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Simulation of Fischer-Tropsch Fluidized Bed Reactor for the Production of Methane from Synthesis Gas (Gas to Liquid Technology)

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Abstract
Models describing the steady state behavior of the Fischer-Tropsch Fluidized Bed Reactor has been developed. Kinetics and operating parameters of an industrial plant obtained from Dry, (2002) were adopted and used in the solution of the developed models. The model equations were integrated numerically using the Fourth-Order Runge-Kutta algorithm. Results obtained had a deviation ranging from 1.3% to 23.2% between model prediction and industrial plant output data indicating reasonable agreement. Reactor simulation with the model equations of process parameters such as superficial velocity, bubble diameter and total pressure gave: optimum yield of methane as 73% (the most significant variables) at superficial velocity of 0.0801m/s; bubble diameter of 0.0487m and a total pressure of 18 Bars.
Keywords: Modeling, Simulation, Fluidized Bed Reactor, Fischer-Tropsch Synthesis.

1.0 INTRODUCTION

The Fischer-Tropsch synthesis convert synthesis gas to hydrocarbons, offers a way to produce synthetic fuels from various raw materials such as natural gas, coal or biomass (gas-to-liquids GTL, coal-to-liquids CTL and biomass-to-liquids BTL). The Fischer-Tropsch synthesis (FTS) is the chemical heart of gas-to-liquid technology. GTL is the technology used to convert natural gas to a clean and versatile liquid fuel. This is a complementary rather than competitive technology for the exploitation of stranded natural gas. In the present world's energy scenario, the supply of oil and other natural resources is limited and not uniformly distributed (Dry, 2002; Tiefeng *et al*., 2007). Hence production of syngas from natural gas, coal and biomass and conversion of syngas to high quality fuels via FTS become increasingly of interest. Natural gas is available in large quantities and the reserve is not used to the same extent as crude oil. Although it does have some drawbacks compared to other fuels, mainly issues dealing with its volume, it promises to be an increasingly important energy source in the years to come. It is important to mention here that methane is the principal component of natural gas currently being used for home and industrial heating as well as for generation of electrical power. Also, natural gas burns cleaner and produces fewer pollutants than other fossil fuels. It has the largest heat of combustion relative to the amount of carbon dioxide (CO_2) formed. It produces 45% less CO_2 than coal for a comparable amount of energy, and also emits considerably less NO_x and SO_x gases (De smet, 2000). During the last ten years, there has been a renewed interest in Gas-to-Liquids (GTL) technology, in which natural gas is converted to liquids useful as fuels and chemicals feedstock through the Fischer-Tropsch Synthesis (FTS). In the gas-to-liquid (GTL) technology, natural gas is converted into a liquid product containing hydrocarbons and oxygenates. In general, the GTL technology consists of the following three main processes: synthesis gas manufacturing, Fischer-Tropsch synthesis and product upgrading. Synthesis gas is a mixture of carbon monoxide (CO) and hydrogen (H_2), which can be obtained from any carbon containing feedstock, such as natural gas. On the other hand, the Fischer-Tropsch reaction represents the heart of the process, because it determines the product types and distributions in GTL technology. The highly exothermic Fischer-Tropsch reaction converts synthesis gas into a large range of linear hydrocarbons including gasoline, diesel and wax (Hindermann *et al*., 1993; Van der Laan and Beenackers, 1999; Chowdhury *et al*., 2006). Therefore, a model for Fischer-Tropsch fluidized bed reactor for the production of methane from synthesis gas was developed and used to predict the conversion and yield patterns of reactants and products in the reactor. The reactor was also simulated to study the effects of functional parameters of the model on the reactor performance (conversion of reactants and yield of methane).

2. Reactor Model

Figure 1 shows the hypothetical representation of a two phase fluidized bed reactor comprising of the bubble and emulsion phase. The emulsion phase consists of catalyst particles and the gas flow rate is equivalent to minimum fluidization velocity. The flow rate of gas in the bubble phase is in excess of the minimum fluidization velocity.

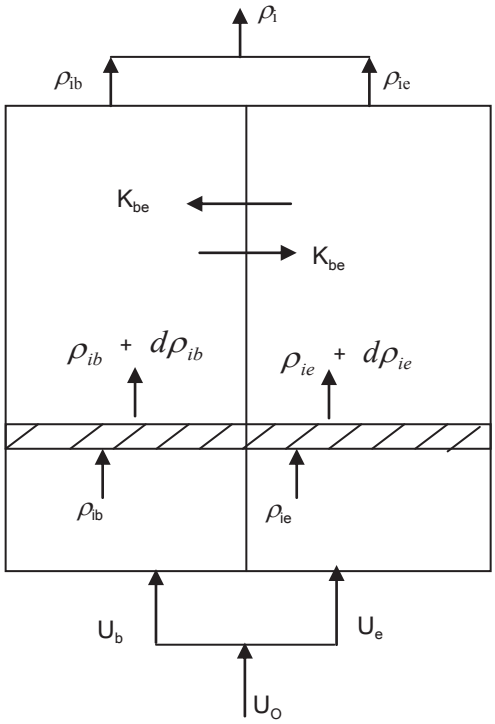

Figure 1: Two phase Fluidized bed reactor model (Kunii and Levenspiel, 1991)

where ρ is the density of the gas phase, ρ_{ib} , ρ_{ie} are the emulsion and bubble phase densities, U_O is the superficial velocity, U_b, U_e are the bubble and emulsion velocities, K_{be} is the mass transfer coefficient between bubble and emulsion phase, U_{mf} is the minimum fluidization velocity.

2.1 Model Assumptions

The following assumptions were made in the derivation of the reactor model:

i) The feed enters the bed at incipient velocity U_o and is partitioned between the emulsion and the bubble phase.
ii) The bubble phase is particle free with negligible catalytic reaction.
iii) Reaction occurs only in the emulsion phase.
iv) Axial diffusion i.e. transport by effective diffusion in the emulsion phase is negligible hence plug flow is assumed in the emulsion phase.
v) There is exchange of mass between bubble and emulsion phase.
vi) Solids are perfectly mixed and of uniform size.
vii) Catalyst decay functions are identical for the reactants and products.
viii) Steady state and isothermal conditions are assumed.

Under these assumptions, the component balance for the mass fractions of the reactants and products in the bubble and emulsion phase of the fluidized bed reactor for a dimensionless catalyst bed height were obtained as follows:

Bubble phase:

$$-U_b \frac{dy_{ib}}{H_f\, dZ} = K_{be}(y_{ib} - y_{ie}) \tag{1}$$

Emulsion phase:

$$-\frac{U_e dy_{ie}}{H_f\, dZ} = (-r_i)\varepsilon_{gT} - Kbe\left[y_{ib} - y_{ie}\right] \tag{2}$$

where; y_{ib}, y_{ie} is the mass fraction of component in the bubble and emulsion phase respectively, Z is the dimensionless catalyst bed height and H_f the catalyst bed height.

2.2 Fluidized Bed Parameter Specification

The following parameters U_b, U_e, U_0, U_{mf}, K_{be}, in two-phase fluidized bed were estimated using the following equations:

Bubble and Emulsion Phase Velocities

U_b can be estimated using the formula (Kunii and Levenspiel, 1991):

$$U_b = U_0 - U_{mf} + U_{br} \tag{3}$$

where U_{br} is the rise velocity of a single bubble in the bed and is given as:

$$U_{br} = 0.711(gd_b)^{1/2} \tag{4}$$

where d_b is the bubble diameter.

The emulsion phase velocity is assumed to be equal to the minimum fluidization velocity, given as:

$$U_e = U_{mf} \tag{5}$$

Interchange Transfer Coefficient

Bubble-cloud Transport Coefficient (K_{bc})

$$K_{bc} = 4.5\left[\frac{U_{mf}}{d_b}\right] + 5.85\left[\frac{D^{1/2}g^{1/4}}{d_b^{5/4}}\right] \tag{6}$$

where D is the diffusivity; g is the acceleration due to gravity

Cloud-Emulsion Transport coefficient (K_{ce})

$$K_{ce} = 6.78\left(\frac{\epsilon_{mf} D U_{br}}{d_b^3}\right) \tag{7}$$

where ϵ_{mf} is the void fraction at minimum fluidization

Bubble-emulsion Transport Coefficient (K_{be})

The K_{be} is obtained by the addition of the two parallel resistances.

$$\frac{1}{K_{be}} = \frac{1}{K_{bc}} + \frac{1}{K_{ce}}$$

$$K_{be} = \frac{K_{bc} . K_{ce}}{K_{bc} + K_{ce}} \tag{8}$$

2.3 Kinetic Model

The kinetic model used to simulate the production of methane from synthesis gas is represented by the following reaction:

$$CO + 3H_2 \xrightarrow{K_{FTS}} CH_4 + H_2O \tag{9}$$

Let: CO = A, H_2 = B, CH_4 = C, H_2O = D

The rate expression for the reactants A and B to produce C and D were written from the stoichiometry of equation (9) in terms of mass fraction and total pressure as:

$$r_A = -K_{FTS}\left(\frac{y_{Ae} P_T}{RT}\right)\left(\frac{y_{BeP_T}}{RT}\right)_3 \tag{10}$$

$$r_B = -3K_{FTS}\left(\frac{y_{Ae} P_T}{RT}\right)\left(\frac{y_{BeP_T}}{RT}\right)_3 \tag{11}$$

$$r_c = K_{FTS}\left(\frac{y_{Ae} P_T}{RT}\right)\left(\frac{y_{BeP_T}}{RT}\right)_3 \tag{12}$$

$$r_D = K_{FTS}\left(\frac{y_{Ae} P_T}{RT}\right)\left(\frac{y_{BeP_T}}{RT}\right)_3 \tag{13}$$

Substituting the kinetic models (equations 10 – 13) into the emulsion phase model (equation 2) gives:

$$\frac{-U_e dy_{Ae}}{H_f dz} = \left[K_{FTS}\left(\frac{y_{AeP_T}}{RT}\right)\left(\frac{y_{BeP_T}}{RT}\right)\text{^}3\right] \varepsilon_{gT} . K_{be}(y_{Ab} - y_{Ae}) \tag{14}$$

$$\frac{-U_e dy_{Be}}{H_f dz} = \left[3K_{FTS}\left(\frac{y_{AeP_T}}{RT}\right)\left(\frac{y_{BeP_T}}{RT}\right)\text{^}3\right]\varepsilon_{gT}_K_{be}(y_{Bb}-y_{Be}) \quad (15)$$

$$\frac{-U_e dy_{Ce}}{H_f dz} = \left[-K_{FTS}\left(\frac{y_{A\,P_T}}{RT}\right)\left(\frac{y_{BeP_T}}{RT}\right)\text{^}3\right]\varepsilon_{gT}_K_{be}(y_{Ce}-y_{Ce}) \quad (16)$$

$$\frac{-U_e dy_{De}}{H_f dz} = \left[-K_{FTS}\left(\frac{y_{A\,P_T}}{RT}\right)\left(\frac{y_{BeP_T}}{RT}\right)\text{^}3\right]\varepsilon_{gT}_K_{be}(y_{DB}-y_{De}) \quad (17)$$

The exit concentration from the bubble and emulsion phase can be linked together using the formula given by Dagde and Puyate, (2012) as:

$$y_i = \beta y_{ib} + (1-\beta)\, y_{ie} \quad (18)$$

where i = A, B, C, and D for CO, H_20, CH_4 and H_20 respectively, substituting gives:

$$y_A = \beta y_{Ab} + (1-\beta)\, y_{Ae} \quad (19)$$

$$y_B = \beta y_{Bb} + (1-\beta)\, y_{Be} \quad (20)$$

$$y_C = \beta y_{Cb} + (1-\beta)\, y_{Ce} \quad (21)$$

$$y_D = \beta y_{Db} + (1-\beta)\, y_{De} \quad (22)$$

where $\beta = 1 - \frac{U_{mf}}{U_0}$ (23)

2.4 Solution Techniques

The model equations were solved using MATLAB 7.5 ode 45 solver employing the algorithm of the 4th order of Runge Kutta algorithm.

From the stoichiometry of the reaction, the initial conditions are:

Z = 0 : $Y_{A_{b0}} = Y_{A_{e0}} = 0.75$; $Y_{B_{b0}} = Y_{B_{e0}} = 0.25$

$Y_{C_{b0}} = Y_{C_{e0}} = Y_{D_{b0}} = Y_{D_{e0}} = 0$

2.5 Operating Parameters

The model equations developed contain certain unknown hydrodynamic and kinetic parameters such as the reaction rate constants for the various reaction paths (K_{ij}), the interchange transfer coefficient K_{be}, the various velocities U_e, U_b, U_{br} and other reaction and reactor parameters. These were obtained from the works of Dry, (2002) and given in Table 1.

Table 1: Operating and Hydrodynamic parameters (Dry, 2002)

Parameters	Values (units)
Superficial gas velocity, U_o	0.0801 m/s
Minimum fluidization velocity, U_{mf}	0.0148 m/s
Bubble rise velocity, U_{br}	0.49 m/s
Bubble velocity, U_b	0.556 m/s
Void fraction, ε_{gT}	0.122
Bubble diameter, d_b	0.0487m
Diffusivity, D	6.1 x 10^{-5} m^2/s
Acceleration due gravity, g	9.8 m/s^2
Bed porosity at minimum fluidization , ε_{mf}	0.657
Bed height, H_f	9.6m
Mass transfer interchange coefficient between the bubble and cloud phase, K_{bc}	4.92s^{-1}
Mass transfer interchange coefficient between the cloud and emulsion phase, K_{ce}	3.00s^{-1}
Mass transfer interchange coefficient between the bubble and emulsion phase, K_{be}	1.86s^{-1}
Temperature, T	523K
Total pressure, P_T	3 x 10^5 Pa
Universal gas constant	8314J/mol. K

3.0 Results and Discussion

The results of the models solutions showing the conversion and yield patterns of the reactants and products along the fluidized bed height are shown in Figure 2. A comparison of the model predictions of the reactor outlet reactants conversions and product yields with industrial plant output data from the works of Dry, (2002) are presented in Table 2.

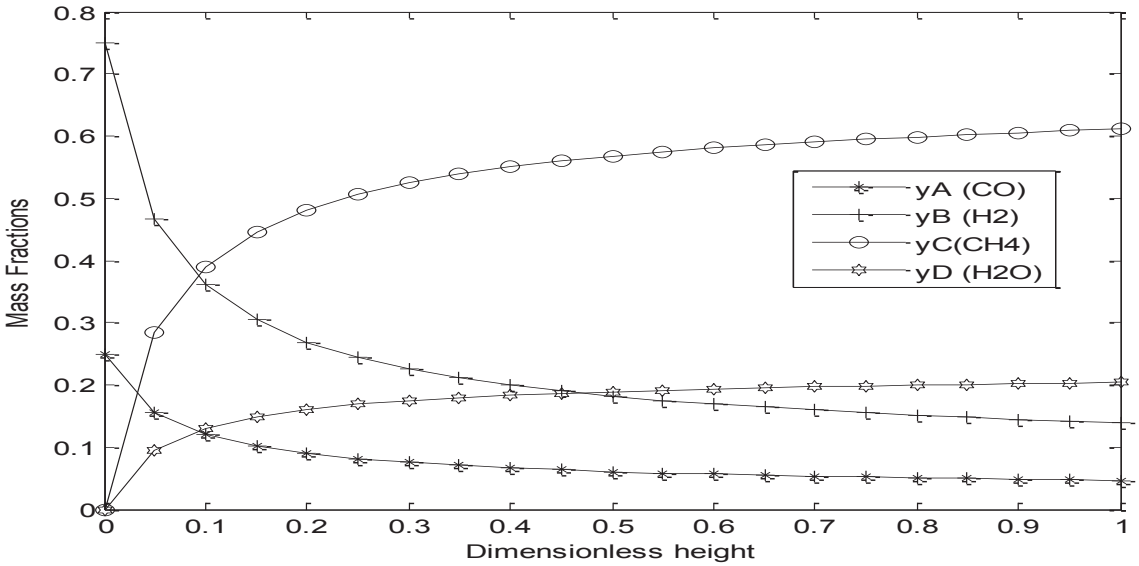

Figure 2: Variations of reactants and products mass fraction along the catalyst bed height.

Table 2: Comparison of Model Predictions with Literature Data.

Parameter	Dry, (2002)	Model predictions	% deviation
Weight fraction of CO (wt%)	6.0	6.08	1.3
Weight fraction of H_2 (wt%)	14.0	18.23	23.2
Weight fraction of CH_4 (wt%)	60.0	56.77	-5.69
Weight fraction of H_2O (wt%)	20.0	18.92	-5.71

Figure 2 showed that the mass fraction of carbon monoxide and hydrogen decrease (conversion increase) along the catalyst bed height while the yield of methane and water increases throughout the catalyst bed height.

Table 1 showed that there is a reasonable agreement between the conversions and yields predicted by the model and those obtained from the industrial plant. The deviations ranged from 1.3 to 23.2. The prediction of methane which is the major advantage of this process matches the industrial plant data very closely with a deviation of 5.69. Therefore, the developed model was used for simulation studies of the reactor.

3.1 Sensitivity Analysis

A sensitivity analysis was performed to determine the effects of process variable such as superficial gas velocity, bubble diameter and total pressure on the reactants conversion and product yield patterns along the catalyst bed height.

i. Effect of Superficial Gas Velocity

The superficial gas velocity is a dominant factor that affects the mass fraction of each component. The effect of superficial gas velocity on the concentration and yield of reactants and products is shown in Figure 3.

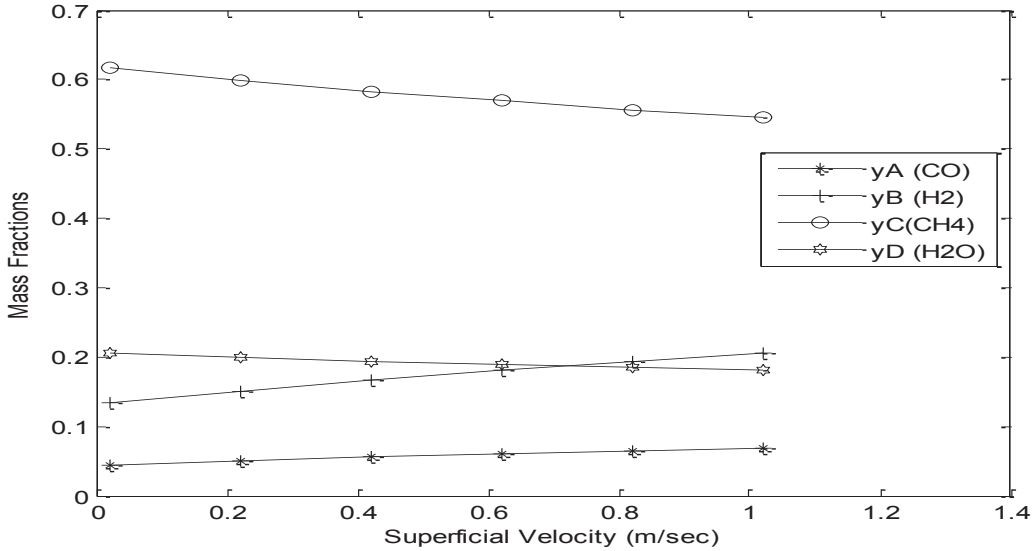

Figure 3: Effect of superficial gas velocity on reactants conversion and products yield.

Figure 3 showed a decrease in the yield of the products and a marginal increase in the conversion of the reactants. The decrease in the yield of the products (components C and D) is attributed to low residence time of the catalyst at high superficial velocity. The low conversion of the reactants (components A and B) is due to channeling and by-passing effects inherent in fluidized bed at higher superficial velocities (Carberry, 1976). At lower superficial velocity the feed spends a longer time in the fluidized bed. Hence, the mass fractions of reactants A and B increases as the superficial velocity increases; the mass fractions of B increasing more than that of A. The mass fractions of product C and D decrease as the superficial gas velocity increases; the mass fractions of C decreasing more than that of D along the catalyst bed height as the selectivity of the catalyst is favorable for the desired component C.

ii. Effect of Bubble Diameter

The influence of bubble diameter is a very important factor that affects the mass fraction of the various components. The effect of bubble diameter on the concentration and yield profiles of reactants and products is shown in Figure 4.

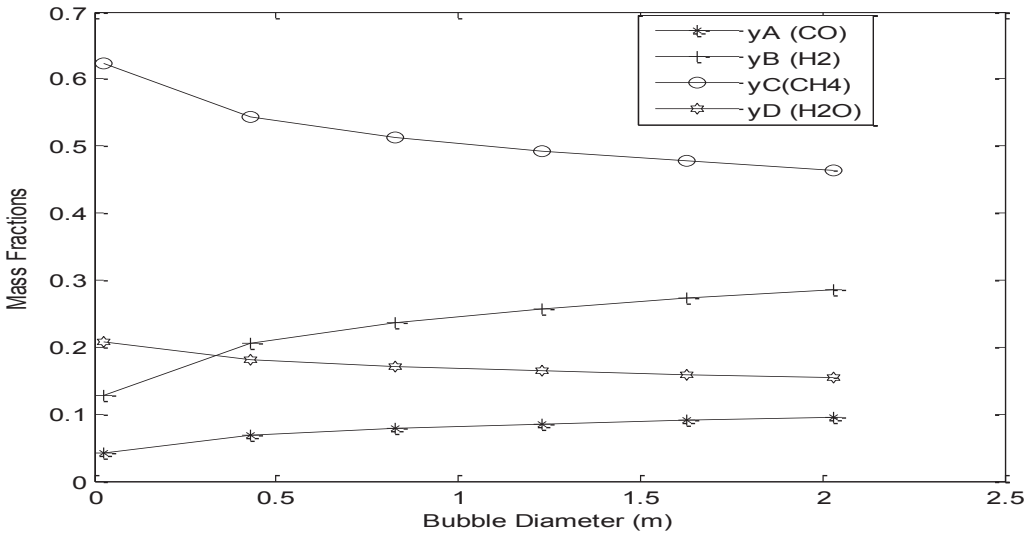

Figure 4: Effect of Bubble diameter on reactants conversion and products yield.

The reactants concentrations increased while the yield of products decreased with bubble diameter.

The decrease in the yield of component C and D can be attributed to slugging effect and the fact that increase in the bubble size causes the bubble to move upward in a piston-like manner, then disintegrates and rains down thereby creating a local space velocity different from the overall space velocity. (Cheremisionff and Cheremisinoff, 1984). Thus, the mass fractions of the reactants (components A and B) increases as the bubble diameter increases while the mass fractions of components C and D decreases as the bubble diameter increases.

iii. Effect of Pressure

The effect of total pressure on the performance of fluidized bed Fischer-Tropsch reactor is seen from the concentration and yield patterns of reactants and products as depicted in Figure 6.

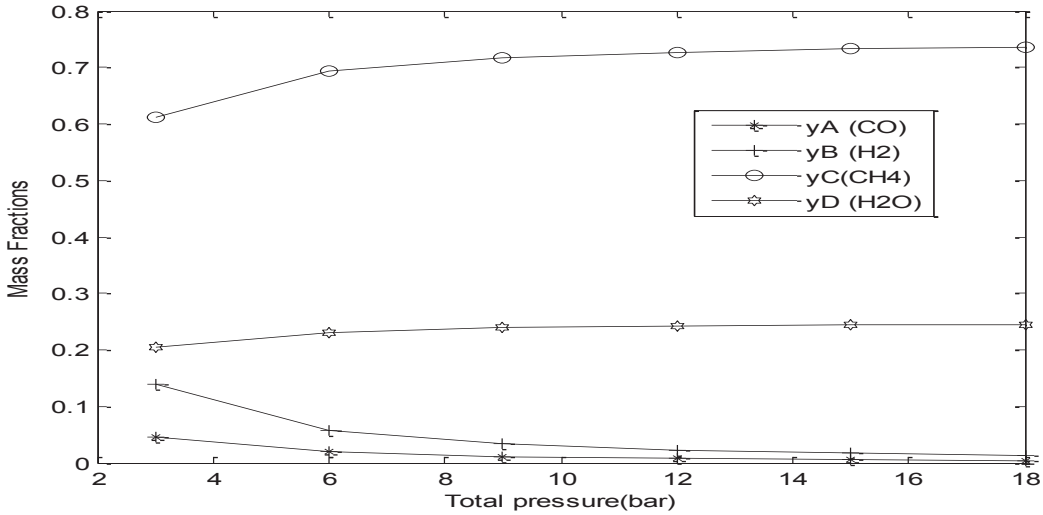

Figure 6: Effect of Total pressure on the reactants conversion and product yield.

The mass fractions of the reactants (components A and B) decreased while the mass fractions of the products (components C and D) increased with increase in total pressure.

4. CONCLUSION

Models describing the steady state fluidized bed Fischer-Tropsch reactor for methane production from natural gas has been presented. Kinetics and operating parameters obtained from Dry, (2002) were adopted and used for solution of the model equations. Models were validated by comparing model predictions with industrial plant output data in Dry, (2202) and a maximum deviation of 23.2% was obtained. Hence the models were used for simulation of the reactor. Simulation results indicate that superficial velocity, bubble diameter, reaction temperature and pressure are major process variables that affect yield of methane.

NOMENCLATURE

A	cross-sectional area of the reactor	m^2
D	diffusivity	m^2/s
d_b	bubble diameter	m
ε_{gt}	void fraction	
ε_{mf}	bed porosity at minimum fluidization	
F_b	fraction of the bed volume occupied by the bubble	
g	Acceleration due to gravity	m/s^2
dH	Differential height	m
H	Incremental bed height	m
H_f	Bed height at final stage	m
H_{mf}	Bed height at minimum fluidization	
K_{fts}	Reaction constant for fischer- tropsch synthesis	
K_{be}	Mass transfer interchange coefficient between the bubble and emulsion phase	s^{-1}
K_{bc}	Mass transfer coefficient interchange between the bubble and cloud phase	s^{-1}
K_{ce}	Mass transfer interchange coefficient between the cloud and emulsion phase	s^{-1}
P_i	Pressure of the gas component i (gas)	Pa
P_T	Total pressure of the gas mixture	Pa
P_{gT}	Density of the gas	kg/m^3
P_{ib}	Density of the gas at bubble phase	kg/m^3

P_{ie} kg/m^3	Density of the gas at emulsion phase	
r_i	Reaction rate	mol/s.kg
T	Temperature	K
U_o	Superficial velocity	m/s
U_b	Bubble phase velocity	m/s
U_{br}	Bubble rise superficial velocity	m/s
U_e	Superficial emulsion phase velocity	m/s
U_{mf}	Superficial minimum fluidizing velocity	m/s
y_{ib}	Vapour phase mass fraction of component i in the bubble	
y_{ie}	Vapour phase mass fraction of component i in the emulsion phase	
z	Dimensionless height	

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