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Two aspects of slurry reactors for Fischer-Tropsch synthesis make them different from fixed bed reactors.

1. Carbon formation and resulting deactivation do not occur as readily in slurry reactors, even at low H_2/CO ratios (1). Two explanations have been put forth for this:

   a) Better heat transfer in a slurry eliminates hot spots, which have been shown to increase the rate of carbon formation. This was investigated in the first phase of this project.

   b) The diffusivity of H_2 in paraffinic oils is about 20 times that of CO; therefore, mass transfer limitations in a slurry act to reduce the CO/H_2 ratio at the catalyst surface. Calculations based on McKee's fixed bed kinetic data (2) and Calderbank's correlations for mass transfer coefficients (3) seem to show that typical F-T reactors operate in a reaction limited regime. However, work by Storch, et al (4) with a trickle bed reactor indicates that mass transfer resistances may be significant. At high temperature, conversion doesn't vary much with temperature; this could result from mass transfer limitations.

2. Product distributions in slurry reactors are different from those in fixed beds: slurries yield more high molecular weight products (5). This may be a mixing effect. Hall, et al (6), and more recently, Kellar and Bell (7) and Somorjai (8) have shown that ethylene will recombine with reactants to form heavier products. Increased mixing

acts to increase the average concentration of products throughout the reactor, so the rate of recombination increases.

The objective of the present phase of the investigation, then, is to see if mass transfer limitations exist to an extent that catalyst deactivation is reduced to determine the extent to which recombination occurs in the slurry, and to assess, through modeling, whether the well-mixed slurry could result in product distributions that differ significantly from those observed with fixed bed reactors.

To answer these questions, 3 sets of experiments are being undertaken. In the first, the rate of reaction will be measured at varying amounts of catalyst per reactor volume, with constant gas flow rate and concentration. For a first-order reaction, we can write:

$$R = k_L a(C^* - C_L) = Wk_s a_s (C_L - C_s) = W k C_s$$

R = rate per unit reactor volume; $k_L a$ = mass transfer coefficient x interfacial area per reactor volume.

$k_s a_s$ = area per mass of catalyst x mass transfer coefficient to catalyst surface

W = mass of catalyst per reactor volume; k = rate constant per mass of catalyst

C = reactant concentration; subscripts: s - catalyst surface; L - bulk liquid; * - Gas-liquid interface

Solving for C_s and C_L in terms of C^*, we get:

$$(C^*/R) = \frac{1}{k_L a} + \frac{1}{W}\left(\frac{1}{k_s a_s} + \frac{1}{k}\right).$$

A plot of $\frac{C^*}{R}$ vs $\frac{1}{W}$ Yields a straight line. For non linear kinetics, such a plot will not be a straight line, but the intercept will still be indicative of mass transfer from gas-liquid interface to bulk liquid, and the scope will be related to intrinsic kinetics and bulk liquid-to-solid surface mass transfer.

The second set of experiments is aimed at examining the role of recombination of products to shift product distributions; it involves the addition of ethylene to reactant gases. If recombination occurs, increased amounts of heavier hydrocarbons will be seen in the reaction products. Runs at higher conversion will also be made; if recombination occurs, the product distribution at higher conversion will be slanted towards heavier products.

In the third set of experiments, a series of runs at conditions known to be reaction limited will be done to examine intrinsic kinetics and look at the effect of H_2/CO ratio on deactivation.

These experiments will be carried out on equipment used by McKee (2) and modified in the following way:

1. The reactor shown in Figure 1 is used in place of the fixed bed reactor. The condenser on top reduces oil loss through evaporation.
2. Two traps, one cooled by water, the other by ice, are used after the reactor.
3. A heated line before the traps allows analysis of the gas with a gas chromatograph.
4. Rotameters and metering valves have been replaced by Matheson flow controllers.

A number of runs have been completed, but results are too preliminary to permit meaningful disucssion at this time.

A sketch of the equipment being used, which has been newly built, is attached as Fig. 1.

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SLURRY REACTOR

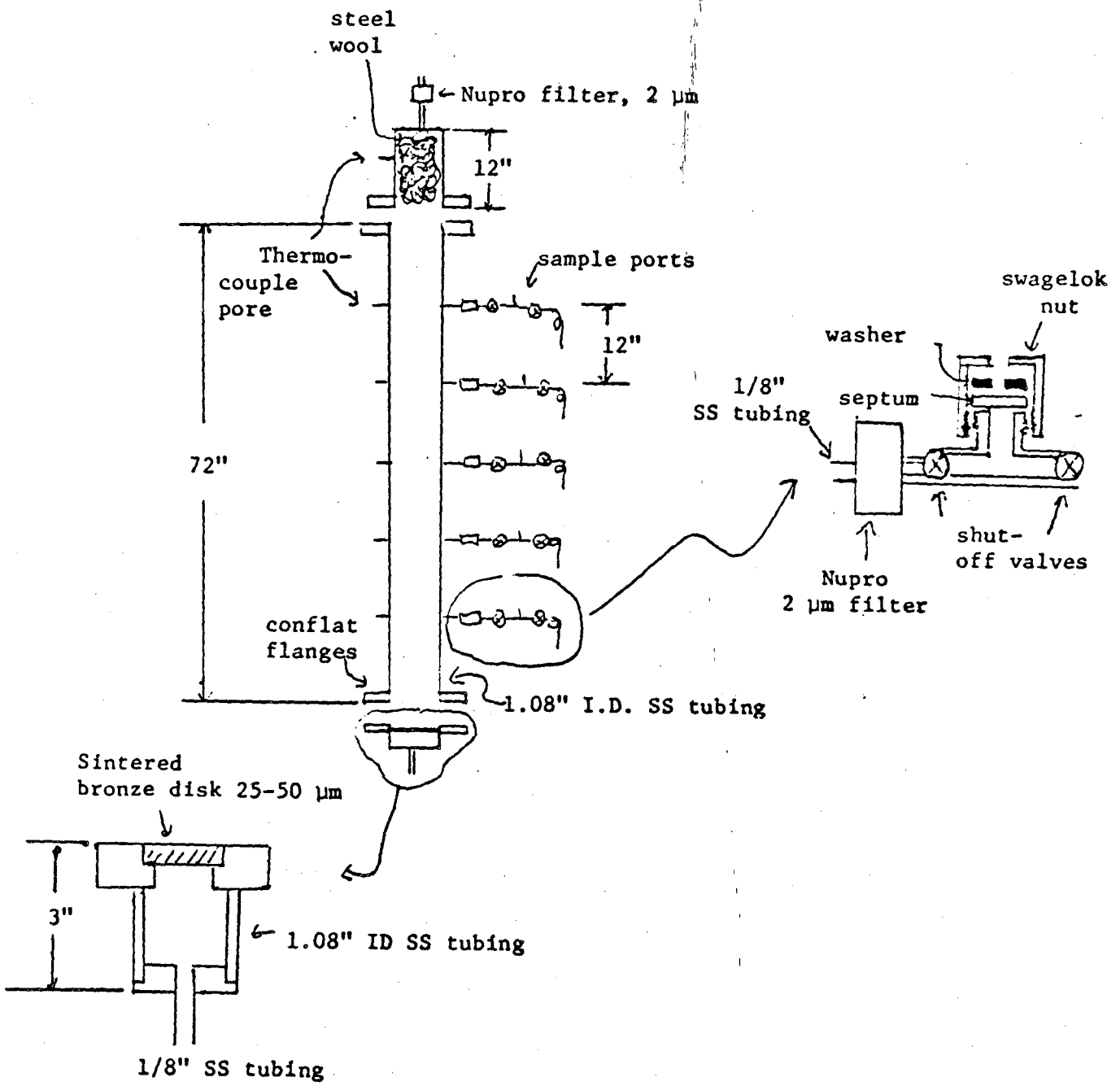

Figure 1

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