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Effect of the operation parameters on the Fischer Tropsch synthesis process using different reactors

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Abstract

There are a number of factors that affect the output of the Fischer Tropsch process, change in the process parameters like catalyst used, residence time, temperature, pressure, particle size, bed height, flowrate and even the type of reactor used. A small manipulation of the parameters is enough to change completely the conversion, selectivity; therefore, these parameters have to be monitored. This paper presents the effect of the operation parameters on the Fischer Tropsch synthesis. The method that was used for this observation was that all the adjustable process parameters were manipulated, one parameter was subjected to variation while others were kept constant so that its effect on the conversion and selectivity can be easily monitored. It is not always very easy to obtain results that favour all the aspects of measuring efficiency: conversion, yield and selectivity e.g. if the selectivity increases, conversion decreases and the yield also changes. It has been found that an increase in the residence time or lowering the concentration of the feed increases the conversion by up to 90% without a significant effect on the selectivity. Investigations of the operation of the fluidized bed reactor using mathematical models in polymerizing syngas was done, simulation results revealed that iron catalyst is best for the optimization of liquid hydrocarbon products. Operation at high reactor pressure has positive effect on the reaction i.e. there is an increase in overall CO conversion which, the chain length of the products. Coupling, high reactor pressure and the use of an iron catalyst leads to the production of heavy molecular weight hydrocarbons. At high pressure there is a reduction in the olefin/paraffin ratio. It can be concluded that iron catalyst, high feed rates and high pressure mostly favour the Fischer Tropsch reactions.

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1.0 Introduction

1.1 Theoretical background

The Fischer Tropsch synthesis process is the hydrogenation of carbon monoxide to produce hydrocarbons in the range of C₄-C₇. The fact that a hydrocarbon (methane) could be catalytically produced from carbon monoxide and hydrogen over an iron or cobalt catalyst at atmospheric pressure was first reported by Sabatier and Senderens in 1902 [1]. However, the greatest breakthrough in the conversion of carbon monoxide into liquid hydrocarbons was made by Franz Fischer and Hans Tropsch in 1923 at the Kaiser Wilhelm Institute for Coal Research (presently Max Plank Institute) in Mülheim, Germany. These scientists reported obtaining synthon, a mixture of hydrocarbons and oxygenated compounds, from the reaction of H₂ and CO over alkalized iron at 400- 450 °C and 150 atmospheres pressure [2]. To test the usefulness of the products as transportation fuels, the oil layer was separated from the aqueous layer, de-acidified and fractionated by distillation and then subsequently road tested using a 1922 model NSU motorbike carrying two persons. The results were reported to be encouraging with the performance appearing to be similar to, or better than, a reference fuel. The Fischer Tropsch process was used by Japan and Germany during the Second World War to produce alternative fuels to substitute crude oil. In the year 1944, Germany's annual synthetic fuel production reached more than 124,000 barrels per day and to about 6.5 million tons from their 25 plants.

Fischer-Tropsch (FT) synthesis is an important gas-to-liquids (GTL) technology which converts syngas obtained from the gasification of coal, and also derived from natural gas or biomass to transportation fuels and petrochemical substituents [3]. This process is a promising option for environmentally sound production of chemicals and fuels from coal since the reserves of crude oil are being depleted and the price of crude oil continues to rise.

The FT process is made up of a variety of reactions producing a diverse number of molecules of dissimilar types and carbon numbers. There are two main processes (coal to Syngas, syngas to FT Fuels) with two major needs being the coal gasifier and FT reactor. The gasification of coal produces Syngas, and the syngas is the main reactant in the Fischer Tropsch production of fuels.

1.2 Fischer Tropsch catalysts

The determination of which type of catalyst to use depends on a wide range of components; cost, ease of availability, the nature of the feed, how well the catalyst achieves desired goal and quantity needed per batch. A suitable catalyst will be the one that achieves or gives high conversion of desired product over undesired products; the conversion should also be over a small residence time. The mostly used catalysts in the FT process are iron and cobalt [4]. Iron catalysts are mostly used because of their eases of availability, lower methane selectivity and low cost [5]. These catalysts are also known to operate over a wide range of temperatures (220 to 350°C) and at pressures between 10 and 60 bar [6].

1.2.1 Cobalt based catalysts

Cobalt catalysts are promoted through the use of little amounts of noble metals (ruthenium, rhodium, palladium, silver, gold, osmium, iridium and, platinum). The noble metals are those that are resistant to corrosion and oxidation by moist air. This type of catalysts decrease the temperature at which the natural gas is reduced but increasing the chemical reactivity in the process. According to [8] the oxides of transition metals should be added to the cobalt if the selectivity of waxes is to be improved over all other products. Cobalt catalysts can be operated at very low pressures of between 1-10bar where they yield few olefins and oxygenated products. The rate of catalytic activity is directly proportional to concentration of Cobalt available [9].

1.3 Pressure

Product distribution in an FT run is highly dependent on operating conditions i.e. pressure, temperature, gas space velocity and type of catalyst used. FT reactions are usually characterised as highly exothermic reactions, therefore the use of high operating pressure allows heat removal to be controlled properly. Recent studies shows that high pressure also increases CO conversion and according to, [10] high reactor pressure has a positive effect on the extent of reaction and chain length of products. One other benefit of high operating pressure is that, there is reduced selectivity towards methane production which is an unwanted product during an FT run, [8] confirms this statement.

In a study carried out by [11] in which the effects of changing operating conditions on product distribution were investigated, noted that by increasing total pressure i.e. reactor pressure conversion of CO increased across all reactors with an iron based catalyst reduced with CO, H₂, and syngas. Similar results were noticed upon further increase in total pressure. [11], also noted that high operating pressure reduces the olefin/paraffin ratio i.e. there is a significant decrease in olefin selectivity, while selectivity towards paraffinic products is favoured by an increase in total pressure. The reduction in olefin/paraffin ratio could be attributed by the fact that as pressure increases, the particle's time on stream also increases hence allowing the primary products of the reaction to undergo secondary hydrogenation to produce large molecular weight hydrocarbons [11] therefore a decrease in olefin/paraffin ratio.

1.4 Temperature

The nature of FT reaction is generally exothermic which makes temperature the most important variable in FT processing. In order to avoid catalyst deactivation, the temperature has to be kept constant, allowing the temperature to fluctuate will in addition increase the rate at which methane is formed, and usually this is an undesirable effect.

According to the study done by [12] the optimal operating temperature range for cobalt is found to be in the Low Temperature Fischer Tropsch (LTFT) range of 200-250°C, while iron-based catalysts could be used in either the LTFT or high temperature Fischer Tropsch (HTFT) in the range of 300-350°C, depending on their preparation methods and formulation. [13] Used a mathematical model to investigate the effect of temperature on Fischer Tropsch selectivity and production rate. Results reveal that both the selectivity and production rate are affected by temperature. [13] Simulation results are shown in figure 1 below. The figure shows that the selectivity of C₅+ decreases with an increase with temperature whereas production increases with the temperature. The selectivity decreases more rapidly after a cooling temperature of 450K. Therefore, for an optimum output of C₅+, an optimum temperature must be used e.g. 450K.

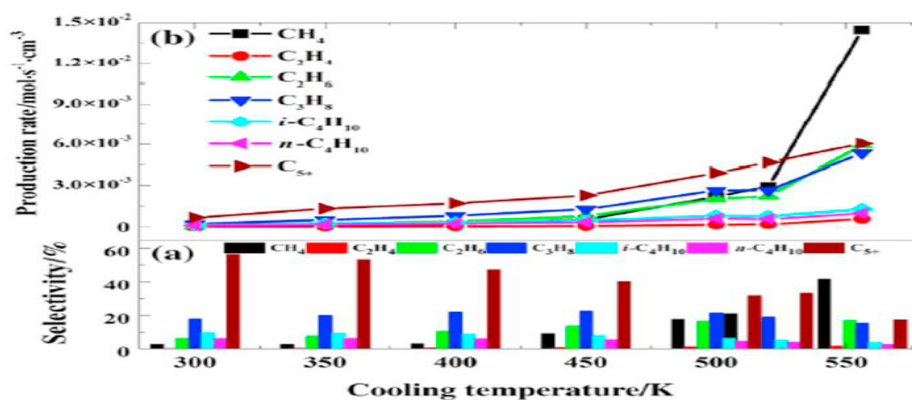


Figure 1: Effect of cooling temperature on the production selectivity and production rates [10]

2.0 Experiments, Results and Discussion

Quan-Sheng [15] carried out an experiment using a precipitated iron catalyst that was promoted with sodium and copper. The sample contained 100 parts by weight (pbw) iron, 4.43 pbw copper, 3.95 pbw sodium and lastly 20.5 pbw silicon dioxide. The sample was divided into 3 parts with different average part diameter. The parent catalyst was grinded, and then sieved to the required size fraction. Catalyst activation was carried out *in situ* by a reductive treatment with a hydrogen/nitrogen mixture at 523 K. Afterwards, the catalyst temperature was reduced with a steam nitrogen to the desired temperature. The results of the iron catalyst prepared as narrated above is shown in the table below:

Table 1: Effect of Catalyst Particle Size on Activity in Synthesis Gas Conversion

Catalyst		Reaction Conditions			Catalyst Performance	
Sample No.	Particle	T(K)	Feed	Conversion(%mol)(H ₂ +CO)	Space Time Yield,	

	diameter(mm)		Ratio(mol/mol)(H ₂ /CO)		kg C ₁₊ (m ³ .cat.h)
1	2.1	493	2	30	62
2	0.64	493	2	46	97
3	0.22	493	2	52	104

As seen from the table [15] found out that the conversion of the syngas and the catalyst performance increase as the average particle size is decreased as shown by the space time yield. [15] Explained that a large particle size limits the diffusion within the particle in a fluidized bed reactor and as a result limiting the average rate of reaction. This means that for increased conversion rates, catalysts of a small average particle size should be used.

On the other hand, according to the second experiment done by [15], it shows that particle size has a higher effect on catalysts prepared by precipitation as compared to those prepared by impregnation on porous silica. The precipitation catalysts usually have a lower voidage and pore diameter than the impregnated ones. For almost the same particle diameter of 2.2 mm, same temperature, feed ratio, the conversion and production as given by the space yield were 17% and 35 % respectively, these two values were significantly lower as compared to those of catalyst prepared by precipitation.

The same experiments as those carried with precipitated iron and impregnated iron were carried out but this time with a cobalt catalyst. Both samples were impregnated, the first on porous alumina and the second on porous silica, nevertheless they had the classical Fischer Tropsch catalysts being magnesium and thorium. The catalyst conditions are shown in table 2 and the results obtained from the different samples shown in table 3.

Table 2: Catalyst make up

Sample No.	Nominal Composition(pbw)	Average pore diameter(mm)	Average part diameter(mm)
1a	25 Co/1.04 Th/1.18 Mg/100 Al ₂ O ₃	15	2.3
1b	25 Co/1.04 Th/1.18 Mg/100 Al ₂ O ₃	15	0.22
2a	25 Co/1.04 Th/1.18 Mg/100 Al ₂ O ₃	100	2.3
2b	25 Co/1.04 Th/1.18 Mg/100 Al ₂ O ₃	100	0.22

Table 3: Effect of Catalyst Particle Size on Activity in Synthesis Gas Conversion

Catalyst		Reaction Conditions			Catalyst Performance	
Sample No.	Particle diameter(mm)	T(K)	Feed Ratio(mol/mol)(H ₂ /CO)	Conversion(%mol)(H ₂ + CO)	Space Yield, C ₁₊ (m ³ .cat.h)	Time kg
1a	2.3	523	1	50	105	
1b	0.22	523	1	55	230	
2a	2.3	523	1	50	105	
2b	0.22	523	1	55	230	

As can be interpreted from table 3, the effect of particle size is clear on the catalyst performance as compared to the syngas conversion which is almost independent of the change in the particle diameter. Catalyst performance profits greatly from the catalyst diameter, a change from 2.3 mm to 0.22mm changed the performance from 105 to 230 for both samples. But one important aspect that should be noted as well is that both conversion and performance

increase with the decrease in catalyst diameter. The productivity of the catalyst seems to be independent of the type of carrier and pore diameter [15].

The influence of the different parameters on Fischer Tropsch synthesis cannot only be shown by experiments but models can also be used to see how the variation in parameters can affects or change the products. Mathematical models have been used in the past to model the FT behaviour; both one dimensional and two dimensional models have been produced by different authors. Models have been previously developed by [14].

[13] did a model whose objectives was to predict the performance of a fixed bed reactor under supercritical fluids to Fischer Tropsch products conditions. The model was to simulate the temperature and concentration profiles inside the catalyst pellet, thus is to be done in both the supercritical and gas phase conditions. The mode was as well expected to show the effect of the main Fischer Tropsch controlling parameters (pressure, temperature), reaction media etc.

After a number of assumptions i.e. steady state conditions, spherical catalyst etc. [5] laid down equations for the model that include the mass balance, heat balance, momentum balance for both the spherical catalyst and the FT reactants being carbon monoxide and hydrogen e.g.

Second order differential equation describing the diffusion and reaction:

$$\frac{D_i}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_i}{dr} \right) = (-r_i) \rho_{cat}$$

(1)

- Equation 2 and 3 are the mass balance equations for the reactants.

$$\frac{D_{CO}}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_{CO}}{dr} \right) = (-r_{CO}) \rho_{cat}$$

(2)

$$\frac{D_{H_2}}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_{H_2}}{dr} \right) = (-r_{H_2}) \rho_{cat}$$

(3)

Where;

i species in the reaction

r= is the radius of the pellet

r_i is the rate of formation of the compound (mol/g.s)

ρ_{cat} is the catalyst density

D_i is the diffusivity of the reactant I in the catalyst (cm/s)

After setting the boundary conditions for the model and defining all equations to deal with the kinetics of the model, the model was run using operation parameters in Table 4 and the results of the model are shown in Table 6.

Table 4: Model operating conditions and catalyst characteristics

Temperature, T	513 K
Total pressure, P	80 Bar
H ₂ /CO feed ratio, V	2
n-Hexane/Syngas ratio, S	3
Catalyst Type	Co/Al ₂ O ₃
Pellet shape	Spherical
Pellet diameter, d Pellet	1 mm
Pellet porosity, ep	0.5
Pellet density, p _{cat}	1.5 g/cm ³
Pellet tortuosity	3

The diffusivity of hydrogen was found to be four times higher than that of carbon monoxide under the model conditions as seen from Table 5. It is also to be noted that the diffusivity in the supercritical phase is much higher than that of the gas phase.

Table 5: Binary diffusion coefficient and effective diffusivity

Supercritical phase	Gas phase
$D_{CO-hexane} = 1.03 \times 10^{-3} \text{ cm}^2/\text{s}$	$D_{CO-wax} = 1.03 \times 10^{-4} \text{ cm}^2/\text{s}$
$D_{H_2-hexane} = 3.86 \times 10^{-3} \text{ cm}^2/\text{s}$	$D_{H_2-wax} = 1.03 \times 10^{-4} \text{ cm}^2/\text{s}$
$D^e_{CO-hexane} = 1.33 \times 10^{-4} \text{ cm}^2/\text{s}$	$D^e_{CO-wax} = 1.03 \times 10^{-5} \text{ cm}^2/\text{s}$
$D^e_{H_2-hexane} = 6.43 \times 10^{-4} \text{ cm}^2/\text{s}$	$D^e_{H_2-wax} = 1.03 \times 10^{-5} \text{ cm}^2/\text{s}$

Looking at the concentration profiles of the reactants carbon monoxide and hydrogen inside the catalyst in figures 4 and 5, the profiles show that the synthesis gas in heavier waxes diffuses much slower in the gas phase when compared to the supercritical phase. The slow diffusion of the syngas is due to the high hydrogen diffusivity under supercritical conditions as compared to carbon monoxide. The simulation profiles are shown in the figures 4 and 5.

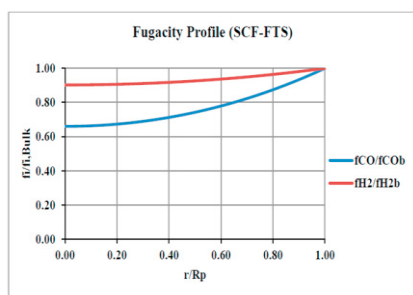


Figure 2: catalyst pellet under supercritical conditions

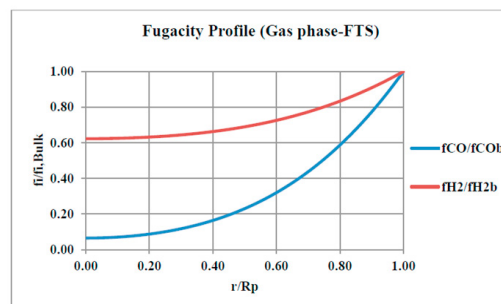


Figure 3: Concentration profile under gas phase conditions

3.0 Conclusion

It can be concluded that precipitated iron catalysts should be prioritised over impregnated iron catalysts if we desire a higher syngas conversion and high catalyst performance. It can therefore be concluded that any temperature can be used for the production of Fischer Tropsch hydrocarbons but optimum temperatures of 450K are used for C_{5+} hydrocarbons. Another observation is that a decrease in the hydrogen to carbon ratio gives a monotonic temperature curve which helps easily arriving at the target condition. Lastly, iron catalyst, high feed rates and high pressure mostly favor the Fischer Tropsch reactions.

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