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Hydrocarbon Distribution of a Catalytic Process - The Fischer-Tropsch Synthesis

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Abstract

Fischer-Tropsch synthesis (FTS) is a catalytic process that can be used to produce hydrocarbons, oxygenates and H₂O among other products from synthesis gas, which can be derived from natural gas, coal, or biomass. It is a key component in Gas-to-Liquid (GTL), Biomass-to-Liquid (BTL) and Coal-to-Liquid (CTL) technology. The goal of the proposed work described in this Final Report was to show the distribution of the major product (hydrocarbon) with carbon number ranging from 1-37 assuming ideal kinetics of Anderson-Schulz-Flory (ASF) distribution model. The distributions of FT hydrocarbon product have best been described by Anderson-Schulz-Flory distribution model. The formation of long chain hydrocarbon product will depend on increasing chain growth probability and that the maximum selectivity of gasoline and diesel range products were 46% and 29% respectively. The selectivity of FT products as described by Anderson-Schulz-Flory (ASF) distribution model is a one parameter factor and does not correspond to the distribution for all ranges of hydrocarbon products as deviations has been reported in literatures for hydrocarbon product yield of C₁, C₂ and products with high molecular weight.

1. Introduction

Crude oil derived fuels have for a long time dominated as a source of transport fuels. Crude oil is a finite and non-renewable resource, and in recent years there has been growing concern about the depleting crude oil reserves. The world's proven reserves of natural gas and coal are much larger than the proven reserves of crude oil. At the end of 1999 the world's proven reserves of crude oil was 140 x 10⁹ tons, the proven reserves of natural gas was 146 x 10¹² m³ which is 132 x 10⁹ tons oil equivalent and coal 984 x 10⁹ tons which is 656 x 10⁹ tons oil equivalent [1]. As a promising route for the production of liquid fuels with high cetane number with little or no sulphur that could be blended with diesel fuel, petrochemicals and lubricant from the abundant natural gas, coal and biomass reserves.

FT (Fischer-Tropsch) process is a set of catalytic processes for the conversion of synthesis gases into a mixture of products that can be refined to produce synthetic fuels, lubricants and petrochemicals as can be seen in Figure 1 [2-3].

FTS is a particularly complex system, where you have a number of different reactions combined into a single mechanism which is the irreversible Fischer-Tropsch reaction. Two phases (vapour and liquid) of hydrocarbons are formed during the synthesis. The lighter components preferentially accumulate in the vapour phase while the heavy oils

and waxes in the liquid phase [4].

The FTS plays a major part in the group of processes called Gas-to-Liquid technologies (GTL). GTL involve the conversion of natural gas, biomass or coal into synthetic crude oil that can be further refined and separated into different fractions of useful hydrocarbons, including liquid fuels [5-6].

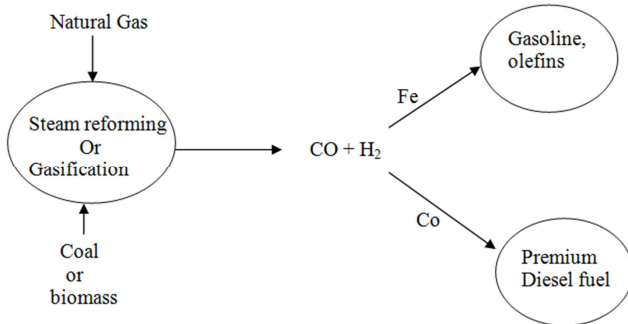


Figure 1. Scheme of FT process [2].

Diesel fuels produced from these processes exhibit outstanding properties compared to diesel fuel derived from crude oil; very high cetane number (typically above 70) and virtually no sulphur, nitrogen and aromatics resulting in reduced pollutants from the engine [7]. Numerous studies have investigated the FT process in different aspects [8-15].

2. Historical Background

Fischer-Tropsch Synthesis has been traced back to catalytic hydrogenation reaction which began in the early 1820s when Dobereiner discovered that finely divided platinum caused hydrogen to burn spontaneously in air. Decades later, scientists began investigating the catalytic properties of a wide range of metals; their focus was on hydrogenation and hydrogen production from hydrocarbons [16]. However, in 1902, Sabatier and Senderans developed a number of catalysts for hydrogenation of vapour phase organic compound. They studied the synthesis of methane by hydrogenation of CO and CO₂ over metal catalyst at high temperature and atmospheric pressure which can be said to be a precursor of FTS [17].

As early as 1923, Franz Fischer and Hans Tropsch at the time worked at the Kaiser Wilhelm institute in Germany invented the FT reaction in petroleum poor but coal rich Germany. It was used by the Germans during the Second World War to produce alternative fuels. Though Fischer and Tropsch made an important breakthrough but it was not until the late 1920s that many Chemical Engineering problems associated with FT reactions were tackled by scientists, and a series of reactors were developed for FT process [2], [18-21].

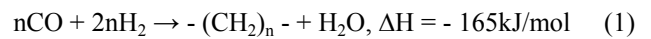
3. Fischer Tropsch Synthesis

Fischer-Tropsch synthesis is a collection of chemical reactions that convert specific mixture of carbon monoxide and hydrogen into liquid hydrocarbon. It is a key component of gas to liquid technology and involves a series of chemical reactions that could yield various hydrocarbons. Two main features of Fischer-Tropsch process are the unavoidable ranges of hydrocarbon product and the liberation of a large amount of heat from the highly exothermic synthesis reaction [22]. FTS has been classified as Low temperature (LTFT) and High temperature (HTFT) which operates at temperature below 250°C and above 250°C respectively.

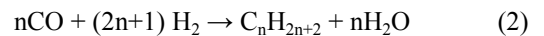
3.1. Chemistry of Fischer-Tropsch Synthesis

The chemistry of FTS consists of a wide variety of linear and branched hydrocarbons and oxygenates products. Although, the major products are linear paraffins and olefins.

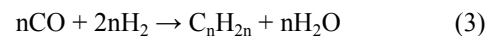
Major FT reactions are:



Temperature ranges from 473 – 573°C, while Pressure ranges from 25 - 40 bar [1].



(Paraffins)



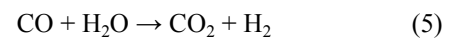
(Olefins)



(Alcohol)

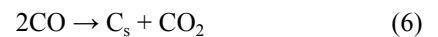
The water-Gas-shift reaction occurs during the process to adjust the H₂/CO ratio.

The WGS reaction is given as



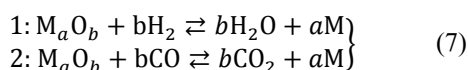
However, it has been discovered that CO₂ may be a significant component in the synthesis gas. Although the need for CO₂ separation before using the synthesis gas in FTS is mentioned in patent literature for some cases, with biomass derived synthetic gas; they could be a potential cost advantage if CO₂ is not removed before the synthesis step in which case the effect of CO₂ on preferably a Co-catalyst under low temperature FTS conditions can be investigated [23].

Also, competing reaction in FTS is the Boudouard reaction which leads to the formation of coke, given as:

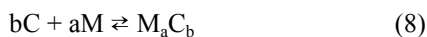


During FTS, catalyst modification may occur resulting in the following reactions:

catalyst oxidation/reduction



Bulk carbide formation



3.2. FT Mechanism

This has been a subject of investigation for many years. Details of the chemical steps that takes place during FT synthesis still remains a contentious topic since several competing reactions with almost equal probabilities are likely to occur during FT synthesis, therefore reducing the selectivity of the desired products likely to occur during FT synthesis [24].

FTS has been recognised as a polymerization reaction with the basic steps.

- CO adsorption on the catalyst surface.
- Chain initiation by CO dissociation followed by hydrogenation.
- Chain growth by insertion of additional CO molecules followed by hydrogenation.
- Chain termination.
- Product desorption from catalyst surface.

Although the product distribution demonstrates the polymerization character of the Fischer-Tropsch synthesis, a great deal of controversy still exists on the chemical identity of the monomeric building block and in relation to the growing hydrocarbon chain [1].

Hence, the following mechanisms are regarded as FT major reaction mechanism.

- The CO insertion mechanism.
- The oxygenates (enol) mechanism.
- The carbide and alkyl mechanism.
- The Vinyl/alkenyl mechanism.

3.3. FT Catalyst

When the FTS process was discovered by Franz Fisher and Hans Tropsch in 1923, an iron catalyst was used to facilitate the conversion of syngas ($CO + H_2$) to liquid fuels. Other catalysts such as cobalt, nickel and ruthenium have also been shown to be catalytically active in FTS.

Most group VIII metals have been noted to be suitable for FTS. It has been reported in literatures that the average molecular weight of hydrocarbon produced by FTS decreases as follows $Ru > Co > Fe > Rh > Ni$ and in terms of cost $Fe > Ni > Co > Ru$ is 1:250:1000:50000, also reported are typical ranges of probability chain growth (α) on Ru, Co, and Fe of: 0.85-0.95, 0.70-0.80, and 0.50-0.70 respectively [16].

3.4. Fischer-Tropsch Reactor

One of the challenges with FTS is the removal of excess heat generated by the reactions. Inadequate heat removal leads to localized overheating which results in high carbon deposition leading to catalyst deactivation. For a large scale

commercial FTS reactors, heat removal and temperature control are most important design features to obtain optimum product selectivity and long catalyst lifetimes [25]. However, FTS has been carried out in the following reactors.

- Fixed Bed FT Reactor
- Fluidized Bed FT Reactor
- Slurry Phase FT reactor

3.5. Kinetics of Fischer-Tropsch Synthesis

The kinetics of FTS has been studied under various catalysts and varies from one catalyst to another. The complexity of the FT reaction mechanism and the large number of species involved is the major problem for development of reliable kinetic expressions.

3.6. Factors That Affects Fischer-Tropsch Synthesis

The study of FTS under different conditions has been influenced by various factors in which studies have shown could affect the product composition. The following factors affects FTS among others:

- presence of H_2O
- H_2/CO composition in the feed Gas
- presence CO_2 in feed Gas
- presence of N_2 in the Feed Gas
- Temperature
- Pressure
- presence of Active Metals

4. Methodology

This is essentially a descriptive work meant to explore and explain the behaviour of hydrocarbon products in Fischer-Tropsch synthesis. However, the model that describe the hydrocarbon products distribution in Fischer-Tropsch synthesis was collected and validated by work presented by the following authors; Arno Klerk [26], Donnelly, *et al* [27], Jin, *et al* [28], Xiaojun [2], Sinee Kraokaw [29].

The distribution of FT products follows the Anderson – Schultz-Flory (ASF) polymerization model. According to the ASF model, the carbon number distribution of the products is a function of the chain growth probability (α) at the surface of the catalyst [30]. Anderson-Schulz-Flory (ASF) distribution obtained from literatures is expressed as:

$$M_n = \frac{W_n}{n} = (1 - \alpha) \alpha^{n-1} \quad (9)$$

Where:

M_n = Molar fraction of hydrocarbon molecules/Carbon atom

W_n = Weight fraction of hydrocarbon molecules
 n = number of carbon atoms

α = chain growth probability or a probability that a molecule will continue reacting to form a longer chain.

Maximum selectivity of LPG, gasoline and diesel range product was computed noting the following assumptions:

- (1) that the ASF distribution follows ideal kinetics.
- (2) C₅-C₁₁ hydrocarbon products boils at a temperature of gasoline products.
- (3) C₁₂-C₂₀ hydrocarbon products boils at a temperature of diesel products.

5. Results and Discussion

5.1. Results

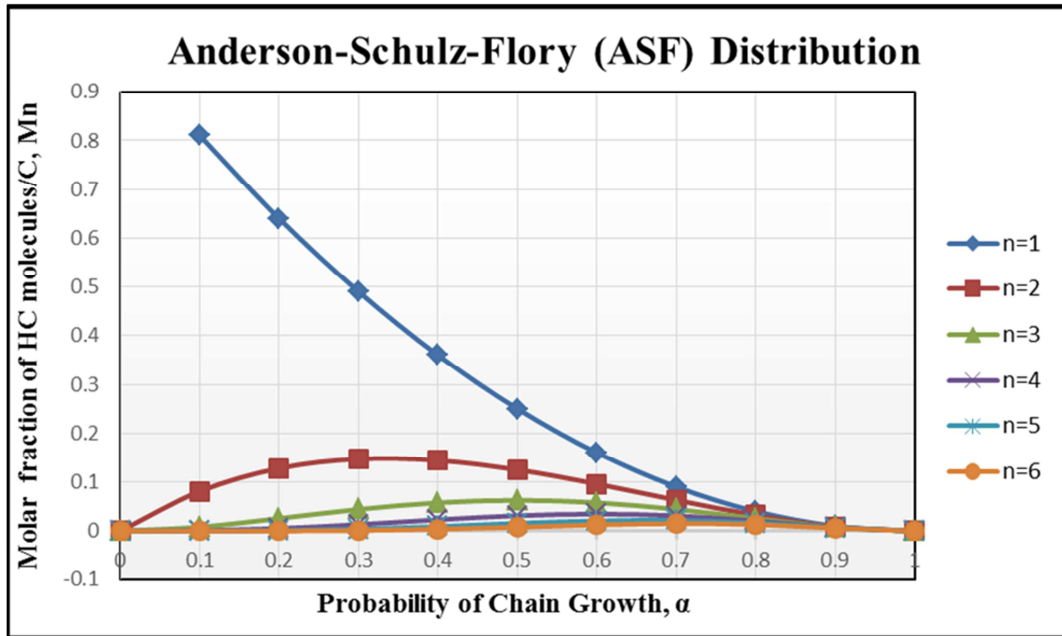


Figure 2. ASF distribution for n ranging from 1-

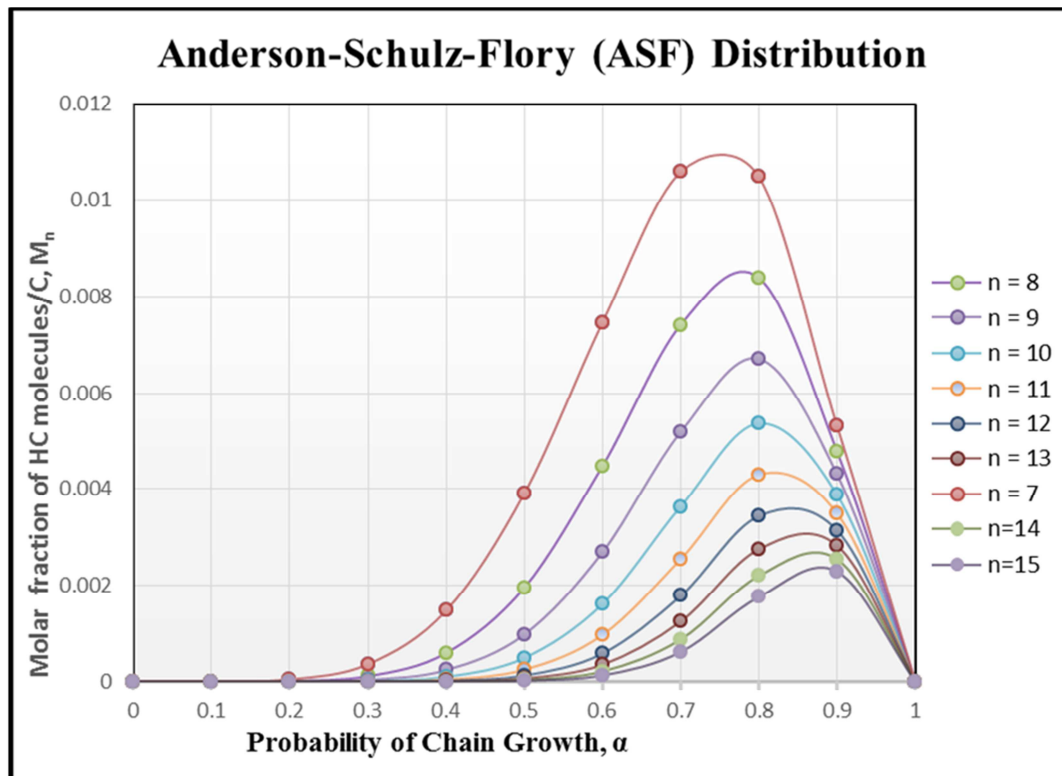


Figure 3. ASF distribution for n ranging from 7-15.

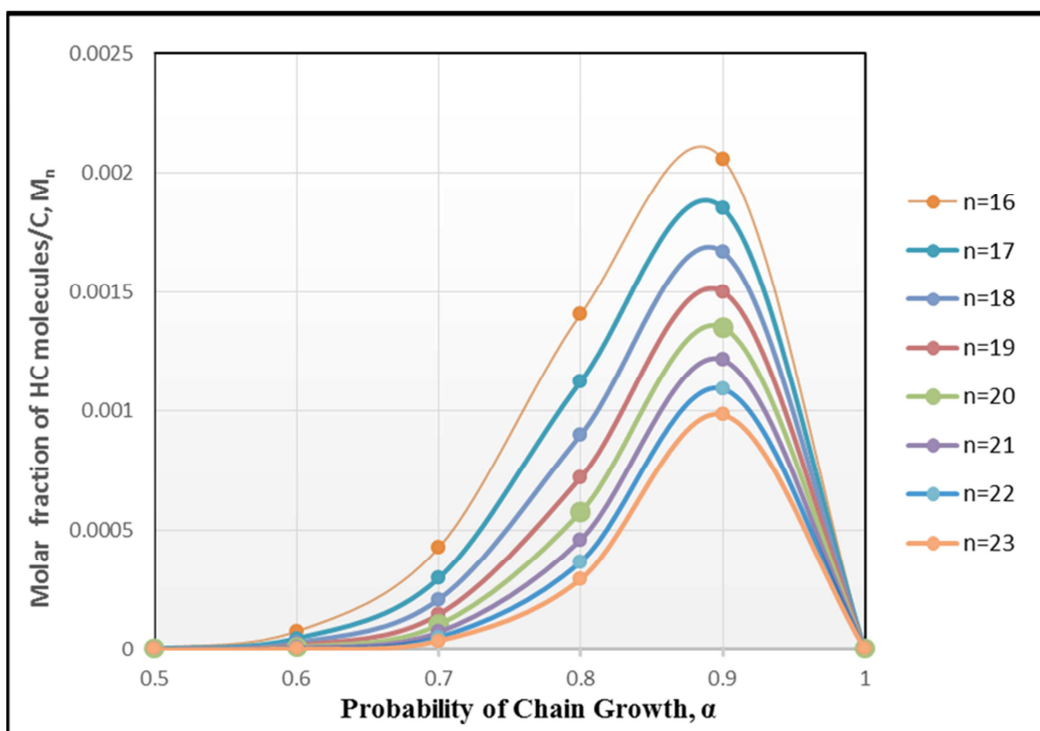


Figure 4. ASF distribution for n ranging from 16-23.

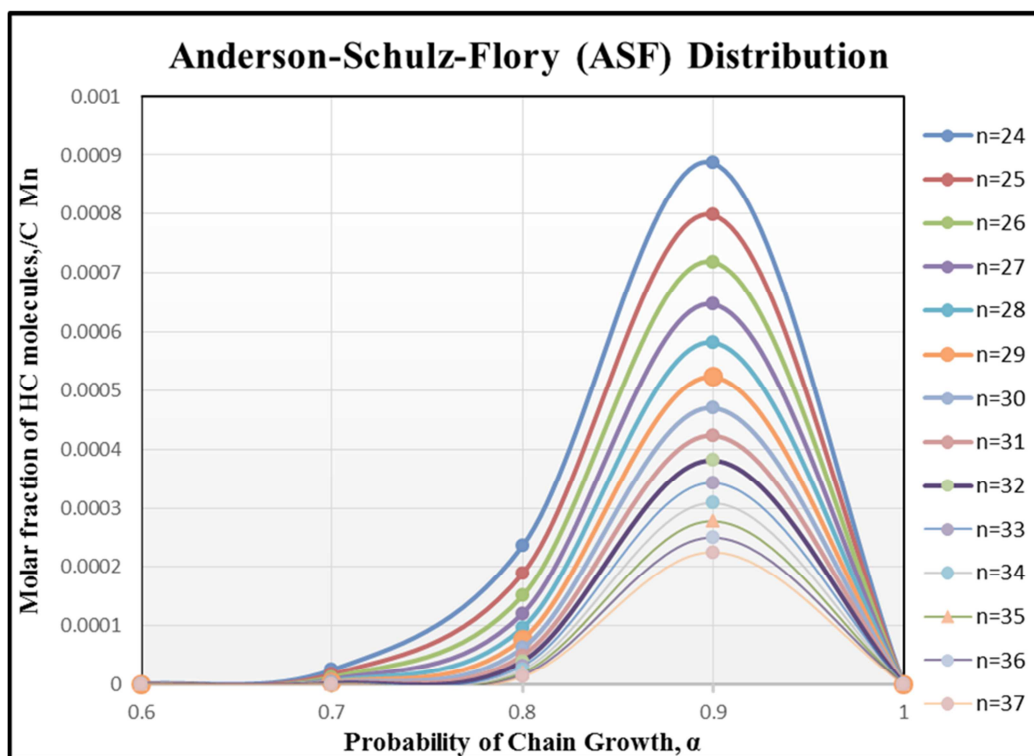


Figure 5. ASF distribution for n ranging from 24-37.

The ASF distribution obtained here which was the plot of the molar fraction of hydrocarbon molecules per carbon atom against chain growth probability.

5.2. Discussion

Figures 2, 3, 4 and 5 shows the distribution of FT

hydrocarbon products from carbon number of 1-6, 7-15, 16-23 and 24-37 respectively and in an ascending order of carbon atom.

However, from Figures 2-5, it is observable that the selective synthesis of a product with a narrow range of chain lengths is not possible, except for methane when α equals 0 or

for infinite chain length if α equals 1, the selectivity to a certain product or product range will always be limited [2]. It is also clear from Figure 2 that the largest single product will always be methane so long as $\alpha < 0.5$ since it corresponds to a carbon number of 1. This may confirm why the use of catalyst and operating at conditions which could yield a chain growth probability that is above 0.5 had been in use. Clearly shown here is that the selectivity of product will favour the production of methane as a single product among wide range of products

that can be obtained at that probability chain growth.

Also, Figure 2 shows that by increasing α , the total amount of methane formed can be minimized compared to the sum of all of the various long-chained products which shows that increasing α favors the formation of long-chained hydrocarbons which supports the definition of α [7].

Assuming ideal ASF kinetics, the maximum distribution of FT reaction major products from the ASF plot is summarized as given in the Table 1 below:

Table 1. Maximum distribution of FT product.

Carbon number	General name	$\alpha = 0.5$	$\alpha = 0.6$	$\alpha = 0.7$	$\alpha = 0.8$	$\alpha = 0.9$
C ₂ -C ₄	LPG	56.5%	50.3%	38.1%	22.3%	7.1%
C ₅ -C ₁₁	Gasoline range	18.4%	31.6%	44.3%	46.1%	25.3%
C ₁₂ -C ₂₀	Diesel range	0.4%	4.4%	10%	19.1%	29.3%

Following information presented in Table 1, the selectivity of methane decreases as α increases, while for gasoline range products, selectivity increases gradually till $\alpha = 0.8$ where the selectivity is observed to decrease while the selectivity of diesel range product increases till $\alpha = 0.9$.

Maximum selectivity of gasoline range product and diesel range product obtained by Jin and Yongwu are approximately 45% and 30% respectively while that obtained by Xiaojun [2] is approximately 43% and 28% respectively. Clearly shown here is that the maximum selectivity of gasoline range product and diesel range product are 46% and 29% at $\alpha = 0.8$ and 0.9 respectively. Considering the catalyst that are applicable in FTS and knowing the maximum chain growth probability, it is noticeable that Ru will result in the production of heavy distillate FT product (waxes), Co favours the production of gasoline and diesel range product and Fe will favour the formation of LPG and gasoline range products.

Although the distribution of FT hydrocarbon products is best described by this model, deviations have been reported in literatures that C₁ and C₂ never fits the ASF distribution. Methane is generally higher than predicted while C₂ is lower [31]. Also the distribution of FT product for carbon number above 30 since they include heavy waxes which are undesirable in FTS cannot be predicted by ASF model [32]. Selectivity for longer chain products is governed by the ability of a catalyst to preferentially enhance the rate of chain propagation above that of chain termination.

The ASF distribution leads to a gradual decrease in selectivity of hydrocarbon as shown in Figures 2-5. An increase in carbon number (n), will limit the formation of desired middle distillates (diesel range product) to favour the formation of heavy waxes.

6. Conclusion

FTS hydrocarbon products distribution is a one parameter factor known as the chain growth probability which depends on several factor that makes it difficult to control. ASF distribution does not show different hydrocarbon product type such as paraffin and olefin, neither does it practically corresponds to every hydrocarbon distribution for all carbon number. Selectivity of range of hydrocarbon product such as

diesel or gasoline was obtained by considering selectivity of hydrocarbon products with specific carbon number atoms in such product range.

The main challenge in Fischer-Tropsch Synthesis is maximizing the selectivity of desired product. Also, the polymerization-like nature of FTS is a strong limitations on efforts to maximize desired products

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