Simulation of Fixed Bed Reactor for Iron Catalyzed Fisher-Tropsch Reactor Using MATLAB

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NUST-2012-60738-MCES-64112-F

Session 2012-14

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

MASTERS of SCIENCE in

ENERGY SYSTEMS ENGINEERING

Center for Energy Systems (CES)
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August 2014

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Dedication

I dedicate my thesis to all my family members for their continuous support.

Acknowledgments

I am extremely grateful to everyone who has helped me on this journey. I would also like to express my profound gratitude to my honorable supervisor, Mr. Shahid Hussain Ansari, for his support, and invaluable guidance. He has been a constant source of inspiration, and without his support, this work would not have been possible.

Additionally, I would like to thank all of the members of the supervisory and examination committees of the MSc. Program. Dr Adeel Waqas, Assistant Professor Center For Energy Systems Engineering NUST, for his sincere and inspire guideance and research assitance. Dr ahsan Ali, professor Center For Energy Systems Engineering NUST, for his help and guidance during lab work. Dr Bilal Khan Niazi for his continous support during the research.

The support of Assistant Professor, Muhammad Noman Aslam Khan is also acknowledged who gave me all the help required about the simulation software MATLAB, and guide about the key for making my reseach successful and effective. I doubt that I will ever be able to convey my appreciation fully, but I owe him my eternal gratitude.

This work is performed on the CTL pilot unit, kindly sponsored by FFCL. Their support is greatly acknowledged.

Filnally I want to thank my family for their moral support and encouragement when it was most required.

Abstract

Demand for liquid fuel for more energy and rapid depletion of crude oil reserves, the importance of alternate energy has been increasing day by day. Fischer–Tropsch synthesis on a large scale is playing important role as a means for conversion of remote natural gas to high-quality products, particularly liquid transportation fuels. In order to give more reliable data about operating conditions and yield before bulk production this research is used to simulate the fixed bed micro reactor used for Fisher-Tropsch synthesis.

In this work we have used the one dimensional heterogeneous model equations of energy and mass balance to investigate various parameters like hydrogen and carbon monoxide conversion, yield of hydrocarbons and CO2 production during water gas shift reaction as we considered iron based catalyst. Temperature and pressure along the length of fixed bed micro reactor is also investigated. Heat and mass transfer correlations are used to find out the design parameters and MATLAB code is made to utilize syngas as efficiently as possible. The results of this theoretical work revealed that the concentration of CO is decreased from 0.27 to 0.24, concentration of hydrogen from 0.7 to 0.58 and concentrations of hydrocarbons are increased along the length of the reactor. The temperature is increased from 573 to 573.6 K and pressure drop increased from 17 to 17.05 bars.

Iron catalysts supported on silica, alumina and mixture of alumina and silica were prepared by incipient wetness impregnation method. Pore sizes of both the catalysts were established using BET and SEM characterization techniques. Fisher-Tropsch activity of these catalysts was evaluated by using 1-D heterogeneous model of fixed bed reactor under operating conditions of temperature 573K, pressure 17 bars and H/CO ratio 2.1. The CO conversion and higher hydrocarbons production was highest in SiO2 supported catalyst. This indicates that silica supported catalysts shows high FTS activity, higher water-gas shift reaction and higher selectivity to C5+ hydrocarbons and facilitates the CO adsorption. The FTS activity of both Al_2O_3 and SiO_2/Al_2O_3 was very similar and lesser than SiO_2.

JOURNALS/ CONFERENCE PROCEEDINGS

Title	Authors	Journal/Conference	Status
1. Investigation of various parameters in a fixed bed Fisher-Tropsch reactor*	Sarwat Hameed, Shahid Ansari	Nova journal of Engineering and Applied Sciences	Abstract Accepted Manuscript under review
2. Effect of different supports on performance of Fe-Cu based catalysts for fixed bed FT synthesis**	Sarwat Hameed,Shahid Ansari	Comptes rendus chimie	Published

*(Attached as Annexure 1)

**(Attached as Annexure 2)

ABBREVIATIONS

a_v	Specific surface area of catalyst pellet (m^2m^{-3})
A_c	Cross section area of each tube (m^2)
c	Total concentration (mol m^{-3})
C_p	Specific heat of the gas at constant pressure ($Jmol^{-1}$)
D_i	Tube inside diameter (m)
E_i	Activation energy for elementary reaction step i, (kJ/kmol)
F	Total molar flow rate (mol s^{-1})
$\Delta H_{f,,i}$	Enthalpy of formation of component i ($Jmol^{-1}$)
k	Rate constant of reaction (mol $Kg^{-1}bar^{-1}/2s^{-1}$)
k_g	Mass transfer coefficient for component i (ms^{-1})
P	Total pressure (bar)
P_i	Partial pressure of component i (Pa)
r_i	Reaction rate of component i (mol $kgcat^{-1}$ $s-^{1}$)
R	Universal gas constant (J mol^{-1} K^{-1})
Re	Reynolds number
Sci	Schmidt number of component i
T	Temperature (K)
u	Superficial velocity of fluid phase (m s^{-1})
u_g	Linear velocity of fluid phase (m s^{-1})
U	Overall heat transfer coefficient between shell and tube sides (W m^{-2} K^{-1})

v_{ci}	Critical volume of component i ($cm^3 mol^{-1}$)
y_i	Mole fraction of component i
z	Axial reactor coordinate (m)

Greek letters

ε_b	Void fraction of catalyst bed
μ	Viscosity of fluid phase ($kg\ m^{-1}\ s^{-1}$)
ρ	Density of fluid phase ($kg\ m^{-3}$)
ρ_b	Density of catalytic bed ($kg\ m^{-3}$)
η	Catalyst effectiveness factor

Superscripts

g	In bulk gas phase
s	At surface catalyst

Subscripts

0	Inlet conditions
i	Chemical species
k	Reaction number index

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Chapter 1
Introduction

1.1 Overview

Demand for liquid fuel sources combined with political unrest in some of the regions of the world most abundant in oil and natural gas and the recent natural gas boom from hydraulic fracturing have pushed global and domestic energy policies to focus on domestic production and sustainability. This push for domestic supplies of fuel provides opportunities for innovation in industry to develop and improve alternative liquid fuel sources including natural gas, biomass, and coal. Processes which convert natural gas, biomass, or coal to liquid fuels are referred to as natural gas to liquids (GTL), biomass to liquids (BTL), or coal to liquids (CTL). The Fischer-Tropsch (FT) Synthesis (FTS) is one commercially proven process for producing hydrocarbon products from carbon monoxide and hydrogen (syngas) and is a key step in GTL, BTL, and CTL projects.

1.2 Fisher Tropsch Technology

1.2.1 History

Two German scientists Franz Fischer and Hans Tropsch during 1920's have developed a gasification reaction known as FT synthesis[1]. Nazi Germany commercialized this process to support the war effort and obtained a peak production of 4.1 Mbbl/y (11,500 bbl/d) [2]. After World War II, South Africa Coal and Oil (SASOL) continued commercialization and development of the FTS and continues production of synthetic fuels to the present. At various times in the past, usually due to high oil prices, massive government programs and many industrial players have explored FTS development. These include SASOL, Exxon Mobil, Shell, Synfuels China, and a number of other companies.

1.2.2 Current status of Fisher Tropsch industry

Current world FTS production is about 410,000 bbl/d. Mostly from facilities built and operated by SASOL, Shell, and Synfuels China. Several projects have been announced or are under construction in China, South Africa, Germany, Qatar, Malaysia, Nigeria, and the United States amounting to an additional 260,000 bbl/d of potential capacity, though the completion of these projects will depend on complex economic variables. The Fischer-Tropsch industry is well established and will continue to be an important alternative fuel source.

Fixed-bed (FB), fluidized-bed, or slurry bubble columns (SBC) are the reactors in which FTS is carried out. The reaction is catalyzed by either iron or cobalt. Selection of reactor and catalyst depends on the accessibility and source of the syngas feed as well as the desired product (e.g. chemicals, gasoline, diesel, or jet fuel). The availability of local resources determines the choice of feedstock. Biomass is most widely present on earth but biomass contains the lowest energy density as compared to coal and natural gas and is not concentrated in deposits as natural gas and coal so that BTL processes are generally limited to smaller scale operation as the cost of transporting feedstock quickly becomes unaffordable. GTL and CTL processes are typically located near natural gas and coal sources. Syngas derived from natural gas is hydrogen rich and the catalyst preferred for hydrogen rice gas is Cobalt while iron catalysts are used with hydrogen-lean syngas derived from biomass and coal as iron's water-gas shift (WGS) activity can significantly reduce the stoichiometric ratio of required H2 to CO for FTS in exchange for making CO2. When heavier liquid and wax products are desired products, FB reactors and SBC reactors are used while fluidized-bed reactors have mainly been used to produce gasoline and olefins.

Table 1-1 Worldwide fossil energy reserves [3], [4]

Fossil Energy	**Units**	**Quantity**
Oil	$\times 10^{12}$ tons	0.13-0.2
Coal	$\times 10^{12}$ tons	0.9-1.0
Natural gas	$\times 10^{12}$ m3	171-198

1.2.3 Fisher Tropsch process

Fischer-Tropsch synthesis is the process that converts synthesis gas, i.e. a mixture of carbon monoxide and hydrogen, into a wide range of long chain hydrocarbons and oxygenates. Fischer-Tropsch synthesis constitutes a practical way for the chemical liquefaction of solid (coal) or gaseous (natural gas) carbon resources. In relation to the classic refining of crude oil, the liquefaction of these carbon sources via the Fischer-Tropsch synthesis provides alternative routes for the production of transportation fuels and petrochemical feedstock.

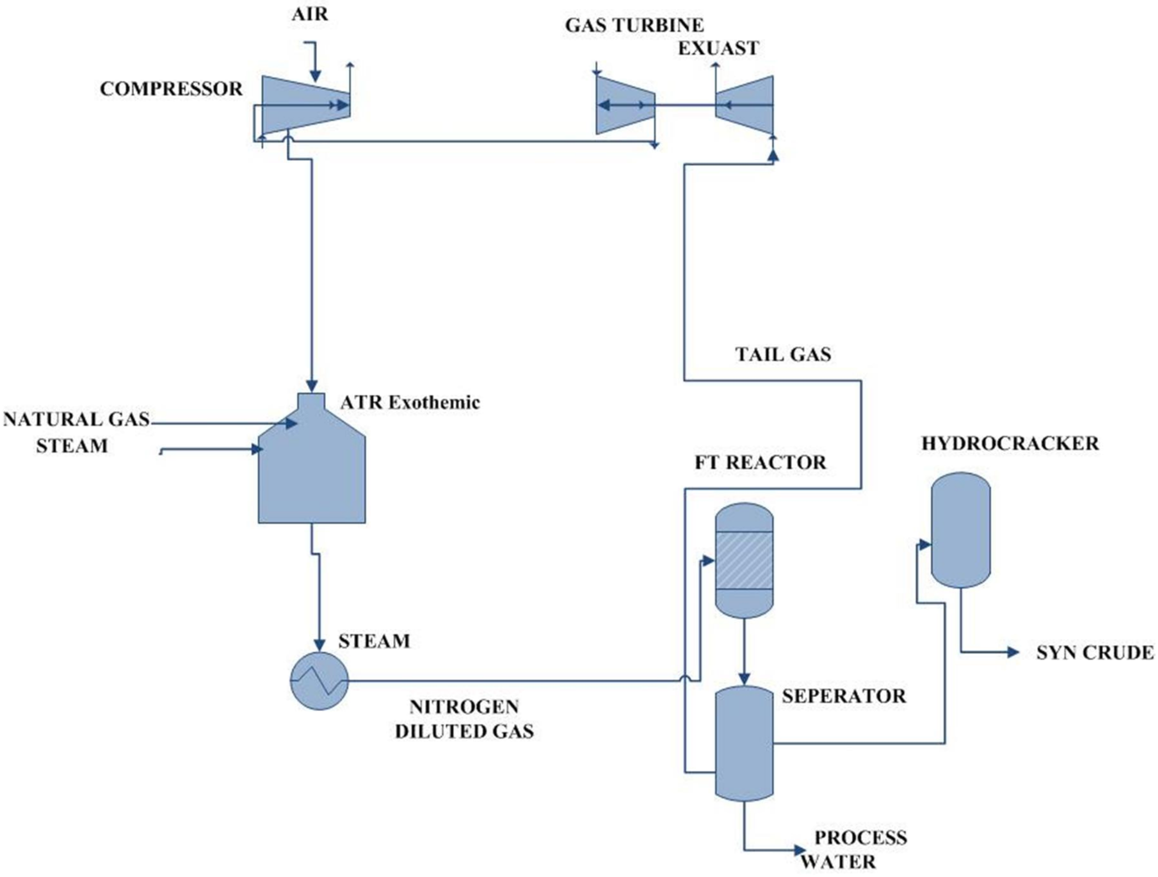


Figure 1-1 Fisher-Tropsch Synthesis Process Diagram

1.2.4 Reactions involved in FTS

The components of Fischer–Tropsch synthesis reactions include H_2, CO, CO_2, H_2O, CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, i-C_4H_{10} and C_5+.

The synthesis of HCs from the hydrogenation of carbon monoxide over transition metal catalysts was discovered in 1902 by Sabatier and Sanderens. They produced methane from hydrogen and carbon monoxide mixtures over nickel, iron and cobalt catalysts. In 1923, Fischer and Tropsch reported the use of alkalized iron catalysts to produce liquid HCs rich in oxygenated compounds [5]. In FT synthesis, the reaction of H_2 and CO on the surface of the catalyst in situ can be regarded as a surface polymerization reaction. First, monomer units are formed from the reagents. Then, a wide product spectrum of HCs (mainly paraffins) is formed by the successive addition of C units to growing chains on the surface of the catalyst. The main reaction of the FT synthesis is represented by [6].

$nCO + 2nH_2 \rightarrow (-CH_2-)_n + nH_2O \qquad \Delta_R H_{298} = -152 kJmol^{-1}$

Where the term (-CH2-) represents a methylene group, which is a building block for the longer HCs. The main reaction (R20) is highly exothermic with a reaction enthalpy of −152 kJ per mole converted CO. Undesirable side reactions such as the formation of methane (R19) and alcohols (R21) are represented by:

$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \Delta_R H^o_{298} = -206 kJmol^{-1}$

$nCO + 2nH_2 \rightarrow C_nH_{2n}+2O+(n-1)H_2O \qquad \Delta_R H^o_{298} = -124 kJmol^{-1}$

In addition, the co-product, HO, can be converted with CO to carbon dioxide and hydrogen by the WGS reaction (R2). The reaction stoichiometry is expressed as:

$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta_R H^o_{298} = -41 kJmol^{-1}$

1.2.5 FTS Reactors

There are four types [7] of Fischer-Tropsch reactors in commercial applications: the circulating fluidized bed reactor, the standard fluidized bed reactor, the fixed packed bed reactor, and the slurry-phase reactor. However, fluidized bed reactors are not suitable for producing liquid phase products because liquid phase products may cause catalyst agglomeration and a loss of fluidization [8]. FT reactors are categorized as either high temperature (HTFT) or low temperature (LTFT) reactors. The key difference is that a liquid phase forms when operating in LTFT reactors, while HTFT reactors operate entirely in the gas phase. LTFT fixed bed and slurry-phase systems are appropriate for producing liquid phase products. Packed bed reactors may have hot-spots causing catalyst deactivation, and thermal runaway [7]. Despite these drawbacks, the packed bed reactor is widely used for F-T process studies such as catalyst development, kinetics measurement, and so on. A packed bed reactor has some benefits, such as ease of operation, no need for additional separation device, and scale-up for large scale reactors.

Abundant experimental and modeling research effort concerning slurry-phase FT reactors are reported, however the literature on the packed bed reactor modeling and design is very limited.

1.2.5.1 Fixed Bed Reactor

Many process industries are based on solid catalysts and the main catalytic process in being done in the fixed-bed reactors. The solid catalyst is in the form of pellets, packed in as a fixed bed inside the reactor. The syngas is introduced in the reactor and is passed through the catalyst bed. Due to direct contact of gas with catalyst, a series of reactions takes place. Since the reaction takes place only on the surface of the catalyst so the reaction is limited by the available surface area. This problem can be overcome by allowing more than one "bed" in the reactor for the gas to pass over, under, and/or through. The catalysts in fixed-bed reactors do not need to be as resilient, as they do not travel in the bed. As the FTS process is highly exothermic, fixed-bed reactors demand cooling of the bed. If the excess heat is not removed from the reactor bed, the reactor may have hot-spots causing catalyst deactivation, and thermal runaway [5]. Fixed-bed reactors are equipped with internal tubes where a heat transfers fluid, such as boiler feed water, can circulate inside the tubes to control the temperature rise in the reactor.

Despite these drawbacks, the packed bed reactor is widely used for F-T process studies such as catalyst development, kinetics measurement, and so on. A packed bed reactor has some benefits, such as ease of operation, no need for additional separation device, and scale-up for large scale reactors.

1.2.1 FTS Catalysts

Both iron and cobalt catalysts are currently used in commercial FB and SBC FT reactors. Sasol uses iron catalysts in its Arge FB and fluidized bed SAS reactors in South Africa and cobalt catalysts in its SBC reactors at its Qatar-based joint venture. Shell uses cobalt catalysts in its FB reactors at Bintulu, Malaysia and in its Pearl GTL facility in Qatar. Synfuels China uses iron catalysts in its FB and SBC reactors located in Inner Mongolia.

Iron based catalyst is low cost and has a high WGS activity. Due to its WGS activity, it is best suited for CO rich syngas created from coal gasification. However, there are some drawbacks; like it is prone to attrition and the water produced by the F-T synthesis may decrease its activity[9], [10]. Cobalt-based catalyst on the other hand is more expensive see Table 1.2.

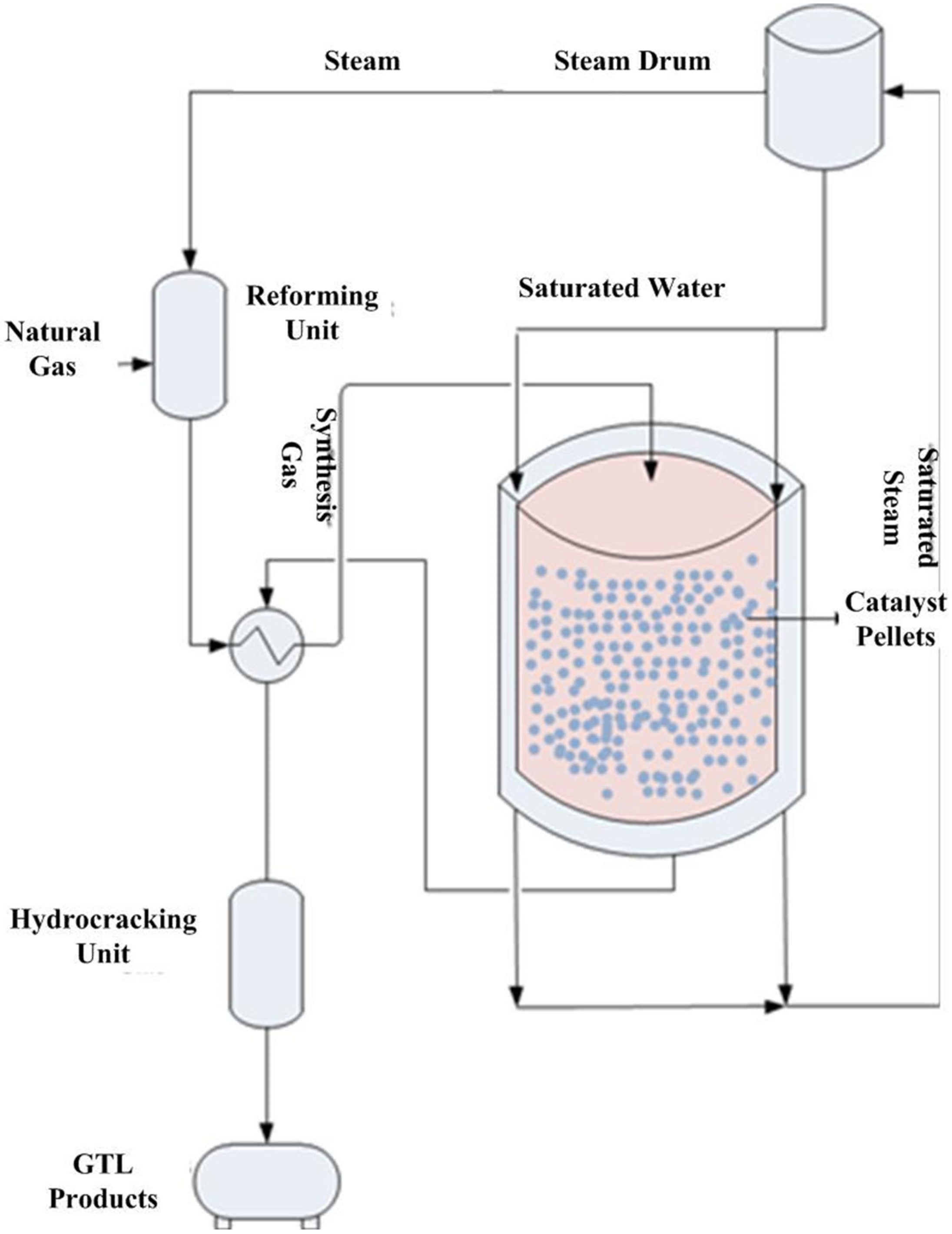


Figure 1-2 Conventional fisher Tropsch fixed bed reactor

But it has higher activity since there is no WGS activity so it is not inhibited by water. It also has longer life than iron catalyst as it is more resistant to attrition. The Co based catalyst has no WGS activity and consequently it is best suited for H-rich syngas, such as that produced from natural gas reforming. It is important to note that presence of sulfur compounds can cause poisoning to both iron and cobalt-based catalysts. It is therefore recommended to keep the sulfur content in the syngas below 0.02 mg/m^3 at standard conditions of pressure and temperature [10]. Incidentally, this is the reason why F-T fuels contain very few amount of sulfur than compared with those produced from oil, and as such F-T fuels are considered more environmental friendly.

Cobalt catalyzed FTS produces mainly normal paraffins while the product slate for iron also includes significant amounts of olefins, oxygenates (e.g. valuable, high molecular weight alcohols), and a large fraction of CO during WGS. FTS products are inherently free of sulfur and heavy metals that typically accompany crude oil all the way through the production process and into the fuel tank. As a clean fuel source free of these contaminants, FTS products are sold at a superior rank. In addition, environmental regulations obligation that transportation fuels incorporate oxygen containing compounds to encourage more complete combustion. The health concerns surrounding MTBE and other additives have increasingly favored long chain alcohols and paraffinic oxygenates, which are produced on iron FT catalysts, as the preferred source of oxygenates in fuel. New iron catalysts can increase the selectivity of these oxygenates alongside the fuel products. A significant amount of work continues in developing new iron and cobalt FT catalysts [10].

Fe as FT catalyst is more resistant to organic sulfur poisons and has a more flexible product slate than Co or Ru. However, it also has the lowest activity among these three. To achieve high activity and stability, Fe catalysts require alkali promotion. With different iron catalyst designs, two ways of selectivity have been followed [11]. One direction has directed at generating a low molecular weight olefinic hydrocarbon mixture to be produced in an entrained phase or fluid bed process. The temperature is comparatively high (~340°C) and the average molecular weight of the product is low. The other direction has aimed at highest catalyst activity to be used at low reaction temperature where most of the hydrocarbon product is in the liquid phase under reaction conditions. The main product fraction is paraffin wax.

This thesis is based on Fe catalyst which aimed to produce olefinic hydrocarbon mixture.

Table 1-2 Comparative prices of different catalysts based on Fe [10]

Catalyst type	Price index
Iron	1
Nickel	250
Cobalt	1000
Ruthenium	50000

Nickel- (Ni) and Ruthenium- (Ru) based catalyst have been used as F-T catalyst only in the laboratory; they have not been used in industry. Nickel-based catalysts produce too much methane over most operating conditions and are poorly performing at high pressure due to the production of volatile carbonyls. Ruthenium-based catalysts, although they have high activity and produce high molecular weight compounds at low temperatures and high pressures, they are very expensive (see Table 1.2) and therefore could not yet be applied at industrial scale.

1.2.2 FTR Model

Reactor design, construction, and operation can be among the most significant costs in building and running a chemical facility. Optimum design and efficient operation of reactors can be realized through the use of accurate, well-crafted computer models.

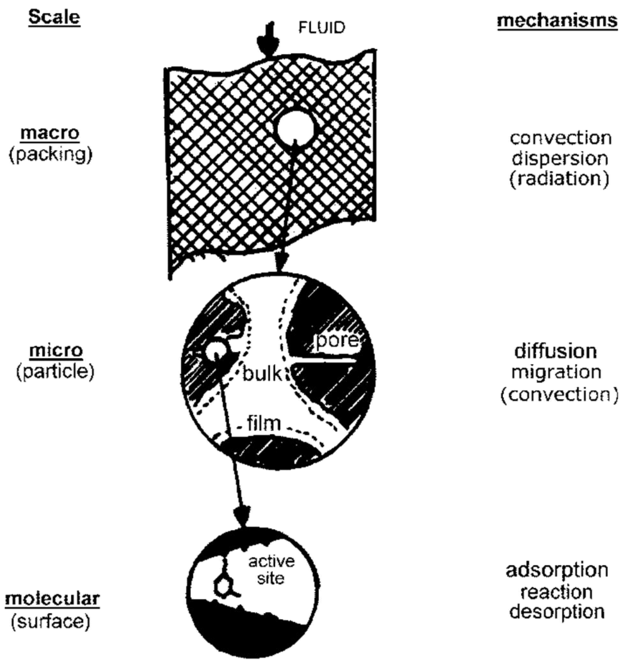
1.2.7.1 Selection of fixed bed reactor models

The model should be simple but should also explain all the mechanisms involved in the chemical reactors.

The main mechanisms involved in chemical reactors are:

In real reactors, in all space directions there will be gradients of

Figure 1-3 Mechanisms involved in fixed bed reactors[12]



- Temperature
- Concentration
- Pressure
- Velocity

The model should cater all the gradients involved but there are some limitations to this approach:

- The dynamics of individual mechanisms are very different from each other
- To describe these dynamics we have to describe the interactions of the flow, chemical system properties and operating conditions
- The mathematical task will be very complex

To overcome these limitations, the common practice is to consider only those mechanisms which have influence on reactor performance. So the required degree of sophistication of model depend upon

- The reaction scheme
- Sensitivity to perturbation in operating conditions

- Degree of accuracy in kinetics and transport parameters
- Degree of dependency of macro reactor on micro reactor mechanisms

1.2.5.2 Classification of fixed bed reactor models

In fixed bed reactors there are two broad categories of models:

- Pseudo homogeneous
- Heterogeneous models

Pseudo homogeneous models do not account explicitly the presence of catalyst; they reflect that the bulk and intra particle conditions are same.

These models are for the systems with:

$$T_g \approx T_s \text{ or } C_g \approx C_s \qquad (1.1)$$

While heterogeneous models reflect that the bulk and intra particle conditions are different and they have separate equations for fluid phase and solid phase.

These models are for the systems with:

$$T_g \neq T_s \text{ or } C_g \neq C_s \qquad (1.2)$$

For FB reactors, the models could be

- 1-D models
- 2-D models

1-D models are less detailed models since they ignore radial gradients of temperature and concentration, but they are easily formulated as they are simple while giving results that are suitable for preliminary reactor design and optimization.

2-D models give more realistic estimates of radial gradients and overall performance but require more time and experience to develop and run.

Several groups have produced computational reactor models for FTS in FB reactors [21-26]; however, few models are flexible enough to model FTS on both iron and cobalt. In addition, little work has been done to model recycle and none of the models include generally-applicable, theoretically-based, industrially-relevant kinetic models for iron and cobalt. A model that addresses these issues could help to further reduce the barriers to entry into the FT industry and reduce further investment and development.

Thesis progress Flow Chart

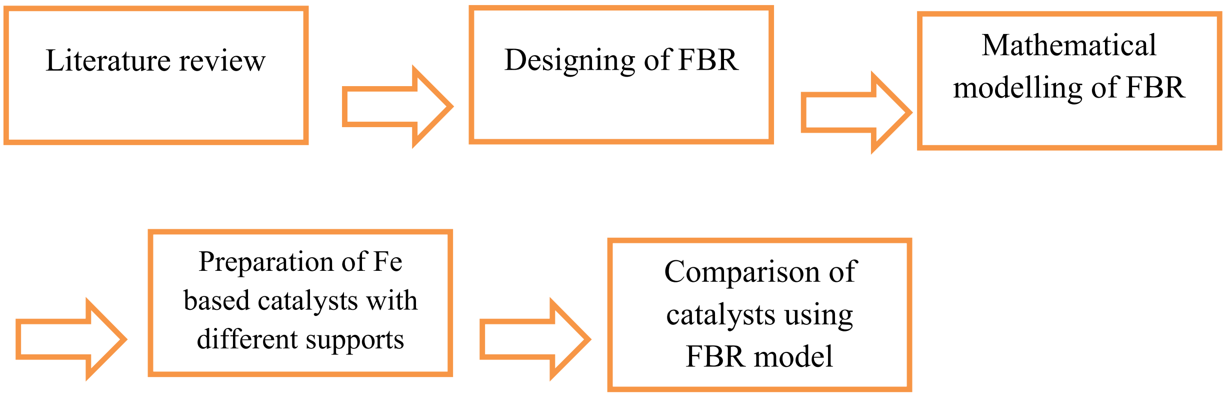


Fig 1-4 Overall Thesis Progress

Summary of the Chapter

In this chapter history of Fisher-Tropsch synthesis is discussed briefly, and then the detailed explanation of FT synthesis process is discussed. The FT reactor used in this thesis is fixed bed reactor, so its structure and working is also explained. The FTS occurs in the presence of metal based catalyst, so the characteristics of all the catalysts used are also explained in this chapter.

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Chapter 2

Literature Review

2.1 Experimental

2.1.1 Catalyst Preparation

The catalyst samples were prepared by using incipient wetness impregnation method. Following this method, required amount of supports are calcinated at 600˚C for 6 hours. Then metal precursor was dissolved in 50ml distilled water and these solutions were poured in the calcinated support and stir it for 40 to 45 minutes rigorously. After stirring, the sample was evaporated by setting the evaporation temperature between 100˚C. After complete evaporation the sample was ground to fine powder. The powdered samples were dried in vented oven for 16 hours at 120˚C. Finally the sample was calcinated in the furnace at 550˚C for 5 hours. The final weight compositions of catalysts samples are 90Fe/3.2Cu/50SiO_2, 90Fe/3.2Cu/50Al_2O_3 and 90Fe/3.2Cu/25SiO_2/25Al_2O_3.

2.1.2 Catalyst Characterization

2.1.2.1 Pore size distribution, pore volume and surface area

Pore size, BET surface area and pore volume were measured by nitrogen physisorption at 77K by using Micrometrics instrument. The sample was degassed at 250K for 4 hrs in flowing helium (30ml/min).

2.1.2.2 SEM

Particle size was determined under scanning electron microscope of both the catalysts. The sample was magnified 100 times operating at 20kV. The particle size was compared with BET to confirm the results.

Shouli, 2000 [1] Prepared cobalt based catalysts by using two different salts Co acetate and Co nitrate with ratios. They used wet impregnation method for preparation of catalyst. They characterized the prepared catalysts by using techniques, like TPR, XRD, TGA, FTIR and TEM. After carrying out FT reaction in the slurry phase reactor, they found out that N/A ratio has strong effect on FT performance as it has effect on reduction degree and metal particle size.

Robert J Obrien, 2000 [2] Investigated the FTS performance and attrition of supported and unsupported Fe based catalysts. They used co-precipitation method for support preparation and wet impregnation for catalyst preparation. They carried out the FTS experiment in CSTR and slurry bubble column. They compared CO conversion and HCs selectivity for supported and unsupported catalysts. Further they characterized the catalysts before and after the FTS experiment and studied the attritional effects on catalysts they prepared in CSTR and slurry bubble column.

Junling, 2003 [3] Studied the effect of support used for Co based catalysts for FTS. They used three types of alumina supports. They prepared the catalyst samples using wetness impregnation method. They characterized these samples by applying different techniques to study the physic-chemical properties and carried out FTS experiments with different alumina supports. They found that the support with low acidity increases the reducibility of cobalt, which in turns increases the C_{5+} hydrocarbons production and less C_1-C_4 hydrocarbons and methane.

Yong 2004[4] Investigate the effect of K on Fe Mn catalyst. They prepared the catalyst samples by Co-precipitation method with different weight fractions (0-0.7%) of K. the characterization techniques BET, TGA, XRD, and MES revealed that, by the weight fraction of K the pore diameter of catalyst increases, so the surface area decreases and the Fe/Mn reduction retarded. The FTS experiment showed that the addition of K promoter restrains the formation of methane and C1-C4 and increases the selectivity of higher hydrocarbons. The selectivity of oxygenates decreases up to 0.7wt% and then increases slowly. At the same time temperature increase also decrease the oxygenate selectivity.

Yang, 2005 [5] Prepared SiO_2 supported Fe-Mn catalysts with different drying methods the spray drying and normal drying. They also changed the method by which they incorporated SiO_2 support in the catalyst. The two methods were adding precipitated SiO_2 or binder SiO_2. They prepared the catalyst by using co-precipitation method and characterize these catalysts before and after FTS experiment. The purpose of characterization was to investigate the effects of SiO_2 contents, addition methods of SiO_2, and drying process of catalyst on physic-chemical properties and FTS performance of Fe-Mn catalyst.

Chang-Hua, 2006 [6] Studied the effect of Cu in Fe/Mn based catalyst on FTS. They prepared the catalyst with and without Cu promoter by co-precipitation method and carried out FTS experiment in slurry stirred tank reactor. They characterized the catalysts by using TPR/TPD, FTIR, and Mossbauer spectroscopy. They studied the reduction of catalyst with and without Cu promoter and also the carburization behavior of Cu promoted catalyst. They investigated the HCs selectivity in the FTS experiment and revealed that with Cu promoter heavier HCs and olefins are formed while without Cu more light HCs are produced.

Song, 2006 [7] Studied the effect of pore size of support of Co based catalyst on FT selectivity. They prepared Al_2O_3 supports with four different pore size diameters and prepared Co/Al_2O_3 catalyst by wet impregnation method. They characterize the catalyst samples by using techniques like N_2 physisorption, TPR, H_2 (TPD) and O_2 pulse reoxidation, DRIFT and XRD to find out the pore diameter, volume, surface area, reduction behavior and dispersion behavior of catalyst. They found that the pore size of support affects the selectivity of FT greatly. The appropriate pore size of support gives the maximum FT performance and also affects the structure and reducibility of cobalt catalyst. Diameter 6-10nm displayed high FT activity and higher C_5+ selectivity.

Wen, 2007 [8] Compared the Fe based catalysts with two different supports of Al_2O_3 and SiO_2. They prepared the catalyst by co-precipitation and spray-drying methods. They analyzed the behaviors of two catalysts by using TPD to find the adsorption of H_2 and CO on the two catalyst and MES to find the carburization behavior. They studied the FTS performance and hydrocarbon selectivity by using these two catalysts and compared the results with TPD and MES.

Heijun et al, 2008 [9] studied the effect of addition of Cu and K in iron based catalyst on FTS. They used characterization techniques like BET, MES, and TPR. The results showed that addition of Cu increases the hydrogenation reaction and deactivates the catalyst, while K addition increases the chain growth by CO adsorption and improves FTS and WGS reaction activity.

Pravakar et al, 2011 [10] prepared CuO-CoO-Cr2O3 catalyst by co-precipitaion method. They added zeolite in it to see the performance of FTS. They characterize the catalyst by using different characteriazation techniques and carried out FTS in fixed bed reactor with different temperature, preesure and H/CO ratios. They found out that higher T&P, increases C5+ production. Higher H/CO ratio inhances the production of methane. Addition of zeolite to catalyst increases the surface area of catalyst hence it results in more active sites in catalyst. This results in high FTS activity by increasingthe conversion of CO-hydrogenation.

Satyen et al, 2013 [11] prepared five Fe-Cu-SiO3 catalysts by adding 0-5% of K promotor to investigate the effect on properties of catalyst that in turn effects CO hydrogenation. They characteraize the cataltsys by using different techniques and performed the FTS experiment in fixed bed reactor. They found that optimum concentration of K is required for FTS activity and that was 1 wt% as K loading incrases the acidity of catalyst that in turn causes the increase in coke on spent catalyst.

Satyen et al, 2014 [12] preapred Fe-Cu-K/SiO2 catalysts and investigate the effect of different active components on FT activity, selectivity, HC distribution and coke formation. They preapared catalysts by co-precipitaion method for silica support and wetness impreganation for K promotor. They found that the catalyst properties by using different characterization techniques and performed FTS in FBR. They found that addition of SiO2 suppresses the FT activity while K addition inhances it.

2.2 Reactor Modeling

The Fischer Tropsch synthesis is highly dependent on such parameters as temperature, pressure, catalyst, gas feed flow rate, and carbon monoxide to hydrogen molar ratio. Scientists often conduct experiments involving many parameters, especially in the development of new catalysts, and cannot afford the time and cost to pursue every combination of these parameters. Therefore they must rely on computer modeling and simulation to assist them in exploring the parameter space to understand the effects of new processing conditions, catalyst kinetics and different kinetic mechanisms.

FT reactors are categorized as either high temperature (HTFT) or low temperature (LTFT) reactors. The key difference is that a liquid phase forms when operating in LTFT reactors, while HTFT reactors operate entirely in the gas phase. LTFT fixed bed and slurry-phase systems are appropriate for producing liquid phase products. Packed bed reactors may have hot-spots causing catalyst deactivation, and thermal runaway[13]. Despite these drawbacks, the packed bed reactor is widely used for F-T process studies such as catalyst development, kinetics measurement, and so on. A packed bed reactor has some benefits, such as ease of operation, no need for additional separation device, and scale-up for large scale reactors.

There are many situations when an engineer needs to have an understanding of how different substances flow and react in a system. The system is may be an industry where a substance should be produced, destroyed or redistributed. The studies of such processes are based on the principle of conservation of matter, and these methods are built upon mass and energy balance. In the chemical industry, and in chemical engineering, process and reactor calculations based on mass and energy balances are the single most vital tool for the analysis and design of chemical processes.

In the literature, several levels of superiority of mathematical models have been proposed to study the behavior of fixed bed reactors [21-26], the models are grouped in two categories: the pseudo-homogeneous (PH) models and heterogeneous (HT) models. The PH models study the catalyst at the same conditions as the fluid and the HT models explain the differences between concentration and temperature in the bulk phase and concentration and temperature inside the catalyst and at its surface. Each group of mathematical models includes one- or two dimensional models, in order to take into account the gradients at the reactor scale in less or more detail.

Atwood and Bennet [14] developed one dimensional, heterogeneous model and simulate the reactor to find the product distribution and effect of catalyst used on CO conversion on commercial scale reactors.

Bub and Baerns [15] studied the distribution of products in fixed bed reactor for FT synthesis by using kinetic measurements. They used pseudo-homogeneous one dimensional model and not consider the intra particle diffusion.

Jess et al [16] proposed pseudo-homogeneous two dimensional fixed bed reactor models to compare the N_2 rice and N_2 free syngas as the reactants on the performance of reactor. Intra particle diffusion was neglected as model is pseudo-homogeneous.

Wang et al [17] developed one dimensional heterogeneous fixed bed reactor model by using SRK equation of state. Model validation was performed using pilot plant data developed internally. Nevertheless, this model is not general. Because it was developed for a specific catalyst, modification to suit another catalyst would require obtaining extensive experimental activity and selectivity data for the new catalyst.

Wen et al [18] developed a model of gas phase using a two bubble class hydro dynamics model in slurry bed reactor for FTS reaction. They considered detailed kinetics and calculate the variation of supercritical gas velocity which changes with gas volume contraction. The value of superficial gas velocity was assumed before. The equation for large bubble was solved by using Gear method and equations for small bubbles and liquid phase were numerically solved by hybrid iteration method.

M.R. Rahimpour and A.M. Bahmanpour [19] modified a thermally coupled reactor having FT reaction in exothermal side and dehydrodenation of cyclohexane in endothermic side. They used hydrogen perm-selective membrane that separates hydrogen produced from dehydrogenation. They developed one dimensional model to determine temperature and concentration profile. They used differential evolution method to predict the conditions at which the conversion of reactants and H_2 recovery yield is maximized and CO2 and CH4 are minimized. The results were compared with conventional reactor data of RIPI (research institute of petroleum industry).

Summary of the Chapter

In this chapter literature review of experimental work done to prepare different combinations of catalysts are developed for FT synthesis is discussed. Also recent work published on reactor modeling and simulation is also discussed.

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Chapter 3

Methodology

3.1 Fisher-Tropsch kinetics

For model development of Fisher-Tropsch fixed bed reactor, we have considered that the source of syngas is coal so iron based catalyst should be used as the syngas has lean hydrogen in it and the system will be HTFT. For these conditions the reactions involved in FT synthesis will be taken as follows [1]:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{3.1}$$

$$2CO + 4H_2 \rightarrow C_2H_4 + 2H_2O \tag{3.2}$$

$$2CO + 5H_2 \rightarrow C_2H_6 + 2H_2O \tag{3.3}$$

$$3CO + 7H_2 \rightarrow C_3H_8 + 3H_2O \tag{3.4}$$

$$4CO + 9H_2 \rightarrow n - C_4H_{10} + 4H_2O \tag{3.5}$$

$$4CO + 9H_2 \rightarrow i - C_4H_{10} + 4H_2O \tag{3.6}$$

$$6.05CO + 12.23H_2 \rightarrow C_{6.05}H_{12.36} + 6.05H_2O \tag{3.7}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{3.8}$$

The rate equation for FT reactions is as follows:

$$R_i = 0.278k_i\exp.\left(\frac{-E_i}{RT}\right)^{\cdot} P_{co}^{m}P_{H_2}^{n} \tag{3.9}$$

The kinetic parameters are summarized in the following table:

The FT hydrocarbon reactions are irreversible but the water shift reaction is reversible so the rate equation for reaction 8 will be different and it is proposed by (Pour, 2010) which is as follows:

$$R_{WGS} = k_w(P_{CO}P_{H_2} - P_{CO_2}P_{H_2}/K_P)/(1 + K_1P_{CO} + K_3P_{H_2O})\text{^}2 \tag{3.10}$$

$$k_W = k_5K_1K_3 \tag{3.11}$$

$$logK_p = \left(P_{CO}P_{H_2}\middle|P_{CO_2}P_{H_2O}\right) = \left(\frac{2073}{T} - 2.029\right) \tag{3.12}$$

Table 3-1 Kinetic parameters of FT hydrocarbon reactions [2]

Reaction no.	m	N	K	E
1	-1.0889	1.5662	142,583.8	83423.9
2	0.7622	0.0728	51.556	65,018
3	-0.5645	1.3155	24.717	49,782
4	0.4051	0.6635	0.4632	34,885.5
5	0.4728	1.1389	0.00474	27,728.9
6	0.8204	0.5026	0.00832	25,730.1
7	0.5850	0.5982	0.02316	23,564.3

The kinetic parameters of WGS reaction rate equations are given in the following table

Table 3-2 Kinetic parameters of WGS reaction rate equation [2]

K_w(mmolg^{-1}s^{-1}bar^{-2})	K_1	K_3(bar^{-1})
0.21	0.39	3.54

3.2 Heat Transfer Parameters

3.2.1 Heat transfer coefficient between gas phase and reactor wall (h_{wall})

In literature the effective heat transfer coefficient (h_{wall}) accounts for interaction of solid liquid and gas within the reactor tube. Since the volumetric flow rate of liquid is very small as compared to gases. So, there will be only little interaction of gas and liquid. In less gas/liquid interaction flow regimes, h_{wall} approached to only one phase (gas/solid) interaction because most of the wall of reactor does not have any liquid contact. That is why gas/solid wall heat transfer correlation is used in the model.

Accordingly the gas/solid equation was used to model the reactor situation (Eq. 13) [3]:

$$\frac{h}{C_p\mu\rho}\left(\frac{C_p\mu}{K}\right)^{\frac{2}{3}} = \frac{0.458}{\varepsilon_b}\left(\frac{\rho u d_p}{\mu}\right)^{-0.407} \tag{3.13}$$

3.2.2 Overall heat transfer coefficient (U)

Overall heat transfer coefficient U accounts for heat transfer in radial direction by conduction, convection and radiation through the catalyst particles, liquid and gas within the reactor. After defining and analyzing the heat transfer in the catalyst bed and the wall of reactor the overall heat transfer coefficient value is found by using following formula[4]:

$$\frac{1}{U} = \frac{1}{h_i} + \frac{A_i \ln(D_o/D_i)}{2\Pi L K_w} + \frac{A_i}{A_o h_o} \tag{3.14}$$

3.3 Catalyst physical properties

3.3.1 Void fraction

Void fraction is affected by pellet geometry and size. Thereby it influences the pressure drop within the reactor. Void fraction is estimated by the equation given by [5].

$$\varepsilon = 0.38 + 0.073\left[1 + \frac{\left(\frac{D}{d_p} - 2\right)^2}{\left(\frac{D}{d_p}\right)^2}\right] \tag{3.15}$$

Where dp is particle dia which is calculated by the formula

$$d_p = 6V_p/S_p \tag{3.16}$$

3.3.2 Effectiveness Factor, Thiele Modulus and Diffusivity

The overall effectiveness factor (η) reconciles observed reaction rate with intrinsic reaction rate by accounting for transport limitations due to internal and external heat and mass transfer. Only internal mass transfer (pore diffusion) resistance is considered in this paper since criteria calculations show that external heat and mass transfer and internal heat transfer resistances are negligible. The effectiveness factor is calculated from the Thiele modulus (φ) as given by Equation

$$\eta = \frac{\tanh(\varphi)}{\varphi} \tag{3.18}$$

The Thiele modulus quantifies the ratio of the reaction rate to the diffusion rate in the pellet.

The effective diffusivity (D) in Equation 5.24 is calculated from the Wheeler pore diffusion model given by

$$D_e = \frac{D\varepsilon_p}{\tau} \tag{3.19}$$

D is the resistance sum of Knudsen (D_k) and bulk (D_{ab}) diffusivities given by Equation

$$\frac{1}{D} = \frac{1}{D_k} + \frac{1}{D_{ab}} \tag{3.20}$$

There are several methods in the literature to obtain binary diffusion coefficients of ideal gases using known properties of the gases under investigation. This creates a challenge when attempting to model the hydrocarbon gases under investigation in this work, because many some of the required properties are not known for many of the species. Therefore, the method of Fuller is attractive because it relies on a concept of diffusion volumes which depend only on the molecular structure, which is known in this case. The Fuller correlation, as stated by Taylor and Krishna [6], is:

$$D_{12} = 1.013 * 10^{-2} T^{1.75} \frac{-b \pm \sqrt{M_1 + M_2}}{P(\sqrt[3]{v}_1 + \sqrt[3]{v_2})^2} \tag{3.21}$$

where the V-terms are the Fuller diffusion volumes and are readily calculated. The coefficient in the front is used to give D_{12} in [m^2/s] when T is [K], P is [Pa], and the molecular weights are [g/mol].

3.4 Reactor Model Development

This chapter describes the development of I-D heterogeneous model and all the designing equations and terms used for the development of model.

3.4.1 Assumptions

For the development of the fixed bed reactor model, some assumptions are considered that include:

- The model is 1-dimensional heterogeneous
- Radial flow is considered
- Gas mixture is considered as ideal
- The system is in steady state condition

- Axial dispersion of heat and mass is neglected

- Plug flow design is considered

- The reactor is in adiabatic condition

Only effective radial thermal conductivity terms accounts in this model and effectiveness factor accounts for pore diffusion resistance.

3.4.2 Model Equations

The mass and energy equations for heterogeneous model are:

Gas phase equations

$$-\frac{F_t}{A_c}+\frac{dy_i}{dz}+a_v c k_{gi}(y_{is}-yi)=0$$

(3.22)

$$-\frac{F_t}{A_c}*C_p*\frac{dT}{dz}+a_v h_f(T_s-T)+\frac{\pi D_i}{Ac}*U_{shell}(T_{shell}-T)=0$$

(3.23)

Solid phase equations

$$a_v c k_{gi}(yi-y_{is})+\eta r_i \rho_b=0$$

(3.24)

$$a_v h_f(T-T_s)+\eta\rho_b\sum_{i=1}^{N} ri\left(-\Delta H_{,f,i}\right)=0$$

(3.25)

Boundary Conditions

Z = 0, $y_i=y_{i,in}$ $T=T_{in}$

Pressure drop

The Ergun momentum balance equation is used in this work, in order to evaluate the pressure drop along the axial direction of the reactor[7]:

$$\frac{dP}{dz}=150(1-\varepsilon)2\mu\frac{u_g}{\varepsilon d_{p^2}}+1.75(1-\varepsilon)u_{g^2}\rho/\varepsilon^3 d_p \qquad (3.26)$$

where dP is pressure gradient across the reactor, ε is void fraction, µis viscosity of gas phase.

Table 3-3 Operating conditions of laboratory fixed bed micro reactor

Parameter	**Value**
H_2/CO ratio	2
Tube dia	28 mm
Tube length	1 ft
Bulk density	27 kg/m^3
Feed temperature	573 K
Feed pressure	17 bar
Bed void fraction	0.52
Number of tubes	1
Catalyst equivalent diameter	$3.35*10^{-5}$ m
Total molar flow rate	1.17

Table 3-4 Predicted and experimental results

Parameter	Conventional plant	Model predictions	Error
CO conversion (%)	77.94	79.04	1.10
H_2 conversion (%)	92.83	90.53	2.30
Methane selectivity (%)	44.15	41.90	1.40
Gasoline selectivity (%)	42.55	45.78	2.07

3.4.1 Model Validity

Table 3-3 shows the operating parameters of lab scale fixed bed reactor. The conversion of reactants and selectivity of hydrocarbons are validated with conventional plant. It validate that the model credibility. The comparison with conventional rector is shown in fig 3-4.

Summary of the Chapter

In this chapter complete methodology of 1-D heterogeneous model is explained that includes the heat and mass balance equations of 1D model, design equations used, their explanation and theory and kinetics of the FT model is discussed.

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Chapter 4

Results and Discussions

The software package developed in this thesis is able to predict the consumption of carbon monoxide and hydrogen, and production of hydrocarbons inside the catalyst particle and along the reactor. The software also predicts the temperature and pressure change along the reactor length. As the catalyst used in the FT reactor is iron based so the CO_2 production due to WGS reaction is also predicted. In this chapter, composition, temperature and pressure profiles along the axis of the rector and factors affecting the FTS will be addressed.

As discussed in previous chapters, iron copper based catalysts by using two different supports are also made by using incipient wetness impregnation method. In this chapter their characterization results, that reveals the catalysts properties will be discussed. Also the effect on the effectiveness factor of catalysts by using two different supports is also discussed.

4.1 MATLAB Illustration

The 1-D heterogeneous model is developed by solving the model equations using RK1 method. The user has to determine all the design parameters of the reactor. They include reactor length, diameter, and surface area and cross sectional area. The user has to find mass and heat transfer coefficient. As the model is heterogeneous, the user has to find the effectiveness factor of the catalyst too.

4.1.1 Composition Profiles

The software package is able to track composition profiles of feedstock and hydrocarbons down the reactor and exhibit them graphically. The composition profiles for carbon monoxide and hydrogen are summarized in Figure 4.1-2.

The concentration of CO decreasing initially as rate of reaction is high at the start of reactor and then it became constant as reaction rate slows down as shown in fig 4.1.

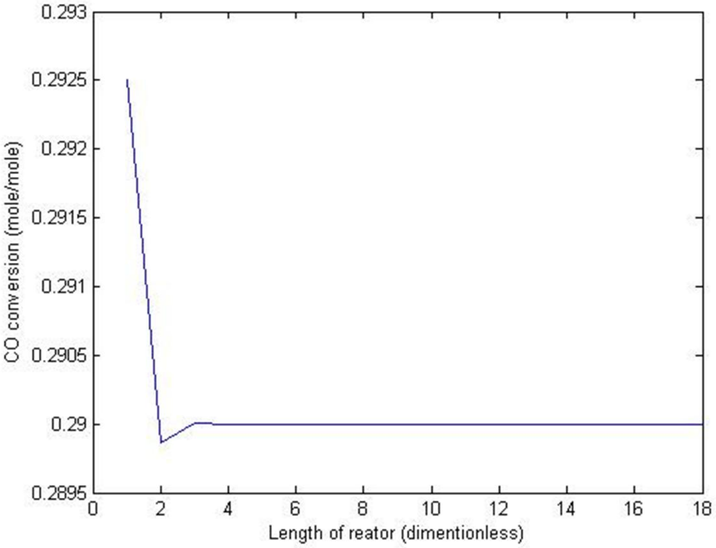


Figure 4-1 Conversion of CO w.r.t length of the reactor

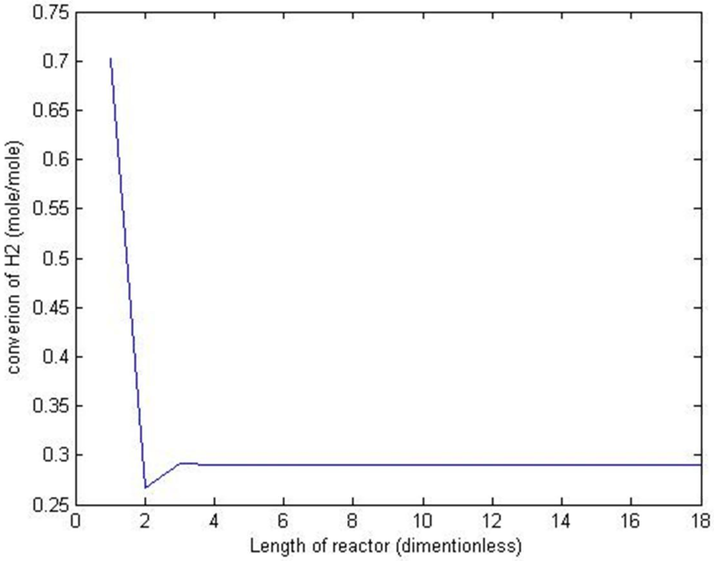


Figure 4-2 Conversion of H_2 w.r.t length of the reactor

Fig 4.2 shows the change in mole fraction of H_2 along the length of reactor the trend is almost same as of CO but with less slope this means that the H_2 is used more quickly during reaction, so it is limiting reactant.

Fig 4-3 is representing all the hydrocarbons yields in one graph. Here the production of hydrocarbon produced can be compared more easily. The trend in this fig shows that highest production is of iso-butane and then C6+ hydrocarbon production which is the desired product the gasoline. The methane which is undesirable product, its yield is not very high but it could be reduced further as the reactor is conventional reactor not the optimized one.

Fig 4-4 shows the production of CO_2 during water gas shift reaction. The CO_2 gas is greenhouse gas and is a byproduct of FTS. Hence is amount of production should be minimized.

4.1.2 Temperature and Pressure profiles

Fig 4-5 shows the temperature profile of the fixed bed reactor. The temperature is increased to its peak point at 573.12 due to exothermic nature of the reaction. The temperature is controlled by circulating the boiling water in shell side of the reactor; due to this the temperature descends to the boiling water temperature of shell side**.**

Fig 4-6 shows the pressure drop across the length of reactor. The pressure drop is increasing along the length of the reactor from 17 to 17.06 bars.

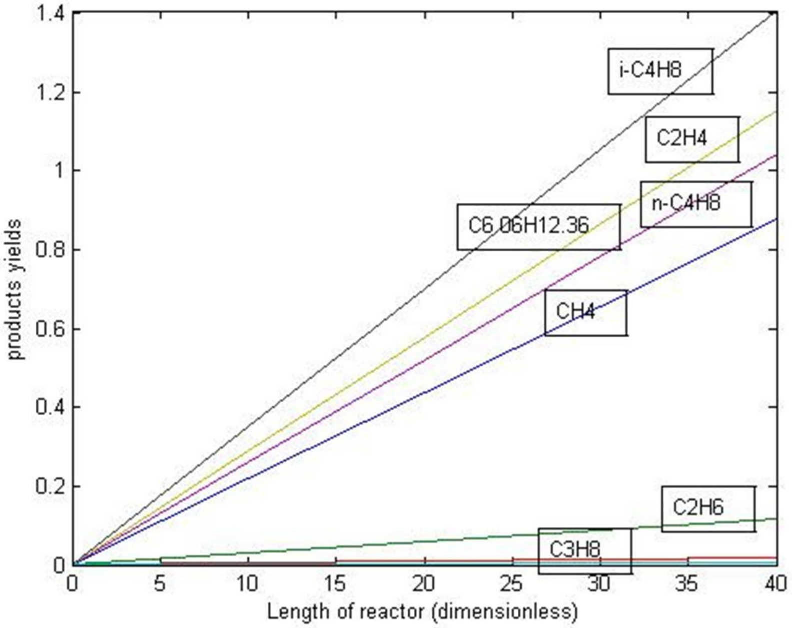


Figure 4-3 Product yields along the reactor length

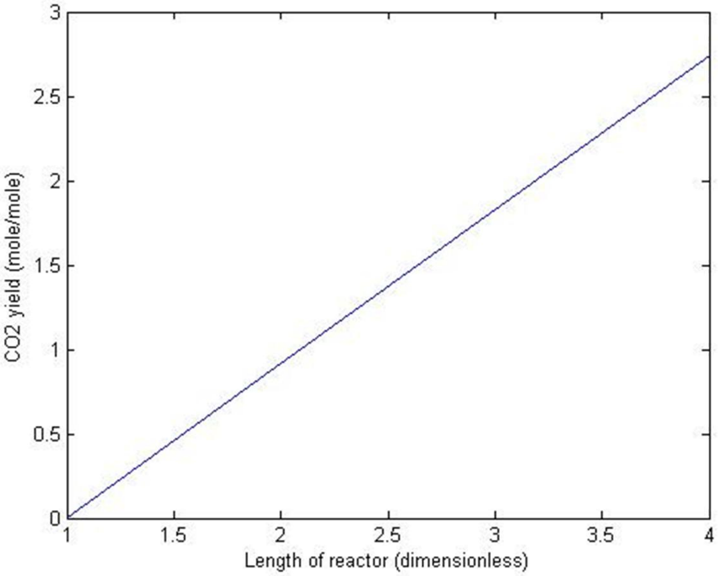


Figure 4-4 Yield of CO_2 during WGS reaction

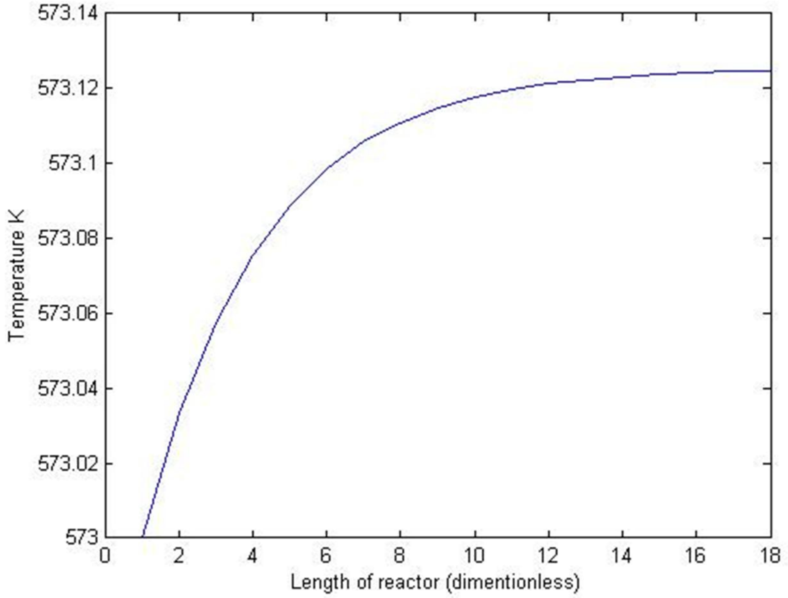


Figure 4-5 Change in Temperature (K) across the reactor

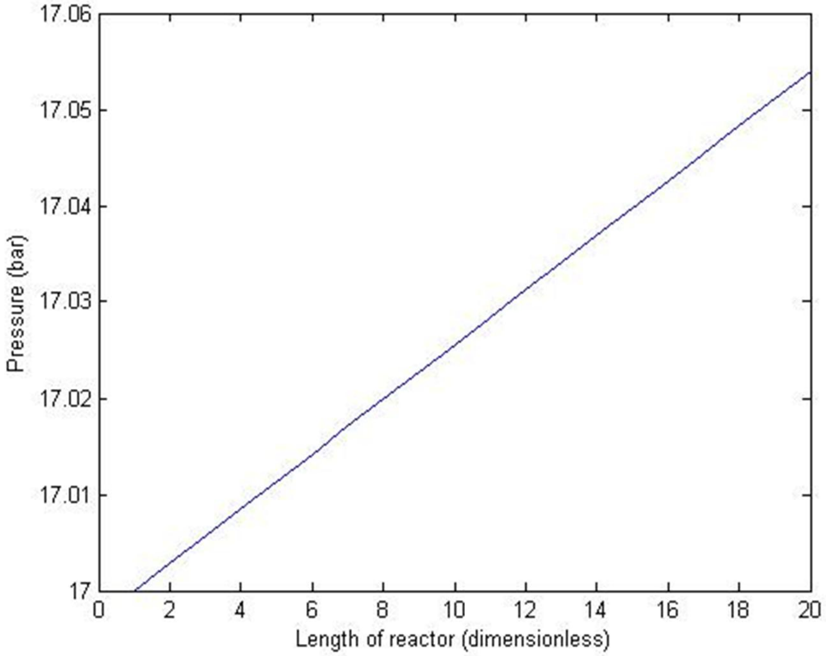


Figure 4-6 Pressure across the reactor length

4.2 Factors effecting FT synthesis

4.2.1 Catalysts support used

Iron catalysts supported on silica, alumina and mixture of alumina and silica were prepared by incipient wetness impregnation method. Pore sizes of both the catalysts were established using BET and SEM characterization techniques. Catalysts with different pore size have different CO adsorption property, which in turn affects the Fisher-Tropsch activity. Fisher-Tropsch activity of these catalysts was evaluated by using 1-D heterogeneous model of fixed bed reactor under operating conditions of temperature 573K, pressure 17 bars and H/CO ratio 2:1. The CO conversion and higher hydrocarbons production was highest in SiO_2 supported catalyst. This indicates that silica supported catalysts shows high FTS activity, higher water-gas shift reaction and higher selectivity to C5+ hydrocarbons and facilitates the CO adsorption. The FTS activity of both Al_2O_3 and SiO_2/Al_2O_3 was very similar and lesser than SiO_2.

4.2.1.1 Nitrogen physisorption measurements

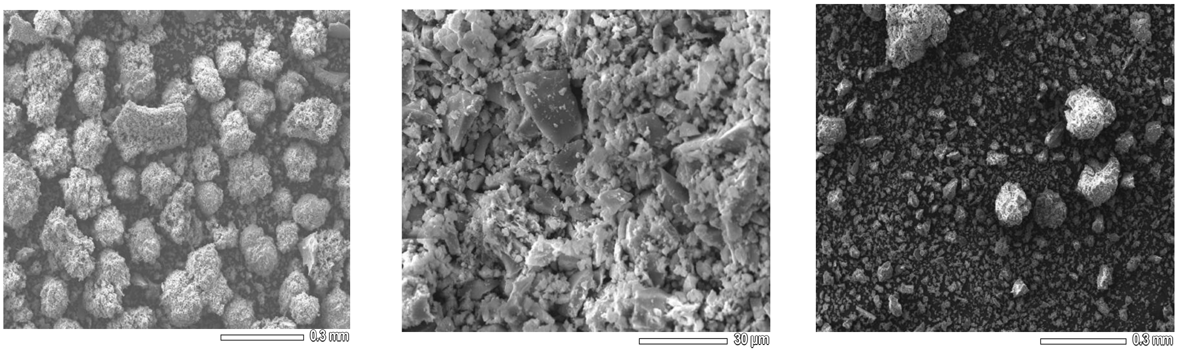
BET surface area, pore volume and pore size of the samples are given in table 4-1. It can be seen that catalyst with silica support has highest value of BET and pore volume. This shows that catalyst with silica support is highly porous and has high internal surface area available for the reaction. The BET and pore volume of catalyst with alumina and alumina/silica combined are almost equal but have lesser porosity and internal surface area than catalyst with silica support alone.

Table 4-1 Texture Properties of Catalysts

Catalyst	**BET (m^2/g)**	**Pore vol (cm^3/g)**	**Pore size (A^o)**
$Fe/Cu/SiO_2$	174	0.22	14.80
$Fe/Cu/Al_2O_3$	54.35	0.249	18.37
$Fe/Cu/SiO_2/Al_2O_3$	52.6	0.249	18.37

4.3 SEM Micrographs

The particle sizes of catalysts with different supports were investigated with SEM micrographs shown in Fig 4-7 and particle sizes in table 4-2. The results of particle sizes of all three catalysts are also supported by Nitrogen physisorption measurements. This obtained data is used in the MATLAB code to confirm the FTS activity is highest in case of using silica as a support with Fe and Cu precursors.



(a) **(b)** **(c)**

Figure 4-7 The SEM images Fe-Cu catalysts with supports (a) Al_2O_3 (b) SiO_2 (c) Al_2O_3/SiO_2

Table 4-2 Catalyst particle size

Catalyst	**Particle size**
$Fe/Cu/SiO_2$	45.6nm
$Fe/Cu/Al_2O_3$	50nm
$Fe/Cu/SiO_2/Al_2O_3$	50.6nm

4.4 Modelling Results

4.4.1 CO and H_2 Conversion

The conversion of CO and H_2 for SiO_2, Al_2O_3 and combined SiO_2/Al_2O_3 supported Fe-Cu based catalysts is shown in Figs 4-8 and 4-9. The FTS activity increases with decreasing particle and pore diameters. As the characterization results revealed that particle size and pore diameter of SiO_2 supported catalyst are smaller than Al_2O_3 and combined

SiO_2/Al_2O_3 supported catalysts. Therefore the conversion of CO and H_2 should be greater for SiO_2 supported Fe catalyst. This is supported by modelling result.

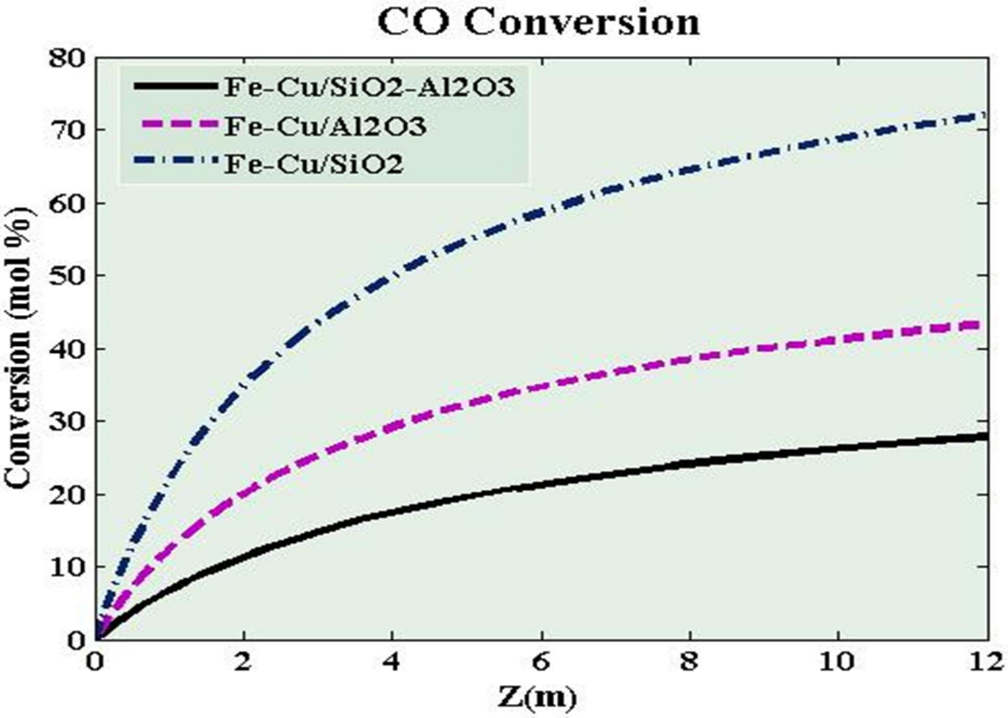


Figure 4-8 CO conversion

4.4.2 Temperature

The temperature change for SiO_2, Al_2O_3 and combined SiO_2/Al_2O_3 supported Fe-Cu based catalysts is shown in Fig 4-10. Here we can see that the silica supported catalyst gives the best range of temperature in which we can get maximum C5+ hydrocarbons. The temperature is not dropped beyond 300K. When using other two catalysts, the temperature is dropped too much which is not helpful in getting the desired product of FTS which is C6 to C10. The temperature change along the length of reactor also shows that for Fe-Cu based catalysts, SiO_2 support is most appropriate.

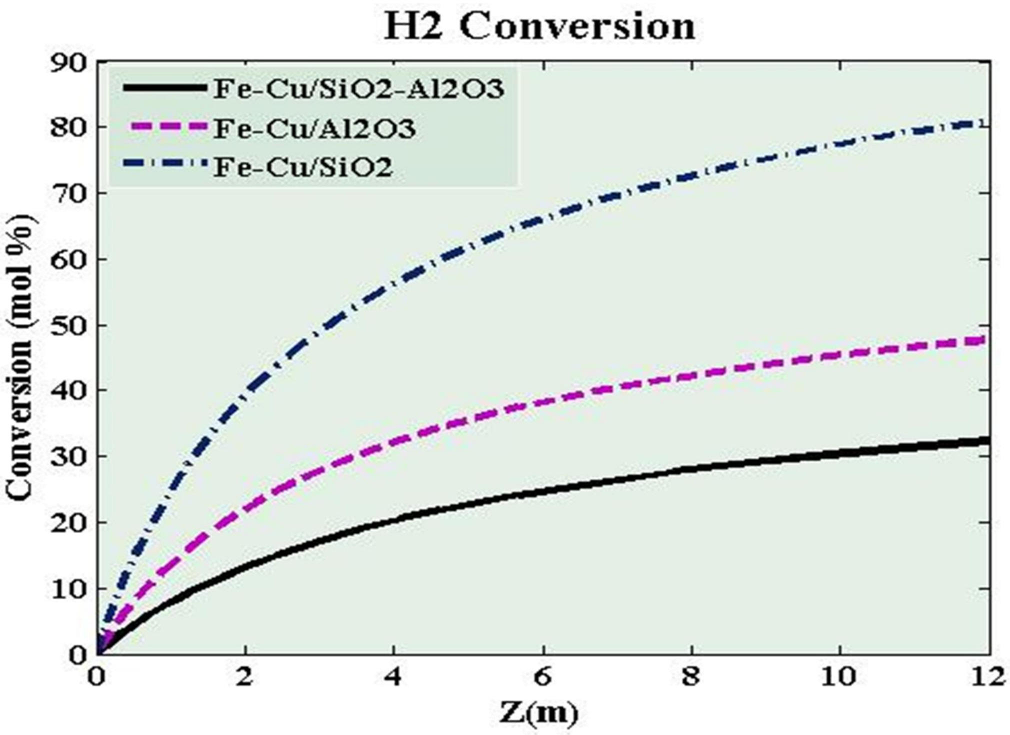


Figure 4-9 H_2 conversion

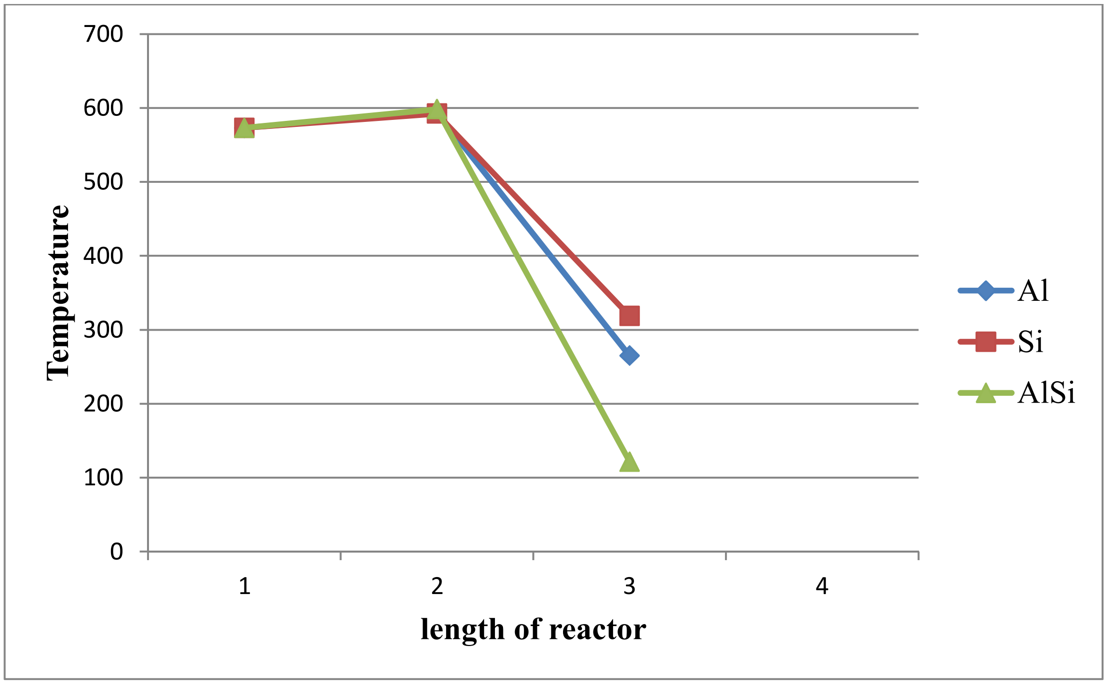


Figure 4-10 Temperature change

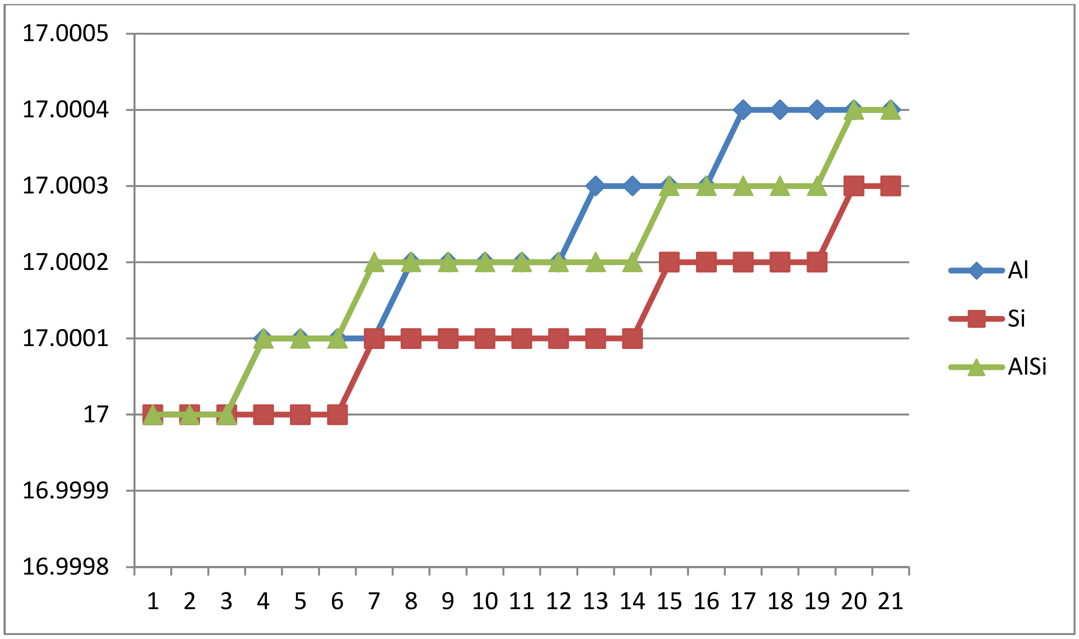


Fig 4-11 Pressure Change

4.4.3 Pressure

Fig 4-11 shows the pressure change along the reactor. The change is not very much significant in each case and does not have effect on the FTS performance. In comparison of catalysts, in case of Si supported Fe-Cu catalyst the pressure change is minimum this means that the catalyst porosity is maximum and this is also been seen by characterization results.

4.4 Product yield

The product yield of methane and C5+ hydrocarbons is shown in Figs 4-11 and 4-12. During FTS methane is the undesirable hydrocarbon and C5+ hydrocarbons are most desirable as they are mainly gasoline. It is clear from the figures that by using catalyst $90Fe/3.2Cu/50SiO_2$ in fixed bed reactor during FTS we will get more desirable hydrocarbon yield, which is C5+ and less CH4 yield that is undesirable FTS product. Moreover there is not much difference in the yields of hydrocarbons if $90Fe3.2/Cu/50Al_2O_3$ or $90Fe/3.2Cu/25SiO_2/25Al_2O_3$ is used.

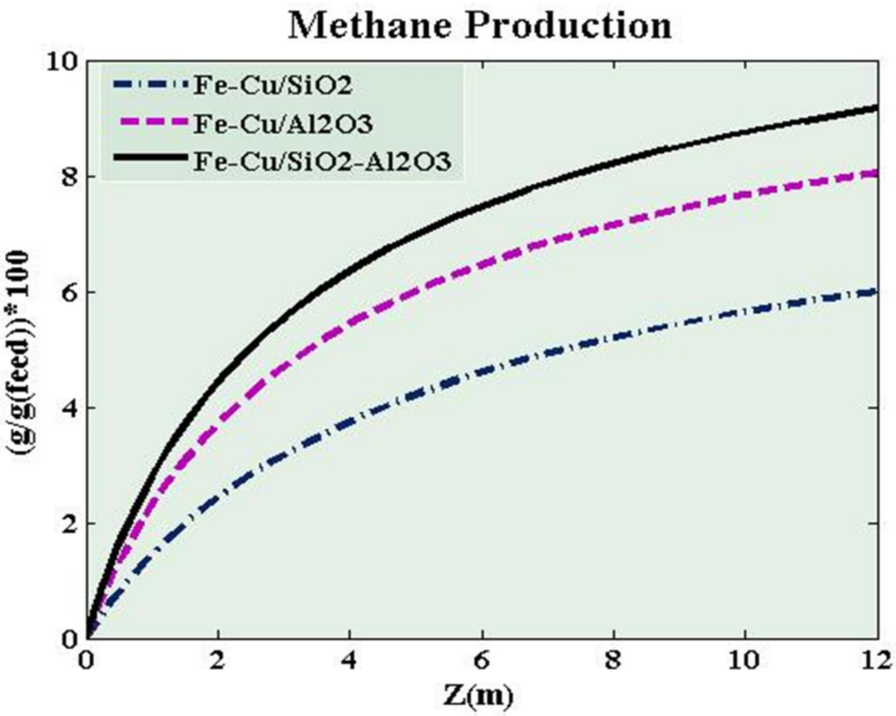


Figure 4-11 CH_4 yield

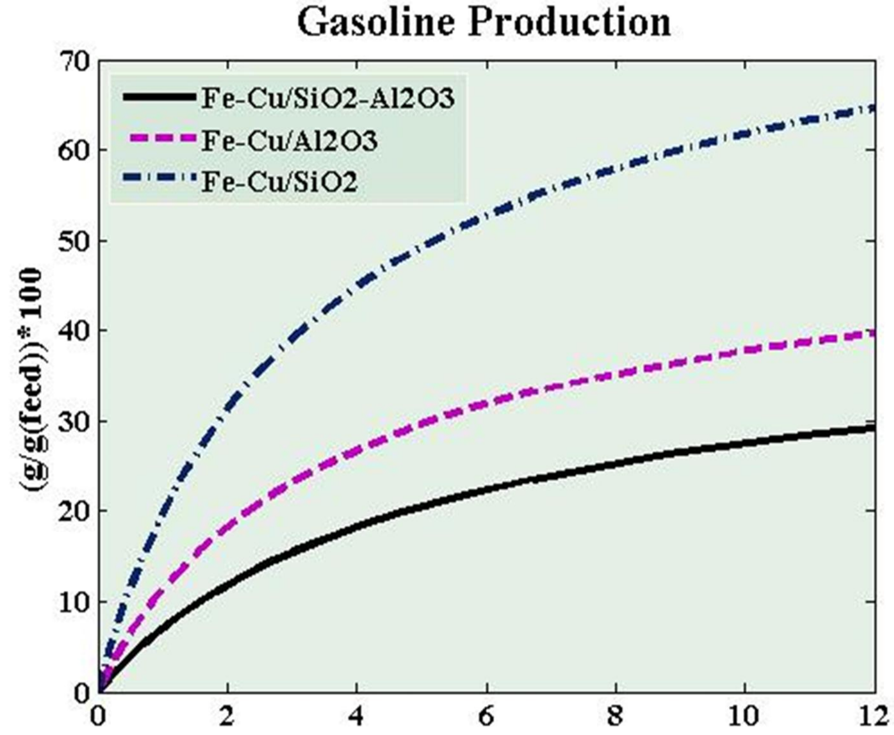


Figure 4-12 C_5^+ yield

Summary of the chapter

In this chapter, model results of operating conditions like temperature and pressure along the reactor is shown. Also the CO and H_2 conversion and product yield along the length of reactor is shown by graphs obtained by simulation model. Also the characterization and modeling results of Si/Al/SiAl supported catalyst are shown to compare the FTS activity of theses catalysts.

Chapter 5

Conclusions

5.1 Conclusions

One dimentional hetrogeonous model of fixed bed reactor is made to predict the performance of FTS. The change in reactor conditions like temperature and pressure are investigated.The conversion of H_2 and CO and product yeild is also forcasted by using MATLAB as simulation tool. This simulation helps to get relialble data about the parameters on which the fixed bed reactor performance greatly depends. Also prior information about the FTS performance helps to optimize the process by applying various techniques. however this is a theoretical study, the industrial application of this model may requires experimental studies too.

Al_2O_3, SiO_2 and Al2O3/SiO_2 supported Fe-Cu based catalyst were prepared to compare their FTS activity. The characterization and modelling results show that silica supported iron-copper based catalyst has high activity than alumina and combined silica and alumina.

5.2 Future Recommendation

Following future word could be done for further improvement and development of work done up to now in FT modelling and simulation.

5.2.1 Development of 2-D Model

In order to make the modelling more detailed 2-D heterogeneous model of the fixed bed reactor could be made by using different simulation tools available. The software FLUENT could be used instead of MATLAB in which the 2-D heterogeneous modelling ispossible.

Annex I Simulation *of Fixed Bed Iron Catalyzed Fisher-Tropsch Reactor Using* MATLAB

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Keywords: fixed bed reactor; Fisher -Tropsch synthesis; heterogeneous reactor model; mathematical modelling; MATLAB simulation;

Abstract

One dimensional heterogeneous model equations are used to investigate various parameters that govern the performance of Fisher-Tropsch synthesis reactor. These parameters include $H_2$and CO conversion, yield of hydrocarbons and CO_2 production during WGS reaction. Temperature and pressure along the length of fixed bed micro reactor are also calculated. MATLAB code is evaluated to simulate the fixed bed reactor for utilizing syngas as efficiently as possible. The results of this theoretical work revealed that along the length of the reactor, the concentration of CO and hydrogen is decreased from 0.29 to 0.289 and 0.70 to 0.58 respectively. In contrast, the hydrocarbons concentrations are increased along the length of the reactor. The temperature is increased from 433 to 434.6K and pressure drop increased from 17 to 17.06 bars. CO_2 is also produced during water gas shift reaction which is a byproduct of FTS process.

Introduction

The depletion of crude oil reserves and higher cost and complexities associated with heavy oil recovery has diverted the research to alternate energy resources. Therefore this scenario has resulted in a rapid increase in demand for liquid fuels. Fischer–Tropsch synthesis is playing an important role in producing high-quality products, particularly liquid transportation fuels from natural gas. However there is scarcity of reliable data about yield and operating conditions for this process to be successful on a large industrial scale. Hence this study is aimed to simulate the fixed bed micro reactor used for Fisher-Tropsch synthesis.

Fischer-Tropsch synthesis is the process of converting synthesis gas, i.e. a mixture of carbon monoxide and hydrogen, into a wide range of long chain hydrocarbons and oxygenates. These products are produced after series of reactions in the presence of catalyst in the reactor. Fischer-Tropsch synthesis is a practical way for the chemical liquefaction of solid (coal) or gaseous (natural gas) carbon resources. It provides alternative routes for the production of liquid transportation fuels and petrochemical feedstock. The fixed-bed Fischer–Tropsch process is one of the most promising reactor technologies, occupies a distinct position in FTS industrial process, as well exemplified by the large-scale commercial operations of Sasol (Dry, 1996) and Shell(Sie, 1998)[1].

FT reactors are categorized as either high temperature (HTFT) or low temperature (LTFT) reactors. The key difference is that a liquid phase forms when operating in LTFT reactors, while HTFT reactors operate entirely in the gas phase. LTFT fixed bed and slurry-phase systems are appropriate for producing liquid phase products[2].

In FT synthesis both iron and cobalt based catalysts could be used. The choice of catalyst depends on the product required. Iron catalyzed FTS mainly produces olefins and oxygenates while cobalt catalyzed FTS produces normal paraffin[3].

The Fisher-Tropsch synthesis could be summarized by two main reactions, the FT reaction and water gas shift reaction[4].

FT Reaction

$$nCO + 2nH_2 \rightarrow (-CH_2-)_n + nH_2O \quad (1)$$

Shift Reaction

$$\mathrm{CO} + \mathrm{H_2O} \leftrightarrow \mathrm{CO_2} + \mathrm{H_2} \qquad (2)$$

Where the (-CH2-) represents the methylene group and which is the main building block of long chain hydrocarbons. The water gas shift reaction is only important when iron basedcatalyst is used. Water is the main product of FT reaction and CO_2 is produced only during WGS reaction.WGS reaction is parallel-consecutive reaction w.r.t. CO.

The modelling of FTS reactors could be done by basic pseudo-homogenous model. In this model, heat and mass transfer effects on catalyst and fluid are not considered separately. Also the temperature and concentration are same for fluid and catalyst. While in more detailed heterogeneous models heat and mass transfer effects on both solid and fluid phases are considered separately. More over the models could be one dimensional where the temperature and concentration changes only in the axial direction are considered. The more detail model is two dimensional models in which these changes are considered axially and also in radial direction[5].

Fixed bed reactor

Many process industries are based on solid catalysts and the main catalytic process in being done in the fixed-bed reactors. The solid catalyst is in the form of pellets, packed in as a fixed bed inside the reactor. The syngas is introduced in the reactor and is passed through the catalyst bed. Due to direct contact of gas with catalyst, a series of reactions takes place. Since the reaction takes place only on the surface of the catalyst so the reaction is limited by the available surface area. This problem can be overcome by allowing more than one "bed" in the reactor for the gas to pass over, under, and/or through. The catalysts in fixed-bed reactors do not need to be as resilient, as they do not travel in the bed. As the FTS process is highly exothermic, fixed-bed reactors demand cooling of the bed. If the excess heat is not removed from the reactor bed, the reactor may have hot-spots causing catalyst deactivation, and thermal runaway[5]. Fixed-bed reactors are equipped with internal tubes where a heat transfers fluid, such as boiler feed water, can circulate inside the tubes to control the temperature rise in the reactor.

Despite these drawbacks, the packed bed reactor is widely used for F-T process studies such as catalyst development, kinetics measurement, and so on. A packed bed reactor has some benefits, such as ease of operation, no need for additional separation device, and scale-up for large scale reactors.

Reactor modelling

The Fischer Tropsch synthesis is highly dependent on such parameters as temperature, pressure, catalyst, gas feed flow rate, and carbon monoxide to hydrogen molar ratio. Scientists often conduct experiments involving many parameters, especially in the development of new catalysts, and cannot afford the time and cost to pursue every combination of these parameters. Therefore they must rely on computer modeling and simulation to assist them in exploring the parameter space to understand the effects of new processing conditions, catalyst kinetics and different kinetic mechanisms.

There are many situations when an engineer needs to have an understanding of how different substances flow and react in a system. The system is may be an industry where a substance should be produced, destroyed or redistributed. The studies of such processes are based on the principle of conservation of matter, and these methods are built upon mass and energy balance. In the chemical industry, and in chemical engineering, process and reactor calculations based on mass and energy balances are the single most vital tool for the analysis and design of chemical processes.

In the literature, several levels of superiority of mathematical models have been suggested to study the performance of fixed bed reactors. In fixed bed reactors there are two broad categories of models, Pseudo homogeneous models and heterogeneous models. Pseudo homogeneous models do not account explicitly the presence of catalyst; they reflect that the bulk and intra particle conditions are same.

These models are for the systems with:

$T_g \approx T_s$ or $C_g \approx C_s$

Parameter	**Value**
H_2/CO ratio	2
Tube diameter	28 mm
Tube length	1 ft.
Bulk density	27 kg/m^3
Feed temperature	433 K
Feed pressure	17 bar
Bed void fraction	0.52
Number of tubes	1
Catalyst equivalent diameter	3.35*10^{-5} m
Total molar flow rate	1.17 moles/s

Table 3 Operating conditions of laboratory fixed bed micro reactor

While heterogeneous models reflect that the bulk and intra particle conditions are different and they have separate equations for fluid phase and solid phase.

These models are for the systems with:

$T_g \neq T_s$ or $C_g \neq C_s$

Atwood et al(1979) [6] developed one dimensional, heterogeneous model and simulate the reactor to find the product distribution and effect of catalyst used on CO conversion on commercial scale reactors. Bub et al(1980) [7]studied the distribution of products in fixed bed reactor for FT synthesis by using kinetic measurements. They used pseudo-homogeneous one dimensional model and not consider the intra particle diffusion. Jess et al(1999) [8]proposed pseudo-homogeneous two dimensional fixed bed reactor models to compare the N_2 rice and N_2 free syngas as the reactants on the performance of reactor. Intra particle diffusion was neglected as model is pseudo-homogeneous. Wang et al (2003)[9]developed one dimensional heterogeneous fixed bed reactor model by using SRK equation of state. Model validation was performed using pilot plant data developed internally. Nevertheless, this model is not general. Because it was developed for a specific catalyst, modification to suit another catalyst would require obtaining extensive experimental activity and selectivity data for the new catalyst.

Wen et al (2007) [10]developed a model of gas phase using a two bubble class hydro dynamics model in slurry bed reactor for FTS reaction. They considered detailed kinetics and calculated the variation of supercritical gas velocity which changes with gas volume contraction. The value of superficial gas velocity was assumed before. The equation for large bubble was solved by using Gear method and equations for small bubbles and liquid phase were numerically solved by hybrid iteration method. M.R. Rahimpour A.M. Bahmanpour (2011) [11]modified a thermally coupled reactor, having FT reaction in exothermal side and dehydrogenation of cyclohexane in endothermic side. They used hydrogen perm-selective membrane that separates hydrogen produced from dehydrogenation. They developed one dimensional model to determine temperature and concentration profile. They used differential evolution method to optimize the reactor so that conversion of reactants and H_2 recovery yield is maximized and CO_2 and CH_4 are minimized. The results were compared with conventional reactor data of RIPI (research institute of petroleum industry).

Objective

The objective of this research is to develop a one dimensional heterogeneous model to simulate CO and H_2 consumption yield of hydrocarbons and temperature changes during the reaction in a fixed bed micro reactor in which the catalyst used is iron based and the reaction is HTFT. To accomplish this objective mathematical method i.e., RK1 method is applied in MATLAB.

Mathematical modelling

Fisher-Tropsch kinetics

For model development of Fisher-Tropsch fixed bed reactor, we have considered that the source of syngas is coal so iron based catalyst should be used as the syngas has lean hydrogen in it and the system will be HTFT. For these conditions the reactions involved in FT synthesis will be taken as follows[12]:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (3)$$

$$2CO + 4H_2 \rightarrow C_2H_4 + 2H_2O \qquad (4)$$

$$2CO + 5H_2 \rightarrow C_2H_6 + 2H_2O \qquad (5)$$

$$3CO + 7H_2 \rightarrow C_3H_8 + 3H_2O \qquad (6)$$

$$4CO + 9H_2 \rightarrow n - C_4H_{10} + 4H_2O \qquad (7)$$

$$4CO + 9H_2 \rightarrow i - C_4H_{10} + 4H_2O \qquad (8)$$

$$6.05CO + 12.23H_2 \rightarrow C_{6.05}H_{12.36} + 6.05H_2O \qquad (9)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (10)$$

The rate equation for FT reactions is as follows:

$$R_i = 0.278k_i \exp.\left(\frac{-E_i}{RT}\right)^{\cdot} P_{co}^{m} P_{H_2}^{n} \qquad (11)$$

The kinetic factors are summarized in the following table:

Table 4 Kinetic parameters of FT

Reaction no.	M	N	K	E
1	-1.0889	1.5662	142583.8	83423.9
2	0.7622	0.0728	51.556	65018.0
3	-0.5645	1.3155	24.717	49782.0
4	0.4051	0.6635	0.4632	34885.5
5	0.4728	1.1389	0.00474	27728.9
6	0.8204	0.5026	0.00832	25730.1
7	0.5850	0.5982	0.02316	23564.3

The FT hydrocarbon reactions are irreversible but the water shift reaction is reversible so the rate equation for reaction 8 will be different and it is proposed by [14] which is as follows:

$$R_{WGS} = \frac{k_w\left(P_{CO}P_{H_2} - P_{CO_2}P_{H_2}/K_P\right)}{\left(1 + K_1P_{CO} + K_3P_{H_2O}\right)^2} \quad (12)$$

$$k_W = k_5K_1K_3 \quad (13)$$

$$logK_p = \left(P_{CO}P_{H_2} \middle| P_{CO_2}P_{H_2O}\right) = \left(\frac{2073}{T} - 2.029\right) \quad (14)$$

The kinetic parameters of WGS reaction rate equations are given in the following table:

Table 5 kinetic parameters of WGS reaction rate equation [13]

k_w(mmolg^{-1}s^{-1}bar^{-2})	K_1	K_3(bar^{-1})
0.21	0.39	3.54

Model assumptions

Assumptions are considered for the mathematical modeling of fixed bed Fischer-Tropsch synthesis reactor. These include that the system is in steady sate condition, the gas mixture is considered as ideal, the model assumed to be one dimensional heterogeneous model, axial dispersion of heat and mass is neglected, plug flow design is considered and the reactor is in adiabatic condition.

Mathematical model

The mass and energy conservation equations for heterogeneous one dimensional model are:

Gas phase equations

$$-\frac{F_t}{A_c} + \frac{dy_i}{dz} + a_v c k_{gi}(y_{is} - yi) = 0 \quad (15)$$

$$-\frac{F_t}{A_c} * C_p * \frac{dT}{dz} + a_v h_f(T_s - T) + \frac{\pi D_i}{Ac} * U_{shell}(T_{shell} - T) = 0 \quad (16)$$

Solid phase equations

$$a_v c k_{gi}(yi - y_{is}) + \eta r_i \rho_b = 0 \quad (17)$$

$$a_v h_f(T - T_s) + \eta \rho_b \sum_{i=1}^{N} ri\left(-\Delta H_{,f,i}\right) = 0 \quad (18)$$

Boundary Conditions

Z=0, $y_i=y_{i,in}$ $T=T_{in}$

Pressure drop

The Ergun momentum balance equation is used in this work, in order to evaluate the pressure drop along the axial direction of the reactor [15]

$$\frac{dP}{dz} = 150(1 - \varepsilon)2\mu\frac{u_g}{\varepsilon d_{p^2}} + \frac{1.75(1-\varepsilon)u_{g^2}\rho}{\varepsilon^3 d_p} \quad (17)$$

Where dP is pressure gradient across the reactor, ε is void fraction, μis viscosity of gas phase.

Design Equations

Some design equations are used to complete the heterogeneous model. To analyze the heat and mass transfer phenomena between gas phase and catalyst particles and evaluation of physical properties of the chemical components and overall heat transfer coefficient some correlations are used. These equations include component heat capacity equation by[16], viscosity and thermal conductivity equations from[17], mass transfer coefficient between gas and solid phase by [18] and overall heat transfer coefficient from[19].

Results and discussions

Conversion of CO and H2, % yield of FT products and change of temperature and pressure across the length of reactor has been investigated in model.

Hydrogen and carbon monoxide conversion is shown in fig 1 and 2. Fig 1 shows the change in mole fraction of CO along the length of reactor. The concentration is decreasing initially as rate of reaction is high at the start of reactor and then it became constant as reaction rate slows down. Fig 2 shows the change in mole fraction of H_2 along the length of reactor the trend is almost same as of CO but with less slope this means that the H_2 is used more quickly during reaction, so it is limiting reactant. To optimize the reaction injection of H_2 during the reaction will help.

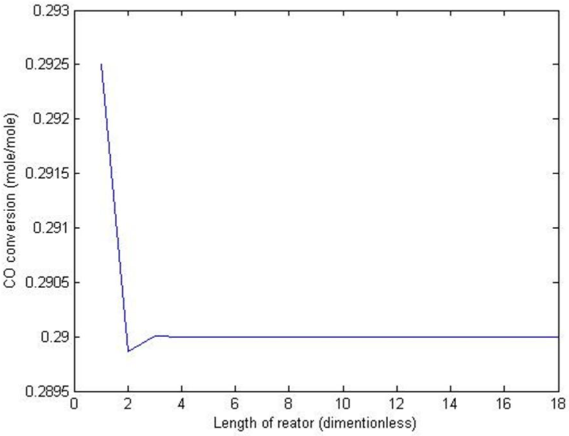

Figure 13 Conversion of CO w.r.t length of the reactor

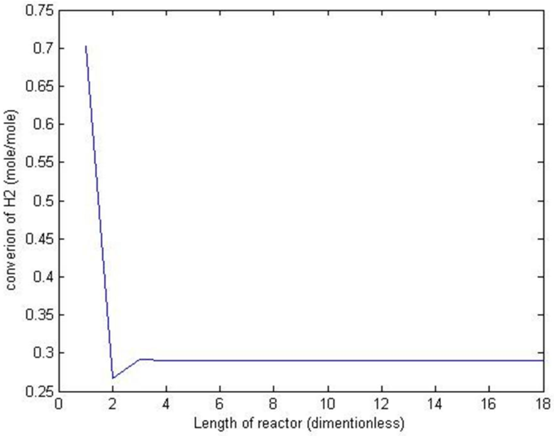

Figure 14 Conversion of H_2 w.r.t length of the reactor

The production yield of hydrocarbons produced during FT reaction is presented in fig. 3 to 9. Methane is undesirable product in and its production yield is shown in fig 3. Its yield is smaller than ethane in this reactor, so it can be deduced that its efficiency is quit decent. But its production could be reduced further by optimizing the performance of reactor.

Fig 4 illustrate the production yield of ethylene (C_2H_4) which is larger than methane which shows that the micro reactor is working efficiently under these process conditions can could be optimized which could give great results.

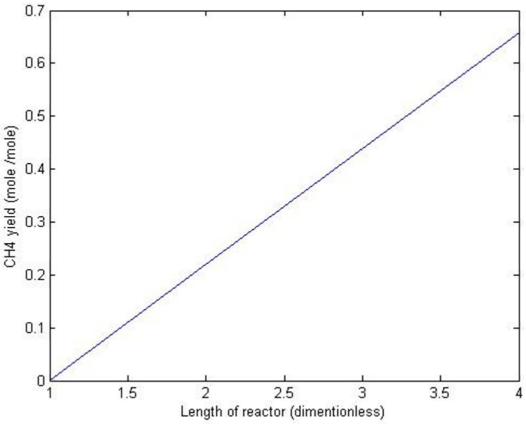

Figure 15 Methane yield along the length of the reactor

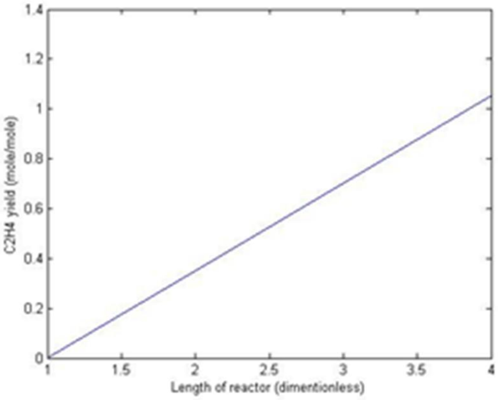

Figure 4 C_2H_4 yield along the length of the reactor

Fig (5, 6) demonstrates the yield of ethane (C_2H_6) and propane (C_3H_8). The production of these two hydrocarbons is not very high and theses two hydrocarbons are important products.

To increase their production yield we have to improve the performance of reactor by injecting more hydrogen in the inlet of reactor or by removal of water or by adjusting any other process parameter.

Fig (7, 8) shows the yield of n-butane (n-C_4H_{10}) and i-butane (i-C_4H_{10}) their production yield is good but their yields are not very important and their production yield is not significant in comparison with gasoline which is thedesirable product.

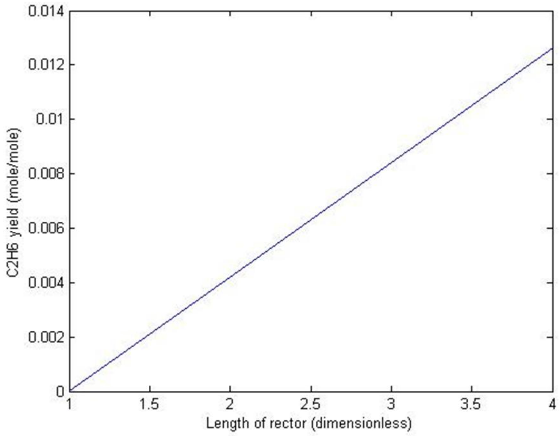

Figure 5 yield of C_2H_6 along the length of the reactor

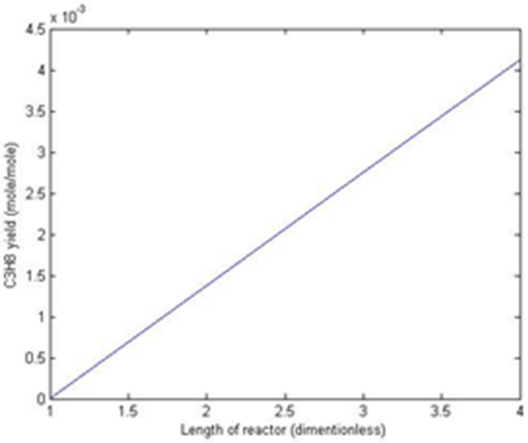

Figure 6 yield of C_3H_8 along the length of the reactor

Fig 9 shows the gasoline production which is better than other hydrocarbons but not very high so we have to increase its production by applying different actions of optimization.

Fig 10 is representing all the hydrocarbons yields in one graph. Here the production of hydrocarbon produced can be compared more easily. The trend in this fig shows that highest production is of iso-butane and then C6+ hydrocarbon production which is the desired product the gasoline. The methane which is undesirable product, its yield is not very high but it could be reduced further as the reactor is conventional reactor not the optimized one.

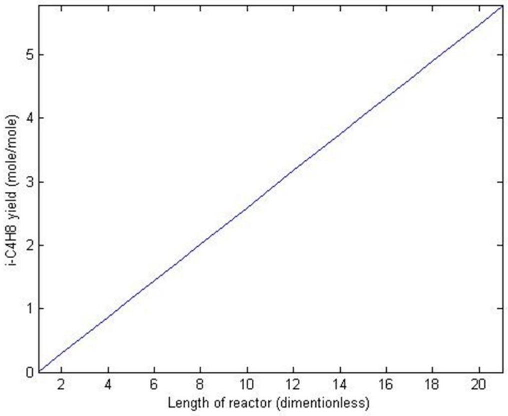

Figure 7 Yield of i-C_4H_8 along the length of the reactor

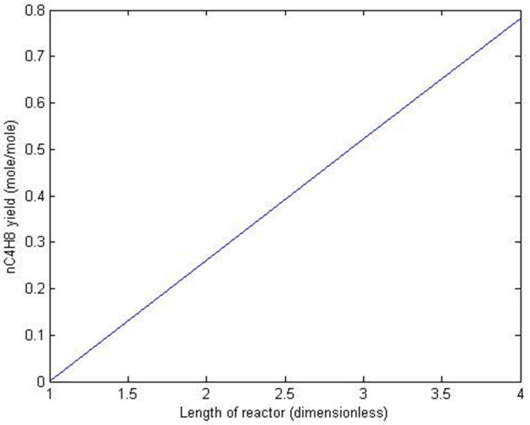

Figure 8 yield of n-C_4H_8 along the length of the reactor

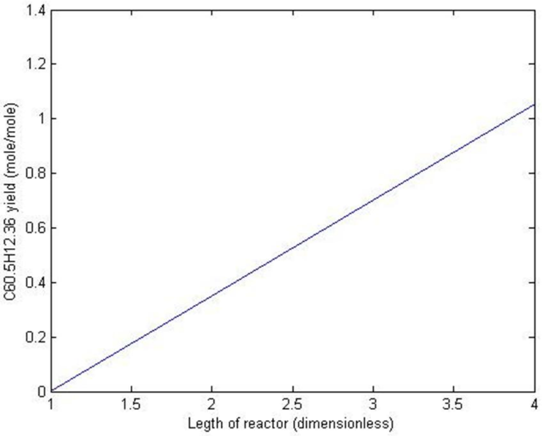

Figure 9 Yield of $C_{6.06}H_{12.36}$ along the length of reactor

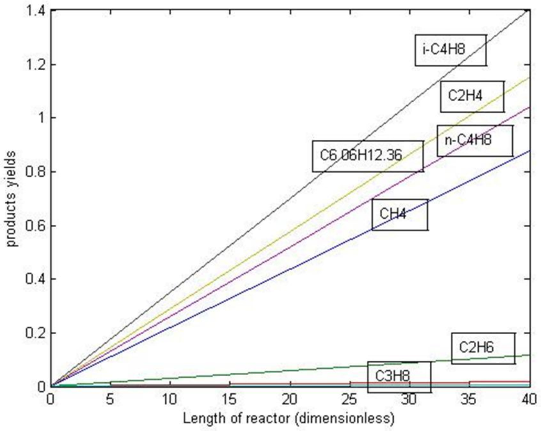

Figure 10 product yields along the reactor length

Fig 11 shows the temperature profile of the fixed bed reactor. The temperature is increased to its peak point at 573.12 due to exothermic nature of the reaction. The temperature is controlled by circulating the boiling water in shell side of the reactor; due to this the temperature descends to the boiling water temperature of shell side**.**

Fig 12 shows the pressure drop across the length of reactor. The pressure drop is increasing along the length of the reactor from 17 to 17.06 bars.

Fig 13 shows the production of CO_2 during water gas shift reaction. The CO_2 gas is greenhouse gas and is a byproduct of FTS. Hence is amount of production should be minimized.

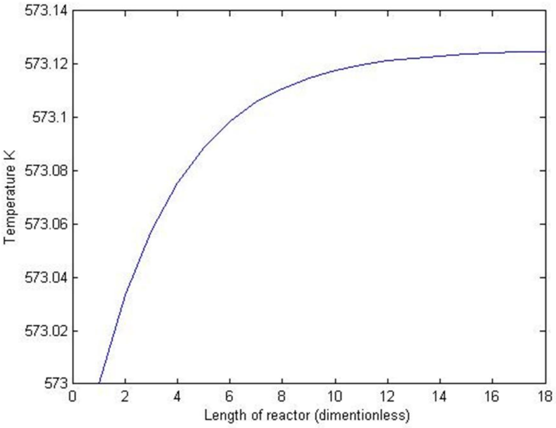

Figure 11 Change in Temperature (K) across the reactor

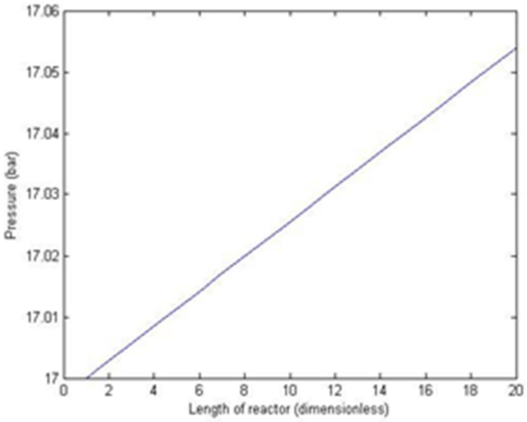

Figure 12 pressure drop across the reactor length

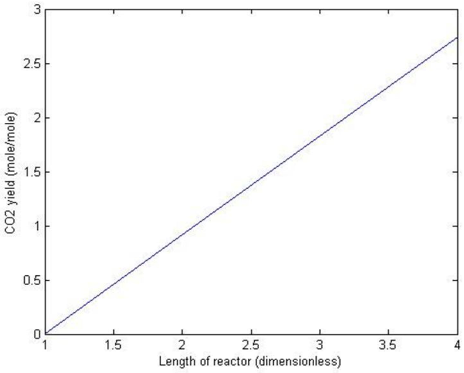

Figure 13 yield of CO_2 during WGS reaction

Conclusion

One dimentional hetrogeonous model of fixed bed reactor is made to predict the performance of FTS. The change in reactor conditions like temperature and pressure are investigated.The conversion of H_2 and CO and product yeild is also forcasted by using MATLAB as simulation tool. This simulation helps to get relialble data about the parameters on which the fixed bed reactor performance greatly depends. Also prior information about the FTS performance helps to optimize the process by applying various techniques. however this is a theoretical study, the industrial application of this model may requires experimental studies too.

Acknowledgement

Mr Shahid Hussain Ansari my supervisor is acknowledged gracefully. The support of Muhammad Noman Aslam Khan is also acknowledged.

Nomenclature

a_v	Specific surface area of catalyst pellet (m^2m^{-3})
A_c	Cross section area of each tube (m^2)
c	total concentration (mol m^{-3})
C_p	Specific heat of the gas at constant pressure (Jmol^{-1})
D_i	Tube inside diameter (m)
E_i	Activation energy for elementary reaction step i, (kJ/kmol)
F	Total molar flow rate (mol s^{-1})
$\Delta H_{f,,i}$	Enthalpy of formation of component i (Jmol^{-1})
k	Rate constant of reaction (mol Kg^{-1}bar^{-1}/2s^{-1})
k_g	Mass transfer coefficient for component i (ms^{-1})
P	Total pressure (bar)
P_i	Partial pressure of component i (Pa)
r_i	Reaction rate of component i (mol kgcat^{-1} s-^{1})
R	Universal gas constant (J mol^{-1} K^{-1})
Re	Reynolds number
Sci	Schmidt number of component i
T	Temperature (K)
u	Superficial velocity of fluid phase (m s^{-1})
u_g	Linear velocity of fluid phase (m s^{-1})
U	Overall heat transfer coefficient between shell and tube sides (W m^{-2} K^{-1})
v_{ci}	Critical volume of component i (cm^3mol^{-1})
y_i	Mole fraction of component i
z	Axial reactor coordinate (m)

Greek letters

ε_b	Void fraction of catalyst bed
μ	Viscosity of fluid phase (kg m^{-1} s^{-1})
ρ	Density of fluid phase (kg m^{-3})
ρ_b	Density of catalytic bed (kg m^{-3})
η	Catalyst effectiveness factor

Superscripts

g	In bulk gas phase
s	At surface catalyst

Subscripts

0	Inlet conditions
i	Chemical species
k	Reaction number index

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Annex II Effect of different supports on performance of Fe-Cu based catalysts for Fixed-bed FT synthesis

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Abstract

Iron catalysts supported on silica, alumina and mixture of alumina and silica were prepared by incipient wetness impregnation method. Pore sizes of both the catalysts were established using BET and SEM characterization techniques. Catalysts with different pore size have different CO adsorption property, which in turn affects the Fisher-Tropsch activity. Fisher-Tropsch activity of these catalysts was evaluated by using 1-D heterogeneous model of fixed bed reactor under operating conditions of temperature 573K, pressure 17 bars and H/CO ratio 2.1. The CO conversion and higher hydrocarbons production was highest in SiO_2 supported catalyst. This indicates that silica supported catalysts shows high FTS activity, higher water-gas shift reaction and higher selectivity to C5+ hydrocarbons and facilitates the CO adsorption. The FTS activity of both Al_2O_3 and SiO_2/Al_2O_3 was very similar and lesser than SiO_2.

Keywords: *Fe Catalyst; F-T synthesis; FTS activity; support; wetness impregnation*

Introduction

The depletion of crude oil reserves and higher cost and complexities associated with heavy oil recovery has diverted the research to alternate energy resources. Therefore this scenario has resulted in a rapid increase in demand for liquid fuels. The spectrum of FT synthesis is very broad and many researchers are working on the controlling and limiting the product selectivity. The most desired products of FTS are those having low methane and oxygenate content, high C5+ content [1] and high alkene/alkane ratio. This control of product selectivity could be achieved by modification of catalyst used during the reaction, the reactor and operating conditions of the reactor [2]. Ruthenium (Ru), Nickel (Ni), cobalt (Co) and iron (Fe) are three most common catalysts used in FTS. Co and Fe are mostly used in industry. Iron based catalyst is low cost and has a high WGS activity. Due to its WGS activity, it is best suited for CO rich syngas created from coal gasification. Fe as FT catalyst is more resistant to organic sulfur poisons and has a more flexible product slate than Co or Ru. However, it also has the lowest activity among these three. Fe catalyst is less resistant to attrition than Co. Addition of structural promoter can improve the attrition resistance. SiO_2 and Al_2O_3 are the main promoters used in FT catalysts. SiO_2 is mostly used in Fe catalysts and Al_2O_3 in Co catalysts. To achieve high activity and stability, Fe catalysts require alkali promotion. FT reactors are categorized as either high temperature (HTFT) or low temperature (LTFT) reactors. The key difference is that a liquid phase forms when operating in LTFT reactors, while HTFT reactors operate entirely in the gas phase. LTFT fixed bed and slurry-phase systems are appropriate for producing liquid phase products. Packed bed reactors may have hot-spots causing catalyst deactivation, and thermal runaway[3]. Despite these drawbacks, the packed bed reactor is widely used for F-T process studies such as catalyst development, kinetics measurement, and so on. A packed bed reactor has some benefits, such as ease of operation, no need for additional separation device, and scale-up for large scale reactors.

Many researchers investigated the influence of different supports used in FT catalyst on FT activity. Robert J Obrien et al [4] investigated the FTS performance and attrition of supported and unsupported Fe based catalysts. Junling et al [5] studied the effect of support used for Co based catalysts for FTS using three types of alumina supports. Yang et al [6] investigated the effects of SiO_2 contents, addition methods of SiO_2, and drying process of catalyst on physic-chemical properties and FTS performance of Fe-Mn catalyst. Song et al [7] Studied the effect of pore size of support of Co based catalyst on FT selectivity. Wen et al [8] compared the Fe based catalysts with two different supports of Al_2O_3 and SiO_2. They prepared the catalyst by co-precipitation and spray-drying methods. Wan el at [9] studied the promotional effect of Cu and K promoters on Fe catalyst on FTS activity. Mohanty et al [10] added zeolite to $CuO–CoO–Cr_2O_3$ to investigate the FTS activity in a fixed bed reactor. They changed the operating conditions of the reactor and optimize the FT reactor. Satyen et al [11] checked the FTS activity by using a range of weight fractions of K in SiO_2 supported Fe catalyst. Satyen et al [12] also investigated the effects of change in amount of active components in silica supported Fe-Cu-K catalyst on activity, selectivity, carbon number distribution of liquid hydrocarbon product and its physiochemical properties. Arsalanfar et al [13] used different supports for Fe-Cu-Mn catalyst and investigate the FTS selectivity and catalytic performance.

The Fischer Tropsch synthesis is highly dependent on such parameters as temperature, pressure, catalyst, gas feed flow rate, and carbon monoxide to hydrogen molar ratio. Scientists often conduct experiments involving many parameters, especially in the development of new catalysts, and cannot afford the time and cost to pursue every combination of these parameters. Therefore they must rely on computer modeling and simulation to assist them in exploring the parameter space to understand the effects of new processing conditions, catalyst kinetics and different kinetic mechanisms.

In the literature, several levels of superiority of mathematical models have been suggested to study the performance of fixed bed reactors. In fixed bed reactors there are two broad categories of models, Pseudo homogeneous models and heterogeneous models. Pseudo homogeneous models do not account explicitly the presence of catalyst; they reflect that the bulk and intra particle conditions are same.

These models are for the systems with:

$T_g \approx T_s$ or $C_g \approx C_s$

While heterogeneous models reflect that the bulk and intra particle conditions are different and they have separate equations for fluid phase and solid phase.

These models are for the systems with:

$T_g \neq T_s$ or $C_g \neq C_s$

Atwood et al [14] developed one dimensional, heterogeneous model and simulate the reactor to find the product distribution and effect of catalyst used on CO conversion on commercial scale reactors. Bub et al [15] studied the distribution of products in fixed bed reactor for FT synthesis by using kinetic measurements. They used pseudo-homogeneous one dimensional model and not consider the intra particle diffusion. Jess et al [16] proposed pseudo-homogeneous two dimensional fixed bed reactor models to compare the N_2 rice and N_2 free syngas as the reactants on the performance of reactor. Intra particle diffusion was neglected as model is pseudo-homogeneous. Wang et al [17] developed one dimensional heterogeneous fixed bed reactor model by using SRK equation of state. Model validation was performed using pilot plant data developed internally. Nevertheless, this model is not general. Because it was developed for a specific catalyst, modification to suit another catalyst would require obtaining extensive experimental activity and selectivity data for the new catalyst.

In this study catalysts with weight compositions of $90Fe/3.2Cu/50SiO_2$, $90Fe/3.2Cu/50Al_2O_3$ and $90Fe/3.2Cu/25SiO_2/25Al_2O_3$ were prepared by wetness impregnation technique. The catalyst samples were characterized by using BET and SEM techniques. In order to confirm the results of characterization, the values of pore sizes were used in 1D heterogeneous model. The model was developed using RK-1 method in MATLAB.

Experimental Procedure

The catalyst samples were prepared by using incipient wetness impregnation method. Following this method, required amount of supports are calcinated at 600˚C for 6 hours. Then metal precursor was dissolved in 50ml distilled water and these solutions were poured in the calcinated support and stir it for 40 to 45 minutes rigorously. After stirring, the sample was evaporated by setting the evaporation temperature between 100˚C. After complete evaporation the sample was ground to fine powder. The powdered samples were dried in vented oven for 16 hours at 120˚C. Finally the sample was calcinated in the furnace at 550˚C for 5 hours. The final weight compositions of catalysts samples are $90Fe/3.2Cu/50SiO_2$, $90Fe/3.2Cu/50Al_2O_3$ and $90Fe/3.2Cu/25SiO_2/25Al_2O_3$.

Characterization Techniques

Pore size, BET surface area and pore volume were measured by nitrogen physisorption at 77K by using Micrometrics instrument. The sample was degassed at 250K for 4 hours in flowing helium (30ml/min).

Particle size was determined under scanning electron microscope of both the catalysts. The sample was magnified 100 times operating at 20kV. The particle size was compared with BET to confirm the results.

Reactor Modelling

Model assumptions

Assumptions are considered for the mathematical modeling of fixed bed Fischer-Tropsch synthesis reactor. These include that the system is in steady sate condition, the gas mixture is considered as ideal, the model assumed to be one dimensional heterogeneous model, axial dispersion of heat and mass is neglected, plug flow design is considered and the reactor is in adiabatic condition.

Mathematical model

The mass and energy conservation equations for heterogeneous one dimensional model are:

Gas phase equations

$$-\frac{F_t}{A_c} + \frac{dy_i}{dz} + a_v c k_{gi}(y_{is} - yi) = 0 \qquad (15)$$

$$-\frac{F_t}{A_c} * C_p * \frac{dT}{dz} + a_v h_f(T_s - T) + \frac{\pi D_i}{Ac} * U_{shell}(T_{shell} - T) = 0 \qquad (16)$$

Solid phase equations

$$a_v c k_{gi}(yi - y_{is}) + \eta r_i \rho_b = 0 \qquad (17)$$

$$a_v h_f(T - T_s) + \eta \rho_b \sum_{i=1}^{N} ri\,(-\Delta H_{,f,i}) = 0 \qquad (18)$$

Boundary Conditions

Z=0, $y_i = y_{i,in}$ $T = T_{in}$

Design Equations

Some design equations are used to complete the heterogeneous model. To analyze the heat and mass transfer phenomena between gas phase and catalyst particles and evaluation of physical properties of the chemical components and overall heat transfer coefficient some correlations are used. These equations include component heat capacity equation by [18], viscosity and thermal conductivity equations from[19], mass transfer coefficient between gas and solid phase by [20]and overall heat transfer coefficient from [21].

Results and discussions

Nitrogen physisorption measurements

BET surface area, pore volume and pore size of the samples are given in table 1. It can be seen that catalyst with silica support has highest value of BET and pore volume. This shows that catalyst with silica support is highly porous and has high internal surface area available for the reaction. The BET and pore volume of catalyst with alumina and alumina/silica combined are almost equal but have lesser porosity and internal surface area than catalyst with silica support alone.

SEM Micrographs

The particle sizes of catalysts with different supports were investigated with SEM micrographs shown in Fig 1 and particle sizes in table 2. The results of particle sizes of all three catalysts are also supported by Nitrogen physisorption measurements. This obtained data is used in the MATLAB code to confirm the FTS activity is highest in case of using silica as a support with Fe and Cu precursors.

Modelling Results

CO and H_2 Conversion

The conversion of CO and H_2 for SiO_2, Al_2O_3 and combined SiO_2/Al_2O_3 supported Fe-Cu based catalysts is shown in Fig 2&3. The FTS activity increases with decreasing particle and pore diameters. As the characterization results revealed that particle size and pore diameter of SiO_2 supported catalyst are smaller than Al_2O_3 and combined SiO_2/Al_2O_3 supported catalysts. Therefore the conversion of CO and H_2 should be greater for SiO_2 supported Fe catalyst. This is supported by modelling result.

Table 16 Texture Properties of Catalysts

Catalyst	BET (m^2/g)	Pore vol (cm^3/g)	Pore size (A^o)
Fe/Cu/SiO_2	174	0.22	14.80
Fe/Cu/Al_2O_3	54.35	0.249	18.37
Fe/Cu/SiO_2/Al_2O_3	52.6	0.249	18.37

Table 2 catalyst particle size

Catalyst	Particle size
Fe/Cu/SiO_2	45.6nm
Fe/Cu/Al_2O_3	50nm
Fe/Cu/SiO_2/Al_2O_3	50.6nm

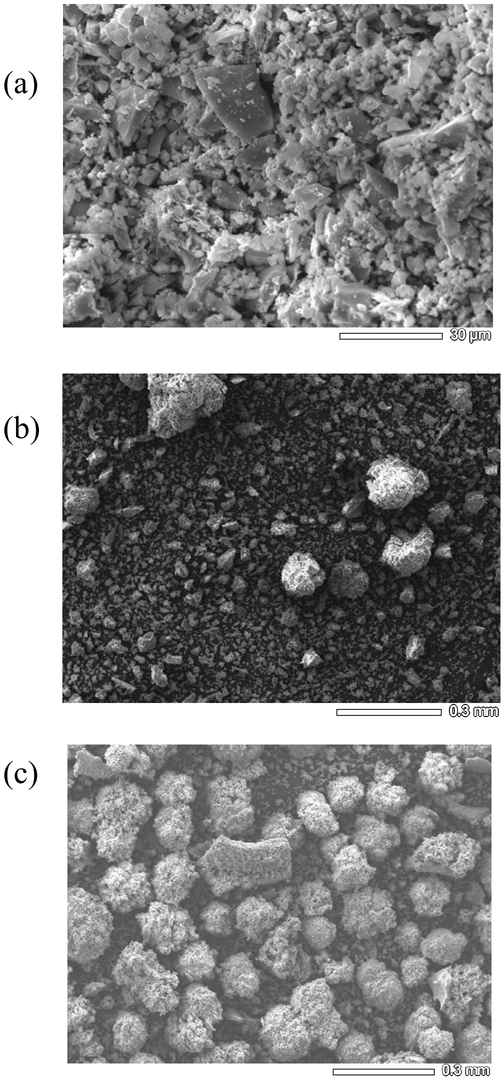

Figure 1 The SEM images Fe-Cu catalysts with supports (a) Al_2O_3 (b) SiO_2 (c) Al_2O_3/SiO_2

Temperature

The temperature change for SiO_2, Al_2O_3 and combined SiO_2/Al_2O_3 supported Fe-Cu based catalysts is shown in Fig 4. Here we can see that the silica supported catalyst gives the best range of temperature in which we can get maximum C5+ hydrocarbons. The temperature is not dropped beyond 300K. When using other two catalysts, the temperature is dropped too much which is not helpful in getting the desired product of FTS which is C6 to C10. The temperature change along the length of reactor also shows that for Fe-Cu based catalysts, SiO_2 support is most appropriate.

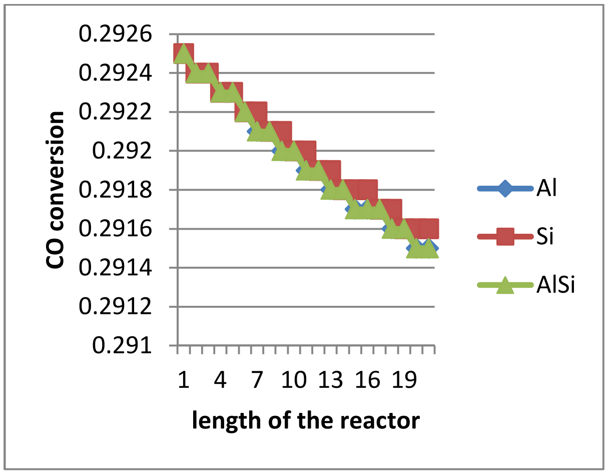

Figure 17 CO conversion

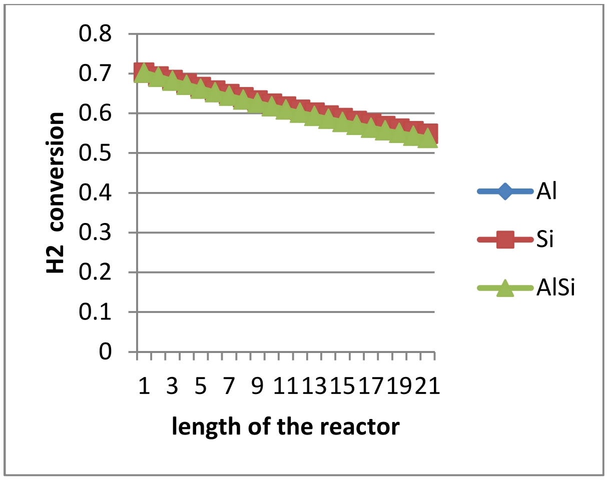

Figure 18 H2 conversion

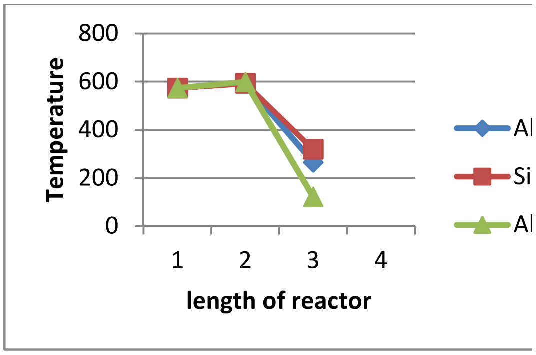

Figure 19 Temperature change

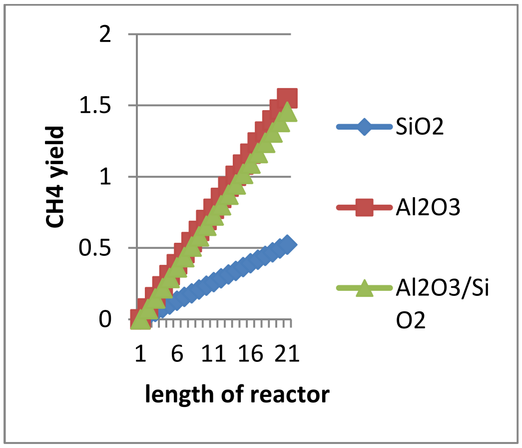

Figure 20 CH4 yield

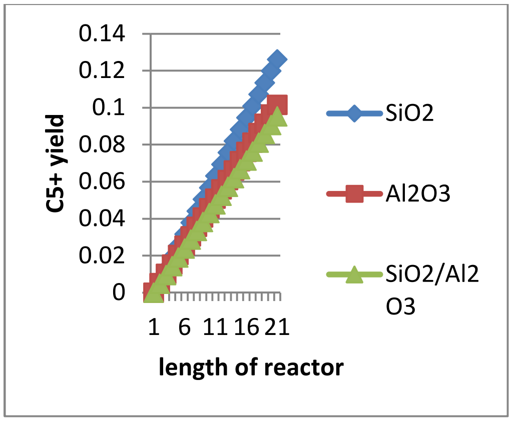

Figure 21 C5+ yield

Product yield

The product yield of methane and C5+ hydrocarbons is shown in fig 5&6. During FTS methane is the undesirable hydrocarbon and C5+ hydrocarbons are most desirable as they are mainly gasoline. It is clear from the figures that by using catalyst $90Fe/3.2Cu/50SiO_2$ in fixed bed reactor during FTS we will get more desirable hydrocarbon yield, which is C5+ and less CH4 yield that is undesirable FTS product. Moreover there is not much difference in the yields of hydrocarbons if $90Fe3.2/Cu/50Al_2O_3$ or $90Fe/3.2Cu/25SiO_2/25Al_2O_3$ is used.

Conclusion

Al_2O_3, SiO_2 and $Al2O3/SiO_2$ supported Fe-Cu based catalyst were prepared to compare their FTS activity. The characterization and modelling results show that silica supported iron-copper based catalyst has high activity than alumina and combined silica and alumina.

Acknowledgement

Mr Shahid Hussain Ansari my supervisor is acknowledged gracefully. The support of Muhammad Noman Aslam Khan is also acknowledged.

Nomenclature

a_v	Specific surface area of catalyst pellet (m^2m^{-3})
A_c	Cross section area of each tube (m^2)
c	total concentration (mol m^{-3})

C_p	Specific heat of the gas at constant pressure ($Jmol^{-1}$)
D_i	Tube inside diameter (m)
E_i	Activation energy for elementary reaction step i, (kJ/kmol)
F	Total molar flow rate (mol s^{-1})
$\Delta H_{f,,i}$	Enthalpy of formation of component i ($Jmol^{-1}$)
k	Rate constant of reaction (mol $Kg^{-1}bar^{-1}/2s^{-1}$)
k_g	Mass transfer coefficient for component i (ms^{-1})
P	Total pressure (bar)
P_i	Partial pressure of component i (Pa)
r_i	Reaction rate of component i (mol $kgcat^{-1}$ s-^{1})
R	Universal gas constant (J mol^{-1} K^{-1})
Re	Reynolds number
Sci	Schmidt number of component i
T	Temperature (K)
u	Superficial velocity of fluid phase (m s^{-1})
u_g	Linear velocity of fluid phase (m s^{-1})
U	Overall heat transfer coefficient between shell and tube sides (W m^{-2} K^{-1})
v_{ci}	Critical volume of component i (cm^3mol^{-1})
y_i	Mole fraction of component i
z	Axial reactor coordinate (m)

Greek letters

ε_b	Void fraction of catalyst bed
μ	Viscosity of fluid phase (kg m^{-1} s^{-1})
ρ	Density of fluid phase (kg m^{-3})
ρ_b	Density of catalytic bed (kg m^{-3})
η	Catalyst effectiveness factor

Superscripts

g	In bulk gas phase
s	At surface catalyst

Subscripts

0	Inlet conditions
i	Chemical species
k	Reaction number index

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