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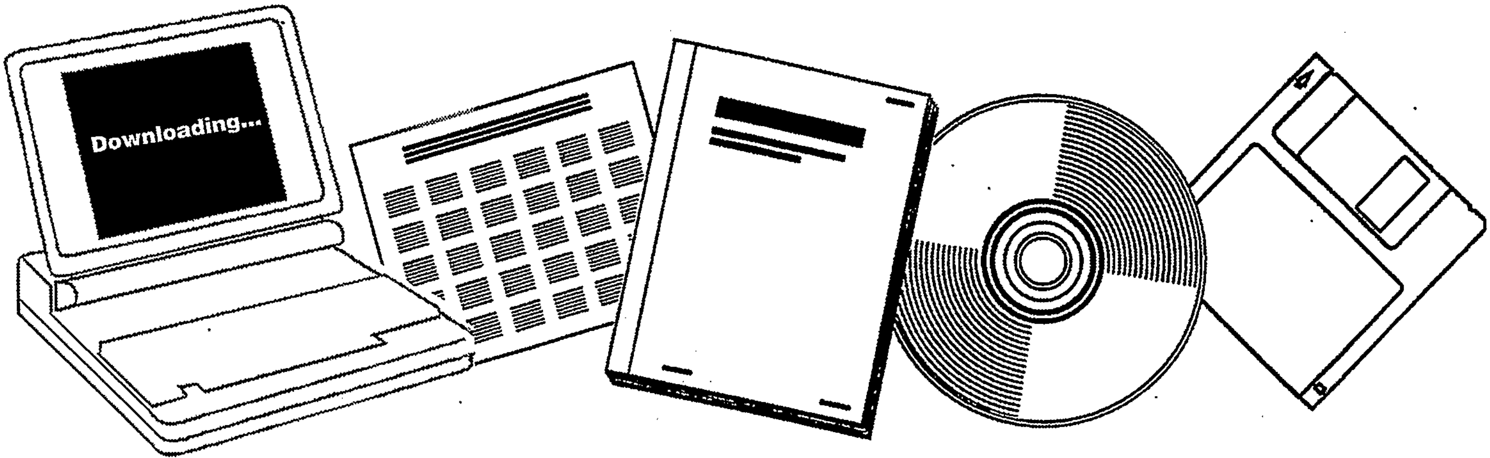

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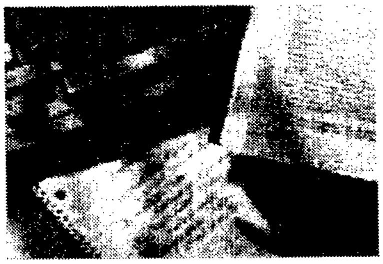

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Quarterly Progress Report

NOVEL EXPERIMENTAL STUDIES
FOR COAL LIQUEFACTION

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NOVEL EXPERIMENTAL STUDIES FOR COAL LIQUEFACTION

Research is being carried out in this project in two areas which are of interest to ongoing investigations at the Pittsburgh Energy Technology Center (PETC). They are: (a) behavior of slurry reactors used for indirect coal liquefaction, and (b) coal liquefaction under supercritical conditions. The current status of each of these tasks is summarized in this report.

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TASK 1: BEHAVIOR OF SLURRY REACTORS USED FOR INDIRECT COAL LIQUEFACTION

The conversion of synthesis gas to liquid products is usually carried out with the reactants in the gas phase and a solid catalyst. Because of relatively poor heat transfer from the gas to the solid, the exothermic heat of reaction is difficult to remove, and care must be taken to prevent the catalyst from overheating with loss of selectivity and activity. Slurry reactors in which the catalyst is suspended in a liquid medium and the gases are bubbled through the slurry have intrinsically better heat transfer characteristics and appear promising for indirect liquefaction processes.

1.1 Scope of Work

Experimental work is presently being concentrated on the synthesis of methanol from CO and H_2 via methyl formate. The process consists in the carbonylation of a molecule of methanol to methyl formate followed by hydrogenation to form two molecules of methanol. The kinetics of the individual reactions were first studied and the results have been included in previous progress reports. They are also presented in a paper which has been published in Fuel Processing Technology(1). Subsequently, the two reactions were carried out concurrently -- both reactions taking place simultaneously in a single reactor. The concurrent reaction is very promising and we are concentrating experimental work in Task 1 on further elucidation of the effect of important design parameters. A paper describing some of these results has been submitted for publication.

A modeling study is also being carried out by Dr. Y. T. Shah at the University of Tulsa. He is investigating the non-isothermal unsteady state Fischer-Tropsch reaction. Experimental work which was begun on a previous project and which was extended on this project demonstrated that multiple steady states can exist for this reaction.

1.2 Results and Highlights

During the quarter experimental studies were concentrated on the study of the concurrent synthesis--specifically the effect of the ratio of the homogeneous to the heterogeneous catalyst and the effect of using alternative homogeneous catalysts. In addition, a paper describing work done on the concurrent synthesis was submitted to Fuel Processing Technology for publication. A copy is attached as an Appendix. Some anomalous experimental data was obtained near the end of the quarter, and no explanation has been found as yet. In brief, the difficulty is that changing the amount of heterogeneous catalyst seems to have little effect on conversion rate. This is contrary to previous work which has indicated that the controlling reaction is the hydrogenation step. Work is continuing to resolve this difficulty.

1.3 Effect of Ratio of Homogeneous to Heterogeneous Catalyst

The concurrent synthesis of methanol (MeOH) is a combination of two sequential reactions--the carbonylation of a molecule of MeOH to form methyl formate (MeF) followed by the hydrogenolysis of MeF to two molecules of MeOH. Both reactions take place in the same reactor. The carbonylation reaction uses a homogeneous catalyst, and the hydrogenolysis reaction uses a heterogeneous catalyst. The effect of changing the ratio of the two catalysts was investigated.

Five runs were made in the 300 cc autoclave at a temperature of 160 C, a pressure of 63.5 bar and a H_2/CO ratio of 2. A fixed amount (6 gm) of heterogeneous catalyst (copper-chromite, United Catalyst G-89) was used with varying amounts of homogeneous catalyst (potassium methoxide, KOMe). The ratios used were 0.0, 0.0007, 0.0024, 0.0048, and 0.0108 moles of KOMe/gm Cu-Cr. In-situ reduction of the catalyst was used. The results are shown in Figure 1. For the run with no carbonylation catalyst, the conversion rate is very low. The fact that there was any conversion at all may be due to some residual KOMe left in the reactor from previous runs. No detectable MeF was found in the liquid. For the other four runs the conversion rates at 30 hours are very similar, and the MeF composition in the liquid corresponded to equilibrium. All conversion rates decreased with temperature. However, the runs using low and high ratios (0.007 and 0.0108) decreased more rapidly than the two runs with intermediate value ratios (0.0024 and 0.0048). The reason for this is not clear, but it does substantiate the conclusion drawn earlier in this work that there is an interaction between the two catalysts.

The rate of change of conversion in the initial transient period is different for the five ratios used. The higher the ratio the more rapidly the conversion rate increases. This is undoubtedly due to the fact that more homogeneous catalyst produces MeF more rapidly, allowing the MeF composition to attain equilibrium more quickly.

1.4. Alternate Homogeneous Catalysts

The homogeneous catalyst used for the carbonylation reaction is MeOK. The source of the catalytic activity for the carbonylation reaction is in dispute. On the one hand, it has been attributed to the methoxide ion by Christiansen (3). This is supported by the findings of Trimm et al. (4) and others that the potassium can be replaced by other cations. On the other hand Imyanitov et al. (5) have reported that salts other than methoxides can be used as catalysts. In the concurrent reaction the situation is still more complicated. We have reported previously that

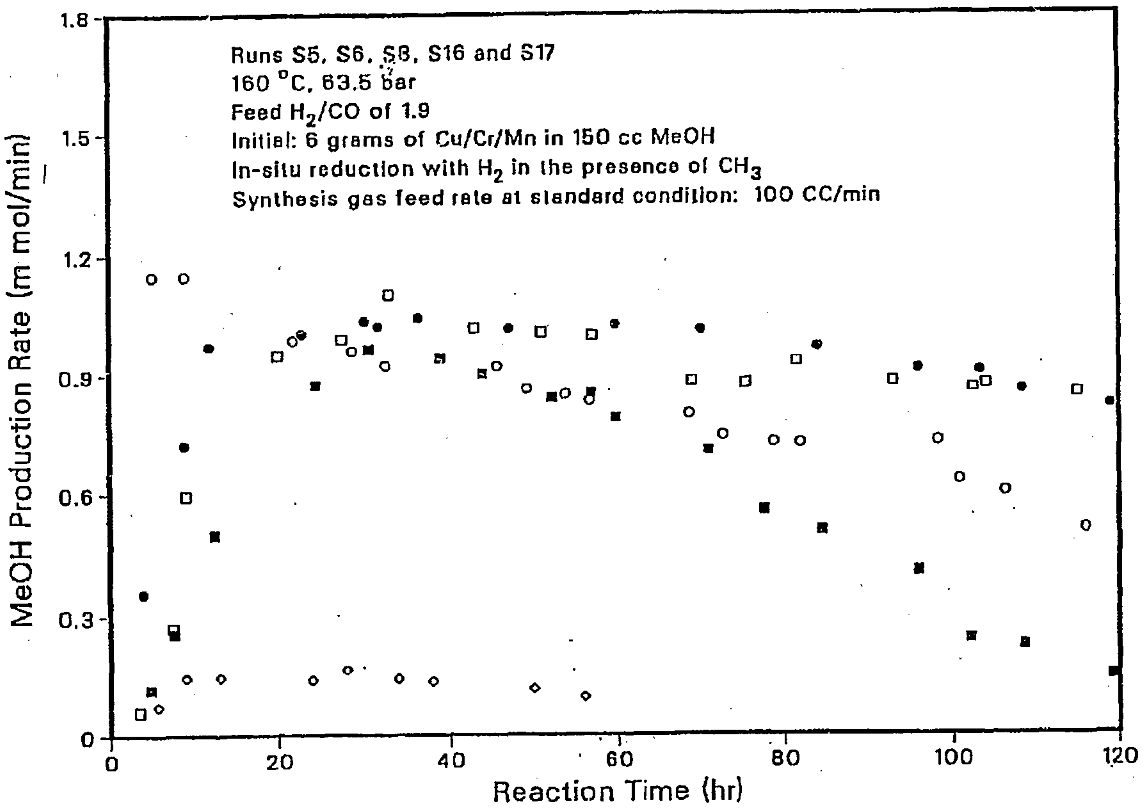

Figure 1: Effect of catalyst ratio (CH_3OK to Cu/Cr/Mn) on the concurrent MeOH synthesis rate.
○ 0.0108 mol/g; ● 0.0048 mol/g; □ 0.0024 mol/g;
■ 0.0007 mol/g; ◇ 0.0000 mol/g.

there is an interaction between the homogeneous catalyst and the heterogeneous catalyst--probably by adsorption of the homogeneous catalyst on the solid heterogeneous catalyst. To evaluate the possibility of using alternative homogeneous catalysts we carried out concurrent runs using potassium acetate, potassium carbonate, and sodium acetate instead of potassium methoxide. All runs were carried out at the same operating conditions, and the results are summarized in Figure 2. Equilibrium MeF concentrations were found for all catalysts after an initial transient period. However, the MeOH formation rates for the three alternative salts were much lower than obtained using MeOK.

A comparison of the performance of NaOMe and KOMe was also made during the quarter. The results are shown in Figure 3. In each case equilibrium concentrations of MeF were observed after the initial transient period. The rate of MeOH formation with NaOMe is smaller in every case than the rate for the potassium salt. There is also a significant difference in the rate of deactivation for the two salts--with the sodium salt deactivating more rapidly. These results are being analyzed.

1.5. Modeling of Non-Isothermal Fischer-Tropsch Slurry Reactors

Modeling studies for the Fischer-Tropsch reaction when carried out adiabaticaly in a slurry reactor were concluded by Dr. Y.T. Shah at the University of Tulsa. A final report was prepared and will be included with the final report for the project. A paper describing the work was completed and submitted for publication. It will be included in the next quarterly report.

1.6 References Cited

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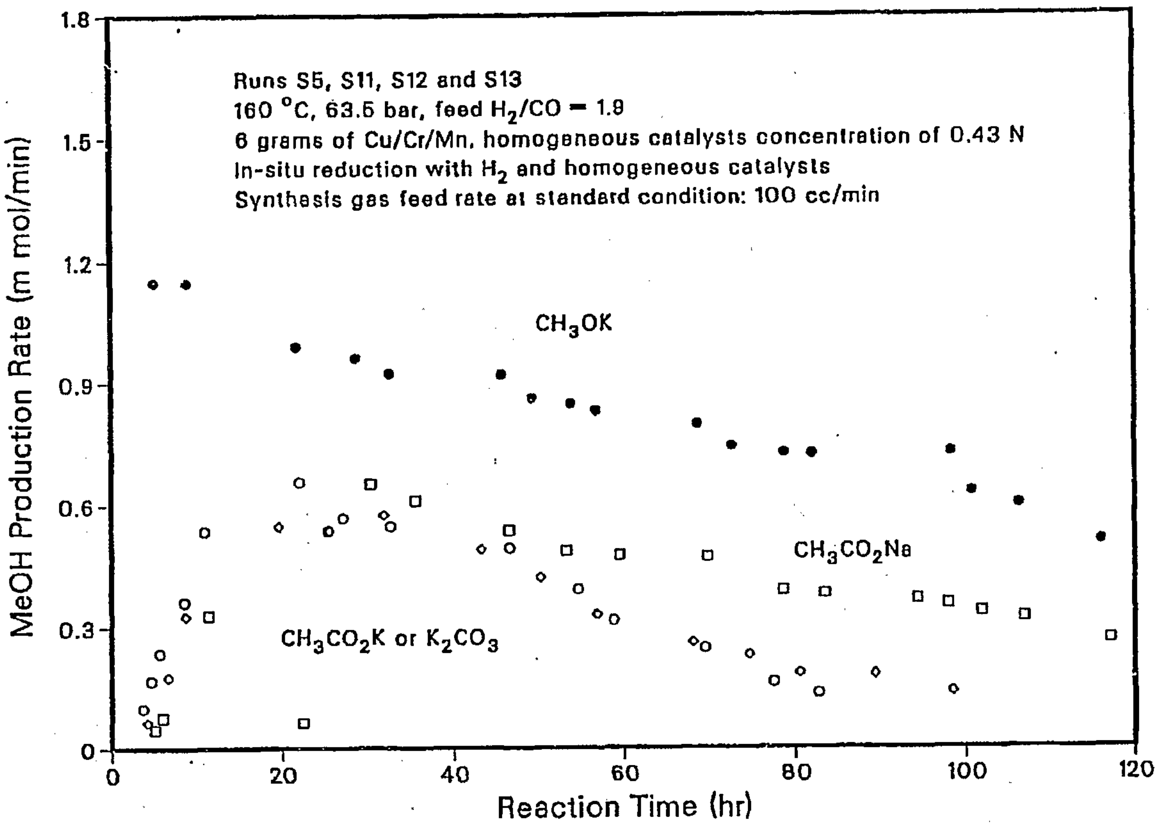

Figure 2: Concurrent MeOH production rates using three homogeneous catalysts and Cu/Cr/Mn (G-89) catalyst.

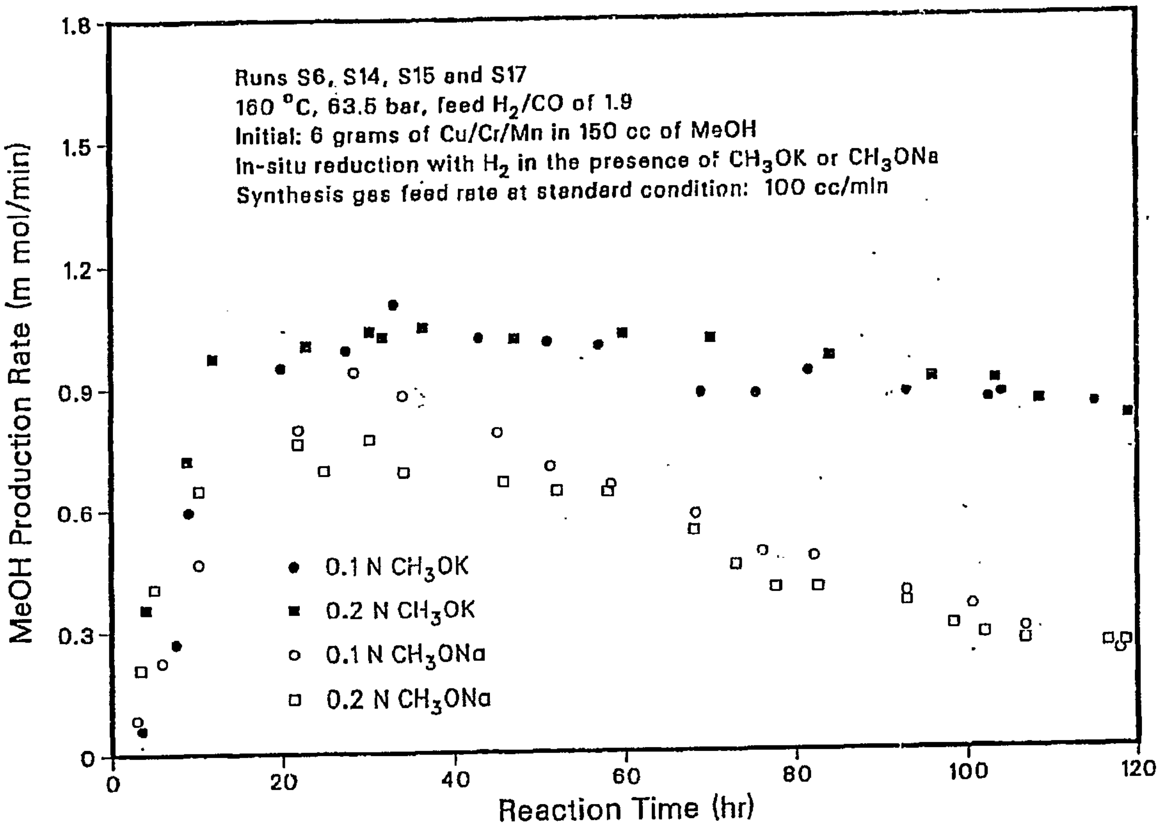

Figure 3: Comparison of concurrent MeOH production rates using CH_3OK and CH_3ONa as the homogeneous catalyst.

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TASK 2: COAL LIQUEFACTION UNDER SUPERCRITICAL CONDITIONS

Supercritical fluid extraction is an attractive process primarily because the density and solvent power of a fluid change dramatically with pressure at near critical conditions. During the extraction of coal, the density of a supercritical fluid should also change the extractability of the coal. During earlier quarters a non-reacting supercritical fluid, toluene, was studied to determine the effect of density on the coal extraction/reaction process. Extractions were carried out for 2 to 60 minutes at reduced densities between 0.5 and 2.0 and at temperatures between 647 and 698 K. The data obtained can be explained by the hypothesis that coal dissolution is required preceding liquefaction reactions and that the degree of dissolution depends upon solvent density and temperature. A kinetic model shows that higher solvent densities result in faster conversion rates and in higher total conversions. Two papers have resulted from this study.

A second factor that makes supercritical extraction attractive is high mass transfer rates. At high pressures, mass transfer rates in a supercritical fluid are much higher than in a liquid, despite the fact that the supercritical fluid has liquidlike solvent powers. The objective of this work is to measure mass transfer rates for naphthalene extraction by carbon dioxide to enable us to determine how mass transfer coefficients vary with pressure, flow rate, and bed height, since these parameters will influence the design of extraction or reaction processes which utilize supercritical fluids. Ultimately, such measurements will be extended to coal/supercritical fluid systems to help define the flow rate and liquid/solvent ratios that would be appropriate for a supercritical system.

2.1 Results and Highlights

During this quarter, we obtained data for equilibrium solubilities and mass transfer coefficients in multiple layers of solid naphthalene pellets at subcritical conditions (35°C and 10-50 atm).

Those equilibrium mole fractions of naphalene in CO_2 at 35°. were 4.58×10^{-5} and 7.00×10^{-5} at 10 atm and 50 atm, respectively. The obtained mass transfer coefficient data were shown in Table O.

2.2 Future Work

Next quarter, we will continue experimental studies of mass transfer in multi layers of solid naphalene pellets at 45°C and 55°C. We will also review the implication of these results for coal liquefaction.

Table 1: **MASS TRANSFER COEFFICIENTS AND DIMENSIONLESS GROUPS FOR TWO LAYERS OF NAPHTHALENE PELLETS AT 35°C AND 10 - 50 ATM**

Run No.	Velocity (1/min) at 0 C, 1 atm	$y \times 10^2$ (mole-fraction)	$G \times 10^2$ (gr/cm2 sec)	$k_y\ 10^4$ (gmole/cm2 sec)
10 - 2	1.060	0.00442	0.373	0.832
10 - 8	1.134	0.00424	0.399	0.589
10 - 9	1.840	0.00380	0.647	0.557
10 - 4	3.825	0.00342	1.346	0.836
50 - 6	2.184	0.00649	0.769	1.144
50 - 7	4.141	0.00622	1.458	1.698

Run No	Re	Jd	Sh	$Gr \times 10^{-6}$	$Sh\ Sc^{-1/3}$	$Gr\ Sc \times 10^{-7}$
10 - 2	11.450	1.620	23.846	0.00008	18.555	0.00002
10 - 8	12.248	1.071	16.864	0.00008	13.122	0.00002
10 - 9	19.837	0.625	15.940	0.00009	12.403	0.00002
10 - 4	41.205	0.451	23.898	0.00010	18.595	0.00002
50 - 6	21.348	1.520	49.429	0.01133	32.450	0.00400
50 - 7	40.338	1.189	73.076	0.01162	47.974	0.00411

2.1: NOMENCLATURE

d_p: Average diameter of sphere possessing the same surface area as a piece of packing [cm].

D_v: Molecular diffusivity [cm^2/sec].

g: Gravitational acceleration [cm/sec^2].

G: Average superficial mass velocity [g/cm^2 sec].

Gr: Grashof number = $d_p^3 \, g \, \rho \, \Delta\rho / m^2$.

Jd: Mass transfer factor = $ShRe^{-1} \, Sc^{-1/3}$.

ky: Mass transfer coefficient [g mole / cm^2 sec mole-fraction].

M_{av}: Average molecular weight [g/g mole].

Re: Reynolds number = $\rho \, d_p \, U_s / M$.

Sc: Schmidt number = $M / \rho \, D_v$.

Sh: Sherwood number = $ky \, M_{av} \, d_p \, / \, \rho \, D_v$.

U_s: Superficial velocity [cm/sec].

GREEK LETTERS

ρ: Average denisty over the bed length [g/cm^3].

ρ_i: Density at solid-solvent interface [g/cm^3].

$\Delta\rho$: Average density difference = $\rho_i - \rho$ [g/cm^3].

μ: Viscosity [g/cm sec].

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