DESIGN OF SLURRY REACTOR FOR INDIRECT LIQUEFACTION APPLICATIONS. QUARTERLY TECHNICAL PROGRESS REPORT, JANUARY 1991--MARCH 1991

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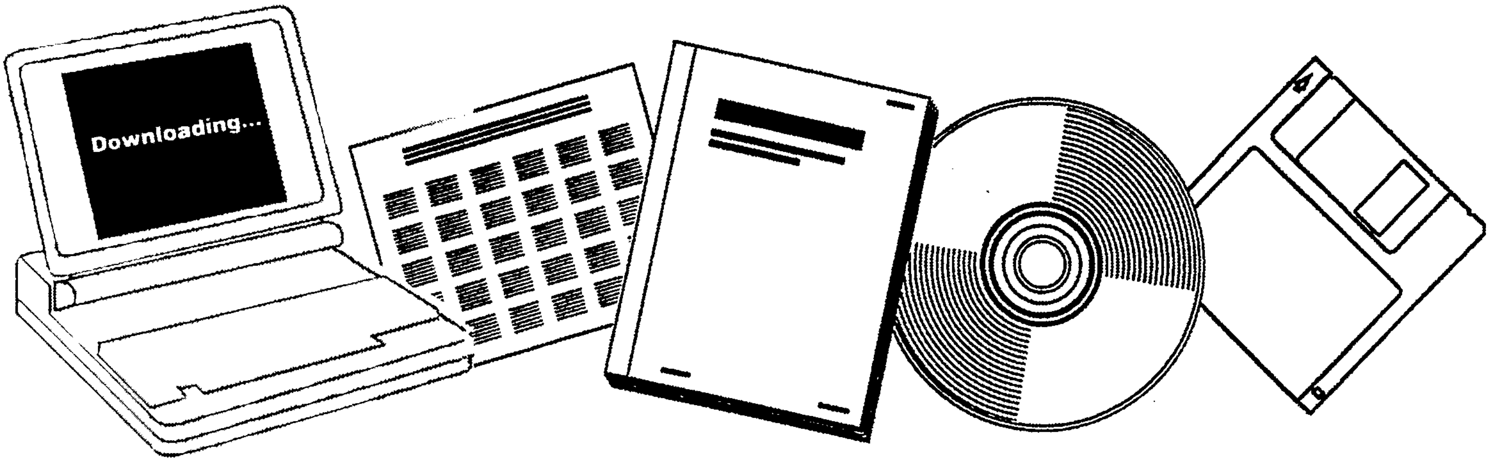

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QUARTERLY TECHNICAL PROGRESS REPORT

January 1991 - March 1991

DESIGN OF SLURRY REACTOR FOR INDIRECT LIQUEFACTION APPLICATIONS

by

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Introduction

The objective of this project is to design a conceptual slurry reactor for two indirect liquefaction applications;production of methanol and production of hydrocarbon fuels via Fischer-Tropsch route. The work will be accomplished by the formulation of reactor models for both the processes and use computer simulation. Process data, kinetic and thermodynamic data, heat and mass transfer data and hydrodynamic data will be used in the mathematical models to describe the slurry reactor for each of the two processes. The cost of current vapor phase reactor systems will be compared with cost estimated for the slurry reactor systems. For the vapor phase systems, upstream and downstream processing equipments may have to be included during cost analysis for a meaningful cost comparison.

Finally, we will point out any inadequacies in the technical database currently available for a commercial design of the slurry reactor and identify research needs to improve upon the slurry reactor design. Assumptions used in the design will be documented.

Project Status

During last month, work was performed in the following areas:

Fischer-Tropsch synthesis:

- Assumptions for FT synthesis
- Product distribution and stoichiometry

- Kinetics of Fischer-Tropsch synthesis
- Differences between FT synthesis and methanol synthesis

Methanol synthesis:

- Effects of gas phase modeling
- Test of kinetic models
- Effects of slurry concentration
- Minor changes in the reactor model

Fischer-Tropsch Synthesis:

Fischer-Tropsch synthesis is essentially hydrogenation of CO which yield saturated and unsaturated compounds of the homologous series. It permits the synthesis of hydrocarbons ranging from methane to high melting paraffins depending on the catalyst, temperature and type of process employed. A small quantity of byproducts such as alcohols, aldehydes, ketones etc. are also formed. Given the large number of products formed during FT synthesis, it is necessary to make some simplifying assumptions for reactor design.

Assumptions for FT synthesis:

1) The FT synthesis products obey Schulz-Flory distribution. This assumption has been found to

be valid over the entire range of products of an iron catalyst (Satterfield and Huff, 1982).

$$m_n = \alpha m_{n-1} = \alpha^{n-1} m_1 \tag{1}$$

Here m_n refers to the product distribution as formed on the catalyst. The probability of chain growth α is taken to be constant over the entire carbon distribution.

2) The products consist only of n-alkanes. These are in fact the main products on many catalysts and little design error will be introduced by lumping the methyl branched isomers and n-alkenes with the n-alkanes.

3) The liquid and gas phases exhibit ideal behavior. A mixture of n-alkanes is a good approximation to an ideal liquid mixture. Although the pressure in the FT synthesis usually exceeds that for which ideal gas behavior may be assumed, the partial pressures of the individual product components are very small.

Product Distribution and Stoichiometry:

The FT synthesis reaction for the production of n-alkanes can be written as

$$xCO + (2x+1)H_2 \rightarrow C_xH_{2x+2} + xH_2O \tag{2}$$

If the distribution is S-F, then the mean carbon number of the products (on a molar basis) is given as

$$x=\frac{1}{1-\alpha} \qquad (3)$$

Substituting for x in Equation 2 shows that (3-α) mole of H_2 is consumed when 1 mole of CO reacts to paraffin products.

The water formed as a primary product is converted to carbon dioxide by the water gas shift reaction.

$$H_2O+CO-CO_2+H_2 \qquad (4)$$

A more general approach for the stoichiometry of FT synthesis was presented by Stern et al. (1985). The reaction was approximated as

$$\gamma_{CO}CO+\gamma_{H_2}H_2-\gamma_{HC}C_xH_y+\gamma_{H_2O}H_2O \qquad (5)$$

The values of γ_i, x and y are expressed in terms of following variables

α the probability of chain growth

λ the fraction of paraffinic hydrocarbons

$$\gamma_{CO}=\frac{1}{D} \tag{6}$$

$$\gamma_{H_2}=\frac{2+(1-\alpha)^2+\lambda\alpha(1-\alpha)}{D} \tag{7}$$

$$\gamma_{HC}=\frac{(1-\alpha)}{D} \tag{8}$$

$$\gamma_{H_2O}=\frac{1}{D} \tag{9}$$

$$D=3+(1-\alpha)^2+\lambda\alpha(1-\alpha) \tag{10}$$

$$x=(1-\alpha)^{-1} \tag{11}$$

$$y=2[(1-\alpha)^{-1}+(1-\alpha)+\lambda\alpha] \tag{12}$$

The value of chain growth probability factor (α) and fraction of paraffins in the product (λ) are a function of the catalyst and operating conditions. For the production of high molecular weight products, value of α has been found to be in the range of 0.85-0.95.

Although the FT reaction stoichiometry presented by Stern et al. (1985) is more general (i.e. it accounts for the production of both paraffins and olifins), however, for the purpose of reactor design FT reaction can be approximated for the production of only n-alkanes with little error.

The composition of the gas and liquid product streams will be determined by phase equilibria calculations using the product analysis data from literature.

Kinetics of Fischer-Tropsch Synthesis:

Iron Catalyst

The reaction kinetics of Fischer-Tropsch synthesis over iron catalyst have been investigated by a number of researchers. The various kinetic expressions have been reviewed by Huff and Satterfield (1984) and Zimmerman and Bukur (1990). The rate expression proposed by Anderson (1956) was found to be particularly useful

$$r_{FT}=\frac{k_o P_{CO} P_{H_2}}{P_{CO}+aP_{H_2O}} \tag{13}$$

This equation includes water inhibition effect. At synthesis gas conversion below about 60 % Equation (13) reduces to

$$r_{FT}=k_1 P_{H_2} \tag{14}$$

Huff and Satterfield (1984) derived an alternate form of expression based on the observed hydrogen dependance for a fused-magnetite catalyst.

$$r_{FT}=\frac{k_o P_{CO} P_{H_2}^2}{P_{CO} P_{H_2}+b P_{H_2O}} \tag{15}$$

Equations (13) and (15) have the same form if the constant 'a' in Equation (13) depends on the H_2 partial pressure i.e. $a = b/H_2$.

For precipitated iron catalyst (100Fe/0.3Cu/0.2K), Zimmerman and Bukur (1990) observed that Equation (3) gave a better fit to their data compared to Equation (5). Similar observations were made by Nettelhoff et al. (1985) using a precipitated, unpromoted iron catalyst. Based on these observations, kinetic expression given by Equation (3) will be used for precipitated iron catalyst in the FT reactor model.

Water gas shift reaction:

The water gas shift reaction occurs readily over potassium promoted iron catalyst. The shift reaction enables CO rich feeds to be utilized efficiently without the need for external shift. Both Equations (1) and (2) for the FT and WGS reaction must be considered to accurately predict both H_2 + CO conversions and H_2/CO usage ratio which requires knowledge of WGS kinetics.

The following rate expression for water gas shift reaction has been selected based on literature information (Kuo, 1983; Zimmerman and Bukur, 1990).

$$r_{WGS}=k_{wo}\frac{(P_{CO}P_{H_2O}-P_{CO_2}P_{H_2}/K_P)}{P_{CO}+aP_{H_2O}} \tag{16}$$

Cobalt Catalyst:

Fischer-Tropsch synthesis on a cobalt catalyst has been investigated by a number of researchers (Sarup and Wojciechowski, 1988, 1989; Yates and Satterfield, 1991). Specific activity of cobalt catalyst is high for FT synthesis (Withers et al., 1990). The FT synthesis over cobalt catalysts produce mostly n-alkanes and 1-alkenes. However, in contrast to most iron-based FT catalysts, cobalt is not very active for the water gas shift reaction. Yates and Satterfield (1991) reviewed and tested various literature rate expressions for FT synthesis over cobalt catalyst. The following kinetic equation was recommended based on their study.

$$r_{FT}=\frac{k_cP_{CO}P_{H_2}}{(1+cP_{CO})^2}. \tag{17}$$

Differences between FT synthesis and methanol synthesis:

FT synthesis differs from methanol synthesis in a number of ways. Some of the important differences which affect the reactor design are listed below:

1) Due to conversion of synthesis gas to liquid products in a FT reactor, the gas flow rate decreases more rapidly along the reactor height thus affecting the hydrodynamics of the reactor. The effects of decreasing gas flow rates on hydrodynamics and mass transfer in a slurry bubble column have not been reported in literature. Following approximations can,however, be made in absence of direct information.

i) Hydrodynamic parameters can be estimated at short intervals of reactor height. using the actual gas velocity at that height.

ii) Hydrodynamic parameters can be estimated using an average gas velocity. Some of the hydrodynamic parameters such as liquid backmixing and catalyst particles suspension are expected to be more strongly dependent on the inlet gas velocity.

We plan to investigate and compare the effects of these approximations on the reactor performance, using our reactor model.

2) In commercial reactors ,the influence of hydrostatic head on total pressure is usually less than 2 % for methanol synthesis, while for FT synthesis the hydrostatic head can contribute up to 6

% of the total pressure. Therefore, for FT reactor model the influence of hydrostatic head on gas expansion will be taken into consideration.

3) Due to higher heat of reactions, the internal heat exchanger can occupy between 16 to 20 % of the reactor volume in a FT synthesis reactor thus reducing the free cross-sectional area for gas flow. The actual superficial gas velocity will be based on free cross-sectional area of the reactor. Presence of large number of heat exchanger tubes could also affect the mixing patterns inside the reactor. However, there is a lack of information on this subject in the literature.

Methanol Synthesis:

Effects of Gas Phase Modeling:

Our computer model allows simulation of the slurry reactor for the following modes:

1) Gas plug flow; Liquid axial dispersion

2) Gas axial dispersion; Liquid axial dispersion

The simulation of methanol synthesis reactor with the two modes showed that the productivity of the reactor decreased by about 10% when the gas was assumed to be axially dispersed. In large reactors, both gas and liquid phases are expected to axially dispersed. Therefore, PDU reactor for methanol synthesis was modeled assuming axial dispersion for both phases.

Test of kinetic models:

Earlier kinetic models of Berty et al. (1983) and Wedel et al. (1988) were tested in methanol synthesis reactor model. It was, however, pointed out that these power law models have limited applicability. The kinetic model of Graff et al. (1988) is based on a proper analysis of reaction mechanism for methanol synthesis. This model was further tested to simulate the PDU reactor data. The reaction rates predicted by this kinetic model were found to be too low to predict the performance of PDU reactor. This indicated that the activity of the catalyst used by Air Products was significantly higher. In order to obtain a suitable correction factor for the kinetic expression, data for a run at the highest gas velocity (0.194 m/s) was selected. This ensured that the reaction was not mass transfer limited. The reactor model was then used to predict the performance of the PDU reactor for runs with different conditions. The effects of slurry concentrations observed on reactor performance are discussed below.

Effects of Slurry Concentration:

The effect of slurry concentration on reactor performance was analyzed for a set of runs for which slurry concentration was varied from about 30 wt % to 42.5 wt % while other operating variables did not change significantly. Tables 1 gives the experimental and predicted production rates for this set of runs. It can be seen that the predicted rates were higher as the slurry concentration increased beyond 31 wt %. This can be attributed to changes in mixing patterns in the reactor with increasing slurry concentration. Higher slurry concentration can result in poor gas-liquid mixing in some part of the reactor (mainly in the distributor region) and/or reduced gas-liquid mass transfer due to increased bubble coalescence. It was determined, however, that

Table 1. Effects of slurry concentration on reactor performance (PDU run E8)

Run #	Gas Velocity (m/s)	Slurry Conc. (wt %)	Production Rate STD		Error (%)
			Exptl.	Predicted	
28	0.154	29.2	8.98	8.78	2.0
11	0.155	31.0	9.28	9.1	2.0
6	0.155	34.3	10.0	10.56	5.6
1	0.15	38.3	10.04	11.29	11.0
2	0.154	42.5	9.1	10.57	16.0

mass transfer coefficient for run # 2 (42.5 wt %) had to be decreased by about 60 % of the estimated value in order to match the predicted and experimental reactor performances. This also meant that the estimated mass transfer coefficient for run # 2 (42.5 wt%) had to decrease by about 70 % as compared to run # 11 (31.0 wt%). Such a large decrease in mass transfer coefficient over this range of slurry concentration is not supported by literature data. It is thus likely that changes in both mixing patterns and mass transfer rate contribute to lower the performance of slurry reactor at high slurry concentrations.

Based on the literature results, the performance of a slurry reactor can be affected by catalyst particle size and concentration in the following ways

* Gas-liquid mass transfer rate can be reduced with increasing slurry concentration due to increase in apparent slurry viscosity.

* There can be stagnant zones in the reactor at high slurry concentration and/or low gas velocities.

* Small catalyst particles can penetrate the diffusional liquid film and enhance absorption rate until the film gets saturated with catalyst particles.

In view of the above, the PDU data from APCL for methanol synthesis in a slurry reactor was analyzed to explain some of the discrepancies observed in the predicted and experimental reactor performances. It was shown in the last report (Jan, 1991) that the predicted values of production rate were higher as the slurry concentration increased beyond 31 wt % (based on weight of reduced catalyst). The runs at a gas velocity of 0.15 m/s were compared. It was also mentioned that these differences could not be explained by the reported decrease in mass transfer rate with increasing slurry concentration. There is a possibility of increase in the volume of stagnant zones in the reactor with increasing slurry concentration. However, for the high gas velocity used for these runs (0.15 m/s) and low volume fraction of solids (7.0 -10.0 %), used for these runs, it is unlikely to have any significant volume of stagnant zones in the reactor, for a properly designed gas distributor. The volume of stagnant zones may, however, become significant at low gas velocities (< 0.1 m/s).

It has been pointed out recently that small catalyst particles in a slurry reactor can enhance absorption rate by penetrating the diffusional liquid film (Alper et al., 1980; Wimmers and Fortuin, 1988). Using fine catalyst particles (< 5 μm), Alper et al. (1980) observed an enhancement of up to 2 with increase in catalyst concentration. Any subsequent increase in catalyst concentration had no measurable effect. Unlike gas-liquid reactions, the absorption rate failed to increase after a certain catalyst concentration. Wimmers and Fortuin (1988) compared Pd/C and Pd/Al_2O_3 catalyst particles to study the effects on absorption enhancement. It was observed that Pd/C catalyst particles enhances the gas absorption considerably while no enhancement was observed with Pd/Al_2O_3 catalyst particles. This difference in behavior was attributed to a difference in adhesion between the catalyst particles and the surface of the hydrogen bubbles.

The PDU data is being further analyzed, in view of above.

Minor changes in the reactor model:

Following minor changes were incorporated into the reactor model:

1) To calculate final reactor length, the volume occupied by the heat exchanger tubes and the volume of vapor space is added to the active reactor volume.

2) The gas velocity at the reactor bottom is calculated using pressure at reactor bottom which includes pressure due to hydrostatic head of the slurry.

NOTATION

a	H_2O adsorption coefficient, Equation (13), (16)
b	H_2O adsorption coefficient, Equation (15) Pa
c	CO adsorption coefficient, Equation (17), 1/Pa
k_o	FT rate constant, Equation (13) kmol/kg-cat.s.Pa
k_1	FT first order rate constant, Equation (14), kmol/kg-cat.s.Pa
k_c	reaction rate constant, Equation (17), kmol/kg-cat.s.Pa^2
K_P	WGS equilibrium constant
m_n	mole fraction of products with carbon number n
P_j	partial pressure of species j, Pa
r_k	rate of reaction k, kmol/kg-cat.s
x	average number of carbon atoms in the product hydrocarbon
y	average number of atomic hydrogen in the product hydrocarbon

Subscripts

FT	Fischer-Tropsch
j	species index ($j=C_xH_y,CO,H_2,H_2O$)
WGS	Water-gas shift

Greek Letters

α	probability of chain growth
γ	stoichiometric coefficient of species j
λ	fraction of paraffins in the product

REFERENCES

Alper,E., Wichtendahl,B., and Deckwer, W.D., "Gas Absorption Mechanism in Slurry Reactors", Chem. Eng. Sci., Vol. 35, p. 217-22 (1980).

Anderson, R.B., "Catalysts for the Fischer-Tropsch Synthesis", in catalysis, Vol. iv, Emmett,P.H.,Van Nostrand Reinhold New York p. 257-371 (1956).

Berty, J.M., Lee, S., Parekh, V., Gandhi, R., and Sivagnanam, K., "Diffusional Kinetics of Low Pressure Methanol Synthesis", Proceedings of PACHEC 83, Vol. 11, 191 (1983).

Graff, G.H., Winkelman, J.G.M., Stamhuis. E.J., and Beenackers, A.A.C.M., "Kinetics of the Three-Phase Methanol Synthesis", Chem. Eng. Sci., Vol. 43, No. 8, p. 2161-68 (1988).Wedel, W.V., Ledakcwicz, S., and Deckwer, W.D., "Kinetics of Methanol Synthesis in the Slurry Phase"Chem. Eng. Sci., Vol. 43, No. 8, p. 2169-74 (1988).

Huff, G.A. Jr., Satterfield, C.N., "Intrinsic Kinetics of the Fischer-Tropsch Synthesis on a Reduced-Magnetite Catalyst", Ind. Eng. Chem. Process Des. Dev., vol. 23, p. 696-705 (1984).

Nettelhoff, H.R., Kokuun, S., Ledakowicz, Deckwer, W.D., "Studies on the Kinetics of Fischer-Tropsch Synthesis in Slurry Phase", Ger. Chem. Eng., Vol. 8, p.177-85 (1985).

Sarup, B., Wojciechowski, B.W., "Studies of the Fischer-Tropsch Synthesis on a Cobalt Catalyst 1. Evaluation of Product Distribution Parameters from Experimental Data", Can. J. Chem. Eng., Vol. 66, p. 831-42 (1988).

Sarup, B., Wojciechowski, B.W., "Studies of the Fischer-Tropsch Synthesis on a Cobalt catalyst. II. Kinetics of Carbon Monoxide Conversion to Methane and Higher Hydrocarbons", Can. J. Chem. Eng., Vol.67, p.62-74 (1989).

Satterfield, C.N., Huff, G.A.,Jr., J. Catalyst, Vol. 73, p.187 (1982).

Stern, D., Bell, A.T., and Heinemann, H., "A Theoretical Model for the Performance of Bubble-Column Reactors Used for Fischer-Tropsch Synthesis", Chem. Eng. Sci., Vol. 40, No. 9, p.1665-77 (1985).

Wimmers, O.J., Fortuin, J.M.H., "The Use of Adhesion of Catalyst Particles to Gas Bubbles to Achieve Enhancement of Gas Absorption in Slurry Reactors-II. Determination of the Enhancement in a Bubble-Containing Slurry Reactor", Chem. Eng. Sci., Vol. 43, p.313-19 (1988).

Withers, H.P., Eliezer, K.F., and Mitchell, J.W., Ind. Eng. Chem. Res., Vol. 29, p. 1807 (1990).

Yates, I.C., Satterfield, C.N., "Intrinsic Kinetics of the Fischer-Tropsch Synthesis on a Cobalt Catalyst", Energy & Fuels, Vol. 5, p. 168-73 (1991).

Zimmerman, W., Bukur, D.B., "Reaction Kinetics over Iron Catalysts used for the Fischer-Tropsch Synthesis", Cand. J. of Chem. Eng., Vol. 68, p. 292-301 (1990).

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