Overview of Slurry phase bubble column Fischer Tropsch Synthesis reactor and relevant design parameters

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Abstract

Slurry phase bubble column Fischer Tropsch (F-T) reactor with Iron catalyst is chosen for conversion of syngas into F-T liquids due to good heat and mass transfer properties. The parameters that affect the conversion rate of CO and molecular mass distribution of final products are considered. Calculations are performed for heat exchanged in the reactor and total mass flow. The correlation between design and performance parameters are shown graphically. The rationale behind design parameter choices are explained. Distillation and refining processes explained qualitatively.

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1. Introduction

Slurry phase bubble column type of reactor has been chosen for F-T synthesis process. The slurry phase reactor offers an isothermal operating condition and better heat transfer than alternative reactor designs[1]. The schematic of slurry phase reactor is shown in Figure 1. The reactor vessel is 7m in diameter and 30m in height. Syngas enters from the bottom of vessel through an inlet nozzle and bubbled vertically in churn turbulent flow regime to maximize the mass and heat transfer [2]. The reactor is filled with inert oil in which Fe catalyst particles are suspended. The heat generated in the chemical reactions is absorbed by a large number of vertical coolant tubes of diameter 50mm. The reactor operates at temperature of T=240°C and pressure of 24.0 bar. Figure 1 also shows the bubble cross section in slurry. The spacing between the coolant tubes is important factor that affect the performance of the reactor and is discussed in Section 3.

2. Fischer Tropsch reaction and the catalyst

Following reactions take place inside FT reactor

$$CO + 2H_2 \rightarrow -(CH_2)- + H_2O + 170kJ \tag{1}$$

$$H_2O + CO \rightarrow CO_2 + H_2 \tag{2}$$

where $-(CH_2)-$is methylene group and it polymerizes into larger molecules[1]. Reaction 2 is called the water shift reaction and its rate is controlled by the type of catalyst used which may or may not be active to it. Depending on the type catalyst used and CO/H_2 ratio of feed syngas stream, the final FT liquid may have different paraffin composition. If we assume that final product consists predominantly of paraffins or hydrocarbons with formula C_nH_{2n+2},then the mass fraction of paraffin with carbon number n in final FT liquid is given by

$$\chi_n = n(1-\alpha_{ASF})^2\alpha_{ASF}^{n-1} \tag{3}$$

where α is the chain growth probability that depends on the type of catalyst and CO/H_2 ratio of syngas stream[2]. Figure 2 shows the mass fraction of different molecules as a function of chain growth probability. In decreasing order of activity, the most commonly used catalyst are Ru>Fe>Ni>Co>Rh[3]. Although Ru is the most active in producing high C number molecules, its price consideration forbids its economic utilization for commercial plants. Therefore as the second most active catalyst, Fe ($\alpha = 0.9$) is chosen as a catalyst for F-T reactor[1]. The major suppliers of catalysts are Dycat International, Haldor Topsoe, ICI Katalco and United Catalysts.

Preprint submitted to Elsevier *November 13, 2011*

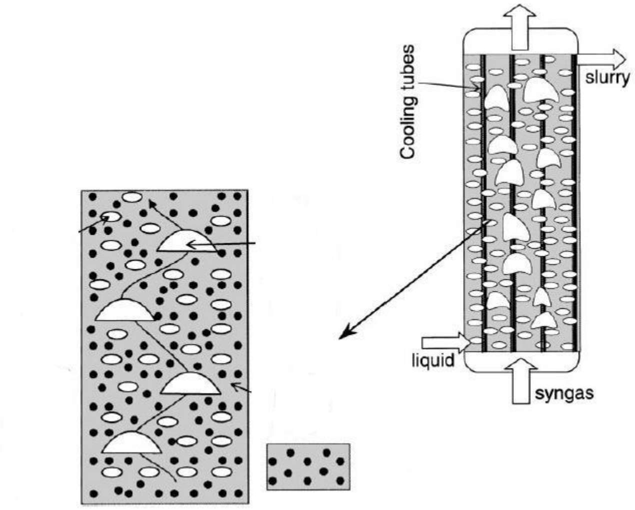

Figure 1: Slurry phase bubble reactor schematic [1]

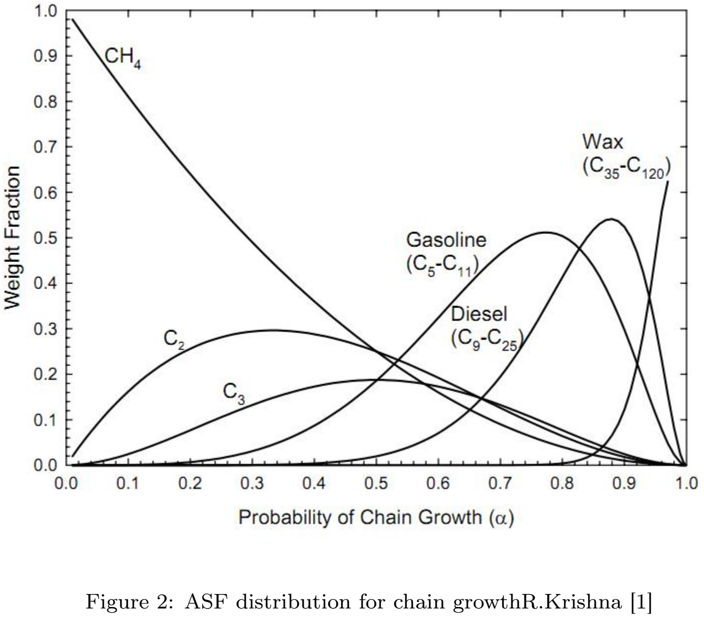

Figure 2: ASF distribution for chain growthR.Krishna [1]

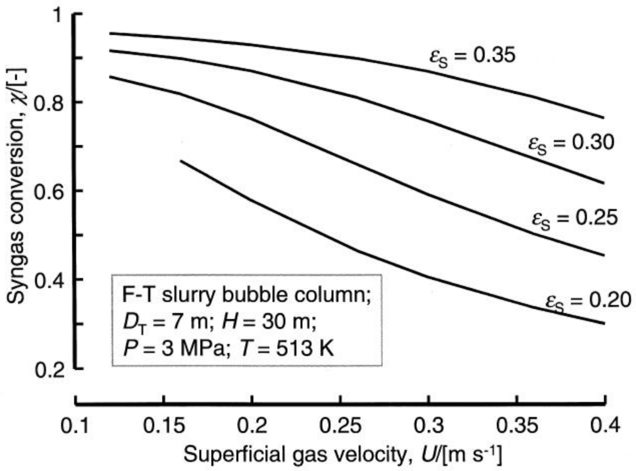

Figure 3: Effect of catalyst concentration on conversion ratio

3. Performance parameters

The fraction of CO molecules in feed syngas stream converted into larger paraffins through F-T process is called the conversion ratio and is a major determinant of the performance of F-T reactors [1]. The conversion factor can be influenced by concentration of catalyst in the slurry, temperature and the H_2/CO ratio of feed syngas among other factors. In literature, the total flow rate of syngas through the reactor is characterized by the superficial velocity which is defined as the volumetric flow rate of syngas per unit cross sectional area of reactor.

$$U_s = \frac{\dot{V}}{A} = \frac{\dot{n}RT}{PA} = 0.05m/s \tag{4}$$

where $\dot{n}$ denotes the molar flow rate and P and A represent the pressure and the cross sectional area of the reactor respectively. Given the chosen parameters for our design the calculation for superficial velocity gives $U_s = 0.12m/s$. The effect of the catalyst concentration on conversion ratio is shown in Figure 3. Increasing catalyst concentration increases conversion ratio and $\varepsilon_{smax} = 0.4$ is considered the limit for feasible commercial operation of F-T plant [2]. For our design, $\varepsilon_s = 0.35$ is used to maximize conversion within reasonable margin from the limit.

The number of vertical coolant tubes needed for heat absorption and to keep the flow in churn turbulent flow regime depends on catalyst concentration and superficial velocity. As illustrated in Figure 3, the number of tubes needed is increased with faster flow rate and larger catalyst concentration. The number of coolant tubes that corresponds to the superficial velocity of this design is 6000 and pitch is 0.15m.

H_2/CO ratio affects the the product selectivity via change in chain growth probability α and the reaction temperature. Song et al (2004) derived a widely accepted model for chain growth probability [4].

$$\alpha = \left(\frac{0.23}{H_2/CO+1} + 0.63\right) \cdot [1 - 0.0039(T - 533K)] \tag{5}$$

Figure 4 and Figure 5 shows the effect of varying feed ration H_2/CO and reaction temperature on selectivity of F-T synthesis.

Our design employs feed syngas ratio $r = H_2/CO \approx 2.0$ which is dictated by the biomass composition. The reaction temperature is chosen as T=245°C. However, it will be possible to change reaction temperature by altering the coolant flow rate in reactor.

Heat transfer coefficient is estimated to be $1450W/m^2$ from Figure 6. This gives for the heat exchanged with the coolant

$$\dot{Q} = 6000 * 30m * \pi * 0.05m * 1450W/m^2 = 41.0MW \tag{6}$$

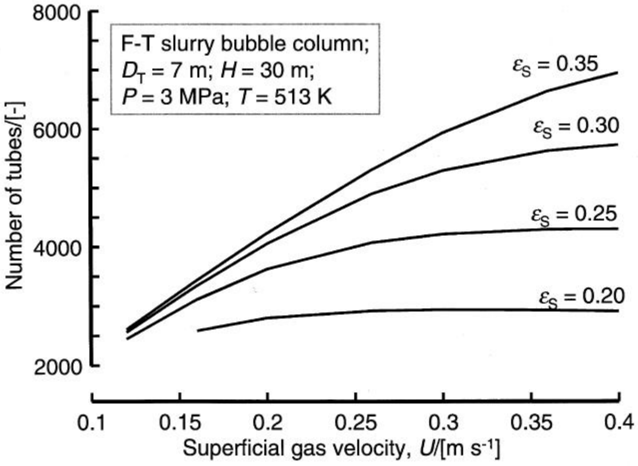

Figure 4: Effect of superficial velocity, catalyst concentration on the number of coolant tubes R. Krishna [2]

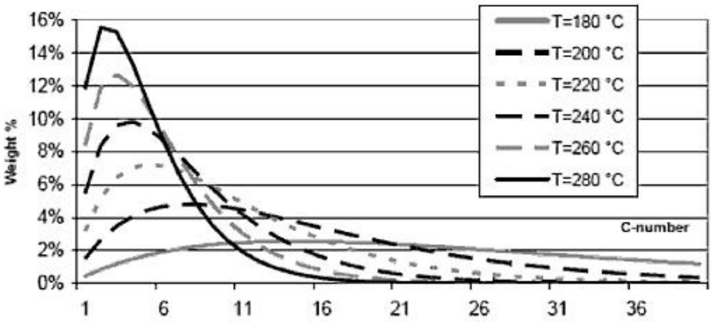

Figure 5: The effect of temperature on selectivity at $H_2/CO = 2.0$

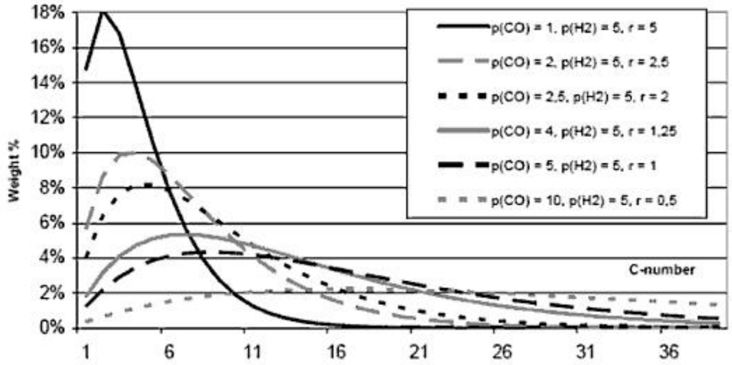

Figure 6: The effect of feed ratio $r = H_2/CO$ on selectivity at T=300°C

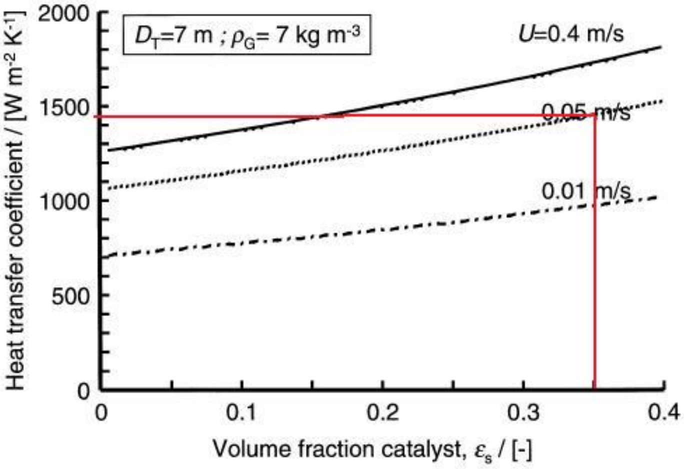

Figure 7: Heat transfer coefficient as a function of catalyst concentration

For coolant flow, we propose to use a one loop system at pressure P=33.5 bar which corresponds to the saturation pressure at T=245°C. The coolant enters FT reactor as a condensed saturated liquid at T=245°C and leaves the FT reactor as a saturated vapor. We can calculate the mass flow rate required for coolant flow as

$$\dot{m}_c = \frac{\dot{Q}}{h_g - h_f} = \frac{41.0MW}{1740kJ/kg} = 23.5kg/s \tag{7}$$

As we are planning to use river water for condensing, the temperature of the coolant water must be within the limit imposed by EPA. The maximum temperature that one can discharge coolant intake water into environment is 20F over the intake water as imposed by EPA [5]. We can then find the coolant water flow rate from heat balance as

$$\dot{m_{intake}} = \frac{\dot{Q}}{C_w \triangle T} = 888kg/s \tag{8}$$

4. Impact of gasifier design on FT product selectivity

Gasifier produces syngas stream which is then fed into FT reactor. Different gasifier designs will produce syngas streams of different composition and H2/CO ratio. Since H2/CO ration critically impacts product selectivity, it is necessary to evaluate how different gasifier design choices affect final; product composition. Two designs of gasifier are proposed and this section provides analysis of the final product selectivity for them. The probability of chain growth is given by following relation.

$$\alpha = \quad \frac{0.23}{H_2/CO + 1} + 0.63 \quad \cdot [1 - 0.0039(T - 533K)] \tag{9}$$

T=240C=513K is the operating temperature of the reactor and for Silva gas gasification process which is an American design, the hydrogen to CO ratio in the syngas stream is $H_2/CO = 22/38.2 = 0.57 \approx 0.5$. Whereas for Swedish FICBC process $H_2/CO = 44.4/22.9 = 1.94 \approx 2$. We can then compare the chain growth probability of the two different gasifier designs at the same temperature as

$$\alpha_{Silva} = \quad \frac{0.23}{H_2/CO + 1} + 0.63 \quad \cdot [1 - 0.0039(T - 533K)] = 0.84 \tag{10}$$

$$\alpha_{FICBC} = \quad \frac{0.23}{H_2/CO + 1} + 0.63 \quad \cdot [1 - 0.0039(T - 533K)] = 0.76 \tag{11}$$

We can then apply ASF distribution to calculate mass fraction of molecules with carbon number n

$$\chi_n^{Silva} = 0.16^2 n * 0.84^{n-1} \tag{12}$$

$$\chi_n^{FICBC} = 0.24^2 n * 0.76^{n-1} \tag{13}$$

Figure 1 shows mass fraction as a function of carbon number for both processes

Naphtha is a term that refers to mixture of hydrocarbon molecules having carbon numbers between 5-12. The term distillate covers hydrocarbons with n between 12-20. Wax refers to carbon number 20 or more hydrocarbons. Using this definition, we can tabulate the mass flow rate for naphtha, distillate and wax streams. Silva gas is chosen as it produces more heavy diesel products and is a design that is patented in the US. This will impact positively on feasibility of our design.

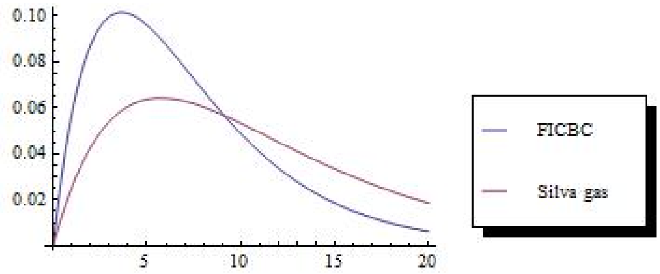

Figure 8: Silva gas and FICBC for product selectivity

Mass flow rates	Silva gas (%)	FICBC(%)
Naphtha (gasoline)	52.2	73.5
Distillate(diesel)	31.7	22.1
Wax(diesel)	16	4.3

Table 1: Product mass flow rates for Silva and FICBC

5. Distillation

Fischer Tropsch liquid is distilled to separate the product into three different product streams according to the molecular mass. The liquid fraction up to 180°C is sent out as naphtha, from 180°C to 320°C as distillate, and the remainder as a heavy wax streamThomas G. Kreutz [6]. Distillation is a standard process in chemical engineering and design of a distiller is relatively simple compared to other units in the whole design. Figure 8 shows a simple schematic of a generic distiller design. The vessel consists of trays for condensing separated products and heat exchangers. The three streams of separated FT hydrocarbons are then sent to refinery unit.

6. Refining

We employ FTL refining design developed by Kreutz et al [6]. Schematic of the refining process is shown on Figure 9. FTL is separated into streams of naphtha, distillate, and heavy wax by distillation process and fed directly into refining. The final product will be biodisel and bio gasoline blend stocks along with light bio gas that is left from distillation or produced as a byproduct of refining.

Naphtha hydrotreating and heavy wax hydrocracking are similar subprocesses that convert the organic sulfur and nitrogen in feed stream into H_2S and NH_3. Figure 10 shows the reactions that take place inside a hydrotreatment reactor. Hydroprocessing step is essential for reducing the sulfur content of final fuel product

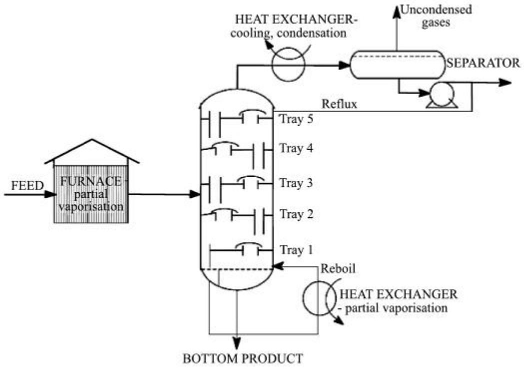

Figure 9: Distillation unit

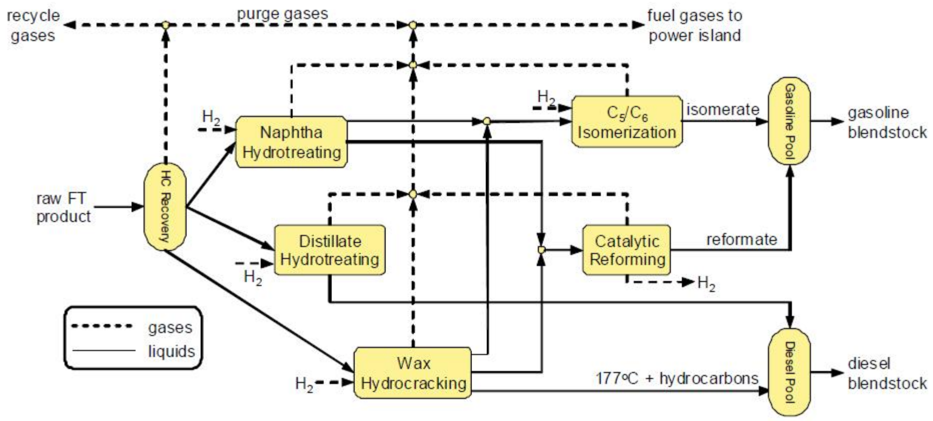

Figure 10: Schematic of FTL refining process

Reaction Type	Illustration	ΔH_R*
Minimal C-C Bond Breaking		
Hydrodesulfurization (HDS) †	R-S-R' + 2 $H_2 \rightarrow$ RH + R'H + H_2S	-2.5 to -3.0
Hydrodenitrogenation (HDN)	R=N-R'+ 3 $H_2 \rightarrow$ RH + R'H + NH_3	-2.5 to -3.0
Hydrodeoxygenation (HDO)	R-O-R' + 2 $H_2 \rightarrow$ RH + R'H + H_2O	-2.5 to -3.0
Hydrodemetallation (HDM)	R-M + ½ H_2 + A $\rightarrow$ RH + M-A	-3
Saturation of aromatics	$C_{10}H_8 + 2\ H_2 \rightarrow C_{10}H_{12}$	-3
Saturation of olefins	R=R' + $H_2 \rightarrow$ HR-R'H	-5.5
Isomerization	n-RH $\rightarrow$ i-RH	n/a
Significant C-C Bond Breaking		
Dealkylation of aromatic rings	Φ-CH_2-R + $H_2 \rightarrow$ Φ-CH_3 + RH	-1.3 to -1.7
Opening of naphthene rings	Cyclo-$C_6H_{12} \rightarrow C_6H_{14}$	-1.3 to -1.7
Hydrocracking of paraffins	R-R' + $H_2 \rightarrow$ RH + R'H	-1.3 to -1.7
Other Reactions		
Coke formation	2 ΦH $\rightarrow$ ΦΦ + 2 H_2	+3
Mercaptan formation	R=R' + $H_2S \rightarrow$ HS-R-R'H	-3

* Kilojoules per standard m^3 of H_2 consumed. For exothermic reactions, ΔH_R is negative.

† R = alkyl; Φ = aromatic; M = Fe, Ni or V; A = metals-adsorbing material

Figure 11: Hydrotreatment reactions and enthalpies

and preparing the feed stream to catalytic reforming stage. In a A stream of high pressure (4bar) hydrogen is needed for the hydrotreatment stage and total estimate of hydrogen is based on refinery design by Kreutz et al and is 0.1kg/sec [6].

Distillate hydrotreatment is identical in principle to naphtha hydrotreating except that the hydroprocessed distillate goes directly to diesel pool without further refining.

Hydroisomerisation of linear alkanes into their higher branched isomers increases the octane value of the fuel and makes the combustion cleaner. In the design we are considering, the output from naphtha hydrotreatment reactor and part of hydrocracking outputs are fed directly into C_5/C_6 isomerization unit. The heat of reaction, H, for the hydroisomerization of C5/C6 paraffin is negligible, making it preferable from energy utilization perspective. High pressure hydrogen stream is supplied to the reaction.

Catalytic reforming is another step to increase the isomerization of the product for greater octane rating. Low C number gases are produced as a byproduct and removed from the product stream. Unlike hydroisomerization units, the isomerization process is carried out without hydrogen input to the reactor with the appropriate catalyst.

7. Conclusion

Slurry phase bubble column reactor is considered. Design parameters that affect the conversion ratio and product selectivity are the type of catalyst, the concentration of the catalyst, reactor size, reaction temperature, feed flow rate and the H_2/CO in feed syngas. Depending on the final product requirement, the conditions of the reactor can be modified to alter the composition of product F-T liquid. The parameters of the reactor has been chosen so as to maximize the production of carbon number 5-20 molecules which can be used for biogasoline and biodisel production.

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22.033 / 22.33 Nuclear Systems Design Project
Fall 2011