Modelling and Simulation of a Fixed-Bed Reactor for the Production of Liquid Fuel from Synthesis Gas

By

Yasir Waheed

Reg# NUST201260719MCES64112F

Session: 2012-14

Supervised by: Asst. Prof. Shahid Hussain Ansari

A Thesis Submitted to the Centre for Energy Systems in partial
fulfilment of the requirements for the degree of

MASTER of SCIENCE in

ENERGY SYSTEMS ENGINEERING

Center for Energy Systems

National University of Sciences and Technology

H-12, Islamabad 44000, Pakistan

August 2014

DEDICATION

This work is dedicated to my beloved parents and my brother and sisters for their endless love support and encouragements.

ACKNOWLEDGEMENTS

First, I am thankful to All Mighty ALLAH for helping me in successful completion of my thesis. I express my gratitude towards my family and especially my parents for their love and support.

I would like to thank my supervisor Asst. Prof. Shahid Hussain Ansari for his guidance, support, helpful comments and questions and especially his confidence in me. My thanks are also extended to my GEC members Dr. Ehsan, Dr. Adeel Waqas, Dr. Bilal Khan Niazi, my HoD-CES, Dr. Zuhair S. Khan and Sir Nouman Aslam for their support in this thesis. I would like to thank all my classmates for their understanding and encouragement in the moment of hardship.

ABSTRACT

Producing transportation and energy generation fuels and chemicals from abundant resources of coal and natural gas has been steadily gaining popularity as the age of conventional crude oil is nearing its end. Over the past decade oil prices have skyrocketed and the involvement of international politics is becoming increasingly problematic due to oil not being globally available including countries like Pakistan as it majorly relies on imported crude for its major energy and transportation needs. The use of this indirect coal liquefaction process of syngas conversion and Fischer Tropsch synthesis can greatly benefit the country in terms of low cost, cleaner fuel production and research in this area in Pakistan must be started on an urgent basis.

In this study the effect of some of the reaction parameters were investigated with a two-dimensional pseudo homogeneous tubular fixed bed reactor model for fischer tropsch synthesis of syngas using cobalt/titania catalyst. The model was applied using suitable kinetics and the initial operating conditions were taken from experimental data. At first, the model was used to predict the general effects of variation in catalyst activity, tube temperature and diameter. A hotspot problem for all the three cases was noted as well as an increase in conversion and reduction in C_5^+ selectivity so an optimized approach was considered. The reactor length was divided into fifteen sections and the tube wall temperature of each section was adjusted according to the axial temperature profile. As a result, nearly isothermal condition was achieved axially while radial-wise, the temperature declined to close to the set tube temperature of that section. Therefore the selectivity of methane reduced and of C_5^+ increased significantly.

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

MFB	Multi-tubular fixed bed
FFB	Fixed fluidized bed
CFB	Circulating fluidized bed
SBC	Slurry bubble column
FT	Fischer-Tropsch
HC	Hydrocarbon
NG	Natural Gas
ASF	Anderson Shulz Flory
SAS	Sasol Advanced Synthol

JOURNALS/ CONFERENCE PROCEEDINGS

Title	Authors	Journal/Conference	Status
1. Optimization and Performance Investigation of FB Reactor on Bench Scale Fischer Tropsch Facility*	Yasir Waheed, Shahid Ansari	3rd International conference of Energy, Environment and Sustainable Development	Abstract Accepted Manuscript under review
2. Modeling of a Fixed Bed Reactor for the Production of Liquid Fuel from Syngas**	Yasir Waheed, Shahid Ansari	Journal of Clean Energy Technologies	Accepted

*(Attached as Annexure 1)

**(Attached as Annexure 2)

TABLE OF CONTENTS

Chapter 1: Introduction

Chapter 2: Literature Review

Chapter 3: Review on Reactor Modelling and Methods

Chapter 4: Experimental Modelling and Validation

Chapter 5: Results and Discussions

Chapter 1

Introduction

1.1 Current scenario of Pakistan and the benefits of CTL

Pakistan, like most of the third-world countries is suffering from severe energy crisis and inflated transportation fuel costs. The economy growth of the world's seventh populous country is nearly crippled due to continuous import of the precious crude oil and unpaid debts both domestic and foreign [14]. Pakistan's natural gas reserves are at a threatening low level. According to 2011 estimates by CIA world fact book, the total reserves are 670 billion cubic meters and annual consumption stands at 49.2 billion cubic meters and are expected to exhaust in nearly 20 years time [13,15]. Large shale oil and gas reserves have been recently discovered in the country but it doesn't have the budget to cover the expensive extraction and processing technology. The fuel prices have increased six-fold from 1995 to 2012 (table 1.1) and diesel fuel, which was cheaper than petrol 14 years back, is now 10 rupees more expensive today and currently stands at PKR 118 whereas petrol is at PKR 108. Due to this most of the local and inter-city and inter-province transport vehicles (excluding trucks and busses) have converted their diesel-powered vehicles in to CNG, which ultimately shifted the burden to Natural Gas. As of today the only fossil fuel that is abundantly available and easily extractable is the massive coal reserves in the Thar Desert, Sindh with an estimated 190 billion tonnes [1]. Coal/Gas to liquid technology (CTL&GTL) is one of the most promising near future options to produce liquid fuels. This is a great opportunity for Pakistan to use this technology for producing domestic and less toxic transportation and power generation fuels in order to boost its economy. Research in the country has been published only on one key component of the FTS technology, i.e, catalysts [2,3]. The FTS reactor, being the second major component, is still under R&D in some of the major universities of Pakistan and publishing is yet to be done. The promotion of small scale CTL and GTL plants must be done in the country in order to understand the potential that this technology can offer. Currently, the known global reserves of natural gas and coal exceed the crude oil reserves by a factor of 2.5 and 25 respectively [4]. Throughout the world this technology is being gaining interest day by day particularly for diesel production due to the following reasons:

- Abundant reserves of coal and NG.
- Diesel produced is virtually clean of sulphur and of relatively high cetane number [5].
- CO_2 sequestration underground can reduce emissions
- Combustion of synthetic fuel produces less pollution [5].
- Synthetic diesel can be used in existing engines and is cheaper than conventional diesel [6,7].

Table 1.1: Diesel price for the past 17 years in Pakistan [17]

Year	**Price (US$/litre)**
1995	0.20
1998	0.19
2000	0.27
2002	0.35
2004	0.41
2006	0.64
2008	0.77
2010	0.92
2012	1.20

1.2 FTS Technology

1.2.1 History

For nearly a century, Fischer Tropsch synthesis has gone through extensive R&D and it is now one of the most popular and major option for making clean transportation fuels and chemicals. Due to the change in the environment and the depletion of oil reserves, the world is shifting its energy requirements towards natural gas and vast coal reserves and that’s why FT synthesis has gained importance [8]. During the pioneering times of FT process (1925—1945), Franz Fischer laboratories in collaboration with the Ruhrchemie Company helped to commercialise this process and, in 1945, a 600,000t/yr capacity plant was erected [4]. Since that time there were a lot of discoveries of large reserves coal and the FT synthesis became a major importance in the first half of the 20th Century, particularly for the Germans in the Second World War. When the war was ended, developments of pilot scale facilities were taken place in the US and South Africa. The original FT process was studied and evaluated in the US Bureau of Mines after WW2 and it lead them to different and improved processes such fluid bed, circulating catalyst, lurgi, etc. Then came the ‘Oil

Age' (1955—1970) when large discoveries of oil fields in the Middle East, North Sea, Alaska were made and the coal based FT process lost its ground to the 'Big Oil'. But in the 1970s during the oil embargo, when the world's major oil producing countries (OPECs) boycotted their export of oil to the western parts of the world, energy programs in the US, Japan and Europe set their attention towards the production of coal based fuels through FT synthesis. Since then, the world became aware that they will run out of oil in the future and as of now the US, Europe and the countries in the Arabian Gulf are the early ones gearing up in developing commercial FT process plants integrated with refineries and coal/natural gas/biomass gasification/reforming units.

1.2.1 FTS Definition and Reactions

FT process involves the catalytic hydrogenation of carbon monoxide to give clean and ordered liquid hydrocarbon composition from syngas by the use of a catalyst that can be supported or unsupported.

A combination of reactions in the fischer tropsch synthesis are shown in table 1.2 [9]

Main products are paraffins, the ratio used is commonly between 2 and 2.2 and the reaction is said to be exothermic, (heat released= -165KJ/mol at room temperature).

In Water gas shift reaction, water produced by the FT reaction reacts with carbon monoxide and produces hydrogen and carbon dioxide and this reaction is also said to be exothermic (heat released = 41.2KJ/mol at room temperature).

The boudouard reaction emerges at very high temperatures when hot spots are formed due to heat removed inefficiently. It generates coke on the catalyst surface making it less active.

Table 1.2: Main and side reactions of the FT process

Main Reactions	
1. Paraffins	$nCO + 2nH_2O \rightarrow (CH_2)n + nH_2O$
2. Olefins	$nCO + (2n+1)H_2 \rightarrow H(CH_2)nH + nH_2O$
3. Alcohols	$nCO + 2nH_2 \rightarrow H(CH_2)nOH + (n-1)H_2O$
Side Reactions	
1. Water-Gas shift	$CO + H_2O \Leftrightarrow CO_2 + H2$
2. Boudouard reaction	$2CO \rightarrow C(s) + CO_2$
3. Methane	$CO + 3H_2 \rightarrow CH_4 + H_2O$
4. Catalyst reduction & oxidation	$M_xO_y + yH_2 \Leftrightarrow yH_2O + xM$
	$M_xO_y + yCO \Leftrightarrow yCO_2 + xM$
5. Carbide formation	$xM + yC \rightarrow M_xC_y$
6. Overall stoichiometry of the reaction	$CO + (1 + (m / 2n))H_2 \rightarrow (1/n)C_nH_m + H_2O$

Heat released = -170KJ/mol at room temperature (extremely exothermic). So it must be avoided.

1.2.2 Process of a CTL Plant

A typical XTL (CTL/BTL/GTL) system consists of four main sections; synthesis gas ($CO+H_2$) production, gas cleaning and upgrading, FT synthesis and FT product workup (Figure1.1). In this chapter, FT synthesis is described on general basis. Further details regarding FTS reactors and catalysts are discussed in chapter 2.

In a commercial SASOL CTL plant (Figure1.2), lurgi coal gasifiers produce syngas with the help of steam and O_2 and with H_2/CO ratio of 1.6--2.0, depending on coal quality. The gas is purified and sent to FT reactors where products formed are mostly the first three shown in the previous section. C_5 to C_{10} cuts undergo refining over $Ni(C_5/C_6)$ and $Pt(C_7/C_{10})$ catalysts for increasing in octane number of gasoline. Of the lighter cuts, methane is either reformed or sold, ethane and propylene are converted to polyethylene and polypropylene. Rest of the olefins are oligomerised for diesel production [4]. Current list of commercial FT plants in operation is shown in table 1.3 [10]. As shown in section 1.2.2, the main FT reaction is highly exothermic and the heat released by the formation of monomers is higher than typical reactions in the oil industry so this should be removed by attaining isothermal condition in the system which is also one of the main focuses in this thesis.

Table 1.3: Commercial FT facilities

Company	**Country**	**Capacity(barrels/day)**	**Raw material**
Sasol	South Africa	150,000	Coal
	Qatar	34,000	Natural gas
Shell	Qatar	140,000	Natural gas
	Malaysia	14,700	Natural gas
Shell Choren	Germany	300	Biomass
Mossgas	South Africa	22,500	Natural gas
EniTechnologie	Italy	20	Natural gas
BP	USA	300	Natural gas
Rantech	USA	1,000	Natural gas
Syntrol-Tyson foods	USA	5,000	Biomass

1.2.3 Process Conditions

Two kinds of processes are used for the synthesis at different temperatures. These are the low temperature fischer tropsch (LTFT) and the high temperature fischer tropsch (HTFT). The processes are summarized in Table 1.4 [6].

Table 1.4: Main processing conditions of FT synthesis

Parameter	**LTFT**	**HTFT**
Temperature(K)	450 – 533	540 – 620
Pressure(Bar)	12 – 45	Around 20
Main products	Heavy oil, wax, diesel	Gasoline, light HCs

1.2.4 Reaction mechanisms:

The reaction mechanism of FT synthesis has been extensively studied by many authors due to its complexity. Most of the researchers found this mechanism involving a polymerization process including the steps initiation, propagation and termination. Following shown are the three possible reaction mechanisms that are proposed [11]:

- **Carbide mechanism:** First found in the late 1920s it is still one of the favourite mechanisms discussed in the research communities. Both carbon monoxide and hydrogen are dissociatively absorbed on the catalyst surface and carbon monoxide is hydrogenated to CH_2 and H_2O. The absorbed CH_2 can be further hydrogenated to CH3 or it can form bond with another absorbed CnHm species, thus allowing chain propagation. Termination can occur by reduction of the absorbed hydrogen to form alkanes or by beta- elimination to form alpha-olefins.
- **Enolic mechanism:** In this, hydrogen reacts with absorbed carbon monoxide and forms oxygenated intermediates (CHOH-metal). Chain growth occurs by surface condensation of two of these intermediates where water is eliminated where as termination occurs by removal of hydroxyl group with the help of hydrogen.
- **CO-insertion mechanism:** This mechanism is the same as the carbide mechanism in terms of forming alkyl metal species and chain termination. However, the difference arises in the propagation step where the chain growth occurs by direct insertion of the carbonyl intermediate (CO-metal) into the carbon metal bond.

1.2.5 FT Crude, Diesel and Gasoline

Processing of FT crude and conventional crude oil is of nearly equal complexity but due to the absence of nitrogen and sulphur compounds, FT crude processing is much less hazardous (table 1.6) [12]. Furthermore, FT derived gasoline has a high octane number in LTFT and has a high cetane number diesel production in LTFT (table 1.5). A high octane number accounts for good anti knocking properties due to the presence of olefins whereas a high cetane number represents good combustion quality during ignition due to high amount of linear paraffins [4].

Table 1.5: Comparison of FT and Conventional diesel and gasoline

Property	Crude oil	High Temp. FT	Low Temp. FT
RON	30 to 60	68	42
Cetane number	57	55	75

Table 1.6: Comparison of FT crude with Conventional crude

Compounds	Crude oil	High Temp. FT	Low Temp. FT
Paraffins	Major	>8%	Major
Olefins	None	Major	> 9%
Aromatics	Major	5-10%	< 1%
Oxygenates	<1%	5-15%	5-15%
Sulphur	0.1 to 5%	None	None
Nitrogen	<1%	None	None
Water	<2%	Major	Major

1.3 Objectives

Based on the issues regarding the temperature in the fixed bed reactor and the requirement of reduced methane selectivity and increased C_5^+ productivity, this thesis focuses on a possible solution for maintaining near isothermal operation of the reactor. For achieving this objective, a two-dimensional plug-flow model is applied in for FT synthesis on a cobalt catalyst using finite difference method in MATLAB software. The experimental work is divided into three sections.

1. Validity of the model with the bench-scale experimental results.
2. Upscale the model of single tube to the length of that found in a commercial tubular reactor and study the effect of various parameters on conversion and thermal stability of reactor.

3. Optimization of the reactor for axially isothermal operation and reduced methane production.

Figurative flowchart of this thesis is shown below:

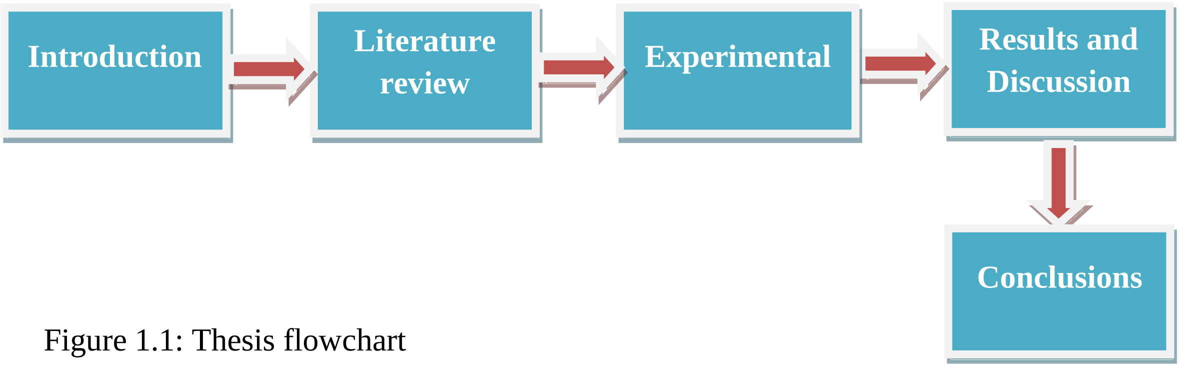


Figure 1.1: Thesis flowchart

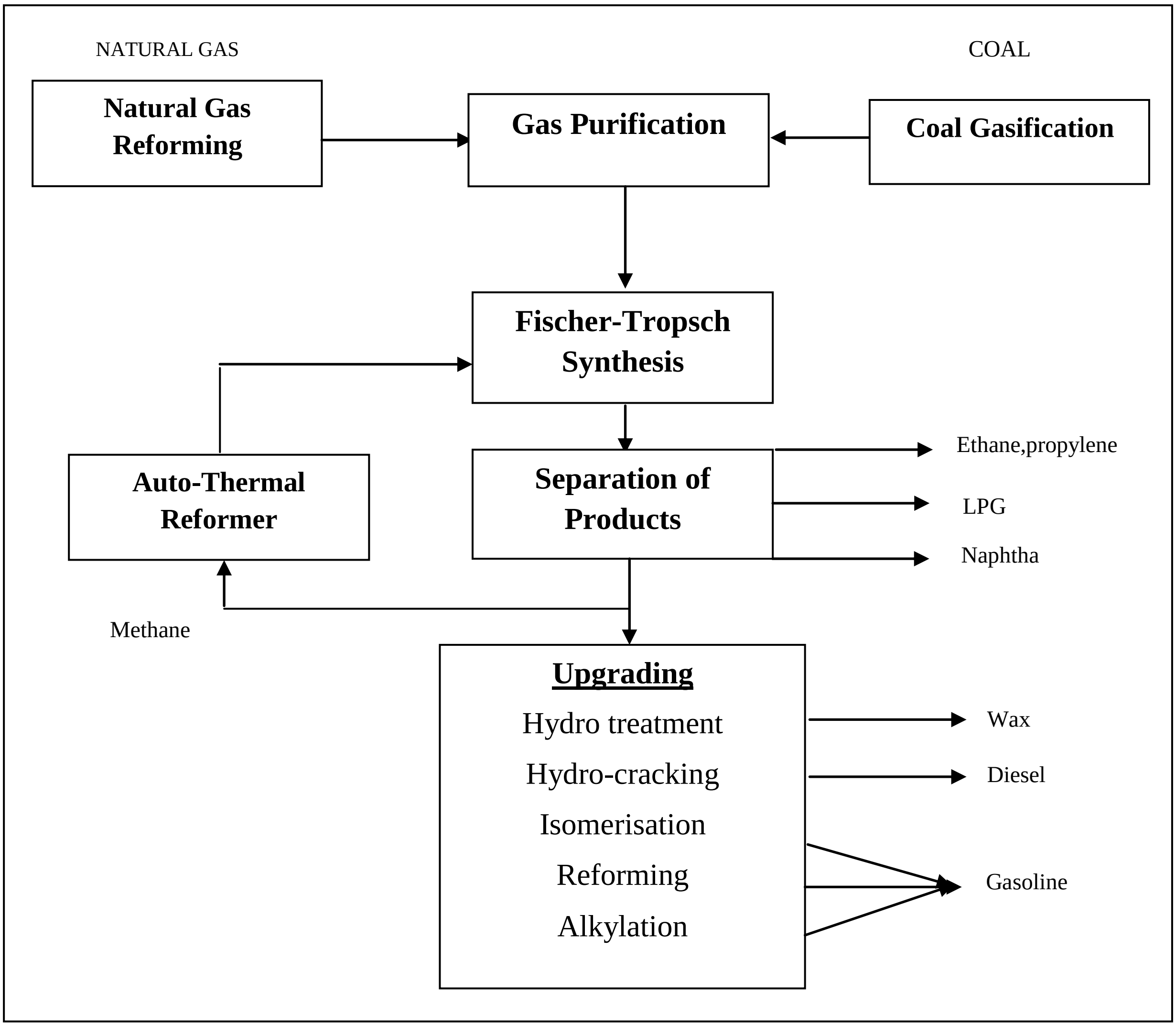


Figure 1.2: FT Process Scheme [6]

Figure 1.3: Secunda CTL SASOL[16]

SUMMARY

In this section the current scenario of Pakistan followed by the importance of the implementation of CTL technology is reviewed. It can be of great benefit to utilize this technology in a coal-rich country like Pakistan. FT synthesis has existed in this world for nearly a century and there is a lot of development going on throughout the globe in making this as an answer to crude oil depleted reserves. Syngas can either be produced from coal or biomass gasification or by methane reforming and it is treated in FT reactors to produce various types of hydrocarbons. Two types of process conditions are applied, namely, LTFT for diesel and wax production or HTFT for gasoline. A brief overall process description along with different reaction mechanisms is also discussed. Comparison between FT synthesis and conventional crude oil is also tabulated.

REFERENCES

[1] I. Shahzad, Final Report Environmental Impact Assessment (Eia) For Sinjhoro Block : Exploration Project, (2011).[www.ogdcl.com].

[2] N. Ahmad, J.A. Anderson, Influence of Gold Promoter on Fischer Tropsch Synthesis Over Col Al203 Catalysts ., (2013) 11–15.

[3] N. Ahmad, S.T. Hussain, B. Muhammad, T. Mahmood, Z. Ali, N. Ali, et al., Effect Of The Reaction Conditions On Al-Pillared Montmorillonite Supported Cobalt-Based Catalysts For Fischer Tropsch Synthesis, 8 (2013) 347–358.

[4] M.E. Dry, The Fischer–Tropsch process: 1950–2000, Catal. Today. 71 (2002) 227–241.

[5] C. White, D. Gray, Production of Zero Sulfur Diesel Fuel from Domestic Coal : Configurational Options to Reduce Environmental Impact, (2012), www.netl.doe.gov.

[6] T.Tarka, Affordable, Low-Carbon Diesel Fuel from Domestic Coal and Biomass, (2009), www.netl.doe.gov.

[7] L. Van Bibber, E. Shuster, J. Haslbeck, M. Rutkowski, Baseline Technical and Economic Assessment of a Commercial Scale Fischer-Tropsch Liquids Facility, (2007), www.netl.doe.gov.

[8] H. Schulz, Short history and present trends of Fischer–Tropsch synthesis, Appl. Catal. A Gen. 186 (1999) 3–12.

[9] M. Ebert, Process synthesis and design of low temperature Fischer-Tropsch crude production from biomass derived syngas, (2013).

[10] R. Luque, A.R. de la Osa, J.M. Campelo, A.A. Romero, J.L. Valverde, P. Sanchez, Design and development of catalysts for Biomass-To-Liquid-Fischer–Tropsch (BTL-FT) processes for biofuels production, Energy Environ. Sci. 5 (2012) 5186.

[11] B.H. Davis, Fischer–Tropsch synthesis: current mechanism and futuristic needs, Fuel Process. Technol. 71 (2001) 157–166.

[12] A. de Klerk, Environmentally friendly refining: Fischer?Tropsch versus crude oil, Green Chem. 9 (2007) 560.

[13] Pakistan Natural Gas consumption [http://www.indexmundi.com](2014)

[14] Pakistan Energy Data [http://www.eia.gov](2014)

[15] Energy Sector of Pakistan [http://www.cia.gov](2014)

[16] Secunda CTL Plant [http://member.zeusintel.com](2014)

[17] Diesel Prices [www.indexmundi.com](2014)

Chapter 2

Literature Review

2.1 FT Reactors

Certain variables are critically important for achieving high results from the reaction. High temperature increases the formation of methane as well as carbon deposition on the catalyst and thus deactivating it at a faster pace. It also favours more production of lower molecular weight hydrocarbons or Olefins (C_1—C_4) which is also a menace to tackle when your major consideration is towards the yield of gasoline and diesel fuel for transportation. It is, therefore, important for the process to be isothermal, a condition that cannot be easily obtained due to the highly exothermic hydrogenation of Carbon Monoxide. Different reactors were studied, built and commercialised for the FT synthesis[1]. The major commercial reactors used today are discussed in the following sections.

The Reactor to be chosen also depends upon the type of catalyst used e.g., Fluidized Bed reactors use dispersed Iron catalyst in HTFT process and bubble column or fixed bed reactors use Cobalt supported catalyst in LTFT Process.

2.1.1 Two-phase Multi-tubular Fixed bed Catalytic reactors (MFB)

These reactors are the first and the oldest type used in process industries. The basic phenomenon is a gaseous reaction taking place on a solid catalyst bed. They were first commercialized in 1955 by SASOL and at that time four of them were built for LTFT synthesis (ID=5cm, L=12.8m, 230^0C, 27 bars), each with a 21,000 t/year capacity[2,3]. Later, a modified one was installed using 45 bars of pressure. Shell erected a 12,500 bpd FT plant consisting bigger MFB reactors and utilizing cobalt catalysts[2]. MFB reactor still holds the advantage of having highest catalyst loading (thus, highest productivity potential) per reactor volume. It can be easily scaled-up from micro to commercial level. Wax product can be easily separated from catalyst and, lastly, only the catalysts near the reactor inlet are affected by impurities. Nevertheless, its major disadvantage is the inefficient heat removal due to transfer limitations[4]. Also, reactor gets bulky when exceeding over 10,000 tubes, increasing its weight as well as complexity and cost. Moreover, short diameter tubes, higher gas velocities and small particle size produce significant pressure drop across the reactor so the particle size of 1—2mm range is acceptable enough to avoid it[5]. Additionally, certain amount of difficulty arises when loading or unloading the catalyst in the tubes. Higher diameter tubes used commercially produce a hot spot, thereby, producing more methane and reducing catalyst life. So feed and tube temperature is kept low, which results in less liquid production[4]. Diagram of FT reactors are shown in Figure 2.1.

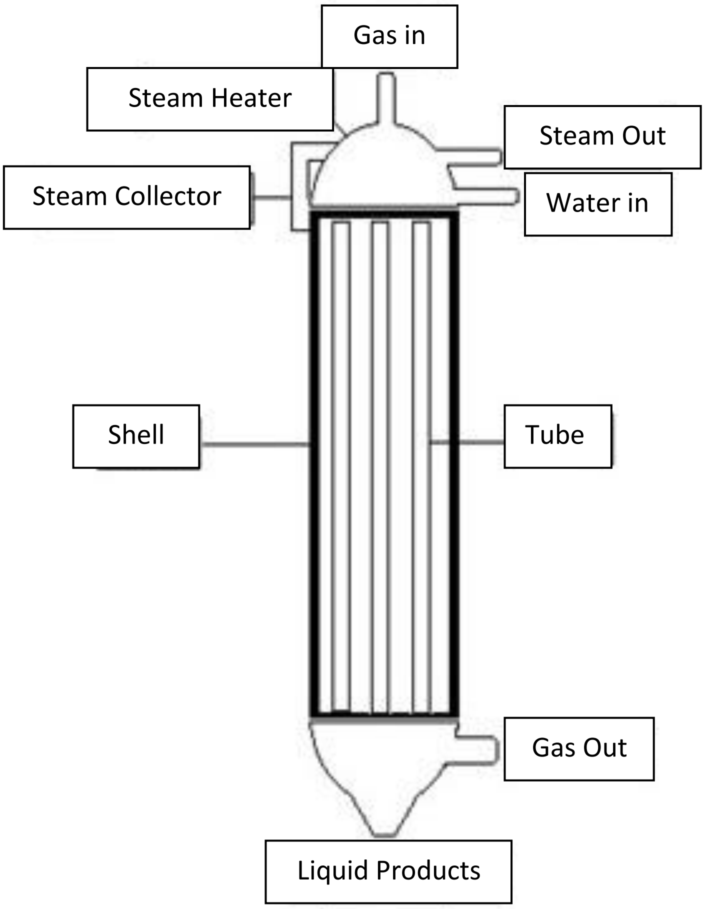


Figure 2.1: Multi-tubular Fixed-bed (MFB) Reactor

2.1.2 Two-phase Fluidized-bed Reactors

Unlike the fixed bed reactor, fluidized bed reactor contains the catalyst in a fluid state that can either be suspended in an inert liquid or in a gas flowing through the reactor. These reactors allow better access to a catalyst as their particles are continuously mixed with in inert liquid or gas flow thus allowing maximum possible surface area for the reactions to occur[5]. Due to the fluidized state of the catalyst bed, these reactors face much less heating issues than fixed bed as there is a much better heat transfer which results in reduction of different heat gradient build-ups that, on the other side, happens on the fixed bed reactor due to the catalyst being immobile.[4] Also, the catalyst can be removed for regeneration or replacement without shutting down the reactor. Like the fixed bed, this reactor can also operate under near-isothermal conditions. There are three types of reactors in this category:

1. Circulating-Fluidized bed (CFB).

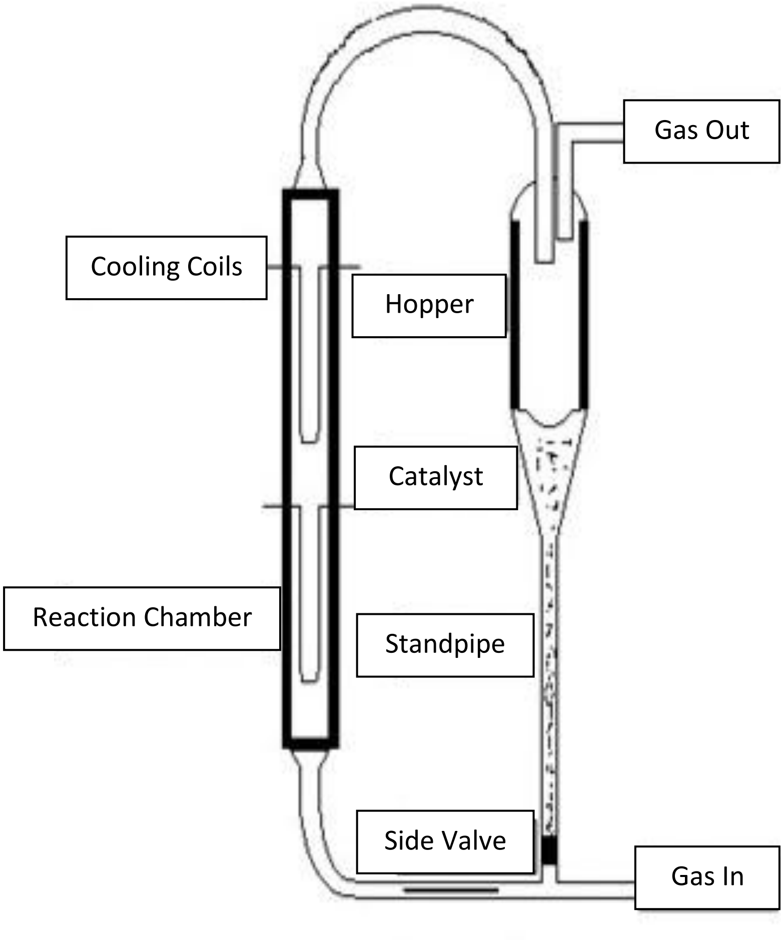


Figure 2.2 Circulating Fluidized-bed (CFB) reactor.

The feed enters from the bottom and meets the downward moving hot catalyst (through vertical stand pipe) and enters the hot zone (reaction) where it encounters several heat exchangers to remove unwanted heat. Then comes the hopper section where the low velocity allows the catalyst particles to break-up from gas stream and falls down in the hopper for cycle continuation. The remaining fine catalyst particles are removed from the stream via series of cyclones (figure 2.2)[6]. These were also built by SASOL and commercialised as HTFT synthesis reactors along with MFBs. These reactors are very complex to build and require excessive amounts of catalysts for circulating. As a result, erosions in different parts of the reactor occur. SASOL first commercialised them in the 1950s for HTFT synthesis. Later they installed 2nd Gen. CFBs with increased capacities[2].

2. Fixed Fluidized-bed (FFB).

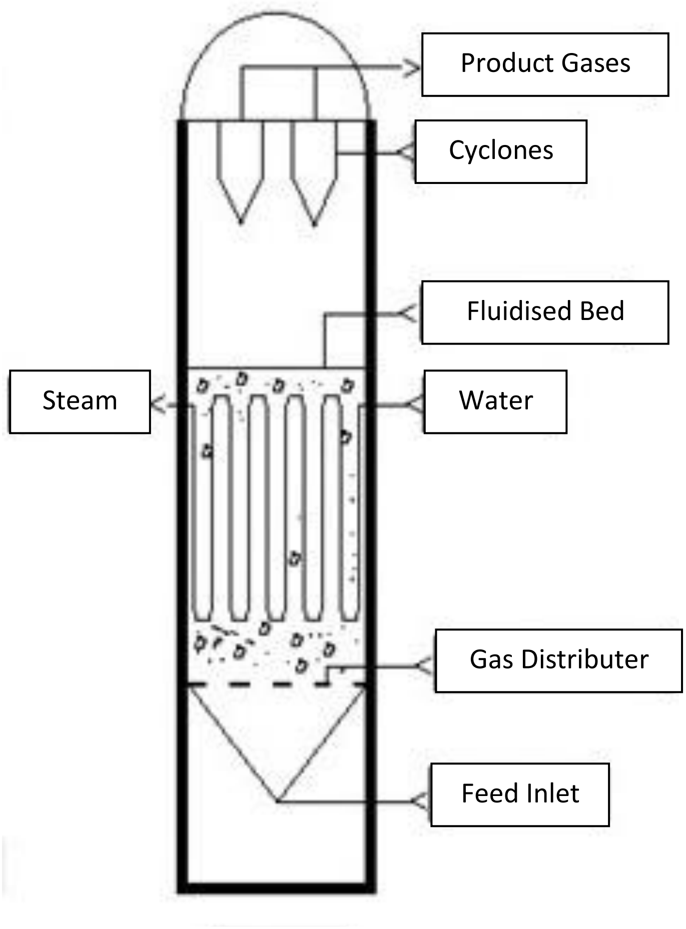


Figure 2.3: Fixed fluidized bed (FFB) Reactor

The feed enters a vertical cylindrical from the bottom, beneath the bed on which the catalysts are residing. Heat is exchanged via tubes inserted in the reactor and the produced gas leaves from the top (figure 2.3)[6]. FFBs, also known as SASOL Advanced Synthol (SAS) reactors, were first successfully commercialised in 1989 by SASOL who later replaced their 2nd Gen. CFBs with FFBs. These steps were taken due to some major advantages of FFBs over CFBs.

1. Smaller size needed for same capacity so nearly 40% less construction costs than CFBs.

2. Since these reactors are wider than CFBs, their capacity of production can be increased by introducing more syngas and cooling coils.
3. Carbon deposition on the catalyst surface is of lower extent in FFBs than in CFBs so less fresh catalyst is required for maintaining conversions.
4. Velocity is linear in FFBs where as it gets higher in the narrower section than in the wider section of CFBs.

2.1.3 Three-phase Slurry Bubble Column Reactors (SBC)

A diagram of Slurry Bubble Column (SBC) reactor is shown in figure 2.3. These reactors are a modification of a normal bubble column reactor and are used for gas-liquid-solid slurry reactions. The basic construction consists of a vertical cylindrical column in which the gas is introduced from the bottom and causes a turbulent stream to obtain optimum gas exchange. The slurry can be parallel or counter flow to the gas. Like the fixed bed reactors, they are also used for LTFTS[7].

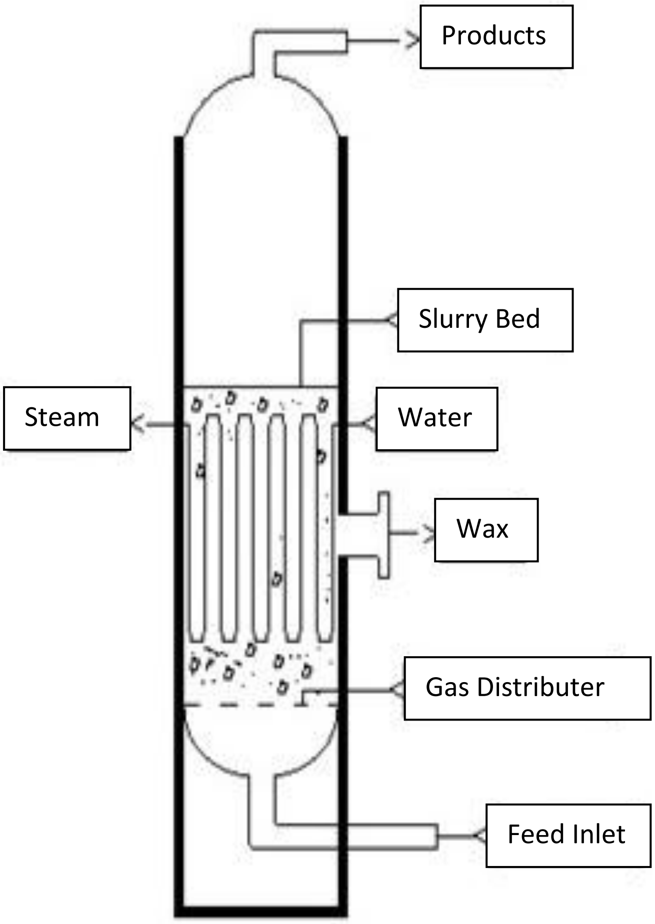


Figure 2.4: Slurry bubble Colum (SBC) Reactor

Fine particle sized catalysts are used thus resulting in negligible mass transfer limitations so better selectivity and activity can be achieved[3]. They have a higher average temperature than MFBs and good catalyst utilization. SBC design was first tested in the 1950s and the reactor was first commercialized in 1993 by Sasol (Dia=5m, 22m length, 2500bpd), and then by Exxon mobil (Dia=1.2, 200bpd) and again by Sasol and Qatar petroleum joint venture (70,000bpd). These reactors have a number of advantages over the fixed bed reactors, the main being:

1. Catalyst used = 1/3rd of that used in MFB with better performance and higher average temperature.
2. Good temperatures control of the reaction same as the fluidized bed.
3. Higher production capacity than MFBs

Major disadvantage of SBC and the other two fluidised bed reactors is that if a poisoned gas is entered, then it will damage the entire catalyst bed. Moreover, the separation of wax from the catalyst and the industrial scale up are still a major problem in commercialization of SBCs. Some of the models are published recently that may help in scale-up[8,9].

2.2 FT Catalysts

Commonly known as the workhorses of chemicals transformations, catalysts are the primary source for accelerating a chemical reaction rate. It has a basic phenomenon of forming bonds with the reactant molecules, allowing them to react for forming product and then disengaging from the products for another round. Catalysts enjoy the advantage of providing a new reaction path that has lower reaction initiation energy than the un-catalyzed path, thereby increasing reaction rate without altering the overall reaction’s energy of activation. The catalytic reactions can either be of **homogeneous, heterogeneous** or **auto-catalytic** types. The basic difference between the first two is of same phase (homo) and different phase (hetro) whereas auto-catalysis occurs when one of the formed products is itself a catalyst thus explaining the fact that the reaction of this type starts very slow as compared to the other two types and then gradually increases as more and more of the product (for catalysis) is formed.

Like for most of the other major chemical reactions carried out around the globe, catalysts are the cornerstone of the Fischer Tropsch synthesis and the heart of its reactors. The catalyst contains the material that is catalytically active. There are many aspects that are needed to be considered during catalyst preparation such as chemical stability, mechanical strength, intra-particle thermal and diffusion resistances, particle size distribution, large scale production. These catalysts are sensitive to reactor operating conditions, especially the operating temperature, that affects the chain growth probability of products on the catalyst surface due to the shifting of desorption and hydrogenation rates[2,7]. Only the group 4 metals Co, Ni, Fe, Ru are active enough for this synthesis and commercially, dispersed iron catalyst and supported cobalt catalyst are being used because of Ruthenium being expensive (Table 1) and Nickel having a major drawback of high methane and volatile carbonyls production[10].

Table 2.1: Activity and price compared to Iron

	Fe	**Co**	**Ni**	**Ru**
Mass	55.85	58.93	58.69	101.07
Price	1	240	130	78,000
Activity	1	250	150	140,000

2.2.1 Iron FT Catalysts

Iron is an effective, cheap and can be easily obtained but it has a major disadvantage of poor selectivity and activity. In order to enhance this, the iron catalyst undergo chemical and physical modifications by applying special additives, e.g. to decrease the catalyst deactivation rate and increase its selectivity, the catalyst is modified by introducing promoters that can either enhance its chemical stability or its mechanical strength or both at the same time. Promoters can be added to the catalyst via impregnation method using a salt solution. Commercially used promoters for this catalyst are copper and K_2O[11]. They do not affect the products formed but lower carbon sintering and also enhance the activation rate of the catalyst. Another aspect of iron catalyst is its high activity towards the WGS reaction inside the reactor. Since this reversible reaction is mainly responsible for balancing the H2/CO ratio, the ratio less than 2 can be used in case of iron catalysts. Therefore, an upstream WGS reactor is not necessary[12].

2.2.2 Cobalt FT Catalysts

Cobalt catalyst usually requires itself to be highly dispersed on a ceramic support that further complicates its preparation and characterisation due to the metal being expensive. Without the supports, these catalysts have short life and high carbon sintering problems. The most common supports used are alumina (Al_2O_3) and silica (SiO_2) on a commercial scale where as Titanium Oxide (TiO_4) and the recently discovered silicon carbide (SiC) and Zirconium Oxide (ZrO_2) are being currently investigated on a lab scale[13]. Promoters used in these catalysts have a primary function to strengthen the interactions between the metal and the support so as to protect it from carbon sintering. Other than this they also have influence on the product selectivity (hence, the yield), reduction temperature and deactivation rate. Being 250 times more active than iron, these catalysts are also highly resistive to corrosion by water or oxygen than iron. They also require fewer or smaller reactors than required by iron for the same product volume. However, they do have the disadvantage of producing volatile cobalt carbonyls at low temperatures and high pressures and also of producing more methane gas at high temperatures[14]. Also cobalt has little to no WGS activity and thus mandatorily requires an upstream WGS reactor. This catalyst produces more diesel than gasoline and is favourably used for slurry bubble column and fixed bed reactors or for LTFT synthesis[2].

2.2.3 Impact of Water on Cobalt and Iron Catalysts:

For an iron based catalyst, the partial pressure of the water accounts for a negative impact on the rate of CO conversion as well as it increases the oxidation of the catalyst surface due to water not allowing hydrogen to adsorb because of hydrogen’s weaker adsorption power[15]. For cobalt, however, the scenario is different where water does not negatively influence the CO conversion. Still it is necessary to remove water as it is a product of every hydrocarbon, especially in the case of some recycling of the products otherwise there will be a water build-up that will decrease the partial pressures of CO and H_2 and, hence, reduce conversion[16].

2.2.4 Methods for Catalyst Preparation

The principal catalyst-preparation technique involves two stages. First, the metal-salt component is dispersed into a finely divided form on a support and secondly; conversion of the supported metal salt to a metallic or oxide state via heat treatment process. The first stage is achieved by impregnation, adsorption from solution, co-precipitation, or deposition, while the second stage is a thermal treatment in either an inert atmosphere or an active atmosphere of either oxygen or hydrogen(reduction). Calcination/reduction does cause major problems in catalyst preparation on a large scale, but it can be safely concluded that the metal’s degree of dispersion will remain unchanged during treatments once it is restrained on the support. The primary aim of the highly dispersed form is highly active form when expressed as a function of the weight of the active component so that the metal can be utilized safely if it is a rare or an expensive metal to be used. Base-metal catalysts use support primarily for improving stability by achieving suitable interaction between the active material and the support. A summary of the most widely used techniques is given below.

Table 2.2: Comparison between iron and cobalt catalysts

Factor	**Iron**	**Cobalt**
Selectivity	Good	250 times that of iron
Single pass conversion	More than one reactor needed for high conversion	65-75 % conversion can be achieved
Low hydrogen content	High WGS activity, WSG reactor not necessary	Low/no WGS activity, WSG reactor is mandatory
Resistance against contaminants	Highly resistant to sulphur	Requires a cleaner gas than does iron
Resistance against water vapour	Water vapour inhibits FT reaction and influences the catalyst depending on the catalyst type	
Partial pressure of water	Negative impact, water extracted before enterance	Water should be extracted when in recirculation mode.
Operation mode	Harsher and more severe conditions favourable for Fe	Less harsher and less severe conditions as selectivity is higher at lower temperatures.
Stability	Life of roughly 7 months under optimized conditions	

1. Impregnation:-

This process involves filling the pores of the support with the solution of the metal salt that can either be sprayed or added drop-wise on the support in powder form till the point when the supported powder almost becomes like a paste. Although this type of execution practice looks simple the phenomena inside impregnation and drying is too much complicated as it requires careful control of temperature and time of drying and metal loading rate. Moreover, the interactions, prior to the drying, are weak so redistribution of the metal occurs during drying and heat treatments. Also, the supports have different points of zero charge (PZC) so electrostatic interactions along with pH of the metal solution also responsible for affecting the homogeneous distribution. If the solution’s pH is lower than PZC repulsion between the metal ions and support will occur therefore, non-homogeneous distribution. If the pH is higher than PZC, the result will be vice-versa. However, the support will face dissolution in the impregnating solution at higher pH values[17,18].

2. Co-precipitation:-

This method produces an intimate mixing of catalysts and support. The solutions of metal and support precursors are mixed to produce precipitated support gel containing the metal hydroxide. This precipitate, when calcined, produces a refractory support with active component dispersed throughout the bulk as well as at the surface. This type of technique is very popular in making iron based catalyst but little research has been done on cobalt. Co-precipitation of cobalt-alumina catalyst has been performed by Khassin et al[19] and Chen et al[20]. Addition of small amount of Mg or Zn improved reducibility and heavy cobalt loading on ZrO_2 improved reaction rate.

3. Deposition precipitation:-

Deposition is process performed in the liquid phase by the deposition of a metal solvent onto a suspended support with careful introduction of the precipitating agent. It has the same advantages of Co-precipitation regarding size distribution and dispersion and it also reduces the risk of bulk compounds of support and metal phase. This technique is used for preparing cobalt catalysts with high metal loading and high dispersion on the oxide supports and on carbon nano-fibres that are studied extensively by Burattin et al[21,22,23], Geus[24] and De Jong at al[25].

4. Sol-Gel method:-

This method is mainly used for improving surface area, porosity and particle size and is greatly considered over incipient wetness impregnation in case of high metal loadings[26]. The end results are highly depended upon the preparation procedure. One such procedure on cobalt-silica catalyst starts with dissolving required quantity of metal precursor solution in ethylene glycol and, afterwards, addition of tetraethyl ortho-silicate and vigorous stirring and heating for achieving homogeneous solution. Form-amide or poly-ethene glycol were added during this time as pore modifiers, followed by reducing temperature to room condition and drop-wise addition of water and ethanol. After that, hydrolyzing of sol was done at T>353K for 40 h for gel formation. The gel, then, underwent drying and heat-treatment for 15hr at 823K. In the end, it was reduced in hydrogen for 15 hr. TEM showed even dispersion of Cobalt particle size of 3—5 nm[27]. Different sol-gel methods were published afterwards[28,29].

5. Monolithic coating:-

Generally three types of monoliths can be used; cordierite, γ-Alumina, and steel[30]. These include long parallel channels separated by thin walls (cordierite or γ-Alumina). Coating of cobalt species can either be done by co-impregnation or deposition precipitation[31]. They have major advantages of reducing pressure drop in large scale commercial reactors and reducing mass transfer limitations[32,33].

SUMMARY

Reactors used in the FT synthesis are discussed along with their advantages and limitations. Fixed bed reactors are the oldest type and still hold the advantage of high productivity and high catalyst life but has a drawback of inefficient heat removal. Slurry reactors have advantages completely to opposite of fixed beds. Cobalt is 200 times more active than iron but is expensive and thus needs to be efficiently and highly dispersed. Ruthenium and Nickel are rare metals therefore they cannot be suitable for commercial applications. Catalyst preparation methods have also been elaborated.

REFERENCES

[1] B.H. Davis, Fischer-Tropsch Synthesis : Overview of Reactor Development and Future Potentialities, 48 (2003) 787–790.

[2] M.E. Dry, The Fischer–Tropsch process: 1950–2000, Catal. Today. 71 (2002) 227–241.

[3] A.P. Steynberg, M.E. Dry, M.E. Davis, Fischer-Tropsch Technology, Elsevier, 2004. [http://books.google.com] (accessed August 21, 2014).

[4] R. Guettel, T. Turek, Comparison of different reactor types for low temperature Fischer–Tropsch synthesis: A simulation study, Chem. Eng. Sci. 64 (2009) 955–964.

[5] S.T. Sie, Process Development And Scale Up: Iv. Case History Of The Development Of A Fischer-Tropsch Synthesis Process, Rev. Chem. Eng. 14 (1998).

[6] J.G. Speight, Hydrocarbons from Synthesis Gas. Handbook of Industrial Hydrocarbon Processes, Gulf Professional Publishing, 2011. http://books.google.com] (accessed August 21, 2014).

[7] R.L. Espinoza, A.P. Steynberg, B. Jager, A.C. Vosloo, Low temperature Fischer–Tropsch synthesis from a Sasol perspective, Appl. Catal. A Gen. 186 (1999) 13–26.

[8] R. Krishna, A Scale-Up Strategy for a Commercial Scale Bubble Column Slurry Reactor for Fischer-Tropsch Synthesis, Oil Gas Sci. Technol. 55 (2000) 359–393.

[9] R.Ã. Krishna, J.M. Van Baten, A strategy for scaling up the Fischer – Tropsch bubble column slurry reactor, 26 (2003) 21–28.

[10] F. Diehl, A.Y. Khodakov, Promotion of Cobalt Fischer-Tropsch Catalysts with Noble Metals : a Review, 64 (2009) 11–24.

[11] M.E. Dry, The fischer-tropsch process - commercial aspects, Catal. Today. 6 (1990) 183–206.

[12] Y. Lu, T. Lee, Influence of the Feed Gas Composition on the Fischer-Tropsch Synthesis in Commercial Operations, J. Nat. Gas Chem. 16 (2007) 329–341.

[13] X. Zhu, X. Lu, X. Liu, D. Hildebrandt, D. Glasser, Heat transfer study with and without Fischer-Tropsch reaction in a fixed bed reactor with TiO2, SiO2, and SiC supported cobalt catalysts, Chem. Eng. J. 247 (2014) 75–84.

[14] M.E. Dry, Catalytic aspects of industrial Fischer-Tropsch synthesis, J. Mol. Catal. 17 (1982) 133–144.

[15] M. Arabpour, M.R. Rahimpour, D. Iranshahi, S. Raeissi, Evaluation of maximum gasoline production of Fischer–Tropsch synthesis reactions in GTL technology: A discretized approach, J. Nat. Gas Sci. Eng. 9 (2012) 209–219.

[16] I.C. Yates, C.N. Satterfield, Intrinsic Kinetics of the Fischer-Tropsch Synthesis on a Cobalt Catalyst, (1991) 168–173.

[17] J.A. Schwarz, The adsorption/impregnation of catalytic precursors on pure and composite oxides, Catal. Today. 15 (1992) 395–405.

[18] G.A. Parks, The Isoelectric Points of Solid Oxides, Solid Hydroxides, and Aqueous Hydroxo Complex Systems, Chem. Rev. 65 (1965) 177–198.

[19] A.A. Khassin, T.M. Yurieva, G.N. Kustova, I.S. Itenberg, M.P. Demeshkina, T.A. Krieger, et al., Cobalt–aluminum co-precipitated catalysts and their performance in the Fischer–Tropsch synthesis, J. Mol. Catal. A Chem. 168 (2001) 193–207.

[20] J.-G. Chen, Y.-H. Sun, Natural Gas Conversion VII, Proceedings of the 7th Natural Gas Conversion Symposium, Elsevier, 2004.

[21] P. Burattin, M. Che, C. Louis, Characterization of the Ni(II) Phase Formed on Silica Upon Deposition−Precipitation, J. Phys. Chem. B. 101 (1997) 7060–7074.

[22] P. Burattin, M. Che, C. Louis, Metal Particle Size in Ni/SiO 2 Materials Prepared by Deposition−Precipitation: Influence of the Nature of the Ni(II) Phase and of Its Interaction with the Support, J. Phys. Chem. B. 103 (1999) 6171–6178.

[23] P. Burattin, M. Che, C. Louis, Ni/SiO 2 Materials Prepared by Deposition−Precipitation: Influence of the Reduction Conditions and Mechanism of Formation of Metal Particles, J. Phys. Chem. B. 104 (2000) 10482–10489.

[24] J.W. Geus, Preparation of Catalysts III - Scientific Bases for the Preparation of Heterogeneous Catalysts, Elsevier, 1983.

[25] G. Bezemer, P. Radstake, V. Koot, A. Vandillen, J. Geus, K. Dejong, Preparation of Fischer–Tropsch cobalt catalysts supported on carbon nanofibers and silica using homogeneous deposition-precipitation, J. Catal. 237 (2006) 291–302.

[26] J.C. In, Structures and properties of silica gels prepared by the sol—gel method, J. Non. Cryst. Solids. 130 (1991) 8–17.

[27] K. Okabe, X. Li, M. Wei, H. Arakawa, Fischer–Tropsch synthesis over Co–SiO2 catalysts prepared by the sol–gel method, Catal. Today. 89 (2004) 431–438.

[28] P. Moggi, G. Predieri, F. Di Silvestri, A. Ferretti, Ru/SiO2 catalysts prepared by the sol–gel method from Ru3(CO)12, Appl. Catal. A Gen. 182 (1999) 257–265.

[29] B. Ernst, A. Bensaddik, L. Hilaire, P. Chaumette, A. Kiennemann, Study on a cobalt silica catalyst during reduction and Fischer–Tropsch reaction: In situ EXAFS compared to XPS and XRD, Catal. Today. 39 (1998) 329–341.

[30] F. Kapteijn, R.M. de Deugd, J.A. Moulijn, Fischer–Tropsch synthesis using monolithic catalysts, Catal. Today. 105 (2005) 350–356.

[31] T.A. Nijhuis, A.E.W. Beers, T. Vergunst, I. Hoek, F. Kapteijn, J.A. Moulijn, Preparation of monolithic catalysts, Catal. Rev. 43 (2001) 345–380.

[32] F. Kapteijn, T.. Nijhuis, J.. Heiszwolf, J.. Moulijn, New non-traditional multiphase catalytic reactors based on monolithic structures, Catal. Today. 66 (2001) 133–144.

[33] P.S. Hagan, M. Herskowitz, C. Pirkles, A simple approach to highly sensitive tubular reactors, SIAM J. Appl. Math. 48 (1988) 1083–1101.

Chapter 3

Review on Reactor Modelling and Methods

3.1 FT Fixed-bed Reactor modelling

The details regarding the model equations and catalyst kinetics are given in chapter 3.

Reactor modelling does play a pivotal role in scaling up to the industrial levels. It helps researchers to study and compare the basic trends of the process and predict the best possible operating parameters for higher yield of the desired products. However, research published on fixed bed reactor in case of FT synthesis is considerable. Table 2.3 summarize some of the published works on FT fixed bed reactor modelling. The optimizations were mainly performed for improving liquid (Gasoline/ Diesel) productions and some of the published work was done on discussing the main trends in HTFT and LTFT synthesis.

Altogether, there are two main reactor models used for reactor simulation. Homogeneous model assumes there is only one phase throughout the reactor tube length whereas heterogeneous model includes two different phases, gas-solid or liquid solid. Both models can one or two dimensional variations types. In one dimensional, the process variation is simulated across the reactor length whereas two dimensional adds the radial variable along with axial variable. One dimensional homogeneous model is accurate enough to give the general idea about the reactor behaviour. For higher accuracy 1D heterogeneous, 2D homogeneous and 2D hetero generous model are applied. However, too much computational work is required for heterogeneous model so the 1D and 2D homogeneous models are used[1,2,3].

As mentioned in earlier (Chapter 1), research regarding FT technology has only been conducted on the development of catalysts in Pakistan. Modelling, simulations and designing of an FT plant has not been published from the country as of yet. Therefore, in this thesis, a 2-D homogeneous model on a fixed bed reactor is developed in MATLAB via finite difference method for simulating the main trends. Furthermore, an optimization was applied to the model for controlling its axial temperature variation.

Table 3.1: Recent works published on Fischer-tropsch reactor modelling [4,5,2,6,7,8]

Author, Journal, Year	**Title**	**Objectives**	**Results**
A. Jess, R. Popp, K. Hedden,Appl. Catal. A. 186 (1999) 321–342.	FT synthesis with nitrogen-rich synthesis gas: Fundamentals and reactor design aspects.	Study the performance of nitrogen-rich syngas using a 2-D pseudo homogeneous model.	Nitrogen helps in removing the heat from the reactor and also increased the diesel/wax production.
R. Guttel, T. Turek, Chem. Eng. Sci. 64 (2009) 955–964.	Comparison of different reactor types for low temperature FT synthesis: A simulation study,	1-D models of MFB and SBC were studied.	SBR has a higher productivity than FBR but has a major disadvantage of wax-catalyst separation.
M.H Rafiq, H.A. Jakobson, Fuel Processing Technology 92(2011) 893—907	Experimental studies and modeling of a fixed bed reactor for FT synthesis using bio-synthesis gas.	2-D pseudo homogeneous model was studied using synthesis gas and bio synthesis gas.	High GHSV leads to lower syngas conversion and higher C5+ selectivity. Larger diameter tube produces more CH4.
M. Bayat, M.R. Rahimpour, J. Nat. Gas Sci. Eng. 11 (2013) 52–64	Boosting the gasoline production via a novel multifunctional Fischer–Tropsch reactor: Simulation and optimization	Enhance gasoline yield using an optimized multifunctional fixed bed reactor model on iron catalyst with the help of differential evolution algorithm.	Enhancement of upto 40.91% for gasoline and reduction of 75% and 34.6% in methane and carbon dioxide yield was achieved.
N.A. Momnov, L.M. Kustov, Catal. Ind. 5(2013) 223-231	1D heterogeneous model of a FT synthesis reactor with a fixed catalyst bed in the isothermal granules approximation	Reduce overheating and increase conversion by determining the optimum tube diameter.	Less than 18mm inner diameter is required for normal conversion and less than 12mm for high conversions.
S.K. Mazidi, M.T. Sadeghi, Chem. Eng. Technol. 36(2013) 62-72	Optimization of FT process in a fixed bed reactor using non-uniform catalyst	Maximized yield using combination of non-uniform and uniform shaped catalysts.	C_5^+ production increased with combination of eggshell & surface layered catalysts.

3.2 Software and Method for Simulation

The major software that are used for optimization of Fischer-Tropsch synthesis, especially MFB reactors are FLUENT, Aspen plus and MATLAB. In this thesis, modelling is performed using finite difference method in MATLAB (developed by MATHWORKS inc) which is a fourth generation programming language and interactive environment that is used by over a million industrial, research and academic users of engineering science and economics backgrounds. It is easily accessible, free to download (Aspen and FLUENT require purchasing) and can be used for optimization and many more purposes as it is primarily developed for numerical computing. FLUENT is mostly used for more complex estimations and simulations and is mainly considered for computational fluid dynamics ASPEN plus is used for detailed simulations and total plant designing and cost analysis. Following tables show the software used by some of the researchers for reactor modelling and plant design simulations.

Table 3.2: Recent work on reactor simulation using MATLAB[2,9,10,3]

Author	**Title**	**Software**
Rafiq and Jakobson	Experimental studies and modeling of a fixed bed reactor for fischer-tropsch synthesis using bio-syngas	MATLAB, Finite difference method
Arabpour et al.	Evaluation of maximum gasoline production of Fischer–Tropsch synthesis reactions in GTL technology: A discretized approach	MATLAB, Differential evolution algorithm
Emrani et al.	Modeling and Optimization of Fixed-Bed Fischer-Tropsch Synthesis Using Genetic Algorithm,	MATLAB, Genetic algorithm.
Park et al.	Modeling of a pilot-scale fixed-bed reactor for iron-based Fischer–Tropsch synthesis: Two-dimensional approach for optimal tube diameter	MATLAB, Finite difference method

Table 3.3: Work on FT synthesis published using FLUENT[11,12]

Author, Year	**Title**	**Software**
M. Irani, G. Division, 55 (2013) 82–92.	Modeling of fischer – tropsch synthesis packed bed reactor for producing liquid fuels from natural gas,	ANSYS FLUENT, Computational Fluid Dynamics.
Andrey A. Troshko ANSYS Inc., Fluid Business Unit, USA, (n.d.).	CFD modeling of slurry bubble column reactor for Fischer-Tropsch synthesis	ANSYS FLUENT, Computational Fluid Dynamics

Table 3.4: Work on FT plant design using ASPEN Plus[13,14,15]

Author	**Title**	**Software**
Mario R. Eden, Auburn University	Modelling of Gasification and Fischer tropsch processes	ASPEN plus
M. Elbert	Process synthesis and design of low temperature Fischer-Tropsch crude production from biomass derived syngas.	ASPEN plus
Gerald N. Choi	Simulation models and designs for advanced fischer-tropsch technologies	ASPEN plus

SUMMARY

Recent work published regarding reactor modelling and process simulation and optimization using different software are discussed in this chapter.

REFERENCES

[1] M. a. Marvast, M. Sohrabi, S. Zarrinpashne, G. Baghmisheh, Fischer-Tropsch Synthesis: Modeling and Performance Study for Fe-HZSM5 Bifunctional Catalyst, Chem. Eng. Technol. 28 (2005) 78–86.

[2] M.H. Rafiq, H. a. Jakobsen, R. Schmid, J.E. Hustad, Experimental studies and modeling of a fixed bed reactor for Fischer–Tropsch synthesis using biosyngas, Fuel Process. Technol. 92 (2011) 893–907.

[3] N. Park, J.-R. Kim, Y. Yoo, J. Lee, M.-J. Park, Modeling of a pilot-scale fixed-bed reactor for iron-based Fischer–Tropsch synthesis: Two-dimensional approach for optimal tube diameter, Fuel. 122 (2014) 229–235.

[4] A. Jess, R. Popp, K. Hedden, Fischer – Tropsch-synthesis with nitrogen-rich syngas Fundamentals and reactor design aspects, 186 (1999) 321–342.

[5] R. Guettel, T. Turek, Comparison of different reactor types for low temperature Fischer–Tropsch synthesis: A simulation study, Chem. Eng. Sci. 64 (2009) 955–964.

[6] M. Bayat, M.R. Rahimpour, Boosting the gasoline production via a novel multifunctional Fischer–Tropsch reactor: Simulation and optimization, J. Nat. Gas Sci. Eng. 11 (2013) 52–64.

[7] N. a. Mamonov, L.M. Kustov, S. a. Alkhimov, M.N. Mikhailov, One-dimensional heterogeneous model of a Fischer-Tropsch synthesis reactor with a fixed catalyst bed in the isothermal granules approximation, Catal. Ind. 5 (2013) 223–231.

[8] S.K. Mazidi, M.T. Sadeghi, M. a. Marvast, Optimization of Fischer-Tropsch Process in a Fixed-Bed Reactor Using Non-uniform Catalysts, Chem. Eng. Technol. 36 (2013) 62–72.

[9] M. Arabpour, M.R. Rahimpour, D. Iranshahi, S. Raeissi, Evaluation of maximum gasoline production of Fischer–Tropsch synthesis reactions in GTL technology: A discretized approach, J. Nat. Gas Sci. Eng. 9 (2012) 209–219.

[10] A.S. Emrani, M. Saber, F. Farhadi, Modeling and Optimization of Fixed-Bed Fischer-Tropsch Synthesis Using Genetic Algorithm, 46 (2012) 1–11.

[11] M. Irani, G. Division, Modeling of fischer – tropsch synthesis packed bed reactor for producing liquid fuels from natural gas, 55 (2013) 82–92.

[12] A.A. Troshko, CFD modeling of slurry bubble column reactor for Fischer-Tropsch synthesis Andrey A. Troshko ANSYS Inc., Fluid Business Unit, USA, (n.d.).

[13] M.R. Eden, Modeling of Gasifica0on and Fischer-Tropsch Synthesis, (n.d.).

[14] M. Ebert, Process synthesis and design of low temperature Fischer-Tropsch crude production from biomass derived syngas, (2013).

[15] G.N. K. Sheldon, Choi, Simulation models and designs for advanced Fischer-Tropsch Technology, (1996) 269–282.

Chapter 4

Experimental Modelling and Validation

4.1 Development of the Reactor Model

4.1.1 Methodology

A two dimensional steady-state pseudo homogeneous model was chosen to simulate the basic trends and effect of change in different parameters on the reactants' conversion and product yield. The following assumptions were made:

1. Non isothermal condition due to noticeable change in reactor.
2. 2-D plug-flow gas-liquid system without radial concentration gradients.
3. Axial dispersion of mass and heat were neglected.

Radial concentration gradients are neglected. The main FT reaction rate on Cobalt/Titania catalyst by Zennaro et al. [1] is taken for this study which is a simple langmunir-hanshelwood (L-H) rate form. The equation is the same as that derived by Yates and Satterfield [2] with a minor difference of having a power of 0.74 on P_{H2} in the numerator. Since the catalyst used was cobalt no water-gas shift reaction is taken into account due to cobalt catalyst's negligible in-situ WGS activity and the H_2/CO ratio taken in this study being 2. This ratio used is the one that is obtained from Sasol's lurgi coal gasifiers. Since C_1 and C_2 compounds deviate from the ASF theory, the chain growth probability factor, alpha-value, was used for higher HCs whereas individual rate laws were given for the compounds mentioned above. The temperature dependant constants were calculated according to the experimental results and the energies of activation were taken from the available literature [2,3,4]. The mass and energy balance equations can be written as follows:

Mass balance:

$$u_{sv}\rho_g \frac{\delta\, C_a}{\delta L} = \rho_g C_a \frac{\partial u_{sv}}{\delta L} + C_a u_{sv} \frac{\delta \rho_g}{\delta L} - r_m \rho_{\boldsymbol{B}} \qquad (1)$$

Energy balance:

$$u_{sv}\rho_g C_p \frac{\delta T}{\delta L} = (-\Delta H)\rho_B r_m + \lambda_{efr}.\left(\frac{1}{r}.\frac{\delta T}{\delta r} + \frac{\delta^2 T}{\delta r^2}\right) \qquad (2)$$

Overall Pressure Drop (Ergun law):

$$-\frac{\delta P}{\delta L} = f.\frac{\rho.u_{sv}^2}{d_p} \qquad (3)$$

Change in density and superficial velocity were calculated by:

$$\frac{\delta \rho_g}{\delta L} = \frac{M}{R} \cdot \left(\frac{1}{T} \cdot \frac{\delta P}{\delta L} - \frac{P}{T^2} \cdot \frac{\delta T}{\delta L} \right) \tag{4}$$

$$\frac{\delta u_{sv}}{\delta L} = \frac{u_{sv}}{\rho} \cdot \frac{\delta \rho_g}{\delta L} \tag{5}$$

Boundary conditions:

$$\frac{\partial C}{\partial r} = 0 \qquad for\ all\ L\ and\ r \tag{6}$$

$$\frac{\partial T}{\partial r} = 0 \qquad for\ all\ L\ at\ r = 0 \tag{7}$$

$$\frac{\partial T}{\partial r} = -\frac{U}{\lambda_{efr}} \left((T\ at\ r = R) - T_W \right) for\ all\ L \tag{8}$$

Main kinetic equation used in this study:

$$r_m = \frac{a P_{H_2}^{0.74} P_{CO}}{(1 + b P_{CO})^2} \tag{9}$$

Component and mixture heat capacities were calculated using equations derived by Poling [5]. The overall heat transfer coefficient equation was taken from the co-relations used for 2-D model [6]. The effective radial thermal conductivity was calculated from equations derived by Forment [7]. The superficial gas velocity was obtained based on overall mass flux and gas mixture density. Finite difference method was applied. MATLAB’s ODE solver was used to conduct the numerical simulation.

Overall Heat transfer coefficient:

$$\frac{1}{U} = \frac{1}{a_w} + \frac{d_i}{2\lambda_s} ln \frac{d_o}{d_i} \tag{10}$$

Effective radial thermal conductivity:

$$\lambda_{efr} = \lambda_{efr}^0 + 0.111 \lambda_g \cdot \frac{Re_p + Pr^{1/3}}{1 + 46 \left(\frac{d_p}{2 \cdot R_O} \right)^2} \tag{11}$$

Where

$$\lambda_{efr}^0 = \varepsilon \cdot \left(\lambda_g + 0.95 + \alpha_{ru} + d_p \right) + \frac{0.95 \cdot (1 - \varepsilon)}{2/(3 \cdot \lambda_s) + 1/\left(10 \cdot \lambda_g \cdot \alpha_{rs} \cdot d_p\right)} \tag{12}$$

Is the thermal conductivity of the catalyst bed without any fluid and α_{ru} and α_{rs} are:

$$\alpha_{ru} = \left(\frac{0.8171 \cdot (T/100)^3}{1 + \varepsilon/2(1 - \varepsilon)((1 - p)/p)} \right) \tag{13}$$

$$\alpha_{rs} = 0.8171 \left(\frac{p}{2 - p} \right) (T/100)^3 \tag{14}$$

Where p is the emissivity of catalyst, assumed to be 0.8 and λ_s is the catalyst thermal conductivity taken as 0.875 $kW.m^{-1}.K^{-1}$ for cobalt based catalyst [8].

The α-value is calculated from equation derived by song et al [9]:

$$\ln \frac{M_n}{n} = n \ln(\alpha) + \ln \frac{(1-\alpha)^2}{\alpha} \qquad (15)$$

Selectivity can be calculated by[3]:

$$S_n = n(1-\alpha)^2 \alpha^{n-1} \qquad (16)$$

4.2 Catalyst Preparation

4.2.1 Method Outline

Un-promoted Cobalt metal was used on TiO_2 support. The preparation method chosen was a two-step incipient wetness impregnation. The required weight of metal was 11%. The properties of metal precursor and the support powder used are shown in the following tables

Table 4.1: Properties of active metal precursor

Property	Cobalt nitrate hexa-hydrate
Molecular formula	$Co(NO_3)_2.6H_2O$
Molecular weight	291.03 g/mol
Solubility in water	103.8g/100ml (25^0C)
Melting point	55^0C
Boiling point	74^0C

Table 4.2: Properties of oxide ceramic support

Property	Titanium Dioxide
Molecular formula	TiO_2
Molecular weight	79.866 g/mol
Density	3.78 g/cm^3, (4.23 g/ cm^3 at heating above 600^0C)
Melting point	1843^0C
Boiling point	2972^0C

4.2.2 Calculations

Weight of the catalyst = 5g

Weight of support (89%) = 4.45g

Weight of metal required = 0.55g

For cobalt:

58.93 g cobalt in one mole of $Co(NO_3)_2.6H_2O$

0.55 g of cobalt requires = (291.03×0.55) / 58.93 = 2.48 g $Co(NO_3)_2.6H_2O$

4.2.3 Apparatus

1. 100ml beaker.
2. Weight balance.
3. Hot plate.
4. Mechanical stirrer.
5. Oven.
6. Muffle furnace.
7. Crucibles.

4.2.4 Preparation Procedure

1. Treat the required amount of support powder at 650^0C for 6hrs.
2. Dissolve the half of the required amount of metal precursor in distilled water having weight ratio of 1:10 (precursor: distilled water).
3. Pour the treated support powder in the solution.
4. Stir the solution containing support powder for 30 to 45 minutes vigorously.
5. Set the evaporation temperature between 80 and 100^0C.
6. After 80% evaporation, stop the stirrer and let it evaporate completely.
7. Grind the sample and dry it in vented oven for 24 hrs at 120 to 140^0C.
8. Repeat steps 2 to 7 for loading of the second half of precursor amount.
9. Heat-treat the sample at 550^0C for 6 hrs (5^0C/min temperature elevation rate).

The final catalyst properties are shown in table below:

Table 4.3: Catalyst properties

Property	Value
BET area	$35m^2/g$
Pore volume	$0.13g/cm^3$
Void fraction	0.45
Weight percent	11%CO, 89% TiO_2
Average pellet diameter	0.002m

4.3 Bench-scale FT Reactor:

A single tube fixed bed bench-scale reactor was used with ID of 9mm and tube length of 0.4m .Co/TiO_2 was inserted in the middle of the reactor, occupying 5mm of the reactor length (figure 3.1). The rest of the reactor was packed with ceramic balls and special type of cloth material.CO, H_2 flow was controlled through separate mass flow controllers (Sevenstar D07 MFC). Prior to the synthesis the catalyst went under reduction in H_2 for 16 hr at 350^0C at 0.4bar. Then the reactor was cooled down to 180^0C and pressurized to 1bar. Each run was started at 200^0C with H_2/CO ratios of 1, 2 & 3. After leaving the reactor the products pass through two traps, one hot and one cold. The hot and cold traps separate the heavy and light hydrocarbons from the product stream respectively. The samples were collected from the manual valves situated beneath the traps after 10 hrs of each run. Liquid sample analysis was done on an offline GCMS. Temperature of the reactor was controlled by placing one thermocouple near the wall at reactor's half length and the other in the catalyst bed. Pressure was controlled using a back-flow regulator.

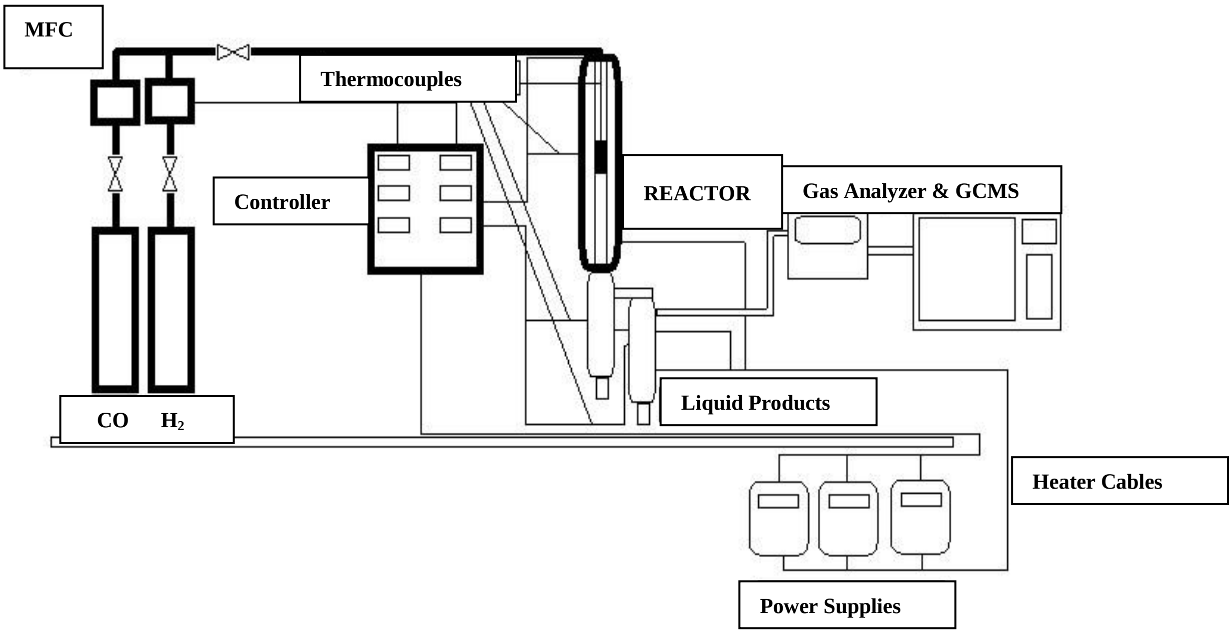


Figure 4.1: Bench-scale FT synthesis setup

3.3.1 Validity and up-scaling of the model:

Table 3.4 shows the operating conditions and dimensions of the bench scale plant. The model was validated via experimental results obtained. The results of the experimented and predicted values are shown in the table 3.5. It provides assurance of the validity of the model as well as the affect of different feed ratios on conversion and selectivity which decreased and increased respectively with decrease in ratios.

Table 4.4: Bench scale reactor dimensions

Property	Value
Length	30mm
Tube ID	9mm
Tube OD	11mm
Temperature	473K (200^{0}C)
Pressure	1bar

Table 4.5: Predicted and experimental results

H_2/CO	**3/1**		**2/1**		**1/1**	
	EXP	**PRE**	**EXP**	**PRE**	**EXP**	**PRE**
X_{CO}%	10.2	12.9	6.9	8.6	4.5	5.2
X_{H2}%	13.4	14.1	9.7	10.5	6.8	7.2
S_{CH4}%	6.11	5.90	4.54	5.10	3.20	3.70
S_{C5+}%	82.2	83.7	86.8	86.4	87.2	87.9
α-value	0.830	0.810	0.850	0.865	0.895	0.883

Table 4.6: Dimensions and conditions of a single tube in a commercial reactor

Parameter	Value
Length	12 m
Tube ID	0.03 m
H_2/CO Ratio	2/1
Pressure	25 bar
Temperature	493 K (220^{0}C)
Space Velocity	600h^{-1}

For parametric study the model was scaled up to industrial dimensions (Table 4.6).

SUMMARY

Detail about the catalyst preparation and bench scale reactor is outlined in this chapter. Equations of the 2-D model along with kinetic expressions of the fischer tropsch reaction on cobalt titanium oxide catalyst are also shown along with certain correlations needed for modelling and simulation. Comparisons between predicted and experimental results show good agreements and the model is up-scaled to commercial level for further predictions and optimization.

REFERENCES

[1] R. Zennaro, M. Tagliabue, C.H. Bartholomew, Kinetics of Fischer–Tropsch synthesis on titania-supported cobalt, Catal. Today. 58 (2000) 309–319.

[2] I.C. Yates, C.N. Satterfield, Intrinsic Kinetics of the Fischer-Tropsch Synthesis on a Cobalt Catalyst, (1991) 168–173.

[3] S. Storsæter, D. Chen, A. Holmen, Microkinetic modelling of the formation of C1 and C2 products in the Fischer–Tropsch synthesis over cobalt catalysts, Surf. Sci. 600 (2006) 2051–2063.

[4] M.J. Keyser, R.C. Everson, R.L. Espinoza, Fischer - Tropsch Kinetic Studies with Cobalt - Manganese Oxide Catalysts, (2000) 48–54.

[5] B.E. Poling, J.M. Prausnitz, The Properties Of Gases And Liquids, n.d.

[6] J. Xu, G.F. Froment, Methane steam reforming, methanation and water-gas shift: I. Intrinsic kinetics, AIChE J. 35 (1989) 88–96.

[7] J. Xu, G.F. Froment, Methane steam reforming: II. Diffusional limitations and reactor simulation, AIChE J. 35 (1989) 97–103.

[8] S. Yagi, D. Kunii, Studies on effective thermal conductivities in packed beds, AIChE J. 3 (1957) 373–381.

[9] H.-S. Song, D. Ramkrishna, S. Trinh, H. Wright, Operating strategies for Fischer-Tropsch reactors: A model-directed study, Korean J. Chem. Eng. 21 (2004) 308–317.

Chapter 5

Results and Discussions

5.1 Influence of Operating Parameters on the Reactor Behaviour

5.1.1 Reaction Rates:

The effects of all three parameters are shown in figures 5.1 and 5.2. Much research has been done on increasing the catalytic activity of cobalt based catalysts by adding little amounts of promoters to the cobalt supported catalysts. A study done by Morales et al [1] on MnO promoted Co/TiO_2 catalyst revealed that activity almost doubled after the introduction of MnO. Bao et al [2] experienced significant increase in heavy HCs selectivity after introducing CaO on Co/Al_2O_3 catalyst. Promotion of ruthenium on TiO_2 and SiO_2 supported cobalt catalyst increased TOF three times and C_5^+ selectivity from 84 to 91 [3]. Therefore, a factor of 3 has been added to the main rate equation in order to support the above said findings. The rate increased the conversions of both syngas components with an increase of 32% (CO) and 27% (H_2) from normal. Production C_5^+ and CH_4 also increased significantly.

5.1.2 Tube Diameter:

Tube diameter is an important parameter to be considered in reactor designing due to the requirement for high rate of heat transfer in order to minimize temperature variation in the reactor. Therefore, the diameter is minimized for attaining near isothermal conditions [4,5]. Hence the effect of tube diameter along with the high reaction rate of promoted cobalt catalyst on production and syngas conversion is shown. Model's prediction shows a further increased conversion. Production of heavy hydrocarbons was also increased but it was of less extent in comparison to methane.

5.1.3 Wall Temperature:

As the prediction shows, the conversion continues to increase with an increase in temperature and so does the production of hydrocarbons. However, high temperatures favour the formation of lighter hydrocarbons and as such the production of methane, an undesirable product and it increases with increase in temperature and there are some rational reasons for its unusual growth at high temperatures. A conclusion made by Wang et al. [5] on increasing the wall temperature was that higher temperatures would cause the species on the surface to desorb rather than propagate to higher molecular weight compounds resulting in an increase in methane selectivity. Consequently, high temperature favours the formation of branched alkanes and aromatics which is an advantage if high octane gasoline production is being considered [6]. Favourable results occur both in terms of syngas conversion and C_5^+ production although the production change is of a lesser extent whereas production of methane increased significantly, thus, indicating a change in product selectivity towards lower molecular weight hydrocarbons.

5.1.4 The Problem of a 'Hot Spot'

All three parameters have one major side effect; the famous hotspot. As shown in figure 5.3(a), increasing the reaction rate by a factor of three caused a steep temperature rise due to reactions occurring thrice faster than normal. A slight shift of the hotspot near the reactor inlet was also noted. Increase in tube diameter not only increased hotspot but also moved it towards the reactor exit as well as it broadened its range over the reactors length, thus increasing the average bed reaction temperature of the reactor and increasing its exit temperature. Ultimately it can be seen that the tube wall temperature further complicates the situation [5]. However, these temperature profiles were noted at the centre of the reactor in previous publications and the same prediction is seen here [7]. Radial temperature profiles show that the where the temperatures were maximum at the centre, the temperatures were close to the set reaction temperature near the tube wall (figures 5.3(b) & 5.4). Anyway, there are two general solutions to this problem. One is to increase overall gas space velocity. It will surely diminish the hotspot but will reduce the residence time and, hence, the conversion and production [4]. The other is to introduce nitrogen gas in the main syngas stream. Nitrogen plays an important role as an inert material that absorbs the reaction heat so as to help in reducing the average bed temperature. A downside to this is the suppression of partial pressures of H_2 and CO [8].

5.2 Performing Optimization

An optimized approach is put into practice for reducing the temperature variation in the reactor. The reactors length is divided in to fifteen sections and the cooling temperature of each section is adjusted according to the temperature rise in the reactor centre (figure 5.5) so the temperature can remain nearly constant in the axial direction at r=0 (figure 5.6(a)). Furthermore, due to cobalt's high activity narrower tube diameters are needed (section 5.2.2). However, with the above mentioned optimization even high tube diameters can be safely used. Increasing the pressure along with the gas inlet flow rate will also increase the production per reactor volume without altering the conversion due to residence time being the same [9]. Therefore it can be concluded that optimized cooling temperature in the 15 sections across the reactor along with increased pressure and flow rate will let conversion reduce a little but will increase the production volume and reduce methane selectivity and hence production yield. But since the increase in pressure and flow-rate have little effect on selectivity as compared to temperature [10], their effect is not covered in this thesis. The reason behind this reduction is the near isothermal optimization (at r=0) of the reactor. Highly exothermic reactions give sudden rise to temperature at the reactor inlet in case of an altered and un-optimized process (e.g, r=3r, ID=0.05m). The sudden spike in temperature that contributes in generating a reactor ‘hot spot’ also contributes in methane selectivity due to heat transfer limitations as well as the reasons mentioned in sub-section 5.2.4. Moreover, the radial temperature variation of the optimized process show the same trend as of the previous trends described in section 5.1 (figure 5.6(b)). Therefore, average temperature of the bed is decreased after applying optimization. Figure 5.7 depict the production of methane and heavy HCs after optimization. Table 5.1 summarizes the above parameter effects and the optimized solution on reactor temperature and Table 5.2 on alpha-value and selectivity. The reduction in average temperature and near isothermal temperature along the length at the centre of the reactor improved the selectivity better than the first four.

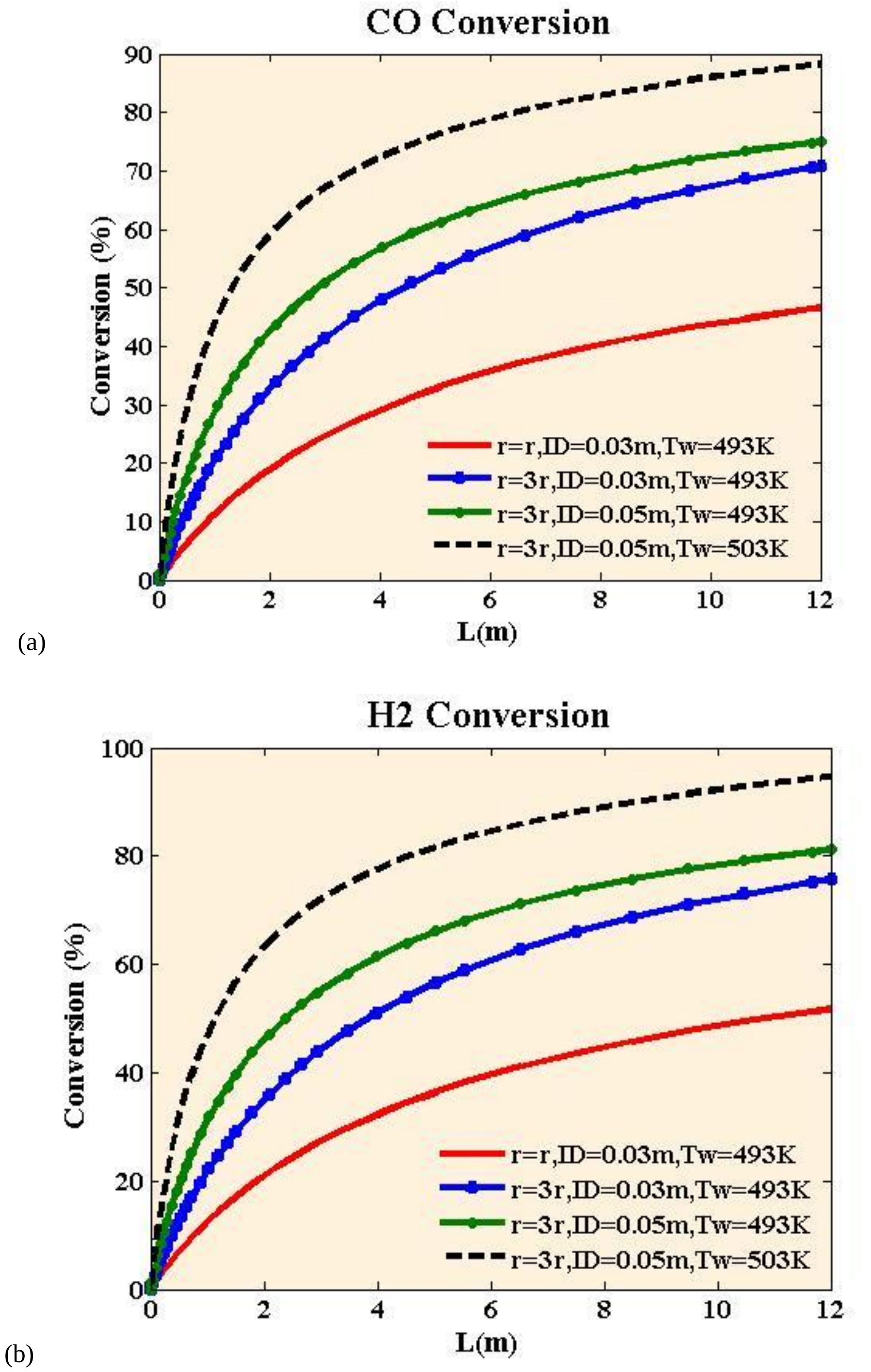
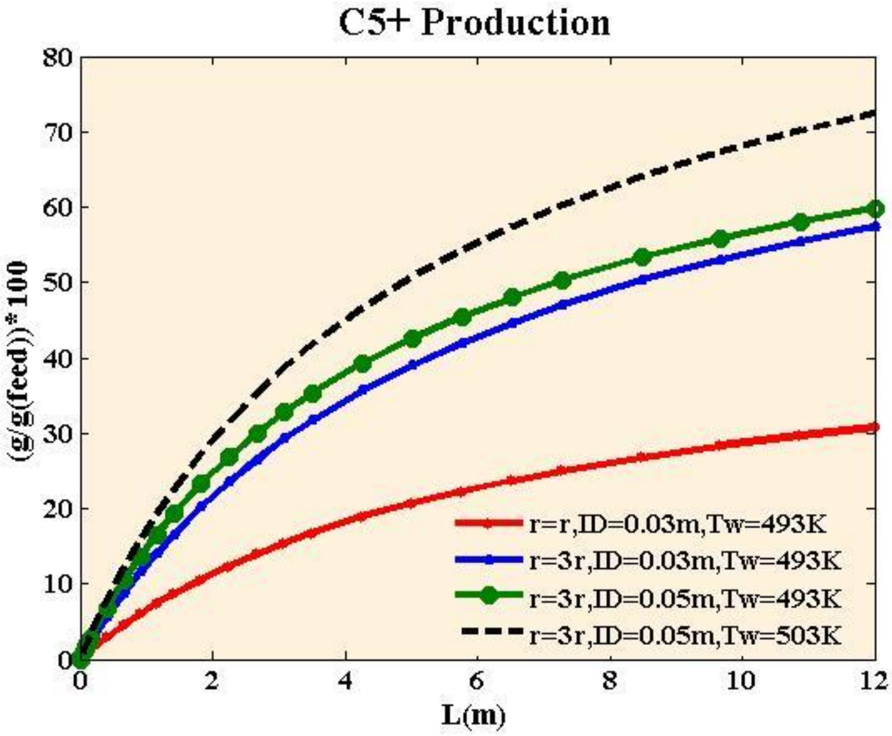
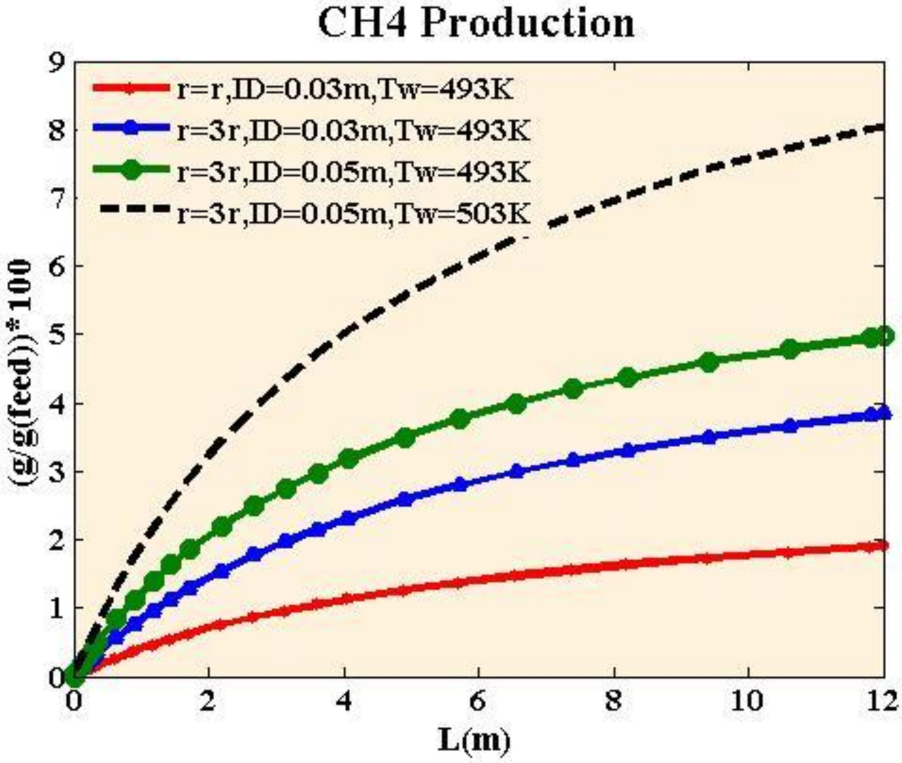


Figure 5.1: Synthesis gas conversion at different conditions 600h^{-1}12m 25bar



(a)



(b)

Figure 5.2: Production variation of at different conditions, 600h^{-1} 12m 25bar

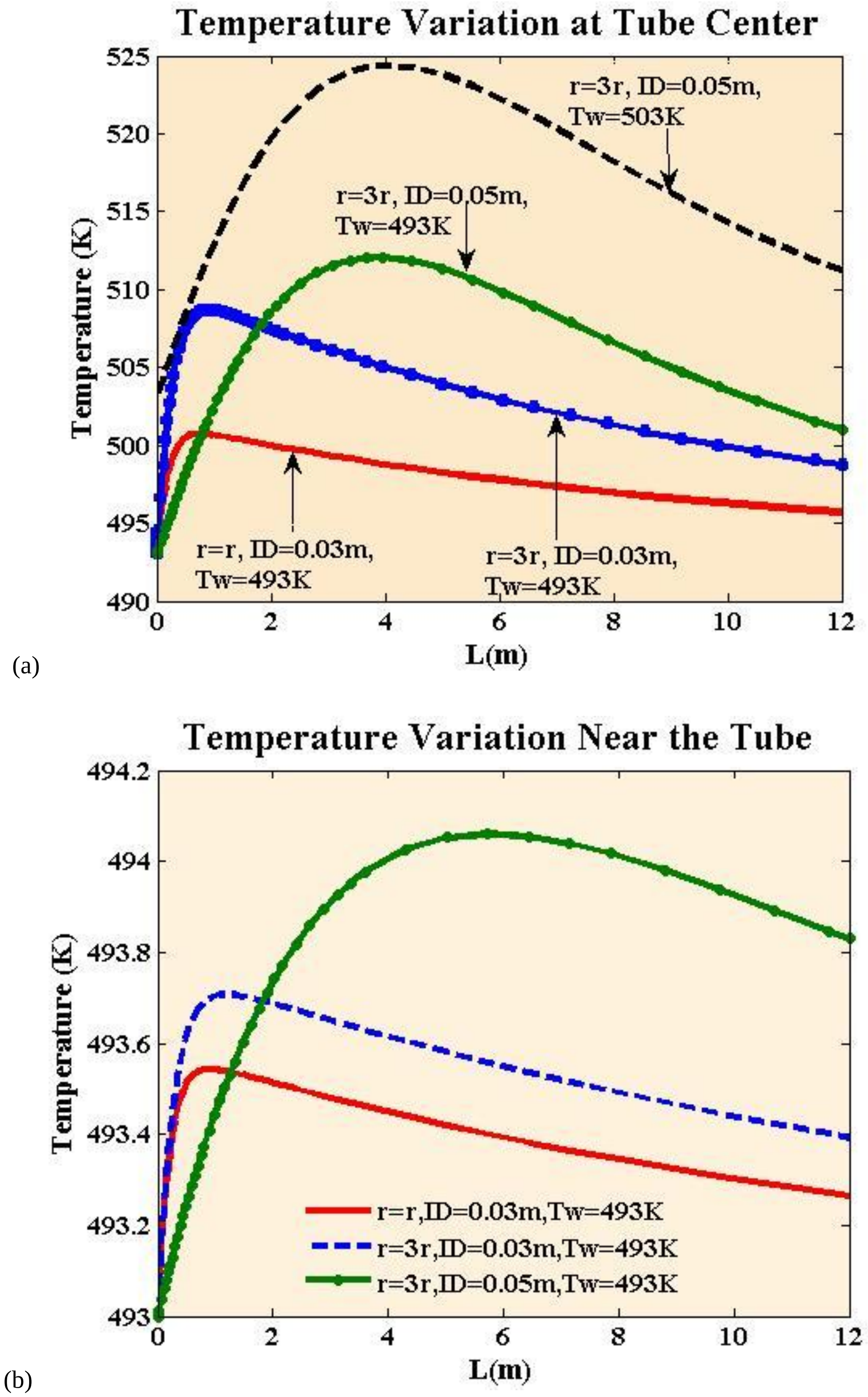
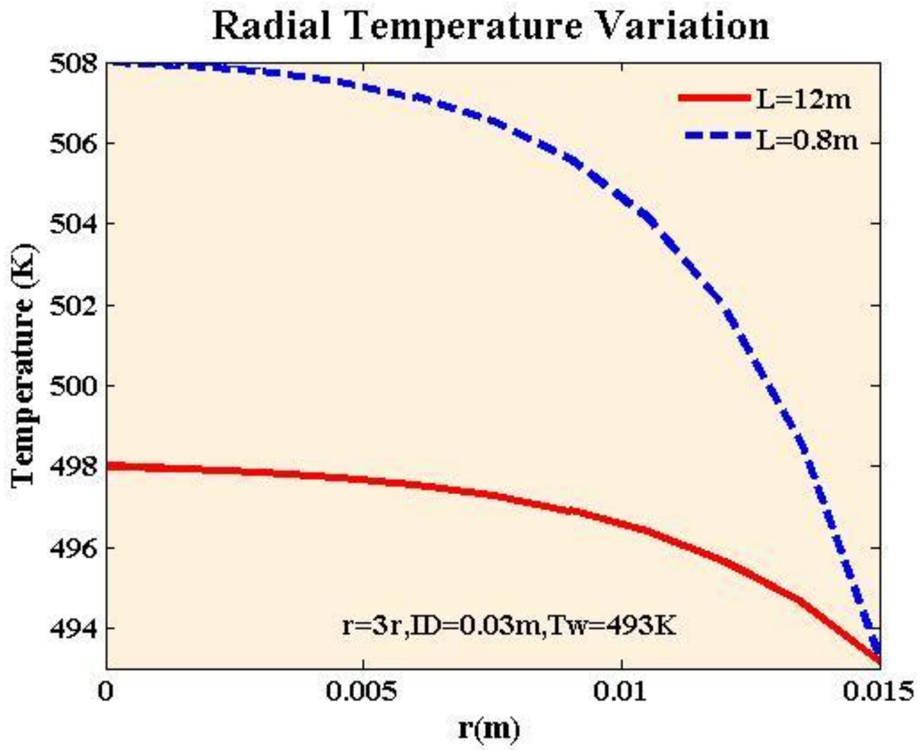
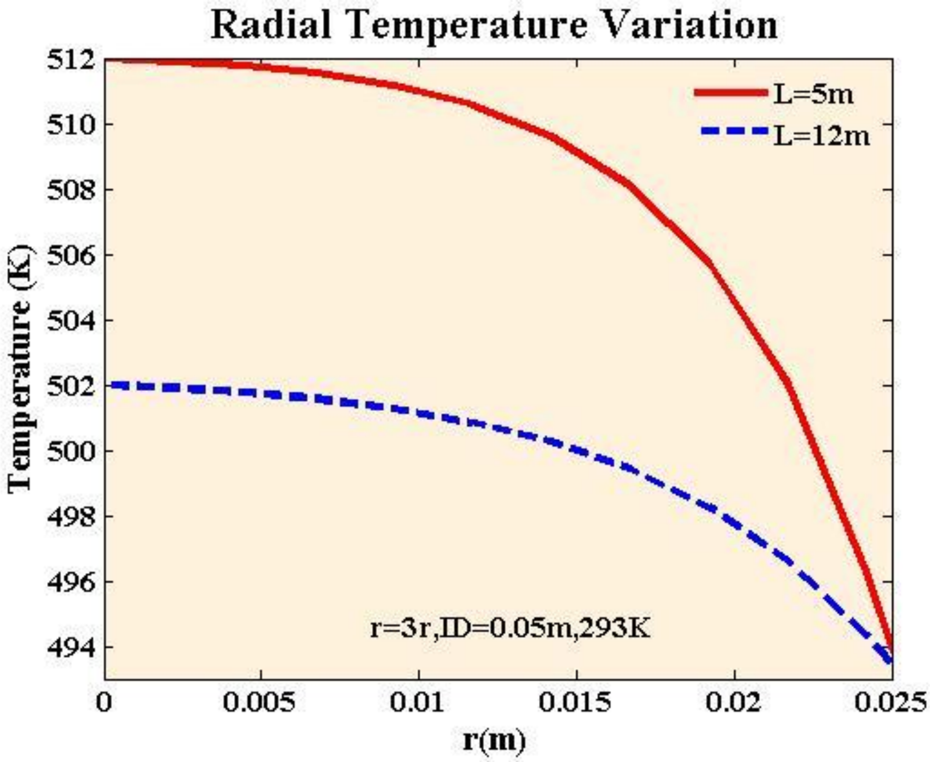


Fig 5.3: Axial temperature variation at centre and near the tube wall 600h^{-1} 25bar 12m



(a)



(b)

Figure 5.4: Radial temperature profile at different parameters 600h^{-1} 12m 25bar

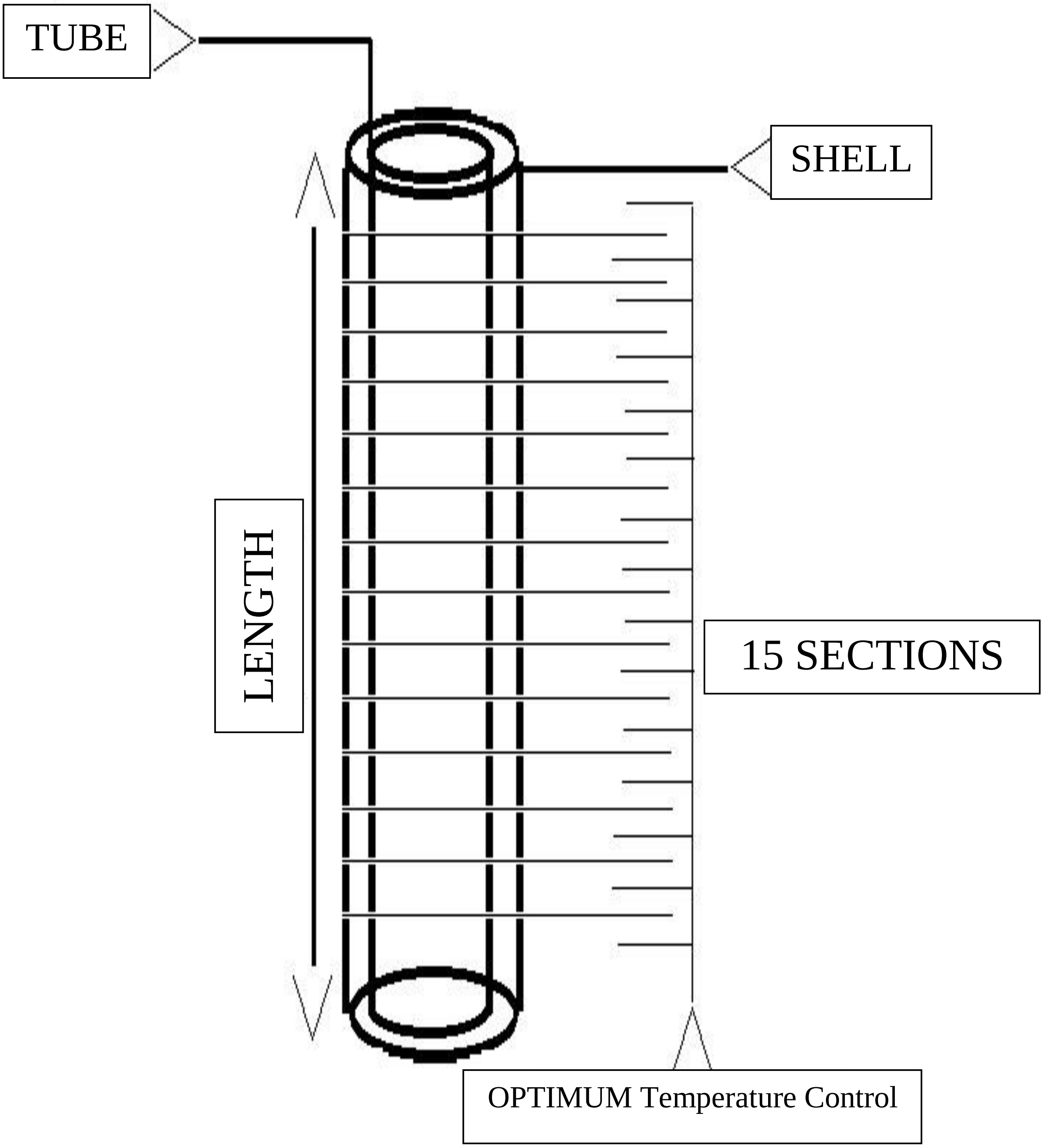
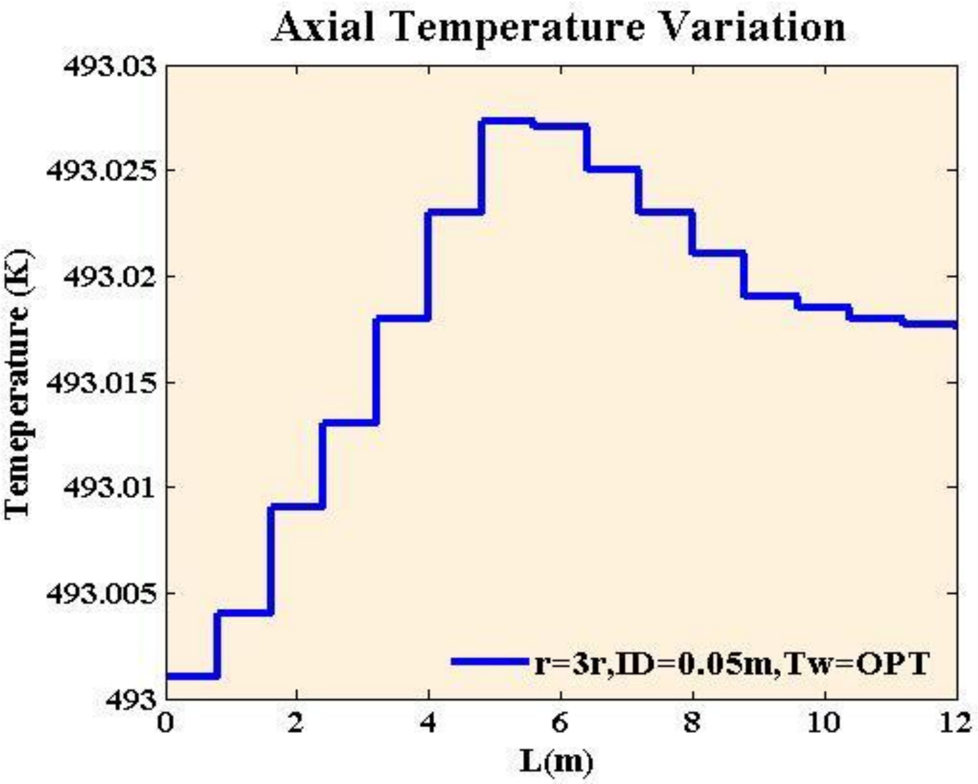
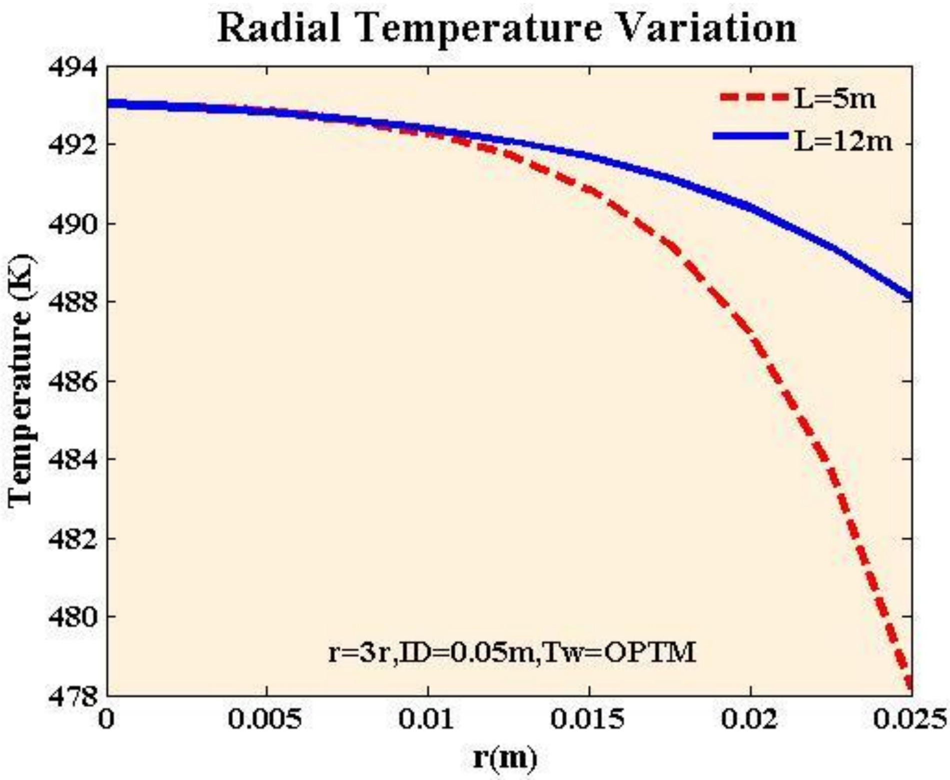


Figure 5.5: Optimized approach for temperature control



(a)



(b)

Figure 5.6: Axial(r=0) and Radial temperature variation after optimization, 600h^{-1} 12m 25bar

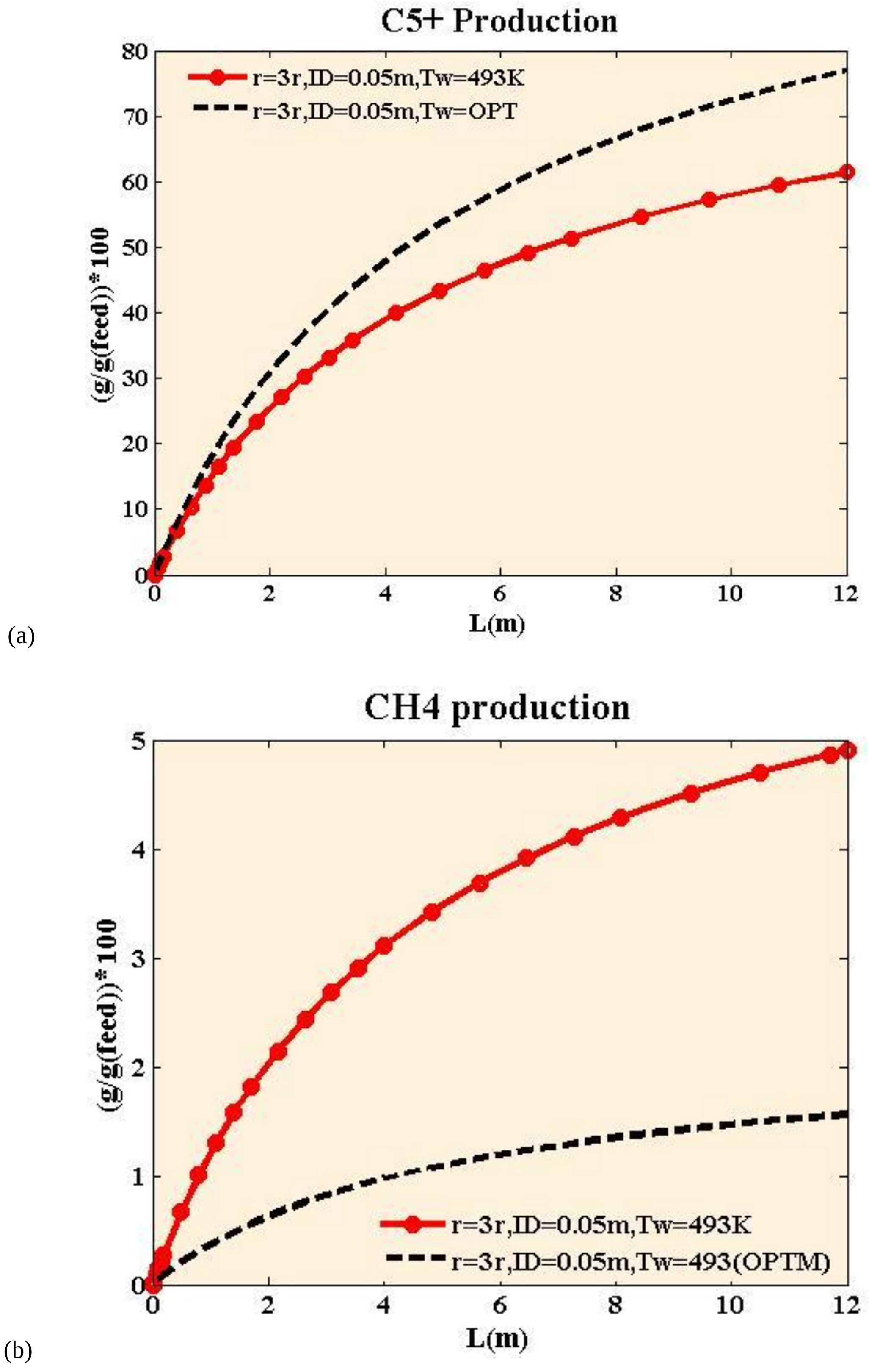


Figure 5.7: Production of CH_4 and C_5^+ after optimization, 600h^{-1}12m 25bar

Table 5.1: Average Reactor temperature under different conditions

RATE	**D_t (m)**	**T_w (K)**	**P (bars)**	**Avg. T_{react} (K).**
R	0.030	493	25	497
3r	0.030	493	25	502
3r	0.050	493	25	505
3r	0.050	503	25	512
3r	0.050	(L=6m)=477 (L=12m) =488 (L=0m)=493	25	484

Table 5.2: Selectivity at different average reactor temperatures

Avg. T_{react} (K).	**Alpha value**	**$S_{Light\ HC}$ %**	**$S_{Gasoline}$%**	**S_{Diesel}%**	**S_{wax}%**
497	0.806	22.05	39.93	34.20	3.42
502	0.795	25.29	41.94	30.83	2.65
505	0.787	26.54	42.51	27.14	2.19
512	0.770	30.5	43.32	22.64	1.45
484	0.837	17.9	34.74	41.68	6.86

SUMMARY

I this chapter, the 2-D pseudo homogeneous model on a single tube was up-scaled from laboratory size to commercial size after its validation from the experimental results and then effects of major parameters on conversion and production and temperature profiles were investigated. Finally, optimization of the axial temperature profile was achieved by adjusting the tube wall temperature from fifteen places along the length of the reactor. Axially the temperature remained nearly isothermal and radial-wise the same trend was noted as it was due the change in parameters discussed before. As a result, the average bed temperature was lowered which indicated a further improved selectivity in heavy hydrocarbons.

REFERENCES

[1] F. Morales, E. Desmit, F. Degroot, T. Visser, B. Weckhuysen, Effects of manganese oxide promoter on the CO and H2 adsorption properties of titania-supported cobalt Fischer–Tropsch catalysts, J. Catal. 246 (2007) 91–99.

[2] A. Bao, K. Liew, J. Li, Fischer–Tropsch synthesis on CaO-promoted Co/Al2O3 catalysts, J. Mol. Catal. A Chem. 304 (2009) 47–51.

[3] E. Iglesia, Bimetallic Synergy in Cobalt Ruthenium Fischer-Tropsch Synthesis Catalysts, J. Catal. 143 (1993) 345–368.

[4] N. Park, J.-R. Kim, Y. Yoo, J. Lee, M.-J. Park, Modeling of a pilot-scale fixed-bed reactor for iron-based Fischer–Tropsch synthesis: Two-dimensional approach for optimal tube diameter, Fuel. 122 (2014) 229–235.

[5] Y.-N. Wang, Y.-Y. Xu, Y.-W. Li, Y.-L. Zhao, B.-J. Zhang, Heterogeneous modeling for fixed-bed Fischer–Tropsch synthesis: Reactor model and its applications, Chem. Eng. Sci. 58 (2003) 867–875.

[6] M.E. Dry, The Fischer–Tropsch process: 1950–2000, Catal. Today. 71 (2002) 227–241.

[7] M.H. Rafiq, H. a. Jakobsen, R. Schmid, J.E. Hustad, Experimental studies and modeling of a fixed bed reactor for Fischer–Tropsch synthesis using biosyngas, Fuel Process. Technol. 92 (2011) 893–907.

[8] P. Hunpinyo, P. Narataruksa, S. Tungkamani, K. Pana-Suppamassadu, N. Chollacoop, H. Sukkathanyawat, et al., A comprehensive small and pilot fixed bed reactor approach for testing Fischer-Tropsch catalyst activity and performance on BTL route, Arab. J. Chem. (2013).

[9] M.E. Dry, The fischer-tropsch process - commercial aspects, Catal. Today. 6 (1990) 183–206.

[10] Y. Lu, T. Lee, Influence of the Feed Gas Composition on the Fischer-Tropsch Synthesis in Commercial Operations, J. Nat. Gas Chem. 16 (2007) 329–341.

Conclusions and Recommendations

The world is shifting towards unconventional means of producing transportation and energy generation fuels and chemicals from abundant resources of coal and natural gas as the age of conventional crude oil is nearing its end. Over the past decade oil prices have skyrocketed and the involvement of international politics is becoming increasingly problematic. Pakistan is also in this crisis as it majorly relies on imported crude for its needs. The country can use this new technology to boost its economy by producing domestic fuels from its abundant coal and gas reserves. In the present work a two-dimensional pseudo homogeneous plug-flow model was successfully developed for predicting general trends and optimization in a fixed bed reactor for Fischer Tropsch synthesis. Predicted results were validated with the experimental values and the model was upscaled to a single tube of commercial standard dimensions. Syngas conversion, methane and heavy HCs production and temperature profiles were observed by varying wall temperature, tube diameter, reaction rate. An increase in these significantly increased the gas conversion and heavy HCs but also added a noticeable increase in methane production. Furthermore, the reactor's bulk temperature was increased by increasing the parameters' values due to uneven heat removal. To minimize the effect an approach was taken to optimize the axial temperature profile. The length of the tube was divided into 15 sections and the tube wall temperature of each section was adjusted according to the temperature at the centre of the reactor. Simulation results show improved yields of heavy HCs and selectivity of diesel cuts although the conversion was reduce a little due to a drop in average reactor temperature.

Research on FT reactor modelling via MATLAB has not been carried out in Pakistan and thus further digging in this era needs to be carried out. Moreover, investigation on the use of high thermal conductivity and high heat coefficient material for tubes needs to be implemented.

NOMENCLATURE

u_{sv}	Superficial velocity	$(m.s^{-1})$
Ca	Component concentration	$(mol.dm^{-3})$
$-r_m$	Reaction rate	$(kmol.kg_{cat}^{-1}.s^{-1})$
ρ_B	Catalyst Bulk density	$(kg.m^{-3})$
ρ_g	Average Gas density	$(kg.m^{-3})$
C_p	Specific heat capacity	$(J.kg^{-1}.K^{-1})$
$-\Delta H$	Reaction Enthalpy	$(J.kmol^{-1})$
U	Heat Transfer Coefficient	$(W.m^{-2}.K^{-1})$
T_W	Wall Temperature	(K)
P	Pressure	(Bar)
d_p	Particle Diameter	(m)
R	Molar Gas Constant	$(J.kmol^{-1}.K^{-1})$
f	Friction Factor	
λ_{efr}	Effective radial thermal conductivity	$(W.m^{-1}.K^{-1})$
λ_g	gas thermal conductivity.	$(W.m^{-1}.K^{-1})$
r_o	outer tube radius	(m)
Re_p	Reynolds number	
a_w	Heat transport coefficient	$(W.m^{-2}.K^{-1})$
L	length	(m)
γ	Composition	(%)

SUBSCRIPTS

CO	Carbon monoxide
H_2	Hydrogen
CH_4	Methane
C_5^+	Heavy Hydrocarbons

Annex I

Optimization and Performance Investigation of FB Reactor on Bench Scale Fischer-Tropsch Facility

Y. Waheed[1], S. Iqbal[2], S. H. Ansari [3]

[1]MS Energy Systems Engg. , Centre for Energy Systems, NUST, Sector H-12, Islamabad, Pakistan

[2]. MS Energy Systems Engg. , Centre for Energy Systems, NUST, Sector H-12, Islamabad, Pakistan,

Abstract

Producing transportation and energy generation fuels and chemicals from abundant resources of coal and natural gas has been steadily gaining popularity as the age of conventional crude oil is nearing its end. Over the past decade oil prices have skyrocketed and the involvement of international politics is becoming increasingly problematic due to oil not being globally available including countries like Pakistan as it majorly relies on imported crude for its major energy and transportation needs. The use of Coal/natural gas to liquids technology will boost it struggling economy by producing low cost domestic fuel from its abundant coal reserves. A comprehensive two-dimensional homogeneous plug-flow model was developed for predicting general trends in a fixed bed reactor for Fischer Tropsch synthesis on un-promoted cobalt/titania catalysts. Predicted results were validated with the experimental values by changing feed ratios and after that, syngas conversion, methane and heavy HCs production and temperature profiles were observed by varying different operating parameters. It was concluded that high wall temperature, reaction rate and tube diameter will significantly increase the gas conversion and heavy HCs but will also increase methane production. Furthermore, the reactor temperature was increased by increasing the parameters

Keywords: Fischer-tropsch; syngas; conversion; production; fixed bed reactor

Introduction

Fischer-Tropsch process has gone through extensive R&D over nearly a century and is now one of the most popular and major option for making clean transportation fuels. The technology involves a catalytic polymerization of carbon monoxide to give clean and ordered liquid hydrocarbon composition using catalysts that are either supported or un supported. Paraffins are its major products and the major side products are methane and carbon dioxide. However, the production of methane is highly un-desirable as the technology's sole purpose is to produce liquid products only[1]. Cobalt or iron are commercially used as catalysts for this synthesis. Cobalt is expensive than iron but is almost 250 times more active and it produces more higher molecular weight hydrocarbons than iron at a relatively low temperature. Raw syngas contains CO, H_2, CO_2, CH_4 and N_2. More H_2 and CO can be obtained via air reforming of methane and CO_2 can be separated by conventional means. Therefore, syngas with a ratio of 2/1 was used for this study. Since the cost of diesel is more than gasoline in many countries, especially south-asian and European countries, promotion of the use of cobalt in this process can have great advantage.

Multi Tubular, Fluidized and slurry reactors are the commercially used designs for this purpose. The tubular fixed bed reactor (TFBR) has the distinctive advantage of not requiring separation of the product from catalyst and also the ease of scale up from one tube to thousands of tubes. It also has the highest possible catalyst loading per reactor volume and, therefore, has the highest potential of productivity per reactor volume. Plus, only the catalyst area near the inlet tube is affected by the reactants impurities while other areas remain fully functional. Furthermore, wax product can be easily separated from the catalyst. Still, heat removal in reactor requires attention for maximizing heavy HC production[2]. Considerable amount of literature has been found on TFBR modeling and design. Irani et al[3] used computational fluid dynamics as a technique to check the prediction of the reactor model using a novel iron catalyst. A 1D dimensional heterogeneous model was applied by Wang et al[4] to study the performance of the fixed bed reactor. Atwood and Bennett[5] discussed parameter effects on commercial reactors using a 1D heterogeneous model. Mazidi and Sadeghi[6] researched on the maximum gasoline yield using non uniform catalysts in a one dimensional heterogeneous model. Guttel and Turek[7] compared SBCRs and FBRs on a 1D approach with cobalt based catalysts. Momonov and Kustov[8] investigated the effects of linear gas velocity and tube diameter using a 1D heterogeneous model Research has being carried out in Pakistan only on the practical preparation and performance of cobalt –based catalysts[9,10]. Pakistan having the 7th largest coal reserves is a very potential place where FT process can be used as today the country is facing high inflation and high oil prices. Also, this unconventional means of fuel production guarantees sulfur and nitrogen free product than the conventional[11]. Therefore, to understand its trends, it has to be studied at a micro level before the domestic industrial level and software modeling and simulation of such a process can be extremely useful for the better future of the country and its engineers. In this work, a two dimensional pseudo homogeneous plug flow model was first used to predict the general effects of operating parameters on conversion, production and thermal stability of the reactor.

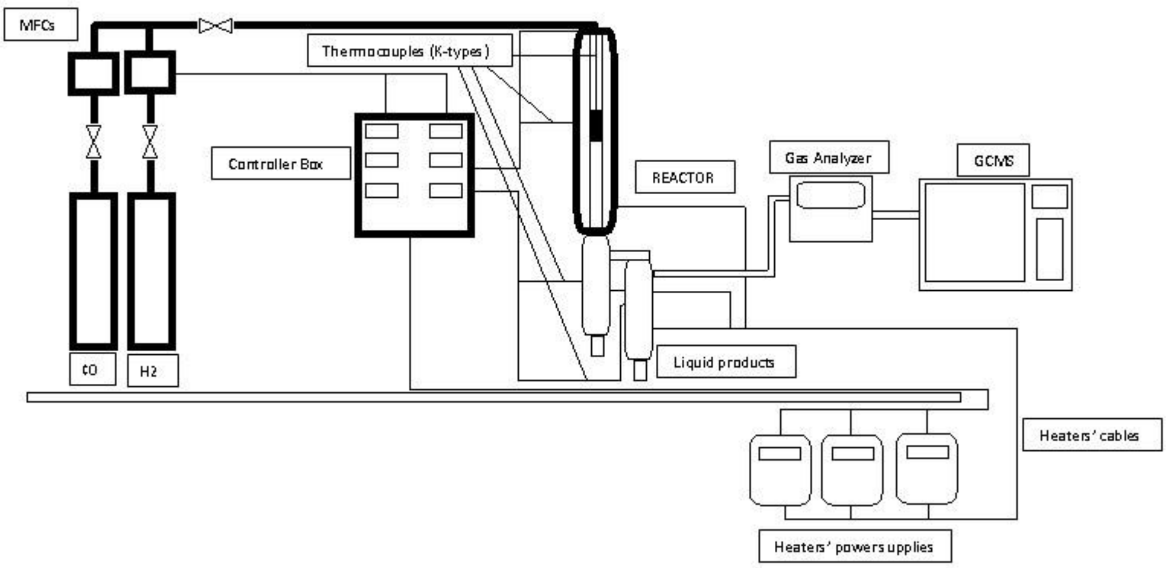


Fig 2: Schematic diagram of bench scale fixed-bed reactor

Table 1:Catalyst Properties

Property	**Unit**	**Content**
Titania	Wt%	89
Cobalt	Wt%	11
Surface Area	m^2/g	255
Diameter	Milimeters	2
Bulk density	kg/m^3	800

Annex I

Experimental Section

A. *FT reactor*

A single tube fixed bed bench-scale reactor was used with ID of 9mm and tube length of 0.3m (figure 1) .Co/TiO_2 catalyst with the properties shown in table 1 was inserted in the middle of the reactor. The rest of the reactor was packed with ceramic balls and special type of cloth material.CO, H_2 flow was controlled through separate mass flow controllers (Sevenstar D07 MFC). Prior to the synthesis the catalyst went under reduction in H_2 for 16 hr at 350^0C at 0.4bar. Then the reactor was cooled down to 180^0C and pressurized to 1bar. The synthesis was started at 200^0C with H_2/CO ratio of 2. A run time of 10 hrs for three runs with different feed ratios was conducted under constant pressure and temperature. After leaving the reactor the products pass through two traps, one hot and one cold. The hot and cold traps separate the heavy and light hydrocarbons from the product stream respectively. The samples from each run were collected from the manual valves situated beneath the traps. Sample analysis was done on an offline GCMS. Temperature of the reactor was controlled by placing one thermocouple near the wall and the other in the catalyst bed. Pressure was controlled using a back-flow regulator.

Table 2: Bench-scale reactor operating conditions

Parameter	**Unit**	**Value**
Pressure	Bar	1
Wall Temperature	K	473
Metal heat coeff.	$W.m^{-1}.K^{-1}$	45
Length	M	0.4
ID	Mm	9
OD	Mm	11
Space velocity	h^{-1}	230

B. *Reactor model*

Reactor dimensions and operating conditions are outlined in table 2. Following assumptions were made in the model:

1. Plug-flow regime so no axial dispersion.
2. Steady-state conditions.
3. Pseudo homogeneous model is applied.
4. No external mass transfer limitations.
5. Non-isothermal condition due to a noticeable temperature change along the reactor.

Radial concentration gradients are neglected. The main FT reaction rate on Cobalt/Titania catalyst by the Zennaro expression[12] is taken for this study. Since the catalyst used was cobalt no water-gas shift reaction is taken into account due to cobalt catalyst's negligible in-situ WGS activity and the H_2/CO ratio taken in this study being above 2. Since C1 and C2 compounds deviate from the ASF theory, it was used for higher HCs whereas individual rate laws were given for the compounds mentioned above [13] The temperature dependant constants were calculated according to the experimental results and the energies of activation were taken from the. available literature[14][15]. The mass and energy balance equations can be written as follows.

Mass balance:

$$u_s\rho_g \frac{\delta\, C_a}{\delta Z} = \rho_g C_a \frac{\partial u_s}{\delta Z} + C_a u_s \frac{\delta u_s}{\delta Z} - r_a \rho_{\boldsymbol{B}} \tag{1}$$

Energy balance:

$$u_s\rho_g C_p \frac{\delta T}{\delta Z} = (-\Delta H)\rho_B r_a + \lambda_{er}.\left(\frac{1}{r}.\frac{\delta T}{\delta r} + \frac{\delta^2 T}{\delta r^2}\right) \tag{2}$$

Overall pressure drop was calculated using Ergun Law:

$$-\frac{\delta P}{\delta Z} = f.\frac{\rho.u_s^2}{d_p} \tag{3}$$

Change in density and superficial velocity were calculated by:

$$\frac{\delta\rho_g}{\delta Z} = \frac{M}{R}\cdot\left(\frac{1}{T}\cdot\frac{\delta P}{\delta Z} - \frac{P}{T^2}\cdot\frac{\delta T}{\delta Z}\right) \tag{4}$$

$$\frac{\delta u_s}{\delta Z} = \frac{u_s}{\rho}\cdot\frac{\delta\rho_g}{\delta Z} \tag{5}$$

Boundary conditions:

$$\frac{\delta C}{\delta r} = 0 \qquad for\ all\ Z\ and\ r \qquad (6)$$

$$\frac{\delta T}{\delta r} = 0 \qquad for\ all\ Z\ at\ r = 0 \qquad (7)$$

$$\frac{\delta T}{\delta r} = -\frac{U}{\lambda_{er}}\left((T\ at\ r = R) - T_W\right) for\ all\ Z \qquad (8)$$

Component and mixture heat capacities were calculated using equations derived by Poling[16]. The overall heat transfer coefficient equation was taken from the co-relations used for 2-D model[17]. The effective radial thermal conductivity was calculated from equations derived by Forment[18]. The superficial gas velocity was obtained based on overall mass flux and gas mixture density. Finite difference method was applied. MATLAB's ODE solver was used to conduct the numerical simulation.

Overall Heat transfer coefficient:

$$\frac{1}{U} = \frac{1}{a_w} + \frac{d_i}{2\lambda_s} ln \frac{d_o}{d_i} \qquad (9)$$

Effective radial thermal conductivity:

$$\lambda_{er} = \lambda_{er}^0 + 0.111\lambda_g \cdot \frac{Re_p + Pr^{1/3}}{1 + 46\left(\frac{d_p}{2 \cdot r_o}\right)^2} \qquad (10)$$

Where

$$\lambda_{er}^0 = \varepsilon \cdot \left(\lambda_g + 0.95 + \alpha_{ru} + d_p\right) + \frac{0.95 \cdot (1-\varepsilon)}{2/(3 \cdot \lambda_s) + 1/\left(10 \cdot \lambda_g \cdot \alpha_{rs} \cdot d_p\right)} \qquad (11)$$

Is the thermal conductivity of the catalyst bed without the presence of fluid and α_{ru} and α_{rs} are taken from literature[19].

Main equation of the kinetic model:

$$r = \frac{a(\frac{E_a}{RT}) C_{H_2}^{0.74} C_{CO}}{\left(1 + b(\frac{E_b}{RT}) C_{CO}\right)^2} \qquad (12)$$

Table 3: Experimental and Predicted Results 473K, 1Bar

H_2/CO	**3/1**		**2/1**		**1/1**	
	EXP	PRE	EXP	PRE	EXP	PRE
A	0.83	0.81	0.85	0.845	0.895	0.883
X_{CO}%	10.2	10.9	6.9	7.5	4.5	4.9
X_{H2}%	13.4	14.1	9.7	10.5	6.8	7.2
S_{CH4}%	6.11	5.90	4.54	5.10	5.20	5.70
S_{C2}%	1.45	2.11	1.95	2.32	1.34	1.97
S_{C3}%	3.53	3.30	3.84	3.47	2.70	3.15
S_{C4}%	3.70	3.95	2.95	3.75	2.53	3.67
S_{C5+}%	85.2	84.7	86.7	85.4	87.2	85.5

The conversion equation can be shown as:

$$Conversion = \frac{amount\ entered - amount\ left}{amount\ entered} \times 100$$

The experimented and predicted values are shown in the table 3 which shows a good overall agreement and ensures the reduction in conversion with decrease in feed ratio. To investigate other parameters and the thermal stability of the reactor, the single tube was scaled-up to the size of that found in a conventional multi tubular reactor with Co/TiO_2 catalysts fitted throughout the tube (table 4).

Results and Discussion

A. *Effect of parameters*

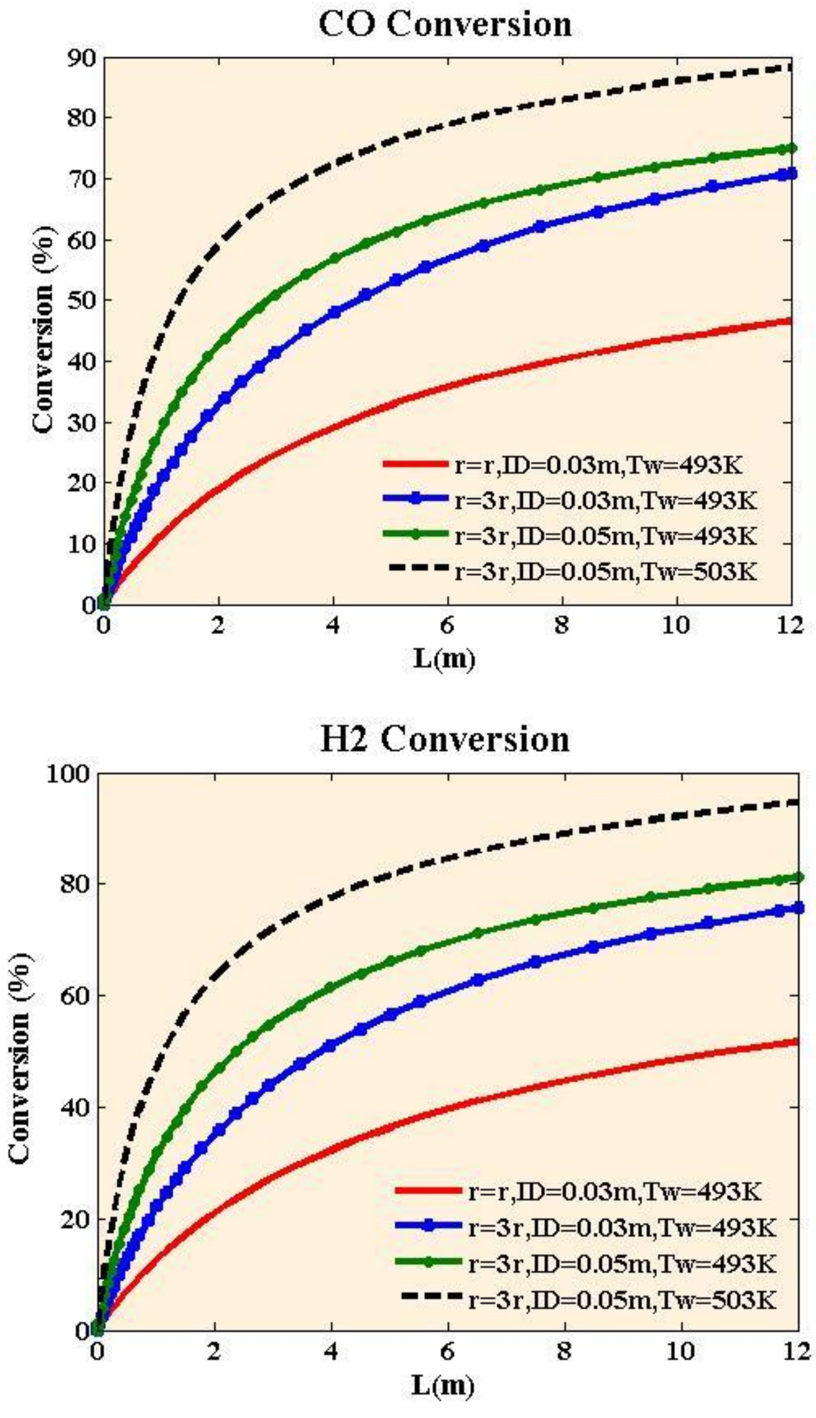
The effects of all three parameters are shown in figures 2 and 3 and tables 5 and 6**.** Much research has been done on increasing the catalytic activity of cobalt based catalysts by adding little amounts of promoters to the cobalt supported catalysts. A study done by Morales et al[20] on MnO promoted Co/TiO_2 catalyst revealed that activity almost doubled after the introduction of MnO. Bao et al[21] experienced significant increase in heavy HCs selectivity after introducing CaO on Co/Al_2O_3 catalyst. Therefore, a factor of 3 has been added to the main rate equation in order to support the above said findings. The rate increased the conversions of both syngas components with an increase of 32% (CO) and 27% (H_2) from normal. Production C_5^+ and CH_4 also increased significantly.

Table 4: Single Tube Dimensions (Commercial Standards)

Property	**Value**
Length	12 m
Tube ID	0.03 m
H_2/CO ratio	2/1
Pressure	25 bar
Temperature	493 K (220^{0}C)
Volumetric flow-rate	(600h^{-1})

Tube diameter is an important parameter to be considered in reactor designing due to the requirement for high rate of heat transfer in order to minimize temperature variation in the reactor. Therefore, the diameter is minimized for attaining near isothermal conditions [4] [12]. Hence the effect of tube diameter along with the high reaction rate of promoted cobalt catalyst on production and syngas conversion is shown. Model’s prediction shows a further increased conversion. Production of heavy hydrocarbons was also increased but it was of less extent in comparison to methane.

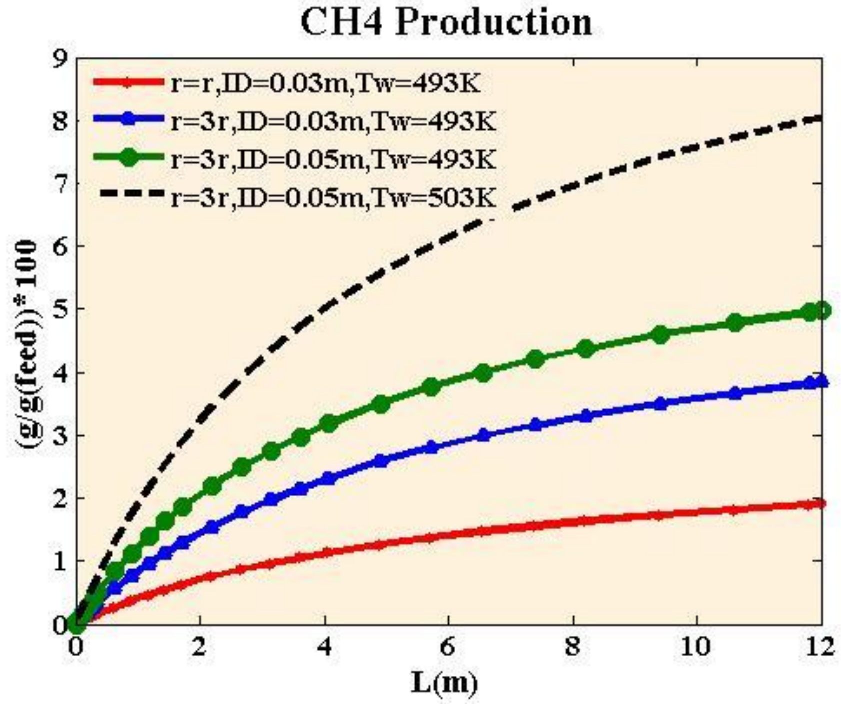
For wall temperature, as the prediction shows, the conversion continues to increase with an increase in this parameter and so does the production of hydrocarbons. However, high temperatures favor the formation of lighter hydrocarbons and as such the production of methane, an undesirable product and it increases with increase in temperature and there are some rational reasons for its unusual growth at high temperatures. A conclusion made by Wang et al. [4] on increasing the wall temperature was that higher temperatures would cause the species on the surface to desorb rather than propagate to higher molecular weight compounds resulting in an increase in methane selectivity. Consequently, high temperature favors the formation of branched alkanes and aromatics which is an advantage if high octane gasoline production is being considered. Favorable results occur both in terms of syngas conversion and C_5^+ production although the production change is of a lesser extent whereas production of methane increased significantly, thus, indicating a change in product selectivity towards lower molecular weight hydrocarbons.



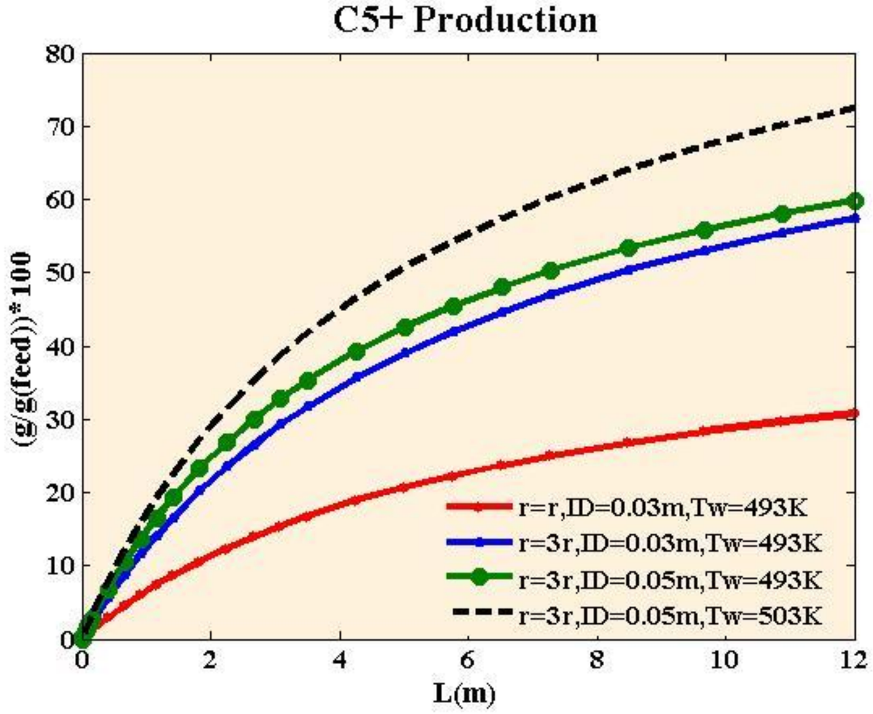
(a)

(b)

Fig 2: Conversion at different operating conditions $600h^{-1}$, 12m, 25bar



(a)



(b)

Fig 3: Production at different operating conditions 600h^{-1}, 12m, 25bar

B. *The 'Hot Spot' problem:*

All three parameters have one major side effect; the famous hotspot. As shown in figure 4(a), increasing the reaction rate by a factor of three caused a steep temperature rise due to reactions occurring thrice faster than normal. A slight shift of the hotspot near the reactor inlet was also noted. Increase in tube diameter not only increased hotspot but also moved it towards the reactor exit as well as it broadened its range over the reactors length, thus increasing the average bed reaction temperature of the reactor and increasing its exit temperature (table 5), plus, reduction in selectivity (table 6). Ultimately it can be seen that the tube wall temperature further complicates the situation. However, these temperature profiles were noted at the centre of the reactor in previous publications and the same prediction is seen here [1].Radial temperature profiles show that the where the axial temperatures were maximum at the centre, the temperatures were close to the set reaction temperature near the tube wall (figures 4(b) & (c)). Anyway, there are two general solutions to this problem. One is to increase overall gas space velocity [3]. It will surely diminish the hotspot but will reduce the residence time and, hence, the conversion and production. The other is to introduce nitrogen gas in the main syngas stream. Nitrogen plays an important role as an inert material that absorbs the reaction heat so as to help in reducing the average

Table 5: Average Reactor Temperatures under Different Conditions

Sr No.	**Rate**	**D_t (m)**	**T_w (K)**	**P (bars)**	**Avg. T_{react} (K).**
1	r	0.030	493	25	496.07
2	3r	0.030	493	25	502.21
3	3r	0.050	493	25	505.12
4	3r	0.050	503	25	512.27

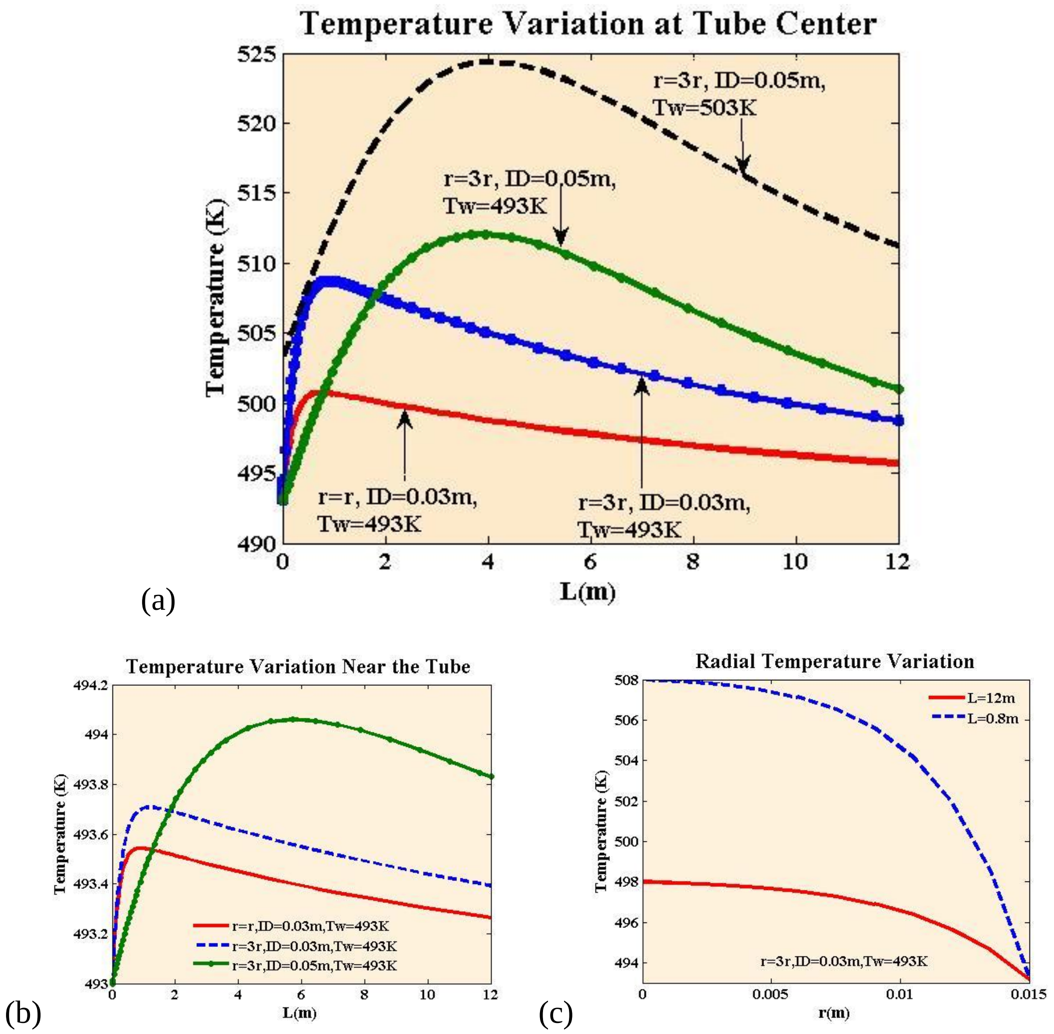
Table 6: Selectivity at Different Average Reactor Temperatures

Sr No.	**Avg. T_{react} (K).**	**Alpha value**	**$S_{Light\ HC}$ %**	**$S_{Gasoline}$%**	**S_{Diesel}%**	**S_{wax}%**
1	496.07	0.806	22.05	39.93	34.20	3.42
2	502.21	0.795	25.29	41.94	30.83	2.65
3	505.12	0.787	26.54	42.51	27.14	2.19
4	511.27	0.770	30.5	43.32	22.64	1.45

bed temperature. A downside to this is the suppression of partial pressures of H_2 and CO[22].

Conclusions

In the present work a two-dimensional pseudo homogeneous plug-flow model was successfully developed for predicting general trends and optimization in a fixed bed reactor for Fischer Tropsch synthesis. Predicted results were validated with the experimental values. Syngas conversion, methane and heavy HCs production and temperature profiles were observed by varying wall temperature, tube diameter, reaction rate. An increase in these significantly increased the gas conversion and heavy HCs but also added a noticeable increase in methane production. Furthermore, the reactor's bulk temperature was increased by increasing the parameters' values. Research on FT reactor modeling via MATLAB has not been carried out in Pakistan



(a)

(b)

(c)

Fig 4: Axial and radial temperature profile at different conditions, 600h^{-1}, 12m, 25 bar and thus further digging in this era needs to be carried out. Moreover, investigation on the use of high thermal conductivity and high heat coefficient material for tubes needs to be implemented.

Acknowledgements

We thank Fauji Fertilizer Company (FFCL) for providing funds for the bench scale FT facility.

ABBREVIATIONS

TFBR	Tubular Fixed-Bed Reactor
SBCR	Slurry Bubble-Column Reactor
GHSV	Gas hourly space velovity
HC	Hydro-Carbon
ASF	Anderson Schulz Flory

Nomenclature

u_{sv}	Superficial velocity	$(m.s^{-1})$
ρ_B	Catalyst Bulk density	$(kg.m^{-3})$
C_p	Specific heat capacity	$(J.kg^{-1}.K^{-1})$
$-\Delta H$	Reaction Enthalpy	$(J.kmol^{-1})$
U	Heat Transfer Coefficient	$(W.m^{-2}.K^{-1})$
T_W	Wall Temperature	(K)
P	Pressure	(Bar)
d_p	Particle Diameter	(m)
R	Molar Gas Constant	(J/kmol.K)
λ	Thermal conductivity	$(W.m^{-1}.K^{-1})$
L	length	(m)

Annex I

References

[1] M.H. Rafiq, H. a. Jakobsen, R. Schmid, J.E. Hustad, Experimental studies and modeling of a fixed bed reactor for Fischer–Tropsch synthesis using biosyngas, Fuel Process. Technol. 92 (2011) 893–907.

[2] J.H. Yang, H.-J. Kim, D.H. Chun, H.-T. Lee, J.-C. Hong, H. Jung, et al., Mass transfer limitations on fixed-bed reactor for Fischer–Tropsch synthesis, Fuel Process. Technol. 91 (2010) 285–289.

[3] M. Irani, G. Division, Modeling of fischer – tropsch synthesis packed bed reactor for producing liquid fuels from natural gas, 55 (2013) 82–92.

[4] Y.-N. Wang, Y.-Y. Xu, Y.-W. Li, Y.-L. Zhao, B.-J. Zhang, Heterogeneous modeling for fixed-bed Fischer–Tropsch synthesis: Reactor model and its applications, Chem. Eng. Sci. 58 (2003) 867–875.

[5] H.E. Atwood, C.O. Bennett, Kinetics of the Fischer-Tropsch Reaction over Iron, Ind. Eng. Chem. Process Des. Dev. 18 (1979) 163–170.

[6] S.K. Mazidi, M.T. Sadeghi, M. a. Marvast, Optimization of Fischer-Tropsch Process in a Fixed-Bed Reactor Using Non-uniform Catalysts, Chem. Eng. Technol. 36 (2013) 62–72.

[7] R. Guettel, T. Turek, Comparison of different reactor types for low temperature Fischer–Tropsch synthesis: A simulation study, Chem. Eng. Sci. 64 (2009) 955–964.

[8] N. a. Mamonov, L.M. Kustov, S. a. Alkhimov, M.N. Mikhailov, One-dimensional heterogeneous model of a Fischer-Tropsch synthesis reactor with a fixed catalyst bed in the isothermal granules approximation, Catal. Ind. 5 (2013) 223–231.

[9] N. Ahmad, J.A. Anderson, Influence of Gold Promoter on Fischer Tropsch Synthesis Over Col Al203 Catalysts ., (2013) 11–15.

[10] N. Ahmad, S.T. Hussain, B. Muhammad, T. Mahmood, Z. Ali, N. Ali, et al., Effect Of The Reaction Conditions On Al-Pillared Montmorillonite Supported Cobalt-Based Catalysts For Fischer Tropsch Synthesis, 8 (2013) 347–358.

[11] U. States, Z. Ft, U. Diesel, A. Force, C. C-, T. Transit, et al., Zero-Sulfur Diesel Fuel from Non-Petroleum Resources : The Key to Reducing U . S . Oil Imports, (n.d.).

[12] R. Zennaro, M. Tagliabue, C.H. Bartholomew, Kinetics of Fischer–Tropsch synthesis on titania-supported cobalt, Catal. Today. 58 (2000) 309–319.

[13] R.B. Anderson, R. a. Friedel, H.H. Storch, Fischer-Tropsch Reaction Mechanism Involving Stepwise Growth of Carbon Chain, J. Chem. Phys. 19 (1951) 313.

[14] I.C. Yates, C.N. Satterfield, Intrinsic Kinetics of the Fischer-Tropsch Synthesis on a Cobalt Catalyst, (1991) 168–173.

[15] M.J. Keyser, R.C. Everson, R.L. Espinoza, Fischer - Tropsch Kinetic Studies with Cobalt - Manganese Oxide Catalysts, (2000) 48–54.

[16] B.E. Poling, J.M. Prausnitz, The Properties Of Gases And Liquids, n.d.

[17] J. Xu, G.F. Froment, Methane steam reforming: II. Diffusional limitations and reactor simulation, AIChE J. 35 (1989) 97–103.

[18] J. Xu, G.F. Froment, Methane steam reforming, methanation and water-gas shift: I. Intrinsic kinetics, AIChE J. 35 (1989) 88–96.

[19] S. Yagi, D. Kunii, Studies on effective thermal conductivities in packed beds, AIChE J. 3 (1957) 373–381.

[20] F. Morales, E. Desmit, F. Degroot, T. Visser, B. Weckhuysen, Effects of manganese oxide promoter on the CO and H2 adsorption properties of titania-supported cobalt Fischer–Tropsch catalysts, J. Catal. 246 (2007) 91–99.

[21] A. Bao, K. Liew, J. Li, Fischer–Tropsch synthesis on CaO-promoted Co/Al2O3 catalysts, J. Mol. Catal. A Chem. 304 (2009) 47–51.

[22] A. Jess, R. Popp, K. Hedden, Fischer – Tropsch-synthesis with nitrogen-rich syngas Fundamentals and reactor design aspects, 186 (1999) 321–342.

Modeling of a fixed bed reactor for the production of liquid fuel from syngas

Yasir Waheed[1], Ansari S.H[2], Dr. Shahid Naveed[3]

[1] Yasir Waheed[1] MS Energy Systems Engineering, Centre for Energy Systems (CES-NUST), National University of Sciences and Technology (NUST), Islamabad Pakistan
[2]Asst. Prof, Centre for Energy Systems (CES-NUST), National University of Sciences and Technology (NUST) Islamabad, Pakistan shahid.ansari@ces.nust.edu.pk; ipofficer@gmail.com
[3] Ex-Dean, Faculty of Chemical Engineering, University of Engineering and Technology, Lahore

ABSTRACT

Fischer-Tropsch process can be used as a viable option for producing diesel and gasoline fuel via indirect liquefaction of coal in Pakistan. Pakistan is being faced with terrible energy crisis and unaffordable transportation and power generation fuel prices due to such fuels being not domestically extracted. The use of this indirect coal liquefaction process can greatly benefit the country in terms of low cost sulfur-free fuel and research in this era in Pakistan need to be given importance today. In this study the effect of temperature and space velocity was investigated with a one-dimensional pseudo homogeneous tubular fixed bed reactor model for fischer tropsch synthesis of syngas using cobalt based catalyst. The model was applied using appropriate kinetics and the base operating conditions were taken from the experimental data. A good overall agreement was concluded in the comparison between experimental and calculated results based on the accuracy of the model. Prediction of the model reviled an increase in Syngas conversion and net increase in C_5^+ production by increasing space velocity and temperature. However, high temperature did increased the gas conversion but was not favoured due to increase in methane production.

Key words: Pakistan, Fischer tropsch, Syngas, C_5^+*, methane, Cobalt.*

Introduction:

Over the past eighty years, fischer-tropsch process has gone through extensive R&D and is now one of the most popular and major option for making clean transportation fuels and chemicals. This phenomenon involves the catalytic hydrogenation of carbon monoxide to give clean and ordered liquid hydrocarbon composition via a combination of polymerisation reactions using catalyst that are either supported or un supported. The major products of this process are the long chain hydrocarbons and the major side product is methane and carbon dioxide [1]. Since this process was invented to produce high quality transportation liquid fuels, the production of methane is highly un-desirable [2]. The commercial catalysts used for this process are cobalt or iron based catalyst [3]. Cobalt is expensive than iron but is almost 250 times more active and it produces more higher molecular weight than iron at a relatively low temperature [3]. Raw syngas contains CO, H_2, CO_2, CH_4 and N_2. Methane can be further converted to H_2 and CO via air reforming and CO_2 can be separated by conventional means. Using these assumptions, a nitrogen-rich syngas was used for this study containing 35% H_2, 15% CO and 50% N_2. The major advantage of the use of nitrogen is its ability to reduce the exothermic hydrogenation temperature and it promotes the production of diesel [4]. Since the cost of diesel is more than gasoline in many countries, especially south-asian countries, promotion of the use of cobalt in this process can have great advantage.

The four major reactor designs used in this process are tubular fixed bed, fixed fluidized bed, circulating fluidized bed and slurry bubble column reactors. The tubular fixed bed (TFBR) still holds the advantage of not requiring separating the product from the catalyst and also the ease of scale up from one tube to thousands of tubes. It also has the highest possible catalyst loading per reactor volume and, therefore, has the highest potential of productivity per reactor volume [5]. Still, reactor optimization is required for maximizing heavy HC production. Not a lot of literature has been found on TFBR modelling and design. Wang et al [6] proposed a 1D dimensional heterogeneous model to study the performance of the fixed bed reactor. De Swart et al [7] used 1D heterogeneous model to study TFBRs on cobalt based catalyst. Guttel and Turek [8] compared SBCRs and FBRs on a 1D approach with the inclusion of all the mass transfer limitations using cobalt based catalysts. Irani et al [23] used computational fluid dynamics as a technique to check the prediction of the reactor model usin a novel iron catalyst. Atwood and Bennett [9] studied parameter effects on commercial reactors using a 1D heterogeneous model. Momonov and Kustov [24] studied the effects of linear gas velocity and tube diameter using a 1D heterogeneous reactor. Marwast et al [10] used both 1D and 2D homogeneous models to study the performance of FBRs using Bi-functional iron catalyst. Mazidi and Sadeghi [25] checked the maximum gasoline yield using non uniform catalysts in a one dimensional heterogeneous model. Nonam et al [26] studied the effect of tube diameter on conversion and thermal behavior using a 2D mathematical model for an iron-based Fischer-tropsch synthesis.

Very little research is being carried out in Pakistan and it is only on the practical designing and performance of catalyst [11, 12]. Pakistan having the 4th largest coal reserves is a very potential place where FT process can be used as today the country is facing high inflation and high oil prices. Also, synthetic fuel is very less polluting than conventional [13]. In order to establish an industrial plant, it has to be studied at a micro level and software modeling and simulation of such a process can be extremely useful for the better future of the country and its engineers. Therefore, for a start, a one dimensional pseudo homogeneous model was developed. Although it is not as accurate as the 2D model when predicting the temperature runaway of the reactor [10], it can be used to give some basic predictions about the process. The model was validated by comparing with the experimental results obtained from the works of Rafiq et al [14].

Reactor model development:

A single tube fixed bed reactor with ID of 0.0272m and tube length of 2m was considered packed with a bed of commercial Co/Al_2O_3 catalyst of spherical shape with the properties shown in Table 1. The reactor operating conditions were set at 473K, 20 bars and the following assumptions were made in the model:

6. One dimensional plug-flow model without axial dispersion.
7. Non-isothermal condition due to a noticeable temperature change along the reactor.
8. No external mass transfer limitations.

The main FT reaction rate on cobalt catalyst by the Yates and Satterfield expression [15] is taken for this study. Since the catalyst used was cobalt no water-gas shift reaction is taken into account due to cobalt catalyst's negligible in-situ WGS activity and the H_2/CO ratio taken in this study being above 2. Specific rate laws were given for methane and ethane formation while the higher HCs, ASF theory was applied using α, the chain growth probability value [16]. The pre-exponential factors of the four kinetic parameters in the kinetic model were taken from Rafiq et al [14]. Activation energies were taken from the literature available [15, 17, 18]. The above parameters are shown in table 2. The model used was a one dimensional pseudo homogeneous plug-flow type to simulate the TFBR. It is a tubular reactor with boiling water as a coolant in the shell. The mass and energy balance equations can be written as follows.

<u>Mass balance:</u>

$$\frac{\partial u_s\, C_a}{\partial Z} = -r_a\rho_{\boldsymbol{B}}$$

<u>Energy balance:</u>

$$u_s\rho_g C_p\frac{\partial T}{\partial Z} = (-\Delta H)\rho_B r_a - 4\frac{U}{d_t}(T_w - T_g)$$

<u>Overall pressure drop was calculated using Ergun Law:</u>

$$-\frac{\partial P}{\partial Z} = f.\frac{\rho. u_s^2}{d_p}$$

Component and mixture heat capacities were calculated using equations derived by Reid et al [19]. The overall heat transfer coefficient was calculated using leva's correlation [20]. The superficial gas velocity was obtained based on overall mass flux and gas mixture density. MATLAB's ODE solver was used to do the numerical integration of the independent variable i.e. reactor length (z).

Validity of the model

The model was validated by comparing it with the experimental results of Rafiq et al [14]. AARE (Absolute average relative error) equation showed the model’s accuracy. This equation was also used by Emrani and Saber [21] for accuracy calculation. The results are shown in table 3 and are in fair agreement with the experimental results.

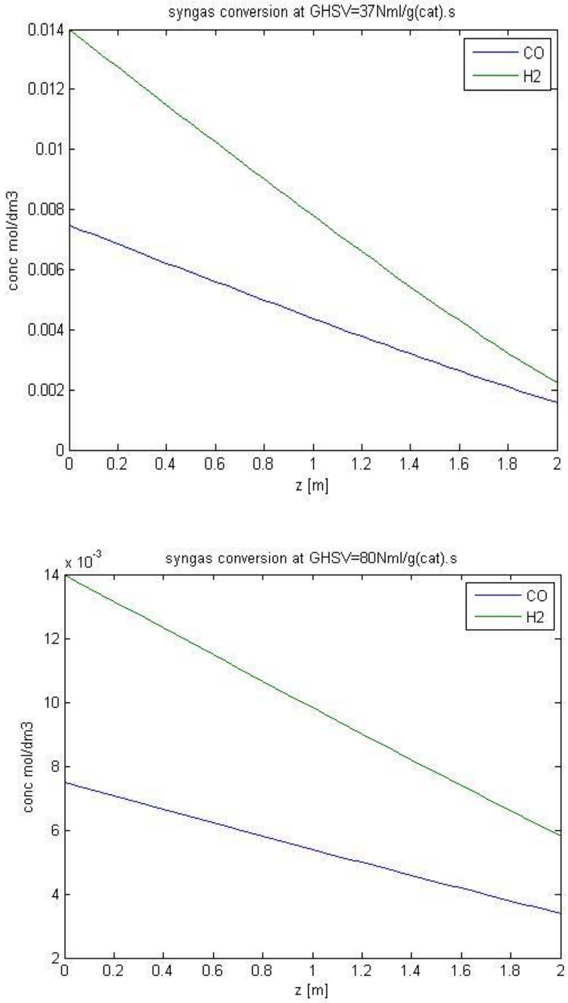


Fig 1: Effect of GHSV on syngas conversion (T=473K, P=20 bars and Tube Diameter = 27.2mm)

Kinetic model used in this study:

$$r_{FT} = \frac{a.\exp\left(\frac{E_a}{RT}\right) C_{CO} C_{H_2}}{\left(1 + b.\exp\left(\frac{E_b}{RT}\right) C_{CO} C_{H_2}\right)}$$

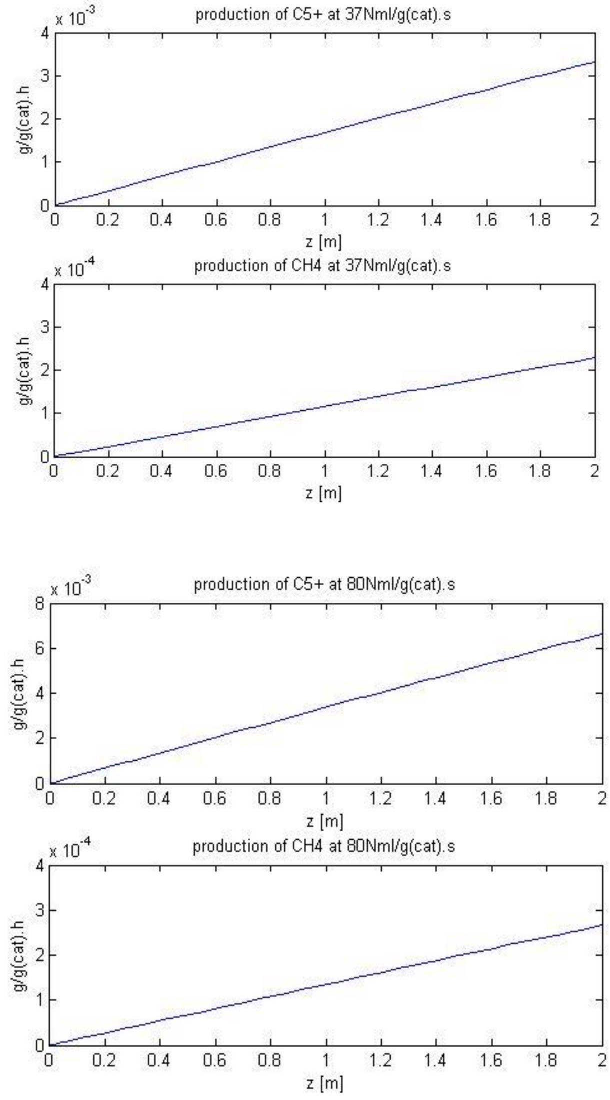
$$r_{CO} = -r_{FT}$$

$$r_{H_2} = -2r_{FT}$$

$$r_{CH_4} = c.\exp\left(\frac{E_c}{RT}\right) r_{FT}$$

$$r_{C_5^+} = \alpha . r_{FT}$$

$$\boldsymbol{ARRE} = \frac{1}{n}\sum_{i=1}^{n}\left|\left(\frac{C(cal)_i - C(ex)_i}{C(ex)_i}\right)\right| \times 100$$



(a)

(b)

Fig 2: Effect of GHSV on product formation (T=473K, P=20 bars and Tube Diameter = 27.2mm)

Results and discussion

I. *Effect of GHSV*

The model along with the reaction kinetics outlined by Rafiq et al [14] was used to investigate the effect of operating parameters on the product yield and syngas conversion. **Figs. 1(a)** and **1(b)** represent the effect on syngas conversion by change in GHSV. The effect on the production of methane and C_5^+ HCs by GHSV is also presented in **Figs. 2(a)** and **2(b)**.

Table 1: Catalyst used in this study

Property	**Unit**	**Real content**
Alumina	Wt%	88
Cobalt	Wt%	9.5
Surface Area	m^2/g	255
Diameter	Mm	3
Bulk density	kg/m^3	700
Voidage		0.44

The results indicate that the syngas conversion is higher at low GHSV. This can be reasoned with the fact that at higher space velocities, the contact time or residence time is decreased, thus affecting the conversion. However, higher GHSVs suppress the formation of lower molecular weight HCs with low syngas conversion on the basis that high GHSVs results in the enhancement of the propagation of higher molecular weight compounds by the surface species thus slightly shifting the product distribution towards higher molecular weight of HC [14]. The predicted overall production of C_5^+ HCs and CH_4 indicates an increasing effect when GHSV is increased.

Table 2: Kinetic parameters

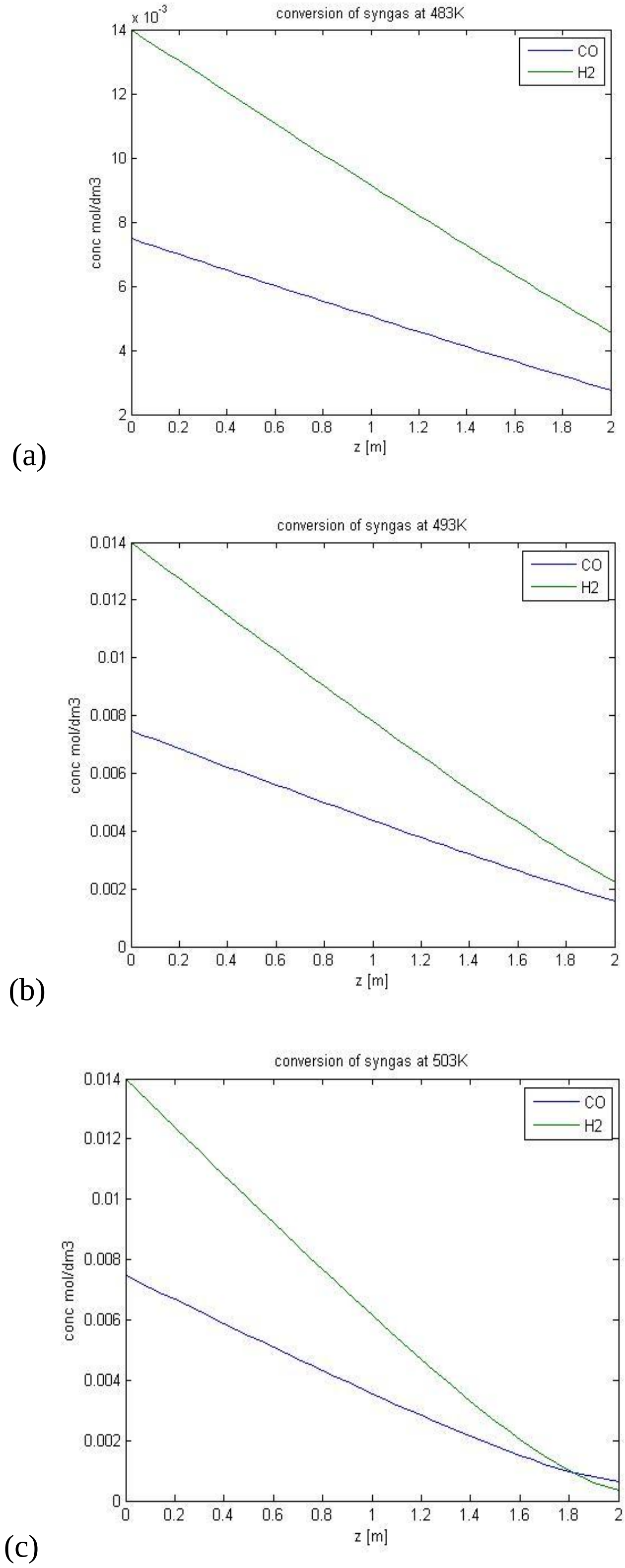
Parameters	**Unit**	**Value**
A	$m^6/mol.g_{cat}.s$	18.41
E_a	kJ/mol	100
B	m^3/mol	3.69
E_b	kJ/mol	20
C		$2.08x10^8$
E_c	kJ/mol	81

Table 3: AARE for major products

Component	**AARE%**
C_5^+	5.11
CH_4	9.44

I. Effect of wall temperature

Figures 3 and 4 show the models prediction about the effect of wall temperature on both the conversion and production. It is clearly shown that the overall syngas conversion is lower at 483K and considerably higher at 503K. Moreover, the production of methane and heavier hydrocarbons has also been increased with rise in wall temperature. Since methane is an undesirable product, there are many explanations for its increased production at high temperatures. Wang et al. [6] reported that an increase in wall temperature caused reactions to occur more rapidly near the entering zone of the reactor and releasing too much reaction heat that became



(a)

(b)

(c)

Fig 3: Effect of wall temperature on syngas conversion (P=20 bars, Tube diameter = 27.2mm)

difficult to be removed. Chernobev and Yakubovich reasoned that due to the increase in temperature, carbide formation on the catalyst surface increases and thus the hydrogenization of CO is reduced [2]. In easy words, higher temperatures would

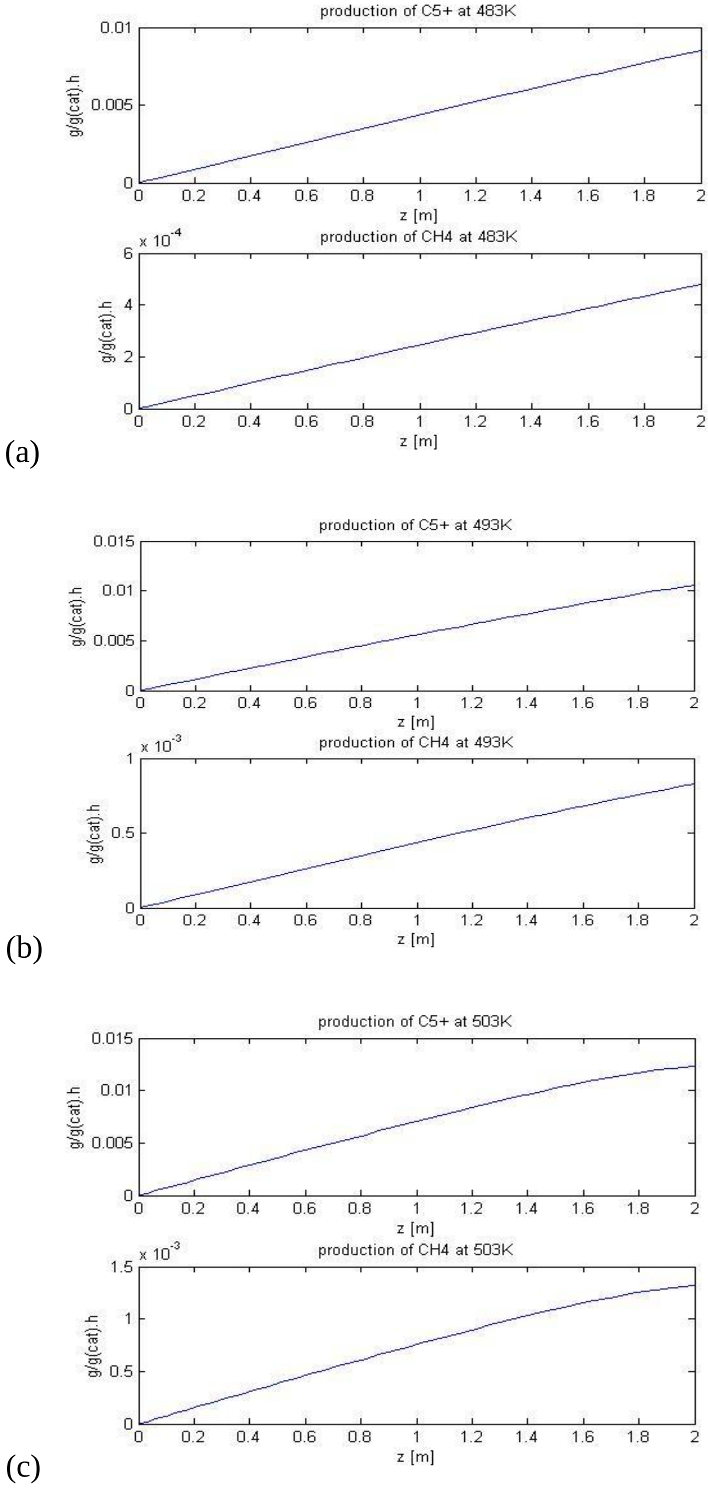


Fig. 4: Effect of wall temperature on product formation. (P=20bars, Tube diameter = 27.2mm)

cause the surface species to desorb rather than propagate to higher molecular weight compounds. Another possible reason for increased methane production can be the thermal cracking of higher molecular weight compounds at elevated temperatures as explained by Irani and co-workers [22]. Therefore it can be concluded that increasing the wall temperature would not be good for reactor safety and would favour methane production.

Conclusions

A one dimensional pseudo homogeneous plug-flow model was successfully developed to predict the performance of a fixed bed reactor. The results were validated and were within the acceptable error limits. Syngas conversion and methane and heavy HCs production were observed by varying GHSV and the wall temperatures. It was concluded that conversion is gradually lowered with increasing GHSV whereas production of heavy HCs are increased. As for wall temperature, an increase in this significantly increased the gas conversion and heavy HCs but also added a noticeable increase in methane production. The reactor model can be used for basic prediction and not for scale-up. Research on FT reactor modeling via MATLAB has not been carried out in Pakistan and thus further digging in this era needs to be carried out by developing a more accurate two dimensional model.

Acknowledgements:

The support of Muhammad Noman Aslam Khan is acknowledged.

Nomenclatures:

u_s	Superficial velocity (m/s)
Ca	Component concentration (mol/dm^3)
$-r_a$	Reaction rate (kmol/kg$_{cat}$.s)
ρ_B^{cat}	Catalyst Bulk density (kg/m^3)
ρ_g	Average Gas density (Kg/m^3)
C_p	Specific heat capacity (J/Kg.K)
$-\Delta H$	Reaction Enthalpy (J/kmol)
U	Heat Transfer Coefficient (W/m^2.K)
T_W	Wall Temperature (K)
T_G	Gas Temperature (K)
P	Pressure (Bar)
d_p	Particle Diameter (m)
E	Activation energy (KJ/Kg)
R	Molar Gas Constant (J/kmol.K)

TFBR	Tubular Fixed-Bed Reactor
SBCR	Slurry Bubble-Column Reactor
f	Friction Factor

Subscripts:

CO	Carbon monoxide
H_2	Hydrogen
CH_4	Methane
C_5^+	Heavy Hydrocarbons
FT	Fischer tropsh

References

[1] A. Steynberg, M. Dry, M.E. Davis, B.B. Breman, Fischer–Tropsch Technology, in: A.Steynberg, M. Dry (Eds.), Studies in Surface Science and Catalysis, 152, Elsevier,Amsterdam, 2004

[2] I.I. Chernobaev, M.N. Yakubovich, A.I. Tripolskii, N.V. Pavlenko, V.L. Struzhko, Investigation of the mechanism of methane formation in the Fischer–Tropsch synthesis on a Co/SiO2ZrIV catalyst, Theor. Exp. Chem. 33 (1997) 38–40.

[3] H. Schulz, Short history and present trends of Fischer–Tropsch synthesis, Appl.Catal. A 186 (1999) 3–12

[4] A. Jess, R. Popp, K. Hedden, Fischer–Tropsch synthesis with nitrogen-rich syngas: Fundamentals and reactor design aspects, Appl. Catal. A. 186 (1999) 321–342.

[5] J.H. Yang, H.K. Kim, D.H. Chun, H.T. Lee, J.C. Hong, H. Jung, J. Yang, Mass transfer limitations on fixed-bed reactor for Fischer–Tropsch synthesis, Fuel Process. Technol. 91 (2010) 285–289.

[6] Y.N. Wang, Y.Y. Xu, Y.W. Li, Y.L. Zhao, B.J. Zhang, Heterogeneous modelling for fixed-bed Fischer–Tropsch synthesis: Reactor model and its applications, Chem. Eng. Sci. 58 (2003) 867–875.]

[7] J.W.A. de Swart, R. Krishna, S.T. Sie, Natural gas conversion IV, in: M. de Pontes, R.L.Espinoza, C.P. Nicolaides, J.H. Scholz, M.S. Scurrell (Eds.), Studies in Surface Science and Catalysis, 107, Elsevier, Amsterdam, 1997.

[8] R. Guttel, T. Turek, Comparison of different reactor types for low temperature Fischer–Tropsch synthesis: A simulation study, Chem. Eng. Sci. 64 (2009) 955–964.

[9] H.E. Atwood, C.O. Bennett, Kinetics of the Fischer–Tropsch reaction over iron, Ind. Eng. Chem. Process Des. Dev. 18 (1979) 163–170.

[10] M.A. Marvast, M. Sohrabi, S. Zarrinpashne, G. Baghmisheh, Fischer–Tropsch Synthesis: Modelling and performance study for Fe-HZSM5 bifunctional catalyst, Chem. Eng. Technol. 28 (2005) 78–86.

[11] N.Ahmad, S.T.Hussain, Jim A. Anderson, Influence of Gold promoter on Fischer-Tropsch Synthesis over Co/Al2O3 catalysts, Appl. Sci. Technol. (2013) 11-15

[12] N.Ahmad, S.T.Hussain, Effect of the reaction conditions on AL-Pillared Montmorillonite Supported Cobalt based catalyst for Fischer-Tropsch Synthesis, Nanomat. Biostr. 8 (2013) 347-358.

[13] FTA research, USA, Zero-sulfur diesel fuel from non-petroleum resources: the key to reducing US oil imports.

[14] M.H.Rafiq, H.A. Jakobsen, Experimental studies and modelling of a fixed bed reactor for Fischer-Tropsch Synthesis using Biosyngas.

[15] I.C. Yates, C.N. Satterfield, Intrinsic kinetics of the Fischer–Tropsch synthesis on a cobalt catalyst, Energy Fuels 5 (1991) 168–173

[16] R.B. Anderson, R.A. Friedel, H.H. Storch, Fischer–Tropsch Reaction mechanism involving stepwise growth of carbon chain, J. Chem. Phys. 19 (1951) 313–319.

[17] M.J. Keyser, R.C. Everson, R.L. Espinoza, Fischer–Tropsch Kinetic studies with cobalt-manganese oxide catalysts, Ind. Eng. Chem. Res. 39 (2000) 48–54.

[18] S. Storsaeter, D. Chen, A. Holmen, Microkinetic modelling of the formation of C1and C2products in the Fischer–Tropsch synthesis over cobalt catalysts, Surf. Sci. 600 (2006) 2051–2063.

[19] R.C. Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases and Liquids, 4th edition McGraw-Hill, New York, 1988.

[20] Holman, J. P. (1997). Heat transfer. 8th Ed. McGraw Hill, USA.

[21] Arezoo S.Emrani, M Saber, Modelling and Optimization of Fixed Bed Fischer-Tropsch Synthesis using Genetic Algorithm, Che. Pet. Engg. 46 (2012) 1-11.

[22] C.K.R. Depoorter, A compressive mechanism for the Fischer–Tropsch synthesis, Chem. Rev. 81 (1981) 447–474.

[23] M.Irani, Modeling of Fischer-Tropsch synthesis packed bed reactor for producing liquid fuel from natural gas, petroleum and coal 55(2) (2013) 82-92

[24] N.A Mamonov, L.M Kustov, 1D heterogeneous model of FT synthesis with a fixed catalyst bed in the isothermal granules approximation, Catal. In Indust. 5(3) (2013.)223-231

[25] S.K Mazidi, M.T Sadeghi, Optimization of FT process in a fixed bed reactor using non-uniform catalysts, Chem. Eng. Technol. 36(1) (2013) 62-72

[26] Nonam Park, J. Kim, Modeling of a pilot scale Fix-bed reactor for Fe-based FT synthesis:Two dimensional approach for optimal tube diameter, Fuel 122 (2014)229-235