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

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QUARTERLY REPORT

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Principal Investigators

**Aydin AKGERMAN
Rayford G. ANTHONY**

**Chemical Engineering Department
Texas A&M University
College Station, TX 77843**

Organization

**Texas A&M Research Foundation
Box 3578
College Station, TX 77843**

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I. Objectives for the Second Quarter, Year 1:

During the second quarter our objective was to continue with Task II and start on Task III. Task II involved standardization and automation of GC analysis protocols. Task III, as stated in the work breakdown schedule, was the modification and automation of the trickle bed reactor and performing the initial factorial design experiments. We have decided to modify this task by expanding it to incorporate determination of the hydrodynamic and transport parameters of the trickle bed reactor in order to isolate and study just the reaction parameters. This task, which was scheduled to take 21 months will now take 25 months, still enabling us to complete the project as scheduled, and is divided into the following subtasks.

Task IIIA. Development of a model for the two phase concurrent down flow trickle bed assembly and identification of the relevant parameters to be determined. (2 Months)

Task IIIB. Development of a dynamic response technique to determine the relevant parameters. Development of the algorithms for data acquisition and data analysis for parameter estimation and writing the computer codes. (5 months)

Task IIIC. Establishment of the methodology in a micro reactor assembly we have available in our laboratories. Determination of the relevant parameters in the micro reactor. (6 months)

Task IIID. Automation and modification of the trickle bed reactor assembly. (3 months)

Task IIIE. Determination of the reactor hydrodynamic and transport parameters at the actual reaction conditions of 250°C and 1000 psia. (6 months)

Task IIIF. Long duration studies in the trickle bed reactor to determine the effects of reaction and reactor parameters on the productivity. (9 months)

After these modifications, Task III schedule becomes as follows:

where Month 4 corresponds to January 1990 and Month 28 to January 1992.

II. Accomplishments, Second Quarter, Year 1:

We have continued with Task II, our GC analysis standardization protocols. We are planning to use two GC's on the slurry reactor. The first one will be used to analyze for methanol and water as well as the reaction intermediates such as dimethyl ether and formaldehyde. The sample will be in the gas phase taken by using a heated sampling valve. The reaction gases, CO, CO₂ and H₂ will be analyzed by a second GC after condensing of the liquid products.

Task IIIA is completed. The design equations we developed for the trickle bed reactor are as follows:

GAS PHASE

$$D_z \frac{\partial^2 (C_A)_g}{\partial z^2} - u_g \frac{\partial (C_A)_g}{\partial z} + K_L a \left((C_A)_l - \frac{(C_A)_g}{K_A} \right) - (1-f) \frac{3(1-\epsilon_b)}{R} (D_{Ac})_s \frac{\partial (C_A)_s}{\partial r} \bigg|_{r=R} = 0 \quad (1)$$

where f is the wetting efficiency, $(C_A)_g$ and $(C_A)_l$ are the gas and liquid phase concentrations respectively and $(C_A)_s$ is the concentration at the gas covered surface of the catalyst particle.

LIQUID PHASE

$$D_Z \frac{\partial^2 (C_A)_l}{\partial Z^2} - u_L \frac{\partial (C_A)_l}{\partial Z} - K_L a \left((C_A)_l - \frac{(C_A)_g}{K_{lg}} \right) - f \frac{3(1-\epsilon_b)}{R} (D_{Ae})_l \frac{\partial (C_A)_l}{\partial r} \Big|_{r=R} = 0 \quad (2)$$

where $(C_A)_l^s$ is the concentration at the liquid covered surface. Similarly for the liquid phase non-volatile reactant

$$D_Z \frac{\partial^2 (C_B)_l}{\partial Z^2} - u_L \frac{\partial (C_B)_l}{\partial Z} - f \frac{3(1-\epsilon_b)}{R} (D_{Be})_l \frac{\partial (C_B)_l}{\partial r} \Big|_{r=R} = 0 \quad (3)$$

SOLID PHASE

$$(D_{Ae})_g \left[\frac{\partial^2 (C_A)_g}{\partial r^2} + \frac{2}{r} \frac{\partial (C_A)_g}{\partial r} \right] = 0 \quad (4)$$

$$(D_{Ae})_l \left[\frac{\partial^2 (C_A)_l}{\partial r^2} + \frac{2}{r} \frac{\partial (C_A)_l}{\partial r} \right] = R_A \quad \frac{R_A}{v_A} = \frac{R_B}{v_B} = kf(C_A, C_B) \quad (5)$$

$$(D_{Be})_l \left[\frac{\partial^2 (C_B)_l}{\partial r^2} + \frac{2}{r} \frac{\partial (C_B)_l}{\partial r} \right] = R_B \quad (6)$$

BOUNDARY CONDITIONS

$$(D_{Ae})_g \frac{\partial (C_A)_g}{\partial r} \Big|_{r=R} = (k_A)_{gs} a_{gs} \left((C_A)_g - (C_A)_g^s \Big|_{r=R} \right) \quad (7)$$

$$(D_{Ae})_l \frac{\partial (C_A)_l}{\partial r} \Big|_{r=R} = (k_A a)_{ls} \left((C_A)_l - (C_A)_l^s \Big|_{r=R} \right) \quad (8)$$

$$(D_{Be})_l \frac{\partial (C_B)_l}{\partial r} \Big|_{r=R} = (k_B a)_{ls} \left((C_B)_l - (C_B)_l^s \Big|_{r=R} \right) \quad (9)$$

$$r = 0 \quad \frac{(\partial C_i)_j}{\partial r} = 0 \quad (10)$$

$$z = 0 \quad (C_A)_g = C_{AG}^o \quad (C_A)_l = C_{AL}^o \quad (C_B)_l = C_{BL}^o \quad (11)$$

$$z = L \quad \frac{(\partial C_i)_j}{Z} = 0 \quad \text{or} \quad (C_i)_j \text{ is finite} \quad (12)$$

$$R_A = k C_A^n C_B^m = \frac{v_A}{v_B} R_B \quad (13)$$

The reactor parameters needed for design are then the axial dispersion coefficients, gas-liquid mass transfer coefficient, the effective diffusivities, the wetting efficiency, Henry's Law constants, gas-solid and liquid-solid mass transfer coefficients.

If we assume plug flow in both phases, reaction in the liquid phase with a first order reaction, and non-volatile liquid phase reactant then the equations reduce to:

$$-u_L \frac{\partial C_B}{Z} - f \frac{3(1-\epsilon_s)}{R} D_{B_s} \left(\frac{\partial C_B^s}{\partial r} \right)_{r=R} = 0 \quad (14)$$

$$D_{B_s} \left(\frac{\partial C_B^s}{\partial r} \right)_{r=R} = k_B a_p (C_B - C_B^s|_{r=R}) \quad (15)$$

$$D_{B_s} \left[\frac{d^2 C_B^s}{dr^2} + \frac{1}{r} \frac{dC_B^s}{dr} \right] = k_r C_B^s \quad k_r \text{ rxn rate constant} \quad (16)$$

which have the simple first order exponential solution

$$\frac{(C_B)_{out}}{(C_B)_{in}} = \exp\left(-\alpha_2 \frac{Z}{u_L}\right) \quad (17)$$

where the modified constant α_2 is now given in terms of the parameters wetting efficiency, liquid solid mass transfer coefficient, and effective diffusivity as well as the modified Thiele Modulus.

$$\alpha_2 = \frac{3f(1 - \epsilon_B)}{u_L R} \frac{k_B a_p (\beta R \coth \beta R - 1)}{\left(\beta R \coth \beta R - 1 + \frac{k_B a_p R}{D_B}\right)}; \quad \beta = \sqrt{\frac{k_r}{D_B}} \quad (18)$$

In case of methanol synthesis, both reactants are in the gas phase, therefore Equations 1, 2, 5, 7 and 8 are written for both reactants, CO and H₂, and Equations 3, 6, and 9 are eliminated.

We have also started with Task III B, development of a dynamic response technique for measuring the relevant parameters. The micro reactor setup is shown Figure 1 which is designed for liquid fill operation initially. The solvent, or the liquid phase is pumped by pump for, through the reference side of the refractive index detector, through a switching valve, to the column and from the column to the sample side of the detector, back to the solvent reservoir. A tracer is pumped by pump 9 and a pulse input is introduced by the switching valve. The response is detected by the RI detector and data acquisition accomplished via a computer.

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- 1 Backpressure Regulator
- 2 Solvent Reservoir
- 3 Refractive Index Detector
- 4 Solvent Pump

- 5 Waste Reservoir
- 6 Injection Valve
- 7 Dispersion Column
- 8 Sample Reservoir
- 9 Sample Pump

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