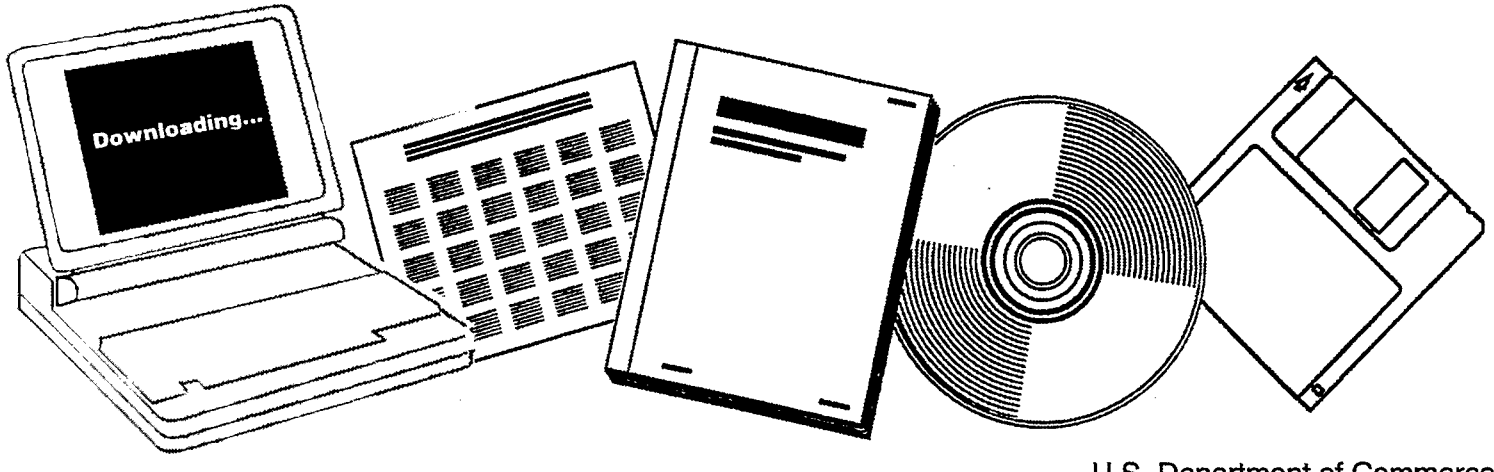
DESIGN OF SLURRY REACTOR FOR INDIRECT LIQUEFACTION APPLICATIONS: QUARTERLY TECHNICAL STATUS REPORT, APRIL--JUNE 1990

VIKING SYSTEMS INTERNATIONAL, INC.
PITTSBURGH, PA

10 JUL 1990



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DE92008957
DOE/PC/89870--T7
DE92 008957

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 this quarter, work was performed in the following areas:

* Review of kinetic models for methanol synthesis reactions
* Estimations of physical, transport and thermodynamic properties
* Development of computer codes

Kinetic Models for Methanol Synthesis:

In the synthesis of methanol, the following chemical reactions are primarily discussed:

$$CO + 2H_2 = CH_3OH \qquad (1)$$

$$CO_2 + H_2 = CO + H_2O \qquad (2)$$

$$CO_2 + 3H_2 = CH_3OH + H_2O \qquad (3)$$

Several researchers have investigated the kinetic rate for methanol synthesis, using $Cu/ZnO/Al_2O_3$ catalyst. The proposed models can be divided into power law rate expressions and mechanistic models.

Graff et al. (1988) proposed a mechanistic model for the kinetics of three-phase methanol synthesis based, on extensive set of experiments. The proposed model is given below:

$$r_{MeOH,1} = \frac{k_{ps,1}K_{CO}(f_{CO}f_{H2}^{3/2} - f_{CH3OH}/(f_{H2}^{1/2}K_{p1}^{\circ}))}{(1 + K_{CO}f_{CO} + K_{CO2}f_{CO2})(f_{H2}^{1/2} + K_{H2O}/K_{H2}^{1/2})f_{H2O})}$$

$$r_{H2O,2} = \frac{k_{ps,2}K_{CO2}(f_{CO2}f_{H2} - f_{H2O}f_{CO}/K_{p2}^{\circ})}{(1 + K_{CO}f_{CO} + K_{CO2}f_{CO2})(f_{H2}^{1/2} + (K_{H2O}/K_{H2}^{1/2})f_{H2O})}$$

$$r_{MeOH,3} = \frac{k_{ps,3}K_{CO2}(f_{CO2}f_{H2}^{3/2} - f_{CH3OH}f_{H2O}/(f_{H2}^{3/2}K_{p3}^{\circ}))}{(1 + K_{CO}f_{CO} + K_{CO2}f_{CO2})(f_{H2}^{1/2} + (K_{H2O}/K_{H2}^{1/2})f_{H2O})} (=r_{H2O,3})$$

The kinetic and the adsorption constants are described by

$$k_{ps,1} = (2.12 + 0.23)\ 10^{3} \exp((-23600 + 120)/R_gT)$$

$$k_{ps,2} = (2.58 + 0.66)\ 10^{15} \exp((-52580 + 260)/R_gT)$$

$$k_{ps,3} = (1.09 + 0.05)\ 10^{-2} \exp((-11544 + 48)/R_gT)$$

$$K_{CO} = (5.15 + 1.16)\ 10^{-11} \exp((21870 + 240)/R_gT)$$

$$K_{CO2} = (7.83 + 1.29)\ 10^{-5} \exp((9800 + 170)/R_gT)$$

$$K_{H2O}/K_{H2}^{1/2} = (2.3 + 1.46)\ 10^{-12} \exp(27270 + 500)/R_gT)$$

Power law models for methanol synthesis in three-phase slurry reactors have been proposed by Berty et al. (1983), Wedel et al. (1988) and Lee (1990). The proposed models are shown below:

Berty et al. (1983)

$$r_{MEOH,1} = k_1 (C_{H2} - \frac{C_{MEOH}}{K_{eq,1}C_{H2}C_{CO}})$$

$$r_{H2O,2} = k_2 \left(C_{H2} - \frac{C_{CO}C_{H2O}}{K_{eq,2}C_{CO2}}\right)$$

Here $K_{eq,1}$ and $K_{eq,2}$ are equilibrium constants for reactions 1 and 2 respectively.

Reported values for rate constants:

$$k_1 = 3.914 \exp(-7489/T)$$

$$k_2 = 1.189 \times 10^{-2} \exp(-5068.4/T)$$

Wedel et al. (1988)

$$r_{MeOH} = 5.5 \exp(-13466/R_gT)\, p_{H2}^{0.4}\, p_{CO}^{0.18} - 5970 \exp(-20537/R_gT)\, p_{CH3OH}^{0.13}$$

The model proposed by Lee (1990) is based on extensive set of data, covering range of syngas composition from H_2-rich to CO-high.

$$r_{MeOH} = A \exp(-E/R_gT)(C_{H2} - C_{H2,eq})$$

here

$A = 3380\ m^3/kg.s$

$E = 18{,}800$ kcal/kmol

Estimation of Liquid and Slurry Phase Properties:

Various literature correlations and models were reviewed to select suitable methods for estimation of physical properties (e.g. density, viscosity), thermodynamic properties (e.g. phase equilibria) and transport properties (e.g. diffusivities, thermal conductivity). Available experimental data was used to develop suitable correlations, whenever necessary.

Properties of Liquid

Two liquids namely, Freezene-100 and Drakeol 10 have been used by Air Products and Chemicals for its liquid phase methanol process development program. The oil, Drakeol 10 from Penreco was selected, based on plant trials, when Witco announced discontinuation of Freezene-100.

Following correlations were developed for density and viscosity of Freezene 100 and Drakeol 10, based on the data from the reports of Air Products and Chemicals:

Density:

Freezene 100

$\rho_L = 1037 - 0.645\ T$ in kg/m^3

where T is in K

Drakeol 10

$\rho_L = 1038.8 - 0.635\ T$ in kg/m^3

Viscosity:

The following equation was obtained for viscosity of Freezene 100, from linear regression of the data, from Figure VII-C-1 in the final report of Air Products and Chemicals (1987).

$\mu_L = 10^{-3} \exp(-2.84 + 1570/T)$ in kg/m.s

where T is in K

A similar equation for oil Drakeol 10 was obtained, based on data from Air Products and Chemicals.

$\mu_L = \exp(-12.415 + 2561.88/T)$ in kg/m.s

where T is in K

Specific Heat:

Following correlation was obtained for the specific heat of Drakeol 10, based on the data available from Air Products and Chemicals:

$$C_{PL} = 0.668 + 0.0042\,T \qquad \text{in kJ/kg.K}$$

Properties of Suspension

Suspension Density:

$$\rho_{sus} = V_{cat}\rho_{cat} + (1-V_{cat})\rho_L \qquad kg/m^3$$

where

$$V_{cat} = \frac{\rho_L W_{cat}}{\rho_{cat} - W_{cat}(\rho_{cat} - \rho_L)}$$

and

$$W_{cat} = M_{cat}/M_{sus}$$

Suspension Viscosity:

Several correlations have been proposed in the literature for estimation of slurry viscosities (i.e. Thomas (1965); Deckwer et al. (1980)). These correlations, however, couldn't be tested in absence of experimental data. At Air Products and Chemicals, the slurry viscosities were determined using the correlation by Kunitz (Perry's Hand Book 5th ed. 3-247). We plan to use this correlation for estimation of slurry viscosities.

$$\mu_{SL} = \mu_L \frac{(1 + 0.5e_s)}{(1 - e_s)^4}$$

Specific Heat:

Heat capacity of the slurry can be estimated, knowing the individual heat capacities of the liquid and solid.

$$C_{PS} = W_{Cat} * C_{PC} + [(1-W_{Cat}) * C_{FL}]$$

Diffusivities

Akgerman measured the diffusion coefficients for synthesis gas in high molecular weight liquids ($n\text{-}C_{20}$ and $n\text{-}C_{28}$) and FT waxes under DOE contract DE-AC22-84PC 70032 at temperatures ranging from 373 to 534°K. Based on this study, Akgerman proposed the following equation to estimate the diffusion coefficients.

$$\frac{10^9 D_i}{T^{0.5}} = \frac{94.5}{M_i^{0.239} M_s^{0.781} (\sigma_i\ \sigma_s)^{1.134}} (V_s - b_i V_{so})$$

Here $b_i V_{so} = b_i N \sigma_s^3 / 2$

and $b_i = 1.206 + 0.0632\ (\sigma_i/\sigma_s)$

Available literature correlations for estimation of diffusion coefficients were also tested. These correlations, however, predicted the diffusivities with large errors. It was, therefore, decided to use the correlation proposed by Akgerman to estimate diffusion coefficients for synthesis gas.

Henry's Law Constants

Chao and Lin investigated the solubilities of synthesis gas in high molecular weight solvents ($n\text{-}C_{20}$,$n\text{-}C_{28}$ and $n\text{-}C_{36}$) and Fischer-Tropsch waxes under DOE contract No. DE-AC22-84PC 70024. Solubilities of hydrogen, carbon monoxide, methane and ethylene were measured at

temperatures in the range of 100-300°C and pressure 10-50 atm. The solubilities of methanol and water, however, were not measured.

In a separate study, Graff et al. (1988) measured solubility of CO, CO_2, H_2, CH_3OH and H_2O in the temperature range of 210 to 260 °C in another high molecular weight solvent (squalene). These authors observed that the Henry's coefficients could be well approximated by an equation of the form:

$$H_i = A_i \exp(B_i/T)$$

The available solubility data of different components in high molecular weight solvents would be used to obtain best estimates for coefficients A_i and B_i.

Development of Computer Codes

Following is a summary of the work done so far in developing computer codes for the reactor model.

Computer codes for the reactor model are being developed with a modular approach to computer programming in order to ensure easy modifications by the user. The model equations for the slurry reactor constitute a set of coupled second order nonlinear differential equations. Since these equations are not amenable to analytical solution, a numerical technique was selected. The selected software package COLSYS, developed by Ascher et al. (1981) is based on spline collocation at Gaussian points using a B-spline basis. In order to improve the accuracy

and speed of convergence for the numerical technique, an analytical solution was included in the program. The analytical solution was obtained assuming mass transfer without chemical reaction.

In order to select a suitable correlation for gas holdup estimations, experimental data from Air Products and Chemicals was obtained, to test various literature correlations. This data is being used to estimate the average absolute error, minimum and maximum errors for the selected correlations.

The new reactor configuration at Air Products and Chemicals does not include external recirculation of slurry. The model equations change slightly, in absence of slurry recirculation. However, we plan to keep the reactor model flexible enough, to allow evaluation of reactor performance both with and without external recirculation of slurry.

NOTATIONS

A	Arrhenius frequency factor (m^3/kg.s)
A_i, B_i	constants for component i in the equation for Henry's coefficient
b_i	coefficient which is a function of molecular sizes of solute and solvent
C_{H2}	concentration of hydrogen in liquid (kmol/m^3)
$C_{H2,eq}$	concentration of hydrogen at equilibrium (kmol/m^3)
C_{PC}	specific heat of catalyst particles (kJ/kg.K)
C_{PL}	specific heat of liquid (kJ/kg.K)
C_{PS}	specific heat of slurry (kJ/kg.K)
D_i	diffusivity of component i in the reactor liquid (m^2/s)
E	energy of activation (kcal/kmol)
f_i	fugacity of component i (bar)
H_i	Henry's coefficient for component i (kmol/m^3.atm)
$k_{ps,1}$	pseudo reaction rate constant for reaction 1 (kmol/kg.s.bar)
$k_{ps,2}$	pseudo reaction rate constant for reaction 2 (kmol/kg.s.bar)
$k_{ps,3}$	pseudo reaction rate constant for reaction 3 (kmol/kg.s.bar)
K	adsorption equilibrium constant (1/bar)
K_p	chemical equilibrium constant based on partial pressures
M_{cat}	mass of catalyst in the suspension (kg)
M_{sus}	total weight of the suspension (kg)
M_i	molecular weight of diffusing component i (kg/kmol)
M_s	molecular weight of solvent (kg/kmol)
N	Avogadro number

p_i partial pressure of component i (MPa)

r reaction rate based on weight of catalyst (kmol/kg.s)

R_g gas law constant (1.987 kcal/kmol.°K)

T temperature (°K)

V_{cat} volume fraction of catalyst in suspension

V_s solvent molar volume (m^3/kmol)

V_{so} the theoretical close-packed volume for solvent spheres of diameter o_s (10^{-6} m^3/mol)

W_{cat} weight fraction of catalyst in suspension

Greek

ρ_L density of liquid phase (kg/m^3)

ρ_{cat} density of catalyst (kg/m^3)

ρ_{sus} density of suspension (kg/m^3)

μ_L viscosity of liquid phase (kg/m.s)

μ_{SL} viscosity of slurry (kg/m.s)

σ_i molecular diameter of component i molecule (Angstroms)

σ_s molecular diameter of solvent molecule (Angstroms)

e_S volume fraction of solid particles in slurry

Superscripts

o standard pressure (1.013 bar)

Subscripts

CO	component CO
CO2	component CO_2
CH3OH	component CH_3OH
H2O	component H_2O
1	methanol from CO reaction
2	water gas shift reaction
3	methanol from CO_2 reaction
ps	pseudo

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