

RELATIONSHIPS OF COAL STRUCTURE TO MOLYBDENUM CATALYST ACTION IN LIQUEFACTION

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INTRODUCTION

Previous work in this laboratory has shown that the addition of ammonium tetrathiomolybdate catalyst precursor (ATTM) to coal at low severity conditions primarily increased the asphaltene yield from subbituminous coals, while for bituminous coals, ATTM primarily increased the oil yield [1]. For coals with higher crosslink density (lower rank coals), the catalyst promoted dissolution, while coals with lower crosslink density did not need catalyst to dissolve, and the catalyst instead mainly participated in the hydrogenation of asphaltenes to oils [1]. Our earlier work has now been extended to several additional coals to include liquefaction data with and without catalyst. This data will be compared with coal aromaticity data determined by ^{13}C NMR and solvent swelling data in pyridine.

EXPERIMENTAL

Two different catalyst precursors were used. Sulfided ammonium molybdate (SAM) was prepared, as described in several publications [1-6], by bubbling H_2S into a solution of ammonium heptamolybdate. Ammonium tetrathiomolybdate (ATTM) was purchased from Aldrich.

The coal was impregnated in the same manner as reported previously [1-8]. Coal was slurried with catalyst precursor solutions for 2 hours and dried to less than 1% moisture. Although several molybdenum sulfide precursors were used, previous data have shown that the predominant active catalyst species is MoS_2 [1-8] and relative comparisons can be made about the effect of molybdenum catalysts on coal liquefaction. However, it should be recognized that the degree of dispersion of the precursors on coal could be different because two different catalyst precursors were used.

A total of eight coals was used. Data on the elemental composition of each coal are contained in Table 1. All reactions were carried out in 25 ml microautoclave (tubing bomb) reactors, and heating was accomplished in a temperature controlled fluidized sandbath. The catalyst loading was 1% expressed as weight of molybdenum (not of molybdenum compound) on a daf basis. The reactor was flushed three times with hydrogen, with the final addition pressurized to 6.9 MPa (cold). The reactor was vertically oscillated 2.5 cm at 200 cycles per minute. The coals PSOC-487, PSOC-831, PSOC-1379, and DECS-12 were reacted in a single stage reaction at 360°C for 1 h (PSOC-1488 for 350°C for 1 h). The solvent used was phenanthrene (naphthalene for PSOC-1488) at a 2/1 solvent-to-coal ratio, and the mass of the coal reacted was 2.5 g. The coal PSOC-1488 was reacted in a temperature-staged reaction (350°C for 1 h followed by 425°C for 10 min). A Texas lignite and a hvB bituminous coal used the following reaction conditions: phenanthrene solvent at a 1/1 solvent-to-coal ratio, with the coal mass 5 g, and the reaction was temperature-staged at 275°C for 30 min and 425°C for 30 min. The Çan (Turkish) coal was reacted in phenanthrene and dihydrophenanthrene (5 g of each of solvent and coal) in temperature-staged reactions of 275°C for 30 min and 425°C for 30 min.

For PSOC-1488, the cooled reactor was vented into a glass expansion bulb, and the contents were analyzed by gas chromatography using a Varian model 3700. The contents of the reactor were then rinsed with tetrahydrofuran (THF) into a dried Soxhlet thimble and extracted for about 12 h under nitrogen. The THF was removed by rotary evaporation. The solid residue was dried at 100°C

for 12 h before weighing. Conversion was calculated by subtracting the weight of the residue from the weight of the coal and dividing by the dmmf weight of the coal. Liquids were further separated into asphaltenes and oils by adding hexane to the THF-soluble portion. This mixture was refluxed for 12 h under nitrogen, followed by filtration into hexane-solubles and insolubles. The hexane was removed by rotary evaporation, and the samples were dried at 100°C for 1 h before weighing. The oil (hexane-soluble) yield was calculated by difference from the conversion percentages of the gas yield, THF solubles, and the THF insolubles.

For the rest of the coals, the work-up procedure was changed slightly. Gas percentages were not determined, so the calculated difference for the oils includes the gas yield as well. Gas yields vary only slightly, so any trend in oil plus gas really reflects changes in oil yield. Once the pressure was vented from the reactor, the contents of the tubing bomb were rinsed with hexane into a dried, weighed ceramic thimble and Soxhlet extracted for about 24 h under nitrogen. The hexane was removed from the extract by rotary evaporation. The hexane-insoluble residue was then Soxhlet extracted with toluene to separate asphaltenes from the residue. Toluene was removed from the extract by rotary evaporation. The toluene-insoluble residue was then Soxhlet extracted with THF to separate preasphaltenes from the residue. THF was removed from the extract by rotary evaporation. Preasphaltenes, asphaltenes, and residue were dried overnight under vacuum at 110°C. Conversion was calculated by subtracting the weight of the residue from the weight of the coal and dividing by the daf weight of the coal.

Solid state ^{13}C NMR was performed using a Chemagnetics NMR Model M100S. The experiment was the standard CPMAS and pulsed Fourier transform (PFT) technique to collect the NMR spectrum. This technique was used for determination of f_a and to characterize the structure of each coal. The conditions used for this were: contact time, 1000 μs ; acquisition count, 10,000; carbon frequency, 25 MHz; the time of the 90° pulse, 5.5 μs ; and a pulse delay of 1 s. Table 2 contains f_a data.

Solvent swelling was performed according to the same procedure as Artok et al. [7] and Davis et al. [8]. About 1 g of coal (-60 mesh) was placed into a graduated centrifuge tube fitted with a screw cap. The coal was centrifuged for 30 min at 3000 rpm (room temperature), and the height of the coal (H_0) was recorded. Pyridine (6-7ml) was added to the coal, and the sample was shaken to ensure that all the coal was wetted with the pyridine. The samples sat for ~24 h. The sample was again centrifuged for 30 min at 3000 rpm, and the new height of the coal (H_s) was recorded. The solvent swelling index, Q , was calculated by H_s/H_0 . Table 2 contains the results of this experiment.

RESULTS AND DISCUSSION

It is important to mention that much of the data discussed in this paper were obtained as part of several different projects. Because each of the projects had somewhat different objectives, different reaction conditions were used to obtain the original data. Therefore it would be impossible to draw quantitative statistical conclusions. However, some useful qualitative comparisons can be discussed. Tables 2 and 3 contain the solvent swelling data, the aromaticity data, and the liquefaction data for all the coals. Table 2 contains single-stage data and Table 3 contains temperature-staged data. The first part of the discussion will focus on the low temperature single-stage data.

For the low temperature single-stage reactions, at every reaction condition, using molybdenum sulfide catalyst shows an increase in the total conversion, even at 275°C. The principal factor of concern in this paper is the change in the light fraction-to-heavy fraction ratio (L/H) compared to the coal rank, the solvent swelling index, and the aromaticity (f_a). The L/H ratio is calculated by dividing the oil plus gas yield by the preasphaltene plus asphaltene yield. For all the subbituminous coals (PSOC-487, -1488, and DECS-1), the L/H ratio decreases when comparing the catalyzed reaction to the uncatalyzed reaction. It appears at low severity that the catalyst functions to depolymerize the coal, not to hydrotreat preasphaltenes and asphaltenes to oils and gas. For the bituminous coals (PSOC-831, PSOC-1379, DECS-6, and DECS-12), the L/H ratio increases when comparing the catalyzed reaction to the uncatalyzed reaction. It appears that the catalyst functions not only to depolymerize the coal, but also to hydrogenate asphaltenes to oils and gas. These data are

similar to data presented in the previous work [1]. It was shown by Burgess et al. [1] that earlier work by Weller and Pelipetz [9] and Garg and Givens [10] fits into this pattern.

There are some other comparisons that can be made for the liquefaction data at 350-360°C. The organic sulfur in the coals can be qualitatively classified as high ($\geq 0.83\%$) or low; the crosslink density can be high (~ 1.7), medium (~ 1.5), or low (~ 1.1); organic oxygen can be high ($\geq 15\%$) or low; and the solvent quality is high (phenanthrene) or low (naphthalene). For the uncatalyzed reactions, the two systems indicating the highest conversions - PSOC-831 and DECS-12 - share the following characteristics: high organic sulfur, a medium crosslink density, and low organic oxygen, while using a relatively good solvent during liquefaction. Organic sulfur is a point of macromolecular decomposition [11] and is important for liquefaction reactivity [12]. It seems odd that a coal with a medium crosslink density would be a better liquefying coal than one with a low crosslink density, but the coal with the medium crosslink density liquefies better than the coal with the high one (the fewer the crosslinks to cut, the easier the liquefaction). High organic oxygen can mean a high percentage of carboxyl groups, and it is thought that carboxyl groups play a role in preventing the hydrogenation of free radicals that can lead to retrogressive crosslinking during liquefaction [13].

For the single stage catalyzed reactions at 350-360°C, liquefaction reactions giving the highest conversions are PSOC-1379 and DECS-12. However, there is no apparent distinction for these coals based on coal properties (at least sulfur, f_a , oxygen, and Q). However, consider the comparison of PSOC-487 and -1379. These coals have comparable Q and oxygen. Note that the higher conversion is obtained with the higher sulfur coal, and furthermore, the higher sulfur coal gives a significant increase in oils. For PSOC-831 and DECS-12, both have comparable Q and oxygen, though lower Q and oxygen values than those of PSOC-487 and -1379. In this case, the coal with higher sulfur gives lower conversion. A possible explanation for these observations is that sulfur is not as important as a reactive site in the higher rank coals (Given found that sulfur was important for lignites [12]). When there is a lower oxygen content, there is less likelihood of retrogressive crosslinking at oxygen sites [13], and hence the intervention of H_2S (generated from hydrogenation of the sulfur compounds) is much less important. For the 487/1379 pair of coals, where sulfur is important, increased conversion comes largely from oils. In the 831/12 pair, where sulfur apparently has no effect, the increased conversion comes largely from asphaltenes and preasphaltenes. It is possible that H_2S facilitates conversion to oils [11, 12].

The discussion will now focus on temperature-staged reactions without catalyst. If PSOC-1488 and DECS-1 are compared, they both have similar oxygen contents, with DECS-1 giving much better liquefaction conversion. Notice the big increase in conversion is due to oils. The better conversion of DECS-1 is consistent with its relatively high organic sulfur content, although the effects of solvent quality and crosslink density must also be considered.

The reaction conditions of temperature-staging plus catalyst give comparable conversions for the three coals (not including the ultra-reactive high organic sulfur coal Çan). However, this is consistent with previous arguments [1], that if a sufficiently severe reaction condition is used (and in the context of the work discussed here catalytic temperature-staging is severe), then the severity of the reaction conditions simply overwhelms effects of coal structure and most coals can be driven to high conversions. The main difference in the reaction for the Çan coal is that the conversion in phenanthrene and catalyst is quite high (96.3% for total conversion and 62.0% for the oil + gas yield) and that the conversion in DHP without catalyst is quite high (93.8% for total conversion and 49.0% for the oil + gas yield). When reacting the Çan coal in DHP and catalyst, there isn't much otherwise reactive coal left to break apart, so the catalyst acts mainly in hydrogenating preasphaltenes and asphaltenes to oil and gas. It is also evident with the Çan coal that even without using catalyst or hydrogen donor solvent, the temperature-staged liquefaction conversion would be very good, hence the coal itself is quite reactive. The Çan coal is also very high in sulfur.

CONCLUSIONS

For the single stage liquefaction experiments, using a catalyst with a subbituminous coal will likely be an asset to help depolymerize the coal, and using a catalyst with a bituminous coal will help

depolymerize the coal and hydrogenate asphaltenes to produce higher oil yields. For the temperature-staged data, there is no correlation for rank. There is no correlation for solvent swelling and aromaticity to the liquefaction data when comparing catalyzed experiments to uncatalyzed experiments. For the low rank coals, coals with higher sulfur content tend to have higher conversions, mainly in the oil fractions. For the bituminous coals, the effect of sulfur is minimal. Future work includes more extensive analysis of the structure of these coals as well some additional coals.

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Table 1: Data for Coal Samples.

Penn State Sample Bank No.	PSOC-487	PSOC-831	PSOC-1379	PSOC-1488	DECS-1	DECS-6	DECS-12	Çan
Scan	Bed # 53	Brazil Block	Colorado F	Deitz	Big Brown	Blind Canyon	Pitt #8	
State	Wyoming	Indiana	Colorado	Montana	Texas	Utah	Penn	
Country	USA	USA	USA	USA	USA	USA	USA	Turkey
ASTM Rank	Sub A	hvC b	hvC b	Sub B	Sub C	hvA b	hvA b	Sub A
Moisture (as received, w%)	11.55	13.02	11.99	23.66	30.00	4.70	2.40	20.20
Mineral Matter (dry, wt%)	6.89	4.16	5.09	6.05	7.62	6.67	11.88	8.80
Elemental Composition								
Carbon	75.91	83.28	76.74	76.57	75.90	81.72	84.75	77.00
Hydrogen	4.78	4.97	4.97	5.20	5.80	6.22	5.66	5.60
Nitrogen	1.21	1.61	1.69	0.95	1.50	1.56	1.39	2.00
Sulfur (organic)	0.42	0.94	0.63	0.51	1.10	0.40	0.83	3.30
Oxygen (by difference)	17.67	8.64	15.96	16.78	15.70	10.10	7.37	12.10
Petrographic Composition								
Virginite	89.60	79.20	92.20	88.60		69.10	83.00	n.d.*
Exinite	2.50	4.90	0.60	3.50		17.00	8.10	n.d.
Inertinite	7.90	15.90	7.20	7.90		13.60	8.90	n.d.

* n.d. = not determined.

Table 2: Data for Solvent Swelling, Aromaticity, and Liquefaction Conversion for Single Stage Reactions.

Coal	Solvent Swelling Q (in pyridine)	f _a	%O Org	%S Rank	Reaction Conditions	Tot Conv wt %	Oils + Gas wt %	Asph wt %	Preasph wt %	L/H ^a
PSOC-487	1.7	0.654	17.67	0.42	Sub A 360°C, phor ^b 360°C, phen, cat ^c	20.4 54.5	0.8 -4.8	7.3 18.6	12.2 40.8	0.04 -0.08
PSOC-831	1.5	0.658	8.64	0.94	hvC b 360°C, phen, cat	29.0 43.2	0.1 4.1	7.0 8.9	21.9 30.2	0.00 0.10
PSOC-1379	1.7	0.634	15.96	0.63	hvC b 360°C, phen	18.1	3.5	5.4	9.3	0.24
DECS-12	1.5	0.633	7.37	0.83	hvA b 360°C, phen, cat 360°C, phen, cat	65.8 70.6	16.2 8.1	19.7 18.0	29.9 44.5	0.32 0.13
PSOC-1488	1.1	0.600	16.78	10.51	Sub B 350°C, naph ^d 350°C, naph, cat	18.3 47.8	11.2 14.0	7.1 33.9	1.58 0.40	
DECS-1 ^e	1.3	0.438	15.70	1.10	Sub C 275°C, phen 275°C, phen, cat	6.6 9.0	1.6 1.5	2.2 3.6	2.8 3.9	0.32 0.20
DECS-6 ^e	2.0	0.598	10.10	0.40	hvA b 275°C, phen 275°C, phen, cat	17.7 25.0	4.9 6.9	2.1 3.0	10.7 15.1	0.38 0.38

a L/H = Light-to-heavy ratio.

b phen = phenanthrene

c cat = catalyst

d naph = naphthalene

e Referenced data from [1], [7], [14].

Table 3: Data for Solvent Swelling, Aromaticity, and Liquefaction Conversion for Temperature-Staged Reactions.

Coal	Solvent Swelling Q (in pyridine)	f_a	%O	%S Org	Rank	Reaction Conditions	Tot Conv	Olis + Gas	Asph	Preasph	L/H ^a
PSOC-1488	1.1	0.600	16.78	0.51	Sub B	2-stg ^b naph ^c	30.8	16.9	13.9		1.21
						2-stg naph, cat ^d	78.5	21.7	57.7		0.38
DECS-18	1.3	0.438	15.70	1.10	Sub C	2-stg, phen ^e	53.1	34.0	10.9	8.2	1.78
						2-stg, phen, cat	78.9	49.0	19.3	10.6	1.63
DECS-68	2.0	0.598	10.10	0.40	hvA b	2-stg, phen	48.0	27.2	8.5	12.3	1.31
						2-stg, phen, cat	85.1	38.9	32.5	14.7	0.82
Çan	1.7	12.10	3.30	Sub A		2-stg, phen, cat	96.3	62.0	27.8	6.5	1.81
						2-stg, DHP ^f	93.8	49.0	27.8	16.9	1.10
						2-stg, DHP, cat	98.4	74.1	22.6	1.7	3.05

a L/H = Light-to-heavy ratio.

b 2-stg = temperature-stage, see text for temperatures and times

c naph = naphthalene

d cat= catalyst

e phen = phenanthrene

f DHP = dihydrophenanthrene

g Referenced data from [1], [7], [14].