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**NOVEL REACTOR CONFIGURATION FOR SYNTHESIS GAS
CONVERSION TO ALCOHOLS**

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QUARTERLY REPORT

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I. Objectives for the Third Quarter, Year 1:

Our objective during this quarter was to complete Task II, calibration and automation of GC analysis protocols, and Task IIIB, development of a dynamic response technique to determine the relevant parameters and of the algorithms for data acquisition and analysis for parameter estimation including the computer codes. In addition, we have started to work on Task IV, determination of the reaction kinetics in the CSTR we have designed.

II. Accomplishments, Third Quarter, Year 1:

Task II is completed. We have developed the protocols for analysis of reactor effluents as well as the Witco Freezene oil. The reactor effluent is analyzed on GowMac GC for the products alcohols, water and CO₂. A Carle GC is used for the analysis of the products after condensing out the condensables for CO, CO₂ and H₂. We use a capillary GC, off line, for periodic analysis of the oil.

We have designed a cold-flow dynamic response system to measure the hydrodynamic and transport parameters. The model equations have to be written for the gas phase, the liquid phase and the solid phase together with the appropriate mass transfer terms at the phase boundaries. In the general case, if a tracer that distributes between all three phases and that can also adsorb on the catalyst is used, then the equations would be as follows.

Gas Phase Assuming Plug Flow

$$H_G \frac{\partial C_g}{\partial t} = -u_g \frac{\partial C_g}{\partial z} + K_L a \left(C_l - \frac{C_g}{K_{lg}} \right) - (1-f) \frac{3(1-\epsilon_b)}{R} (D_s)_l \frac{\partial C_l^i}{\partial r} \bigg|_{r=R} \quad (1)$$

Liquid Phase Assuming Axial Dispersion

$$H_L \frac{\partial C_l}{\partial t} = D_L \frac{\partial^2 C_l}{\partial z^2} - u_l \frac{\partial C_l}{\partial z} - f \frac{3(1-\epsilon_b)}{R} (D_s)_l \frac{\partial C_l^i}{\partial r} \bigg|_{r=R} \quad (2)$$

Solid Phase

$$(D_e)_g \left[\frac{\partial^2 C_g^i}{\partial r^2} + \frac{2}{r} \frac{\partial C_g^i}{\partial r} \right] - (\epsilon_p)_g \frac{\partial C_g^i}{\partial t} - \rho_p \frac{\partial C_g^s}{\partial t} = 0 \quad (3)$$

$$(D_e)_l \left[\frac{\partial^2 C_l^i}{\partial r^2} + \frac{2}{r} \frac{\partial C_l^i}{\partial r} \right] - (\epsilon_p)_l \frac{\partial C_l^i}{\partial t} - \rho_p \frac{\partial C_l^s}{\partial t} = 0 \quad (4)$$

$$\frac{\partial C_g^s}{\partial t} = k_{g,s} a_{g,s} \left(C_g^i - \frac{C_g^s}{K_{g,s}} \right) \quad (5)$$

$$\frac{\partial C_l^s}{\partial t} = k_{l,s} a_{l,s} \left(C_l^i - \frac{C_l^s}{K_{l,s}} \right) \quad (6)$$

Boundary Conditions at the Gas-Solid and Gas-Liquid Interfaces

$$(D_e)_g \left(\frac{\partial C_g^i}{\partial r} \right)_{r=R} = k_{fg} \left(C_g - C_g^i|_{r=R} \right) \quad (7)$$

$$(D_e)_l \left(\frac{\partial C_l^i}{\partial r} \right)_{r=R} = k_{fl} \left(C_l - C_l^i|_{r=R} \right) \quad (8)$$

Initial Conditions

$$t = 0 \quad C_l = C_g = C_l^i = C_g^i = C_l^s = C_g^s = 0 \quad (9)$$

Boundary Conditions

$$z = 0 \quad C_l = f(C_l^s); \quad \text{some cases} = \delta(t) \quad (10)$$

$$z = L \quad C_l \neq \pm \infty \quad (11)$$

$$r = 0 \quad \frac{\partial C_g^i}{\partial r} = \frac{\partial C_l^i}{\partial r} = 0 \quad (12)$$

Thus the parameters for the dynamic response would be:

- a. Gas and Liquid Hold-Ups: H_L , H_G , $(\epsilon_p)_l$, $(\epsilon_p)_g$
- b. Liquid Phase Axial Dispersion Coefficient: D_z
- c. Wetting efficiency: f
- d. Pore diffusion effective diffusivities: $(D_e)_l$, $(D_e)_g$
- e. Gas liquid mass transfer coefficient and equilibrium partition coefficient (Henry's Law Constant): K_{La} , K_{lg}
- f. Liquid-solid and gas-solid mass transfer coefficients: k_{fl} , k_{fg}
- g. Adsorption rate and equilibrium constants: $k_{gs}a_{gs}$, K_{gs} , $k_{ls}a_{ls}$, K_{ls}

Of all these parameters only the ones that also appear in the reactor design equations given in the previous Quarterly Report are relevant. If a non-adsorbing, non-volatile liquid phase tracer is used, then the system of equations reduce to:

$$H_L \frac{\partial C_l}{\partial t} = D_z \frac{\partial^2 C_l}{\partial z^2} - u_l \frac{\partial C_l}{\partial z} - f \frac{3(1-\epsilon_b)}{R} (D_e)_l \left(\frac{\partial C_l^i}{\partial r} \right)_{r=R} \quad (13)$$

$$(D_e)_l \left[\frac{\partial^2 C_l^i}{\partial r^2} + \frac{2}{r} \frac{\partial C_l^i}{\partial r} \right] - (\epsilon_p)_l \frac{\partial C_l^i}{\partial t} = 0 \quad (14)$$

$$(D_e)_l \left(\frac{\partial C_l^i}{\partial r} \right)_{r=R} = k_{fl} (C_l - C_l^i|_{r=R}) \quad (15)$$

In this system of equations C_l is the concentration of the tracer in the bulk liquid, C_l^i is the concentration of the tracer in the catalyst pores. The parameters are D_z , H_L , f , k_{fl} , and D_e . Normally, unless the operation is at very high gas to liquid fluid ratios or the reactor operates with dry zones, the catalyst pores will be completely saturated with the liquid due to capil-

lary action, the $(\epsilon_p)_1 = \epsilon_p$. The solution to the above system of equations, in the Laplace's domain, is given by:

$$E(s) = \exp\left(-\frac{uL}{2D_s}\left(\sqrt{1 + \frac{4D_s\gamma}{u}} - 1\right)\right) \quad (16)$$

$$\gamma = \frac{HLs}{u} + f \frac{3(1 - \epsilon_b)k_f}{Ru} \left[\frac{\beta R \coth \beta R - 1}{\frac{k_f R}{D_s} + \beta R \coth \beta R - 1} \right] \quad (17)$$

$$\beta^2 = \frac{\epsilon_p s}{D_s} \quad (18)$$

If an adsorbing tracer is used, then Equation 14 becomes

$$(D_s)_l \left[\frac{\partial^2 C_l^i}{\partial r^2} + \frac{2}{r} \frac{\partial C_l^i}{\partial r} \right] - (\epsilon_p)_l \frac{\partial C_l^i}{\partial t} - \rho_p \frac{\partial C_l^s}{\partial t} = 0 \quad (19)$$

and an additional equation is needed for the adsorption rate:

$$\frac{\partial C_s}{\partial t} = k_s a_s \left(C_i - \frac{C_s}{K_s} \right) \quad (20)$$

introducing the adsorption rate and equilibrium parameters $k_s a_s$ and K_s . The solution is still given by the same transfer function, but now β is given by:

$$\beta^2 = \frac{\epsilon_p s}{D_s} + \frac{\rho_p}{D_s} \frac{K_s s}{k_s a_s + 1} \quad (21)$$

Thus the number of parameters to be estimated increases to 7.

The parameter estimation procedure we developed consists of fitting of the tracer response with a Fourier series and optimization of the parameters in the real time domain by equating the coefficients for the model and the data.

In order to overcome the uncertainties associated with estimating this many parameters from a single experiment, we first make experiments with a liquid filled column. In this case $H_L = \epsilon_b$ and $f = 1.0$. Therefore for liquid filled operation the parameters are k_f , D_z , D_e , $k_s a_s$, and K_s . Of these 5 parameters, D_e , $k_s a_s$, and K_s will not change in gas liquid operation whereas D_z and k_f might. Liquid filled runs will be followed by gas-liquid runs with a non-volatile tracer. The remaining 4 parameters, H_L , D_z , k_f , and f will be extracted from the data. Finally, a gas phase tracer would yield $K_L a$.

We have developed our model and algorithms and started testing our model with liquid fill column studies in the micro system in our laboratory. The packing used is alumina, characteristics of which are given in Table I. The liquid phase is heptane with hexadecane as the tracer. Figure 1-3 represent the fit of the model to the experimental data. We expect to finish our liquid fill operation during the next quarter.

In this quarter we have also started Task IV which involves measuring the kinetics of the reaction in the CSTR slurry reactor. We have encountered certain experimental difficulties which are summarized below and are not solved yet.

III. Problems Encountered:

In our parameter estimation program we use a optimization routine based on decreasing grid sizes to extract the five parameters of interest. In the

model there are three processes that take place in series, namely mass transfer to the catalyst surface, diffusion into the pores and adsorption in the pores. Testing the parameter estimation routine with simulated data we observe that if all these three processes are of the same order of magnitude, we determine the parameters quite accurately, however if one of the phenomena is much slower than the others (and hence is rate controlling) we determine that correctly, but the values we converge at for the other parameters do not make sense. We are still working on the optimization routine to solve the problem.

We also had some problems with our CSTR slurry reactor. As mentioned in our first Quarterly Report, we would like to keep the oil in the reactor in the batch mode with the catalyst dispersed in it, feed in synthesis gas and withdraw the products in the gas phase. So far we were unable to keep the oil in the reactor. We believe that due to the rigorous mixing in the reactor, the oil is swirled around and any oil that hits the porous metal filter in the gas exit line is carried away with the gas phase effluent. We have tried to redesign the filter with an enclosure to prevent the oil from contacting the surface, so far unsuccessfully. We are now planning to circulate the oil phase continuously which will necessitate solving some experimental difficulties associated with it. In addition we observe that we deactivate the catalyst very rapidly, in a matter of 10-20 hours indicating some source of carbonyl poisoning. We are checking every item in the reactor assembly to make sure that everything is made of stainless steel.

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Table I

Properties of Alumina used in the Packed bed Study

Supplier: All-Tech Associates, Unibeads A 80/100, (Catalogue No. 2778)

Mesh Size: 80/100 Mesh

Particle Size: 0.149 - 0.177 mm

Average Diameter: 0.163 mm

Bulk Density from Mercury Penetration Data: 0.7745 g/cm^3

Solid Density from Mercury Penetration Data: 2.1401 g/cm^3

Average Pore Diameter from Mercury Penetration Data: 68 $\text{\AA}$

Average Pore Diameter from BET Adsorption: $74.0 \pm 5.0 \text{ \AA}$

Particle Porosity from BET Adsorption: 47.8 %

Bed Porosity: 38 %

Heptane and Hexadecane

FIG. 1.

$$u = 0.03 \text{ cm/s}$$

P.S. = 4 %

Heptane and Hexadecane

P. S. = 24 %

Fig. 2:

$$\eta = 0.21 \text{ cm}^2/\text{s}$$

Heptane and Hexadecane

P. S. = 60 %

Fig. 3:
 $u = 0.53 \text{ cm/s}$

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