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ADVANCED LIQUEFACTION USING COAL SWELLING
AND CATALYST DISPERSION TECHNIQUES

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For

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

By

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Prepared by
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EXECUTIVE SUMMARY

Research in this project centers upon developing a new approach to the direct liquefaction of coal to produce an all-distillate product slate at a sizable cost reduction over current technology. The approach integrates all aspects of the coal liquefaction process including coal selection, pretreatment, coal swelling with catalyst impregnation, coal liquefaction experimentation, product recovery with characterization, alternate bottoms processing, and a technical assessment including an economic evaluation. The project is being carried out under contract to the United States Department of Energy.

On May 28, 1992, the Department of Energy authorized starting the experimental aspects of this projects; therefore, experimentation at Amoco started late in this quarterly report period. Research contracts with Auburn University, Pennsylvania State University, and Foster Wheeler Development Corporation were signed during June, 1992, so their work was just getting underway. Their work will be summarized in future quarterly reports.

A set of coal samples were sent to Hazen Research for beneficiation. The samples were received and have been analyzed. The literature search covering coal swelling has been up-dated, and preliminary coal swelling experiments were carried out. Further swelling experimentation is underway. An up-date of the literature on the liquefaction of coal using dispersed catalysts is nearing completion; it will be included in the next quarterly report.

PROGRAM OBJECTIVES

The objective of this project is to develop a new approach to the direct liquefaction of coal to generate an all-distillate product slate at a sizable cost reduction over current technology. The approach will integrate all aspects of the coal liquefaction process including coal selection, pretreatment, coal swelling with catalyst impregnation (and parallel runs with dispersed catalyst), coal liquefaction experimentation including solvent evaluation, product recovery with characterization, alternate bottoms processing, and a technical assessment including an economic evaluation. The three tasks of this program are:

1. Task 1: Laboratory-Scale Experimentation--The goals are to obtain samples of coals and Wilsonville-derived solvents and vacuum tower bottoms and to establish experimental procedures.

2. Task 2: Laboratory-Scale Operation--The goals are to:
(1) reduce the concentration of mineral matter and alkali metals in low rank coals, (2) swell and impregnate coals with dispersed catalysts, (3) characterize the resulting catalyst solids, (4) evaluate the effectiveness of the procedures using liquefaction runs, and (5) study solids separation and alternative bottoms handling, which includes observing pumping characteristics, deasphalting and coking.

3. Task 3: Technical Assessment--The goals are to analyze the data, develop descriptive models, and carry out an economic evaluation.

The research will be carried out in cooperation with the following subcontractors: Foster Wheeler Development Corporation, Auburn University, Pennsylvania State University, and Hazen Research Incorporated. Appropriate meetings and correspondence will be maintained to insure effective completion of the project.

PROGRAM MILESTONES

For practical purposes, the experimental program schedule started on May 28, 1992, with the approval of the NEPA document by DOE. The first key milestone was to obtain the appropriate feed stocks for the experiments. The second milestone is preparing the beneficiated bulk samples of coal for subsequent experiments. The feedstocks have been obtained and the beneficiation of samples of Martin Lake lignite and Black Thunder subbituminous coal have been done by Hazen Research, Inc. The small-scale coal swelling and catalyst screening program has started. Sufficient data must be obtained from the latter program to establish conditions for bench-scale liquefaction experiments to start during the fourth quarter. The batch deasphalting and coking experiments will be completed by the end of the fifth quarter after the start of experimentation by FWDC. Experimentation should be essentially complete by the end of the seventh quarter in order to complete the project within a two year period that started on May 28, 1992.

SUMMARY OF RESULTS AND ACTIVITY

Initial activity was limited to carrying out non-experimental work covered under Subtasks 1.1 and 2.2. The coal swelling literature search was brought up-to-date, and that of coal liquefaction using dispersed catalysts was almost completed during the quarter (it will be included in the next report). Exploratory coal swelling experiments were carried out with the three coals (Martin Lake lignite, Black Thunder subbituminous, and Burning Star Illinois No. 6 seam bituminous) using 10 solvents. Low levels of swelling were observed with aliphatic and aromatic solvents, moderate levels with alcohols, and high levels with solvents having highly polar functionality.

Project Documentation

The Project Management Plan, Milestone Schedule/Manpower Plan, and Cost Plan had been completed and approved; however, they will have to be modified to reflect the late approval (NEPA) to start experimentation on May 28, 1992.

Task 1.0: Laboratory-Scale Experimentation

Subtask 1.1: Laboratory Support

Fresh, bulk samples of Black Thunder subbituminous coal and Martin Lake Texas lignite are on-hand. Analyses have been obtained from Commercial Testing Laboratories, Inc. These analyses are attached in the Appendix.

Sufficient quantities of coal-derived liquids (atmospheric tower bottoms and solvent) were obtained from Wilsonville in order to complete this project. Two 55-gallon samples of Wilsonville atmospheric tower bottoms derived from the liquefaction of Black Thunder subbituminous coal were sent to Foster Wheeler Development Corporation.

Task 2.0: Laboratory-Scale Operation

Subtask 2.1: Coal Pretreatment

Bulk samples of both Martin Lake lignite and Black Thunder subbituminous coal were pretreated to recover beneficiated coal for subsequent swelling, catalyst impregnation, and liquefaction experiments. The treatment was to include crushing, sizing, contacting the coarse fraction with aqueous SO_2 to remove alkali and alkaline metals, and subsequent gravity separation to recover a fraction having particularly low ash content. It was proposed that conditions for the heavy-media gravity separation be chosen that would result in a high recovery (about 85%) of the float coal fractions.

Two 55-gallon drums of Martin Lake (Texas) lignite and 3 of Black Thunder subbituminous coal were processed at Hazen Research, Inc. The coals were first crushed to pass 8 mesh, and the raw coals were wet screened twice at 65 mesh (Taylor) to recover 8x65 mesh and minus 65 mesh fractions. All of the minus 65 mesh fines and portions of the 8x65 coarse fractions were retained as raw coal.

Bulk samples of the 8x65 mesh coals were contacted in batch mix tanks with concentrated aqueous sulfurous acid for times up to 5 hours. The contact time included the sparging of gaseous SO_2 into the coal/water mixture along with a subsequent 1 hour mixing time. Previous experience has indicated that only about 15 minutes is necessary for effective removal of the alkali and alkaline earth metal ions from these coals. The coals were then screened and immediately flushed with water. This was followed with a second slurring with fresh water and another screening.

The SO_2 -treated subbituminous and lignitic coals were subjected to heavy media (finely dispersed magnetite) cyclone tests. The exploratory tests were carried out at specific gravities of 1.25, 1.35, and 1.40. The results are given in the research results attached as Appendix B. In summary, it was not possible to isolate an overhead (float) fraction having a coal recovery of about 80 wt%. The bulk samples of raw and SO_2 -treated coals were returned to Amoco for characterization and use. Due to the unusual gravity separation results, further exploratory runs

will be done at Hazen Research using the SO₂-treated coals (previous heavy media runs with similar coals had resulted such a separation).

About one 55-gallon drum of SO₂-treated Black Thunder has been partially dried using a stream of nitrogen at ambient temperature. This coal is being characterized and used in swelling experiments.

Subtask 2.2: Catalyst and Swelling Studies

The literature concerning coal swelling, both alone and in combination with coal liquefaction has been up-dated using Amoco's library computer search facilities. The search is attached as Appendix C.

The literature pertinent to coal liquefaction using dispersed catalysts is being up-dated, and it will be included in the next quarterly report.

Preliminary Swelling Experiments:

Three coal samples, that were prepared in a previous DOE project, were used: 1) Martin Lake lignite, 2) Black Thunder subbituminous and 3) Illinois No. 6 bituminous coals. The coals were handled in nitrogen whenever possible. All samples were sieved and ground to -325 mesh under nitrogen and dried overnight at 60°C in a vacuum oven. The analyses are given in Table I.

The following ten swelling agents ranging from hydrocarbon solvents to more polar liquids were used: hexane, cyclohexane, benzene, toluene, methylene chloride, methanol, ethanol, acetone, tetrahydrofuran (THF) and tetrabutylammonium hydroxide (TBAH). These swelling agents were used without further purification.

Coal Swelling (Determination of Swelling Index, Q):

(Note, see Appendix C for the list of references.)

A convenient way of measuring swelling of coals by solvents is the volumetric technique which was developed by Dryden¹² and used by Liotta¹³

and Larsen¹⁴. This technique does not require the corrections for pore filling required by gravimetric measurements 3, 9-11. The two techniques have been directly compared and shown to be equivalent.

In the volumetric swelling technique used in these preliminary experiments, dry coal was placed in a volumetric calibrated tube and centrifuged for 60 minutes. The height of the coal was measured as h_1 . After breaking up the column of packed coal, excess solvent was introduced and the tube was vigorously shaken to ensure thorough mixing. The mixture sat for one day, and the coal was again centrifuged and the height was measured. The mixing and centrifuging were repeated after the fourth day, and a height, h_2 , was obtained. The swelling ratio was $Q = h_2/h_1$.

Results of Coal Swelling Experiments:

The results in Table II and Figure 1 show that the hydrocarbon solvents do not swell coals. Acetone and the alcohols (methanol and ethanol) swell coals slightly, and tetrahydrofuran (THF) and tetrabutylammonium hydroxide (TBAH) are effective. TBAH is the best swelling solvent for all the coals. Figure 2 shows the swelling ratios of the coals in three solvents; methanol, THF and TBAH. Coal swelling by TBAH decrease with increasing coal rank, while the opposite trend is observed in THF. Methanol appears to be the least effective swelling polar solvent.

The differences in swelling is attributed to the interaction of the solvent with the various bonds present in coal. The low rank coals contain significant amounts of ionic and hydrogen bonds due to the presence of relatively large number of polar functional groups, while the high rank coals contain more charge transfer complexes because of their higher aromatic content. TBAH, which is a very basic solvent, interacts with the ionic and hydrogen bonds readily, thus swelling the Martin Lake lignite to the greatest extent. This is followed by Black Thunder coal and Illinois No. 6. On the other hand, THF disrupts charge transfer complexes, which are predominant in Illinois No. 6, a higher rank coal, thus resulting in a swelling trend opposite to that of TBAH.

CONCLUSIONS AND FUTURE WORK

Experimentation is just getting underway due to the late approval of the NEPA form by the Department of Energy. The coals have been obtained, and the first stages of beneficiation are complete. Some follow up work is necessary on the gravity separation aspect of beneficiation. Appropriate samples of coals and atmospheric tower bottoms have been supplied to the subcontractors, and their experimentation is also just getting underway. Preliminary coal swelling experiments have yielded results that can be explained.

ACKNOWLEDGMENTS

This work is being supported by the United States Department of Energy under Contract DE-AC22-91PC91051. Appreciation is particularly extended to Mr. C. Guttermann of Foster Wheeler Development Corporation, Dr. C. W. Curtis of Auburn University, and Dr. S. Chander of Pennsylvania State University for participating in this program.

TABLE I
ELEMENTAL ANALYSES OF COALS, WT%, DAF

	Martin Lake	Black Thunder	Illinois #6
Carbon	73.01	73.85	75.51
Hydrogen	5.25	5.39	5.12
Nitrogen	1.37	1.00	1.69
Oxygen	20.95	19.70	14.81
Sulfur	2.16	0.52	4.11
Ash	10.27	6.50	14.12

TABLE II

SWELLING RATIOS, Q, OF COALS IN DIFFERENT SWELLING SOLVENTS

Solvent	Martin Lake	Black Thunder	Illinois #6
Hexane	0.95	1.01	1.00
Cyclohexane	1.00	1.00	1.02
Benzene	1.14	1.12	1.06
Toluene	1.00	1.04	1.16
Chloroform	1.03	1.17	1.19
Methanol	1.25	1.28	1.20
Ethanol	1.24	1.31	1.26
Acetone	1.25	1.32	1.24
Tetrahydrofuran	1.34	1.53	1.61
Tetrabutylammonium Hydroxide	2.84	2.52	2.16

Figure 1

SWELLING RATIOS

Figure 2
SWELLING RATIOS

APPENDICES

APPENDIX A

Analyses of Martin Lake Lignite and Black Thunder Subbituminous Coal.

COMMERCIAL TESTING & ENGINEERING CO.

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

SINCE 1908

Member of the SGS Group (Société Générale de Surveillance)

February 18, 1992

PLEASE ADDRESS ALL CORRESPONDENCE
16130 VAN DRUNEN RD., P.O. BOX
SOUTH HOLLAND, IL 60
TELEPHONE: (708) 331-1100
FAX: (708) 333-1100

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

Sample taken at -----

Sample taken by Amoco Research Center

Date sampled February 10, 1992

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

Date received February 13, 1992

Analysis Report No. 71-27775

Page 1 of

PROXIMATE ANALYSIS

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

ULTIMATE ANALYSIS

	<u>As Received</u>	<u>Dry Basis</u>
% Moisture	25.81	xxxxxx
% 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)	<u>13.88</u>	<u>18.70</u>
	100.00	100.00

Respectfully submitted,
COMMERCIAL TESTING & ENGINEERING CO.

Manager, South Holland Laboratory

SINCE 1908

COMMERCIAL TESTING & ENGINEERING CO.

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

Sample taken at -----

Sample taken by Amoco Research Center

Date sampled February 10, 1992

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

Date received February 13, 1992

Analysis Report No. 71-27774

Page 1 of 1

PROXIMATE ANALYSIS

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

ULTIMATE ANALYSIS

	<u>As Received</u>	<u>Dry Basis</u>
% 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)	<u>10.87</u>	<u>16.68</u>
	100.00	100.00

Respectfully submitted,
COMMERCIAL TESTING & ENGINEERING CO.

Manager, South Holland Laboratory

OVER 40 BRANCH LABORATORIES STRATEGICALLY LOCATED IN PRINCIPAL COAL MINING AREAS, TIDEWATER AND GREAT LAKES PORTS, AND RIVER LOADING FACILITIES

F-465
Original Watermarked For Your Protection

TERMS AND CONDITIONS ON REVERSE

APPENDIX B

Research Report of Hazen Research, Inc.

Hazen Research, Inc.
4601 Indiana Street • Golden, CO 80403
Tel: (303) 279-4500 • Telex 45-860
Fax: (303) 278-1523

June 12, 1992

Dr. Donald C. Cronauer
Research and Development Department
Mail Station H-4
Amoco Oil Company
P.O. Box 3011
Naperville, IL 60566

Re: HRI Project 7818
SO₂/Heavy Medium Coal Cleaning

Dear Dr. Cronauer:

This letter reports the results of a study to reduce the ash content of coal using SO₂ scrubbing and heavy medium separation methods.

Previous work by Amoco Oil Company (Amoco) and Hazen Research, Inc. (Hazen) has shown that agitating crushed coal in an aqueous solution saturated with SO₂ significantly improves the capability of heavy media cyclones to separate the ash component. Two samples of coal were processed at Hazen using this technique with the objective of providing processing conditions and samples of clean coal for further study at the Amoco Research and Development Department.

Approximately 500 pounds of a sample identified as Martin Lake lignite and 1000 pounds of a sample identified as Black Thunder subbituminous coal were processed in this study. The as-received coal was nominal two-inch lump coal.

PROCESS DESCRIPTION

SAMPLE PREPARATION

Each sample was crushed to pass 8 mesh. The crushed coal was wet screened at 65 mesh (Tyler) using a Derrick vibrating screen. Each sample was screened two times. The plus and minus fractions were collected and weighed wet. One hundred pounds of the wet Black Thunder coal sample and 75 pounds of the wet Martin Lake lignite sample were split for further study.

SO₂ TREATMENT

The screened coal was scrubbed in a saturated SO₂ solution, as shown in Figure 1 and described below.

- Approximately 75 pounds of wet screened coal (minus 8 plus 65 mesh) was added to an agitated tank along with 30 gallons of water.
- Twenty pounds of SO₂ were sparged into the agitated tank. This procedure took from one to four hours depending upon the SO₂ cylinder temperature.
- After the SO₂ was sparged, the slurry was agitated for an additional hour.
- The SO₂-treated slurry was then discharged to a Sweco shaking screen with a 65-mesh screen. The coal was collected in buckets and the SO₂ solution, along with fines, was pumped to a neutralization tank for discharge.
- The SO₂-treated coal was then returned to the agitation vessel along with an additional 30 gallons of fresh water and agitated for 15 minutes.
- The slurry was again discharged to the Sweco for solid/liquid separation. This washing procedure was repeated three more times.

This entire procedure was repeated on each sample of minus 8 plus 65-mesh coal until all the sample was processed. The product distributions for each sample are shown in Table 1.

HEAVY MEDIUM CYCLONE SEPARATION

Exploratory heavy medium (magnetic medium) cyclone tests were conducted to determine conditions for producing a cyclone overflow product representing 70 to 80 weight percent of the feed. To this end, four tests were conducted using a Krebs D3B hydrocyclone with inlet, vortex finder and apex openings of 1, 0.5, and 0.5 inches, respectively. The specific gravity of the medium was varied through 1.25, 1.35, and 1.40 for the four exploratory tests. The results of these tests are shown in Tables 2 and 3. For the Martin Lake lignite, weight distributions (dry basis) of the corresponding cyclone overflow products were 23.3%, 98.9%, 98.7%, and 98.9%. The Black Thunder subbituminous weight distributions of the corresponding cyclone overflow products were 28.0%, 99.5%, 99.5%, and 99.4%.

Based upon the results of the exploratory testing, the bulk pretreated coal samples were batch processed through the heavy medium separator using a medium density of 1.27 and 1.28 for the Martin Lake lignite and Black Thunder subbituminous coals, respectively. The bulk cyclone products (overflow and underflow) were screened at 65 mesh to remove the magnetite medium. The dewatered wet material was then weighed to determine the fraction of feed reporting to the overflow. Reporting as overflow in these tests were 40% of the SO₂-treated Martin Lake lignite and 46.4% of the SO₂-treated Black Thunder subbituminous samples.

Analysis of the heavy medium products showed that heavy medium separation did not significantly upgrade the SO₂-treated coal. The ash concentration of the upgraded coal was only slightly lower than the feed to the heavy medium cyclone; i.e. 5.12% ash versus 6.66% for Martin Lake lignite and 2.74% versus 3.81% for Black Thunder subbituminous.

The low ash content in the feed to heavy medium concentration apparently precludes upgrading. The reasons for the low ash content could be: 1) lower ash content of the original feed to SO₂ treatment and/or 2) more efficient SO₂ treatment than was attained in the previous test runs. With respect to the latter (2) cause, the operation during this campaign differed from previous campaigns. The SO₂ was weighed into the mix tank to insure saturation. This sometimes took a long period of time (four hours or more). In addition, the method of dewatering and washing SO₂-treated coal differed in this study, the coal was dewatered using a vibrating 65-mesh screen. In previous work the coal was dewatered by decantation. Compared to decantation, screening removes fine materials more efficiently.

Products from each of the testing procedures were packaged and returned to Amoco Research and Development for further analysis.

Hazen appreciates the opportunity to be of service to Amoco Oil Company in this research study. Please call at your convenience if there are any questions or if further information is required.

Sincerely,

Tom Bolles
Senior Project Engineer

Enclosures

xc: D. Erik Spiller

TB/aw

Figures and Tables

Table 1

Product Distribution of Crushed Screened Coal

<u>Sample Identification</u>	<u>Black Thunder Subbituminous</u>	<u>Martin Lake Lignite</u>
	<u>HRI 46115-1</u>	<u>HRI 46115-2</u>
Initial weight (crushed to minus 8 mesh)	992 lb	456 lb
Minus 65 mesh	138 lb	73 lb
Minus eight plus 65 mesh	850 lb	380 lb

Table 2

Heavy Medium Separation

<u>Cyclone Test Number</u>	<u>Specific Gravity</u>	<u>% Weight Distribution</u>	
	<u>Medium</u>	<u>Overflow</u>	<u>Underflow</u>
Martin Lake Lignite			
1	1.25	23.3	76.7
2	1.30	98.9	1.1
3	1.35	98.7	1.3
4	1.40	98.8	1.2
9	1.27	48.4	51.6
Black Thunder Subbituminous			
5	1.25	28.0	72.0
6	1.30	99.5	0.5
7	1.35	99.4	0.6
8	1.40	99.6	1.4
10	1.28	40.0	60.0

Table 3

Analysis of Heavy-Medium Products

Cyclone Product	Wt %	As-Received		Dry
		% Moisture	% Ash	% Ash
Martin Lake Analyzed		44.31	3.12	5.61
Test 1 Overflow	23.3	4.44	4.98	5.21
Test 1 Underflow	76.7	6.13	6.68	7.12
Calculated Head				6.66
Test 2 Overflow	98.9	23.62	4.24	5.55
Test 2 Underflow	1.1	4.24	54.72	57.12
Calculated Head				6.12
Black Thunder Analyzed		3.86	3.23	3.36
Test 5 Overflow	28.0	4.88	2.61	2.74
Test 5 Underflow	72.0	4.15	4.06	4.23
Calculated Head				3.81
Test 6 Overflow	99.5	5.29	2.63	2.78
Test 6 Underflow	0.5	4.21	49.35	51.52
Calculated Head				3.24

Schematic of SO₂ Coal Treating Process

Figure 1

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 monographs¹⁻⁴.

More than 25 years ago, van Krevelen proposed that coals were three-dimensionally cross-linked macromolecular networks and successfully treated them as such⁵. 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 universally⁶⁻⁹, 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 available¹⁻⁴.

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 in the solid, 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 ($\bar{M}_c$). 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 $\bar{M}_c$ 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. $\bar{M}_c$ 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 $\bar{M}_c$, 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 $\bar{M}_c$ of the coal.

The size of $\bar{M}_c$ governs many of the mechanical properties of coals. A highly cross-linked (low $\bar{M}_c$) material will be stiffer, less flexible than a less cross-linked material. Mechanical properties such as shear-moduli depend directly on $\bar{M}_c$. It is necessary to know $\bar{M}_c$ 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 literature¹⁻¹⁵. 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 raised¹⁶⁻¹⁸. 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 Brenner²³ is consistent only with a covalently crosslinked structure and rules out entanglements as the sole associative force¹⁸⁻²¹. 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 cleaved³. 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 macromolecules 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 electron³¹. 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 technique³²⁻³⁶ 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 Liotta³⁸ and Larsen³⁷. 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 1-6³⁹ 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 17²⁹ was milled and sieved and the <0.43 mm fraction was dried under vacuum at 179°C and kept under nitrogen. Coals 18-25⁴¹ were ground to pass a sieve with 900 mesh/cm² and dried to constant weight in an oven at 150°C. Coals 26-28³³ were Soxhlet extracted successively with DMF, pyridine, benzene, acetone and methanol. Coals 29-31⁴² were ground to pass a 200 (IMN) sieve and were heated in an oven at 150°C. Coals 32-41⁴³ were pyridine extracted and dried under vacuum at 60°C and stored in a nitrogen purged glove box. Coals 42-47⁴⁴ were pyridine extracted and dried in vacuum. Finally, coals 48-51⁴⁵ 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 interactions³¹.

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 coal²⁶.

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 Sanada⁴⁰ and Peppas and Lucht⁴³ 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. Non-hydrogen Bonding Solvents:

The extent of coal swelling is directly related to the affinity of the coal for the solvent³⁵. Regular solution theory³⁷ has often been used to describe coal-solvent interactions²³. 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 solvents⁹.

Larsen, Green and Kovac²⁶ 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 state²³.

An in-situ microscopic study of the swelling of polished coal surfaces and thin sections was done by Brenner²³. 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 coal¹⁵.

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 macromolecules¹⁻⁴. 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.

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

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 stiff²⁶. 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 way⁴⁶. 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.

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

The earlier work on the cross-link density of coal was done by Kirov et. al.²¹ and Sanada & Honda²². 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 rank⁴⁷. This raises the question of

whether regular solution theory will lead to accurate determinations of the interaction parameter (χ) in coal systems⁴⁸.

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 Windle⁴⁹, Peterlin, Astarita and Sarti⁵⁰, and Hopfenberg⁵¹. 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.

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

For analysis of dynamic swelling or sorption in coals, a slightly modified form of the empirical transport equation is used as shown below²⁹. M_t is the mass of the solvent taken up at time t , and k 's

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

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 coals³² using equation 4 is shown in Figures 7 and 8. These coals are (A) Fettkohle (bituminous), (B) Chinolinrestkohle, (C) G1, 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%. 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 state²⁷. 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^{33,34}.

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 links²¹ (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 Cruz⁵⁹ found that the conversion of a Colombian coal increased when it was swollen with tetrahydrofuran (THF) prior to liquefaction using different solvents, Table IV. Joseph⁶⁰ 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. Liotta⁶⁵ 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 compounds⁶⁶⁻⁶⁹. 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) ■ Kirov et al. (cyclohexane)
 ○ Green (benzene) ○ Green (cyclohexane)
 △ Moore (benzene)

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

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

● Honda and Sanada

▼ Szeliga and Marzec

● Honda and Sanada

■ Kirov et al.

Fig. 7. Dynamic swelling by pyridine vapors.

□ Gasflammekohle; ■ Fettkohle; ● Chinolinrestkohle;
○ Gl

Fig. 8. Solvent swelling in pyridine.

□ Gasflammekohle; ■ Fettkohle; ● Chinolinrestkohle;
○ 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	1.72±0.02
	Pyridine	2.12±0.06
	Ethanol	1.30±0.06
	Methanol	1.46±0.04
	Ethanol	1.54
	Acetone	1.29±0.08
	2-Propanol	1.64
North Dakota	Methylene Chloride	1.74
	Chloroform	1.78
	1,4-Dioxane	2.04
	Pyridine	1.28±0.04
	Methanol	1.36±0.02
	Ethanol	1.44
	Acetone	1.45±0.06
	2-Propanol	1.94
	Methylene Chloride	2.21
	Chloroform	1.23
	Formamide	2.31
	Aniline	1.79
	2,6-Lutidene	1.46
	Chlorobenzene	1.61
Bruceton	o-Dichlorobenzene	1.44±0.07
	Carbon Disulfide	2.07
	1,4-Dioxane	2.32
	Pyridine	1.32±.08
	Methanol	1.44±.01
	Ethanol	1.40±.04
	2-Propanol	1.65
	Methylene Chloride	2.00
	Chloroform	1.16
	Formamide	2.22
	Aniline	1.90
	2,6-Lutidene	1.81±0.06
	Chlorobenzene	1.72
	o-Dichlorobenzene	2.07
	Tetrahydrofuran	2.03
	Ethylenediamine	1.82±0.06
	N,N-Dimethylaniline	1.54
	Diethylether	2.21
	Dimethyl Sulfoxide	

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-Dioxane	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 Leopold	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
Buili (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 THF⁵⁹.

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 solvents⁶⁰.

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

END

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