

Modeling the Fischer-Tropsch Reaction In a Slurry Bubble Column Reactor

F. Gholami, M. Torabi Angaji, and Z. Gholami

Abstract—Fischer-Tropsch synthesis is one of the most important catalytic reactions that convert the synthetic gas to light and heavy hydrocarbons. One of the main issues is selecting the type of reactor. The slurry bubble reactor is suitable choice for Fischer-Tropsch synthesis because of its good qualification to transfer heat and mass, high durability of catalyst, low cost maintenance and repair. The more common catalysts for Fischer-Tropsch synthesis are Iron-based and Cobalt-based catalysts, the advantage of these catalysts on each other depends on which type of hydrocarbons we desire to produce. In this study, Fischer-Tropsch synthesis is modeled with Iron and Cobalt catalysts in a slurry bubble reactor considering mass and momentum balance and the hydrodynamic relations effect on the reactor behavior. Profiles of reactant conversion and reactant concentration in gas and liquid phases were determined as the functions of residence time in the reactor. The effects of temperature, pressure, liquid velocity, reactor diameter, catalyst diameter, gas-liquid and liquid-solid mass transfer coefficients and kinetic coefficients on the reactant conversion have been studied. With 5% increase of liquid velocity (with Iron catalyst), H_2 conversions increase about 6% and CO conversion increase about 4%, With 8% increase of liquid velocity (with Cobalt catalyst), H_2 conversions increase about 26% and CO conversion increase about 4%. With 20% increase of gas-liquid mass transfer coefficient (with Iron catalyst), H_2 conversions increase about 12% and CO conversion increase about 10% and with Cobalt catalyst H_2 conversions increase about 10% and CO conversion increase about 6%. Results show that the process is sensitive to gas-liquid mass transfer coefficient and optimum condition operation occurs in maximum possible liquid velocity. This velocity must be more than minimum fluidization velocity and less than terminal velocity in such a way that avoid catalysts particles from leaving the fluidized bed.

Keywords—Modeling, Fischer-Tropsch Synthesis, Slurry Bubble Column Reactor.

I. INTRODUCTION

THE Fischer-Tropsch reaction involves the conversion of syngas, carbon monoxide (CO), and hydrogen (H_2) to various hydrocarbons and oxygenates, including alkanes, alkenes, alcohols, aldehydes, ketones, ethers, and acid [1], for

use as fuel and chemical feedstock. As an important type of Fischer-Tropsch synthesis reactors, slurry bubble column (SBC) reactor attracts more and more interests because of its advantages relative to other type of reactors. These advantages mainly include: (1) nearly isothermal operation, (2) small solids particle size that results in good productivity, (3) good interface contacting, (4) low pressure drop, and (5) low construction and operation costs [2].

Modeling the operation of Fischer-Tropsch synthesis in an SBC reactor is an important part of reactor design R&D. Modeling can be used to predict the effect of various process variables on conversion and concentration profiles in the reactor as well as hydrodynamic characterization. The objective of this study is to develop a concise approach to Fischer-Tropsch SBC modeling, incorporating F-T kinetics with a set of equations governing hydrodynamic behavior and constraints on the SBC reactor.

A set of mass and momentum balance equations will be developed and combined with empirical relationships from literature to model F-T synthesis in an SBC reactor. Reactant concentration profiles are determined for different values of liquid-phase velocity, rate constant, reactor diameter, catalyst diameter, pressure, and temperature, gas to liquid mass transfer coefficient and liquid to solid mass transfer coefficient.

II. MATHEMATICAL MODELING

Slurry bubble column reactors can operate either in the homogeneous flow regimes or in heterogeneous (churn-turbulent) flow regime. Homogeneous regime is established within the reactor, when operating at low gas flow rates: small bubbles of gas (1-10 mm) are uniformly distributed into the slurry phase (liquid+solid catalyst). With increasing gas through put, transition from homogeneous to churn-turbulent regime occurs [3]. In the heterogeneous regime, small bubbles combine in clusters to form large bubbles (20-70 mm). The liquid phase is a mixture of heavy hydrocarbons that has an average density 640kg/m^3 , a surface tension of 0.01 N/m , and viscosity of 2.9E-4 Pa.S [4].

In this study Iron-based and Cobalt-based catalysts are used. Fe catalyst with intrinsic density of 3500 kg/m^3 and average particle diameter of 0.0005m [5]. Co catalyst with intrinsic density of 2030 kg/m^3 and average particle diameter of 0.0005m [4]. For modeling, 10 kg catalyst with a packed-

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bed porosity of 0.5 will be used. The reactor will be operated at 523 K and 2 MPa [6].

Assuming steady-state operation, no phase change within the gas phase, no condensation of the syngas, uniform concentration in r and θ directions, no reactions in the gas phase, insignificant diffusion / axial dispersion in the gas phase, and constant gas-phase holdup and gas-phase velocity.

The gas-phase component balance can be written as follows:

$$\varepsilon^\alpha V_z^\alpha \frac{dC_{H_2}^\alpha}{dz} + (K_{L\alpha L})_{H_2} \left(\frac{C_{H_2}^\alpha RT}{He_{H_2}} - C_{H_2}^\beta \right) = 0 \quad (1)$$

$$\varepsilon^\alpha V_z^\alpha \frac{dC_{CO}^\alpha}{dz} + (K_{L\alpha L})_{CO} \left(\frac{C_{CO}^\alpha RT}{He_{CO}} - C_{CO}^\beta \right) = 0 \quad (2)$$

Where $C_{H_2}^\alpha$ and C_{CO}^α are the gas-phase H_2 and CO concentrations, $C_{H_2}^\beta$ and C_{CO}^β are the liquid-phase H_2 and CO concentrations, ε^α is gas-phase volume fraction (gas phase holdup), V_z^α is the average gas-phase velocity, $K_{L\alpha L}$ is gas phase to liquid phase mass transfer coefficient, He_{H_2} and He_{CO} are Henry's Law constant for H_2 and CO.

The same assumptions were used to obtain the component balances in the liquid phase:

$$\varepsilon^\beta V_z^\beta \frac{dC_{H_2}^\beta}{dz} - (K_{L\alpha L})_{H_2} \left(\frac{C_{H_2}^\alpha RT}{He_{H_2}} - C_{H_2}^\beta \right) + (K_{s\alpha s})_{H_2} (C_{H_2}^\beta - C_{H_2}^\gamma) = 0 \quad (3)$$

$$\varepsilon^\beta V_z^\beta \frac{dC_{CO}^\beta}{dz} - (K_{L\alpha L})_{CO} \left(\frac{C_{CO}^\alpha RT}{He_{CO}} - C_{CO}^\beta \right) + (K_{s\alpha s})_{CO} (C_{CO}^\beta - C_{CO}^\gamma) = 0 \quad (4)$$

C_{CO}^γ and $C_{H_2}^\gamma$ are the solid-phase H_2 and CO concentrations, ε^β is liquid-phase volume fraction (liquid phase holdup), V_z^β is the average gas-phase velocity, $K_{s\alpha s}$ is liquid phase to solid phase mass transfer coefficient. The main difference between the gas-phase and liquid-phase equations is in the interphase transfer terms, the last two terms in equation (3) and (4), which must account for species entering liquid phase from the gas phase and species

exiting the liquid phase into the solid phase, where CO and H_2 adsorb on the catalyst surface.

To derive the component balances for the solid phase, it is assumed steady-state operation, uniform catalyst particle distribution, absence of phase change, homogeneous reactions, and no species concentration gradients within the catalyst particle, the reactant concentration within the catalyst pores is the same as that at the liquid-solid boundary.

The most critical part of writing the balance equation is inserting the appropriate rate law for the heterogeneous reaction term.

Although the F-T reaction generally follows Langmuir-Hinshelwood kinetics, it is convenient to use a simplified rate expression, $r_{H_2}^\gamma = k C_{CAT} C_{H_2}^\gamma$ which is valid in a limited range.

This simplified kinetic expression, which has shown to be valid for 2.0 MPa pressure, temperature up to 588K, and conversion up to 70% [7], will be used for the purposes of this simulation.

The final form of the solid-phase species balances with Iron-based catalyst can be written as follows:

$$-K_{s\alpha s} (C_{CO}^\beta - C_{CO}^\alpha) + U k C_{CAT} C_{H_2}^\gamma = 0 \quad (5)$$

$$-K_{s\alpha s} (C_{H_2}^\beta - C_{H_2}^\alpha) + k C_{CAT} C_{H_2}^\gamma = 0 \quad (6)$$

U is the CO/ H_2 usage ratio and for Iron-based catalyst, U is 1.5 [8] due to the water-gas shift reaction, and for Cobalt-based catalyst is 0.5.

C_{CAT} is catalyst concentration and k is constant rate for the conversion of H_2 . k is determined using an Arrhenius expression from literature for a supported iron catalyst [8]:

$$k = 1.12 \times 10^5 \exp\left(\frac{-70000}{8.314 \times T}\right) [S \text{ wt\% Fe}]^{-1} \quad (7)$$

$$C_{cat} = \frac{\varepsilon^\gamma \rho^\gamma}{\varepsilon^\gamma \rho^\gamma + \varepsilon^\beta \rho^\beta} \times 10 \text{ wt\% Fe} \quad (8)$$

With Cobalt-based catalyst, the intrinsic kinetic equation for the consumption rate of syngas, chosen in literature, was that proposed by Yates and Satterfield[9], which is a Langmuir-Hinshelwood type

$$-R_{CO+H_2} = \frac{a P_{H_2} P_{CO}}{(1 + b P_{CO})^2} \quad (9)$$

The ranges of operating conditions used were 220-240 °C, 5-15 bar, 1.5-3.5 as H_2 /CO feed ratios. The kinetic constant, a , and the absorption coefficient of species CO, b , were determined by means of non-linear fit of experimental data [4]:

$$a = 8.8533 \times 10^{-6} \exp[4494.41(\frac{1}{493.15} - \frac{1}{T})] \quad (10)$$

$$b = 2.226 \times 10^{-5} \exp[-8236(\frac{1}{493.15} - \frac{1}{T})] \quad (11)$$

Costa et al. (1986) [10] have provided an empirical correlation for determination of liquid minimum fluidization velocity that includes the effect of the gas-phase velocity. This correlation, assuming spherical particles, is given below:

$$V_{mf}^{\beta} = 6.96 \times 10^{-4} (V_z^{\alpha})^{-0.328} \times (\mu^{\beta})^{-0.355} \times (D_t)^{0.042} \times (D_p)^{1.086} \times (\rho^{\gamma} - \rho^{\beta})^{0.865} \quad (12)$$

Typical values of V_z^{α} to ensure bubbly flow, homogeneous flow, are less than or equal to 0.05 m/s [11].

Terminal velocity can be estimated via Kunii-Levenspiel method (1991) [12]. The pertinent equations, assuming a particle sphericity, are given below :

$$d_p^* = D_p \left[\frac{\rho^{\beta} (\rho^{\gamma} - \rho^{\beta})_g}{(\mu^{\beta})^2} \right]^{\frac{1}{3}} \quad (13)$$

$$V_t^* = \left[\frac{d_p^*}{18.591} \right] \quad (14)$$

$$V_t = \frac{V_t^*}{\left[\frac{(\rho^{\beta})^2}{\mu^{\beta} (\rho^{\gamma} - \rho^{\beta})_g} \right]^{\frac{1}{3}}} \quad (15)$$

Han et al. (1990) [13] have derived an empirical correlation for ε^{β} and Bloxom et al. (1975) [14] have derived an empirical correlation for ε^{α} for F-T slurry bubble column operated under conditions similar to those used in this study.

$$\varepsilon^{\beta} = \left(\frac{V_z^{\beta}}{V_t^{\beta}} \right)^{\frac{1}{n}} \times (1 - 0.347 Fr_s^{0.176} We_m^{-0.173}) \quad (16)$$

$$\varepsilon^{\alpha} = 0.159 \left(\frac{(V_z^{\alpha})^5 (\rho^{\gamma} - \rho^{\beta})}{g V_z^{\beta} \sigma} \right)^{0.150} \quad (17)$$

$$\varepsilon^{\alpha} + \varepsilon^{\beta} + \varepsilon^{\gamma} = 1 \quad (18)$$

The gas to liquid correlation for mass transfer is shown below [15]:

$$(K_L \alpha_L)_i = 3.31 \frac{D_i \varepsilon^{\alpha}}{D_B^2} \left(\frac{\mu^{\beta}}{\rho^{\beta} D_i} \right)^{\frac{1}{3}} \quad (19)$$

Where D_i is the diffusivity for CO or H₂, 1.72E-8 and 4.55E-8 m²/s [4], and D_B is the gas bubble diameter. D_B will be assigned a value of 2 mm, which is reasonably close to estimates in the literature [16]. The liquid to solid correlation for mass transfer in a slurry bubble column is taken from Sanger and Deckwer (1981) and it is $K_{sas} = 0.011 S^{-1}$ [17].

Henry's Law constants for CO and H₂ are shown below [18]:

$$He_{Co} = 1952 \times \exp\left[\frac{248}{T}\right] \quad (20)$$

$$He_{H2} = 6954 \times \exp\left[\frac{555}{T}\right] \quad (21)$$

III. RESULTS AND DISCUSSION

The model equation have been solved for different specified value of T, P, V_z^{β} , D_p , D_t , $K_L \alpha_L$, $K_S a_S$, k, a.

V_z^{β} and k are having the largest impact on concentration and conversion. It is crucial to identify the minimum liquid fluidization velocity and terminal velocity. The slurry bubble column reactor cannot be operated outside these constraints. Results are shown in Table I.

Increasing in Temperature, pressure, liquid-solid mass transfer coefficient and constant rate have an insignificant effect on CO and H₂ conversions. With 5% increase of liquid velocity (with Iron catalyst), H₂ conversions increase about 6% and CO conversion increase about 4%. With 8% increase of liquid velocity (with Cobalt catalyst), H₂ conversions increase about 26% and CO conversion increase about 4%. With 20% increase of gas-liquid mass transfer coefficient (with Iron catalyst), H₂ conversions increase about 12% and CO conversion increase about 10% and with Cobalt catalyst H₂ conversions increase about 10% and CO conversion increase about 6%. Increasing on catalyst diameter and reactor diameter will decrease H₂ and CO conversions.

IV. CONCLUSION

The results suggest that the reaction is kinetically limited because of the observed increases in conversion with increases in k. In addition, overall conversion was found to increase with an increase in liquid-phase velocity. Results show that the process is sensitive to gas-liquid mass transfer coefficient and optimum condition operation occurs in maximum possible

liquid velocity. This velocity must be more than minimum fluidization velocity and less than terminal velocity in such a way that avoid catalyst particles from leaving the fluidized bed.

TABLE I
1-MODELING RESULTS

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Parameter	Iron		Cobalt		
Pressure	XCO	XH2	XCO	XH2	
1.8 MPa	42.2	16	49	9.5	
2 MPa	42.3	16	49	9.5	
2.2MPa	42.3	16	49	9.5	
Temperature	XCO	XH2	XCO	XH2	
513K	41.4	15	48.5	9.2	
523K	42.3	16	49	9.5	
533K	42.8	17	49.5	9.8	
Reactor Diameter	XCO	XH2	XCO	XH2	
0.15m	60	25	49	9.4	
0.2m	42.3	16	49	9.5	
0.25m	35	13.5	49	9.8	
Catalyst Diameter	XCO	XH2	XCO	XH2	
0.0004m	47	18	49	9.5	
0.0005m	42.3	16	49	9.5	
0.0006m	36.8	13.7	49	9.5	
$K_{L\ a\ L}$	XCO	XH2	XCO	XH2	
*0.8	37.1	13.8	44	8.2	
*1.0	42.3	16	49	9.5	
*1.2	46.5	18	52	10.4	
$K_{S\ a\ S}$	XCO	XH2	XCO	XH2	
*0.8	42	16	49	9.3	
*1.0	42.3	16	49	9.5	
*1.2	42.4	16.2	49.5	9.9	
Parameter	Iron		Parameter	Cobalt	
Liq. Velocity	XCO	XH2	Liq. Velocity	XCO	XH2
0.034m/s	40.5	15	0.024m/s	47	7.2
0.036m/s	42.3	16	0.026m/s	49	9.5
0.038m/s	44	17	0.028m/s	51	11.8
A	XCO	XH2	k	XCO	XH2
*0.8	42.3	15.8	*0.8	49	9.4
*1.0	42.3	16	*1.0	49	9.5
*1.2	42.4	16	*1.2	49.3	9.5

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