PARAMETRIC STUDY OF FISCHER-TROPSCH SYNTHESIS IN SUPERCRITICAL PHASE CARBON DIOXIDE

by

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TITLE: PARAMETRIC STUDY OF FISCHER-TROPSCH SYNTHESIS IN SUPERCRITICAL PHASE CARBON DIOXIDE

MAJOR PROFESSOR: Dr. Kanchan Mondal

The results from studies on Fischer Tropsch synthesis wherein syngas was dissolved in CO_2 are presented. The syngas generally used was typical of that obtained from coal gasification, i.e. CO:H_2 of one. Under these conditions Co-based catalysts without any water gas shift catalyst does not perform well while Fe – based catalysts have been found to be useful. However, the Fe based catalysts have a propensity towards CO_2 selectivity via the primary FT reaction, Boudouard reaction and the water gas shift reaction. The use of CO_2 as a solvent was found to suppress the CO_2 and CH_4 selectivity while enhancing the hydrocarbon selectivity and CO conversion when FT synthesis was conducted using coal derived syngas on Fe-Zn-K catalysts. The effects were found to be significantly pronounced at pressures higher than or equal to 1200 psig. It should be noted that CO_2 is supercritical at pressures higher than 1070 psig and 31.4 ^{o}C. The effect of CO_2 partial pressure, reactor pressure, reaction temperature, catalyst loading and H_2:CO ratio in syngas on the liquid product distribution was evaluated. Some of the notable findings include product tenability by varying temperature and pressure as well as varying the CO_2 partial pressure and the syngas composition. Increasing the reactor pressure was found to favor longer chain growth. In addition, it was noted that the ratio between CO_2:syngas in the reaction mixture is an important factor in the liquid product distribution. A higher value of the ratio is seen to favor hydrocarbon synthesis, while

a lower value of the ratio favors oxygenate production particularly pentanols and butanols. In addition, the data on the once through fractionation of the products utilizing the solubilities in supercritical CO_2 and pressure tuning were encouraging. It was found that the products can be easily fractionated into narrow carbon chain length distributions downstream of the reactor by simply reducing the pressures in each collection vessel. It was generally observed that oxygenates and higher n-alkanes were collected in the higher pressure trap and lower hydrocarbons in the subsequent lower pressure traps.

DEDICATION

I would like to dedicate this body of work to my mother, Dhani Maya Gautam, and father, Dil Prasad Gautam, who always loved and supported me through all obstacles in my life. Also, dedication is deserved to my brothers, Jeevan Gautam and Jagadish Gautam. They also offered me love and support during the completion of this study.

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CHAPTER 1

INTRODUCTION

It is expected that the demand for diesel fuel will rapidly grow in future. Along with this rise in demand, there are other various causes such as decreased supply, natural disaster and political conflicts that will contribute to the price of the said fuels. There is a very close correlation between the usage of fossil fuels and the economic condition of individual. Hence, reduction of people's dependence on fossil fuels is a major challenge for most economically advanced countries of the world. This is where sustainability comes into play since it will aid in sustaining the available high density fuel source. So there is an immediate need of exploration of alternative sources for the fossil fuels resulting in the wave of today's interest in renewable and synthetic fuels. With the production of renewable fuels like ethanol and bio diesel, dependency of United States in foreign oil can be decreased to some extent. But the extreme supply/demand is driving the interest of the world towards the production of synthetic fuels from coal.

Synthetic liquid fuels were first produced in Germany at the beginning of 20th century. One of the well-known routes for the conversion of coal, natural gas and biomass to fuels is through their conversion to an intermediate syngas or (synthesis gas). This offers the opportunity to furnish a broad range of environmentally clean fuels, additives and chemicals which can be clearly seen in figure 1 below.

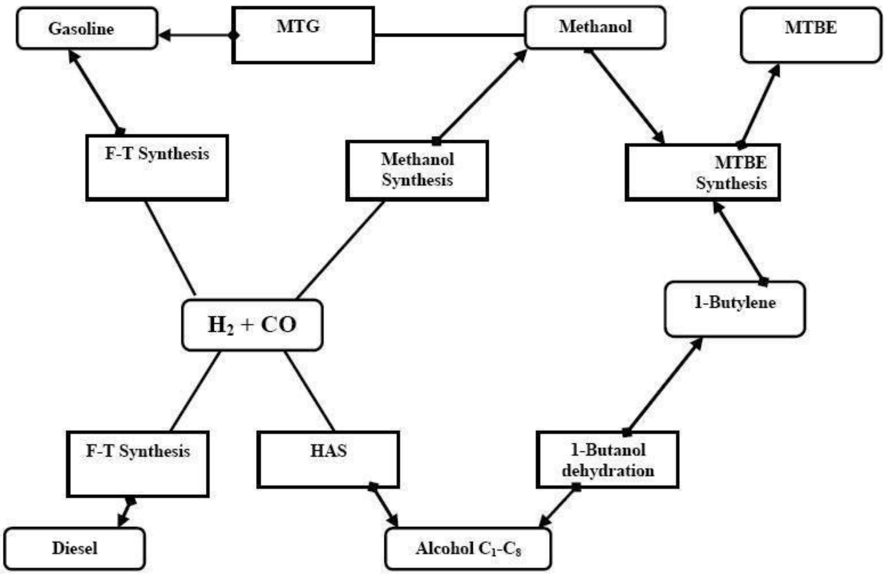


Figure 1: Syngas Applications [2]

The most common way for the production of synthetic liquid fuels is by the Fischer Tropsch Synthesis (FTS) reaction which can be carried out at both high and low temperatures. FTS is a catalyzed reaction through which coal, biomass or natural gas reservoirs can be exploited in order to obtain high grade synthetic fuels in areas where petroleum reserves are not available. Aside from hydrocarbons, FT synthesis also generates oxygenates (alcohol and ethers), aromatics, carbon dioxide and water. High quality gasoline and diesel products can be obtained from FTS compared to crude oil derives (fuels and liquid) which can further be processed for the fractionation of products employing distillation.

For the catalytic FTS process, cobalt, iron, nickel, and ruthenium are known to be active catalysts for the synthesis gas conversion to distinctive hydrocarbon chains during the FTS. Ni-based catalysts have demonstrated a higher selectivity for the formation of methane, while Ru-based catalysts have shown a higher selectivity for paraffin waxes. Cobalt and iron are the most preferred catalyst because of their relatively low cost and high availability and are preferred for the production of gasoline, kerosene, and diesel fuels. Because of high cost, scarcity and patents on Co-based catalysts, Fe catalysts are preferred. However, it should be noted that Co catalysts, with higher activity, have been shown to produce a broad distribution of the carbon chain molecules, varying from light to heavy hydrocarbons with little water-gas shift (WGS) activity. The deactivation of catalyst, caused by the heat generated and the waxes builds up on the catalyst surface preventing the active sites from converting CO and H_2 to hydrocarbons for chain growth to liquid fuels, reduces the life of the catalysts and in turn increases the cost of production. Fe-based catalysts are often used for high temperature FTS and for low H_2:CO ratio in the feed syngas. The latter is primarily due to its known WGS activity. In addition, it should be noted that Fe-based catalysts are best known for higher selectivity of oxygenated hydrocarbons, olefins, and CO_2.

Majority of the reactors for FTS today in commercial use are fixed-bed, slurry-bubble, and fluidized-bed type. The fixed-bed reactor (gas phase) provides exceptional reactant diffusivity for the FT process but presents problems due to the overheating of the catalyst, as a result of the high exothermic FT reaction. Also, gas phase FTS lacks the capacity to prevent the buildup of heavy hydrocarbons that deactivate the catalyst. In addition to excellent solvent properties, slurry-bubble reactors also have excellent heat transfer properties to keep the catalyst surface free of hot spots and waxes, because of the heat capacity of the liquid solvent, and, thus, impede deactivation. But these reactors lack the diffusivity of gases inside the reactor resulting in relatively low conversion of CO when compared with gas phase system than that in gas phase rectors. To overcome the problem of diffusivity, fluidized bed reactors are utilized but these are often plagued with problems of deposition of heavy waxes and their agglomeration on the catalyst surface. This causes shutdowns due to de-fluidization as well as catalyst deactivation. So the search for a new medium that provides for diffusivity like gas and heat transfer capacity like that of liquid led to the development of supercritical phase FTS with selective liquid and gas phase properties. This type of reactor systems are expected overcome the limitations of traditional reactors by providing high diffusivity of gas phase properties and the heat transfer and wax removal properties of the slurry-bubble reactors.

For supercritical FTS, supercritical fluids in common use are hexane, methanol, benzene, and heptanes. Much research has not been done for use of Sc-CO_2 as supercritical FTS media. When supercritical CO_2 was used for supercritical FTS, then it was found that the selectivity of CO_2 and CH_4 was inhibited [7]. Major prospective advantages of FTS in supercritical CO_2 are suppression of CO_2 formation that reduces the carbon utilization, enhancement of syngas conversion, enhancement of heat removal from FT catalyst surface, facilitation for wax removal from the catalyst surface and reduction in re-adsorption of crucial olefins.

FTS in supercritical CO_2 was studied at SIUC by Benoit [7] in a batch mode. He observed the enhancement in reaction rate and suppression in the CO_2 and CH_4 selectivity. Later, to identify its feasibility in continuous flow mode, Perry [6] continued the research with continuous flow fixed bed reactor, He compared the FTS in gas phase, non critical and supercritical phase. It was found that the influence of CO_2 enhances the hydrocarbon production and affects its distribution.

Further research in supercritical phase FTS with $ScCO_2$ was continued. The experiments testing the effectiveness of using CO_2 as the solvent in the supercritical phase FT synthesis were conducted in a continuous flow reactor system with online GC connected for gas product analysis. Each FT reaction was run for average of 7 days. Different sets of experiments were conducted to find out the effect of variation in different process parameters in the product distribution and composition. FTS experiments were conducted in different temperature and pressures. Amount of catalyst loading was varied for the experiment with all other parameters constant. Amount of CO_2 was varied so as to provide variation in dilution. Different types of syngas with different ratios of hydrogen and carbon monoxide were used for the experiment. The effect of the supercritical phase properties on the FTS was evaluated. FTS experiments were conducted in supercritical phase in different temperatures and pressure. Variation in catalyst loading was done to find the deviation in the product distribution. Feed source were supplied in different proportions to see the subsequent results.

CHAPTER 2

LITERATURE REVIEW

The lack of domestic petroleum supply in Germany at the beginning of 20th century encouraged the German government to support the research on alternative fuel resources at that time. The German researchers came up with the invention and early development of the Bergius coal liquefaction (hydrogenation) and Fischer Tropsch synthesis (FTS) which was followed by Germany's commercialization of Bergius and FT synthesis resulting in the global transfer of the German technology [1]. One of the first and largest commercial plants in United States for the production of liquid fuels from carbon monoxide and hydrogen went into operation in 1950, in Brownsville, Texas. The plant was designed by Hydrocarbon Research Inc., for Carthage Hydrocol, Inc. [2].

Bergius began the German mission for energy independence with his invention and early development of high pressure coal hydrogenation (1910-1925) in Rheinau-Mannheim. Bergius crushed coal (containing less than 85% carbon) and dissolved in a heavy oil to form a paste. The paste was reacted with hydrogen gas at high pressure (around 200 atmospheres) and high temperature of 400^{o}C to obtain petroleum like liquids. Matthias Pier, in 1925 at BASF, made major advancements in the process that notably improved product yield and quality. Pier separated the conversion into two stages, a liquid stage and a vapor stage by developing sulphur-resistant catalysts, such as Tungsten Sulphide (WS2) [1].

A decade after Bergius began his work, Franz Fischer and Hans Tropsch played a key role in invention of second process for the synthesis of liquid fuel from coal at the Kaiser-Wilhelm Institute. Fisher and Tropsch reacted coal with steam to produce a gaseous mixture of carbon monoxide and hydrogen and then converted the mixture at low pressure from 1 to 10 atmospheres and temperature from 180°C – 200°C to petroleum like liquids. In the 1920s-30s, development of cobalt catalysts by Fischer and his coworkers were critical to the FT success [3].

In 1925, almost 70 % of the world's petroleum was produced by the United States. However during the 1940s, there was a serious fear that the United States and the world were running out of petroleum reserves. The United States Bureau of Mines established a program to develop a coal based supply of transportation fuel in 1943 [2]. The Japanese scientists conducted an excellent laboratory scale demonstration of coal hydrogenation and FTS at that time; however they were not successful in large-scale production. This unsuccessful attempt was accredited by many historians to bypassing of intermediate plant levels and rushing to construct large synthetic plants [3].

Sasol Company, South Africa's largest oil company, has played a major role on recent developments in FTS Technology, especially in the reactor design and new FTS catalytic systems [4]. Lately, many countries became involved in developing or using existing Fischer –Tropsch technologies for the production of liquefied fuels from natural gas and coal [2].

Fisher Tropsch Synthesis Reaction Chemistry

The stoichiometry, in case of the Fischer Tropsch Synthesis process, is primarily concerned with the ratio of consumption of hydrogen and carbon monoxide [5]. The chemistry that takes place in a Fischer Tropsch reactor is complex but can be simplified into the following chemical reactions.

Methane

$CO + 3H_2 \rightarrow CH_4 + H_2O$ (1)

Heavier hydrocarbons

$nCO + (2n+1) H_2 \rightarrow (-CH_2-)_n + nH_2O$ (2)

Alcohols

$nCO + 2nH_2 \rightarrow C_nH_{2(n+1)}O + (n-1) H_2O$ (3)

Water Gas shift (WGS)

$CO + H_2O \rightarrow CO_2 + H_2$ (4)

From the equation (2), it is seen that the theoretical stoichiometric ratio of CO and H_2 for FT is 1:2. The carbon monoxide and hydrogen adsorb and dissociate at the catalyst surface to form hydrocarbon chains. The ratio of the consumption of carbon monoxide and hydrogen may vary significantly depending on the extent of other reactions shown and secondary reactions [5].

The equation (2) is a simplification of a polymerization reaction of which the primary products are α-olefins. It can undergo secondary reactions as hydrogenation, carbon chain propagation, isomerization and hydro cracking [6].

An excess of CO or H_2 can be added to the reactants to control the syngas ratio (H_2: CO). However, an excess of CO results in the formation of more CO_2 via the Boudouard reaction, causing deposition of soot (C) on the catalyst surface rendering it inactive. The Boudouard reaction is given by equation (5) [7].

$2CO \rightarrow C + CO_2$ (5)

Also, the carbon can react with hydrogen in syngas to form another undesirable product i.e. methane, in FTS as shown in equation (6) [6].

$C + 2H_2 \rightarrow CH_4$ (6)

If the preferred ratio of syngas is used, it supplies H_2 in the FT reaction for the CO reduction which in turn results in a corresponding decrease in the disproportionation of CO. Moreover, the H_2 also acts as scavenger for oxygen. It should be noted that, use of Fe based catalysts results in the participation of carbon monoxide for scavenging the oxygen radical as shown by equation (7).

$$2nCO+nH_2 \rightarrow (CH_2)_n + nCO_2 \qquad (7)$$

It is thus found that there is a probability of the formation of additional carbon dioxide in FTS reaction, which is always an indication of loss of carbon utilization for the formation of useful hydrocarbons [8].

The initial attempt to understand the polymerization behavior of non homogeneous materials led to the development of first FTS chain growth model which went through series of development resulting in current well-known Anderson-Shultz-Flory (ASF) product distribution model. [2]

According to the model, the polymerization reaction in FTS was assumed to be initiated on the surface of the catalyst by a monomer containing one carbon atom, while chain growth takes place by the addition of one monomer at a time. The weight fraction (W_n) of a chain with length n can be measured as a function of chain growth probability (α) as shown in equation (8).

$$W_n=n\,\alpha^{(n-1)}\,(1-\alpha)^2 \qquad (8)$$

$$\ln(W_n/n)=n\ln\alpha+\ln((1-\alpha)^2/\alpha) \qquad (9)$$

To evaluate the product distribution based on the ASF model, a plot of $\ln(W_n/n)$ vs. n (as in equation (9)) provides a straight line for all hydrocarbon products, whose slope is related to α. It can be seen from the above equations that as α increases, heavier hydrocarbon products are produced. A number of studies have reported deviations from ASF distribution line.

The way to explain the phenomena of hydrocarbon formation is to understand the mechanism of FTS reaction [7]. Today, it is generally accepted that the FTS is a polymerization reaction of surface species that contains one carbon molecule (CH_2). But there is still ambiguity about the mechanism by which the polymerization takes place to form variety of products as olefins, oxygenates, and isomers, to CO_2, H_2O and coke [1].

The metals that have the required FT activity for commercial use as FT catalyst are iron (Fe), nickel (Ni), cobalt (Co) and ruthenium (Ru). If the price of making iron catalyst is x, the relative approximate cost of Ni is 250x, Co is 1000x and Ru is 50000x. Also under pragmatic conditions, Ni produces CH_4 in excess amounts. The availability of ruthenium (Ru) is insufficient and is too expensive for large scale production. Overall, it leaves Co and Fe as viable catalysts [9].

Generally, Co and Fe based catalysts are used for Fischer Tropsch Synthesis. Co catalysts are found to give the highest yields and have the longest life time, producing mainly linear alkanes (paraffins) [10] at reaction temperatures ranging from 180-240^{o}C. The extent of water gas shift reaction (equation 4) for the cobalt catalysts is negligible [5], so it gives higher syngas conversion [11]. The use of iron catalysts is at the upper end of the operating temperatures range (250^{o}C -350^{o}C) and is known for its water gas shift activity, and can thus be used with syngas composition with less than the stoichiometrically required H_2:CO ratio [5]. Typical forms of iron catalysts used for FTS are prepared by precipitation and fusion [2]. Iron based catalysts are generally prepared by precipitation techniques, promoted with Cu, K_2O and bound with SiO_2. For high temperature applications, they are prepared by fusing magnetite together with the required chemical and structural promoters such as aluminum oxide (Al_2O_3) or magnesium oxide (MgO) [9]. These iron catalysts needs to be reduced as they are typically oxides before use, which can be done by reacting it with hydrogen to metallic iron or with carbon monoxide or syngas to various iron carbides. During FTS reaction, phase transition takes place on iron catalysts either due to some of the products (such as water) or the operating conditions (such as temperature) [2]. As Fe-based catalysts exhibit activity at relatively higher temperature and wide range of syngas feed ratios, the Fe based catalysts are found to be an attractive option to complement the Co based catalysts which normally work at lower temperatures [2]. However, Fe catalysts have turnover frequencies of about three times lower than that of Co based catalysts for condition of 200°C and 2.0 MPa. Although the hydrocarbon synthesis rate (per catalyst mass or volume) on Fe-Zn-Cu-K catalysts were similar to those on Co based catalysts, Fe based catalysts was reported to result in much lower CH_4 selectivity [12].

Currently there are two operating modes in FTS. The high temperature (300-350°C) process using Fe based catalysts for the production of gasoline and linear low molecular mass olefins. The low temperature (200-240°C) process using either Fe or Co based catalysts for the production of high molecular mass linear waxes. Since the FT reactions are highly exothermic, it is very important to remove the heat of reaction from the catalyst surface in order to avoid overheating of the catalyst which would otherwise result in an increased rate of catalyst deactivation due to sintering and fouling and also in the undesirable high production of methane [9]. Heavy wax may plug microbes of the catalyst and the catalyst bed itself, resulting in catalyst deactivation as well [13]. For iron catalysts the primary products are found to be 1-alkenes and, to a smaller extent, n-alkanes, of which the 1 alkene may subsequently undergo hydrogenation to an n-alkane, isomerization to the 2-alkane or re-adsorption on the active sites to initiate further chain growth. [14]. No measurable hydrocarbon production from CO_2 could be found under typical FT conditions with cobalt catalysts in slurry reactors. The formation rate of heavier hydrocarbon was significantly higher (about 200 %) for catalysts prepared by impregnation compared to the catalysts prepared by precipitation [15].

The comparison of slurry and fixed bed reactor by C.N. Satterfield [16] showed that there was no significant difference in carbon number distribution, and catalyst activity was slightly less in slurry bubble than fixed bed reactor, while the olefin/paraffin ratio of products from slurry reactor was found to be greater than that obtained from experiments in fixed bed reactors. The Fischer Tropsch reaction is highly exothermic and requires the use of heterogeneous catalysts in a temperature range between 200 and 350^{o}C under elevated pressure. Both fixed bed and slurry reactor are found to have different disadvantages. The fixed bed reactor system exhibits high pressure drop, low catalyst separation, less ideal residence time behavior, and highly demanding scale up, whereas the slurry reactor (bubble column) faces the need for catalyst separation, less ideal residence time behavior, and highly demanding scale up [17]. It is found that traditional fixed bed FTS reactors are susceptible to local overheating of the catalyst surface and condensation of heavy wax in the catalyst pores under heterogeneous catalytic gas phase reaction conditions. This, in turn, shortens the catalyst life time and reduces syngas conversion. Although reaction rates and product diffusivities are exceptionally high in the gas phase, inadequate heat removal during exothermic reaction can increase methane formation [18]. Despite these drawbacks, gas phase reactors are used on a commercial scale, mainly due to their ability to produce heavy molecular weight waxes which can then be hydro cracked to form diesel fuels [19].

Slurry-phase bubble-column ("slurry") reactors are found to be superior in terms of heat removal capabilities when compared to the traditionally used fixed-bed reactors for carrying out the F-T reaction with constant reaction temperature without deactivation. In addition, liquid phase reaction media is capable of dissolving the higher molecular weight products compared to gas phase reaction media [19]. However, the separation of the catalyst from the wax product is an issue that yet needs to be resolved [20]. The slurry reactors suffered from mass transfer limitations which reduces the concentration of reactant at the catalyst surface. To overcome the mass transfer limitations, relatively large reactor volumes are required which is also an issue for research [21]. It was found that the mass transfer rate of syngas into the micro pores of the catalyst is low in the slurry phase because of which the overall reaction rate is considerably lower than that in gas phase FTS [22]. So, the ideal FTS medium would therefore be one with gas-like transport properties and liquid-like heat capacity, thermal conductivity, and solubility characteristics. These considerations have driven research on FTS towards the application of supercritical fluids (SCFs) and compressed gas solvents as the reaction medium. SCF solvents combine the desirable properties of gas-like diffusion along with liquid-like heat transfer and solubilities to provide well-controlled FTS. Also the steady state condition was achieved much faster in SCF-FTS than in gas phase [22].

The model proposed by Fujimoto and Yokota suggests that the mass transfer rates of gaseous components to catalyst surface is highest in gas phase and in supercritical phase but was found very low in liquid phase [23]. Overall catalyst activity is found to be slightly higher in the supercritical mode of operation due to higher diffusivities of reactants in supercritical fluids relative to conventional mode of operation [13]. Using near critical n-hexane as the FTS reaction media at 240^{o}C, it was observed that the syngas conversion and product selectivity on Fe based catalyst was significantly changed [19]. The supercritical phase FT reaction employs unique SCF characteristics such as high diffusion rates of reactant gas, in situ extraction of high molecular weight hydrocarbons, and effective removal of reaction heat [13].

By introducing supercritical phase n-pentane into the FTS reaction, waxy hydrocarbon formation rate was increased significantly while light hydrocarbon formation rate was suppressed, [24] which noticeably suggest the deviation from ASF model. Elbashir adds that many researchers have used this modification for the control of the FTS product distributions and obtain the narrow carbon number selectivity. A number of models have been developed and modified in course of time to explain the observed deviations from ASF model such as Surface Reaction Model, Langmuir-Hishelwood-Hougen-Watson Models, and Diffusion Enhanced Olefin Readsorption Model [2]

Existence of a very fine balance between gas like diffusivity and liquid like density is found in supercritical FTS. The density of supercritical fluid can be related to the extent of extraction of heavy hydrocarbons and wax from inside catalyst pores, while the diffusivity is important for the transport of reactant and olefins to the active sites and contribute the chain growth [28]. When the gas phase and supercritical phase FTS are compared with consideration of pressure, solvent type, supercritical media/syngas molar ratio, it was found that the unique properties of supercritical media can improve FTS catalyst activity and selectivity in supercritical FTS due to higher heat and mass transfer rates in comparison to gas phase FTS [18]. With supercritical media, the conversion of CO was found to be much more than or close to that in gas phase because of rapid desorption and dissolution of heavy hydrocarbons effectively creating more vacant reactive sites available to reactants [18]. Since overheating of catalyst surface leads to higher methane selectivity, the better heat transfer in supercritical media, lead to considerable decrease in CH_4 selectivity with shifting of overall product distribution towards heavier products compared to gas phase FTS [18]. Heat transfer is enhanced because of the higher thermal conductivity in case of supercritical phase FT. The primary products of the FTS can be extracted and transported out of the catalyst by supercritical fluid before the start of re adsorption and hydrogenation to paraffins. The olefin content in supercritical media is found to be much more than other reaction phases [18], which was first reported by Yokota and Fujimoto. Supercritical phase FTS using supercritical fluid yields the highest olefin content compared to the gas and liquid phase. This was observed in supercritical phase n-hexane when used with cobalt based catalyst [23]

Fujimoto and Fan [29] also analyzed the FTS in experimental and simulation methods. They were able to achieve efficient transportation of reactants and products to the inside of the catalyst bed and pellet, quick heat transfer and in situ wax extraction from catalyst by supercritical fluid were accomplished. This process can be applied for the effective production of wax in supercritical phase reaction; especially by the addition of heavy olefin to the supercritical fluid. It is a generally accepted model that the CO inserts into a metal-methyl group or metal-methylene carbon bond, which is then hydrogenated to produce either an alcohol or an alkene (olefin) which in case of SCF-FTS is not likely to hydrogenate [21].

Experiments on a fixed bed reactor with precipitated Fe catalyst for a variety of process conditions during conventional and supercritical FTS showed that the total olefin content decreased whereas 2-olefin content increased with both, an increase in conversion or H_2/CO molar feed ratio. Total olefin content was greater but 2-olefin content is smaller in case of SCF-FTS. The result of this test suggested the primary products of FTS are 1-olefins and to a smaller extent n-paraffins. Because of higher diffusivities and desorption rates of α-olefins in the supercritical propane than in liquid filled catalyst pores, the secondary reactions as isomerization, hydrogenation and readsorption of higher molecular weight of α- olefins occur to smaller extent [25].

A new FT process was developed for producing wax products selectively with reduced gaseous products which led to efficient transportation of reactants and products to the inside of catalyst bed and pellet, quick heat transfer, and in situ wax extraction from catalyst by supercritical fluids containing light paraffins and small amount α-olefins. [13]. FTS under SCF hexane was examined by Roberts[22] in a continuous high pressure reactor employing traditional Co catalyst where it was found that enhanced olefins readsorption and increased availability of active sites in the supercritical state contribute to the increased olefin selectivity and chain growth probability in the supercritical phase [22]. The study by Bukur was carried out in a fixed bed reactor with precipitated iron catalyst and evaluated the effect of process conditions on olefin selectivity during the conventional FTS and FTS in supercritical propane. Due to higher diffusivities and desorption rates of α –olefins in the supercritical propane, the undesired secondary reactions as isomerization, hydrogenation and readsorption of higher molecular weight is suppressed during the supercritical operation [25].

An on-line GC method for analysis of C_1-C_{30} products from FT synthesis was conducted in a supercritical hexane medium over a Fe catalyst in a continuous fixed-bed reactor. It was shown that that pressure and temperature affects the elution order of oxygenates relative to hydrocarbon in the non-polar capillary column. This phenomenon was exploited for obtaining improved resolution in the product analysis [26].

Today the need of environmentally friendly techniques is most. So it is very important to find a way to suppress the production of carbon dioxide- a generally accepted green house gas. However, in case of FTS, there are multiple routes which produce CO_2 as their product. Those routes can be water gas shift reaction (equation 4), the Boudouard reaction (equation 5)- which also forms CO_2 along with soot, and even the primary FTS reaction can produce hydrocarbon chains and either H_2O or CO_2.

Supercritical carbon dioxide has been considered as an ideal a polar solvent for chemical reactions due to its moderate critical parameters and easy product separation compared to conventional solvents. It is an environmentally benign fluid which is nontoxic and nonflammable. However, little is known about its application as a solvent in supercritical FTS. [26]

Benoit [7], at SIUC first conducted research on feasibility of CO_2 as supercritical fluid medium in FTS in a batch mode. It was found that the use of supercritical CO_2 enhances the reaction rate for FTS and more importantly suppresses the CO_2 and CH_4 selectivity. Also, the temperature and pressure range for CO_2 as supercritical fluid is fairly easy to maintain making it the perfect option. For CO_2 to be in supercritical state the temperature and pressure must be at least 31.4^oC (88^oF) and 72.8 atmospheres (1070 psig) respectively [28]. The increment in surface area was observed in supercritical phase FTS while with non critical/low pressure FTS, the area was found to be decreased [7].

The use of CO_2 as a medium was further widened by setting up of a continuous flow reactor system and testing it for non critical to supercritical phase FT reaction. The research compared the result of FTS, with and without the use of CO_2 and showed that the influence of CO_2 enhances product distribution to yield higher diesel fraction (C_{13}-C_{15}) when conducted without CO_2 dilution, it favored the gasoline fraction (C_7-C_9) [6].

CHAPTER 3

RATIONALE FOR THE CURRENT RESEARCH

The FTS process is a catalytic reaction for the conversion of gaseous fuel to liquid fuel. The gaseous fuel is syngas which can be derived from biomass, coal, natural gas etc. The catalysts used for the catalytic FT reaction are Ni, Ru, Co, Fe etc. The cheap and popular catalysts under research are Co and Fe. The catalytic reaction occurs on the spots of surface of catalyst which are known as active sites. There is problem of overheating of catalyst and deactivation in most cases as FT itself is an exothermic reaction. Along with this, the issue of deposition of heavy molecular weight wax on the catalyst surface is yet to be resolved. The gas phase FTS provide exceptional diffusivity characteristics but lower heat transfer from catalyst bed, while slurry FT reaction system have very good heat transfer property to remove heat from catalyst surface. Additionally, in case of slurry reactor system the heavy molecular weight waxes deposition is reduced. So, supercritical fluid reactor system combines the advantages of gas like diffusivity property and liquid like heat transfer property. The supercritical fluid will provide two-phase system for the reaction that enhances the diffusivity of reactants, and remove the heat and heavy molecular wax from catalyst bed.

Being specific, CO_2 when used as supercritical fluid for FT reaction will inhibit the CO_2 production and CH_4 selectivity. There are several pathways for the formation of CO_2 as primary FT reaction itself, the Boudouard reaction, and if Fe catalyst is used, the water gas shift reaction. So for FTS reaction in supercritical CO_2, there will be an addition of CO_2 content to the mixture which cause an equilibrium shift and reverses the Boudouard reaction and water gas shift reaction (Le Chatelier's principle). The presence of excess CO_2 will also prevent the CO to act as primary oxygen remover.

The primary objective of this proposed research was to develop comprehensive parametric evaluation of the $ScCO_2$-FTS. The concept of the use of $ScCO_2$-FTS has already been proven [7] in batch reactor. Perry [6] designed a flow reactor to prove the feasibility of continuous $ScCO_2$-FTS. However, significant (up to 80%) amount of alcohols were produced during these tests. It was hypothesized that the low ratio of CO_2:Syngas resulted in participation of CO_2 in the reaction and thus resulting the formation of these oxygenates. Preliminary tests where the CO_2:Syngas ratio was increased proved that at higher CO_2 contents, it behaved as an inert rather than a reactant. The aim of this research was to conduct $ScCO_2$-FTS at these CO_2 contents and evaluate the affect of temperature, pressure, catalyst loading, CO_2:syngas ratio and H_2:CO ratio on the liquid product distribution.

CHAPTER 4

STATEMENT OF OBJECTIVE

The main objective of this research was to comprehensively evaluate the effect of parameters on $ScCO_2$-FTS.

The specific objectives were to:

1. Determine the effect of pressure and temperatures on $ScCO_2$-FTS.

2. Determine the effect of feed composition i.e. (a) ratio of hydrogen and carbon monoxide in syngas; (b) ratio of carbon dioxide and syngas.

3. Identify the optimal catalyst loading.

4. Explore the possibility of fractionation of liquid products.

CHAPTER 5

EXPERIMENTAL SETUP AND PROCEDURES

5.1 Experimental Setup and Modification

A Supercritical Fluids Technology reactor was used for the FTS experiments in continuous flow mode with supercritical CO_2. It was setup (figure 2) to work as a continuous flow fixed bed reactor system equipped with an online GC analysis system. The reactor should be able to routinely handle high temperatures and pressures in supercritical region. The stainless steel reactor used in this work is six inches in diameter with an effective volume of 300ml, and a maximum pressure rating of 10,000 psig. The reactor temperature is monitored using a temperature controller with PID control (Rxtrol Jr. Controller). If mixing is needed, the controller can also maintain the speed of the reactor’s agitator. The side wall of the large tube furnace reactor is covered with ceramic elements. The reactor’s outlet is located directly at the bottom of the reactor. The catalyst is loaded into a small cylindrical box and then inserted into the reactor before closing the reactor. The cylindrical box was made by fine mesh of stainless steel wires with a layer of quartz wool on all sides to prevent the catalyst from spilling out of the box. The size of the box is 1.5 inch diameter and 3 inch height. The volume of the cylindrical box was enough to hold a maximum of 40 gm of FT catalyst (Fe-Zn-K).   The reactor system is illustrated in figure 2.

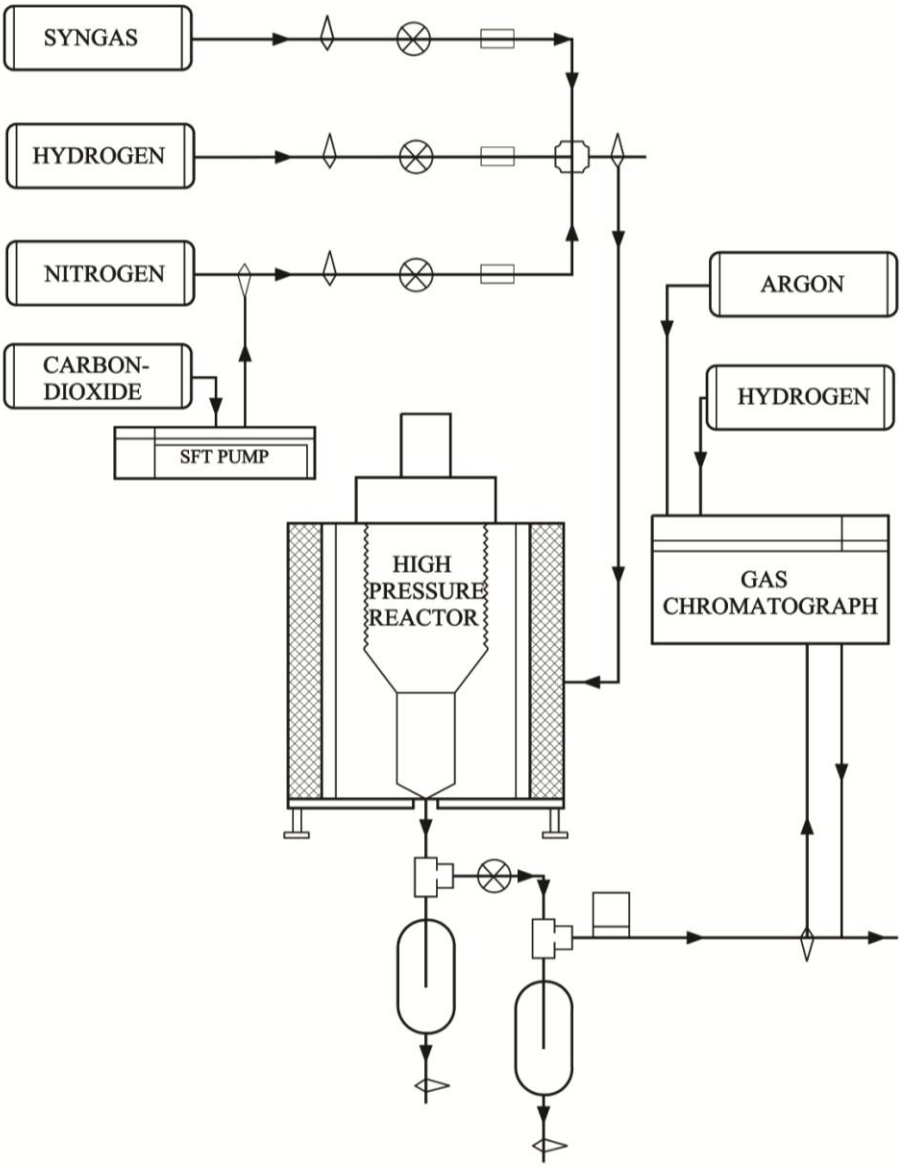


Figure 2: Model of the continuous flow reactor system.

The exhaust line of the reactor was modified in such a way that the catalyst particles were prevented from reaching the BPR and damage the BPR. The modifications completed were:

(a) A filter was inserted just after the exhaust so that the catalyst particles would first stopped in the filter. The filter was a connection of two male and female connectors with fine quartz wool on it, so that it would allow the liquid to flow through but prevent the catalyst particles.

(b) The exhaust line went deep into the first collection vessel and exhaust gases passed through the cylinder (on the exterior of the exhaust line) and again up to the three way connection so that if any catalyst particles were not filtered will be settled out at the bottom of the first collection vessel. This type of modification was done for the other collection vessels too. This type of setup also facilitated for the maximum collection of liquid in the collection vessels unlike previously done. In the previous setup [6], the connection lines used to contain the produced liquid.

The modifications are illustrated as in the figure 3.

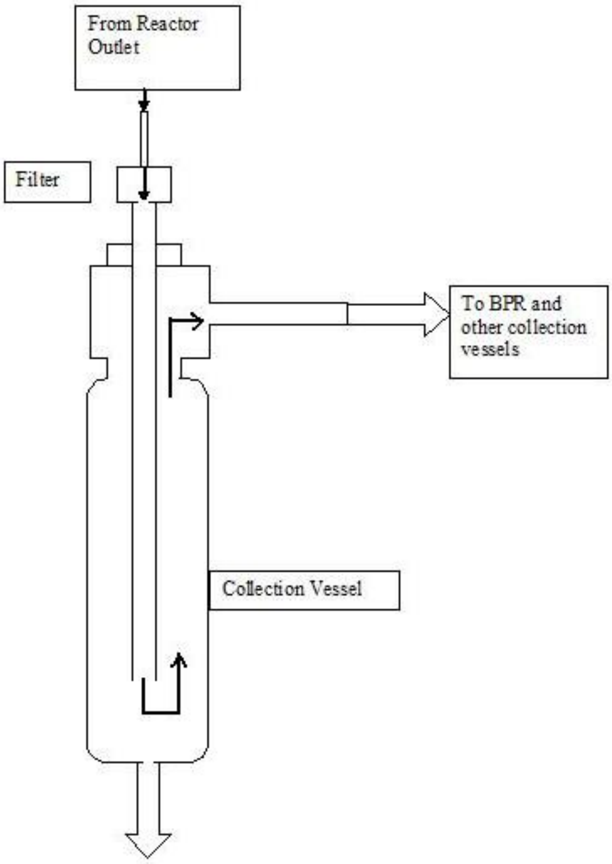


Figure 3: Reactor modification for the collection vessels

For the controlled supply of the different gases to the 300 ml stainless steel reactor, a series of pressure regulators, shutoff values, and metering valves were connected in the line. The minimum pressure of carbon dioxide to be in supercritical phase is 1070 psig. However the CO_2 liquid cylinder has a pressure rating of around 900 psig, so a SFT-10 constant flow/constant pressure dual piston pump with flow rates up to 24 ml/min and a maximum pressure of 10,000 psig was used to meet the requirements of supercritical phase FTS.

Figure 4: Picture of the reactor system

The catalyst was first loaded in the reactor. The catalyst was reduced with continuous flow of hydrogen at elevated temperature of 350^{o}C. Then the reactor was filled with syngas and CO_2 to desired pressure. BPR was used to hold the pressure. The series of back pressure regulators with different pressures upstream of them aided in the fractionation of liquid products from FTS. The back pressure regulator after the first vessel was maintained at the pressure of reactor so that the heavy hydrocarbons, polar alcohols and waxes would collect in first vessel. The back pressure regulator after the second cylinder was reduced to the pressure sufficiently enough to precipitate out the lower hydrocarbons. The remaining liquids would be collected at atmospheric pressure in the third vessel. And the other gasses (consisting of solvent gas, gaseous hydrocarbons, and remaining syngas) were passed through a gas chromatograph. The collected liquid and wax analysis was carried out by an online gas chromatograph (Buck Scientific, Model 910) using a silica gel columns and a cross-linked methyl silicone capillary column with FID (flame ionization) and TCD (thermal conductivity) detectors. The previous research from continuous flow test [6] had provided enough data to determine an optimized range of required pressure and temperature. Length of the experiments was of 7 days.

5.2 Experimental Procedure

The past research experience had setup a basic procedure for the FTS experiment. The procedure was identified and modified several times for optimization. The procedure followed for the FTS experiments are listed below. Same process was repeated for each experiment to maintain consistency.

1. The stainless steel reactor was cleaned and polished.
2. FT catalyst (Fe-Zn-K/alumina) was loaded into the small cylindrical box.
3. Before reactor assembly, a layer of TiO_2 based anti seize was applied to prevent the seizing of two steel reactor parts during the experiment. This is applied to make it easy to dissemble and prevent change in shape and size of reactor parts during the time of elevated temperatures.
4. The set-screws (hex nuts) were tightened up to 20 ft-lb torque which is a company standard value for tightening the reactor.

5. The reactor was then pressurized with nitrogen slowly up to the desired pressure. Back pressure regulator was used for steady build-up of pressure in the reactor. The supply was controlled through the two stage regulator in the nitrogen tank.

6. Entire leak test was done with bubble spray bottle and an ultrasonic leak detector. After the leak test, the reactor pressure was relieved slowly by venting out the nitrogen through the exhaust line.

7. As the catalyst must be reduced before the start of the reaction, a continuous flow of hydrogen was passed through the catalyst at elevated temperature of 350°C. The flow rate was maintained constant using a mass flow controller for the flow rate of 50ml per minute for period of 12 hours.

8. The reactor was again pressurized with nitrogen to the pressure which is 100 psig less than the desired experiment pressure. For instance, if the experimental desired pressure is 1200 psig, the reactor is pressurized up to 1100 psig with nitrogen.

9. After the pressure is raised to the 100 psig below the desired pressure, nitrogen flow was stitch with CO_2 flow by the help of 3-way shut-off valve.

10. Before initiating carbon dioxide flow, it is to be noted that the carbon dioxide tank pressure was around 900 psig. The pressure was raised to desired pressure with the help of SFT-10 pump. The pump was pre-cooled for 20 minutes before operation to remove heat from the pump heads. A small amount of carbon dioxide was bleed through the line before running the pump. This

bleeding of CO_2 helps to remove the possible water vapor in the lines that could potentially damage the pump.

11. To raise the pressure of carbon dioxide, two chips (one for each operational mode –constant pressure and constant flow) were used. The CP (Constant Pressure) chip was inserted into the logic board of the pump which would make the pump run at constant pressure. The range of minimum to maximum pressure is 50 psig in constant pressure mode. So when the pump reaches the maximum set point for the experiment, it reads variable range of 50 psig. For example, if the desired pressure of the experiment is 1200 psig, the pump could read 1150-1200 psig.

12. Once the system reaches the desired pressure, the CP chip was replaced with identical looking CF (Constant Flow) chip in the logic board of the pump. Then the pump was set to run with desired constant flow of CO_2 throughout the experiment (0 to 0.25 ml per min for this research).

13. To initiate the syngas flow, the two stage regulator in the syngas tank was preset to the desired pressure of the experiment. The flow was opened slowly by the help of needle valve so that once the syngas starts to flow it balances out with the carbon dioxide flow. Mass flow meter was used to monitor the flow of the syngas to the reactor. Once the mass flow meter starts to read positive values, syngas was assumed to flow.

14. As the system is already connected with online Gas Chromatograph (Buck 910 Series), the gas sample was analyzed every 12 hours.

15. The reaction was constantly maintained at the desired flow rates, pressures and temperatures for the period of seven days. To stop the experiment after 7 days the CO_2 and syngas flow rates were stopped first. The heater and the pump were turned off.

16. The pressure of the reactor was slowly vented out. Once the reactor reached the atmospheric pressure, the liquid samples from first and second cylinder were collected into a small jar with tight seal and septum. A sample of used catalyst was also collected for further analysis.

5.3 Pressure Tuning

For fractionation of liquid products, pressure tuning was employed. The pressure of first BPR was maintained in such a way that collection vessel before the first BPR was maintained at reactor pressure and lowered temperature (above 32^oC). The vessel between the first BPR and the second BPR was maintained above supercritical conditions but at pressures closer to the critical pressure. The supercritical CO_2 was expected to carry the relatively lighter hydrocarbons through the first BPR leaving the heavy waxes in the first collection vessel and the mid weighted hydrocarbons would be collected in the second cylinder and then the lightest hydrocarbons were carried out to the third vessel (operating at atmospheric pressure) and the lower hydrocarbons or gaseous products to the online connected GC system. So proper tuning of the pressure was done to acquire the required allocation of products in different collection vessels.

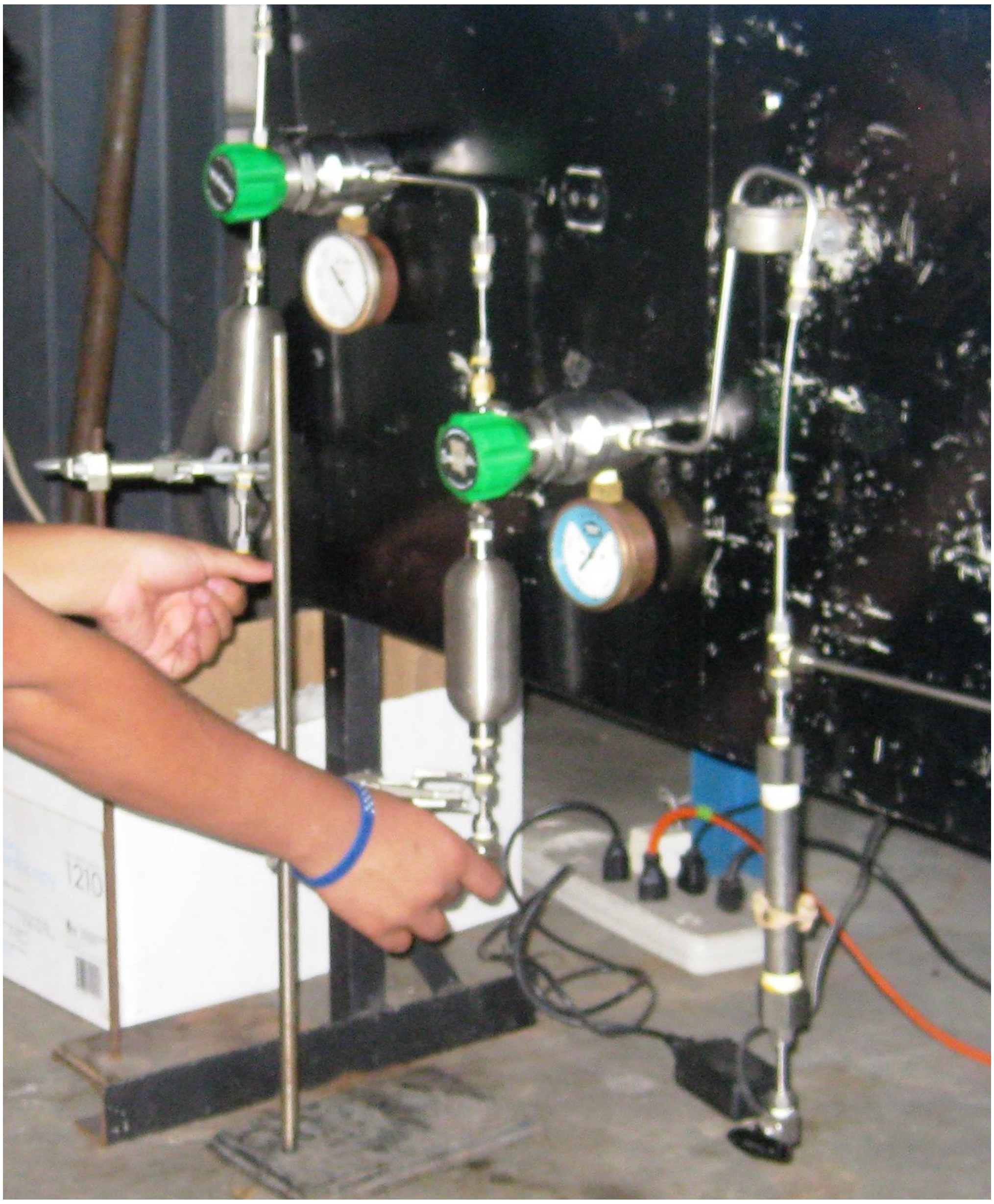


Figure 5: Exhaust line of the reactor with a series of BPRs and collection vessels.

5.4Catalyst Preparation

The basic steps followed for the preparation of iron based catalysts (Fe-Zn-K/alumina) for this research are as follows:

1. Make 50ml Iron Nitrate Solution(3.0M)
2. Add 1.78gm Zinc Nitrate (on 25:1 molar basis)

3. Add 20 gm Alumina
4. Stir 2-3 Hours
5. Filter Using 2.5micron Particle Filtration Paper
6. Dry at 100°C for 10 hours
7. Add Filtered and dried portion to waste Solution
8. Stir 2-3 hours
9. Filter
10. Dry at 100°C for 10 hours
11. Calcine at 350°C for 15 hours
12. Add to 50 ml of Potassium Carbonate Solution(0.16M)
13. Stir 2-3 Hours
14. Filter
15. Dry at 100°C for 10 hours
16. Calcine at 350°C for 4 hours

5.4 Catalyst Characterization

The method followed for the preparation of catalyst was exactly same with the technique used before in the SIUC Catalyst Preparation Lab by Perry [7] and Benoit [6]. The results from the catalyst characterization performed by Perry and Benoit were found to be consistent. Hence the catalyst characterization results obtained then were taken as standard data for Fe-Zn-K catalyst for this research.

Among many techniques of catalyst characterization, three of them were practiced in past for Fe-Zn-K catalyst by Perry [7] and Benoit [6] in SIUC Catalyst Preparation Lab. They are explained below briefly as follows:

i. Particle Size Analysis

Microtrac S3500 Particle Size Analyzer was used to determine the pore size distribution of catalyst. The result of the analysis was represented in figure 9.

The alumina support which was used to make catalyst was found to have an average size of the particle size of 63.78 microns. The unused catalyst average size was found to be 68.87 microns [7]. A typical graph obtained from particle size analyzer showing the results on sample catalyst is as shown in figure 6.

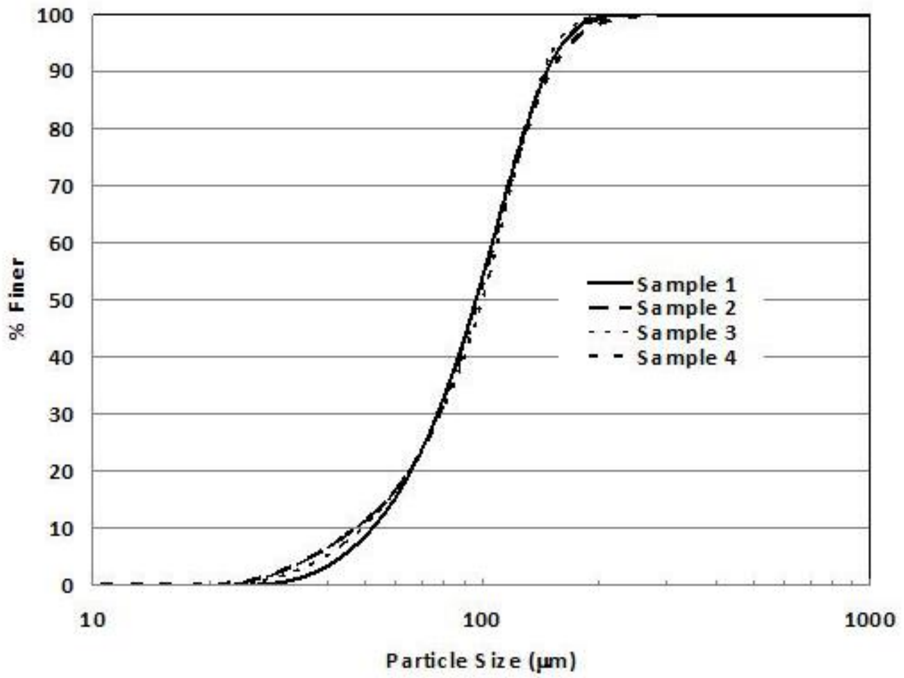
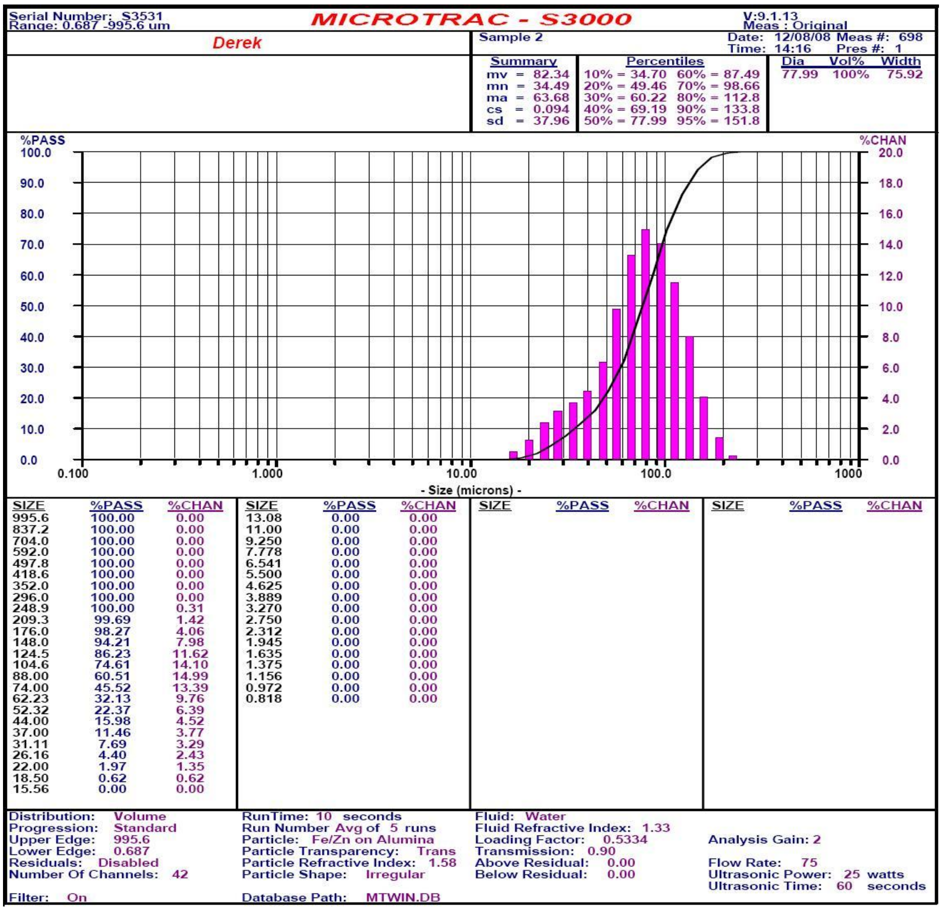


Figure 6: Particle size distributions of fresh catalysts [7]

ii. BET Analysis

The average surface area of the fresh unused catalyst was found to be 112.95 m^2/gm. The average pore volume of unused catalyst was 0.149 cc/gm, and the average pore radius of unused catalyst was 30.25 A^o. [7]



Serial Number: S3531
Range: 0.687 -995.6 um

MICROTRAC - S3000

V:9.1.13
Meas : Original

Derek

Sample 2

Date: 12/08/08 Meas #: 698
Time: 14:16 Pres #: 1

Summary
mv = 82.34
mn = 34.49
ma = 63.68
cs = 0.094
sd = 37.96

Percentiles
10% = 34.70 60% = 87.49
20% = 49.46 70% = 98.66
30% = 60.22 80% = 112.8
40% = 69.19 90% = 133.8
50% = 77.99 95% = 151.8

Dia	Vol%	Width
77.99	100%	75.92

SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN
995.6	100.00	0.00	13.08	0.00	0.00						
837.2	100.00	0.00	11.00	0.00	0.00						
704.0	100.00	0.00	9.250	0.00	0.00						
592.0	100.00	0.00	7.778	0.00	0.00						
497.8	100.00	0.00	6.541	0.00	0.00						
418.6	100.00	0.00	5.500	0.00	0.00						
352.0	100.00	0.00	4.625	0.00	0.00						
296.0	100.00	0.00	3.889	0.00	0.00						
248.9	100.00	0.31	3.270	0.00	0.00						
209.3	99.69	1.42	2.750	0.00	0.00						
176.0	98.27	4.06	2.312	0.00	0.00						
148.0	94.21	7.98	1.945	0.00	0.00						
124.5	86.23	11.62	1.635	0.00	0.00						
104.6	74.61	14.10	1.375	0.00	0.00						
88.00	60.51	14.99	1.156	0.00	0.00						
74.00	45.52	13.39	0.972	0.00	0.00						
62.23	32.13	9.76	0.818	0.00	0.00						
52.32	22.37	6.39									
44.00	15.98	4.52									
37.00	11.46	3.77									
31.11	7.69	3.29									
26.16	4.40	2.43									
22.00	1.97	1.35									
18.50	0.62	0.62									
15.56	0.00	0.00									

Distribution: Volume
Progression: Standard
Upper Edge: 995.6
Lower Edge: 0.687
Residuals: Disabled
Number Of Channels: 42

Filter: On

RunTime: 10 seconds
Run Number Avg of 5 runs
Particle: Fe/Zn on Alumina
Particle Transparency: Trans
Particle Refractive Index: 1.58
Particle Shape: Irregular

Database Path: MTWIN.DB

Fluid: Water
Fluid Refractive Index: 1.33
Loading Factor: 0.5334
Transmission: 0.90
Above Residual: 0.00
Below Residual: 0.00

Analysis Gain: 2

Flow Rate: 75
Ultrasonic Power: 25 watts
Ultrasonic Time: 60 seconds

Figure 7: Particle size analysis results [7]

5.5 Gas Chromatography

As this is a continuous flow fixed bed reactor system with an online GC analysis system, the exhaust gas mixture was passed through the GC for analysis. The GC was setup to auto sample from the exhaust line of continuous flow and display the result in the computer screen with the help of executable program named Peak Simple

3.29. It could also be used to run batch samples which were collected in sealed sample bags or jars.

The gas chromatograph that was used in this research is Buck Scientific Model 910 with FID and TCD detectors installed. The general procedure followed to operate a gas sample in the gas chromatograph is listed as follows:

1. The flow of the carrier gases (argon and hydrogen) was initiated with standard supply pressure for GC.
2. The GC was turned on.
3. The far right switch was switched to upward position to see the set points.
4. Wait 10-20 minutes for the detectors and columns to heat up to the set points. The blinking of the indicator lights of each Chromatograph components shows that the set points were reached.
5. The executable Peak Simple 3.29 program was opened in the computer connected to GC for data acquisition.
6. The required initial conditions for the GC for running a sample are: column temperature: $90^{o}C$, TCD oven temperature: $250^{o}C$ and TCD detector temperature: $150^{o}C$.
7. The internal air compressor was switched to the on position. The air compressor is integrated with the FID detector on Chromatograph.
8. The flame was ignited with the ignite switch up.
9. The TCD filament switch was turned on by setting the switch to lower position.

10. Highlighting the required number of channels in Peak Simple program the spacebar on key board was pressed to auto sample the exhaust gas.
11. After running it for total specified run time (50 minutes), the results from each detector were saved separately
12. Then the program was closed, TCD filament was turned off, internal air compressor was turned off.
13. The GC was turned off.
14. And the carrier gas supply was shut off.

5.6 Experimental Conditions

There were various process conditions common to almost all of the experiments in this study. All experiments were done on continuous flow mode for period of 7 days. Hydrogen was used to reduce the catalyst at 350°C with continuous flow of 50 ml/min for 12 hours. The experimental procedure explained in Section 5.2 outlines the baseline procedure which was repeated for each experiment.

The variables which were analyzed in this research are:

1. Reaction Pressure
2. Reaction Temperature
3. Carbon Dioxide Flow rate
4. Syngas Composition Ratio
5. Catalyst Loading.

With following variables listed above, the test matrix for this research is tabulated below:

Table1: Experimental Parameters

PARAMETERS					
Temperature	350^{o}C	300^{o}C	250^{o}C		
Pressure	1200 psig	1350 psig	1500 psig		
CO_2:Syngas	5:1	4:1	3:1	2:1	1:1
H_2:CO	1:1	2:1	3:1		
Catalyst Loading	10 gm	20 gm	30 gm		

CHAPTER 6

RESULTS AND ANALYSIS

All of the FTS experiments were carried out in fixed bed continuous flow supercritical reactor system with supercritical carbon dioxide. So it is to be noted that the effective volume of the reactor for all experiments is constant which is equal to about 300 ml. Experiments were conducted at temperature ranging from 250^{o}C to 350^{o}C, pressure between 1200 psig to 1500 psig. Each experiment was run for 7 days to reach and maintain the steady state for a significantly long period to obviate the effects of initial unsteady state and for the uniformity in the desired product and analysis. The exhaust gas sample from the reactor was analyzed by the online GC system every 12 hours. The liquid sample was collected from the collection vessel every 2 days and then it was analyzed by GC/MS in the Geology Lab. The results of all the experiments and analysis can be grouped into following sets:

1. Effect of Catalyst Loading

2. Effect of Pressure

3. Effect of Temperature

4. Effect of CO_2 Dilution

5. Effect of the Ratio of H_2:CO (Feed Type)

6. Prospect of Fractionation

6.1 EFFECT OF CATALYST LOADING

A total of three experiments were conducted to evaluate the effects of catalyst loading in supercritical phase FTS. Keeping all other process parameters constant, amount of catalyst used for the experiment was varied. 10 gm, 20 gm and 30 gm of catalyst were used for each experiment. It is to be noted that the volume of the reactor and flow of the gases supplied are identical for all three experiments, so the catalyst loading here can be related to the catalyst loading per unit volume of the reactor. All of the experiments in this set were carried out at constant reaction temperature of 350°C and constant reaction pressure of 1200 psig. Equal amounts of carbon dioxide and syngas were passed into the reactor for all experiments in this set i.e. the mass flow rates for each gas was maintained identical, so the ratio of CO_2 and syngas supplied to all experiments was 1:1. The ratio of hydrogen and carbon monoxide for the syngas that was used for this set of experiments is 1:1.

The effect of catalyst loading per unit volume for hydrocarbon (alkane) distribution in terms of carbon number was analyzed (figure 8). When 10 gm of catalyst was used for the same volume of reactor and flow of reactant gases, the distribution lies between C_7 to C_{22}. When the loading was increased to 20 gm of catalyst the hydrocarbons in the products were in the range of C_{10} to C_{26}. With further increment of catalyst amount to 30 gm, the range of carbon number lies between C_7 to C_{21}. The carbon number distribution was found to vary with the amount of catalyst. However, the, main aim of this set of experiments was to determine a suitable catalyst loading that would provide sufficient syngas conversion. A loading of 20 gm was observed to provide the required syngas conversion.

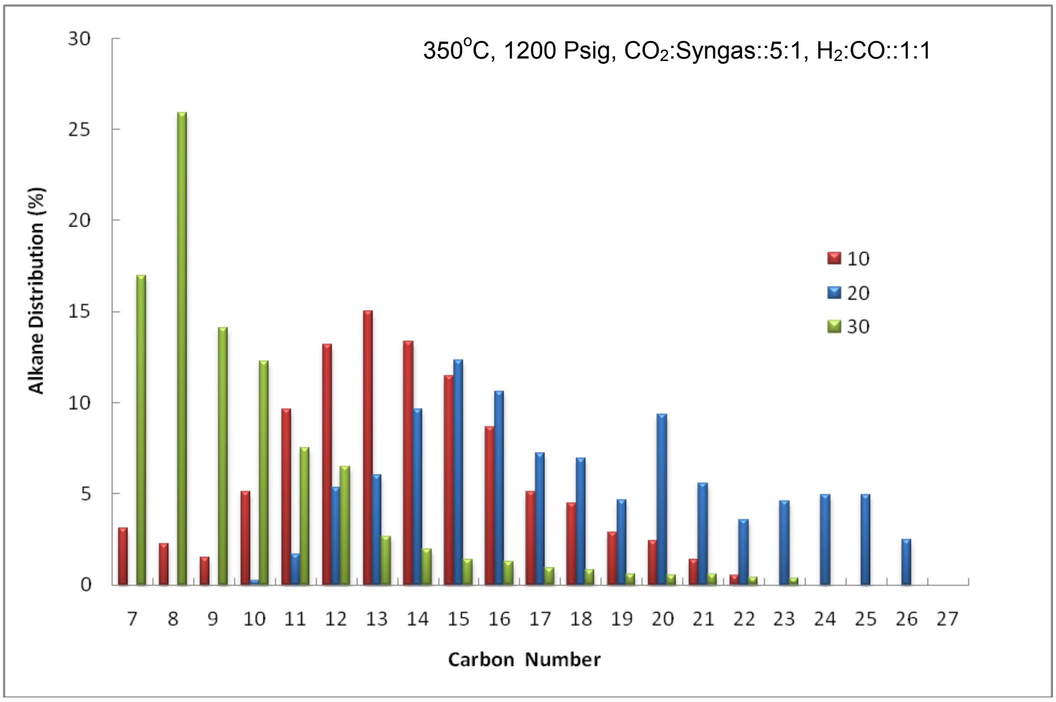


Figure 8: Effects of catalyst loading on the distribution of alkanes

Figure 9 shows the composition of the liquid products obtained from FTS experiments for different catalyst loading. For 10 gm catalyst loading, it was found that the liquid product contains 20 % of alkanes, 2 to 3 % of alkenes, 75% of oxygenates and 2 to 3 % of aromatics. Similarly, for 20 gm catalyst loading, the composition was found to be 70% alkanes, 20% alkenes, 2 to 3% oxygenates and about 5% aromatics. For 30 gm of catalyst loading, content of alkanes was about 65%. About 25% alkenes, 10 % of aromatics and almost no oxygenates were found. Since the product distributions of 20gm and 30 gm loadings were similar and sufficient liquids were generated with 20gm of catalyst, this value of loading (20 gm) was found to be optimal.

From the aforementioned detail of the distribution of product composition, it was apparent that an increase in the amount of catalyst loading suppressed the production of oxygenates. For 10 gm of catalyst loading, it was found that the product consists of 80% of oxygenates while there was almost no oxygenates with 30 gm of catalyst. However, traces of oxygenates were seen in the product from 20 gm catalyst loading. In case of aromatics, it was found that higher the catalyst loading, higher the production of aromatics. For 20 gm and 30 gm catalyst loading, the amount of alkane in the product was almost constant i.e. about 60 to 70% but for 10 gm of catalyst loading the amount of alkanes formed was 20%. Similar trend was observed in case of alkenes. For 20 gm and 30 gm catalyst loading, amount of alkenes formed were about 20 to 25 % of total composition while with 10 gm catalyst loading about 2% of alkenes in total product was measured. The variation in the alkane distribution and in the overall product distribution may be explained as follows. When a low loading is used, a significant proportion of the sites is used for FT synthesis as a result a small fraction of the sites may be responsible for water gas shift that results in an increase in hydrogen content responsible for both O radical removal as well as for reduction of CO. Since sufficient hydrogen is not available, CO may act as an O radical scavenger. However, the high CO_2 partial pressure reduces the extent of occurrence of this phenomenon and thus terminates as alcohols. Since alcohols are formed, there is a negligible increase in the CO_2 content in the product gases. The alkene to alkane ratio is also observed to be the highest at low catalyst loading which may also be explained by the low H_2:CO ratio and fewer sites for WGS. When the catalyst loading is increased, the number of sites for the same number of moles of reactant gas is increased, thereby facilitating the movement of O radical from the FT reaction site to be removed by CO or H_2 (produced locally by water gas shift). The excess CO_2 in the reactant mixture ensures that any excess H_2 is used up in the reverse water gas shift to maintain nearly no net CO_2 generation. Nonetheless, due to the low H_2 content, formation of alkenes is favored (although amount of oxygenates is reduced). A further increase in the loading increases the number of active sites to a degree that the reactant concentration in the vicinity of each site is too low and thus results in the termination of the chain growth at lower carbon numbers. Thus, while the product distribution in terms of alkanes, alkenes, oxygenates and aromatics remain nearly the same, the alkane distribution is skewed towards lower carbon chain lengths. Overall, we can conclude that we can get the desired variation in the product distribution by varying the amount of catalyst.

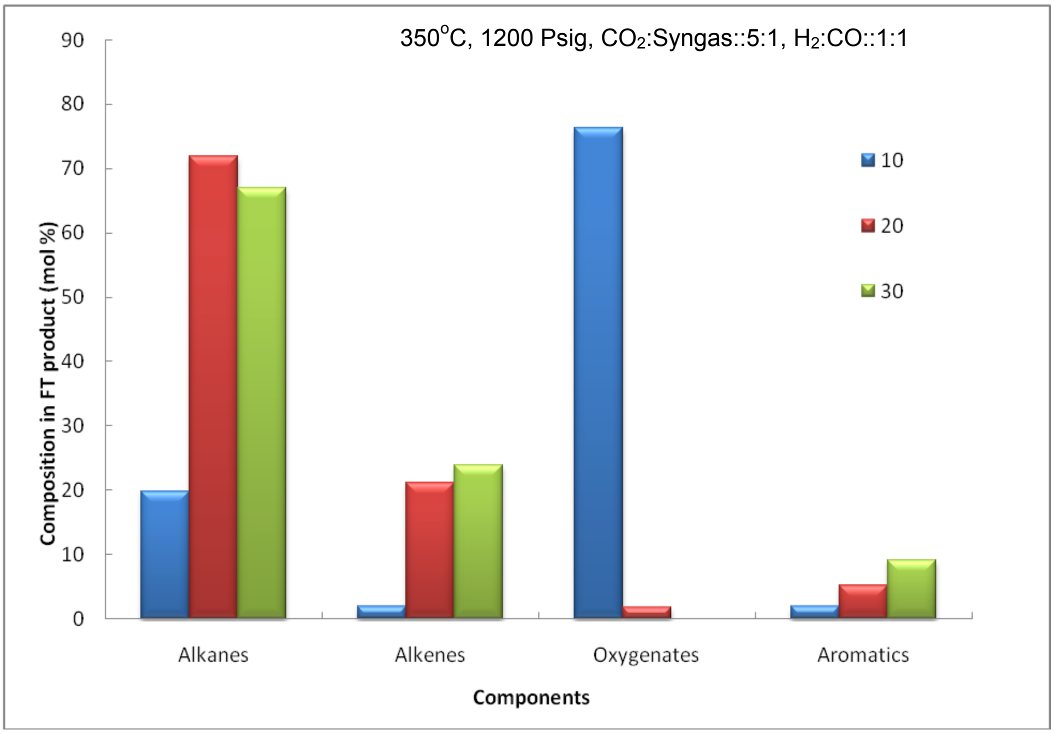


Figure 9: Effects of catalyst loading on the composition of liquid fraction

6.2 EFFECT OF CARBON DIOXIDE DILUTION

As mentioned earlier in this thesis, there is no literature available outside of SIUC for the FTS in supercritical CO_2. Thus the nature and of FTS and the extent of required dilution needs to investigated thoroughly. In a previous study by Perry [6], it was found that at a CO_2:syngas ratio of 1, the CO_2 probably acts as a reactant and results in the formation of oxygenates. A series of experiments varying the CO_2

content in the feed was evaluated to understand its effect in supercritical phase FTS. A total of five different experiments were conducted in this set to find out the effects of change in amount of CO_2 supply to the FTS reaction. The ratio of CO_2 to syngas was altered for each experiment as 5:1, 4:1, 3:1, 2:1, 1:1 and respective liquid products were analyzed to determine the comparative effects. The data from these experiments were also analyzed to evaluate the effect of variation in the supply of supercritical fluid/media (dilution) on the reaction. The type of syngas used for this experiment is the coal derived syngas with hydrogen and carbon monoxide ratio of 1:1. The temperature and pressure of all five experiments was maintained constant with 350°C and 1200 psig respectively. 20 gm of Fe-Zn-K/alumina catalyst was used for all experiments.

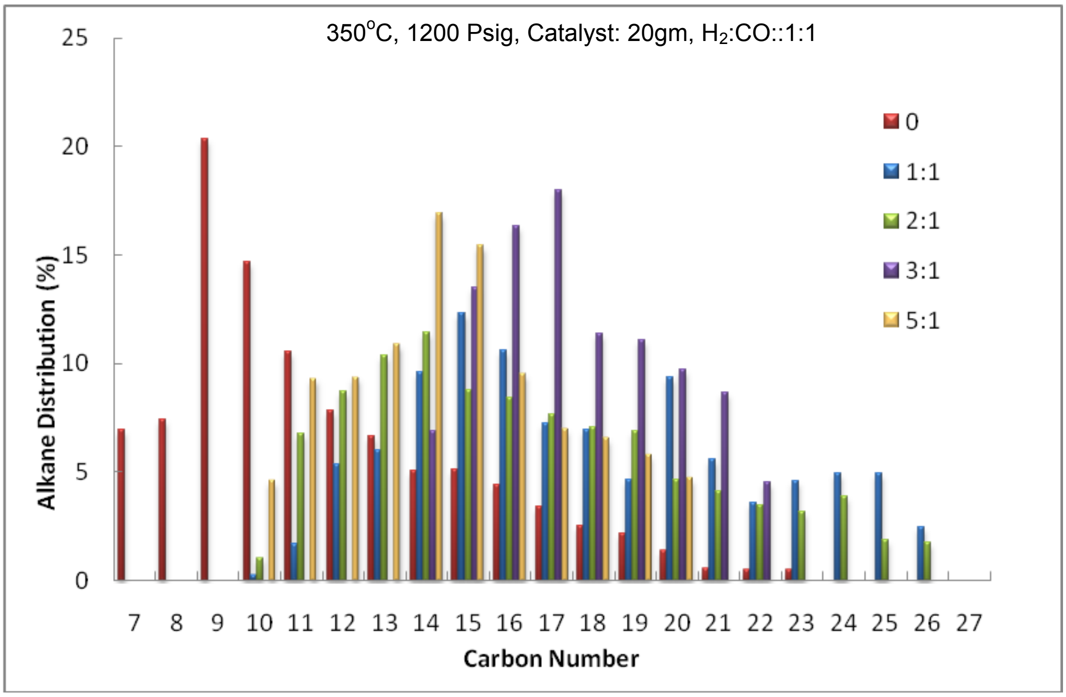


Figure 10: Effects of dilution on the distribution of alkanes

Figure 10 shows the distribution of alkanes in terms of carbon numbers for different feed ratio of carbon dioxide and syngas. For the experiment with no carbon dioxide i.e. with pure syngas or the experiment with ratio of carbon dioxide to syngas is 0:1, the alkane distribution was found to be from C_7 to C_{23} with its peak distribution ranging between C_9 and C_{11}. With addition of little carbon dioxide in the reaction i.e. when the ratio of carbon dioxide to syngas was made around 1:1, the distribution of the alkanes shifted towards higher carbon chain lengths which were from C_{10} to C_{26}. So the insertion of the carbon dioxide to the reaction actually favored the production of higher hydrocarbons. The peak of the distribution for this experiment ranged from C_{14} to C_{16}. Further increase in the amount of carbon dioxide in the feed, so that the ratio of carbon dioxide to syngas comes out to be 2:1, the distribution of the alkane did not change significantly compared to distribution obtained from the experiment conducted with a feed composition of CO_2:syngas of 1:1, which was from C_{10} to C_{26}, and peak distribution lying from C_{13} to C_{16}. However the peaks for the latter were observed to be higher than the previous case that indicated a larger quantity production of those hydrocarbons. Based upon the comparison of these two experiments, it can be concluded that the contents of the carbon chain lengths in the peak region were increased although no shifting of the distribution was observed or in other words sharper distributions were obtained. The amount of carbon dioxide was further increased so that the feed ratio of carbon dioxide to syngas was 3:1. For this experiment the distribution of alkanes was observed to lie from C_{14} to C_{22} which is comparatively narrower than the previous distributions. The peak of this distribution lies from C_{15} to C_{17}. So a further increase in the amount of carbon dioxide resulted in a narrower product distribution. The amount of carbon dioxide was further increased to make the ratio of carbon dioxide to syngas about 5:1. The observable distribution of the alkane for 5:1 ratio of carbon dioxide to syngas was found to be from C_{10} to C_{20} for which the peak distribution lies from C_{14} to C_{15}. As a whole, the conclusion derived from this set of experiment is variation in the amount of carbon dioxide in the reaction actually can result narrower alkane distribution in the products. This gives us the variation of carbon dioxide amount as an option to control the product distribution.

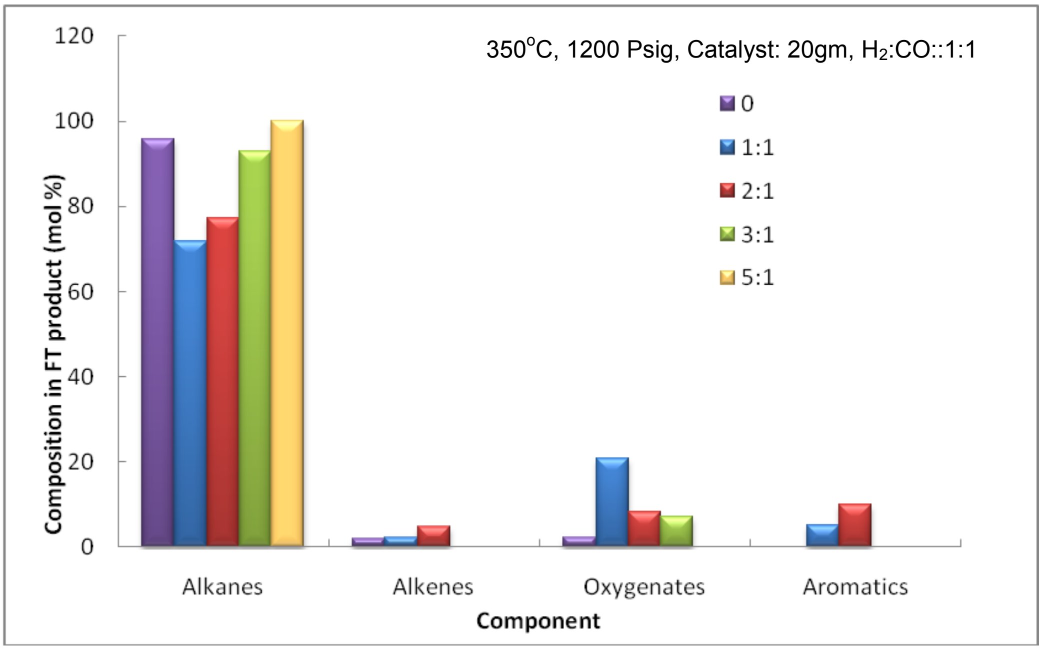


Figure 11: Effects of dilution on the composition of liquid fraction

Figure 11 is a bar graph of the relative composition of the products as the function of the extent of dilution of the feed (syngas) with supercritical carbon dioxide. Without the supply of carbon dioxide in the reaction, almost 95 % of alkanes were observed while rest of the composition contained 2% of alcohols and 3 % of oxygenates. With an addition of carbon dioxide in equal amounts of syngas making the ratio of carbon dioxide to syngas 1:1, it was found that the amount of alkane was decreased to about 70 % of the total composition. A corresponding increase in the amount of oxygenates was observed which went up to 25%. Around 2% of alkenes and 7% of aromatics were found in the composition. At these low CO_2 contents, CO_2 behaves as a reactant rather than as a diluent and thus resulting in the formation of oxygenates by CO_2 reduction either by the CO or formate intermediate routes. When CO_2 participates as a reactant, there is even higher amount of oxygen that needs to be cleaved and a significant portion of it may not be removed and report to the product stream as oxygenates. As the CO_2 content in the feed is increased, the CO_2 behaves more as a diluent and results in the suppression of oxygenate production as reported in the following. Further increase in the amount of carbon dioxide in the feed so that the ratio of carbon dioxide to syngas becomes 2:1, slight increment in the production of alkanes, alkenes and aromatics were observed while the production of oxygenates was decreased to10%. 75% alkanes, 7% alkenes and 12 % aromatics were found in the product composition. For the carbon dioxide to syngas ratio of 3:1, the amount of alkanes observed was about 90% of total composition. About 10 % of oxygenates were observed in the composition leaving no production of alkenes and aromatics. Further increase in the carbon dioxide amount in the feed making the ratio of carbon dioxide to syngas about 5:1, it was observed that almost all the products contained only alkanes. No production of alkenes, oxygenates and aromatics were observed in this experiment. From the above observation it is apparent that the increment of the content of carbon dioxide in feed increased the production of alkanes. Also, suppression in the production of oxygenates was observed as a result of the increase in the ratio of carbon dioxide and syngas. In addition, it was found that the increase in the carbon dioxide content in the reaction actually inhibits the production of alkenes and aromatics too and further studies need to be conducted to confirm and evaluate the reasons behind these observations. The formation of oxygenates after the addition of carbon dioxide in small amount could be because the carbon dioxide instead of acting as a supercritical media or solvent acted as reactant. Therefore, it can be concluded that by controlling the amount of carbon dioxide in the reaction as solvent one can vary the product composition as per our requirement.

6.3 EFFECT OF PRESSURE

To evaluate the effects of variation in pressure in the supercritical phase FTS, experiments were carried out at three different reaction pressures; 1200 psig, 1350 psig and 1500 psig. All other parameters were kept constant. 20 gm Fe-Zn-K/alumina catalyst was used for all three experiments. The constant reaction temperature of 350°C was selected for this set of experiment. Ratio of CO_2 and syngas was maintained 5:1 for the all three experiments. Syngas with 1:1 ratio of hydrogen to carbon monoxide was used for this set of experiments.

A variation in alkane distribution was observed as a result of the variation in reaction pressure as illustrated in figure 12. The alkane distribution is shown in terms of carbon number for three different reaction pressures. It can be seen from the figure that at 1200 psig, the distribution lies between C_{10} to C_{20} with its peak lying between C_{13}-C_{15}. Increasing the reaction pressure to 1350 psig, the distribution shifted towards C_{14} to C_{22} with its peak lying between C_{15}-C_{16}. A further increase in the reaction pressure to 1500 psig, the distribution is shifted towards even higher hydrocarbons with carbon chain lengths in product from C_{16} to C_{23} with the peak lying between C_{19}-C_{21}. From the analysis of the results above, it is seen that the pressure increment results in a shift of the product distribution curve from lower hydrocarbons to higher hydrocarbons or in other words increase in pressure favors chain growth. The above results are a confirmation of the observations by past FT researchers during conventional FT studies. So, it can be concluded that reaction pressure can be varied based upon product requirement.

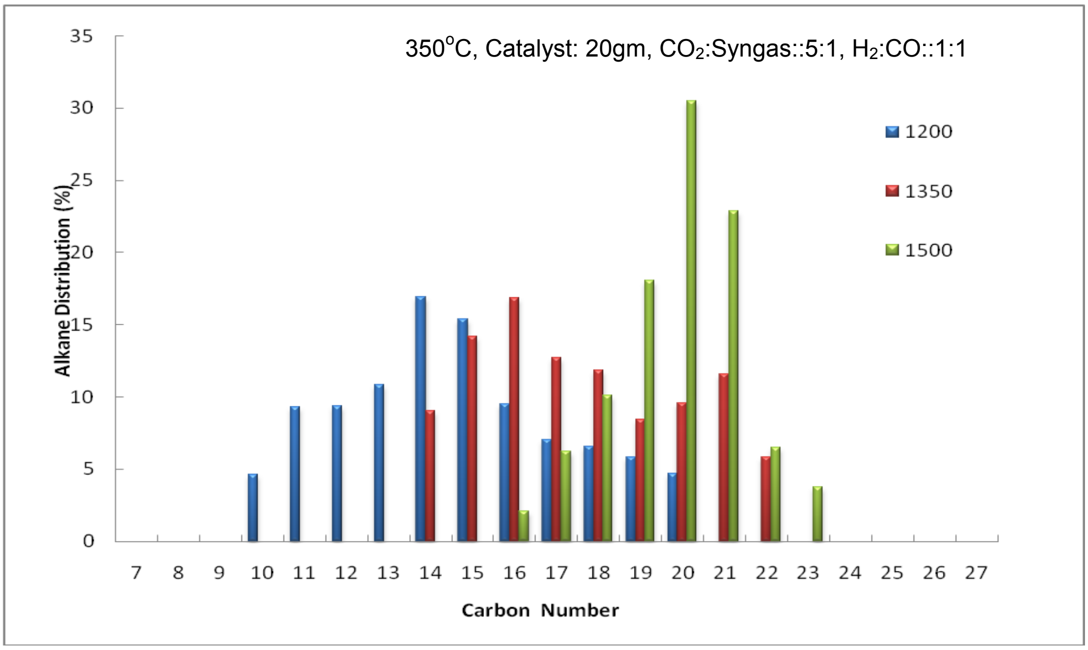


Figure 12: Effects of pressure on the distribution of alkanes

Figure 13 shows the effect of pressure on the composition of the liquid fraction. At a reaction pressure of 1200 psig, almost the entire liquid product contained alkanes. Upon increasing the reaction pressure to 1350 psig, it was found that the amount of alkanes was slightly decreased to about 90% of the total composition. About 2 % of alkenes and 4% of aromatics were also observed at 1300 psig. At the highest reaction pressure used in this study (1500 psig), amount of alkanes observed was about 85%. About 1 to 2 % of alkenes were found in the total composition of liquid product. The amount of aromatics found was 5-7 % of total composition. For all three pressures, almost no formation of oxygenates were observed. Overall it can be seen that an increment in the reaction pressure favors the production of aromatics.

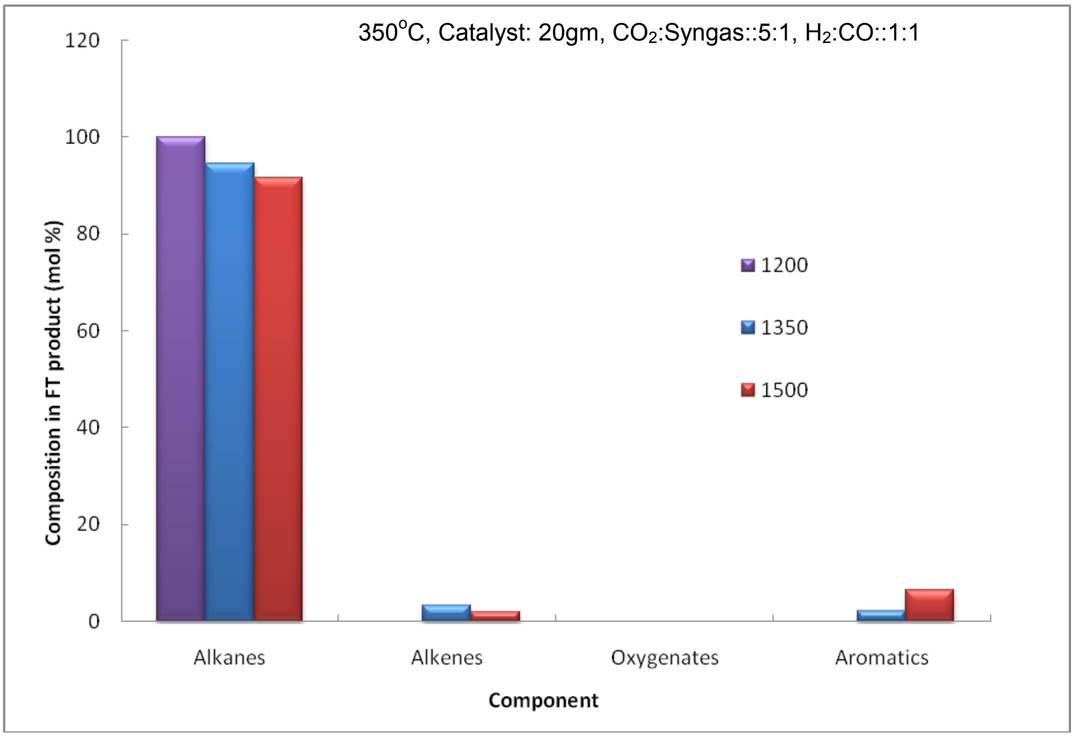


Figure 13: Effects of pressure on the composition of liquid fraction.

6.4 EFFECT OF TEMPERATURE

A total of three different reaction temperatures were taken to determine the effects of temperature in the FTS experiments. 250°C, 300°C and 350°C were the three different temperatures chosen for the three experiments conducted to evaluate the relationship between temperature and FT product distribution. A constant pressure of 1200 psig was maintained throughout all of these three experiments. The amount and type of catalyst used for this set of experiments is 20 gm Fe-Zn-K/alumina. Syngas used for this set of experiment had a 1:1 ratio of hydrogen and carbon monoxide. The mass flow rate of CO_2 was maintained in such a way that the ratio of CO_2 to syngas is 5:1.

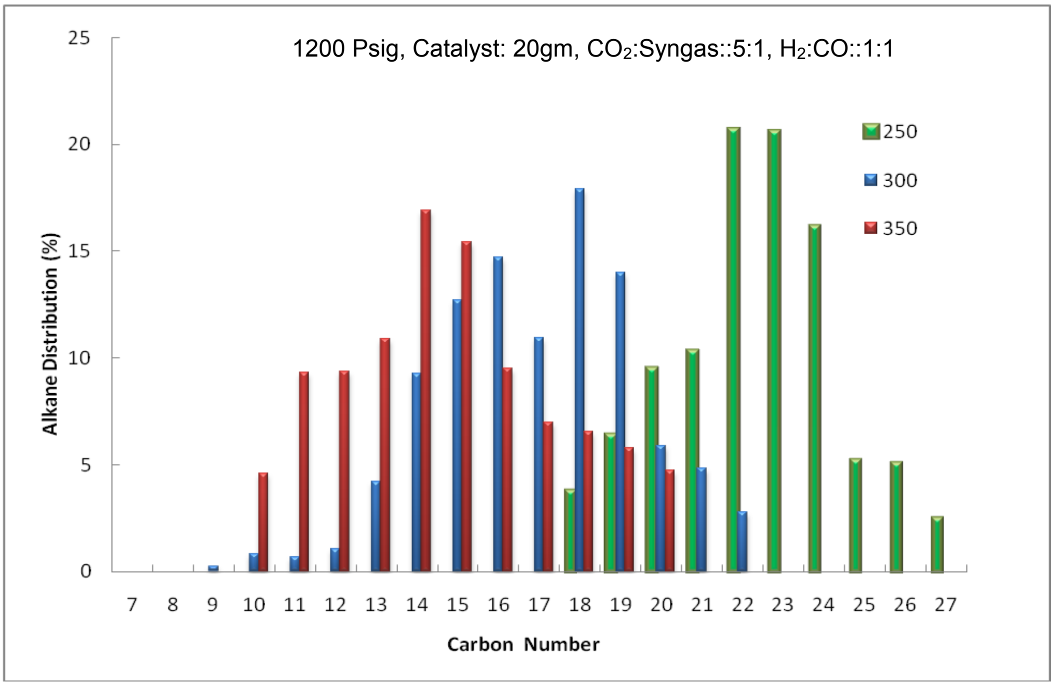


Figure 14: Effect of temperature on distribution of alkanes

Figure 14 contains the plots of the alkane distribution in terms of carbon number for different reaction temperatures. At a reaction temperature of 250°C, it was observed that the distribution of alkane lies between C_{17} to C_{27} with its peak area lying between C_{22} and C_{24}. Similarly, the range of carbon chain lengths observed in the liquid product distribution when the experiments were conducted at 300 °C was C_9 to C_{22} for which the peak distribution lies between C_{16} to C_{19}. When the experiment was conducted at 350°C, the carbon number distribution in the liquid product was observed to lay between C_{10} and C_{20} with peak between C_{13} and C_{15}. From the nature of the liquid product distribution, it is seen that the increase in temperature shifts the carbon number distribution in the product towards the lower carbon numbers which technically means that the decrease in the temperature favors the chain growth which is consistent with previous studies conducted at SIUC as well as other researchers conducting conventional gas phase, slurry phase or supercritical phase FTS.

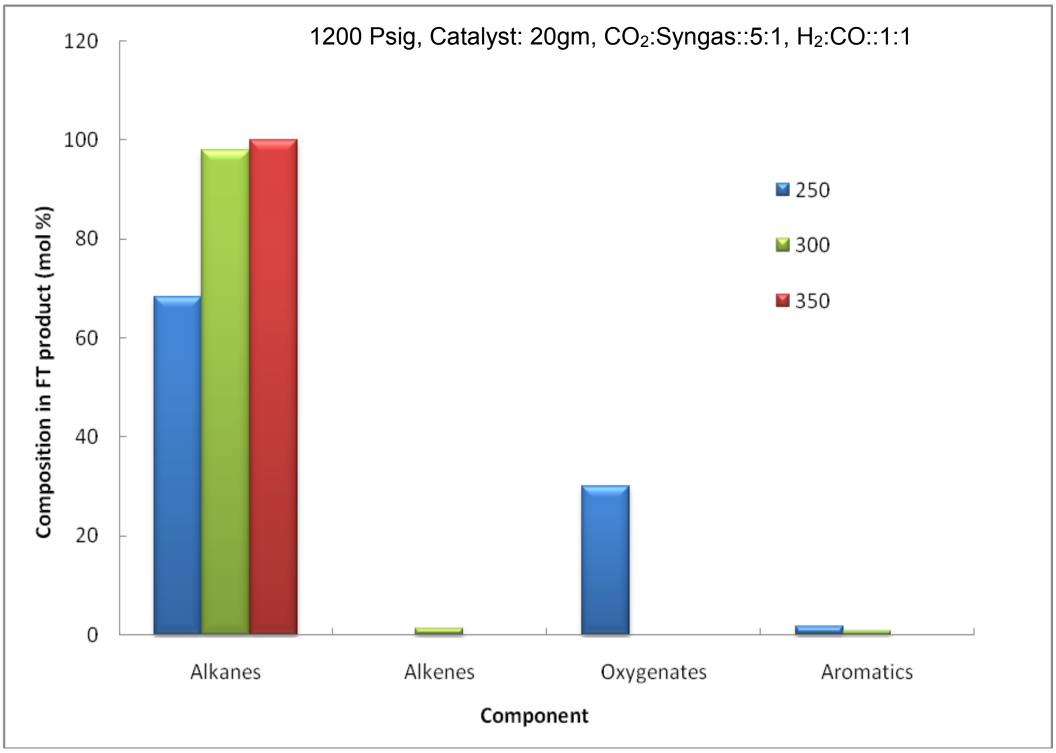


Figure 15: Effects of temperature on the composition of liquid fraction

Figure 15 shows the composition of the liquid fraction as an effect of variation in temperature of the reaction. At the reaction temperature of 250°C, amount of alkanes was observed to be about 65% of the total composition. The remaining composition of the liquid product from the experiment at 250°C contains about 30% of oxygenates and 2-3% of aromatics. No alkenes were found in the products. With an increase in 50°C of the reaction temperature making it up to 300°C, a considerable increase in the production of alkanes was observed. The percentage of alkanes went up to 95 % from 65% at 250°C. The rest of the product contained a very small amount of alkenes (about 2%) and aromatics (about 1%). At a reaction temperature of 350°C, almost all the product composition contained alkanes with none or very small amount of other products. The most apparent conclusion from the above explanation is that the increase in the reaction temperature actually increases the formation of alkanes.

Also, increase in temperature actually suppresses the formation of oxygenates. This is contrary to the observation by Perry [6] where an increase in temperature was found to increase the oxygenate content. The primary difference between the two studies was that Perry [6] conducted the tests with a CO_2:syngas ratio of 1 while, in this study, the ratio used was 5. The probable reason for these above observed trends may be a result of the kinetics of hydrogenation rates and the adsorption and desorption kinetics of intermediates and products. The primary reason for the difference between Perry's results [7] and this study is that CO_2 no longer behaves as a reactant but more as a diluent and thus alcohol formation by CO_2 reduction either by the CO or formate intermediate routes are suppressed and thus reduces the amount of alcohols. When CO_2 participates as a reactant, there is even higher amount of oxygen that needs to be cleaved and a significant portion of it may not be removed and report to the product stream as oxygenates. From the above analysis, it can be concluded that by varying the reaction temperature one can vary the product distribution and composition. Thus, one can vary the temperature of the reaction as per the requirement of desired product.

6.5 EFFECT OF SYNGAS RATIO

Although syngas used for most of the experiments were with 1:1 ratio of hydrogen and carbon monoxide, it was very important to evaluate the effect of variation in the composition of hydrogen and carbon monoxide itself. Syngas produced from various sources result in different H_2:CO ratios and it is essential to evaluate the characteristics of the process as it relates to the source of the syngas to identify if further syngas processing is required before the process. It should be noted that ideally hydrogen to CO ratio of 2 is stoichiometrically favored and this is generally obtained by steam methane reforming or by processing of the syngas produced by gasification of coal or biomass. Five experiments were conducted in this set. The reaction temperature of 350°C was maintained for all experiments of this set. The reaction pressure chosen for this experiment was 1200 psig. 20 gm of Fe-Zn-K/alumina catalyst was used for all five experiments. The amount of carbon dioxide supply was maintained constant at a ratio of 5:1 carbon dioxide to syngas for all experiments in this set. Considering the fact that the syngas from different sources have different composition ratios of hydrogen and carbon monoxide, a total of 4 different compositions of syngas was chosen. One additional experiment was conducted with only hydrogen instead of combination of hydrogen and carbon monoxide. Hence, the ratios of hydrogen to carbon monoxide for the experiments were 1:0, 3:1, 2:1, 1:1 and 1:2.

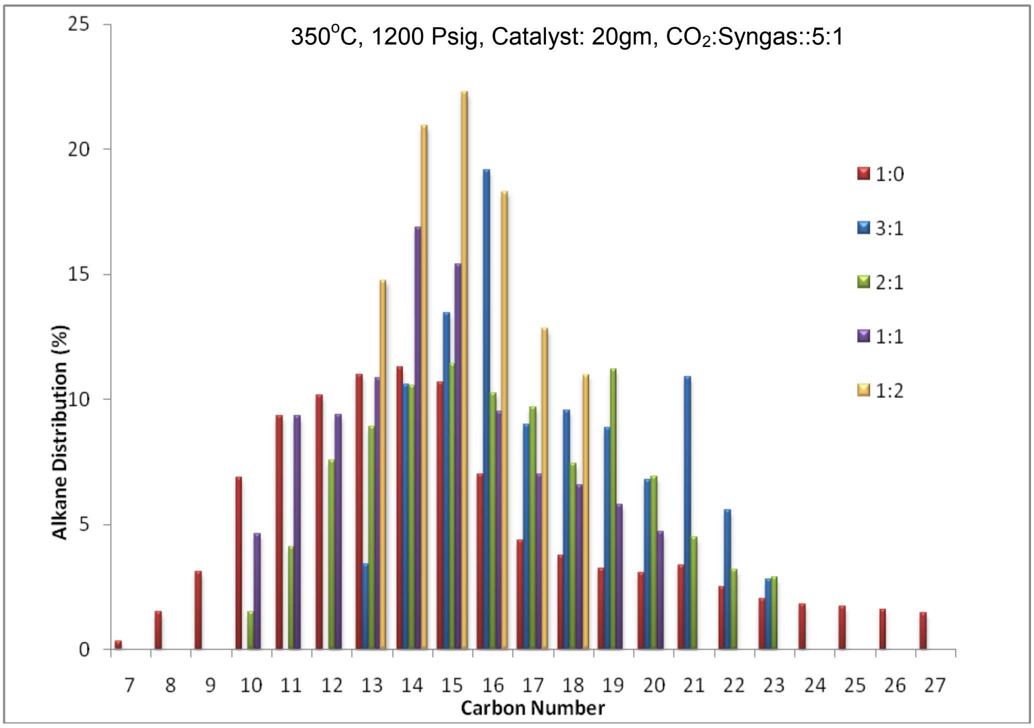


Figure 16: Effects of syngas ratio on distribution of alkanes

Figure 16 contains the plots of the alkane distribution for different ratios of hydrogen and carbon monoxide in the syngas feed. For the reaction without carbon monoxide i.e with only hydrogen in supercritical carbondioxide, the alkane distribution range all the way from C_7 to C_{27} for which the peak distribution lied from C_{11} to C_{15} was observed. This experiment reflects the results of CO_2 hydrogenation in the absence of CO in the feed. The distribution of alkanes for 3:1 hydrogen to carbon monoxide synagas is from C_{13} to C_{22} with its peak from C_{15} to C_{16}. Further decrease in the hydrogen percentage in the syngas feed i.e for 2:1 hydrogen to carbon monoxide synagas, the distribution ranged from C_{10} to C_{23} with its peak lying from C_{14} to C_{19}. For 1:1 hydrogen to carbon monoxide synagas, the distribution of alkanes were found to start from C_{10} to C_{20} with is peak at C_{14} to C_{15}. The alkane distribution was found to be narrower ranging from C_{13} to C_{18} with its peak being at C_{15} for syngas with hydrogen to carbon monodixe ratio 1:2. Although not much of a difference is observed in the hydrocarbon range (and distribution) as a result of syngas composition, it appears that reducing the H_2 concentration in the feed results in a narrower modal range and higher contents in these ranges. The only significant difference in the experiment conducted with no carbon monoxide.

Figure 17 are bar plots of the composition of the components in the products from the FTS experiments with different types of feed. The difference in feed was created by varying the ratio of hydrogen and carbon monoxide in the feed syngas. For the reaction with hydrogen with supercritical CO_2, identical amounts of alkanes and oxygenates were produced which was about 50% each of total composition. Almost no production of alkenes and aromatics were observed during this reaction.

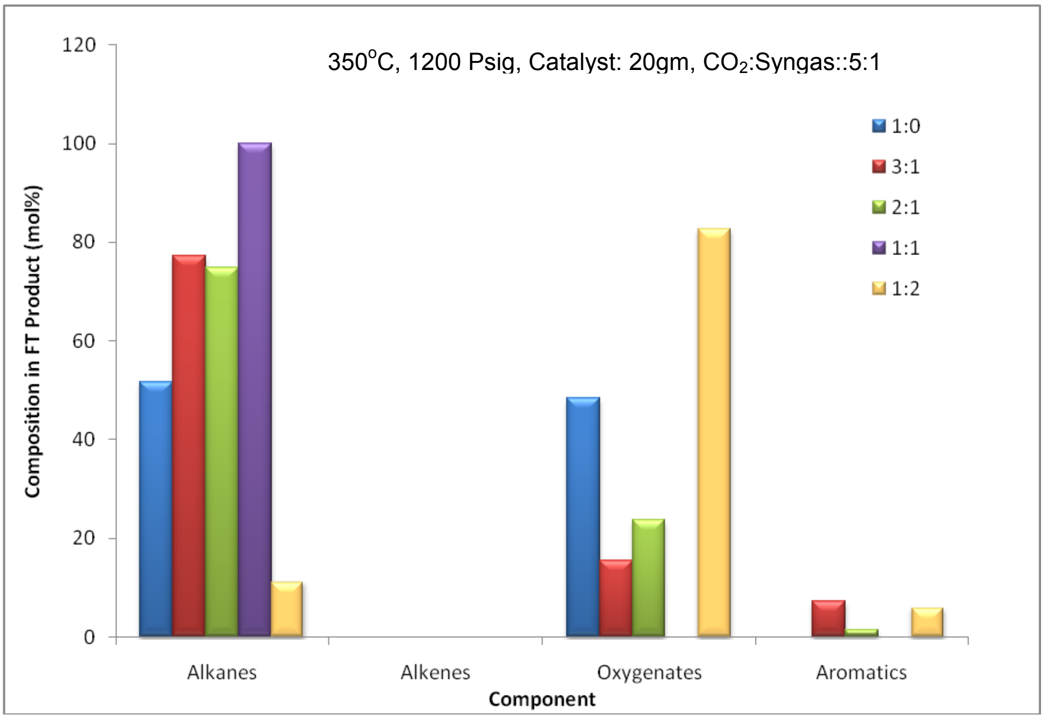


Figure 17: Effects of syngas ratio on the composition of liquid fraction

Upon introducing CO into the mixture of hydrogen and supercritical carbon dioxide (syngas with a H_2:CO is 3:1) ,the amount of alkane production was increased to about 75% with 15 % of oxygenates and 10% of aromatics. Further increasing the percentage of carbon monoxide in the syngas making the hydrogen to carbon monoxide ratio 2:1 another experiment was conducted. For 2:1 hydrogen to carbon monoxide synagas, the amount of alkanes produced were about 70% which is almost like the previous experiment with 3:1 syngas. The rest of the composition contained about 25% of oxygenates and 5 % o aromatics. With a further increase in the percentage of carbon monoxide i.e. for 1:1 hydrogen to carbon monoxide synagas, the entire product was almost all alkanes with no or very few other products. From the observation of the pattern of the product composition it can be said that with increase in carbon monoxide in the feed actually favored for the production of alkanes and suppressed the production of oxygenates. Two plausible reasons for this observation can be hypothesized. When no CO is introduced, CO_2 behaves as the reactant and significant oxygenates are produced since more O has to be cleaved to reduce to hydrocarbons and the reaction rates and hydrogen content did not favor complete reduction at the given space velocities. In addition, the reduction of CO_2 may proceed through two mechanisms – reduction to CO or reduction to formate. The reduction to formate would favor production of oxygenate. Upon introduction of CO, it favored pathways towards the production of hydrocarbons. Still approximately 25 % oxygenates were produced. However increasing the CO content, such that H_2:CO ratio was 1:1, suppressed oxygenate formation. Thus, it can be concluded that the relative ratio of CO and CO_2 plays a significant role in the reaction pathways and needs to be investigated. However, for 1:2 hydrogen to carbon monoxide synagas, there was very high decrease in the production of alkanes which is about 10% of the total composition. This feed actually favored the production of oxygenates which increased to about 85% of total composition. The rest of the composition contained aromatics (about 5%). Another observation (data not provided) was the relatively small amount of liquids being formed in this experiment. When the hydrogen content is too low, oxygenate production is favored. The current mechanistic view of the FT reaction and chain propagation is that CO is converted to CH_2O followed by cleavage of the O to form carbenes unlike the previously held view of CO being reduced to carbide on the surface which is then followed by H_2 addition to form carbenes. The chain propagation is believed to follow through the CO insertion into the C-M (where M is the metal) bond of the carbene rather than CH_2 addition to another CH_2. Thus, a CH_2-CO species is formed which is reduced to CH_2-CH_2O on the metal surface. These mechanisms were found to be thermodynamically and kinetically favored over the competing mechanisms. On the basis of the above mechanism, it can be seen that oxygenate species exist at every chain growth and the cleavage of O form an alkene or H addition to form an alcohol or further reduction of these species to alkanes is going to be competitive depending on the hydrogen concentration and the reaction conditions. In the case of 1:2, H_2:CO feed, the hydrogen content was too low which resulted in a relatively high oxygenate concentration.

6.6 PROSPECT OF FRACTIONATION

The exhaust line of the reactor passes through the first collection vessel and then to the back pressure regulators as shown in figure 3.

As the first collection vessel was placed right after the reactor and before the first BPR, the pressure of the collection vessel is same as the reaction pressure. After BPR, the exhaust gases were then passed through other collection vessels at atmospheric pressure. The two vessels were used to trap the liquid products from the reaction. The products collected in two vessels were analyzed separately and a comparative study was done. The purpose of the analysis and study was to find the prospect of fractionation without using any external unit, but by simply tuning the pressure which in this case was reaction pressure and atmospheric pressure.

The figure 18 is a very encouraging example of the fractionation of liquid products downstream the reactor. This is the representation of the distribution of products in the two different traps for the experiment with 1500 psig reaction pressure. The ratio of carbon dioxide and syngas for this experiment was 5:1. The syngas used for this experiment had a H_2:CO ratio of 1:1. 20 gm of Fe-Zn-K/alumina catalyst was used for this experiment. The reaction temperature for this experiment was 350°C.

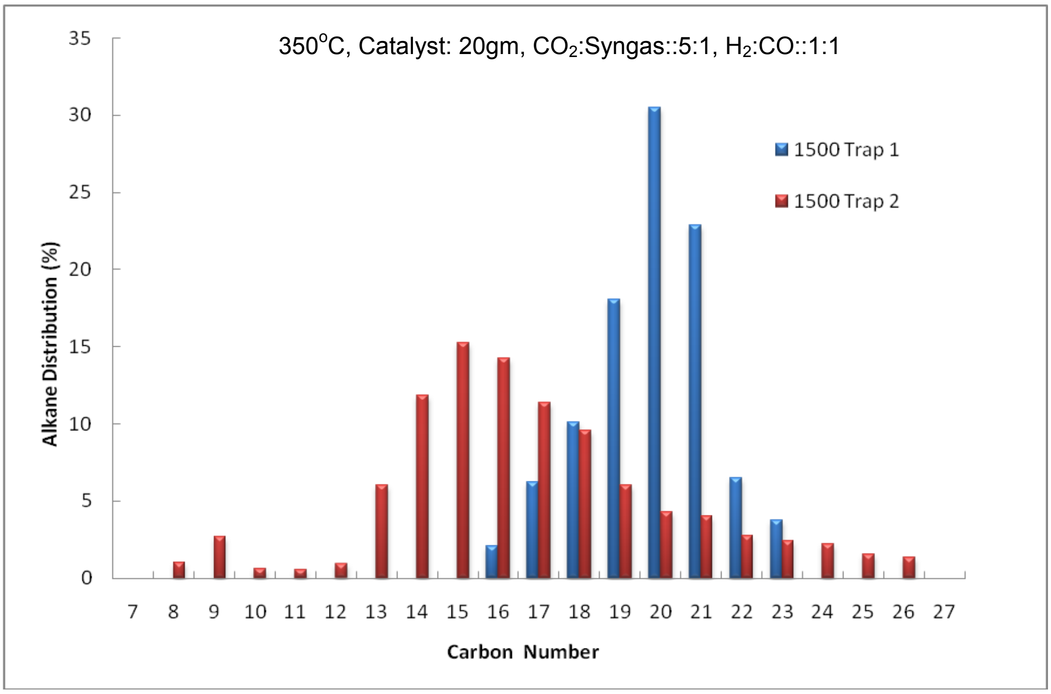


Figure 18: Distribution of alkanes in the product collected at two collection vessels

From the figure it can be seen that the carbon number distribution in the liquid product for the first trap ranges between C_{16} and C_{23} while the distribution of carbon chain lengths in the liquid products from second trap ranges between C_8 to C_{26} with its peak from C_{14} to C_{17}. So it is apparent that the heavier hydrocarbons were collected in trap 1 while the lighter hydrocarbons were collected in the second trap. This can be because the lighter hydrocarbons were more soluble in supercritical carbon dioxide i.e at supercritical pressure and travelled to the other trap. However, as a result of the lower solubility of the heavier hydrocarbons in supercritical CO_2, these species precipitated in the first collection vessel.

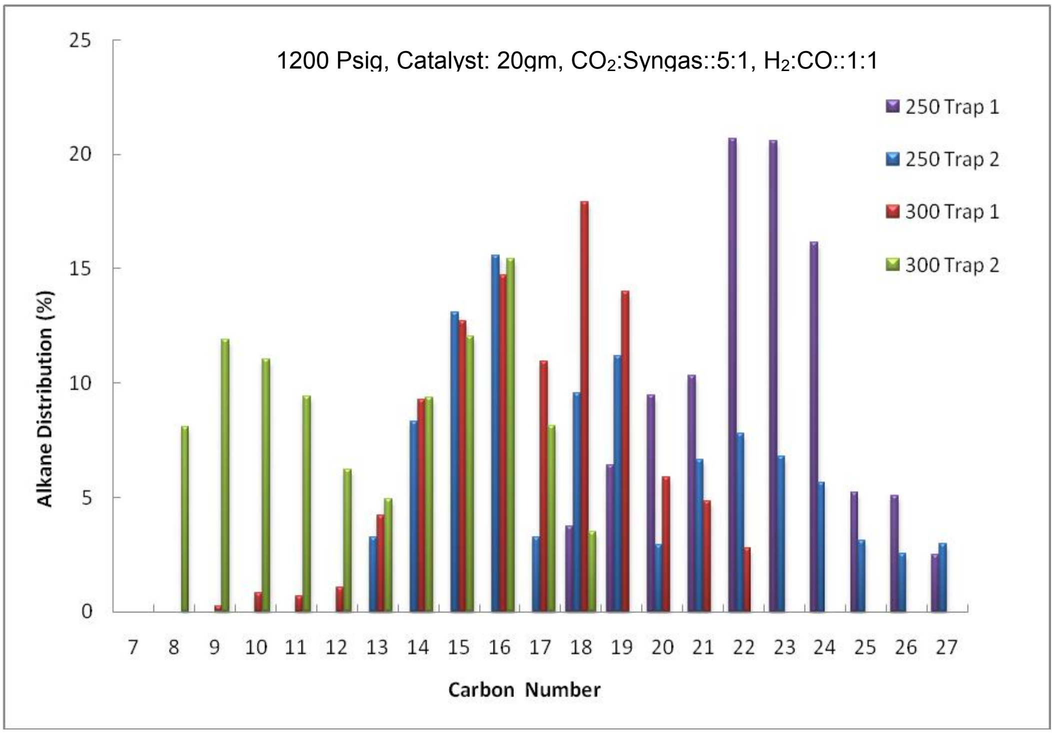


Figure 19: Distribution of alkanes in the product collected at two collection vessels

Figure 19 is representation of the product distribution in terms of carbon number. Two traps for the experiment with 250°C and 300°C. The carbon dioxide and syngas (H_2:CO:1:1) ratio was 5:1 for both of this experiment. The reaction pressure for this experiment was 1200 psig. For this experiment 20 gm of Fe-Zn-K catalyst was used.

For 250°C, the distribution of product in trap 1 has its alkane distribution from C_{18} to C_{27} with its peak distribution from C_{21} to C_{24}. For trap 2, C_{13} to C_{27} is the total alkane distribution with its peak from C_{14} to C_{16}. So this pattern of product distribution also supports the idea of dissolution of lighter hydrocarbons with the supercritical carbon dioxide and precipitate in the second trap where the pressure is atmospheric. The heavier hydrocarbons were precipitated in the first trap which was at the reaction pressure.

Similarly, at a reaction temperature of 300°C, the heavier hydrocarbons (C_9-C_{22} with peak contents around C_{18}) were collected in first trap and the second trap collected the lighter hydrocarbons (C_8-C_{18}).

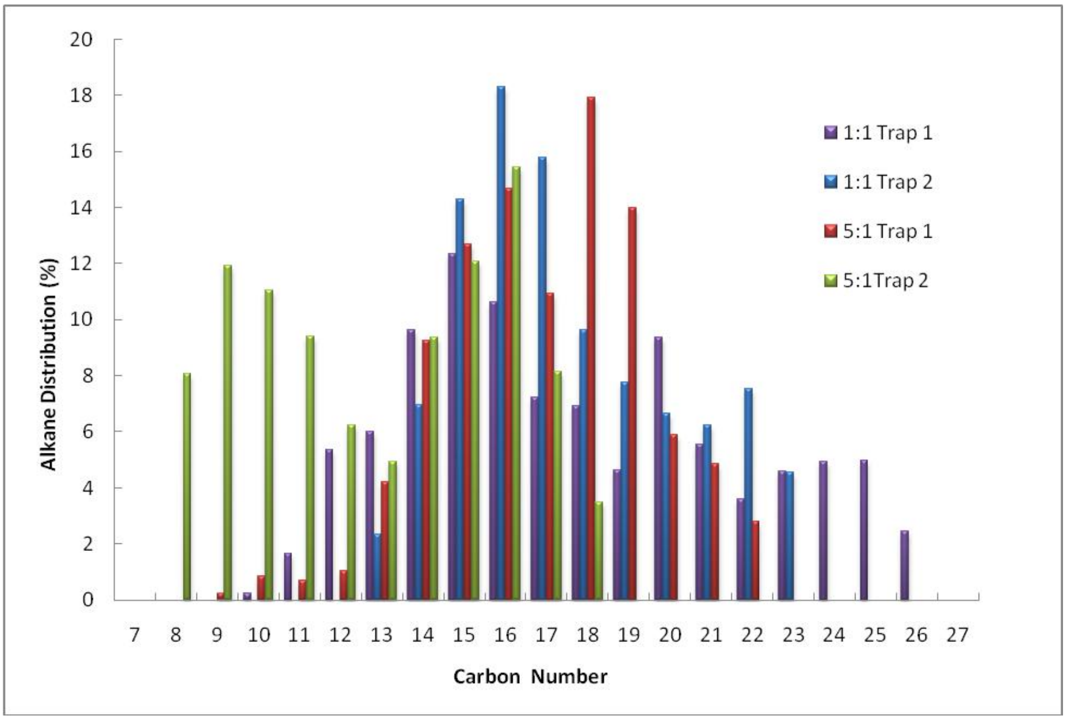


Figure 20: Distribution of alkanes in the product collected at two collection vessels

Additional studies of fractionation by pressure tuning were also conducted and shown in figure 20. For the experiment with carbon dioxide to syngas(H_2:CO=1:1) ratio 5:1, a reaction temperature and pressure of 300°C and 1200 psig, respectively, the second trap collected hydrocarbons ranging from C_8 to C_{21} with fairly uniform contents of species from C_9 and C_{16}. The first trap collected the alkanes ranging from C_{10} to C_{22} with its peak around C_{16} and C_{18}.

For the experiment with feed containing carbon dioxide and syngas in the ratio of 1:1, and reaction pressure and temperature of1200 psig and 300°C reaction, respectively, over with 20 gm Fe-Zn-K/alumina catalyst, the first trap collected the alkanes from C_{13} to C_{24} with its peak distribution lying from C_{15} to C_{17}. The second vessel trapped the alkanes from C_{10} to C_{26} with its peak around C_{14} to C_{16}. The separations of the components in this experiment were not as distinctive as the previous experiments and thus the pressure tuning feature needs to be investigated further to understand the unit operation better and to achieve better control.

Overall, very positive and encouraging results of fractionation of liquid products downstream the reactors with the help of pressure tuning were obtained.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

The batch mode reactor system to evaluate the Sc CO_2 as supercritical fluid was successfully converted to continuous flow reactor system. However, several problems were encountered. The problems encountered were solved by modifying the system and installing additional parts in the system to give the steady and continuous flow of the reactor.

Conclusions

1. Experiments were conducted for different catalyst loading for the reactor. It was found that the increase in the amount of catalyst loading increased the amount of alkanes. However, the amount of oxygenates formed were suppressed as the amount of catalyst loading was increased.

2. Experiments were conducted at different pressures between 1200 – 1500 psig,. It was found that the increase in pressure shifted the liquid product distribution towards higher hydrocarbons. Moreover, it was found that at lower end of the pressure (1200 psig) no alkenes or aromatics were formed while small amount of alkenes and aromatics were found in the experiment with 1350 psig and 1500 psig.

3. To determine the effect of different reaction temperatures in FTS, experiments were conducted at different temperatures ranging between 250 to 350^{o}C. Higher temperatures favored production of lower hydrocarbons. Formation of oxygenates was suppressed as the temperature was increased. At 350^{o}C, only alkanes were found in the liquid product.

4. Different percentage of carbon dioxide was supplied with syngas for different experiments to evaluate the effect of dilution n FTS experiments. It was

found that an increase in the extent of dilution increased the extent of the suppression of oxygenates and formation of alkanes.

5. Syngas with different compositions (proportions of hydrogen and carbon monoxide) were used to determine the effect of feed type/ratio in the product distribution. It was found that, for syngas with a H_2:CO of 0.5, maximum amount of oxygenates was formed. Similarly for syngas with H_2:CO of 1, maximum amount of alkanes was formed.

6. Fractionation of the liquid products by tuning the pressure was achieved.

Recommendations

As discussed in the results section, onsite fractionation of liquid products can be done and further research into the pressure tunable fractionation should be be conducted in more extensive manner. It is preliminarily proved that it is possible to fractionate the liquid products obtained by tuning the pressure in the collection vessels. The current flow system can be re-designed by adding more BPRs and collection vessels so the FT synthesis products are passed through and collected by a series of liquid traps at different temperatures and pressures. Pressure regulators after each collection vessel could be maintained such that the solubility of the heavy hydrocarbons and oxygenates in the supercritical fluid is negligible. Those heavy hydrocarbons will accumulate and be collected in the first vessel. The back pressure regulator after the second vessel should be maintained so that the certain fraction of hydrocarbon with medium weight will precipitate. The back pressure regulator after the third chamber will hold a reduced pressure which would cause the remaining lower or lighter hydrocarbon fraction to precipitate out.

As from the online GC analysis it was found that the exhaust gas contained small amounts of unused carbon monoxide and hydrogen along with lower hydrocarbons in the form of gas. Redirecting the exhaust gases through recycling loop would definitely increase the conversion of carbon monoxide and help in the formation of longer chains of hydrocarbon with negligible amount of undesired losses at high throughputs. Also, addition of lower hydrocarbon gases such as heptanes, hexane and pentane would enhance the solubility of waxes from the catalysts surface in addition to the traditional advantages of using supercritical CO_2.

As all of this research was done with Fe-Zn-K catalyst, it would be productive to test the whole set of this experiment with other types of catalyst including commercially available catalysts.

It was claimed that the supercritical fluid will increase the life of catalyst so study of used and unused catalyst the gas and supercritical phase should be studied to justify that claim. Further investigations should include long-term tests that focus on catalyst deactivation in the supercritical phase FT synthesis with CO_2 as a medium. To determine catalyst life, steady-state flow experiments should be conducted with and without CO_2 as a medium, where CO and H_2 conversions are recorded hourly. Similarly, CO_2, CH_4, and other low carbon number hydrocarbons (chain) selectivity can be monitored. To show the overall catalyst deactivation, the decrease in syngas conversion and increase in CO_2 and CH_4 selectivity should be used.

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