

Temperature-Staged Catalytic Coal Liquefaction

Frank Derbyshire, Alan Davis, Mike Epstein, and Peter Stansberry

College of Earth and Mineral Sciences
The Pennsylvania State University
University Park, PA 16802, USA

Abstract

Coal liquefaction has been investigated under conditions where reaction is conducted in successive stages of increasing temperature and in the presence of a dispersed sulfided Mo catalyst. This sequence leads not only to high conversions but also greatly increases the selectivity of the products to oils at the expense of asphaltenes, with only marginal increase in gas make. The product distribution is strongly influenced by the solvent composition and the reaction conditions in the two stages. Examination of the liquefaction residues from the liquefaction of a bituminous and a subbituminous coal has provided supporting evidence to show that the temperature-staged reaction sequence favors hydrogenative processes. Moreover, the choice of reaction conditions for optimum performance is rank-dependent; for example, low-rank coals appear to require a lower first stage temperature than bituminous coals in order to minimize the potential for regressive reactions.

Introduction

In some earlier reported research (1,2) a bituminous and a subbituminous coal were pretreated by dry catalytic hydrogenation, using a molybdenum catalyst at 350°C for 1 h, following which they were mixed with naphthalene (2:1 solvent to coal ratio) and reacted at 425°C for 10 min. The results showed that the low-temperature pretreatment improved both the net coal conversion, based upon solubility in tetrahydrofuran, and the product distribution. Notably, the oil to asphaltene ratio was substantially increased with only marginal additional gas make.

Based upon these findings, further research has been directed to investigating the chemistry and the potential of temperature-staged coal liquefaction. The results of this research are presented in this paper. Similar studies are being conducted on a larger scale by Hydrocarbon Research Inc. (3).

Experimental

Coal Preparation

Samples of bituminous and subbituminous coal were provided by the Penn State Coal Sample Bank for use in this research. The coals were obtained undried and in lump form about 12 mm size and were crushed in a glove box under oxygen-free nitrogen to 0.8 mm top size. The crushed coals were subdivided by riffing into a number of 10 g representative samples and sealed in vials under nitrogen. Properties of the coals are shown in Table 1.

The coals were impregnated with Mo catalyst by slurring with an aqueous solution of ammonium tetrathiomolybdate in the concentration necessary to attain a loading of 1% wt Mo on a dmf basis. The quantity of coal impregnated was sufficient for a complete series of experiments. After slurring, the excess water was removed by vacuum freeze-drying.

Liquefaction

The impregnated coal was mixed in a ratio of 1:2 with liquefaction solvent. In most of the experiments, naphthalene was selected as the solvent because, at least

at the onset of reaction, no H-donor would be present, which would allow the effects of added catalyst and low-temperature coal pretreatment to be more clearly discerned. Approximately 0.1 g of CS₂ was added to the reaction mixture to ensure that the molybdenum was maintained in the fully sulphided state.

Reactions were carried out in tubing bomb reactors of about 30 cm³ capacity which were heated by immersion in a fluidized sandbath. More detailed descriptions of the experimental procedures have been given elsewhere (4). Reactions were conducted either at 425°C for 10 min or under these same conditions after first pretreating at 350°C for 60 min. The initial hydrogen pressure (cold) for both pretreatment and the higher temperature reaction was 7 MPa.

When the low-temperature pretreatment was carried out, the bombs were quenched to room temperature at the end of the reaction period and the yields of light gases were determined by volumetric measurement and gas chromatographic analysis. The main purpose of the cooling and venting procedure was to ensure that there was a high partial pressure of hydrogen in the reactor at the beginning of the higher temperature stage. The rationale for choosing a short reaction time for the high-temperature stage (10 min at 425°C) was the same as that used for solvent selection; namely to accentuate the effects which would be caused by the low-temperature reaction.

Following high-temperature reaction, the gas yield and composition were determined and the solid and liquid products were worked-up to obtain the yields of insoluble residue (tetrahydrofuran, THF) asphaltenes (hexane-insoluble, THF-soluble) and oils (hexane-soluble). In these calculations, it was assumed that the naphthalene reported to the hexane-solubles. Despite extensive precautions, some of the lighter liquefaction products were lost during product work-up and especially during the removal of solvents. Oil yields are therefore calculated from the mass balance assuming that most of the mass balance deficit is attributable to the loss of light ends.

A further factor, which is not accounted in the product distribution, is the yield of water produced by reaction. It is not anticipated that this will constitute more than a few percent of the liquid yields, even with the subbituminous coal, although firm estimates have not yet been made. Because of the method of calculation of the oil yield, any water which is produced is considered as oil. Consequently, the actual oil yield will be somewhat lower than reported.

A few experiments were conducted to explore the effects of extended reaction time at 425°C and the influence of a more reactive solvent than naphthalene. In the latter instance, the solvent was a process-derived recycle solvent fraction (454+°C) obtained from the Lummus Integrated Two-Stage Liquefaction (ITSL) process, when operating on Wyodak subbituminous coal.

In determining the product distribution, quantities of oil and asphaltene, equivalent to those present in the original solvent, were subtracted from the product yields in order to obtain the net yields attributable to coal.

Residue Microscopy

The dried liquefaction residues (THF insolubles) were embedded in epoxy resin and polished with a series of alumina slurries. Examination was undertaken with a polarizing reflected-light microscope under oil immersion at a magnification of 625; a rotatable compensation plate was used as an aid in distinguishing between isotropic and anisotropic materials. Some observations were made in blue-light irradiation, in order to observe the proportions of liptinite macerals present.

Results and Discussion

Reactions in Naphthalene

The conversions and product distributions obtained by the liquefaction of the subbituminous and bituminous coals under various combinations of pretreatment and liquefaction reactions are summarized in Tables 2 and 3. Similar trends are apparent for both of the coals. Reaction in the presence of the catalyst produced higher net conversions than the 'thermal' experiments, as would be expected. However, the combination of low-temperature catalytic pretreatment followed by the higher temperature catalytic reaction had the greatest influence in improving the product selectivity concomitant with attaining the highest conversion. In particular, the highest oil yields were obtained without any attendant increase in the production of light hydrocarbon gases.

An examination of the liquefaction products by gas chromatography showed that there was no significant conversion of naphthalene to tetralin (less than 1%) in any of these experiments. While this finding does not exclude the possibility that the catalyst may promote liquefaction through the successive generation and dehydrogenation of donor solvent, it does suggest that other reaction pathways are operative and may be more important.

The addition of catalyst, without pretreatment, significantly increased the conversion of both coals over that obtained in the thermal experiments. At the same time, these conditions produced the lowest oil yields and the lowest ratios of oils to asphaltenes. The pretreatment evidently allows the catalyst to perform certain functions which ultimately lead to higher oil yields and these functions appear to be not as readily performed during a short catalytic reaction at the higher temperature of 425°C.

Microscopic Examination of Liquefaction Residues

There were notable differences in the appearance of the residues from the bituminous and subbituminous coals. The bituminous coals hydrogenated in the absence of catalyst showed clear evidence of the development of plasticity, i.e., rounded particle outlines and the formation of spheres of vitroplast. Vitroplast is a low-reflecting, isotropic, pitch-like material, usually derived from vitrinite, that occurs as spheres and agglomerates (5). The vitroplast observed in this study is the type which Shibaoka (6) has referred to as a primary vitroplast, being derived directly by softening of vitrinite.

In contrast, the residues derived from the catalytically hydrogenated bituminous coals had apparently undergone more extensive reaction. There was no evidence of simple melting, and the vitrinite-derived material was considerably reduced in volumetric proportion relative to that of other macerals. The reflectance of this vitrinite-derived material was lower than either that of the vitrinite in the feed coal or that of the vitroplast in the residues of uncatalyzed runs. These observations are consistent with the action of the catalyst being instrumental in the hydrogenation and breakdown of the vitrinite structure. An unexpected feature of the residues was the large proportion of remaining, although not necessarily unchanged, liptinite (sporinite and cutinite) present in samples from the catalysed experiments with bituminous coal.

None of the residues from the subbituminous coal contained vitroplast or showed other evidence of plasticity during treatment. Rather, the residues of the vitrinite (huminite) consisted of tattered skeletons of the structures present in the original coal. However, the vitrinite reflectance was significantly higher in the residues than in the parent coal; that of the residue from the catalysed and pretreated coal was judged to be somewhat lower than that of other residues. This

run also resulted in more particle disintegration than was observed in the other residues.

The microscopic studies of the liquefaction residues reflect the trends shown by the yield data in confirming that the staged catalytic liquefaction produced the conditions most conducive to coal hydrogenation and liquefaction.

From the residue analysis for the subbituminous coal, it appears that the temperature selected for the low-temperature stage was too high as shown by the increase in reflectance of the vitrinite-derived materials in the residues relative to the vitrinite (huminites) in the untreated coal. In contrast, the residues from catalysed bituminous coal hydrogenation display the predominance of hydrogenation reactions as evidenced by the lower vitrinite reflectance compared to the parent coal. Without catalyst, the very obvious development of plasticity indicates the dominating effect of thermal treatment.

Effect of Other Reaction Conditions

The data presented above have illustrated the potential advantages to be derived by liquefying coals in stages of increasing temperature and in the presence of a catalyst. Verification of these phenomena has been demonstrated more comprehensively and on a larger scale by Hydrocarbon Research Inc. (3).

In the laboratory scale studies, no systematic attempt has yet been made to investigate how independent variables such as the reaction conditions in the first and second stages, the solvent composition and the catalyst type and concentration affect the performance attainable in such a reaction sequence. Some preliminary data are presented in Figure 1 which show the comparative effects on the product distribution for the subbituminous coal (PSOC-1401) due to (i) increasing the high temperature residence time from 10 to 45 min while employing naphthalene as solvent and (ii) using the more reactive process solvent and the 45 min high-temperature residence time.

With naphthalene, increasing the reaction time at high-temperature is evidently advantageous in promoting further interconversion of oils to asphaltenes (the oil to asphaltene ratio increased from 0.8 to 2:1) with some simultaneous increase in gas make; the CO_x yield increased from 7.9 to 9.8% and the yield of C₁-C₄ hydrocarbons increased from 0.8 to 3.0%. As in the other experiments using naphthalene as solvent, there was no significant conversion of naphthalene to tetralin.

A much more dramatic change in product selectivity was achieved by using the process solvent when the oil to asphaltene ratio increased to approximately 14:1. To offset this gain there was a more significant increase in gas make; the CO_x and C₁-C₄ yields being 12.2 and 4.7%, respectively. Quite evidently, the composition of the solvent is an important parameter even in the presence of an active catalyst.

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TABLE 1

Coal Properties	Penn State Sample Bank No.	FSOC-1266	FSOC-1401
Seam	L. Kittanning	Lower Wyodak	
County	Mahoning	Cambell Co.	
State	Ohio	Wyoming	
Province	Eastern	Northern Great Plains	
ASTM rank class	hVAb	sub. B. (apparent)	
Moisture content, % wt (a.r.)	3.4	16.3	
Mineral Matter, % wt dry coal	6.1 [†]	6.6*	
<u>Elemental Composition % dmmf</u>			
C	83.2	74.3	
H	5.0	5.2	
O**	8.6	19.3	
N	2.1	1.1	
S	0.5	0.2	
<u>Maceral Analysis, % vol</u>			
Vitrinite	91	85	
Exinite	3	2	
Inertinite	6	13	
<u>Sulfur Forms (% dry coal)</u>			
Organic	0.46	0.19	
Pyritic	0.79	0.01	
Sulfate	0.02	0.00	
Total	1.27	0.20	

[†] By low-temperature ashing; * Reported as ASTM "Ash"; ** By difference

TABLE 2

Product Yields from the Liquefaction of Subbituminous Coal (PSOC 1401)

Conditions		Product Yields (% dmmf)									
Pretreatment	Liquefaction	Conversion	Asphaltenes	Oils ¹	CO ₂	CO ₂	C ₁ -C ₄ ²	CO ₃	CO ₂ ³	C ₁ -C ₃	C ₁ -C ₄ ³
a)	None	Thermal	42.5	4.7	28.8	--	--	--	0.6	7.9	0.5
b)	Thermal	Thermal	41.9	9.9	22.1	0.2	7.3	0.1	0.4	9.3	0.2
c)	None	Catalytic	66.7	41.8	17.6	--	--	--	0.5	6.3	0.5
d)	Catalytic	Catalytic	90.7	46.7	35.3	0.3	6.5	0.3	1.1	6.8	0.8

TABLE 3

Product Yields from the Liquefaction of Bituminous Coal (PSOC 1266)

Conditions		Product Yields (% dmmf)									
Pretreatment	Liquefaction	Conversion	Asphaltenes	Oils ¹	CO ₂	CO ₂	C ₁ -C ₄ ²	CO ₃	CO ₂ ³	C ₁ -C ₃	C ₁ -C ₄ ³
a)	None	Thermal	58.1	42.8	13.7	--	--	--	0.3	0.9	0.4
b)	Thermal	Thermal	59.0	47.3	10.2	0.03	0.9	0.05	0.2	1.1	0.24
c)	None	Catalytic	72.6	66.7	4.8	--	--	--	0.2	0.6	0.3
d)	Catalytic	Catalytic	77.3	36.8	38.8	0.09	0.5	0.06	0.3	0.8	0.6

Conditions: 2/1 solvent (naphthalene) to coal (dmmf); catalyst MoS₂, 1% wt dmmf; pretreatment 350°C, 1 h, 7 MPa H₂ (cold); liquefaction 425°C, 10 min 7 MPa H₂ (cold).

¹ By difference; ² After pretreatment; ³ Net yield (pretreatment + liquefaction)

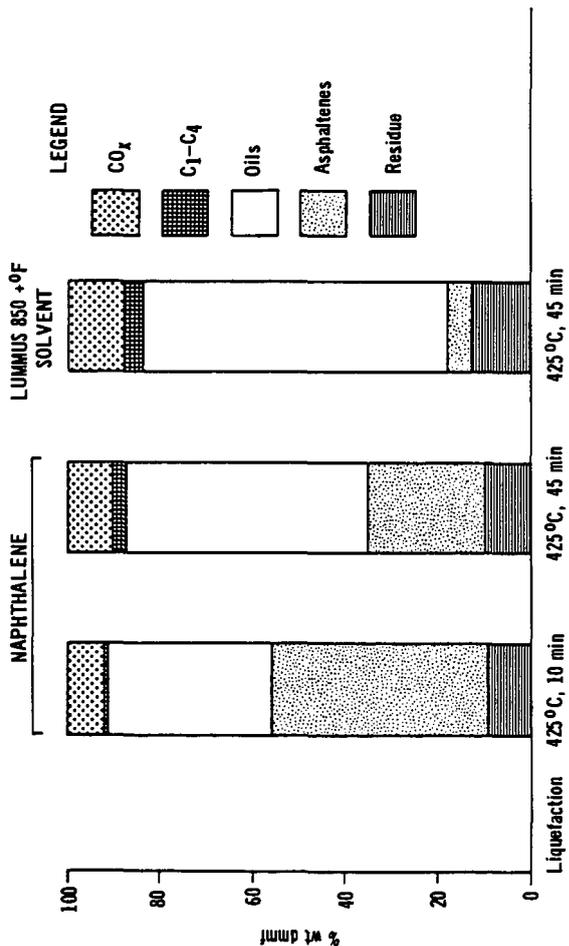


Figure 1. INFLUENCE OF LIQUEFACTION CONDITIONS AND SOLVENT COMPOSITION ON TEMPERATURE STAGED CATALYTIC LIQUEFACTION; SUBBITUMINOUS COAL, WYODAK (PSOC-1401)
 Pretreatment 350°C, 1h, 7 MPa H₂, 1% wt MoS₂