chain growth probability and selectivity to light hydrocarbons is also important. Discussion about the effect of selectivity on the chain growth probability (α) are placed in the next section.

6.3.4 Product selectivity and chain growth probability in the gas phase

The influence of the product selectivity on the product distribution in the gas phase for the light hydrocarbons was also determined. The light hydrocarbons

selectivities (olefins (O_3-O_5); paraffins (P_3-P_5) and the overall hydrocarbons (C_3-C_5)) were plotted as a function of the chain growth probability (α) from carbon numbers 3 to 6. The results are displayed in **Figure 6.8 (A)** for olefins (O_3-O_5) versus α (O_3-O_6), (B) for paraffins (P_3-P_5) versus (P_3-P_6), and (C) for the overall hydrocarbons (C_3-C_5) versus (C_3-C_6). As usual the selectivity to carbon number 2 was left out due to its strange behaviour. **Figure 6.8 (A)** reveals that the α values of olefins (O_3-O_6) increased with increasing selectivity to light olefins (O_3-O_5). At steady state when the chain growth probability reached 0.76 (refer to region 4 (R4)), the product selectivity increased exponentially for all the carbon numbers C_3 to C_5 . **Figure 6.8 (B)** demonstrates that the increase of the light paraffin (P_3-P_6) α values is not affected significantly by the increase in the product (P_3-P_5) selectivity (see all four regions R1 to R4). On the other hand, **Figure 6.8 (C)** reveals that the overall light hydrocarbons (C_3-C_5) have similar patterns to the ones obtained for the light olefins (see all four regions R1 to R4). Based on these findings, we can see that the product selectivity strongly affects the chain growth probability of the total light hydrocarbons including light olefins while light paraffins are hardly affected. Previous studies have also reported that the product selectivity impacts on the product distributions in FTS [31,32].

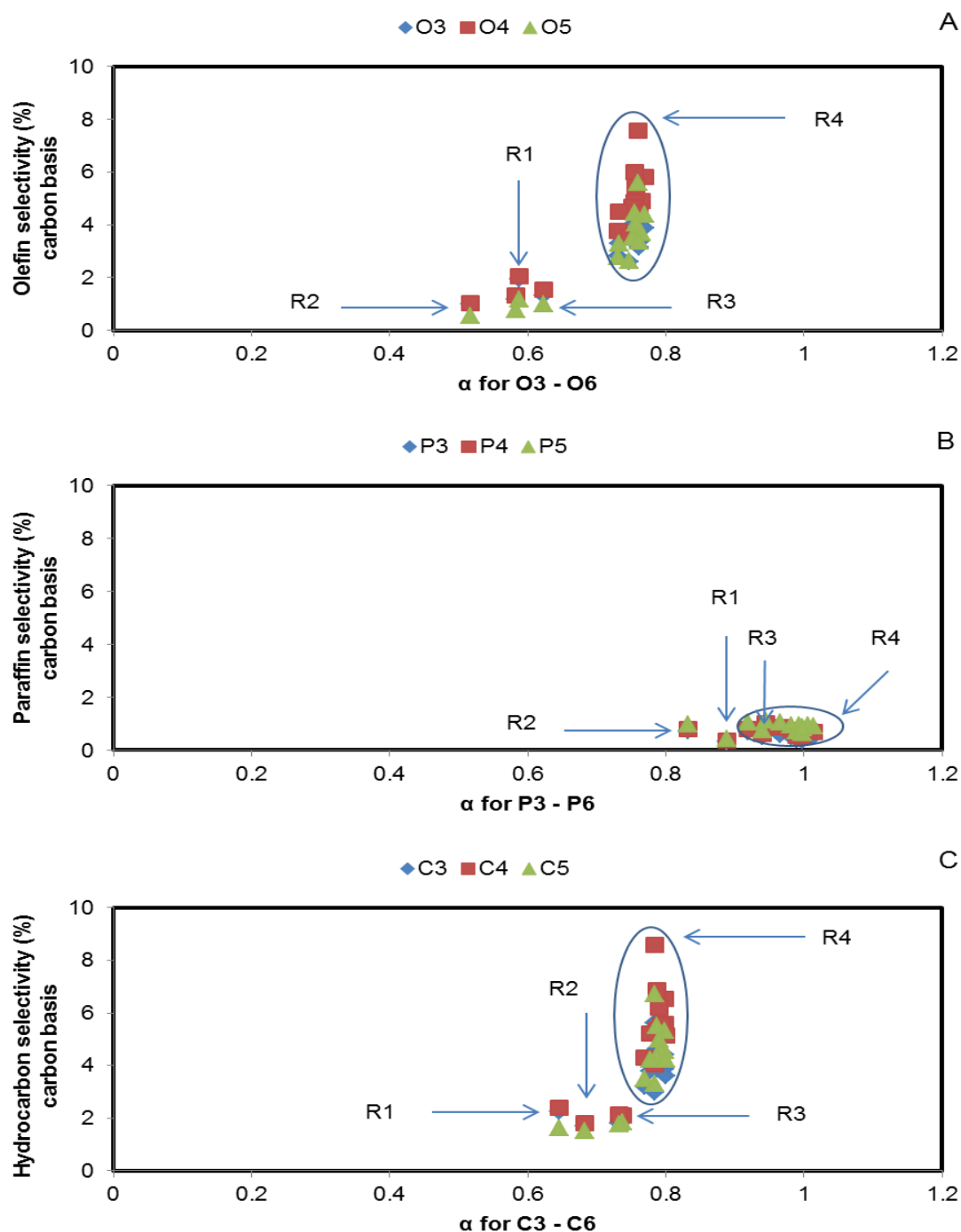


Figure 6.8: The product growth probabilities as a function of light hydrocarbon products selectivity α : (A) for the light olefins; (B) for the light paraffins and (C) for the overall light hydrocarbons as per the FT runs feed switches and time on stream duration as given in **Table 6.2**. Arrows R1, R2, R3 and R4 displayed here refer to four regions according to **Table 6.2**.

What is very clear from **Figure 6.8 (A)** is there is a clear relationship between the alpha value and the conversion to olefins. For high conversions the alpha value asymptotes to a value of about 0.8. However, when the conversion drops below about 2% for each of the olefins the alpha values begin drop significantly (see regions R1 to R3). The situation for the paraffins **Figure 6.8 (B)** is, however, very different. In this case the alpha values do not really depend on the paraffin conversion. Because generally the olefins are in excess or not less than the paraffins, the overall hydrocarbon patterns in **Figure 6.8 (C)** follow that of the olefins (see all four regions R1 to R4).

It is interesting that the correlation between the alpha value and selectivity is only true for the olefins whereas the alpha value for the paraffin seems to be fairly independent of selectivity. What this means is that the olefin to paraffin ratio will be very different for low and high selectivities, with the olefins dominating at low selectivities. Another interesting point is that the alpha value of the olefins asymptotes to a fixed value for high relative amounts of olefins (low overall conversion). This seems to suggest some sort of pseudo-equilibrium at low overall conversions. The same is clearly not true for paraffins.

Plotting the growth probability of short chain hydrocarbon against their selectivity as presented in this study is not readily available in the literature. However, Masuku et al. [25] were the first to report findings based on the constrained equilibrium approach, which shows that the chain growth probability is dependent on the intercept of the Gibbs free energy of reaction/formation (G_0) versus carbon number. Furthermore, they minimised Gibbs free energy for olefins and predicted that the chain growth probability of olefins decreased with increasing the temperature as illustrated in **Table 6.3**.

Table 6.3: The predicted chain growth probability factor (α) at various temperatures for olefins [25]

Intercept/ G_0 (kJ/mol)	Temperature ($^{\circ}\text{C}$)	Alpha (α)
10.997	200	0.945
3.4047	250	0.746
-4.1876	300	0.469

It is logical to assume that if there was some sort of equilibrium the alpha value for olefins at the researcher's experimental temperature of 220°C would range from 0.746 to 0.945. In his experimental work, when the FT reaction reached steady state, the olefin alpha value reached 0.79 (see **Figure 6.3**), while the reactor temperature was set at 220°C . As can be seen from **Figure 6.8**, the chain growth probability increased with selectivity increasing and reached the asymptotic value of 0.79, which might indicate some species reaching equilibrium.

The results indicate that the chain growth probability might be affected by the CO conversions possibly due to the secondary reaction of primary olefins, which is consistent with the literature [22,30,33]. The selectivity to olefins increases with decreasing CO conversions. We see that when the selectivity to light olefins increases, the chain growth probability also increases. The present data indicate a possible link between the product distributions and the chain growth mechanism. According to previous publications the chain length distributions of products obtained on cobalt catalysts are slightly modified by secondary chain growth of readsorbed alkenes and hydrogenolysis of hydrocarbons [9].

Besides temperature, other FT operating conditions including pressure and flow rate influence the product distributions. The researcher observed changes to the chain growth probability of the light products even though the reactant partial and flow rate were kept constant. It has been suggested that the deviation from the ASF distribution and dependence of product distributions on the reactants

(hydrogen and carbon monoxide) partial pressure indicate that the products which have lower growth probability are formed by the well accepted CH_2 insertion mechanism [9]. Previously, Qian et al. considered the readsorption of alkenes and the following secondary reaction to analyse the deviation from ASF distribution [34]. Other authors who studied the ASF plots confirmed that the product distribution of the FTS shows significant deviations from the ASF distribution on iron, cobalt, and ruthenium catalysts [5,9,33].

Another report suggested that the change of the ASF slope with growing carbon number is accounted for by the model due to the adopted dependence on the carbon number of the vapour-liquid equilibrium (VLE) involving olefins in the liquid surrounding the catalyst pellets [27]. The liquid hydrocarbons which accumulate can also impact the product distribution when diffusion limitations and product hold up due to VLE occur [35]. To repeat what was mentioned above, if the liquid phase hydrocarbon data was included in the calculations, different results may have been obtained. However, several authors have different ways of analysing the product distribution from FT processes. For instance, it is understood that the apparent products of the FTS reaction is a mixture of freshly produced FTS products and the products left in the reactor. In order to obtain the correct product distribution, Shi and Davis believed it is necessary to find a way to evaluate or eliminate the product left in the reactor, which requires conducting FTS research in a different way [35]. On the other hand, Kruit et al. suggested that the correct product distribution should be obtained by volume-based summation of local product distributions, weighted with the local reaction rate [24]. In brief, based on the literature, despite all these studies over several decades and a certain consensus, the product distribution and mechanism of the FTS remain controversial topics. Therefore, the present experimental data obtained based on short chain hydrocarbons show that even though there is not global equilibrium, there is the possibility of an approach to equilibrium between the olefin product species.

6.4 Conclusion

The product distributions of gas phase light hydrocarbons (C_1 – C_6) in a fixed bed Fischer-Tropsch reactor were analysed at different stages of a Fischer-Tropsch synthesis (FTS) run over a 10% Co/TiO₂ catalyst. The investigation was carried out with FT feeds periodically switched from FT runs with syngas to FT runs with syngas + N₂, while the reactant partial pressures (P_{CO} and P_{H_2}) and volumetric flow rates remained constant at 200 °C and 220 °C.

Looking at the FT reaction conversion and the product selectivity with time on stream, the results showed that both the reaction temperature and the catalyst activity affect the product selectivity to short chain hydrocarbons. At higher temperatures, relatively more short chain paraffins than short chain olefins were initially produced. Moreover, at the same temperature (220 °C), the short chain olefin selectivity was increased when the catalyst gradually deactivated, but the selectivity to paraffins did not change much.

The chain growth probabilities (α) of short chain hydrocarbons with carbon number from 3 to 6 were calculated and the data were obtained for different stages of the FT experiment. In these FT experiments, the researcher found that the α values for the olefins (O_3 – O_6) were smaller than those for the paraffins (P_3 – P_6) under all the FT reaction conditions studied. The results showed that the co-feeding of N₂ to the syngas during FT runs slightly increased the chain growth probability (α) values for most cases of the FT runs. At the time when the reaction conversion was lower (approximately 13%), the olefin selectivity was higher than that of the selectivity to paraffin. Interestingly, the light paraffin α values were about 1 (a value often not reported).

The effect of CO conversions on the chain growth probability is slightly more complex since it reveals both an increase and a decrease of the α values. On the other hand, the results about the relationship between the chain growth probability and selectivity of light hydrocarbons show that light olefins α values increased with increasing selectivity up to an asymptotic value of about 0.79, whereas the α

values of paraffins were not affected. Comparing the present laboratory data and the value calculated by a model with minimised the Gibbs Free Energy for olefins, it is found that the experimentally measured data approximately agreed with the value expected at the temperature between 200 °C and 250 °C, which suggests that even though there is not global equilibrium, there is a possibility of some sort of equilibrium between the olefin product species in FT processes.

Overall, these results show that the operating conditions affect olefin and paraffin product distributions differently in FTS. Although the feed reactant partial pressures were kept constant in all these experiments, the short chain hydrocarbons product distributions varied for different conditions and different stages of the results. A simple kinetic model is unlikely to be able to explain all these phenomena.

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CHAPTER 7

A STUDY OF FISCHER-TROPSCH SYNTHESIS: DOES THE PRODUCT DISTRIBUTION FOLLOW THERMODYNAMICS?

The data contained in this chapter have been written in a paper format and is submitted to Applied Catalysis: A General Journal.

Abstract

The olefin to paraffin ratio is often linked to the product distribution in Fischer-Tropsch synthesis (FTS). As such, the researcher looked at the relationship between the ratios paraffin (P) to olefin (O) namely P_{n+1}/O_{n+1} and P_n/O_n where n is a carbon number from 2 to 5. Plotting molar ratios of paraffin to olefin (P/O) with carbon number $n+1$ (P_{n+1}/O_{n+1}) against P_n/O_n with carbon number n revealed a linear relationship which is independent of feed gases, catalyst activity and reaction temperature. This result implied that the product distribution might be determined by quasi-reaction equilibrium or vapour-liquid equilibrium, or the combination of the two factors.

During FTS the hydrocarbon C_nH_{2n} (low olefin) can be converted into an immediate high olefin ($C_{n+1}H_{2n+2}$) and/or paraffin (C_nH_{2n+2}) products where n is the carbon number 2, 3 and 4. The relative amounts of these three kinds of hydrocarbons (C_nH_{2n} , $C_{n+1}H_{2n+2}$ and C_nH_{2n+2}) were normalised and plotted in a ternary diagram in an order determined by their boiling points. The ternary diagram (referred to as Lu's plots) indicated that the product distribution tends to achieve equilibrium during FTS.

Our findings revealed that FT processes cannot be explained fully by kinetics alone. There might be factors including vapour-liquid equilibrium or quasi-reaction equilibrium worthy of consideration to explain FTS. Data in this work could prove worthwhile for the design of FTS and comprehending its product distribution.

7.1 Introduction

Fischer-Tropsch synthesis (FTS) is a chemical catalysed process that converts synthesis gas (syngas) into, among other things, a transportation fuel. During FTS a wide range of materials including reactants, products and catalyst are in the reactor. The products are hydrocarbons, mainly alkenes and alkanes. Some oxygenates are also produced. These substances can be found in phases such as gas, vapour, liquid and solid. Raje and Davis reported that products (vapour phase) exiting the reactor are merely in thermodynamic equilibrium with the liquid phase remaining in the reactor [1]. Thermodynamic equilibrium analysis can be an important tool which assists in reactor modelling, kinetic schemes or reaction mechanisms examination, and identifies rate-controlling processes in the reaction system [2]. Although overall thermodynamic equilibrium does not occur in FTS, Masuku et al [2] have reported that olefin product distribution is equilibrium determined, and that some paraffins might be primary products while others are the product of a secondary reaction. Furthermore, researchers have conducted experiments which showed that vapour–liquid equilibrium (VLE) was set up between the liquid and the gas in the reactor and this equilibrium could be adequately described by Raoult's Law [3]. Others have said that VLE plays an essential role in the Fischer-Tropsch (FT) reaction [4,5].

Fairly recently Visconti [6] found that process variables have only minor effects on the VLE when working in the narrow range of conditions of industrial interest. In this regard, the most relevant process variable is pressure, which affects both the product distribution and the vapour–liquid split. Another factor is the temperature; for the low temperature Fischer-Tropsch (LTFT) operated at below 250 °C, the reaction products of cobalt-based (but also iron-based) catalysts are partially vapour and partially liquid [6]. It is also known that when the temperature increases the selectivity moves towards the lower carbon number products regardless of the types of FT catalysts. Thermodynamics predicts that the products should consist mainly of CH_4 and graphite in the temperature range where FT is normally operated. The increase in CH_4 selectivity at higher temperatures may therefore mean that thermodynamic factors are starting to 'take

over' from mechanistic kinetic factors [7]. On the other hand, when temperature and/or total pressure increases, total conversion of propylene is expected from thermodynamic and kinetic considerations resulting in the increase of the reaction rate [8].

From a simple criterion Caldwell and Van Vuuren reported that with Schulz-Flory product distributions it is possible to predict when a liquid phase will form in FT reactors [9]. Moreover, the composition and quantity of the liquid can be calculated from the chain-growth probability and the usual operating data [4]. In addition, Marano et al [4] developed a VLE model which predicts accurately product phase splits. The ASF describes the carbon number distribution when the chain growth and termination are independent of chain size [2]. The FT product distribution may not be described by global thermodynamic equilibrium; yet Masuku et al. [2] reported that there might be aspects of it that can be described by equilibrium. Furthermore, the thermodynamically expected distributions of the products of FTS, with regard to molecular weight distribution and olefin formation, are shown to closely resemble distributions which have been observed experimentally [10]. The Flory distribution that is often observed in FT reactors could be described by reaction equilibrium between species [11].

It is well documented that the ratio of olefins to paraffins provides crucial information in FTS and depends on the reaction operating conditions, catalyst type and structure [12]. Yao et al. [13] showed that, based on experimental evidence, there is a linear relationship when the paraffin to olefin ratios of species of the lower hydrocarbons n are plotted versus $n + 1$ for a wide range of catalysts, reactor types and experimental conditions. Yao and co-workers developed models based on which the experimental results are quite close to the equilibrium calculations, and they postulated that the product distribution might be determined by considering reaction equilibrium or vapour-liquid equilibrium [13]. In addition, Lu et al. [14] performed conventional FT experiments and reported that the olefin/paraffin ratio of adjacent olefins such as C_4H_8/C_3H_6 is fixed. The ratio remained constant even when the reactor temperature and feed flow rates were varied. They proposed a thermodynamic model for olefin product distribution and

found that there is good agreement between the thermodynamic predictions and the measured distributions [14].

Generally the literature suggests that the environment in which FTS is operating renders the mechanism and thermodynamic studies of FT reaction very complicated. For instance, Glasser et al. [15] reported that the major problem in describing the FT reaction kinetics is the apparent complexity of the reaction mechanism and the large number of species involved. On the other hand, the kinetic description of the FT reaction is a very important task for the industrial practice. Yet the complexity of the reaction products makes it quite hard to accurately describe the kinetics of the process [16]. The FT reaction is usually regarded as kinetically controlled, as opposed to thermodynamically controlled, due to simulations having shown that thermodynamically methanation is preferred to heavy product formation [17]. However, the present researcher has shown in Chapter 5 (paper manuscript) that there might be more in FT processes than kinetics alone. Therefore, in this chapter, he investigates whether the product distributions in FTS have thermodynamic features. Moreover, he intends to expand on previous publications from his research group which indicated that the overall product distribution is possibly thermodynamically affected [2], the product distribution might be determined by considering reaction equilibrium [13], and finally that the olefin distribution in the FTS reaction might be determined by thermodynamics [14]

7.2 Experimental procedure

The FT reaction was performed in a laboratory scale fixed bed reactor loaded with 1 g of 10% Co/TiO₂. The catalyst reduction was carried out overnight with the reactor temperature set at 350 °C, at atmospheric pressure and under pure hydrogen flowing at 60 (NTP)mL/min. During FTS two kinds of syngas (S): H₂ 60% by volume, CO 30% and 10% N₂ and syngas with extra N₂ (S+N₂): H₂ 48% by volume, CO 24% and 28% N₂ were periodically switched and fed into the reactor with a constant partial pressure of H₂ at 12.5 bar (abs) and CO at 6.20 bar (abs) by adjusting the total flow rate and pressure. The researcher started the FT reaction,

at the reaction temperature 200 °C and for two days. Thereafter, the reaction temperature was increased to 220 °C for the remainder of the experiments. The operating conditions are summarised in **Table 7.1**. The vapour phase products exited the reactor at the bottom and passed through two traps placed in series. First the hot trap was set at 150 °C and secondly the cold trap was maintained at room temperature. The uncondensed gases from these two traps passed through a backpressure regulator and the tail gas was monitored with a DANI GC fitted with a flame ionisation detector (FID) and two thermal conductivity detectors (TCD A and TCD B). The condensed products (wax, oil and water) from both the hot and cold traps were collected when required for further analysis with an off-line GC.

Table 7.1: Reaction and feed conditions for the FTS experiments over 1 g of cobalt based catalyst

Region	FT runs	TOS (hours)		Reactants' partial pressure (bar abs)	
	Feed switch/Temperature	From	To	H ₂	CO
Region R1	{ S ^a : 200°C	4.63	44.52	12.51	6.26
Region R2	{ S: 220°C	110.88	255.37	12.51	6.26
	{ S+N ₂ ^b : 220°C	281.86	422.33	12.41	6.20
Region R3	{ S: 220°C	446.98	667.00	12.51	6.26
	{ N ₂ only: 220°C				
Region R4	{ S: 220°C	859.06	931.02	12.51	6.26
	{ S+N ₂ : 220°C	951.32	1029.49	12.41	6.20
	{ S: 220°C	1055.76	1109.89	12.51	6.26
	{ S+N ₂ : 220°C	1150.74	1266.25	12.41	6.20
	{ S: 220°C	1292.75	1409.66	12.51	6.26
	{ S+N ₂ : 220°C	1462.86	1603.94	12.41	6.20
	{ S: 220°C	1631.05	1792.34	12.51	6.26
	{ S+N ₂ : 220°C	1822.08	2028.67	12.41	6.20
	{ S: 220°C	2063.60	2271.12	12.51	6.26
	{ S+N ₂ : 220°C	2299.69	2533.24	12.41	6.20
	{ S: 220°C	2559.60	2687.40	12.51	6.26

^a: S refer to syngas (60% H₂ / 30% CO / 10% N₂ by volume)

^b: S + N₂ refer to syngas with extra N₂ (48% H₂ / 24% CO / 28% N₂ by volume)

7.3 Results

7.3.1 Paraffin to olefin ratio

The researcher plotted the paraffin to olefin (P/O) ratio as a function of time on stream for the light hydrocarbon C₂ to C₅ under various operating conditions, such as: keeping the reactants' partial pressure the same while periodically switching syngas to syngas + N₂ throughout the experiments; and temperature was set at 200 °C for two days at the start and increased to 220 °C for the remainder of the FT runs. The graphs are presented in **Figure 7.1 (A)** for the P/O with carbon number 2, **(B)** for the P/O with carbon number 3, **(C)** for the P/O with carbon number 4, and **(D)** for the P/O with carbon number 5. The patterns of the P/O ratios are identical for all the light hydrocarbons. The graphs in **Figure 7.1** also revealed that when the reactor's temperature was increased by 20 °C (200 °C to 220 °C) a significant increase in the P/O was obtained. Thereafter the P/O ratio values decreased with time on stream increment from 110 to 859 hours, where the values remained quite similar for the rest of the experiment. The decrease observed in this section of the experiment, 110 to 859 hours, is quite similar to the trend acquired for the catalyst deactivation period presented in **Figure 7.2**.

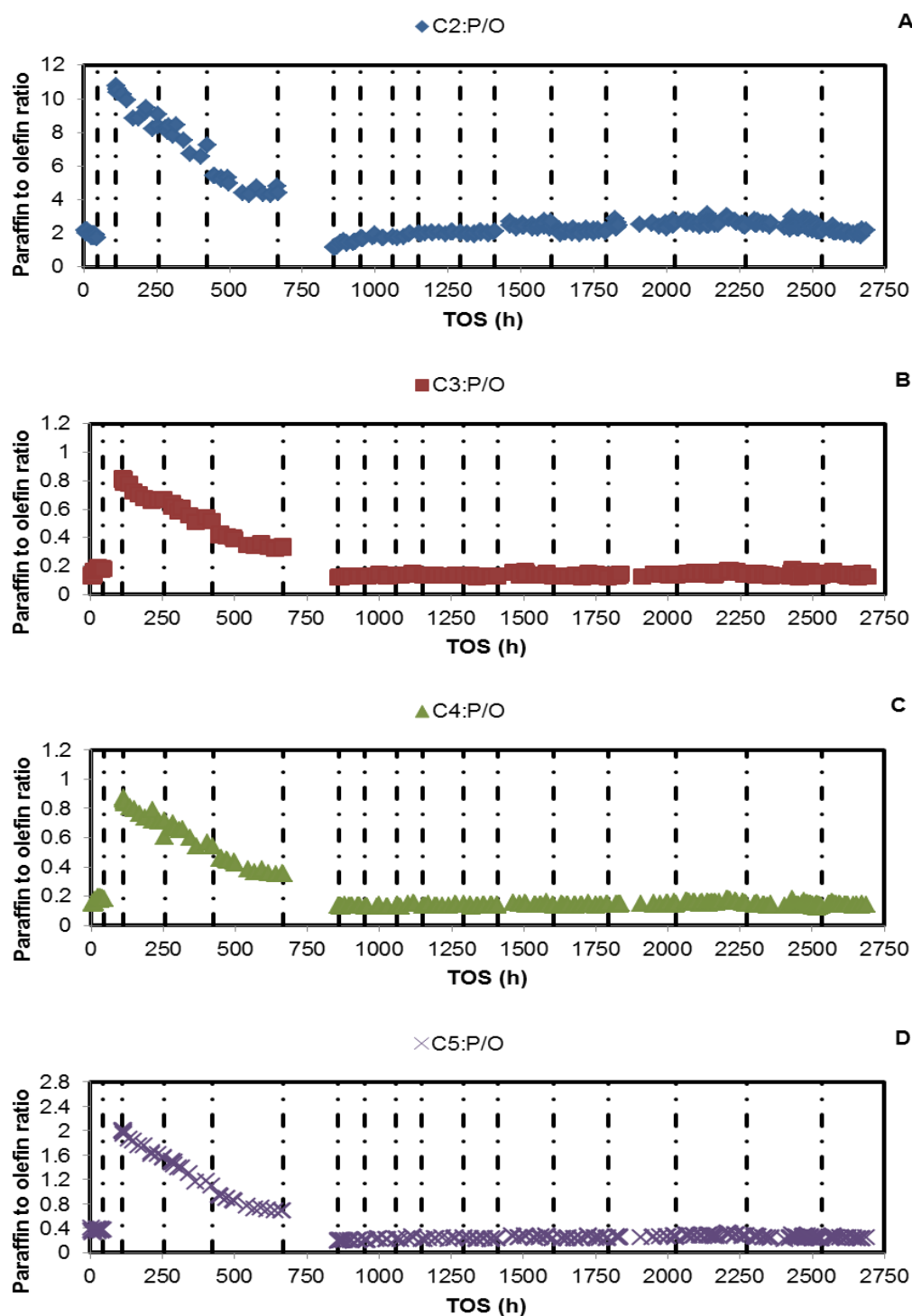


Figure 7.1: The paraffin to olefin ratio as a function of time on stream for the light hydrocarbons (O_2 – O_5 and P_2 – P_5) under the operating conditions summarised in **Table 7.1**.

The P/O ratio values did not change noticeably from 859 to 2750 h, although the feed compositions were switched periodically from syngas to syngas + N₂. However, the ethane to ethylene ratio value is higher than for any other carbon number. The graphs also show that the P/O ratio values obtained when the FT run started at 200 °C appear similar to those obtained when the FT runs reached steady state. It is important to note that the dashed lines in all figures (in this study) represent the starting points of switching the two kind of feed gases: syngas to syngas + N₂; the reaction conditions with time on stream for each run are listed in **Table 7.1**.

Figure 7.2 shows the reactant conversions with time on stream depicting zones such as 14.69 to 16.90% (for the first 48 hours of FT run with syngas at 200 °C), 16.90 to 46% (when the reactor temperature was increased from 200 to 220 °C at TOS 48 to 110 hours), 46 to 30% (during the catalyst deactivation TOS 110 to 667 hours), and 30 to 13% (from TOS 667 to 859 hours), and thereafter the reaction reached steady state at CO conversion approximately 13% until 2700 hours of time increment.

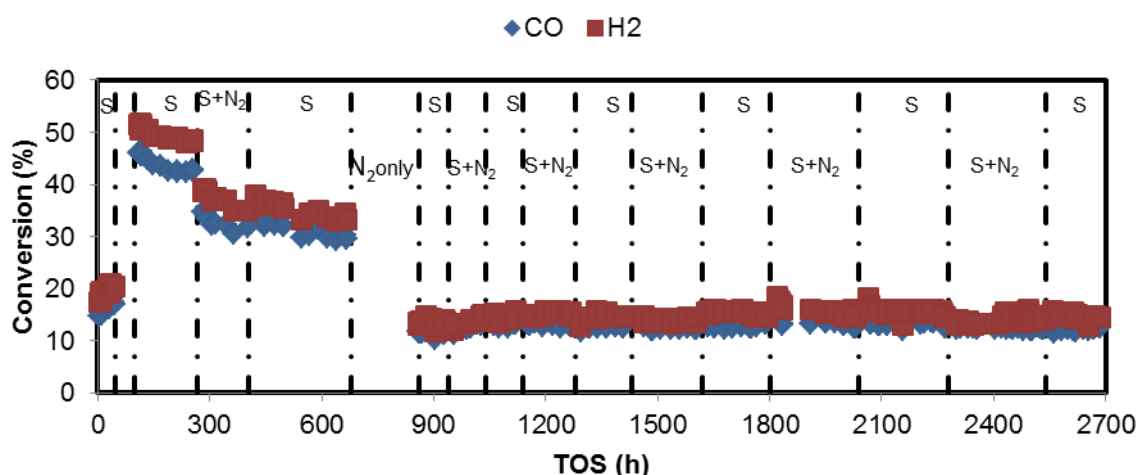


Figure 7.2: Reactant conversions as a function of time on stream (TOS) during FT runs with 10% Co/TiO₂ in a fixed bed reactor at 200 °C for 48 hours and 220 °C thereafter, while keeping the reactants' partial pressure and volumetric flow rate the same (see **Table 7.1**) for the remainder of the experiment. There was nitrogen flow only during TOS between 667 and 859 hours.

7.3.2 Paraffin to olefin ratio: Yao's plot

Yao et al. [13] have conducted research using a fixed bed reactor on both cobalt and iron catalyst and found that there is a linear relationship when P_{n+1}/O_{n+1} is plotted against P_n/O_n . For convenience these are referred to here as Yao's plots.

In order to investigate the product distributions, the present researcher plotted P_{n+1}/O_{n+1} as a function P_n/O_n and the results are displayed in **Figure 7.3 (A)–(D)** where $n = 2$ to 5. In **Figure 7.3**, the data points which are furthest from the origin of the graphs are those obtained at the CO conversions 46% at time on stream 110 hours. The data points' direction is toward the origin with decreasing in the CO conversions from 46 to 13% as shown in **Figure 7.2**. The results also reveal that the data obtained, when the CO conversions were between 13% and 16% including those from the FT runs with periodic switching of the feeds from syngas to syngas + N₂, are superimposed on each other and found close to the origin of the graphs for all carbon numbers studied.

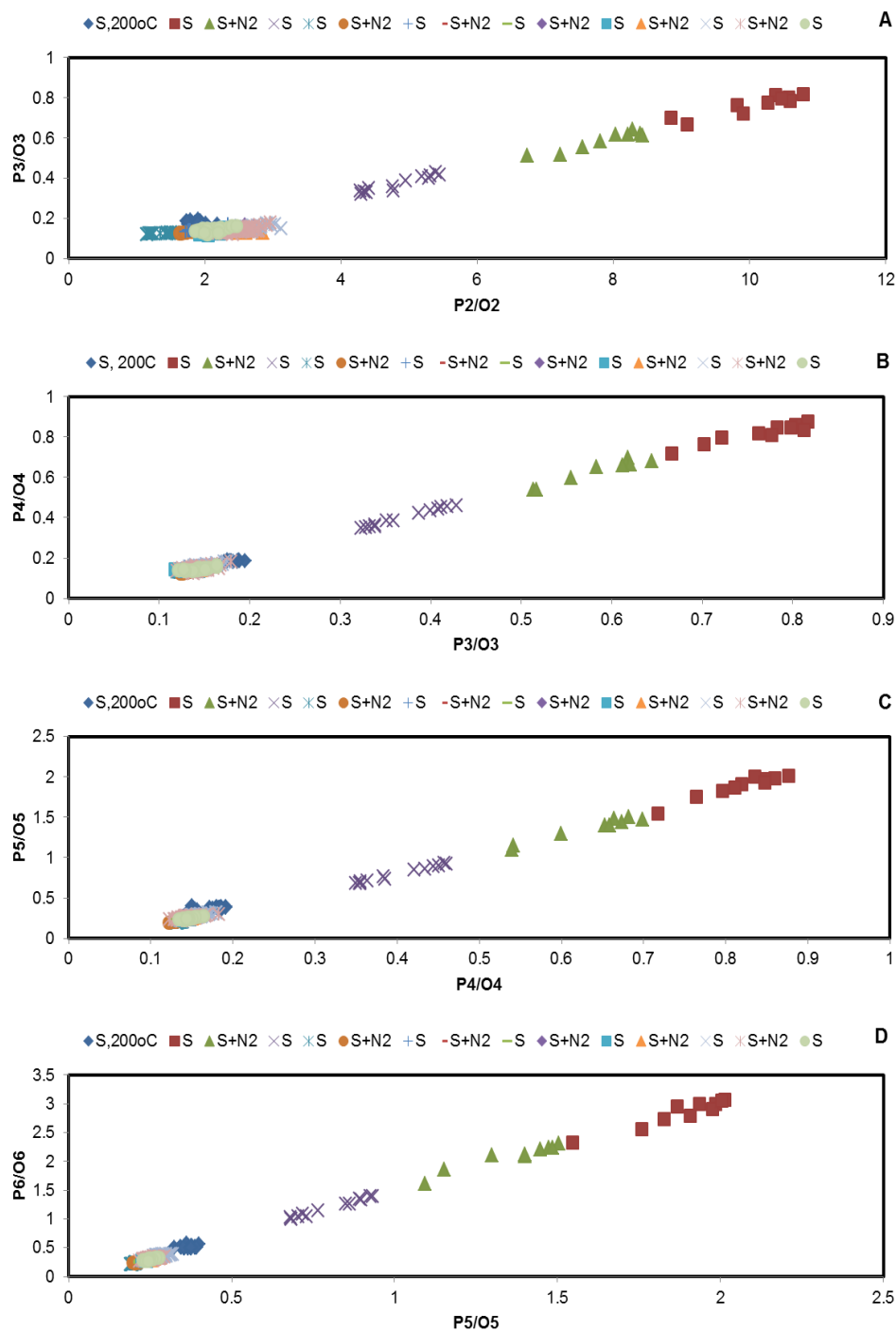


Figure 7.3: The paraffin to olefin ratio of P_{n+1}/O_{n+1} as a function of P_n/O_n where P is paraffin and O is olefin. (A) for $n=2$, (B) for $n=3$, (C) for $n=4$ and (D) for $n=5$. S,200 °C means syngas at 200 °C; S: syngas at 220 °C and S+N₂: syngas + N₂ at 220 °C and the legend above each graph represents changes in the order of the TOS as shown in **Figure 7.2**.

From **Figure 7.3**, it is clear that the experimental data tend to follow nearly straight lines and the slopes and goodness of fit (R^2) are displayed in **Figure 7.4** for each chain length (2 to 5) of the hydrocarbons plotted. In order to obtain a clear image of all the data, the data for each chain length have been plotted as one set of data and the results from the ratios are graphically presented in **Figure 7.4**. By comparing the trends of the $P_{(n+1)} / O_{(n+1)}$ versus $P_{(n)} / O_{(n)}$, the researcher found (1) with carbon number $n = 2$, the trend of P_3/O_3 versus P_2/O_2 is nearly straight with a lower slope value of 0.07; (2) with carbon number $n > 2$, the trends are straight lines with different slopes, however, the values of the slopes are: 1.06 for $n = 3$; 2.05 for $n = 4$ and 1.45 for $n = 5$. The trends demonstrated are consistent with a previous finding by Yao et al. [13]. The only difference between the present data and those from reference 13 is the values of slope, for example in their case the slope is near to 0.144 with $n = 2$, and is near to 1.391 with $n > 2$ over cobalt catalyst at 200 °C.

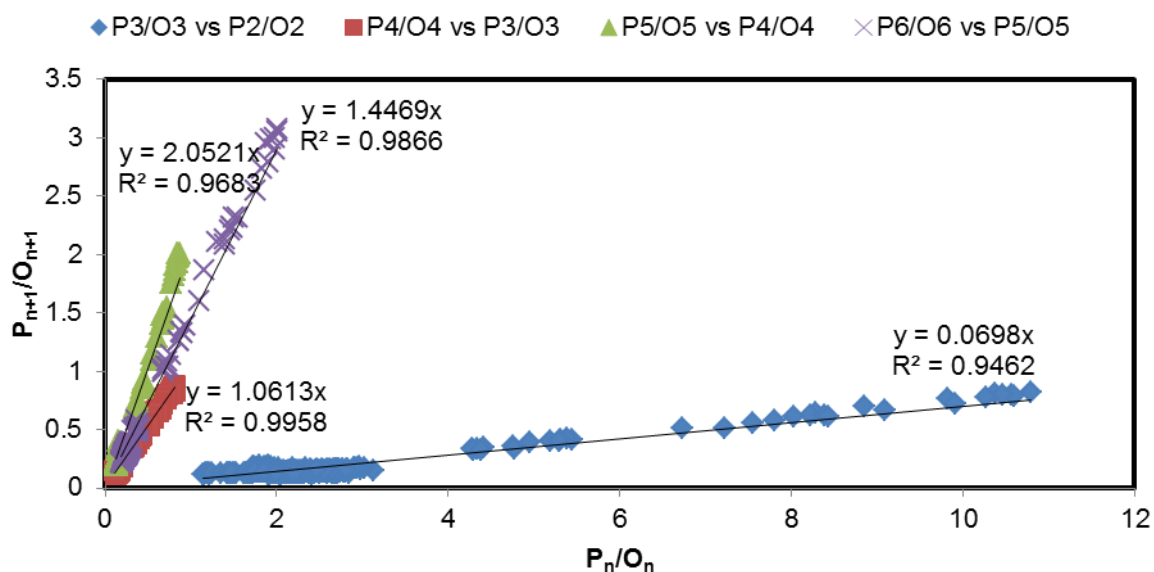


Figure 7.4: The paraffin to olefin ratio of P_{n+1}/O_{n+1} as a function of P_n/O_n where P is paraffin and O is olefin. The legend of the graphs follows this order, $n = 2$ (blue diamond), $n = 3$ (red square), $n = 4$ (green triangle) and $n = 5$ (purple cross). Results are from data presented in **Figure 7.3 (A) to (D)**.

In addition to the linear relationship between P_{n+1}/O_{n+1} and P_n/O_n , Yao et al. [13] have developed two simple models: one based on vapour–liquid equilibrium (VLE) assumptions and the other based on quasi-reaction equilibrium.

- i. The model based on VLE [13]: the ratio of $P_{(n+1)} / O_{(n+1)}$ to $P_{(n)} / O_{(n)}$ changes in a range of $(1, 1/\beta)$ where β is the variation of the vapour pressure coefficient, which is related to the increment of the energy of vaporisation per CH_2 unit of the hydrocarbon chain. β can be obtained through the following equation (1)

$$\beta = e^{\left[-427218 \left(\frac{1}{T} - 1.029804 \times 10^{-3} \right) \right]} \quad (1)$$

$\beta = 0.63$ for 200°C and 0.65 for 220°C which gives $1/\beta$ as 1.59 and 1.53 for 200°C and 220°C , respectively.

The present experimental results with carbon number $n = 3$ (the ratio is 1.06), $n = 4$ with (the ratio of 2.05) and $n = 5$ (the ratio is 1.45) approximately support the expression $[1, 1/\beta]$. However, with chain length $n = 2$, the ratio 0.07 is far away from the range of $[1, 1/\beta]$, so that the expression is unable to explain the relationship between P_3/O_3 and P_2/O_2 , which is a similar result to that obtained by Yao et al. [13].

- ii. Based on quasi-reaction equilibrium, Yao et al. assumed that the reaction of $\text{C}_{n+1}\text{H}_{2n+2} + \text{C}_n\text{H}_{2n+2} = \text{C}_{n+1}\text{H}_{2n+4} + \text{C}_n\text{H}_{2n}$ reaches a quasi-equilibrium which is developed to explain the linear relationship between $P_{(n+1)}/O_{(n+1)}$ and $P_{(n)}/O_{(n)}$ [13]. This assumption can explain why the ratio of P_3/O_3 to P_2/O_2 is far lower than the ratio of $P_{(n+1)} / O_{(n+1)}$ to $P_{(n)} / O_{(n)}$ with $n > 2$.

This agrees with the present researcher's results, where the ratio for $n = 2$ is far lower than the ratio of $n > 2$, as in **Figure 7.3**.

Because the experimental results obtained by the current work are quite close to those predicted by the equilibrium calculations from the above models, the researcher suggests that kinetics alone cannot explain the FTS fully and the FT product distribution might be determined by either VLE or quasi-reaction equilibrium, or by a combination of those two factors.

Seeking to further understand these results, the researcher has looked at another way of plotting FT data in a ternary graph (developed in his research group and reported by Lu et al. [14]). These figures are here referred to as Lu's plots.

7.3.3 Ratio of compounds normalised mole fractions: Lu's plots

Lu et al. [14] have introduced a triangular plot that is commonly used in research on distillation to depict the relationship between the olefin and paraffin products from FT reaction. The idea was to normalise the molar amounts of C_nH_{2n} (olefin), C_nH_{2n+2} (paraffin), and $C_{n+1}H_{2n+2}$ (olefin), where n is the length of the carbon number 2, 3 and 4, so that the total mole fraction of these three components was one and show them in one triangular plot, which we refer to as Lu's plot for convenience. **Figure 7.5** displays an example of Lu's plot. **Figure 7.5** indicates that a straight line from the right angle corner for the data points shows there is a constant ratio for $C_{n+1}H_{2n+2}/C_nH_{2n}$, and the intersection of the line with the sloping edge of the triangle at point A (see red circle on the graph) gives this ratio of $C_{n+1}H_{2n+2}/C_nH_{2n}$. A point in the triangle then corresponds to some fixed composition of the three species. A line parallel to the sloping edge means the paraffin concentration remains the same while varying the relative amounts of the olefins.

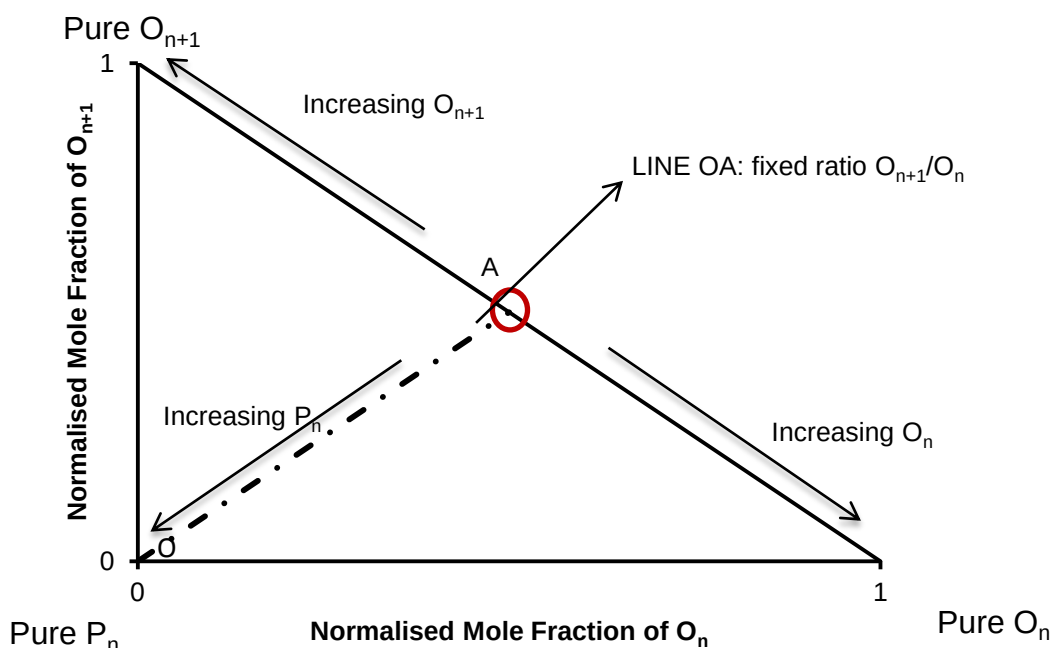


Figure 7.5: The Lu plot: A plot of the normalised mole fractions O_{n+1} (corresponding to the vertical axis), O_n (corresponding to the horizontal axis) and P_n .

The results for the three cases, namely 223 (olefin 2, paraffin 2 and olefin 3), 334 and 445, are plotted in **Figures 7.6, 7.7 and 7.8** respectively. We can immediately see for all the cases the results lie only on 2 lines that move towards a single point. These lines are either roughly parallel to the sloping edge, namely ratio of olefins changing but paraffin constant or one that approximately comes from the right angle corner namely paraffin changing and ratio of the olefins constant. Clearly, something as striking as this must have implications for some important underlying phenomenon or phenomena.

Note from the direction of the arrows that every time the operating conditions were changed, the experiment took a step away from the single point towards which it was previously moving. Thus there are three lines moving towards the single point, namely when the process started at 200 °C, then when it was started at 220 °C, and finally after the nitrogen alone period. It is as if, when the initial conditions were changed, something was disturbed and that then gradually returned to a

stable point. Remember that a fixed point on the triangular plot represents a fixed relationship between the three species. This stable operating point strongly suggests some sort of equilibrium relationship.

The major difference between the three graphs is where the stable point is on the graph. These points are shown on **Figure 7.9**. All the results suggest a smaller amount of paraffin at the stable points. These results are slightly different from the previous results [14] as those results only showed the line from the right angle corner to the stable point; however, in those experiments there were no changes and disturbances as in the present results.

What seems to happen is that the subsystems 223, 334 and 445 all tend to a stable operating point, but when disturbed move away and move back slowly along well-defined directions. The slowness is very interesting as it suggests something much slower than normal kinetics. These graphs show this result quite clearly.

Let us look at the results mainly after the nitrogen purging period. The overall conversion settles into its new steady state very quickly. Now it is well-known that there is a liquid layer on the catalyst. If the reaction conditions change, the liquid layer will change much more slowly than the gas phase. Thus if the composition effects of the liquid layer affect the composition of the products formed, the response to the gas-phase changes could be quite slow as observed in these results. The Lu graphs that have been plotted here show this phenomenon quite clearly.

If one is dealing with a liquid and gas phase with reaction then one might think of reactive distillation as a phenomenon that could help to explain these results. The fact that the positions of the stable points are not the same as those from Lu [14] is not all that surprising, as it is known that the nodes in reactive distillation can move depending on the relative amounts of reaction to separation [18].

One may then ask why all the points lie on only two lines on the Lu graph and not all over the place. Now again from reactive distillation it is known that all the

trajectories approach the stable operating point along eigenvectors. The researcher therefore suggests that these two directions actually represent the directions of the eigenvectors in this case.

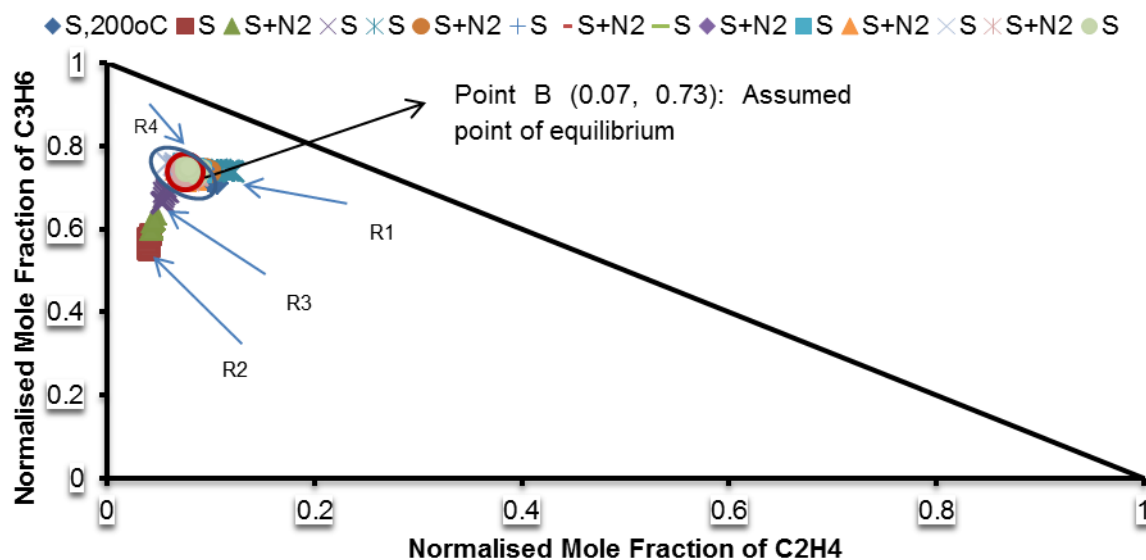


Figure 7.6: The ratio of normalised mole fraction between C_2H_4 , C_3H_8 and C_3H_6 . Where S,200 °C means syngas at 200 °C; S: syngas at 220 °C and S+N₂: syngas + N₂ at 220 °C. The reactants' partial pressure and volumetric flow rate were kept the same. Arrows R1, R2, R3 and R4 displayed in this figure refer to four regions according to **Table 7.1**.

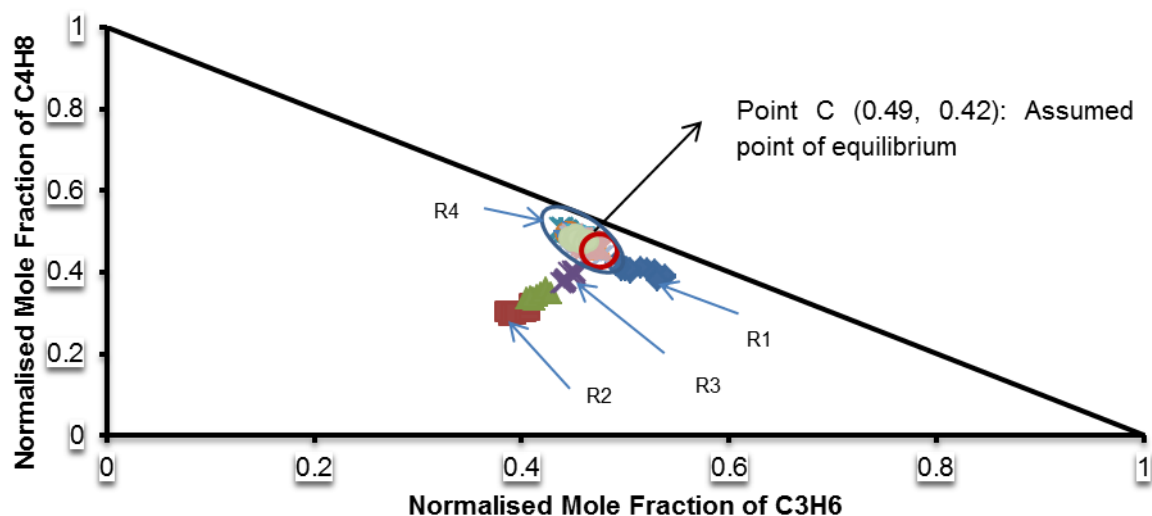


Figure 7.7: The ratio of normalised mole fraction between C_3H_6 , C_4H_8 and C_3H_8 . Where S, 200°C means syngas at 200 °C; S: syngas at 220 °C and S+N₂: syngas + N₂ at 220 °C. The reactants' partial pressure and volumetric flow rate were kept the same. Arrows R1, R2, R3 and R4 displayed in this figure refer to four regions according to **Table 7.1**.

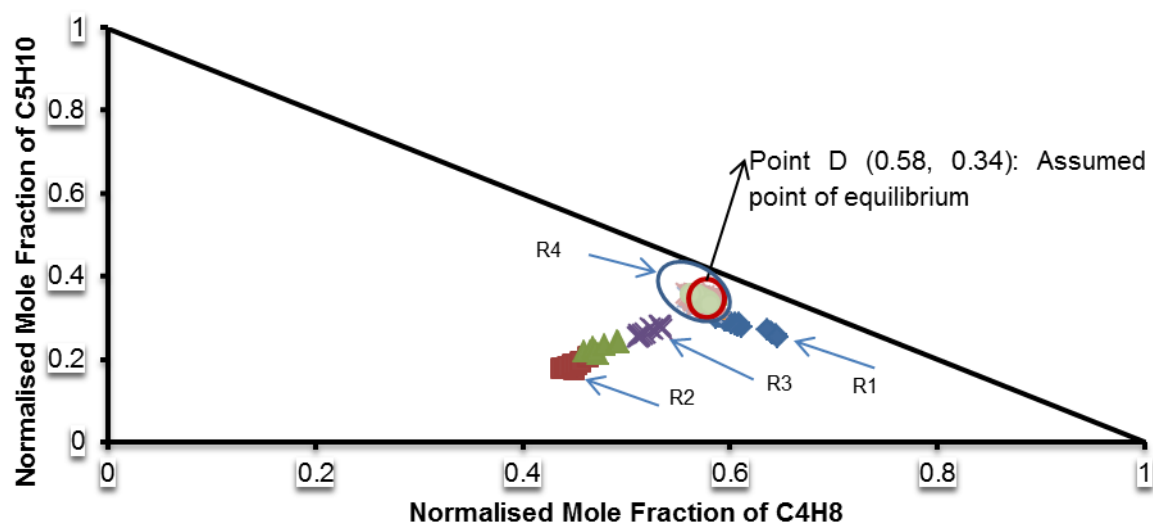


Figure 7.8: The ratio of normalised mole fraction between C_4H_8 , C_5H_{10} and C_4H_{10} . Where S, 200°C means syngas at 200 °C; S: syngas at 220 °C and S+N₂: syngas + N₂ at 220 °C. The reactants' partial pressure and volumetric flow rate were kept the same. Arrows R1, R2, R3 and R4 displayed in this figure refer to four regions according to **Table 7.1**.

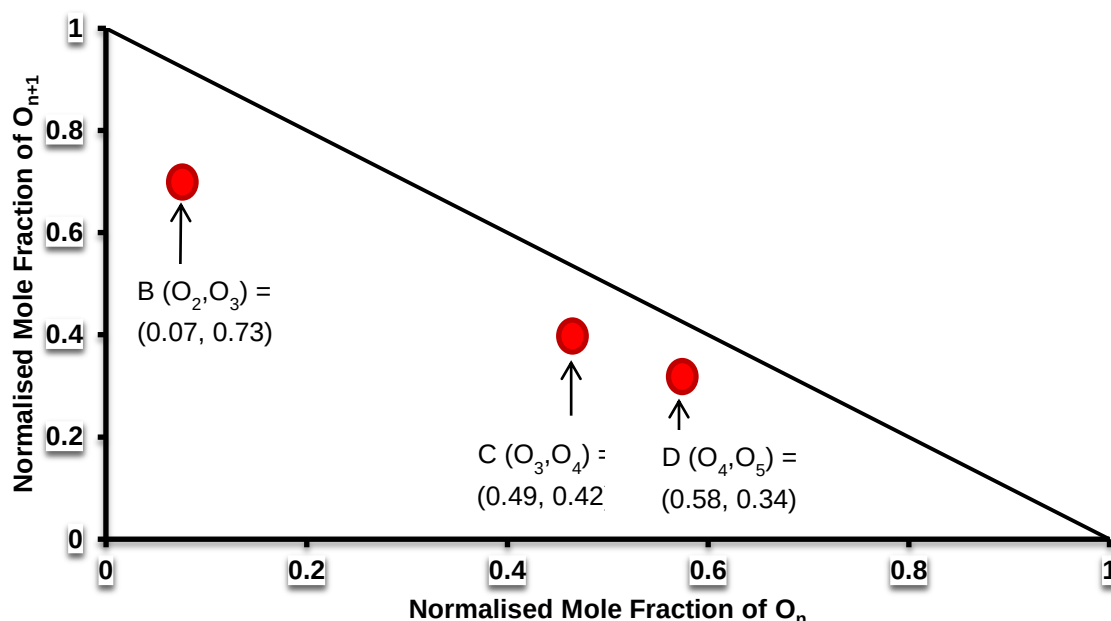


Figure 7.9: Equilibrium points (from **Figures 7.6 to 7.8**) for the different olefin pairs on a normalised mole fraction plot.

7.4 Discussion

Both the Yao and the Lu plots suggest that there are some sorts of equilibria happening between the lower molecular mass hydrocarbons (gas phase). The fact that for both plots the results for a wide range of conditions as the catalyst deactivates lie on good lines on these plots strongly suggests that there are underlying phenomena that have up to now not been taken account of in modelling these systems.

For the Yao plot the results show that the ratio O_n/P_n versus O_{n+1}/P_{n+1} lie on a straight line through the origin or, put another way, $O_n/O_{n+1} = K P_n/P_{n+1}$ where K is a constant. As all the species above have virtually the same straight lines, what this means is that if either of the species O or P obeys an ASF distribution so must the other one. Furthermore, as K is the same constant for all species after the one involving $n = 2$, this says once the ASF value for either O or P is set so is the other one. This is a very powerful result and as these are good straight lines it can clearly be seen that the system is very constrained.

Now for the Lu plots it is very clear that changing the operating conditions causes a jump away from the apparent stable operating conditions, but in the end the results slowly move back to the stable operating conditions. This is even the case when the overall conversion is very constant. The researcher suggests that these results could be explained by reactive distillation where the liquid layer in the catalyst plays a big part, because when conditions change the gas-phase will respond quickly unlike the liquid.

The results are shown in a more standard way in **Figures 7.1** and **7.2**. From these figures it is not easy to see what is happening. Thus to get a deeper understanding of what is happening it is often very important to be able to find other ways of presenting the data. The Yao and Lu plots help us to understand that the system is very constrained, and certainly normal kinetic models are not able to describe the underlying phenomena. This is why the researcher has suggested that equilibria of some kind play a part. This is whether it is reaction or vapour-liquid equilibrium.

7.5 Conclusion

This chapter discusses the study of Fischer-Tropsch synthesis over a long period of time, during which a number of changes were made and catalyst deactivation occurred. In order to try to make sense of the data, the researcher has looked at the relationship between the ratios of paraffin (P) to olefin (O) namely P_{n+1}/O_{n+1} and P_n/O_n where n is a carbon number from 2 to 5. He also looked at the relative amounts of three kinds of hydrocarbons (C_nH_{2n} , $C_{n+1}H_{2n+2}$ and C_nH_{2n+2}) which were normalised and plotted in a ternary diagram.

Plotting molar ratios of paraffin to olefin (P/O) with carbon number $n+1$ (P_{n+1}/O_{n+1}) against P_n/O_n with carbon number n (Yao plot) revealed a remarkable linear relationship which is independent of feed gases, catalyst activity and reaction temperature. This result implied that the product distribution could be determined by quasi-reaction equilibrium or vapour-liquid equilibrium, or a combination of the two factors.

The three plots of normalised mole fractions of C_nH_{2n} , $C_{n+1}H_{2n+2}$, and C_nH_{2n+2} for $n = 2$ to 4 (Lu plots) showed that after a disturbance the product distributions tended to single stable operating points along unique directions that were parallel to the hypotenuse, or were lines from the right hand corner to the stable points. This result suggested that the liquid phase played a role in the approach to the stable points.

The conclusion that the researcher came to was that the results could best be explained by some complicated equilibria between species that could not be accounted for in normal kinetic models, and he has suggested that a better model might be one of reactive distillation.

Note that one was not able to see these relationships when the raw data set was plotted in the normal way. It is only by using these novel plots that one was able to see these underlying phenomena.

Therefore the present researcher suggests that in addition to kinetics there are phenomena such as thermodynamic equilibrium and vapour–liquid equilibrium that need to be considered when designing FT processes. The consideration of these aspects might enhance the understanding of FT and its product distributions.

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CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

Many reports in the open literature focus on the kinetics of Fischer-Tropsch synthesis (FTS), most of which show that the FT reaction rate depends on the reactants' partial pressures; however, none of them can yet explain FTS fully. Furthermore, some researchers revealed that the vapour-liquid equilibrium (VLE) or reaction partial equilibrium may occur during FTS. Moreover, most of the reviewed papers reported the catalytic activity of FTS but only a few of them mentioned the formation rate and selectivity of olefin and paraffin separately. In order to study whether the selectivity of olefin and paraffin follow the same trends during FTS and whether FT kinetics alone suffice to explain FT phenomena, the researcher conducted a series of FT experiments by repeatedly switching the feed gas from syngas to syngas + N₂ in a fixed bed reactor, while keeping the partial pressures of the reactants (H₂/CO) the same.

The experiments were carried out for around 2700 hours. Catalyst deactivation, 'CO conversion dropped from 46% to 13%', was observed during the time on stream (TOS) from 110 hours to 1200 hours. By comparing the product formation rates during deactivation, the researcher found that the olefin formation rate is fairly constant (with some variation but not major), and in some cases it even increased, while that of paraffin dropped for FTS with both of the two feeds (syngas and syngas + N₂), which indicates that the deactivation is mainly caused by the change of paraffin formation rate. Currently, none of the published kinetics models can be used to explain the phenomenon that the trends of the reaction rates of olefin and paraffin were not the same during catalyst deactivation.

The experiments were continued repeatedly switching from syngas to syngas + N₂ from 1055 hours to 2700 hours. The data showed that the FT catalytic activity

reached steady state. For this period of time similar FT reaction conversions were achieved of approximately 13% for both using syngas only and syngas + N₂. However, when the researcher compared the product formation rates and selectivity, he found that the addition of the extra N₂ into the reactor decreased the selectivity and formation rate of all light hydrocarbons whereas the overall reaction rate did not change noticeably. Classic kinetics cannot describe these findings because the P_{CO} and P_{H₂} were held constant. It is not clear why this phenomenon occurred. But the present laboratory data suggest that there is a possibility to increase the selectivity and formation rate of long chain hydrocarbons (C₅₊) by feeding an extra amount of N₂ in FTS.

The Anderson-Schulz-Flory (ASF) distribution for light hydrocarbons (C₁-C₆) was evaluated and the value of chain growth probability (α) was calculated based on the hydrocarbons with carbon number 3 to 6 for each run. The finding was that the α values for the olefins (O₃-O₆) were smaller than those for the paraffins (P₃-P₆) under all the FT reaction conditions studied. The results showed that the co-feeding of N₂ to the syngas during FT runs slightly increased the chain growth probability (α) values for most cases of the FT runs. At the time when the reaction conversion was lower (approximately 13%), the olefin selectivity was higher than that of the selectivity to paraffin. Interestingly the light paraffin α values were about 1 (a value often not reported). Furthermore, the relationship between the chain growth probability and selectivity of light hydrocarbons show that light olefins α values increased with increasing selectivity up to an asymptotic value of about 0.79 whereas the α values of paraffins were not affected. Comparing these laboratory data and the value calculated by a model which minimised the Gibbs Free Energy for olefins, it is found that the experimentally measured data approximately agreed with the value expected at the temperature between 200 °C and 250 °C, which suggests that even though there is no global equilibrium, there is a possibility of some sort of equilibrium between the olefin product species in FT processes.

Intent to find new explanations for the results obtained, the researcher re-plotted his laboratory data in two different ways. Firstly, the molar ratio of paraffin to olefin

(P/O), with carbon number $n+1$ (P_{n+1}/O_{n+1}) against the molar ratio of P_n/O_n , was plotted by using all the data obtained in his experiments. The linear relationship between P_{n+1}/O_{n+1} and P_n/O_n was obtained, which is independent of the kinds of feed gases, the catalyst activity under unsteady state and steady state, and the reaction temperature. This result suggested that the product distribution might be determined by some kind of quasi-equilibrium.

Secondly, because the hydrocarbon C_nH_{2n} might be converted into subsequent $C_{n+1}H_{2n+2}$ and/or paraffin C_nH_{2n+2} products during FTS, the researcher plotted the mole fractions of C_nH_{2n} , $C_{n+1}H_{2n+2}$, and C_nH_{2n+2} in a ternary diagram to display the relationship between these 3 components in the FT reactor. The position of the data points in the triangular diagram changed with different reaction conditions, however, the data on the diagram followed 3 separate curves, and these curves tend to one 'midpoint', which suggests the product distribution tends to a single stable value during FTS. It was noted that whenever the reaction conditions changed, the results on the triangular diagram jumped away from this stable point and then slowly returned to it. As stated above, the perturbed results then slowly returned to this stable point along three directions only, two parallel to the sloping edge and the other one from the right angle corner towards the stable point.

The research conclusion was that the results could best be explained by some complicated equilibria between species that could not be accounted for in normal kinetic models, suggesting that a better model might be one of reactive distillation.

Although not all the results acquired in this study could be explained, it is important to emphasise that kinetics alone cannot fully explain FT processes. There might be some other factors, such as VLE or quasi-reaction equilibrium, that need to be accounted for in the explanation of FTS. Moreover, designing a cobalt based FTS should consider the formation rates of olefin and paraffin separately. The data provided in this thesis can prove to be important for the design of FTS and for understanding product distributions.

8.2 Recommendations and future work

- Liquid phase hydrocarbons should be included in all analyses as well as the determination of the chain growth probability and product distributions.
- The outcome of the work in the thesis is a strong suggestion that there are equilibria involved in FTS. A suggestion that is made is that this could be due to the equivalent of reactive distillation. This idea should be tested both theoretically and experimentally.
- It would be useful if the literature could be scanned to find other experimental results that could also be used to test these theories.

APPENDIX A:

CATALYST (10% Co/TiO₂) CHARACTERISATION TECHNIQUES

A.1. Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) was performed to study the reduction behaviour of the cobalt catalyst used in the current research work. The TPR was carried out using a self-made TPR apparatus in a U-shaped quartz tube reactor. Prior to the reduction, a sample of 0.1 g sieved (1000–500 μm) was placed in the tube reactor and degassed with pure nitrogen at 150 °C for 30 minutes. A reducing gas 5% hydrogen mixed in argon was passed over the sample for the reduction. A flow rate of 5 mL/min was used while the temperature was increased at a rate of 10 °C/min from 50° to 800 °C. The amount of H₂ consumed by the catalyst was detected by the thermal conductivity detector (TCD) at the exit of the reactor. The results are shown in **Figure A1**.

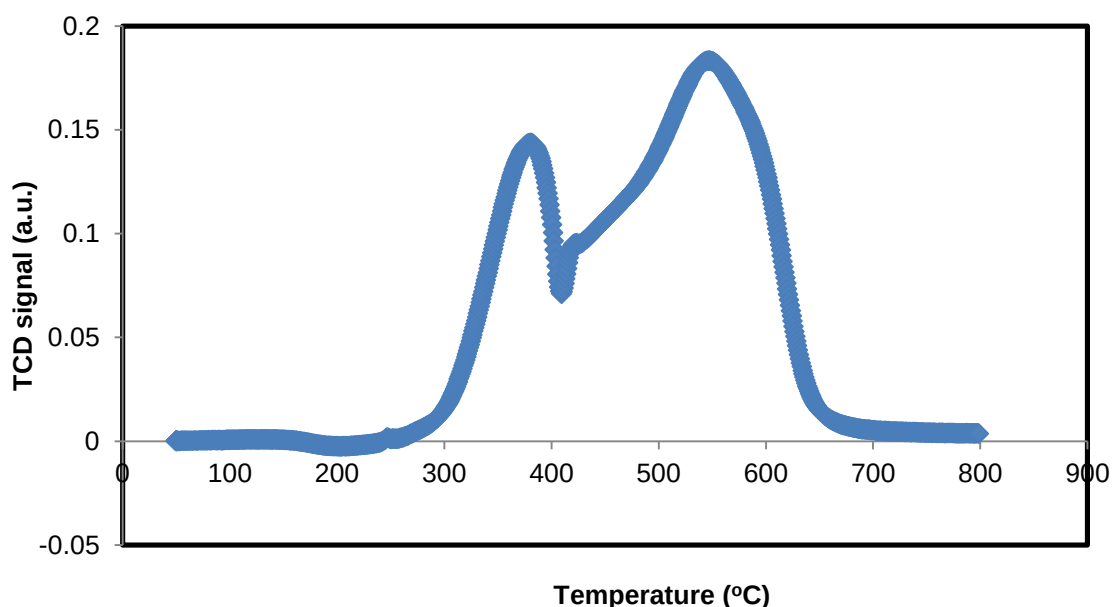


Figure A1: TPR spectrum of the 10% Co/TiO₂ FT catalyst used in this thesis.

A.2. X-ray diffraction (XRD)

X-ray diffraction (XRD) measurements were performed to obtain information concerning the phase composition and the crystallite size distribution. Prior to the analysis, samples of the catalyst and catalyst support were crushed to very fine powder and loaded into the holder. The tube voltage and current of the instrument were set at 40 kV and 30 mA respectively. The XRD instrument operated on a rhodium tube and K-beta filter mounted to it. The samples were run in a Rigaku XRD instrument equipped with scintillation counter detector. The powder samples were scanned in the 0° – 75° 2θ range at the rate of $0.2^{\circ}/\text{min}$. The XRD spectra obtained are shown in **Figure A2**.

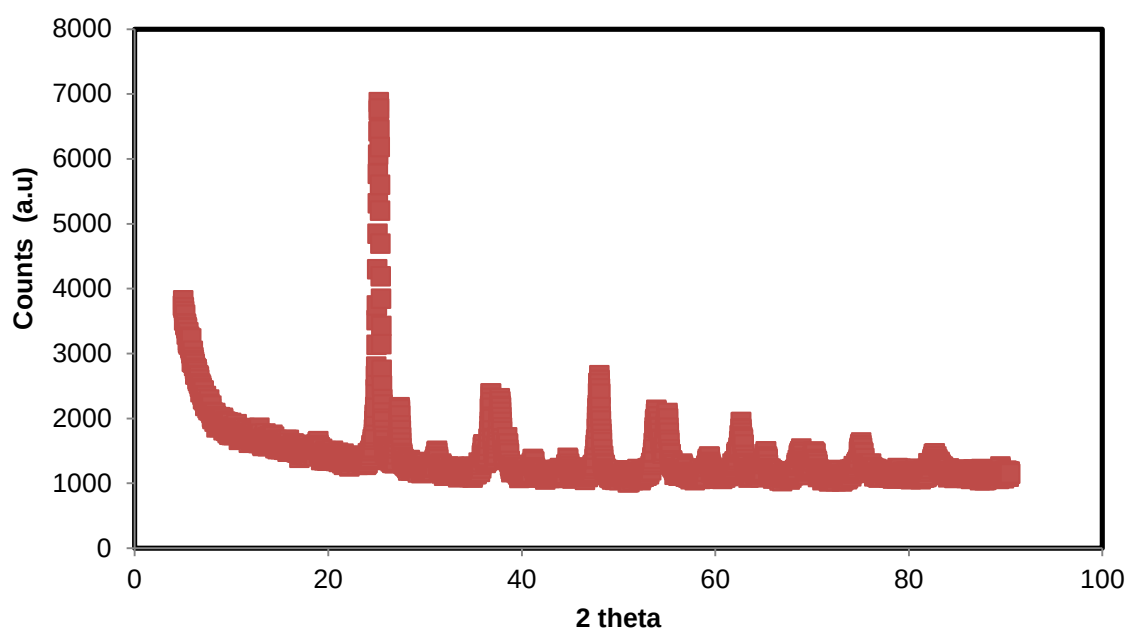


Figure A2: XRD pattern of the 10% Co/TiO₂ FT catalyst used in this thesis.

A.3. Brunauer-Emmet-Teller (BET)

The BET analysis was performed as the technique which looks at the measurement of the specific surface area and the pore volume of the cobalt

catalyst. The sample was out-gassed under vacuum overnight. The temperature of the drying was 80°-100 °C to drive any moisture away in the samples. BET analysis was conducted under liquid nitrogen at -196 °C. Equilibration intervals considered were of five seconds. The surface area and porosity of the sample were measured with a Micromeritics TriStar II - Surface Area and Porosity analyser. The BET results are depicted in **Table A1**.

Table A1: Surface area, pore volume and pore size of the 10% Co/TiO₂ FT catalyst used in this thesis

Summary report	
Surface Area	
Single point surface area at P/Po = 0.1999:	108.578 m ² /g
BET Surface Area:	114.173 m ² /g
BJH Adsorption cumulative surface area of pores between 1.70 nm and 300.00 nm diameter:	111.781 m ² /g
BJH Desorption cumulative surface area of pores between 1.70 nm and 300.00 nm diameter:	137.011 m ² /g
Pore Volume	
BJH Adsorption cumulative volume of pores between 1.70 nm and 300.00 nm diameter:	0.354 cm ³ /g
BJH Desorption cumulative volume of pores between 1.70 nm and 300.00 nm diameter:	0.372 cm ³ /g
Pore Size	
BJH Adsorption average pore diameter (4V/A):	12.673 nm
BJH Desorption average pore diameter (4V/A):	10.849 nm

A.4. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) technique was performed to study the imaging structure of the cobalt catalyst. The sample was dispersed in 100% ethanol and sonicated for 15 seconds. Carbon-coated grids were briefly immersed into the suspension and allowed to dry before observation in a JEOL JEM 2100 High Resolution TEM (JEOL, Japan). Calibrated images were captured using a Gatan Ultrascan camera and Digital Micrograph software (Gatan, USA). One of the pictures acquired from the imaging process is presented in **Figure A3**.

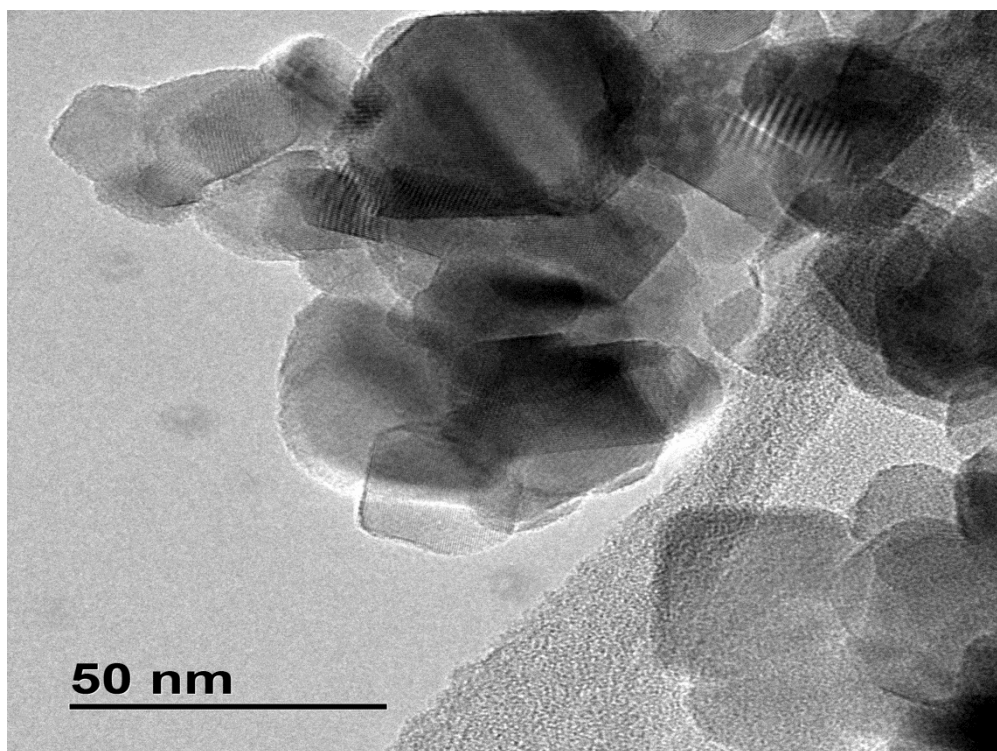


Figure A3: TEM micrograph of the 10% Co/TiO₂ FT catalyst used in this thesis.

A.5. Scanning electron microscopy (SEM)

The SEM technique was performed to look at the morphology of the sample. Calcined cobalt catalyst was crushed and sprinkled on double-sided carbon adhesive tape and rendered conductive by sputtering a 4 nm layer of Au/Pd using

a Quorum 950 coater. A JEOL 7500 SEM instrument was used. One of the micrographs acquired is exhibited in **Figure A4**.

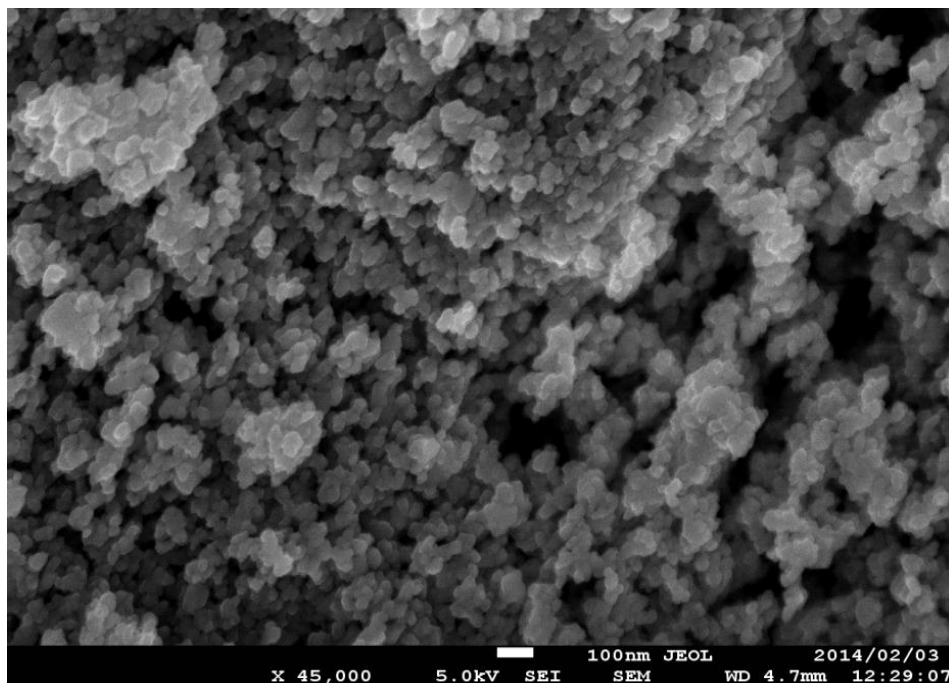


Figure A4: SEM micrograph of the 10% Co/TiO₂ FT catalyst used in this thesis.

A.6. Energy dispersive X-ray spectroscopy (EDS)

The energy dispersive X-ray spectroscopy (EDS) is a technique that was employed to identify chemical elements present on the cobalt catalyst. EDS was utilised along with electron microscopy imaging to give complementary chemical information of the different species in the samples. Calcined cobalt catalyst was crushed and sprinkled on double-sided tape and fixed on copper sample holder. The sample was then analysed using a VEGA3 TESCAN SEM instrument. One of the spectra resulting from the sample analysis is depicted in **Figure A5**.

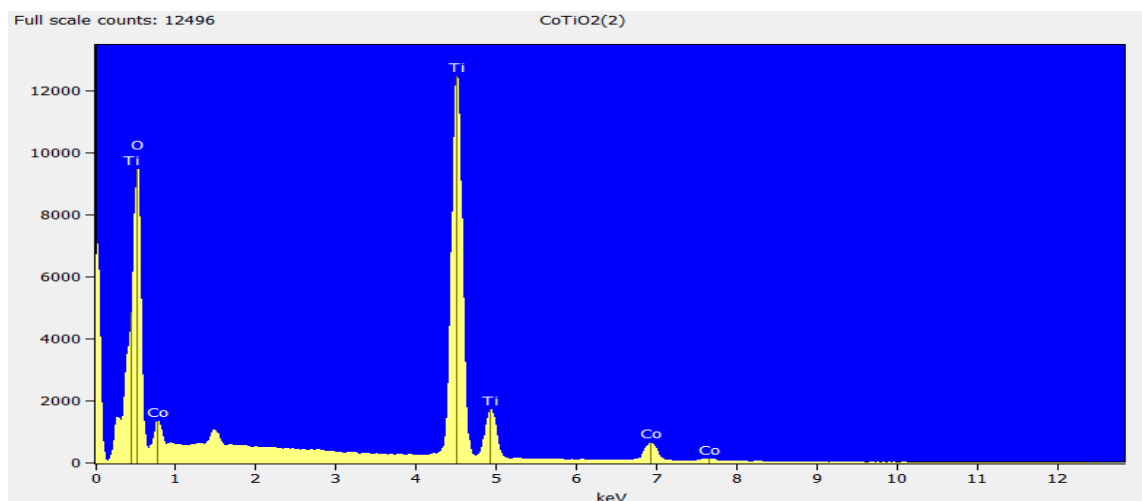


Figure A5: EDS micrograph of the 10% Co/TiO₂ FT catalyst used in this thesis.

The percentages of the identified elements as per EDS result in **Figure A5** are summarised in **Table A3**.

Table A2: Elements, weight and atomic percentage of the 10% Co/TiO₂ FT catalyst used in this thesis

Element	Weight%	Atomic%
O K	42.59	69.60
Ti K	48.21	26.32
Co K	9.20	4.08
Totals	100.00	100.00

A.7. Dynamic light scattering (DLS)

The dynamic light scattering technique (DLS) was conducted to measure the nanoparticle size of the cobalt catalyst. The technique also assisted in measuring the particle size distributions. This analysis was performed using a Horiba L550 DLS (Horiba Instruments, Japan). The sample was dispersed in water and measured under the conditions shown in the spread sheet header (especially see number of measurements). The conditions of measurement, average data and one of the spectra resulting from the sample analysis are given in **Table A3** and **Figure A6**.

Table A3: Conditions of measurement and average data of the 10% Co/TiO₂ FT catalyst used in this thesis

Filename	Average
Sampling Times	10
Particle Refractive Index	2.490 - 0.000i
Dispersant Refractive Index	1.333
Measurement Temperature	21.4(21.3- 21.4)(°C)
Temperature Sensor	Liquid Sensor
Axis Selection	LogX-LinY
Median	0.0952(μm)
Mean	0.1008(μm)
Mode	0.0940(μm)
Variance	1.4731E-3(μm ²)
S.D.	0.0384(μm)
Coefficient of Var	38.066
Geo. Mean	0.0945(μm)
Geo. Variance	1.0571(μm ²)
Geo. S.D.	1.4297(μm)

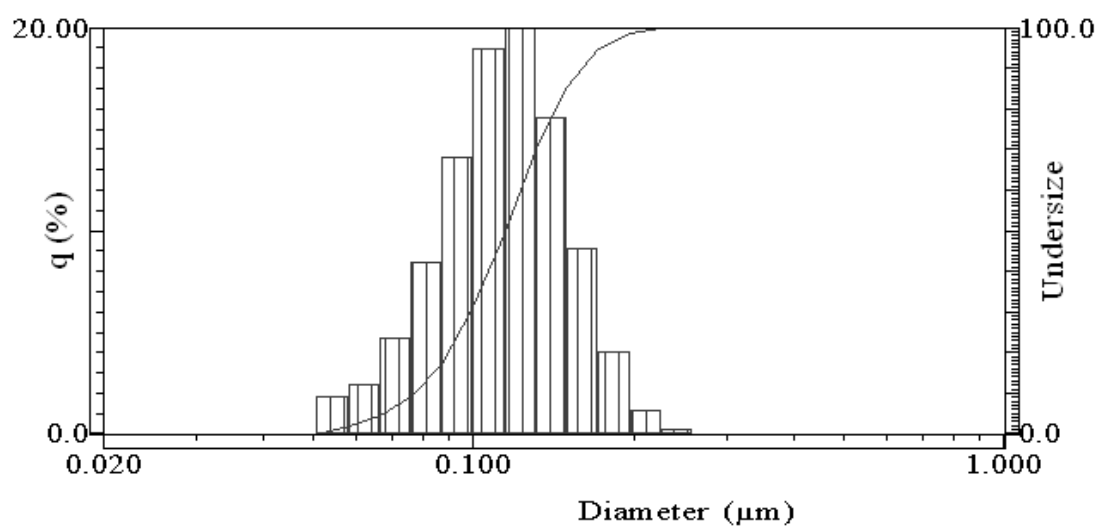


Figure A6: Particle size of the 10% Co/TiO₂ FT catalyst used in this thesis.

APPENDIX B:

REACTANT CONSUMPTION RATE AND PRODUCT FORMATION RATES

The reactant consumption rates were calculated and the results were plotted against the later TOS (1055 to 2700 hours when the overall conversions had stabilised) and are presented graphically in **Figure B1 (A)**. Basically this figure shows the effect on the reactant consumption rates of feeding extra nitrogen into the reactor while keeping the partial pressures of the reactants the same. These results are as per the operating conditions listed in **Table B1** with the switching numbers of the FT runs as tabulated in **Table B2**.

Table B1: Reaction and feed conditions for the FTS experiments on a cobalt based catalyst

Case	S	S+N ₂
Catalyst	10% Co/TiO ₂	10% Co/TiO ₂
Mass (gram)	1	1
Temperature (°C)	220	220
Reactants partial molar flow rate (mol/min) for: FR _{H2} FR _{CO}	0.075 0.038	0.075 0.037
Reactants partial pressure (bar abs) for: P _{H2} P _{CO}	12.51 6.26	12.41 6.20

Table B2: Summary of the reaction and feed conditions for the FT experiments over a cobalt based catalyst

Switching number	FT runs	Starting time on Stream	Reaction conditions (see Table B1)
First	1	At 1055.76 hours	S
	2	At 1150.74 hours	S+N ₂
Second	3	At 1292.75 hours	S
	4	At 1462.86 hours	S+N ₂
Third	5	At 1631.06 hours	S
	6	At 1822.08 hours	S+N ₂
Fourth	7	At 2063.60 hours	S
	8	At 2299.69 hours	S+N ₂

As would be expected from the selectivity results, the CO consumption rate reveals that when extra nitrogen was added to the syngas the overall reaction rate seems not to change noticeably as is clearly exhibited in **Figure B1 (A)**. **Figure B1 (B)** was constructed as a bar chart from the average data acquired as a function of switching the feed of the FT runs from syngas (S) to syngas + N₂ (S+N₂). The average reaction rate values were plotted for the different FT runs (**Figure B1 (B)**) in order to demonstrate clearly that the switching of feeds during FT processes did not noticeably affect the rate as **Figure B1 (A)** tended to suggest.

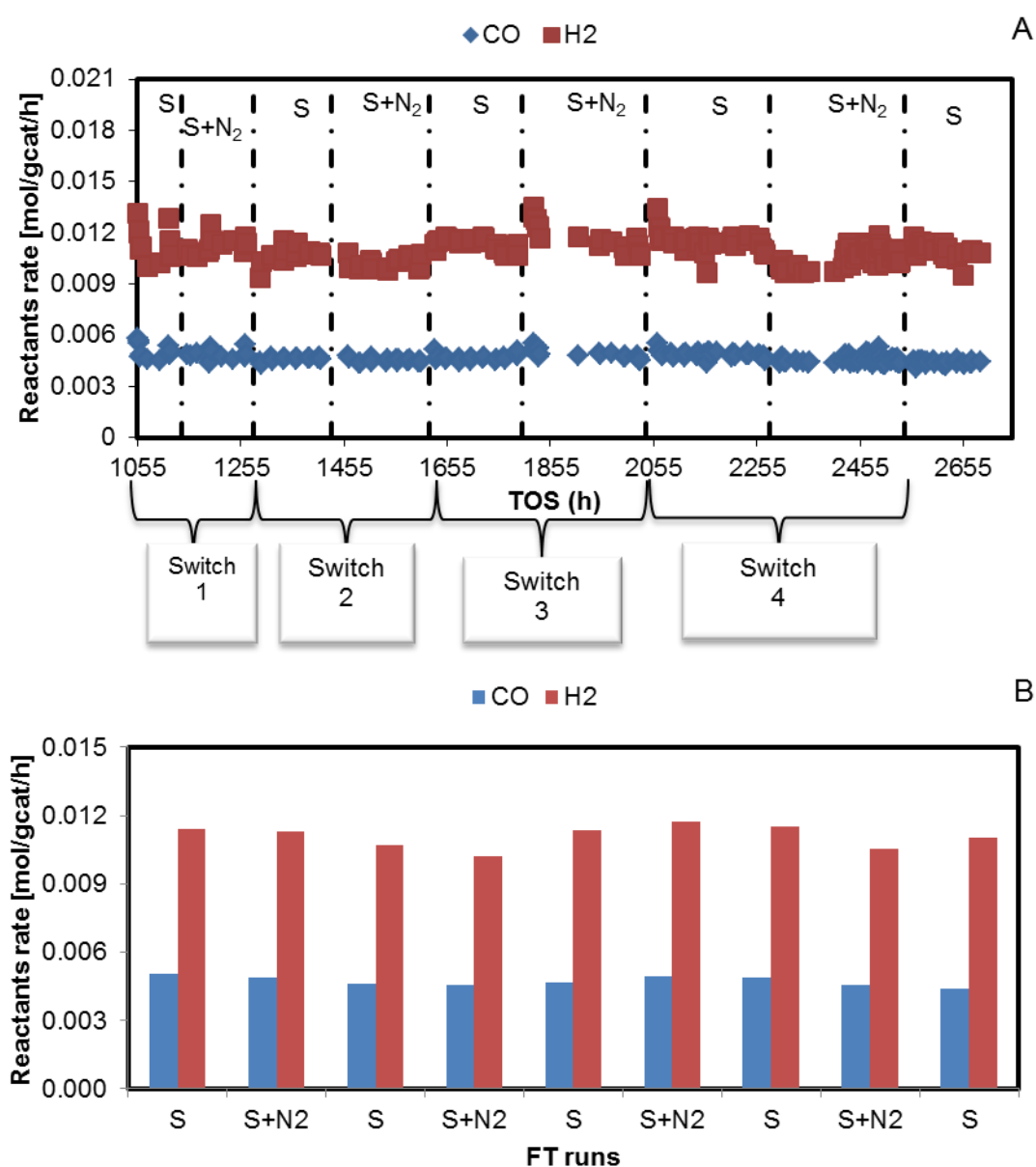


Figure B1: Effect of feeding extra nitrogen into the reactor while keeping the reactant partial pressures the same on: (A) the reactants CO and H₂ consumption rates as a function of TOS under the reaction conditions listed in **Table B1** and (B) average data of the CO and H₂ consumption rates for the eight FT runs of syngas (S) and syngas + nitrogen (S+N₂) representing four switches as shown in **Table B2**.

The methane formation rate was measured as a function of the time on stream and the values obtained were plotted in the graph shown in **Figure B2 (A)**. The

graph reveals that when extra nitrogen was added to the syngas in the fixed bed FT reactor, the methane formation rate declined. This can be regarded as a positive effect for an FT process. Although the changes can be seen by just looking at the graph, the changes are more easily seen when we plotted the average values of the methane formation rate for the four switches of the FT runs as a bar chart in **Figure B2 (B)**. It is now clear that when the extra amount of N_2 was fed into the reactor, the rate of methane formation declined by about 15%.

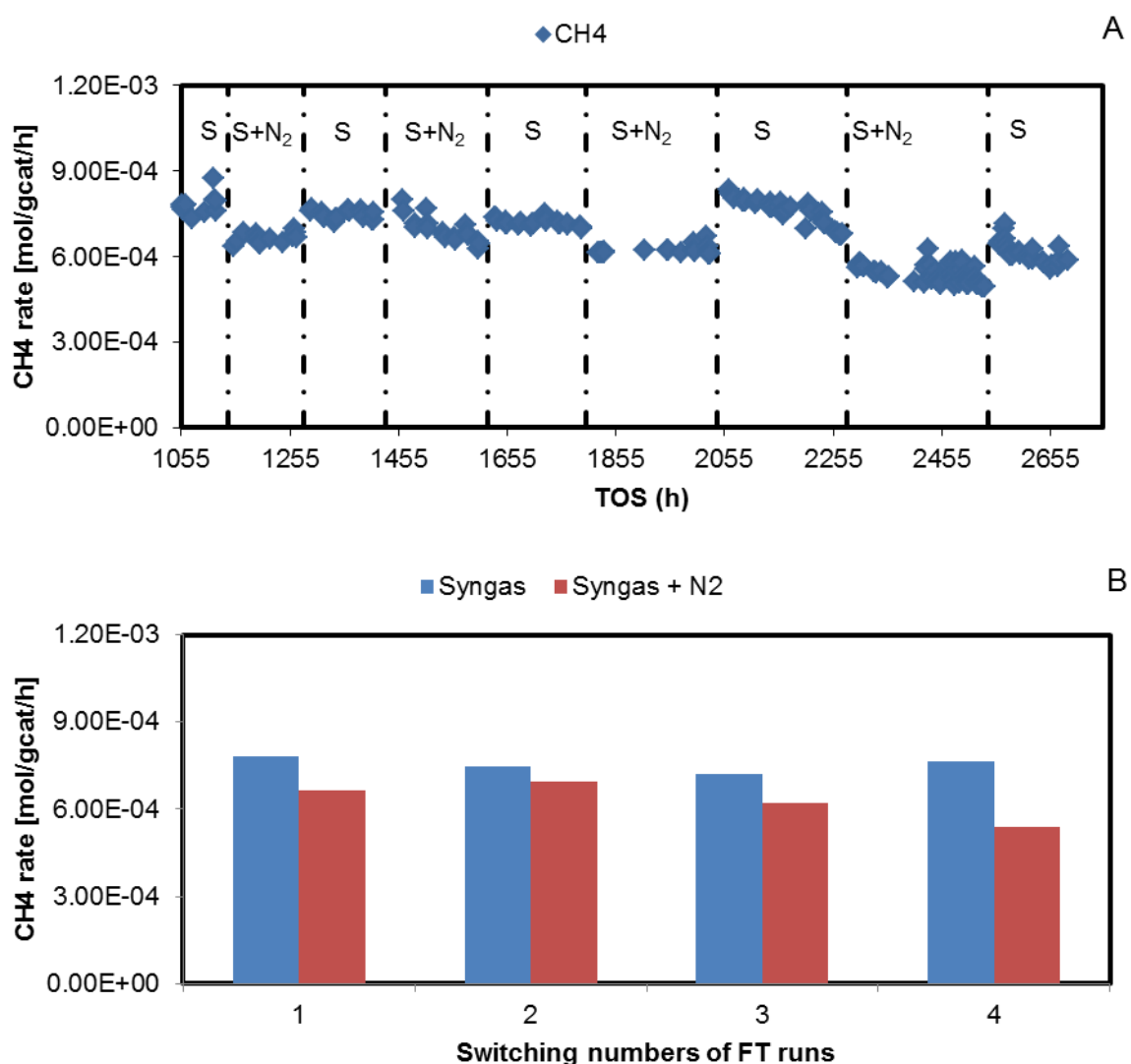


Figure B2: Effect of feeding extra nitrogen into the reactor while keeping the reactant partial pressures the same on: (A) CH₄ formation rate as a function of TOS under the reaction conditions listed in **Table B1** and (B) the average data of CH₄ formation rate as a function of the four switches representing eight total FT runs of syngas (S) and syngas + nitrogen (S+N₂) respectively, as shown in **Table B2**.

In addition to the methane rate, the formation rates of the other light hydrocarbons were also calculated and plotted against TOS in a graph displayed in **Figure B3 (A)**. The findings demonstrate that adding extra nitrogen into the fixed bed FT reactor while keeping the reactant partial pressures constant decreases the formation rate of all the light hydrocarbons (C₂–C₅). As in the previous paragraph,

bar charts were also constructed based on the average values of these formation rates for all the eight FT runs. The results shown in **Figure B3 (B)** reveal that as the feeds of the FT runs were changed from syngas to syngas + N₂ while keeping the partial pressure of CO and H₂ the same, the formation rates decreased by up to about 20% for all the light hydrocarbons.

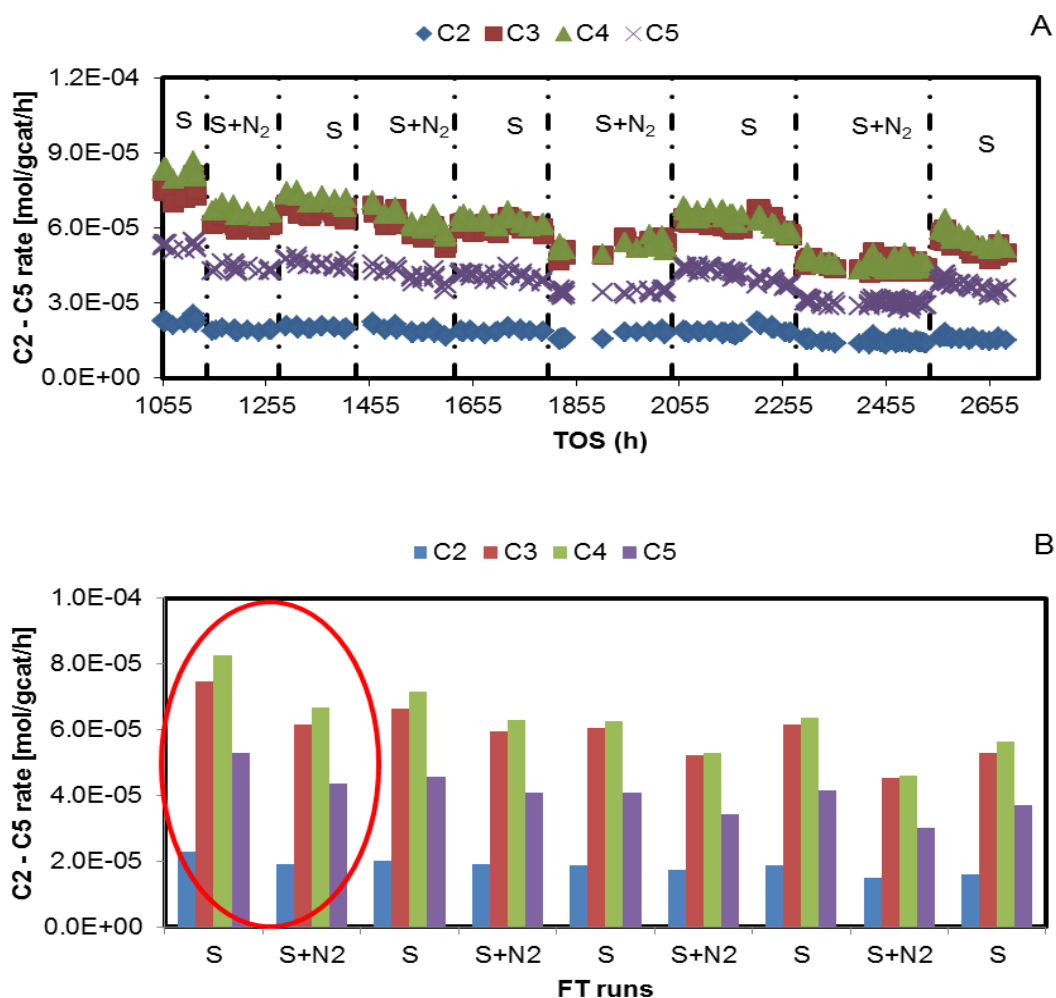


Figure B3: Effect of feeding extra nitrogen into the reactor while keeping the reactant partial pressures the same on: (A) the formation rate of the total light hydrocarbons (C₂–C₅) as a function of TOS under the reaction conditions listed in **Table B1** and (B) for the average data of light hydrocarbons (C₂–C₅) formation rate for the eight FT runs of syngas (S) and syngas + nitrogen (S+N₂) respectively representing four switches as shown in **Table B2**.

The effect of adding extra nitrogen into the reactor on the formation rates of light olefins (O_2 – O_5) and paraffins (P_2 – P_5) was also determined separately. The results are presented in **Figure B4** and **Figure B5** for the light olefins and paraffins, respectively. It is quite clear from both **Figures B4 (B)** and **B5 (B)** that the formation rate of both olefins and paraffins decreased when FT runs were carried out with syngas + N_2 .

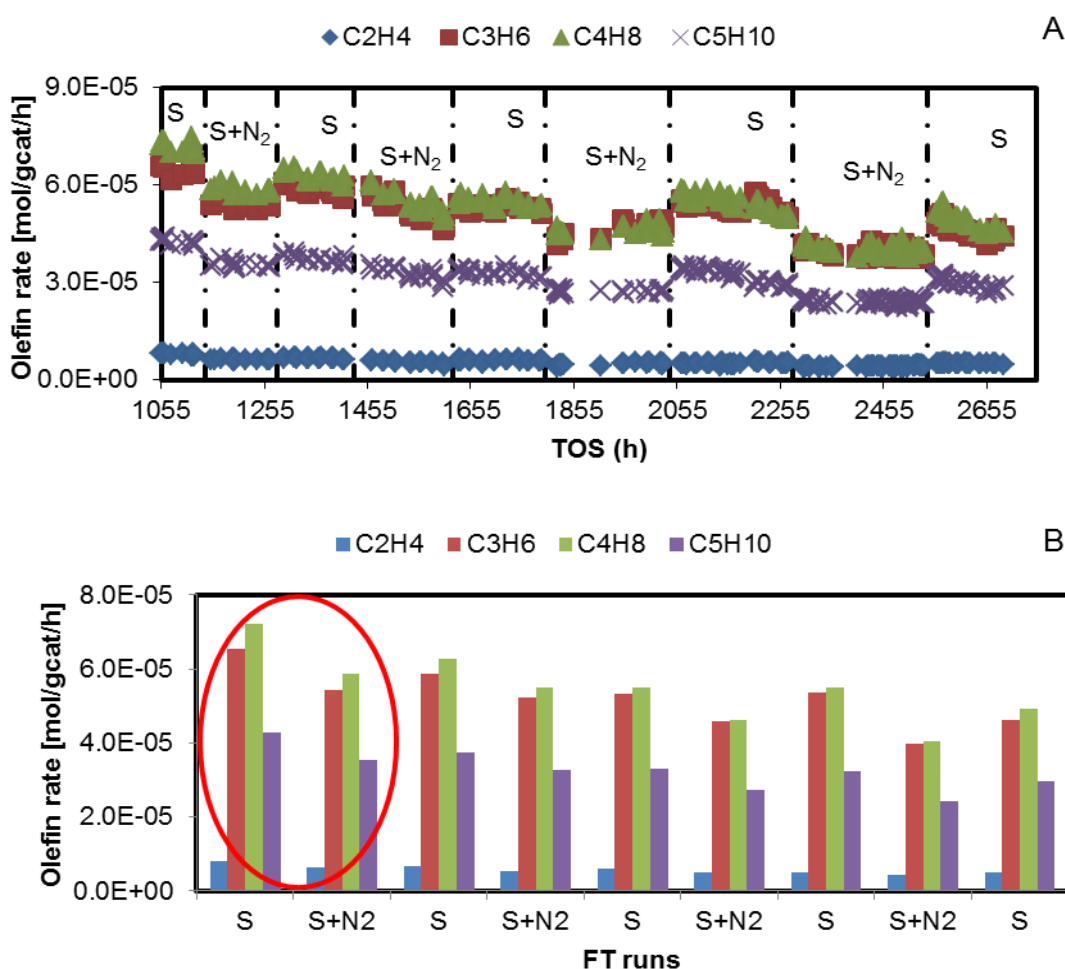


Figure B4: Effect of feeding extra nitrogen into the reactor while keeping the reactant partial pressures the same on: (A) the formation rate of light olefins (O_2 – O_5) as a function of TOS under the reaction conditions listed in **Table B1** and (B) for the average data of light olefins (O_2 – O_5) formation rates for the eight FT runs of syngas (S) and syngas + nitrogen ($S+N_2$) respectively, representing four switches as shown in **Table B2**.

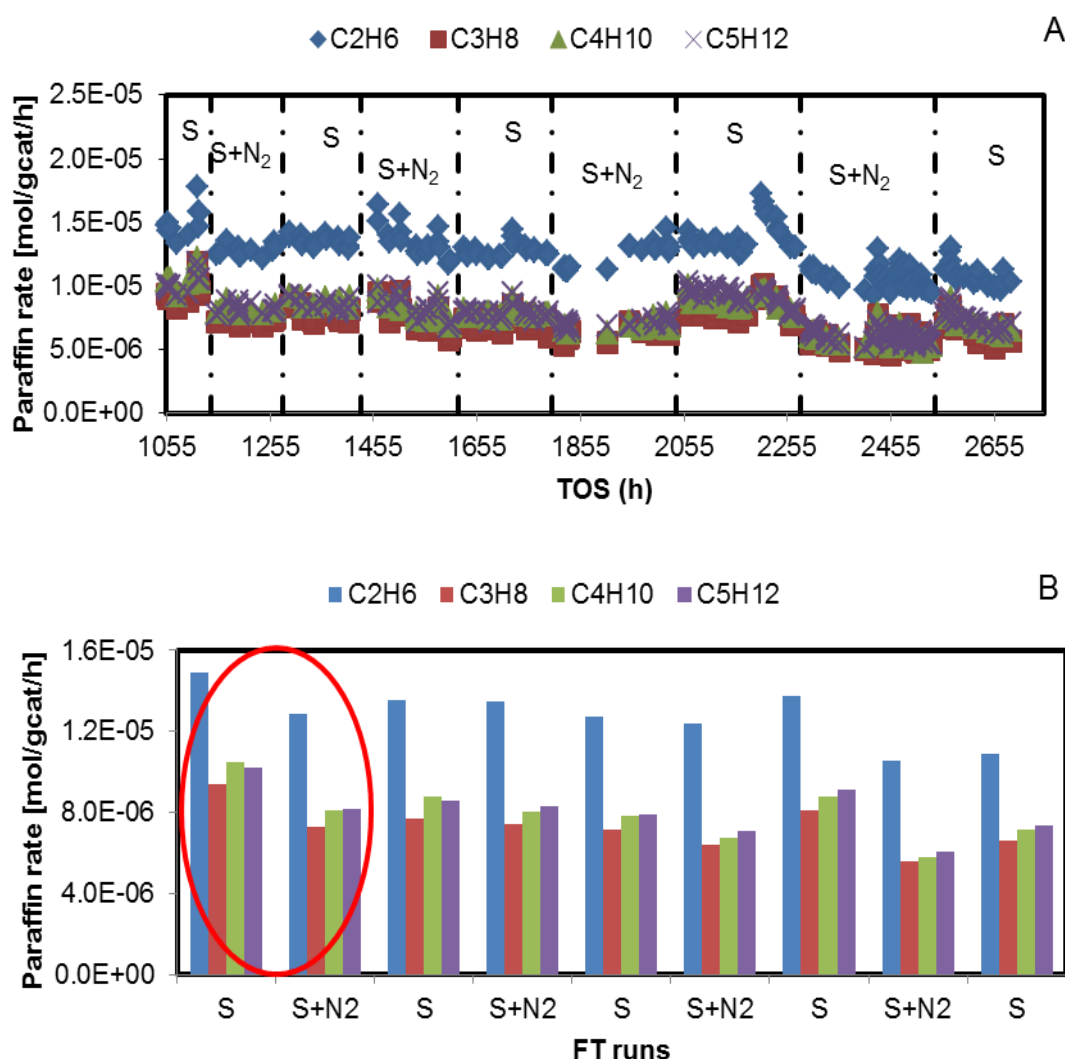


Figure B5: Effect of feeding extra nitrogen into the reactor while keeping the reactant partial pressures the same on: (A) the formation rate of light paraffin (P₂–P₅) as a function of TOS under the reaction conditions listed in **Table B1** and (B) for the average data of light paraffin (P₂–P₅) formation rates for the eight FT runs of syngas (S) and syngas + nitrogen (S+N₂) respectively, representing four switches as shown in **Table B2**.

From these data, it is obvious that the addition of extra nitrogen in a fixed bed FT reactor while keeping the P_{CO} and P_{H₂} constant decreases the formation rates of total light hydrocarbons (C₂–C₅), olefins (O₂–O₅) and paraffins (P₂–P₅) as depicted in **Figures B3**, **B4** and **B5** respectively. Another important point to note is that the

trends of the overall light hydrocarbons are similar to the olefin patterns because of the high olefin to paraffin ratio. It is also of interest to see what the effect of co-feeding extra nitrogen will be when the formation rate data are plotted against the carbon number. In order to clearly see the effect, the first switch was chosen at random as exhibited by the red oval shape in **Figures B3 to B5**. The findings are shown in **Figure B6**.

Figure B.6 illustrates trends of formation rates of **(A)** light hydrocarbons (C_2 – C_5), **(B)** olefins (O_2 – O_5) and **(C)** paraffins (P_2 – P_5) as a function of carbon number for the average values when steady state had been reached. The results reveal that the rates of formation increased with the increase in carbon number from C_2 to C_4 and olefins O_2 to O_4 but not for the paraffins (P_2 to P_5). The most important finding is the product formation rates dropped for all FT runs done with syngas + N_2 ($S+N_2$) for the carbon number (C_2 – C_5) even though the P_{CO} and P_{H_2} were kept constant. From these results, the researcher infers that the co-feeding of nitrogen in FTS affected positively the rate of liquid products by reducing the rate of formation of the light hydrocarbons. This is a positive improvement because heavy hydrocarbons, C_{5+} , are the most sought after molecules in FTS.

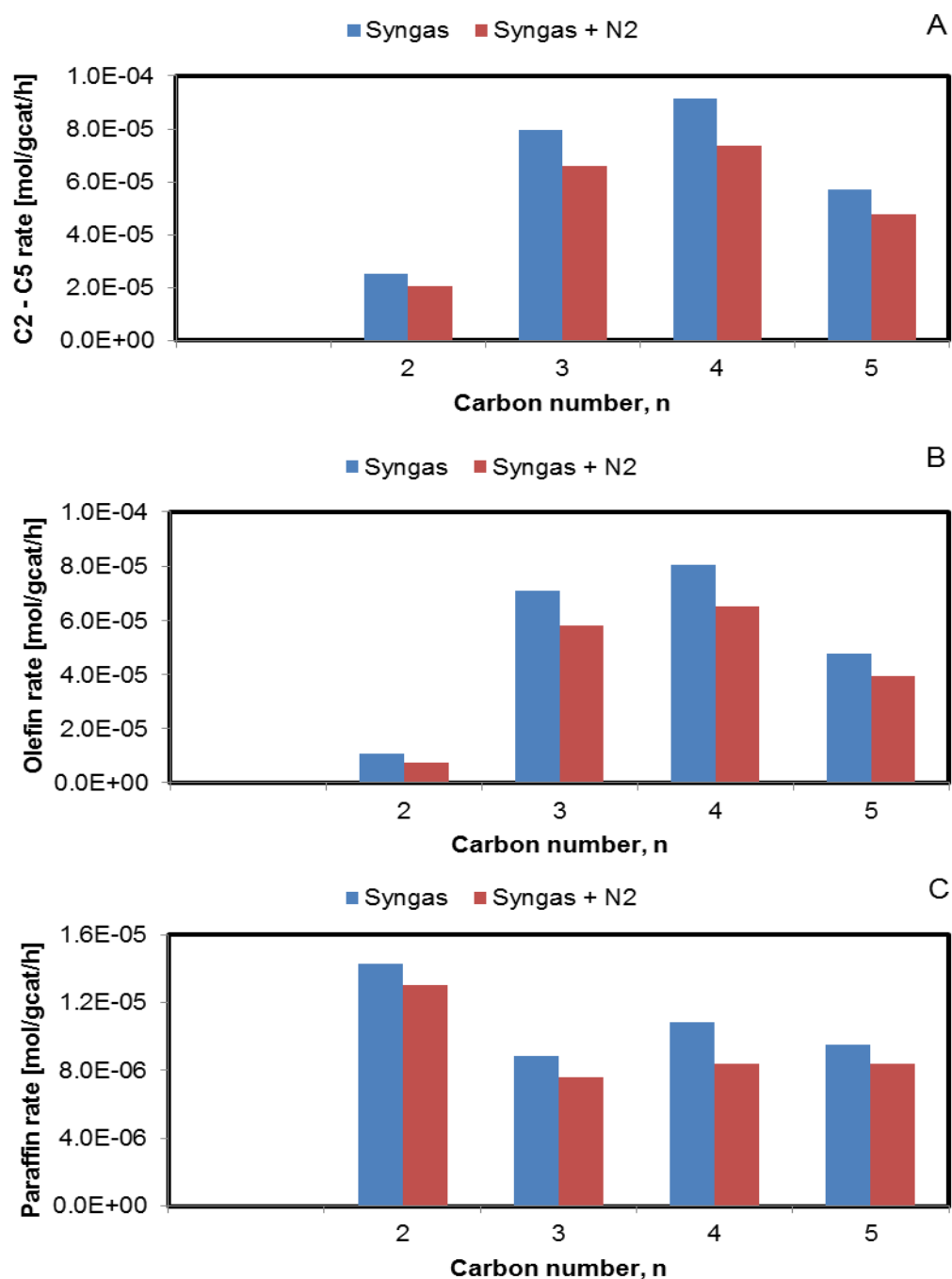


Figure B6: Effect of feeding extra nitrogen into the reactor while keeping the reactant partial pressures the same on the formation rates: (A) for light hydrocarbon; (B) for olefins and (C) for paraffins as a function of carbon number under the reaction conditions listed in **Table B1** for the first switch of FT runs as shown by the red oval shape in **Figures B3 to B5**.

In summary, **Figure B6** shows the formation rates of total hydrocarbons, olefins and paraffins from chain lengths 2 to 5 at a fairly stable CO conversion (ranging on average from about 12% to 13%) as a function of carbon number. It is evident from **Figure B6** that the paraffin formation rate is quite low as compared to the olefin formation rate. Importantly, lower paraffin and olefin formation rates of the lower hydrocarbons were obtained for FTS with syngas + N₂. The data in **Appendix B** imply, adding extra N₂ while keeping the reactants P_{CO} and P_{H2} has very little effect on the overall rate but has an effect on the selectivity to CH₄, light olefins and light paraffins, which suggests that a classic kinetic model cannot be the only explanation for this phenomenon.