Volume II
Appendices

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DVORSCAK

ADVANCED LIQUEFACTION USING COAL SWELLING AND CATALYST DISPERSION TECHNIQUES

Final Technical Report
for
October 1, 1991-September 30, 1994

Project Manager:
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Work Performed Under Contract No: DE-AC22-91PC91051

For

U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By

Amoco Oil Company
Research and Development Department
Post Office Box 3011
Naperville, IL 60566

We have no objection from a patent standpoint to the publication or dissemination of this material.

Mark P. Dvorscak 3-6-95
Office of Intellectual Property Counsel Date
DOE Field Office, Chicago

MASTER

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APPENDIX A

COMMERCIAL TESTING & ENGINEERING CO.
GENERAL OFFICES: 1919 SOUTH HIGHLAND AVE., SUITE 210-B, LOMBARD, ILLINOIS 60148 • (708) 953-9300

SINCE 1908

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369

PLEASE ADDRESS ALL CORRESPONDENCE
16130 VAN DRUNEN RD., P.O. BOX
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TELEPHONE: (708) 331-
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February 18, 1992

AMOCO RESEARCH CENTER
Warrenville Road & Mill St.
P.O. Box 3011
Naperville, IL 60566
ATTN: D.C. Cronauer
Mail Station H-4

Sample identification by
Amoco Research Center

Kind of sample reported to us: Coal

Sample taken at: -----

Sample taken by: Amoco Research Center

Date sampled: February 10, 1992

Date received: February 13, 1992

Sample No: 14007-117-C2
Sample ID: Raw Coal - Black Thunder

Project No.: 70-6186-15
P.O. No. 099P25960

Analysis Report No. 71-27775

Page 1 of

PROXIMATE ANALYSIS

	As Received	Dry Basis
% Moisture	25.81	xxxxx
% Ash	5.11	6.89
% Volatile	31.06	41.86
% Fixed Carbon	38.02	51.25
	100.00	100.00
Btu/lb	8808	11872
% Sulfur	0.30	0.41
MAF Btu		12751

ULTIMATE ANALYSIS

	As Received	Dry Basi
% Moisture	25.81	xxxxx
% Carbon	50.76	68.42
% Hydrogen	3.77	5.08
% Nitrogen	0.37	0.50
% Sulfur	0.30	0.41
% Ash	5.11	6.89
% Oxygen(diff)	13.88	18.70
	100.00	100.00

Respectfully submitted,
COMMERCIAL TESTING & ENGINEERING CO.

Manager, South Holland Laboratory

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Warrenville Road & Mill St.
P.O. Box 3011
Naperville, IL 60566
ATTN: D.C. Cronauer
Mail Station H-4

Sample identification by
Amoco Research Center

Kind of sample reported to us: Coal

Sample taken at: -----

Sample taken by: Amoco Research Center

Date sampled: February 10, 1992

Date received: February 13, 1992

Sample No: 14007-116-C4
Sample ID: Raw Coal - Lignite

Project No.: 70-6186-15
P.O. No. 099P25960

Analysis Report No. 71-27774 Page 1 of

PROXIMATE ANALYSIS

	As Received	Dry Basis
% Moisture	34.83	xxxxx
% Ash	6.92	10.62
% Volatile	30.18	46.31
% Fixed Carbon	28.07	43.07
	100.00	100.00
Btu/lb	7367	11304
% Sulfur	1.30	1.99
MAF Btu		12647

ULTIMATE ANALYSIS

	As Received	Dry Basis
% Moisture	34.83	xxxxx
% Carbon	42.13	64.64
% Hydrogen	3.15	4.84
% Nitrogen	0.80	1.23
% Sulfur	1.30	1.99
% Ash	6.92	10.62
% Oxygen(diff)	10.87	16.68
	100.00	100.00

Respectfully submitted,
COMMERCIAL TESTING & ENGINEERING CO.

Manager, South Holland Laboratory

APPENDIX B

SUMMARY OF EXPERIMENTS PERFORMED AT PENN STATE UNIVERSITY

Interim Report Submitted to Amoco Oil Company For Sub-Contract Under DOE Contract No. DE-AC22-91PC91051

Date: April 26, 1994

Project: Advanced Liquefaction Using Coal Swelling and Catalyst Dispersion Techniques

Principal Investigator: S. Chander

ADVANCED BENEFICIATION STUDIES WITH THE SO_2 TREATED LIGNITE SAMPLE

The as-received sample was a sulphurous acid (aqueous SO_2) treated lignite material of 8x60 mesh in size. It had an ash content of about 6%. A microscopic examination of the as-received sample showed that this relatively coarse material did not contain any liberated ash particles. The sample was ground to various feed sizes in order to liberate the ash material. A series of flotation tests were carried out at these feed sizes under varying conditions. Dodecane and MIBC were used as the collector and the frother, respectively. It was reported in the previous quarterly reports that a block copolymer of ethylene and propylene oxide was very effective as a flotation promoter in floating lignite. The same polymer was used with the new coal sample for flotation tests in order to increase the combustible matter recovery and to decrease the ash content. For some tests an advanced flotation technique, where the fine feed material was mildly agglomerated prior to flotation, was employed to increase the ash rejection. A summary of experimental conditions for these tests is given in Table 1.

Grinding

The as-received lignite sample was wet-ground in a planetary mill for preset times to liberate the ash material. The grinding times employed were 10, 20 and 40 minutes which are similar to those used with the coal samples tested earlier. A plot of flotation feed size distributions corresponding to these grinding times is given in Figure 1. The nominal feed sizes of the products for the three grinding times were -75 μm, -60 μm and -45 μm, respectively.

Flotation

Flotation with Dodecane as Collector

Flotation tests were carried out at different dodecane concentrations for the three materials produced by grinding. The experiments were carried out at three collector concentrations of 15, 60 and 240 kg per ton of coal. MIBC concentration was kept constant at 1.5 kg per ton of coal in these tests. The result are given in Tables 2, 3 and 4 for the three feed sizes, respectively. An increase in the combustible matter recovery was observed with the addition of the oily collector for the three feed materials. The ash content decreased with the addition of dodecane, except for the -75 μm feed material. As the feed size for flotation became finer a decrease in the

Table 1. Summary of experimental conditions used in the study.

Grinding	Wet grinding in a planetary mill
Feed size	8x60 Mesh
Sample size	50 grams
Solids concentration	33% by weight
Grinding Times	10, 20 and 40 minutes.
Mild oil agglomeration	A blender with a 1.0 liter cell
Solids concentration	5% by weight
Blending sequence	Addition of oil+surfactant to water to make 500 ml of solution - blending for 3 min. in high shear; addition of pulp of 100 ml containing solids - blending for 3 min. in high shear; blending in low shear for 2 min. - transferring the pulp to flotation cell.
Flotation	Wemco flotation machine a with 1 liter cell
Solids concentration	2.5% by weight
Impeller speed	1000 rpm
Dodecane	15 to 240 kg/ Ton of coal
MIBC	1.5 kg/ Ton of coal
Surfactant	0 to 8 kg/Ton of coal
Conditioning sequence	1 min. conditioning of pulp - oil+surfactant addition*; 3 min. conditioning - MIBC addition; Flotation at preset time intervals.

* : This step is omitted if a mild oil agglomeration step is involved.

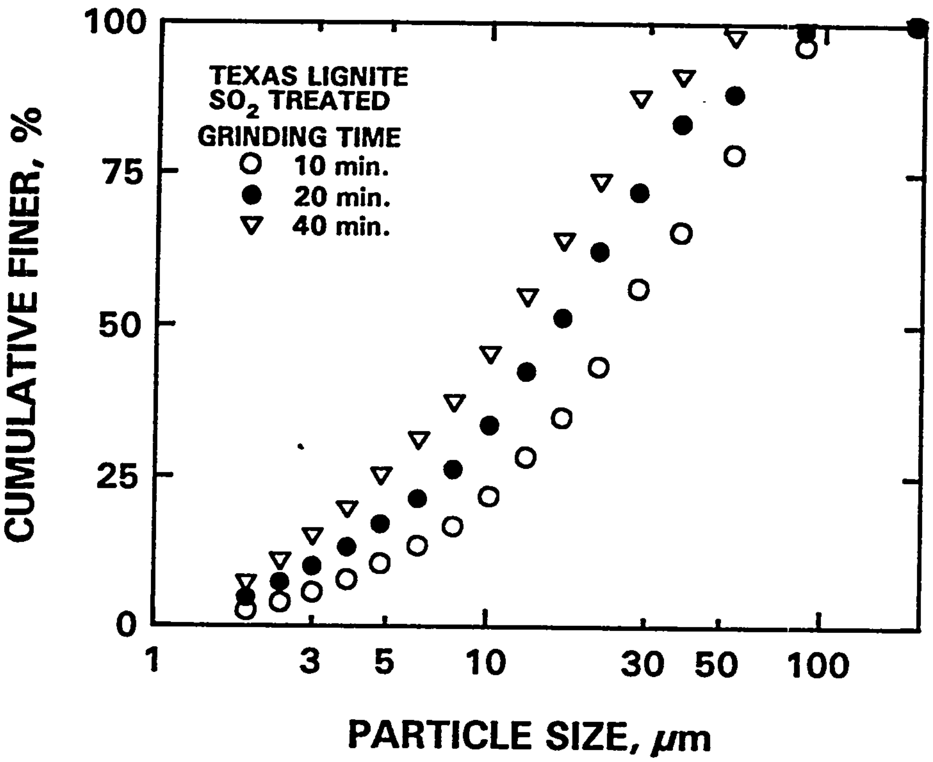

Figure 1. Size distribution of the grinding products used as flotation feed in the experiments.

Table 2. Results of flotation test for varying collector concentrations at a nominal feed size of -75 μm.

	Collector concentration, kg/Ton of coal					
	15		60		240	
Time, min.	Ash, %	CMR, %	Ash, %	CMR, %	Ash, %	CMR, %
0.5	4.9	4.5	5.0	11.2	5.0	13.9
1	5.1	11.4	5.0	18.3	5.1	27.2
2	5.1	21.4	5.0	26.4	5.2	43.1
4	5.0	36.9	5.3	42.3	5.7	59.9
8	5.3	52.8	5.4	60.2	5.7	78.8
Refuse	6.5	100.0	6.5	100.0	6.5	100.0

Table 3. Results of flotation test for varying collector concentrations at a nominal feed size of -60 μm.

	Collector concentration, kg/Ton of coal					
	15		60		240	
Time, min.	Ash, %	CMR, %	Ash, %	CMR, %	Ash, %	CMR, %
0.5	5.1	6.3	5.0	10.8	4.6	13.2
1	5.1	14.0	5.0	17.4	4.9	23.2
2	5.2	24.5	5.0	28.2	5.0	37.6
4	5.3	40.5	5.2	44.5	5.1	50.7
8	5.5	59.3	5.4	61.1	5.3	69.0
Refuse	6.3	100.0	6.3	100.0	6.1	100.0

Table 4. Results of flotation test for varying collector concentrations at a nominal feed size of -45 μm.

	Collector concentration, kg/Ton of coal					
	15		60		240	
Time, min.	Ash, %	CMR, %	Ash, %	CMR, %	Ash, %	CMR, %
0.5	5.9	5.9	5.5	7.2	5.3	6.5
1	5.7	12.3	5.3	12.8	5.2	11.8
2	5.6	21.2	5.4	22.8	5.2	21.2
4	5.6	32.3	5.4	37.4	5.2	34.4
8	5.7	48.6	5.5	54.5	5.3	54.0
Refuse	6.6	100.0	7.0	100.0	6.5	100.0

combustible matter recovery was observed for a given collector concentration. The ash content of the clean coal product generally increased with the decrease in the feed size, except for the oil concentration of 240 kg per ton of coal. The decrease in the quality of separation was not surprising since flotation is known for its lack of selectivity at very fine sizes. In summary, it can be seen from the results that the ash rejection is not very satisfactory and the combustible matter recoveries are quite low for all the three feed materials when only dodecane was used as collector. For a combustible matter recovery of about 50% the ash in the product was around 5.5%, which was much too high. The results show that use of dodecane alone is not enough to beneficiate the treated lignite sample.

In another test, carried out with the -45 μm material at an oil concentration of 240 kg/T of coal, dodecane was emulsified in a blender prior to its addition to the flotation cell. By this procedure fine collector droplets were produced to improve the separation by enhancing the collector-particle interactions at these fine sizes. The results are given in Table 5 for both "no-emulsification" and "emulsification" case for the same amount of dodecane. It can be seen that emulsification of the oily collector resulted in an appreciable increase in the combustible matter recovery while no discernable improvement in the ash rejection was observed.

Flotation in the Presence of Dodecane and a Copolymer of Ethylene and Propylene Oxide

Flotation tests were carried out using a copolymer of ethylene and propylene oxide as a flotation promoter in addition to dodecane. The collector concentrations used in these tests were 15 and 60 kg per ton of coal. The block copolymer to collector ratio was kept constant at 0.1 for these tests. The results are given in Tables 6, 7 and 8 for the three feed sizes of -75 μm, -60 μm and -45 μm, respectively. It can be seen that addition of the surfactant resulted in a substantial decrease in ash while significantly increasing the combustible matter recovery when compared to dodecane alone. The flotation results were better if 60 kg of collector per ton of coal was used when the polymeric surfactant is present. Both the product quality and the combustible matter recovery decreased as the feed size became finer.

Table 5. Results of flotation test with or without emulsifying the collector at a nominal feed size of -45 μm.

	Collector concentration: 240 kg/Ton of coal			
	Non-emulsified		Emulsified	
Time, min.	Ash, %	CMR, %	Ash, %	CMR, %
0.5	5.3	6.5	5.2	10.7
1	5.2	11.8	5.1	17.6
2	5.2	21.2	5.0	27.2
4	5.2	34.4	5.1	42.3
8	5.3	54.0	5.2	62.5
Refuse	6.5	100.0	6.4	100.0

Table 6. Results of flotation tests for varying collector concentrations at a nominal feed size of -75 μm in the presence of a block copolymer.

	Collector concentration, kg/Ton of coal			
	15		60	
Time, min.	Ash, %	CMR, %	Ash, %	CMR, %
0.5	4.6	11.5	4.2	24.9
1	4.6	26.3	4.2	42.2
2	4.6	43.3	4.3	65.6
4	4.8	61.0	4.5	86.2
8	4.9	67.5	4.7	93.5
Refuse	6.3	100.0	6.1	100.0

Table 7. Results of flotation test for varying collector concentrations at a nominal feed size of -60 μm in the presence of a block copolymer.

	Collector concentration, kg/Ton of coal			
	15		60	
Time, min.	Ash, %	CMR, %	Ash, %	CMR, %
0.5	4.7	10.4	4.2	17.0
1	4.7	13.9	4.3	25.8
2	4.7	28.2	4.4	44.3
4	4.7	44.8	4.5	64.1
8	4.9	62.0	4.6	79.3
Refuse	6.2	100.0	6.3	100.0

Table 8. Results of flotation test for varying collector concentrations at a nominal feed size of -45 μm in the presence of a block copolymer.

	Collector concentration, kg/Ton of coal			
	15		60	
Time, min.	Ash, %	CMR, %	Ash, %	CMR, %
0.5	5.2	8.3	4.8	10.9
1	4.9	16.5	4.6	20.7
2	4.8	27.3	4.6	31.9
4	4.8	40.4	4.8	45.6
8	5.0	53.5	5.0	65.1
Refuse	6.7	100.0	6.2	100.0

Advanced Flotation in the Presence of Dodecane and a Copolymer of Ethylene and Propylene Oxide

In this set of flotation experiments the flotation pulp was conditioned in high shear (in a blender) in the presence of the oily collector and the polymer. The flotation test conditions were similar to those reported in Tables 6, 7 and 8. After mixing in the blender the material was transferred to the flotation cell and the flotation test was carried out. A visual observation showed that the material from the blender consisted of loose agglomerates of about 0.5 mm in diameter. A photo-micrograph of the agglomerates from the blender is given in Figure 2. The conditions were chosen to obtain such loose agglomerate structure so that the entrapment of the ash material inside the agglomerates would be minimized. The results of these tests are given in Tables 9, 10 and 11 for the three feed sizes, respectively. The amount of the oily collector was 15 and 60 kg per ton of coal and the polymer-to-collector ratio was 0.1 as before.

The results show that a mild agglomeration of the feed material prior to flotation results in a substantial decrease in the ash content. The corresponding combustible matter recovery was also higher if the feed material is agglomerated prior to flotation than that obtained in the case of flotation alone. A clean coal product of about 4.0% was obtained with a combustible matter recovery of about 90%. The feed size to obtain this product was nominal passing 60 μm, suggesting that further grinding under these conditions is not necessary. Better results were obtained with 60 kg of collector per ton of coal than that obtained with the small amount. Further improvement might be possible by optimizing the amount of collector and the surfactant.

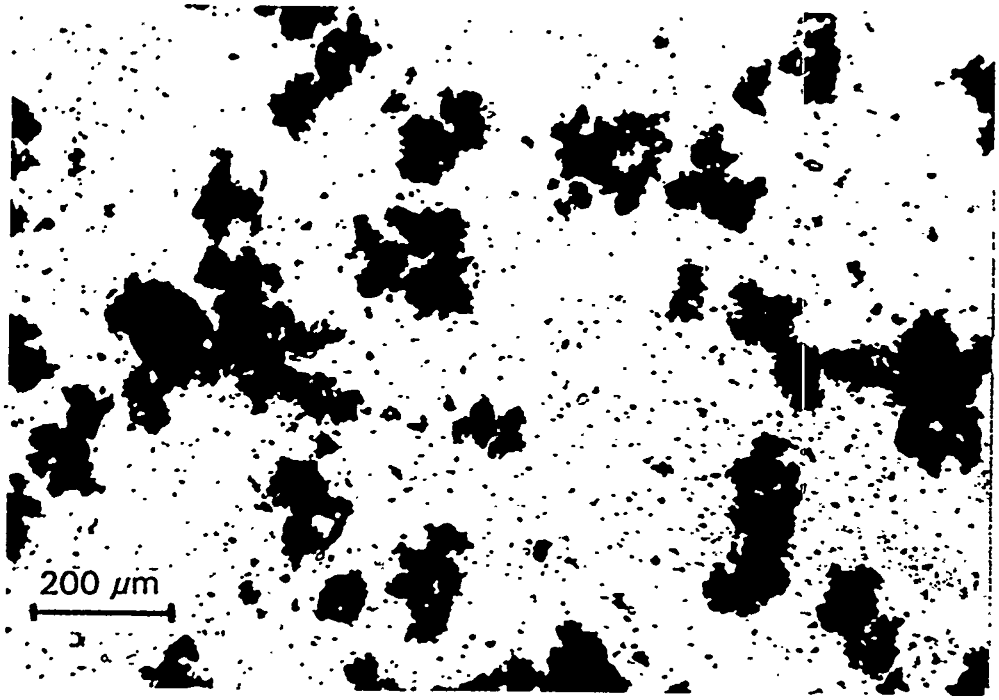

Figure 2. A photo-micrograph of the loose agglomerates generated by the mild oil agglomeration stage.

Table 9. Results of advanced flotation test for varying collector concentrations at a nominal feed size of -75 μm in the presence of a block copolymer.

	Collector concentration, kg/Ton of coal			
	15		60	
Time, min.	Ash, %	CMR, %	Ash, %	CMR, %
0.5	4.8	13.0	4.1	24.2
1	4.7	22.3	4.2	42.9
2	4.5	38.7	4.2	72.9
4	4.4	54.4	4.2	88.0
8	4.5	63.5	4.2	92.5
Refuse	6.5	100.0	6.5	100.0

Table 10. Results of advanced flotation test for varying collector concentrations at a nominal feed size of -60 μm in the presence of a block copolymer.

	Collector concentration, kg/Ton of coal			
	15		60	
Time, min.	Ash, %	CMR, %	Ash, %	CMR, %
0.5	4.7	10.0	4.3	15.4
1	4.7	16.8	4.2	29.1
2	4.4	30.7	4.1	54.2
4	4.3	47.2	4.0	79.0
8	4.3	58.1	4.0	88.3
Refuse	6.3	100.0	6.3	100.0

Table 11. Results of mild advanced flotation test for varying collector concentrations at a nominal feed size of -45 μm in the presence of a block copolymer.

	Collector concentration, kg/Ton of coal			
	15		60	
Time, min.	Ash, %	CMR, %	Ash, %	CMR, %
0.5	5.0	6.3	4.1	13.8
1	5.0	9.5	4.2	26.7
2	50	18.1	4.1	50.0
4	5.1	29.6	4.1	71.7
8	5.3	41.8	4.1	84.5
Refuse	6.4	100.0	6.3	100.0

APPENDIX C

APPENDIX C

LITERATURE REVIEW: SOLVENT SWELLING OF COALS

1. INTRODUCTION

When brought into contact with most organic solvents, coals absorb the solvent and swell. The amount of swelling depends on both the coal and the solvent. The necessary background for that interpretation is the physical chemistry of cross-linked polymers. An extensive discussion of that well developed, active science can be found in standard texts and monographs[1-4].

More than 25 years ago, van Krevelen proposed that coals were three-dimensionally cross-linked macromolecular networks and successfully treated them as such[5]. This idea was largely ignored for almost 20 years. Recently this suggestion has been extensively developed by several groups and is now generally, but not universally[6-9], accepted. It has changed the way chemists think about coals and led to new research and insights.

Bakelite, the polymer once used to make billiard balls, and rubber are two familiar materials which are cross-linked networks. Their properties are quite different and the structural features responsible for the differences are well and quantitatively understood. There exist a variety of experimental techniques for studying macromolecular networks and a well developed theoretical framework to guide their application and evaluate their results. The experiments discussed in this review are a principal technique of modern polymer chemistry and the data obtained with coals are intelligible within the framework of macromolecular structures. A brief, qualitative introduction to cross-linked networks will therefore be provided. More thorough and quantitative introductions to this topic are available[1-4].

Consider the set of linear macromolecules shown in Plate 1A. They will, in principal, dissolve in a good solvent. Plate 1B shows these chains linked together to form a three-dimensionally cross-linked network with the dots (●) indicating a covalent bond between chains. This network is insoluble in all solvents, because it is one large molecule. A rubber stopper is such a large molecule, that is obviously too large to dissolve. When contacted by a solvent for which it has an affinity, the solvent will dissolve <u>in the solid,</u> and the solid will expand to hold it. This experiment, done quantitatively, is capable of revealing a good deal about the nature of the macromolecular network. This background will be used in discussing the effects of swelling coals with solvents.

The two factors which control the amount by which a coal swells in a solvent are the magnitude of the solvent-coal interactions, usually expressed as the Flory interaction parameter, χ, and the cross-link density of the coal, usually expressed as the number average molecular weight between branch points ($\overline{M}_c$). The more favorable the interactions between the solvent and the coal, the greater the amount of solvent present in the coal at equilibrium and the greater the swelling will be. The effect of $\overline{M}_c$ is more complex. The molecular chains in the cross-linked network shown in Figure 2 are linked together in a three-dimensional array. The links between the chains, shown as black dots at chain intersections, are called branch points. $\overline{M}_c$ is the number average molecular weight of the chain between branch points. As the coal swells, these branch points move away from each other. The farther they can move, the more the coal can expand. Their limits of motion are set by the length of the chains connecting them. Therefore, the longer the chain segments, that is the larger $\overline{M}_c$, the more the coal can swell. The two factors whicH must be considered in any rationalization of coal swelling are the coal-solvent interactions (χ) and the cross-link density or $\overline{M}_c$ of the coal.

The size of $\overline{M}_c$ governs many of the mechanical properties of coals. A highly cross-linked (low $\overline{M}_c$) material will be stiffer, less flexible than a less cross-linked material. Mechanical properties such as shear-moduli depend directly on $\overline{M}_c$. It is necessary to know $\overline{M}_c$ to understand a coal's mechanical properties.

A coal can exist as either a glass or a rubber with a transition zone. In the rubbery state, the macromolecular chains can move relatively freely and the coal will be somewhat flexible. Diffusion rates in the solid will approach those in liquids because the macromolecules can move readily to allow passage of the diffusing molecule. In a glassy state, the same macromolecular chains are constrained and can only move a little. The material is no longer flexible and diffusion through it is quite slow. Coals as mined exhibit glass-like properties. Some solvents can cause a glass-to-rubber transition to occur in coals. Whether the thermal glass to rubber transition occurs at a temperature below that at which a coal thermally decomposes is an important question. The mobility of reagents and coal products in coals has a large effect on the chemistry which occurs. For example, a trapped pyrolysis product eventually reacts with the coal matrix trapping it. If it could diffuse freely, this might not happen. Therefore, the state of the network has a large effect on its chemical reactivity.

The measurement of solvent swelling is one of the best methods for probing the macromolecular network structure of coals. The swelling of coals also provides opportunities for modifying their properties in technologically useful ways, such as providing routes for catalyst precursors to penetrate into the coal matrix.

2. COAL STRUCTURE MODELS

Different models of the molecular structure of coal have been proposed and reviewed quite extensively in the literature[1-15]. Recently, a consensus that coal is a covalently crosslinked macromolecular network structure composed largely of aromatic and hydroaromatic "clusters" has been reached among most scientists in this area. However, some objections have been raised[16-18]. The following arguments support a crosslinked macromolecular network structure. 1. Only a small amount of most coals is soluble without reaction[19,20] in any known solvent; this is consistent with crosslinked macromolecular structure or a highly entangled or associated mixtures of large molecules. 2. Coals swell and expand by as much as 2.5-fold in volume when brought into contact with a good solvent.[21,22] This is consistent with crosslinked macromolecular structure or a highly entangled or associated mixtures of large molecules. The high degree of reversibility of the dimensional swelling of coal particles recently observed by Brenner[23] is consistent only with a covalently crosslinked structure and rules out entanglements as the sole associative force[18-21]. 3. Coals are viscoelastic.[24,25] 4. Hydrogenolysis increases the amount of soluble material in a coal and these new soluble materials are very similar to those naturally occurring in coal. Coals behave as if they are very large molecules being cleaved[5]. It is concluded from the foregoing considerations that coals must be covalently crosslinked networks.

Other noncovalent interactions also play important structural roles. Larsen, et al[9,26] proposed that coals consist of a covalently bonded network of clusters which are extensively hydrogen bonded to each other and that the hydrogen bonding between clusters provide most of the crosslinks responsible for the brittle, rock-like, character of bituminous coals. Peppas and Lucht[27,28] proposed a crosslinked macromolecular coal structure in which entanglements among the chains play a large role. Szeliga and Marzec proposed that coal macromolcules are bound together through electron-donor interactions[29,30].

3. EQUILIBRIUM SWELLING

Coals do not dissolve, rather they swell when they come in contact with a good solvent[21,22]. Dryden developed a classification of suitable solvents for coals based on his extensive studies on the extraction of low rank coals. The best solvents contain a nitrogen or oxygen atom possessing an available unshared pair of electron[31]. This phenomenon is particularly striking with solvents containing nitrogen atoms such as ethylenediamine and pyridine. Solvents which extract large amounts of soluble material from coals are also good swelling solvents.

Equilibrium swelling is an important investigative tool to study the thermodynamic interactions and physicochemical structure of coal. The swelling ratio (Q) of coal by solvents is defined as the ratio of the volume of swollen coal at equilibrium with the swelling solvent to the original coal volume . Several days may be needed to reach equilibrium due to slow diffusion rates. The gravimetric technique[32-36] for measuring the expansion of coal is quite simple, but often takes a long time. The coal is exposed to solvent vapors in a vacuum desiccator. The swelling ratio is the ratio of the mass of swollen coal after equilibration to the mass of dry coal corrected for the mass of the solvent which fills the coal pores and does not contribute to the swelling. The equilibration time often is several days. A more rapid and convenient way of measuring swelling of coals by solvents was developed by Dryden[10c] and used by Liotta[38] and Larsen[37]. The dry coal is placed in an 8 mm o.d. Pyrex tube and is centrifuged for 5 min. in a Fisher centrifuge at 1725 rpm. The height of the coal is measured as h_1. After breaking up the column of packed coal excess amount of solvent (3-4 ml) is introduced and the tube is vigorously shaken to ensure thorough mixing. The coal is again centrifuged and the height is measured as h_2. The mixing and centrifuging are repeated until a constant height, h_2, is obtained. The swelling ratio (Q) is h_2/h_1. This technique does not require the corrections for pore filling required by gravimetric measurements. The two techniques have been directly compared and shown to be equivalent.

Swelling ratios of a number of coals using a variety of solvents are presented in this report. The elemental analyses of the coals are given in Table I. Coal samples 1-6[39] were pyridine extracted and dried in vacuum at 110°C overnight. Coals 7-16[22,40] were pulverized to pass through a 30 mesh Tyler sieve and the vitrain of specific gravity less than 1.30 was isolated by the float/sink method using mixtures of benzene and carbon tetrachloride. These vitrains were dried in vacuum for a few hours and stored in a calcium chloride desiccator. Coal 17[29] was milled and sieved and the <0.43 mm fraction was dried under vacuum at 179°C and kept under nitrogen. Coals 18-25[41] were ground to pass a sieve with 900 mesh/cm^2 and dried to constant weight in an oven at 150°C. Coals 26-28[33] were Soxhlet extracted successively with DMF, pyridine, benzene, acetone and methanol. Coals 29-31[42] were ground to pass a 200 (IMN) sieve and were heated in an oven at 150°C. Coals 32-41[43] were pyridine extracted and dried under vacuum at 60°C and stored in a nitrogen purged glove box. Coals 42-47[44] were pyridine extracted and dried in vacuum. Finally, coals 48-51[45] were impact-milled, sieved and pyridine extracted.

4. SWELLING: EFFECT OF SOLVENT HYDROGEN BONDING

Solvents can be divided into two classes: non-hydrogen bonding and hydrogen bonding. The swelling ratios of the coal samples in non-hydrogen bonding solvents (Table II) are less (<25-50%) than those in hydrogen bonding solvents (Table III).

The data from Kirov et al.[33] for non-hydrogen bonding solvents are significantly higher than the others. These unusually high swelling ratios may mean that the Kirov coal samples are different from the other coal samples. The swelling ratios in benzene, toluene and cyclohexane are plotted in Figure 3 versus the carbon content of the different coal samples. The Kirov et al. data stand out as different from the rest of the coal samples. There are not enough data to decide whether Kirov's high values are due to differences in coal properties or experimental errors. There is no relationship between elemental composition and swelling in non-polar solvents.

a. Hydrogen Bonding Solvents:

In the classification of coal solvents developed by Dryden, a good solvent for coal is a hydrogen bonding solvent that contains a nitrogen or oxygen atom possessing an unshared pair of electrons. Other things being equal, nitrogen compounds are better solvents than compounds containing oxygen. He inferred that hydrogen bonding played a part in these interactions[31].

The high swelling caused by such nitrogen-containing solvents (hydrogen bond-accepting solvents in general) was attributed to the replacement of coal-coal hydrogen bonds with coal-solvent hydrogen bonds. This phenomenon causes the coal to swell more because the replacing of a coal-coal hydrogen bond by a coal-solvent hydrogen bond reduces the cross link density of the coal[26].

From the data presented in Table III, the swelling ratios in hydrogen bonding solvents are much higher than those in the non-hydrogen bonding solvents. Swelling ratios of different coal samples published by a variety of different researchers are shown in Figures 2 and 3. The swelling ratios seem to be constant for coals containing 60% to 85% C (dry-mineral matter-free, dmmf), then abruptly drop off above 85% C. This trend is observed for most of the coal samples.

The data from Bunte et. al.[41] are unusually low (Figures 4-6). Similar to the other results, the swelling ratios are constant for coals containing 60% to about 88% C. A careful examination of the experimental details revealed no obvious sources of errors. Perhaps these coals are significantly weathered.

Figures 2 and 3 show correlations between swelling in pyridine and coal carbon content. This correlation is most apparent in individual data sets. The swelling ratio is constant up to about 85%C then drops sharply. The Bunte et. al. data are low, but show the same trends as the other data. The data are consistent with the conclusion made by Honda and Sanada[40] and Peppas and Lucht[43] that swelling is constant from 65%C-87%C and then decreases abruptly above 87%C. This correlation extends to one being observed between swelling and the oxygen-carbon ratio of coal, because the O/C ratio directly correlates with coal carbon content. The swelling ratios are relatively constant between about 0.10 O/C and 0.35 O/C and drop off below 0.10 O/C. Again, the Bunte data are low. No correlations are observed between swelling and hydrogen content and H/C ratios.

The most startling feature of these data is the rapid decrease in pyridine-induced swelling in coals above about 85%C. Two explanations are possible. The coals may be increasingly cross-linked at these high ranks, and this causes decreased swelling. There are no obvious indications of increasing cross-link densities at carbon contents as low as 85%C, although most coal properties undergo sharp changes between 85%C and 89%C. Alternatively, the coal-pyridine interactions may decrease sharply, because of a decrease in phenolic hydroxyl groups which can strongly interact with the basic pyridine. It is clear that an important structure transition of coals occurs here and an understanding of it should be assiduously sought.

Figures 4-6 present the plots of the swelling ratio versus carbon and hydrogen contents of some coal samples in hydrogen bonding solvents other than pyridine. No correlations are observed.

b. <u>Non-hydrogen Bonding Solvents</u>:

The extent of coal swelling is directly related to the affinity of the coal for the solvent[35]. Regular solution theory[57] has often been used to describe coal-solvent interactions[23]. In this context, a number of correlations of coal swelling with the solubility parameter of the solvent have been noted[21,22,54]. Larsen et. al. has claimed that regular solution theory can only be used with non-hydrogen bonding solvents[9].

Larsen, Green and Kovac[26] observed a large increase in swelling in non-hydrogen bonding solvents after extraction of the coal samples with pyridine. This was attributed to the destruction of coal-coal hydrogen bonds during pyridine extraction. The derivatization of the hydroxyl groups in coal resulted in maximum swelling which supports the importance of internal hydrogen bonds in coals.

5. PHYSICAL CONSEQUENCES OF COAL SWELLING

The swelling of coal occurs as an increase in the volume of coal due to absorption of a solvent. It is not necessarily true that when coal swells, the weight uptake corresponds to the dimensional change in coal, because coals have pores which are occupied by the solvent. Therefore, the necessity of correcting for the pore volume is critical in the gravimetric measurement of coal swelling. Methods for making this correction have been developed[34,35].

Dryden's studies of particulate coal swelling resulted in dramatic changes in the appearance of the coal[10d]. With good swelling agents, an appreciable fraction of the coal was extracted. The dried sample was highly distorted. The coals expanded greatly in size and cracked. These changes were interpreted as a consequence of the reorientation of the macromolecular chains, the driving force coming from the free energy of mixing of the liquid and the coal structure. This model assumes a gel structure of coal in which there are cross-links between the various macromolecular subunits of the coal. In the presence of selected liquids, the gel structure swells, but the cross-linkages prevent dissolution of the coal structure. The high degree of swelling (about 100%) indicates that there are a number of flexible molecular subunits between cross-links in the average chain, however the high modulus of the unswelled coal suggests a relatively short chain length. This contradiction was finally resolved recently by the realization that native coals are in a glassy state[23].

An in-situ microscopic study of the swelling of polished coal surfaces and thin sections was done by Brenner[23]. A high degree of reversibility of the dimensional swelling was observed after the removal of the swelling solvent. This observation is typical of cross-linked networks. When the swelling was allowed to continue for a long period of time, it proceeded beyond the point where it can be reversed. This irreversibility was attributed[23b] to fractures or dislocations within the coal structure which occur when sufficiently high stresses are generated by uneven swelling of the coal structure. The non-uniform swelling of the coal was attributed to kinetic effects or differences in the swellability of the various microscopic subcomponents of the coal sample. The various inner regions of the coal particles are reached by the swelling agent at different times or the different subcomponents are swelled at different rates. Both of these occurrences will cause large mechanical stresses. Also, the different macerals are likely to have different swellabilities, hardnesses, and shapes and all of these differences can contribute to stresses as swelling occurs. Such stresses can result in cracking, dislocation, and fracturing of the structure which can not be reversed when the swelling agent is removed.

The studies involving the swelling of thin sections of coal in pyridine, ethylenediamine and n-propylamine were especially revealing[23b]. Swelling was reversible and the swollen samples were substantially more flexible than the original samples or the redried samples. The shapes of the thin dried coal samples were similar to the shapes of the samples before they were swollen. The most dramatic result observed in Brenner's study was the high degree of reversibility of the observed swelling. Samples which roughly doubled in volume, shrunk to the original size after drying. This could be repeated several times. The first time a thin section was swollen and dried, the resulting piece of coal was slightly smaller than the original, although retaining the same shape. This reduction in size was attributed to extraction of some of the coal material by the solvent and provides additional evidence for the mobility of the chains in the coal macromolecular structure. It may also be due to the change in packing efficiency of the coal macromolecular chain segments. The decrease in modulus which occurred upon swelling was attributed to the solvation of strong non-covalent interactions between chains such as hydrogen-bonds, which are present in the dry coal[15].

In a macromolecular structure, the amount of swelling is controlled by the cross-link density and by the magnitude of the interactions between the solvent and the macromolecules[1-4]. Thus, the measurement of swelling and the interactions between solvent and the macromolecules can be used to calculate the number average molecular weight between cross-links ($\bar{M}_c$) with the Flory-Rehner equation (equation 1). In this equation, $\bar{M}_c$ is the number average molecular weight between branch points, ρ is the coal density, V_s is the solvent molar volume, V is the volume fraction polymer at equilibrium swelling and the Flory χ parameter for coal-solvent pairs.

$$M_c = \frac{\rho_c \, V_s \, V^{1/3}}{-[\,\ln(1-V) + \chi \, V^2]} \qquad (1)$$

Larsen, Kovac and Green pointed out that the Flory-Rehner equation is not applicable to coals because they are too highly cross-linked and their chains too stiff[26]. Kovac developed a simple non-Gaussian theory which describes the swelling of coal better and accounts for chain stiffness and the finite extensibility of the network in an approximate way[46]. The N in the Kovac equation describes the deviation from Gaussian behavior. In the limit of very low cross-link density, the Kovac equation (equation 2) reduces to the Flory-Rehner equation.

$$M_c = \frac{\rho_c \, V_s \, V^{1/3} + \rho_c \, V_s \,/\, N \, V}{-[\,\ln(1-V) + V + V + \chi \, V^2\,]} \qquad (2)$$

The earlier work on the cross-link density of coal was done by Kirov et. al.[21] and Sanada & Honda[22]. The measurement of the interaction parameter (χ) between solvent and the coal macromolecular structure is experimentally difficult. However, in spite of the difficulty, several researchers were able to measure indirectly and calculate the cross-link density of some coal samples[22,33]. The results showed a minimum in cross-link density at about 86%C which shows that as coalification process continues, the coal does not become increasingly cross-linked. Recently, researchers have published results which show no dependence of the interaction parameter (χ) on coal rank[47]. This raises the question of whether regular solution theory will lead to accurate determinations of the interaction parameter (χ) in coal systems[48].

6. DYNAMIC SWELLING

Dynamic swelling or sorption measurements of macromolecular systems yield information about the physical state (glassy or rubbery) of the network, the time scale of major relaxation processes, and the diffusion coefficient of solvent into the macromolecule. If the system is in the glassy state, it is possible to determine whether the sorption is due to Fickian diffusion and/or due to relaxations of the macromolecular chains. It is possible to estimate values of the diffusion coefficients and the relaxation constants of the macromolecular chains can be determined.

Sorption mechanisms in macromolecular systems may be defined in terms of two limiting cases. These are Fickian diffusion and Case II transport. Case II transport systems have been described in detail by Thomas and Windle[49], Peterlin, Astarita and Sarti[50], and Hopfenberg[51]. This system is characterized by a change of state from a glassy to rubbery state as it is penetrated by the solvent. In Case II, solvent uptake is directly proportional to time. On the other hand, Fickian diffusion usually occurs in rubbery systems and the solvent uptake is proportional to the square root of time.

The analysis of sorption data in macromolecular systems involves fitting the sorption data to the empirical equation below[28,43]. M_t is the mass of the solvent taken up at time t, M is the mass of solvent taken up at long times, and k is a constant which depends on the structural characteristics of the material and the solvent-material interactions. The exponent n is used to indicate the type of diffusion and to infer state changes in the macromolecular systems. When n equals 0.50 the diffusion is Fickian; when n is 1.0, it is a Case II transport; when n is between 0.5 and 1.0, it is an anomalous transport and when $n>1.0$ the swelling material is likely to craze and fracture due to the tremendous osmotic pressure differences at the accelerating and advancing front. This type of transport mechanism is called Super Case II transport.

$$M_t / M = kt^n \qquad (3)$$

For analysis of dynamic swelling or sorption in coals, a slightly modified form of the empirical transport equation is used as shown below[29]. M_t is the mass of the solvent taken up at time t, and k'is

$$M_t = k't^n \qquad (4)$$

a constant the same as k in equation 3. Equation 4 can only be used up to about 60% of the final volume uptake.

An analysis of the dynamic swelling data of four coals[52] using equation 4 is shown in Figures 7 and 8. These coals are (A) Fettkohle (bituminous), (B) Chinolinrestkohle, (C) Gl, and (D) Gasflammkohle. The elemental analyses of these coals are not available; however, bituminous coal carbon content is between 87-89% or higher and gas flammable coal carbon content is between 80-85%[5]. The data are from reference 50. The plotted data in Figure 7 demonstrate a Fickian type of diffusion. The values of n as determined from the slopes of the straight lines in Figure 7 are between 0.42-0.58. The plot of the solvent uptake versus the square root of time in Figure 8 shows deviation from straight lines after about 25-30 hours. This is attributed to the change in the physical state of coal from a glassy state to a rubbery state[27]. When a macromolecular structure is in its glassy state, large molecular motions are restricted, although segmental motion may still be exhibited. Increased concentration of a diluent in a macromolecular system like coal causes it to swell, decreasing its density and allowing increased bond rotation. In polymeric systems, this phenomenon effectively lowers the glass transition temperature of the polymer. In coals, however, no conclusive evidence yet has been found that a glass transition temperature exists, although several researchers have observed temperature-dependent transitions which are suggestive of glass transition temperatures[53,54].

The solvent uptake plot, Figure 8, shows that Fettkohle bituminous coal absorbs more solvent than the rest of the coal samples and the Gasflammkohle absorbs the least solvent. There are not enough data to support any conclusions regarding the correlation of elemental composition with solvent uptake.

7. STRUCTURAL MODEL

The structural model of coal that is in best agreement with the swelling data is that of a covalent macromolecular network containing many hydrogen bonds which are cross links[21] (Figure 9). In a covalently bonded network, clusters are extensively hydrogen bonded to each other. The removal of the hydrogen bonds causes a large increase in $\bar{M}_c$ and the covalently cross-linked coal is somewhat flexible. In low rank bituminous coals the hydrogen bonds between clusters provide most of the cross-links. With the hydrogen bonds in place, $\bar{M}_c$ is low and this is responsible for the brittle character of bituminous coals. The destruction of the network of internal hydrogen bonds greatly increases $\bar{M}_c$ changing the character of bituminous coals and making them more flexible. The existence of extensive hydrogen bonding in the coal structure is a significant difference from classical coal structure models.

The observed high swelling in hydrogen bond-accepting solvents is explained by the existence of hydrogen bond cross-links in coals. The strong hydrogen bonding solvents replace the coal-coal hydrogen bonds with a new coal-solvent hydrogen bond. This increases $\bar{M}_c$ so swelling can increase. Non-hydrogen bonding solvents do not show enhanced swelling because the coal-coal hydrogen bonds remain intact.

8. EFFECT OF SWELLING ON COAL LIQUEFACTION

Swelling may play a significant role in coal liquefaction. Several researchers have shown that liquefaction conversion increased after coal swelling in suitable swelling agents. Rincon and Cruz[59] found that the conversion of a Colombian coal increased when it was swollen with tetrahydrofuran (THF) prior to liquefaction using different solvents, Table IV. Joseph[60] reported the effect of several swelling agents on coal liquefaction. His results showed that preswelling a lignite, a subbituminous coal and a bituminous coal in tetrabutyl ammonium hydroxide (TBAH) improved liquefaction yields and product quality. Preswelling the subbituminous and the bituminous coals in THF and methanol also enhanced liquefaction yields and product quality.

Artok et. al.[58] studied the effect of preswelling with and without catalyst impregnation and found that the combined effect of catalyst addition and swelling enhanced conversion of a lignite using TBAH as the swelling agent. Liotta[65] has shown that swelling with TBAH increased the rate of alkylation of the phenolic hydroxyl groups in coal which suggests that the rate and extent of liquefaction can be enhanced by using suitable swelling solvents. High conversions were observed during liquefaction of coal in the presence of basic nitrogen compounds[66-69]. The high conversions were ascribed in part to the ability of these compounds to disrupt and swell the coal macromolecular structure. However, these solvents exhibit some disadvantages. They react with the liquefaction products resulting to the incorporation of undesirable amounts of nitrogen. Even THF poses some problems, because it decomposes/polymerizes near its boiling point and gets incorporated into the coal and its liquefaction products. Hence, finding a good swelling agent which does not participate in liquefaction, or a technique to remove all the swelling agent is a desired.

Although the mechanism by which coal liquefaction conversion is improved by preswelling is not yet completely understood, it can be assumed that swelling causes structural changes in the coal macromolecular network which results in increase reactivity of the coal. Swelling expands the coal structure as well as the pore structures within the coal, thereby allowing faster and more complete accessibility of the donor solvent to the coal reactive sites. This may aid in capping coal-derived free radicals, thereby limiting the occurrence of retrograde reactions.

Temperature-programmed coal liquefaction with dispersed catalysts has been studied at Penn State under DOE Program DE-AC22-89PC89877. The results are given in Quarterly Reports(70) and an ACS Preprint.(71) The objectives of their work were "1. to investigate the use of highly dispersed catalysts for the pretreatment of coal by mild hydrogenation, 2. to identify the active forms of catalysts under reaction conditions, and 3. to clarify the mechanisms of catalysis."(70) Their research has been directed toward the use of ammonium tetrathiomolybdate as the catalyst precursor. At reaction temperatures below 300°C (572°F), the precursor apparently was not converted to an active form. At a reaction temperature of 400°C (750°F) in batch microautoclave runs, it was demonstrated that the addition of precursor (1% Mo) increased coal conversion greatly and that better results occurred when water/THF solvent was used for the catalyst transfer than with water alone.

The literature dealing with the use of dispersed catalysts is being updated, and will be included in the next quarterly report.

9. SUMMARY OF OBSERVATIONS AND CONCLUSIONS

Based upon recent literature and published data, the proposal of van Krevelen that coals are three-dimensionally cross-linked macromolecular networks is generally being accepted. When brought into contact with most organic solvents, coals absorb the solvent and swell. The amount of swelling depends on both the coal and the solvent. The two factors which control the amount of swelling are the magnitude of the solvent-coal interactions and the cross-link density of the coal. Expressions have been derived to describe these terms. Another aspect is that coals can behave as either a glass or rubber with a transition zone. In a glassy state, the macromolecular chains are constrained and diffusion through the coal matrix is quite slow. For reference, as-mined coals exhibit glass-like properties. In the rubbery state, the macromolecular chains can move relatively freely, and diffusion rates in the solid approach those in liquids. Some solvents can cause a glass-to-rubber transition to occur in coals.

Coal swelling solvents can be divided into two classes: non-hydrogen bonding and hydrogen bonding. The swelling ratios of the coal samples in non-hydrogen bonding solvents are significantly less than those in hydrogen bonding solvents. The most effective solvents are those containing a nitrogen or oxygen atom possessing an unshared pair of electrons.

The swelling data are consistent with a covalent cross-linked structure of coal. This is supported by the high swelling observed in hydrogen bonding solvents. The strong hydrogen bonding solvents replace the coal-coal hydrogen bonds with new coal-solvent hydrogen bonds. If the coal-coal hydrogen bonds are active cross links, the replacement would result in a lower cross-link density which would cause swelling to increase. The weak hydrogen bonding solvents result in less swelling since more coal-coal hydrogen bonds remain intact. The decrease in swelling in high carbon content coals could be attributed to possible physical stacking interactions between polynuclear aromatics (PNA's) in the coal structure although there is no supporting evidence in the literature. These interactions will not be easily altered by materials which are liquids.

The best correlation between the extent of swelling and coal rank is that derived from experimentation with pyridine. A relatively constant swelling ratio was observed in pyridine for coal samples with carbon contents of 65% to 85. A dramatic decrease in the swelling ratio was observed above 86% C.

It appears that swelling coal in suitable solvents prior to liquefaction could improve conversion and product quality. This has been demonstrated, and the application of this technique in combination with catalyst impregnation in coal liquefaction should decrease the costs of commercial liquefaction.

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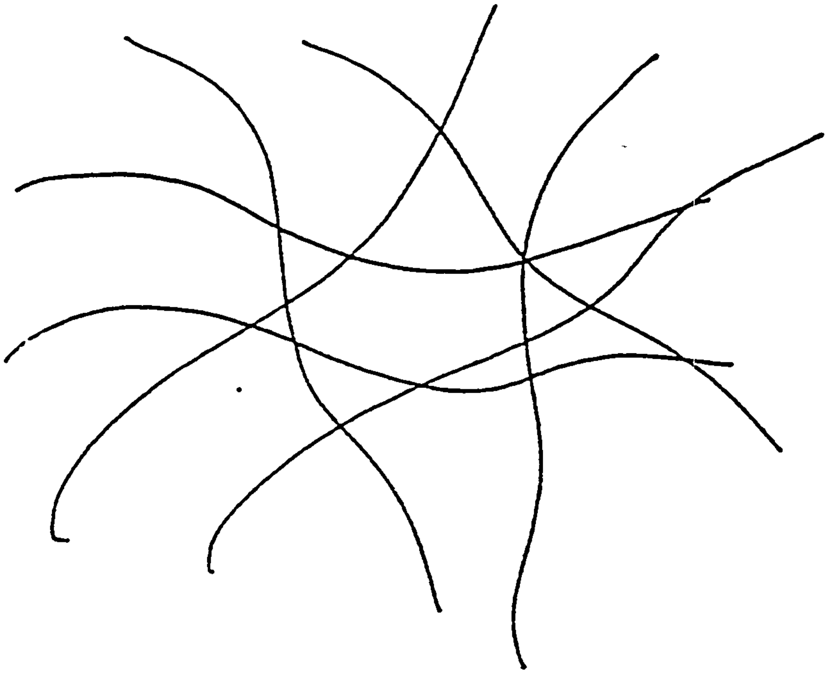
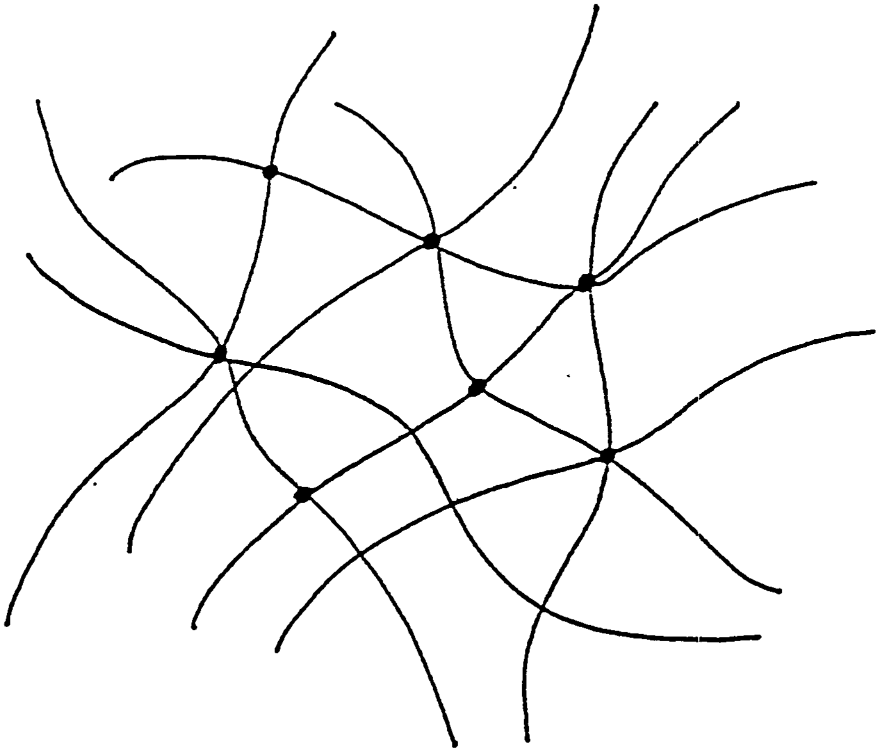
Plate 1

Schematic of Coal Macromolecules



A. MIXTURE OF LINEAR MACROMOLECULES



B. A CROSS-LINKED MACROMOLECULAR NETWORK

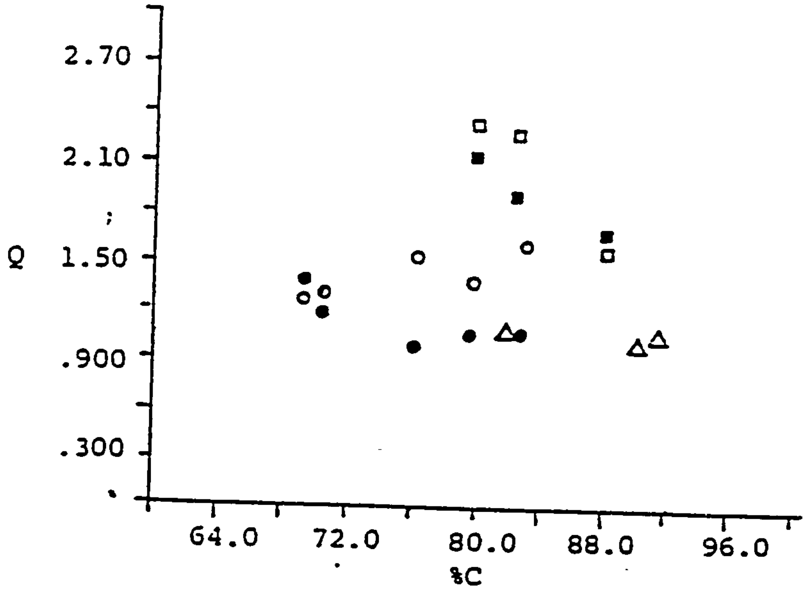


Fig. 1. Relation between equilibrium swelling and the carbon content of coals in non-hydrogen bonding solvents at room temperature.

□ Kirov et al. (benzene)
○ Green (benzene)
△ Moore (benzene)
■ Kirov et al. (cyclohexane)
○ Green (cyclohexane)

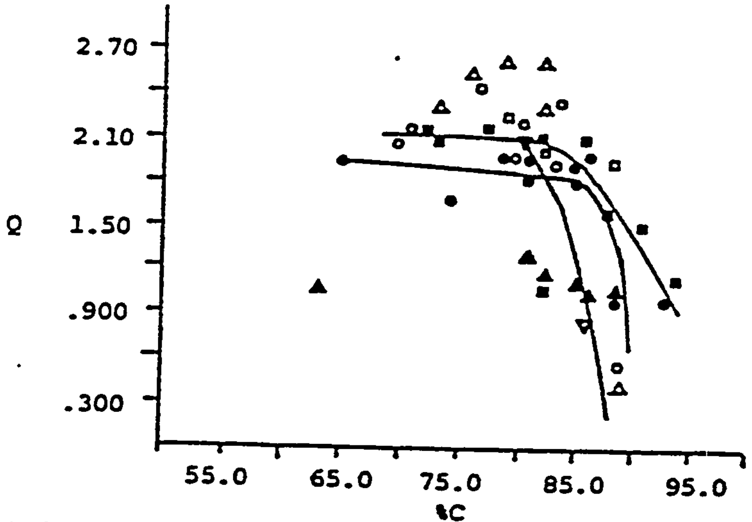


Fig. 2. Relation between equilibrium swelling and carbon content in pyridine at room temperature.

▼ Szeliga and Marzec
● Honda and Sanada
△ Larsen and Lee
▽ Van Bodegom et al.
□ Kirov et al.
○ Green
■ Peppas and Lucht
▲ Bunte et al.

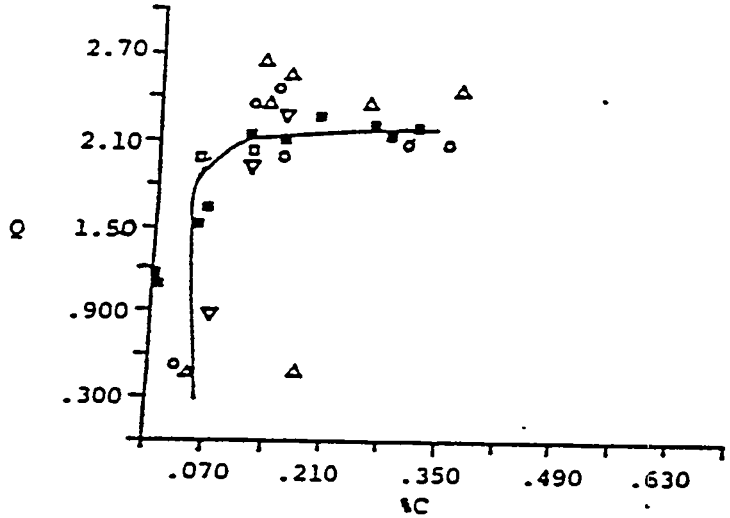


Fig. 3. Relation between equilibrium swelling and the oxygen-carbon ratio of coals in pyridine at room temperature.
○ Green
■ Peppas and Lucht
▽ Van Bodegom et al.
□ Kirov et al.
△ Larsen and Lee

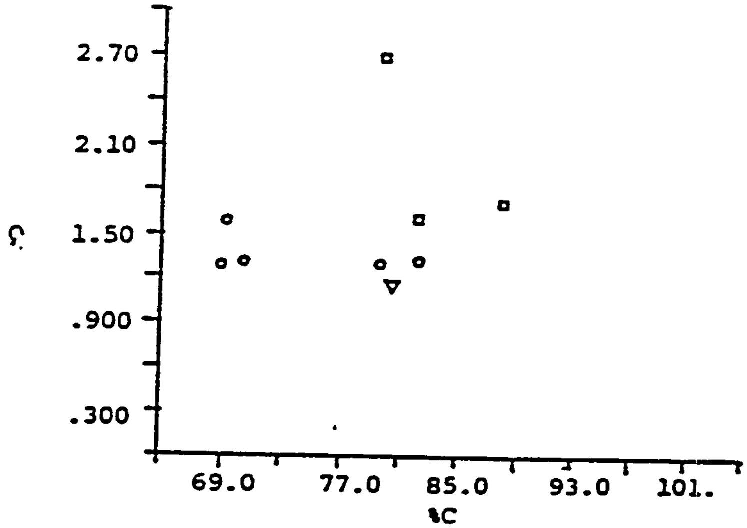


Fig. 4. Relation between equilibrium swelling and the carbon content of coals in methanol at room temperature.
○ Green
□ Kirov et al.
▼ Szeliga and Marzec

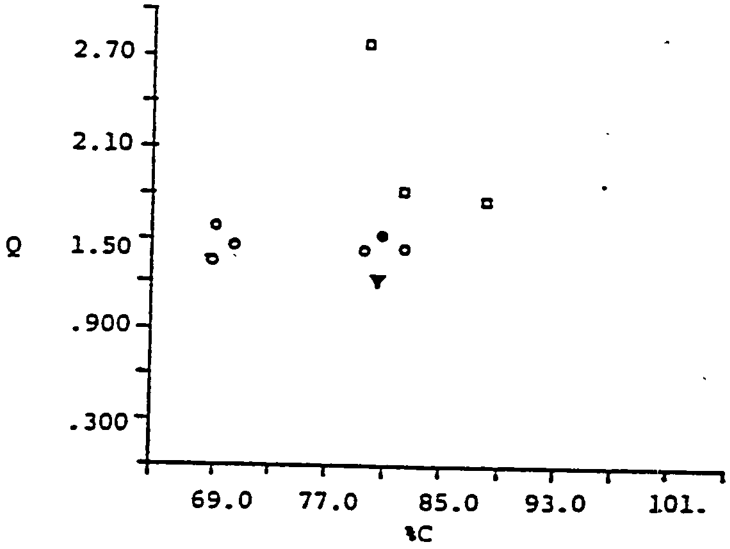


Fig. 5. Relation between equilibrium swelling and the carbon content of coals in ethanol at room temperature.

○ Green ● Honda and Sanada
□ Kirov et al. ▼ Szeliga and Marzec

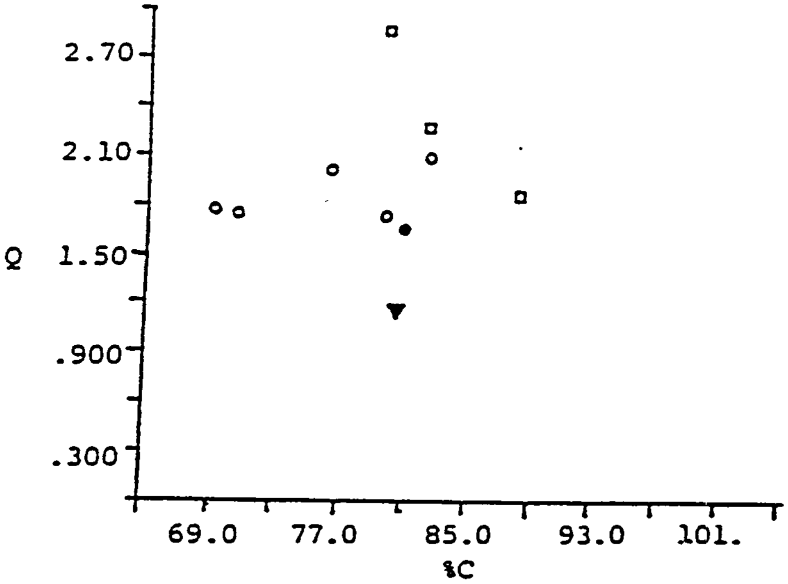


Fig. 6. Relation between equilibrium swelling and the carbon carbon content of coals in 1,4-dioxane at room temperature.

○ Green ● Honda and Sanada
▼ Szeliga and Marzec □ Kirov et al.

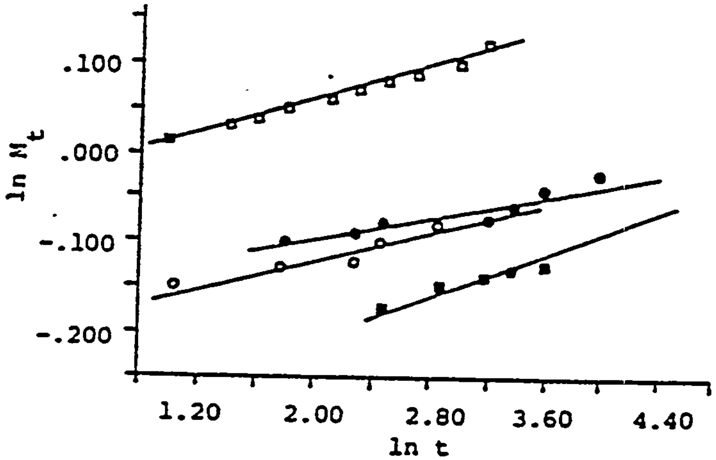


Fig. 7. Dynamic swelling by pyridine vapors.

□ Gasflammekohle; ■ Fettkohle; ● Chinolinrestkohle;
○ Gl

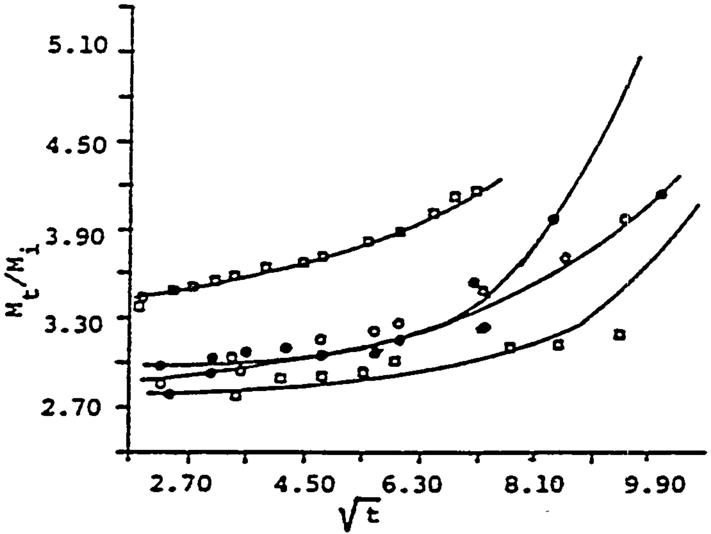


Fig. 8. Solvent swelling in pyridine.
□ Gasflammekohle; ■ Fettkohle; ● Chinolinrestkohl;
○ Gl

Table I. Coal Elemental Analysis

Coal Name	%C	%H	%O	%O+N	%O+N+S
1. Big Brown Lignite		64.45	5.62	21.09	
2. Wyodak (Rawhide)	70.57	5.01	21.62		
3. North Dakota	69.16	5.31	23.93		
4. Bruceton	82.57	5.20	8.84		
5. Illinois No. 6(1)		79.80	5.03	11.85	
6. Illinois No. 6(2)		76.35	5.71	10.38	
7. Ashibetsu Bituminous	81.1	5.5			13.4
8. Odaira Lignite	65.1	5.0			29.9
9. Nakago	74.3	5.3			20.4
10. Takamatsu	79.0	5.0			16.0
11. Bibai	80.9	5.9			13.2
12. Yubari I	84.9	6.2			8.9
13. Yubari II	85.2	6.3			8.5
14. Hashima	86.6	5.6			7.8
15. Yatake	88.7	3.3			6.9
16. Hongei	93.0	3.3			3.7
17. Bituminous Coal (hvB Coal)	80.7	5.6		10.9	
18. Furst Leopold	80.9	5.4		12.0	
19. Hohenzollen	82.5	5.2		11.9	
20. Heinitz	85.4	5.5		8.3	
21. Heinitz vitrain	82.5	5.05		12.2	
22. Heinitz durain	82.05	5.75		11.7	
23. Heinitz Fusain	63.15	2.7		32.9	
24. Emscher Emil	86.5	5.1		7.25	
25. Escheiler	88.6	4.7		5.7	
26. Hebe (W. A)	79.9	4.5	14.6		
27. Greta (N.S.W.)	82.4	6.2	8.7		
28. Bulli (N.S.W.)	88.2	5.1	4.7		
29. Coal A (Bituminous)		82.32	5.51	5.89	
30. Coal E (Anthracite)		91.29	2.91	2.10	
31. Coke No.0	89.96	0.91	2.39		
32. PSOC Code No. 418	69.94		21.40		
33. " 791	72.25		20.17		
34. " 414	72.99		19.25		
35. " 211	77.08		14.68		
36. " 207	79.82		12.23		
37. " 402	82.48		9.00		
38. " 341	86.01		5.29		
39. " 1029		88.12		4.81	
40. " 647	91.54		1.37		
41. " 384	94.17		0.62		
42. Bruceton	82.3	5.2	9.7		
43. PSOC-219	82.1	5.7	10.9		
44. PSOC-213	78.9	5.7	9.7		
45. Illinois No. 6	76.2	5.8	11.5		
46. Wyodak	73.3	6.3	18.3		
47. Big Brown	67.5	5.4	24.7		
48. SRS 800	80.5	5.3	12.3		
49. SRS 600	83.6	5.4	9.2		
50. SRS 400	86.6	5.5	6.0		
51. SRS 300	89.5	4.8	4.3		

Table II. Non-hydrogen bonding solvents and their swelling ratios.

Coal Name	Solvent	Q
Big Brown Lignite	Benzene	1.29
	Toluene	1.23
	Methyl Chloride	1.45
Wyodak(Rawhide)	Cyclohexane	1.23
	Toluene	1.32±0.01
	Nitromethane	1.34
	Nitrobenzene	1.42±0.01
	Acetonitrile	1.27
North Dakota	Cyclohexane	1.32
	Toluene	1.18±0.03
	Benzene	1.42
	Nitrobenzene	1.67±0.06
	Acetonitrile	1.33±0.01
	Nitromethane	1.44
	n-Pentane	1.19
Bruceton	Cyclohexane	1.08±0.02
	Toluene	1.55±0.02
	Benzene	1.58±0.03
	Carbon Tetrachloride	1.46
	Nitromethane	1.43
	Nitrobenzene	1.62±0.06
	Acetonitrile	1.43±0.03
	Naphthalene	1.58
	n-Pentane	1.17
	Biphenyl	1.15
	o-Xylene	1.51
	Tetralin	1.65
	n-Heptane	1.16
Illinois No. 6(1)	Pentane	1.14
	Cyclohexane	1.11±0.04
	Toluene	1.39±0.05
	Benzene	1.38±0.01
	Carbon Tetrachloride	1.34
	Nitrobenzene	1.67±0.06
	Acetonitrile	1.39±0.01
Illinois No. 6(2)	Biphenyl	1.11±0.01
	Cyclohexane	1.00
	Benzene	1.52±0.02
	o-Xylene	1.41
	Tetralin	1.52±0.02
	n-Heptane	1.00
	Methylcyclohexane	1.03

Table II (cont'd.)

Coal Name	Solvent	Q
Ashibetsu Bitum.	Benzene	1.53
Odaira Lignite	Benzene	1.05
Bituminous Coal	Benzene	1.0
hvB Coal	Nitrobenzene	1.1
	Acetonitrile	1.15
	Nitromethane	1.18
Hebe (W.A.)	Cyclohexane	2.13
	Xylene	2.32
	Toluene	2.32
	Benzene	2.32
	Carbon Tetrachloride	1.49
Greta (N.S.W.)	Cyclohexane	1.89
	Xylene	2.32
	Toluene	2.50
	Benzene	2.27
	Carbon Tetrachloride	2.22
	Nitrobenzene	2.44
Bulli (N.S.W.)	Cyclohexane	1.67
	Xylene	1.72
	Toluene	1.78
	Benzene	1.56
	Carbon Tetrachloride	1.64
	Nitrobenzene	1.62
Coal A (Bitum.)	Benzene	1.07
	Pentane	1.02
	Heptane	1.02
	Octane	1.00
	Nonan	1.00
	Decane	1.00
	Toluene	1.03
	Xylene	1.01
Coal E (Anthra.)	Benzene	1.06
Coke No.0	Benzene	1.01

Table III. Hydrogen bonding solvents and their swelling ratios,

Coal Name	Solvent	Q
Big Brown Lignite	Pyridine	2.03
	Methanol	1.57
	Ethanol	1.58
	Ethylenediamine	1.97
	2-Propanol	1.53
Wyodak(Rawhide)	1,4-Dioxane Pyridine	1.72±0.02
	Ethanol	2.12±0.06
	Methanol	1.30±0.06
	Ethanol	1.46±0.04
	Acetone	1.54
	2-Propanol	1.29±0.08
	Methylene Chloride	1.64
	Chloroform	1.74
North Dakota	1,4-Dioxane	1.78
	Pyridine	2.04
	Methanol	1.28±0.04
	Ethanol	1.36±0.02
	Acetone	1.44
	2-Propanol	1.45±0.06
	Methylene Chloride	1.94
	Chloroform	2.21
	Formamide	1.23
	Aniline	2.31
	2,6-Lutidene	1.79
	Chlorobenzene	1.46
	o-Dichlorobenzene	1.61
Bruceton	Carbon Disulfide	1.44±0.07
	1,4-Dioxane	2.07
	Pyridine	2.32
	Methanol	1.32±.08
	Ethanol	1.44±.01
	2-Propanol	1.40±.04
	Methylene Chloride	1.65
	Chloroform	2.00
	Formamide	1.16
	Aniline	2.22
	2,6-Lutidene	1.90
	Chlorobenzene	1.81±0.06
	o-Dichlorobenzene	1.72
	Tetrahydrofuran	2.07
	Ethylenediamine	2.03
	N,N-Dimethylaniline	1.82±0.06
	Diethylether	1.54
	Dimethyl Sulfoxide	2.21

Table III (cont'd.)

Coal Name	Solvent	Q
Illinois No.6(1)	Carbon Disulfide	1.46
	1,4-Dioxane	1.73
	Pyridine	1.94
	Methanol	1.28±0.04
	Ethanol	1.44
	Acetone	1.54
	Methylene Chloride	1.48
	2Propanol	1.45±0.05
	Chloroform	2.21
	Formamide	1.26
	216-Lutidene	1.79
	Chlorobenzene	1.52
	o-Dichlorobenzene	1.60±0.02
	Aniline	1.82
Illinois No. 6(2)	1,4-Doxane	2.00
	Pyridine	2.42±0.17
	Carbon Disulfide	1.41±0.01
	Diethylether	1.60
	Dimethyl Sulfoxide	2.15±0.08
Ashibetsu Bituminous	Chloroform	1.71
	1,4-Dioxane	1.66
	Pyridine	1.95
	Ethylenediamine	1.81
	Ethanol	1.51
	Dimethyl Sulfoxide	1.62
Odaira Lignite	Acetophenone	1.02
	1,4-Dioxane	1.15
	Pyridine	1.92
	Dimethyl Formamide	1.50
Nakago	Pyridine	1.66
Takamatsu	Pyridine	1.94
Bibai	Pyridine	1.82
Yubari I	Pyridine	1.89
Yubari II	Pyridine	1.80
Hashima	Pyridine	1.97
Yatake	Pyridine	1.02
Hongei	Pyridine	1.02

Table III (continued)

Coal Name	Solvent	Q
Bituminous Coal hvB Coal	2-Propanol	1.14
	Diethylether	1.15
	Dioxane	1.16
	Methanol	1.19
	n-Propanol	1.23
	Ethanol	1.25
	Ethyl Acetate	1.26
	Acetone	1.30
	Methyl Acetate	1.32
	Methyl Ethyl Ketone	1.49
	Tetrahydrofuran	1.59
	1,2-Dimethoxyethane	1.60
	Dimethylformamide	1.69
	Dimethyl Sulfoxide	2.04
	Pyridine	2.08
	Ethylenediamine	2.08
	1-Methyl-2-Pyrolidone	2.38
Furst Leopol	Pyridine	1.28
Hohenzollern	Pyridine	1.17
Heinitz	Pyridine	1.11
Heinitz vitrain	Pyridine	1.11
Heinitz durain	Pyridine	1.10
Heinitz fusain	Pyridine	1.05
Emscher Emil	Pyridine	1.05
Eschweiler	Pyridine	1.03
Greta (N.S.W.)	Chloroform	2.13
	Methyl Ethyl Ketone	2.44
	Dioxane	2.27
	Acetone	2.27
	Aniline	2.78
	Pyridine	2.00
	Quinoline	2.86
	Dimethylformamide	2.78
	n-Propanol	2.78
	Ethanol	1.82
	Methanol	1.61

Table III (cont'd.)

Coal Name	Solvent	Q
Bulli (N.S.W.)	Chloroform	1.82
	Methyl Ethyl Ketone	1.82
	Dioxane	1.85
	Acetone	2.70
	Aniline	1.89
	Pyridine	1.92
	Quinoline	1.89
	Dimethylformamide	1.92
	Ethanol	1.75
	Methanol	1.72
PSOC Code No. 418	Pyridine	2.13
791	Pyridine	2.10
414	Pyridine	2.15
211	Pyridine	2.22
207	Pyridine	2.07
402	Pyridine	2.10
341	Pyridine	1.59
1029	Pyridine	1.49
647	Pyridine	1.10
384	Pyridine	1.14
Bruceton	Pyridine	2.6
PSOC-219	Pyridine	2.3
PSOC-213	Pyridine	2.6
Illinois No. 6	Pyridine	2.5
Wyodak	Pyridine	2.3
Big Brown	Pyridine	2.4
SRS 800	Pyridine	2.2
SRS 600	Pyridine	1.9
SRS 400	Pyridine	0.85
SRS 300	Pyridine	0.45

Table IV. Liquefaction conversions in THF[59].

Sample	Tetralin		PHO		AO		PHO:AO(1:1)	
	RC	SC	RC	SC	RC	SC	RC	SC
03	49.1	52.4	38.9	45.1	36.2	41.6	46.5	48.3
10	68.4	84.7	44.8	56.7	47.1	59.7	62.7	73.5
15	77.6	87.7	45.2	58.1	49.1	51.9	66.4	76.8

RC - Raw Coal
SC - Swollen Coal
PHO - Petroleum Heavy Oil
AO - Anthracene Oil

Table V. Liquefaction conversions in different solvents[60].

Swelling agent	Q	Conversion (wt. %)			
		Total	Oil	Asph	PA
		Illinois No. 6			
None		69	22	31	16
TBAH	2.3	83	37	33	13
THF	2.0	89	28	37	24
Methanol	1.5	88	28	31	29
		Wyodak			
None		67	32	22	13
TBAH	3.1	78	50	22	6
THF	1.5	74	52	13	9
Methanol	1.4	67	44	13	10
		Kinneman Creek Lignite			
None		56	33	15	8
TBAH	3.5	68	51	12	5
THF	1.3	56	33	16	7
Methanol	1.5	56	34	15	7

Q - Swelling Ratio
PA - Preasphaltenes

APPENDIX D

DISPERSED CATALYSTS IN COAL LIQUEFACTION: A LITERATURE AND PATENT REVIEW

1. INTRODUCTION

1.1 Objectives and scope

This review reports on a literature and patent survey on the use of dispersed (unsupported) catalysts in coal liquefaction. It is in support of the overall goal of the DOE contract on "Advanced Coal Liquefaction Concepts" to identify an effective dispersed catalyst process for low-rank subbituminous coal and lignite. This review was conducted to provide leads on effective dispersion techniques and catalytic components, and to summarize the current understanding on the mechanisms for catalysis, particularly by Fe and Mo.

Several reviews on the general area of coal liquefaction catalysts have excellent discussions on dispersed catalysts. Among these are those of Derbyshire (1988)[1] and Charcosset and Genard (1987)[2]; the latter cites other literature reviews, such as the review of Narain, et. al. (1987)[3] which concentrated on iron-based dispersed catalysts. This review updates these previous ones with recent developments in both process and fundamental studies, particularly in catalyst dispersion methods and characterization of catalyst activity. Most of the recent work addresses these previous reviews' recommended work in these areas of research. Although there is an emphasis on catalysis by molybdenum and iron in this review, other dispersed catalysts reported in both the patent and open literature are also surveyed.

It is also to be noted that dispersed catalysts were the original coal liquefaction catalysts used by the Germans, who did a lot of developmental work which led to embarking on a commercialization program as early as 1925. Literature abstracting services do not go as far back as this. Donath (1982)[4] provides both a good review of this early history and references to key patents and publications summarizing the early work. However, the importance of this early work is not and cannot be ignored. This review provides a brief discussion of the importance of this early work, which also laid the foundation for later work on the transition metal sulfides as petroleum hydroprocessing catalysts. This review also discusses some recent developments in this field that are relevant to our current interest in coal liquefaction dispersed catalysts. Interestingly, the original pre-World War II interest in these catalysts has now gone full-circle. Although active catalysts have been identified and recent progress in analytical techniques have allowed better catalyst characterization, the basis and origin of catalytic activity is still little understood.

Although every effort at an exhaustive search has been made, this review is by no means complete. A computerized search on the field was performed using the keywords "dispersed, slurry, catalysts, coal, liquefaction". It is possible that some of the relevant literature were indexed under other keywords. In most cases, references for a researcher's or research group's work are confined only to selected, more contemporary articles or to those considered key articles for that particular researcher or group.

Finally, no attempt is made to compare catalysts studied by different researchers or groups, other than in general terms. In addition to variations in experimental conditions, the lack of standardization, particularly in product work-up and characterization, precludes any meaningful ranking of catalyst performance. Any comparisons presented in this review will be of catalysts prepared and/or tested by the same researcher or group.

1.2 Catalysis in coal liquefaction

In conventional coal liquefaction, hydrogen is added to coal using catalyst at elevated pressure and temperature. Although there is overlap to some extent, liquefaction is generally regarded to proceed via two consecutive steps: coal dissolution primarily by depolymerization followed by upgrading via molecular weight reduction and heteroatom removal.[1] Liquefaction has been conducted in a single stage or in stages,[5] with the same or different catalysts in each stage.

The emphasis of this review will be on catalysis in conventional coal liquefaction. However, pertinent literature in processes such as pyrolysis (the first step in liquefaction), hydropyrolysis, and coal/residuum coprocessing will also be cited.

1.2.1 Liquefaction catalysts

Derbyshire's (1988)[1] discussion of catalysis in coal liquefaction is based on the broad categories of dispersed and supported (or heterogeneous) catalysts. The terms slurry, disposable, soluble, homogeneous, or once-through have been used synonymously with "dispersed" in the literature. Dispersed catalysts are usually used as dissolution catalysts while supported catalysts are primarily for hydrotreating. There can be overlaps in these categories and functions. For example, supported catalysts when ground and added as fine powder to coal can be considered as slurry catalysts. A pulverized catalyst containing a transition metal compound supported on sepiolite, palygorskite, or attapulgite has been claimed as a coal liquefaction slurry catalyst.[6] Some dispersed catalysts can have both dissolution and upgrading functionalities, such as multicomponent catalyst systems.

Based on the requisite dissolution and upgrading steps during coal liquefaction, a desirable liquefaction catalyst must possess activities for:

1) hydrogenation of polycyclic aromatic compounds,
2) cleavage of C-C or C-O bonds through hydrocracking reactions, and
3) desulfurization and denitrogenation.

The development of such a catalyst is driven by the cost reduction incentives associated with increasing hydrogen utilization efficiency and reducing capital and operating costs by lowering reaction severity. These cost reductions may be substantial to offset the possibly higher cost of a dispersed catalyst.

1.2.2 Catalyst mechanisms for liquefaction

During pyrolysis (or liquefaction without a solvent), it is reasonable to assume that liquefaction occurs only in the vicinity of the catalyst; in which case, the catalytic action is associated with cleaving coal linkages and hydrogenation. The catalyst and H_2 also suppress cross-linking or retrogressive reactions. In this case, a high degree of dispersion and/or mobility of the catalyst is important.

During liquefaction with a H-donor solvent, there are three possible pathways for hydrogen transfer to the coal:

1) Direct hydrogenation -- the catalyst can promote direct reaction of hydrogen (probably in the form of dissociatively adsorbed H_2) with the coal, thus effectively reducing the requirement for hydrogen donation from the solvent.

2) Hydrogen transfer from the solvent -- the catalyst can generate or regenerate the solvent H-donors by reaction with H_2. Since liquefaction can occur even in the absence of a solvent, this pathway does not appear to be the only one operative during liquefaction.

3) Hydrogen transfer from other H donors -- although the generation of H-donating groups in coal can also occur thermally, this can be enhanced by addition of a catalyst.

For a given coal and set of reaction conditions, the competition among these pathways is affected by the catalyst activity and solvent composition, which can also be interdependent.[1] Derbyshire's (1988) review[1] has a good summary of proposed mechanisms for liquefaction, e.g., solvent-mediated hydrogenolysis and radical hydrogen transfer mechanisms for hydrogenation catalysts.

The role of dispersed catalysts during the initial stages of liquefaction when retrogressive reactions can take place, especially in low-rank coals, has been actively investigated, particularly with respect to altering initial reaction pathways. Dispersed iron catalysts have been researched extensively by DOE-sponsored programs but the question on how iron catalyzes initial reactions has remained unanswered. The mechanisms for catalysis by Fe and Mo have also been studied and this review will present results from recent work in later sections.

1.3 Dispersed catalysts

Although there has been a dramatic increase in interest in dispersed catalysts for coal liquefaction in recent years, these catalysts were originally used in the primary step of brown coal liquefaction in the Bergius-Pier process developed in Germany. In this process, coal is hydrogenated in the liquid phase at elevated pressure and temperature with a dispersed catalyst; the liquid from this primary stage is then hydrogenated over supported catalyst in the second stage. In addition to a commercialization program, the Germans also had a catalyst development program. This section will briefly discuss some of the milestones in that program; there will also be a brief discussion of coal minerals, ores, and manufacturing residues as disposable catalysts.

1.3.1 Early developments

Donath (1982)[4] reviews the history of the German developments in coal liquefaction. Using cresylic acid as a coal tar model compound, Pier and others determined that sulfides and oxides of Mo, W, and Co, and sulfides of Fe were active sulfur-resistant hydrogenation catalysts at 200 bar H_2 (2900 psi). This study was extended to brown coal tar with testing of nearly all elements singly or in combination, with limited testing of noble metals because of cost and availability considerations. Mo and W and Groups V and VI elements were the most active catalysts, using conversion to gasoline as criterion. The combinations of molybdic acid/zinc oxide/magnesia and molybdic/chromic acids were found to be effective as well. In the liquefaction of bituminous coal, tin in combination with HCl was found to be active. Later work with bituminous coal at 600 bar H_2 (8700 psi) using an iron catalyst demonstrated similar performance. The results from this early catalyst testing program were applied in the various commercial plants started up between 1927 and 1943; by 1944, there were a total of 12 plants with a combined motor fuel product capacity of about 4 million metric tons per year. Table 1, adapted from Donath[4], shows the various hydrogenation plants and their feeds. It also shows the catalysts and pressures used in the primary liquefaction first stage. The catalysts used in the coal oil refining in the second stage evolved from a catalyst mixture of oxides of Mo, Zn, and Mg to WS_2 and combinations of these two catalysts. After 1940, the "workhorse" refining catalyst was WS_2-NiS supported on alumina or WS_2 supported on montmorillonite earth.

The main drawback in the early work was the high catalyst concentrations required to obtain the refined products. For example, concentrations of 20-25% of the coal slurry of pulverized Mo-containing catalysts were used for brown coals whose high alkali content decreased Mo activity. Experiments with low Mo concentration were effective if the MoO_3 was supported. This then led to the development of supported catalysts which later impacted petroleum refining.

In the development of bituminous coal liquefaction, the use of high pressure, i.e. 600-700 bar (8700-10,155 psi) vs. 200-300 bar (2900-4350 psi) for brown coal, gave satisfactory performance with low-cost catalysts such as iron compounds impregnated on to coal or to char. The main iron catalyst was an iron-oxide-containing residue of aluminum production from bauxite (Bayer Masse or red mud). Ferrous sulfate was also used.

1.3.2 Disposable catalysts

In the development of the Bergius-Pier liquefaction process, the advantage of a disposable catalyst was recognized, i.e., no catalyst aging/recovery concern and low catalyst cost. This was also recognized in the modern SRC-II process which used finely-divided coal minerals as catalysts. The beneficial effects of mineral matter in coal liquefaction have been investigated extensively; Narain, et. al.[3] have a good review of this. In general, the investigations show that removing mineral matter from coal decreases coal conversion, indicating that coal minerals are catalytically active in liquefaction. Canada Centre for Mineral and Energy Technology (CANMET) has reported lighter products from the two-stage coprocessing of coal and heavy oil with coal minerals compared to single-stage processing, at a given level of residuum conversion.[7]

Some of the previous work also attempt to determine what the catalytically active components in the mineral matter are. Iron sulfides (pyrites), magnetite, diaspore, and limonite have been reported as active components. Narain's (1987)[3] review indicates that pyrite (FeS_2) and its decomposition products, such as pyrrhotite ($Fe_{1-x}S$, $0<x<1$), are the most active catalysts. A more detailed discussion of catalysis by pyrite will be presented in a later section. Table 2 lists other disposable catalysts, such as ores, ore concentrates,[8-14] and wastes or residues from manufacturing processes[15-25] that have been investigated as liquefaction catalysts.

Ores and ore concentrates have also been investigated as disposable catalysts in coal liquefaction. Mathur, et. al. (1984)[8] liquefied Pittsburgh seam (WV) bituminous in SRC-II heavy distillate using mixtures of pyrite with ores and ore concentrates containing minerals of potentially-active metals as slurry catalysts. Mixtures of pyrite and Ni limonite were more active than pyrite alone (of equivalent mass). FeS_2 + Mo oxide (small amounts), with or without Co oxide or hydroxide gave high yields of low-viscosity liquid. Ores containing Mo gave comparable oil yields, higher preasphaltene yields, and marginally lower asphaltene yields than commercial catalysts (e.g., Co-Mo/alumina.) In a subsequent study, Mathur and Karri (1986)[9] showed that a synthetic mixture of MoO_3 ore, limonite, and bauxite used for first stage liquefaction followed by liquefaction with Ni-Mo/Al_2O_3 gave results comparable to those using a commercial Co-Mo catalyst.

Manganese nodules which are naturally found on ocean and lake floors have been claimed as hydrogenation catalysts.[10,11] When pretreated by leaching and/or sulfiding, they have also been claimed as hydrodesulfurization, hydrodemetallization, and hydrodenitrogenation catalysts for coal,[12] along with bog iron and nickel laterites.

Residues from various manufacturing processes that contain active metals have also been investigated as disposable catalysts. As previously mentioned, Bayer-Masse or red mud, a by-product of aluminum oxide processes, has also been used in coal hydrogenation. Veba Oel has numerous patents on red mud catalyst preparation and its use (with sulfur and/or with other oxides, such as Mn) in high pressure hydrogenation of coal and/or heavy oil.[15-18] Catalytic activity has also been claimed for waste from production of lithopone, a pigment containing ZnS and $BaSO_4$.[19,20] Most of the patent claims cover 0.1-5.0 wt% addition of the disposable catalyst.[21]

Unfortunately, the low to medium activity of coal minerals and the other disposable catalysts requires more severe operating conditions than those used with supported catalysts. Sato, et. al. (1987)[26] liquefied Taiheyo coal at 440 & 450°C, 85 bar (1235 psi) initial pressure, and coal:tetralin of 1:3 using red mud and a catalyst prepared from gasification of coal liquefaction distillation bottoms. Although the latter gave higher oil yield, commercial NiMo and CoMo gave higher yields than both iron-based catalysts. Batenin and Lipovich (1991)[14] investigated short-contact-time liquefaction of Kansk-Achinsk brown coal at 420-430°C using ore tailings, iron-based catalyst, and a Fe-Mo catalyst with 1% Fe (as $Fe_2(SO_4)_3$) and 0.2% Mo (as ammonia paramolybdate). Coal conversion improved with 0.5 wt% tailings. However, compared with the ore tailings, the Fe-Mo catalyst was less sensitive to donor solvent, especially at lower temperature. The inferiority of red mud compared to synthetic iron oxide and the beneficial effect of Mo doping was also observed by Bacaud, et. al. (1990)[27] in their liquefaction of Freyming and Gardanne coals at 300-450°C and 150 bar H_2 (2180 psi) with 1-methylnaphthalene (1-MNP). Multicomponent catalysts will be discussed in greater detail in Section 3.4.

1.4 Catalyst activity

Catalyst activity is determined by the degree of dispersion and the morphology (form/phase/composition) of the catalyst. These factors are in turn affected by factors such as the nature of the catalyst precursor, the mode of catalyst addition or impregnation, and the catalyst activation conditions for a given coal and set of liquefaction conditions. Exactly how and to what extent they affect catalyst activity is not known. Moreover, most catalyst characterizations are reported for the catalyst either before or after the liquefaction. Obviously, the dispersion and morphology of the catalyst during liquefaction conditions are the determining factors.

1.4.1 Degree of dispersion

In most cases, the degree of catalyst dispersion is a qualitative description and is often inferred from the observed liquefaction performance. The ideal dispersed catalyst has a high surface area to volume ratio, intimate contact with, and uniform dispersion within the coal. Reucroft and Kim (1992)[28] performed an XPS study of various catalysts and catalysts impregnated onto coals. These included mixed oxides (such as Fe_2O_3/MoO_4^{-2}), sulfated oxides (such as $FeOOH/SO_4^{-2}$, SnO_2/SO_4^{-2}, and $FeOOH/SnO(OH)_2/SO_4^{-2}$) and promoted oxides (such as $Mo/FeOOH/SO_4^{-2}$ and $Mo/Fe_2O_3/SO_4^{-2}$. For their catalysts, the analysis showed that the bulk concentration differed from the surface concentration; lower concentrations of both O and S were detected when going from the surface to the bulk. Dispersion methods (to be discussed in Section 2) attempt to increase the degree of dispersion.

The various studies which compare liquefaction using fine catalyst powders added to the coal with using impregnated catalyst precursors illustrate the greater coal-catalyst contact that can be attained with impregnation. Table 3 shows how impregnation can result in dramatic improvements in conversion to solubles for a bituminous coal compared to fine powder addition. However, this improvement may decrease as the powder size becomes small, e.g., sub-micron.

The impregnating solvent can also determine the level of dispersion. For example, organic solvents may be better able to penetrate the coal compared to water and so may produce better catalyst dispersion. The nature of the catalyst precursor is also important. For example, organometallic precursors may facilitate dispersion because they are miscible with the solvent which may be able to wet the coal better. The extent of wetting for the high-moisture low-rank coals may be different from that for the higher-rank coals. Moreover, there is the possibility of interaction between the precursor and the coal which can interfere with the transformation of the precursor into the catalyst active form. Buchanan, et. al. (1992)[29] have reported evidence for the possibility of solid-state interactions in dispersed catalysts. The activation conditions and the catalyst active form, in most cases, are unknown or not optimized. Catalyst dispersion methods will be discussed in greater detail in Section 2.

1.4.2 Catalyst active form/phase/composition

There are very few studies that attempt an in-situ characterization of the liquefaction catalyst. The catalysts are either characterized before or after liquefaction. Table 4a lists some studies on the characterization of active forms for catalysts, such as Sn, Mo, Ni, and Ru, based on analyses of the catalyst after liquefaction. Table 4b lists similar studies for Fe catalysts.

Since for most metals the sulfide is the most thermodynamically stable form under liquefaction conditions (if sulfur is present), it has generally been regarded as the active form for metal compounds that have demonstrated catalytic activity. However, this may not always be the case depending on the coal, the presence of other metals, and the amount of sulfur present. For example, Rogers and Agnew (1981)[30] analyzed the inorganic constituents present before and after liquefaction of Morwell and Gelliondale (Australian) coals to determine the form of the catalytic components. They found that iron sulfides reduced to pyrrhotite, iron carboxylates to magnetite (Fe_3O_4), calcium carboxylates to vaterite ($\mu CaCO_3$), and tin oxide (precipitated onto the coal by hydrolysis of stannous chloride) to liquid tin, some of which reacted with H_2S to form herzenbergite (SnS). A later Japanese (1985) study of tin oxide as a dispersed fine particle catalyst found the oxide to be reduced to metallic tin, which was detected as small molten tin particles dispersed in the coal slurry under the liquefaction conditions studied.[31] In a more recent study, Besson, et. al. (1990)[32] investigated the liquefaction of French high-volatile bituminous Freyming coal at 350-430°C using various tin precursors (i.e., non-porous SnO_2 aerosol, presulfided SnO_2, or commercial metallic tin). SnS was observed as the main product with small amounts of oxidized tin, although $FeSn_2$ was also observed in some cases. The active species was thought to be SnS, based on Mossbauer spectroscopy on the residues. In a study of ruthenium dispersed catalysts generated from organometallic complexes by Suzuki, et. al. (1992),[33] XPS analysis indicated the possibility of the existence of metallic Ru, in addition to the sulfide.

The iron sulfide system has been most studied (as seen from Table 4b) and the general consensus is that pyrrhotite, a non-stoichiometric sulfide, is the active form under liquefaction conditions. Section 5 presents a more detailed discussion of this. The studies for the iron sulfide system can be extended to other metal sulfide systems. Molybdenum sulfide has also been extensively studied, primarily in the petroleum refining field. It is generally recognized that MoS_2 is the active catalyst form with the edge planes as the active sites. However, recent studies[34] in coal liquefaction indicate that the active form may be a non-stoichiometric sulfide, as in the iron sulfide system. Mitchell, et. al. (1991)[34] formed MoS_2 from sulfided ammonium molybdate (SAM) as precursor. Even under liquefaction with excess sulfur, the SAM was not fully converted to MoS_2 although the imperfectly sulfided precursor was more active. This may suggest a non-stoichiometric active form for the Mo sulfide, as for Fe. Section 4 presents a more detailed discussion of catalysis by molybdenum.

1.4.3 Catalyst activation and activity maintenance

The activation conditions vary with the catalyst precursor, as will be discussed with the various dispersion methods in Section 2. Ideally, these should be at conditions milder than or similar to liquefaction conditions. In the study of Mitchell, et. al. (1991)[34] with sulfided NH_4 molybdate (discussed in the previous section), the coal was liquefied under either H_2 or N_2 atmosphere with excess sulfur. Various temperature sequences were used: pretreatment (PT) to 275°F for 30 minutes; high-temperature treatment (HT) at 425°C for 30 minutes; or temperature-staged treatment (TS) combining PT and HT. Analyses of the catalyst residues after liquefaction did not show major differences in the catalysts, suggesting that the activation at 275°C may have been sufficient. Cugini, et. al. (1991)[34a] found a similar optimum preactivation temperature of 275°C for Fe impregnated as FeOOH in the liquefaction of Illinois No. 6. An interesting finding in the Mitchell study is that the S/Mo under H_2 < S/Mo under N_2 suggesting H was actively involved in the reduction of SAM (but not necessarily to MoS_2).

For disposable once-through catalysts, long-term activity maintenance may not be a concern. However, for catalysts based on expensive metals, such as Mo, catalyst recovery may need to be addressed. Recovery methods based on extraction[35-38] have been claimed to be effective. For example, DOE has investigated the recovery of Mo from the coprocessing of model coal-ash/metal oxide mixtures,[39] Illinois No. 6, or deep-cleaned Kentucky with Maya atmospheric tower bottoms[35] using NH_4 molybdate at 435°C and 170 bar (2500 psig) for 2 hr. The THF-insolubles were ashed, then the ash was extracted with dilute aqueous NH_4OH at 65°C for one hr. A refractory Mo-V complex can be formed at high ashing temperatures; moreover, Ca molybdate can be formed from Ca in the Illinois coal. A Mo recovery of >90% was obtained from cleaned coal from which most of Ca had been removed.

1.5 Overview of some DOE programs on dispersed catalysts

Work on process developments has essentially revolved around refinements to integrated two-stage liquefaction, which has been demonstrated on the pilot-scale at Wilsonville. Until recently, most of the Wilsonville work has been with supported catalysts (unimodal and bimodal Ni-Mo/alumina) all of which have proven effective. Recent work at Wilsonville has investigated liquefaction with combinations of dispersed Mo with supported catalyst; this will be discussed in a later section. PETC is currently focusing on dispersed catalysts and preliminary work has successfully achieved finely dispersed, highly-active Fe and Mo catalysts.[40] Several DOE-sponsored programs are involved in the development of similar catalysts using various synthesis and dispersion techniques, such as precipitation of nanoscale catalyst particles from microemulsions and production of catalysts using flame methods and laser pyrolysis, among others. The results from these investigations will be discussed in greater detail in various sections.

DOE has sponsored process development of UOP's coprocessing with dispersed catalyst since 1984. Gatsis at UOP has been developing coal liquefaction and coal/residuum coprocessing using a slurry catalyst. UOP's process patents[41-43] cover the use of finely divided dispersed metal catalyst -- selected from Groups IVB, VB, VIB, VIIB, and VIII. The precursor may be an oil-soluble or oil-insoluble compound (10 wppm to 4 wt% metal).[44] Specific catalyst preparations are claimed for V and Mo oxides (such as V_2O_5 and MoO_3) contacted with H_2S or NH_4S.[45-48] The current effort is on the development of the Mo slurry catalyst. In this single-stage process, part of the liquid product from the high-pressure separator is recycled (5:1 recycle-to-fresh-feed ratio). For the coprocessing of Illinois No. 6 with Lloydminster resid (1:2 weight ratio, respectively), even at 0.05 wt% Mo, plant operability was good with no evidence of reactor fouling.[49] Temperatures as high as 465°C have been achieved with no reactor fouling with 0.12 wt% Mo, an improvement over what was achieved with the previous V-based catalyst.[50] The improved high-temperature conversion and stability has been attributed to either or both of the more active Mo catalyst or/and the liquid recycle.[50] Moreover, catalyst recovery of >95% has been obtained on the bench-scale.[51]

2. CATALYST DISPERSION METHODS

This section discusses the methods for catalyst dispersion; the methods are classified according to the mode of introduction or addition of the catalyst. The broad classifications are: 1) catalysts introduced as fine powders; 2) catalysts generated in-situ from oil-soluble precursors; 3) catalysts generated in-situ from water-soluble precursors; and 4) catalysts introduced or generated via impregnation techniques. In the first class of methods, where the catalyst or catalyst precursor is mixed with the coal in the feed slurry, coal-catalyst contact may not be intimate. The other classes of methods attempt to increase this contact by incorporating the catalyst within the coal structure.

2.1 Finely-divided powders

The catalyst or precursor can be mixed with the coal/solvent slurry as a very fine powder which may be in the form of metals, oxides, oxyhydroxides, sulfides, oxysulfides, borides, carbides, nitrides, or phosphides, among others. In general, the contact achieved with dry mixing of the catalyst with coal is not as intimate as that achieved with the other dispersion techniques. However, if the powder particle size is small enough, the dispersion achieved may be satisfactory. The various methods discussed here deal with the production of the fine powder form of the catalyst; Table 5 lists these methods along with the catalyst forms that can be synthesized with the methods.

2.1.1 Precipitation methods for supported catalysts

The literature on preparation of supported catalysts reports on precipitation methods that form oxides or mixed oxides. If sulfides or oxysulfides[52] are desired, they can then be generated by sulfidation. Nitrides,[53] borides, carbides, and phosphides can be generated in a similar manner, if they are the desired catalysts or precursors. Oyama (1992)[54] reviews the preparation and catalytic properties of transition metal carbides and nitrides which have been evaluated for hydrodenitrogenation of coal-derived liquids, among others.

Sulfides can also be directly prepared using a non-aqueous precipitation method wherein a metal chloride is dissolved in ethyl acetate followed by addition to a slurry of Li_2S to precipitate the metal sulfide.[55]

Precipitation methods used for supported catalyst preparation, in general, involve the precipitation of a metal salt on to an oxide support surface by varying the pH of the solution heterogeneously or homogeneously, e.g., by dropwise addition of the precipitating agent.[56] The catalyst fine powder may be obtained by detachment from the support.[57] The following are some precipitation methods (the descriptions are generalized for multicomponent systems):[58]

1) <u>Gel precipitation</u>: organic gelling agent is added to aqueous metal salt solution before precipitation; for a bimetallic system, contact with an alkali precipitant (e.g., NH_4OH) results in formation of a co-precipitate such that the metallic hydroxide is held rigidly within the framework of the organic gel

2) <u>Sol-gel formation</u>: colloidal solution of metallic oxide(s) or hydroxide(s) is converted to a semi-rigid gel by a number of mechanisms, such as removal of water, neutralization with base, or removal of acid by solvent extraction. The gel is then dried and calcined to the oxide.

3) <u>Aerogel formation</u>: Mixed aerogel is prepared by addition of small amount of water to a solution containing the dissolved metal compound(s). The solvent is then stripped under supercritical conditions.

4) <u>Homogeneous pH control</u>: the precipitant (OH^-) is generated homogeneously throughout a suspension in a solution of the active metal by thermal or chemical decomposition of urea.

-- For example, catalyst prepared by mixing urea with $FeSO_4$ has been claimed to result in less gas make during conventional coal liquefaction conditions.[59]

2.1.2 Microemulsion-based synthesis techniques

There is a growing interest in production of very fine catalyst particles using microemulsion-based synthesis techniques. Matijevic (1988)[60] reviews the principles involved in the formation of colloidal dispersions of metal oxides, carbonates, sulfides, selenides, phosphates, titanates, and ferrites by precipitation from homogeneous solutions. Microemulsions have also been used to prepare monodisperse colloidal transition metal particles[61-64] and alloy powders[65,66]. Although most of the applications have been in ceramics,[67] the synthesis methods have been increasingly used to produce catalysts for Fischer-Tropsch synthesis[68,69] and coal liquefaction. Work at Sandia National Laboratories has looked at colloidal titanates as potential coal liquefaction catalysts.[70,71] For example, Snape, et. al. (1988)[71] have investigated the hydropyrolysis of a bituminous coal at 500°C and 152 bar (2205 psi) H_2 with various catalysts, including a titanate. The tar yields achieved were 26% with no catalyst, 36% with $ZnCl_2$, 54% with $SnCl_2$, 59% with MoS_2, and 64% with 0.7% Pd on hydrous TiO_2.

Various DOE-sponsored programs at Sandia,[72,73] Batelle,[74] and West Virginia University[75] are investigating the production of iron-based liquefaction catalysts using emulsion techniques. Linehan, et. al. (1992)[74] prepare nanometer-sized iron oxide catalysts from reverse micelles by rapid thermal decomposition of soluble precursors such as $FeNH_4(SO_4)_2$. The catalysts prove to be good, selective catalysts for C-C bond scission.

Pennsylvania State University is synthesizing molybdenum sulfide particles in microemulsions by adding ammonium molybdate to sulfuric acid-solubilized microemulsions containing a non-ionic surfactant. By varying the water to surfactant mole ratio, catalyst particle size and surface area can be varied.[76] Liquefaction of Wyodak coal at 350°C with 100 ppm

Mo of this catalyst has resulted in a yield of 80% hexane-solubles, which was equal to or greater than those obtained from impregnation with ammonium molybdate.[77]

An attractive advantage of the microemulsion route to dispersed catalyst is the production of very fine (up to nanosized) particles with a narrow size distribution. The effects of the surfactants used in the emulsions on liquefaction behavior may be adverse. However, microemulsions can be prepared without surfactants, e.g., from hexane, water, and isopropanol.[78]

2.1.3 Deposition via surface wetting

Incipient wetness techniques as developed for supported catalysts have been used to deposit the catalyst or precursor onto coal, which acts as the support for the dispersed catalyst. In the standard method, a strongly bridging solvent, such as water, is used to dissolve the metal salt precursor. Then the mixture is added dropwise to the coal until the coal is at "incipient wetness", i.e., the point where unbound moisture is about to become available.[58]

There are other techniques that are referred to as incipient wetness methods that are variants of the above. In some of these, the support (or coal) is first impregnated with an organic liquid until only a thin surface element of the coal is left dry. Then, the coal is impregnated with an aqueous solution of the metal salt to give a surface-coated coal particle. The coal particles are subsequently dried. In yet another variation, the coal is first slurried with a water-immiscible liquid before the aqueous impregnating solution is added to displace the water-immiscible liquid from the pores of the coal.

Obviously, the variety in the methods results in differences in properties of the catalysts generated. For example, Milburn, et. al. (1989)[79] looked at the effects of solvent and method of solvent removal for alumina-supported liquefaction catalysts. The use of a less polar solvent and subsequent rapid removal of the solvent minimized compaction of the colloidal alumina particles.

For multicomponent catalysts, e.g., bimetallic systems, the general procedure is to use one reactant as a high-surface area template (e.g., Mg). This is then reacted with the other metal carrier, e.g., ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$), to form the surface compound. The excess template is removed by solubilization techniques (e.g, remove excess MgO with dilute HCl; the dried product is $Mg_2Mo_3O_8$).[58]

2.1.4 Other methods

Flame decomposition is usually used to form metals. In this method, the vapor of a metal salt, such as metal chloride, is directed into the flame of an O_2-H_2 burner, followed by reduction by H_2 of the product to convert the oxide to the metal. The H_2 reduction may be replaced by a sulfidation to form the sulfide.[58] Fe_2O_3 and SnO_2 (10-200 nm) aerosols prepared from such a flame method were used in the liquefaction of Freyming coal, a French high-volatile bituminous coal.[32,80,81] These flame processes, used primarily in the production of ceramic powders like the microemulsion-based techniques, also have the potential to produce nanometer-sized particles.[82]

Radiation chemistry techniques have also been used to produce fine metal particles. Argonne Laboratory has been investigating the evolution of chalcogenide particles by laser photolysis that allow good control of particle size.[83] Ongoing work at University of Kentucky is on the production of nanometer-sized iron-based catalysts using a CO_2 laser pyrolysis system.[84,85] Spherical 3-13 nm orthorhombic Fe_3C and metastable hexagonal Fe_7C_3 were prepared by laser pyrolysis of gas mixtures of $Fe(CO)_5$ and ethylene. After in-situ sulfidation with dimethyldisulfide, these carbides were tested and compared with metal sulfides prepared from $Fe(CO)_5$, $Fe(C_5O_2H_7)_3$, and Mo naphthenate in the liquefaction of Western Kentucky No. 6 bituminous and Wyodak subbituminous at 405°C and 55 bar

(800 psi) H_2 (cold) for 15 minutes. All catalysts enhanced coal conversion over thermal or non-catalytic liquefaction.

Both spray drying and freeze drying of an aqueous metal salt solution with subsequent H_2 or chemical reduction of the salts can be used to produce finely-dispersed powders.

2.1.5 Relative activities of powdered catalysts

There have been numerous studies comparing the activities of various fine powder catalysts or catalyst precursors for a given reaction and set of conditions. For example, Tarrer, et. al. (1988)[86] compared the hydrodenitrogenation (HDN) performance of the precipitated transition metal sulfides Cr_2S_3, MoS_2, WS_2, RuS_2, FeS_x. The sulfides, prepared using a non-aqueous precipitation method,[55] had surface areas of 5-80 m^2/g. Activity and selectivity of these sulfides were evaluated using both a quinoline model compound system (380°C, 30 min.) and Kentucky #1 coal (400°C, 60 minutes) at 1250 psi (cold) H_2. RuS_2 was the most active in terms of quinoline hydrogenation. The precipitated catalysts were more active than commercial $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$, except for FeS_x. For HDN of quinoline, the most active were $NiMo/Al_2O_3$ and RuS_2 which showed similar HDN activities; precipitated catalysts had coal HDN activity but $NiMo/Al_2O_3$ was more active.

Tekely, et. al. (1988)[87] liquefied French Freyming coal for one hr at 140 bar H_2 (2030 psi) using sulfided Fe, Mo, and Sn aerosols produced from the combustion of metal chloride vapors. At 2 wt% catalyst on coal loading, the catalysts accelerated hydrogenolysis of bridging bonds (especially ether bonds) and hydrogenation of polyaromatic units, with the relative activities being $Fe_2O_3 \sim MoO_3 >> SnO_2$.

2.2 Oil-soluble precursors

Sections 2.2 and 2.3 discuss oil- and water-soluble catalyst precursors, respectively. Tables 6a and 6b lists various oil- and water-soluble precursors (respectively) that have been studied or claimed for coal liquefaction. The table includes precursors that have been used with pretreatments (to be discussed in Section 2.4.2).

Oil-soluble catalysts and precursors can be mixed in with the coal/solvent slurry. Most of the precursors that have been used are organometallics. As homogeneous catalysts, organometallic compounds may maximize contacting with coal. They can be highly active, specific, and selective; they may also be more poison-resistant than heterogeneous systems. Advances in the synthesis of polynuclear cluster complexes (e.g., Pt and Ir, Au and Rh) and the ability to anchor such complexes to heterogeneous surfaces have been used. In the latter case, there is a possibility of complex cross-linking, though.

In general, oil-soluble and water-soluble precursors (to be discussed in Section 2.3) give liquefaction performance better than thermal liquefaction. For example, Hirschon and Wilson (1989)[88] found that the use of either aqueous salts or organometallic complexes of Mo gave superior conversions over thermal liquefaction with Illinois No. 6 in tetralin at 34 bar (500 psi) H_2 (cold) and 400°C. The best organometallic precursor was a dimeric molybdenum sulfido complex that did not require high-temperature activation.

The catalyst effectiveness can also be a function of coal type and the catalyst precursor. In a subsequent SRI study, Hirschon and Wilson (1992)[89] found that Fe catalyst precursors were not effective for Illinois No. 6; however, Fe catalysts were effective for Beulah Zap ND lignite. Moreover, catalysts from organometallic precursors gave higher yields of toluene-solubles than catalysts from water-soluble salts or than reaction without catalyst. Yields with organometallic precursors were as high as those in tetralin with no catalyst, indicating that donor solvents may be unnecessary with a good catalyst precursor. In a microscopic study of Fe and Mo liquefaction catalysts by Mitchell et. al. (1991)[34], he found that Mo generated from sulfided NH_4 molybdate was associated with the organic phase unlike Fe from $FeSO_4$ which was in agglomerates. This may explain why Mo was more effective than Fe. However, there was also indication from energy dispersive analysis of the catalyst residues that the Mo was only dispersed on the surface and did not penetrate throughout the coal particle. Moreover, the Mo catalyst coating "peeled" from the coal surface with reaction time.

2.2.1 Naphthenates and octoates

Naphthenates and octoates are among the most studied organometallic catalyst precursors for coal liquefaction. Curtis et. al. (1988)[90] tested Mo naphthenate, Amocat 1B, and precipitated MoS_2 with model compounds at a concentration of 1 or 2 wt% in hexadecane solvent, 380°C, and 87 bar (1250 psi) H_2 (cold). While all three catalysts had the same hydrodesulfurization (HDS) activities and were ineffective for hydrocracking, Mo naphthenate was most effective for hydrogenation, hydrodeoxygenation (HDO), and HDN. In the liquefaction of Illinois No. 6 in anthracene at 425°C, 1250 psi H_2 (cold), Mo naphthenate was most effective for coal conversion, HC production, production of $MeCl_2$/MeOH-soluble material, HDN, and HDO.

The relative activities of Mo, Ni, and V organometallic complexes have also been investigated in Auburn University studies by Kim, et. al. (1990).[91] Oil-phase naphthenates or octoates, and solid-phase acetylacetonates were used in the coprocessing of Illinois No. 6 with Khafji or Maya resid at 400°C, 195 bar (2820 psi) H_2 and 425°C, 208 bar (3000 psi) H_2. The relative activities were in the order Mo ~ Ni > Ni-Mo/Al_2O_3 > S(thermal) > V.

Kim, et. al. (1991)[92] further investigated the effectiveness of Ni in the hydrogenation of the model systems naphthalene, indan and indene, benzothiophene, o-cresol and benzofuran, or quinoline and indole in hexadecane solvent. The catalysts were generated from Ni naphthenate, octoate, acetylacetonate, or citrate. At a level of 2900 ppm Ni, all precursors except for naphthenate were active for hydrogenation and the relative activities were in the order acetylacetonate > citrate > octoate.

In an Exxon patent, it is claimed that mixing 0.1-2 wt% of an oil-soluble Cr compound, such as naphthenate, with a hydrocarbon oil and heating the mixture with an H_2S-containing gas in the absence of coal, produces a catalyst precursor that when added to the coal/solvent slurry, results in good liquefaction performance at 425-480°C and 29-345 bar (400-5000 psi) H_2.[116]

2.2.2 Carbonyls

Fe and Mo carbonyls have been among the most studied carbonyls. A 1983 Japanese patent[93] claims that $Fe(CO)_5$ with free or coal sulfur converts to a high-activity catalyst for coal liquefaction at about 300°C. Watanabe, et. al. (1984)[94] liquefied Japanese Mi-ike bituminous and Taiheiyo subbituminous coals at 445°C with $Fe(CO)_5$, $[Fe(CO)_2Cp]_2$ (Cp=cyclopentadienyl), ground red mud, $FeCl_3$, $FeSO_4$, and Fe(III) acetylacetonate. In general, the presence of these Fe compounds resulted in increases in the lighter fractions (oil and asphaltenes) but $Fe(CO)_5$ showed the highest activity. $[Fe(CO)_2Cp]_2$ did not show high activity probably because higher temperatures (>445°C) are required to form the active species.

Herrick, et. al. (1990)[95] used $Fe(CO)_5$ in the coprocessing of Illinois No. 6 with Maya atmospheric residue. The use of 0.5 wt% Fe as $Fe(CO)_5$ increased coal conversion to $MeCl_2$-solubles from 39% to 82%. 95% of the Fe in the $Fe(CO)_5$ precursor decomposed to a mixture of highly-dispersed pyrrhotite with a 12 nm mean crystallite size. The remainder of the Fe decomposed to Fe_3C and other iron compounds.

In addition to $Fe(CO)_5$, Pennsylvania State University researchers have also done work with $Mo(CO)_6$ and mixtures of $Fe(CO)_5$ and $Mo(CO)_6$. In general, the order of catalyst activities is $Fe(CO)_5/Mo(CO)_6 > Mo(CO)_6 >$

$Fe(CO)_5$ with respect to yield of pentane-soluble products.[96,97] This work by Pradhan, et. al. on carbonyls will be discussed in greater detail in Section 3.3 as their performance relate to that of sulfated oxides.

Suzuki, et. al. (1992)[33] studied Ru-based catalysts generated from the following precursors: Ru (cyclooctadiene) (cyclooctatriene), Ru (acetylacetonate)$_3$, and $Ru_3(CO)_{12}$. Liquefaction with 1-MNP at 400-425°C and 55 bar (800 psi) H_2 (cold) were conducted with Australian Yallourn brown coal, Wyoming, Illinois No. 6, and Mi-ike Japanese bituminous coals. All coals were liquefied with high conversion with only small amounts of the Ru complexes (0.02-0.07%). Ru complexes were found to be more effective in promoting preasphaltene to asphaltene and asphaltene to oil conversions compared to $Fe(CO)_5$-S. $Ru_3(CO)_{12}$, when used as a promoter for supported CoMo, was also found to be effective as an active amine transalkylating catalysts for hydrogenolysis reactions of C-N bonds based on reactions with the model compound tetrahydroquinoline by Hirschon, et. al. (1988).[98]

Warzinski, et. al. (1992)[99] at DOE investigated an alternative method of impregnating $Mo(CO)_6$ into coal. The method utilizes supercritical CO_2; the solubility and phase behavior of the carbonyl in supercritical CO_2 at 40, 50, and 60°C have been reported and preliminary liquefaction results with Illinois No. 6 impregnated by this method suggest that coal dissolution is promoted.

2.2.3 Molybdic and phosphomolybdic acids

Molybdic acid (H_2MoO_4) in combination with other compounds, such as ZnO+magnesia or chromic acid, was found to be effective in liquefaction by the early German work. Exxon has several patents on various formulations containing molybdic acid[100] and phosphomolybdic acid $H_7[P(Mo_2O_7)_6]$[101-104] for the hydroconversion of carbonaceous material. The latter has been claimed to have higher activity and better coke control.[101] On a Mo basis, sulfided molybdic acid at a 0.2-2 wt% Mo on oil loading is claimed to be 57% more active than Mo naphthenate.[100]

Bearden and Aldridge of Exxon patented catalysts that contain phosphomolybdic acid for the hydroconversion of coal, oil, and coal/oil mixtures. In the parent patent, 10-950 ppm Mo (preferred are phosphomolybdic acid and Mo naphthenate) is used as catalyst in the coprocessing of 2-50% coal at 375-415°C.[104] In a second patent, the catalyst consists of 1-2000 ppm of Mo (especially phosphomolybdic acid and Mo naphthenate) with 0.1-20 moles/g-atom metal of a hydrogen halide. In the hydroconversion of coal or oil at 315-455°C and 35-345 bar (500-5000 psi) H_2, the halide is claimed to improve metals removal, Conradson carbon conversion, and coke suppression.[103] In these patents, H_2S is added to produce the active catalyst. In a later Exxon patent by Lewis and Mayer (1987)[105], the catalyst precursor preparation did not require the addition of H_2S. 0.2-2 parts weight Mo as phosphomolybdic acid was mixed with 100 parts weight of the oil prior to contacting with a H_2-containing gas at 40-370°C to remove the water. A portion of the resulting mixture is then mixed with the oil then reheated in a 370-565°C H_2-containing gas.

2.2.4 Others

Commercial oil-soluble Mo-based additives, such as Molyvan L or Molyvan 822, have been used to liquefy Illinois No. 6[106] and Black Thunder subbituminous[107] coals. These additives, which already have Mo-S bonds, have an advantage in that no sulfiding is required. Results with these relatively new catalysts will be discussed in greater detail in Section 4.4.

Tetraethyl lead has also been investigated as a catalyst precursor with bituminous Australian, mostly Millmeran, coal.[108] It improved conversions although yields were not as high as those from iodomethane as catalyst; lead acetate or tetramethyl tin also gave reasonable oil yields.

Cobalt-based catalysts have also been investigated for coal liquefaction. Wilson, et. al. (1988)[109] liquefied Illinois No. 6 (River King) with SRC-II recycle solvent at 425°C for 15 min. using bis(dihydrobis(pyrazolyl)borate)cobalt(II), an oil-soluble organometallic salt. At 0.2 wt% Co loading, coal conversion (based on daf coal) and conversions to cyclohexane- and THF-soluble products at 2010 psig were about the same as those obtained with the water-soluble precursor NH_4 molybdate at 1.6 wt% Mo and 125 bar (1800 psi) H_2. With water-soluble cobalt(II) sulfate heptahydrate as precursor, conversions were only slightly better than in the absence of catalyst.

Another cobalt-based catalyst that has been studied is Co phthalocyanine (Co-PhCy). Sakamoto, et. al. (1989)[110] obtained a liquid yield of 4% without catalyst and 15% with catalyst for liquefaction at 380°C and 100 bar (1450 psi) H_2 (cold). They claim that the Co-PhCy catalyst held a lot of H_2 and promoted the decomposition of asphaltene by donating H_2 to the radicals produced during hydrocracking.

A Japan Synthetic Rubber patent115 outlines the synthesis of a thiolate, Mo(t-C4H9S)4, a dark red crystalline solid unstable to moisture and air, which may be used to synthesize other Mo complexes that can be used as soluble catalysts.

<u>Organic sulfur compounds</u> have also been claimed as effective catalysts. Charcosset, et. al. (1986)[111] have used benzenethiol as soluble catalyst for coal liquefaction. Rudnick has European patents on the use of thiol, thiophenol, benzothiopene, and 2- to 12-carbon alkyl mercaptans as hydrogen transfer agents.[112,113] A French patent[114] claims that an oil-soluble ferric complex of at least one sulfonic acid and containing 6-12 g-atoms Fe per g-equiv of acid can be effective for liquefaction with donor solvent at 400-470°C, and 60-250 bar (870-3630 psi). For example, for a catalyst prepared from $Fe(OH)_3$ and a 10- to 35-carbon alkylbenzene sulfonic acid, higher conversions (84-86%) and distillate yields compared to no catalyst or to $FeCl_2$ are obtained.

The use of colloidal metals as fine powder catalysts was mentioned in a previous section. In a study by Bonnemann, et. al. (1992)[61], nanometer colloidal metals were produced by the reduction of the metal salts with hydrotriorganoborates. The quaternary ammonium halides that were formed coated the colloidal particles and provided solubility in organic solvents and high stability. It was reported that hydrogenation catalysts made by this method had twice the activity of standard catalysts. It is possible then to alter the solubility of the metal catalyst precursor by this selective halide coating.

2.3 Water-soluble precursors

These precursors can be introduced onto the coal by any of the surface wetting deposition methods discussed in Section 2.1.2.

2.3.1 Molybdates

Various molybdates, particularly ammonium molybdates, have been investigated as catalyst precursors. Li, et. al. (1991)[117] have found that with 0.5% Mo added as ammonium tetrathiomolybdate, NH_4MoS_4 (ATM), higher yields of oil and phenols, and lower sulfur in oil compared to the non-catalytic case were attained. Burgess, et. al. (1991)[118] have used sulfided ammonium molybdate, $(NH_4)_2MoO_4$ (AM), sulfided tetrahydroquinolinium molybdate, and ATM as MoS_2 precursors with five coals using naphthalene or phenanthrene as solvents. Their results with bituminous coals indicate that Mo provided atomic H to help crack asphaltenes to oils. In the investigation of Davis, et. al. (1991)[119] of ATM as precursor, H_2 or N_2 atmosphere was used in the liquefaction of lignite, subbituminous, high-volatile C, and high-volatile A coals. As in the Burgess, et. al. study,[118] the catalyst minimized retrogressive reactions in the subbituminous coal. H_2 and catalyst promoted liquid conversion and the thermoplastic development of vitrinite, due to enhanced H transfer and catalyst dispersion.

This catalyst enhancement of conversion was also demonstrated by Derbyshire, et. al. (1988)[120] in the liquefaction of PSOC-1403P subbituminous coal with no donor solvent using ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}\ 4H_2O$ (AHM). The results suggest that the catalyst provides a source of H atoms by dissociating molecular hydrogen and that the H atoms induce cleavage of bridging linkages and stabilize the resulting fragments. Garcia and Schobert (1989)[121] studied the liquefaction of a high-sulfur (12% S) lignite with no solvent using ATM, sulfided AHM, and MoS_2 as catalysts. The best conversions, liquid yields, and HDS were obtained with the impregnated sulfided AHM at 325°C. At temperatures <325°C, the other precursors did not decompose to the active catalyst form.

The catalyst activation temperature is also a function of the form of the catalyst precursor. Bockrath, et. al. (1992)[122] mixed Illinois No. 6 coal with 40% of its weight of an aqueous solution of AHM or ATM followed by vacuum drying at 60°C. In another case, AHM was added as a powder. During liquefaction at 350°C, the AHM powder performed only marginally better than coal without added catalyst even though twice as much Mo was added in the powder form. At this low temperature liquefaction, it is important that the catalyst be in its active form. Utz, et. al. (1990)[123] liquefied Illinois No. 6 with tetralin (1:2 coal:solvent) at 425°C and 70 bar (1000 psi) H_2 (cold) for one hr using 1000 ppm Mo on coal. At these conditions, the catalyst precursors (aqueous AHM, ATM, aqueous suspension of MoS_3, and dry MoS_3) were sufficiently activated.

The impregnation solvent can also have an effect on the catalyst effectiveness. Huang, et. al. (1992)[124] liquefied Montana subbituminous using ATM as catalyst precursor dispersed by an incipient wetness method. Water and a mixture of water/THF were employed as impregnation solvents. The volume of water/THF required to achieve incipient wetness was thrice that of pure water so that better liquefaction (probably due to better catalyst dispersion) was achieved with coal impregnated using water/THF.

2.3.2 Sulfates

As mentioned in the early history of coal liquefaction, ferrous sulfates were used as slurry catalysts in the liquefaction of brown coals. In a recent study, Yokohama, et. al. (1989)[125] used diphenylether and diphenylmethane to study the activities of FeS_2, $Fe_2O_3 + S$, $Fe_3O_4 + S$, red mud (contg. 40% Fe_2O_3) + S, and $FeSO_4$ at 101 bar (1465 psi) H_2 or N_2 (cold) and 450°C. The sulfate always formed in the presence of water (but never without it) and promoted formation of radicals from phenyl and benzyl groups by dehydrogenation; these radicals polymerized to less volatile compounds under both N_2 and H_2.

Ammonium sulfate has also been tested by Yokohama, et al. (1991)[126] for the liquefaction of a pyrite-containing Japanese bituminous coal and a pyrite-free Australian lignite; however, it did not demonstrate any activity for coal hydrogenation with tetralin at the same conditions stated previously. Moreover, there was a difference in the products from liquefaction of Japanese bituminous with $(NH_4)_2SO_4$ compared with that from FeS_2. The coal liquids from FeS_2 consisted of aromatics with short side chains and fewer heteroatoms whereas with $(NH_4)_2SO_4$, the side chains were longer and had more heteroatoms.[125]

The use of sulfated metal (particularly iron) oxides as coal liquefaction catalysts with excellent hydrogenation and hydrocracking activities has been researched extensively by groups at University of Pittsburgh and in Japan. This work will be discussed in greater detail in Section 3.3.2.

2.3.3 Others

In a study by McCandless, et. al. (1981),[127] metal chloride was impregnated at 3 wt% on pulverized Montana Rosebud subbituminous coal which was then liquefied at 450°C, 69 bar (1000 psi) H_2 with 5% HCl/H_2. The alkaline earth metal (Ca, Sr, Ba, Ra) chlorides had some catalytic effect, but the alkali metal (Group IA) chlorides seemed to act as poisons. The relative reactivities were in the order $FeCl_2 < ZnCl_2 < NiCl_2 < CuCl_2 < SnCl_2 < CoCl_2$. Nonvolatile chlorides remained in the unreacted residue in chloride form but they could be easily removed by water leaching. Exxon has several patents on the use of one or more iron or zinc chlorides[128] and hydrogen halides[103,129] for the hydroconversion of coal and oil.

Takemura and Saito (1984)[130] found that Ni <u>acetate</u> was effective for coal conversion in the liquefaction of Morwell brown coal with phenolics as solvent at relatively low temperatures of 230-270°C. XRD analysis of the catalysts after runs showed the presence of metallic Ni, indicating that Ni acetate converted to acetic acid and Ni. Ihara (1985)[131] claims a similar advantage with the use of phenol and/or alkylphenol; a partially hydrogenated product with good H-donor properties can be produced with one or more Group VI and/or VIII metal sulfides.

Exxon has numerous patents on other water-soluble catalysts for hydroconversion of coal and/or oil, such as aqueous solutions of <u>oxalates</u> of V and Mo[37] and aqueous solutions of <u>CrO_3</u> to which a water-soluble compound such as an alcohol or carbohydrate has been added.[132-134] In the case of t-butanol added to CrO_3, it has been claimed that hydroconversion performance for a vacuum residue was comparable to that obtained with Cr naphthenate.[132] In another Exxon patent, the salt of a <u>metal-sulfur analog of cubane</u> or a mixture of such analogs mixed with solid HC feed, and an ammonium and/or <u>hydrocarbyl substituted ammonium</u> has been claimed to be effective in the hydroconversion of solid carbonaceous materials. The metal-sulfur cubane analog is converted to the sulfide during hydroconversion at 260-480°C and 35-483 bar (500-7000 psig) H_2 and is claimed to be highly dispersed and gives high conversion.[135]

2.4 Impregnation techniques

In the deposition by surface wetting methods discussed in Section 2.1.3, both the metal salt and its counter ion are deposited on to the support (i.e., coal for dispersed catalysts). The metal salt is then dispersed by diffusion through the liquid-filled pores, or by capillarity if the support is dry. These methods are usually used when there is little interaction between the metal salt and the support, which just acts as a solid surface.[56] In the impregnation techniques discussed in this section, there may be an interaction between the deposited catalyst precursor and the coal support.

2.4.1 Ion-exchange

Ion exchange takes advantage of ion adsorption properties to prepare catalysts in solution from metal salts. Unlike deposition by surface wetting, only the adsorption of a given type of ions occurs; none of the corresponding counterions are adsorbed. If the surface charge and charge density are properly selected by appropriate pH control, it may be possible to have dispersion of the metal ion at the atomic level. The pH of the metal salt solution can be viewed to act as a "surface charge selection switch".[56]

The ability to introduce metals by ion-exchange is particularly promising with low-rank coals which contain ion-exchangeable functional groups like carboxyls. These carboxyl groups can occur either as carboxylic acids or as groups associated with cations such as Ca, Mg, Na, and Fe. For example, Fe has been successfully ion-exchanged into Taiheyo Japanese subbituminous coal[136,137] and Morwell brown coal,[136] among others. In the latter case, ion-exchange with ferrous sulfate or acetate resulted in a catalyst that had higher activity than Fe_2O_3 powders mixed with the coal.[138] It has also been found that coal conversion was unaffected by changing the counter anion (e.g., sulfate, chloride, or acetate) of the treatment solution.[139]

2.4.2 Pretreatment combined with soluble precursors

In general, incipient wetness, impregnation, and soluble precursor techniques produce catalysts that are more effective than precipitated fine powders that are mixed with the coal. For example, in a study of various molybdenum-based catalysts, Mo naphthenate was more active than a precipitated poorly crystalline MoS_2.[140] A possible exception may be ultrafine, nanosized powders precipitated via microemulsion techniques which may result in good dispersion that can be comparable to that obtained by the other techniques. For example, the 3-13 nm iron carbide precursors synthesized at University of Kentucky enhanced conversion of

Wyodak in tetralin at 385°C, 55 bar (800 psi) H_2 (cold) to a greater extent than that obtained with $Fe(CO)_5$ precursor.[141]

Solvent swelling of coal combined with catalyst impregnation followed by liquefaction can result in enhanced conversions and yields. Artok, et. al. (1992)[142] swelled Blind Canyon high-volatile bituminous and Big Brown lignite with methanol, pyridine, tetrahydrofuran (THF), or 10% t-butyl ammonium hydroxide (TBAH) in aqueous 50% methanol. Swollen and unswollen coals were impregnated with NH_4 tetrathiomolybdate and MoS_3 then liquefied in phenanthrene at 275°C and 69 bar (1000 psi) H_2. Without swelling, the catalysts increased conversion mainly due to increased yield of preasphaltenes; without catalyst, swelling improved conversion mainly due to higher yield of oil + gas. For bituminous coals, preswelling with methanol or pyridine had little effect but THF and TBAH enhanced conversion. Pre-swollen coals impregnated with ferrous sulfate, $Mo(CO)_6$, and $Fe(CO)_5$ gave better liquefaction behavior than the unswollen coals.[143] In ion-exchanging Taiheyo Japanese subbituminous coal using aqueous $FeSO_4$ solution, Miki, et. al. (1991)[136,137] also added ethanol to improve coal swelling. In another Japanese study,[144] Morwell Australian brown coal was impregnated with $ZnCl_2$ or $SnCl_2$ from a methanol solution, followed by sulfidation of the metal chloride with 5% H_2S at room temperature. Flash pyrolysis of the swollen/impregnated coal resulted in increased coal conversion and oil yields.

Prehydrogenation of swollen impregnated coals at mild H_2 pressure and ambient temperature followed by liquefaction is one embodiment of a patent by Joseph (1991).[145] Bolton and Derbyshire (1988)[146] prehydrogenated Linby high-volatile bituminous coal that had been impregnated with 1 wt% Mo from aqueous NH_4 tetrathiomolybdate. Compared to the unhydrogenated coal, the treated coal resulted in increases in overall conversion and liquid yield during pyrolysis; hydropyrolysis increased these even more. In hydropyrolysis, the same conversion was achieved using catalyst-impregnated but unhydrogenated coal, indicating that reactions occurring in catalytic hydrogenation and early in hydropyrolysis may be the same. In a subsequent study, Derbyshire, et. al. (1990)[147] impregnated a lignite and two bituminous coals with Mo, Fe, or Fe/Mo prior to prehydrogenation at 7 MPa H_2 and 275°C for 30 minutes. For liquefaction at 425°C and 30 minutes, the performance of the Mo and Fe/Mo catalysts were comparable and superior to Fe. Increasing coal rank decreased oil yield, oil/asphaltene ratio, and CO_x yield.

Baldwin and Miller (1990)[148] combined <u>mild alkylation</u> and addition of a dispersed catalyst (chlorine) via HCl as alkylation catalyst. The presence of the dispersed catalyst was more effective than alkylation in terms of net reactivity enhancement.

The effectiveness of <u>organic reductions</u> with sodium or potassium as pretreatments was investigated by Nomura, et. al. (1985).[149] Taiheyo coal impregnated with $FeBr_2$ was co-reduced with either Na in NH_3 or with K in refluxing THF prior to liquefaction with tetralin. Non-catalytic (no Fe) liquefaction of pretreated coals resulted in higher hexane solubles yields than those obtained without the pretreatment. Fe increased benzene- and hexane-solubles compared to non-catalytic liquefaction of K-treated coal. The slight increase of H atoms added to coal and the loosening of clusters of aromatic sheets was a possible explanation.

Ha, et. al. (1988)[150] deposited either a water-soluble Fe or Mo catalyst onto coal particles before or after <u>agglomeration</u> with SRC-II heavy distillate at 0.35:1 to form 2-3 mm diameter agglomerates which were then reacted at 400°C and 91 bar (1300 psig) H_2 (cold). When the catalyst was Fe (+H_2S addition), higher THF-solubles yield resulted when impregnation was prior to agglomeration. However, the reverse was true with Mo. It is possible that some of the Fe may have been removed by the H_2O during the agglomeration step. A patent has been issued on this agglomeration of catalyst-impregnated coals.[151]

The use of <u>ultrasound</u> to enhance catalyst dispersion during coal liquefaction has been investigated by Bendale, et. al. (1991).[152] Two-stage liquefaction experiments have been conducted with Mo naphthenate or Mo carbonyl as catalyst precursors along with stoichimetric amounts of elemental sulfur.

3. DEVELOPMENTS IN DISPERSED CATALYSTS

This section provides a general review of relevant developments in dispersed catalysts for petroleum hydroprocessing and coal liquids upgrading, and fundamental research in the areas of effect of sulfur during liquefaction, sulfated oxide ("superacid") catalysts, and multicomponent catalysis.

3.1 Applications in petroleum hydroprocessing

As mentioned in Section 2, the preparation and characterization of supported catalysts developed for petroleum hydroprocessing have been applied accordingly to dispersed catalysts. For example, techniques for the addition of metals introduced as inorganic salts or organometallic complexes onto supported hydrotreating catalysts have been effectively used in the impregnation of these same metals onto coal particles.[153] This section will also review recent developments in dispersed catalysts for petroleum refining, particularly in the patent literature. The use of coal and other residues as supports, which has direct relevance, will also be briefly reviewed.

3.1.1 Dispersed catalysts for petroleum refining

In Bearden and Aldridge's (1981)[154] Exxon M-coke hydroconversion process, where M-coke stands for micrometallic coke, the catalysts are micron-sized particles which consist of a catalytic metal (Mo preferred) sulfide component combined with a carbonaceous component. They report that as little as 100 ppm Mo can obtain 95% petroleum residuum conversion at 400-454°C and 69-172 bar (1000-2495 psi) total pressures. Catalyst is formed in-situ from oil soluble metal compounds and catalyst dispersion is claimed to be high.

Exxon has numerous patents on dispersed catalysts introduced as soluble (oil- or water-) precursors for heavy oil hydrocracking. Thermally decomposable compounds containing metals from Groups II, III, IV, V, VIB, VIIB, and VIII (preferably Mo, Cr, and V) have been claimed.[155-158] The form of the compounds can be any of the following oil-soluble compounds: carbonyl, halide, inorganic acid, or the salt of an organic acid. In a recent embodiment,[158] the catalyst concentrate is prepared by mixing 565°C$^+$ hydrocarbon oil with the metal compounds to provide 0.2-3 wt% metal (based on oil), then heating the concentrate in the absence of H_2 at 275-425°C and 0-35 bar (0-500 psig) for a time to convert to the solid catalyst. The sulfiding agent is elemental S (claimed to be less hazardous than H_2S) and can be used at any stage of the preparation.

Two Exxon patents cover dihydrocarbyl substituted dithiocarbamates of metals of Groups IVB, VA, VIA, VIIA, VIIIA (especially Mo, Fe, Co, and Ni) for hydroconversion of carbonaceous materials, including coal.[159,160] These precursors do not require sulfiding since they already contain the Mo-S bond. Phillips Petroleum holds several patents on the use of molybdenum dithiphosphates, carboxylates, molybdates, sulfonates, catechols, and mixtures of these compounds.[161-164] In addition to superior coke suppression performance, these soluble catalysts can also perform some conversion and upgrading.

In a patent by Lang, et. al. (1989)[165], it is claimed that Group IB, IVB, IVA, VA, VIA, VIIA, and/or VIII metal oxides or sulfides of up to 150 Å on a carbon support are at least as effective as the corresponding metal naphthenate or phosphomolybdate.

The use of organometallic precursors as petroleum hydrotreating catalysts has also been investigated by other groups. Chen, et. al. (1988)[166] studied naphthenates of Ni, Mo, and Co; acetylacetonates of Ni, Mo, Co, V, Cr, and Fe. At 100 ppm, the most active precursors were Ni carboxylate and Mo acetylacetonate. Using %gas yield < %coke yield and %asphaltene conversion as criteria, the relative activities were in the order Ni > Mo > V > Co > Fe > Cr > thermal.

Ojima, et. al. (1985)[167] synthesized molybdenyl acetylacetonate [$MoO_2(C_5H_7O_2)_2$] from MoO_3 and acetylacetone in the presence of water. The use of 500-200 ppm Mo of this precursor gave performance comparable to finely divided Ni-V/Al_2O_3 (3% on feed) and vanadyl acetylacetonate precursor (1000 ppm V). Ho (1991)[168] prepared his dispersed catalyst by sulfiding tris(ethylenediamine) cobalt molybdate in 10% H_2S/H_2 or 1% H_2S/H_2 at 400°C for 2 hr. The catalysts were tested for HDS of light cat cycle oil. Steady-state HDS of the catalyst formed by sulfidation in 10% H_2S/H_2 was twice that from the catalyst formed in 1% H_2S/H_2. The HDN activity difference was small, indicating that sulfur vacancies used for HDN were not the same as those for HDS. Thiotunstantonickelate has also been claimed as hydrotreating catalyst precursor.[169]

3.1.2 Alkali metal addition

The effect of alkali earth metal addition during the hydrotreatment of petroleum or coal liquids, particularly with respect to coking, has been studied. Masuyama, et. al. (1990)[170] liquefied Australian Victorian brown coal with iron catalyst then deashed the product via extraction with toluene and/or THF. The deashed coal liquid bottoms was hydrotreated in hydrogenated creosote oil over a commercial NiMo/Al_2O_3 catalyst. Preasphaltenes deactivated the catalyst probably because N compounds that were strongly adsorbed on the acid sites were converted to coke. Doping the catalyst with Ca (2.7% CaO) resulted in less coke, lower N in the catalyst coke, and stable activity. Baker, et. al. (1987)[171], in impregnating aqueous $NaNO_2$ on Shell 324 M, found that increasing Na reduced surface acidity and decreased coke on the catalyst. Sulfided catalysts, with or without Na, had stable hydrogenation and HDN activities for the hydrotreatment of Pittsburgh coal tar fraction.

The addition of alkali metals has also been used with coal liquefaction catalysts. For example, activity of a Fe-based catalyst promoted with small amounts of other metals like Sn, Mo, Co, Ni, or Zn, can be improved by adding 0.1-0.5 wt% of a Ca compound, preferably $Ca(NO_3)_2$.[172] In a German patent,[173] catalyst prepared from reaction of $FeSO_4$ with stoichiometric amount of alkali, such as NaOH (4.5-7.5 pH) has been claimed to be effective at 1.5 wt% addition for the liquefaction of Rhine browm coal at 420°C and 80-500 bar (1160-7255 psi).

3.1.3 Disposable additives in petroleum refining

Coal has been used as disposable additive in several petroleum upgrading processes, such as the CANMET[174] and Veba Oel[15,16] processes. Both these processes use coal impregnated with an iron-based compound. Bisaria and Bakhshi (1990)[175] used Sheerness subbituminous coal as disposable additive with Mobil Celtic whole crude from Saskatchewan. With no H_2 and catalyst, 20-30% oil conversion was achieved although coking occurred at coal concentrations > 9%. The addition of iron oxide benefitted viscosity reduction and API gravity improvement. As additive, the CANMET process uses up to 10 wt% (usually 5 wt%) coal which has been coated with an iron salt; other coatings that have been claimed in the patent literature include salts of Co, Mo, Zn, Sn, Ni, or W.[174] Concentrations as high as 40 wt% (maf coal) of Forestburg subbituminous have been coprocessed with Cold Lake vacuum bottoms at high severity.[176,177, 177a]

As with coal liquefaction, clay minerals and spent catalysts have also been investigated as potential disposable additives for petroleum upgrading. Itoh and Tsuchida (1989)[178] used clay minerals and FCC catalysts with Arabian Heavy vacuum residue at 450°C and 85 bar (1235 psi) H_2 (cold). The minerals gave higher yields of middle distillate and lower yields of gum and coke than FCC catalyst, which were impregnated with iron and iron removed from allophane, one of the minerals. The results suggest that iron and macropores are important for suppressing coke formation. Kondo, et. al. (1983)[179] have used spent Co molybdate HDS catalyst with Cold Lake tar sand bitumen. Although the catalyst was active in hydrocracking, the products did not meet fuel specifications.

3.2 Effect/role of sulfur

As mentioned in Section 1.4.2, the sulfide has generally been regarded as the active form for metals that demonstrate catalytic activity during coal liquefaction. Therefore, sulfur, usually in the form of H_2S, elemental sulfur, or dimethyldisulfide (DMDS), is added to non-sulfide catalyst precursors. For example, iron oxide (Fe_2O_3 or Fe_3O_4) alone had no effect but the addition of DMDS or elemental S increased conversion and inhibited retrogressive reactions during the liquefaction of Alberta subbituminous coals by Aitchison, et. al. (1986)[180] or of Zalarroure lignite by Wang, et. al. (1992).[181] The use of molten sulfur as sulfiding agent has also been reported.[182]

Even in the absence of catalyst, the addition of sulfur or sulfur compounds has been found to enhance performance. For example, the addition of sodium sulfide[183] or zinc sulfide[184] has been found to improve coal conversion and the yield of pentane-soluble oils. ZnS addition increased coal conversion from 77% (without catalyst) to 96% and increased oil yield from 16% (without catalyst) to 41%.[184] This improvement has been postulated to be due to the sulfides being free radical initiators and/or sulfiding agents.

The use of H_2S during CANMET corpocessing of Forestburg subbituminous and Cold Lake vacuum bottoms improved both coal conversion and distillate yields at 400-425°C compared to those obtained with Fe (as $FeSO_4$) impregnation alone. However, at higher severities, $FeSO_4$ impregnation resulted in better coprocessing performance, possibly due to the stronger hydrogenation activity of $FeSO_4$.[176]

In a study of coal/oil coprocessing using model coal compounds by Kim, et. al. (1990),[185,186] excess sulfur enhanced hydrogenation during thermal reactions. This same study also looked at the effect of excess sulfur with catalysts. The MoS_2 catalyst generated from Mo napthenate with excess S promoted partial saturation of the multiring aromatic to hydroaromatic species but did not promote further saturation of the hydroaromatic or of single-ring alkyl-substituted aromatics.[185] Organic N compounds deactivated the MoS_2 catalyst; excess elemental S and organic S compounds alleviated this poisoning by the N compounds but inhibited deoxygenation.[186] The addition of sulfur can also help maintain the catalyst in the active sulfided form. Kamia, et. al. (1988)[187] used Fe, $Fe(CO)_5$, and ferrocene as catalyst precursors with Yallourn brown coal at 400°C. The in-situ water in this high-moisture low-rank coal may reoxidize the catalyst but S addition was found to prevent this.

The organic sulfur content of the coals has also been found to affect the liquefaction performance with dispersed catalysts. Garcia and Schobert (1990)[188] liquefied US Hagel seam, Turkish Cayhiran, and Spanish Mequinenza lignites with or without NH_4 tetrathiomolybdate under several conditions, i.e., N_2, H_2, and no solvent. Without the catalyst, conversions and yields for a given lignite were similar regardless of atmosphere; with the Mo catalyst, higher conversions and yields were obtained in H_2 than in N_2. The liquid yields and increase in yield in H_2 relative to N_2 correlated with the organic sulfur content of the coal. These results suggest that the thermolysis of relatively weak C-S bonds are important in these lignites and that in the absence of a solvent, the dispersed catalyst was important to facilitate hydrogenolysis.

Without external S addition during liquefaction, the organic sulfur content of the coal can also determine the effectiveness of the catalyst. Cook, et. al. (1988)[189] liquefied two Victorian brown coals of similar H/C with different organic S contents: Morwell (0.35 wt% organic S) and Coolungoolum (4.6 wt% organic S). They used aqueous impregnation with Fe acetate or $SnCl_2$ and liquefaction conditions of 100 bar (1450 psi) H_2 or N_2 (cold) at 300-400°C. Sn was more effective for the low-S coal and Fe was more effective for the high-S coal where Fe was converted to the active pyrrhotite with a 0.92:1 Fe/S ratio and the tin converted to the relatively inactive SnS.

3.3 Sulfated oxides ("superacids")

TiO_2-SO_4^{-2}, ZrO_2-SO_4^{-2}, and Fe_2O_3-SO_4^{-2} are among a new type of solid superacids that have been developed for use as catalysts for various acid-catalyzed reactions,[190, 190a] including coal liquefaction. In a study of the mechanism for the formation of sulfate in sulfur-promoted iron oxide catalysts for coal liquefaction, Kotanigawa, et. al. (1988)[191] heated mixtures of pure Fe compounds (such as FeS, FeS_2, Fe_3O_4, and Fe_2O_3) with sulfur and water to 450°C at 2.5 °C/min under H_2 or N_2 at an initial pressure of 101 bar (1465 psi). Both sulfate and sulfide formed simultaneously via reaction of S with H_2O to form SO_2, H_2S, and H_2.

A recent study investigated sulfated zirconia, titania, and alumina with CO and pyridine adsorption and methanol hydration to dimethyl ether as test reactions. Sulfation enhanced the strength of weak Lewis acid sites but poisoned the strong Lewis acid sites. At high sulfate levels, Bronsted acidity was generated.[190]

In the generation of acidity on sulfate addition, the acidity has been found to disappear on reduction but reappears on oxidation.[192] Yamaguchi, et. al. (1986)[193] studied Fe_2O_3 promoted by $(NH_4)_2SO_4$, SO_3, SO_2, or H_2S. Strong acidity was generated by all promoters as long as the sulfur oxidation state was brought to +6. Different conditions, such as temperature, may be necessary to generate this oxidation state for the various promoters. It is also to be noted that the sulfur species can interconvert between S^{+6} and S^{-2} by redox treatment. A sulfur oxide species, in which two covalent S=O bonds play an important role, is proposed to be responsible for the generation of strong acidity, although the structure of the acid sites is unclear.

Most of the recent liquefaction work in this area has been done by Pradhan and co-workers at University of Pittsburgh and Kotanigawa and co-workers at the Government Industrial Development Laboratory in Japan. Pradhan, et. al. have investigated Fe oxides and Sn oxides treated with various amounts of sulfate. Liquefaction have been conducted with Illinois No. 6,[194] Blind Canyon bituminous,[195] and Wyodak-Anderson subbituminous[195,196] in tetralin at 400°C and 70 bar (1000 psig) H_2 (cold). They have also studied coprocessing of Illinois No. 6 in Maya atmospheric tower bottoms (1:4 coal:oil ratio) with these sulfated oxides.[96] Recent work has also investigated bifunctional catalyst systems such as Mo on sulfated iron oxides ($Mo/Fe_2O_3/SO_4$). Bifunctional 0.5-2.0 wt% Mo on sulfate-promoted ferric oxide, equivalent to 20-100 ppm Mo on coal, has been found to give performance comparable to or better than that obtained with the sulfated oxides.[96,97]

In general, sulfate addition resulted in promotion of coal conversion and oil yield. Sulfated iron oxides were significantly more active than the unsulfated oxides.[196] For example, use of <0.7 wt% sulfated ferric oxide gave 86% maf coal conversion with >50 wt% pentane-soluble oil in the liquefaction of Illinois No. 6. Moreover, elemental S added to this catalyst further increased both coal conversion and oil yield (90% and >60%, respectively); similar results were obtained with sulfated SnO_2.[194] The bifunctional Mo/Fe catalysts were more active than the sulfated Fe oxides and Sn oxides. For example, in the coprocessing study, a bifunctional 3500 ppm Fe + 50 ppm Mo catalyst gave higher coal conversion (78%) and oil selectivity (80%) than those obtained with ferric sulfate and the catalyst precursors $Fe(CO)_5$ or $Mo(CO)_6$. The order of catalyst activities at 400°C, based on the yields of pentane soluble products was bifunctional > sulfated Fe_2O_3 > $Fe(CO)_5/Mo(CO)_6$ > $Mo(CO)_6$ > $Fe(CO)_5$. It is postulated that the Mo contributed hydrogenation function, and that the sulfate ion possibly prevented sintering or agglomeration of the bifunctional catalyst.[96,97]

This sulfate promotion has been attributed to an increase in catalyst dispersion and surface acidity.[194] In a study of finely-divided FeOOH, Fe_2O_3, and Mo/Fe_2O_3 containing 3-4 wt% sulfate ion (with elemental sulfur for sulfidation), the surface areas increased and particle sizes decreased on sulfate addition. This facilitated conversion of the oxides to the active sulfide phase. Moreover, Mo was more effective with calcined sulfated iron oxide than with its uncalcined form.[195]

The effects of the sulfate group in these oxides may be due to an increase in catalyst dispersion, a (probable) inhibition of agglomeration of the metal oxide catalysts at the high temperature, and superacidity of the surface. The superacidity attained with sulfate promotion also achieved significant HDN and HDS. A small amount of moisture in the catalyst system helps maintain high acidic activity, maybe due to transformation of the catalyst to its Bronsted acid form, responsible for generating carbocations. The pyrrhotites formed from iron in coal had a much larger particle size (d_{avg} = 30 nm) than that formed from iron added as sulfated iron oxide (10 nm).[197]

The Japanese work with sulfated oxides has also been conducted with coals of various ranks: Taiheyo bituminous,[198] Akabira bituminous,[126] and Yallourn Australian lignite (which contains no pyrite).[126] Liquefaction experiments have been conducted in tetralin at 100 bar (1450 psi) H_2 or N_2 (cold) with FeS_2, $Fe_2O_3(SO_4)^{-2}$, and $(NH_4)_2SO_4$ as catalysts. With Taiheyo, FeS_2 and $Fe_2O_3(SO_4)^{-2}$ gave similar coal conversions; however, bifunctional FeS_2-$Fe_2O_3(SO_4)^{-2}$ gave excellent results.[198] Fe_2O_3 with 1.2% added sulfate had highest activities for hydrogenation and hydrocracking of tetralin for Akabira and Yallourn coals although HDN and HDO activities were not very good. FeS_2 showed slightly lower activity (was active only for Akabira) and $(NH_4)_2SO_4$ was inactive for both coals (only showed activity for hydrogenation of tetralin). These results indicate that the catalytic action is via reaction with H_2 rather than through participation of the donor solvent.[126] A Japanese patent issued to the Agency of Industrial Science and Technology[199] claims coal conversions of up to 79% with FeS-$FeSO_4$ or $FeSO_4$ sulfated on an Fe oxide composite. The patent also claims that addition of $(NH_4)_2SO_4$ can accelerate hydrogenation.

3.4 Multicomponent catalysts

In coal liquefaction, the need for both hydrogenation and cracking functionalities may be achieved with multicomponent catalysts. For example, tin, which has been used in commercial coal liquefaction developments along with molybdenum and iron, has been found to be very active in combination with HCl or HI[200], although this caused corrosion problems. Maa, et. al. (1989)[200] claim that tin and iodine (as HI) are effective for coal hydroconversion, preferably at 70-207 bar (1000-3000 psig) total pressure and 56-172 bar (800-2500) psig H_2; higher naphtha is obtained if sulfides of metals other than Sn added. Sn + NH_4Cl has also been found to be effective as a bifunctional catalyst with both cracking and hydrogenative functions.[201]

A special case of multicomponent catalysts is that of bimetallic catalysts; Cusumano, et. al.[58] have a good (although old, 1976) review. The points brought out in the review could be extended to nonmetallic catalysts, i.e., sulfides. Although catalyst systems with two or more components (metals) have been disclosed or discussed in the patent or open literature, bimetallic systems are best understood. The earliest approach to their study has looked at their electronic properties with the view that control of the density of d-electrons was instrumental in explaining their properties. Since then, other models have provided better pictures. Moreover, recent developments in characterization techniques have shown that surface and bulk compositions of these catalyst can differ significantly. These bimetallic catalysts can be supported or unsupported, with the latter easier to study and characterize. Supported catalysts occur as alloys or metal clusters; they are usually supported on high-surface area materials since it is difficult to maintain highly-dispersed metals in the unsupported state without sintering and crystallite growth. The general observation is that supported metal catalysts are more stable than unsupported metal catalysts with respect to sintering.

The combination of two metal catalysts can result in promotional effects and better activity maintenance; in the latter case, alloy formation can increase resistance to coking by diluting primary active centers, or by properly balancing hydrogenation and cracking activities. Alloying can also enhance selectivity; for example, alloying with an inert metal can enhance selectivity to products which require single sites and can decrease formation of products from pathways requiring several contiguous active metal sites. It is to be noted, though, that during coal liquefaction conditions where high concentrations of H_2S may be present, the catalyst system is a mixture of sulfides, and not of the metals. The sulfides may also occur as mixed sulfides. Diaz, et. al. (1990)[202] performed an X-ray diffraction study of a CoMo sulfide formed by the decomposition of a thiosalt. Their analysis indicated the presence of a mixed Co-Mo sulfide in addition to the MoS_2 and Co_9S_8 phases.

A special class of multimetallic catalyst systems is the ultrastable intermetallic compound which is an alloy of two or more metals that has a characteristic crystal structure and definite stoichiometry. It usually consists of two metals from opposite ends of the periodic table (e.g., $ZrIr_3$, $ZrPt_3$). It is difficult to prepare the more stable ones because of the high temperatures needed for the alloying.

The promotion of supported catalysts with soluble catalysts has also been investigated. Work at SRI by Hirschon and co-workers[98,203] have been investigating promotion of supported CoMo, NiMo, and WMo with soluble Ru carbonyl. Ru exhibited a synergistic relationship with Mo. RuCoMo > RuNiMo > RuNiW in terms of activity but RuNiW > RuNiMo > RuCoMo in terms of selectivity. In terms of conversion to THF-solubles, RuCoMo was more effective in the liquefaction of Wyodak coal in tetralin than CoMo; RuCoMo was also more effective than unpromoted CoMo in HDN of coal liquids.

In Section 3.3, the use of bifunctional dispersed Fe+Mo was briefly discussed in sulfated oxide catalyst systems. Combinations of metals other than Fe+Mo have been investigated. Table 7 lists some of the combinations, mostly from the patent literature. The promotion of Fe with other metals will be discussed in greater detail in Section 5.3.

4. CATALYSIS BY MOLYBDENUM

Petroleum hydroprocessing catalysts containing transition metal sulfides have been widely used in HDS, HDN, and product quality improvement (hydrotreating). Original interest (pre-WWII) in these catalysts were in their activity for hydrogenating high-sulfur coals (hence maintaining the metal in the sulfided state). Co, Ni, Mo, and W sulfides and their mixtures were most active and least expensive; after WWII, major uses shifted to Co- and Ni-promoted Mo and W catalysts usually supported on Al_2O_3. Unfortunately, there is still little understanding of the basis for and origin of catalytic activity.

This section provides a more detailed discussion on Mo-based dispersed catalysts, MoS_2 (chalcogenides), and liquefaction results with various precursors. It also discusses oil-soluble Molyvan as a coal liquefaction catalyst, and the promoting effect of phosphorus, based on resid hydroprocessing/hydrotreating work on alumina-supported Mo catalysts.

4.1 Morphology and properties of MoS_2

MoS_2 from low-temperature precipitation is amorphous, but highly disordered rag-like morphology can develop when MoS_2 is annealed in H_2S/H_2 at 400°C. It has a high surface/volume ratio. Weak bonding between adjacent basal planes leads to "lubricity", which results in MoS_2's intercalative properties that have found it applications in electronics, for example. MoS_2 (and WS_2 to lesser extent) have HDS and HDN activity; the edge plane has been proposed as the source of this activity.

Chianelli and co-workers[204-207] have reviewed the properties of MoS_2, particularly as it relates to petroleum hydroprocessing. In general, the catalytic activity, e.g. for hydrodesulfurization (HDS), can be correlated with the electronic configuration of the d-orbitals as "percentage d character" of the metallic bond (based upon Pauling's valence bond theory) or with the strength of the metal adsorbate bond. A relation among HDS activity, heat of adsorption of a reacting molecule, and heat of formation of the corresponding sulfide exists (Sabatier's principle), i.e., compounds exhibiting maximum activity will have intermediate heats of formation, presumably because the stability of the surface complex formed by the sulfur-bearing molecule will be intermediate. The metal-sulfur bond at the surface of the catalyst must not be too strong or too weak to obtain maximum HDS; this appears consistent with idea that sulfur vacancies on catalyst surface are active HDS sites (but this is not the entire picture). Some electronic factors, such as number of electrons in the highest occupied molecular orbital of each cluster and relative metal-sulfur d-p covalent strength, provide a basis for the observed trends in catalytic activity but there is still a need to define a relation between these factors (which are based on bulk electronic structure of the metal sulfides) and the electronic structure of active sites on the catalyst surface (i.e., need to define relation between bulk and surface electronic structures).

In the determination of catalyst activity, geometric properties, such as crystal structure, appear to be of secondary importance. Heat treatment conditions can be optimized to obtain highest activity. For example, for anisotropic MoS_2, HDS activity does not correlate with surface area, but does with O_2 chemisorption. However, for isotropic RuS_2 (cubic), linear correlations between HDS activity and both surface area and O_2 chemisorption exist. There is indication that the edge plane of MoS_2 is active but this cannot be confirmed by single-crystal studies since MoS_2 can only be grown in very thin crystals which do not permit study of edge planes.

The structural nature of the active site and the concentration of these sites on the edge plane are chemical properties that may affect catalyst activity. ESR has been used to characterize the defect sites; one work has correlated defect site density with activity for benzene hydrogenation over WS_2 catalysts.

Promotional factors, such as the presence of a second metal, can result in activities greater than the sum of activities of the two catalysts, as discussed in the section on multicomponent catalysts. No consensus exists as to the origin of this synergistic effect, although there appears to be a relation between the activity of these synergic pairs and the average heats of formation of the sulfides of the pairs. Elements to the left of the periodic table have high heats of formation, bind sulfur too strongly, and are poisoned by sulfur; those to the right have low heats of formation and sulfur-containing molecules are too weakly bound for reaction to take place. Averages of these heats of formation can fall into the optimum range; examples are Co/Mo, Ni/Mo. In the case of Fe, if the heat of formation of FeS_2 is used, then Fe/Mo average heat of formation falls outside the optimum range, suggesting no synergy. However, recent work (discussed in Sections 3.3 and 3.4) indicate synergy; this suggests that the active form may not be FeS_2.

In general, surface areas of synergic pairs are lower than those of the pure phases; this suggests that the number of active sites is not increasing but rather that the quality of the active site may be enhanced. Microscopic theory for promotion suggests that somewhere at the edge, sulfur atoms (which upon leaving create vacancies) are shared by the metals (promoter and Mo for example) and behave in an average electronic fashion, i.e., metal-sulfur bonds are adjusted to intermediate values which are necessary for high activity.

4.2 Molybdenum catalysts and precursors

As discussed in examples in Section 2, molybdenum has been introduced in the form of MoO_3, MoS_2, and MoS_3 fine powder, soluble organometallics (such as Mo naphthenate, octoate, carbonyl, acetylacetonate, oxalate), phosphomolybdic and molybdic acid, oil-soluble Molyvan additives, and water-soluble molybdates (ammonium molybdate, AHM, and ATM). The relative effectiveness of these precursors depend on the coal and liquefaction conditions. In general, the soluble precursors result in improvements in coal conversion and oil yield compared to no catalyst or to the use of fine powder Mo oxides or sulfides. An exception to the latter case is the use of nanometer-sized particles. Tables 6a and 6b lists selected references for the studies on molybdenum-based dispersed catalysts, most of which have been discussed in Section 2.

The high activity of Mo-based catalysts are of particular interest in the liquefaction of low-rank coals. Derbyshire and co-workers have found that low-rank coals can be liquefied to obtain similar to higher yields than bituminous coals (even at lower temperatures) if the coals are vacuum-dried to ~4 wt% moisture at room temperature and then heated slowly to liquefaction (>400°C). This mild pretreatment is necessary to prevent cross-linking reactions that normally occur during coal drying and heat-up prior to liquefaction.[208-210] Similar improvements were observed with coals that had been impregnated with water-soluble Mo precursors, such as NH_4 tetrathiomolybdate. For example, the highest yields of chloroform-solubles during liquefaction with no solvent at 350-400°C in 70 bar (1000 psig) H_2 (cold) for 1 hr was obtained from subbituminous coals and the least was for a low-volatile B bituminous coal.[208]

Cugini and co-workers at DOE have also used AHM and ATM as catalyst precursors in coprocessing. In the coprocessing of 0-30% Illinois No. 6 with North Slope vacuum resid, Boscan, or Maya atmospheric resid at 84 bar (1200 psig) H_2 (cold) and 425°C for 1 hr, the addition of 0.1-1.0 wt% Mo as AHM increased yields of heptane solubles.[36] In a more recent study of the coprocessing of Illinois No. 6 or Ohio No. 5/6 in process-derived H donor solvent or with Maya atmospheric residuum or Cold Lake vacuum residuum at 420-450°C and 173 bar (2500 psig) H_2 for 0.5-1.5 hr, high catalyst activities were obtained with the addition of up to 1000 ppm Mo (based on coal), added as ATM or MoS_3.[211]

Other metals can be added to Mo as co-catalysts, as seen in Table 7. For example, a Japanese patent claims good removal of S and metals at 100-1000 ppm Co, Ni, Fe, V, Ti, Zn, Cu, or W added to Mo as co-catalyst.[212] Koo, et. al. (1992)[213] studied various bimetallic systems and found that bimetallic $Mo\text{-}P/RuCl_3\text{-}H_2O$ offered the highest activity.

4.3 Mo-S-P catalysts

In supported MoS_2-γAl_2O_3 hydrotreating catalysts, the active phase consists of small slabs of MoS_2, generally well-dispersed on the support, with the coordinatively unsaturated Mo edge atoms considered as the active sites. The addition of phosphorus generally improves catalytic performance of Al_2O_3-supported MoS_2 catalysts but it is a poison for C-supported ones. Poulet, et. al. (1991)[214] reviews the effects of phosphorus on alumina-supported MoS_2 catalysts; in general, the effects are in morphological changes in the MoS_2 and/or the support and in the surface properties of the support. This section will review those effects that may be relevant to dispersed MoS_2 catalysts.

The direct effects of phosphorus addition on the MoS_2 active phase are probably the most relevant to dispersed catalysts. One effect may be the direct replacement of some sulfide species by phosphide-like species which can induce modification in the site structure. Another effect is that of the P-O-Mo bridges on the ordering of the stacked MoS_2 layers.

1) Alteration of the stacking of MoS_2 layers
-- More stacked layers of MoS_2 have been observed when P is present. This may be due to the different (i.e., weaker) interaction of MoS_2 with the support surface. If the stacked platelets have irregular superposition, there may exist a diffusion limitation for the reactants to reach the active sites.

In the electron microscopy study by Ramirez, et. al. (1992),[215] P addition to the supported catalysts with low Mo promotes formation of single- and double-layered MoS_2 when P and Mo are impregnated simultaneously. P addition before Mo impregnation resulted in higher stacking of the MoS_2 crystallites and promoted formation of partly sulfided MoO_3 particles. Moreover, P addition to catalysts with high Mo prevented agglomeration of MoS_2 particles.

2) Change in the coordination of the sites

-- In the case of catalysts where Ni is present along with Mo, the interaction of P with the active Mo sites can induce changes in the site coordination of both Mo and Ni. For example, in an FTIR and NMR study of supported Mo by DeCanio, et. al. (1992),[216] the addition of up to 1.5 wt% P promotes the formation of reducible octahedrally coordinated molybdena on the alumina surface. The electron density of the site is modified as well. The addition of >2.0 wt% P results in formation of bulk MoO_3 and $Al_2(MoO_4)_3$. It is postulated that the presence of low amounts of P causes an increase in the number of sites adsorbing CO and increasing P further decreases the number of these adsorbing sites, probably due to the formation of either Ni phosphate of Ni molybdate.

The trend of increase in number of CO-adsorbing sites with P addition up to a maximum was observed by Kushiyama, et. al. (1991)[217,218] in the HDS of Morichal Venezuelan crude at 470°C using the soluble catalyst precursors Mo naphthenate, Co octylate, and di-2-ethylhexylphosphate. (H_2S generated from elemental sulfur addition can accelerate decomposition of the precursors below 240°C.) P addition increased HDS activity up to a maximum and this optimum level was unchanged by Mo concentration. The improvement was attributed to the formation of oil-insoluble P-V compounds that separated from the active Mo-Co-S phases. This interaction of P with V also led to better hydrodevanadation, thereby preventing catalyst deactivation by V. Excess P can poison the catalyst, though.

3) Change in the acidic properties of the (coal) support

-- Depending on the P loading and the structure of the surface phosphates, acidity can be increased or decreased. Lewis sites may be created by elimination of H_2O and/or H_2S from the surface OH and/or SH groups upon P treatment. Lower coke yields have been reported with phosphorus addition.

4) Enhancement of dispersion of metals

-- In a recent study of thiophene HDS using MoO_3-Al_2O_3 hydroprocessing catalyst promoted with 0 or 1 wt% P, Al-OH groups were more reactive toward molybdena, resulting in higher Mo dispersion for the P-promoted catalyst.[219,220]

4.4 Oil-soluble Molyvan additives

Oil-soluble Molyvan additives, marketed by Vanderbilt Inc. as commercial anti-oxidant and anti-friction agents for engine lubrication, have recently been investigated as coal liquefaction catalysts. Molyvan L and Molyvan 822 are two such additives which already contain Mo-S bonds so that no sulfiding is necessary. Phillips Petroleum has investigated their use as catalysts and coke suppresants during resid hydroconversion.[161-164]

Swanson (1992)[106] studied the liquefaction performance of oil-soluble Molyvan L (molybdenum di-2-ethylhexylphosphorodithioate in mineral oil) in a Wilsonville-type two-stage process. In this study, Molyvan L and sulfided Mo octoate both gave high Illinois No. 6 residuum conversion although the distilled fractions contained more heteroatoms that must be removed by subsequent hydrotreatment.

The performance of Molyvan additives in combination with supported catalyst has been tested in the close-coupled integrated mode at the Wilsonville coal liquefaction facility.[107] Solids buildup can be a problem during subbituminous coal operation so the potential use of these Molyvan additives in the maintenance of low coke levels was investigated with Black Thunder subbituminous coal. The addition of 100 ppm Mo (on moisture-free coal) as Molyvan L or Molyvan 822 with or without Criterion 324 unimodal supported catalyst was tested. With the additive alone, both coal and residuum conversions were increased so that operation at lower thermal severity in the first stage and higher thermal severity in the second stage (compared to with the supported catalyst) was possible. With the hybrid (dispersed Mo + supported catalyst) system, C_4^+ distillate product yields increased 30-60% compared to that with either of the individual catalysts. Distillate product quality was similar to that obtained with supported catalyst alone, although of higher quality than that obtained with the dispersed Mo alone.

5. CATALYSIS BY IRON

Although Mo, in general, has higher activity compared to Fe, Fe-based catalysts, such as pyrite, have the advantages of a disposable catalyst -- low cost, availability and environmental compatibility. The relative low activity of Fe may be improved by methods that can modify its compositions. A composition modification reported to increase activity of iron-based catalysts is mixing different forms of iron. For example, a mixture of Fe oxide and pyrite increases oil yields to 39% from the maximum of 27% attainable with the catalysts separately.[221] Greater activity enhancements are possible; Derbyshire and Hager (1992)[222] review some of these methods such as sulfation to change surface properties, promotion with low concentrations of other metals (such as Mo, Ni, Ti), and formation of intermetallic hydrides which can store H_2. Sulfated oxides and promotion in multicomponent catalysts have been discussed previously in this review.

Increasing the surface area of iron oxide catalysts can also improve hydrogen incorporation, although oil production is not substantially improved.[27] For example, Stohl (1983)[223] studied various forms of FeS_x -- synthetic FeS_2 (46.6 wt% Fe) of 2-10 m^2/g areas, FeS_x (60 wt% Fe) of 6 and 10 m^2/g areas, and iron sulfides of unknown composition of 40 and 80 m^2/g areas. In the liquefaction of W. Va. Blacksville No. 2 in SRC-II heavy distillate, catalytic conversions were to a lesser extent than those obtained with Co-Mo/Al_2O_3. Moreover, although surface areas changed drastically during heat-up, no large differences in conversion among these catalysts were observed.

5.1 Reaction mechanism

Cook and Cashion (1987)[138] summarized the prevailing (sometimes contradictory) ideas on the role of iron during coal liquefaction at that time. Based on some early 1982-1983 studies by Cassidy and others with coal model ethers where adsorption of phenoxy radicals on iron surfaces was observed, it was inferred that iron slows the propagation of coal radicals that were initially formed during liquefaction. Hence, because these retrograde reactions are reduced, more asphaltene is formed. The activity of iron in coal conversion was, therefore, thought to be confined mainly to asphaltene production rather than subsequent upgrading to oil. Moreover, iron appeared to influence mechanistic steps not associated with the solvent. Brooks, et. al. (1984)[224] studied liquefaction at longer residence times and determined that pyrite accelerated coal conversion to (pentane-soluble) oils, although the effects on other product fractions were less pronounced. Moreover, their model compound work suggested that pyrite catalysis involved acceleration of both direct hydrogenation reactions involving molecular H_2 (e.g., replenishing solvent hydroaromaticity) and reactions involving H-transfer from donor solvent. Thus, iron appears to effect both short-term reduction and long-term enhancement of coal conversion.

Farcasiu, et. al. (1991)[225], in testing various Fe compounds with a model compound 4-(1-naphthylmethyl)bibenzyl, found that non-stoichiometric Fe-S compounds can selectively catalyze cleavage of C-C bonds between condensed polyaromatic moieties and aliphatic carbons. The nature of the active sites was found to depend on the water content of the catalysts: without water, the reaction was of an ion-radical type mechanism, whereas with water, the reaction was of an ionic mechanism.

In a spectroscopic study of depolymerization with an iron-based catalyst of coal macerals from Hiawatha Utah coal, Wang, et. al. (1992)[226] determined that the iron catalyst was evenly dispersed inside vitrinite and that this uniform dispersion was preserved upon mild hydrotreatment. Iron did not completely penetrate into the resinite due to lack of microporosity.

Although not generally regarded as a good hydrogenation catalyst, iron possesses hydrogenation capability. A catalyst prepared from the reaction of Fe_2O_3 with H_2S at 260-315°C in a non-oxidizing atmosphere or at 350°C in a H_2 atmosphere and stored in inert atmosphere before use, has been claimed to have high activity for hydrogenating polycyclic aromatics in coal liquids.[227]

Based on the above studies, for liquefaction of low-rank coals, where initial retrogressive reactions can limit conversion, iron may catalyze cracking to form radicals which must be capped by a good donor solvent and/or a good hydrogenation catalyst in order to get good conversion. For example, subbituminous coals such as Wyoming Black Thunder have been successfully liquefied at the Wilsonville coal liquefaction facility with pyrite (+DMDS) + supported catalyst. High conversions and yields have also been obtained with pyrite + oil-soluble Molyvan L. Wilsonville experience has shown that the addition of iron as pyrite is almost necessary for a high level of liquefaction of low-rank coal, although the actual mechanism is still unknown. Good dispersion of iron may be achieved with low-rank coals. Aggregation of iron atoms can occur more readily over bituminous coals than lower-rank coals at the same loading because low-rank coals have more surface functional groups that can interact with the iron.[228]

5.2 Pyrrhotite as active form

Table 8 shows the various crystalline phases in the Fe-S system. Pyrrhotite ($Fe_{1-x}S$) is the stable form during coal liquefaction conditions and the general consensus is that it is the catalyst active form. Mixing pyrrhotite in with coal did improve liquefaction over thermal but not as much as when pyrrhotite is produced in-situ from pyrite decomposition. This difference may be due to the more intimate contact between coal and the coal-derived pyrrhotite. It can also be due to the difference in morphology between pyrite in coal vs. synthesized pyrite.

There have been numerous studies to determine the active form of the iron catalyst during liquefaction, using model compounds and coals (see Table 4b). In their model compound investigations, Suzuki, et. al. (1989)[229] used the following iron catalyst precursors: $Fe(CO)_5$-S, FeS_2, and Fe_2O_3. Active carbon was added to simulate coal and to improve dispersion; $Mo(CO)_6$-S was also used for comparison. The model compound reactions studied were the hydrogenation (with decalin) of phenanthrene and pyrene, and the hydrogenolysis (without solvent) of diphenylmethane, dibenzyl ether, and biphenyl ether. Mossbauer spectroscopy on $Fe(CO)_5$-S deposited on active carbon from hydrogenolysis of diphenylmethane showed pyrrhotite and an unidentified doublet peak that was not seen for the other Fe-S catalysts. This catalyst (and the $Mo(CO)_6$-S) showed higher catalytic activity than the other catalysts. This doublet peak (the definite species of paramagnetic iron giving this peak is not known) may be responsible for the higher activity of $Fe(CO)_5$-S. It is to be noted that the spectrum of $Fe(CO)_5$ without S indicated Fe metal and cementite.

Olson and Yagelowich (1992)[230] formed pyrrhotite from calcination and sulfidation of iron-pillared clays. During hydrocracking and hydrogenation test reactions with bibenzyl and pyrene, respectively, the presence of pyrrhotite resulted in minimal coking and condensation reactions. The iron tended to migrate from its originally dispersed state as surface area decreased as the layers collapsed.

In the coal liquefaction studies, the initial form of the iron catalyst is usually as an oxide. Huffman, et. al. (1992)[231] studied the precursors sulfated Fe_2O_3, iron added by chemical impregnation, and iron added by ion exchange. In their as-dispersed state, all were in the form of superparamagnetic ferric oxides or oxyhydroxides. Djega-Mariadassou, et. al. (1986)[81] observed pyrrhotite stoichiometries (1-x) of 0.87 and 0.90 after hydroliquefaction of sulfided Fe_2O_3 aerosols prepared by a flame method. Moreover, the hexagonal habit was preserved as pyrite transformed to pyrrhotite; this may explain the absence of sintering. Srinivasan, et. al. (1992)[232] characterized iron oxide and sulfided iron oxide catalysts generated from Fe_2O_3 precursor with 300 m^2/g surface area under simulated coal liquefaction conditions. Sulfidation was at 385°C. The majority of the diffraction patterns in the electron microdiffraction analysis corresponded to the Fe_7S_8 phase. Ferric naphthenate sulfided at the same conditions yielded catalysts of a different morphology containing FeS_2, FeS, and Fe_7S_8. There was no evidence for the presence of Fe metal.

In the examples above, the catalyst precursors were sulfided. If no additional source of sulfur is provided, the form of the iron catalyst during liquefaction conditions can depend on the precursor and the Fe-S ratio in the coal. Cook and Cashion (1987)[138] liquefied Morwell Victorian brown coal using <40 μm hematite (α-Fe_2O_3) powders physically mixed with the coal and $Fe_3(CO)_{12}$. For this coal, which had Fe/S - 3, it appeared that FeS was the active species for the Fe_2O_3 precursor for long residence times (they proposed an ionic divalent species which stabilizes radicals during short residence times). For brown coals with Fe/S - 0.3, such as Loy Yang and Coolungoolun), they report that pyrrhotite was formed. They proposed the following iron transformation: rapid reduction from FeOOH via a transient divalent species to magnetite (Fe_3O_4). When H_2 is present, magnetite is further reduced to elemental iron, which in turn forms Fe_3C; inherent or added sulfur reacts with Fe_3O_4 to form FeS or $Fe_{1-x}S$. For Fe carbonyl, they proposed that elemental Fe may be the active form, promoting coal hydrocracking and producing Fe_3C in the process. Yamashita, et. al. (1989)[228], in their investigation of Loy Yang impregnated with $Fe(NO_3)_39H_2O$ also proposed a similar iron transformation scheme. Based on Mossbauer, XAFS, XANES, and XRD analysis of the liquefaction residues, the following scheme is the proposed progression of the iron species: highly dispersed iron species to ultrafine FeOOH, and then crystalline reduced species (α-Fe, γ-Fe, Fe_3C, depending on iron loading).

5.3 Promotion by other elements

Section 3.4 presented a general discussion of the principles involved in multicomponent catalysis. The promotion of Fe coal liquefaction catalysts with other elements is the subject of many patent claims. In one of them, Kleppel, et. al. (1987),[233] mixes coal containing a fine iron compound, i.e., oxide, hydroxide or hydrated oxide, with Ni, Mn, Cr, Mo, W, Ti, Al, and/or Sn, and with a P-containing oil (0.03-3 wt% in form of organophosphorus compounds). It is claimed that the P increases distillate yields without causing excessive corrosion from phenols. Table 7 lists other patents and investigations on the promotion of Fe-based catalysts with small amounts of other metals, primarily Groups VI or VIII such as Mo, Sn, Mn, and Ru.

Promotion of dispersed Fe catalysts by Mo has been actively pursued recently. Garg (1984)[234] reports that during liquefaction at 400°C, conversion to oil with 1% Fe (added as $FeSO_4$) and 0.02% Mo (added as NH_4 molybdate) is 36% compared to 25% with 1% Fe alone. During the liquefaction of high-volatile Freyming bituminous coal, Bacaud (1991)[32,235] improved the effectiveness of iron oxide aerosols produced by a flame method by the addition of small amounts of Mo. Asahi Chemical Industries claim improved liquefaction rates and oil production and less gas generation with Fe promoted by Mo or other metals (Co, Ni, W, Ti, Sn, Zn, V, Cr, and Sb).[236a,b,c]

The addition of low amounts of Mo (20-100 ppm on coal)[96] to sulfated Fe oxide resulted in improvements in coal conversion and oil yield which was partially attributed to the contribution of hydrogenation function by Mo. Davis, et. al. (1988)[237] also looked at a bifunctional Fe+Mo catalyst. A high-volatile C coal (PSOC-1498) was impregnated with Mo, Fe, or Fe+Mo using NH_4 heptamolybdate and NH_4 tetrathiomolybdate. The bimetallic Fe+Mo catalyst was very effective for liquefaction with or without a low-boiling recycle solvent. In terms of total conversion and H_2 consumption, the order of activity (without solvent) was 1% Fe+0.1% Mo ~ 1% Mo >> 1% Fe; a similar relative activity order was obtained during liquefaction with solvent. Miki, et. al. (1992)[137] also found that the addition of small amounts of soluble Mo to ion-exchanged iron on Taiheyo resulted in higher activity that that from either Mo or Fe alone.

Cook and Cashion (1988)[238] investigated catalysis by Fe+Sn with a Victorian coal (from which quartz and pyrite/marcasite has been removed) which was treated with aqueous $FeSO_4/SnCl_2$ solutions, then dried under N_2 at 105°C. Although there was no evidence of association between the initial ferric and stannic species, some $FeSn_2$ formed during liquefaction. Tin accelerated the formation of iron sulfide while iron retarded the formation of tin sulfide during initial liquefaction. Tin also prevented the carbiding of elemental α-Fe to Fe_3C.[238] High liquid yields have been claimed using an FeSn sulfided catalyst prepared by dissolving Fe in an HCl solution containing Sn halides or organohalides at a Fe:Sn ratio >

3.[239] Effective FeSn catalysts have also been prepared by flame decomposition of $FeCl_3$ and $SnCl_4$.[80]

Wallach, et. al. (1990)[25] claim a disposable Fe+Mn catalyst formulation containing 5-25 wt% Fe, 15-25 wt% Mn, and 8-12 wt% S for coal liquefaction at 200-500°C, 50-400 bar (725-5800 psi) for 15-200 minutes. The Fe and Mn are preferably in oxide, hydroxide, or sulfate forms and added in a concentration of 0.2-5 wt% based on the feed. In a patent issued to the Agency of Industrial Science and Technology (1991)[240] in Japan for an Fe+Ru catalyst, FeS_2 impregnated with $RuCl_3$ at 120°C (0.013 wt% Ru in catalyst) can conduct liquefaction at moderate conditions, compared to FeS_2.

Table 1. German Commercial Coal Liquefaction Plants, 1944
(Adapted from Donath, ref. 4)

Start-up	Location	Owner	Feed	Catalyst (1^{st} stage)	P, psi (1^{st} stage)	Product	Product capacity (10^3 t/yr)
1927	Leuna	ICI Farbenindustrie (licensee)	Brown coal, brown coal tar	Mo	200	Motor fuels	650
1936	Boehlen Magdeburg	Braunkohle Benzin AG	Brown coal tar	Mo	300	Motor fuels (char by-product)	250 220
1939	Zeitz		Brown coal tar	Mo	300	Motor fuels, lube oils, paraffin wax	280
1941	Wesseling	Rheinische Braunkohle	Brown coal	Fe	700	Motor fuels, diesel fuel	250
1942	Bruex		Brown coal tar	Mo	300	Motor fuels	600
1936	Scholven	Hibernia AG Mining Co.	Bituminous coal	Sn-HCl	300	Motor fuels	280
1937	Welheim	Stinnes AG	Coal tar pitch	Fe	700	Motor fuels	130
1939	Gelsenberg	Vereinigte Stahlwerke AG	Bituminous coal	Fe	700	Motor fuels	400
1940	Poelitz		Bituminous coal oils	Fe	700	Motor fuels	700
1940	Luetzkendorf	Wintershall AG	Tar oils	Fe	500	Motor fuels	50
1943	Blechhammer		Bituminous coal tar, pitch	Fe	700	Motor fuels, navy fuel oil	420

Table 2. Some Disposable Catalysts for Coal Liquefaction (Other than Coal Minerals)

ORES AND ORE CONCENTRATES:	Active component(s)	References
Pyrite	Fe	Mathur, et. al. (1984)[8], US Patents[12,13]
Limonite	Ni, Fe	Mathur, et. al. (1984)[8], US Patent[13]
Bauxite	Al	Mathur, et. al. (1986)[9]
Laterite	Ni, Fe, Al	US Patent[12]
Manganese nodules	Mn	US Patents[10-12]
Ore tailings	Fe	German Patent[25]
MoO_3 ore	Mo	Mathur, et. al. (1986)[9]
MANUFACTURING RESIDUES:		
Red mud	Fe	Donath (1982)[4], Sato, et. al. (1987)[26], German Patents[16-18]
Lithopone production waste	Zn, Fe	German Patents[19-21]
Coal liquefaction and/or residuum hydroprocessing residues	Fe, Mn	German Patent[24]
Galvanic slurries	Ni, Zn, Cr(III), Cu	German Patent[19]
Leather industry waste water	Cr	German Patent[19]
Electrochemical metal processing waste water	Zn	German Patents[19,21]
Spent catalyst	Fe	Japanese Patent[22]
Blast furnace flue dust		US Patent[23]
Production wastes from plastics, fungicides, anti-fouling agents	Sn	German Patent[24]
Pigment production wastes	Fe	German Patent[23]

Table 3. Effect of Catalyst Dispersion on Liquefaction Performance
Solvent-free Hydrogenation at 450°C, 1 hr, 70 bar (1015 psi) H_2 (cold)

(Weller and Pelipetz (1951)[243] study as reported in ref. 1)

Catalyst	Mode of catalyst addition	Liquefaction yield, % maf coal			
		Conversion (benzene-solubles)	Asphaltene (hexane-insolubles)	Oil (by difference)	Gas
None	--	33.4	2.8	21.6	9.0
$FeSO_4$ (1% Fe)	Powder Impregnated	38.9 84.9	6.9 38.9	18.9 31.0	13.1 15.0
$NiCl_2$ (1% Ni)	Powder Impregnated	44.2 88.3	6.8 15.5	24.0 54.8	13.4 18.0
$SnCl_2$ (1% Sn)	Powder Impregnated	82.3 88.3	26.5 19.9	41.3 52.9	14.5 15.5
NH_4 molybdate	Powder Impregnated	33.7 92.7	1.0 27.2	24.6 51.9	8.1 13.6
$+H_2SO_4$	Impregnated	94.7	10.0	70.8	13.9

Table 4a. Chemical Forms of Some Dispersed Catalysts
(Based on catalyst characterization after liquefaction)

Active Metal(s)	Catalyst Precursor	Sulfidation	Catalyst Form(s) Detected	Comments	Refs.
Sn	SnO_2 powder	No	Liquid Sn	Molten tin dispersed in coal	31
	SnO_2 aerosol	Presulfiding or in-situ (elemental S)	SnS + $Fe_{1-x}S$ + some $FeSn_2$	Presulfidation gave more SnS; $Fe_{1-x}S$ from coal (French Freyming; $FeSn_2$ from reaction of Sn with coal pyrite	32
	Sn metal	No	SnS + some $FeSn_2$		
	SnO_2 from hydrolysis of $SnCl_2$	In-situ (H_2S)	Liquid Sn + SnS	Morwell and Gelliondale (Australian) coals	30
Mo	NH_4 molybdate	Presulfiding H_2S	non-stoichiometric MoS_2	S/Mo = 2.5 with H_2, 2.7 with N_2 (hvC coal)	34
Ni	Ni acetate	No	Ni metal	230-270°C with phenolics as solvents (Morwell)	130
				310-350°C with tetralin (Morwell, Wandoan, Akabira, Liddell)	130a
Ru	$Ru_3(CO)_{12}$	No	RuS_2 + Ru metal	400-425°C, Illinois No. 6 (high-S)	33
Co, Mo	Co-Mo thiosalt	--	MoS_2, Co_9S_8, and mixed Co-Mo sulfide	Catalyst prepared from thiosalt decomposition	202
Fe, Sn	$FeSO_4/SnCl_2$	No	Fe, FeS, Sn, SnS, $FeSn_2$	Morwell, >380°C: with Sn/Fe = 0.073	238
			FeS, Sn, SnS, SnS_2, $FeSn_2$	with Sn/Fe > 1.7	

Table 4b. Active Forms of Dispersed Fe Catalysts
(Based on catalyst characterization after liquefaction)

Catalyst Precursor	Sulfidation	Catalyst Active Form	Comments	Refs.
Coal pyrite (FeS_2)	In-situ (H_2S)	$Fe_{1-x}S$	Morwell and Gelliondale (Australian) coals	30
	No		Illinois No. 6 (high-S)	197
FeS_2 or Fe_2O_3	In-situ (elemental S)	$Fe_{1-x}S$	Model compound study (active carbon to simulate coal)	229
Fe_2O_3 aerosols	In-situ (elemental S)	$Fe_{1-x}S$	Freyming French coal; $1-x = 0.87, 0.90$	81
Fe_2O_3 powder	Yes (DMDS)	Fe_7S_8	catalyst generated from fine powder sulfided at 380°C	232
$Fe(CO)_5$	No	$Fe_{1-x}S$ (mostly) + Fe_3C + other Fe compounds	Illinois No. 6 in Maya atmospheric resid; 12 nm pyrrhotite	95
	No	Fe metal + cementite	Model compound study	229
	In-situ (elemental S)	Pyrrhotite	Mossbauer spectra of $Fe_{1-x}S$ has an unidentified doublet peak	
Fe_2O_3 powders or $Fe_3(CO)_{12}$	No	FeS	if coal $Fe/S = 3$	138
		$Fe_{1-x}S$	if coal $Fe/S = 0.3$	
Ferric naphthenate	Yes (DMDS)	FeS_2, FeS, Fe_7S_8	Simulated coal liquefaction conditions	232
$Fe(NO_3)_2$ $9H_2O$	No	α-Fe, γ-Fe, Fe_3C	Loy Yang coal; distribution of catalyst forms depends on iron loading	228
Sulfated Fe_2O_3	No	$Fe_{1-x}S$	Size of pyrrhotite from this precursor < that from coal pyrite	238

Table 5. Production of Catalyst Fine Powders

Method	Chemical Form	Examples	References
PRECIPITATION	Oxides	Fe_2O_3	125, 180, 181, 194-196
		Fe_3O_4	125, 180, 181
		SnO_2	31, 194, 196
		MoO_3, V_2O_5	US Patents 45-48
		CrO_3	US Patents 132-134
	Oxyhydroxides	FeOOH	195
		$SnO(OH)_2$	28
	Sulfides	MoS_2,MoS_3	121, 140; 123, 142, 211
		Cr_2S_3, WS_2, RuS_2, FeS_x, MoS_2	55, 86
	Nitrides & carbides	Transition metal	53, 54 (HDN of coal liquids)
	Others: Oxysulfides, borides, phosphides, metals		
MICROEMULSION-BASED TECHNIQUES	Oxides	Fe_2O_3	74
	Sulfides	MoS_2	76, 77
	Titanates	TiO_2 w/ 0.7% Pd	70, 71
	Metals	Transition metals	61-64 (ceramic applications)
	Alloys		65, 66 (ceramic applications)
	Others: Carbonates, ferrites, selenides, phosphates		
SURFACE DEPOSITION (Incipient wetness)	Metal salts		58 (general reference)
FLAME DECOMPOSITION	Metals, oxides, sulfides	Fe_2O_3, SnO_2, MoO_3	32, 80, 81, 87
LASER PHOTOLYSIS/ PYROLYSIS	Carbides, sulfides, oxides	Fe_3C, Fe_7C_3	84, 85, 141

Table 6a. Oil-Soluble Catalyst Precursors

COMPOUNDS	EXAMPLES	REFERENCES
NAPHTHENATES	Mo	90, 185, 186 (model cpds.); 91 (coprocessing), 140 (>MoS_2), 152 (with ultrasound)
	V	91 (coprocessing)
	Ni	92 (model cpds.), 91 (coprocessing)
	Cr	US Patents 116, 132-134
OCTOATES	Mo, Ni, V	91 (coprocessing)
	Ni	92 (model compounds)
CARBONYLS	$Fe(CO)_5$	94 (Japanese coals), 95 (coprocessing), 141 (Wyodak subbitum.), 187 (Yallourn Australian), 143 (with preswelling); Japanese Patent 93 (high activity at 300°C)
	$Fe_3(CO)_{12}$	138
	$Mo(CO)_6$	99 (impregnation with supercritical CO_2), 143 (with preswelling); 152 (with ultrasound)
	$Fe(CO)_5$ + $Mo(CO)_6$	112, 113 (coprocessing; Fe+Mo > Mo > Fe)
	$Ru_3(CO)_{12}$	33 [> $Fe(CO)_5$], 98 (model compounds)
ORGANIC ACIDS	Molybdic acid	4 (with ZnO/magnesia or chromic acid); US Patent 100
	Phosphomolybdic acid	US Patents 101, 102, 103 (with hydrogen halide), 104 (sulfiding unnecessary)
	Sulfonic acids	French Patent 114 ($Fe(OH)_3$ + 10- to 35-C alkylbenzene)

Table 6a. Oil-Soluble Catalyst Precursors
(Continued)

COMPOUNDS	EXAMPLES	REFERENCES
ORGANIC SULFUR COMPOUNDS	Benzenethiol	111
	Thiol, thiophenol benzothiophene, alkyl mercaptans	European Patents 112, 113
OTHER ORGANOMETALLICS	Molyvan additives	106, 107
	Citrate	92 (Ni)
	Acetylacetonates	91 (Mo, Ni, V); 92 (Ni); 106 (Fe); 56 (Ru)
	Others	110 (Co phthalocyanine), 187 (ferrocene); 108 (tetraethyl lead, tetramethyl tin); 33 (Ru[cyclooctadiene][cyclooctatriene]); 94 ($[Fe(CO)_2Cp]_2$, Cp-cyclopentadienyl); Jap. Patent 115 ($Mo[t\text{-}C_4H_9S]_4$)

Table 6b. Water-Soluble Catalyst Precursors

COMPOUNDS	EXAMPLES	REFERENCES
MOLYBDATES	NH_4 tetrathiomolybdate (ATM)	117-119, 122, 123 ; 36, 211 (coprocessing); 121, 188 (with high-S coals); 124 (impregnation with THF/H_2O); 142 (with preswelling); 146 (with prehydrogenation); 208 (with mild vacuum drying pretreatment)
	NH_4 molybdate (AM)	34, 118
	NH_4 heptamolybdate (AHM)	122, 123; 120 (no donor solvent); 36 (coprocessing); 121 (with high-S coals)
	Tetrahydroquinolium molybdate	118
SULFATES	$FeSO_4$	94 (Jap. coals); 125 (model cpds.); 176 (coprocessing); 136, 137, 143 (with preswelling)
	$(NH_4)_2SO_4$	125 (model cpds.); 126 (Jap. coals)
	$CoSO_4$ $8H_2O$	109 (only slightly better than thermal)
	Sulfated Fe and Sn oxides	194-196; 126, 198 (Fe, Jap. and Australian coals); 96, 97 (coprocessing)

Table 6b. Water-Soluble Catalyst Precursors
(Continued)

COMPOUNDS	EXAMPLES	REFERENCES
HALIDES	Metal chlorides	127 ($FeCl_2 < ZnCl_2 < NiCl_2 < CuCl_2 < SnCl_2 < CoCl_2$)
	$FeCl_3$	94 (Jap. coals); US Patents 103, 129
	$ZnCl_2$	144 (with methanol for swelling); US Patents 103, 129
	$SnCl_2$	144 methanol for swelling); 189 (Victorian coals)
	$FeBr_2$	149 (with organic preduction pretreatments)
	Hydrogen halides	148 (HCl with mild alkylation); US Patent 128
ACETATES	Ni	130 (with phenolics as liquefaction solvent)
	Fe	189 (Victorian coals)
	Pb	108 (Milmerran Australian coal)
OTHERS	Oxalates	US Patent 37 (V and Mo)
	Nitrates	228 ($Fe[NO_3]_3$ $9H_2O$)

Table 7. Examples of Multicomponent Catalysts

Components	Form and concentration of components	References
Fe, Mo	1% Fe as $Fe_2(SO_4)_3$ 0.2% Mo as ammonia paramolybdate	14
	1% Fe as $FeSO_4$ 0.02% Mo as NH_4 molybdate	234
	Fe as iron oxide aerosols	27, 32, 235
	<0.7 wt% Fe as sulfated Fe_2O_3 20-100 ppm Mo (as AHM and ATM) on coal	96, 195, 196
	Mo as AHM or ATM; 1% Fe + 0.1% Mo ~ 1% Mo >> 1% Fe (in terms of conv.)	237
	Fe as sulfated and non-sulfated Fe_2O_3 or FeOOH; Mo as molybdate	28
	Fe as ion-exchanged; Mo as soluble precursor	137
	Fe and Mo as ores	8
	Fe and Mo as metals or sulfides; Mo could be replaced by Co, Ni, W, Ti, Sn, Zn, V, Cr, or Sb)	Japanese Patents 236a,b,c
	Mo could be replaced by Ni, Mn, Cr, W, Ti, Al, and Sn; 0.03-3 wt% P added	German Patent 233
Fe, Sn	Fe as FeOOH or Fe_2O_3 or FeOOH; Sn as $SnO(OH)_2$ or SnO_2; oxides may be sulfated	28
	Fe and Sn from flame decomposition of $FeCl_3$ and $SnCl_4$	80
	Fe from $FeSO_4$; Sn from $SnCl_2$	238
	Fe dissolved in HCl solution containing Sn halides	German Patent 239

Table 7. Examples of Multicomponent Catalysts (Continued)

Components	Form and concentration of components	References
Fe, Mn	Fe and Mn as mixed oxides, hydroxides, or sulfates (0.2-5 wt% based on feed)	25
	Fe and Mn as ores	8
Fe, Ru	Fe as FeS_2; Ru as $RuCl_3$	241
Mo, Ru, P	Mo-P/$RuCl_3$-H_2O (high activity for quinoline hydrogenation)	213
Mo, Halide	Halide as hydrogen halide	US Patent 103
Cu, Mo (or W, Co, Ni)	5000-15,000 ppm as $CuSO_4$; 100-1000 ppm NH_4 molybdate	US Patent 241
Zn, Mo (or W, Co, Ni)	5000-15,000 ppm Zn as $ZnSO_4$, $ZnCl_2$, nitrate, oxalate, acetate, bromide, octoate, or naphthenate; 100-1000 ppm Mo as NH_4 molybdate or phosphomolybdic acid	US Patent 241
Cu, Al (or Mg, Ni, Zn, Cr)	10-70% Cu; 1-30% Al (or Mg, Ni, Zn, Cr); catalyst 0.2-5 wt% of feed	US Patent 241
Mo, P and one of Co, Ni, Fe, V, Ti, Zn, Cu, or W)	Mo as soluble complex; 10-1000 ppm of co-catalyst	Japanese Patent 212
Fe, Mo, Co	Fe, Mo, Co as ores	8
Mo, Ni, Al	Mo, Ni, Al as ores	8

Table 8. Crystalline Phases in the Fe-S System
[From Srinivasan, et. al. (1992)[232]]

Formula	Crystal Structure	Lattice Parameters, Å		
		a	b	c
FeS_2	Cubic	5.417	--	--
FeS_2	Orthorhombic	4.436	5.414	3.381
FeS	Cubic	5.423	--	--
FeS	HCP(1)	5.967	--	11.735
FeS	Tetragonal	3.676	--	5.032
$Fe_{1-x}S$	HCP(1)	6.88	--	22.90
β-$Fe_{1-x}S$	HCP(1)	6.894	--	40.15
Fe_9S_8	Tetragonal	3.679	--	5.047
Fe_7S_8	HCP(1)	6.867	--	17.062
Fe_7S_8	Monoclinic	11.902	6.859	22.787
Fe_3S_4	HCP(1)	3.47	--	34.5
Fe_3S_4	Cubic	9.876	--	--

(1) HCP - hexagonal close packed

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APPENDIX E

TAB. 2-1

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: IMPREGNATION SOLUTION: 30/70 IPA/TOLUENE (Part 1)

COAL MESH	CATALYST		SAMPLE ID 16103-	IMPREGNATION		Mo_{soln} (ppm)	ICP or XRF	EST. UP-TAKE [1]	CALCULATED [2]		COMMENTS
	TYPE	ppm		Temp. (°F)	Time (h)				Mo_{coal} (ppm)	UP-TAKE	
None	None	0	76-1	--	--	0.1ND	ICP	--	--	--	Reference soln.
8x60	MVL	100	77-2A	70	0.08	0.2	ICP	99.8	--	--	CARN 92-021871 76-1 ref. - used pressure filtration
			77-2B		0.17	110		100	--	--	
			77-2C		0.5	119		100	--	--	
			77-2D		1.0	84		16.0	--	--	
			77-2E		12.0	35		65.0	--	--	
8x60	MVL	100	78-2A	70	0.5	88	ICP	12.0	60	12.0	CARN 92-022728 76-1 ref.
			78-2B		1.0	96		10.0	60	12.6	
			78-2C		2.0	87		13.0	73.5	16.1	
			78-2D		4.0	81		19.0	99	22.8	
			78-2E		7.0	72		28.0	135	32.6	
			78-2F		23.0	39		61.0	258.8	65.4	
			78-2G		48.0	18.8		81.2	329.5	85.4	
-70	MVL	105	78-3D	70	67.5	10.4	ICP	90.1	--	--	CARN 92-022734 76-1 ref.
None	None	0	79-1	--	--	0.1ND	ICP	--	--	--	Reference soln.
8x60	MVL	275	79-2A	70	0.5	250	ICP	9.1	125	9.1	CARN 92-022728 (2A to 2D) CARN 92-022732 (2E to 2G) 79-1 ref.
			79-2B		1.0	246		10.5	144	11.0	
			79-2C		2.0	228		17.1	225	18.0	
			79-2D		4.0	213		22.5	288.8	24.2	
			79-2E		7.0	197		28.4	352.8	30.9	
			79-2F		24.0	141		48.7	562.8	51.6	
			79-2G		48.0	79		71.3	779.8	73.8	

Notes:

[1] Estimated % Uptake = $(1 - Mo_{soln,i}/Mo_{soln,0}) \times 100$

[2] Calculated % Uptake = $(Mo_{coal,i}/Mo_{max,i}) \times 100$ (See Appendix A)

TABLE 1

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: IMPREGNATION SOLUTION: 30/70 IPA/TOLUENE (Continued--Part 2)

COAL MESH	CATALYST		SAMPLE ID 16103-	IMPREGNATION		Mo_{soln} (ppm)	ICP or XRF	EST. UP-TAKE [1]	CALCULATED [1]		COMMENTS
	TYPE	ppm		Temp. (°F)	Time (h)				Mo_{coal} (ppm)	UP-TAKE	
None	None	0	79-1	--	--	0.1ND	ICP	--	--	--	Reference soln.
8x60	Mo oct.	105	79-3A	70	0.5	99	ICP	5.7	--	--	CARN 92-022732 79-1 ref. -- large scatter in Mo_{soln} so only estimated uptake
			79-3B		1.0	94		10.5	--	--	
			79-3C		2.0	99		5.7	--	--	
			79-3D		4.0	81		22.9	--	--	
			79-3E		6.0	85		19.1	--	--	
			79-3F		23.0	50		52.4	--	--	
			79-3G		46.0	35		87.3	--	--	
None	None	0	139-2	--	--	5ND	XRF	--	--	--	Reference soln.
8x60	Mo oct.	105	139-2A	150	0.5	66	XRF	37.1	195	37.1	CARN 93-005940 139-2 ref. -- No precipitate observed in samples with standing (up to 6 days)
			139-2B		1.0	35		66.7	342.2	67.3	
			139-2C		2.0	19		81.9	414.2	82.9	
			139-2D		3.5	13		87.6	439.7	88.8	
			139-2E		6.17	13		87.6	439.7	89.4	
			139-2F		24.0	6		94.3	466	95.4	
			139-2G		48.17	6		94.3	466	95.7	

Notes:

[1] Estimated % Uptake = $(1 - Mo_{soln,i}/Mo_{soln,0}) \times 100$

[2] Calculated % Uptake = $(Mo_{coal,i}/Mo_{max,i}) \times 100$ (See Appendix A)

TABLE E

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: IMPREGNATION SOLUTION: THF/TOLUENE (Part 1)

(30% THF unless specified otherwise)

COAL MESH	CATALYST		SAMPLE ID 16103-	IMPREGNATION		Mo_{soln} (ppm)	ICP or XRF	EST. UP-TAKE [1]	CALCULATED [2]		COMMENTS
	TYPE	ppm		Temp. (°F)	Time (h)				Mo_{coal} (ppm)	UP-TAKE.	
None	None	0	82-1	--	--	0.5ND	ICP	--	--	--	Reference soln.
8x60	MVL	109	82-2	70	137	4.9	ICP	95.5	520.5	95.5	CARN 92-023765
8x60	MVL	109	82-3A	70	0.5	96	ICP	11.9	545	11.9	CARN 92-023765 82-1 ref. - no 4-hr sample withdrawn
			82-3B		1.0	91		16.5	521	17.0	
			82-3C		2.0	89		18.3	498.2	19.6	
			82-3E		6.5	73		33.0	476	34.8	
			82-3F		24.0	50		54.1	457.8	56.3	
			82-3G		48.0	36		67.0	445.3	69.7	
-70	MVL	110	82-4A	70	0.5	79	ICP	28.2	155	28.2	CARN 92-023765 82-1 ref. - no 4-hr sample withdrawn
			82-4B		1.0	75		31.8	174	32.8	
			82-4C		2.0	72		34.5	187.5	36.7	
			82-4E		6.5	56		49.1	255.5	51.8	
			82-4F		24.0	33		70.0	347.5	72.5	
			82-4G		48.0	8.9		91.9	437.9	92.9	
-200	MVL	105	83-6A	70	0.5	72	ICP	31.4	165	31.4	CARN 92-023769 82-1 ref.
			83-6B		1.0	70		33.3	174.5	34.4	
			83-6C		2.0	67		36.2	188	38.4	
			83-6D		4.0	60		42.9	217.8	46.1	
			83-6E		6.0	56		46.7	233.8	51.1	
			83-6F		24.0	30		71.4	331.3	74.6	
			83-6G		48.0	16.2		84.6	379.6	87.0	

Notes:

[1] Estimated % Uptake = $(1 - Mo_{soln,i}/Mo_{soln,0}) \times 100$

[2] Calculated % Uptake = $(Mo_{coal,i}/Mo_{max,i}) \times 100$ (See Appendix A)

TABLE

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: IMPREGNATION SOLUTION: THF/TOLUENE (Continued--Part 2)

(30% THF unless otherwise specified)

COAL MESH	CATALYST		SAMPLE ID 16103-	IMPREGNATION		Mo_{soln} (ppm)	ICP or XRF	EST. UP-TAKE [1]	CALCULATED [2]		COMMENTS
	TYPE	ppm		Temp. (°F)	Time (h)				Mo_{coal} (ppm)	UP-TAKE	
None	None	0	84-1	--	--	0.3ND	ICP	--	--	--	Reference soln.
-70	MVL	110	84-2A	70	0.5	81	ICP	26.4	145	26.4	CARN 93-000215 84-1 ref.
			84-2B		2.0	73		33.6	183	34.5	
			84-2C		4.0	65		40.9	219	42.9	
			84-2D		6.0	59		46.4	244.5	49.5	
			84-2E		24.0	30.5		72.3	358.5	74.7	
			84-2F		48.0	17		84.5	409.1	86.7	
None	None	0	108-1	--	--	0.3ND	ICP	--	--	--	Reference soln.
8x60	MVL	106	108-5A	120	0.5	82	ICP	22.6	120	22.6	CARN 93-002361 108-1 ref. - rotavap water bath level low for sample 5G
			108-5B		1.0	78		26.4	139	27.3	
			108-5C		2.0	71		33.0	170.5	34.8	
			108-5D		4.0	59		44.3	221.5	46.9	
			108-5E		6.17	52		50.9	249.5	54.5	
			108-5F		24.0	21.3		79.9	364.6	82.0	
			108-5G		48.0	7.9		92.5	411.5	93.7	
None	None	0	122-1	--	--	0.3ND	ICP	--	--	--	Reference soln.
-70	MVL	102	122-1A	120	0.5	97	ICP	4.9	25	4.9	CARN 93-004764 122-1 ref.
			122-1B		1.0	85		16.7	82	16.9	
			122-1C		2.0	75		26.5	127	27.3	
			122-1D		4.0	58		43.1	199.2	44.7	
			122-1E		6.0	48		52.9	239.2	55.5	
			122-1F		24.0	13		87.2	370.4	88.3	
			122-1G		48.0	6.6		93.5	392.8	94.4	

Notes:

[1] Estimated % Uptake = $(1 - Mo_{soln,i}/Mo_{soln,0}) \times 100$

[2] Calculated % Uptake = $(Mo_{coal,i}/Mo_{max,i}) \times 100$ (See Appendix A)

TABLE E

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: IMPREGNATION SOLUTION: THF/TOLUENE (Continued--Part 3)

(30% THF unless otherwise specified)

COAL MESH	CATALYST		SAMPLE ID 16103-	IMPREGNATION		Mo_{soln} (ppm)	ICP or XRF	EST. UP-TAKE [1]	CALCULATED [2]		COMMENTS
	TYPE	ppm		Temp. (°F)	Time (h)				Mo_{coal} (ppm)	UP-TAKE	
-70	Mo oct.	103	123-2A	120	0.5	52	ICP	49.5	260	49.5	CARN 93-004771 122-1 ref.
			123-2B		1.0	47		54.4	283.8	56.5	
			123-2C		2.33	36.9		64.2	329.2	67.1	
			123-2D		4.0	28.5		72.3	364.9	75.9	
			123-2E		6.5	20		80.6	398.9	84.2	
			123-2F		24.0	7.2		93.0	446.9	95.3	
			123-2G		48.0	9		91.3	446.9	95.7	
None	None	0	138-1	--	--	5ND	XRF	--	--	--	Reference soln.
8x60	MVL	103	136-7A	120	24.0	29	XRF	71.8	370	718	CARN 93-005931 138-1 ref. - no precipitate with standing (up to 13 days)
8x60	MVL	102	136-8A	70	24.0	58	XRF	43.1	510	43.1	CARN 93-005932 138-1 ref. - no precipitate with standing (up to 13 days)

Notes:

[1] Estimated % Uptake = $(1 - Mo_{soln,i}/Mo_{soln,0}) \times 100$

[2] Calculated % Uptake = $(Mo_{coal,i}/Mo_{max,i}) \times 100$ (See Appendix A)

TABL .-2

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: IMPREGNATION SOLUTION: THF/TOLUENE (Continued--Part 4)

(30% THF unless otherwise specified)

COAL MESH	CATALYST		SAMPLE ID 16103-	IMPREGNATION		Mo_{soln} (ppm)	ICP or XRF	EST. UP-TAKE [1]	CALCULATED [2]		COMMENTS
	TYPE	ppm		Temp. (°F)	Time (h)				Mo_{coal} (ppm)	UP-TAKE	
None	None	0	138-1	--	--	5ND	XRF	--	--	--	Reference soln.
8x60	Mo oct.	104	138-1A 138-1B 138-1C 138-1D 138-1E 138-1F 138-1G	120	0.5 1.0 2.0 4.0 6.0 24.0 48.0	46 39 32 26 24 9 17	XRF	55.8 62.5 69.2 75.0 76.9 91.3 83.6	290 323.2 354.7 380.2 388.2 444.4 444.4	55.8 63.6 71.1 77.5 80.2 92.9 93.4	CARN 93-005936 138-1 ref. - trace of blue immiscible film at bottom of 1A and 1B; none in others after 8 days standing
None	None	0 (20% THF)	110-1	--	--	0.3ND	ICP	--	--	--	Reference soln.
8x60	MVL	107 (20% THF)	109-6A 109-6B 109-6C 109-6D 109-6E 109-6F 109-6G	120	0.33 1.0 2.0 4.0 6.0 24.25 48.0	92 89 79 74 67 38 18.6	ICP	14.0 16.8 26.2 30.8 37.4 64.5 82.6	75 89.2 134.2 155.4 183.4 292.2 360.1	14.0 17.4 27.4 33.1 40.6 67.2 84.1	CARN 93-002362 110-1 ref.
8x60	MVL	104 (20% THF)	110-7A 110-7B 110-7C 110-7D 110-7E 110-7F 110-7G	70	0.5 1.0 2.0 4.0 6.0 24.0 48.0	101 97 93 88 84 65 53	ICP	2.9 6.7 10.6 15.4 19.2 37.5 49.0	15 34 52 73.2 89.2 160.4 202.4	2.9 6.9 11.1 16.4 21.0 39.7 52.1	CARN 93-002359 110-1 ref.

Notes:

[1] Estimated % Uptake = $(1 - Mo_{soln,i}/Mo_{soln,0}) \times 100$

[2] Calculated % Uptake = $(Mo_{coal,i}/Mo_{max,i}) \times 100$ (See Appendix A)

TAi E-3

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: IMPREGNATION SOLUTION: 30/70 DMSO/TOLUENE (Part 1)

COAL MESH	CATALYST		SAMPLE ID 16103-	IMPREGNATION		Mo_{soln} (ppm)	ICP or XRF	EST. UP-TAKE [1]	CALCULATED [2]		COMMENTS
	TYPE	ppm		Temp. (°F)	Time (h)				Mo_{coal} (ppm)	UP-TAKE	
None	None	0	99-1	--	--	0.2ND	ICP	--	--	--	Reference soln.
8x60	MVL	110	99-2A	70	0.5	31.5	ICP	71.4	392.5	71.4	CARN 93-001880 99-1 ref.
			99-2B		1.0	18.6		83.1	453.8	83.7	
			99-2C		2.25	14.3		87.0	473.2	88.0	
			99-2D		4.0	13.2		88.0	477.9	89.5	
			99-2E		6.33	10.7		90.3	487.9	92.0	
			99-2F		24.0	9.8		91.0	491.3	93.1	
			99-2G		48.0	8.0		92.7	497.6	94.7	
8x60	MVL	109	100-3A	150	0.5	10.1	ICP	90.7	494.5	90.7	CARN 93-001880 99-1 ref. - rotavap heater malfunctioned for sample 3B; * assumed Mo_{soln} for sample 3B was 9.2 ppm (ave. of 10.1 and 8.4)
			100-3B		1.25	--		--	498.8*	91.9*	
			100-3C		2.17	8.4		92.3	502.4	93.0	
			100-3D		4.08	6.9		93.7	508.8	94.6	
			100-3E		6.0	6.0		94.5	512.6	95.6	
			100-3F		24.0	--		--	--	--	
			100-3G		48.0	--		--	--	--	
8x60	MVL	109	101-4A	150	0.5	10.4	ICP	90.5	493	90.5	CARN 93-001882 99-1 ref. - repeat of 100-1 series
			101-4B		1.0	8.7		92.0	501.1	92.4	
			101-4C		2.0	7.8		92.8	505.2	93.5	
			101-4D		4.0	6.1		94.4	512.4	95.2	
			101-4E		6.0	5.3		95.1	515.6	96.1	
			101-4F		24.0	3.5		96.8	522.4	97.6	
			101-4G		48.0	3.4		96.9	522.8	97.8	

Notes:

[1] Estimated % Uptake = $(1 - Mo_{soln,i}/Mo_{soln,0}) \times 100$

[2] Calculated % Uptake = $(Mo_{coal,i}/Mo_{max,i} \times 100$ (See Appendix A)

TA E-3

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: IMPREGNATION SOLUTION: 30/70 DMSO/TOLUENE (Continued-Part 2)

COAL MESH	CATALYST		SAMPLE ID 16103-	IMPREGNATION		Mo_{soln} (ppm)	ICP or XRF	EST. UP-TAKE [1]	CALCULATED [2]		COMMENTS
	TYPE	ppm		Temp. (°F)	Time (h)				Mo_{coal} (ppm)	UP-TAKE	
None	None	0	124-3	--	--	0.5ND	XRF	--	--	--	Reference soln.
8x60	Mo oct.	103	124-3A	70	0.58	76	XRF	26.2	--	--	CARN 93-005921 124-3 ref - after 18-20 days standing, precip. observed in 3A to 3E; no sediments in 3F and 3G - large scatter in Mo_{soln} so only estimated uptake
			124-3B		1.0	87		15.5	--	--	
			124-3C		2.0	79		23.3	--	--	
			124-3D		4.0	72		30.1	--	--	
			124-3E		6.0	69		33.1	--	--	
			124-3F		24.0	42		59.2	--	--	
			124-3G		48.0	30		70.9	--	--	
8x60	Mo oct.	104	125-4A	150	0.5	51	XRF	51.0	--	--	CARN 93-005924 124-3 ref. - after 18-20 days standing, immiscible film observed at bottom of sample vials - large scatter in Mo_{soln} so only estimated uptake
			125-4B		1.0	30		71.2	--	--	
			125-4C		2.0	33		68.3	--	--	
			125-4D		4.0	11		89.4	--	--	
			125-4E		6.0	13		87.5	--	--	
			125-4F		24.0	5ND		95.2	--	--	
			125-4G		48.0	5ND		95.2	--	--	

Notes:

[1] Estimated % Uptake = $1 - Mo_{soln,t}/Mo_{soln,0} \times 100$

[2] Calculated % Uptake = $Mo_{coal,t}/Mo_{max,t}) \times 100$ (See Appendix A)

TABLE 4

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: IMPREGNATION SOLUTION: TOLUENE

COAL MESH	CATALYST		SAMPLE ID 16103-	IMPREGNATION		Mo_{soln} (ppm)	ICP or XRF	EST. UP-TAKE [1]	CALCULATED [2]		COMMENTS
	TYPE	ppm		Temp. (°F)	Time (h)				Mo_{coal} (ppm)	UP-TAKE	
None	None	0	134-5	--	--	5ND	XRF	--	--	--	Reference soln.
-70	MVL	101	134-5A	150	0.5	84	XRF	16.8	85	16.8	CARN 93-005926 134-5 ref - after up to 15 days standing, no precipitates observed in the samples
			134-5B		1.0	78		22.8	113.5	23.4	
			134-5C		2.0	77		23.8	118	25.4	
			134-5D		4.0	74		26.7	130.8	29.4	
			134-5E		6.0	68		32.7	154.8	36.3	
			134-5F		24.0	54		46.5	207.3	50.6	
			134-5G		48.0	39		61.4	259.8	65.6	
-70	MVL	103	135-6A	70	0.5	92	XRF	10.7	55	10.7	CARN 93-005927 134-5 ref. - after up to 15 days standing, no precipitates observed in the samples
			135-6B		1.0	92		10.7	55	11.2	
			135-6C		2.0	90		12.6	64	13.6	
			135-6D		4.0	87		15.5	76.8	17.2	
			135-6E		6.0	88		14.6	76.8	18.1	
			135-6F		24.0	82		20.4	95.6	23.7	
			135-6G		48.0	73		29.1	127.1	33.2	

Notes:

[1] Estimated % Uptake = $(1 - Mo_{soln,i}/Mo_{soln,0}) \times 100$

[2] Calculated % Uptake = $(Mo_{coal,i}/Mo_{max,i}) \times 100$ (See Appendix A)

TABLE 5

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: FURTHER SWELLING OF COALS SWOLLEN/IMPREGNATED WITH 30/70 THF/TOLUENE

Ambient swelling with fresh 30/70 THF/toluene
Mo in coal and swelling solution measured by ICP

COAL MESH	SAMPLE ID 16103-			Swelling time	Mo_{soln} (ppm)	Mo_{coal} (ppm)		COMMENTS
	Starting coal	Final swollen coal	Final swelling solution			Meas.	Calc. [1]	
8X60	83-3	--	--	0	--	2ND	--	Dry coal analysis
8x60	82-3	83-1	83-4	48.0 hr	1.0	370	445	CARN 92-023766
-70	82-4	83-2	83-5	48.0 hr	1.7	500	511	CARN 92-023766
-70	84-3	—	--	0	--	420	409	CARN 92-00218 part of dried coal from 84-2 series
-70	84-2	84-4	84-5	14 days	0.9	410	409	CARN 92-00218

Notes:

[1] Calculated Mo concentration on the simultaneously swollen and impregnated coals as outlined in Appendix A (i.e., on the starting coal for the subsequent swelling performed). Comparison of the measured Mo on the subsequently swollen coal and the calculated concentration on the starting coal indicates no re-extraction of the Mo by the swelling solution.

APPENDIX F

CALCULATION OF MOLYBDENUM UPTAKE BY COAL

For the simultaneous swelling and impregnation experiments where samples were withdrawn at given times from the same starting coal-solvent slurry, the sample withdrawal depletes the solvent in molybdenum. The corrections for Mo concentration on the coal and the remaining available Mo for uptake by the coal are discussed.

The major assumptions are: (1) there is negligible coal loss from the slurry with the sampling; and (2) the solution density is approximately unity.

At a given sampling schedule i, the concentration of Mo on the coal is given by:

$$Mo_{coal,i} = Mo_{coal,i-1} + (Mo_{soln,i-1} - Mo_{soln,i}) \times \frac{V_{soln,i}}{W_{coal}} \qquad (1)$$

where the subscripts i and i-1 refer to any two successive sampling schedules

Mo_{coal} is the concentration of Mo (on coal)

Mo_{soln} is the concentration of Mo in the sampled solution

V_{soln} is the volume of the solution remaining

W_{coal} is the weight of the coal in the slurry (assumed constant at 100 g).

At any given time, the amount of available Mo for uptake by the coal is $Mo_{coal} = Mo_{max}$. This is calculated from

$$Mo_{max,i} = Mo_{max,i-1} - Mo_{soln,i-1} \times \frac{V_{sample,i-1}}{W_{coal}} \qquad (2)$$

where V_{sample} is the volume of the sample withdrawal (constant at 25 ml)

Note that

$$Mo_{max,0} = Mo_{soln,0} \times \frac{V_{soln,0}}{W_{coal}} \qquad (3)$$

where $Mo_{soln,0}$ is the initial Mo solution concentration (e.g., 100 ppm)

$V_{soln,0} = 500$ ml

Catalyst uptake is then estimated by

$$Uptake_i = \frac{Mo_{coal,i}}{Mo_{max,i}} \qquad (4)$$

Assuming the catalyst uptake is irreversible (see discussion in Experimental section), then the concentration of Mo on the coal can either increase or remain constant with time. This can only happen if $Mo_{soln,i-1} >= Mo_{soln,i}$. For cases where $Mo_{soln,i-1} < Mo_{soln,i}$ (due to experimental error), it is assumed that

$Mo_{coal,i} = Mo_{coal,i-1}$ and $Mo_{max,i}$ is calculated from Equation (3) using the measured value of $Mo_{soln,i-1}$.

In cases where there is fluctuation of $Mo_{soln,i}$ values, no correction is applied and uptake is estimated by

$$Uptake_i = 1-\frac{Mo_{soln,i}}{Mo_{soln,0}} \tag{5}$$

APPENDIX G

Advanced Liquefaction Using Coal Swelling and Catalyst Dispersion Techniques

DOE Contract No. DE-AC22-91PC91051
Subcontract to Amoco

Final Report
September 1994

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Part I

THE EFFECT OF COAL BENEFICIATION AND SWELLING ON LIQUEFACTION BEHAVIOR OF BLACK THUNDER COAL

Abstract

Liquefaction experiments were undertaken using subbituminous Black Thunder mine coal to observe the effects of aqueous SO_2 coal beneficiation and the introduction of various coal swelling solvents and catalyst precursors. Aqueous SO_2 beneficiation of Black Thunder coal removed alkali metals and alkaline earth metals, increased the sulfur content and increased the catalytic liquefaction conversion to THF solubles compared to untreated Black Thunder coal. The liquefaction solvent had varying effects on coal conversion, depending upon the type of solvent added. The hydrogen donor solvent, dihydroanthracene, was most effective, while a coal-derived Wilsonville solvent promoted more coal conversion than did relatively inert 1-methylnaphthalene. Swelling of coal with hydrogen bonding solvents tetrahydrofuran (THF), isopropanol, and methanol, prior to reaction resulted in increased noncatalytic conversion of both untreated and SO_2 treated Black Thunder coals, while dimethylsulfoxide (DMSO), which was absorbed more into the coal than any other swelling solvent, was detrimental to coal conversion. Swelling of SO_2 treated coal before liquefaction resulted in the highest coal conversions; however, the untreated coal showed the most improvements in catalytic reactions when swelled in either THF, isopropanol, or methanol prior to liquefaction. The aprotic solvent DMSO was detrimental to coal conversion.

Introduction

The effect of aqueous SO_2 coal beneficiation on the thermal and catalytic liquefaction behavior of Black Thunder subbituminous coal was investigated. Aqueous SO_2 beneficiation has potential for improving coal liquefaction behavior because SO_2 treatment has been shown to reduce substantially the ash content of both bituminous and subbituminous coals as well as lignite.[1-5] Aqueous SO_2 beneficiation of bituminous Illinois No. 6 coal resulted in both positive and negative effects on liquefaction behavior. The positive effects resulted from a reduction in the solids introduced into the reactor and, hence, less difficulties arose from processing the solids; however, the reduction in the mineral matter resulted in less inherent reactivity of the coal.[1] A subbituminous coal, Clovis Point, gave equivalent liquefaction results for both untreated and SO_2 treated materials,[3] while Martin Lake lignite showed improved conversions with SO_2 treatment.[1,3] SO_2 beneficiation of coal involves first crushing and sizing coal and then contacting the coarse fraction with aqueous SO_2 to remove alkali metals and alkaline earth metals. This deashing treatment is followed by gravity separation to recover the size fraction that contains the lowest ash content.[6] Metals that are typically removed from subbituminous coals using aqueous SO_2 are Ca, Mg, Na, and K.[3-5] The iron content is also frequently reduced, which is possibly caused by the solubilization of siderite.[3] This reduction in iron also probably accounts for the reduction in the inherent catalytic activity of the coal mineral matter.

Swelling of coal by organic solvents has been investigated by a number of researchers[7-12] after Van Krevelen first proposed that coal was composed of a three dimensional cross-linked macromolecular network.[13] Organic solvent when contacted with coal becomes incorporated in the structure and swells the coal. The degree of swelling achieved depends on the chemical composition of the solvent. Hydrogen bonding solvents swell coals significantly more than non-hydrogen bonding solvents. Liquefaction of solvent-swollen coals by Joseph[6] showed that bituminous and lower rank coals yielded enhanced conversion and product slates. The improvement in yield was postulated to be caused by the opening of the coal pore structure allowing greater accessibility to hydrogen donor solvents.

In this study, hydrogen bonding solvents were utilized in conjunction with the aqueous SO_2 beneficiation of coal. Possible synergetic effects of the two modes of pretreatment were examined. In order to evaluate the effects of these pretreatment, thermal and catalytic liquefaction reactions were performed with both untreated and SO_2 treated Black Thunder coal. In the catalytic reactions, the effect of different slurry-phase catalyst precursors on the liquefaction behavior for both untreated and SO_2 pretreated coal was examined. The first set of liquefaction experiments used a probe hydrogenation species, pyrene, as the solvent. In the second set of experiments, the amount of pyrene was decreased and an additional solvent was added for the liquefaction reaction. The solvents used ranged from a nondonor solvent, 1-methylnaphthalene, to a hydrogen donor solvent, 9,10-dihydroanthracene, to a coal-derived solvent, V1074. The last set of experiments evaluated combining two types of coal pretreatment, in which SO_2 treated as well as untreated Black Thunder coal was swelled prior to liquefaction reactions. The swelling solvents chosen were methanol, isopropanol, tetrahydrofuran (THF), and dimethylsulfoxide (DMSO) on the basis that these solvents swell coals to different degrees.[14,15] The alcohols had a swelling index of 1.35 to 1.39 for Black Thunder coal, while THF and DMSO had larger swelling indices of 1.53 and 2.39, respectively.[14,15] Molyvan L and nickel octoate were chosen as the catalysts because of their demonstrated activity in the slurry-phase catalyst screening study. 1-Methylnaphthalene was chosen as the reaction solvent for the swelled coals because of its relative inertness under the reaction conditions and apparent lack of interaction with the coal and pyrene during liquefaction. The use of this noninteracting solvent allowed the effect of swelling untreated and SO_2 treated coals on their liquefaction behaviors to be more clearly demonstrated.

Experimental

Catalyst Screening Test. The catalytic activity of a number of different slurry-phase catalysts for coal conversion of untreated and SO_2 treated Black Thunder coal to THF solubles and for pyrene hydrogenation was evaluated. The system, was composed of 1.5 g of pyrene, 0.33 g of moisture and ash free (maf) coal and a nominal 600-800 ppm of active metal from the catalyst precursor based on the coal feed. These reactions were performed without an additional solvent. The coals used were untreated and SO_2 treated Black Thunder coals. Proximate and ultimate analyses for both coals are given in Table 1. The catalyst precursors tested were Molyvan L (Vanderbilt), molybdenum naphthenate (Shepherd Chemical) (MoNaph), iron naphthenate (Aldrich) (FeNaph), nickel naphthenate (Shepherd Chemical) (NiNaph), nickel octoate (Shepherd Chemical) (NiOct), chromium 2-ethylhexanoate (Strem Chemical) (Cr2-EH), and vanadium naphthenate (Strem Chemical) (VNaph).

The reactions were performed at 410 °C for 30 min using ~20 cm^3 stainless steel microtubular reactors which were agitated horizontally at 450 cpm. The pyrene reaction products were analyzed by gas chromatography using a Varian Model 3400, J&W DB-5 column and flame ionization detector. Pyrene conversion and hydrogenation to partially saturated products were determined to evaluate the effect of different catalysts and SO_2 pretreatment on the hydrogenation reactions.

Table 1. Proximate and Ultimate Analysis of Untreated and SO_2 Treated Black Thunder Coals[a]

Proximate Analysis[b]			Ultimate Analysis[c]		
	Untreated	SO_2 Treated		Untreated	SO_2 Treated
% Moisture	11.2	9.9	% Carbon	69.7	70.5
% Ash	5.4	3.1	% Hydrogen	4.9	5
% Volatile Carbon	44.5	41.7	% Nitrogen	0.9	0.9
% Fixed Carbon	38.8	45.3	% Sulfur	0.4	0.8
Total	100	100	% Ash	6.1	3.4
Btu/lb	10606	10993	% Oxygen (by difference)	18	19.4

[a] Commercial Testing and Engineering Co., Birmingham, AL
[b] As Received
[c] Dry Basis

7 ml of swelling solvent. After 2 hr the amount of coal swelling that occurred was determined by measuring the height of the coal and comparing that to the height of the coal prior to swelling. The change in the volume was calculated by

$$\% \Delta V = \frac{h_1}{h_o} \times 100\%$$

where, ΔV is the volume change of the coal, h_0 is the initial height of the coal in the tube in an unswelled state, and h_1 is the height of the coal in the tube in a swelled state. The coal remained in the swelling solvent for a total of 24 hr, after which the nonabsorbed solvent was removed from the coal and the coal was contacted for 7 hr in ambient air, but remained in a swelled state; the weighed coal and any absorbed solvent was placed in the liquefaction reactor and then reacted at 410 °C for 30 min under well-agitated conditions. Each reaction contained a nominal 1.33 g of maf coal, 2.00 g of 1-MN as solvent, 0.67 g of pyrene, and any residual swelling solvent remaining in the coal for those reactions performed with swelled coal. Hydrogen gas was introduced at 1250 psig at ambient temperature. Reactions, performed thermally and catalytically, were duplicated. The catalysts used were Molyvan L and NiOct which were both introduced at a level of 600 to 800 ppm of active metal on a coal basis.

Discussion of Results

Effect of Catalyst Precursors on Coal and Pyrene Conversion. Liquefaction reactions were performed with untreated and SO_2 treated Black Thunder coals using pyrene as both a probe hydrogenation species and a solvent. When Black Thunder coal was treated with aqueous SO_2, the amount of ash present in the coal was halved, but the amount of sulfur doubled. Residual sulfur from the SO_2 treatment was retained in the coal (Table 1). The amount of

Pyrene hydrogenation is defined as the moles of hydrogen required to form the liquid hydrogenation products from pyrene as a percentage of the moles of hydrogen required to form pyrene's most hydrogenated product, perhydropyrene. Coal conversion to THF solubles was also determined and is defined as percent coal conversion = [1-((g of IOM) / (g of maf coal charged))] where IOM is insoluble organic matter which is ash-free.

Liquefaction reactions were conducted in which an additional solvent was employed; one of the three following solvents was used: 9,10-dihydroanthracene (DHA) from Aldrich, 1-methylnaphthalene (1-MN) from Aldrich, and V1074 was a solvent produced from the liquefaction of Black Thunder coal and was obtained from the Wilsonville Coal Liquefaction Research and Development facility. The V1074 nominal boiling range was 650-900 °F. The coals used were untreated and SO_2 treated Black Thunder coals. The catalysts employed with the different solvents were Molyvan L, NiOct, cobalt naphthenate (Strem) (CoNaph), and chromium naphthenate (Strem) (CrNaph) with 9,10-DHA; Molyvan L and NiOct with V1074; and Molyvan L, NiOct, and CrNaph with 1-MN. The liquefaction conditions used were 410 °C, 1250 psig H_2 at ambient temperature, 30 min reaction time, 1.33 g of maf coal, 0.67 g of pyrene, 2.00 g of solvent, and catalyst loading of 600 to 800 ppm of active metal based on coal feed. The reactors were the same as previously described. The pyrene reaction products and coal conversion were obtained as stated earlier.

Coal Swelling Reactivity Test. For the coal swelling reactivity test, four swelling solvents were used: methanol, isopropanol, THF, and DMSO, all of which were obtained from Fisher Scientific and were used as received. Untreated and SO_2 treated Black Thunder coals were swelled prior to reaction by introducing 1.33 g of maf coal to a pyrex swelling tube along with conversion of beneficiated and raw coal to THF solubles achieved with the different catalyst precursors is presented in Table 2. Pyrene conversion and the %HYD, which is a measure of the hydrogenation of pyrene to partially saturated products, is also given in Table 2.

The amount of coal conversion achieved in the liquefaction reactions was dependent upon the presence of a catalyst, type of catalyst, and pretreatment of coal. The thermal coal conversions for untreated and SO_2 treated Black Thunder coals with no additional solvent present were similar, although the SO_2 treated coal showed more variability. The most active catalysts for the untreated coal were Molyvan L and NiOct, both yielding conversions of about 73%. Three of the slurry-phase catalysts appeared to be detrimental to coal conversion, yielding conversion values that were less than the thermal conversion. These catalysts, which were reacted without any additional sulfur being added to the reaction, were MoNaph, FeNaph, and Cr 2-EH. Two of these catalyst precursors, MoNaph[16,17] and FeNaph,[18,19] have shown considerably more activity in systems that contain excess sulfur. Since the liquefaction reactions were performed without the addition of any sulfur, the catalyst precursors which required sulfur for their activity, had to rely on sulfur that was either indigenous to themselves as with Molyvan L or was released from coal.

The activity of each catalyst precursor increased in the presence of the SO_2 treated coal. Two factors were probably responsible for the increase: the removal of the alkali and alkaline earth metals such Ca[3,5] and the presence of additional S which was residual in the coal from the SO_2 treatment (Table 1). A number of the catalyst precursors increased coal conversion with SO_2 treated coal; these included Molyvan L, MoNaph, FeNaph, NiNaph, NiOct, and Cr 2-EH. The largest improvement in activity was with MoNaph where both the increase in sulfur content

Table 2. Effect of Catalyst Type on Coal and Pyrene Conversions Using Untreated and SO_2 Treated Black Thunder Coal With and Without Solvents[a]

Catalyst	Untreated Black Thunder Coal			SO_2 Treated Black Thunder Coal		
	% Coal Conversion	% Pyrene Conversion	% Pyrene HYD[b]	% Coal Conversion	% Pyrene Conversion	% Pyrene HYD
No Solvent						
None	59.6±0.9	1.6±0.1	1.0±0.1	57.5±11.5	1.3±0.4	0.8±0.3
Molyvan L	72.9±4.6	22.9±4.6	8.3±1.7	90.3±0.1	28.0±2.8	9.8±1.2
MoNaph	48.2±1.8	3.4±1.7	1.1±0.6	85.7±2.0	26.3±2.5	9.2±0.9
FeNaph	54.2±11.2	1.4±0.1	1.0±0.3	63.4±2.8	4.9±4.2	2.1±1.6
NiNaph	62.7±10.9	13.1±6.8	5.7±1.5	73.9±5.7	15.8±0.4	5.7±0.1
VNaph	64.4	4.2	2.0	66.1±1.8	3.9±0.7	1.9±0.3
NiOct	73.8±6.0	25.6±0.1	9.1±0.0	84.4±7.6	21.9±2.0	7.8±0.7
Cr 2-EH	48.0±7.9	1.2±0.3	0.8±0.2	54.8±1.5	3.3±1.6	1.5±0.6
Solvent: 1-Methylnaphthalene						
None	49.3±0.8	3.5±1.1	2.1±0.6	47.3±1.1	1.5±1.1	0.7±0.7
Molyvan L	82.4±3.0	30.0±5.4	11.2±2.4.	88.5±0.7	27.8±3.0	10.4±0.6
NiOct	70.7±4.1	6.8±0.3	2.3±0.1	76.3±4.2	12.5±3.5	4.2±1.2
CrNaph	52.8±1.8	0.0±0.0	0.0±0.0	51.7±1.1	0.0±0.0	0.0±0.0
Solvent: V1074						
Molyvan L	84.7±1.0	14.9±2.8	5.7±1.1	90.5±1.9	20.8±2.2	7.6±0.8
NiOct	81.5±0.9	6.8±4.3	2.4±1.6	82.1±3.0	2.0±2.8	0.7±0.9
Solvent: 9,10-Dihydroanthracene						
Molyvan L	89.7±0.2	15.2±4.5	5.4±1.8	92.4±0.7	20.8±4.4	7.4±1.6
NiOct	87.0±1.7	4.4±1.1	2.1±0.4	92.4±5.0	3.7±1.4	1.8±0.5
CoNaph	83.2±0.1	2.2±0.2	1.3±0.1	85.9±0.8	2.7±0.4	1.6±0.3
CrNaph	76.8±4.2	4.0±0.0	2.6±0.0	78.6±5.7	2.9±1.3	2.0±0.9

[a] Reaction Conditions: 410 °C, 30 min, 1250 psig H_2 at ambient temperature, agitated at 450 cpm.

[b] HYD = hydrogenation

[c] MoNaph = molybdenum naphthenate; FeNaph = iron naphthenate; NiNaph = nickel naphthenate; VNaph = vanadium naphthenate; NiOct = nickel octoate; Cr2-EH = chromium 2-ethylhexanoate; CrNaph = chromium naphthenate; CoNaph = cobalt naphthenate

of the coal and removal of ash from the coal had positive effects. In previous studies, the addition of sulfur to MoNaph improved its activity in both model compound[16] and coal liquefaction reactions.[20] The catalyst precursors, FeNaph, Molyvan L, NiNaph, and NiOct, also showed noticeable improvements with SO_2 treated coal. While in the process of removing alkali metals and alkaline earth metals, the SO_2 treatment most likely opened up the porous structure of the coal, thereby allowing more contact between the finely dispersed catalyst and the reactive coal moieties. The removal of the alkali metals and alkaline earth metals also allowed the metals present as finely dispersed catalysts to exhibit their full activity, since the Ca and other interfering metallic species are largely removed from the system.[3,5] The coal conversion with SO_2 treated coal showed less variability in coal conversion than did the reactions with untreated coal. The activity of some of the catalyst precursors tended to stabilize when additional sulfur was present in the system. Similar effects of sulfur have been observed with supported oxide catalysts.[21]

Pyrene conversion varied considerably depending upon the type of catalyst precursor present and the pretreatment of the coal (Table 2). Pyrene conversion for the untreated coal systems was greatest with NiOct, Molyvan L, and NiNaph while MoNaph, FeNaph, Cr 2-EH, and VNaph showed low activity. Molyvan L and NiOct were active for pyrene conversion with the SO_2 treated coal. The activity of NiNaph for pyrene conversion was intermediate regardless of whether the coal was pretreated or not. The presence of the additional sulfur in the SO_2 treated coal and the reduced ash content affected some of the activity of the different catalysts for pyrene conversion. The activity of MoNaph for pyrene conversion increased substantially from 3.4% in the untreated system to 26.3% in the SO_2 treated system. This increase was probably influenced most by the additional sulfur in the coal system since MoNaph is most effective when substantial amounts of readily available sulfur are present in the reaction system.[16,17] Pyrene conversion with Cr 2-EH was low but doubled with SO_2 treated coal.

The primary hydrogenation product from pyrene observed with all of the catalyst precursors was dihydropyrene (DHP) while the more active catalysts also yielded tetrahydropyrene (THP) and hexahydropyrene (HHP) as the reaction products. The percent pyrene hydrogenation (% HYD) given in Table 2 gives an indication of the degree of saturation achieved in the reaction products produced. The higher values indicate that DHP with small amounts of THP and HHP was formed while the lower values indicate that DHP was the only product although trace amounts of the other two products may have also been formed.

Effect of Additional Solvent on Liquefaction Behavior. The effect of introducing an additional solvent to the liquefaction reaction on the thermal and catalytic liquefaction of untreated and SO_2 treated coals was also examined as shown in Table 2. In these reactions, the primary solvent present was either DHA, 1-MN, or V1074 at 2.00 g; pyrene was also present at 0.67 g. Hence, the solvent to pyrene to maf coal ratio was 2.00:0.67:1.33 so that the total solvent (added solvent plus pyrene) to coal ratio was 2:1. When the liquefaction behavior of the solvent plus pyrene systems was compared to that of pyrene alone, interactions among the solvent, coal, and catalyst precursor became evident.

The nondonor solvent, 1-MN, used without a catalyst precursor, decreased the amount of coal conversion for both untreated and SO_2 treated coals compared to pyrene alone. Pyrene served as a better solvating medium than 1-MN for both untreated and SO_2 treated coals. Pyrene has been shown to be an effective shuttler of hydrogen in some coal liquefaction systems.[22]

Pyrene also because of its four-ring structure has the propensity to be a better solvating agent for coal than the two-ring 1-MN. Hence, both factors may be responsible for the higher conversion in pyrene than in to 1-MN. The addition of both Molyvan L and NiOct catalyst precursors to the 1-MN system resulted in substantial increases in coal conversion. Molyvan L was the more active of the two in terms of both coal and pyrene conversions. In the case of Molyvan L and untreated coal, the use of 1-MN as solvent was beneficial for coal conversion compared to using pyrene as solvent. Coal conversion increased from 72.9 to 82.4% while pyrene conversion increased from 22.9 to 30.0%. These increases in conversion may have resulted from increased mass transfer of the system with 2.0 g of 1-MN being present in the reactor. The coal conversion in 1-MN achieved in the presence of CrNaph was only slightly higher than the thermal reaction. The presence of 1-MN was detrimental to the activity of NiOct, particularly for pyrene conversion.

Aqueous SO_2 treatment of Black Thunder coal prior to liquefaction increased the apparent reactivity of the coal as demonstrated by an increase in catalytic coal conversion for both the pyrene alone and 1-MN and pyrene systems. The solvent combination of 1-MN with pyrene was a less effective solvent for the catalytic medium than was pyrene alone. For reactions with both Molyvan L and NiOct, both coal and pyrene conversion decreased with 1-MN and pyrene compared to pyrene alone.

Use of V1074, a coal-derived reaction solvent from Black Thunder coal, with Molyvan L and NiOct increased the untreated coal conversion compared to similar reactions with 1-MN or pyrene alone. The increase was most obvious with NiOct where the coal conversion for untreated coal increased from 70.7% with 1-MN to 81.5% with V1074; likewise, with SO_2

treated coal, coal conversion increased from 76.3 to 82.1% with V1074. However, the V1074 solvent was detrimental to pyrene conversion as shown in Table 2. Coal-derived V1074 contains a multiplicity of compounds which could partially poison the finely dispersed catalyst and render the catalyst less active for pyrene hydrogenation.

The hydrogen donor solvent, DHA, yielded an increased coal conversion for both Molyvan L and NiOct compared to the other solvents. This increase in activity was particularly noticeable for untreated Black Thunder coal. The hydrogen donability of DHA promoted coal conversion in the catalytic reactions utilizing Molyvan L, NiOct, CoNaph, and CrNaph. Hence, a synergetic interaction occurred between the catalysts and solvent when the untreated subbituminous coal was used. Synergism was also observed when DHA, the catalysts Molyvan L or NiOct, and SO_2 treated coal were reacted together compared to these reactions with 1-MN. The activity of CrNaph substantially increased in DHA compared to 1-MN.

A previous activity study of MoNaph and excess sulfur compared to presulfided $NiMo/Al_2O_3$ showed that the presence of a hydrogen donor in the reaction system had the most effect on the catalyst with the lesser activity.[24] The same phenomenon was also demonstrated in this study with the reaction of coal in DHA with CrNaph. Coal conversions in DHA using the low activity CrNaph catalyst were 76.8% and 78.6%, for untreated and SO_2 treated coal, respectively, while in 1-MN the conversions were 52.8% and 51.7%, respectively. However, DHA had less effect on the more active catalysts which was the same result as obtained in the previous study.[24] Both Molyvan L and NiOct exhibited small increases in activity but to a lesser degree than did CrNaph. Pyrene conversions as a result of using Molyvan L and NiOct were less than those that occurred in 1-MN, but similar to those obtained with V1074.

Of the three solvents used, DHA produced the highest coal conversion, followed by coal-derived V1074, with the nondonor solvent, 1-MN yielding the least conversion. This ranking of solvents appears quite reasonable since DHA is a hydrogen donor solvent, V1074 is a coal-derived solvent with solvating characteristics that should be effective for converting coal and 1-MN should be least effective since 1-MN is a relatively inert solvent containing a limited amount of partially saturated methylnaphthalenes produced under these reaction conditions. In contrast, pyrene conversions were the highest with 1-MN as the solvent. The primary hydrogenation products from pyrene in the reactions with the added solvents were DHP; only minor amounts of THP were formed when DHA was solvent while neither THP or HHP was formed with the other two solvents.

Effect of Swelled Coal on Liquefaction Reactions. Four swelling solvents, THF, methanol, isopropanol, and DMSO, were employed to swell untreated and SO_2 treated Black Thunder coals. The swelling solvents ranked in effectiveness as methanol $\approx$ isopropanol $<$ THF $<$ DMSO. DMSO swelled the untreated coal by 100% so that the volume of the coal doubled as shown in Table 3. The other swelling solvents, methanol, isopropanol and THF, swelled the untreated coal by 16 to 42% with THF being the most effective among the three. Methanol and isopropanol remained in the coal in similar amounts which ranged from 0.9 to 1.3 g for 1.6 to 1.7 g of coal. More THF was absorbed in the coal, leaving between 1.45 to 1.7 g in 1.6 to 1.7 g of coal. Dimethylsulfoxide absorbed the most, giving 3.1 to 4.3 g of DMSO in 1.62 g of untreated coal.

All of the swelling solvents increased the volume of the SO_2 treated coal more than that of the untreated coal. Ca^{+2} ions, which may serve to cross-link acid groups in coal, were

Table 3. Effect of Preswelling Coal on Reactions of Untreated and SO$_2$ Treated Black Thunder Coal in 1-Methylnaphthalene[a]

Swelling Solvent	Catalyst	Untreated Black Thunder Coal			SO$_2$ Treated Black Thunder Coal		
		Change in Volume (% ΔV)	Coal Conversion (%)	Pyrene Conversion (%)	Change in Volume (% ΔV)	Coal Conversion (%)	Pyrene Conversion (%)
None	None	NA	49.3±0.8	3.5±1.1	NA	47.3±1.1	1.5±1.1
	Molyvan L	NA	82.4±3.0	30.0±5.4	NA	88.5±0.7	27.8±3.0
	Ni Octoate	NA	70.7±4.1	6.8±0.3	NA	76.3±4.211	12.5±3.5
THF	None	34.2±7.0	59.7±8.9	0.0±0.0	87.6±2.7	58.0±9.5	0.0±0.0
	Molyvan L	37.8±1.9	87.3±1.6	18.6±1.3	79.5±0.8	91.2±1.5	25.4±0.1
	Ni Octoate	41.3±0.6	77.0±0.1	2.4±0.1	97.4±3.7	72.5±5.8	2.2±0.4
Methanol	None	26.7±0.8	53.9±2.8	1.0±0.3	38.4±2.3	41.8±2.4	1.5±0.1
	Molyvan L	18.6±0.6	88.0±0.9	24.3±1.8	36.9±7.4	90.0±1.3	30.0±4.4
	Ni Octoate	18.6±0.6	85.5±0.1	10.9±0.4	31.6±7.4	78.7±1.1	4.9±0.8
Isopropanol	None	16.9±5.5	61.7±1.1	0.8±1.1	45.0±0.0	56.4±3.0	1.6±0.1
	Molyvan L	17.9±6.9	88.1±0.4	18.7±0.8	38.6±5.0	91.3±0.6	21.3±2.4
	Ni Octoate	16.3±3.8	77.6±1.1	2.2±0.4	32.3±6.4	73.9±5.1	3.9±0.6
DMSO	None	111.7±3.7	29.3±4.0	1.2±0.5	176.5±26.2	29.8±3.2	1.3±0.4
	Molyvan L	115.9±2.2	79.9±1.9	11.6±0.1	178.9	78.1	13.7
	Ni Octoate	102.4±9.5	63.6±3.6	5.0±0.8	171.6±11.9	50.1±9.5	7.1±1.1

[a] Reaction Conditions: 410 °C, 30 min, 1250 psig at ambient temperature agitated at 450 cpm.

removed by SO_2 treatment, thereby allowing freer movement within the coal molecule. Methanol and isopropanol swelled SO_2 treated coal by 31 to 45% while THF swelled SO_2 treated coal by 79 to 98% and DMSO by 170 to 180%. More swelling solvent was retained in the SO_2 treated coal than in the untreated coal. Again DMSO remained strongly absorbed in the coal after removal of the swelling solvent with amounts ranging from 4.0 to 5.7 g for 1.6 to 1.7 g of coal. A lesser, though still substantial amount of the other solvents was retained in the SO_2 treated coal. Nearly 2.0 g of THF and about 1.0 g of either methanol or isopropanol were retained in an equivalent amount of coal.

Liquefaction reactions using swelled, untreated and SO_2 treated coals were performed noncatalytically and catalytically with Molyvan L and NiOct using 1-MN as the solvent (Table 3). Pyrene was added as a probe hydrogenation agent. Molyvan L and NiOct were chosen because of their demonstrated high activity for coal conversion as shown in the previous set of experiments given in Table 2. When the catalytic reactions, regardless of swelling solvent, were compared to the noncatalytic reactions, the amount of coal conversion increased substantially with the presence of a catalyst. Likewise, pyrene conversion increased when either Molyvan L or NiOct was present.

The effect of swelling coal prior to liquefaction was clearly demonstrated by comparing the coal conversion achieved in the noncatalytic reactions with and without preswelling. For untreated coal, the greatest improvement in coal conversion occurred when using isopropanol as the swelling solvent. Coal conversion increased from 49.3 to 61.7% after the untreated coal was swelled with isopropanol and to 59.7% with THF. The absorbed DMSO present in untreated coal was detrimental to noncatalytic coal conversion, decreasing the amount of coal conversion by almost half. When either Molyvan L or NiOct was used as the catalyst precursor, all of the swelling solvents except for DMSO increased the amount of coal conversion achieved for untreated coal. Among the three other swelling solvents, THF, methanol and isopropanol, the amount of the coal conversion achieved for untreated coal with Molyvan L was very similar. By contrast, methanol, as compared to the other swelling solvents, appeared to enhance the coal conversion of untreated coal when NiOct was used. The swelling solvents directly influenced the coal liquefaction behavior. The swelling solvent affected liquefaction behavior positively by the opening of the coal structure and allowing accessibility to the finely dispersed catalyst during the liquefaction reaction. But retention of aprotic DMSO diminished the reactivity of the coal.

Swelling of SO_2 treated coal with THF and isopropanol improved noncatalytic coal conversion compared to no swelling, while methanol and DMSO did not. Smaller improvements in coal conversion were obtained with Molyvan L with SO_2 treated coal swelled with THF, methanol and isopropanol compared to swelled untreated coal. The conversion increased from 88.5 to 90 or 91%. Only a slight improvement was observed with NiOct and one swelling solvent, methanol; all of the other swelling solvents were detrimental to coal conversion when NiOct was present compared to that achieved in the reaction without prior swelling. Since the swelling solvents, except DMSO, enhanced coal conversion of untreated coal, the presence of THF, isopropanol and methanol in the reactor was not detrimental to coal conversions.

Influence of Swelling Solvent on Liquefaction Behavior. The influence of the swelling solvent on liquefaction behavior appeared to be specific for a given coal and catalyst system. The swelling solvent which showed the most improvement for noncatalytic coal conversion compared to no swelling solvent was isopropanol for untreated coal and THF for the SO_2 treated coal.

Isopropanol yielded the greatest improvement in the reactions with Molyvan L for both untreated and SO_2 treated coals while methanol interacted more favorably with NiOct for both coals. By contrast, DMSO, which was the most effective solvent for swelling coal but also incorporated the most into the coal of all of the swelling solvents, was detrimental to coal conversion. The SO_2 treated coal reacted with catalysts was more adversely affected by DMSO than the untreated coal reacted with catalysts.

Beneficiation of coal with SO_2 reduced the benefit of swelling prior to liquefaction with Molyvan L and NiOct as catalysts as shown in Table 4. Untreated Black Thunder coal was more positively affected by preswelling than SO_2 treated coal. The only swelling solvent that was detrimental to coal conversion for both the untreated and SO_2 treated coals was DMSO. The differences between untreated and SO_2 treated coal were not as large for Molyvan L as for NiOct; the SO_2 treated coal showed some improvement with preswelling using THF, methanol and isopropanol but not as much as with the untreated coal. Coal swelling as a pretreatment was more effective for promoting coal conversion of untreated Black Thunder coal than of SO_2 treated coal. Almost all of the pyrene reactions were negatively affected by preswelling.

SUMMARY

Aqueous SO_2 beneficiation of Black Thunder coal removed alkali metals and alkaline earth metals from subbituminous Black Thunder coal; the sulfur content of the coal also increased. Both factors enhanced coal conversion of SO_2 treated Black Thunder coal when slurry-phase catalysts were present. The reduced ash content decreased the amount of potential catalyst poisons, and linked carboxylic acid groups while the available sulfur helped to sulfide the slurry-phase catalysts.[18,23] Noncatalytic reactions did not show any benefit of SO_2 treatment

Table 4. Comparison of the Effect of Swelling Solvents on the Liquefaction of Untreated and SO_2 Treated Black Thunder Coal

Swelling Solvents	Coal Conversion			Pyrene Conversion			Swelling Index
	Thermal	Molyvan L	Ni Octoate	Thermal	Molyvan L	Ni Octoate	(ΔV%)
	Untreated Black Thunder Coal Percent Change (%)						
THF	+10.4	+4.9	+6.3	-3.5	-11.4	-4.4	37.3
Methanol	+4.6	+5.6	+14.8	-2.5	-5.7	4.1	21.3
Isopropanol	+12.4	+5.7	+6.9	-2.7	-11.3	-4.6	17
DMSO	-20	-2.5	-7.1	-2.3	-18.4	-1.8	110
	SO_2 Treated Black Thunder Coal Percent Change(%)						
THF	+10.7	+2.7	-3.8	-1.5	-2.4	-10.3	88.1
Methanol	-5.5	+1.5	+2.4	0	+2.2	-7.6	35.6
Isopropanol	+9.1	+2.8	-2.4	0.1	-6.5	-8.6	38.6
DMSO	-17.5	-10.4	-26.2	-0.2	-14.1	-5.4	175

when reacted under the same conditions as the catalytic reactions. The addition of a hydrogen donor solvent, dihydroanthracene, further enhanced coal conversion for most of the catalytic agents used. A coal-derived reaction solvent also had a positive effect on coal conversion compared to a nondonor solvent.

The coupling of aqueous SO_2 beneficiation with coal swelling resulted in a slight improvement in coal conversion with Molyvan L but not with NiOct. Swelling of the coal prior to liquefaction showed a greater benefit for untreated coal than SO_2 treated coal. The swelling of untreated coal opened the coal structure and increased reactivity sufficiently to improve both thermal and catalytic coal conversion.

Nomenclature For Part I

% HYD = percent hydrogenation
1-MN = 1-methylnaphthalene
CoNaph = cobalt naphthenate
Cr2-EH = chromium 2-ethylhexanoate
CrNaph = chromium naphthenate
DHA = dihydroanthracene
DHP = dihydropyrene
FeNaph = iron naphthenate
HHP = hexahydropyrene
IOM = insoluble organic matter
maf = moisture and ash free
MoNaph = molybdenum naphthenate
NiNaph = nickel naphthenate
NiOct = nickel octoate
THF = tetrahydrofuran
THP = tetrahydropyrene
VNaph = vanadium naphthenate

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Part II

LIQUEFACTION BEHAVIOR OF COAL IMPREGNATED WITH CATALYST DURING PRESWELLING

Abstract

The effect of impregnating coal with slurry phase catalysts during solvent preswelling on coal conversion was investigated. Black Thunder subbituminous coal which was either untreated or pretreated with aqueous SO_2 was used. The coal was placed into the swelling solvent, THF, methanol or isopropanol, for 96 hr prior to liquefaction. Slurry phase catalysts, Mo naphthenate, Molyvan L and Ni octoate, were introduced into the swelling solvents; catalyst uptake by coal was 90 to 95% of the catalyst introduced. Coal conversions of these impregnated coals were obtained in a reaction solvent of 1-methylnaphthalene at 385 °C and in reaction solvents of 1-methylnaphthalene, coal-derived V1074, and dihydroanthracene at 410 °C. These coal conversions were compared to those obtained with swelled and nonswelled coals. The swelling solvent and the SO_2 pretreatment affected the amount of coal conversion obtained. Coal conversions achieved with impregnated coals were somewhat less than those achieved when the catalyst was added directly to the reactor.

Introduction

Increases in the liquefaction conversion and production of upgraded product from subbituminous coal are desirable to make the process a feasible option for production of transportation of fuels. To this end, a process was conceptualized and tested. The conceptual process involves several steps: (1) coal is pretreated with aqueous SO_2; (2) the pretreated coal is then swelled in a hydrogen bonding solvent in which is placed a slurry phase catalyst; (3) during swelling the slurry phase catalyst is deposited within the pores of the coal; and (4) the impregnated coal is liquefied having the catalyst in intimate contact with the reacting coal molecules.

The research described herein tested the conceptual process using both untreated and SO_2 treated coal. The reason that a substantial number of experiments were performed with the untreated coal was that previous results[1,2] indicated that swelling coal prior to liquefaction was more beneficial to coal conversions of untreated coal than of SO_2 treated coal. Reactions were performed (1) without swelling prior to liquefaction; (2) with swelling prior to liquefaction with the catalyst being added directly to the reactor; and (3) with swelling prior to liquefaction with catalyst being added to the swelling solvent. Three different swelling solvents, tetrahydrofuran (THF), isopropanol, and methanol, were used[3]; three different catalysts, Mo naphthenate, Molyvan L and Ni octoate, were used; and three different reaction solvents, 1-methylnaphthalene, a relatively inert solvent; V1074, a coal-derived solvent, and dihydroanthracene, a hydrogen donor solvent, were also used. The effect of the reaction temperature on the preswelled catalyst impregnated coal was investigated.

Experimental

Materials. Liquefaction reactions were performed using untreated and aqueous SO_2 treated Black Thunder coals. The swelling solvents, THF, methanol, and isopropanol were obtained from Fisher and were used as received. The liquefaction reaction solvents used were 1-methylnaphthalene (1-MN) (98% purity) and 9,10-dihydroanthracene (DHA), which were obtained from Aldrich, and V1074, a coal-derived solvent, from the Wilsonville Coal Liquefaction Research Facility. The catalysts used were Molyvan L from Vanderbilt Chemical Company and Mo naphthenate (MoNaph) and Ni octoate (NiOct) from Shepherd Chemical Company.

Swelling and Reaction Procedures. Untreated and SO_2 treated Black Thunder coals were swelled by introducing 1.33 g maf coal to the swelling tube and then adding 7 ml of solvent. Catalysts were charged to the swelling solvent at 1.05 times 600 to 800 ppm of active metal, the amount used when the catalyst was added directly to the liquefaction reactions. The coal was then allowed to sit unagitated in the swelling solvent for 96 hr. These experiments were designated with a "N" on the tables. Several experiments, designated with an "A" on the tables, were performed in which the coal and swelling solvent were agitated using an orbital shaker at 250 rpm during the 96 hr swelling period. Molyvan L was also added to the swelling solvent at twice the loading typically used, 1400 to 1600 ppm of active metal. These experiments in which the catalyst level was doubled are designated with a "D" on the tables.

Liquefaction reactions using untreated Black Thunder coal in 1-MN were performed at 385 °C for 30 min and at 410 °C for 10, 20, and 30 min in stainless steel tubular microreactors. The liquefaction reactions for SO_2 treated Black Thunder coal in 1-MN and for untreated Black

Thunder coal in V1074 and DHA were conducted for 30 min. Each reaction contained ~1.33 g of maf coal, 2 g of solvent, 0.67 g of pyrene and residual swelling solvent that remained in the swelled coal. The amount of solvent absorbed in the coal after swelling differed for each swelling solvent. The amount of solvent retained in the coal ranged from 0.6 to 1.0 times the coal mass. The amount of catalyst taken up by coal was obtained for selected reactions using X-ray fluorescence spectroscopy and equalled between 90 and 95% of that introduced into the reaction. Hydrogen gas was introduced at 1250 psig at ambient temperature. The reactor was well-agitated at 450 cpm. Recovery of the reaction products were generally 95% or higher.

Analysis. Products from the liquefaction reactions were removed from the reactor with THF. The conversion of the coal to THF solubles was determined. For the reactions where analysis of catalyst uptake was obtained, the values for the catalyst loading are given; otherwise, the presumed amount deposited ranged from 90 to 95% of the 600 to 800 ppm of active metal loaded on a per gram of coal basis. The amount of pyrene hydrogenation to hydrogenated products was obtained by gas chromatographic analyses using a Varian Model 3400, a J&W DB-5 fused silica capillary column and flame ionization detection. Pyrene hydrogenation is defined as the moles of hydrogen required to form the liquid hydrogenation products from pyrene as a percentage of the moles of hydrogen required to form the most hydrogenated product, perhydropyrene. The hydrogenation products obtained from pyrene were dihydropyrene (DHP), tetrahydropyrene (THP) and hexahydropyrene (HHP).

Results and Discussion

In the liquefaction reactions performed in this research, two primary parameters were measured to evaluate the efficacy of the catalyst impregnation step. The first parameter evaluated was the conversion of Black Thunder coal to THF soluble material. The second parameter measured was the hydrogenation reactivity of the added aromatic, pyrene, in the system. By determining the pyrene conversion to hydrogenated species and the percent hydrogenation to partially saturated products, the intrinsic activity of the catalyst added to the reaction system in a particular manner could be obtained. The only products observed from pyrene were DHP, THP, and HHP. Usually, higher conversions resulted in the production of all three products. However, DHP was the primary hydrogenation product produced in all reactions. Both THP and HHP, when formed, were always minor products.

The liquefaction reactions were performed at two temperatures, 385 °C and 410 °C. The basic premise for performing these reactions at 385 °C was to achieve a greater sensitivity for evaluating catalytic activity. Since the effect of the noncatalytic reactions would be less at the lower temperature, the effect of the catalyst and its method of introduction should be more apparent at 385 °C than at 410 °C. The reactions performed at the higher temperature of 410 °C were more representative of the reaction temperatures that are used in commercial processing.

Liquefaction Reactions at 385 °C. Liquefaction reactions were performed at 385 °C to examine the liquefaction behavior of coal impregnated with catalyst during preswelling as compared to the behavior of coal contacted with slurry phase catalyst by adding the catalyst directly to the reactor. The three slurry phase catalysts used were Mo naphthenate with sulfur, Molyvan L and Ni octoate. Isopropanol and THF were used as the swelling solvents. The data presented in Table 5 represent two types of reactions performed at 385 °C, reactions in which the catalysts were added directly to the reactor which contained the preswelled coal and reactions which contained coal that had been preswelled with catalyst. For each reaction, the amount of coal conversion, pyrene conversion and pyrene hydrogenation to saturated products was determined and is given in Table 5. Two sets of reactions are described: those in which coal

Table 5. Coal and Pyrene Conversions in Reactions of Untreated Black Thunder Coal in 1-Methylnaphthalene at 385 °C

Catalyst Type	Catalyst Loading (ppm)	Conditions During Swelling	%ΔV	Coal Conversion (wt %)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Time: 30 minutes			**Swelling Solvent: THF**		**Catalyst: added to reactor**	
Mo Naphthenate+S	655±35	N[a]	39.7±4.6	73.8±1.6	34.4±1.5	14.2±0.6
Molyvan L	602±6.4	N	34.1±9.6	72.5±3.5	25.7±7.2	10.4±3.3
Ni Octoate	803±108	N	34.9±2.2	69.4±7.8	16.2±11.2	6.7±4.2
Time: 30 minutes			**Swelling Solvent: THF**		**Catalyst: added to swelling solvent**	
Mo Naphthenate+S	646±42.4	N	41.9±1.4	76.8±0.3	35.4±0.1	14.6±0.1
Molyvan L	583±4.9	N	33.4±4.2	50.4±3.9	4.5±1.0	2.3±0.2
Ni Octoate	641±23.3	N	33.4±6.7	57.0±1.0	3.6±0.1	1.9±6.1
Time: 30 minutes			**Swelling Solvent: Isopropanol**		**Catalyst: added to reactor**	
Mo Naphthenate+S	758±8.5	N	11.2±3.5	80.0±7.9	29.0±1.8	11.7±0.5
Molyvan L	650±50	N	14.3±6.7	76.7±0.3	23.1±8.0	9.2±3.0
Ni Octoate	698±112	N	14.0±0.4	65.3±0.9	7.7±1.3	3.5±0.4
Time: 30 minutes			**Swelling Solvent: Isopropanol**		**Catalyst: added to swelling solvent**	
Mo Naphthenate+S	616±1.4	N	11.7±3.7	79.3±3.8	32.3±0.8	13.2±0.3
Molyvan L	633±19.1	N	13.6±0.0	55.9±0.3	5.0±0.4	2.6±0.1
Ni Octoate	725±94.0	N	14.3±6.7	62.2±2.7	5.0±0.4	2.6±0.2

[a] N = not agitated for 96 hr swelling period.

was preswelled in THF prior to reaction and those in which coal was preswelled in isopropanol.

For the reactions with THF as the swelling solvent, the amount of coal conversion achieved with the three slurry phase catalysts added directly to the reactor were very similar, ranging from 69.4% for NiOct to 73.8% for MoNaph+S. When the three catalysts were added to the swelling solvent, substantial differences in the catalytic activity for coal conversion were observed. Molyvan L yielded the lowest conversion at 50.4%, NiOct was intermediate at 57.0% and MoNaph+S was highest at 76.8%. Only MoNaph+S yielded a higher coal conversion when impregnated into the coal rather than being added directly to the reactor. Both Molyvan L and NiOct were negatively affected by contact with the swelling solvent THF and the coal prior to reaction.

Likewise, pyrene conversion and hydrogenation, in the reactions in which the coal was preswelled in THF and the catalyst added directly to the reactor, were fairly high for all three catalysts. The pyrene conversions ranged from 16.2% for Ni Oct to 34.4% for MoNaph+S. The primary hydrogenation product was DHP with only minor amounts of THP and HHP being formed. The catalyst impregnation process had the same effect on pyrene conversion as it did on coal conversion. Pyrene conversion with MoNaph+S added to the THF swelling solvent remained high at 35.4% while pyrene conversion for both Molyvan L and NiOct decreased substantially to 3.6 and 4.5%, respectively.

Similar catalytic activity was observed when isopropanol was used as the swelling solvent. Coal conversion ranged from 65.3% for NiOct to 80% for MoNaph+S when the catalyst was added directly to the reactor. Again, MoNaph+S was the only catalyst to retain its activity when impregnated into the coal during preswelling. Both Molyvan L and NiOct decreased in their activity when preswelled in isopropanol; however, the decrease was not as great as when these catalysts were preswelled in THF.

Pyrene conversion and hydrogenation followed the same trends as the coal conversion for the isopropanol system. Pyrene conversion was higher for MoNaph+S after impregnation to the coal compared to direct catalyst addition. Pyrene conversion for the NiOct system only decreased slightly from 7.7% for direct catalyst addition to 5.0% for catalyst impregnation. The activity of Molyvan L decreased substantially upon contact with isopropanol just as it did with THF. Pyrene conversion for the Molyvan L system decreased from 23.1% for direct catalyst addition to 5.0% for catalyst impregnation.

Coal conversion was sensitive to the type of swelling solvent used. Both Mo catalysts performed better when contacted with coal that had been swelled in isopropanol or when impregnated in coal during preswelling with isopropanol. The presence of the swelling solvent was slightly detrimental to the activity of MoNaph+S but was highly detrimental to the activity of Molyvan L. By contrast, NiOct performed similarly when added to the reactor with either isopropanol or THF swelled coal. However, direct contact between either THF or isopropanol and NiOct was detrimental to its catalytic activity. Pyrene conversion was also sensitive to the type of swelling solvent used. The catalyst which showed the greatest effect of the two swelling solvents, both THF and isopropanol, was Molyvan L.

Liquefaction Reactions in 1-Methylnaphthalene at 410 °C. Liquefaction reactions performed in the nondonor solvent 1-MN using untreated and SO_2 treated Black Thunder coal are presented in Tables 6 and 7, respectively. Evaluation of the coal conversions obtained with the untreated (Table 6) or SO_2 treated coal (Table 7) indicated that the presence of a Mo or Ni based catalyst regardless of method of introduction increased coal conversion.

Table 6. Coal and Pyrene Conversions for Untreated Black Thunder Coal Reacted in 1-Methylnaphthalene at 410 °C

Catalyst Type	Catalyst Loading (ppm)	Conditions During Swelling	% ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Reaction Time: 30 min		**Swelling Solvent: None**				
None	0	NA[a]	NA	49.3±0.8	3.5±1.1	2.1±0.6
Molyvan L	709±39	NA	NA	82.4±3.0	30.0±5.4	11.2±2.4
Ni Octoate	604± 6	NA	NA	70.7±4.1	6.8±0.3	2.3±0.1
Reaction Time: 30 min		**Swelling Solvent: THF**		**Catalyst Added to Reactor**		
None	0	N[b]	34.2±7.0	59.7±8.9	0.0	0.0
Molyvan L	661±33	N	37.8±1.9	87.3±1.6	18.6±1.3	6.2±0.4
Ni Octoate	615± 6	N	41.3±0.6	77.0±0.1	2.4±0.1	1.2±0.1
Reaction Time: 30 min		**Swelling Solvent: THF**		**Catalyst Added to Swelling Solvent**		
Mo Naphthenate	672±16	A	35.0±4.5	62.3±0.6	3.5±0.2	1.8±0.4
Molyvan L	607±88	N	40.4±1.8	81.9±1.6	15.1±1.8	5.7±0.4
Molyvan L	653±94	A	52.3±3.2	73.6±3.0	14.7±5.0	5.7±1.9
Molyvan L	1188±64	D	41.0±2.7	84.8±1.1	28.6±2.5	11.0±1.2
i Octoate	624±78	N	38.9±5.7	74.8±12.9	11.1±11.0	4.7±4.1
Reaction Time: 20 min		**Swelling Solvent: THF**		**Catalyst Added to Swelling Solvent**		
Mo Naphthenate	608±9.2	A	37.1±12.0	53.1±3.3	2.6±0.5	1.7±0.2
Molyvan L	599±7	N	38.7±3.2	67.5±5.4	4.8±3.5	2.1±1.3
Ni Octoate	652±74	N	34.1±3.3	60.8±3.2	2.4±0.3	1.3±0.1
Reaction Time: 10 min		**Swelling Solvent: THF**		**Catalyst Added to Swelling Solvent**		
Molyvan L	599±16	N	43.2±3.3	49.4±3.7	6.1±0.9	2.6±0.2
Reaction Time: 30 min		**Swelling Solvent: Methanol**		**Catalyst Added to Reactor**		
None	0	N	26.7±0.8	53.9±2.8	1.0±0.3	0.8±0.2
Molyvan L	690±19	N	18.6±0.6	88.0±0.9	24.3±1.8	8.5±1.1
Ni Octoate	698±70	N	18.6±0.6	85.5±0.1	10.9±0.4	4.0±0.4
Reaction Time: 30 min		**Swelling Solvent: Methanol**		**Catalyst Added to Swelling Solvent**		
Molyvan L	666±31	N	25.2±4.9	68.4±0.0	3.0±0.8	1.7±0.5
Molyvan L	1269±4	D	26.2±3.4	88.8±0.5	25.7±2.7	9.9±1.3
Ni Octoate	644±13	N	23.3±0.8	70.1±1.1	3.5±0.4	1.9±0.1

Table 6. Coal and Pyrene Conversions for Untreated Black Thunder Coal Reacted in 1-Methylnaphthalene at 410 °C(Continued)

Catalyst Type	Catalyst Loading (ppm)	Conditions During Swelling	% AV	Coal Conversion (wt%)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Reaction Time: 20 min		**Swelling Solvent: Methanol**		**Catalyst Added to Swelling Solvent**		
Molyvan L	652±21	N	25.4±9.1	67.6±0.1	2.8±0.8	1.9±0.1
Ni Octoate	613±6.4	N	20.6±4.5	64.4±0.4	2.3±0.4	1.4±0.3
Reaction Time: 30 min		**Swelling Solvent: Isopropanol**		**Catalyst Added to Reactor**		
None	0	N	16.9±5.5	61.7±1.1	0.8±1.1	0.6±0.8
Molyvan L	623±37	N	17.9±6.9	88.1±0.4	18.7±0.8	6.6±0.3
Ni Octoate	658±1.4	N	16.3±3.8	77.6±1.1	2.2±0.4	1.1±0.1
Reaction Time: 30 min		**Swelling Solvent: Isopropanol**		**Catalyst Added to the Swelling Solvent**		
Molyvan L	645±26	N	18.2±1.1	79.9±0.8	16.9±2.3	6.5±0.8
Molyvan L	NM	D	22.8±1.5	81.9±1.8	28.2±0.4	10.9±0.3
Ni Octoate	667±70	N	15.6±3.7	75.2±0.8	3.9±0.6	1.9±0.3
Reaction Time: 20 min		**Swelling Solvent: Isopropanol**		**Catalyst Added to the Swelling Solvent**		
Molyvan L	583±16	N	18.6±0.6	68.2±4.0	4.5±1.8	1.9±0.7
Ni Octoate	678±30	N	15.6±3.7	64.8±3.7	4.3±0.4	2.2±0.1

[a] A = agitated: samples were agitated with catalyst for 96 hr; N = not agitated for 96 hr swelling period; D = catalyst level doubled; NA = not applicable.

Table 7. Coal and Pyrene Conversions for SO_2 Treated Black Thunder Coal Reacted in 1-Methylnaphthalene at 410 °C

Catalyst Type	Catalyst Loading (ppm)	Conditions During Swelling	% ΔV	Coal Conversion (wt %)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Reaction Time: 30 min Swelling Solvent: None						
None	0	NA[a]	NA	47.3±1.1	1.5±1.1	0.7±0.7
Molyvan L	623±12	NA	NA	88.5±0.7	27.8±3.0	10.4±0.6
Ni Octoate	696±143	NA	NA	76.3±4.2	12.5±3.5	4.2±1.2
Reaction Time: 30 min Swelling Solvent: THF Catalyst Added to Reactor						
None	0	N[b]	87.6±2.7	58.0±9.5	0.0±0.0	0.0±0.0
Molyvan L	683±53	N	79.5±0.8	91.2±1.5	25.4±0.1	9.1±0.1
Ni Octoate	665±23	N	97.4±3.7	72.5±5.8	2.2±0.4	1.2±0.1
Reaction Time 30 min Swelling Solvent: THF Catalyst Added to Swelling Solvent						
Molyvan L	617±30	N	76.1±18.2	86.0±2.2	31.4±0.8	12.5±0.4
Ni Octoate	632±38	N	58.9±26.7	71.4±4.1	6.9±1.2	3.1±0.4
Reaction Time: 30 min Swelling Solvent: Methanol Catalyst Added to Reactor						
None	0	N	38.4±2.3	41.8±2.4	1.5±0.1	1.0±0.0
Molyvan L	672±18	N	36.9±7.4	90.0±1.3	30.0±4.4	11.2±1.5
Ni Octoate	655±2.1	N	31.6±7.4	78.7±1.1	4.9±0.8	1.8±0.6
Reaction Time: 30 min Swelling Solvent: Methanol Catalyst Added to Swelling Solvent						
Molyvan L	648±37	N	43.7±5.2	85.1±5.7	26.8±2.8	11.1±1.6
Ni Octoate	685±1	N	33.4±4.8	78.4±0.2	7.1±0.5	3.1±0.1
Reaction Time: 30 min Swelling Solvent: Isopropanol Catalyst Added to Reactor						
None	0	N	45.0±0.0	56.4±3.0	1.6±0.1	1.1±0.1
Molyvan L	642±25	N	38.6±5.0	91.3±0.6	21.3±2.4	8.0±1.1
Ni Octoate	674±26	N	32.3±6.4	73.9±5.1	3.9±0.6	2.1±0.0
Reaction Time: 30 min Swelling Solvent: Isopropanol Catalyst Added to Swelling Solvent						
Molyvan L	638±1.0	N	32.5±1.2	87.6±1.0	26.0±0.2	10.4±0.1
Ni Octoate	637±25	N	25.0±0.0	67.9±2.3	5.0±0.2	2.4±0.0

[a] NA = not applicable. [b] N = not agitated during 96 hrs swelling period.

The Molyvan L catalyst was more active for both untreated coal conversion and pyrene hydrogenation than was either NiOct or Mo naphthenate reacted without sulfur. Longer reaction times of 30 min resulted in higher coal and pyrene conversions than did shorter reaction times of 20 or 10 min. The type of swelling solvent used affected coal conversion, depending on the catalyst used. Methanol was particularly detrimental to Molyvan L. Agitation of the swelling solvent with coal and catalyst present did not increase coal conversion. Doubling the catalyst loading and the amount of catalyst impregnated into the coal yielded only a slight improvement in coal conversion but a more substantial improvement in pyrene conversion. When the coal conversion of coal impregnated with catalyst during the swelling process was compared to that achieved when the catalyst was added directly to the reactor, the Molyvan L systems with all three swelling solvents yielded less conversion with impregnated catalyst. For NiOct, all of the impregnated coals yielded less conversion than the coal reacted with the catalyst in the slurry phase. Pyrene conversions were also higher when the catalyst was added directly to the reactor.

Reactions with SO_2 treated coal showed that swelling of the pretreated coal had less effect on liquefaction behavior than swelling the untreated coal.[1,2] Impregnation of Molyvan L with any of the three swelling solvents resulted in approximately 5% less coal conversion than adding the catalyst directly to the reactor (Table 7). Pyrene conversion remained high with Molyvan L; in some reactions adding the catalyst directly to the reactor yielded more activity while in other reactions the impregnated catalyst was more active. The type of swelling solvent had a stronger influence on coal conversion when NiOct was used as a catalyst. Higher coal and pyrene conversions were achieved with NiOct when methanol was used as a swelling solvent than when either THF or isopropanol was used. More coal conversion was achieved with NiOct when NiOct was added directly to the reactor rather than being preswelled with coal. When methanol was used as a swelling solvent, pyrene conversion was less when the catalyst was preswelled with coal than when the catalyst was added directly to the reaction. The opposite result was obtained when isopropanol was used as the swelling solvent.

Liquefaction Reactions in V1074 at 410 °C. A series of reactions was performed using THF as the swelling solvent and coal-derived V1074 as the reaction solvent (Table 8). Comparison of the reaction solvent V1074 to 1-MN for liquefaction of untreated Black Thunder coal showed a higher coal conversion with Molyvan L when no swelling prior to liquefaction was used. This advantage of the coal-derived solvent was maintained when the coal was swelled prior to reaction and reacted without catalyst. However, when coal was swelled prior to liquefaction and Molyvan L was added either directly to the reactor or to the swelling solvent, the reaction solvent 1-MN yielded slightly higher coal conversion and nearly equivalent pyrene conversions. The coal and pyrene conversions were quite similar with NiOct in the two reaction solvents. The amount of coal conversion achieved with NiOct was similar regardless of the introduction method. By contrast, the highest coal conversion achieved with Molyvan L in V1074 occurred without prior swelling, followed by swelling with THF and adding Molyvan L to the reactor; the least coal conversion was obtained when Molyvan L was added to the THF swelling solvent. Substantial variability in coal and pyrene conversion occurred when Molyvan L was introduced into the swelling solvent indicating nonuniform absorption of the catalyst by the coal.

Liquefaction Reactions in Dihydroanthracene at 410 °C. Higher conversions of untreated Black Thunder coal occurred in DHA when no catalyst was used than occurred in the

Table 8. Coal and Pyrene Conversions for Untreated Black Thunder Coal Reacted in V1074 at 410 °C

Catalyst Type	Catalyst Loading (ppm)	Conditions During Swelling	% ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Reaction Time: 30 min Swelling Solvent: None Catalyst Added to Reactor						
Molyvan L	652±18	NA[a]	NA	84.7±1.0	14.9±2.8	5.7±1.1
Ni Octoate	668±41	NA	NA	79.8±3.5	5.5±4.4	2.0±1.6
Reaction Time: 30 min Swelling Solvent: THF Catalyst Added to Reactor						
None	0	N[b]	25.0±3.3	72.0±1.7	5.3±0.1	3.0±0.1
Molyvan L	670±57	N	38.7±9.7	82.8±2.0	28.0±0.3	11.8±0.3
Ni Octoate	663±4.2	N	35.0±4.5	77.2±1.8	6.4±0.0	3.3±0.1
Reaction Time: 30 min Swelling Solvent: THF Catalyst Added to Swelling Solvent						
Molyvan L	648±0.0	N	38.3±1.1	76.0±8.1	14.1±2.3	6.1±0.8
Ni Octoate	683±0.5	N	26.7±0.8	79.5±3.5	4.6±1.5	2.5±0.7

[a] NA = not applicable. [b] N = not agitated for 96 hr swelling period.

other two reaction solvents (Table 9). The hydrogen donor solvent promoted noncatalytic conversion of Black Thunder coal yielding 82.4% coal conversion after swelling in THF while 72.0% was achieved in V1074 and 59.7% in 1-MN. The highest coal conversion with Molyvan L in DHA was achieved without prior swelling, intermediate coal conversion occurred with swelling in THF and catalyst added directly to the reactor, while the lowest coal conversion occurred when the catalyst was added to the swelling solvent. The difference between the high and low values, though, was only 5%. Pyrene conversion was highest in DHA when Molyvan L was added directly to the reactor after the coal had been preswelled in THF. The addition of the catalyst to the THF swelling solvent was detrimental to pyrene conversion reducing the amount from 23.5% when the catalyst was added directly to the reactor to 8.9% when preswelled with THF.

Effect of Catalyst Introduction Method in Coal and Pyrene Conversion at the Two Reaction Temperatures. The effect of catalyst introduction method on coal and pyrene conversions at 385 and 410 °C was evaluated. In Table 10, the difference in coal conversion between placing the catalyst in the swelling solvent (Method A) or placing the catalyst directly in the reactor (Method B) was evaluated. The difference of Method A-Method B yielded a positive number when the swelling solvent method yielded more coal conversion than the direct addition method. A negative value was obtained when the direct catalyst addition yielded more coal conversion than addition of the catalyst to the swelling solvent. The effect of the catalyst introduction on pyrene conversion is given in Table 11. The same terminology, definitions, and sign conventions are used in Table 11 as in Table 10.

MoNaph plus sulfur was the only catalyst which gave a positive difference indicating that

Table 9. Coal and Pyrene Conversions for Untreated Black Thunder Coal Reacted in Dihydroanthracene at 410 °C

Catalyst Type	Catalyst Loading (ppm)	Conditions During Swelling	% ΔV	Coal Conversion (mol %)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Reaction Time: 30 min		**Swelling Solvent: None**		**Catalyst Added to Reactor**		
Molyvan L	677±23	NA[a]	NA	89.7±0.2	15.2±4.5	5.4±1.8
Reaction Time: 30 min		**Swelling Solvent: THF**		**Catalyst Added to Reactor**		
None	0	N[b]	36.5±2.3	82.4±2.1	9.3±0.2	6.0±0.1
Molyvan L	658±33	N	22.2±0.7	87.3±2.8	23.5±4.7	9.4±1.8
Reaction Time: 30 min		**Swelling Solvent: THF**		**Catalyst Added to Swelling Solvent**		
Molyvan L	641±41	N	41.0±6.4	84.5±0.4	8.9±2.3	4.6±0.8

[a] NA = not applicable. [b] N = not agitated for 96 hr swelling period.

Table 10. Difference in Coal Conversions between Placing Catalyst in Swelling Solvent or into the Reactor at Liquefaction Temperatures of 410 and 385 °C

Catalyst	Method A[1] Coal Conversion	Method B[2] Coal Conversion	Method A-Method B	Method A Standard Deviation	Method B Standard Deviation
Coal: untreated Swelling Solvent: THF Temperature 410 °C					
MoNaph + S	89.9	89.8	+ 0.1	0.1	1.2
Molyvan L	81.9	87.3	- 5.4	1.6	1.6
Ni Octoate	74.8	77.0	- 2.2	12.9	0.1
Coal: untreated Swelling Solvent: THF Temperature: 385 °C					
MoNaph + S	76.8	73.8	+ 3.0	0.3	1.6
Molyvan L	50.4	72.1	-21.7	3.7	3.5
Ni Octoate	57.0	69.4	-12.4	1.0	7.8
Coal: untreated Swelling Solvent: Methanol Temperature: 410 °C					
Molyvan L	68.4	88.0	-19.6	0.0	0.9
Ni Octoate	70.1	85.5	-15.4	1.1	0.1
Coal: untreated Swelling Solvent: Isopropanol Temperature: 410 °C					
Molyvan L	79.9	88.1	- 8.2	0.8	0.4
Ni Octoate	75.2	77.6	- 2.4	0.8	1.1
Coal: SO_2 treated Swelling Solvent: THF Temperature: 410 °C					
Molyvan L	86.0	91.2	- 5.2	2.2	1.5
Ni Octoate	71.4	72.5	- 1.1	4.1	5.8
Coal: SO_2 treated Swelling Solvent: Methanol Temperature: 410 °C					
Molyvan L	85.1	90.0	- 4.9	5.7	1.3
Ni octoate	78.4	78.7	- 0.3	0.2	1.1
Coal: SO_2 treated Swelling Solvent: Isopropanol Temperature: 410 °C					
Molyvan L	87.6	91.3	- 3.7	1.0	0.6
Ni Octoate	67.9	73.9	- 6.0	2.3	5.1
Coal: untreated Swelling Solvent: Isopropanol Temperature: 385 °C					
MoNaph + S	79.3	80.0	−0.7	3.8	7.9
Molyvan L	55.9	76.7	−20.8	0.3	0.3
Ni Octoate	62.2	65.3	−3.1	2.7	0.9

1: Method A - Catalyst placed into swelling solvent for 96 hours with coal.
2: Method B - Catalyst placed directly into the reactor.

Table 11. Difference in Pyrene Conversions between Placing Catalyst in Swelling Solvent or into Reactor at Liquefaction Temperatures of 410 and 385 °C

Catalyst	Pyrene Conversion Method A[1]	Pyrene Conversion Method B[2]	Method A - Method B	Method A Standard Deviation	Method B Standard Deviation
Coal: untreated		Swelling Solvent: THF		Temperature: 410 °C	
MoNaph + S	26.0	24.8	+ 1.2	0.5	0.8
Molyvan L	15.1	18.6	−3.5	1.8	1.3
Ni Octoate	11.1	2.4	+8.7	11.0	0.1
Coal: untreated		Swelling Solvent: THF		Temperature: 385 °C	
MoNaph + S	35.4	34.4	+1.0	0.1	1.5
Molyvan L	4.5	25.7	−21.2	1.0	7.2
Ni Octoate	3.6	16.2	−12.6	0.1	11.2
Coal: untreated		Swelling Solvent: Methanol		Temperature: 410 °C	
Molyvan L	3.0	24.3	−21.3	0.8	1.8
Ni Octoate	3.5	10.9	−7.4	0.4	0.4
Coal: untreated		Swelling Solvent: Isopropanol		Temperature: 410 °C	
Molyvan L	16.9	18.7	−1.8	2.3	0.8
Ni Octoate	3.9	2.2	+1.7	0.6	0.4
Coal: untreated		Swelling Solvent: Isopropanol		Temperature: 385 °C	
MoNaph + S	32.3	29.0	+3.3	0.8	1.8
Molyvan L	5.0	23.1	−18.1	0.4	8.0
Ni Octoate	5.0	7.7	−2.7	0.4	1.3
Coal: treated		Swelling Solvent: THF		Temperature: 410 °C	
Molyvan L	31.4	25.4	+6.0	0.8	0.1
Ni Octoate	6.9	2.2	+4.7	1.2	0.4
Coal: SO_2 treated		Swelling Solvent: Methanol		Temperature: 410 °C	
Molyvan L	26.8	30.0	−3.2	2.8	4.4
Ni Octoate	7.1	4.9	+2.2	0.5	0.8
Coal: SO_2 treated		Swelling Solvent: Isopropanol		Temperature: 410 °C	
Molyvan L	26.0	21.3	+4.7	0.2	2.4
Ni Octoate	5.0	3.9	+1.1	0.2	0.6

1: Method A - catalyst placed into swelling solvent for 96 hours with coal.
2: Method B - catalyst placed directly into the reactor.

more coal conversion was achieved when catalyst was introduced in the swelling solvent than in the reactor. A positive value of 3.0 was obtained at 385 °C while a positive value of 0.1 was obtained at 410 °C. All of the other reaction systems contained Molyvan L or NiOct which were reacted at either 385 or 410 °C. The largest differences for those two catalyst occurred at 385 °C using THF or isopropanol as the swelling solvent. All of these differences were negative. At 410 °C the largest differences were obtained for both catalysts in systems that used methanol and untreated Black Thunder coal. Again these differences were negative, indicating that contact with the swelling solvent and impregnation into the coal structure was detrimental to the catalytic activity of Molyvan L or NiOct. The untreated Black Thunder was more sensitive to the method of catalyst introduction than the SO_2 treated coal.

The effect of catalyst introduction method for pyrene conversion gave a somewhat different result. Nearly one-half of the reactions using both untreated and SO_2 treated coals yielded positive pyrene conversions. This result indicated that pyrene conversion was not as adversely affected by preswelling the catalyst with coal catalyst as was coal conversion.

Summary

The improvement in coal conversion expected by impregnating slurry phase catalysts into the coal pores during swelling prior to liquefaction was not achieved. Swelling of untreated Black Thunder coal increased the accessibility of the interstices of the coal structure to the catalyst and increased coal reactivity under liquefaction conditions. However, absorbing the catalyst into coal, prior to liquefaction, thereby making the catalyst more accessible to the dissolving coal molecule, did not necessarily achieve increased coal conversion. In fact, only Mo naphthenate with sulfur showed improved coal conversions with the swelling process.

Neither Molyvan L nor Ni octoate showed any improvement in coal conversion with preswelling. Pyrene conversion and hydrogenation provided a sensitive measure of catalyst activity. Pyrene conversion showed a more positive response to swelling the catalyst with coal than did coal conversion.

References for Part II

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Part III

EFFECT OF SWELLING AND REACTION PARAMETERS ON CATALYTIC ACTIVITY

Abstract

The conceptual process of swelling coal with slurry phase catalyst and then liquefying the coal was tested further. Swelling and reaction parameters were evaluated and included the composition of the reaction solvent, composition of the swelling solvent, catalyst loading and swelling time. Since Molyvan L had been proven in pilot scale continuous reactions at the Wilsonville Coal Liquefaction Research facility, the effect of swelling parameter of the activity and stability of Molyvan L was evaluated, in particular. The activity of Molyvan L like the other catalysts tested, was sensitive to the particular swelling solvent used. Addition of a carbon black support to the slurry phase Mo naphthenate only served to decrease the reactivity of the entire system. A variety of slurry phase catalysts were tested in the conceptual process using either isopropanol or isopropanol and water as the swelling solvent and a hydrogen donor-enriched coal-derived solvent as the reaction solvent. The Mo catalysts showed the most activity followed by the Ni catalysts with Co catalyst showing the least activity.

Introduction

In Part III of this report, a number of parameters that affected the preswelling and liquefaction reactions were investigated. The parameters included the composition of the reaction solvent, composition of the swelling solvent, catalyst loading, and swelling time. In addition, several different types of experiments were performed evaluating Molyvan L stability. These experiments included examining the effect of contact between the swelling solvent and Molyvan L and evaluating the effect adding phosphorus to Molyvan 822, which was a similar additive to Molyvan L, but did not contain phosphorus. The effect of adding a solid support such as carbon black to the system was also evaluated.

The conceptual process described in Part II was expanded to include a variety of slurry phase and powdered catalysts. These catalysts included metals of Mo, Ni and Co. The swelling solvent isopropanol was used since contact with isopropanol seemed to have a less deleterious effect on the catalyst than THF. One of the catalysts tested was not soluble in isopropanol so that a swelling solvent of 20% isopropanol and 80% water was used. The reaction solvent was composed of 80% coal-derived V1074 and 20% DHA. This solvent was chosen to simulate a hydrogenated coal recycle solvent.

Experimental

Materials. Liquefaction reactions were performed using untreated and aqueous SO_2 treated Black Thunder coals. The swelling solvents, THF, methanol, isopropanol, and toluene were obtained from Fisher Scientific and were used as received. Distilled water was also used as a swelling solvent. The liquefaction reaction solvents used were 1-methylnaphthalene (1-MN) (98% purity) and 9,10-dihydroanthracene (DHA), which were obtained from Aldrich, and

V1074, a coal-derived solvent, from the Wilsonville Coal Liquefaction Research Facility. The catalysts used were Molyvan L and Molyvan 822 from Vanderbilt Chemical; Mo naphthenate, Ni octoate, Ni acetylacetonate, and Ni citrate from Shepherd Chemical Company; and Ni naphthenate, molybdic oxide, molybdenum dioxide bis acetylacetonate, and ammonium tetrathiomolybdate from Strem Chemical Company. Carbon black, Regal 660, from Cabot Industries was used as a solid support for Mo naphthenate. Triphenylphosphine obtained from Aldrich was used as a phosphorous additive.

Swelling and Reaction Procedures. Untreated and SO_2 treated Black Thunder coals were swelled by introducing 1.33 g maf coal to the swelling tube and then adding 7 ml of solvent. Catalysts were charged to the swelling solvent at 1.05 times 600 to 800 ppm of active metal, the amount used when the catalyst was added directly to the liquefaction reactions. The coal was then allowed to sit unagitated in the swelling solvent for 96 hr. Reactions were also performed at lower catalyst loading of 100-150 ppm and higher catalyst loading of 1400 to 1600 ppm. Catalyst uptake into the coal during preswelling averaged ~92% of the catalyst introduced into the swelling solvent.

Liquefaction reactions using untreated Black Thunder coal were performed using a reaction solvent of either 1-MN, DHA or V1074 at 410 °C for 30 min in stainless steel tubular reactors. Each reaction contained ~1.33 g of maf coal, 2 g of solvent, 0.67 g of pyrene and residual swelling solvent that remained in the swelled coal. The amount of solvent absorbed in the coal after swelling differed for each swelling solvent. The amount of solvent retained in the coal ranged from 0.6 to 1.0 times the coal mass. The amount of catalyst taken up by coal was obtained for selected reactions using X-ray fluorescence spectroscopy. Hydrogen gas was introduced at 1250 psig at ambient temperature. The reactor was well-agitated at 450 cpm. The recovery of the reaction material from the reactors was typically 95% or higher.

Reaction Using Carbon Black as a Catalyst Support. Experiments were performed in which Cabot Regal 660 carbon black was used as a solid support for Mo naphthenate, a slurry phase catalyst. Four sets of experiments were performed: (1) carbon black and catalyst were placed directly in the reactor; (2) carbon black was placed in the reactor but the catalyst was placed with coal in the swelling solvent; (3) carbon black was placed in the swelling solvent with coal and the catalyst was added to the reactor; and (4) carbon black and catalyst were placed into the swelling solvent with coal for 96 hr. Baseline experiments without carbon black were also performed. The swelling solvent used was THF and the reaction solvent was 1-MN. Sulfur was added to the reactor at a 3:1 weight ratio of S: Mo. The reaction procedures followed the previously described procedures.

Catalyst Screening Experiments. Untreated Black Thunder coal was swelled in isopropanol or 20% isopropanol and 80% water using the same swelling conditions as given above. The slurry phase catalysts, Mo naphthenate, Ni octoate, Co naphthenate, Ni naphthenate, Molyvan L and Molyvan 822 as well as the powder catalysts, MoO_3 , MoO_2AcAc, $(NH_4)_2MoS_4$, Ni acetylacetonate and Ni citrate were used. The slurry phase catalysts were introduced at 600-800 ppm of active metal. The swelling solvent isopropanol was used for the majority of the catalysts, while a 20% isopropanol and 80% water mixture was used only for $(NH_4)_2MoS_4$ for solubility reasons. Molyvan L, Molyvan 822, and Ni naphthenate were tested in both swelling solvents. The coal and catalysts were allowed to sit unagitated in the swelling solvent for 96 hours. The liquefaction solvent used was a mixture of 20% DHA in V1074. The liquefaction conditions used were the same as described above.

Reactions with Added Phosphorus. Molyvan L from Vanderbilt is a sulfurized oxymolybdenum organophosphordithioate which was designed as an antiwear agent. Molyvan 822 from Vanderbilt is an organo molybdenum dithiocarbamate which was designed to be a nonphosphorus containing antifriction agent. Both compounds are soluble in petroleum oils but are insoluble in water. The effect of adding phosphorus in the form of triphenylphosphine to the thermal and catalytic to the reactions was investigated. The experimental set that was performed included: (1) catalyst and phosphorus being added to the reactor; and (2) the catalyst being added to the swelling solvent and the phosphorus to the reactor. The swelling solvent was THF and the reaction solvent was 1-MN. The phosphorus was added at a level of 1300 to 1550 ppm on the basis of the coal charge. Baseline reactions were also performed in which phosphorus was added to the reactor in a noncatalytic reactor.

Analysis. Products from the liquefaction reactions were removed from the reactor with THF. The conversion of the coal to THF solubles was determined. For the reactions where analysis of catalyst uptake was obtained, the values for the catalyst loading are given; otherwise, the presumed amount deposited ranged from 90 and 95% of the 600 to 800 ppm of active metal loading on a per gram of coal basis. The amount of pyrene hydrogenation to hydrogenated products was obtained by gas chromatographic analysis using a Varian Model 3400, a J&W DB-5 fused silica capillary column and flame ionization detection. Pyrene hydrogenation is defined as the moles of hydrogen required to form the liquid hydrogenation products from pyrene as a percentage of the moles of hydrogen required to form the most hydrogenated product, perhydropyrene. The hydrogenation products obtained from pyrene were dihydropyrene (DHP), tetrahydropyrene (THP) and hexahydropyrene (HHP).

Results and Discussion

In Part II of this report, the effect of reaction temperature on the reaction systems was described. The higher temperature reactions at 410 °C, showed greater activity for the Molyvan L and NiOct catalysts than did the reactions at 385 °C. At the lower reaction temperature the catalytic species active for coal and pyrene conversion did not form from either Molyvan L or NiOct when they had been preswelled and impregnated into coal. By contrast, Mo naphthenate did form an active catalytic species and was effective for coal and pyrene conversions at 385 °C although higher conversions were achieved at 410 °C as described herein. Several different reaction sequences were performed and compared at 410 °C. Reactions with Molyvan L and NiOct being added directly to the reactor were more effective for coal and pyrene conversions than when these two catalysts were impregnated into coal and had contact with the swelling solvent.

The research performed in Part III evaluated a number of different reaction parameters and their effect on conversion of untreated Black Thunder coal and on pyrene conversion and hydrogenation. Among the parameters examined were the reaction solvent composition, swelling solvent composition, swelling time, catalyst loading and catalyst type.

Reaction Solvent. The effect of the reaction solvent on the conversion of untreated Black Thunder coal and pyrene is described in Table 12. The effect of the reaction solvent was dependent upon the reaction system and the catalyst introduction method. When THF was used as the swelling solvent, the reaction solvent had much less effect on coal conversion when the catalyst was added directly to the reactor than when the catalyst was impregnated into coal.

Table 12. Effect of Reaction Solvent on Untreated Black Thunder Coal and Pyrene Conversions[a]

Reaction Solvent	Catalyst Type	Coal Conversion (wt%)	Pyrene Conversion (mol%)	Pyrene Hydrogenation (%)
Swelling Solvent: THF		**Catalyst added to THF**		
1-Methylnaphthalene	Molyvan L	81.9±1.6	15.1±1.8	5.7±0.4
V1074	Molyvan L	76.0±8.1	14.1±2.3	6.1±0.8
DHA	Molyvan L	84.5±0.4	8.9±2.3	4.6±0.8
1-Methylnaphthalene	Ni Octoate	74.8±12.9	11.1±11.0	4.7±4.1
V1074	Ni Octoate	79.5±3.5	4.6±1.5	2.5±0.7
Swelling Solvent: THF		**Catalyst added to Reactor**		
1-Methylnaphthalene	Molyvan L	87.3±1.6	18.6±1.3	6.2±0.4
V1074	Molyvan L	82.8±2.0	28.0±0.3	11.8±0.3
DHA	Molyvan L	87.3±2.8	23.5±4.7	9.4±1.8
1-Methylnaphthalene	Ni Octoate	77.0±0.1	2.4±0.1	1.2±0.1
V1074	Ni Octoate	77.2±1.8	6.4±0.0	3.3±0.1
Swelling Solvent: Isopropanol		**Catalyst added to Isopropanol**		
1-Methylnaphthalene	Molyvan L	79.9±0.8	16.9±2.3	6.5±0.8
20% DHA 80% V1074	Molyvan L	81.2±1.1	7.7±1.6	3.6±0.6
1-Methylnaphthalene	Molyvan 822	83.3±0.8	24.3±0.1	9.6±0.1
20% DHA 80% V1074	Molyvan 822	88.0±0.1	21.0±1.1	9.1±0.6
1-Methylnaphthalene	Ni Octoate	75.2±0.8	3.9±0.6	1.9±0.3
20% DHA 80% V1074	Ni Octoate	75.3±1.5	5.7±2.5	2.9±0.8
Swelling Solvent: Isopropanol		**Catalyst added to Reactor**		
1-Methylnaphthalene	Molyvan L	88.1±0.4	18.7±0.8	6.6±0.3
1-Methylnaphthalene	Ni Octoate	77.6±1.1	2.2±0.4	1.1±0.1

[a] Conditions: Swelled for 96 hr; reacted at 410 °C for 30 min with 1250 psi H_2 introduced at ambient temperature.

Direct catalyst addition resulted in equivalent coal conversion of 87% with Molyvan L in 1-MN and DHA as reactions solvents; only V1074 showed a lower conversion of 82.8%. Pyrene conversion, however, followed an opposite trend with V1074 yielding the highest value and 1-MN the lowest. The catalyst NiOct gave equivalent coal conversions and similar pyrene conversions when added directly to either 1-MN or DHA.

When the catalysts were preswelled in THF with coal, the reaction solvent influenced coal conversion to a greater extent than when the catalyst was added directly to the reactor. The hydrogen donor solvent, DHA, yielded the highest coal conversion at 84.5%, followed by an intermediate conversion in 1-MN at 81.9%, and the lowest conversion in V1074 at 76%. Each respective conversion was less than when the catalyst was added directly to the reactor. Pyrene conversion was also less and ranked in a different order when the catalyst was impregnated into coal during preswelling. NiOct when preswelled with coal in THF also was influenced by the reaction solvent with V1074 being a more effective solvent for coal conversion but a less effective solvent for pyrene conversion than 1-MN.

In these reaction systems, contact of Molyvan L with THF and coal prior to liquefaction had a deleterious effect on both coal conversion and pyrene conversion. Since the Molyvan L catalyst seemed to be rendered less effective by preswelling in THF, the reaction solvents had a greater influence on the reactivity of the system. The hydrogen donor solvent under these less favorable catalytic conditions affected the conversion more positively than the other swelling solvents. The NiOct catalyst did not appear to be as strongly affected by THF in preswelling conditions as Molyvan L. Hence, the reaction solvents had a lesser effect on coal conversion in the presence of NiOct than in the presence of Molyvan L.

Three different catalyst were used with isopropanol as the swelling solvent; these catalysts were Molyvan L, Molyvan 822, and NiOct. Two different reaction solvents were used, the relatively inert 1-MN and a solvent mixture of 20% DHA and 80% V1074 which modeled a coal-derived solvent with hydrogen donor capability. Molyvan L and NiOct, which were directly added to the reactor containing 1-MN as the reaction solvent, yielded higher coal conversions than when these catalysts were impregnated into coal. Both Mo catalysts when impregnated into coal yielded higher coal conversions when reacted in the 20% DHA and 80% V1074 solvent than when reacted in 1-MN. However, the opposite result was obtained with pyrene conversion. The impregnated NiOct catalytic systems were insensitive to the reaction solvent and were also much less sensitive than the Mo catalyst to the method of catalyst introduction.

Swelling Solvent. The effect of the chemical composition of the swelling solvent on conversion of untreated Black Thunder coal that had been swelled with a catalyst is presented in Table 13. The effect of the swelling solvent on pyrene conversion is also presented. In the first set of reactions, the reaction solvent used was 1-MN. The swelling solvents ranged in their ability to swell the untreated coal. The 40% THF and 60% H_2O swelling system with Molyvan L yielded the greatest percent change in volume (%ΔV) of 62.4%; while the same swelling solvent with Molyvan 822 gave a %ΔV of 44.2%. THF was also very effective in swelling coal with Molyvan L present. The %ΔV ranged from 40% for the typical addition of Molyvan L to 7 ml of solvent followed by 96 hr of swelling to 55.8% where Molyvan L was added to the coal by treating the coal with 1.5 ml of THF containing Molyvan L followed by 96 hr of swelling in 7 ml of THF. The methanol and isopropanol systems increased the coal volume the least, giving %ΔV's of 25% or less.

Table 13. Effect of Swelling Solvent on Untreated Black Thunder Coal and Pyrene Conversions[a]

Swelling Solvent	Catalyst Type	%ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol%)	Pyrene Hydrogenation (%)
Reaction Solvent: 1-Methylnaphthalene				**Catalyst Added to Swelling Solvent**	
THF	MoNaphthenate + S	35.1±11.0	89.9±0.1	26.0±0.5	10.7±0.2
THF	Molyvan L	40.4±1.8	81.9±1.6	15.1±1.8	5.7±0.4
Methanol	Molyvan L	25.2±4.9	68.4±0.0	3.0±0.8	1.9±0.1
Isopropanol	Molyvan L	18.2±1.1	79.9±0.8	16.9±2.3	6.5±0.8
40% THF/60% H_2O	Molyvan L	62.4±20.6	81.3±7.1	25.1±13.7	13.7±0.2
20% Isopropanol/80% Water	Molyvan L	25.0±3.3	89.6±1.6	34.7±2.9	15.0±2.0
20% Isopropanol/80% Toluene	Molyvan L	21.4±3.4	60.7±1.2	4.8±0.6	2.4±0.1
Water	Molyvan L	6.7±3.0	80.1±3.1	25.0±2.2	9.9±0.7
1.5 ml THF(1)[b]	Molyvan L	20.1±3.7	77.7±4.7	22.8±2.3	8.6±1.1
1.5 ml THF(2)[c]	Molyvan L	55.8±4.7	84.1±1.8	15.4±7.5	6.1±2.8
1.5 ml THF(3)[d]	Molyvan L	49.1±14.1	72.9±1.6	21.4±1.4	8.2±0.2
1-MN + 1.5ml THF[e]	Molyvan L	29.7±5.1	50.8±0.2	3.2±0.6	2.1±0.2
Isopropanol	Molyvan 822	23.9±1.6	83.3±0.8	24.3±0.1	9.6±0.1
20% Isopropanol/80% Water	Molyvan 822	34.1±5.7	60.6±0.1	4.6±0.5	2.4±0.5
40% THF/60% H_2O	Molyvan 822	44.2±1.8	69.4±7.4	9.8±5.1	4.0±1.8
THF	Ni Octoate	38.9±5.7	74.8±12.9	11.1±11.0	4.7±4.1
Methanol	Ni Octoate	23.3±0.8	70.1±1.1	3.5±0.4	1.9±0.1
Isopropanol	Ni Octoate	15.6±3.7	75.2±0.8	12.9±1.3	2.2±0.1
Reaction Solvent: 20% DHA-80% V1074				**Catalyst added to Swelling Solvent**	
Isopropanol	MoNaphthenate + S	10.9±3.0	85.3±0.6	21.3±1.4	9.9±0.6
Isopropanol	Molyvan L	20.1±3.7	81.2±1.1	7.7±1.6	3.6±0.6
20% Isopropanol/80% Water	Molyvan L	28.0±0.9	87.5±1.9	28.6±1.9	11.5±0.6
Isopropanol	Molyvan 822	26.7±0.8	88.0±0.1	21.0±1.1	9.1±0.6
20% Isopropanol/80% Water	Molyvan 822	38.7±3.2	83.2±2.8	11.5±0.9	5.0±0.4
Isopropanol	Ni Octoate	17.8±0.6	75.3±1.5	5.7±2.5	2.9±0.8
Isopropanol	Ni Naphthenate	25.7±4.2	85.5±1.5	11.4±0.7	5.1±0.2
20% Isopropanol/80% Water	Ni Naphthenate	23.8±0.0	84.5±2.3	12.1±2.9	5.2±0.8

[a] Conditions: Swelled for 96 hr; reacted at 410 °C for 30 min with 1250 psi H_2 introduced at ambient temperature; catalyst loading at 600 to 800 ppm. [b] Catalyst impregnated into coal and reacted immediately.
Catalyst impregnated into coal, swelled for 96 hr in THF, and then reacted.
Catalyst impregnated into coal, swelled for 96 hr in THF, dried for 24 hr and then reacted.
[e] Swelling solvent 1-MN was introduced after the coal had been contacted with 1.5 ml THF to open the pores.

No correlation was apparent between the %ΔV and the amount of coal conversion achieved with Molyvan L reacted in 1-MN. The highest coal conversion of 89.6% occurred with the swelling solvent mixture of 20% isopropanol and 80% water, but the %ΔV for the system was only 25%. Coal preswelled with isopropanol, THF, and the mixture of 40% THF and 60% water which had %ΔV's which ranged from 18.2% to 62.4% gave similar coal conversion of 80 to 81%. Methanol was particularly ineffectual as a swelling solvent for Molyvan L yielding only 68.4% coal conversion. The hydrocarbon solvents of toluene in a mixture of 20% isopropanol and 80% toluene and 1-MN introduced after the coal was contacted with 1.5 ml of THF to open the coal pores yielding low coal conversions of 60.7% and 50.8%, respectively. Although both of these swelling solvents yielded %ΔV's of more than 20%, the hydrocarbon solvents were ineffectual in impregnating the catalysts into coal.

Pyrene conversion in the reactions with Molyvan L also reflected the effect of the swelling solvent. The highest pyrene conversion of 34.7% was obtained after coal had been swelled with 20% isopropanol and 80% water. The next most effective swelling solvent was 40% THF and 60% water which yielded 25.1% pyrene conversion. These swelling solvents mixtures evidently opened the coal pores sufficiently to allow Molyvan L to penetrate but were not detrimental to its catalytic activity. Both THF and isopropanol gave similar pyrene conversion of 15 to 17%; although these swelling solvents opened the coal pore structure allowing catalyst access as evidenced by the coal conversion achieved, both swelling solvents were detrimental to Molyvan L catalytic activity as measured by pyrene conversion and hydrogenation.

Molyvan 822 was sensitive to the type of swelling solvent used when liquefied in 1-MN.

The swelling solvents, isopropanol, 20% isopropanol and 80% water, and 40% THF and 60% water, increased the coal volume by ~24, 34, and 44%, respectively. Swelling in isopropanol yielded a coal conversion of 83.3% while the water containing swelling solvents were highly detrimental to the activity of Molyvan 822, giving lower coal conversion. The 20% isopropanol and 80% water system yielded a coal conversion of 60.6% while 40% THF and 60% water yielded a higher coal conversion of 69%. In these two swelling solvent systems the increase in the organic fraction of the swelling solvent and the consequent decrease in the percentage of water improved both coal and pyrene conversion which indicates that Molyvan 822 catalytic activity was negatively affected by water.

The catalyst NiOct was also affected by the swelling solvent but not to the same extent as was Molyvan L. Similar coal conversions of ~75% were obtained with THF and isopropanol. The coal impregnated in the presence of methanol yielded less conversion of 70.1%. The pyrene conversion reflected a larger effect of the swelling solvent on NiOct activity. NiOct after contact with swelling solvents, THF and isopropanol, yielded pyrene conversion between 11 and 13% while after contact with methanol only 3.5% pyrene conversion was achieved.

When the reaction solvent was the coal-derived V1074 to which the hydrogen donor DHA had been added, the type of swelling solvent used still affected the amount of coal conversion achieved. When reacted under the same liquefaction conditions, both Molyvan L and Molyvan 822 were affected by the composition of the swelling solvent. Molyvan L gave higher coal and pyrene conversions when preswelled in 20% isopropanol/80% water compared to isopropanol. In contrast, Molyvan 822 was positively affected by preswelling in isopropanol and negatively affected by the water present in the 20% isopropanol/80% water mixture. When Ni naphthenate was used, the swelling solvent had little effect on the amount of coal or pyrene conversion.

Catalyst Loading. The effect of Molyvan L catalyst loading on coal and pyrene conversion as a function of the three swelling solvents is demonstrated in Table 14. The amount of Molyvan L introduced into THF was 600-800 ppm of Mo on a maf coal basis as a standard loading and the amount was then doubled to 1200-1600 ppm. Reactions were also performed at a low loading level of 100-150 ppm of Mo on a maf coal basis. Doubling of catalyst loading when Molyvan L was swelled with coal in THF only increased coal conversion from 81.9% to 84.8%; however, pyrene conversion increased substantially from 15.1 to 28.6%. The effect of doubling the Molyvan L loading, when methanol was used as a swelling solvent, was more substantial. Coal conversion increased from 68.4% at the standard loading level to 88.8% while the pyrene conversion increased from 3.0% to 25.7%. The methanol swelling solvent system evidently depressed Molyvan L activity or access of Molyvan L to the coal pores. Doubling the amount of Molyvan L overcame these barriers and substantially increased the activity of the system.

The effect of Molyvan L loading on coal and pyrene conversions was also examined using isopropanol as the swelling solvent. Four different methods of catalyst introduction were evaluated. The initial loading level of Molyvan L was 600 to 800 ppm yielding 79.9% conversion. Doubling the amount only increased coal conversion to 81.9% although pyrene conversion increased from 16.9 to 28.2%. The increased amount of catalyst available to the system affected pyrene hydrogenation but had little effect on coal conversion.

Introducing Molyvan L at the low of 100-150 ppm resulted in low coal conversions in the range of 51 to 54% for all three swelling solvents. Pyrene conversions were also low at 1.8

Table 14. Effect of Molyvan L Loading on Untreated Black Thunder Coal and Pyrene Conversions[a]

Swelling Solvent	Catalyst Loading (ppm)	Coal Conversion (wt%)	Pyrene Conversion (mol%)	Pyrene Hydrogenation (%)
Reaction Solvent: 1-Methylnaphthalene			**Catalyst Added to Swelling Solvent**	
THF	100-150	53.7±1.3	2.1±1.3	1.3±0.0
THF	600-800	81.9±1.6	15.1±1.8	5.7±1.9
THF	1200-1600	84.8±1.1	28.6±2.5	11.0±1.2
Methanol	100-150	53.1±2.3	2.1±0.4	1.3±0.2
Methanol	600-800	68.4±0.0	3.0±0.8	1.7±0.5
Methanol	1200-1600	88.8±0.5	25.7±2.7	9.9±1.3
Isopropanol	100-150	51.6±4.0	1.8±0.4	1.2±0.1
Isopropanol	600-800	79.9±0.8	16.9±2.3	6.5±0.8
Isopropanol	1200-1600	81.9±1.8	28.2±0.4	10.9±0.3
Isopropanol	600-800 SS[b] 600-800 R[c]	87.3±1.3	25.9±0.8	10.4±0.4
Isopropanol	300-400 SS 300-400 R	83.0±1.8	17.7±7.9	7.1±3.3

[a] Conditions: Swelling for 96 hr, reacted at 410 °C for 30 min with 1250 psi H_2 introduced at ambient temperature.

[b] SS = added directly to swelling solvent.

[c] R = added directly to reactor.

to 2.1%. Introduction of Molyvan L at 100-150 ppm to the swelling was ineffectual for catalyzing the coal reaction system. The coal conversions achieved were in the range of thermal reactions although the presence of Molyvan L was detectable in the system since some pyrene conversion occurred.

The next two experiments evaluated combining impregnated catalyst with catalyst added directly to the reactor. When half the normal loading, 300-400 ppm, was added to the swelling solvent and the other half to the reactor, more coal conversion, 83%, and more pyrene conversion, 17.7%, were achieved than when that amount of Molyvan L was impregnated into coal. When the doubled loading amount was split between the swelling solvent and reactor, the coal conversion increased to 87.3% while the pyrene conversion remained high at 25.7%. Direct access of the liquefying coal to slurry phase Molyvan L was beneficial at both loading levels. Several factors may have caused this effect: (1) contact of isopropanol with Molyvan L may have limited its catalytic activity, and/or (2) the impregnated catalyst may not have been available to all of the reacting coal sites. Therefore, when the catalyst was in the slurry phase, the catalyst may have had access to more of the reacting sites than when it was impregnated into the coal.

Swelling Time. Liquefaction reactions were performed at 410 °C with untreated Black Thunder coal that had been preswelled in THF or isopropanol with Molyvan L for 12, 24, 48 and 96 hours. These data are given in Table 15. The initial time of no contact between the catalyst and the swelling solvent is designated as catalyst being added directly to the reactor. The reaction systems preswelled in THF were reacted in V1074 and 1-MN while the system preswelled in isopropanol was reacted in 1-MN.

Table 15. Effect of Swelling Time on Untreated Black Thunder Coal and Pyrene Conversions[a]

Swelling Time (hr)	%ΔV	Coal Conversion (wt%)	Pyrene Conversion (%)	Pyrene Hydrogenation
Swelling Solvent: THF	Reaction Solvent: V1074		Catalyst Added to Swelling Solvent	
0	38.7±9.7[b]	82.8±2.0	28.0±0.3	11.8±0.3
12	40.7±6.1[c]	85.4±1.4	31.8±1.6	13.4±0.7
24	32.6±1.7[c]	84.4±0.6	23.5±7.8	9.8±3.0
48	34.1±3.2[c]	80.4±1.1	14.7±1.1	6.3±0.3
96	38.3±1.1[c]	76.0±8.1	14.1±2.3	6.1±0.8
Swelling Solvent: THF	Reaction Solvent: 1-MN		Catalyst Added to Swelling Solvent	
0	37.8±1.9[b]	87.3±1.6	18.6±1.3	6.2±0.4
6	41.9±1.4[c]	76.8±4.0	15.2±6.9	5.9±2.5
16	36.5±9.1[c]	78.2±5.0	18.1±10.3	7.2±4.2
28	41.0±6.4[c]	74.1±1.1	8.8±2.3	3.6±1.0
96	40.4±1.8[c]	81.9±1.6	15.1±1.8	5.7±0.4
Swelling Solvent: Isopropanol	Reaction Solvent: 1-MN		Catalyst Added to Swelling Solvent	
0	17.9±6.7[b]	88.1±0.4	18.7±0.8	6.6±0.3
12	14.3±0.0[c]	71.2±9.4	7.8±2.9	3.7±0.9
24	11.9±3.4[c]	74.1±5.7	10.1±3.9	4.5±1.3
48	16.3±3.8[c]	70.2±0.5	9.5±0.3	4.2±0.0
96	18.2±1.1[c]	79.9±0.8	16.9±2.3	6.5±0.8

[a] Conditions: varied swelling times; reacted at 410 °C for 30 min with 1250 psig H_2 introduced at ambient temperature.

[b] Coal swelled without catalyst

[c] Coal swelled with catalyst.

For the THF swelling solvent and V1074 reaction solvent system, coal conversion increased after 12 and 24 hours of swelling with Molyvan L compared to when coal was not preswelled with catalyst. After 24 hours of contact between THF and Molyvan L, pyrene conversions were less than when the catalyst was added directly to the reactor. After 48 hours of swelling in THF with coal, coal conversion decreased below that obtained when the catalyst was added directly to the reactor. After 96 hours of contact, coal conversion was even less. Pyrene conversions also continued to decrease after this initial increase observed after 12 hours of swelling. Swelling with THF was effective in opening the coal's pores and allowing access of Molyvan L to the coal's inner structure as evidenced by increased coal and pyrene conversion at short swelling times. However, longer contact between THF and Molyvan L was detrimental to the activity of Molyvan L.

When Molyvan L was preswelled in THF and liquefied in 1-MN, the coal conversion achieved was highest at 87.3% when no Molyvan L was not contacted with THF. Coal conversion after 6, 16, and 28 hours of preswelling with THF was less ranging between 74 to 78%. Variability in coal and pyrene conversions was fairly high at the shorter swelling times, indicating that the impregnation process was not stable or complete at short swelling times. After 96 hours the amount of coal conversion of 81.9% was increased and less variable than the shorter swelling time, but was less than that achieved with no contact between Molyvan L and THF. Since ~92% of the catalyst was absorbed by the coal after 96 hours of preswelling and the amount of catalyst present in the reactor when added directly or preswelled was essentially the same, the difference in catalytic activity continually apparent after swelling solvent contact and impregnation were caused by the following two factors. Table 15 presented earlier clearly demonstrated that the type of swelling solvent strongly influenced the activity of the catalyst. Data presented concerning catalyst loading and introduction method evinced that a small amount of catalyst in the slurry phase and freely accessible was beneficial to the entire system resulting in more soluble products.

The effect of swelling time on the isopropanol system was somewhat different. In the case of isopropanol, the increased coal volume was less than that of THF. The length of catalyst contact time with isopropanol and coal was directly related to coal conversion. Contact of 96 hours gave both the highest coal conversion and pyrene conversion, although both of these conversions were substantially less than adding the catalyst directly to the reactor. On the basis of measurements of the amount of catalyst left in the swelling solvent, the longer contact time allowed time for Molyvan L to penetrate into the coal structure; however, the contact between Molyvan L and isopropanol rendered the catalyst less effective than when Molyvan L was added as a slurry phase catalyst.

Effect of THF Contact Time on Molyvan L Activity. To further elucidate the effect of the swelling solvent THF on Molyvan L activity in liquefaction reactions (Table 16). Two additional experiments were performed. First, Molyvan L was contacted with THF for 15 min, then separated from the THF and added to the liquefaction reactor. The amount of coal conversion in the liquefaction reaction was slightly less after contact with THF although the amount of pyrene conversion was slightly more than that achieved when Molyvan L was added to the reactor without contact with THF. The second experiment evaluating the stability of Molyvan L in THF involved placing Molyvan L in THF at an equivalent concentration level as used in liquefaction experiments. After 96 hours of contact, the THF was removed by rotary

Table 16. Effect of Contact with THF and Catalytic Activity of Molyvan L

Catalyst Type	Catalyst Loading (ppm)	%ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol%)	Pyrene Hydrogenation (%)
Time: 30 min			**Catalyst added to Reaction**		
Molyvan L	661±32.5	37.8±1.9	87.3±1.6	18.6±1.3	6.2±0.4
Time: 30 min			**Catalyst Placed in THF, separated and added to Reactor**		
Molyvan L	656±23.3	33.4±4.2	85.2±1.8	22.9±4.2	9.0±1.6

evaporation. No liquid Molyvan L was left in the flask but a solid mass of black residue was stuck to the bottom of the flask. The residue could not be removed from the flask and, therefore, its liquefaction activity could not be tested.

Spectroscopic Analysis of Catalyst in Swelling Solvents. The effect of the swelling solvent on stability of three different slurry phase catalysts was examined by UV-visible spectroscopy. Three catalysts, Molyvan L, Mo naphthenate and NiOct, were evaluated in two swelling solvents, Isopropanol and THF. The analysis wavelengths were 710 nm for Molyvan L, 495 nm for MoNaph and 400 nm for NiOct. All of the catalysts dissolved readily and completely in THF; however, MoNaph and NiOct dissolved very slowly in isopropanol, giving an error for the initial reading.

Each catalyst showed different spectroscopic effects of the two swelling solvents. Mo naphthenate, which converted coal equally well with or without contact with the swelling solvent, showed decreased absorbance in THF with time as presented in Table 17. In isopropanol, MoNaph dissolved slowly showing increased absorbance during the first 24 hours. After MoNaph achieved solubility, the absorbance and apparent concentration of MoNaph decreased with time.

Molyvan L behaved differently from MoNaph. Molyvan L showed decreased absorbance for the first 48 hours in THF and then increased. The final apparent concentration of Molyvan L in THF was quite high giving a concentration value of three times its original concentration. These results suggest that Molyvan L formed a complex with THF which not only affected its spectroscopic properties, but also its liquefaction and hydrogenation activity. Molyvan L acted differently in isopropanol showing decreased absorbance and decreased apparent concentration

Table 17. Change in Concentration of Slurry Phase Catalysts in Swelling Solvents with Time

Catalyst	Isopropanol			THF		
	Absorbance	Concentration (g/l)	Fraction (C / C_o)	Absorbance	Concentration (g/L)	Fraction (C / C_o)
Elapsed Time: 0 hours						
MoNaph[a]	1.007±0.595	1.819±1.074		2.529±0.159	4.567±0.250	
Molyvan L	0.682±0.035	6.263±0.177		0.712±0.066	6.588±0.177	
Ni Octoate	0.111±0.056	7.144±0.044		0.315±0.009	7.800±0.389	
Elapsed Time: 6 hours						
MoNaph	1.294±0.256	2.338±0.463	0.463±0.067	2.438±0.170	4.404±0.308	0.964±0.014
Molyvan L	0.465±0.022	4.266±0.202	0.681±0.013	0.474±0.100	4.389±0.930	0.669±0.159
Ni Octoate	0.171±0.178	4.243±4.422	0.596±0.622	0.269±0.012	6.663±0.298	0.854±0.004
Elapsed Time: 12 hours						
MoNaph	1.326±0.269	2.396±0.486	0.474±0.071	2.379±0.172	4.298±0.310	0.941±0.016
Molyvan L	0.433±0.014	3.976±0.130	0.635±0.003	0.819±0.243	7.579±2.246	1.155±0.372
Ni Octoate	0.310±0.004	7.693±0.105	1.077±0.008	0.279±0.011	6.911±0.263	0.887±0.011
Elapsed Time: 24 hours						
MoNaph	1.365±0.375	2.466±0.678	0.488±0.108	2.323±0.165	4.197±0.298	0.919±0.015
Molyvan L	0.399±0.010	3.664±0.091	0.586±0.002	1.472±0.226	13.625±2.089	2.074±0.373
Ni Octoate	0.260±0.021	6.439±0.509	0.902±0.066	0.265±0.011	6.576±0.281	0.843±0.006
Elapsed Time: 48 hours						
MoNaph	1.246±0.246	2.251±0.444	0.446±0.064	2.199±0.116	3.973±0.209	0.870±0.001
Molyvan L	0.379±0.013	3.476±0.124	0.555±0.004	1.723±0.085	15.954±0.786	2.424±0.184
Ni Octoate	0.294±0.008	7.295±0.211	1.021±0.023	0.266±0.011	6.601±0.281	0.847±0.006
Elapsed Time: 96 hours						
MoNaph	1.112±0.138	2.008±0.249	0.399±0.028	1.872±0.057	3.382±0.102	0.741±0.018
Molyvan L	0.389±0.006	3.572±0.052	0.571±0.008	2.252±0.050	20.848±0.465	3.167±0.155
Ni Octoate	0.280±0.007	6.948±0.175	0.973±0.019	0.255±0.010	6.328±0.245	0.812±0.009

[a] MoNaph = Mo naphthenate

[b] * - concentration of catalyst in solution only. A large portion of catalyst in solvent but not in solution.

of the complex with time.

Ni octoate behaved differently in the two swelling compared to the other two catalysts. the values of the visible absorbance fluctuated over the 96 hours. The general trend was a lowering in the absorbance so that the final concentrations in both THF and isopropanol were somewhat lower than the original concentration. The effect of the swelling solvent on the behavior of NiOct in liquefaction reactions was a decrease in its overall performance.

Reactions with Carbon Black. Slurry phase catalysts were used throughout this work because of their solubility in the reaction medium as well as their ability to diffuse to and deposit on the coal's surface or within swelled coal's pores. Although slurry phase catalyst present a number of benefits such as high activity and accessibility, the hypothesis was tested that providing a support for these catalysts may improve their overall performance in liquefaction. Therefore, Regal 660 carbon black, a carbon black with some oxygen on the surface, was added to the reaction system to evaluate if a surface for deposition would improve the overall activity of MoNaph in the system.

The reaction system that was tested evaluated the liquefaction of untreated Black Thunder coal with 600 to 800 ppm of Mo as MoNaph on a coal basis and sulfur added at three times the Mo loading. The swelling solvent used was THF and the reaction solvent was 1-MN. Experiments were performed as shown in Table 18: (1) MoNaph + S was added to the reactor and one of three conditions existed for carbon black: no carbon black was added; carbon black was added directly to the reactor; and carbon black was added to the swelling solvent; and (2) MoNaph was added to the swelling solvent THF, sulfur was added to the reactor and carbon black was added in the same three ways as described in (1).

Table 18. Effect of Carbon Black Addition on Coal and Pyrene Conversion

Catalyst Type	Catalyst Loading	Compound Added	%ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol%)	Pyrene Hydrogenation (%)
Swelling Solvent: THF				**Catalyst in Reactor**		
Mo Naphthenate + S	659±21	None	36.4±6.4	89.9±1.2	24.8±0.8	10.2±0.2
Mo Naphthenate + S	643±74	Carbon Black in Reactor	31.1±1.0	78.2±0.9	15.8±11.6	6.5±4.7
Mo Naphthenate + S	657±21	Carbon Black in THF	52.0±25	80.0±2.8	21.6±1.3	9.2±0.3
Swelling Solvent: THF				**Catalyst in THF**		
Mo Naphthenate + S	655±66	None	35.1±11.0	89.9±0.1	26.0±0.5	10.7±0.2
Mo Naphthenate + S	578±9	Carbon Black in Reactor	31.8±12.9	78.3±1.1	28.9±0.1	9.0±0.4
Mo Naphthenate + S	593±47	Carbon Black in THF	46.7±17.5	78.8±1.1	21.8±1.6	9.2±0.7

When MoNaph was added directly to the reactor, the highest coal conversion 89.9% was achieved without carbon black. When carbon black was added to the system either directly to the reactor or to the swelling solvent, the amount of coal conversion decreased to 78.2 and 80.0%, respectively. Pyrene conversion decreased likewise to 15.8 and 21.6%, respectively, from 24.8% when Mo Naph + S was added directly reactor without carbon black. When MoNaph was added to the swelling solvent, the same phenomenon occurred. The highest coal and pyrene conversions were achieved without carbon black, yielding 89.9% coal conversion and 26.0% pyrene conversion. When carbon black was added to the system, the amount of coal conversion decreased to 78.8% and pyrene conversion to 21-22%. The carbon black rather than providing a support for MoNaph that helped to activate the system reduced the activity of the system possibly by depositing MoNaph on its surface and effectively removing the catalyst from the system. Carbon black may also have served as a diluent in the system. Carbon black neither catalyzed or promoted reactions for coal conversion or pyrene hydrogenation.

V1074 as a Swelling and Reaction Solvent. In one set of experiments V1074 was used as both a swelling and reaction solvent. The swelling solvent V1074 with coal present was so dark that the amount of coal swelling that occurred could not be measured. Table 19 presents the data from these reactions. The first set of reactions involved preswelling the coal but not using a catalyst. The second experiment involved no preswelling of coal and the catalyst was added directly to the reaction solvent. The three experiments involved V1074 as both the swelling and reaction solvent with the catalyst being introduced into the swelling solvent.

The V1074 solvent converted 70.7% of untreated Black Thunder coal without a catalyst present; this high conversion indicated that V1074 was an excellent solvent for coverting coal.

Table 19. Coal and Pyrene Conversion Using V1074 as Swelling and Reaction Solvent

Catalyst Type	Catalyst Loading (ppm)	Condition	%ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol%)	Pyrene Hydrogenation (%)
None	0.0	N[a]	NM[d]	70.7±1.3	5.8±0.9	3.0±0.4
Molyvan L	645±55	NoPS[b]	NM	76.8±2.3	25.9±2.4	10.7±1.3
Molyvan L	655±33	NC[c]	NM	77.9±0.4	27.3±0.9	11.6±0.5

[a] N = not agitated during preswelling; preswelling solvent used as reaction solvent.
[b] NoPS = No preswelling; catalyst added directly to the reactor.
[c] Catalyst added to preswelling solvent; preswelling solvent used as reaction solvent.

Where the Molyvan L catalyst was added directly to the reactor, coal conversion increased to 76.8% and increased even more to 77.9% when Molyvan L was added to the swelling solvent with untreated Black Thunder coal present. Because of the chemical nature of V1074, the swelling solvent could not readily be removed from coal but was introduced directly into the reactor. The additional reactivity of the preswelled coal with catalyst may have been caused by the portion of slurry phase catalyst remaining dissolved in the reaction solvent.

Addition of Phosphorus to Catalytic and Thermal Reactions. Molyvan L and Molyvan 822 are very similar materials, both being composed of a oxythiomolybdenum compound. The primary difference is that Molyvan L contains phosphorus while Molyvan 822 does not. The reactions that were performed included the addition of phosphorus in the form of triphenylphosphine to the thermal reaction and to the Molyvan 822 reaction when Molyvan 822 was added directly to the reactor. Corresponding reactions without phosphorus were also performed. The other reactions performed was the addition of the phosphorus to the reactor when Molyvan 822 and Molyvan L were added to the swelling solvent. Again, corresponding reactions without phosphorus have been performed. The swelling solvent was THF and the reaction solvent was 1-MN.

The addition of phosphorus to the thermal reactions resulted in a decrease in coal conversion from 59.7% to 54.3% but an increase in pyrene conversion to 4.0% from zero. The addition of phosphorus to Molyvan 822, when Molyvan 822 was added directly to the reactor, also increased coal conversion from 73.4 to 83.6%; pyrene conversion also increased substantially from 8.8% to 26.6%. Molyvan L introduced directly to the reactor yielded the highest coal conversion of 87.3% and an intermediate pyrene conversion of 18.6%.

When Molyvan 822 was added to the swelling solvent, the amount of coal and pyrene conversion decreased markedly. Coal conversion was 64.7% decreased from 73.4% when Molyvan 822 was added directly to the reactor without contact with THF. Molyvan 822 appeared to be quite sensitive to the type of swelling solvent used as shown in Table 13, being adversely affected by THF and a mixture of isopropanol and water. Addition of phosphorus to the reactor decreased both coal and pyrene conversion. Molyvan 822 was also sensitive to contact with the swelling solvent. Addition of Molyvan L to THF also decreased coal and pyrene conversion but not to the extent observed with Molyvan 822. Addition of phosphorus to the reactor with Molyvan L impregnated coal decreased coal conversion but not to the extent observed with Molyvan 822. Pyrene conversion decreased somewhat, also.

Only in the reaction where Molyvan 822 and phosphorus added directly to the reactor did the activity of Molyvan 822 increase with phosphorus in the system. All other additions of phosphorus with Molyvan 822 or Molyvan L were detrimental to the activity of the catalysts.

Effect of Catalyst Type. The effect of catalyst type on coal and pyrene conversions was evaluated for reaction systems in which the catalyst was preswelled with coal (Table 21). The swelling solvent used for most of the systems was isopropanol while 20% isopropanol and 80% water was used for several systems. After catalyst impregnation, the coal was liquefied in a reaction solvent composed of 20% DHA and 80% V1074. The catalysts used were divided into two groups: the slurry phase catalysts were Molyvan L, Molyvan 822, Ni naphthenate, Mo naphthenate and Co naphthenate; and the powdered catalysts used were Ni acetylacetonate, Ni citrate, MoO_3, MoO_2AcAc, and $(NH_4)_2MoS_4$. All of the catalysts were introduced at a nominal 600 to 800 ppm of active metal based on coal.

Table 20. Effect of Adding Phosphorous on Catalytic and Thermal Reactions of Untreated Black Thunder Coal

Catalyst Type	Catalyst Loading (ppm)	Phosphorus Loading (ppm)	Coal Conversion (wt%)	Pyrene Conversion (mol%)	Pyrene Hydrogenation (%)
Swelling Solvent: THF			**Catalyst in Reactor**		
None	0.0	0.0	59.7±8.9	0.0±0.0	0.0±0.0
None	0.0	1348±1	54.3±5.7	4.0±0.2	2.4±0.1
Molyvan 822	611±11	0.0	73.4±0.8	8.8±3.7	3.6±1.3
Molyvan 822	625±15	1343±3	83.6±1.8	26.6±1.6	10.7±0.7
Molyvan L	661±33	0.0	87.3±1.6	18.6±1.3	6.2±0.4
Swelling Solvent: THF			**Catalyst in Swelling Solvent**		
Molyvan 822	600±16	0.0	64.7±9.5	5.5±0.2	3.0±0.1
Molyvan 822	640±23	1338±2	58.5±0.8	4.7±0.0	2.6±0.0
Molyvan L	607±88	0.0	81.9±1.6	15.1±1.8	5.7±0.4
Molyvan L	680±27	1431±130	79.9±3.1	19.6±1.8	7.9±0.6

Table 21. Coal and Pyrene Conversions for Untreated Black Thunder Coal Reacted in DHA and V1074

Catalyst Type	Catalyst Loading (ppm)	Conditions During Swelling	%ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol%)	Pyrene Hydrogenation (%)
Swelling Solvent: Isopropanol					**Catalyst: In Swelling Solvent**	
Mo Naphthenate + S	608±4.9	N	10.9±3.0	85.3±0.6	21.3±1.4	9.9±0.6
Molyvan L	626±26.9	N	20.1±3.7	81.2±1.1	7.7±1.6	3.6±0.6
Molyvan 822	498±0.7	N	26.7±0.8	88.0±0.1	21.0±1.1	9.1±0.6
Molyvan 822 + S	664±40.3	N	25.0±3.3	86.5±0.1	23.6±0.1	10.1±0.5
Ni Naphthenate	682±0.0	N	25.7±4.2	85.5±1.5	11.4±0.7	5.1±0.2
Ni Octoate	626±38.2	N	17.8±0.6	75.3±1.5	5.7±2.5	2.9±0.8
Co Naphthenate	660±9.2	N	28.2±14.1	73.4±0.6	4.8±0.3	3.0±0.2
Ni Acetylacetonate	671±55.9	N	20.9±2.6	80.0±1.3	7.3±2.1	3.6±0.8
Ni Citrate	603±12.0	N	13.6±0.0	77.5±1.4	6.3±1.2	3.3±0.1
MoO_3	746±36.1	N	18.7±7.2	83.6±0.9	9.6±0.8	4.5±0.2
MoO_2AcAc	697±21.9	N	19.6±3.0	78.9±3.2	6.2±0.4	3.2±0.1
Swelling Solvent: 20% Isopropanol/80% Water					**Catalyst: In Swelling Solvent**	
Molyvan L	77±83.4	N	28.0±0.9	87.5±1.9	28.6±0.8	11.5±0.6
$(NH_4)_2MoS_4$	632±10.6	N	18.6±0.6	89.5±0.6	27.6±1.4	11.6±0.6
Molyvan 822	605±15.6	N	38.7±3.2	83.2±2.8	11.5±0.9	5.0±0.4
Ni Naphthenate	619±25.5	N	23.8±0.0	84.5±2.3	12.1±2.9	5.2±0.8

Liquefaction of Molyvan L impregnated coal gave a coal conversion of 81.2%. This reaction was chosen to serve as a benchmark by which to compare the activities of the other catalysts. The activities of Mo naphthenate plus sulfur, Molyvan 822 and Molyvan 822 plus sulfur, and Ni naphthenate were higher than Molyvan L, yielding between 85.3% and 88% coal conversion. The reaction with Ni acetylacetonate yielded 80% coal conversion which was nearly equivalent to Molyvan L while MoO_3 yielded slightly more coal conversion at 83.6%. The four catalysts which had lower conversion than Molyvan L under equivalent conditions were NiOct, Ni citrate, MoO_2AcAc, and Co naphthenate. Co naphthenate gave the lowest conversion of 73.4%.

The pyrene hydrogenation reactions that occurred simultaneously in these liquefaction reactions differentiated among the catalysts. For the catalysts preswelled in isopropanol, Mo naphthenate plus sulfur and Molyvan 822 with and without sulfur yielded pyrene conversions above 20% while all of the other catalysts including Ni naphthenate and Molyvan L yielded much less coal conversion of ~11% or less. By contrast, Molyvan L and $(NH_4)_2MoS_4$ produced pyrene conversions of ~28 to 29% when preswelled in 20% isopropanol and 80% water. By contrast, Molyvan 822 yielded 11.5% pyrene conversion after being preswelled in the isopropanol water mixture. The only difference in the activities of these catalysts for pyrene conversion was the effect of the contact with different swelling solvents, since all other reaction conditions were the same. Contact of Molyvan L with isopropanol was detrimental while contact with 20% isopropanol and 80% water mixture was beneficial. The opposite effect was observed for Molyvan 822. By contrast, Ni naphthenate's activity for pyrene conversion was not affected by the swelling solvent.

Coal conversion showed the same effect of the swelling solvent on the catalysts. Molyvan L converted more coal after being preswelled in the 20% isopropanol and 80% water than after being preswelled in isopropanol. Molyvan 822 showed the opposite effect while Ni naphthenate was not affected by the composition of the swelling solvent.

Summary

A number of parameters affected the activity of a given catalyst in the preswelling and liquefaction reaction process. The most influential of these parameters was the swelling solvent. The swelling solvent both affected the ability of the catalyst to impregnate Black Thunder coal and the inherent activity of the catalyst itself. Length of swelling time also affected the activity of the catalyst; the effect was directly dependent upon the type of swelling solvent used. As in any coal liquefaction system, the reaction solvent in the liquefaction reaction itself affected the overall reactivity of the system. Addition of a relatively inert solid that could serve as a catalyst support was detrimental to the overall reactivity of the system. Addition of phosphorus to the reaction system of Molyvan 822 and Molyvan L was only positive when added directly to the reactor with Molyvan 822. The use of catalyst impregnated coal with phosphorus was detrimental to coal converson. Different catalysts composed of Mo, Ni, and Co displayed inherently different activities under the same swelling and liquefaction conditions. The Mo containing catalysts were the most active and were followed in activity by Ni containing catalyst. The Co containing catalyst had the least activity. Pyrene conversion and hydrogenation were more sensitive measures of catalytic activity than coal conversion although both types of reactions gave corresponding results.

Appendix

Table 1. Proximate and Ultimate Analysis of Black Thunder and SO_2 Treated Black Thunder Coals[a]

	Proximate Analysis			
	Black Thunder		SO_2 Treated Black Thunder	
	As Received	Dry Basis	As Received	Dry Basis
% Moisture	11.20		9.88	
% Ash	5.43	6.12	3.08	3.42
% Volatile	44.53	50.15	41.74	46.32
% Fixed Carbon	38.84	43.73	45.30	50.26
Total	100.00	100.00	100.00	100.00
Btu/lb	10606	11944	10993	12198
% Sulfur	0.39	0.44	0.73	0.81
maf Btu		12723		12630
	Ultimate Analysis			
	Black Thunder		**SO_2 Treated Black Thunder**	
	As Received	**Dry Basis**	**As Received**	**Dry Basis**
% Moisture	11.20		9.88	
% Carbon	61.87	69.67	63.57	70.54
% Hydrogen	4.33	4.88	4.46	4.95
% Nitrogen	0.81	0.91	0.80	0.89
% Sulfur	0.39	0.44	0.73	0.81
% Ash	5.43	6.12	3.08	3.42
% Oxygen (diff)	15.97	17.98	17.48	19.39

[a] Commercial Testing and Engineering Co., Birmingham, AL laboratory.

Table 2. Coal and Pyrene Conversions in Reactions of Untreated Black Thunder Coal in 1-Methylnaphthalene at 385 °C

Catalyst		Added Coal			Pyrene Conversion (mol %)	Coal Conversion (wt %)	Total Recovery (g) [%R]
Type	Loading (ppm)	%ΔV	(g)	wt %			
Time: 30 minutes		Swelling Solvent: THF				Catalyst: added to reactor	
Mo Naphthenate+S	655±35	39.7±4.6	1.66±0.00	29.7±0.1	34.4±1.5	73.8±1.6	4.9±0.7 106.9±1.4
Molyvan L	602±6.4	34.1±9.6	1.65±0.00	30.6±0.0	25.7±7.2	72.5±3.5	5.0±0.0 115.5±0.1
Ni Octoate	803±108	34.9±2.2	1.65±0.00	30.7±0.0	16.2±11.2	69.4±7.8	5.0±0.1 116.0±2.3
Time: 30 minutes		Swelling Solvent: THF				Catalyst: added to swelling solvent	
Mo Naphthenate+S	646±42.4	41.9±1.4	1.66±0.00	29.7±0.1	35.4±0.1	76.8±0.3	4.98±0.00 110.0±0.2
Molyvan L	583±4.9	33.4±4.2	1.65±0.00	30.6±0.0	4.5±1.0	50.4±3.9	4.46±0.16 102.6±3.7
Ni Octoate	641±23.3	33.4±6.7	1.65±0.00	30.7±0.0	3.6±0.1	57.0±1.0	4.87±0.02 112.1±4.9
Time: 30 minutes		Swelling Solvent: Isopropanol				Catalyst: added to reactor	
Mo Naphthenate+S	758±8.5	11.2±3.5	1.67±0.00	29.7±0.1	29.0±1.8	80.0±7.9	4.5±0.6 99.9±13.2
Molyvan L	650±50	14.3±6.7	1.64±0.00	30.6±0.1	23.1±8.0	76.7±0.3	4.8±0.1 111.4±2.3
Ni Octoate	698±112	14.0±0.4	1.64±0.00	30.7±0.1	7.7±1.3	65.3±0.9	4.7±0.05 109.4±1.2
Time: 30 minutes		Swelling Solvent: Isopropanol				Catalyst: added to swelling solvent	
Mo Naphthenate+S	616±1.4	11.7±3.7	1.66±0.00	29.6±0.1	32.3±0.8	79.3±3.8	3.12±0.02 113.2±0.2
Molyvan L	633±19.1	13.6±0.0	1.64±0.00	30.6±0.1	5.0±0.4	55.9±0.3	4.54±0.19 104.4±4.3
Ni Octoate	725±94.0	14.3±6.7	1.64±0.00	30.6±0.0	5.0±0.4	62.2±2.7	4.85±0.06 11.8±1.3

Table 3. Pyrene Product Distributions in Reactions of Untreated Black Thunder Coal in 1-Methylnaphthalene at 385 °C

Catalyst		% HYD (% Coal)	Product Distribution (mole %)			
Type	Loading (ppm)		PYR	DHP	THP	HHP
Time: 30 minutes		Swelling Solvent: THF		Catalyst: added to reactor		
MoNaphthenate+S	665±35	14.2±0.6 29.7±0.1	65.7±1.8	28.3±1.4	3.8±0.8	2.3±0.1
Molyvan L	602±6.4	10.4±3.3 30.6±0.0	74.3±7.2	22.1±5.3	2.0±1.2	1.7±0.7
Ni Octoate	803±108	6.7±4.2 30.7±0.0	83.9±11.2	13.8±10.1	0.9±0.9	1.6±0.2
Time: 30 minutes		Swelling Solvent: THF		Catalyst: added to swelling solvent		
MoNaphthenate+S	646±42.4	14.6±0.1 29±0.1	64.7±0.1	29.1±0.5	4.3±0.4	2.1±0.1
Molyvan L	583±4.9	2.3±0.2 30.6±0.0	95.5±1.0	3.3±1.3	0.0±0.0	1.2±0.1
Ni Octoate	641±23.3	1.9±6.1 30.7±0.0	96.4±0.1	2.7±0.1	0.0±0.0	1.0±0.1
Time: 30 minutes		Swelling Solvent: Isopropanol		Catalyst: added to reactor		
Mo Naphthenate+S	758±8.5	11.7±0.5 29.7±0.1	71.1±1.8	24.6±1.6	2.7±0.6	1.7±0.4
Molyvan L	650±50	9.2±3.0 30.6±0.1	77.0±8.0	20.1±7.1	1.5±1.1	1.3±0.0
Ni Octoate	698±112	3.5±0.4 30.7±0.1	92.4±1.3	6.1±1.4	0.2±0.1	1.4±0.1
Time: 30 minutes		Swelling Solvent: Isopropanol		Catalyst: added to swelling solvent		
MoNaphthenate+S	616±1.4	13.2±0.3 29.6±0.1	67.8±0.8	27.0±0.6	3.3±0.1	2.0±0.0
Molyvan L	633±19.1	2.6±0.1 30.6±0.1	95.1±0.4	3.5±0.3	0.1±0.1	1.4±0.0
Ni Octoate	725±94.0	2.6±0.2 30.6±0.0	95.1±0.4	3.6±0.3	0.0±0.0	1.4±0.1

Table 4. Amount Solvent Uptake into Coal Reacted at 385 °C

Catalyst	Coal Mass (g)	Solvent Mass Absorbed (g)	Catalyst Mass (g)
Time: 30 minutes	**SS[a]: THF**	**Catalyst: added to reactor**	
Mo Naphthenate	1.66±0.00	1.34±0.15	0.05±0.00
Molyvan L	1.65±0.00	1.34±0.07	0.03±0.00
Ni Octoate	1.65±0.00	1.31±0.04	0.03±0.00
Time: 30 minutes	**SS: THF**	**Catalyst: added to SS**	
Mo Naphthenate	1.66±0.00	1.52±0.14	0.05±0.00
Molyvan L	1.64±0.00	1.41±0.04	0.04±0.00
Ni Octoate	1.65±0.00	1.32±0.00	0.03±0.00
Time: 30 minutes	**SS: IPA[b]**	**Catalyst: added to reactor**	
Mo Naphthenate	1.67±0.00	0.90±0.01	0.06±0.00
Molyvan L	1.64±0.00	0.98±0.14	0.04±0.00
Ni Octoate	1.64±0.00	0.92±0.02	0.03±0.00
Time: 30 minutes	**SS: IPA**	**Catalyst: added to SS**	
Mo Naphthenate	1.66±0.00	0.02±0.03	0.05±0.00
Molyvan L	1.64±0.00	0.95±0.03	0.04±0.00
Ni Octoate	1.64±0.00	0.98±0.03	0.03±0.00

[a] SS = Swelling Solvent
[b] IPA = isopropanol

Table 5. Coal and Pyrene Conversion for Untreated Black Thunder Coal Reacted in 1-Methylnaphthalene with Catalyst Introduced During Swelling

Catalyst Type	Catalyst Loading (ppm)[a]	Conditions	Added Coal			Pyrene Conversion (mol %)	Coal Conversion (wt %)	Total Recovery (g) [% R]
			%ΔV	(g)	wt%[c]			
Reaction Time: 30 min			Swelling Solvent: THF					
Molyvan 822	545±2.1	T(40%)[b]	44.2±1.8	1.64±0.00	30.4±0.0	9.8±5.1	69.4±7.4	4.82±0.18 110.5±4.2
Mo Naphthenate	672±16.3	A	35.0±4.5	1.65±0.00	30.6±0.1	3.5±0.2	62.3±0.6	4.82±0.10 110.3±2.4
Molyvan L	607±88.4	N	40.4±1.8	1.65±0.00	30.7±0.1	15.1 ± 1.8	81.9±1.6	4.76±0.15 109.4±3.7
Molyvan L	653±94.0	A	52.3±3.2	1.65±0.00	30.6±0.1	14.7 ± 5.0	73.6±3.0	5.21±0.06 119.5±1.3
Molyvan L	1188±63.6	D	41.0±2.7	1.65±0.00	30.5±0.1	28.6 ± 2.5	84.8±1.1	5.17±0.07 117.8±1.7
Molyvan L	619±33.2	28 h	41.0±6.4	1.65±0.00	30.6±0.0	8.8±2.3	74.1±1.1	4.87±0.09 111.9±2.1
Molyvan L	671±19.8	16 h	36.5±9.1	1.65±0.00	30.7±0.1	18.1±10.3	78.2±5.0	5.18±0.14 118.9±3.3
Molyvan L	632±55.2	6 h	41.9±1.4	1.65±0.00	30.6±0.0	15.2± 6.9	76.8±4.0	4.80±0.27 110.2±6.4
Molyvan L	608±41.0	1.5s+	55.8±4.7	1.65±0.00	30.6±0.0	15.4± 7.5	77.7±4.7	5.15±0.25 118.2±5.7
Molyvan L	684±12.0	1.5s	20.1±3.7	1.65±0.00	30.6±0.0	22.8± 2.5	84.1±1.8	5.05±0.1 115.8±1.2
Molyvan L	226±27.6	1.5s+d	49.1±14.1	1.65±0.00	30.6±0.0	21.4± 1.4	72.9±1.6	50.6±0.05 116.2±1.1
Molyvan L	650±43.7	T(40%)	62.4±20.6	1.64±0.01	30.5±0.1	25.1± 13.7	81.3±7.1	4.81±0.12 110.6±2.8
Ni Octoate	624±77.8	N	38.9±5.7	16.5±0.00	30.7±0.0	11.1±11.0	74,8±12.9	4.98±0.21 114.7±4.9
Reaction Time: 30 min			Swelling Solvent: 1-MN + 1.5 ml THF					
Molyvan L	616±50.2	1.5s + m	29.7±5.1	1.63±0.00	30.4±0.0	3.2±0.6	50.8 ± 0.2	5.48±0.33 126.4±7.4

Table 5. Coal and Pyrene Conversi or Untreated Black Thunder Coal Reacted in 1-Methylnaphthalene wit atalyst Introduced During Swelling(Continued)

Catalyst Type	Catalyst Loading (ppm)^a	Conditions	Added Coal			Pyrene Conversion (mol %)	Coal Conversion (wt %)	Total Recovery (g) [% R]
			%ΔV	(g)	wt%^{c}			
Reaction Time: 20 min Swelling Solvent: THF								
Mo Naphthenate	608±9.2	A	37.1±12.0	1.65±0.00	30.5±0.0	2.7±0.5	53.1±3.3	4.8±0.31 110.8±7.1
Molyvan L	599±7.1	N	38.7±3.2	1.65 ±0.00	30.7±0.1	4.8±3.5	67.5±5.4	4.57±0.34 104.9±7.8
Ni Octoate	652±74.2	N	34.1 ±3.3	1.65±0.00	30.8±0.1	2.4±0.3	60.8±3.2	4.95±0.03 113.9±0.7
Reaction Time: 10 min Swelling solvent: THF								
Molyvan L	599±15.6	N	43.2±3.3	1.65±0.00	30.6±0.0	6.1±0.9	49.4±3.7	4.50±0.31 103.4±7.2
Reaction Time: 30 min Swelling Solvent: Methanol								
Molyvan L	666±31.1	N	25.2±4.9	1.65±0.00	30.6±0.0	3.0±0.8	68.4±0.0	4.84±0.12 111.2±2.8
Molyvan L	1264±4.2	D	26.2±3.4	1.65±0.00	30.4±0.1	25.7±2.7	88.8±0.5	50.5±0.30 115.0±6.9
Ni Octoate	644±12.7	N	23.3±0.8	1.65±0.00	30.7±0.0	3.5±0.4	70.1±1.1	4.99±0.01 115.1±3.5
Reaction Time: 20 min Swelling Solvent: Methanol								
Molyvan L	652±20.5	N	25.4±9.1	1.65±0.00	30.6±0.1	2.8±0.8	67.6±0.1	4.97±0.47 114.1±10.6
Ni Octoate	613±6.4	N	20.6±4.5	1.65±0.00	30.7±0.0	2.3±0.4	64.4±0.4	4.67±0.2 107.6±4.5
Reaction Time: 30 min Swelling Solvent: Isopropanol								
Molyvan 822	674±8.5	N	23.9±1.6	1.64±0.00	30.4±0.1	24.3±0.1	83.3±0.8	4.64±0.33 106.2±7.5
Molyvan 822	623±53.0	J(20%)	34.1±5.7	1.65±0.00	30.4±0.0	4.6±0.5	60.6±0.1	4.61±0.05 105.4±1.3
Molyvan L	645±26.2	N	18.2±1.1	1.64±0.00	30.6±0.1	16.9±2.3	79.9±0.8	4.8±0.3 109.6±7.6

Table 5. Coal and Pyrene Conversion for Untreated Black Thunder Coal Reacted in 1-Methylnaphthalene with Catalyst Introduced During Swelling(Continued)

Catalyst Type	Catalyst Loading (ppm)^a	Conditions	Added Coal			Pyrene Conversion (mol %)	Coal Conversion (wt %)	Total Recovery (g) [% R]
			%ΔV	(g)	wt%^{c}			
Molyvan L	1258±96.9	D	22.8±1.5	1.64±0.00	30.3±0.0	28.2±0.4	81.9±1.8	5.20±0.06 118.5±2.4
Molyvan L	1258±36.1	D2	16.7±3.3	1.64±0.00	30.3±0.0	25.9±0.8	87.3±1.3	4.83±0.10 110.2±2.2
Molyvan L	652±7.8	C(0.5)	21.4±3.4	1.64±0.00	30.5±0.1	17.7±7.9	83.0±1.8	5.24±0.46 120.7±10.7
Molyvan L	629±55.9	I(20%)	25.0±3.3	1.64±0.00	30.5±0.1	34.7±2.9	89.6±1.6	4.51±0.42 103.9±9.8
Molyvan L	699±21.9	J(20%)	21.4±3.4	1.65±0.00	30.6±0.0	4.8±0.6	60.7±1.2	4.21±0.68 96.7±15.6
Molyvan L	590±2.1	K(20%)	16.3±3.8	1.63±0.00	30.5±0.0	34.6±0.8	85.6±0.6	4.79±0.14 110.6±3.2
Ni Octoate	667±70.0	N	15.6±3.7	1.64±0.00	30.6±0.0	3.9±0.6	75.2±0.8	4.6±0.17 105.8±3.7
Ni Octoate	1319±99.0	D2	20.5±9.7	1.64±0.00	30.5±0.0	12.9±1.3	85.1±0.8	4.75±0.21 108.9±4.9
Reaction Time: 20 min Swelling Solvent: Isopropanol								
Molyvan L	583±15.6	N	18.6±0.6	1.64±0.00	30.6±0.0	4.5±1.8	68.2±4.0	5.10±0.30 117.3±6.9
Ni Octoate	678±30.4	N	15.6±3.7	1.64±0.00	30.6±0.0	4.3±0.4	64.8±3.7	4.89±0.01 112.7±0.0

[a] ND = Not determined, but on the basis of analyzed samples the amount of catalyst loading should be between 500 and 750 ppm.

[b] A = agitated: Samples were agitated with catalyst for 96 hr during preswelling; N + not agitated for 96 hr during preswelling; D = double catalyst loading; 28 h, 16 h, 6 h = hours of catalyst solvent contact during preswelling; 1.5 s = catalyst impregnated into coal and reacted immediately; 1.5 s + = catalyst impregnated into coal, swelled for 96 hr in THF, and then reacted; 1.5 s + d = catalyst impregnated into coal, swelled for 96 hr in THF, dried for 24 hr, and then reacted; 1.5 s + m = 1.5 ml of THF solvent swells coal, then new solvent added with catalyst for 96 hr; D2 = double catalyst loading where half the catalyst is placed into the swelling solvent for 96 hr and half into the reactor; C (0.5) = half of catalyst placed in swelling solvent with coal for 96 hr and half directly in reactor; I(20%) = isopropanol swelling solvent is diluted with water; T(40%) = THF swelling solvent is diluted with water; J(20%) = isopropanol swelling solvent is diluted with toluene. K(20) = isopropanol diluted with water and used as a preswelling solvent for 12 hr. Percent strength of swelling solvent is shown in parentheses; [c] Coal percentages should be near 31%.

Table 6. Pyrene Product Distribution Using Untreated Black Thunder Coal Reacted in 1-Methylnaphthalene with Catalyst Introduced During Preswelling

Catalyst Type	Catalyst Loading (ppm)[a]	Conditions[b]	% HYD[c] (% Coal)[d]	Product Distribution (mole %)			
				PYR	DHP	THP	HHP
Reaction Time: 30 min Swelling Solvent: THF							
Molyvan 822	595±2.1	T(40%)	4.0±1.8 30.4±0.0	90.2±5.1	8.5±4.7	0.4±0.2	1.0±0.1
Mo Naphthenate	672±16.3	A	1.8±0.4 30.6±0.1	96.6±0.2	2.5±0.3	0±0	1.0±0.5
Molyvan L	607±88.4	N	5.7±0.4 30.7±0.1	84.9±1.8	14.0±2.3	0.3±0.0	0.8±0.4
Molyvan L	653±94.0	A	5.7±1.9 30.6±0.1	85.4±5.0	13.3±4.6	0.5±0.3	0.9±0.1
Molyvan L	1188±63.6	D	11.0±1.2 30.5±0.1	71.5±2.5	25.3±1.5	2.3±0.7	1.0±0.3
Molyvan L	619±33.2	28 h	3.6±1.0 30.6±0.0	91.2±2.3	7.8±1.8	0.2±0.2	0.9±0.2
Molyvan L	671±19.8	16 h	7.2±4.2 30.7±0.1	82.0±10.3	15.8±8.5	1.2±1.3	1.1±0.5
Molyvan L	632±55.2	6 h	5.9±2.5 30.6±0.0	84.8±6.9	13.6±6.2	0.7±0.6	1.0±0.1
Molyvan L	608±41.0	1.5s +	6.1±2.8 30.6±0.0	84.6±7.5	13.8±6.8	0.5±0.6	1.2±0.1
Molyvan L	684±12.0	1.5s	8.6±1.1 30.6±0.0	77.3±2.5	20.5±1.8	1.5±0.5	0.8±0.1
Molyvan L	226±27.6	1.5s + d	8.2±0.2 30.6±0.0	78.6±1.4	19.3±1.7	1.1±0.3	1.0±0.6
Molyvan L	650±43.7	T(40%)	10.3±5.3 30.5±0.1	74.9±13.7	21.0±11.7	2.5±1.8	1.7±0.3
Ni Octoate	624±77.8	N	4.7±4.1 30.7±0.0	89.0±11.0	9.4±10.0	0.5±0.6	1.3±0.4
Reaction Time: 30 min Swelling Solvent: 1-MN + 1.5 ml THF							
Molyvan L	616±0.2	1.5s + m	2.1±0.2 30.4±0.0	96.8±0.6	1.8±0.5	0.1±0.0	1.4±0.1

Table 6. Pyrene Product Distribution Using Untreated Black Thunder Coal Reacted in 1-Methylnaphthalene with Catalyst Introduced During Preswelling(Continued)

Catalyst Type	Catalyst Loading (ppm)[a]	Conditions[b]	% HYD[c] (% Coal)[d]	Product Distribution (mole %)			
				PYR	DHP	THP	HHP
Reaction Time: 20 min				**Swelling Solvent: THF**			
Mo Naphthenate	608±9.2	A	1.7±0.2 30.5±0.0	97.4±0.5	1.6±0.4	0±0	1.1±0.1
Molyvan L	559±7.1	N	2.1±1.3 30.7±0.1	95.3±3.5	4.0±3.2	0.1±0.1	0.8±0.2
Ni Octoate	652±74.2	N	1.3±0.1 30.8±0.1	97.6±0.3	1.7±0.2	0±0	0.8±0.1
Reaction Time: 10 min				**Swelling Solvent: THF**			
Molyvan L	599±15.6	N	2.6±0.2 30.6±0.0	94.0±0.9	5.3±1.1	0±0	0.8±0.1
Reaction Time: 30 min				**Swelling Solvent: Methanol**			
Molyvan L	666±31.1	N	1.7±0.5 30.6±0.0	97.0±0.8	2.0±0.5	0±0	1.1±0.4
Molyvan L	1261±4.2	D	9.9±1.3 30.4±0.1	74.3±2.7	22.9±1.8	1.6±0.4	1.2±0.4
Ni Octoate	644±12.7	N	1.9±0.1 30.7±0.0	96.6±0.4	2.3±0.3	0±0	1.2±0.1
Reaction Time: 20 min				**Swelling Solvent: Methanol**			
Molyvan L	652±20.5	N	1.9±0.1 30.6±0.1	97.2±0.8	1.9±0.9	0±0	1.0±0.1
Ni Octoate	613±6.4	N	1.4±0.3 30.7±0.0	97.7±0.4	1.4±0.2	0±0	1.0±0.2
Reaction Time: 30 min				**Swelling Solvent: Isopropanol**			
Molyvan 822	674±8.5	N	9.6±0.1 30.4±0.1	75.8±0.1	21.2±0.1	1.9±0.1	1.3±0.1
Molyvan 822	623±53.0	J(20%)	2.4±0.5 30.4±0.0	95.5±0.5	3.2±0.1	0.2±0.0	1.2±0.4
Molyvan L	645±26.2	N	6.5±0.8 30.6±0.1	83.2±2.3	15.2±2.3	0.6±0.1	1.1±0.0

Table 6. Pyrene Product Distribution Using Untreated Black Thunder Coal Reacted in 1-Methylnaphthalene with Catalyst Introduced During Preswelling(Continued)

Catalyst Type	Catalyst Loading (ppm)[a]	Conditions[b]	% HYD[c] (% Coal)[d]	Product Distribution (mole %)			
				PYR	DHP	THP	HHP
Molyvan L	1258±96.9	D	10.9±0.3 30.3±0.0	71.9±0.4	24.7±0.2	2.4±0.0	1.1±0.2
Molyvan L	1258±36.1	D2	10.4±0.4 30.3±0.0	74.2±0.8	22.1±0.4	2.1±0.1	1.7±0.2
Molyvan L	652±7.8	C(.5)	7.1±3.3 30.5±0.1	82.3±7.9	15.4±6.4	1.0±1.0	1.4±0.5
Molyvan L	629±55.9	I(20%)	15.0±2.0 30.5±0.1	65.4±2.9	26.9±0.1	5.4±2.7	2.4±0.1
Molyvan L	699±21.9	J(20%)	2.4±0.1 30.6±0.0	95.2±0.6	3.5±0.6	0.2±0.1	1.2±0.1
Molyvan L	590±2.1	K(20%)	14.2±0.3	65.4±0.8	28.8±0.8	3.7±0.1	2.2±0.0
Ni Octoate	667±70.0	N	1.9±0.3 30.6±0.0	96.2±0.6	2.9±0.6	0±0	1.0±0.1
Ni Octoate	1319±99.0	D2	5.2±0.6 30.5±0.0	87.2±1.3	11.3±1.2	0.4±0.0	1.2±0.1
Reaction Time: 20 min				Swelling Solvent: Isopropanol			
Molyvan L	583±15.6	N	1.9±0.7 30.6±0.0	95.5±1.8	4.0±1.8	0.1±0.1	0.5±0.0
Ni Octoate	678±30.4	N	2.2±0.1 30.6±0.0	95.7±0.4	3.2±0.6	0±0	1.1±0.1

[a] ND = Not determined.

[b] A = agitated: Samples were agitated with catalyst for 96 hr during preswelling; N + not agitated for 96 hr during preswelling; D = double catalyst ; 28 h, 16 h, 6 h = hours of catalyst solvent contact during preswelling; 1.5 s = catalyst impregnated into coal and reacted immediately; 1.5 s + = catalyst impregnated into coal, swelled for 96 hr in THF, and then reacted; 1.5 s + d = catalyst impregnated into coal, swelled for 96 hr in THF, dried for 24 hr, and then reacted; 1.5 s + m = 1.5 ml of THF solvent swells coal, then new solvent added with catalyst for 96 hr; D2 = double catalyst loading where half the catalyst is placed into the swelling solvent for 96 hr and half into the reactor; C (0.5) = half of catalyst placed in swelling solvent with coal for 96 hr and half directly in reactor; I(20%) = isopropanol as swelling solvent water; T(40%) = THF swelling solvent is diluted with water; J(20%) = isopropanol swelling solvent is diluted in toluene. K(20) = isopropanol diluted with water and used as a preswelling solvent for 12 hr. Percent strength of swelling solvent is shown in parentheses; [c] % HYD = % hydrogenation;

[d] Coal percentages should be near 31 %.

Table 7. Comparison of coal and Pyrene Conversions With Untreated Black Thunder Coal With Different Catalyst Introduction Methods Using 1-Methylnaphthalene as Reaction Solvent

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Catalyst	Conditions	% Change in Coal Conversion[a] (weight %)	% Change in Pyrene Conversion[a] (mole %)	Swelling Index (%ΔV)
	Coal: untreated		Swelling Solvent: THF	
Molyvan L	N	−5.4±1.6	−3.5±1.8	40.0±1.8
Molyvan L	A	−13.8±3.0	−4.0±5.0	52.3±3.2
Molyvan L	D	−2.5±1.1	+10.0±2.5	41.0±2.7
Molyvan L	28 h	−13.2±1.1	−9.7±2.4	41.0±6.4
Molyvan L	16 h	−9.2±5.0	−0.6±10.3	36.5±9.1
Molyvan L	6 h	−10.5±4.0	−3.4±6.9	41.9±1.4
Molyvan L	1.5s +	−9.6±4.7	−3.2±7.5	55.8±4.7
Molyvan L	1.5s	−3.2±1.8	+4.2±2.5	20.1±3.7
Molyvan L	1.5s + d	−14.5±1.6	+2.8±1.4	49.1±14.1
Molyvan L	T(40%)	−6.0±7.1	6.5±13.7	62.4±20.6
Ni Octoate	N	−2.2±12.9	+8.7±11.0	38.9±5.7
	Coal: untreated		Swelling Solvent: 1-methylnaphthalene + 1.5 ml THF	
Molyvan L	1.5s + m	−36.6±0.2	−15.4±0.6	29.7±5.1
	Coal: untreated		Swelling Solvent: Methanol	
Molyvan L	N	−19.6±0.0	−21.3±0.8	25.2±4.9
Molyvan L	D	+0.8±0.5	+1.4±2.7	26.2±3.4
Ni Octoate	N	−15.4±1.1	−7.5±0.4	23.3±0.8
	Coal: untreated		Swelling Solvent: Isopropanol	
Molyvan L	N	−8.2±0.8	−1.9±2.3	18.2±1.1
Molyvan L	D	−6.3±1.8	+9.5±0.4	22.8±1.5
Molyvan L	D2	−0.9±1.3	+7.2±0.8	16.7±3.3
Molyvan L	C(0.5)	−5.1±1.8	−1.0±7.9	21.4±3.4
Molyvan L	I(20%)	1.5±1.6	+16.0±2.9	25.0±3.3
Molyvan L	J(20%)	−27.5±1.2	−13.9±0.6	21.4±3.4
Molyvan L	K(20%)	−2.5±0.6	+15.9±0.8	16.3±3.8
Ni Octoate	N	−2.4±0.8	+1.7±0.6	15.6±3.7
Ni Octoate	D2	+7.5±0.8	+10.7±1.3	20.5±9.7

[a] % change in conversion is the difference between the percentage of conversion when the catalyst was added directly to the reactor and the percentage conversion when the catalyst was added to the preswelling solvent.

[b] A = agitated; Samples were agitated with catalyst for 96 hr during preswelling; N = not agitated for 96 hr during preswelling; D = double catalyst loading; 28 h, 16 h, 6 h = hours of catalyst solvent contact during preswelling; 1.5s = catalyst impregnated into coal and reacted immediately; 1.5s + = catalyst impregnated into coal, swelled for 96 hr in THF, and then reacted; 1.5 s+d = catalyst impregnated into coal, swelled for 96 hr in THF, dried for 24 hr, and then reacted; 1.5 s+m = 1.5 ml of THF solvent swells coal, then new solvent added with catalyst for 96 hr; D2 = double catalyst loading where half of the catalyst is placed into the swelling solvent for 96 hr and half into the reactor; I(20%) = isopropanol as swelling solvent in water; T(40%) = THF swelling solvent is diluted in water; J(20%) = isopropanol as swelling solvent in toluene. Percent strength of swelling solvent is shown in parentheses.

* Performed in March.

Table 8. Coal and Pyrene Conversion for SO_2 Treated Black Thunder Coal Reacted in 1-Methylnaphthalene with Catalyst Introduced During Preswelling

Catalyst Type	Catalyst Loading (ppm)	Conditions[a]	Added Coal			Pyrene Conversion (mol%)	Coal Conversion (wt%)	Total Recovery (g) [%R]
			%ΔV	(g)	wt%			
Reaction Time: 30 min			**Swelling Solvent: THF**					
Molyvan L	617±29.7	N	76.1±18.2	1.53±0.00	31.3±0.0	31.4±0.8	86.0±2.2	4.73±0.39 111.7±9.1
Ni Octoate	632±38.2	N	58.9±26.7	1.53±0.00	31.4±0.0	6.9±1.2	71.4±4.1	4.96±0.07 117.5±1.6
Reaction Time: 30 min			**Swelling Solvent: Methanol**					
Molyvan L	648±36.8	N	43.7±5.2	1.53±0.00	31.3±0.1	26.8±2.8	85.1±5.7	5.19±0.07 122.5±1.6
Ni Octoate	685±0.7	N	33.4±4.8	1.53±0.00	31.4±0.1	7.1±0.5	78.4±0.2	4.72±0.34 11.9±8.0
Reaction Time: 30 min			**Swelling Solvent: Isopropanol**					
Molyvan L	638±0.7	N	32.5±1.2	1.53±0.00	31.3±0.1	26.0±0.2	87.6±1.0	5.06±0.06 119.5±1.2
Ni Octoate	637±24.7	N	25.0±0.0	1.52±0.00	31.3±0.0	5.0±0.2	67.9±2.3	4.94±0.02 117.2±0.7

[a] A = Agitated during preswelling; N = not agitated.

Table 9. Pyrene Product Distribution Using SO_2 Treated Black Thunder Coal with 1-Methylnaphthalene as Reaction Solvent

Catalyst Type	Catalyst Loading (ppm)	Conditions[a]	%HYD (%Coal)	Product Distribution (mol%)			
				PYR	DHP	THP	HHP
Reaction Time: 30 min				**Swelling Solvent: THF**			
Molyvan L	617±29.7	N	12.5±0.4 31.3±0.0	68.7±0.8	26.9±0.6	2.8±0.1	1.7±0.1
Ni Octoate	632±38.2	N	3.1±0.4 31.4±0.0	93.2±1.2	5.7±1.3	0.0±0.0	1.2±0.1
Reaction Time: 30 min				**Swelling Solvent: Methanol**			
Molyvan L	648±36.8	N	11.1±1.6 31.3±0.1	73.3±2.8	22.5±1.1	2.3±1.3	2.1±0.4
Ni Octoate	685±0.7	N	3.1±0.1 31.4±0.1	93.0±0.5	6.0±0.6	0.0±0.0	1.1±0.1
Reaction Time: 30 min				**Swelling Solvent: Isopropanol**			
Molyvan L	638±14.1	N	10.4±0.1 31.3±0.1	74.1±0.2	22.3±0.3	2.3±0.1	1.4±0.0
Ni Octoate	637±24.7	N	2.4±0.0 31.3±0.0	95.1±0.2	3.8±0.4	0.0±0.0	1.2±0.1

[a] N = not agitated

Table 10. Comparison of Coal and Pyrene Conversions With SO_2 Treated Black Thunder Coal With Different Catalyst Introduction Methods

Catalyst	Agitated (A) Not Agitated (N) Double Catalyst (D)	% Change in Coal Conversion (weight %)	% Change in Pyrene Conversion (mole %)	Swelling Index (%ΔV)
Coal: SO_2 Treated		Swelling Solvent: THF		
Molyvan L	N	−5.2±2.2	+6.0±0.8	76.1±18.2
Ni Octoate	N	−1.1±4.1	+4.7±1.2	58.9±26.7
Coal: SO_2 Treated		Swelling Solvent: Methanol		
Molyvan L	N	−0.6±0.5	+0.3±2.2	38.4±2.3
Ni Octoate	N	−0.5	+2.5	30.0
Coal: SO_2 Treated		Swelling Solvent: Isopropanol		
Molyvan L	N	−3.7±1.0	+4.7±0.2	32.5±1.2

Table 11. Coal and Pyrene Conversions for Untreated Black Thunder Coal Reacted in V1074

Catalyst Type	Catalyst Loading (ppm)	Added Coal			Conversion		Total Recovery (g)[%R]
		%ΔV	(g)	wt%	Pyrene (mol %)	Coal (wt%)	
Reaction Time: 30 min				**Swelling Solvent: None**			
Molyvan L	652±17.7	NA	1.64±0.00	30.3±0.1	14.9±2.8	84.7±1.0	4.3±0.2 98.8±4.7
Ni Octoate	668±41.2	NA	1.64±0.00	30.6±0.1	5.5±4.4	79.8±3.5	4.3±0.2 98.7±6.5
Reaction Time: 30 min				**Swelling Solvent: THF**			
None	0±0	25.0±3.3	1.65±0.00	30.7±0.0	5.3±0.1	72.0±1.7	5.1±0.01 117.0±0.4
Reaction Time: 30 min				**Swelling Solvent: THF**		**Catalyst Placed in Reactor**	
Molyvan L	670±57.3	38.7±9.7	1.65±0.00	30.2±0.5	28.0±0.3	82.8±2.0	5.5±0.01 123.6±3.3
Ni Octoate	663±4.2	35.0±4.5	1.65±0.00	30.5±0.2	6.4±0.0	76.6±0.9	5.3±0.16 121.6±4.5
Reaction Time: 30 min				**Swelling Solvent: THF**		**Catalyst Placed in Swelling Solvent**	
Molyvan L	648±0.0	38.3±1.1	1.65±0.00	30.7±0.1	14.1±2.3	76.0±8.1	5.55±0.04 127.5±0.9
Ni Octoate	683±0.5	26.7±0.8	1.65±0.00	30.6±0.2	4.6±1.5	78.7±1.7	5.17±0.05 118.7±0.4

Table 12. Pyrene Product Distribution Using Untreated Black Thunder Coal With V1074 as the Reaction Solvent

Catalyst	Catalyst (ppm)	%HYD (% Coal)	Product Distribution (mol%)			
			PYR	DHP	THP	HHP
Reaction Time: 30 min		**Swelling Solvent: None**				
Molyvan L	652±17.7	5.7±1.1 30.3±0.1	85.2±2.8	13.5±2.5	0.7±0.1	0.7±0.1
Ni Octoate	668±41.2	2.0±1.6 30.6±0.1	94.5±4.4	5.1±4.1	0.4±0.3	0±0
Reaction Time: 30 min		**Swelling Solvent: THF**				
None	0	3.0±0.1 30.7±0.0	94.7±0.1	3.2±0.0	0.5±0.1	1.7±0.1
Reaction Time: 30 min		**Swelling Solvent: THF**		**Catalyst: Placed in Reactor**		
Molyvan L	670±57.3	11.8±0.3 30.2±0.5	72.0±0.3	23.2±0.1	2.4±0.0	2.5±0.2
Ni Octoate	645±21.9	3.3±0.1 30.5±0.2	93.6±0.0	4.6±0.1	0.4±0.0	1.5±0.1
Reaction Time: 30 min		**Swelling Solvent: THF**		**Catalyst: Placed in Swelling Solvent**		
Molyvan L	648±0.0	6.1±0.8 30.7±0.1	85.9±2.3	11.7±2.2	0.7±0.1	1.8±0.1
Ni Octoate	683±0.5	2.5±0.7 30.6±0.7	95.5±1.5	2.8±1.1	0.4±0.0	1.4±0.4

Table 13. Coal and Pyrene Conversions for Untreated Black Thunder Coal Reacted in Dihydroanthracene

Catalyst Type	Catalyst Loading (ppm)	%HYD (% Coal)	Added Coal			Conversion		Total Recovery [% R]
			%ΔV	g coal	wt%	Pyrene (mol %)	Coal (wt%)	
Time: 30 min			Swelling Solvent: None					
Molyvan L	677±23.3	5.4±1.8 30.5±0.0	NA[a]	1.64±0.00	30.5±0.0	15.2±4.5	89.7±0.2	4.7±0.25 107.5±5.7
Time: 30 min			Swelling Solvent: THF					
None	0±0	6.0±0.1 30.9±0.1	36.5±2.3	1.65±0.00	30-.9±0.1	9.3±0.2	82.4±2.1	5.4±0.1 125.7±2.2
Time: 30 min			Swelling Solvent: THF			Catalyst: Placed in Reactor		
Molyvan L	658±32.5	9.4±1.8 30.6±0.0	22.2±0.7	1.65±0.00	30.6±0.0	23.5±4.7	87.3±2.8	5.5±0.06 127.3±1.4
Time: 30 min			Swelling Solvent: THF			Catalyst: Placed in Swelling Solvent		
Molyvan L	641±41.0	4.6±0.8 30.6±0.0	41.0±6.4	1.65±0.00	30.6±0.0	8.9±2.3	84.5±0.4	5.42±0.14 124.5±3.2

Table 14. Pyrene Distributions for Untreated Black Thunder Coal Reactions Using Dihydroanthracene as the Reaction Solvent

Catalyst Type	Catalyst Loading (ppm)	%HYD (% Coal)	Product Distribution (mol%)			
			PYR	DHP	THP	HHP
Time: 30 min		**Swelling Solvent: None**				
Molyvan L	677±23.3	5.4±1.8 30.5±0.0	84.8±4.5	14.5±4.1	0.5±4.1	0.3±0.4
Time: 30 mine		**Swelling Solvent: THF**				
None	0±0	6.0±0.1 30.9±0.1	90.8±0.2	3.2±0.1	3.3±0.1	2.8±0.1
Time: 30 min		**Swelling Solvent: THF**	**Catalyst: Placed in reactor**			
Molyvan L	658±32.5	9.4±1.8 30.6±0.0	76.6±4.7	20.3±4.0	1.6±0.6	1.6±0.3
Time: 30 min		**Swelling Solvent: THF**	**Catalyst: Placed in Swelling Solvent**			
Molyvan L *	641±41.0	4.6±0.8 30.6±0.0	91.2±2.3	5.8±2.6	1.4±0.4	1.7±0.1

[a] NA = not applicable.

[b] ND = not determined.

[c] Coal percentages should be near 31%.

Table 15. Coal and Pyrene Conversions for Reaction Systems with Untreated Black Thunder Coal using 1-Methylnaphthalene as the Reaction Solvent and Mo Naphthenate as Catalyst

Catalyst Type	Catalyst Loading (ppm)	Added Coal			Conversion		Total Recovery(g) [%R]
		%ΔV	(g)	wt%	Pyrene (mol%)	Coal (wt%)	
Compound Used: Sulfur		Swelling Solvent: THF		Catalyst: In Reactor			
Mo Naphthenate	659±20.5	36.4±6.4	1.65±0.00	29.5±0.0	24.8±0.8	89.9±1.2	5.13±0.09 113.4±2.0
Compound Used: Sulfur		Swelling Solvent: THF		Catalyst: In Swelling Solvent			
Mo Naphthenate	655±65.8	35.1±11.0	1.65±0.00	29.5±0.1	26.0±0.5	89.9±0.1	5.08±0.10 112.4±2.1
Compound Used: Sulfur + Carbon Black		Swelling Solvent: THF		Catalyst: In Reactor			
Mo Naphthenate	643±74.2	31.1±1.0	1.65±0.00	28.6±0.1	15.8±11.6	78.2±0.9	5.06±0.03 108.2±0.4
Compound Used: Sulfur + Carbon Black		Swelling Solvent: THF		Catalyst: In Swelling Solvent			
Mo Naphthenate	578±9.2	31.8±12.9	1.67±0.00	28.9±0.1	21.1±0.8	78.3±1.1	5.06±0.46 108.1±9.8
Compound Used: Sulfur		Swelling Solvent: THF		Catalyst: In Reactor + Carbon Black in Swelling Solvent			
Naphthenate	657±21.2	52.0±25.0	1.67±0.00	28.9±0.1	21.6±1.3	80.0±2.8	5.24±0.01 111.6±0.1
Compound Used: Sulfur		Swelling Solvent: THF		Catalyst: In Swelling Solvent + Carbon Black in Swelling Solvent			
Mo Naphthenate	593±46.7	46.7±17.5	1.67±0.00	28.9±0.1	21.8±1.6	78.8±1.1	5.52±0.18 117.6±3.5

Table 16. Pyrene Product Distribution in Reactions of Untreated Black Thunder Coal Using 1-Methylnaphthalene as Reaction Solvent and Mo Naphthenate as Catalyst

Catalyst Type	Catalyst Loading (ppm)	%HYD (% Coal)	Product Distribution (mol%)			
			PYR	DHP	THP	HHP
Compound Used: Sulfur		**Swelling Solvent: THF**		**Catalyst In Reactor**		
Mo Naphthenate	659±20.5	10.2±0.2 29.5±0.1	75.2±0.8	21.0±0.8	2.0±0.1	1.8±0.1
Compound Used: Sulfur		**Swelling Solvent: THF**		**Catalyst: In Swelling Solvent**		
Mo Naphthenate	655±65.8	10.7±0.2	74.1±0.5	21.8±0.4	2.3±0.1	1.9±0.0
Compound Used: Sulfur + Carbon Black		**Swelling Solvent: THF**		**Catalyst: In Reactor**		
Mo Naphthenate	643±74.2	6.5±4.7 28.6±0.1	84.2±11.6	13.4±9.8	1.0±1.3	1.4±0.6
Compound Used: Sulfur + Carbon Black		**Swelling Solvent: THF**		**Catalyst: In Swelling Solvent**		
Mo Naphthenate	578±9.2	9.0±0.4 28.9±0.1	79.0±0.8	17.4±0.6	1.3±0.0	2.4±0.2
Compound Used: Sulfur		**Swelling Solvent: THF**		**Catalyst: In Reactor + Carbon Black in Swelling Solvent**		
Mo Naphthenate	657±21.2	9.2±0.3 28.9±0.1	78.4±1.3	17.9±1.4	1.5±0.2	2.3±0.4
Compound Used: Sulfur		**Swelling Solvent: THF**		**Catalyst: In Swelling Solvent + Carbon Black in Swelling Solvent**		
Mo Naphthenate	593±46.7	9.2±0.7 28.9±0.1	78.2±1.6	18.2±1.1	1.4±0.3	2.2±0.1

Table 17. Effect of Swelling on Catalytic Activity of Molyvan L

Catalyst Type	Catalyst Loading (ppm)	Added Coal			Conversion		Total Recovery (g)[%R]
		%ΔV	(g)	wt%	Pyrene (mol%)	Coal (%wt)	
Time: 30 min				**Catalyst: Added directly to reactor**			
Molyvan L	661±32.5	37.8±1.9	1.65±0.00	30.7±0.1	18.6±1.3	87.3±1.6	4.11±0.15 94.3±3.3
Time: 30 min				**Catalyst: Placed in THF, then separated and placed into reactor**			
Molyvan L	656±23.3	33.4±4.2	1.65±0.00	30.6±0.0	22.9±4.2	85.2±1.8	4.78±0.31 109.7±7.0

Table 18. Pyrene Product Distribution from Reactions Evaluating the Catalytic Activity of Molyvan L

Catalyst Type	Catalyst Loading (ppm)	%HYD (% Coal)	Product Distribution (mol%)			
			PYR	DHP	THP	HHP
Time: 30 min Catalyst: Added directly to reactor						
Molyvan L	661±32.5	6.2±0.4 30.7±0.1	81.4±1.3	18.6±1.3	0±0	0±0
Time: 30 Catalyst: Placed in THF, then separated and placed into reactor						
Molyvan L	656±23.3	9.0±1.6 30.6±0.0	77.2±4.2	19.8±3.5	1.8±0.6	1.3±0.0

Table 19. Coal and Pyrene Conversion for Untreated Black Thunder Coal Using V1074 as a Swelling and Reaction Solvent

Catalyst Type	Catalyst Loading (ppm)	Conditions	Added Coal			Conversion		Total Recovery [%R]
			%ΔV	(g)	wt%	Pyrene (mol %)	Coal (wt%)	
Reaction Time: 30 min Swelling Solvent: V1074								
Thermal	None	N[a]	NA	1.64±0.00	21.1±0.1	5.8±0.9	70.7±1.3	7.0±0.3 111.3±4.7
Molyvan L	645±55.2	NoPS[b]	NA	1.64±0.00	20.7±0.1	25.9±2.4	76.8±2.3	7.1±0.01 109.9±0.9
Molyvan L	655±33.2	NC[c]	NA	1.64±0.00	20.8±0.0	27.3±0.9	77.9±0.4	7.1±0.2 111.7±2.8

[a] N = not agitated during preswelling; preswelling solvent used as reaction solvent.
[b] NoPS = no preswelling; catalysts added directly to the reactor.
[c] NC = Catalyst added to preswelling solvent; preswelling solvent used as reaction solvent.

Table 20. Pyrene Distributions for Untreated Black Thunder Coal Using V1074 as a Swelling and Reaction Solvent

Catalyst Type	Catalyst	Conditions	% HYD (% Coal)	Product Distribution (mol %)			
				PYR	DHP	THP	HHP
Reaction Time: 30 min Swelling Solvent: V1074							
Thermal	None	N[a]	3.0±0.4 21.1±0.1	94.3±0.9	3.8±0.7	0.6±0.0	1.4±0.2
Molyvan L	645±55.2	NoPS[b]	10.7±1.3 20.7±0.1	74.1±2.4	22.0±1.5	1.8±0.4	2.2±0.5
Molyvan L	655±33.2	NC[c]	11.6±0.5 20.8±0.0	72.8±0.9	22.6±0.5	2.1±0.1	2.7±0.4

[a] N = not agitated during preswelling; preswelling solvent used as reaction solvent.
[b] NoPS = no preswelling; catalysts added directly to the reactor;
[c] NC = catalyst added to preswelling solvent; preswelling solvent used as reaction solvent.

Table 21. Untreated Black Thunder l Using 1-Methylnaphthalene as the Reaction Solvent and Adding Hexane Soluble Step In the Product Separation Procedure

Catalyst Type	Loading (ppm)	Added Coal			Pyrene Conversion (mole %)	Coal Conversion (wt %)	Total Recovery (g) [%R]
		%ΔV	(g)	wt %			
Time: 30 minutes		Swelling Solvent: Isopropanol				Catalyst: added to swelling solvent	
None	0.0±0.0	19.2±5.7	1.64±0.00	30.8±0.0	2.4±0.5	58.3±2.7	4.9935±0.054 115.7±1.3
Molyvan 822	608±22.6	14.0±0.5	1.64±0.00	30.4±0.0	24.3±2.7	24.3±2.7	3.7479±0.258 85.9±6.2
Mo Naphthenate + S	645±31.1	11.6±2.9	1.66±0.00	29.7±0.1	22.3±0.9	89.1±1.6	3.8361±0.059 84.7±1.3
Molyvan L	650±33.9	13.3±0.4	1.64±0.00	30.5±0.0	15.9±5.6	76.6±1.8	3.5699±0.251 82.1±5.9

Table 22. Product Distribution of Untreated Black Thunder Coal Using 1-Methylnaphthalene as the Reaction Solvent and Adding Hexane Soluble Step in the Product Separation Procedure

Catalyst Type	Loading (ppm)	% H (% Coal)	Product Distribution (mole %)			
			PYR	DHP	THP	HHP
Time: 30 minutes		Swelling Solvent: Isopropanol		Catalyst: added to swelling solvent		
None	0.0±0.0	1.5±0.3 30.8±0.0	97.6±0.5	1.4±0.49	0±0	1.0±0.3
Molyvan 822	608±22.6	10.2±1.2 30.0±0.0	75.7±2.7	20.0±2.1	2.4±0.2	2.0±0.4
Mo Naphthenate + S	645±31.1	10.1±0.6 29.7±0.1	77.8±0.9	17.3±0.4	1.7±0.1	3.3±0.4
Molyvan L	650±33.9	7.2±1.4 30.5±0.0	84.2±5.6	12.3±5.7	1.4±1.1	2.2±1.2

Table 23. Coal and Pyrene Conversions for Reaction Systems With Untreated Black Thunder Coal Using Low Levels of Catalysts

Catalyst Type	Catalyst Loading (ppm)[a]	Added Coal			Conversion		Total Recovery (g)[%R]
		%ΔV	(g)	wt%	Pyrene (mol%)	Coal (wt%)	
Swelling Solvent: THF Catalyst: In Swelling Solvent							
Molyvan L	127±37.5	35.7±7.4	1.65±0.00	30.8±0.0	2.1±1.3	53.7±1.3	4.67±0.39 107.9±9.1
Swelling Solvent: Methanol Catalyst: In Swelling Solvent							
Molyvan L	115±10.6	22.8±1.5	1.65±0.00	30.8±0.0	2.1±0.4	53.1±2.3	4.74±0.01 105.5±6.0
Swelling Solvent: Isopropanol Catalyst: In Swelling Solvent							
Molyvan L	116±32.5	15.9±3.3	1.64±0.00	30.8±0.0	1.8±0.4	51.6±4.0	4.42±0.13 102.3±3.1

Table 24. Pyrene Product Distributions in Reactions of Untreated Black Thunder Coal Using Low Levels of Catalyst

Catalyst Type	Catalyst Loading (ppm)	%HYD (% Coal)	Product Distribution (mol%)			
			PYR	DHP	THP	HHP
Swelling Solvent: THF Catalyst: In Swelling Solvent						
Molyvan L	127±37.5	1.3±0.0 30.8±0.0	97.9±0.0	1.3±0.1	0±0	0.9±0.1
Swelling Solvent: THF Catalyst: In Swelling Solvent						
Molyvan L	115±10.6	1.3±0.2 30.8±0.0	97.9±0.4	1.3±0.4	0±0	0.8±0.0
Swelling Solvent: Isopropanol Catalyst: In Swelling Solvent						
Molyvan L	116±32.5	1.2±0.1 30.8±0.0	98.3±0.4	0.9±0.4	0±0	0.9±0.1

Table 25. Change in Concentration of Molyvan L at Different Reaction Conditions

Reaction Time(min)	Concentration of Catalyst Precursor (ppm)							
	Molyvan L 380 °C		Molyvan L 410 °C		Molyvan L + S 410 °C		MoNaph 380 °C	
	305 nm	345 nm	305 nm	345 nm	305 nm	345 nm	485 nm	460 nm
0	C^i	C^i	C^i	C^i	C^i	C^i	C^o	C^o
2	99	73	76	68	95	76	517	517
5	125	80	81	72	76	72	531	591
10							542	612
15	151	91	51	76	121	81	57	71
30	70	74	30	65	98	79	56	70

Reaction Conditions: C^i = 994 ppm, initial concentration of Molyvan L in solvent, 1-methylnaphthalene, hydrogen pressure: 1250 psig at ambient, S:Mo = 3:1 when sulfur is present.
C^i = 1001 ppm, initial concentration of Mo naphthenate is solvent, hexadecane, hydrogen pressure: 1250 psig at ambient.

Table 26. Coal and Pyrene Conversions for Reactions with Untreated Black Thunder Coal at 410 °C

Catalyst Type	Catalyst Loading (ppm)	Added Coal			Pyrene Conversion (mole %)	Coal Conversion (weight %)	Total Recovery (g) [%R]
		%ΔV	(g)	wt %			
Swelling Time: 96 hours Swelling Solvent: THF Reaction Solvent: V1074							
None	0.0±0.0	25.0±3.3	1.65±0.00	30.7±0.0	5.3±0.1	72.0±1.7	5.1±0.01 117.0±0.4
Molyvan L	648±0.0	38.3±1.1	1.65±0.00	30.7±0.1	14.1±2.3	76.0±8.1	5.55±0.04 127.5±0.9
Swelling Time: 48 hours Swelling Solvent: THF Reaction Solvent: V1074							
Molyvan L	617±39.6	34.1±3.3	1.65±0.00	30.6±0.1	14.7±1.1	80.4±1.1	5.53±0.51 126.8±11.2
Swelling Time: 24 hours Swelling Solvent: THF Reaction Solvent: V1074							
Molyvan L	621±42.4	32.6±1.1	1.65±0.00	30.7±0.1	23.5±7.8	84.4±0.6	5.42±0.39 124.5±9.1
Swelling Time: 12 hours Swelling Solvent: THF Reaction Solvent: V1074							
Molyvan L	659±37.5	40.7±6.1	1.65±0.00	30.5±0.0	31.8±1.4	85.4±1.4	5.16±0.02 118.1±0.3
Catalyst: Placed in reactor Swelling Solvent: THF Reaction Solvent: V1074							
Molyvan L	670±57	38.7±9.7	1.65±0.00	30.2±0.5	28.0±0.3	82.8±2.0	5.5±0.07 123.6±3.3

Table 27. Product Distributions of Pyrene in Reactions of Untreated Black Thunder Coal at 410 °C

Catalyst Type	Catalyst Loading	% HYD (% Coal)	Product Distribution (mole %)			
			PYR	DHP	THP	HHP
Swelling Time: 96 hours Swelling Solvent: THF Reaction Solvent: V1074						
None	0.0±0.0	3.0±0.1 30.7±0.0	94.7±0.1	3.2±0.0	0.5±0.1	1.7±0.1
Molyvan L	648±0.0	6.1±0.8 30.7±0.1	85.9±2.3	11.7±2.2	0.7±0.1	1.8±0.1
Swelling Time: 48 hours Swelling Solvent: THF Reaction Solvent: V1074						
Molyvan L	617±39.6	6.3±0.3 30.6±0.1	85.4±1.1	12.2±1.1	0.6±0.0	1.9±0.1
Swelling Time: 24 hours Swelling Solvent: THF Reaction Solvent: V1074						
Molyvan L	621±42.4	9.8±3.0 30.7±0.1	76.5±7.8	19.9±6.4	1.6±1.3	2.1±0.1
Swelling Time: 12 hours Swelling Solvent: THF Reaction Solvent: V1074						
Molyvan L	659±37.5	13.4±0.7 30.5±0.0	68.2±1.6	26.1±1.1	3.1±0.7	2.7±0.2
Catalyst: Placed in reactor Swelling Solvent: THF Reaction Solvent: V1074						
Molyvan L	670±57	11.8±0.3 30.2±0.5	72.0±0.1	23.2±0.1	2.4±0.0	2.5±0.2

Table 28. Solvent Uptake by Coal During Swelling

Catalyst	Coal Mass (g)	Solvent Mass Absorbed (g)	Catalyst Mass (g)
Swelling Time: 96 hours		**SS[a]: IPA**	**RS[b]: 1-methylnaphthalene**
None	1.6353±0.001	1.2052±0.142	0.0000±0.000
Molyvan L	1.6440±0.002	1.2480±0.038	0.0400±0.001
Swelling Time: 48 hours		**SS: IPA**	**RS: 1-methylnaphthalene**
Molyvan L	1.6407±0.001	0.8838±0.074	0.0333±0.007
Swelling Time: 24 hours		**SS: IPA**	**RS: 1-methylnaphthalene**
Molyvan L	1.6419±0.003	0.9015±0.046	0.0409±0.000
Swelling Time: 12 hours		**SS: IPA**	**RS: 1-methylnaphthalene**
Molyvan L	1.6432±0.003	0.8881±0.018	0.0353±0.002
Catalyst: placed into reactor		**SS: IPA**	**RS: 1-methylnaphthalene**
Molyvan L	1.6365±0.005	1.1893±0.040	0.0338±0.002

[a] SS: swelling solvent.

[b] RS. reaction solvent.

[c] IPA: isopropanol

Table 29. Effect of Swelling Time on Coal and Pyrene Conversions with Untreated Black Thunder Coal at 410 °C

Catalyst Type	Catalyst Loading (ppm)	Added Coal			Pyrene Conversion (mole %)	Coal Conversion (wt %)	Total Recovery (g) [%R]
		%ΔV	(g)	wt %			
Swelling Time: 96 hours Swelling Solvent: Isopropanol Reaction Solvent: 1-MN							
None	0±0	16.9±5.5	1.64±0.00	30.7±0.0	0.8±1.1	61.7±1.1	4.3326±0.304 100.7±7.1
Molyvan L	645±26.2	18.2±1.1	1.64±0.00	30.6±0.1	16.9±2.3	79.9±0.8	4.7718±0.332 109.6±7.6
Swelling Time: 48 hours Swelling Solvent: Isopropanol Reaction Solvent: 1-MN							
Molyvan L	731±112.4	16.3±3.8	1.64±0.00	30.5±0.3	9.5±0.3	70.3±0.5	4.7827±0.127 109.9±3.0
Swelling Time: 24 hours Swelling Solvent: Isopropanol Reaction solvent: 1-MN							
Molyvan L	691±6.4	11.9±3.4	1.64±0.00	30.6±0.1	10.1±3.9	74.1±5.7	4.6069±0.182 105.9±4.2
Swelling Time: 12 hours Swelling Solvent: Isopropanol Reaction Solvent: 1-MN							
Molyvan L	597±29.0	14.3±0.0	1.64±0.00	30.6±0.0	7.8±2.9	71.2±9.4	4.6384±0.241 106.8±5.4
Catalyst: placed in reactor Swelling Solvent: Isopropanol Reaction Solvent: 1-MN							
Molyvan L	623±37.5	17.9±6.9	1.64±0.00	30.5±0.0	18.7	88.1±50.4	4.6732±0.133 107.6±3.3

[a] NA = not applicable.

Table 30. Effect of Swelling Time on Pyrene Product Disturbution in Reactions of Untreated Black Thunder Coal

Catalyst Type	Catalyst Loading (ppm)	% HYD (%Coal)	Product distribution (mole %)			
			PYR	DHP	THP	HHP
Swelling Time: 96 hours Swelling Solvent: Isopropanol Reaction Solvent: 1-MN						
None	0±0	0.6±0.8 30.7±0.0	99.2±1.1	0.3±0.4	0±0	0.5±0.7
Molyvan L	645±26.2	6.5±0.8 30.6±0.1	83.2±2.3	15.2±2.3	0.6±01	1.1±0.0
Swelling Time: 48 hours Swelling Solvent: Isopropanol Reaction Solvent: 1-MN						
Molyvan L	731±112.4	4.2±0.0 30.5±0.0	90.5±0.3	7.8±0.4	0.3±0.0	1.4±0.1
Swelling Time: 24 hours Swelling Solvent: Isopropanol Reaction Solvent: 1-MN						
Molyvan L	691±6.4	4.5±1.3 30.6±0.1	90.0±3.9	8.3±3.7	0.3±0.2	1.5±0.0
Swelling Time: 12 hours Swelling Solvent: Isopropanol Reaction Solvent: 1-MN						
Molyvan L	597±29.0	3.7±0.9 30.6±0.0	92.3±2.9	6.2±2.9	0.2±0.1	1.5±0.1
Catalyst: placed in reactor Swelling Solvent: Isopropanol Reaction Solvent: 1-MN						
Molyvan L	623±37.5	6.6±0.3 30.5±0.0	81.4±0.8	18.7±0.8	0.6±0.1	0.4±0.1

[a] NA = not applicable.

Table 31. Catalyst Screening Reactions: Coal and Pyrene Conversions for Reaction Systems with Untreated Black Thunder Coal Using DHA and V1074 as Reaction Solvent

Catalyst Type	Catalyst Loading (ppm)*	Added Coal			Conversion		Total Recovery (g)[%R]
		%ΔV	(g)	wt%	Pyrene(mol%)	Coal(wt%)	
Swelling Solvent: Isopropanol					Catalyst: In Swelling Solvent		
Mo Naphthenate + S	608±4.9	10.9±3.0	1.65±0.00	29.3±0.2	21.3±1.4	85.3±0.6	4.93±0.68 108.3±14.1
Molyvan L	626±26.9	20.1±3.7	1.64±0.00	30.4±0.3	7.7±1.6	81.2±1.1	5.05±0.03 115.5±0.3
Molyvan 822	498±0.7	26.7±0.8	1.65±0.00	30.2±0.1	21.0±1.1	88.0±0.1	4.87±0.42 110.7±9.2
Molyvan 822 + S	664±40.3	25.0±3.3	1.66±0.00	29.1±0.0	23.6±0.1	86.5±0.1	5.28±0.01 114.1±0.14
Ni Naphthenate	682±0.0	25.7±4.2	1.64±0.00	30.3±0.1	11.4±0.7	85.5±1.5	5.25±0.15 119.5±3.5
Ni Octoate	626±38.2	17.8±0.6	1.64±0.00	30.5±0.1	5.7±2.5	75.3±1.5	5.17±0.02 118.8±1.1
Co Naphthenate	660±9.2	28.2±14.1	1.64±0.00	30.4±0.2	4.8±0.3	73.4±0.6	5.25±0.27 119.7±5.2
Ni Acetylacetonate	201±0.0	15.9±3.3	1.65±0.00	30.8±0.0	5.2±0.0	77.0±0.0	5.01±0.04 115.9±1.0
Ni Acetylacetonate	671±55.9	20.9±2.6	1.64±0.00	30.3±0.4	7.3±2.1	80.0±1.3	5.10±0.2 116.1±2.0
Ni Citrate	603±12.0	13.6±0.0	1.64±0.00	30.4±0.4	6.3±1.2	77.5±1.4	5.0±0.32 113.8±6.2
Mo Oxide	746±36.1	18.7±7.2	1.64±0.00	30.7±0.2	9.6±0.8	83.6±0.9	5.4±0.06 124.8±0.8
Mo dioxide Bis Acetylacetonate	697±21.9	19.6±3.0	1.65±0.00	30.7±0.1	6.2±0.4	78.9±3.2	5.08±0.1 116.9±2.1
Swelling Solvent: 20% Isopropanol/80% Water					Catalysts: In Swelling Solvent		
Molyvan L	777±83.4	28.0±0.9	1.63±0.00	30.3±0.1	28.6±0.8	87.5±1.9	5.3±0.3 121.4±8.3
Ammonium tetrathiomolybdate	642±10.6	18.6±0.6	1.65±0.00	30.7±0.1	27.6±1.4	89.5±0.6	4.7±0.64 108.2±15.7
Molyvan 822	605±15.6	38.7±3.2	1.63±0.00	30.5±0.2	11.5±0.9	83.2±2.8	4.9±0.07 112.5±1.6
Ni Naphthenate	619±25.5	23.8±0.0	1.63±0.00	30.4±0.1	12.1±2.9	84.5±2.3	5.21±0.13 120.1±3.0

* Values obtained by assuming 91.8% of the catalyst absorbed into the coal.

Table 32. Catalyst Screening Reactions: Pyrene Product Distribution in Reactions of Untreated Black Thunder Coal Using DHA and V1074 as the Reaction Solvent

Catalyst Type	Catalyst Loading(ppm)	%HYD (% coal)	Product Distribution (mol%)			
			PYR	DHP	THP	HHP
Swelling Solvent: Isopropanol			Catalyst: In Swelling Solvent			
Mo Naphthenate + S	608±4.9	9.9±0.6 29.3±0.2	78.7±1.4	16.7±1.2	1.2±0.1	3.5±0.1
Molyvan L	626±26.9	3.6±0.6 30.4±0.3	92.4±1.6	5.9±1.6	0.4±0.0	1.4±0.1
Molyvan 822	498±0.7	9.1±0.6 30.2±0.1	79.1±1.1	17.1±0.6	1.6±0.1	2.4±0.4
Molyvan 822 + S	664±40.3	10.1±0.5 29.1±0.0	76.5±0.1	19.4±0.6	1.8±0.1	2.4±0.7
Ni Naphthenate	682±0.0	5.1±0.2 30.3±0.1	88.6±0.7	9.3±0.8	0.5±0.1	1.7±0.1
Ni Octoate	626±38.2	2.9±0.8 30.5±0.1	94.4±2.5	4.0±2.6	0.5±0.1	1.3±0.1
Co Naphthenate	660±9.2	3.0±0.2 30.4±0.2	95.2±0.3	2.4±0.2	0.8±0.0	1.7±0.1
Ni Acetylacetonate	201±0.0	3.0±0.1 30.8±0.0	94.8±0.0	3.0±0.1	0.7±0.1	1.6±0.1
Acetylacetonate	671±55.9	3.6±0.8 30.3±0.4	92.7±2.1	5.4±2.0	0.4±0.1	1.6±0.2
Ni Citrate	603±12.0	3.3±0.1 30.4±0.4	93.8±1.2	4.2±1.7	0.4±0.3	1.7±0-.2
Mo Oxide	746±36.1	4.5±0.2 30.7±0.2	90.5±0.8	7.5±0.8	0.4±0.0	1.7±0.1
Mo Dioxide Bis Acetylacetonate	697±21.9	3.2±0.1 30.7±0.1	93.8±0.4	4.4±0.5	0.5±0.1	1.4±0.0
Swelling Solvent: 20% Isopropanol/80% Water			Catalyst: In Swelling Solvent			
Molyvan L	777±83.4	11.5±0.6 30.3±0.1	71.5±0.8	24.2±0.2	2.9±0.1	1.6±0.5
Ammonium Tetrathiomolybdate	642±10.6	11.6±0.6 30.7±0.1	72.4±1.4	22.7±1.1	2.7±0.2	2.2±0.1
Molyvan 822*	605±15.6	5.0±0.4 30.5±0.2	88.9±0.9	9.6±0.8	0.4±0.0	1.5±0.1
Ni Naphthenate*	619±25.5	5.2±0.8 30.4±0.1	88.0±2.9	10.0±3.2	0.6±0.1	1.5±0.1

* Values obtained by assuming 91.8% of the catalyst absorbed into the coal.

Table 33. Coal and Pyrene Conversions for Thermal Reactions of Illinois No. 6 Coal With Three Different Solvents[a]

Catalyst (ppm)	Added Coal		Pyrene Conversion (mol%)	Coal Conversion (wt %)	Total Recovery (g) [%R]
	(g)	wt %			
Solvent: 9,10-Dihydroanthracene					
None	1.72±0.00	30.4±0.0	10.0±1.1	86.5±2.6	5.71±0.22 130.1±5.1
Solvent: V1074					
None	1.72±0.00	30.3±0.1	17.9±4.7	86.6±0.8	5.36±0.08 121.6±1.2
Solvent: 1-Methylnaphthalene					
None	1.72±0.00	30.4±0.0	9.0±1.5	86.5±0.2	4.98±0.04 113.5±0.9

[a] Reaction Conditions: 410 °C; 30 min; no catalyst; 1250 psig H_2 introduced at ambient temperature.

Table 34. Pyrene Product Distributions from Thermal Reactions of Illinois No. 6 Coal in Three Solvents

Catalyst [Label]	% HYD (% Coal)	Product Distribution (mol %)			
		PYR	DHP	THP	HHP
Solvent: 9,10-Dihydroanthracene					
None	4.4±0.4 30.4±0.0	90.1±1.1	8.4±1.1	0.3±0.0	1.3±0.0
Solvent: V1074					
None	7.4±1.8 30.3±0.1	82.2±4.7	15.4±4.5	0.8±0.0	1.7±0.3
Solvent: 1-Methylnaphthalene					
None	3.9±0.4 30.4±0.0	91.1±1.5	7.5±1.6	0.3±0.1	1.2±0.1

[a] PYR = pyrene; DHP = dihydropyrene; THP = tetrahydropyrene; HHP = hexahydropyrene.

Table 35. Pyrene and Coal Conversions for Thermal Reactions of Wyodak Coal With Three Different Solvents[a]

Catalyst (ppm)	Added Coal		Pyrene Conversion (mole %)	Coal Conversion (%)	Total Recovery (g) [%R]
	(g)	wt %			
Solvent: 9,10-Dihydroanthracene					
None	2.03±0.00	28.3±0.0	4.4±0.0	87.0±1.9	6.56±0.24 139.4±5.1
Solvent: V1074					
None	2.51±0.69	31.4±4.7	3.5±0.8	86.0±2.2	5.87±0.71 112.8±0.8
Solvent: 1-Methylnaphthalene					
None	2.03±0.00	28.3±0.0	2.1±0.4	71.5±0.1	4.95±0.06 105.5±1.2

[a] Reaction Conditions: 410 °C; 30 min; no catalyst; 1250 psig H_2 introduced at ambient temperature.

Table 36. Pyrene Product Distributions from Thermal Reactions of Wyodak Coal in Three Solvents

Catalyst (ppm)	% HYD (% Coal)	Product Distribution (mol %)			
		PYR	DHP	THP	HHP
Solvent: 9,10-Dihydroanthracene					
None	2.5±0.1 28.3±0.0	95.6±0.0	2.5±0.3	0.7±0.0	1.2±0.3
Solvent: V1074					
None	1.7±0.4 31.4±4.7	96.6±0.8	2.6±0.5	0.3±0.1	0.7±0.2
Solvent: 1-Methylnaphthalene					
None	1.2±0.1 28.3±0.0	98.0±0.4	1.3±0.4	0±0	0.8±0.0

[a] PYR = pyrene; DHP = dihydropyrene; THP = tetrahydropyrene; HHP = hexahydropyrene.

Table 37. Coal and Pyrene Conversions for Thermal Reactions of North Dakota Coal with Three Different Solvents[a]

Catalyst (ppm)	Added Coal		Pyrene Conversion (mole %)	Coal Conversion (%)	Total Recovery (g){%R]
	(g)	wt %			
Solvent: 9,10-Dihydroanthracene					
None	2.12±0.00	27.1±0.0	6.0±0.5	76.7±5.1	5.43±0.26 113.3±5.4
Solvent: V1074					
None	2.12±0.00	27.0±0.1	6.1±0.3	74.1±6.2	5.29±0.14 109.8±2.5
Solvent: 1-Methylnaphthalene					
None	2.12±0.00	27.1±0.1	4.7±0.8	73.5±4.0	5.06±0.26 105.7±5.4

[a] Reaction Conditions: 410 °C, 30 min, no catalyst, 1250 psig H_2 introduced at ambient temperature.

Table 38. Pyrene Product Distributions from Thermal Reactions of North Dakota Coal With Three Solvents

Catalyst (ppm)]	% HYD (% Coal)	Product Distribution (mol %)			
		PYR	DHP	THP	HHP
Solvent: 9,10-Dihydroanthracene					
None	3.5±0.5 27.1±0.0	94.1±0.5	3.2±0.1	1.3±0.3	1.5±0.4
Solvent: V1074					
None	2.9±0.1 27.0±0.1	93.9±0.3	4.8±0.6	0.3±0.1	1.1±0.2
Solvent: 1-Methylnaphthalene					
None	2.2±0.3 27.1±0.1	95.3±0.8	3.8±0.9	0±0	1.0±0.1

[a] PYR = pyrene; DHP = dihydropyrene; THP = tetrahydropyrene; HHP = hexahydropyrene.

Table 39. Coal and Pyrene Conversions for Treated Wyodak Coal

Catalyst [Label]	Added Coal		Pyrene Conversion (mole %)	Coal Conversion (%)	Total Recovery (g)[%R]
	(g)	wt %			
Solvent: 9,10-Dihydroanthracene					
None	2.03±0.00	20.3±0.0	4.4±0.0	87.0±1.9	6.56±0.24 139.4±5.1
Solvent: V1074					
None	2.51±0.69	31.4±4.7	3.5±0.8	86.0±2.2	5.87±0.71 112.8±0.8
Solvent: 1-Methylnaphthalene					
None	2.03±0.00	28.3±0.0	2.1±0.4	71.5±0.1	4.95±0.06 105.5±1.2
Iron	2.03±0.00	28.4±0.1	3.3±0.0	47.4±3.0	4.68±0.00 99.0±0.1
Cobalt	2.04±0.00	28.4±0.0	2.3±0.0	46.9±1.5	4.68±0.00 99.4±0.0
Molybdenum	2.04±0.00	28.4±0.0	34.4±0.6	88.3±2.8	5.83±0.07 123.9±1.6
Nickel	2.04±0.00	28.4±0.0	5.1±0.1	60.7±2.2	4.94±0.05 105.1±1.1
Acid Washed	2.04±0.00	28.4±0.0	3.2±0.1	41.6±1.4	4.91±0.02 104.3±0.2

Table 40. Pyrene Product Distribution for Wyodak Coal

Catalyst [Label]	% HYD (% Coal)	Product Distribution (mol %)			
		PYR	DHP	THP	HHP
Solvent: 9,10-Dihydroanthracene					
None	2.5±0.1 28.3±0.0	95.6±0.0	2.5±0.3	0.7±0.0	1.2±0.3
Solvent: V1074					
None	1.7±0.4 31.4±4.7	96.6±0.8	2.6±0.5	0.3±0.1	0.7±0.2
Solvent: 1-Methylnaphthalene					
None	1.2±0.1 28.3±0.0	98.0±0.4	1.3±0.4	0±0	0.8±0.0
Iron	1.8±0.0 28.4±0.1	96.7±0.0	2.0±0.0	0.3±0.0	1.0±0.0
Cobalt	1.4±0.0 28.4±0.0	97.7±0.0	1.3±0.0	0.1±0.0	0.9±0.0
Molybdenum	14.2±0.2 28.4±0.0	65.7±0.6	28.6±0.6	3.5±0.1	2.3±0.1
Nickel	2.8±0.1 28.4±0.0	95.0±0.1	3.4±0.1	0.2±0.1	1.6±0.1
Acid Washed	2.2±0.1 28.4±0.0	96.9±0.1	1.5±0.0	0.2±0.1	1.5±0.0

Table 41. Coal and Pyrene Conversions Using Metal Treated Wyodak Coals

Catalyst (ppm)	Added Coal		Pyrene Conversion (mol%)	Coal Conversion (wt %)	Total Recovery (g) [%R]
	(g)	wt %			
Solvent: 1-Methylnaphthalene					
Iron	2.03±0.00	28.3±0.0	3.3±0.0	74.7±0.1	4.80±0.23 102.0±4.8
Cobalt	1.93±0.14	28.3±0.1	2.5±0.8	53.4±5.0	4.76±0.38 106.5±0.8
Molybdenum	2.03±0.00	28.3±0.0	4.5±2.4	74.2±1.3	5.05±0.01 107.4±0.0
Nickel	2.03±0.00	28.3±0.0	3.2±0.5	75.6±0.1	4.97±0.11 105.8±2.1

Table 42. Pyrene Distributions Using Metal Treated Wyodak Coals

Catalyst (ppm)	% HYD (% Coal)	Product Distribution (mol %)			
		PYR	DHP	THP	HHP
Solvent: 1-Methylnaphthalene					
Iron	2.0±0.1 28.3±0.0	96.7±0.0	2.1±0.1	0±0	1.3±0.1
Cobalt	1.7±0.4 28.3±0.1	97.5±0.8	1.3±0.6	0±0	1.3±0.2
Molybdenum	2.3±1.1 28.3±0.0	95.5±2.4	3.4±2.1	0±0	1.2±0.4
Nickel	1.8±0.4 28.3±0.0	96.9±0.5	2.0±0.1	0±0	1.2±0.4

Table 43. Coal and Pyrene Conversions Using Metal Treated Black Thunder Coal

Catalyst [Label]	Added Coal		Pyrene Conversion (mol%)	Coal Conversion (wt %)	Total Recovery (g) [%R]
	(g)	wt %			
Solvent: 1-Methylnaphthalene					
Nickel [Ni 1]	1.65±0.00	30.9±0.0	2.6±0.1	64.0±0.5	4.52±0.17 104.6±4.0
Nickel [Ni 2]	1.65±0.00	30.9±0.0	3.0±0.6	66.0±5.8	4.59±0.35 106.0±8.1
Cobalt [Co 1]	1.65±0.00	30.9±0.0	2.9±0.3	63.4±1.5	4.79±0.22 110.9±5.0
Cobalt [Co 2]	1.65±0.00	30.9±0.0	3.0±0.6	65.1±2.8	4.32±0.12 99.8±2.8
Molybdenum [Mo 1]	1.64±0.00	30.8±0.0	5.3±0.3	65.6±3.2	4.10±0.02 95.1±0.5
Molybdenum [Mo 2]	1.64±0.00	30.8±0.0	3.2±0.6	63.4±5.6	4.51±0.07 104.7±1.6
Iron [Fe 1]	1.64±0.00	30.8±0.0	3.5±1.3	60.2±1.6	4.41±0.06 102.1±1.4
Iron [Fe 2]	1.64±0.00	30.8±0.0	3.1±0.4	65.9±3.4	4.39±0.14 101.8±3.0
Iron-Nickel [Fe-Ni 1]	1.64±0.00	30.8±0.0	3.9±0.1	67.5±3.0	4.47±0.01 103.6±0.3
Iron-Nickel [Fe-Ni 2]	1.64±0.00	30.8±0.0	4.0±0.1	66.4±3.0	4.43±0.15 102.8±3.3
Iron-Molybdenum [Fe-Mo 1]	1.64±0.00	30.8±0.0	5.3±0.1	69.2±2.9	4.39±0.02 101.8±0.7
Iron-Molybdenum [Fe-Mo 2]	1.64±0.00	30.8±0.0	4.8±0.1	66.5±2.4	4.41±0.03 102.2±0.8

Table 44. Pyrene Product Distributions with Metal Treated Black Thunder Coal

Catalyst [Label]	% HYD (% Coal)	Product Distribution (mol %)			
		PYR	DHP	THP	HHP
Solvent: 1-Methylnaphthalene					
Nickel [Ni 1]	1.5±0.0 30.9±0.0	97.4±0.1	1.7±0.2	0±0	1.0±0.1
Nickel [Ni 2]	1.6±0.2 30.9±0.0	97.1±0.6	2.1±0.6	0±0	0.9±0.1
Cobalt [Co 1]	1.7±0.1 30.9±0.0	97.1±0.3	1.9±0.4	0±0	1.1±0.1
Cobalt [Co 2]	1.7±0.3 30.9±0.0	97.1±0.6	1.9±0.6	0±0	1.1±0.1
Molybdenum [Mo 1]	2.4±0.1 30.8±0.0	94.7±0.3	4.4±0.3	0±0	0.9±0.0
Molybdenum [Mo 2]	1.8±0.4 30.8±0.0	96.9±0.6	2.2±0.5	0±0	1.0±0.1
Iron [Fe 1]	1.8±0.6 30.8±0.0	96.6±1.3	2.5±1.2	0±0	1.0±0.1
Iron [Fe 1]	1.7±0.1 30.8±0.0	97.0±0.4	2.2±0.4	0±0	0.9±0.0
Iron-Nickel [Fe-Ni 1]	2.0±0.1 30.8±0.0	96.1±0.1	2.9±0.1	0±0	1.0±0.0
Iron-Nickel [Fe-Ni 2]	2.1±0.1 30.8±0.0	96.0±0.1	3.0±0.1	0±0	1.1±0.1
Iron-Molybdenum [Fe-Mo 1]	2.5±0.1 30.8±0.0	94.7±0.1	4.3±0.1	0±0	1.0±0.0
Iron-Molybdenum [Fe-Mo 2]	2.4±0.2 30.8±0.0	95.2±0.1	3.7±0.2	0±0	1.2±0.4

Table 45. Change in Concentration of Slurry Phase Catalysts in Swelling Solvents with Time

Catalyst	Isopropanol			THF		
	Absorbance	Concentration (g/l)	Fraction (C / C_o)	Absorbance	Concentration (g/L)	Fraction (C / C_o)
Elapsed Time: 0 hours						
MoNaph[a]	1.007±0.595	1.819±1.074		2.529±0.159	4.567±0.250	
Molyvan L	0.682±0.035	6.263±0.177		0.712±0.066	6.588±0.177	
Ni Octoate	0.111±0.056	7.144±0.044		0.315±0.009	7.800±0.389	
Elapsed Time: 6 hours						
MoNaph	1.294±0.256	2.338±0.463	0.463±0.067	2.438±0.170	4.404±0.308	0.964±0.014
Molyvan L	0.465±0.022	4.266±0.202	0.681±0.013	0.474±0.100	4.389±0.930	0.669±0.159
Ni Octoate	0.171±0.178	4.243±4.422	0.596±0.622	0.269±0.012	6.663±0.298	0.854±0.004
Elapsed Time: 12 hours						
MoNaph	1.326±0.269	2.396±0.486	0.474±0.071	2.379±0.172	4.298±0.310	0.941±0.016
Molyvan L	0.433±0.014	3.976±0.130	0.635±0.003	0.819±0.243	7.579±2.246	1.155±0.372
Ni Octoate	0.310±0.004	7.693±0.105	1.077±0.008	0.279±0.011	6.911±0.263	0.887±0.011
Elapsed Time: 24 hours						
MoNaph	1.365±0.375	2.466±0.678	0.488±0.108	2.323±0.165	4.197±0.298	0.919±0.015
Molyvan L	0.399±0.010	3.664±0.091	0.586±0.002	1.472±0.226	13.625±2.089	2.074±0.373
Ni Octoate	0.260±0.021	6.439±0.509	0.902±0.066	0.265±0.011	6.576±0.281	0.843±0.006
Elapsed Time: 48 hours						
MoNaph	1.246±0.246	2.251±0.444	0.446±0.064	2.199±0.116	3.973±0.209	0.870±0.001
Molyvan L	0.379±0.013	3.476±0.124	0.555±0.004	1.723±0.085	15.954±0.786	2.424±0.184
Ni Octoate	0.294±0.008	7.295±0.211	1.021±0.023	0.266±0.011	6.601±0.281	0.847±0.006
Elapsed Time: 96 hours						
MoNaph	1.112±0.138	2.008±0.249	0.399±0.028	1.872±0.057	3.382±0.102	0.741±0.018
Molyvan L	0.389±0.006	3.572±0.052	0.571±0.008	2.252±0.050	20.848±0.465	3.167±0.155
Ni Octoate	0.280±0.007	6.948±0.175	0.973±0.019	0.255±0.010	6.328±0.245	0.812±0.009

[a] MoNaph = Mo naphthenate

[b] * - concentration of catalyst in solution only. A large portion of catalyst in solvent but not in solution.

APPENDIX H

August 31, 1994

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R. J. Torres-Ordonez, H-4
R. L. Ollendorff, H-9

Routine Service - Closeout Report (CARN 94-011869-000)
IOM Swollen Coal Samples with Catalyst

The three small samples IOM_Molyvan-L A, IOM_Molyvan-822 A, and IOM_Molybdenum Naph. A, were ground and dusted onto zero-background holders. The X-ray powder diffraction patterns were measured on a Philips diffractometer using the standard configuration. Patterns were measured from 6-70° 2θ in 0.04° steps, counting for 16 sec/step. The patterns (Figure 1, on the same relative, but not absolute, scale) are in general similar, and indicate varying concentrations of the same set of crystalline phases. Amorphous material, indicated by the broad feature in the background at approximately 20° 2θ, is also present.

The observed patterns were searched against the Powder Diffraction File using the μPDSM software from PSI International. The major crystalline phases present (Figure 2) are α-quartz (SiO_2, PDF 33-1161) and vaterite ($CaCO_3$, 33-268). Vaterite is a metastable hexagonal form of calcium carbonate, and its presence presumably reflects the treatment of the samples.

Present at lower (intermediate to minor) concentrations (Figures 3 and 4) are calcite ($CaCO_3$, 5-586, the normal form of calcium carbonate), dickite ($Al_2Si_2O_5(OH)_4$, 10-446, or another clay mineral), pyrrohtite ($Fe_{1-x}S$, 29-726), talc ($Mg_3Si_4O_{10}(OH)_2$, 29-1493), and molybdenite (MoS_2, 37-1492). An additional peak at $2\theta = 25.6°$ may indicate the presence of corundum (Al_2O_3, 42-1468), anatase (TiO_2, 21-1272), or a graphite-like phase. The concentrations of the various minerals vary among the samples.

The presence of MoS_2 is indicated most clearly by the peak at $2\theta = 14.5°$ (Figure 1). This is the strongest peak in the molybdenite pattern. From the width of this peak, the average crystallite size of the MoS_2 can be calculated:

Sample	Average Crystallite Size, Å
IOM_Molyvan-L A	650
IOM_Molyvan-822 A	440
IOM_Molybdenum Naph. A	440

The pattern of sample IOM_Molybdenum Naph. A was measured twice, on different instruments on successive days. In the second pattern (Figure 1) two additional peaks appeared, peaks which are not accounted for by any of the reported phases. We are not certain whether they reflect the presence of a few large grains of a phase, or a change in the sample on exposure to the atmosphere.

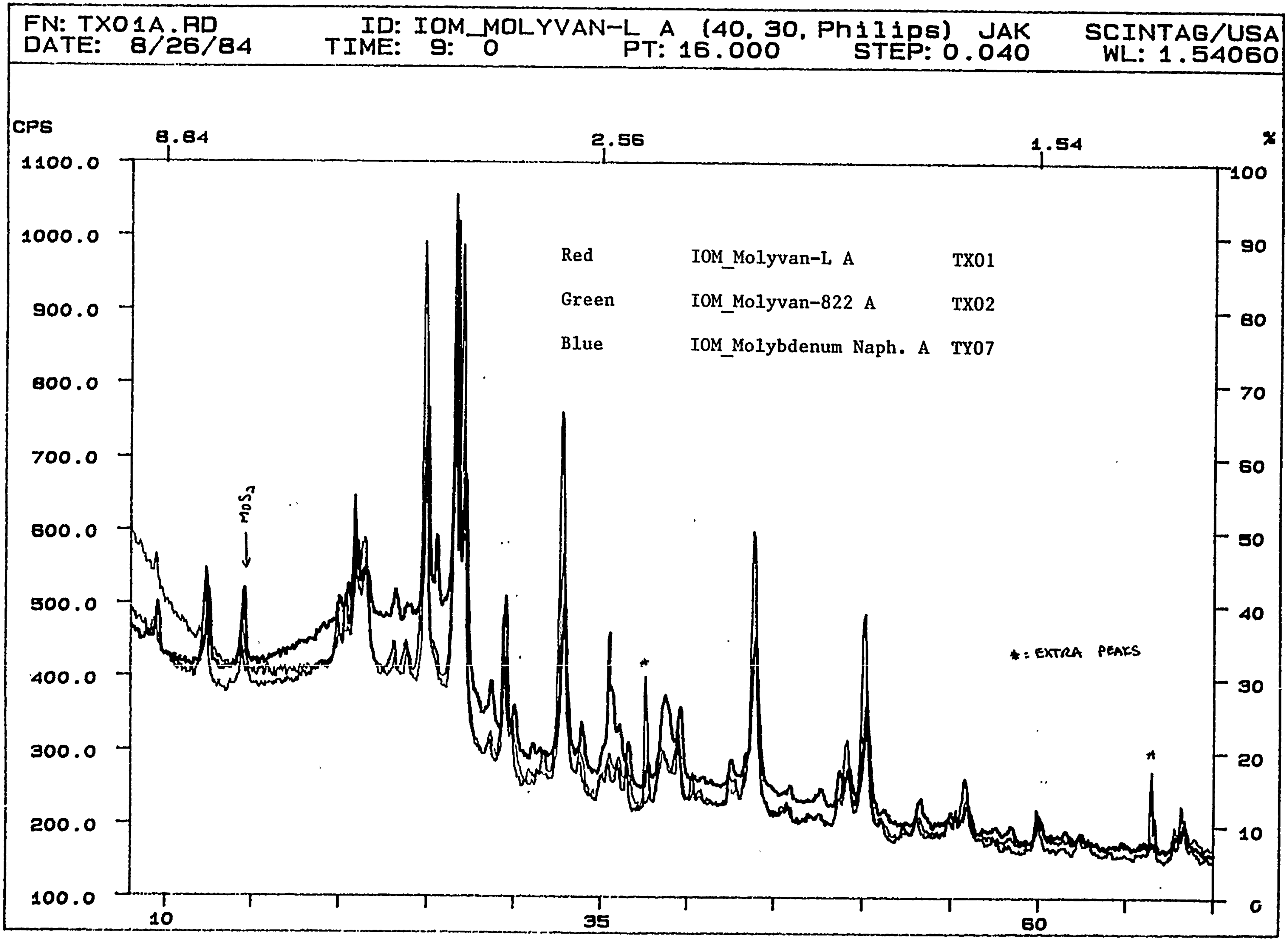
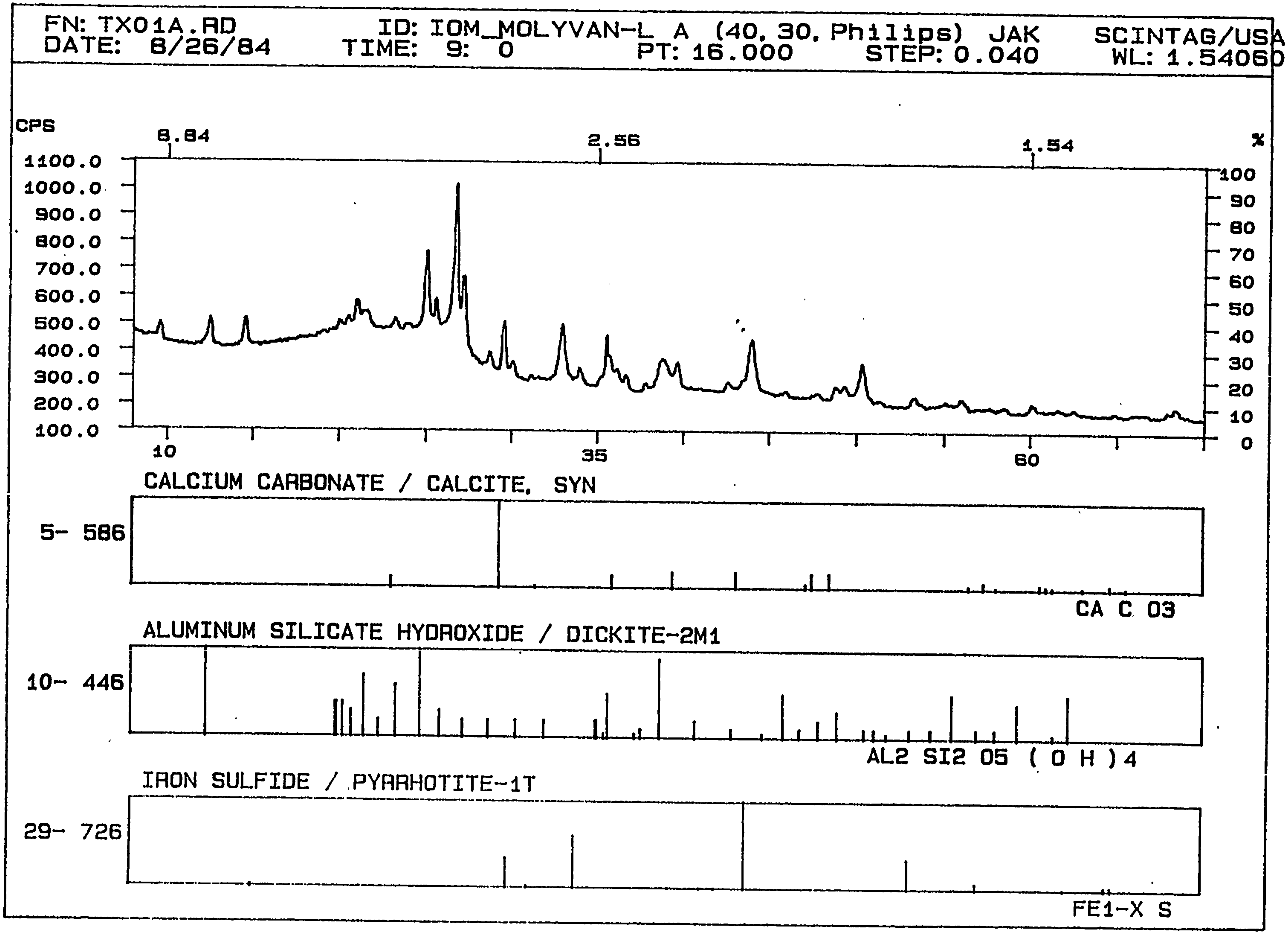

FN: TX01A.RD
DATE: 8/26/84
ID: IOM_MOLYVAN-L A (40, 30, Philips) JAK
TIME: 9: 0
PT: 16.000
STEP: 0.040
SCINTAG/USA
WL: 1.54060
CPS
1100.0
1000.0
900.0
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
8.84
2.56
1.54
%
100
90
80
70
60
50
40
30
20
10
0
10
35
60
Red
IOM_Molyvan-L A
TX01
Green
IOM_Molyvan-822 A
TX02
Blue
IOM_Molybdenum Naph. A
TY07
MoS2
*
*
*: EXTRA PEAKS

FIGURE 1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8.84
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%
100
90
80
70
60
50
40
30
20
10
0
10
35
60
CALCIUM CARBONATE / CALCITE, SYN
5- 586
CA C 03
ALUMINUM SILICATE HYDROXIDE / DICKITE-2M1
10- 446
AL2 SI2 05 (O H) 4
IRON SULFIDE / PYRRHOTITE-1T
29- 726
FE1-X S

FIGURE 3

APPENDIX I

SULFUROUS ACID PRETREATMENT OF WYOMING BLACK THUNDER COAL FOR COAL LIQUEFACTION

Final Technical Report

to

Amoco Oil Company

by

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August 16, 1994

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1. Introduction

The removal of mineral matter prior to liquefaction may be beneficial for a number of reasons. The most obvious is that the demands on solids removal equipment will be reduced. Also, the precipitation of solids in processing equipment is a problem with some coals. Calcium is a particularly bad actor in this regard. The solids buildup in a dissolver has been related to the calcium content of the feed coal[1]. Several groups of investigators have observed the presence of alkali and alkaline earth elements to retard the liquefaction of low rank coals[2,3,4,5]. Again, calcium seems to be the major problem. It has been postulated that calcium inhibits hydrogen transfer to the coal free radicals produced during liquefaction[3,4]. Alternatively, the calcium might serve to increase crosslinking by interacting with carboxylate ions[2,3,5,6].

Pretreatment of the feed coal with mineral acid has shown promise as a means of removing metal cations from the coal and improving coal liquefaction performance. Mochida and coworkers have reported that pretreatment of lignites with 0.4 M HCl significantly increased the conversion during liquefaction[2]. Our research group has performed a study of pretreatment of Wyoming Black Thunder coal with dilute nitric acid[7]. Most of the calcium was removed by this treatment, and the calcite deposit surrounding the used catalyst particles which had been observed in earlier runs with untreated coal was eliminated. Unfortunately, this treatment did not result in an enhancement of catalyst life. Nitric acid is known to oxidize certain functional groups of the type found in coal. The expense aside, nitric acid is unsuitable as a coal pretreatment.

Recently, Cronauer and coworkers[8] reported success in removal of metal cations from a Texas lignite using aqueous SO_2. The sulfurous acid treatment is preferred to nitric acid and other treatments because it is not an oxidant, it is more cost effective, and it is noncorrosive by comparison to hydrochloric acid.

In collaboration with Dr. Cronauer of the Amocao Oil Company, we initiated a series of runs to further explore the effects of demineralization with aqueous SO_2. The catalyst selected for this study is Amocat 1C, a nickel molybdate analog of the cobalt molybdate Amocat 1A which has been employed in our previous work. The switch to a different catalyst necessitated the establishment of a new baseline run with the untreated Black Thunder coal. Upon establishment of the baseline, the coal was treated with aqueous SO_2 and then subjected to coal liquefaction in a catalytic coal liquefaction microreactor unit to explore the effects of the pretreatment on catalyst activity maintenance.

2. Catalyst Deactivation for Amocat 1C

The catalyst selected for this study is Amocat 1C, A nickel molybdate analog of the cobalt molybdate Amocat 1A which has been employed in our previous work. The switch to a different catalyst necessitated the establishment of a new baseline run with the untreated Black Thunder coal. A thermal run was also performed in order to determine the thermal level for the Wyoming Black Thunder coal.

2.1 Experimental

The catalyst deactivation runs were conducted in the Catalytic Coal Liquefaction Microreactor (CCLM) unit of Figure 1. This unit employs a novel ebullated bed reactor which charges only five grams of catalyst. The development of this reactor is described in previous reports[9,10,11]. The coal paste feed was comprised of Black Thunder coal (as received, or acid washed, 96% through 100 mesh), residuum material derived from this coal, and raw creosote oil (Allied Signal, 24CB) in the weight ratios 3/1/2. The coal paste was extruded into the feed line by means of a high pressure syringe pump (Isco Model LC-5000). In order to obtain the desired solvent/coal ratio, a makeup solvent (raw creosote oil) was fed to the reactor separately by means of a liquid chromatography pump (Eldex Model A-30-S) from a tank placed on an analytical pan balance which reads to 0.01 gram.

Hydrogen was compressed into a reservoir from which high pressure hydrogen was introduced to the reactor through a pressure

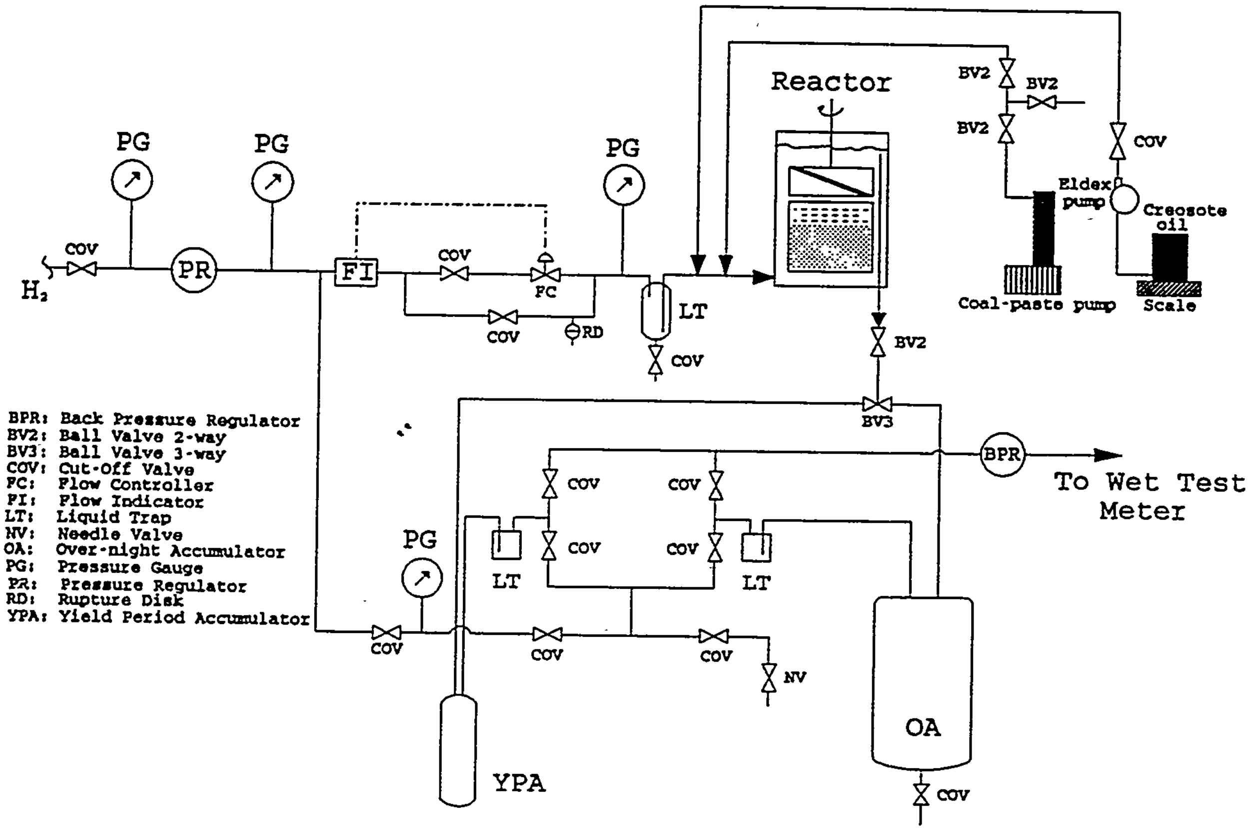

Figure 1. Schematic Diagram of the Catalytic Coal Liquefaction Microreactor Unit.

regulator and a mass flow controller (Brooks Model 5850 TRB).

The liquid/solid product was directed by a three way ball valve to either of two high pressure accumulators. Gas leaving the accumulator passed through a back pressure regulator, a wet test meter, and was collected in a butyl rubber bag for gas chromatographic analysis.

A computerized data acquisition system (Omega WB-FAI-B16) was coupled with the CCLM unit to monitor and record important operation parameters such as reactor temperature, cartridge temperature, feed temperature, reactor pressure, ISCO pump pressure, hydrogen flow rate, exit gas flow rate, and the weight of creosote oil in the feed tank.

The coal employed in this study is Wyoming Black Thunder coal provided by the Amoco Oil Company. Proximate and the ultimate analyses are presented in Table 1. A mineral ash analysis is provided in Table 2.

The deactivation run was conducted at nominal conditions: 800°F,(427°C), 2000 psig, 4000 scf/bbl hydrogen treat rate, WHSV=2 and a solvent/coal weight ratio of 3.

The products workup consisted of forward sequential extraction first in cyclohexane, then in toluene and finally in pyridine. The solubility class conversions were calculated on an MAF coal + residuum basis acceding to the formula:

$$\%Conversion=\frac{g\ mf\ coal+residuum-g\ insol.prod.residue}{g\ maf\ coal+g\ residuum}\times 100$$

The catalyst was first presulfided with CS_2/heavy mineral oil and then subjected to about 20 hours of hydrotreating creosote oil. At this point the reactor was brought to 800°F, coal paste was cut in, and the unit was set to the desired operating conditions.

The used catalyst was Soxhlet extracted in tetrahydrofuran, air dried and finally vacuum dried at 105°C. A portion of the used extracted catalyst was fired in a muffle furnace at 500°C to obtained the loss on ignition and percent catalyst recovery. A small portion was used for Carbon-Hydrogen-Nitrogen analysis conducted on a Leco CHN600 analyzer.

BET surface area analyses and pore size distribution analyses were performed for fresh, used and fired used catalysts.

Table 1. Proximate and Ultimate Analyses for the Original Wyoming Black Thunder Coal

	As-Received (wt.%)	Moisture Free (wt.%)	Moisture & Ash Free (wt.%)
Proximate:			
Moisture	22.67		
Ash	4.76	6.16	
Volatile Matter	33.66	43.53	46.39
Fixed Carbon	38.91	50.31	53.61
Total	100.00	100.00	100.00
Ultimate:			
Hydrogen	6.32	4.89	5.21
Carbon	58.61	75.79	80.77
Nitrogen	0.63	0.81	0.86
Sulfur	0.39	0.50	0.53
Oxygen	29.29	11.85	12.63
Ash	4.76	6.16	
Total	100.00	100.00	100.00

Table 2. Mineral Ash Analysis of Untreated BT Coal

Oxide	% of Ash
SiO_2	31.67
Al_2O_3	15.47
Fe_2O_3	4.74
CaO	24.70
MgO	4.69
Na_2O	0.95
K_2O	0.21
TiO_2	1.10
MnO	0.02
P_2O_5	0.93
SrO	0.35
BaO	0.46
SO_3	14.71
SUM	100.00

2.2 Results from Run ZHQ08

A run summary for the baseline run, identified as Run ZHQ08, is reported in Table 3. The run proceeded smoothly except for a minor temperature excursion (to 430°C) during the 9th yield period, and a partial plug in the makeup pump filter on the 8th and 17th yield periods. The run was shut down as planned after the 21st yield period at which time approximately 1000 weights of coal had been processed per weight of catalyst. As shown in Figure 2., the material balances for most of the yield periods are within the acceptable range of 97-103%.

Solubility class conversion for this run are plotted in Figure 3. A steady deactivation of the catalyst is observed over the duration of the run. The deactivation is, however, less rapid as compared to previous results obtained for the Amocat 1A catalyst

Table 3. Summary of Run ZHQ08

Yield Period No.	1	2	3	4	5
Yield Period Length,Hr	2.0	2.0	2.0	2.0	2.0
Average Temperature,°F	800	800	800	800	800
Average Pressure,Psig	1980	2000	1990	1990	1990
Stirrer Speed,rpm	1205	1205	1205	1205	1205
Makeup Solvent Rate,GM/Hr	20.15	20.15	20.00	19.90	19.80
Coal Paste Rate,GM/Hr	19.99	20.00	20.12	20.00	20.00
Residence Time,Hr	1.510	1.510	1.511	1.520	1.524
Space Velocities:					
GM Coal/Hr/GM Cat	1.998	2.000	2.012	2.000	2.000
GM Dry Coal/Hr/GM Cat	1.545	1.546	1.556	1.546	1.546
GM MAF Coal/Hr/GM Cat	1.450	1.451	1.460	1.451	1.451
Solvent/Coal Wt Ratios:					
GM CO/GM Coal	2.682	2.681	2.654	2.656	2.646
GM CO+Resid/GM Coal	3.016	3.015	2.988	2.990	2.980
GM CO/GM Dry Coal	3.469	3.467	3.432	3.435	3.422
GM CO+GM Resid/GM Dry Coal	3.900	3.898	3.864	3.866	3.853
GM CO/GM MAF Coal	3.696	3.695	3.658	3.660	3.646
GM CO+Resid/GM MAF Coal	4.156	4.154	4.117	4.120	4.106
H_2 Treat Rate,L(STP)/Hr	25.05	25.05	25.05	25.05	25.05
H_2 Treat Rate,SCF/BBL	3992	3991	3995	4017	4028
Exit Gas Rate,L(STP)/Hr	17.30	18.20	18.55	20.10	20.15
Cumulative Quantities:					
Hours on Catalyst	24.7	49.1	72.8	96.6	120.6
Wt Makeup Solvent/Wt Cat	138.0	236.9	332.1	427.7	523.8
Wt Resid/Wt Cat	16.5	32.6	48.3	63.9	79.7
Wt Coal/Wt Cat	49.4	97.7	144.8	191.5	238.9
Overall Material Balance,Wt%	103.1	103.2	104.1	105.3	100.1
Yields(Total Feed Basis):					
Carbon Monoxide,Wt%	0.00	0.00	0.00	0.00	0.00
Carbon Dioxide,Wt%	0.20	0.23	0.24	0.29	0.36
Hydrocarbon Gases(C_1-C_4),Wt%	1.34	1.20	1.27	1.32	1.34
Slurry Product,Wt%	104.8	104.9	105.8	106.5	100.8
H_2 Consumption (Total Feed Basis),Wt%	3.03	2.86	2.78	2.40	2.39
Conversions (MAF Coal+Resid Basis),Wt%					
Wt% Cyclohexane Soluble	81.8	82.4	79.2	68.7	71.0
Wt% Toluene Soluble	84.0	84.6	81.7	74.7	75.7
Wt% Pyridine Soluble	86.2	86.4	85.6	78.3	81.1

Table 3. (Continued)

Yield Period No.	6	7	8	9	10
Yield Period Length,Hr	2.0	2.0	2.0	2.0	2.0
Average Temperature,°F	800	800	800	805	800
Average Pressure,Psig	1990	1980	1990	1980	1990
Stirrer Speed,rpm	1205	1205	1205	1205	1205
Makeup Solvent Rate,GM/Hr	20.15	20.25	16.25	20.15	20.25
Coal Paste Rate,GM/Hr	19.94	19.93	20.02	20.04	20.08
Residence Time,Hr	1.512	1.508	1.681	1.508	1.503
Space Velocities:					
GM Coal/Hr/GM Cat	1.994	1.992	2.001	2.003	2.007
GM Dry Coal/Hr/GM Cat	1.542	1.541	1.557	1.549	1.552
GM MAF Coal/Hr/GM Cat	1.447	1.446	1.452	1.454	1.456
Solvent/Coal Wt Ratios:					
GM CO/GM Coal	2.687	2.699	2.624	2.678	2.684
GM CO+Resid/GM Coal	3.021	3.032	2.962	3.011	3.017
GM CO/GM Dry Coal	3.475	3.490	3.393	3.463	3.471
GM CO+GM Resid/GM Dry Coal	3.906	3.921	3.393	3.894	3.902
GM CO/GM MAF Coal	3.703	3.718	3.156	3.690	3.698
GM CO+Resid/GM MAF Coal	4.162	4.178	3.615	4.149	4.158
H_2 Treat Rate,L(STP)/Hr	25.05	25.05	25.05	25.05	25.05
H_2 Treat Rate,SCF/BBL	3997	3987	4443	3988	3974
Exit Gas Rate,L(STP)/Hr	20.59	20.39	20.06	19.90	21.48
Cumulative Quantities:					
Hours on Catalyst	144.3	168.9	192.1	216.6	240.5
Wt Makeup Solvent/Wt Cat	620.1	720.0	807.7	904.8	1002.2
Wt Resid/Wt Cat	95.3	111.5	126.8	142.8	158.6
Wt Coal/Wt Cat	285.9	334.4	380.3	428.4	475.8
Overall Material Balance,Wt%	101.2	103.5	102.8	100.3	100.4
Yields(Total Feed Basis):					
Carbon Monoxide,Wt%	0.00	0.00	0.00	0.00	0.00
Carbon Dioxide,Wt%	0.37	0.37	0.49	0.39	0.46
Hydrocarbon Gases(C_1-C_4),Wt%	1.31	1.29	1.63	1.42	1.41
Slurry Product,Wt%	101.9	104.5	103.6	101.2	100.6
H_2 Consumption (Total Feed Basis),Wt%	2.33	2.38	2.58	2.77	2.03
Conversions (MAF Coal+Resid Basis),Wt%					
Wt% Cyclohexane Soluble	71.3	67.0	67.3	64.9	64.2
Wt% Toluene Soluble	75.6	72.5	73.3	72.9	72.4
Wt% Pyridine Soluble	80.5	78.3	77.3	79.1	79.8

Table 3. (Continued)

Yield Period No.	11	12	13	14	15
Yield Period Length,Hr	2.0	2.0	2.0	2.0	2.0
Average Temperature,°F	800	800	800	800	800
Average Pressure,Psig	1990	1980	1990	1980	1970
Stirrer Speed,rpm	1205	1205	1205	1205	1205
Makeup Solvent Rate,GM/Hr	20.30	20.55	20.10	20.04	20.17
Coal Paste Rate,GM/Hr	20.09	19.96	20.00	20.04	20.17
Residence Time,Hr	1.501	1.496	1.512	1.508	1.504
Space Velocities:					
GM Coal/Hr/GM Cat	2.008	1.995	2.000	2.003	2.016
GM Dry Coal/Hr/GM Cat	1.553	1.543	1.451	1.549	1.559
GM MAF Coal/Hr/GM Cat	1.457	1.448	1.451	1.454	1.463
Solvent/Coal Wt Ratios:					
GM CO/GM Coal	2.688	2.726	2.676	2.678	2.664
GM CO+Resid/GM Coal	3.021	3.060	3.010	3.011	2.998
GM CO/GM Dry Coal	3.476	3.525	3.461	3.463	3.446
GM CO+GM Resid/GM Dry Coal	3.907	3.956	3.892	3.894	3.877
GM CO/GM MAF Coal	3.704	3.757	3.688	3.690	3.672
GM CO+Resid/GM MAF Coal	4.163	4.216	4.147	4.149	4.131
H_2 Treat Rate,L(STP)/Hr	25.05	25.05	25.05	25.05	25.05
H_2 Treat Rate,SCF/BBL	3968	3954	3996	3988	3975
Exit Gas Rate,L(STP)/Hr	21.92	21.81	22.40	21.82	22.33
Cumulative Quantities:					
Hours on Catalyst	264.9	288.1	312.0	336.1	360.6
Wt Makeup Solvent/Wt Cat	1101	1195	1292	1389	1484
Wt Resid/Wt Cat	174.8	190.0	205.8	221.7	237.9
Wt Coal/Wt Cat	524.2	569.9	617.2	664.9	713.5
Overall Material Balance,Wt%	100.0	101.2	97.7	103.4	103.1
Yields(Total Feed Basis):					
Carbon Monoxide,Wt%	0.00	0.00	0.00	0.00	0.00
Carbon Dioxide,Wt%	0.52	0.46	0.53	0.57	0.57
Hydrocarbon Gases(C_1-C_4),Wt%	1.35	1.36	1.36	1.22	1.23
Slurry Product,Wt%	100.0	101.5	97.5	103.8	103.3
H_2 Consumption (Total Feed Basis),Wt%	1.88	2.00	1.84	1.88	1.79
Conversions (MAF Coal+Resid Basis),Wt%					
Wt% Cyclohexane Soluble	65.4	61.7	66.7	59.9	60.5
Wt% Toluene Soluble	73.9	69.7	73.6	66.8	68.9
Wt% Pyridine Soluble	78.3	78.4	79.4	76.8	77.0

Table 3. (Continued)

Yield Period No.	16	17	18	19	20
Yield Period Length,Hr	2.0	2.0	2.0	2.0	2.0
Average Temperature,°F	800	800	800	800	800
Average Pressure,Psig	1990	1990	1990	1980	1990
Stirrer Speed,rpm	1205	1205	1205	1205	1205
Makeup Solvent Rate,GM/Hr	20.10	12.50	20.35	20.40	19.90
Coal Paste Rate,GM/Hr	19.96	19.99	19.97	19.94	19.92
Residence Time,Hr	1.513	1.888	1.503	1.502	1.523
Space Velocities:					
GM Coal/Hr/GM Cat	1.995	1.998	1.996	1.994	1.991
GM Dry Coal/Hr/GM Cat	1.543	1.545	1.544	1.542	1.540
GM MAF Coal/Hr/GM Cat	1.448	1.450	1.449	1.447	1.445
Solvent/Coal Wt Ratios:					
GM CO/GM Coal	2.681	1.917	2.705	2.712	2.665
GM CO+Resid/GM Coal	3.014	2.250	3.038	3.046	2.998
GM CO/GM Dry Coal	3.467	2.479	3.498	3.507	3.446
GM CO+GM Resid/GM Dry Coal	3.898	2.910	3.929	3.939	3.877
GM CO/GM MAF Coal	3.694	2.642	3.727	3.738	3.672
GM CO+Resid/GM MAF Coal	4.154	3.101	4.187	4.197	4.131
H_2 Treat Rate,L(STP)/Hr	25.05	25.05	25.05	25.05	25.05
H_2 Treat Rate,SCF/BBL	4001	4991	3974	3971	4025
Exit Gas Rate,L(STP)/Hr	22.89	22.63	24.17	24.63	25.29
Cumulative Quantities:					
Hours on Catalyst	385.1	409.1	432.5	456.8	481.2
Wt Makeup Solvent/Wt Cat	1583	1676	1773	1873	1973
Wt Resid/Wt Cat	253.9	269.7	285.2	300.9	317.0
Wt Coal/Wt Cat	761.5	809.1	855.4	902.6	950.8
Overall Material Balance,Wt%	99.9	99.1	103.7	98.9	101.7
Yields(Total Feed Basis):					
Carbon Monoxide,Wt%	0.00	0.00	0.00	0.00	0.00
Carbon Dioxide,Wt%	0.60	0.88	0.71	0.76	0.88
Hydrocarbon Gases(C_1-C_4),Wt%	1.27	1.71	1.24	1.18	1.15
Slurry Product,Wt%	99.6	98.2	103.5	98.1	101.0
H_2 Consumption (Total Feed Basis),Wt%	1.60	1.83	1.39	1.24	1.10
Conversions (MAF Coal+Resid Basis),Wt%					
Wt% Cyclohexane Soluble	62.0	72.5	55.8	55.1	48.8
Wt% Toluene Soluble	71.2	77.6	64.9	64.9	58.5
Wt% Pyridine Soluble	78.6	83.2	69.0	68.2	69.6

Table 3. (Continued)

Yield Period No.	21
Yield Period Length,Hr	2.0
Average Temperature,°F	800
Average Pressure,Psig	1990
Stirrer Speed,rpm	1205
Makeup Solvent Rate,GM/Hr	20.40
Coal Paste Rate,GM/Hr	20.11
Residence Time,Hr	1.496
Space Velocities:	
GM Coal/Hr/GM Cat	2.010
GM Dry Coal/Hr/GM Cat	1.555
GM MAF Coal/Hr/GM Cat	1.459
Solvent/Coal Wt Ratios:	
GM CO/GM Coal	2.695
GM CO+Resid/GM Coal	3.029
GM CO/GM Dry Coal	3.485
GM CO+GM Resid/GM Dry Coal	3.917
GM CO/GM MAF Coal	3.714
GM CO+Resid/GM MAF Coal	4.173
H_2 Treat Rate,L(STP)/Hr	25.05
H_2 Treat Rate,SCF/BBL	3995
Exit Gas Rate,L(STP)/Hr	25.84
Cumulative Quantities:	
Hours on Catalyst	505.3
Wt Makeup Solvent/Wt Cat	2064
Wt Resid/Wt Cat	332.8
Wt Coal/Wt Cat	998.1
Overall Material Balance,Wt%	100.1
Yields(Total Feed Basis):	
Carbon Monoxide,Wt%	0.00
Carbon Dioxide,Wt%	0.93
Hydrocarbon Gases(C_1-C_4),Wt%	0.99
Slurry Product,Wt%	99.1
H_2 Consumption (Total Feed Basis),Wt%	0.93
Conversions (MAF Coal+Resid Basis),Wt%	
Wt% Cyclohexane Soluble	48.8
Wt% Toluene Soluble	58.4
Wt% Pyridine Soluble	67.7

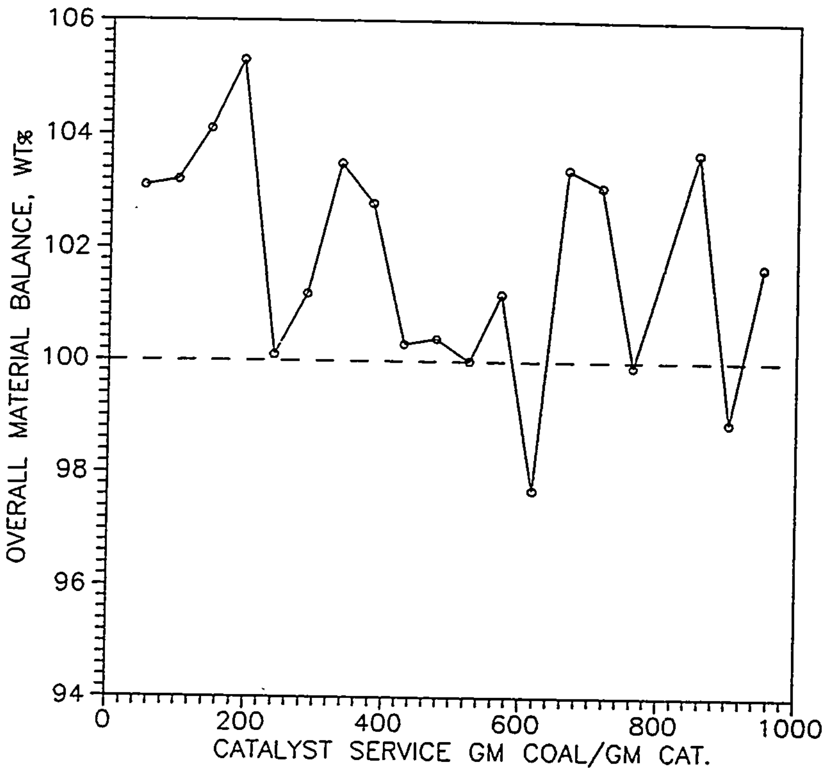

Figure 2. Overall Material Balance for Run ZHQ08

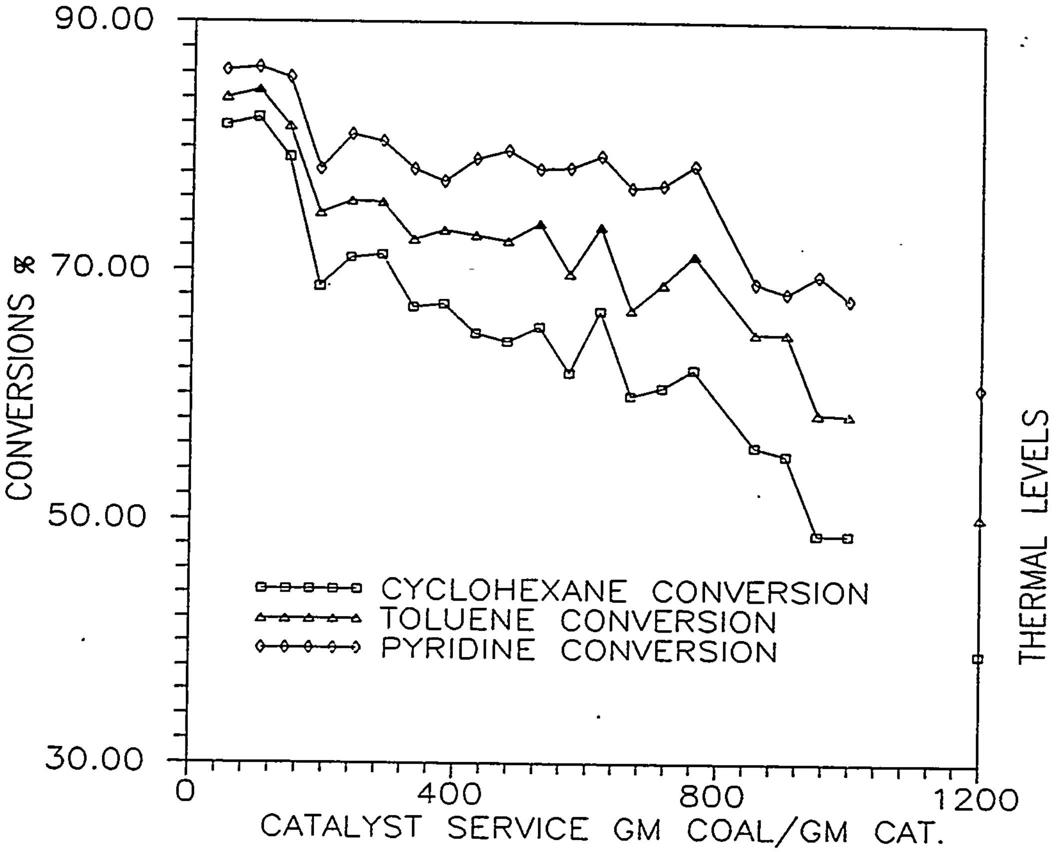

Figure 3. Solubility Class Conversions for Run ZHQ08.

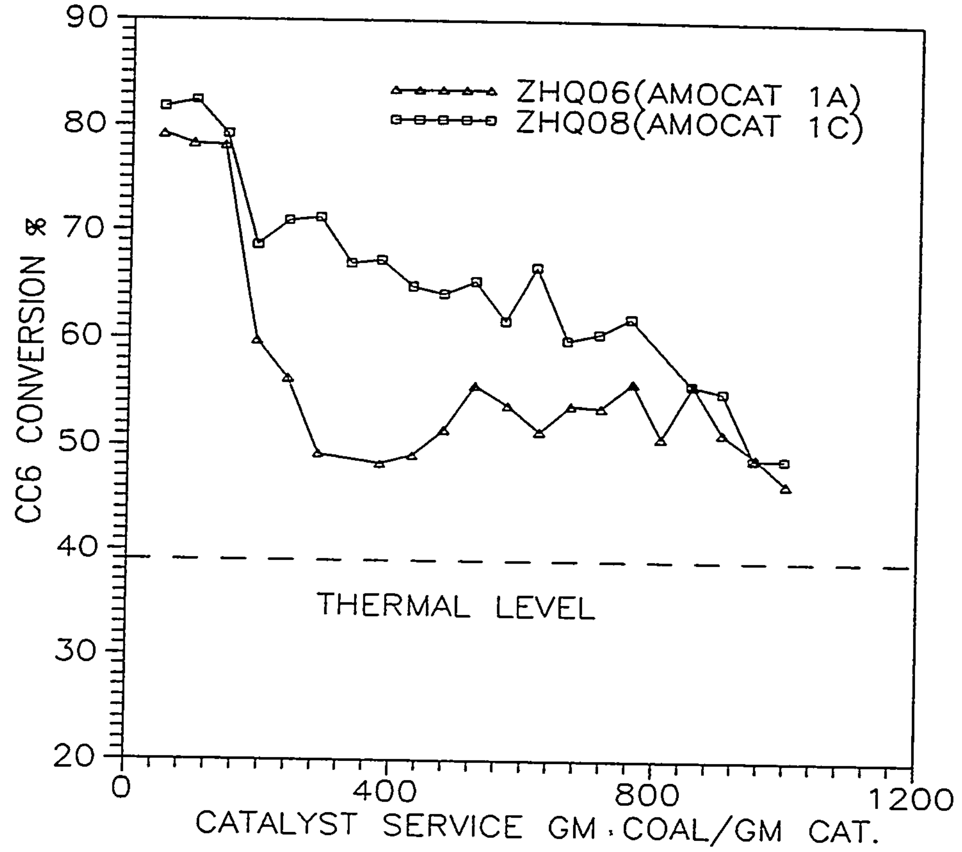

Figure 4. Comparison of Cyclohexane Solubility Conversions for Amocat 1A and Amocat 1C Catalysts.

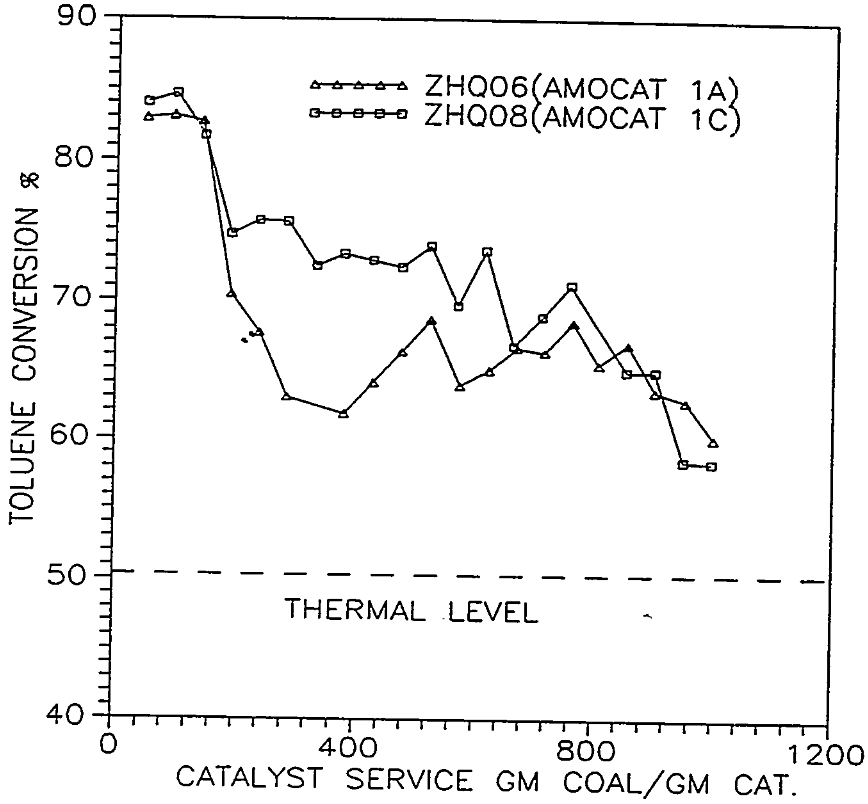

Figure 5. Comparison of Toluene Solubility Conversions for Amocat 1A and Amocat 1C Catalysts.

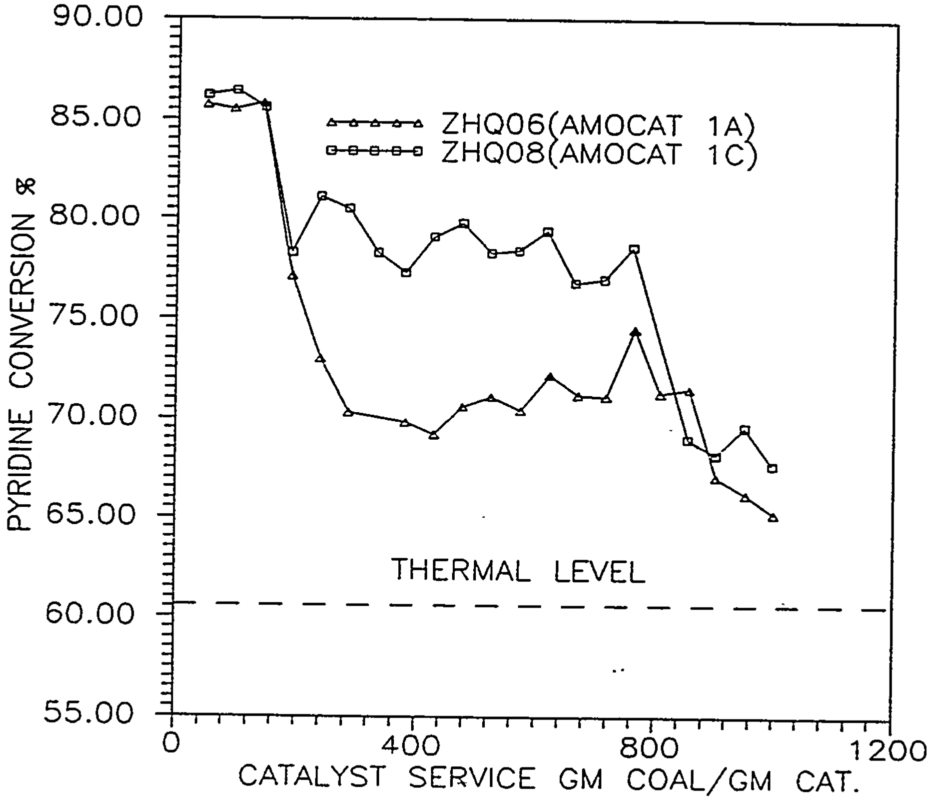

Figure 6. Comparison of Pyridine Solubility Conversions for Amocat 1A and Amocat 1C Catalysts.

under identical operating conditions. This is shown in Figures 4 through 6.

From the information thus far available, it is not possible to identify the reason for this improvement. However, one can speculate based on the pore size distributions for the two catalysts, Figure 7. It is evident that the pore size distributions for these two catalysts are very different in the macropore range. The much smaller macropore sizes for the Amocat 1C catalyst might serve to slow penetration of the large coke deposition precursors to the interior of the catalyst, and thereby maintain a higher level of activity for this catalyst. In analyzing the effects of macroporosity on activity and activity maintenance, Leung and Haynes[12] concluded that an optimum macroporosity generally exists with regard to activity maintenance. Of course it is also plausible that the improvement observed for the Amocat 1C catalyst is due to the difference in active metals - nickel molybdate vs. cobalt molybdate. Cobalt sintering has been observed in used cobalt molybdate catalysts taken from coal liquefaction pilot plants[13,14].

A comparison of BET surface areas for fresh, used and fired used Amocat 1C and Amocat 1A catalysts is presented in Table 4. The results show that the Amocat 1C catalyst with smaller macropores has a somewhat larger BET surface area. Figure 8 and Figure 9 present the pore size distributions for fresh, used and fired Amocat 1A and Amocat 1C catalysts, respectively. Other used catalyst properties are reported in Table 5. A interesting observation is that after twenty one days on coal, the two used catalysts contain approximately the same amount of deposits (about 86 wt.% of the original catalyst). But much less metals and much more carbon were deposited on the Amocat 1C catalyst as compared with Amocat 1A. Again, the difference in pore size distributions may be responsible for this observation.

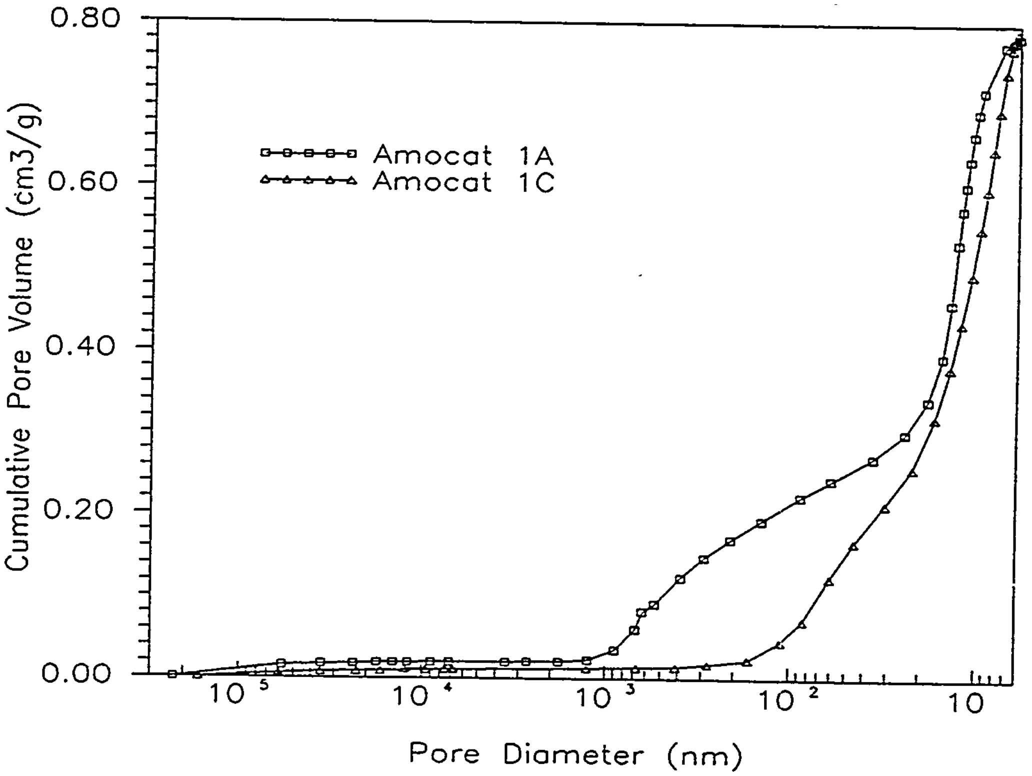

Figure 7. Cumulative Pore Size Distributions for Fresh Amocat 1A and Amocat 1C Catalysts.

Table 4. BET Surface Areas for Fresh, Used and Fired Used Amocat 1A and Amocat 1C Catalysts(m^2/g)
(All surface areas are on fresh catalyst weight basis)

	Fresh	Used	Fired Used
Amocat 1A	174.0	143.3	146.7
Amocat 1C	228.7	185.0	173.9

Table 5. Spent Catalyst Properties for Amocat 1A and Amocat 1C Catalysts

	ZHQ06(Amocat 1A)	ZHQ08(Amocat 1C)
Run Duration(hrs)	507	505
Catalyst Charged(g)	5.0019	5.0019
Dried Extracted Spent Catalyst Weight(g)	9.2178	9.4415
Loss on Ignition(%)	16.6	27.5
Percent Recovery(%)	153.7	139.6
Percent Metals*(%)	53.7	36.9
Percent Carbon*(%)	28.5	45.7
Percent Hydrogen*(%)	1.1	1.8
Percent Nitrogen*(%)	0.5	0.6

*. On Fresh Catalyst Weight Basis.

During Run ZHQ08, aliquots of centrifuged liquid product were collected after each yield period. These samples were subjected to various analyses to try to obtain a better understanding of the compositional changes in the liquefaction solvent as the catalyst deactivates and liquefaction yields decrease. Thus far, only CHN elemental analyses are available. These results are reported in Table 6, and the data are plotted in Figures 10 and 11. Referring to Figure 10, it is seen that as the run progresses, the carbon content remains essentially unchanged, the hydrogen content drops, and the nitrogen content increases progressively. There is a steady decrease in the H/C ratio as shown in Figure 11. It is hoped that NMR analyses in progress will provide further insight into the nature of the solvent as the catalyst deactivates.

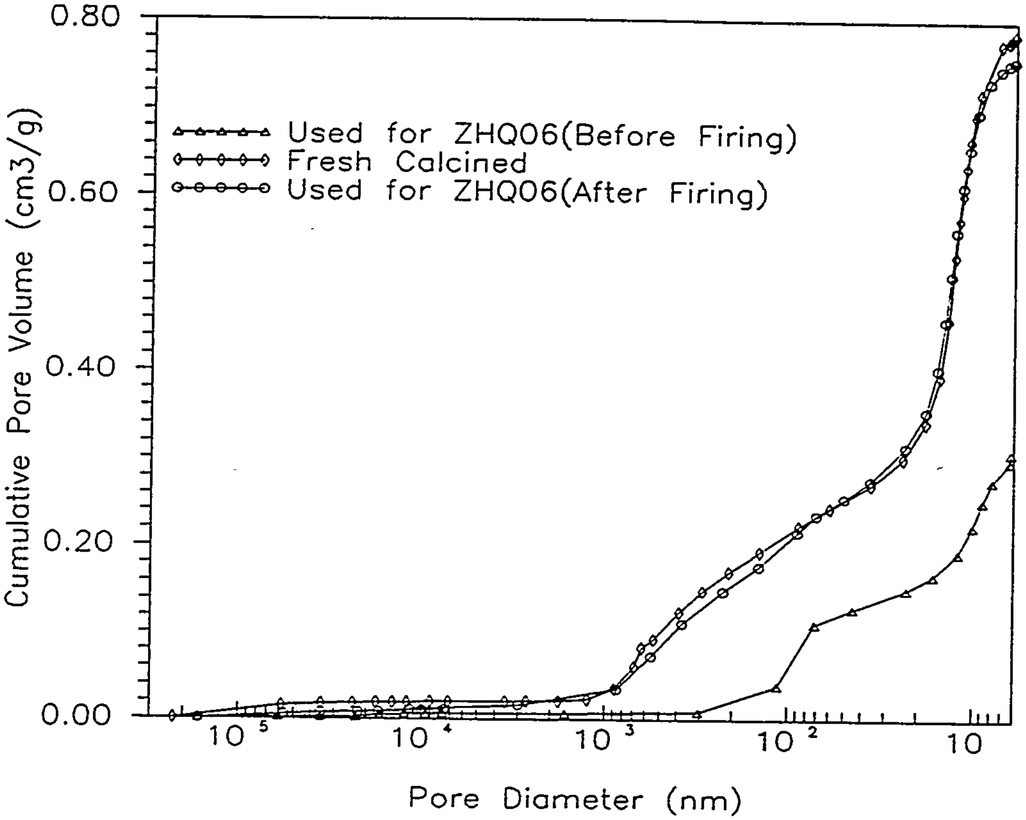

Figure 8. Cumulative Pore Size Distributions for Amocat 1A.

Table 6. CHN Analyses for Liquid Samples from ZHQ08

Yield Period	Cat. Service	Carbon (wt.%)	Hydrogen (wt%)	Nitrogen (wt.%)	H/C
1	49.4	90.49	8.33	0.66	0.092
2	97.7	90.44	8.27	0.69	0.091
3	144.8	90.05	8.10	0.70	0.090
4	191.5	90.45	7.91	0.82	0.087
5	238.9	88.72	7.88	0.77	0.089
6	285.9	90.29	7.85	0.77	0.087
7	334.4	90.13	7.75	0.74	0.086
9	428.4	90.03	7.69	0.80	0.085
10	475.8	89.39	7.69	0.84	0.086
11	524.2	88.60	7.66	0.84	0.086
12	569.9	89.24	7.52	0.92	0.084
13	617.2	89.77	7.54	0.81	0.084
14	664.9	88.93	7.56	0.92	0.085
15	713.5	88.19	7.39	0.97	0.084
16	761.5	90.58	7.27	0.86	0.080
18	855.4	90.23	7.05	0.89	0.078
19	902.6	89.13	6.93	0.98	0.078
20	950.8	88.59	6.82	1.02	0.077
21	998.1	87.46	6.81	1.04	0.078

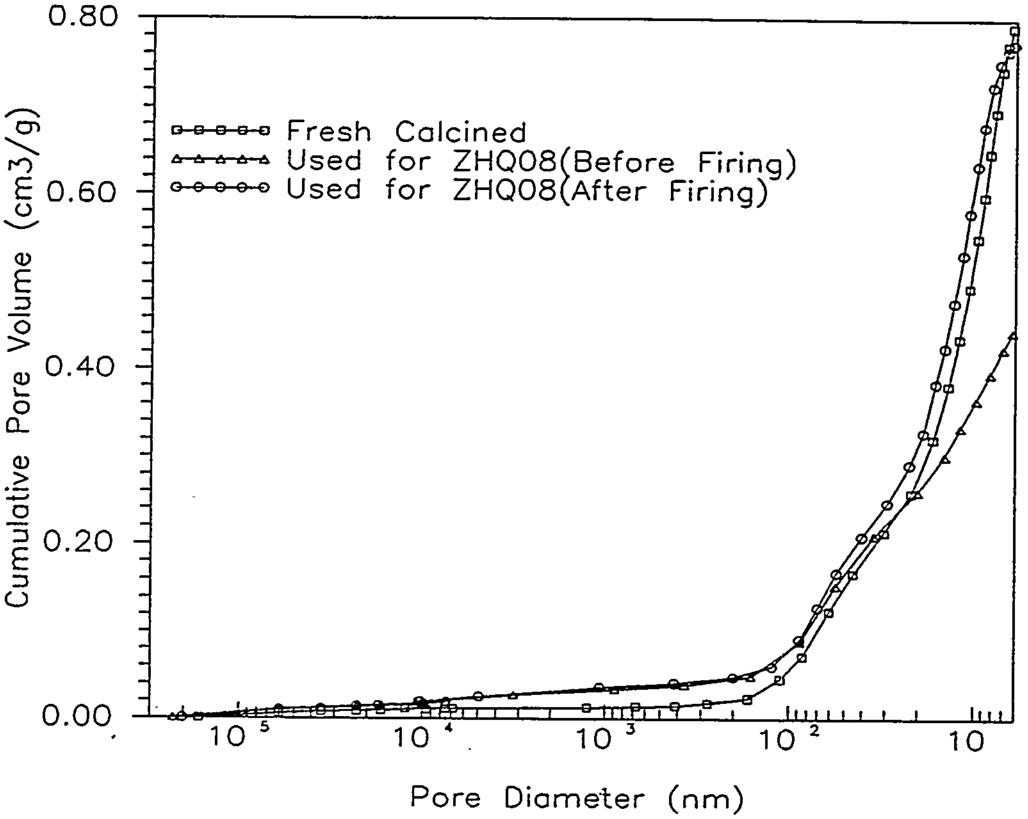

Figure 9. Cumulative Pore Size Distributions for Amocat 1C.

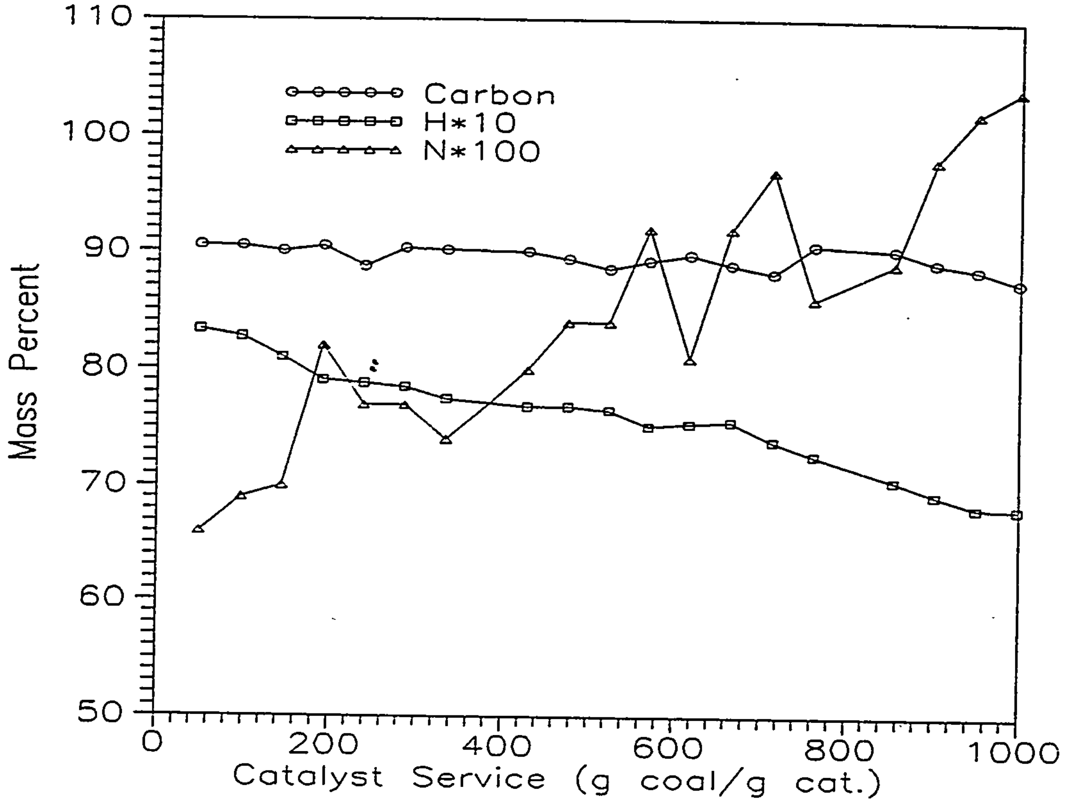

Figure 10. Solvent Carbon, Hydrogen and Nitrogen Contents vs. Catalyst Service for Run ZHQ08

2.3 The Thermal Run

The thermal run for the untreated Black Thunder coal, identified as Run ZHQ07, was conducted in the CCLM unit under identical nominal operating conditions as Run ZHQ08. The catalyst, however, was replaced with an equal volume of 3 mm diameter glass beads. Four balance periods were completed, and the results are recorded in Table 7.

Results from balance period ZHQ07-02, -03 and -04 were taken to calculate the average thermal conversions. The ZHQ07-01 results were considered unreliable due to a low material balance. The thermal conversions are listed in Table 8.

2.4 Conclusions

A new base line has been established for processing Black Thunder coal with Amocat 1C catalyst. The Amocat 1C catalyst out performed the Amocat 1A catalyst. The cause cannot be stated with certainty, but significant differences in pore structure may have been a factor. Decreased liquefaction yields are accompanied by a decrease in H/C ratio of the solvent.

Table 7. Run summary for ZHQ07

Yield Period No.	01	02	03	04
Yield Period Length,Hr	2.0	2.0	2.0	2.0
Average Temperature,°F	797	797	799	796
Average Pressure,Psig	2000	1990	1990	1990
Stirrer Speed,rpm	1205	1205	1205	1205
Makeup Solvent Rate,GM/Hr	20.75	19.90	20.60	20.20
Coal Paste Rate,GM/Hr	19.98	19.98	19.98	19.98
Residence Time,Hr	1.487	1.520	1.493	1.509
Solvent/Coal Wt Ratios:				
GM CO/GM Coal	2.774	2.659	2.729	2.689
GM CO+Resid/GM Coal	3.077	2.992	3.062	3.022
GM CO/GM Dry Coal	3.548	3.438	3.529	3.477
GM CO+GM Resid/GM Dry Coal	3.979	3.869	3.960	3.908
GM CO/GM MAF Coal	3.781	3.663	3.760	3.705
GM CO+Resid/GM MAF Coal	4.240	4.123	4.219	4.164
H_2 Treat Rate,L(STP)/Hr	25.05	25.05	25.05	25.05
H_2 Treat Rate,SCF/BBL	3932	4020	3947	3988
Exit Gas Rate,L(STP)/Hr	25.84	25.45	26.70	26.60
Cumulative hours on Catalyst*	20.5	23.4	32.6	46.5
Overall Material Balance,Wt%	93.3		104.1	102.6
Yields(Total Feed Basis):				
Carbon Monoxide,Wt%	0.00		0.00	0.00
Carbon Dioxide,Wt%	0.97		0.97	1.03
Hydrocarbon Gases(C_1-C_4),Wt%	0.70		0.81	0.77
Slurry Product,Wt%	92.0		103.5	101.9
H_2 Consumption (Total Feed Basis),Wt%	0.97		0.74	0.82
Conversions (MAF Coal+Resid Basis),Wt%				
Wt% Cyclohexane Soluble	45.9	38.1	42.6	36.3
Wt% Toluene Soluble	55.8	48.4	51.9	50.5
Wt% Pyridine Soluble	67.7	58.2	61.5	62.0

* Glass Beads

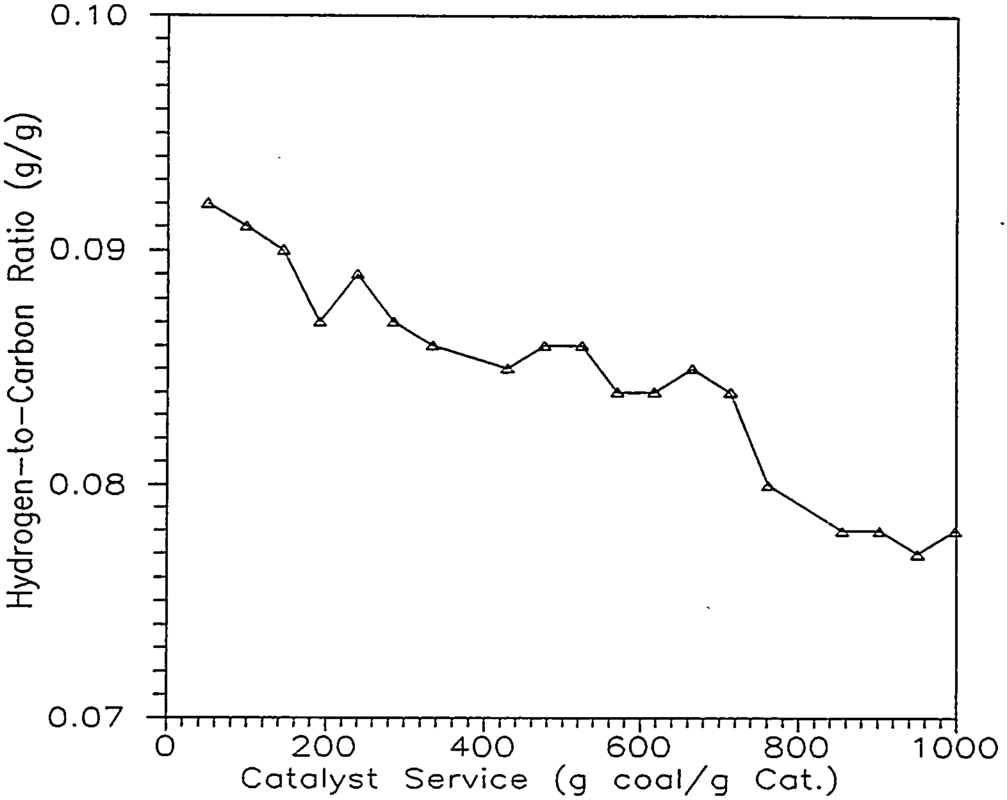

Figure 11. Solvent H/C Ratios vs. Catalyst Service for Run ZHQ08

3. Pretreatment of The Black Thunder Coal

In an earlier study we investigated the processing demineralized coal from Black Thunder Mine, Wyoming[7]. Demineralization was accomplished by washing with dilute nitric acid. Most of the calcium was removed by this treatment, and the calcite deposit surrounding the used catalyst particles which had been observed in earlier runs with untreated coal was eliminated. Unfortunately, this did not result in an enhancement of catalyst life. The acid washed coal was more reactive than the untreated coal, and this could be related to the increased oxygen content of the feed coal.

The acid selected for this investigation is sulfurous acid. This treatment is preferred to nitric acid and other mineral acid treatments because it is not an oxidant, it is more cost effective, and it is noncorrosive by comparison to hydrochloric acid. Recently, Cronauer and coworkers[8] reported success in removal of metal cations from a Texas lignite using aqueous SO_2. Partial removal of mineral matter by aqueous SO_2 was also reported to enhance liquefaction yields from low rank coals[15].

3.1 Experimental

Pretreatment Procedures:

The procedure recommended by Dr. Cronauer of the Amoco Oil Company were employed for the pretreatment without major modification. The procedure consists of the following steps:

1. Bubble SO_2 through distilled water by introducing SO_2 via a fretted tube until near saturation conditions are reached. This can be determined by weight. Saturation occurs at approximately 5.5-6.5% SO_2 by weight. The actual SO_2 introduction was terminated at 5.7-5.8% increase in weight.
2. Contact 1 weight of coal with 5 weights of solution. Let sit for one and a half hours at room temperature while maintaining stirring by means of a magnetic stirrer.
3. Filter quickly and wash with distilled water using approximately 10 weights of distilled water to 1 weight of coal.
4. Dry the coal cake at ambient conditions under the protection of nitrogen to about 11% moisture. This was accomplished by drying the coal under nitrogen in a filter funnel with #4 filter paper. The coal was stirred two to three times per day.

The moisture content for every batch of the coal was monitored using a modification of the ASTM Standard D3173-87. The coal paste was made immediately after the drying step to prevent oxidation.

A deactivation run for the acid treated coal identified as Run ZHQ10 was performed in the CCLM unit under the same nominal conditions employed in Run ZHQ08. All other procedures such as products analyses, used catalyst treatment and CHN analyses remained the same as described earlier. Also, a thermal run for the acid treated coal was conducted using the same conditions as in Run ZHQ07 to determine the thermal levels for the aqueous SO_2 treated coal.

3.2 Results of the Pretreatment

The proximate and ultimate analyses of the SO_2 treated coal are presented in Table 8. A mineral ash analysis of the coal ash is reported in Table 9. From a comparison of these data with the data recorded in Tables 1 and 2, respectively, it is seen that the pretreatment is effective in removal of the metal cations. Calculation shows that about 86.5% of the calcium in the original coal was removed by this treatment, and the losses of sodium and magnesium were over 90%. The loss of iron, however, was only 42%. Similar results were reported by Cronauer and coworkers[8] when they treated a Texas lignite using aqueous SO_2.

The oxygen content was substantially increased by the SO_2 pretreatment. The observed increase of 9.0% (maf basis) is far in excess of the approximate 1.1% that can be accounted for by possible sulfonation of the coal suggested by the increase in sulfur content. Evidently, air oxidation of the coal took place during the pretreatment despite efforts to protect the coal from exposure to air.

About 10% of ZnO was found in the ash of the treated coal. A metal pan was employed to dry the first batch of coal, and perhaps the source of the zinc was the coating on the metal pan. This batch of pretreated coal was only employed during the thermal run and the first yield period of Run ZHQ10. Subsequent drying was conducted in a ceramics container, so the pretreated coal used for the balance of Run ZHQ10 should not contain any Zn.

Table 8. Proximate and Ultimate Analyses for the Aqueous SO_2 Treated Wyoming Black Thunder Coal

	As-Received (wt.%)	Moisture Free (wt.%)	Moisture & Ash Free (wt.%)
Proximate:			
Moisture	11.24		
Ash	3.56	4.01	
Volatile Matter	42.15	47.49	49.47
Fixed Carbon	43.05	48.50	50.53
Total	100.00	100.00	100.00
Ultimate:			
Hydrogen	4.72	3.90	4.06
Carbon	61.38	69.15	72.04
Nitrogen	0.87	0.98	1.02
Sulfur	1.06	1.19	1.24
Oxygen	28.41	20.77	21.64
Ash	3.56	4.01	
Total	100.00	100.00	100.00

Table 9. Mineral Ash Analysis of Sulfurous Acid Washed Coal

Oxide	% of Ash
SiO_2	48.24
Al_2O_3	20.30
Fe_2O_3	4.19
CaO	5.09
MgO	0.55
Na_2O	0.05
K_2O	0.20
TiO_2	1.93
MnO	0.01
P_2O_5	1.21
SrO	0.23
BaO	0.86
SO_3	3.97
ZnO	10.10
SUM	96.93

Sample had a loss on ignition @1000°C of 3.07%

3.3 Results of the Deactivation Run

A summary for the deactivation run with the SO_2 pretreated coal, Run ZHQ10, is provided in Table 10. The run proceeded smoothly until an elevated reactor temperature of 434°C was experienced shortly after yield period number eight. This was accompanied by a sudden drop of the intermediate pressure causing the inlet hydrogen flow rate to drop to about 7 liters(stp)/hr. The reactor pressure was unchanged. After about ten minutes adjustments were made to bring the hydrogen flowrate and reactor temperature back to their target values. This disturbance was considered to have no significant effect on the catalyst activity. An inlet line plug was encountered right before the time at which the number twelve yield period was to have been completed. The reactor temperature rose to 432°C, and the inlet hydrogen flow dropped to about 7 liters(stp)/hr. The plug was freed immediately, coal paste was cut off, and creosote oil only was run through the system at the normal rate (20 g/hr) for about twenty four hours to clean out the inlet line. At this point the stirrer began operating erratically so the unit was shut down in a controlled manner in an attempt to protect the catalyst. The reactor temperature controller was turned off while maintaining hydrogen and oil flow until the reactor temperature dropped to room temperature. Following this, the reactor was depressurized and the unit sat idle while the stirrer motor was replaced.

After installation of the new stirrer moter four days later, the system was restarted with a programmed temperature rise rate of

2°C/min. The system was operated on creosote oil overnight without introducing coal paste. Subsequent conversion results indicated that the catalyst activity was not significantly affected by this upset. Another plug was experienced after the catalyst was fifteen days on coal. The plug was observed and freed immediately, and again, the coal paste was cut off and system was purged with raw creosote oil for about twenty hours. One more yield period was completed before a fatal plug occurred after sixteen days on coal. The system shut down automatically, and the reactor temperature dropped to about 70 °C within two hours. A total of fourteen yield periods were obtained.

The material balances for most of the periods are within the range of 99-103%. No balance values were obtained for the last three yield periods due to a lack of gas analyses resulting from a malfunctioning gas chromatograph.

Solubility class conversion for this run are presented in Figure 12. The initial conversions are high, but the catalyst deactivated quickly during the early stages of the run. The comparison of conversions between Runs ZHQ08 and ZHQ10 and the corresponding thermal conversions are presented in Figures 13 through 15. The results show that the initial activity is slightly higher for the acid washed coal, but the corresponding thermal conversions are also higher by comparison to those obtained for the as-received coal. The catalyst for the acid washed coal run deactivated quickly and assumed a lower level of activity as compared with that for the original coal. Thus, no improvement in catalyst activity maintenance was observed for the acid treated coal run.

The used catalyst properties are reported in Table 11. The dried extracted used catalyst weights from the Run ZHQ10 were greater than those from Run ZHQ08 even though the catalyst was only sixteen days on coal. However, much less metals were deposited on the ZHQ10 catalyst. Plugging of the reactor may be responsible for the much higher coke laydown on the catalyst.

About two grams of fine solids were observed and separated from the catalyst. Firing of a small portion of these fines and further CNH analysis showed that the fines consisted of broken catalyst particles. This catalyst attrition may be attributed to the malfunction of the stirrer motor.

A comparison of BET surface areas for Run ZHQ08 and ZHQ10 is provided in Table 12. Pore size distributions for the fresh, used and fired used catalysts from Run ZHQ10 are provided in Figure 16. Similar to observations for the ZHQ08 catalysts, most of the pores were plugged for the used catalyst, and most of the lost pores were recovered by firing.

Results from CHN analyses of samples of the liquid products are presented in Table 13. Plots of carbon, hydrogen and nitrogen contents vs. catalyst service are presented in Figure 17. A comparison of solvent H/C ratio for the two catalyst deactivation runs is provided in Figure 18. For the acid washed coal run, the carbon, hydrogen, nitrogen contents and the H/C ratio change in same manner as observed during Run ZHQ08. But the decline in H/C ratio is more rapid for Run ZHQ10 consistent with the more rapid catalyst deactivation experienced during this run.

Table 10. Summary of Run ZHQ10

Yield Period No.	1	2	3	4	5
Yield Period Length,Hr	2.0	2.0	2.0	2.0	2.0
Average Temperature,°F	802	800	799	800	800
Average Pressure,Psig	2000	2000	2010	2000	2010
Stirrer Speed,rpm	1205	1205	1205	1205	1205
Makeup Solvent Rate,GM/Hr	20.25	20.10	20.20	20.35	20.40
Coal Paste Rate,GM/Hr	20.02	20.10	20.02	20.02	20.02
Residence Time,Hr	1.505	1.511	1.507	1.501	1.499
Space Velocities:					
GM Coal/Hr/GM Cat	2.001	2.001	2.001	2.001	2.001
GM Dry Coal/Hr/GM Cat	1.776	1.776	1.776	1.776	1.776
GM MAF Coal/Hr/GM Cat	1.705	1.705	1.705	1.705	1.705
Solvent/Coal Wt Ratios					
GM CO/GM Coal	2.690	2.675	2.685	2.700	2.705
GM CO+Resid/GM Coal	3.023	3.008	3.018	3.033	3.038
GM CO/GM Dry Coal	3.034	3.014	3.025	3.042	3.047
GM CO+GM Resid/GM Dry Coal	3.406	3.389	3.401	3.417	3.423
GM CO/GM MAF Coal	3.157	3.140	3.151	3.169	3.175
GM CO+Resid/GM MAF Coal	3.549	3.511	3.543	3.560	3.566
H_2 Treat Rate,L(STP)/Hr	25.05	25.05	25.05	25.05	25.05
H_2 Treat Rate,SCF/BBL	3979	3995	3985	3969	3964
Exit Gas Rate,L(STP)/Hr	16.61	16.77	17.50	17.76	18.35
Cumulative Quantities:					
Hours on Catalyst	24.6	48.9	72.3	95.2	119.8
Wt Makeup Solvent/Wt Cat	138.9	237.8	333.5	426.6	523.0
Wt Resid/Wt Cat	15.5	28.5	43.9	59.0	75.9
Wt Coal/Wt Cat	46.5	85.4	131.6	176.9	227.8
Overall Material Balance,Wt%	99.9	105.2	103.5	101.7	100.9
Yields(Total Feed Basis):					
Carbon Monoxide,Wt%	0.00	0.00	0.00	0.00	0.00
Carbon Dioxide,Wt%	0.15	0.14	0.19	0.25	0.21
Hydrocarbon Gases(C_1-C_4),Wt%	1.15	1.33	1.30	1.37	1.32
Slurry Product,Wt%	101.7	107.5	105.4	103.2	102.2
H_2 Consumption (Total Feed Basis),Wt%	3.18	3.23	3.05	2.96	2.77
Conversions (MAF Coal+Resid Basis),Wt%					
Wt% Cyclohexane Soluble	86.4	83.3	81.3	76.0	70.4
Wt% Toluene Soluble	89.8	86.8	84.8	81.3	76.3
Wt% Pyridine Soluble	93.6	91.1	90.5	91.1	86.8

Table 10. (Continued)

Yield Period No.	6	7	8	9	10
Yield Period Length,Hr	2.0	2.0	2.0	2.0	2.0
Average Temperature,°F	800	800	799	799	800
Average Pressure,Psig	2000	1990	2010	2000	2000
Stirrer Speed,rpm	1205	1205	1205	1205	1205
Makeup Solvent Rate,GM/Hr	20.25	20.35	20.15	20.25	20.20
Coal Paste Rate,GM/Hr	19.99	19.99	19.99	19.99	19.99
Residence Time,Hr	1.506	1.512	1.510	1.506	1.508
Space Velocities:					
GM Coal/Hr/GM Cat	1.999	1.999	1.999	1.999	1.999
GM Dry Coal/Hr/GM Cat	1.774	1.774	1.774	1.774	1.774
GM MAF Coal/Hr/GM Cat	1.703	1.703	1.703	1.703	1.703
Solvent/Coal Wt Ratios					
GM CO/GM Coal	2.692	2.702	2.682	2.692	2.687
GM CO+Resid/GM Coal	3.026	3.036	3.016	3.026	3.021
GM CO/GM Dry Coal	3.033	3.045	3.022	3.033	3.028
GM CO+GM Resid/GM Dry Coal	3.409	3.420	3.398	3.409	3.403
GM CO/GM MAF Coal	3.160	3.172	3.148	3.160	3.154
GM CO+Resid/GM MAF Coal	3.551	3.563	3.540	3.551	3.546
H_2 Treat Rate,L(STP)/Hr	25.05	25.05	25.05	25.05	25.05
H_2 Treat Rate,SCF/BBL	3982	3971	3992	3982	3987
Exit Gas Rate,L(STP)/Hr	18.55	18.88	19.02	19.94	20.66
Cumulative Quantities:					
Hours on Catalyst	144.8	168.6	192.8	216.3	240.3
Wt Makeup Solvent/Wt Cat	630.7	728.1	826.7	922.3	1020.2
Wt Resid/Wt Cat	92.3	107.7	123.3	137.3	152.8
Wt Coal/Wt Cat	276.9	323.2	370.0	411.7	458.4
Overall Material Balance,Wt%	102.7	105.9	101.7	101.2	100.6
Yields(Total Feed Basis):					
Carbon Monoxide,Wt%	0.00	0.00	0.00	0.00	0.00
Carbon Dioxide,Wt%	0.22	0.28	0.26	0.36	0.40
Hydrocarbon Gases(C_1-C_4),Wt%	1.34	1.29	1.27	1.32	1.31
Slurry Product,Wt%	104.1	107.5	103.0	102.0	101.2
H_2 Consumption (Total Feed Basis),Wt%	2.74	2.71	2.67	2.44	2.27
Conversions (MAF Coal+Resid Basis),Wt%					
Wt% Cyclohexane Soluble	67.2	62.0	64.9	60.2	60.8
Wt% Toluene Soluble	73.9	70.4	71.0	68.4	68.0
Wt% Pyridine Soluble	88.0	80.2	82.0	78.8	79.6

Table 10. (Continued)

Yield Period No.	11	12	13	15
Yield Period Length,Hr	2.0	2.0	2.0	2.0
Average Temperature,°F	800	800	800	798
Average Pressure,Psig	1990	1990	1990	1990
Stirrer Speed,rpm	1205	1205	1205	1205
Makeup Solvent Rate,GM/Hr	20.30	20.35	19.95	20.05
Coal Paste Rate,GM/Hr	19.99	19.99	19.99	19.99
Residence Time,Hr	1.504	1.502	1.518	1.514
Space Velocities:				
GM Coal/Hr/GM Cat	1.999	1.999	1.999	1.999
GM Dry Coal/Hr/GM Cat	1.774	1.774	1.774	1.774
GM MAF Coal/Hr/GM Cat	1.703	1.703	1.703	1.703
Solvent/Coal Wt Ratios				
GM CO/GM Coal	2.697	2.702	2.662	2.672
GM CO+Resid/GM Coal	3.031	3.036	2.996	3.002
GM CO/GM Dry Coal	3.039	3.045	3.000	3.011
GM CO+GM Resid/GM Dry Coal	3.415	3.420	3.375	3.386
GM CO/GM MAF Coal	3.166	3.172	3.125	3.137
GM CO+Resid/GM MAF Coal	3.557	3.563	3.516	3.528
H_2 Treat Rate,L(STP)/Hr	25.05	25.05	25.05	25.05
H_2 Treat Rate,SCF/BBL	3977	3971	4013	4003
Exit Gas Rate,L(STP)/Hr	20.98	21.30	21.52	23.67
Cumulative Quantities:				
Hours on Catalyst	263.2	479.6	503.7	574.6
Wt Makeup Solvent/Wt Cat	1112	1539	1636	1936
Wt Resid/Wt Cat	167.5	198.4	213.8	241.3
Wt Coal/Wt Cat	502.3	595.1	641.2	723.8
Overall Material Balance,Wt%	100.7			
Yields(Total Feed Basis):				
Carbon Monoxide,Wt%	0.00			
Carbon Dioxide,Wt%	0.41			
Hydrocarbon Gases(C_1-C_4),Wt%	1.35			
Slurry Product,Wt%	100.0			
H_2 Consumption (Total Feed Basis),Wt%	1.88			
Conversions (MAF Coal+Resid Basis),Wt%				
Wt% Cyclohexane Soluble	59.9	58.9	57.0	49.9
Wt% Toluene Soluble	67.4	67.3	63.3	61.0
Wt% Pyridine Soluble	77.7	78.4	75.4	72.4

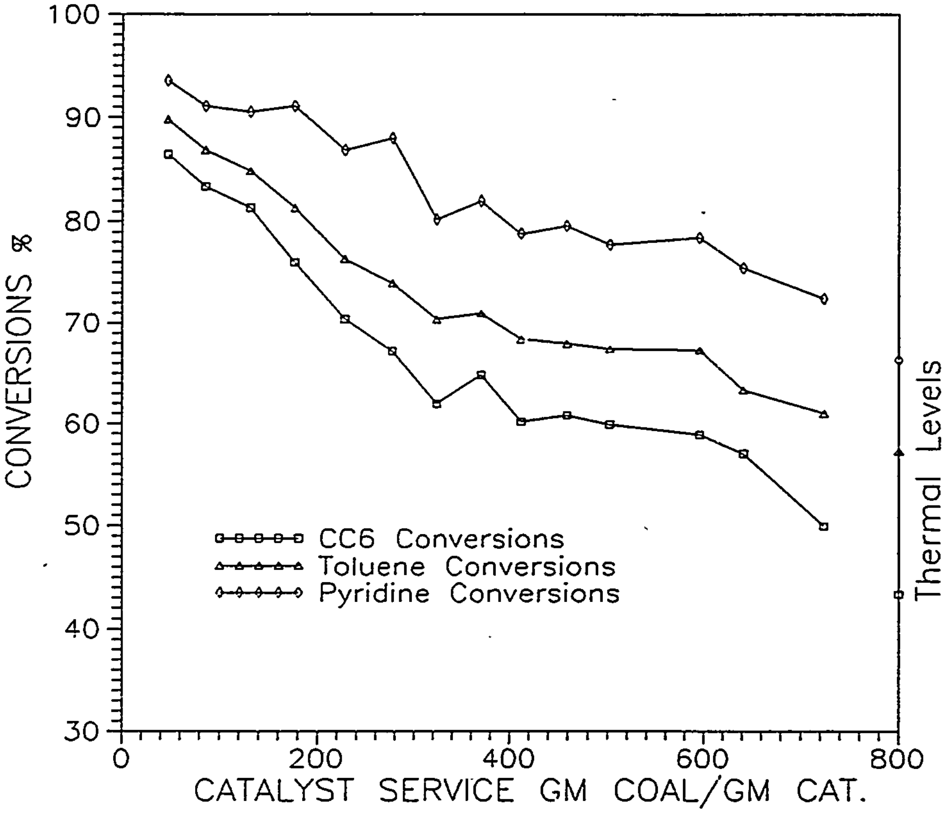

Figure 12. Solubility Class Conversions for Run ZHQ10.

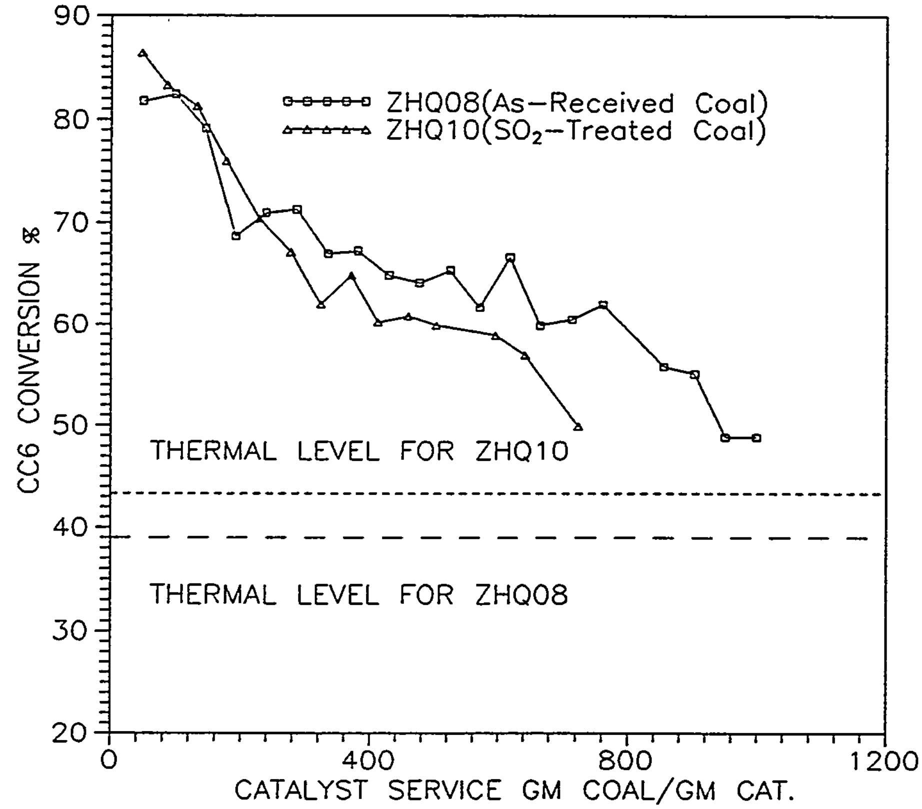

Figure 13. Comparison of Cyclohexane Solubility Conversions for Run ZHQ08 and Run ZHQ10.

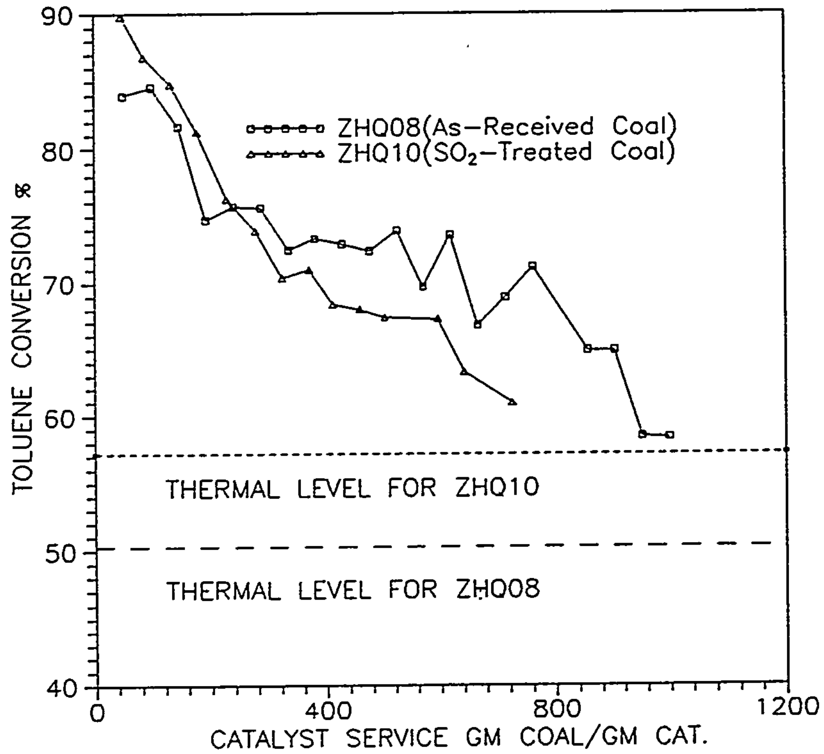

Figure 14. Comparison of Toluene Solubility Conversions for Run ZHQ08 and Run ZHQ10.

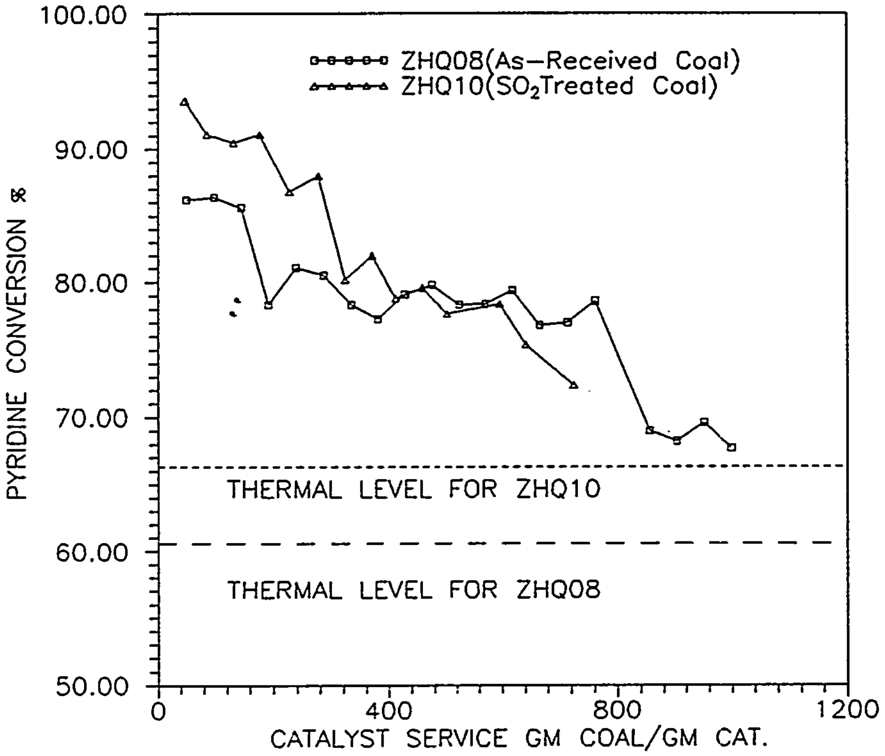

Figure 15. Comparison of Pyridine Solubility Conversions for Run ZHQ08 and Run ZHQ10.

Table 11. Comparison of Used Catalyst Properties for ZHQ10 and ZHQ08

	ZHQ08	ZHQ10
Run Duration(hrs)	505	397
Catalyst Charged(g)	5.0019	5.0013
Spent Catalyst Wt.(g)	9.4415	10.1646
Loss on Ignition(%)	27.5	37.8
Percent Recovery(%)	136.9	126.4
Percent Metals*(%)	36.9	26.4
Percent Carbon*(%)	45.7	76.8
Percent Hydrogen*(%)	1.8	2.3
Percent Nitrogen*(%)	0.8	1.1

* On Fresh Catalyst Basis.

Table 12. BET Surface Areas for Catalysts from Run ZHQ08 and Run ZHQ10 (m^2/g)
(All surface areas are on fresh catalyst weight basis)

	Fresh	Used	Fired Used
ZHQ08	228.7	185.0	173.9
ZHQ10	228.7	94.63	176.6

Table 13. CHN Analyses for Liquid Samples from ZHQ10

Yield No.	Cat. Service (g coal/g cat.)	Carbon (wt.%)	Hydrogen (wt.%)	Nitrogen (wt.%)	H/C
1	46.5	90.70	8.25	0.67	0.091
2	86.4	90.70	8.16	0.72	0.090
3	131.6	90.61	8.16	0.75	0.090
4	176.9	90.72	8.09	0.72	0.089
5	227.8	90.64	8.04	0.72	0.089
6	276.9	90.53	8.05	0.75	0.089
7	323.2	90.53	8.01	0.77	0.088
8	370.0	90.47	7.96	0.75	0.088
9	411.7	90.40	7.67	0.81	0.085
10	458.4	90.16	7.60	0.88	0.084
11	502.3	90.35	7.49	0.90	0.083
12	595.1	90.34	7.38	0.99	0.082
13	641.2	89.42	7.35	0.98	0.082
15	723.8	88.05	6.85	1.10	0.078
Thermal Level		89.50	6.72	1.10	0.075

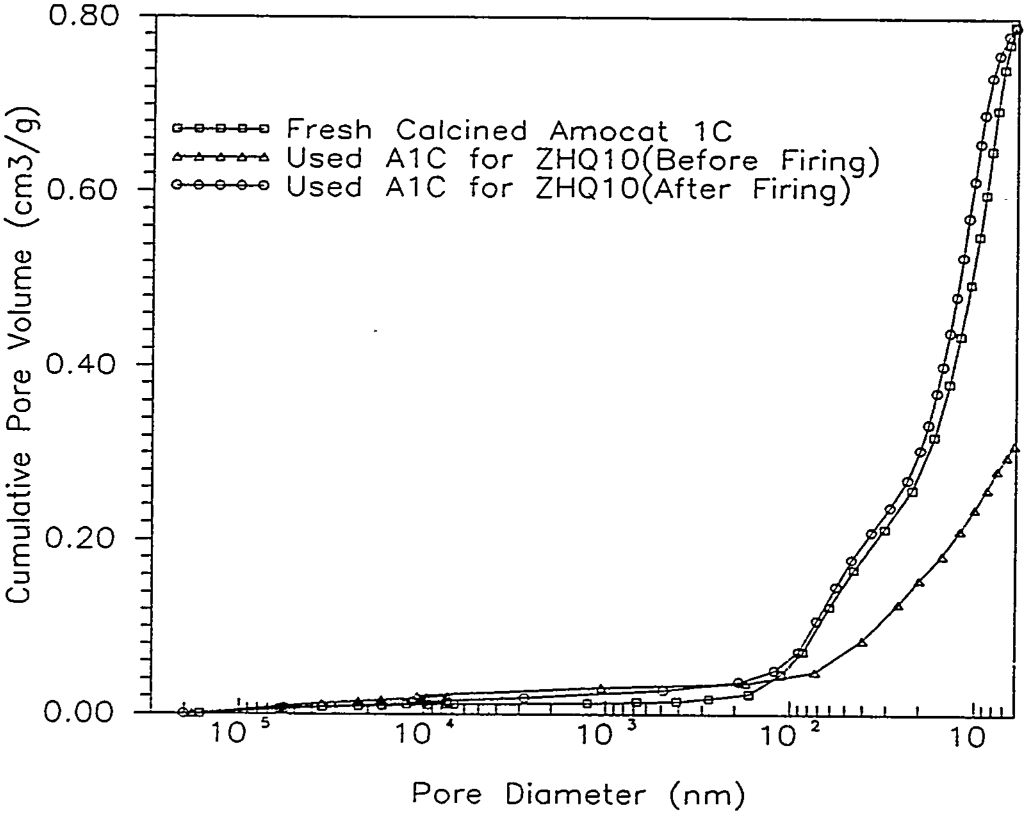

Figure 16. Cumulative Pore Size Distributions form Catalysts from Run ZHQ10.

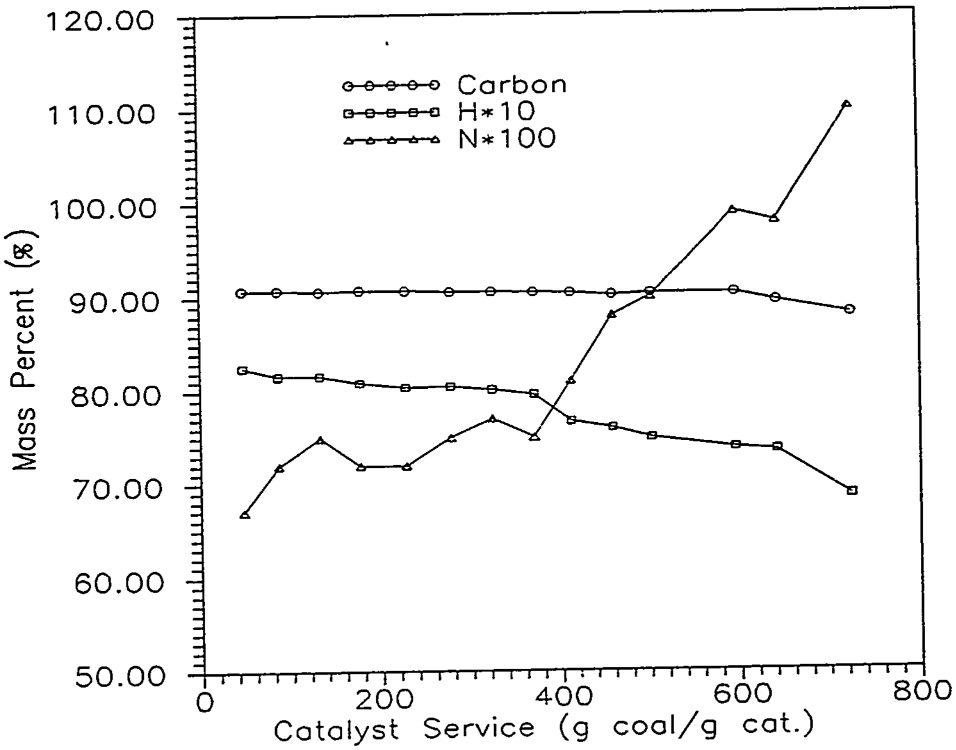

Figure 17. Solvent Carbon, Hydrogen and Nitrogen Contents vs. Catalyst Service for Run ZHQ10

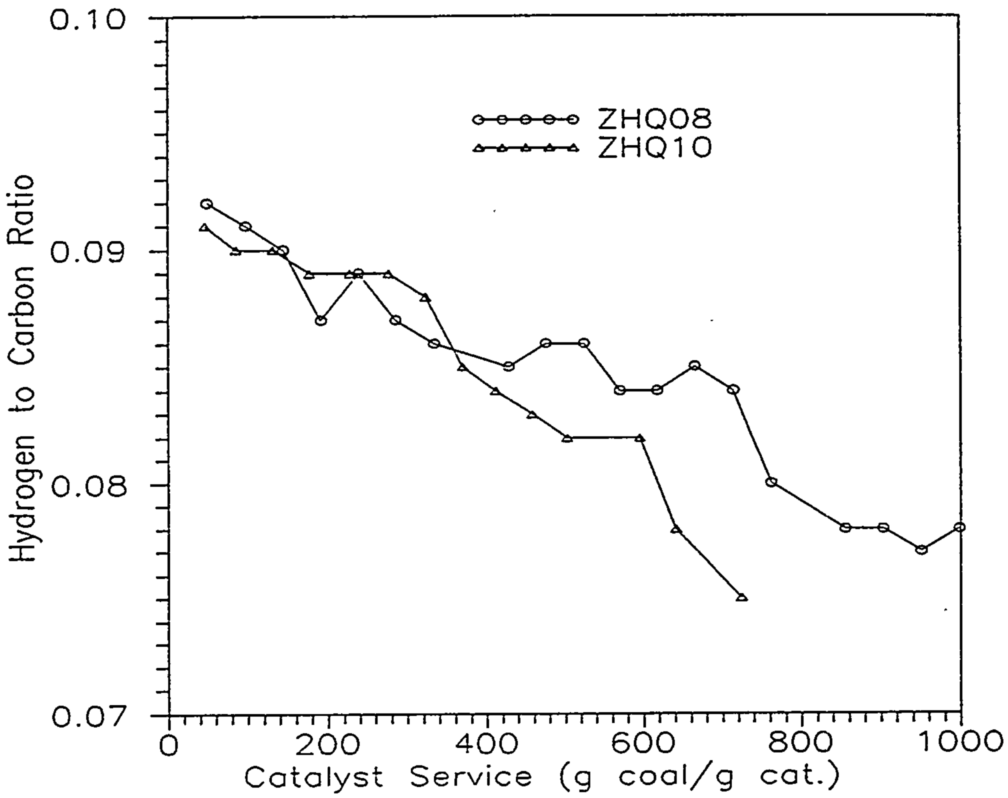

Figure 18. Comparison of Solvent Carbon to Hydrogen Ratio for Run ZHQ08 and Run ZHQ10.

3.4 The Thermal Run

Run ZHQ09 is the thermal run for the sulfurous acid treated coal. As in Run ZHQ07, the catalyst was replaced with an equal volume of 3 mm diameter glass beads. Otherwise, conditions were totally identical to those employed during Run ZHQ10. A summary of the four yield periods is presented in Table 14. Results from balance periods ZHQ09-02, -03 and -04 were taken to compute average thermal conversions. Results from the first yield period were again excluded due to a low material balance. The calculated thermal conversions are presented in Table 15.

3.5 Conclusions

Pretreatment with aqueous SO_2 is effective in removal of the metal cations from a Wyoming Black Thunder coal. About 86.5% of calcium can be removed from the coal. This treatment was accompanied by a small increase in sulfur content, and a much greater increase in oxygen content of the coal. The increased oxygen content suggests that air oxidation occurred despite efforts to minimize air contact. The acid washed coal is slightly more reactive than the untreated coal. However, pretreatment of the feed coal with sulfurous acid does not appear to improve the catalyst activity maintenance.

Table 14. Summary of Run ZHQ09

Yield Period No.	1	2	3	4
Yield Period Length,Hr	2.0	2.0	2.0	2.0
Average Temperature,°F	798	800	800	798
Average Pressure,Psig	2000	2020	2020	2010
Stirrer Speed,rpm	1205	1205	1205	1205
Makeup Solvent Rate,GM/Hr	20.25	20.30	20.40	20.35
Coal Paste Rate,GM/Hr	19.98	19.98	19.98	19.98
Residence Time,Hr	1.507	1.505	1.501	1.503
Solvent/Coal Wt Ratios				
GM CO/GM Coal	2.694	2.699	2.709	2.704
GM CO+Resid/GM Coal	3.027	3.032	3.042	3.037
GM CO/GM Dry Coal	3.114	3.040	3.052	3.046
GM CO+GM Resid/GM Dry Coal	3.499	3.416	3.427	3.422
GM CO/GM MAF Coal	3.256	3.167	3.179	3.173
GM CO+Resid/GM MAF Coal	3.659	3.559	3.570	3.565
H_2 Treat Rate,L(STP)/Hr	25.05	25.05	25.05	25.05
H_2 Treat Rate,SCF/BBL	3983	3978	3967	3972
Exit Gas Rate,L(STP)/Hr	25.45	25.67	25.71	25.87
Cumulative hours on Catalyst*	12.6	15.2	17.8	20.4
Overall Material Balance,Wt%		101.7		101.7
Yields(Total Feed Basis):				
Carbon Monoxide,Wt%		0.00		0.00
Carbon Dioxide,Wt%		1.15		1.10
Hydrocarbon Gases(C_1-C_4),Wt%		1.33		1.12
Slurry Product,Wt%		100.4		100.7
H_2 Consumption (Total Feed Basis),Wt%		1.10		1.02
Conversions (MAF Coal+Resid Basis),Wt%				
Wt% Cyclohexane Soluble	52.1	45.0	39.4	45.6
Wt% Toluene Soluble	62.0	56.9	54.1	45.6
Wt% Pyridine Soluble	69.9	64.3	65.5	69.1

* Glass Beads

Table 15. Thermal Conversions for the Sulphurous Acid Washed Coal and Their Comparison with That for Original Coal

Balance No.	Cyclohexane Conv.	Toluene Conv.	Pyridine Conv.
02	45.0	56.9	64.3
03	39.4	54.1	65.5
04	45.6	60.6	69.1
mean	43.3	57.2	66.3
Thermal Conv.for Original coal	39.0	50.3	60.6

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APPENDIX J

FWC/FWDC/TR-94/05

ALTERNATIVE BOTTOMS PROCESSING FOR PRIME CONTRACT ADVANCED LIQUEFACTION USING COAL SWELLING AND CATALYST DISPERSION TECHNIQUES

PROJECT MANAGER: C. GUTTERMAN

PREPARED FOR

AMOCO OIL COMPANY
RESEARCH AND DEVELOPMENT DEPARTMENT
NAPERVILLE, ILLINOIS
PROJECT MANAGER: R. OLLENDORFF

SEPTEMBER 1994

UNDER PRIME CONTRACT NO. DE-AC22-91PC91051
U.S. DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER
PITTSBURGH, PENNSYLVANIA

FOSTER WHEELER DEVELOPMENT CORPORATION
Livingston, New Jersey

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1.0 INTRODUCTION

The overall objective of this project was to develop a new approach for the direct liquefaction of coal, producing an all-distillate product slate at a sizable cost reduction over current technology. The approach taken was to investigate and integrate all aspects of the coal liquefaction process including coal selection, pretreatment, catalyst and solvent evaluation and alternate bottoms processing. The advanced process that developed would then be subjected to a technical and economic assessment.

The project was carried out under contract to the United States Department of Energy. Amoco Oil Company was the primary contractor, with Foster Wheeler Development Corporation (FWDC), Auburn University, Pennsylvania State University and Hazen Research, Inc. participating as major subcontractors. The primary coal selected for the program was Black Thunder subbituminous coal.

The subject of this report covers Foster Wheeler's effort. FWDC investigated alternative bottoms processing and solids separation through its ASCOT℠ (Asphalt Coking Technology) process and direct delayed coking. The ASCOT℠ process couples solvent deasphalting with delayed coking to maximize the production of coal-derived liquids while rejecting troublesome solids within the coke drum. A portion of the final liquid product is recovered by an appropriate solvent through solvent deasphalting. The asphalt product from this process is then coked to produce additional liquid product and coke. The coke will contain any solids and nearly all the metals that were present in the original feedstock.

FWDC's primary bottoms feedstock was the atmospheric residue generated at DOE's Wilsonville facility from Run 262 with Black Thunder coal. Amoco, as part of their coal liquefaction study, also produced an atmospheric bottoms product which was directly coked (without first being subjected to solvent deasphalting).

A preliminary economic assessment of the battery limits for the ASCOT℠ process and direct delayed coking was completed by Foster Wheeler USA Corporation (FW USA), the commercial offerer of these processes.

The following outline summarizes FWDC's program investigating the ASCOT℠ process and direct delayed coking for producing liquid product and rejecting solids.

- **Batch Solvent Deasphalting Tests**

These tests determined the relationship between deasphalting conditions, yield and product quality. Three differing asphalt yields were then selected to study their transport properties.

- **Transport Tests**

The scope of the program required the use of an existing delayed coking pilot plant. The transport tests were needed to determine the practical transport characteristics of the asphalt as it pertained to the plants design.

- **Delayed Coking Asphalt From Solvent Deasphalting**

The batch deasphalting and transport tests were used to select a practical and promising asphalt feedstock for the delayed coking portion of the ASCOT℠ process. This feedstock was then produced in appropriate quantity and test coked.

- **Direct Delayed Coking Wilsonville Bottoms Product**

The atmospheric bottoms product produced at Wilsonville was directly coked to compare with the ASCOT*m process.

- **Direct Delayed Coking Amoco Bottoms Product**

The atmospheric bottoms product produced by Amoco was directly coked to compare with the results from the Wilsonville feedstock.

- **Economic Assessment**

A preliminary economic assessment for two cases — the ASCOT*m process and direct delayed coking, were completed to define process parameters and estimate a capital cost.

2.0 CONCLUSIONS AND RECOMMENDATIONS

The conclusions drawn from FWDC's alternative bottoms processing test program are:

- The primary technical objective was met. The average liquid yield from Foster Wheeler's ASCOT^{sm} process (62.4 wt%) exceeded the combined liquid yield from the vacuum tower (vacuum distillate) and ROSE-SR^{sm}(Residuum Oil Supercritical Extraction - Solids Rejection) process (58.6 wt%) as operated at DOE's Wilsonville facility. The basis for comparison was the atmospheric residue from liquefying Black Thunder subbituminous coal, as feedstock for both scenarios.

- The ASCOT^{sm} process produces a high quality liquid product. There are very low levels of metals, sulfur and ash present. High levels of sulfur and metals indicate a need for additional steps or potential problems in downstream processing of petroleum substitutes. Corrosion and catalyst deactivation can occur in their presence, leading to operating problems, and lower yield and quality products.

- Direct delayed coking of the Wilsonville feedstock (atmospheric residue) cannot produce as much liquid product as vacuum distillation in tandem with the ROSE-SR^{sm} process, or the ASCOT^{sm} process.

- The coal liquefaction bottoms product (atmospheric residue) generated by Amoco in the course of this program was superior to the Wilsonville atmospheric bottoms used as feedstock during the program. The levels of ash, sulfur, quinoline insolubles and conradson carbon residue were all significantly lower in the Amoco material.

- The Amoco bottoms used by FWDC as feedstock, as follows from the above conclusion, better met the program objective to produce more liquid product from bottoms processing. However, it was generated in small quantity at Amoco's research facility and may not be representative of what would come from more extensive operation of an advanced, integrated process.

- The practical feeding limitations associated with the pilot plant set the maximum level of solids loading and associated softening point of the asphalt that could be test coked during the ASCOT^{sm} process study. Solvent deasphalting can produce more concentrated asphalt products (lower yields) which make the ASCOT^{sm} process more economical and would most likely improve upon the liquid yield attained in this program.

Recommendations are:

- Investigate and modify the delayed coking pilot plants front-end feeding system to handle asphalts with higher solids loadings and softening points.

- Evaluate the ASCOT^{sm} process at higher deasphalted oil yields and associated heavier asphalts for coking than in present program.

- Evaluate the ASCOT process with feedstocks other than the bottoms product generated at Wilsonville from Black Thunder subbituminous coal.

- Complete a technical and economic assessment based on the test programs findings and integration into an advanced liquefaction concept. The coking cycle, which incorporates a continuous feeding period, a steam out period, cool down and decoking would have to be addressed and the proper number of trains determined for a defined integration scheme.

3.0 TEST FACILITIES

The two FWDC test facilities used for this program were the batch deasphalting unit and the 4-inch delayed coking pilot plant (Minicoker). Following is a brief description of these units.

3.1 BATCH SOLVENT DEASPHALTING (SDA) UNIT

The laboratory batch deasphalting unit (Figure 1) is a 16 liter pressure vessel capable of processing 400 to 2000 ml of oil, depending upon the solvent to oil ratio employed. The vessel is Dowtherm jacketed for heating and is traced with an outer coil for water cooling.

The deasphalters main features are:

- Rocker Bomb Design
- Dowtherm jacket heater
- Taps for locating/draining solvent phase
- Batch Feed: 400 to 2000 ml
- Solvent/Feed Ratio: 3:1 to 10:1
- Temperatures to 550°F

The deasphalter is charged with oil and solvent, brought to the desired operating temperature, and agitated until equilibrium is established. After a settling period, the deasphalted oil is withdrawn from the oil outlet immediately above the asphalt level. The asphalt is withdrawn from the bottom outlet, and the vessel is then washed to remove traces of any remaining asphalt. The washings are added to the asphalt after stripping the wash solvent. The deasphalted oil and asphalt are stripped of solvent and inspected for quality characteristics. The yield and material balance are determined.

3.2 4-INCH DELAYED COKING PILOT PLANT (MINICOKER)

The 4-inch minicoker is a versatile and cost-effective pilot plant that bridges the gap between batch cokers and larger more complex and costly units. The minicoker (Figure 2) is designed for once-through or recycle operation over a 4 to 8-hour test period. It can operate up to 200 psi, with a feed rate of 0.25 to 0.5 gal/h.

The minicokers main features are:

- Two drums
- Once-through/recycle operation
- Preheated feedstock
- Coke drum steamout
- Coking pressure to 200 psig
- 7-lb coke/drum
- Feed rate 0.25 to 0.5 gal/h

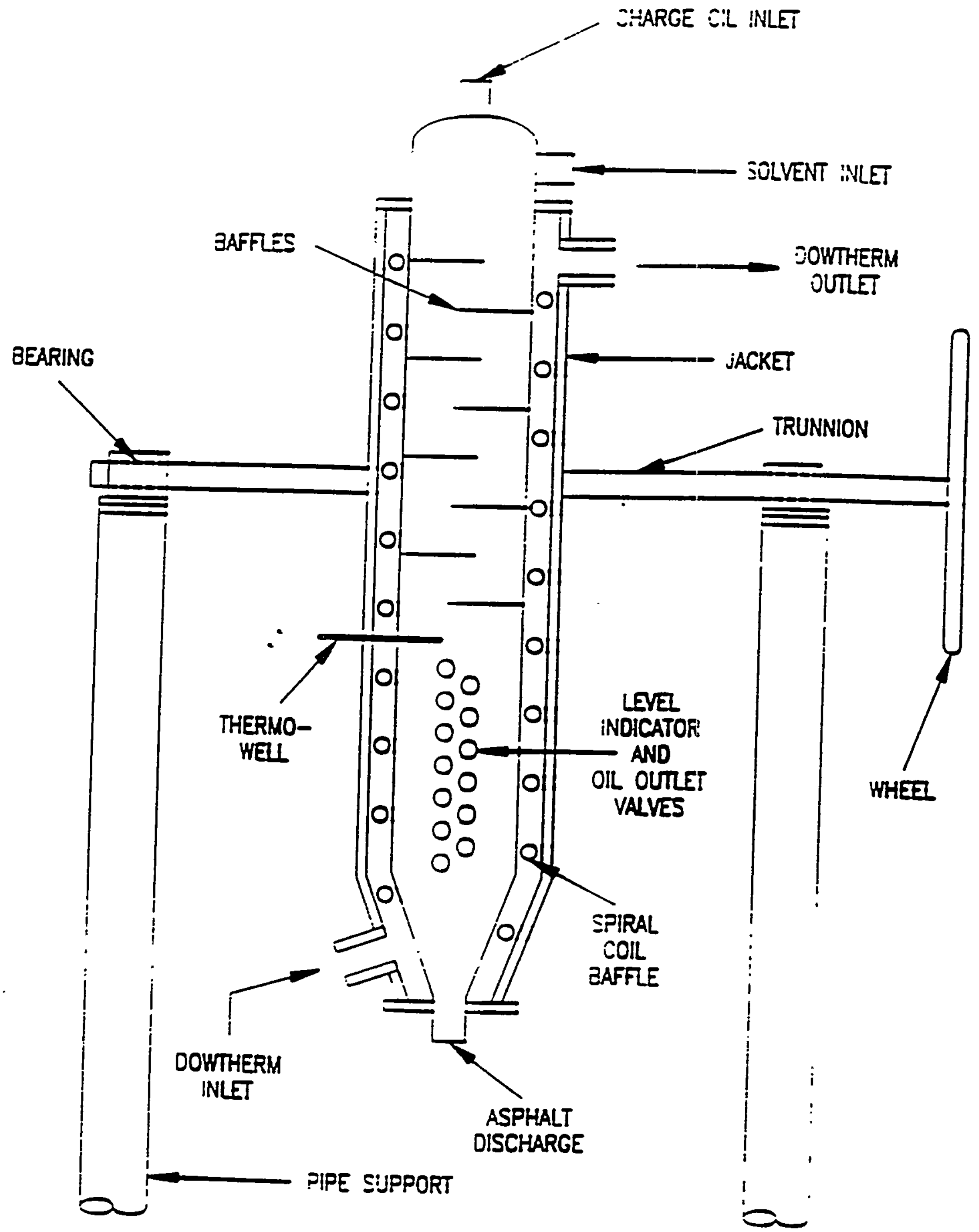

Figure 1 Batch Deasphalting Unit

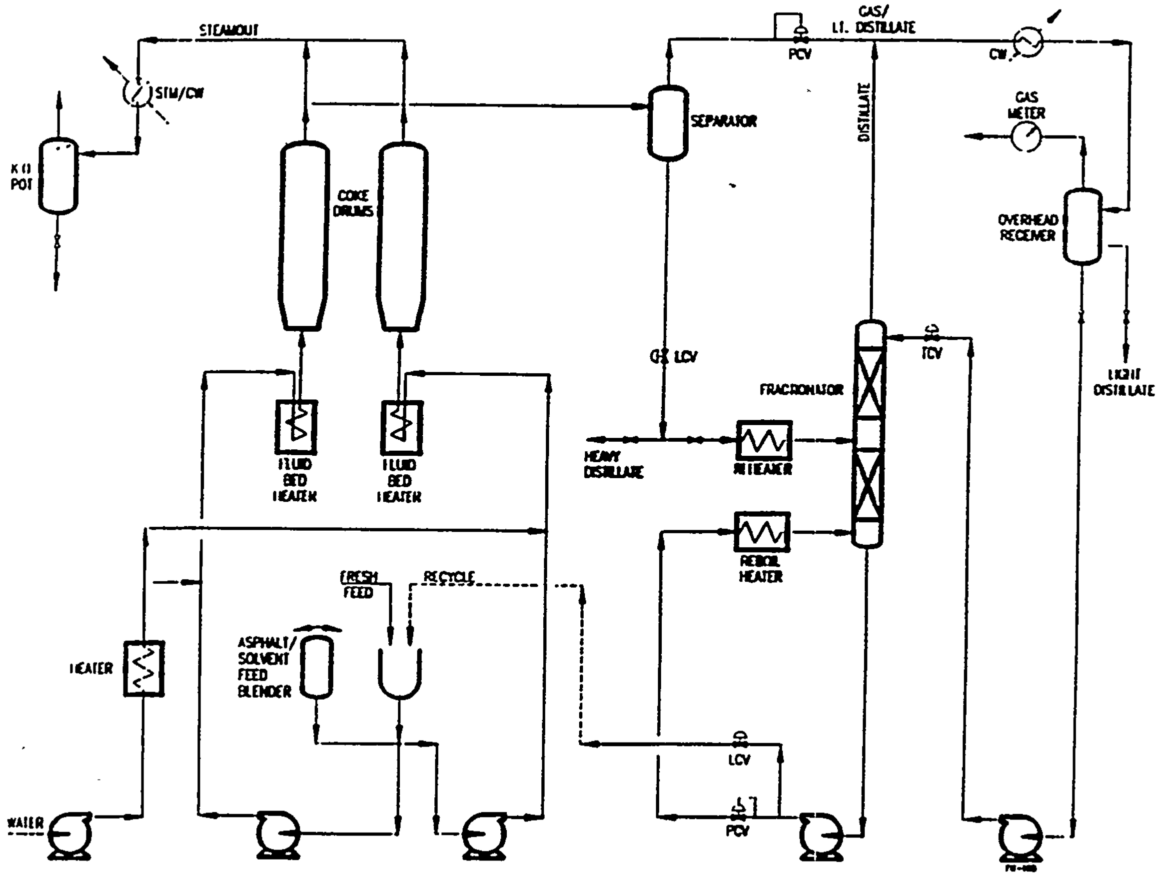

Figure 2 4-Inch Mini-delayed Coking Pilot Plant

Standard bottoms feeds are weighed into the feed tank hourly and pumped through the fluidized bed heater to the coke drum, which is housed in a three-zone tubular heater. ASCOT^{sm} feed (a 1:1 v/v blend of asphalt and deasphalting solvent representative of the composition in the bottom settler of a commercial SDA unit) is weighed, charged and blended in a pressure vessel with mixing capability prior to beginning a test.

Temperature is controlled in the fluid bed heater and coke drum. Vapor effluents from the coke drum pass through a knockout pot, a cooler/condenser, and a receiver. Condensed effluent is collected in the receiver and weighed. The uncondensed vapor leaving the receiver is metered, and an adequate sample taken for analysis.

Immediately after the coke drum is filled, it is steamed out, and the steamed out material is weighed and accounted for. The coke drum is cooled and the coke is removed, weighed, and sampled. All products are inspected according to the specific project requirements.

4.0 LABORATORY-SCALE OPERATION: ALTERNATIVE BOTTOMS PROCESSING

4.1 FEEDSTOCK CHARACTERIZATION

Two different feedstocks were used during the test program. The primary feedstock, used to investigate the ASCOT™ process and compared with direct delayed coking, was an atmospheric residue produced during Run 262 at DOE's Wilsonville facility (FW #22777). It was derived from the liquefaction of Black Thunder subbituminous coal. Amoco also conducted coal liquefaction experiments on Black Thunder coal as part of this program. They produced an atmospheric residue for a direct delayed coking test in a series of dispersed catalyst runs (FW #22779A).

Tables 1 and 2 characterize the Wilsonville material; Tables 3 and 4 the Amoco-derived feed. While the relatively low softening point (124°F) made it easy to handle the Wilsonville feedstock, the high levels of quinoline insolubles (22.2 wt%) and ash (11.5 wt%) set the practical solvent deasphalting range (measured as percent-asphalt on feed), for providing a pumpable asphalt more narrowly than it would have been with lower numbers.

The values for asphaltenes, toluene insolubles, quinoline insolubles and ash were used to characterize the Wilsonville feedstock (Table 2) and approximate what a paraffin solvent, such as heptane, is capable of extracting (65.9 wt% oil) and what a BTX solvent might extract (76.8 wt% oil plus asphaltenes). Based on the feed characteristics we anticipated solvent deasphalting to provide between 40 and 60 wt% distillate yield from this feedstock before coking. Any greater yield will probably not be practical due to the high asphalt solids content. Much lower yields will not take proper advantage of the deasphalting phase.

The sulfur and metals content reported in Table 1 provide an indication of the need for additional steps or potential problems in downstream processing or limitations in final product utilization. Crude oil or intermediates with greater than about 0.5 wt% sulfur are considered "sour" and generally require more extensive processing than those with lower sulfur content. Coal liquids will probably be treated in the same manner. High sulfur can cause corrosion and catalyst deactivation. Fuels for transportation and heating have sulfur specs that range from 0.05 wt% max (aviation gasoline) to 0.5 wt% max (No. 2 heating oil). Sodium at 10 to 15 ppm can cause corrosion problems during refinery processing. in lower-value products. Vanadium in fuel oils, even in concentrations as low as 3 ppm can lead to severe corrosion to turbine blades and deterioration of refractory furnace linings and stacks.

There are significant differences between the Amoco and Wilsonville materials. Some of the differences of note are the percentages of ash, sulfur and sodium, the quinoline insolubles, conradson carbon residue, softening point, and boiling range - all significantly lower for the Amoco material. Total carbon, as must follow from the low ash in the Amoco feedstock, is notably higher (89.5% compared to Wilsonville's 77.6%). The oil content is about the same in both feedstocks, while the mix of the other constituents defined in Tables 2 and 4 (asphaltenes, preasphaltenes, insoluble organic matter and ash) are quite different.

Based on the characterization of both feedstocks, the Amoco material was considered as superior. However, it was produced in too small quantity, late into the program, and is not representative of any sustained process evaluation as was the case with the Wilsonville operation. For these reasons the test program was focused on the Wilsonville feedstock.

Table 1
Feedstock Inspections
Wilsonville Atmospheric Residue (1)

FW Identification No.	22777
Specific Gravity @ 60/60 °F	1.187
Asphaltenes (2), wt%	10.9
Toluene Insolubles, wt%	23.2
Quinoline Insolubles, wt%	22.2
Ash, wt%	11.49
Softening Point (R&B), °F	124
Conradson Carbon Residue, wt%	38.1
Carbon, wt%	77.6
Hydrogen, wt%	7.4
Sulfur, wt%	1.40
Nitrogen, wt%	1.12
Metals, ppm	
Fe	16200
Ni	36
V	43
Cu	46
Na	426
ASTM Distillation (D-1160, °F(3)	
IBP	592
2 vol%	677
5	721
10	764
20	812
30	846
40	883
50	931(4)

---

(1) Source: Liquefaction of Wyoming Black Thunder subbituminous coal

(2) Asphaltenes Precipitation with Normal Heptane. Method IP 143

(3) Corrected to atmospheric pressure

(4) Cracking at still temperature of 650°F

Table 2
Wilsonville Feedstock Characterization[1]
FW# 22777

	wt %
Oil [2]	65.9
Asphaltenes	10.9
Preasphaltenes [3]	1.0
Insoluble Organic Matter [4]	10.7
Ash [5]	11.5
TOTAL	100.0

---

(1) This estimation was developed from following feedstock inspections: Asphaltenes, Toluene Insolubles, Quinoline Insolubles, and Ash.

(2) Toluene solubles minus asphaltenes

(3) Quinoline solubles minus toluene solubles

(4) Defined as quinoline insolubles minus ash. Includes coal fines (mmf)

(5) Includes catalyst fines with coal's mineral matter

Table 3
Feedstock Inspections
Amoco Atmospheric Residue [1]

FW Identification No.	22779A
Specific Gravity @ 60/60 °F	1.148
Asphaltenes [2], wt%	18.0
Toluene Insolubles, wt%	18.1
Quinoline Insolubles, wt%	6.7
Ash, wt%	0.97
Softening Point (R&B), °F	96
Conradson Carbon Residue, wt%	26.8
Carbon, wt%	89.5
Hydrogen, wt%	6.2
Sulfur, wt%	0.27
Nitrogen, wt%	1.68
Metals, ppm	
Fe	4180
Ni	30
V	80
Cu	8
Na	< 20
ASTM Distillation (D-1160, °F[3]	
IBP	654
2 vol%	672
5	687
10	711
20	756
30	793
40	830
50	869
60	919
70	994[4]

---

(1) Source: Liquefaction of Wyoming Black Thunder subbituminous coal
(2) Asphaltenes Precipitation with Normal Heptane. Method IP 143
(3) Corrected to atmospheric pressure
(4) Feedstock cracked

Table 4
Amoco Feedstock Characterization (1)
FW# 22779A

	wt %
Oil (2)	63.9
Asphaltenes	18.0
Preasphaltenes (3)	11.4
Insoluble Organic Matter (4)	5.73
Ash (5)	0.97
TOTAL	100.0

---

(1) This estimation was developed from following feedstock inspections: Asphaltenes, Toluene Insolubles, Quinoline Insolubles, and Ash.

(2) Toluene solubles minus asphaltenes

(3) Quinoline solubles minus toluene solubles

(4) Defined as quinoline insolubles minus ash. Includes coal fines (mmf)

(5) Includes catalyst fines with coal's mineral matter

4.2 BATCH DEASPHALTING TESTS (WILSONVILLE FEED)

A series of sixteen batch deasphalting screening tests (summarized in Table 5) were needed to select the solvents and extraction conditions that would provide the necessary control and product yield range for producing asphalt from the Wilsonville feedstock.

The screening tests were begun using one paraffin (heptane) and one aromatic (xylene) solvent. It soon became apparent that both solvents were "too effective" in the sense that extraction temperature, the primary means of establishing and controlling a yield for any given solvent, could not be properly used. Tests, going down the solvent power scale, with hexane and pentane, also showed these to be too high in solvent power. Even when operating near their critical temperatures, where extraction should be markedly reduced, would not lower the yield of extracted oil.

Figure 3 indicates the effect of temperature on the deasphalted oil (DAO) yield for the solvents that were deemed "too effective;" -- pentane, hexane, heptane and xylene. Here, it is evident that the controlling variable was solvent-type (i.e., paraffin or aromatic), not temperature. The DAO yield was essentially independent of temperature and solvent/feed ratio. The yield was near constant and averaged 61.3 wt% for the paraffin solvents and was 80.6 wt% for the single test with xylene. These numbers are consistent with the feedstock characterization (Table 1 and 2) of 65.9 wt% oil (paraffin-soluble material) and 76.8 wt% soluble in toluene (an aromatic solvent). None of these solvents provide the means for readily achieving lower yields and placing us in the 40 to 60 weight percent DAO yield range we sought for processing the solids-ladened asphalt.

The practical yield range sought could be bracketed with butane (Run 3023--32.5 wt% oil yield). Butane was then screened over its practical temperature range, and butane/pentane blends were also studies. Testing was focused on a solvent/feed ratio (v/v) of 4/1. Results showed this to be an acceptable ratio and it will be more economical from an equipment sizing and throughput perspective than the 8/1 ratio that was also screened.

Figure 4 shows the effect of temperature on the DAO yield when using n-butane as the solvent. This was the first solvent that readily permitted the use of temperature as a controlling variable. Butane's solvent power however, limits the maximum yield to about 50 wt% DAO. It must also be used over an undesirable temperature range as is evident by its yield vs. temperature curve. As the temperature is lowered from near the critical temperature (306°F) the DAO yield increases as it should, peaks, and then falls off precipitously. This occurs in solvent deasphalting when the extraction temperature is reduced to the degree that the asphalt phase becomes too viscous for effective extraction. Potentially extractable material is then trapped in the asphalt.

At this point it appeared that a blend of butane and a more effective paraffin solvent, used close to the critical temperature of butane, would be the best choice for producing a yield/temperature relationship of the proper sensitivity and also minimize the possibility of again encountering a too viscous asphalt phase.

Pentane was selected as the blend component and those results, which are plotted in Figure 5, show a relationship that was able to furnish most of the yield range needed. Temperature was fixed at 290°F, near the critical temperature of butane.

Above 50 vol% pentane, the yield peaks and tends to drop off. This is the same phenomenon noted with 100 percent n-butane as the extraction temperature was lowered. In this case it was suspected that as more and more oil was extracted, with successively higher concentrations of pentane in the blend, the asphalt phase became too viscous for

Table 5 Summary of Batch Deasphalting Test Results

Run No.	Solvent	S/F Ratio V/V @ 60°F	Temp. °F	Yields - wt % Oil	Yields - wt % Asphalt	Yields - wt % Recov	Ash - wt% Oil	Ash - wt% Asphalt
3015	Heptane	8	475	60.4	32.0	92.4	0.010	27.75
3016	Heptane	8	500	58.5	30.5	89.0	0.006	27.23
3017	Xylene	8	565	80.6	25.3	105.9	2.27	33.06
3018	Heptane	4	500	60.6	35.8	96.4	0.030	27.85
3019	Heptane	8	520	60.9	28.8	89.7	0.060	28.44
3020	Heptane	8	550	65.3	40.3	105.6	0.024	28.00
3021	Hexane	4	430	59.8	33.7	93.5	0.017	30.70
3022	Pentane	4	380	63.6	35.7	99.3	0.020	26.00
3023	Butane	4	290	32.5	69.8	102.3	0.017	15.88
3024	Butane	4	240	30.4	68.4	98.8	0.006	17.04
3025	Butane	4	265	49.5	52.5	102.0	0.0044	20.33
3026	80%C_4,20%C_5	4	290	47.9	49.4	97.3	0.0037	21.51
3027	70%C_4,30%C_5	4	290	50.0	47.0	97.0	0.0053	23.77
3028	50%C_4,50%C_5	4	290	54.0	46.3	100.3	0.0055	25.63
3029	70%C_4,30%C_5	8	290	57.9	38.4	96.3	0.0071	25.98
3030	20%C_4,80%C_5	4	290	50.5	44.8	95.3	0.014	25.48

S/F Ratio = Solvent/Feed Ratio

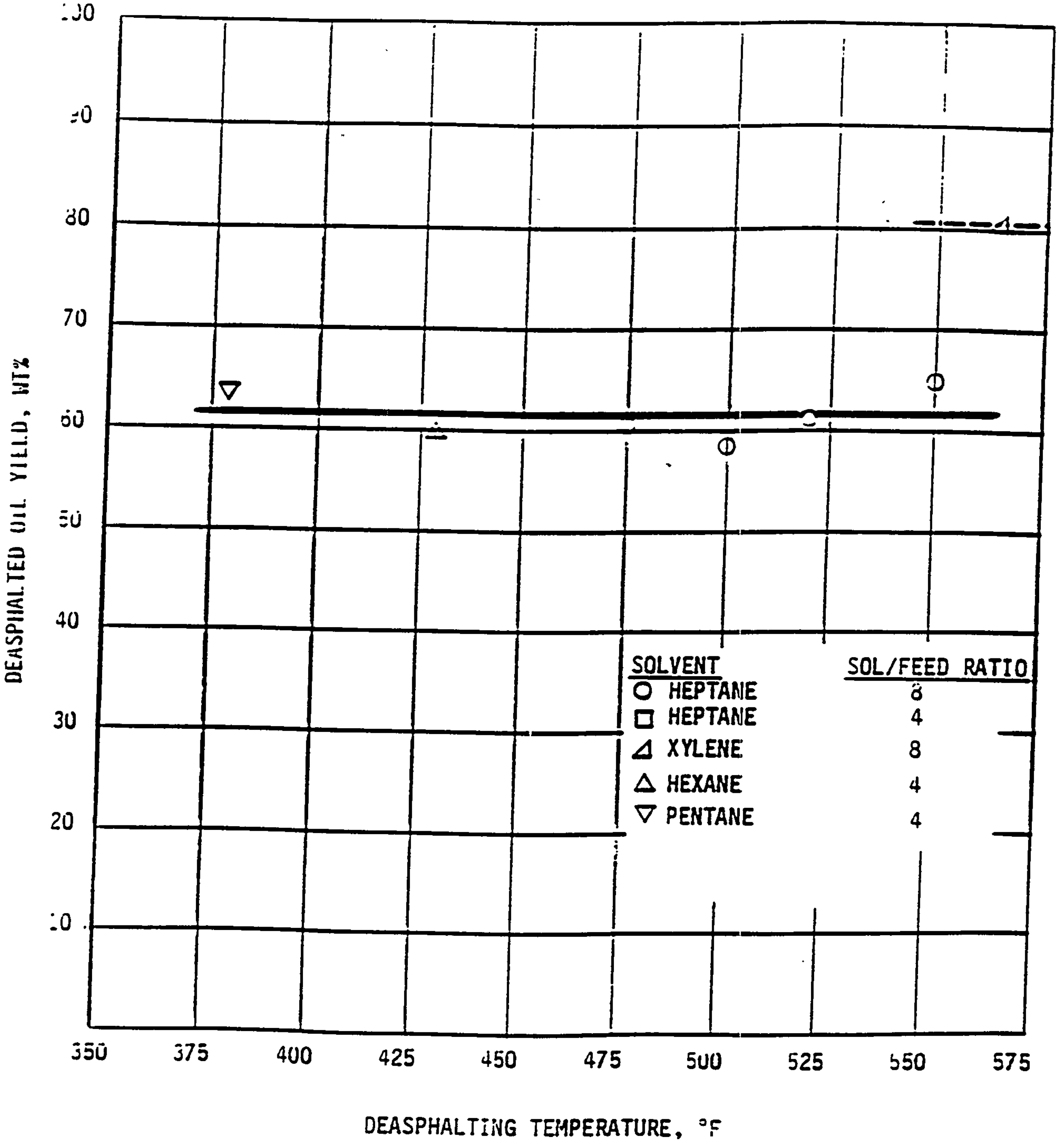

Figure 3 Effect of Temperature on DAO Yield

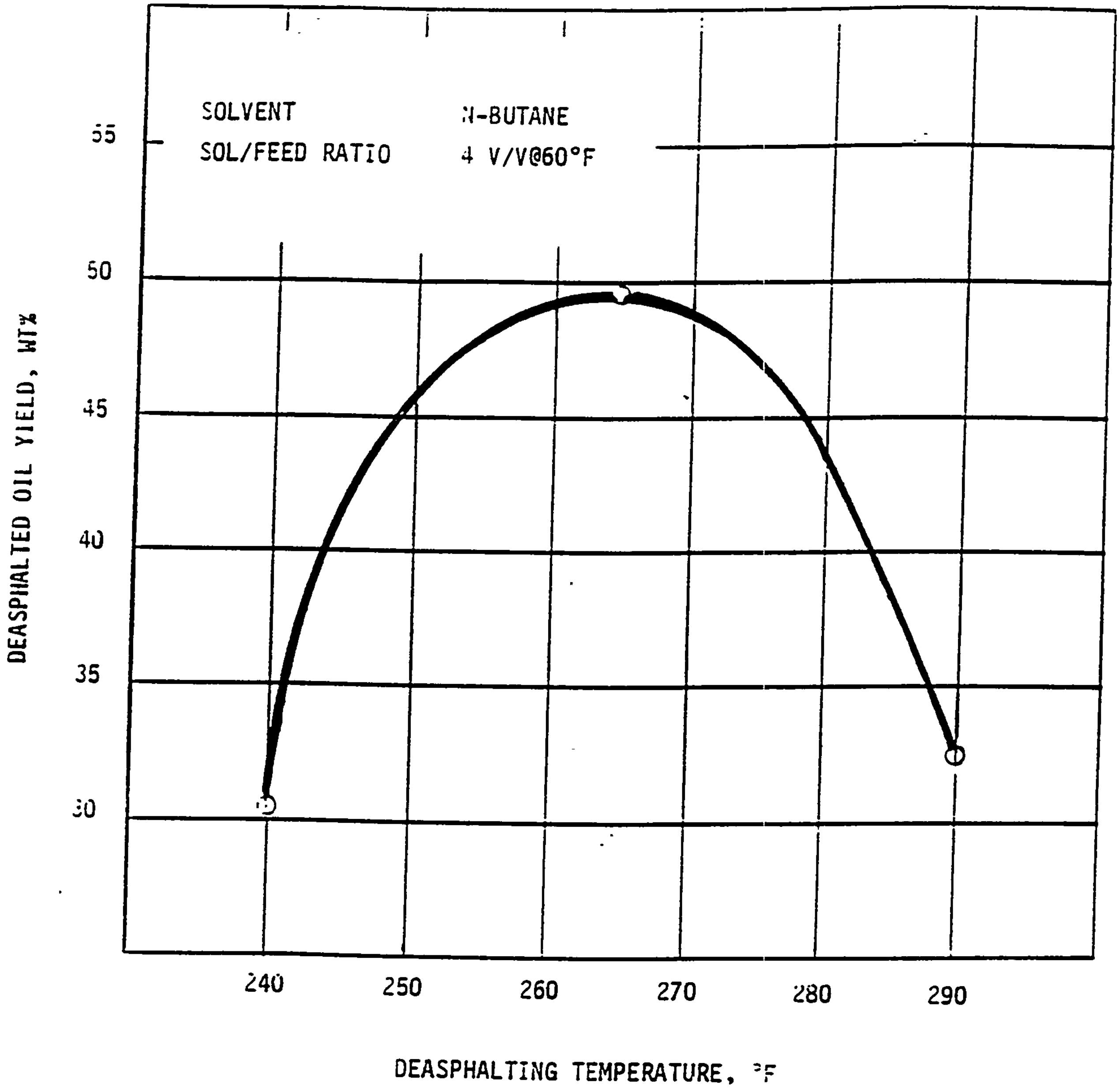

Figure 4 Effect of Temperature on DAO Yield For N-Butane

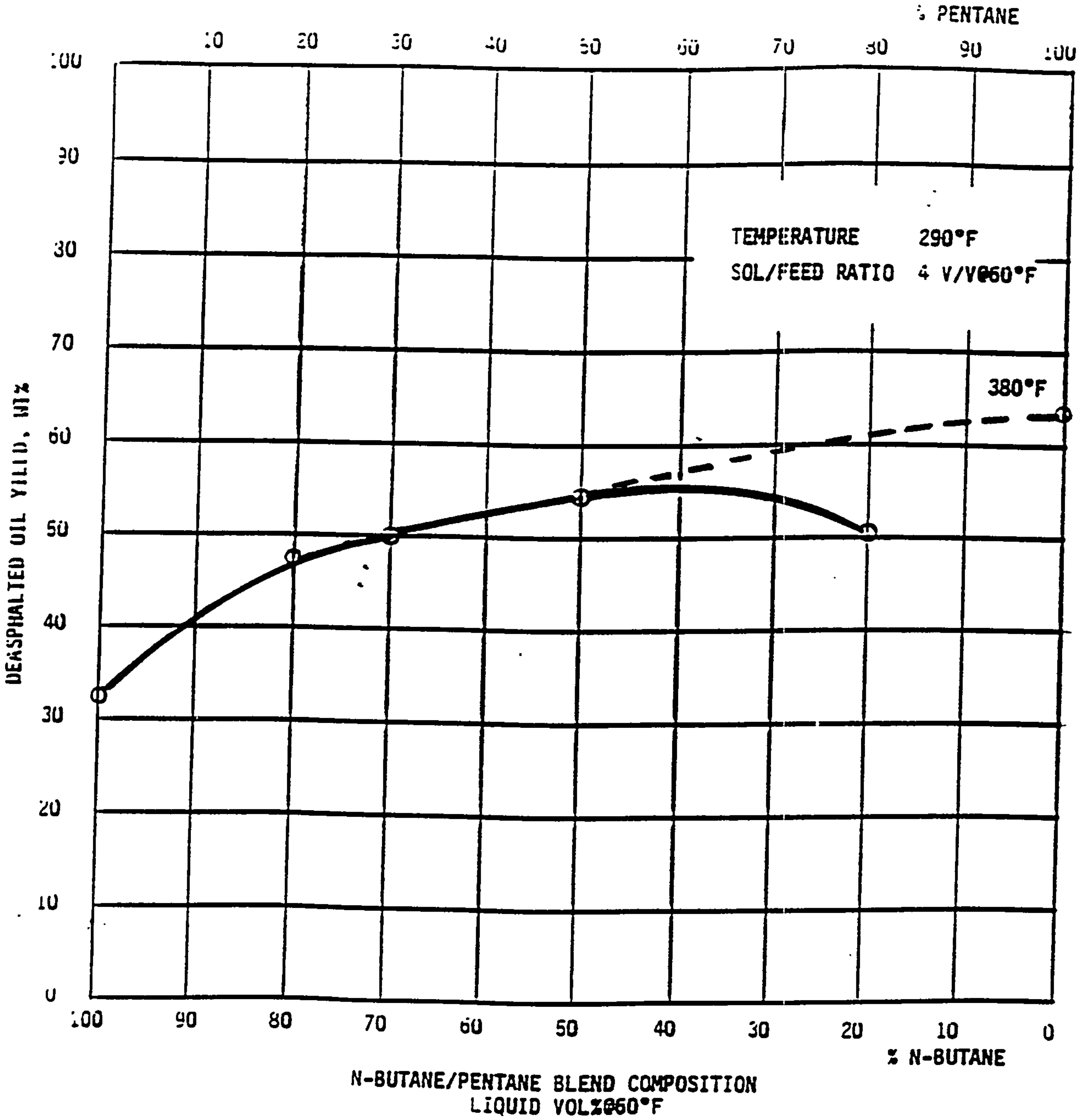

Figure 5 Effect of Butane/Pentane Blend Composition on DAO Yield

effective extraction at the test temperature (290°F). The data indicated that the oil yield at 290°F for n-butane/pentane will not exceed about 55 wt%. However, 100 percent pentane at 380°F does provide an oil yield (63.6 wt%) that will satisfy the need for a higher level of extraction. A dashed line is drawn on Figure 5 to show that a 60+ wt% oil yield is achievable if low temperature is eliminated as the controlling variable.

Table 6 tabulates the ASTM D-1160 distillation data from eight selected batch tests. The distillation data shows that we always extracted a deashed resid fraction through solvent deasphalting. We can use this data to approximate the amount by defining deashed resid as "the volume percent of deasphalted oil (DAO) corresponding to the 900°F + fraction from its ASTM-D-1160 distillation". Figure 6 plots the relationship of DAO yield to deashed resid yield showing the linear regression line and equation. The correlation coefficient, $\underline{r}$ is 0.77.

le 6
Distillations of Deasphalted Oil

Run No.	3015	3017	3018	3023	3024	3026	3027	3028
DAO Yield, wt%	60.4	80.6	60.6	32.5	30.4	47.9	50.0	54.0
°API @ 60°F	4.6	4.4	4.7	14.2	11.6	10.9	10.0	8.9
ASTM D-1160,°F[1]								
IBP	612	574	ND	490	524	539	561	540
2 Vol%	700	717	653	652	601	618	615	619
5	743	753	752	722	671	691	681	676
10	775	783	783	768	719	743	732	721
20	802	819	817	805	759	778	766	758
30	828	855	843	827	784	807	789	772
40	854	914	875	851	811	831	819	810
50	886	928	916	879	828	857	843	838
60	930		977	912	857	890	878	873
70	1010		1014[3]	972	895	932	924	907
80	1044[2]			1048[4]	952	1009	992	961
90					997[5]	1024[6]	1026[7]	1008[5]
95								
EP								

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(1) Temperature reported at 760 mm Hg. Distillation terminated at 750°F flask temperature.
(2) 75 vol%
(3) 68 vol%
(4) 77 vol%
(5) 86 vol%
(6) 81 vol%
(7) 84 vol%

ND = Not Determined

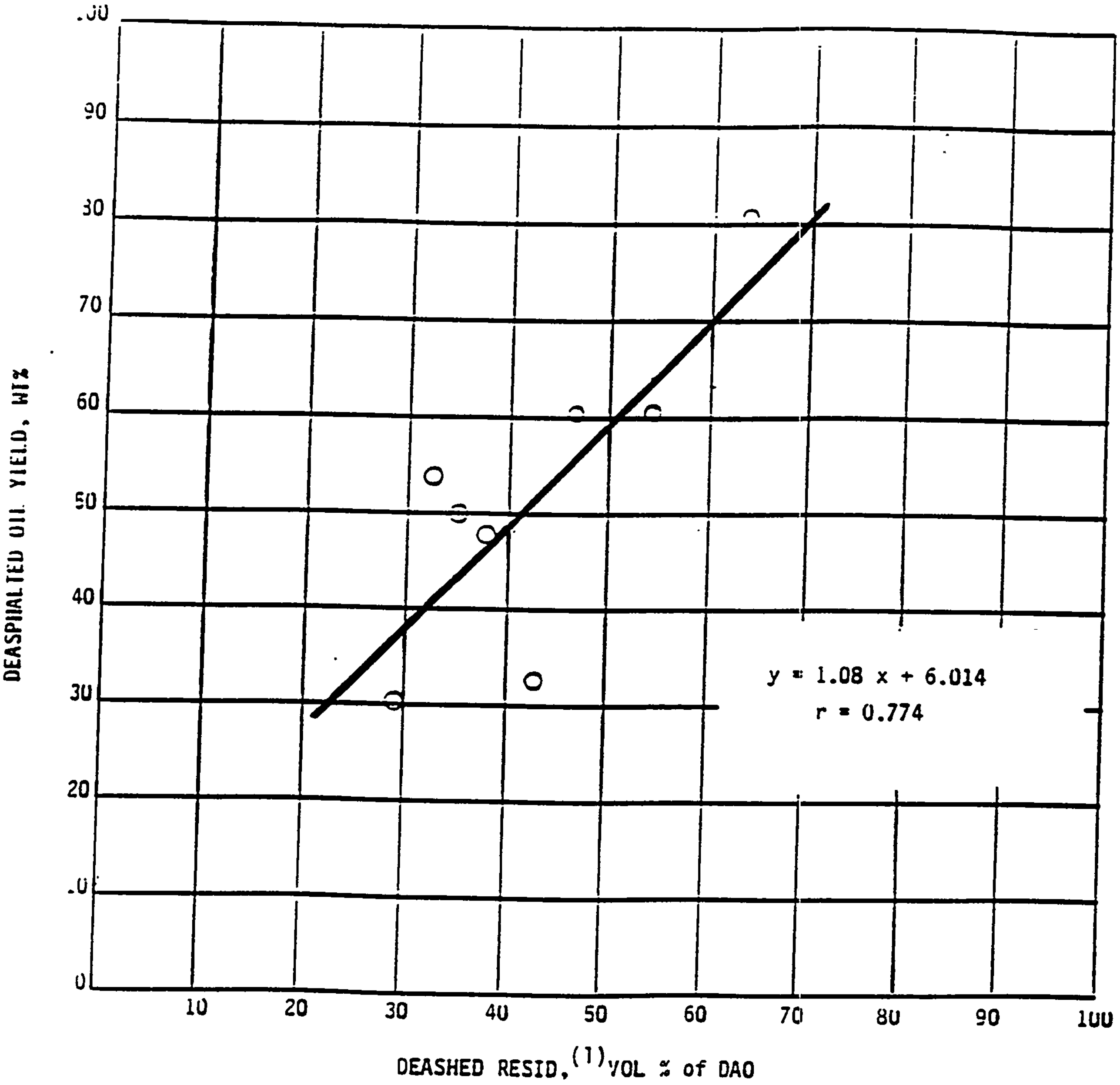

Figure 6 Relationship of DAO Yield to Deashed Resid Yield

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(1) Defined as vol% of deasphalted oil (DAO) corresponding to a 900°F + Resid fraction from its ASTM D-1160 distillation.

4.3 TRANSPORT TESTS (WILSONVILLE FEED)

Three transport tests were completed to determine the practical transport characteristics of asphalt corresponding to oil yields of approximately 40, 50 and 60 wt%. The 4-inch delayed coking pilot plant's (minicoker) front-end ASCOT℠ pumping and piping system was partly used to evaluate the suitability of the asphalt for transport from the pressurized feed tank, through the fluid bed heater to the coke drum.

The data and curves developed during the batch deasphalting screening tests were used as a guide for the asphalt production runs needed for the transport tests. The data shown in Figure 5 was initially used to select the solvent and predict the oil yield for these tests. While the 40 wt% oil yield was produced as the curve predicted, the higher yields were off-target. There is a relative insensitivity to blend composition expressed by a segment of the data - the curve flattens and then falls off, which may account in part for the discrepancy. The flatness and fall off was theorized as due to the high viscosity of the asphalt phase at a 290°F extraction temperature. A rising viscosity, corresponding to increasing the pentane portion of the blend may have been the culprit.

Nonetheless, the remaining screening data provided enough information to allow the quick determination of effective extraction parameters. Straight pentane was used to produce a near 50 wt% yield and hexane was selected as the solvent for a 60 wt% yield because pentane produced a somewhat lower yield than indicated by the screening tests. Therefore, moving up to a better solvent would more readily achieve the desired yield.

The results from the asphalt production runs are shown in Table 7.

Table 7 Asphalt Production for Transport Tests

Run	Solvent	S/F Ratio (V/V at 60°F)	Temp (°F)	Yields (wt%)			Ash (wt%)	
				Oil	Asphalt	Recov.	Oil	Asphalt
3031	90%C_4,10%C_5	4	290	41.0	58.0	99.0	0.001	21.03
3034	Pentane	4	340	54.1	48.9	103.0	0.008	24.14
3035	Hexane	4	400	59.8	41.3	101.1	0.003	27.23

The transport test setup (Figure 7) included the following:

1. A steam heated, pressurized feed tank mounted on a shaker assembly.
2. An electrically-heated flexible metal hose as suction line to the metering pump.
3. A Zenith precision gear metering pump applicable for suspended fine solids slurry transport.
4. A pressure-control valve and controller to maintain the pump discharge pressure above that of the feed tank.
5. A steam-heated and enclosed receiving tank to collect transport product.

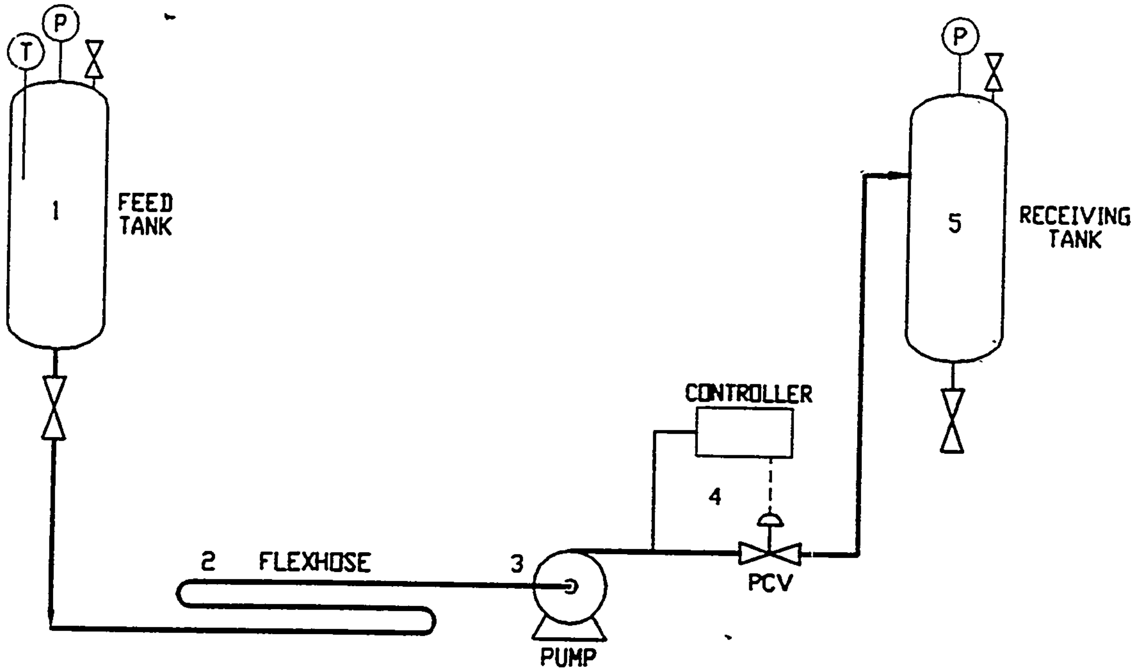


Figure 7 Transport Test Setup

The asphalt was prepared by crushing and screening through a No. 50 sieve (-300 μm). It was then blended at transport temperature (~ 275°F) with an equal volume of its solvent to simulate the composition in the bottom settler of a commercial SDA unit. Commercially this stream would be sent directly to a delayed coker. The blend was mixed for three hours before conducting the pumping test over a three to four hour period.

The asphalt from the butane/pentane blend, containing 21.03 wt% ash, was selected for the first transport test. The test was successful and represented a milestone in the program. This was the first demonstration that a coal-derived asphalt with a high solids loading could be handled with our pilot plant equipment.

Two follow-up transport tests, one on asphalt containing 24.14 wt% ash and the other containing 27.23 wt% ash, were less successful. Neither test was able to demonstrate an ability to properly transport these materials. The visual evidence suggested the asphalt never reached a stage of fluidity where the solvent could effectively aid in its transport through the system. A higher temperature, in the range of 350-400°F, was tried to help in the transport of this heavier material.

The test equipment had to be modified to reach this higher temperature range. This was accomplished by adding three independently controlled electrical trace heaters; to the batch deasphalter, the suction line to the pump and a portion of the line downstream of the pump, respectively, and installing additional thermocouples to monitor transport temperatures.

The two transport tests were repeated at higher temperatures (~ 375°F). Again, neither test was able to demonstrate an ability to properly transport these materials.

The operating parameters had now reached the point where the pressure ratings on some equipment items and frequent failure of the flexible metal hose connection limited any further experimental changes in the direction of still higher temperature. The asphalt containing approximately 21 wt% ash, which was transported successfully with the pilot plant equipment, was therefore selected as the candidate for delayed coking.

4.4 DELAYED COKING ASPHALT FROM SOLVENT DEASPHALTING (WILSONVILLE FEED)

An extended series of batch extractions were needed to produce the required amount of asphalt coker feed corresponding to a targeted 40 wt% DAO yield. The solvent blend had to be adjusted, increasing the percentage of pentane to 40 vol%, to consistently achieve this yield. The overall material balance and ash determinations are reported in Table 8.

Table 8 Asphalt Production for Delayed Coking

Run	Solvent	S/F Ratio (V/V at 60°F)	Temp (°F)	Yields (wt%)			Ash (wt%)	
				Oil	Asphalt	Recov.	Oil	Asphalt
3039/ 3040	60%C_4,40%C_5	4	290	40.2	59.8	100.0	0.010	19.09

All products were inspected from the solvent deasphalting production runs that generated candidate asphalts for transport testing (Runs 3034 and 3035, and the selected candidate for coking [blend of Runs 3039 and 3040]) and are reported in Table 9. Each run number signifies a series of batch extractions, conducted in sequence without closing the material balance by washing the reactor vessel. The final run in the series served to close the material balance with a wash sequence. As an example, Run 3034 was actually a series of five batch extractions further identified as Runs 3034A through 3034E.

The asphalt chosen for delayed coking was produced in sequential production runs 3039 and 3040 which were blended for the needed quantity. The asphalts from reported runs 3034 and 3035 were rejected candidates for coking after evaluating the transport tests. These contained higher solids loadings and prohibitive softening points and did not pass the transport test criteria. Examining the data on toluene and quinoline insolubles, ash and softening point readily indicates the difficulty involved in handling the asphalts that were not selected. If the integrated coal liquefaction process delivered lower solids loaded material, the ASCOT^{sm} process would provide more options as to how deeply to top the feedstock via solvent deasphalting prior to coking. This would, of course, vary a great deal with the coal being processed.

Two asphalt coking tests were completed with the material produced in blended runs 3039 and 3040. The first, Run 3047 reported in Tables 10 and 11, produced a normalized liquid product yield of 38.6 wt% (on asphalt feed). The overall ASCOT^{sm} yield of liquid product was 63.3 wt% (on the atmospheric residue feed); 40.2 wt% from solvent deasphalting and 23.1 wt% from coking.

This run demonstrated that liquid products from the ASCOT^{sm} process are essentially free of ash (< 0.02 wt%) and metals (< 1 ppm Ni and V, ≤ 4 ppm Cu and Na, ≤ 61 ppm Fe). Specific values for the metals in the deasphalted oil and distillate oil from delayed coking are given in Table 9 (Run No. 3039/3040) and Table 11 (Run No. 3047) respectively.

Conducting the second test with the same asphalt/solvent feedstock blend served to confirm the liquid yield data and improve upon the material balance of the first run. The results from this test (Run 3048) are reported in Tables 12 and 13.

Table 9 Inspection of Products from Solvent Deasphalting (Asphalt Considered a Candidate Feed to Delayed Coking)

Run No.	**3039/3040 Blend**	**3034**	**3035**
Deasphalted Oil (DAO)			
DAO yield, wt%	40.2	54.1	59.8
API Gravity @ 60°F	9.8	7.3	6.3
Conradson Carbon Residue, wt%	4.10	7.62	10.23
Heptane Insolubles, wt%	0.89	1.94	6.36
Ash, wt%	0.010	0.008	0.003
Carbon, wt%	87.40	87.56	87.77
Hydrogen, wt%	9.99	9.68	9.50
Sulfur, wt%	0.02	0.03	0.04
Nitrogen, wt%	0.63	0.70	0.90
Metals, ppm			
Fe	5	11	2.6
Ni	0.4	0.2	0.2
V	0.2	0.1	0.1
Cu	0.1	0.1	0.1
Na	0.3	1.6	0.5
ASTM Distillation (D-1160)°F			
IBP	537	526	532
2 vol%	603	602	618
5	665	668	687
10	717	716	728
20	753	754	765
30	779	778	791
40	801	800	820
50	827	828	853
60	859	858	894
70	912	907	963
80	996	983	1107(75%)
90	1045(83%)	1023(84%)	

Table 9 (Cont) Inspection of Products from Solvent Deasphalting (Asphalt considered a Candidate Feed to Delayed Coking)

Run No.	3039/3040[1] Blend	3034	3035
Asphalt			
Yield, wt%	59.8	48.9	41.3
Specific Gravity @ 60/60°F	1.357	1.449	1.532
Conradson Carbon Residue, wt%	58.31	68.58	69.28
Asphaltenes, wt%	19.12	14.45	14.09
Toluene Insolubles, wt%	42.04	57.52	60.82
Quinoline Insoluble, wt%	33.93	49.40	51.23
Ash, wt%	19.09	24.14	27.23
Softening Point, °F	242	348	NA
Carbon, wt%	78.82	73.73	69.62
Hydrogen, wt%	6.36	5.13	4.40
Sulfur, wt%	2.01	2.50	2.73
Nitrogen, wt%	1.18	1.24	1.20
Metals, ppm			
Fe	38900	45300	43600
Ni	21	21	21
V	95	116	137
Cu	29	95	158
Na	480	637	764

NA - Not applicable. Sample decomposed before melting.
(1) - Selected Feedstock for Delayed Coking.

Table 10 Delayed Coking Asphalt [1] Product From Solvent Deasphalting Wilsonville Atmospheric Residue

FWDC Run No.	**3047**	
Operating Conditions		
Coke Drum Pressure, psig	5	
Throughput Ratio (Total feed/Fresh feed)	1.0	
Steam/Feed Ratio, w/w	0.134	
Maximum Drum Temperature, °F (Avg.)	901	
Material Balance		
Product Distribution-Wt%		
	As Measured	**Normalized**
Gas	2.2	2.3
Distillate Oil	36.2	38.6
Coke	55.3	59.1
Recovery	93.7	100.0
Overall ASCOT™ Liquid Yield	**wt%**	
Solvent Deasphalting Yield	40.2	
Asphalt Coking Yield (59.8 x 0.386)	23.1	
Total Liquid Yield (on atm residue)	**63.3**	
Total Liquid Yield (Solids-Free Basis)[2] (63.3/0.778)	**81.4**	

(1) Asphalt produced by blending solvent deasphalting product from SDA Run Nos. 3039/3040.

(2) Feedstock solids defined as Quinoline Insolubles (22.2 wt%).

Table 11 Inspection of Run 3047 Delayed Coking Products
ASCOT℠ Process

Distillate Oil	
API Gravity @ 60°F	5.7
Carbon, wt%	87.68
Hydrogen, wt%	9.02
Sulfur, wt%	0.05
Nitrogen, wt%	1.01
Ash, wt%	0.018
Metals, ppm (w)	
Iron	61
Nickel	0.2
Vanadium	0.1
Copper	4
Sodium	2.2
ASTM Distillation, °F	D1160
IBP	140
2 Vol%	373
5	504
10	618
20	732
30	773
40	798
50	823
60	848
70	880
80	924
90	1032
EP (90.7%)	1076

Coke			
Proximate Analysis, wt%		Ultimate Analysis, wt%	
Fixed Carbon	54.73	Carbon	62.06
Volatile Matter	14.81	Hydrogen	2.55
Ash	29.98	Oxygen	0.09
Moisture	0.48	Nitrogen	1.37
Total	100.0	Sulfur	3.47
		Ash	29.98
		Moisture	0.48
		Total	100.0

Table 11 (Con't) Inspection of Run 3047 Delayed Coking Products

Gas (Composite Sample)	
	Mol% of Gas
Hydrogen	62.01
Carbon Monoxide	0.93
Carbon Dioxide	3.62
Hydrogen Sulfide	0.58
Methane	18.97
Ethane	6.08
Ethylene	0.56
Propane	3.02
Propylene	0.89
Isobutane	1.21
n-Butane	ND
Propadiene	—
Butene-1	0.56
Isobutene	0.93
trans-Butene-2	0.16
cis-Butene-2	0.08
Butadiene	—
Isopentane	0.28
n-Pentane	ND
Pentene-1	0.04
cis/trans-pentene-2	—
2-Methyl butene-2	0.08
n-hexane	—
Unknown C_5's	—

\- none detected

ND Not Determined. N-butane and n-pentane comprised the solvent present with the asphalt feedstock. Their presence in the product gas masked the much smaller yields (< 1.0% each) of these compounds that occurred from coking the asphalt. The gas composition is calculated on a n-butane/n-pentane - free basis.

Table 12 Delayed Coking Asphalt [1] Product From Solvent Deasphalting Wilsonville Atmospheric Residue

FWDC Run No.	**3048**	
Operating Conditions		
Coke Drum Pressure, psig	5	
Throughput Ratio (Total feed/Fresh feed)	1.0	
Steam/Feed Ratio, w/w	0.163	
Maximum Drum Temperature, °F (Avg.)	962	
Material Balance		
Product Distribution-Wt%		
	As Measured	**Normalized**
Gas	3.9	4.0
Distillate Oil	35.1	35.7
Coke	59.2	60.3
Recovery	98.2	100.0
Overall ASCOT Liquid Yield	**wt%**	
Solvent Deasphalting Yield	40.2	
Asphalt Coking Yield (59.8 x 0.357)	21.3	
Total Liquid Yield (on atm residue)	**61.5**	
Total Liquid Yield (Solids-Free Basis)[2] (61.5/0.778)	**79.0**	

(1) Asphalt produced by blending solvent deasphalting product from SDA Run Nos. 3039/3040.

(2) Feedstock solids defined as Quinoline Insolubles (22.2 wt%).

Table 13 Inspection of Run 3048 Delayed Coking Products ASCOT℠ Process

Distillate Oil	
API Gravity @ 60°F	4.9
Carbon, wt%	86.69
Hydrogen, wt%	8.69
Sulfur, wt%	0.07
Nitrogen, wt%	0.97
Ash, wt%	0.05
Metals, ppm (w)	
Iron	170
Nickel	0.5
Vanadium	0.2
Copper	5.8
Sodium	3.4
ASTM Distillation, °F	**D1160**
IBP	342
2 Vol%	430
5	516
10	625
20	741
30	782
40	807
50	832
60	861
70	893
80	933
90	1022
EP (91%)	1078

Coke			
Proximate Analysis, wt%		**Ultimate Analysis, wt%**	
Fixed Carbon	55.42	Carbon	61.96
Volatile Matter	13.51	Hydrogen	2.21
Ash	29.77	Oxygen	0.15
Moisture	1.30	Nitrogen	1.23
Total	100.0	Sulfur	3.38
		Ash	29.77
		Moisture	1.30
		Total	**100.0**

Table 13 (Con't) Inspection of Run 3048 Delayed Coking Products

Gas (Composite Sample)	
	Mol% of Gas
Hydrogen	56.91
Carbon Monoxide	1.67
Carbon Dioxide	6.59
Hydrogen Sulfide	—
Methane	20.94
Ethane	5.83
Ethylene	0.95
Propane	2.65
Propylene	1.33
Isobutane	0.83
n-Butane	ND
Propadiene	—
Butene-1	0.61
Isobutene	0.72
trans-Butene-2	0.15
cis-Butene-2	0.08
Butadiene	—
Isopentane	0.27
n-Pentane	ND
Pentene-1	0.08
cis/trans-pentene-2	0.11
2-Methyl butene-2	0.08
n-hexane	—
Unknown C_5's	0.20

-	none detected
ND	Not Determined. N-butane and n-pentane comprised the solvent present with the asphalt feedstock. Their presence in the product gas masked the much smaller yields (< 1.0% each) of these compounds that occurred from coking the asphalt. The gas composition is calculated on a n-butane/n-pentane - free basis.

The normalized liquid product yield of distillate oil, from coking the asphalt, was 35.7%. The overall ASCOT*m process yield of liquid product was 61.5 wt% (on the atmospheric residue feed); 40.2 wt% from solvent deasphalting and 21.3% wt% from coking. The overall liquid yield from this run was a little lower than from Run 3047 (63.3 wt%). The material balance, at 98.2% was a significant improvement over that of Run 3047 (93.7%), lending confidence to our conclusion that ASCOT*m liquid yields greater than 60 wt% are readily attainable from Black Thunder subbituminous coal.

Run 3048 was conducted at a higher coke drum temperature, higher steam rate and longer steamout period to try and increase the yield of distillate oil. This proved ineffective, as we lost liquid yield to gas and coke formation, when compared with Run 3047 results. The higher drum temperatures and longer steamout period did reduce the cokes volatile manner, however, the overall distillate yield suffered. The metals content of the distillate although low, was greater than in Run 3047. This may be due to the higher drum temperature and extended steamout schedule driving over some heavier material with higher associated metals. The API gravity of the liquid product also indicates a heavier average material than in Run 3047.

4.5 DIRECT DELAYED COKING WILSONVILLE BOTTOMS-PRODUCT

The residue feedstock from the liquefaction of Black Thunder coal at Wilsonville has a high concentration of guinoline insolubles (22.2%) and ash (11.5%). These characteristics set a limit as to the amount of liquid product that can be expected from the feedstock. Direct delayed coking proved less capable of getting the potential liquid product available from this feedstock than the ASCOT*m process did. This is generally the case, as the ASCOT*m process removes a significant amount of liquid through a nondegrading extraction mechanism before delayed cokings thermal treatment can convert a portion of it to gas and coke products.

Data are reported in Tables 14 and 15. The yield was calculated "as measured", normalized and on a solids-free basis, solids being defined as the quinoline insolubles. This helps in comparing results with Amoco's feedstock, which had a lower solids loading even though the same Black Thunder coal was used.

The liquid yield from direct delayed coking was 50.0 wt%, significantly lower than the > 60 wt% from the ASCOT process. On a solids free basis the liquid yield was 64.3 wt%; ASCOT*m produced solids-free yields of 81.4 and 79.0 wt%.

Comparing liquid quality criteria, i.e., ash, metals, and sulfur, shows low levels of these impurities, indicating direct delayed coking and ASCOT*m produce good quality product.

The gas yield was desirably low through higher than ASCOT*m produced, and was comprised mainly of hydrogen and methane with some ethane and propane present. Other hydrocarbons were present in relatively small concentrations. This is consistent with the ASCOT*m data and past results when processing other liquefaction feedstocks.

Table 14 Direct Delayed Coking Wilsonville Atmospheric Residue From Black Thunder Subbituminous Coal

FWDC Run No.	3042		
Operating Conditions			
Coke Drum Pressure, psig	5		
Throughput Ratio (Total feed/Fresh feed)	1.0		
Steam/Feed Ratio, w/w	0.088		
Maximum Drum Temperature, °F (Avg.)	855		
Material Balance			
Product Distribution-Wt%			
	As Measured	**Normalized**	**Normalized Solids-Free Feed**(1)
Gas	2.8	2.8	3.6
Distillate Oil	50.4	50.0	64.3
Coke	47.5	47.2	32.1
Recovery	100.7	100.0	100.0

(1) Feedstock solids defined as Quinoline Insolubles (22.2 wt%). Solids-free basis calculated by subtracting solids from coke product.

Table 15 Inspection of Run 3042 Delayed Coking Products
Direct Delayed Coking Wilsonville Feed

Distillate Oil		
API Gravity @ 60°F	10.4	
Carbon, wt%	87.95	
Hydrogen, wt%	9.99	
Sulfur, wt%	0.05	
Nitrogen, wt%	0.79	
Ash, wt%	0.007	
Metals, ppm (w)		
Iron	22	
Nickel	< 1	
Vanadium	< 1	
Copper	1	
Sodium	3	
ASTM Distillation, °F	D86	D1160
IBP	352	393
2 Vol%	---	468
5	504	540
10	710	635
20		726
30		762
40		787
50		809
60		831
70		856
80		885
90		937
95		1010
EP		1023

Coke			
Proximate Analysis, wt%		Ultimate Analysis, wt%	
Fixed Carbon	59.14	Carbon	67.26
Volatile Matter	15.21	Hydrogen	3.02
Ash	25.24	Oxygen	0.09
Moisture	0.41	Nitrogen	1.20
Total	100.0	Sulfur	2.78
		Ash	25.24
		Moisture	0.41
		Total	100.0

Table 15 (Con't) Inspection of Run 3042 Delayed Coking Products Direct Delayed Coking Wilsonville Feed

Gas (Composite Sample)	
	Mol% of Gas
Hydrogen	74.45
Carbon Monoxide	0.52
Carbon Dioxide	1.17
Hydrogen Sulfide	ND
Methane	13.08
Ethane	4.99
Ethylene	0.44
Propane	1.98
Propylene	0.82
Isobutane	0.17
n-Butane	0.81
Propadiene	—
Butene-1	0.19
Isobutene	0.09
trans-Butene-2	0.08
cis-Butene-2	0.06
Butadiene	—
Isopentane	0.12
n-Pentane	0.27
Pentene-1	0.10
cis/trans-pentene-2	0.08
2-Methyl butene-2	0.05
n-hexane	0.17
Unknown C_5's	0.36

— none detected
ND Not Determined

4.6 DIRECT DELAYED COKING AMOCO BOTTOMS PRODUCT

A delayed coking test was completed using the atmospheric residue generated at Amoco from dispersed catalyst liquefaction of Black Thunder subbituminous coal. Tables 16 and 17 summarize the tests operating conditions, material balance and product characterization.

The Amoco feedstock had characteristics (Tables 3 and 4) that were superior to the feedstock produced at Wilsonville, as most evident by its significantly lower quinoline insoluble matter. QI material will essentially all end up as solid product in the coke drum. The quinoline soluble portion of a feed will produce liquid product to greater or lesser degree depending on its specific composition. The material balance results bear this out, indicating a 66.5 wt% liquid yield from the Amoco material compared with a 50.0 wt% yield from the Wilsonville feedstock (Table 14). Comparing liquid yields on a solids-free feed basis, although closer, still shows the Amoco feedstock to be superior to Wilsonville's for delayed coking application (71.3% vs. 64.3% liquid yield). Feedstock solids is defined as the quinoline insoluble material.

The benefit of the ASCOT℠ process in producing liquid product is also apparent from the programs cumulative data. When solvent deasphalting was combined with delayed coking to process the Wilsonville feed, the liquid yield, on a solids-free basis, averaged 80.2 wt% (Tables 10 and 12), a greater yield than was achieved with the superior Amoco feedstock. Even when the high solids loading of the Wilsonville feed is ignored, the liquid yields are fairly close; 62.4 wt% on average, with ASCOT℠ vs. 66.5 wt% when directly coking the Amoco feed.

The low metals and ash content of the oil product from the Amoco feed are consistent with the general quality of liquid product from delayed coking. These impurities are concentrated and found in the solid coke product. The coke, which has a much lower ash content (4.7 wt%) than that produced from the Wilsonville-derived feedstock (averaged 29.9 wt%), could serve as a supplemental solid fuel in an integrated process.

Table 16 Direct Delayed Coking Amoco Atmospheric Residue From Black Thunder Subbituminous Coal

Feedstock No.	22779A
FWDC Run No.	3054
Operating Conditions	
Coke Drum Pressure, psig	5
Throughput Ratio (Total feed/Fresh feed)	1.0
Steam/Feed Ratio, w/w	0.081
Maximum Drum Temperature, °F (Avg.)	880
Material Balance	
Product Distribution-Wt%	

	As Measured	**Normalized**	**Normalized Solids-Free Feed**(1)
Gas	2.4	2.4	2.6
Distillate Oil	65.9	66.5	71.3
Coke	30.8	31.1	26.1
Recovery	99.1	100.0	100.0

(1) Feedstock solids defined as Quinoline Insolubles (6.7 wt%). Solids-free basis calculated by subtracting solids from coke product.

Table 17 Inspection of Run 3054 Delayed Coking Products
Direct Delayed Coking Amoco Feed

Distillate Oil	
API Gravity @ 60°F	10.4
Carbon, wt%	90.13
Hydrogen, wt%	8.70
Sulfur, wt%	0.07
Nitrogen, wt%	0.80
Ash, wt%	0.005
Metals, ppm (w)	
Iron	38
Nickel	2
Vanadium	0.4
Copper	0.4
Sodium	2
ASTM Distillation, °F	**D86/D1160**
IBP	290
2 Vol%	524
5	614
10	656
20	708
30	742
40	771
50	799
60	823
70	862
80	884
90	928
95	972
EP	1018

Coke			
Proximate Analysis, wt%		**Ultimate Analysis, wt%**	
Fixed Carbon	88.70	Carbon	88.57
Volatile Matter	6.52	Hydrogen	3.69
Ash	4.72	Oxygen	0.01
Moisture	0.06	Nitrogen	2.05
Total	**100.0**	Sulfur	0.90
		Ash	4.72
		Moisture	0.06
		Total	**100.0**

Table 17 (Con't) Inspection of Run 3054 Delayed Coking Products
Direct Delayed Coking Amoco Feed

Gas (Composite Sample)	
	Mol% of Gas
Hydrogen	36.63
Carbon Monoxide	1.43
Carbon Dioxide	0.88
Hydrogen Sulfide	0.11
Methane	40.52
Ethane	10.88
Ethylene	1.00
Propane	3.45
Propylene	1.53
Isobutane	0.26
n-Butane	1.09
Propadiene	—
Butene-1	0.39
Isobutene	0.16
trans-Butene-2	0.14
cis-Butene-2	0.11
Butadiene	—
Isopentane	0.19
n-Pentane	0.48
Pentene-1	0.21
cis/trans-pentene-2	0.12
2-Methyl butene-2	0.14
n-hexane	0.16
Unknown C_5's	0.12

— none detected

4.7 PROCESS COMPARISONS

Solvent deasphalting of the Wilsonville atmospheric residue in tandem with delayed coking of the resultant asphalt product (FW's ASCOT℠ process) can be considered in direct competition with a vacuum distillation in tandem with the ROSE℠ process. The Wilsonville test facility fed their vacuum bottoms to the ROSE℠ process.

FWDC analyzed Wilsonville's Run 262 data on Black Thunder coal to determine the combined liquid yield from the vacuum tower and ROSE℠ process. This was then compared with the ASCOT℠ process and direct delayed coking of the representative atmospheric residue supplied to FWDC for this program. Table 18 details the calculation and basis used to derive the combined Vacuum Tower/ROSE℠ process liquid yield.

The combined liquid yield from the Vacuum Tower/ROSE℠ process was 58.6 wt% (27.2% from vacuum distillation and 31.4% from the ROSE℠ process). To compete, this is the yield the ASCOT℠ process should meet or exceed. FWDC feels the ASCOT℠ process has the advantage of providing greater flexibility to reach a high liquid yield than the ROSE℠ process in tandem with a vacuum tower because solvent deasphalting can cut more deeply into a feedstock than a vacuum distillation to better optimize the process.

The two ASCOT℠ tests produced overall liquid yields (63.3 wt% and 61.5 wt%) that exceeded the combined liquid yields from the vacuum tower and ROSE℠ process. Direct delayed coking of the atmospheric residue fell short, generating a 50.0 wt% yield. Table 19 summarizes the comparison of yields from the atmospheric residue. To look at the results from another perspective, the ROSE℠ process at Wilsonville (Run 262) produced 41.4 wt% of undesirable solid product. The two ASCOT℠ runs produced 35.3% and 36.1 wt%; direct delayed coking 47.2 wt%.

Both elements of the ASCOT℠ process, solvent deasphalting and delayed coking, produce a distillate fraction and a smaller resid fraction. Examining the ASTM distillations in Table 9 (deasphalted oil) and Tables 11 and 13 (coker distillate) show a high temperature tail (> 850°F) that can be considered as the practical resid fraction (essentially the bottoms from a vacuum distillation). This fraction was about 40 vol% in both cases and roughly corresponds to ASCOT℠ producing about three-quarters and direct delayed coking two-thirds the amount of resid as the ROSE℠ process. The theoretical resid fraction defined in the Wilsonville program (the non-distillable fraction at 600°F and 0.1 mm Hg in the laboratory) would be significantly less than actually obtained for all three processes.

Comparing the three processes has shown that the primary technical objective set for the ASCOT℠ process was met. Its liquid yield exceeded the combined liquid yield from the vacuum tower and ROSE℠ process.

Table 18

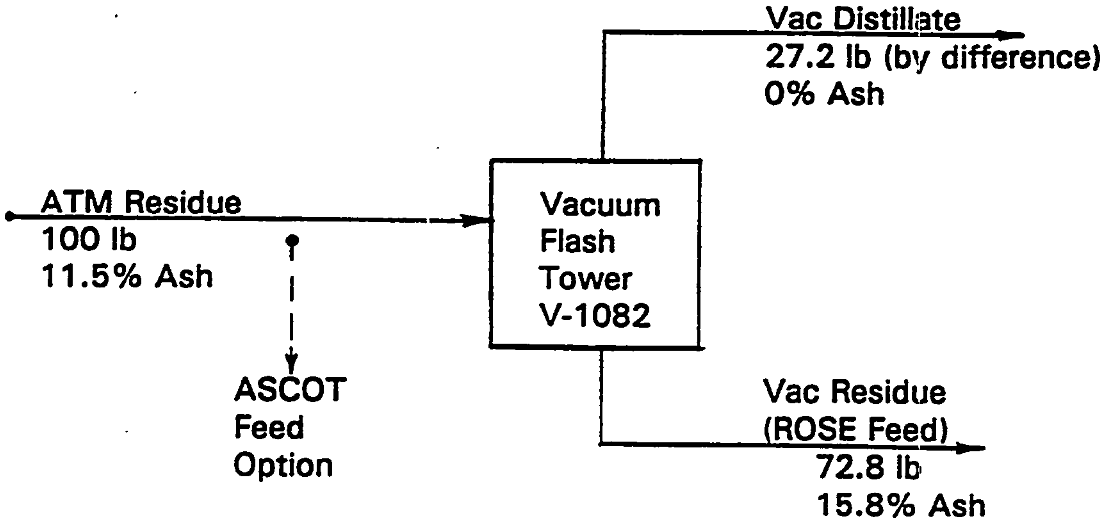
Calculation of Vacuum Tower/ROSE-SR^{TM} Process Liquid Yield
At
Advanced Coal Liquefaction R&D Facility
Wilsonville, Alabama

Basis:

- Draft Technical Progress Report, Run 262, with Black Thunder Subbituminous Coal, by Southern Electric International Inc, 1991 (DOE Contract No. DE-AC22-90PC90033). Figures 25-30, Material Balance Flow Diagrams for Runs 262A Through 262F.
- Feed to ROSE-SR^{TM} contains an average of 15.8% ash (Calculated from Figures 25-30)
- Solid product averages 56.9% of ROSE-SR^{TM} feed (Calculated from Figures 25-30)
- Ash content of Atmospheric Residue 11.5 wt% (Analysis of Residue from Black Thunder subbituminous coal by FWDC)
- Ash in vacuum distillate product assumed at zero percent.

Material Balance Around Vacuum Flash Tower (V-1082)

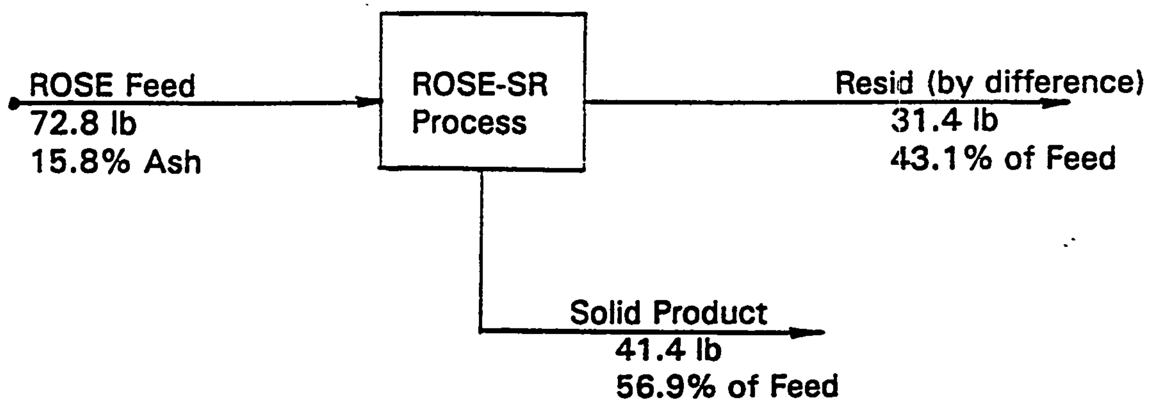
(For Portion of Vac Residue that Feeds ROSE Process)



Vacuum Residue Calculated via Ash Balance
0.115 x 100 lb/0.158 = 72.8 lb

Table 18 Con't

Material Balance Around ROSE-SR™ Process



Solid Product Calculation
72.8 lb x 0.569 = 41.4 lb

Vacuum Tower/ROSE Process Liquid Yield, % of ATM Residue

	wt %
Vacuum Distillate	27.2
Resid (ROSE Process)	31.4
Total Liquid Yield	58.6

NOTE: A technical objective of FW's ASCOT process is to meet or exceed the combined liquid yield from the vacuum tower and ROSE Process.

Table 19 Comparison of Yields from Atmospheric Residue, wt%

	Process			
	Wilsonville Run 262 Vac Tower + ROSE	Direct Delayed Coking	ASCOT	
			3047	3048
Products				
Gas	—	2.8	1.4	2.4
Oil				
Distillate	27.2	50.0	23.1	21.3
Deasphalted Oil	—	—	40.2	40.2
Resid	31.4	*	*	*
Solids/Coke	41.4	47.2	35.3	36.1
Total	100.0	100.0	100.0	100.0

* Included in oil product. The tail end of the ASCOT℠ product oil would provide about three-quarters, and direct delayed coking about two-thirds the amount of Resid as the ROSE Process (Resid fraction defined as >850°F).

5.0 ECONOMIC ASSESSMENT

5.1 INTRODUCTION

This section covers a preliminary economic assessment by Foster Wheeler USA (FW USA) of the battery limits for two case studies -- the ASCOT^{sm} process, employing proprietary technology which integrates Foster Wheeler's solvent deasphalting and delayed coking technologies and their proprietary SYDEC (Selective Yield Delayed Coking) delayed coking process standing alone, as might be incorporated into an integrated direct coal liquefaction processing scheme.

Each case study includes the following:

- Schematic Process Flow Diagram
- Process Description
- Overall Material Balance
- Summary of Operating Utilities
- Estimated Capital Cost

The objective of the study was to determine how cost competitive the ASCOT^{sm} process is compared with direct delayed coking at and around the projected product yields developed from the test data. The investment cost can also be used for comparisons with other processes which are competing to maximize the production of liquid product.

The actual yields of liquid product achieved during the test program are summarized in Table 20. The economic study covers three levels of liquid product from solvent deasphalting (25, 40 and 50 wt% deasphalted oil) and direct delayed coking (standing alone) producing 50 wt% liquid product, the yield reached through testing.

Table 20 Summary of Test Data for Economic Assessment
Coal Source: Black Thunder Subbituminous

Overall Liquid Yield, wt% **(Based on atm residue feedstock)**		
Process	**ASCOT^{sm}**	**Direct Coking**
Solvent Deasphalting	40.2	--
Coking Asphalt (Avg.)	22.2	--
Coking atm Residue	--	50.0
Total Liquid Yield	62.4	50.0

The studies three ASCOT℠ solvent deasphalting yields covered that actually reached through testing (40 wt%), a higher yield (50 wt%), which is considered reasonable but not attained during this program due to asphalt feeding limitations, and a low-end liquid yield of 25 wt%, to present a more complete picture of the relationship between solvent deasphalting liquid yield and overall ASCOT℠ yield and cost.

FW USA calibrated their SDA and delayed coking models based on the test run data to facilitate the development of a basis for evaluating the economics of providing new battery limits for these services.

The ASCOT℠ process was designated as Case 1 and Direct Delayed Coking as Case 2 for the study. Case 1 was further subdivided as follows:

Case 1	50 wt% DAO yield
Case 1A	25 wt% DAO yield
Case 1B	40 wt% DAO yield

5.2 BASIS OF STUDY

5.2.1 Capacity

The capacity of the new units, as set in the study basis package, is 713,334 lb/hr of atmospheric residue from liquefied coal feedstock. Assuming 330 operating days/year (on-stream factor of 0.904), the unit feed capacity is 789,086 lb/hr (45,604 BPSD). This capacity is the same for both cases.

As the liquefied coal residue feedstock is very heavy (-12.29 °API, 38.1 wt% Conradson Carbon), a minimum coke yield operation was selected for the delayed coking sections. A minimum coke yield operation is typified by a low pressure, low recycle type operation.

5.2.2 Feedstock Characteristics

The physical characteristics for the atmospheric residue derived from liquefied Wilsonville Black Thunder Subbituminous Coal are listed in Table 21. This is the feedstock for the SDA section of the ASCOT℠ unit for Case 1, and the SYDEC delayed coking unit for Case 2. This data was developed by FWDC based on their analysis of a sample of the liquefied coal residue.

For Case 1, the feedstock for the delayed coking section of the ASCOT℠ unit is the asphalt product from the SDA section. The Case 1 asphalt yield is specified in the study as 50 wt%, and the estimated properties of this asphalt feedstock are listed in Table 22. These properties were predicted using the SDA model developed by FWUSA. The development of the SDA and delayed coking models is detailed in Section 5.2.5, Study Considerations.

Table 21 Atmospheric Residue from Liquefied Coal

Specific Gravity @ 60/60	1.187
°API	-12.29
Conradson Carbon, wt%	38.1
Sulfur, wt%	1.40
Nitrogen, wt%	1.12
Metals, wppm	
Fe	16200
Ni	36
V	43
Cu	46
Na	426
ASTM D1160 Distillation @ 1 atm	
LV% Distilled	Temperature, °F
IBP	592
2	677
5	721
10	764
20	812
30	846
40	883
50	931

Table 22 Asphalt Feed to Coker Section of ASCOT℠ Unit (50 wt% DAO Yield)

Specific Gravity @ 60/60	1.440
°API	-33.24
Conradson Carbon, wt%	69.7
Sulfur, wt%	2.75
Nitrogen, wt%	1.51
Metals, wppm	
Ni	72
V	86

5.2.3 Overall Theoretical Material Balance

The overall theoretical material balances for both cases are provided in this section. The material balances are for the feedstocks and unit capacities as defined in the preceding sections.

Table 23 Overall Theoretical Material Balance

CASE 1 - ASCOT℠ Unit				
SDA Section				
Product	Yield (Wt%) on Fresh Feed	Lbs/Hr	°API	BPSD
DAO	50.0	394,543	8.65	26,811
Asphalt	50.0	394,543	-33.24	18,793
Fresh Feed	100.0	789,086	-12.29	45,604
CASE 1 - ASCOT℠ Unit				
Delayed Coking Section				
Product	Yield (Wt%) on Fresh Feed	Lbs/Hr	°API	BPSD
Gas	1.71	6,747		
Distillates	24.20	95,479	-6.80	5,772
Coke	74.09	292,317		
Fresh Feed	100.00	394,543		
CASE 2 - Delayed Coking Unit				
Product	Yield (Wt%) on Fresh Feed	Lbs/Hr	°API	BPSD
Gas	3.15	24,868		
Distillates	46.57	367,452	10.09	25,227
Coke	50.28	396,766		
Fresh Feed	100.0	789,086		

5.2.4 Estimated Product Characteristics

The estimated product characteristics from FW USA's models for Case 1 and Case 2 are given in Table 24.

Table 24 Estimated Product Characteristics From FW/ USA Models

CASE 1 - ASCOT℠ Unit	
Deasphalted Oil (DAO), 50 wt% Yield	
Specific Gravity @ 60/60	1.010
°API	8.65
Conradson Carbon, wt%	6.5
Sulfur, wt%	0.05
Nitrogen, wt%	0.73
Metals, wppm	
Ni	0.19
V	0.09
Coker Gas (Dry)	
Molecular Weight	11.7
H_2S, wt%	0.832 (On asphalt feed)
Distillate Liquids	
TBP, °F	C_5-972
°API	-6.80
Sulfur, wt%	0.54
Nitrogen, wt%	0.09
Green Coke	
VCM, wt%	10-12
Moisture	10
Sulfur, wt%	2.48
Nitrogen, wt%	2.01
CASE 2 - Delayed Coking Unit	
Coker Gas (Dry)	
Molecular Weight	7.9
H_2S, wt%	0.328 (On Atm Residue)
Distillate Liquids	
TBP, °F	C_5-972
°API	10.09
Sulfur, wt%	0.52
Nitrogen, wt%	0.22
Green Coke	
VCM, wt%	10-12
Moisture	10
Sulfur, wt%	1.69
Nitrogen, wt%	2.02

5.2.5 Study Considerations

On-Stream Factor and Run Length

The unit capacities have been adjusted to account for potential downtime experienced during a normal year of operation. A typical run length of 330 days per year has been used. This corresponds to an on-stream factor of 0.904.

Operating Conditions

The operating conditions used for the delayed coking processes in this study are typical for minimum coke yield operations. For both cases, a minimum of coke drum overhead pressure, and a minimum throughput ratio are specified for the delayed coking operations. For each case, the coke drum overhead temperature was adjusted in the model to match the test run yields.

Additionally, 48 hour coking cycles (24 hours coking and 24 hours decoking) were assumed for all cases.

Test Run Analysis

The test run data provided by FWDC was used to calibrate solvent deasphalting and delayed coking models for this study. Only the test run data provided as part of the study basis package was used in this study.

Three sets of test run data were provided for solvent deasphalting. This test run data is summarized in Table 9 of the study basis package. The test runs were numbered 3039/3040 blend, 3034, and 3035. Data was provided for both the DAO and asphalt products at 3 different DAO yields. This data was regressed and input into FWUSA's solvent deasphalting model. The model was used to develop DAO and asphalt properties at 50 wt% DAO, 50 wt% asphalt yields for Case 1.

Two sets of delayed coking data were also provided in the study basis package. Data from test run 3042 was provided in Tables 14 & 15, and data test run 3047 was provided in Tables 10 & 11.

Test run 3042 was a delayed coking test on the atmospheric residue from the liquified coal feedstock. This corresponds to Case 2 - SYDEC delayed coking. The test run was operated at a coking pressure of 5 psig, throughput ratio of 1.0 and a maximum drum temperature of 855°F. FWUSA used the results of this run to calibrate our SYDEC yield program. The coke drum overhead temperature was varied to match the test run yields. FWUSA then ran a second set of yields at the minimum coke yield operating conditions. These yields were then used to develop the material balance and basis for the cost estimate for Case 2.

Test run 3047 was a delayed coking test on the asphalt product from SDA test run 3039/3040 blend. This approximated the target ASCOT℠ yields of 50 wt% DAO and 50 wt% asphalt. This test run corresponds to Case 1. Again, this test run was operated at a coking pressure of 5 psig and a throughput ratio of 1.0. For this run the maximum drum temperature was 901°F. The same calibration method used for test run 3042 was applied to this test run to arrive at a final yields for Case 1.

5.3 PROCESS DESCRIPTION

5.3.1 Schematic Process Flow Diagrams

The following schematic process flow diagrams are included in this section.

Description	Figure	Drawing No.
Case 1 - ASCOT Unit	8	37294-1-50-101
Case 2 - Delayed Coker Unit	9	37294-1-50-102

5.3.2 Description of Flow

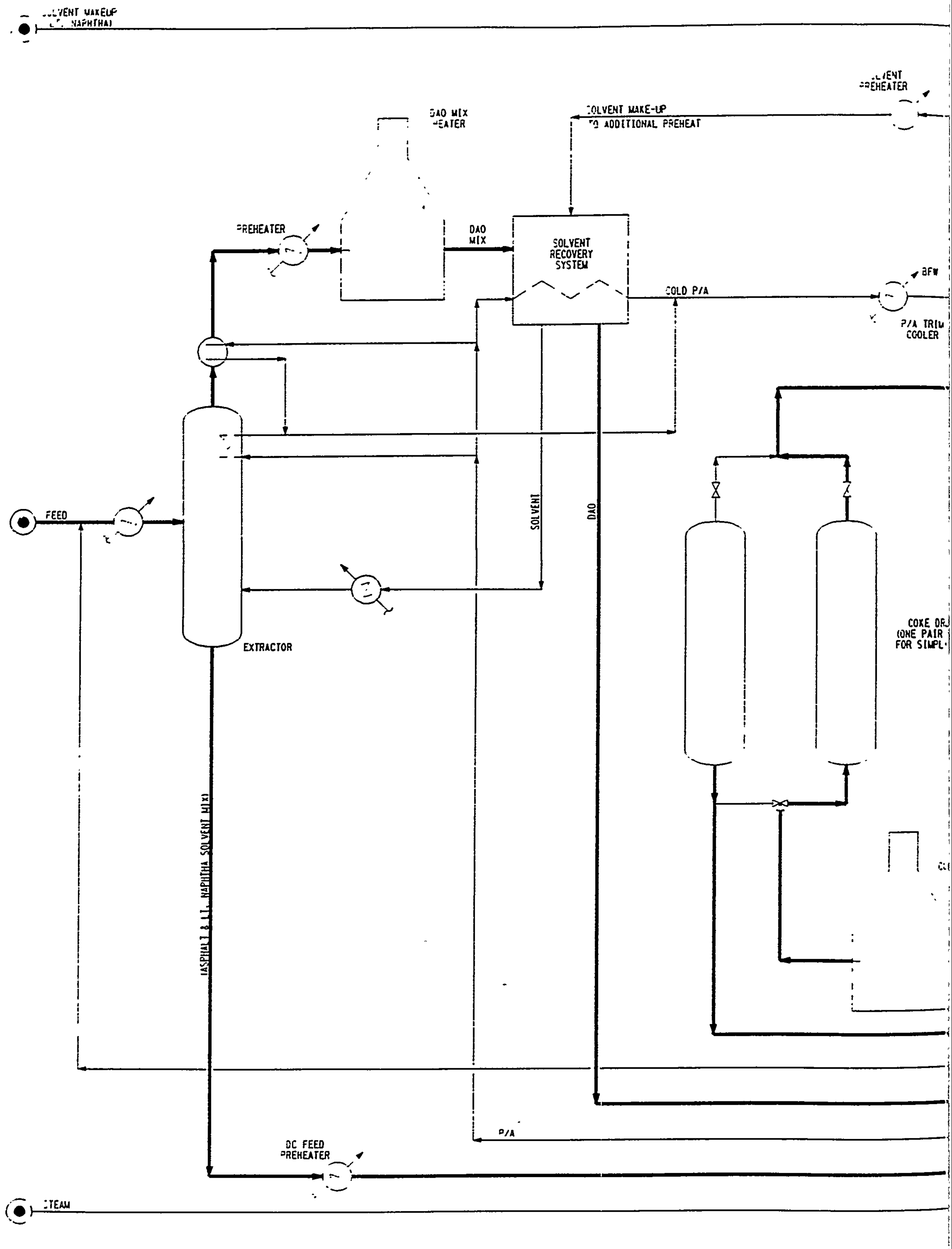
Case 1

The Foster Wheeler ASCOT^{sm} unit is an integration of FW solvent deasphalting (SDA) and delayed coking technologies. This integration takes advantage of the excess heat generated by the delayed coking section, to supply heat to the SDA solvent recovery section. The ASCOT^{sm} unit described in this study does not include a gas plant for light ends processing. The schematic process flow diagram (Dwg. No. 37294-1-50-101) is provided in Section 5.3.1.

The liquefied coal residue feed enters the unit and is mixed with the recycle material from the fractionator. The feed and recycle mixture is preheated and fed to a liquid-liquid multistage extraction column. In the extractor, the feed mixture is contacted counter-currently against a solvent (typically a light hydrocarbon). The extract, or DAO mix, exiting from the top of the extractor is a solution of deasphalted oil (DAO) and solvent. The bottoms product is a mixture asphalt and entrained solvent. The DAO mix is fed to the DAO mix heater and the solvent recovery unit where the solvent is separated from the DAO. The recovered solvent is recirculated to the extractor. The DAO is combined with coker gas oil, stripped, cooled and sent to battery limits. The asphalt is fed to the coker section.

In the coker section of the ASCOT^{sm} unit, the asphalt mix is fed to the coker heater where it is partially vaporized. The heater effluent is delivered to the coke drums, where due to a combination of pressure, temperature and residence time, coke is formed. When the coke drum is filled with coke, the heater effluent is switched to an empty drum and the full drum is decoked. The overhead vapors from the coke drum are sent to the fractionator.

The fractionator typically has three liquid products: unstabilized naphtha, light coker gas oil (LCGO), and heavy coker gas oil (HCGO). A coker off gas, suitable for fuel gas use after H_2S removal, is also produced. The unstabilized naphtha is typically sent to a gas plant for further processing. The LCGO, HCGO are combined with the DAO and stripped, cooled and delivered to battery limits. The LCGO, HCGO and DAO are suitable cracker feedstocks.


SOLVENT MAKEUP
(LT. NAPHTHA)
DAO MIX
HEATER
SOLVENT MAKE-UP
TO ADDITIONAL PREHEAT
SOLVENT
PREHEATER
PREHEATER
DAO
MIX
SOLVENT
RECOVERY
SYSTEM
COLD P/A
BFW
P/A TRIM
COOLER
FEED
SOLVENT
DAO
EXTRACTOR
COKE DR
(ONE PAIR
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(ASPHALT & LT. NAPHTHA SOLVENT MIX)
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DC FEED
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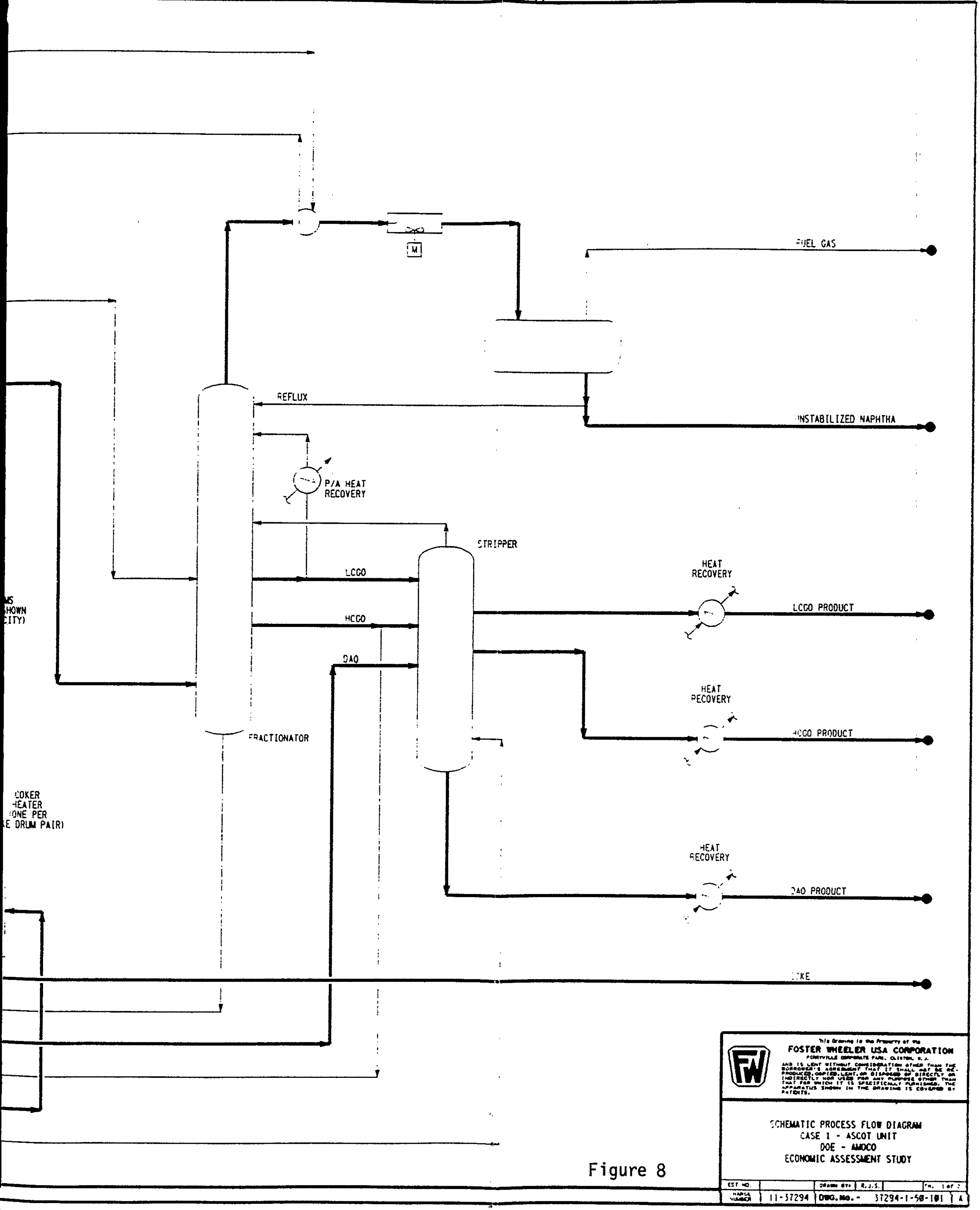
REVISIONS



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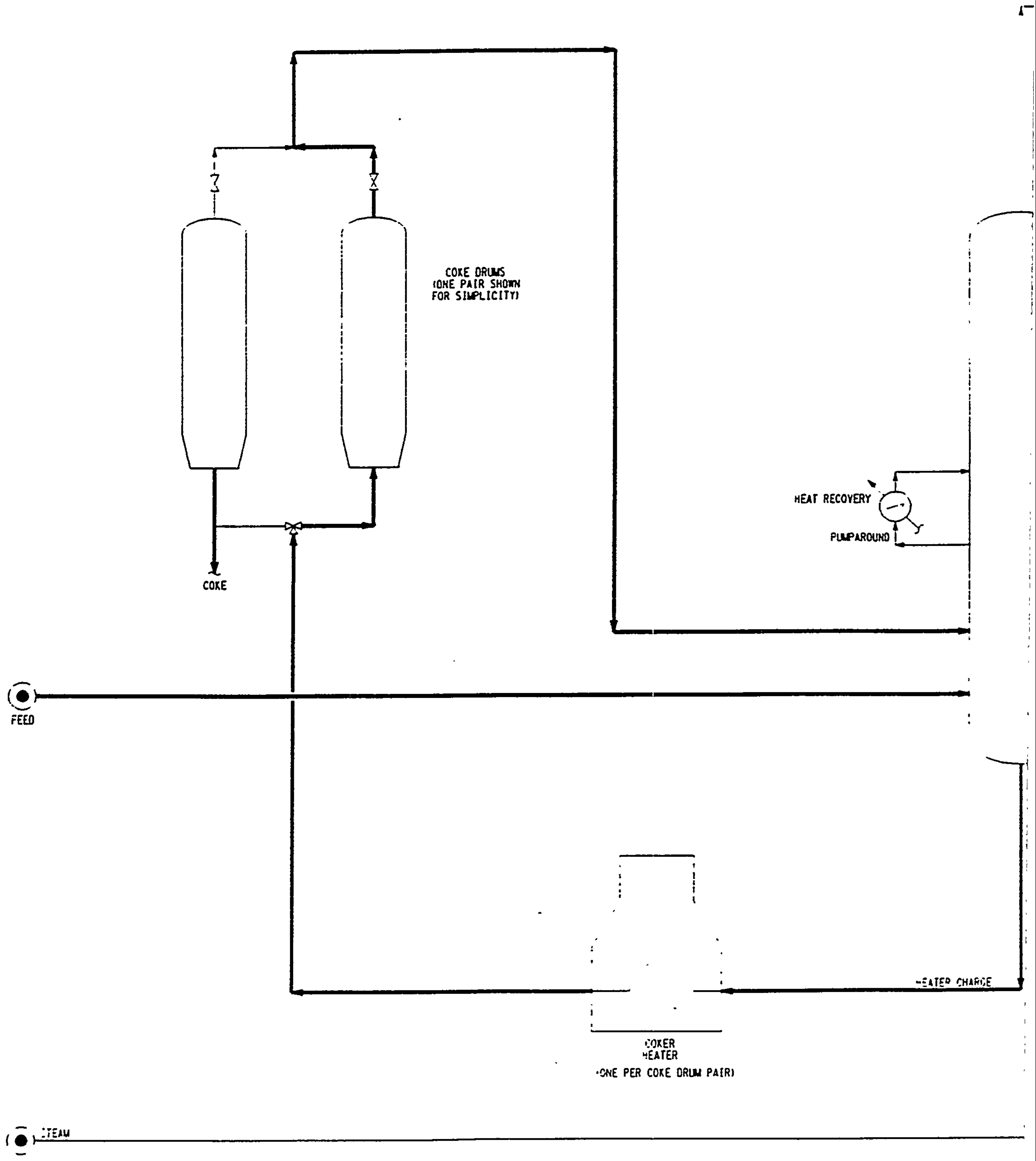
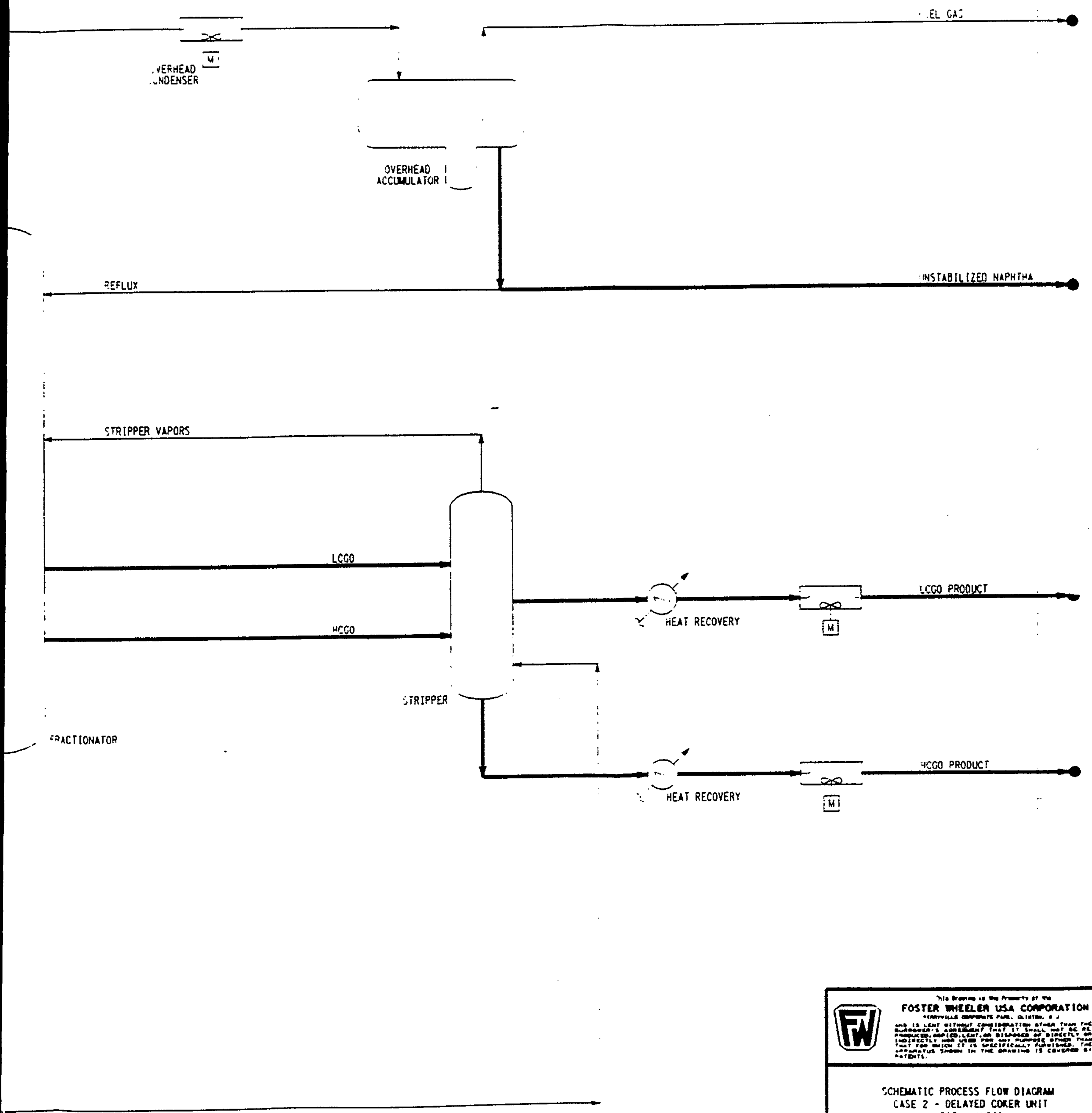
SCHEMATIC PROCESS FLOW DIAGRAM
CASE 1 - ASCOT UNIT
DOE - AMOCO
ECONOMIC ASSESSMENT STUDY

EST NO.		DRAWN BY:	R.J.S.		SH. 1 of 2
CHARGE NUMBER	11-37294	DWG. No. -	37294-1-50-101		A

Figure 8


COKE DRUMS
(ONE PAIR SHOWN
FOR SIMPLICITY)
COKE
HEAT RECOVERY
PUMPAROUND
FEED
HEATER CHARGE
COKER
HEATER
(ONE PER COKE DRUM PAIR)
STEAM



SCHEMATIC PROCESS FLOW DIAGRAM
CASE 2 - DELAYED COKER UNIT
DOE - AMOCO
ECONOMIC ASSESSMENT STUDY

EST. NO.		DRAWN BY:	C. CRIBE	22-MAR-94	SH. 2 OF
CHARGE NUMBER	11-37294	DWG. NO. -	37294-1-50-102		

Figure 9

Case 2

A typical delayed coker unit is very similar in operation to the delayed coker section of an ASCOT^{sm} unit. The primary differences involve the mixing of the feed and recycle, as well as the increased steam generation. Again, no gas plant has been provided. A schematic process flow diagram (DWG. No. 37294-1-50-102) is provided in Section 5.3.1.

The feed to the coker unit is preheated against the pumparound and hot product streams before entering the bottom of the coker fractionator. In the bottom of the tower, the feed mixes with the recycle liquid condensing in the tower. The feed and recycle mixture is fed to the coker heater and then to the coke drums. Coke is produced in the coke drums, and the overhead vapors flow to the coker fractionator.

Again, there are typically three liquid products in the coker fractionator: unstabilized naphtha, LCGO and HCGO. A coker off gas is also produced. The pumparound and product rundown circuits are used for steam generation rather than integration with the SDA section as in the ASCOT unit. The unstabilized naphtha is typically sent to a gas plant, and the LCGO and HCGO are sent to a cracking unit for further processing.

5.4 UTILITY SUMMARY

The estimated utility requirements for both cases are presented in Table 25. The utility estimates were developed based on existing units whenever possible. Actual utility requirements will depend upon finalized heat and material balances as well as downstream processing requirements.

Table 25 Utility Summary

Case 1 - ASCOT℠ Unit	
Continuous Utilities	
Utility	**Amount**
Fuel Liberated, MM BTU/Hr (1)	216
Power Consumed, KW/Day	7,360
Steam Consumed, (150 psi sat) Lbs/Hr	103,300
BFW Consumed, Lbs/Hr	28,400
Cooling Water, GPM ($\Delta T = 25°F$)	100
Raw Water Consumed, GPD	255,000
Recovered Water, GPD	126,000
Net Raw Water Consumed, GPD	129,000
Intermittent Utilities	
Utility	**Amount**
Power Consumed, KW/Day	1,800
Steam Consumed, (150 psi sat) Lbs/Day	242,000
Cooling Water, GPD	375
Case 2 - Delayed Coking Unit	
Continuous Utilities	
Utility	**Amount**
Fuel Liberated, MM BTU/Hr (1)	270
Power Consumed, KW/Day	6,900
Steam Produced, (150 psi sat) Lbs/Hr	33,300
BFW Consumed, Lbs/Hr	69,000
Cooling Water, GPM ($\Delta T = 25°F$)	230
Raw Water Consumed, GPD	340,000
Recovered Water, GPD	168,000
Net Raw Water Consumed, GPD	172,000
Intermittent Utilities	
Utility	**Amount**
Power Consumed, KW/Day	2,400
Steam Consumed, (150 psi sat) Lbs/Day	322,000
Cooling Water, GPD	500

"Fuel Liberated" refers to fuel fired by the heater(s). It corresponds to the "Fuel Absorbed," divided by the heater efficiency.

5.5 ECONOMIC EVALUATION

From the material balances and unit descriptions, curve type total installed cost estimates were developed for both cases. FWUSA's Estimating Department prepared cost estimates for the units involved in this study, and the results are summarized as follows:

Case 1 ASCOT^{sm} Process (50 wt% DAO)

ASCOT^{sm} Unit:	SDA section processing 45,604 BPSD of atmospheric residue and delayed coker section processing 18,793 BPSD asphalt and producing 3,508 STPD coke.
Installed Cost:	$220 Million Dollars

Case 2 Direct Delayed Coking

Delayed Coker Unit: Processing 45,604 BPSD feed and producing 4,761 STPD coke.

Installed Cost: $212 Million Dollars

The estimates include an open type coke collection system, which is a concrete pit with an overhead crane; no further coke handling or storage is included. The estimates do not include a gas plant or coker gas compressor.

Additionally, two other ASCOT^{sm} cases, Alternate A and Alternate B, were developed. Case 1, Alternate A was an ASCOT^{sm} unit with the SDA section operating at 25 wt% DAO yield. Case 1, Alternate B was an ASCOT^{sm} unit with the SDA section operating at 40 wt% DAO yield. The cost estimates for these units are as follows:

Case 1, Alternate A: ASCOT^{sm} Process (25 wt% DAO)

ASCOT^{sm} Unit:	SDA section processing 45,604 BPSD of atmospheric residue and delayed coker section processing 32,345 BPSD asphalt and producing 3,862 coke.
Installed Cost:	$230 Million Dollars

Case 1, Alternate B: ASCOT^{sm} Process (40 wt% DAO)

ASCOT^{sm} Unit:	SDA section processing 45,604 BPSD of atmospheric residue and solvent, delayed coker section processing 23,887 BPSD asphalt and producing 3,697 STPD coke.
Installed Cost:	$225 Million Dollars

These costs were used as points to develop a graph (Figure 10) of DAO yield vs. installed cost for ASCOT^{sm} units operating on this feedstock. A reference line showing the cost of the direct delayed coking unit is also included.

DAO Yield vs Investment Cost

Uprgading Liquified Coal Residue

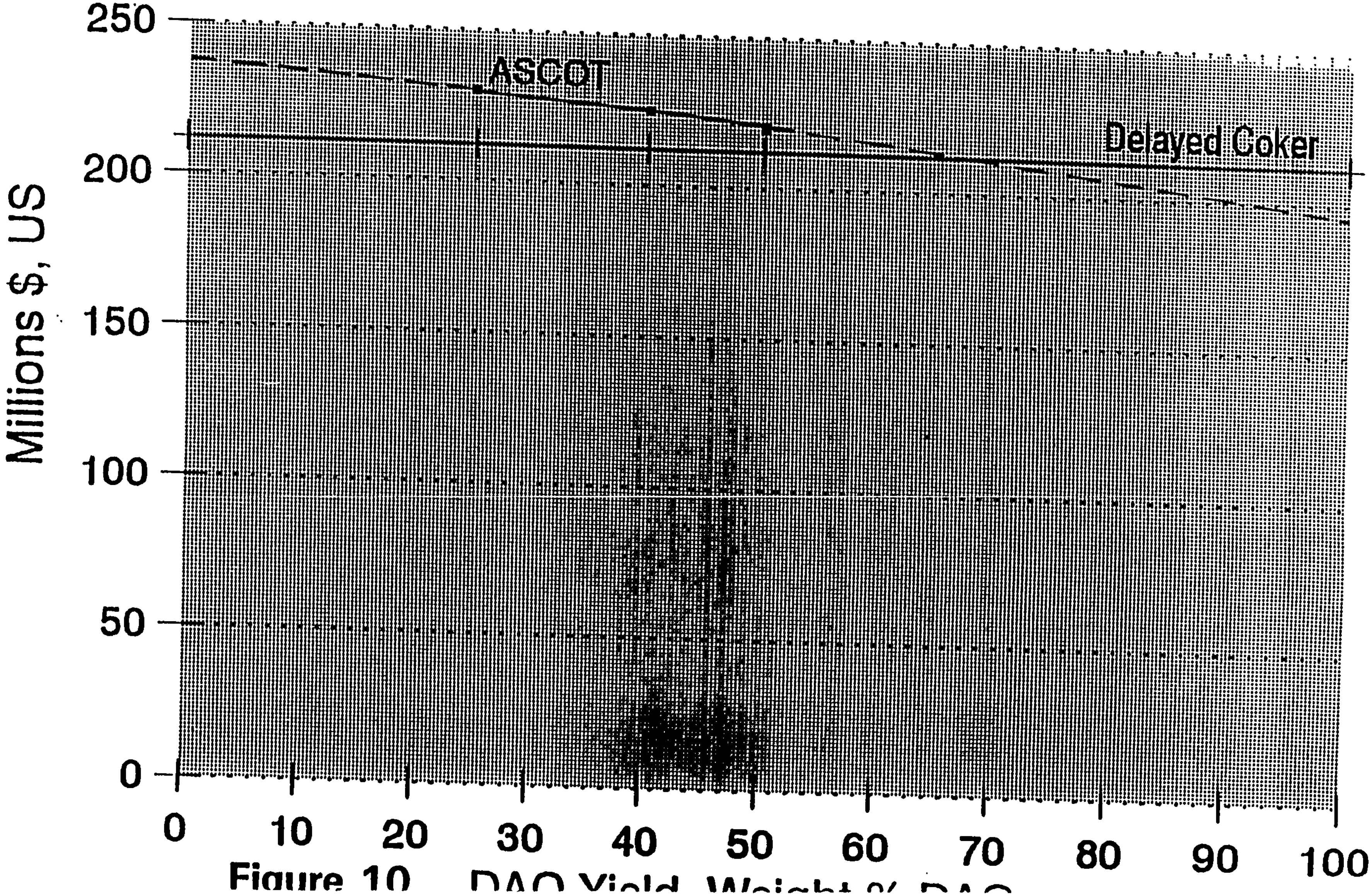


Figure 10

These are conceptual estimates of ±30% accuracy, battery limits process units, based on U.S. Gulf Coast, second quarter 1994, instant execution philosophy, through mechanical completion only, and assumes that land is free of above and underground obstructions. Excluded are cost of land, process licensor fees, taxes, royalties, permits, duties, warehouse spare parts, catalysts, forward escalation, support facilities and all client costs.

The typical percentage breakdown for the bottom-line estimates is as follows:

Process Equipment	28%
Bulk Commodities (steel, concrete, etc.)	22%
Labor	32%
Engineering	18%
Total	100%