

LOW-TEMPERATURE CATALYTIC COAL HYDROGENATION:
PRETREATMENT FOR LIQUEFACTION

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INTRODUCTION

There are certain advantages to liquefying coals in separate and successive stages which are operated under different reaction conditions (1). For practical reasons, most investigations have considered only two stages. The main advantages are to increase the selectivity to oil or distillate products and to enhance flexibility of operation.

Differences of opinion exist about whether the preferred reaction sequence is from low to high or high to low temperature. (Essentially, the low temperature range is typically 250-350°C and the high temperature range 400°C and above. Individual studies will depart from this general distinction). In the authors' experience, the first stage should be operated at a lower temperature than the second. Catalytic hydrogenation under mild conditions appears to effect subtle changes to the coal structure, such as the addition of small amounts of hydrogen and the cleavage of weak crosslinks. The outcome of the first stage conditioning or pretreatment is to render the coal more amenable to further processing in the second stage.

This paper describes the findings of a program of research which was intended to examine the relative effects of catalyst type, coal rank and solvent composition on temperature-staged liquefaction.

EXPERIMENTAL

The three coals used in the study were obtained from the Penn State Coal Sample Bank. Their ASTM rank classifications were lignite, hvC bituminous and hvA bituminous. The coal properties are summarized in Table 1.

The coals were ground to -60 mesh (U.S. sieve size) and sealed in air-tight containers. They were impregnated with catalysts of Mo, Fe or a bimetallic Fe/Mo catalyst, by impregnation from aqueous solutions of ammonium tetrathiomolyb-

date (ATM), $(\text{NH}_4)_2\text{MoS}_4$; iron sulfate, FeSO_4 ; or a mixture of these two salts. The procedure consisted of dissolving the desired quantity of the metal salt(s) in enough distilled water to give an approximate water-to-coal ratio of 1.5:1. The coal was then added to the solution, which was stirred at room temperature for about 30 minutes before the excess water was removed by vacuum drying. The residual moisture was less than 2% by weight in all cases.

ATM was prepared from ammonium heptamolybdate (AHM), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ by bubbling H_2S through a solution of AHM for 30 minutes at room temperature while stirring. The reaction occurs quickly (<1 minute), producing a dark-red solution. The coal was then added to this solution in the manner described above. Related studies have now shown that complete conversion of AHM to ATM may not always be achieved and that the tetrathiomolybdate is metastable and can revert to the heptamolybdate on storage and exposure to oxygen (2). Iron sulfate was used as a precursor for the iron sulfide catalyst. The metal loadings were 1% Mo, 1% Fe and 1% Fe + 0.1% Mo expressed on dmmf coal.

Experiments were made in the absence of added solvent and in the presence of pyrene, tetralin, a high-boiling (850+°F) solvent fraction from the lummus ITSL process and a distillate process solvent fraction (220-500° C) from H-Coal (supplied by Consolidation Coal Company). The reactions were performed in stainless steel tubing bombs of about 25cm³ capacity. For solvent-free reactions, 5g of coal was charged and, when solvent was present, the charge consisted of 2.5g of coal and 5g of solvent. A stoichiometric amount of CS_2 was added to ensure that enough available sulfur was present to convert the metal to its sulfide form. The assumption was made that ATM would convert entirely to MoS_2 , and FeSO_4 to FeS_2 . It has since been shown (2) that the thermal decomposition of ATM produces a molybdenum sulfide with an S/Mo atomic ratio in excess of 2.0.

The following reaction conditions were employed: first stage, 275°C, 30 minutes, 7 MPa H_2 (cold); second stage, 425°C, 30 minutes, 7 MPa H_2 (cold). The reactor was cooled and vented between stages. The gaseous products were analyzed after the first and second stages. The second stage products were worked up to obtain the net conversion to tetrahydrofuran-solubles, asphaltenes (hexane-insoluble) and oils, which were calculated by difference.

Hydrogen consumption was calculated knowing the free reactor volume, the initial and final cold reactor pressures and the partial pressures of product gases (CO , CO_2 and $\text{C}_1\text{-C}_4$ hydrocarbons). The THF-insoluble residues were characterized by measurements of the volumetric swelling in pyridine using the procedure described by Liotta (3).

RESULTS AND DISCUSSION

The research program entailed the investigation of sixty different reaction conditions and a considerably greater number of experiments. Space precludes a comprehensive presentation and discussion of the findings, which can be found in a more extended report (4). The text here will be confined to the more evident trends and observations which were indicated by the experimental evidence.

Solvent Composition

The effects of solvent composition on product distribution are shown in Table 2 for the system Fe + Mo catalyst/hvCb coal (PSOC-1498).

In each of the systems studied, the conversions were higher in the presence of solvent than in the solvent-free experiments. It is not necessary to resort to sophisticated explanations to account for this observation: the solvent helps to reduce heat and mass transfer limitations; it can provide a source of donatable hydrogen; the presence of a liquid medium will aid in the distribution of catalyst and the dispersion of the dissolving coal. For the system shown in the table, the presence of solvent also increased the oil to asphaltene ratio. This was not always the case and lower selectivity to oils was recorded in other experiments. No explanation is offered at this time.

In comparison to pyrene, tetralin effected some increases in conversion and oil yield. The magnitude of the response was more evident with the lignite and the hvCb coal than with the highest rank coal. Still further gains were apparent with the high boiling process solvent; in other experiments the product distributions obtained in tetralin and the 850+°F solvent were more comparable.

Earlier work has shown that this high boiling process solvent is an effective liquefaction medium (5). It contains about 30% condensed aromatics which, like pyrene, could promote H-shuttling. The presence of additional H-donors could account for this solvent affording a more favorable yield structure than pyrene alone.

The results obtained with the distillate solvent were quite different. With the hvCb coal, the liquefaction products had high asphaltene contents which, by the method of calculation, results in negative values of the oil yield. It implies that the interaction of the solvent with the coal produced solvent-solvent or solvent-coal adducts which report to the asphaltene fraction.

Similar phenomena were found previously using another distillate solvent fraction (5). In this case, it was further shown that hexane-insoluble products were formed upon catalytic

hydrogenation even in the absence of coal. Evidently, in both instances, the presence of catalyst and hydrogen overpressure were insufficient to counteract the tendency of the solvent to undergo regressive reactions.

Coal Rank

The effects of coal rank on product distribution are reasonably well represented by the selected data in Table 3. To make inferences about rank-dependent behavior from investigations of only three coals would be unrealistic. However, the findings described below are consistent with the outcome of numerous other studies of the influence of coal rank on liquefaction.

With increasing rank there were decreases in oil yield, oil to asphaltene ratio and the yield of CO_2 . It has been shown that the potential for producing oils or distillates in catalytic liquefaction is greater for lower-rank coals (6,7: see also 1 and 8).

The greater proportion of the CO_2 was due to carbon dioxide; CO production was not clearly related to coal rank. Typically, 20-25% of the CO_2 was produced in the first stage. In contrast, the first-stage production of light hydrocarbons was negligible. The net $\text{C}_1\text{-C}_4$ yield did not correlate with rank but generally increased together with conversion.

When solvent and catalyst were fixed, it was also found that the net hydrogen consumption increased with decreasing coal rank. The trend is predictable and follows the rank-related change in coal oxygen content.

Catalyst Type

Caution must be exercised in drawing conclusions about the relative merits of the different catalyst systems, since so many factors can influence the apparent catalyst activity. With this caveat, the present research showed that the Mo and Fe + Mo catalysts were comparable to each other and superior under all conditions to the Fe catalyst, as illustrated in Table 4. It has been demonstrated elsewhere that Mo catalysts are more active than Fe in coal liquefaction (9-11), and synergism for Fe + Mo combinations has also been reported (12).

The lower activity of the Fe catalyst was reflected by the consistently low hydrogen consumption compared to that for Mo and Fe + Mo. Relatedly, Fe appears to be less active than Mo for promoting hydrocracking reactions. Garg and Givens (11) showed that at similar levels of conversion an Mo catalyst (0.02 wt%) gave higher selectivity to oils than an Fe catalyst at much higher loading (1 wt%).

The high activity of the combination catalyst is worthy of note, since the molybdenum was present at a much lower concentration than when used alone (0.1 vs 1.0 wt%). However, the dependence of liquefaction performance on the concentration of the Mo catalyst has not been established. Hawk and Hiteshue (8) showed that Mo introduced as a naphthenate was equally effective at a concentration of 0.1 wt% as 1.0 wt%. Consequently, one explanation for the high activity of the combination catalyst is that Mo is still the dominant species at the lower concentration level.

Alternatively, the possible existence of synergistic or complementary and non-additive effects is of great interest. It offers the potential for the development of new and enhanced activity coal dissolution catalysts and/or the ability to reduce catalyst cost by the partial substitution of a less expensive catalyst component while providing the same or a higher level of activity. In the case of Fe + Mo, there is some evidence to suggest that the two metals interact with coals and coal liquids in different ways.

The principal functions of sulfided molybdenum catalysts are generally believed to be those of hydrogenation, hydrodesulfurization and hydrocracking (9). As discussed above, Fe is much less effective for hydrogenation and hydrocracking than Mo. Iron catalysts may however exert an important role in the reactions of oxygen-containing groups.

Montano (13) has reported that iron sulfide surfaces are involved in the cleavage of oxygen bonds in coals and coal-derived products. Similarly, Tekely and others (14) found that pyrite promoted the cracking of ether bridges, even in the absence of gaseous hydrogen. The interaction of Fe catalysts with oxygen groups is further indicated in the present work. The difference in activity between the iron catalysts and the other two catalysts distinctly decreased with decreasing coal rank. Moreover, the pyridine swelling ratios tended to be higher, at similar conversion levels, for the residues from Fe-catalyzed reactions than from Mo and Fe + Mo, suggesting an ability to break and stabilize (oxygen-containing?) crosslinks.

A tentative proposition is then that Fe and Mo can act in concert, iron selectively attacking oxygen-containing linkages and molybdenum providing strong hydrogenation activity.

Comments on Temperature-Staged Liquefaction

It was apparent from this work that temperature-staged liquefaction mutes the effects caused by altering various reaction parameters. The magnitude of the shift in product yield due to a change in one of the variables is much less than is experienced in single-stage, high-temperature reactions. Previous studies (4) showed that catalytic temperature-staged liquefaction could accommodate quite significant changes

(reductions) in solvent quality before the consequences became significant.

In this investigation, the poor performance of the distillate solvent was evident but there was no clear distinction between the other three. Differences in liquid product distribution attributable to coal rank were also less than expected. From a process standpoint, this can only be considered advantageous; the relative insensitivity to changes in process conditions will allow easier control and steadier operation. For fundamental research, it means that it is more difficult to study the impact of reaction variables on the liquefaction process

Under conditions where there is a plenitude of sources of available hydrogen, it may not be possible to readily identify the most active catalyst system, or most appropriate solvent. To gain more insight into the chemistry of two-stage liquefaction it is necessary then either to employ different reaction conditions or to seek alternative measures of change which are more sensitive than those used here.

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Table 1. Coal Properties

Penn State Sample Number	PSOC-1482	PSOC-1498	PSOC-1504
Seam	Hagel	Wadge	Upper Sunnyside
State	North Dakota	Colorado	Utah
ASTM Rank	lig	hvc	hva
Mean-Maximum Reflectance of Vitrinite (Romax, %)	0.39	0.60	0.80
Ultimate Analysis (% daf)			
Carbon	72.32	77.52	81.96
Hydrogen	2.26	5.45	5.80
Oxygen	23.46+	14.66+	9.66+
Nitrogen	1.02	1.81	1.75
Organic Sulfur	0.94	0.56	0.83
Proximate Analysis (a.r.%)			
Moisture	34.71	9.45	3.38
Volatile Matter	28.07	38.04	37.49
Fixed Carbon	31.36	46.08	51.84
Ash	5.86	6.43	7.29
Petrographic Composition (mineral-free, % vol)			
Vitrinite	88	89	87
Liptinite	2	2	3
Inertinite	10	9	10
Chloroform-soluble extract (% dmmf)	1.76	1.31	1.06

+ = By difference

Table 2. Effect of Solvent Composition on Temperature-Staged Liquefaction (Fe, 1% + Mo, 0.1% catalyst and hvCb coal, PSOC-1498)

Solvent	Yields (% wt dmmf coal)		O/A Ratio
	Conversion(THF)	Asphaltene Oils	
None	54.3	34.8	12.9 0.37
Pyrene	88.7	55.2	21.3 0.39
Tetralin	90.1	56.3	26.0 0.46
850+F residue	93.1	54.1	34.3 0.63
Process distillate	91.8	94.7	-9.3 n.a.

Reaction conditions: first stage 275°C, 30 min., 7MpaH₂ (cold)
second stage 425°C, 30 min., 7MpaH₂ (cold)

Table 3: Influence of Coal Rank on Temperature-Staged Liquefaction (Mo, 1% wt, catalyst; tetralin solvent)

Coal	ASTM Rank	Yields % wt dmmf Coal			
		Conversion	Asphaltenes Oils	CO _x	C ₁ -C ₄ H ₂ Cons.
PSOC-1482	lignite	44.4	35.0	0.79	8.2 1.7 2.44
PSOC-1498	hVCb	59.2	27.2	0.46	3.9 1.7 1.90
PSOC-1504	hvAb	68.1	18.1	0.27	1.6 1.8 1.80

Reaction conditions: first stage 275°C, 30 min., 7MpaH₂ (cold)
second stage 425°C, 30 min., 7MpaH₂ (cold)

**Table 4. Effect of Catalyst on Temperature-Staged Liquefaction
(tetralin; hvcb coal, ESOC-1498)**

Catalyst	Yield (%wt dmmf coal)		
	Conversion	Asphaltenes Oils	H ₂ Consumption
None	73.9	52.1	14.1
Mo	92.1	59.2	27.2
Fe	88.5	58.4	21.5
Fe + Mo	90.1	56.3	26.0
			0.41
			1.90
			1.02
			1.82