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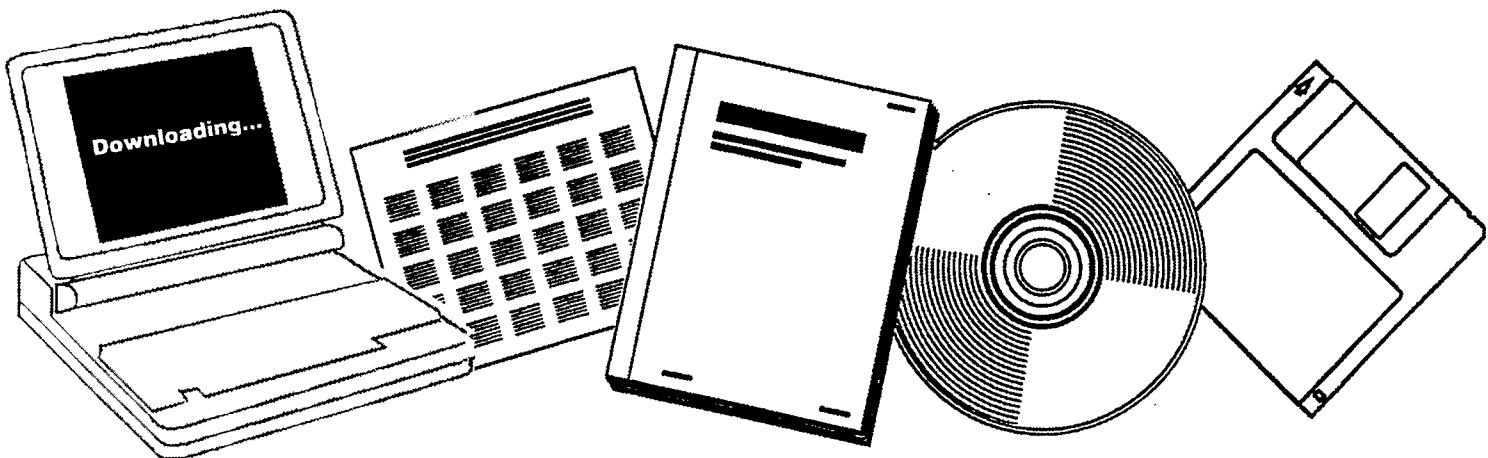
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**DESIGN OF SLURRY REACTOR FOR INDIRECT  
LIQUEFACTION APPLICATIONS: QUARTERLY  
TECHNICAL STATUS REPORT, JULY--SEPTEMBER  
1991**

**VIKING SYSTEMS INTERNATIONAL, INC.  
PITTSBURGH, PA**

**12 OCT 1991**



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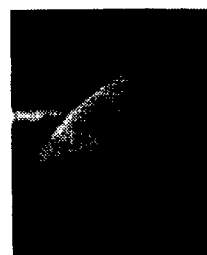
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### Introduction

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 quarter work was performed in the following areas:

- \* Two chain growth probability in Fischer-Tropsch synthesis
- \* Synthesis gas solubility in FT waxes
- \* Review of recent correlations for model parameters estimation.
- \* Estimation of heat transfer area

**MASTER**

- \* Testing and validation of computer codes for Fischer-Tropsch reactor model.
- \* Design of fixed bed reactor for indirect liquefaction applications
- \* Cost estimates for commercial size reactors

### Two Chain Growth Probabilities in Fischer-Tropsch Synthesis:

Evidence for two chain growth probabilities in Fischer-Tropsch synthesis has been shown by some researchers (Huff et al., 1984; Bukur et al., 1989). Huff et al. (1984) observed a marked break on a Flory plot at carbon number of ten. At higher carbon numbers, hydrocarbons are produced with a much higher probability of chain growth than for lower carbon numbers. The carbon number distribution is interpreted in terms of a dual site mechanism that can be described by an extended Flory equation which accounts for the fraction of product formed on each type of site.

$$m_n = \beta(1-\alpha_1)\alpha_1^{n-1} + (1-\beta)(1-\alpha_2)\alpha_2^{n-1} \quad (1)$$

where  $m_n$  is the mole fraction of products containing  $n$  carbon atoms,  $\beta$  is the fraction of type I sites on the catalyst and  $\alpha_1$  and  $\alpha_2$  are the chain growth probabilities associated with the type I and type II sites respectively.

A more general approach for the stoichiometry of FT synthesis should account for the two chain growth probabilities. The Fischer-Tropsch reaction is given by

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$$\gamma_{CO}CO + \gamma_{H_2}H_2 - \gamma_{HC}C_xH_y + \gamma_{H_2O}H_2O \quad (2)$$

The values of  $\gamma_i$ ,  $x$  and  $y$  are expressed in terms of following variables

- $\alpha_1, \alpha_2$  two chain growth probabilities
- $\lambda$  the fraction of paraffinic hydrocarbons
- $\beta$  fraction of type I sites on the catalyst

$$\gamma_{CO} = \frac{\frac{\beta}{1-\alpha_1} + \frac{1-\beta}{1-\alpha_2}}{D} \quad (3)$$

$$\gamma_{H_2} = \frac{2\left(\frac{\beta}{1-\alpha_1} + \frac{1-\beta}{1-\alpha_2}\right) + \lambda[\beta\alpha_1 + (1-\beta)\alpha_2] + [\beta(1-\alpha_1) + (1-\beta)(1-\alpha_2)]}{D} \quad (4)$$

$$\gamma_{H_2O} = \frac{\frac{\beta}{1-\alpha_1} + \frac{1-\beta}{1-\alpha_2}}{D} \quad (5)$$

$$D=3\left(\frac{\beta}{1-\alpha_1} + \frac{1-\beta}{1-\alpha_2}\right) + \lambda[\beta\alpha_1 + (1-\beta)\alpha_2] + [\beta(1-\alpha_1) + (1-\beta)(1-\alpha_2)] \quad (6)$$

$$x = \frac{\beta}{1-\alpha_1} + \frac{1-\beta}{1-\alpha_2} \quad (7)$$

$$y = 2\left[\left(\frac{\beta}{1-\alpha_1} + \frac{1-\beta}{1-\alpha_2}\right) + \lambda\{\beta\alpha_1 + (1-\beta)\alpha_2\} + \{\beta(1-\alpha_1) + (1-\beta)(1-\alpha_2)\}\right] \quad (8)$$

#### Synthesis Gas Solubility:

Solubility of synthesis gas in Fischer-Tropsch waxes has been investigated by Chao and Lin (1987). Following equations were obtained for Henry's constants from regression analysis of the data from Chao and Lin (C<sub>43</sub> wax, temperature range 200 to 300°C).

$$H_{H_2} = 83.35 \exp(604.7/T) \quad (9)$$

$$H_{CO} = 151.0 \exp(136.0/T) \quad (10)$$

$$H_{CO_2}=297.0\exp(-582.4/T) \quad (11)$$

$$H_{CH_4}=204.4\exp(-264.2/T) \quad (12)$$

$$H_{C_2H_6}=558.36\exp(-1118.87/T) \quad (13)$$

Recent Correlations for model parameters:

A recent report by Air Products and Chemicals (Topical Report: Tracer Studies in the LaPorte LPMEOH PDU) presented the results of gas and liquid phase dispersion studies in the process development unit at LaPorte. It was observed that literature correlations (Field and Davidson, 1980; Towell and Ackerman, 1972) for gas phase axial dispersion overpredicted gas phase mixing by a factor of around 3. The following correlation was recommended for gas phase dispersion, based on the best fit of their data:

$$D_e=21.72D^{1.5}U_G^{1.8} \quad (14)$$

Recent correlations for gas holdup are also being tested against experimental data from PDU studies.

#### Estimation of Heat Transfer Area:

A new subroutine (HTAREA) has been now included in the reactor model to calculate the heat transfer area required to remove the heat of reaction for Fischer-Tropsch reactions. The reaction heat is used to generate steam using an internal heat exchanger. The slurry side heat transfer coefficient is estimated with the correlation of Deckwer et al. (1980) based on the observations of Saxena et al. (1990).

#### Testing and Validation of Fischer-Tropsch Reactor Model:

The model equations for the Fischer-Tropsch synthesis reactor constitute a set of coupled second-order non-linear differential equations. These equations are not amenable to an analytical solution and therefore, a numerical method was selected for solution. Orthogonal collocation techniques are particularly suitable for the solution of boundary value problems and the software package, COLSYS, developed by Ascher et al. (1981) was selected for the numerical solution of the model equations. This method is based on spline collocation at Gaussian points using a B-spline basis. Approximate solutions are computed on a sequence of automatically selected meshes until a user-specified set of tolerances is satisfied.

Computer codes for the reactor model have been developed with a modular approach to computer programming, to ensure easy modifications by the user. Standard FORTRAN 77 has been used for writing the codes since this will ensure transfer to other compatible systems.



Computer codes for the slurry reactor model have been developed for the following cases:

With external recirculation of slurry

- o Gas plug flow; Liquid axial dispersion
- o Gas axial dispersion; Liquid axial dispersion

No external recirculation of slurry

- o Gas plug flow; Liquid axial dispersion
- o Gas axial dispersion; Liquid axial dispersion

Results of Computation:

For the results of this section, the slurry reactor for Fischer-Tropsch synthesis was modeled assuming there was no external recirculation of slurry and both gas and liquid phases were axially dispersed. Table 1 gives the range of operating variables studied. The model was used to investigate the following:

- o Concentration profile along the reactor length
- o Effect of operating variables
- o Parameter sensitivity analysis
- o Simulation of demonstration unit

Table 1. Range of input data used to simulate slurry Fischer-Tropsch reactor

Diameter	4.5 m
Length	12.0 m
Temperature	230-270 °C
Pressure	15-20 atm
Gas Velocity	0.10-0.16 m/s
Slurry Conc.	30-35 wt. %
Syngas in Feed	90.0%
H <sub>2</sub> /CO ratio	0.5-1.5
Particle size	0.00003-0.00005 m

Figure 1 shows how the concentration profile varied along the reactor length in both gas and liquid phases. It can be seen that in both phases the CO concentration declines more rapidly compared to hydrogen concentration as a result of the stoichiometry of the synthesis reaction. It may also be noted that the H<sub>2</sub>/CO ratio in the liquid phase is higher than that in the gas phase.

Figures 2 and 3 show the effects of reactor temperature and gas velocity respectively, on syngas conversion. The conversion of syngas increased with increasing reactor temperature while it decreased with increasing gas velocity. Figure 3 also shows the results obtained with the gas plug flow case. It can be seen that predicted conversions were always higher for the gas plug flow mode than the gas dispersion mode and the difference between the two decreased with

decreasing gas velocity. Figure 4 shows the effect of  $H_2/CO$  ratio in the feed gas on the conversion of syngas and CO. It can be seen that conversion of syngas passes through a maximum with increasing  $H_2/CO$  ratio.

Parameter sensitivity analysis for the reactor model was investigated for gas dispersion coefficient and volumetric mass transfer coefficient. Figure 5 shows that, as expected, the conversion decreases with increasing gas phase dispersion coefficient. The gas dispersion coefficient estimated by the selected correlation in the model is also shown on Figure 5. A 50% error in the estimated value of gas dispersion coefficient would result in less than 2% error in the predictions for syngas conversion. Figure 6 shows the significance of proper estimates for volumetric mass transfer coefficient in the model. It can be seen that syngas conversion would be significantly reduced for low gas-liquid mass transfer rates ( $k_{La} < 0.4 \text{ s}^{-1}$ ). The effect, however, becomes less significant for higher values of mass transfer coefficients.

#### Simulation of Demonstration Unit:

The Fischer-Tropsch reactor model was also used to predict the performance of demonstration unit at Rheinpreussen (Kolbel and Ralek, 1980). Table 2 presents the reactor dimensions and operating conditions used. The predicted syngas conversion was 12 % higher than reported conversion. This could be attributed to higher catalyst activity at the Rheinpreussen plant.

Table 2. Operating conditions and reactor dimensions for Rheinpreussen

Demonstration Unit

Diameter	1.29 m
Length	7.7 m
Temperature	268°C
Pressure	11.84 atm
Gas velocity	0.095 m/s
Slurry Conc.	18 wt %

Syngas Conversion

Reported	Predicted
89%	77%

Simulation with Bechtel Design Data:

Bechtel presented a design for a commercial size slurry reactor for Fischer-Tropsch synthesis (Fox and Degen,1990). Our slurry reactor model was used to predict the performance using Bechtel design data. The predicted syngas conversion was within 1% of reported value (Table 3).

Table 3. Bechtel Design Data

Diameter	4.8 m
Length	12.0 m
Net xsect of reactor	15.16 m <sup>2</sup>
Reactor volume	211.0 m <sup>3</sup>
Temperature	257°C
Pressure	28.3 atm
Slurry Conc.	35 wt%
Gas velocity	0.14 m/s

Syngas Conversion

Bechtel Design	Model Prediction
80%	79%

Design of Fixed Bed Reactor:

In order to compare the cost of the conceptual commercial-scale reactor with the costs for the vapor phase systems, it is necessary to size the fixed bed reactor for same production. The fixed bed reactor is being designed using the heterogeneous reactor model which allows for differences in concentrations and temperature between the bulk gas stream and the catalyst pellet. The

effects of internal and external resistances on the reaction rates are accounted for by using overall reaction rates rather than intrinsic rates which requires calculation of effectiveness factor for catalyst particles. The calculation of effectiveness factor involves a solution of solid phase differential mass and energy balance equations with appropriate boundary conditions. The internal resistances are accounted for by differential equations for the gaseous components, and the effect of external resistances are imposed by boundary conditions. The overall reaction rate can therefore, be obtained by multiplying the effectiveness factor with the rate evaluated at bulk conditions.

#### Cost Estimates for Commercial Size Reactors:

For cost estimate purposes, the diameter and operating conditions for commercial size slurry reactors have been selected to be the same as in Bechtel design (Fox and Degen, 1990). The final reactor volume (or reactor length) are expected to be different from Bechtel design. This will provide a good basis for comparison of cost for the two designs.

## NOTATIONS

$D_C$  : Diameter of reactor, m

$D_G$  : Gas phase dispersion coefficient,  $m^2/s$

$H_i$  : Henry's constant for component i,  $atm.m^3/kmol$

$T$  : Temperature, K

$U_G$  : gas superficial velocity, m/s

$U_L$  : liquid superficial velocity, m/s

## Subscripts

L : liquid phase

G : gas phase

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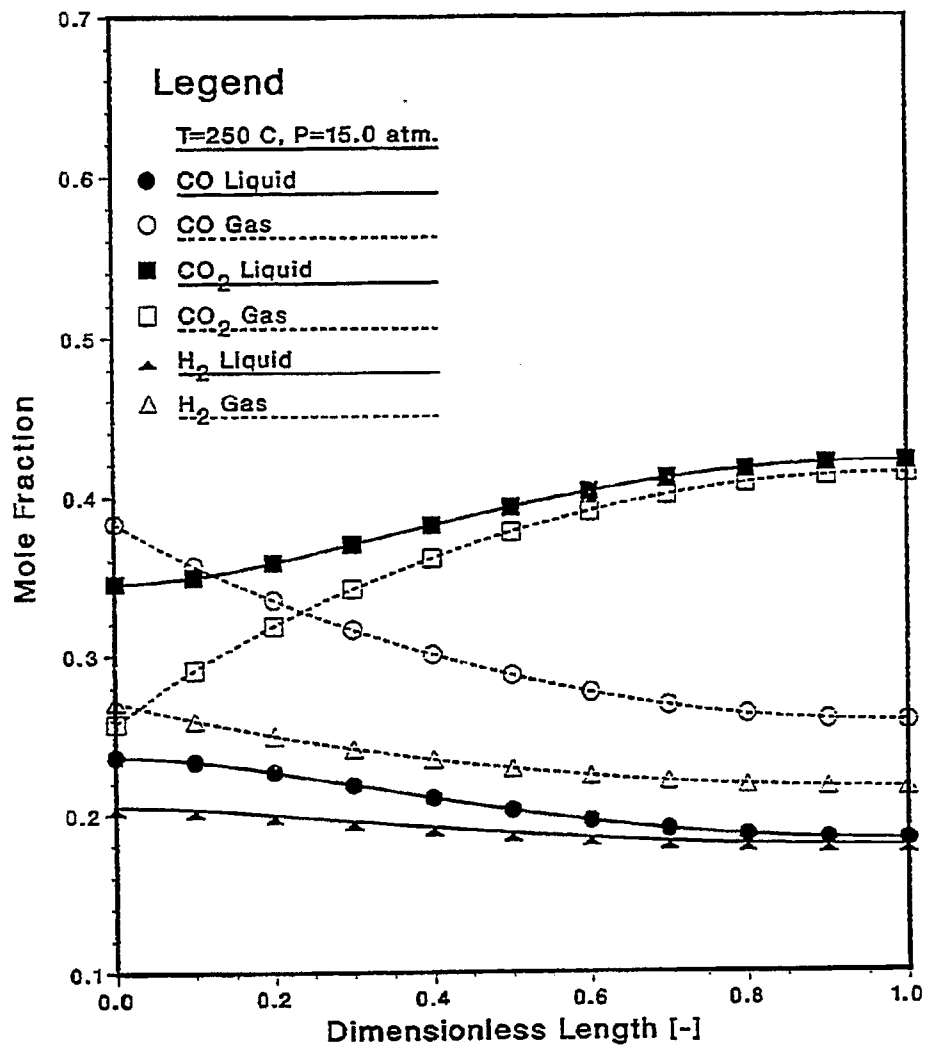


Figure 1: Concentration Profiles in Bubble Column Slurry Reactor

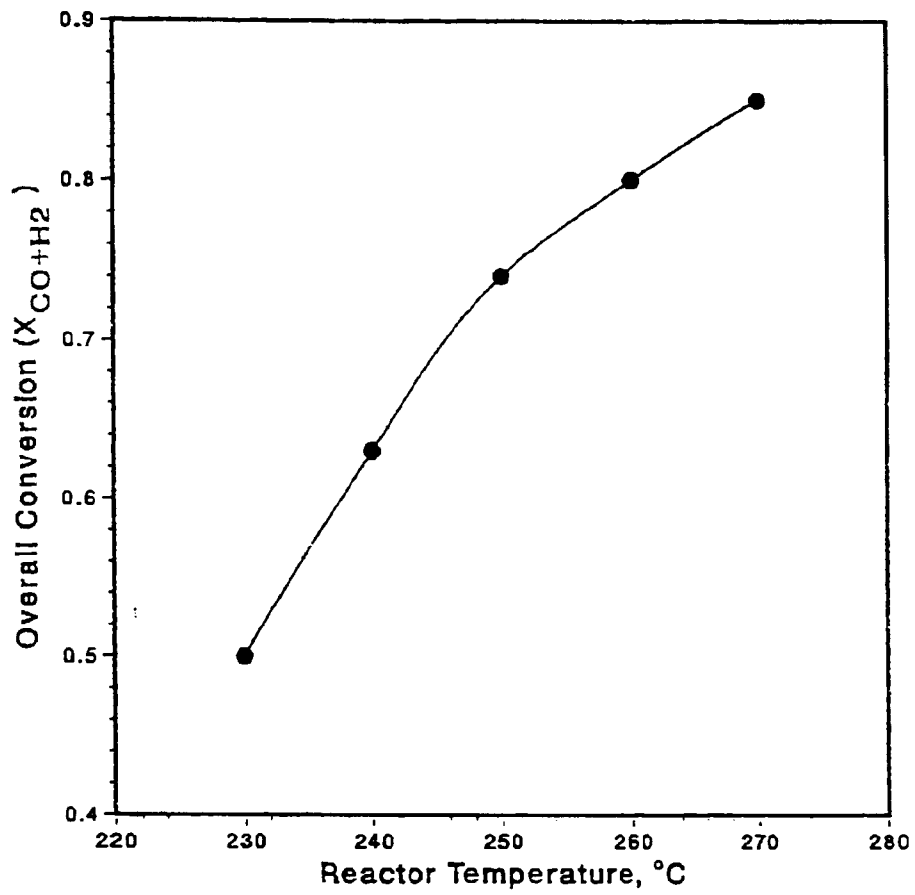


Figure 2: Effect of Reactor Temperature on Syn Gas Conversion

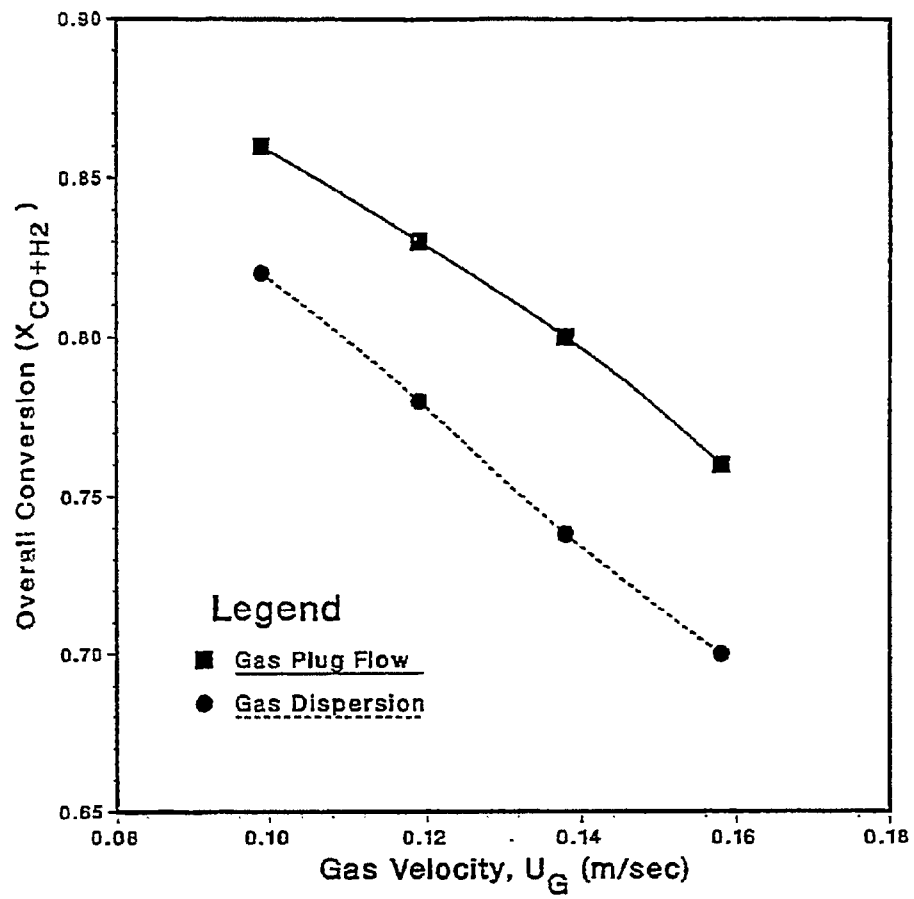


Figure 3: Effect of Gas Velocity on Syn Gas Conversion

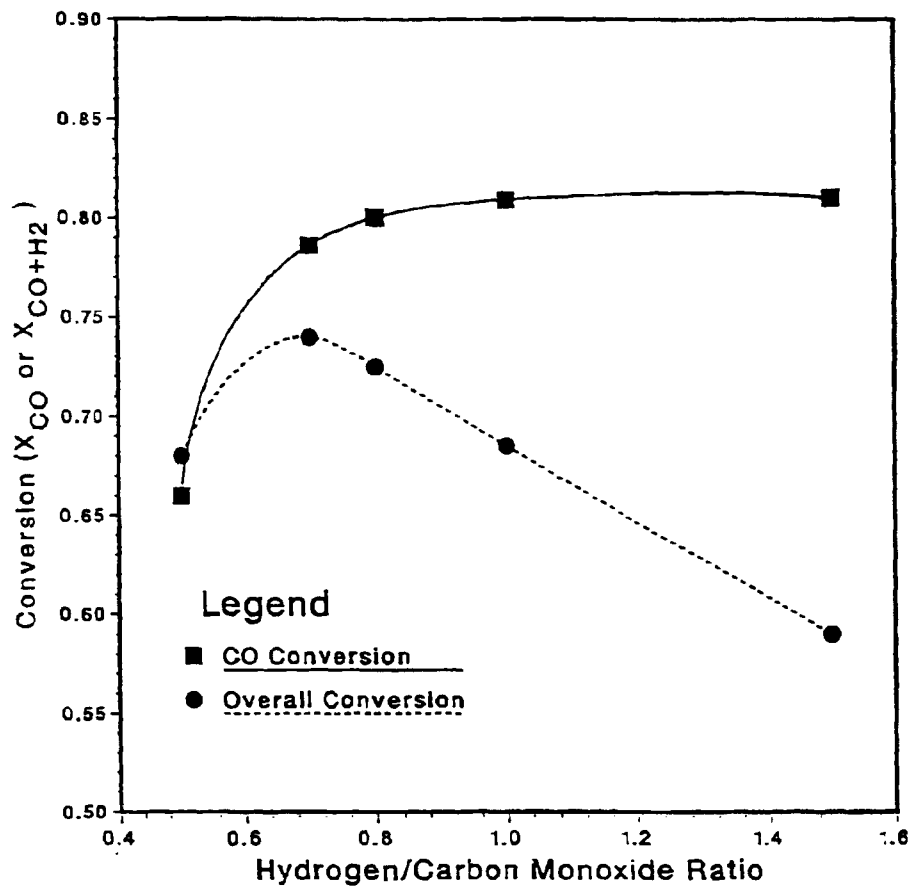


Figure 4: Effect of Hydrogen/Carbon Monoxide Ratio on Syn Gas Conversion

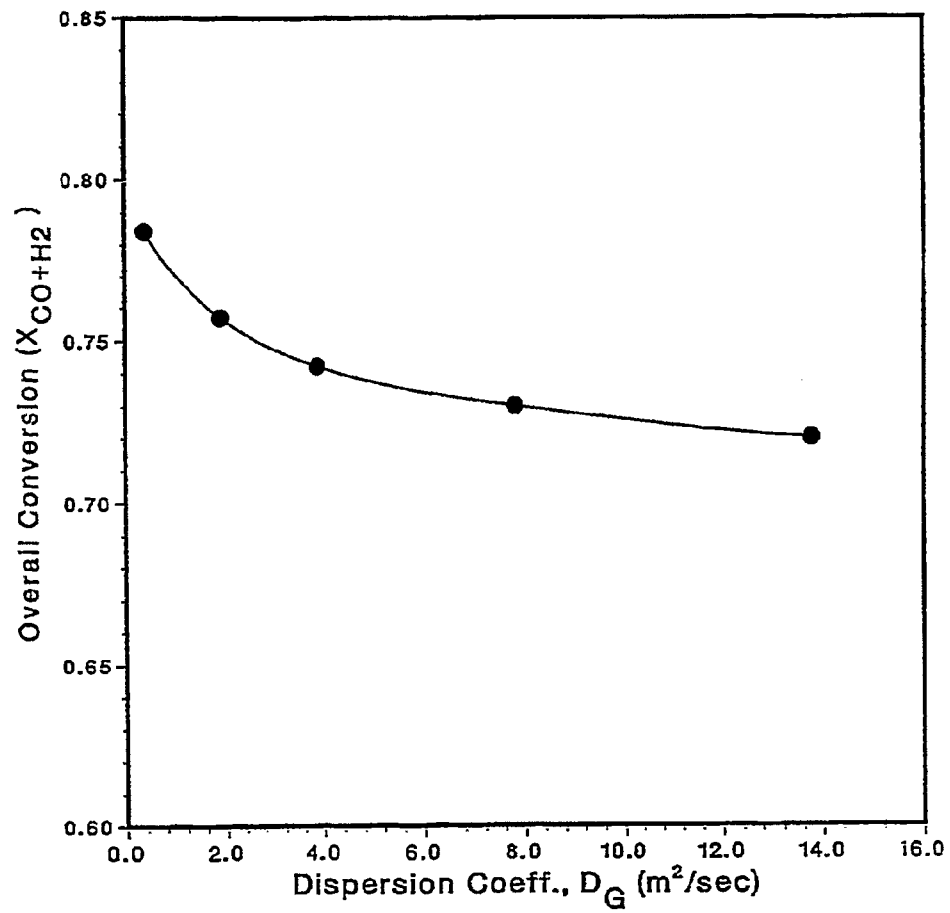


Figure 5: Effect of Gas Phase Dispersion Coefficient on Syn Gas Conversion

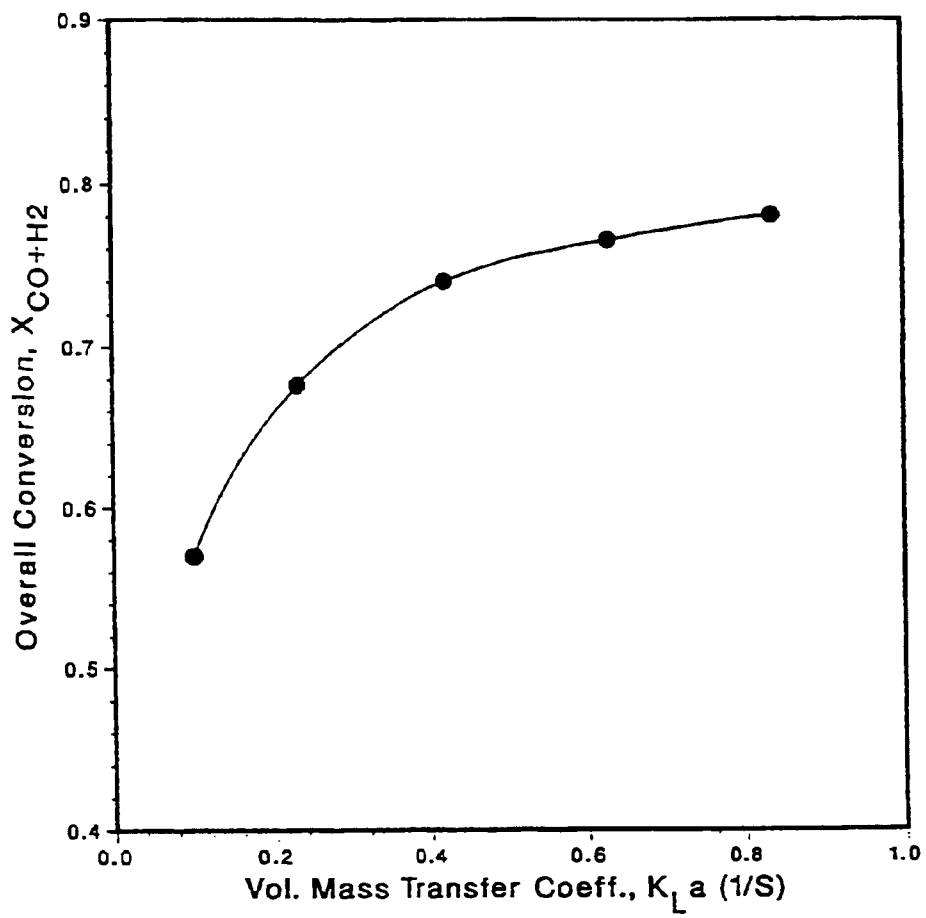


Figure 6: Effect of Volumetric Mass Transfer Coefficient on Syn Gas Conversion

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