Study of Solvent and Catalyst Interactions in Direct Coal Liquefaction

Annual Progress Report

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Report Period: Start Date: 9/30/97 End Date: 10/1/98

DE-FG26-97FT97264

Report Issue Date: 11/9/98

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EXECUTIVE SUMMARY

CATALYST STUDIES

Major objectives of the present project are to develop a better understanding of the roles of the catalyst and the liquefaction solvent in the coal liquefaction process. An open question concerning the role of the catalyst is whether intimate contact between the catalyst and the coal particles is important or required. To answer this question, it had been planned to coat an active catalyst with a porous silica coating which was found to retain catalyst activity while preventing actual contact between catalyst and coal. Consultation with people in DuPont who coat catalysts for increasing abrasion resistance have indicated that only portions of the catalyst are coated by their process (spray drying) and that sections of uncoated catalyst remain. For that reason, it was decided to suspend the catalyst in a basket separated from the coal in the reactor. The basket walls were to be permeable to the liquefaction solvent but not to the coal particles. Several such baskets were constructed of stainless steel with holes which would not permit passage of coal particles larger than 30 mesh. Liquefactions run with the coal of greater than 30 mesh size gave normal conversion of coal to liquid in the absence of catalyst in the basket, but substantially increased conversion when Ni/Mo on alumina catalyst was in the basket. While this result is interesting and suggestive of some kind of mass transfer of soluble material occurring between the catalyst and the coal, it does not eliminate the possibility of breakdown of the coal particle into particle sizes permeable to the basket. Indeed, a small amount of fine coal has been found inside the basket. To determine whether fine coal from breakdown of the coal particles is responsible for the conversion, a new basket is being prepared with 0.5μm pore size.

Table 1 shows the results of some liquefaction runs with and without two kinds of catalyst in the basket.

Table 1. Conversion (wt%) for Illinois #6 coal.

Sample	T, °C	t, min	Gas	Catalyst	Conv, wt%
DOES-028	421	30	H_2	no	46.6
DOES-027	421	30	H_2	Amocat	57.2
DOES-029	420	30	H_2	Shell	61.3
DOES-033	413	35	N_2	Amocat	78.1

TG/MS Coal Studies

In an effort to better understand the structures and compositions of the more labile components of coal and how they perform in liquefaction, a range of coals from lignite to low volatile bituminous were analyzed by Thermogravimetric Analysis/Mass Spectrometry. Not surprisingly, almost all of the volatile matter came over in the narrow temperature range of 370°C to 570°C with a maximum evolution increasing as the coal rank increased. The coals investigated are listed in Table 2.

Table 2. Percentage of ion current for different compound classes identified by MS for a suite of coals.

Sample	Coal Rank	ALK	BTX	PH	DHB	BFU	NAPT	BPH	FLU	PHE
DECS #25	lig A	18.4	13.3	32.5	5.3	6.5	4.9	2.2	1.8	1.3
Beulah Zap	lig	16.7	13.2	36.0	5.5	6.3	5.2	3.1	1.2	0.6
Wyodak	sub C	17.6	11.5	31.3	5.9	7.3	5.5	2.2	1.2	1.1
DECS #1	sub C	22.5	10.8	20.5	5.9	7.2	6.4	4.1	2.1	2.1
DECS #9	sub B	18.6	11.1	29.2	8.0	7.0	5.2	3.0	1.6	1.7
DECS #10	sub B	21.7	12.2	28.5	4.9	6.5	5.8	2.8	1.8	1.3
DECS #27	sub A	19.6	12.1	29.5	5.1	6.4	6.9	2.9	2.1	1.5
Illinois #6	hvb C	17.5	9.4	31.7	8.9	5.9	5.8	2.4	2.6	1.4
DECS #2	hvb C	15.8	8.6	32.1	8.9	5.6	5.5	4.7	2.2	3.1
DECS #18	hvb C	16.0	7.4	29.9	9.9	5.7	5.9	5.4	2.3	3.5
DECS #22	hvb A	30.9	10.4	17.2	3.8	4.4	6.8	6.0	2.1	3.4
Pittsburgh #8	hvb B	19.1	9.2	23.9	4.6	5.2	10.4	7.2	2.4	4.2
DESC #12	hvb A	18.3	8.6	28.4	5.6	5.3	8.7	6.7	1.9	3.3
Lewiston-Stockton	hvb A	20.1	12.8	24.9	3.3	5.8	8.4	5.1	3.4	2.8
Upper Freeport	mvb	22.2	15.6	17.1	1.9	4.5	11.6	6.2	4.1	4.5
DECS #3	mvb	30.7	11.9	12.0	3.3	4.1	11.5	6.4	3.1	3.9
Pocahontas	lvb	21.4	31.4	10.7	0.9	3.3	13.0	5.8	2.3	2.7

ALK - alkenes; BTX - benzenes, toluenes, xylenes; PH - phenols; DHB - dihydroxybenzenes; BFU - benzofurans; NAPT - naphthalenes; BPH - biphenyls; FLU - fluorenes; PHE - phenanthrenes

The thermogravimetric (TG) analyzer is a TGA 2050 instrument (TA Instruments, New Castle, DE). Each run used ~50 mg of sample. The heating rate was 20°C/min to a final temperature of 900°C. A reflectron time-of-flight (RETOF) mass spectrometer (R. M. Jordan co., Grass Valley, CA) was used to detect the volatile hydrocarbons which were photoionized in the source of the mass spectrometer. Photoionization was performed with generated vacuum ultraviolet radiation at 118.2 nm (10.49 eV). The low ionization potential produced only molecular ions with virtually no fragmentation.

As one would expect, the volatile products were a mixture mainly of olefins, phenols, and lower aromatic hydrocarbons (e.g. BTX) with smaller amounts of such compounds as benzofurans, indenes, indanol, biphenyls, fluorenes and phenanthrenes. While these products came over at slightly different temperatures, they all came over in the temperature range mentioned above. This suggested that they were all breakdown products of larger structures in the coal. To determine that these observations were not artifacts of the experiments, cresol (a commonly observed product) was impregnated into the coals and the pyrolysis repeated. In this case, the added cresol came off quite separately suggesting that the pyrolysis product was a cracking product of the coal and not merely adsorbed in the original coal structure.

The labile components in coal may serve as hydrogen transfer agents and as a solvent in the absence of solvents. In order to investigate the chemical composition of this labile material we extracted coal with tetrahydrofuran (THF) and performed TG/MS analysis on the extract and the extracted coals. While the extracted coal gave rather similar products as the original coal, the extraction products were quite different. Specifically, compounds of molecular weight in the vicinity of 220 are prominent and were not previously observed in the pyrolysis of the original coal samples.

Some of the coals have now been extracted with pyridine and the extracted coal and the pyridine extracts are now being examined by TG/MS. Because of the higher boiling point of the pyridine and its excellent solvent characteristics, we would expect the products to be somewhat different that the THF extracts.

Table 3. Extraction yields in wt% daf.

Coal	Wyodak	Pittsburgh #8	Illinois #6	Upper Freeport
THF yields	9.2	16.8	19.0	5.5
Pyridine yields	-	28.6	25.3	-

Three coals (Mequinenza, Rasa and Illinois #6) containing significant amounts of sulfur were also studied by TG/MS. H_2S, methyl mercaptan and S_2 were principal sulfur products produced along with other sulfur containing compounds (particularly thiophenic). From the temperature of evolution of the products, it is clear that S_2 is being evolved from the pyrite but also from the organic sulfur components, perhaps polysulfides.