

CHAPTER 3

RESULTS AND DISCUSSIONS

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Despite the wealth of literature concerning F-T kinetics, bubble column hydrodynamics, and slurry bubble column modeling, there is no application of these models on real existing reactors. Only simulations to study the effect of operating variables on an industrial scale reactor performance have been attempted [Van der Laan et al., 1999] and [Marreto, and Krishna, 1999].

The desired results from a reactor model are the conversion of reactants, productivity [(product produced) / (amount of catalyst)(time.m³)] and product distribution and include the influence of the ratio of reacting species, pressure, temperature, superficial gas velocity, reactor diameter, and catalyst loading. The Software developed is assumed to cover all these requirements.

Two aspects will be covered in this work; the first one is to reproduce the results obtained by Van der Laan et al. [1999] using the software developed above in order to assess the correctness of the proposed method of solution, the second aspect is to use this model to predict the performance of the pilot scale Fischer- Tropsch slurry reactor of DOE's Alternative Fuels Development Unit (AFDU) at LaPorte, Texas [Bhatt, 1999] and compare model predictions with the actual results.

3-1-Simulation of an Industrial Scale Fischer-Tropsch Slurry Reactor

Van der Laan et al. [1999] performed simulation studies to an industrial scale Fischer- Tropsch reactor the characteristics of which and the operating conditions are given in Table (3-1). The kinetic rate equation utilized for the consumption of synthesis gas was equation (3-1) with the constants k, a and b determined for the iron based catalyst utilized by industry [Van der Laan et al., 1999]

$$- R_{CO + H_2} = \frac{k P_{CO} P_{H_2}^{1/2}}{(1 + a P_{CO} + b P_{CO_2})^2} \quad (3-1)$$

where, $k = 0.034 \text{ mol kg}^{-1} \text{ s}^{-1} \text{ Mpa}^{-1.5}$
 $a = 1.185 \text{ Mpa}^{-1}$ and $b = 0.656 \text{ Mpa}^{-1}$

Table (3-1) Operating conditions and system properties

Reactor temperature	523 K
Reactor pressure	30 bar
Reactor diameter	8 m
Reactor dispersion height	24 m
Liquid density, ρ_L	640 kg/m ³
Liquid viscosity, μ_L	2.9*10 ⁻⁴ pa s
Surface tension, σ_L	0.01 N/m
Catalyst particle density, ρ_p	1957 kg/m ³
Catalyst particle pore volume, V_0	0.00105 m ³ /kg
Catalyst particle skeleton density, ρ_{sk}	2030 kg/m ³

Simulations were carried out for a range of superficial gas velocities $U_G = 0.15$ to 0.4 m/s, while the catalyst concentration range was $\epsilon_s = 0.20$ to 0.35 and H₂ to CO feed ratio of 0.67 to 2.0. The same simulation studies are repeated with the software developed above. The major results of the simulations on the reactor performance are shown in (Figs. 3-1 - 3-5).

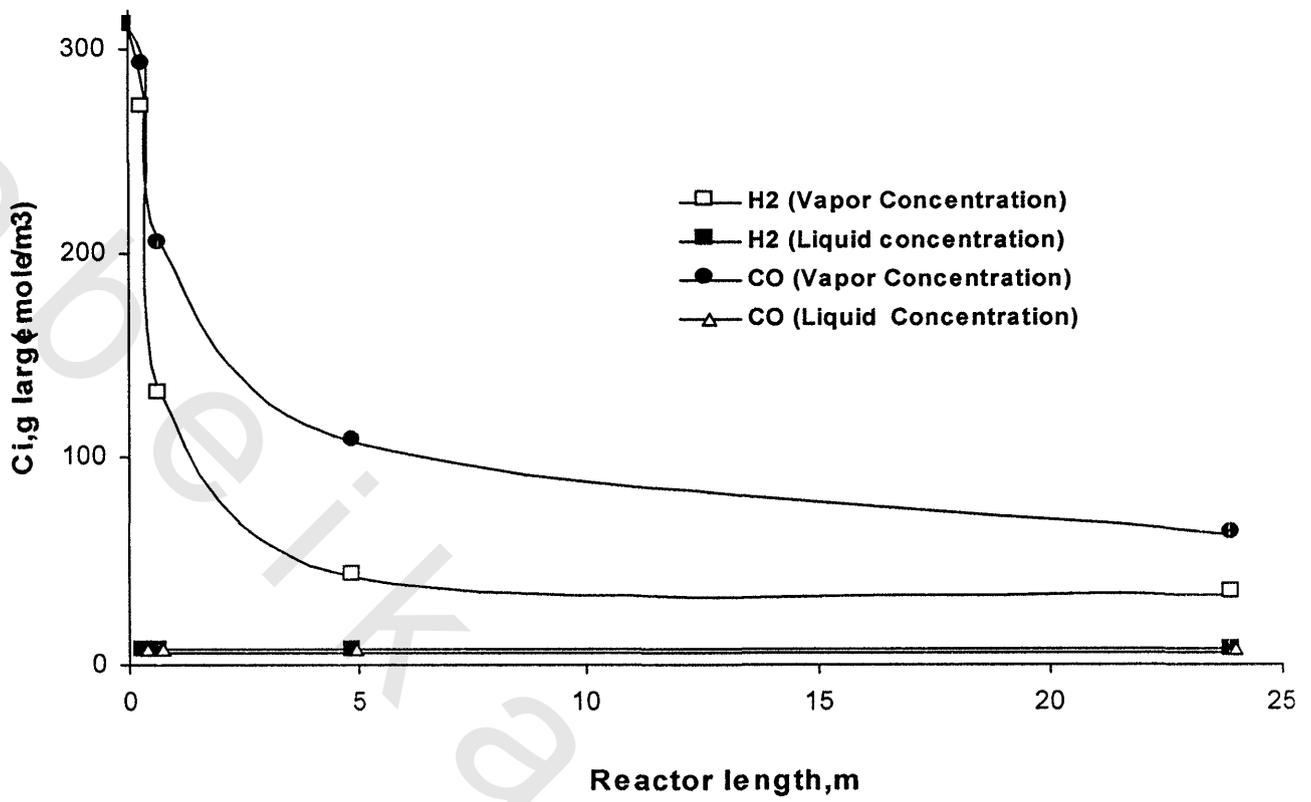


Figure (3-1) Axial concentration profiles in Liquid and Vapor phases for H2 and CO ($F=1$, $U_G = 0.2$ m/s, $\epsilon_s = 0.25$, $D = 8$ m, $H = 24$ m, $T = 523$ K).

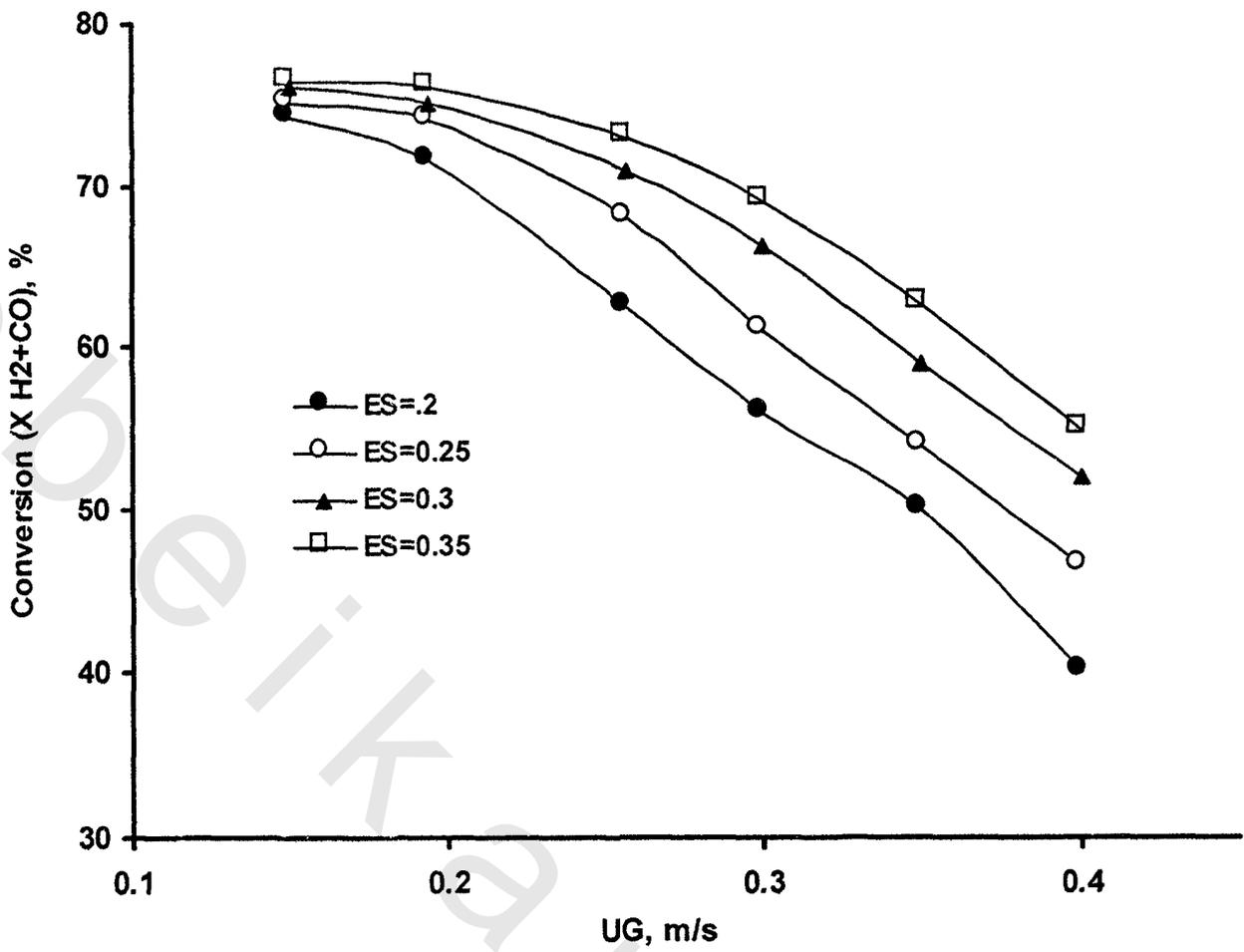


Figure (3-2) Effect of catalyst concentration and gas velocity on the synthesis gas conversion [F=1, T= 523 K, H=24 m, D= 8m]

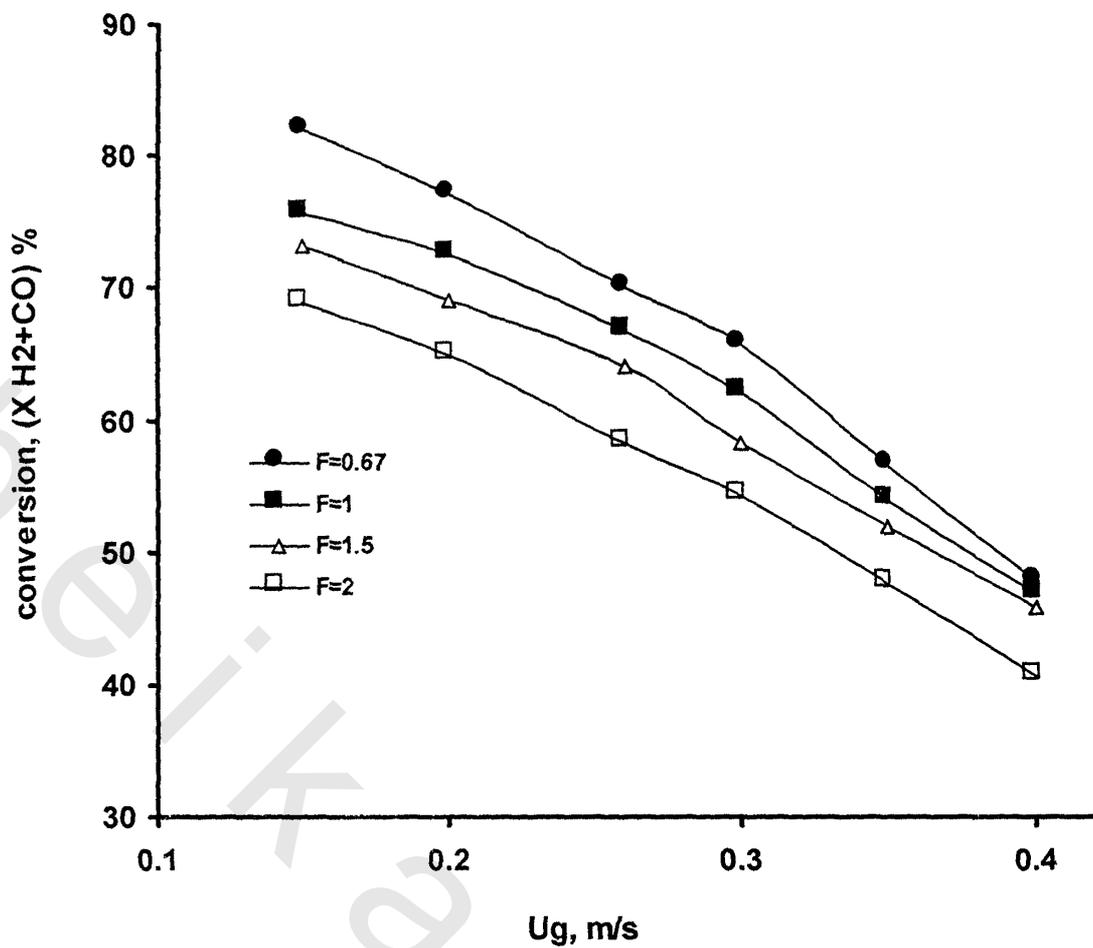


Figure (3-3) Effect of H_2/CO feed ratio F and gas velocity on the synthesis gas conversion [$\epsilon_s = 0.25$, $H=24$ m, $D=8$ m]

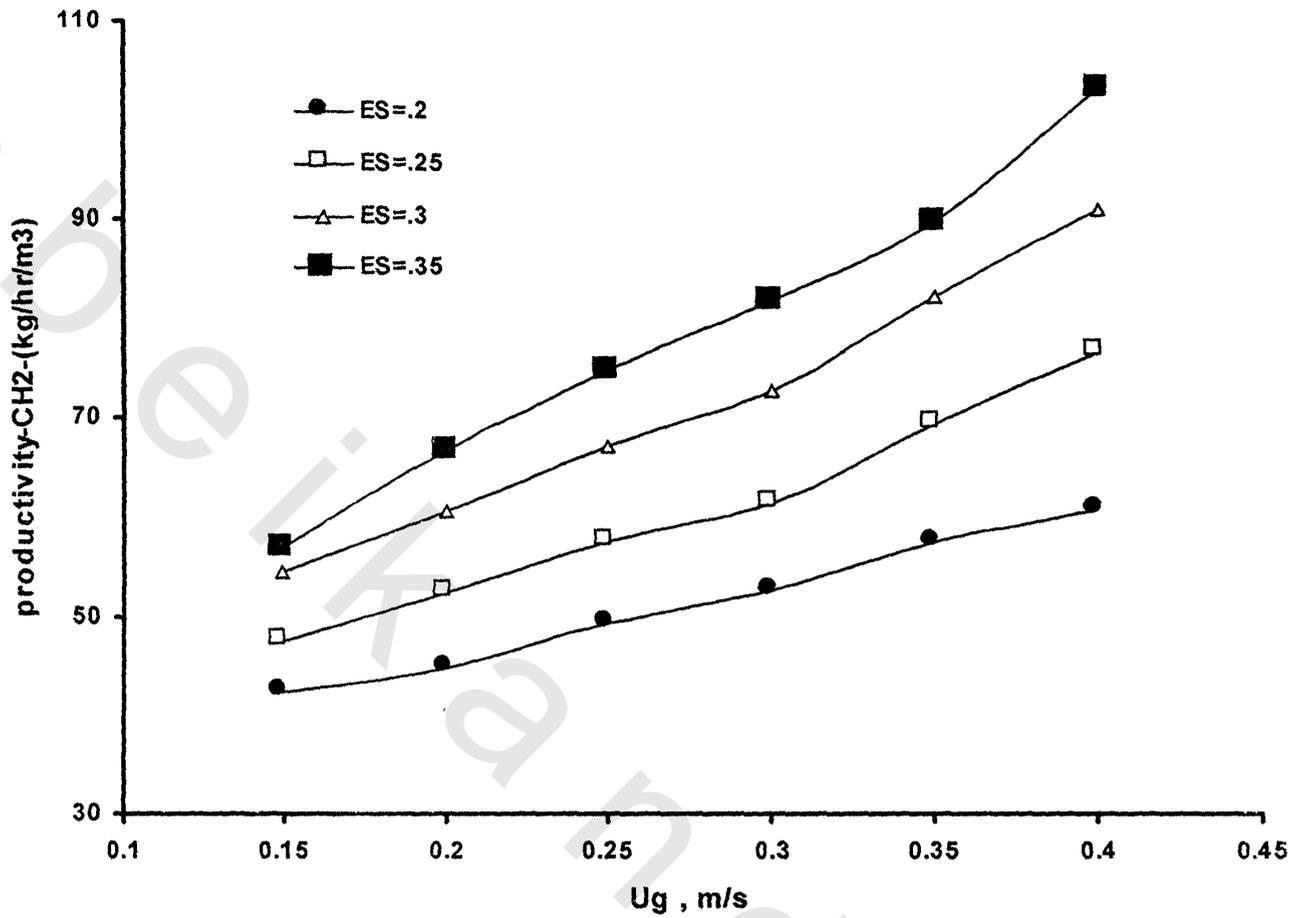


Fig (3-4) Effect of catalyst concentration and gas velocity on the reactor productivity (F=1, T=523K, H=24 m, D=8 m)

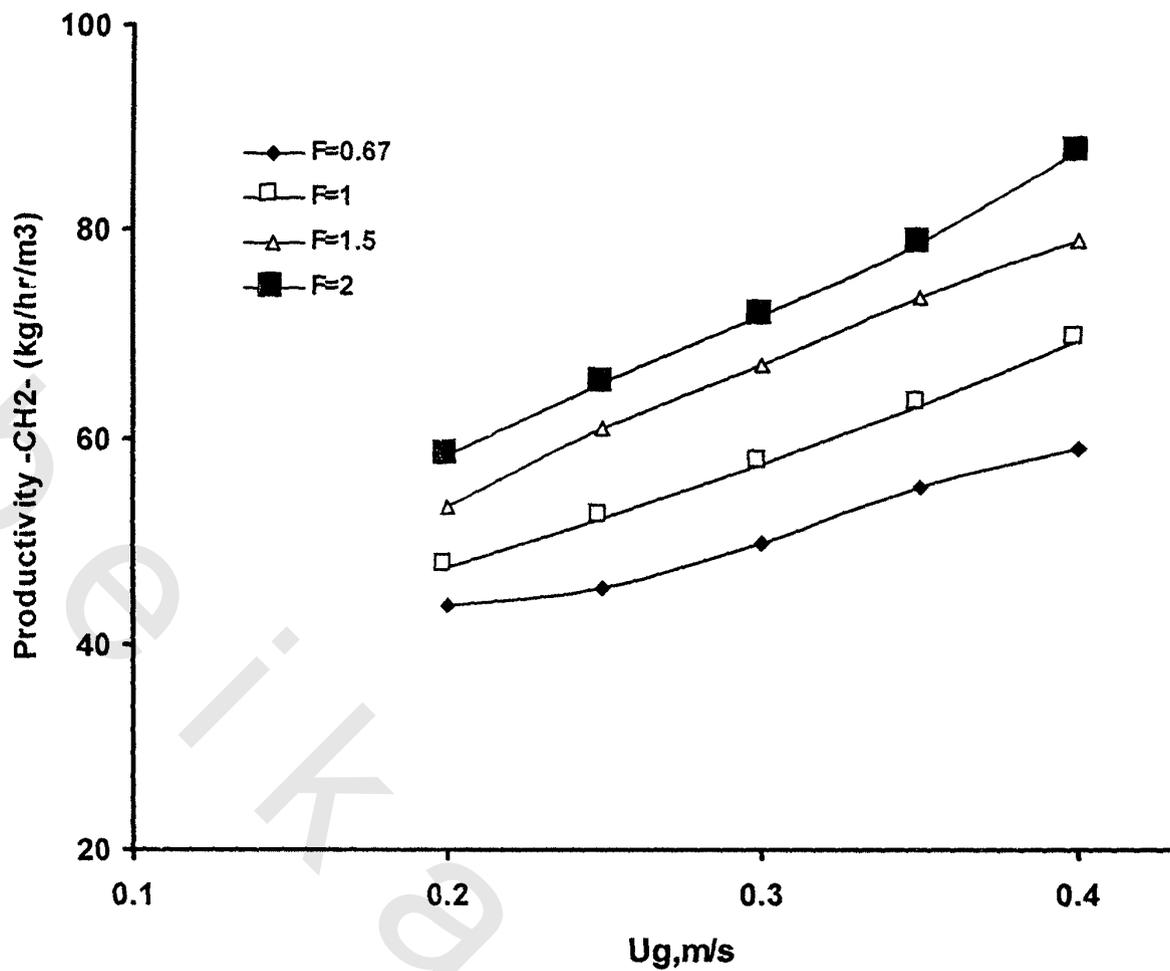


Figure (3-5) Effect of the H₂/CO F and gas velocity on the reactor productivity ($\epsilon_s = 0.25$, T = 523 K, H=24 m, D= 8m)

The reactants (H_2 , CO) concentration (mole/m^3) profile in the large bubbles and the liquid phase concentration as a function of reactor length is shown in **fig. (3-1)** for a representative production case ($F=1$, $U_G = 0.2 \text{ m/s}$, $U_L = 0.007 \text{ m/s}$, $\varepsilon_s = 0.25$, $T = 523 \text{ K}$). Because of the complete mixing in the small bubble phase and the slurry phase, the concentration of the reacting gases in the former phase and their concentration in the later phase are constant throughout the reactor length. On the contrary, being in plug flow, the concentration of each of the reacting species in large bubbles phase decreases as they ascend the reactor. The maximum decrease occurs at the bottom of the reactor the entrance section. Similar results were reported by **Van der Laan et al. [1999]**.

For a constant solids volume fraction, ε_s or feed ratio F , increasing the inlet superficial gas velocity causes a decrease in conversion of the gas phase (**Fig. 3-2, 3-3**) as expected. Higher conversion may be obtained when the operating conditions (P , T) or catalyst is changed or when the dispersion height is increased.

The reactor productivity, expressed as total hydrocarbon production in $\text{kg m}^{-3} \text{ hr}^{-1}$, generally increases with increasing gas velocity (**Fig. 3-4, 3-5**). The effect of catalyst concentration on the reactor performance at feed ratio $F = 1$ is shown in **Figs. (3-2, 3-4)** Increasing the catalyst concentration shows an increase of the conversion and productivity. Highest productivity is obtained at the highest catalyst concentration, $\varepsilon_s = 0.35$ and highest gas velocity, 0.4 m s^{-1} **fig. (3-4)**. The effect of the feed ratio F at a constant catalyst concentration of $\varepsilon_s = 0.25$ on conversion and reactor productivity is shown in **Figs. (3-3, 3-5)** respectively. The decrease of the synthesis gas conversion and increase in reactor productivity with increasing F is mainly caused by the kinetics.

The above results are similar to those obtained by **Van der Laan et al. [1999]**. This confirms the validity of the proposed method of solution.

Table (3-2) shows the effect of feed ratio F on the weight selectivity of the different hydrocarbon classes. The constants p , t_0 , k_R utilized by **Van der Laan et al. [1999]** is utilized here. Four hydrocarbon groups are shown these are namely

methane, C₁, light gases C₂-C₄, gasoline fraction (C₅-C₁₀) and a diesel /wax fraction C₁₀₊, more over the olefin content is shown for the C₂ products (W_{O,2}), C₃₋₄ (W_{O,3-4}) and the total olefin yield of all products, W_O. The total reaction productivity is also given. It is shown that the selectivities for light hydrocarbons W₁, W₂₋₄ W₅₋₁₀ increases while that for the heavy hydrocarbon fraction C₁₀₊ decreases as the feed ratio increases. The olefin content of W_{O,2}, W_{O,3-4} and the overall olefin content in the product decreases as F increases because of the more availability of hydrogen to saturate the produced olefins. The total reactor productivity is also listed for the studied cases. It is clear that productivity in kg/h as F increases. Comparing these results to those obtained by **Van der Laan et al. [1999]** shown as second row in **bold** in each cell, the same trends are reproduced however; selectivity and productivity values are slightly different from the reference case. This difference may be caused by the different methods of model solutions (analytically in this work as opposed to numerically in the reference work). Reactor productivities are higher in the present case than those reported by **Van der Laan et al. [1999]**. These authors erroneously divided the moles produced by $\sum_i n m_i$ in equation (2-33) which is not justified.

Table (3-2) selectivity parameters and product selectivities (wt %) as a function of the feed ratio F ($U_G = 0.2$, m/s, $\varepsilon_s = 0.25$, $T = 523$ K)

F	p	t_0	k_R	w_1	w_{2-4}	w_{5-10}	w_{10+}	$w_{O,2}$	$w_{O,3-4}$	w_O	Productivity (kg/hr)
0.67	17.4	5.6	0.17	5.18	23.3	23.84	53.32	43.2	78.9	35.21	69037.12
				3.7	17.5	26.5	52.3	43.0	85.0	37.7	60000
1.0	12.6	4.6	0.27	7.02	23.8	23.05	46.137	29.11	69.8	27.98	79900.84
				5.7	18.9	27.2	48.2	28.5	79.3	33.5	66330
1.5	9.6	3.9	0.41	8.8	26.2	24.9	40	19.8	62.37	25.6	89142.56
				8.2	20.5	28.4	43.0	18.0	72.7	29.5	71154
2.0	7.9	3.6	0.56	10.11	27.2	25.6	37.566	14.2	55.19	21.2	102351.12
				10.6	21.8	29.3	38.3	13.9	66.8	26.5	71154

Values in **Bold** are those of Van der Laan et al., [1999]

3-2 -Simulation of AFDU Pilot Scale Slurry Reactor

Domestic development of a slurry-phase Fischer-Tropsch (F-T) process is of considerable interest to the U. S. Department of Energy's Indirect Liquefaction program. The Federal Energy Technology Center (FETC) sponsors the Indirect Liquefaction program as part of its Coal Liquefaction program. The overall goal is to develop a scientific and engineering knowledge base with which industry can bring economically competitive and environmentally acceptable advanced technology for the manufacture of synthetic liquid fuels from coal into the marketplace when needed. In addition, several industrial companies have an interest in developing the technology for remote gas conversion.

Slurry phase Fischer-Tropsch technology was successfully demonstrated in DOE's Alternative Fuels Development Unit (AFDU) at LaPorte, Texas. Earlier work at LaPorte, with iron catalysts in 1992 and 1994, had established proof-of-concept status for the slurry phase process. The third campaign (Fischer-Tropsch III), in 1996, aimed at aggressively extending the operability of the slurry reactor using a proprietary cobalt catalyst. These runs were sponsored by the U. S. Department of Energy (DOE), Air Products and Chemicals, Inc., and Shell Synthetic Fuels, Inc. (SSFI). A productivity of approximately 140 grams (gm) of hydrocarbons (HC)/ hour (hr)-liter (lit) of expanded slurry volume was achieved at reasonable system stability. The reactor operated hydrodynamically stable with uniform temperature profile and gas hold-ups.

3-2-1-Process Description

The process flow diagram for Fischer-Tropsch III is given in **Fig. (3-6)**. Carbon monoxide, hydrogen and nitrogen are blended and compressed to obtain desired fresh synthesis gas composition and flow. The fresh feed is then mixed with recycle feed. High pressure hydrogen is used to supplement the fresh feed. The combined feed gas is preheated in the feed/product economizer and a steam heater. The preheated feed gas is introduced to the bottom of the slurry reactor. The synthesis gas flows upward through the slurry and is partially converted to hydrocarbons, water and carbon dioxide. The heat of reaction is absorbed by the slurry medium and then rejected to an internal heat exchanger. Heavier hydrocarbon fraction of the product (heavy wax) is liquid at reaction conditions and accumulates in the reactor. The reactor effluent is first sent through a cyclone separator to remove entrained slurry and then cooled to condense light waxes. Part of the uncondensed vapor is sent to the flare as a purge stream, most of this stream is recycled. The liquids are de-pressurized and sent to a tank trailer in batches, periodically. The excess slurry from the reactor is drained, degassed, cooled and filtered. The concentrated slurry is sent back to the reactor. In the reactor, particles are kept fully suspended by the upward liquid flow (also in the absence of gas flow), as the liquid velocity is well beyond the particle settling velocity. Flows and

compositions are measured at various strategic points in the process including feed and product gas.

3-2-2- The Slurry Bubble Column

The bubble column reactor is 28.3' top to bottom and 22.5" inside diameter. The maximum slurry level is about 20' with the remainder being vapor disengagement space. A goal of 150 grams HC/liter reactor vol. - hr of HC productivity was set. Removal of reaction heat is achieved through an internal heat exchanger. The reactor is fitted with a number of thermocouples, located at various elevations. A nuclear density gauge is mounted on an external track and spans the space occupied by the internal heat exchanger. The maximum temperature for the reactor is 315°C at the maximum pressure of 1000 psig.

3-2-3. Simulation Results

In this work the slurry phase reactor simulation has been performed using the model described above. The kinetic rate equation utilized for the consumption of synthesis gas was that proposed by Yates and Satterfield [1991], which is a Langmuir-Hinshelwood type equation (3-2). This equation has been recommended by Maretto & Krishna [1999] who calculated the equation constants for cobalt based catalysts as given below by equations (3-3, 3-4).

$$-R_{CO+H_2} = \frac{a.P_{H_2}.P_{CO}}{(1+b.P_{CO})^2} \quad (3-2)$$

Where,

$$a = 8.8533 \times 10^{-3} \cdot \exp \left[4494.41 \left(\frac{1}{493.15} - \frac{1}{T} \right) \right] \quad \text{mol}/(\text{s kg}_{\text{cat}} \text{ bar}^2) \quad (3-3)$$

$$b = 2.226 * \exp \left[-8236 \left(\frac{1}{493.15} - \frac{1}{T} \right) \right] \quad \text{1}/\text{bar} \quad (3-4)$$

27-10 slurry reactor 22-65 hairpin exchanger 01.10,20 compressors 22.62 filters 10-52-01A/B,02 pumps 21.85 heat Exchanger 22.11, 22.15
and 22.16 vessels 21.70 catalyst-slurry cooler 22-10 separator 28.30 prep tank 21.38 feed/product economizer 27.15 slurry degasser 02-61
feed gas steam heater 27.11 cyclone separator. 27-12 slurry carryover surge tank 27-13-tank

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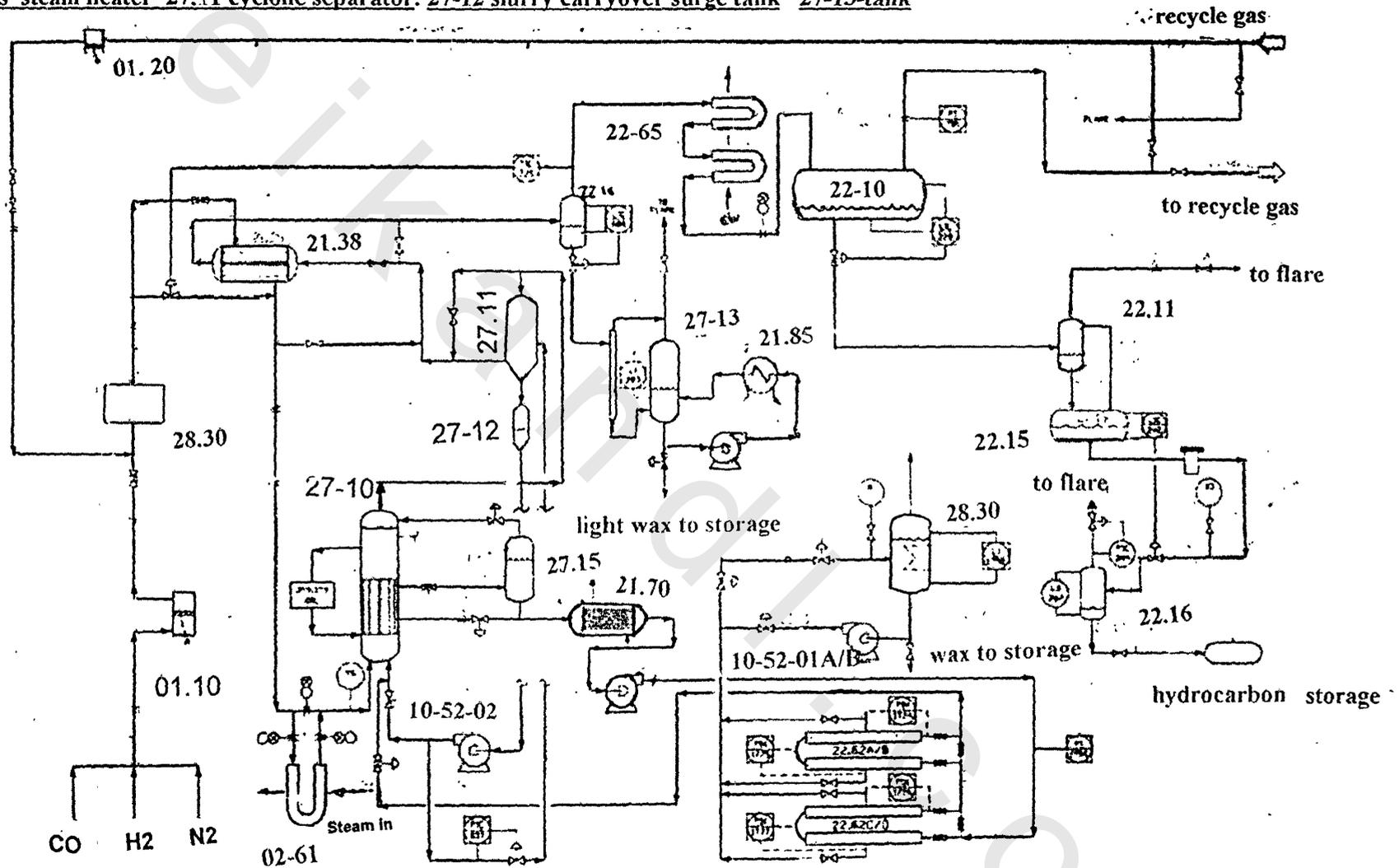


Figure 3-6 Process Flowchart for Liquid Phase Fischer-Tropsch Synthesis in the LaPorte Alternative Fuel Development Unit

Four **RUNS** were chosen for simulation in order to scan different operating conditions. The experimental conditions are those corresponding to Laporte AFDU pilot plant (**RUNS NO.: AF-R16.3A, AF-R16.1B, AF-R16.1C and AF-R15.1C**). Copies of the original documents are displayed in Appendix C. A summary of the reactor conditions for each run is given in **table (3-3)**. Analysis of the feed gas stream in each case is given in **table (3-4)**.

Table (3-3) Reactor Conditions in Laporte AFDU Pilot Plant

Run No.	AF.R.16-1B	AF.R.16-1C	AF.R.16-3A	AF.R.15-1C
Temperature, °K	532	532	534	500
Pressure, bar	49.97	49.97	49.98	49.97
Inlet superficial gas velocity, m/s	0.1248	0.1245	0.1832	0.1318
Slurry velocity, m/s	0.007	0.007	0.007	0.007
Solids holdup ϵ_s in 3-phase (g-l-s)	0.118	0.118	0.116	0.164
Solids holdup ϵ_s in 2-phase (l-s)	0.229	0.23	0.242	0.255
Catalyst weight, kg	176.9	176	173.7	390.1
Catalyst vol. in reactor, lit.	191.9	190.9	188.4	262,4
Expanded bed height, m	6.33	6.33	6.34	6.27
Diameter, m	0.57	0.57	0.57	0.57
Catalyst	cobalt	cobalt	cobalt	cobalt
Catalyst density, kg/m ³	1996	1996	1996	<u>1996</u>
Catalyst diameter, micron	50	50	50	50

Table (3-4) feed gas composition for the Laporte AFDU Pilot Plant for the different RUNS

Run No.	AF.R.16-1B	AF.R.16-1C	AF.R.16-3A	AF.R.15-1C
H ₂	0.4425	0.4637	0.4208	0.5289
CO	0.3772	0.3678	.383	0.3762
H ₂ O	0.0	0.0	0.0	0.0
CO ₂	0.0099	0.009	0.0089	0.0009
N ₂	0.062	0.0582	0.0586	0.0632
Others (recycle HC.)	0.108	0.101	0.09	0.03
Total	1.0	1.0	1.0	1.0
Total, moles/hr	259.55	259.1	379.33	291.89
Total, kg/hr	1905.87	1832.2	2856	1887.39

Taking case (RUN 16-1B) to start with the following results are obtained.

3-2-3-1- Gas holdup:

To start with, model prediction of gas holdup $\epsilon_g = 0.454$ which is close to the two values (0.505 and 0.473) measured by two different techniques as shown in Appendix C. This confirms the validity of the two- bubble class model of Krishna and Ellenberger [1996].

3-2-3-2-Conversion

Conversion of both hydrogen and carbon monoxide are higher than the pilot results, 85 % vs. 60 % for hydrogen and 75 % vs. 33 % for carbon monoxide. Searching for the reason behind this discrepancy it was discovered that Van der Laan et al., [1999] used values for diffusivity necessary to calculate mass transfer coefficients in equations (2-28, 2-29) estimated from the correlation of Erkey,

Rodden and Akgerman [1990], these values are ten times higher than the values reported by **Stern et al. [1982]** under similar conditions as shown in the table (3-5).

Using the diffusivity values utilized by **Stern et al. [1982]** in our calculations reduced the conversion of H₂ to 50 % instead of 85 % as previously calculated and the CO conversion to 45.5 % instead of 75 %, while H₂ conversion is under estimated, CO conversion is still over estimated. It is to be noticed here that the values for H₂ and CO diffusivities are the same for **Stern et al. [1982]**, CO has nearly 1/2 the diffusivity value in case of **Van der Laan et al. [1999]**. In the present work diffusivity values for H₂ shall be taken equal to 3.24×10^{-9} , m²/s, while that for CO will be taken equal to 1.53×10^{-9} , m²/s. Conversion predictions using these values are 49.5 % for H₂ conversion and 39.9 % for CO conversion. Actual experimental values reported in Appendix C are 59.9 % and 33.1 % for H₂ and CO conversion respectively as shown in **table (3-6)**. Diffusivity and hence mass transfer coefficients have strong influence on the reactants concentrations in the bubble column slurry reactor and hence synthesis gas conversion.

3-2-3-3-Product hydrocarbon selectivity

product hydrocarbon molar selectivities and hence weight selectivity were calculated using **Van der Laan et al.[1999]** Olefin Readsorption Product Distribution model described in chapter (1). The results for **RUN 16-1B** are shown in **table (3-7)** compared to the actual pilot plant results. It is clear that there are significant deviations between the model predictions and the actual results. Light hydrocarbons selectivities determined by the model are much higher than the actual results which osculated in a much lower selectivity for the higher carbon number hydrocarbons (C₄₊).

3-2-3-4-Reactor productivity.

The model predicts a reactor productivity of 108 kg/h while the actual production is reported as 1155.1 grams of HC produced/ kg cat oxide –hr, i.e $1155.1 \times 176.9 \times 10^{-3} = 204.34$ kg/h., another measure of the reactor productivity is 139.23 grams of HC/lit.of reactor vol.-hr, i.e. $139.23 \times (3/4 \times (0.57)^2 \times 6.33) / 4 = 224.893$, kg/hr.

This concludes that the model predictions for reactor productivity are much less than the actual as a result of the high selectivity of light hydrocarbons.

Table (3-5) diffusivities values used by Van der Laan et al., [1999] and Stern et al. [1982]

Component	Van der Laan et al., [1999]	Stern et al. [1985]
H ₂	3.851 * 10 ⁻⁸ , m ² /s	3.24 * 10 ⁻⁹ , m ² /s
CO	1.53 * 10 ⁻⁸ , m ² /s	3.24 * 10 ⁻⁹ , m ² /s
N ₂	1.54 * 10 ⁻⁸ , m ² /s	3.24 * 10 ⁻⁹ , m ² /s

Table (3-6) Synthesis gas conversion for run AF.R.16-1B using different values of diffusivity.

Item	Pilot plant	Vander laan et al, 1999	Stern, et al., 1982	present
H ₂ conversion/ pass mole%	59.5	85	50	49.5
CO conversion/ pass mole%	33.1	75	45.5	39.9

Table (3-7) Product Hydrocabons weight and selectivity

Component	Pilot plant	Model
	Wt %	Wt %
CH ₄	13.95	24
C ₂ H ₆	2.06	9.33
C ₂ H ₄	0.08	12.58
C ₃ H ₈	2.4	10.08
C ₃ H ₆	1.46	2.54
Sum C ₄ H ₁₀	1.89	1.15
Sum C ₄ H ₁₀	1.24	2.73
Sum C ₄ +	76.9	30.59

The above mentioned discrepancies are not unexpected since the α -Olefin Readsorption Product Distribution Model (ORPDM) of Van der Laan et al. [1999] parameters were optimized to fit iron based catalyst FT synthesis results. It is known that product distribution is primarily a function of the catalyst type. The data under investigation corresponds to a cobalt based catalyst. Optimizations of the (ORPDM) parameters were attempted but unfortunately data on molar hydrocarbon selectivities were absent which was necessary for the parameter estimation. Several trials were then performed for adjusting the model parameters which ended with the parameters listed in table (3-8) as the best achieved ones. Another modification was necessary that is the CH₄ selectivity is calculated. Now the modified (ORPDM) with the new parameters will be utilized to predict product distribution and reactor productivity for the different investigated runs. Tables (3-9, 3-10) compare the model predictions with the actual pilot plant data as $\theta_1 t_p^1 \wedge 1.5$ instead $\theta_1 t_p^1$ as in (ORPDM) model chapter (1).

Table (3-8) ORPDM model parameters adjusted for cobalt based catalyst

Parameter	Value
t_0	$3.71 P_{H_2}^{-0.5}$
t_p^1	8
t_p^2	1.7
c	0.35
p	$14 P_{H_2}^{-0.26} P_{CO}^{0.40}$
k_R	$3.32 * 10^{-4} \frac{P_{H_2}^{1.4} P_{CO}^{-0.49}}{\phi_{V,0} / w}$

Table (3-9) shows model predictions for gas hold up, synthesis gas conversion and production rates for the four different cases with the operating conditions listed above in **table (3-3)**. It is to be noticed that **RUNS 16-1B and 16-1C** are nearly identical; they are so chosen to reflect the normal variability. Generally speaking estimation of the gas hold up is of remarkable accuracy. The predicted value in most cases represents the average of the two measurements performed by two different techniques. The same talking is also true for the production rate, the model predictions represent the average of the two values calculated from reactor productivity based on the weight of the catalyst and based on the reactor volume. This, despite the variations encountered in the weight selectivity for the light hydrocarbons see **(table 3-10)** reflect the relative accuracy of most of the product distribution. It is known that cobalt catalyst produces predominantly paraffins which are reflected on the estimated high paraffin content of the products which ranged between 80 % and 90 %. The higher value corresponded to the higher initial hydrogen content in the feed gas stream for **RUN NO. 15-1C** (feed ratio).

Table (3-9) Gas hold up, conversions and production rates for different RUNS

RUN NO.	AF.R.16-1B		AF.R.16-1C		AF.R.16-3A		AF.R.15-1C	
	Pilot	Model	Pilot	Model	Pilot	Model	Pilot	Model
Gas hold up	0.505	0.455	0.501	0.455	0.502	0.5	0.414	0.4
	0.473		0.473		0.472		0.358	
H ₂ Conversion / pass, mole %	59.9	50.1	60.5	50.1	43.0	37.7	15.8	28.2
CO conversion / pass, mole %	33.1	39.9	33.2	32.8	20.7	27.5	9.1	26.3
Reactor productivity, kg/hr	204		199.3		185.4		63.7	
	225	212.8	219	217	203.9	195	70.2	67.18

Table (3-10) Product hydrocarbons weight selectivity for different RUNS

RUN NO.	AF.R.16-3A		AF.R.16-1B		AF.R.16-1C		AF.R.15-1C	
	Pilot	Model	Pilot	Model	Pilot	Model	Pilot	Model
CH ₄	17.67	15.2	13.95	15.33	14.61	15.5	13.88	14.23
C ₂ H ₆	2.48	1.82	2.05	1.84	2.42	1.87	1.5	1.75
C ₂ H ₄	-0.05	0.95	0.08	0.86	0.15	0.78	1.01	0.3
C ₃ H ₈	2.64	1.33	2.4	1.34	2.51	1.37	1.90	1.32
C ₃ H ₆	1.73	2.2	1.46	2.12	1.69	2.05	3.57	1.26
Sum C ₄ H ₁₀	1.55	1.5	1.89	1.52	1.90	1.55	2.57	1.54
Sum C ₄ H ₈	1.45	2.2	1.42	2.12	1.21	2.04	3.4	1.21
Sum C ₄ +	72.53	74.8	76.96	75.17	75.51	74.84	72.98	78.4
Olefins %		18.3		17.3		16.5		8.7
Paraffins %		81.7		82.7		83.5		91.3

In conclusion the developed software and the model parameters accurately responded to variations in operating conditions and the predictions are in very good agreement with experimental results.