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### COAL CONVERSION PROCESSES. QUARTERLY REPORT, SEPTEMBER 13-DECEMBER 12, 1983

PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL AND PETROLEUM ENGINEERING

JAN 1984



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DOE/PC/61256--T1 DE84 007529

COAL CONVERSION PROCESSES

### Quarterly Report

### For Period September 13 - December 12, 1983

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### January 1984

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### I. ABSTRACT

Experimental work has begun on four separate projects related to coal conversion processes.

An experimental adiabatic flow reactor has been modified to study the direct digital control of exothermic multiphase reactions. The computer program controlling the reactor has been changed to reflect the equipment modifications. Two Fischer-Tropsch catalysts have been tested preliminarily.

A chromatographic apparatus has been refitted to study the absorption of SO<sub>2</sub>, NO and NO<sub>2</sub> by various liquid chemicals. Amines (including triethylene tetramine), N-cyclohexyl-2-pyrrolidone, liquid membranes and stabilized liquid membranes will be tested.

Tests have begun in another experimental fixed-bed flow reactor system, which uses an on-line mass spectrometer and various isotopes of carbon and hydrogen to study the mechanism of synthesis gas conversion on composite catalysts. Initial tests of this method show that the use of  $^{13}C$  alone is insufficient. The use of both  $^{13}C$  and D (deuterium) will be tested next.

Tests in an experimental apparatus for supercritical extraction of coal with water-piperidine mixtures have been made. Results obtained with Illinois #6 and Bruceton bituminous coals have been compared with earlier results using Powhattan #5 coal. Effects of variations in the preasphaltene content of the coal and the hydrogen donor characteristic of the solvent have been found.

### II. INTRODUCTION

Over the past ten years, the faculty of the Chemical and Petroleum Engineering Department at the University of Pittsburgh have devoted major portions of their research effort toward coal conversion. Its coal related projects have included work on a variety of subjects, such as:

 behavior of multiple-phase reactors and heat exchangers in coal liquefaction

. denitrification of coal liquids

- . Fischer-Tropsch synthesis reaction
- production of light olefins from methanol
- . enhanced recovery of methane from coal seams
- . thermal properties of coal and coal liquids
- . coal sedimentation and dewatering
- pneumatic transfer of coal
- . coal gasifier modeling
- . sulfur dioxide absorption in organic liquids
- organization of ten annual international conferences on coal gasification, liquefaction and conversion to electricity (COGLAC).

It is the purpose of this project to extend the work on three of these subjects:

thermal behavior of slurry reactors and for indirect coal
liquefaction

- use of chromatographic techniques to explore absorbers for  $\mathrm{SO}_2$  and  $\mathrm{NO}_{\mathrm{w}}$ 

. support and promoter effects on composite  $CO/H_2$  conversion catalysts and to expand existing work on supercritical extraction to

 extraction and conversion of coal and oil shale using supercritical fluids.

This quarterly report has been prepared by Professors Paul Biloen (Section V), Gerald D. Holder (Section VI), George E. Klinzing (Section IV) and John W. Tierney (Section III). The overall project is coordinated by Professor James T. Cobb, Jr.

### III. THERMAL BEHAVIOR OF SLURRY REACTORS USED FOR INDIRECT COAL LIQUEFACTION (TASK 1)

A knowledge of thermal effects is important in the design and control of reactors for indirect coal liquefaction. The reactions involved are exothermic, and at high conversions the removal of substantial quantities of heat is necessary. A slurry reactor is a promising candidate for carrying out these reactions because of the good heat transfer beetween the liquid and gas phases and between the catalyst and the fluids. The high state of agitation makes it less likely that hot spots will develop, but it also makes it more likely that the reacting mass will undergo large temperature changes if not properly controlled. A slurry reactor especially equipped to measure heat evolution has been built in the Chemical and Petroleum Engineering Department and is being used in this study. The objectives of this work during the first year and the progress to date are summarized below.

1. To complete the testing and evaluation of the experimental adiabatic reactor for measuring thermal requirements for an exothermic reaction carried out under flow conditions. We have made several modifications to the reactor during the first quarter. These include additional heaters on the transfer lines, a provision for cooling the bottom of the copper jacket, and an improved method for activating the catalyst. The thermal capacity of the reactor including the catalyst and slurrying liquid has been measured and found to be 2589.3 cal/C. The measured value agrees well with a calculated value of 2570.21 cal/C.

2. To write and test the computer programs necesary to control the reactor. A digital computer is being used to control the adiabatic heaters, and several changes were made in the control algorithm. Temperatures on the

reactor surface and the surface of the copper containing vessel are now more uniform.

3. To measure the thermal requirement for a Fischer-Tropsch reaction carried out in a slurry reactor under a range of operating conditions. Work was done previously using a fused iron catalyst supplied by United Catalyst. Some data obtained with that catalyst are shown in Table I. We were unable to obtain high conversions with the iron catalyst, and we have subsequently changed to a supported ruthenium catalyst (5% on alumina) supplied by Englehard. Some preliminary data are shown in Table II. The catalyst gives good conversion, but its activity is short-lived, and it must be frequently reactivated. We are developing procedures to obtain good reproducible data from this catalyst in spite of the activation problems.

### IV. USE OF CHROMATOGRAPHIC TECHNIQUES TO EXPLORE

ABSORBERS FOR SO2 AND NO, (TASK 2)

During this past quarter, the chromatographic apparatus was reinstalled in a new laboratory and shakedown operations were carried out. As a check on the operability and reproducibility of the apparatus, the absorption of NO<sub>2</sub> by methanol was carried cut. It is essential to have the column conditioned before attempting any runs with the liquid phase. The retention times and activity coefficients at infinite dilution were measured and calculated. These values agree with the work of Mohamed [1] thus leading the way to probe the newer components.

The three amines to be studied were obtained for testing. The most promising according to discussions with R. J. Walker of PETC is triethylene tetramine [2]. This compound is seen as having the greatest potential to absorb the troublesome NO gas. The coming quarter will emphasize work on the amines.

A recent announcement by Exxon Research [3] has suggested that hindered amines are good candidates for the absorption of acid gases of which  $SO_2/NO_x$  are included. Though the specific compounds listed as hindered amines are classified literature, work into identifying potential candidates has begun.

Another new compound to be tested for  $SO_2/NO_x$  absorptivity is CHP (Ncyclohexyl-2-pyrrolidone) manufactured by GAF. Tests have been performed on pyrrolidone and found to be acceptable for  $SO_2$  absorption but not acceptable for NO absorption. The unique property of CHP is the wide range of its twophase regime in terms of salt concentration and temperature. The wide insolubility zone could be a benefit in the stripping operation and also would

permit the possibility of using CHP as a membrane material. Tests will be conducted on this compound in the coming quarter.

Another area in which exploratory work has been carried out in  $SO_2/NO_x$ absorption is that of membranes. Examination has focused specifically upon facilitated transport. Work by Ward [4] has identified a solution of ferrous chloride in formamide as a facilitated membrane material that can pump NO across its boundaries against a concentration gradient. This system consists of a chamber having two parts separated by a liquid membrane across which the transport of NO takes place. Because this arrangement may be difficult to scale up, research has begun to identify a liquid-liquid system where a similar operation can be applied. Contacts with experts in liquid membranes at Westinghouse Research have suggested some potential candidate membranes, and have established an experimental procedure for forming the membranes. Essential in all membrane work is the addition of the proper stabilizer or surfactant. This material causes the liquid membrane to form a rigid spherical shell which does not break in the agitation process. The surfactant Span 80 by ICI has proved effective in stabilizing the emulsions formed. Carbosil is an additional additive that further stabilizes a system containing < Span 80.

### V. SUPPORT AND PROMOTER EFFECTS ON COMPOSITE CO/H<sub>2</sub> CONVERSION CATALYSTS (TASK 3)

Prior research at PETC [5] has revealed that promotion affects significantly the performance of transition metal/H-ZSM5 catalysts used in the conversion of  $CO/H_2$ . The present study is based upon this finding and focuses on the question:

Is the action of the promoter merely a structural one (leading to an increased surface area of the transition metal component), or does
the promoter affect the intrinsic properties of the transition metal portion of the composite catalysts?

The experimental approach is one in which the isotopic composition of the feed is switched abruptly:

 $12_{CO/H_2} + 13_{CO/H_2}$ 

and the resulting inclusion of  $^{13}$ C within Fischer-Tropsch products is followed by on-line mass spectrometry. For a given overall rate R:

 $\mathbf{R} = \mathbf{k} \Theta$ 

a situation characterized by a high value for surface area,  $\Theta$ , and a low value for reactivity, k (i.e., a large abundancy of <u>long living</u> intermediates) can be recognized because inclusion of <sup>13</sup>C, which occurs on a time scale  $\tau \approx 1/k$ [6,7], is <u>slow</u>. These experiments therefore essentially monitor the coverage ( $\Theta$ ) and the reactivity (k) of reaction intermediates. In these experiments,

reactivity is on the order of  $(\sec^{-1})$ . Whereas structural promoters merely change the total surface area, intrinsic promoters affect both k and  $\Theta$ . These experiments therefore are able to discriminate between structural and intrinsic promotion effects.

Over the past quarter we have conducted experiments which show that stepwise inclusion of  $^{13}$ C in Fischer-Tropsch hydrocarbons indeed can be observed as shown in Figure 1. However, these epxeriments revealed also that despite the low electron impact energy employed (16.5 ev) there is still substantial fragmentation. This hampers the quantitative determination of rates of inclusion of  $^{13}$ C.

Acting on this finding we changed to a setup employing deuterium:

 $12 co/D_2 + 13 co/D_2$ 

This leads to a window of two mass units between fragmentation products (Figure 2).

Currently we are in the process of collecting fragmentation data of deuterated hydrocarbons at 16.5 ev electron impact energy.

### VI. EXTRACTION AND CONVERSION OF COAL AND OIL SHALE USING SUPERCRITICAL FLUIDS (TASK 4)

### Background

A program for the study of supercritical fluids for extraction of coal and oil shale is being carried out. Emphasis is placed on developing a fundamental understanding of supercritical phase behavior as applied to coal conversion and for coal liquid deashing [8]. Initial experiments which have used supercritical water to convert coal to gases, liquids and THF soluble products at supercritical temperatures have produced high conversion with brown coal (75%) and with bituminous coal (58%). Results obtained to date have shown coal rank, coal type, extraction (reaction) time, extraction temperature and initial density of the supercritical phase are important variables. In the case of supercritical fluid mixtures, composition effects are important, particularly when one of the component is a hydrogen donor and the other is not. This report briefly describes the progress made during the period September 13, 1983 to December 15, 1983.

### Progress

Experiments were done with Illinois #6 coal to study the effect of coal type on conversion to gases, liquids and THF soluble products. The results are given in Table III. It was found that the conversion with Illinois #6 coal was low (28%) compared to that obtained with Bruceton bituminous coal (58%) under identical reaction conditions. This may be attributed to the

relatively high preasphaltene content in raw Bruceton coal (8-9%) as compared to 2-3% in the case of raw Illinois #6 coal [9]. Results with Powhattan #5 coal by Towne support this hypothesis. Conversion of Powhattan #5 under identical conditions was only 17%, the lowest of the three coals, and the preasphaltene content of the raw coal (1%) was also the lowest.

Experiments were done with supercritical fluid mixtures of water and a hydrogen donor (piperidine) to study the effect of the addition of a hydrogen donor to the solvent. The effects studied include the conversion of coal to gases, liquids and THF soluble products. A 20 mole % (54 wt %) piperidinewater mixture was used as a supercritical fluid. The results are given in Table III. The coal conversion was lower (16%) than either water or piperidine under identical reaction conditions of temperature, reduced density, reaction time and agitation conditions. This can be attributed to the adduct-forming tendency of piperidine with coal leading to formation of THF insoluble products. The molar density of the mixture was lower due to the higher wt % (54 wt %) of a high mol. wt. substance (piperidine 85-15%) compared to that of water (18%). It was found earlier using brown coal that by increasing the density ( $\rho$ ) of the supercritical water from  $\rho_c/2$  to  $\rho_c$  the amount of THF solubles obtained after a fifteen minute extraction increased from 40% to 75%. Hence the lower conversion obtained using the piperidinewater mixture is probably due to the lower molar density of the supercritical fluid mixture.

Experiments with piperidine-water mixture were conducted with coal being present during the heat-up period. The mixture composition was 20 mole % piperidine. The results are also given in Table III. For the reaction time of one hour, the conversion obtained was 69%. This was in between the conversion obtained for water (10%) and piperidine (83%) under otherwise

identical conditions. The adducts formed by piperidine with coal may be decomposing into THF soluble products as reaction time increases. Also, the presence of piperidine curbs some of the retrogressive reactions going on when coal is present during the heat-up period. Hence the conversion is higher for the piperidine-water mixture than for water alone. Piperidine is a good hydrogen donor and helps in stabilizing the products of coal decomposition during the heat-up period. Hence the conversion in the case of piperidine is greater than for either water or the piperidine-water mixture.

### Plans for the Next Quarter:

Experiments have been done with toluene and piperidine as a supercritical fluid for extraction of coal. Some more experiments are planned to obtain complete kinetic data at different temperature levels and different reduced densities of piperidine and toluene.

Experiments have been done with toluene and piperidine mixtures at the mixtures critical temperature and density. The results are awaited. The data from pure supercritical fluid experiments will be used to explain any compositional effects on the extraction of coal using supercritical fluid mixtures.

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Table I Conversion Using Iron Catalyst in Experimental Reactor

Catalyst: Ammonia Synthesis, C 73-1-01, United Catalyst Inc., Weight of Catalyst: 80 gms, Catalyst loading: 0.160 gm/m1 slurry, Inlet H<sub>2</sub>/CO: 1.0, Pressure: 996 kPa

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Run Lime (hr)	3,5	4.5	7.5	8.0	10.0	12.0	5.0	5.25	7.00	7.45	10.25	10.75	12.0
% Conversion of H <sub>2</sub>	26.4	23.1	58.6	25.0	20.95	58.85	54.7	50.1	20.45	27.2	40.7	20.1	19.2
% Conversion of CO	19.0	19.56	45.87	10.01	14.54	47.44	42.8	38,9	12.25	18.4	31.3	14.26	12.98
Space Velocity (hr-1)	1539.7	1539.7	1539.7	1539.7	1539.7	i 539.7	1255.2	1255.2	1255.2	1255.2	1255.2	1255.2	1255.2
Outlet Flow Rate (scc/min)	685.08	679.6	671.5	668.9	668.9	668.9	541.1	544.5	536.98	534.27	. 534.27	534.27	532.9
Temperature of the Slurry ( <sup>O</sup> C)	268.3	269,0	269.0	269.0	269.4	269.4	268.6	267.8	266.9	266.0	263.8	263.7	262.4
Inlet •Flow Rate (scc/min)	9.707	707.9	707.9	707.9	707.9	707.9	577.1	577.1	577.1	577.1	577.1	577.1	577.1
Run #		1-2	1-3	1-4	1-5	1-6	2-1	2-2	2-3	2-4	2-5 -5	26	2-7

### Table II

### Conversion and Heat Generation Using Ruthenium Catalyst in Experimental Reactor

Catalyst: 5% Ruthenium on Al<sub>2</sub>0<sub>3</sub>., Weight of Catlayst: 30 gms, Catalyst Loading: .06 gms/ml slurry, Pressure: 1375 kPa

Inlet Flow Rate (scc/mm)	Inlet CO Composition (%)	Temperature ( <sup>o</sup> K)	% Conversion of CO	Heat generated per unit vol. slurry (Kcal/hr ml).
758-48	19.07	526.0	16.30	6.0
751.77	20.62	535.0	19,52	7.35
765.32	20.85	545.0	47.41	16.40
758.48	19.07	546.0	56.27	20.77
746.48	21.22	553.0	52.68	17.68
738.7	21.20	559.0	60.96	20,74
738.7	20.77	568.0	95.29	42.93

### Table III

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Summary of Batch Extraction/Reaction of Coal Using Supercritical Fluids

Run #	33	38	44
Coal Used	BBC	BBC	Illinois #6
Procedure	A	В	A
Water, wt%	46.0	45.9	100
Piperidine, wt%	54.0	54.1	
Fluid Density, kg/m <sup>3</sup>	312.1	340.6	351.9
Coal charged x 10 <sup>3</sup> , kg	11.7	60.43	14.6
Temperature, K	647.0	648.0	647.8
Pressure prior to			
injection, MPA	21,81	N.A.	22.57
Pressure, MPA			
(solvent + Argon)	24.93	23,19	24.15
Reaction time, min	15	60	60
Stirrer speed, rpm	2500	2500	2500
THFI, feed coal, %	91.3	91.3	97.2
THFI, solid product, %	16.0	31.3	72.3
Gaseous Product, %	-	-	-
Solid Product, %*	98.7	-	77.1
Liquids (by diff)	-	-	-
Ash %, in THFI	5,39	11.21	17.85
p <sup>r</sup> of water	-	-	8.7

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Fig. 2: IN-SITU OBSERVATION OF DEUTERATED F.T. PRODUCTS.

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