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Thermal Dissolution of Lignite Under Hydrogen Pressure

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THERMAL DISSOLUTION OF LIGNITE UNDER HYDROGEN PRESSURE

by

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ABSTRACT

The hydrogenation-solution reaction of North Dakota lignite was studied with various organic solvents in a batch microautoclave at reaction conditions of 740 degrees F. and 1500 psig. initial hydrogen pressure. The solvents included aliphatic, aromatic, cycloparaffinic, heterocyclic, phenolic and amino compounds. The extent of dissolution was measured from the amount of residue retained on an asbestos filter-mat after it was washed and dried. It was found that the hydro-aromatic compounds were very effective, giving more than 70 percent solubilization of lignite in solution reaction.

Four lignites from different mines in the Northern Great Plains Provinces were dissolved in tetralin at the same operating conditions to study the effect of composition of lignite on the solution reaction. Lignites studied ranged from 71 percent to 82 percent solubilization. There was no evident correlation between the extent of solubilization and the proximate analysis. Also, the percent solubilization and the heating value of lignite did not show any correlation in the samples studied.

INTRODUCTION

The need to expand the existing markets for coal and coal-derived products has long been recognized. In the past, competition from petroleum products has had a depressing effect on the production of coal. In the future, nuclear energy may well replace coal in some of the electrical energy markets. Also, stringent regulations currently being introduced concerning air pollution may limit use of many coals as fuels.

One possible solution to these problems facing the coal industry is to convert coal into liquid products that can better compete in today's market place. A method of producing liquid products from coal that has attracted considerable interest in recent years is the thermal dissolution of coal in a solvent under hydrogen pressure. The degree of dissolution depends on the rank of coal, the petrographic constitution of coal, physical and chemical properties of the solvent and process variables such as hydrogen pressure, catalyst composition and concentration, coal particle size and moisture content, and the time and temperature of the reaction. In the form of liquid products, coal might reenter markets captured by the petroleum industry. Further, coal hydrogenation can lead to the reduction of sulfur content, providing a possible alternate fuel of lower air pollution potential. The solution process also removes

most of the ash from the coal and hence reduces boiler fouling.

Work on the hydrogenation-solution reaction of coal has been underway for many years. In Germany during World War II, high pressure coal hydrogenation supplied synthetic fuels for the war effort. The most comprehensive work on the solution of bituminous coal in pure compounds has been reported by Orchin et al. (13,14). The Office of Coal Research has sponsored several projects concerned with the hydrogenation of coal. The purpose of "Project Gasoline," one of the OCR projects, is to develop the Consolidation Coal Company's synthetic fuel process for converting coal to liquid fuels.

North Dakota lignite was used in the present study. The Fort Union Coal Region contains an estimated 460 billion tons of low rank coal (8). Despite the large reserve, very little work has been done on dissolution of lignite in comparison to high rank coals. The purpose of the present research is to compare solubility data on lignite with that of bituminous coal, and to determine relative efficacy of different organic solvents.

LITERATURE REVIEW

The behavior of coals toward different solvents has been studied for many years and voluminous literature has been accumulated. Mechanisms have been proposed to explain the reaction, but because the coal matrix is complex, the structure and behavior of coal during the solution reaction have not been clearly elucidated.

According to Storch (18), in 1869 Berthelot showed that pretreatment of coal with 100 parts of hydriodic acid at about 520 degrees F. for 24 hours yielded 60 weight percent oil and 30 weight percent of a bitumen-like residue. DeMarsilly (3) in 1860 extracted coal with boiling benzene, chloroform, ether, alcohol and carbon disulfide. In 1914, Bergius (1) filed a patent on a process for the hydrogenation of coal under pressure at temperatures between 570 and 930 degrees F. The conversion of powdered coal to gases and liquids in the presence of heavy recycle oil is covered in his patent.

The Pott-Broche Process (16) was used in Germany during World War II for the partial dissolution of coal in a hydrocarbon solvent followed by filtration and carbonization of the filtrate to produce a raw material for carbon electrodes used in the aluminum industry.

The literature reviews by Kloepper (10), VanKrevelen (19) and

Dryden (4) encompass most of the papers on solvent extraction of coal published until 1963. A recent Bureau of Mines Bulletin (21) on "Hydrogenation of Coal and Tar" published in 1968, describes the history and economics of coal solution processes.

Dryden (4) has summarized previous work done on the effect of various organic solvents on coal dissolution. According to him, various workers have attempted, without much success, to correlate physical properties of solvents such as surface tension, swelling properties and internal pressure with the extent of coal solubilization. Dryden (4) also proposes that the dissolving power of a solvent depends on the chemical structure and stability of the solvent. A two ring compound with one ring aromatic and the other ring hydroaromatic is particularly effective. Such a compound is tetralin, which has been used successfully in hydrogenation-solution of coal at about 400 degrees C. The hydroaromatic ring is a potential hydrogenation agent. A hydroxyl group on the aromatic ring polarizes the molecule enabling it to donate hydrogen more readily, thus making an even more effective solvent, as for example, 1,2,3,4-tetrahydro 5-hydroxy naphthalene.

According to Dryden (4), D'yakova (5) has found that between 360 and 400 degrees C., the dissolving power of solvents decreases in the following order: amines, phenols, cyclic hydrocarbons and aliphatic hydrocarbons. Dryden concluded that the important factor determining the high dissolving power of amines and related compounds for high

volatile bituminous coal was the availability of an unshared pair of

electrons on a nitrogen or oxygen atom.

The probable role of alternate donation and acceptance of hydrogen

by the hydroaromatic portion of the solvent at a temperature between 200

and 400 degrees C. was pointed out by Oele and coworkers (12). They

also found that diphenylamine was an effective agent for hydrogen

transfer.

The extraction yield of bituminous coal at the normal boiling point

of homologous aromatic solvents was found to increase directly with the

boiling point of the solvent by Orchin and coworkers (13). Some of their

results are presented in Table 1. Gillet (7) supports this view, but

suggests that specific structural arrangement rather than boiling point

may be the important factor.

Some results obtained on uncatalyzed solution of bituminous coal

by Orchin and Storch (14) are presented in Table 2. For catalyzed

reaction with different solvents, at 1000 psig. initial hydrogen pressure

and 400 degrees C., they report that most of the solvents dissolve 80

to 90 percent of bituminous coal.

By a generally accepted view (11,15), coal is composed of a

micellar (lyophobic) core with attached protective (lyophilic) colloids

in a dispersion medium of comparatively low molecular weight. Hirst (9)

presents a similar structure in which coal is considered as an "isogel."

Below the gel-point temperature the lyophilic phase is firmly held to the

TABLE 1

EXTRACTION OF BITUMINOUS COAL BY AROMATIC COMPOUNDS

Solvent	Boiling-Point Degrees C.	Extraction Percent
Pyrene	385	84
Fluoranthene	378	85
9-Methylphenanthrene	360	82
Phenanthridine	360	89
Anthracene	354	24
5,6-Benzoquinaldine	352	93
5,6-Benzoquinoline	351	95
Phenanthrene	340	95
9,10-Dihydrophenanthrene	307	60
Fluorene	295	26
Diphenyloxide	288	25
Diphenyl	255	8

micellar portion, so that the gel is insoluble. Above the gel-point temperature, the dispersing phase becomes freely rotating and mobile, permitting solution and peptization of the micellar portion. According to Orchin and coworkers (13), the above mechanism does not explain the influence of the solvent in the solution process. Thus, according to Orchin (13), the effectiveness of solvent is governed in part by the

TABLE 2

SOLVATION[a] EXPERIMENTS AT 400 DEGREES C.

Solvent	Time Hours	Solubilization Percent
1,2,3,4-Tetrahydro-5, Hydroxy Naphthalene	0.5	85.3
0-Cyclohexyl Phenol	0.5	81.6
Tetralin	0.5	49.4
U.S.P. Cresol	0.5	32.1
Naphthalene	0.5	22.2
Dicyclohexyl	1.0	27.2
o-Phenyl Phenol	0.5	19.6
Diphenyl	0.5	19.4
2-Methoxy-1-Cyclohexyl benzene	0.5	30.2

[a]Initial hydrogen pressure = 1000 psig.

penetration of the solvent molecule into the micropore structure of the coal. The spatial arrangement and size of the solvent molecule becomes an important factor in its ability to dissolve or disperse coal. Orchin illustrates this by comparing the extent of solubilization of bituminous coal in phenanthrene and anthracene which yield 95 and 24 percent solubilization respectively (Tables 1 and 3). He also considers the structure of coal as a very important factor contributing to the solubilization as may be seen from 23 percent solubilization of lignite in

TABLE 3

EFFECT OF RANK ON PHENANTHRENE EXTRACTION

Carbonaceous Material	Extraction Percent
Graphite	Trace
Anthracite	1.0
Bituminous Coal	95.0
Subbituminous Coal	27.0
Lignite	23.0

phenanthrene (Table 3) as to 95 percent for bituminous coal. The mobility of the micellar structure in coal of ranks other than bituminous coal is decreased by the presence of greater number of cross linkages among micelles such as the carbon-oxygen type in lignite.

Extensive work has been done by Franke and coworkers (6) on pretreatment of lignite before carbonization in production of liquid products. They have done comparative work on different lignites from North Dakota, Texas and Washington. Some results are presented in Tables 4 and 5.

Franke and coworkers (6) conclude that there is relatively little relationship between analyses of lignite and solubilization. The yield increases somewhat with increasing hydrogen pressure. They also found the most effective solvents for lignite dissolution to be tetralin

TABLE 4

PRODUCT YIELDS FROM PRESSURE EXTRACTION
OF VARIOUS LIGNITES

Lignite Source	Gas Percent	Extract Percent	Residue Percent	Liquefaction Percent
Washington	4.5	65.8	29.7	86.9
North Dakota	7.9	65.1	27.0	93.7
Texas	4.8	60.5	34.7	75.3

Reaction conditions:

Solvent: 4 parts of tetralin : part of cresol

Solvent to lignite ratio: 2:1

Temperature: 400 degrees C.

and tetralin-cresol mixture.

Results from work of Severson and coworkers (17) are presented in Table 6. The lignite solution runs were made in a one-gallon stirred autoclave. Tar from low temperature carbonization of lignite was found to be a very poor solvent in uncatalyzed test, yielding only 5.6 percent solubilization. Additional work is being done in which the ease of solubilization of various lignites is under investigation. According to these investigators, the most promising commercially available solvent appears to be anthracene oil.

TABLE 5

EFFECT OF SOLVENT AND HYDROGEN PRESSURE ON SOLUBILIZATION OF LIGNITE

Lignite Source	Solvent	Temp. °C.	Initial Hydrogen Pressure	psig. Max.	Gas Percent	Solubilization Percent
North Dakota	4T:C	400	0	1140	8.0	92.8
North Dakota	4T:C	400	1000	2790	8.7	100.0
Texas	4T:C	400	0	990	9.2	86.8
Texas	T	440	1000	2950	8.9	87.0
Texas	4T:C	440	1000	3150	11.3	91.9
Texas	C	400	0	1010	8.8	46.6
Texas	C	400	1000	3000	7.5	75.6
Texas	N	400	760	-	6.5	58.6
Texas	OA	400	0	-	8.1	75.8
Texas	P	400	0	-	9.6	26.2
Texas	OP	400	0	460	6.4	61.3

Solvent:
4T:C 4 parts tetralin : 1 part cresol
OP Octahydrophenanthrene
P Phenanthrene
N Naphthalene
OA Octahydroanthracene
T Tetralin
C Cresol

TABLE 6

SOLUBILIZATION OF LIGNITE WITH VARIOUS SOLVENTS

Solvent	Solubilization Percent
Anthracene Oil	78.1
Tetralin	83.7
o-Cresol + Tetralin (50% + 50%)	96.1
Alpha-Naphthol Tetralin Mixture (50% + 50%)	89.3

Run conditions:

Initial Hydrogen Pressure   =   1550 psig.

Maximum Pressure   =   3000-3300 psig.

Temperature   =   700-800 degrees F.

Lignite   –   Baukol-Noonan Mine,
Burke County, North Dakota

EQUIPMENT AND EXPERIMENTAL PROCEDURE

Equipment

The batch microautoclave used to determine the extent of solubilization of lignite in organic solvents is shown in Figure 1.

Main Reactor

The microautoclave was constructed of a type 316 stainless steel tube, 9/16 in. o.d., 5/16 in. i.d., and 6 in. in length, having an internal volume of 8 ml. It was capped on one end, the other end being connected to a pressure gauge through a cross. The tubing, couplings and nipples were AE Cone(R)[1] fittings designed for 15,000 psig. at 100 degrees F. service, this material supplied by Autoclave Engineers, Inc.

The reactor assembly was inside a pipe 1 1/2 in. i.d. and 8 in. long. A beaded heater coil rated 1200 watts at 110 volts, was wound uniformly on this pipe. The heater was insulated with 1 1/2 in. thick magnesia to minimize heat loss and to maintain a uniform temperature over the length of the reactor.

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[1](R) Registered trademark.

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To recorder

1 Thermocouple
2 Valve
3 Pressure gauge
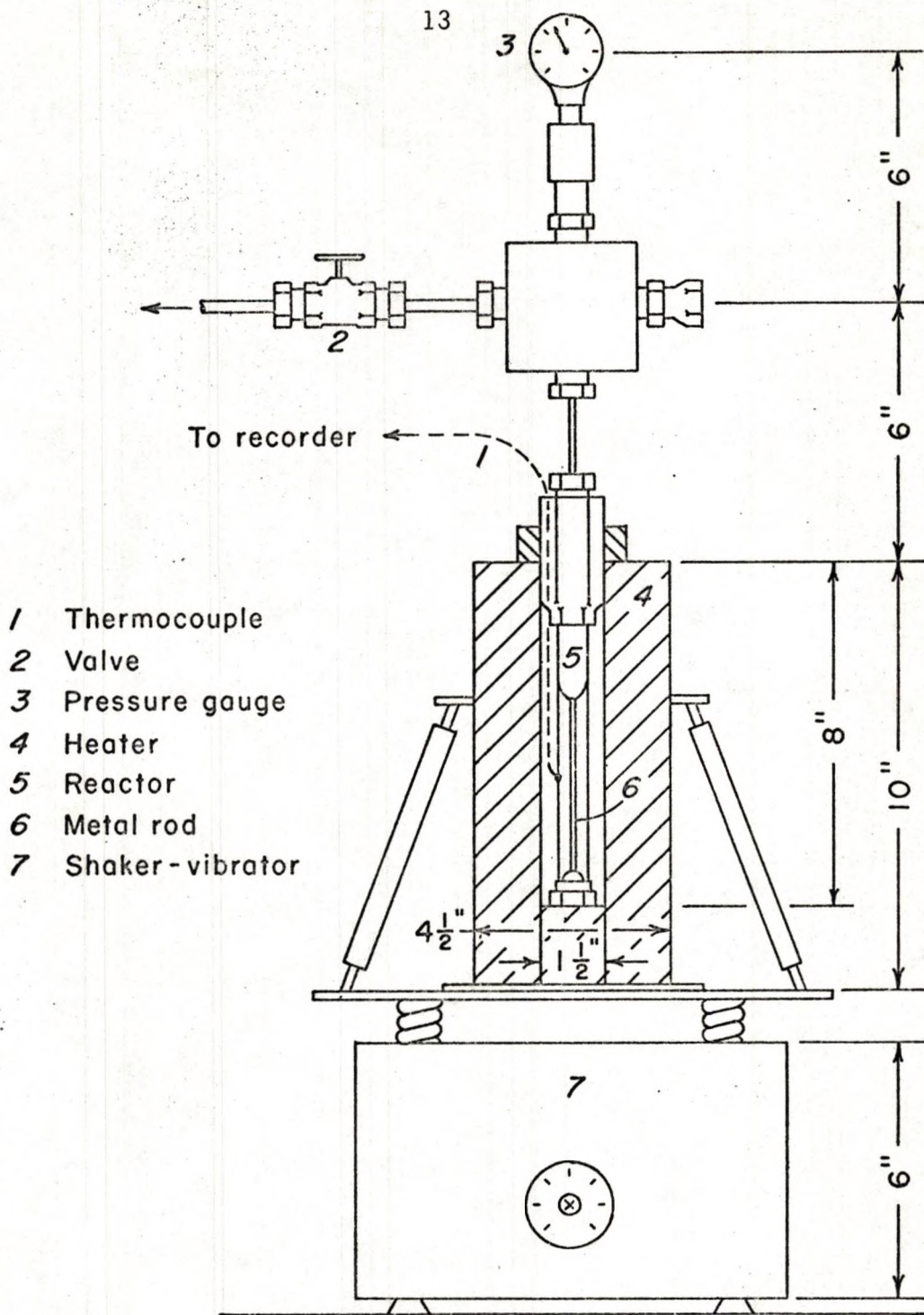4 Heater
5 Reactor
6 Metal rod
7 Shaker-vibrator

FIG. I Schematic diagram of reactor assembly.

Mixing

The reactor and heater assembly was mounted on a shaker-vibrator manufactured by the Central Scientific Company. This Cencomeinzer Sieve Shaker was driven by an electric motor with a double ended shaft. The combined vertical and lateral gyratory motion produced effective agitation. The speed of the motor was controlled by using a rheostat.

A 1/16 in. stainless steel rod, 3 in. long with a flattened end was placed inside the reactor to improve the mixing. In a Lucite model, it was observed visually that the reaction material was well mixed and was uniformly distributed when the reactor was one-half full or less, with shaker speed at No. 2 rheostat position.

Instrumentation

A chromel-alumel thermocouple was silver-soldered to the outside wall of the reactor, 2 in. from the bottom of the tube, to give an approximate temperature of the reactor contents. The outside thermocouple was connected to a Honeywell Temperature Recorder. Power supply to the heaters was controlled through a variac arrangement with manual adjustment.

Experiments were conducted to find the reliability and accuracy of this temperature measurement. The reactor was charged with tetralin-lignite slurry. Another chromel-alumel thermocouple was inserted inside the reactor tube and then the outside and inside temperatures were

recorded as the system was heated. It was found that the difference in temperature was 10 degrees F. at outside temperatures from 100 to 300 degrees F., and this temperature difference was independent of the temperature level for the range investigated. It was assumed that at operating temperatures of 735-750 degrees F. the difference in outside and inside temperatures would not be significantly different from this value. Thus, only the outside temperature was recorded as it was difficult to mount a thermocouple well inside the small reactor and still maintain a pressure seal at high operating pressures.

A pressure gauge, 0-5000 psig., was fitted onto the reactor. Pressure was recorded at 15 minute intervals during the reaction. A rupture disk was installed on the unit for safety purposes. In operation, the unit was placed behind a steel barricade.

Materials

Hydrogen was obtained from a commercial supplier in tanks at 2000 psig. and was used as received. Various organic solvents were purchased from different sources and are listed in Appendix B, with their grade, boiling point and structural formula. Lignite from the Baukol-Noonan mine, Burke County, North Dakota, was used to investigate the effect of various solvents in solution reaction. Other samples include one each from Velva and Beulah, North Dakota, and Savage, Montana, mines. Proximate analyses and heating value are shown in Appendix C.

The heating values reported are of the samples from the same mines with similar composition. All samples were pulverized to minus 200 mesh, and dried in a nitrogen atmosphere at 110 degrees C. for 4 hours.

Performing the Run

The reactor was charged with lignite and solvent in a ratio of 1 to 4 by weight. In a typical experiment, 0.63 gm. of dried pulverized lignite and 2.6 gm. of tetralin were placed in the reactor. After sealing, the reactor was pressurized to 1500 psig. initial pressure with hydrogen. The unit was tested for leakage by holding at room temperature for 2 hours and noting the constancy of pressure. The reactor was then fitted inside the heater assembly, heated to 735-750 degrees F. in about 30 minutes, and maintained at this temperature for 2 hours. Vibrator-shaker speed during the run was at No. 2 rheostat position. Pressure and temperature were recorded at 15 minute intervals. After 2 hours, the heaters were shut off, and the reactor was removed from the heater assembly. The reactor was cooled to room temperature, and the pressure released slowly. The reacted material was transferred quantitatively to a 500 ml. beaker. A mixture of acetone and benzene was used to wash the inside walls of the reactor, and the washings collected.

Filtration

The reaction material collected in the acetone-benzene mixture was vacuum filtered through a gooch crucible with an asbestos-mat.

Filtration time was noted. The residue was washed with hot tetralin until a colorless filtrate was obtained (the quantity of tetralin required was generally less than 50 ml.). The residue was washed with acetone to remove traces of tetralin, and the crucible dried at 110 degrees C. for 1 hour, and weighed. The weight of the residue retained on the filter-mat was used in the calculation of percent solubilization. Sample calculations and a typical temperature-pressure history of a run are shown in Appendix A.

EXPERIMENTAL RESULTS

The results from the hydrogenation-solution reaction experiments
are given in Tables 7 and 8. No attempt was made to determine separate
yield of gas and liquid products. The extent of solubilization was cal-
culated from the amount of residue retained on the filter-mat after it was
washed and dried. Solubility is the weight of 1 gm. of moisture and ash
free (MAF) lignite converted to either gas or liquid during the solution
reaction. Thus,

$$\text{Percent Solubilization} = (1 - \frac{\text{Weight of MAF residue}}{\text{Weight of MAF lignite}}) \times 100$$

The temperature, initial hydrogen pressure, solvent to lignite
ratio and reaction time were held constant to compare the relative dis-
solving power of solvents. In Table 7, percent solubilization of
Baukol-Noonan, North Dakota lignite in 15 different solvents is shown.
Solvents studied include aromatic, aliphatic, amino, phenolic, hetero-
cyclic and cycloparaffinic compounds. In Table 8, solubilization in
tetralin for four lignites from different mines is presented.

The ease of filtration with different solvents is reported as an
index of the time taken for filtration of the reaction mass in the

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acetone-benzene mixture, according to the following nomenclature:

Filtration Time (Minutes)	Ease of Filtration	
5-10	Very Easy	(VE)
10-20	Easy	(E)
20-40	Difficult	(D)
40-60	Very Difficult	(VD)

In Table 7, percent solubilization, ease of filtration, maximum reaction pressure and average solubilization of the duplicate runs are summarized. R1 and R2 represent the results of duplicate runs made with the same solvent to study the reproducibility. Average percent solubilization is the arithmetic mean of R1 and R2. A detailed sample calculation is shown in Appendix A.

Reaction conditions for all tests were:

Temperature:	735-750 degrees F.
Initial Hydrogen Pressure:	1500 psig.
Reaction Time:	2 hours
Vibrator-Shaker Speed:	No. 2 rheostat position
Solvent to Lignite Ratio:	4 gm. of solvent to 1 gm. of lignite
Lignite Particle Size:	-200 mesh

Results from tests with different lignites indicating the effect of change in composition on the extent of solubilization are summarized in

Table 8. Tetralin was used as solvent with conditions being the same as for other experiments. Analysis of various lignites used is given in Appendix D.

In Table 7, the various solvents are divided into three groups--A, B and C; the least effective, moderately effective and very effective solvents respectively, depending upon the extent of solubilization. Effort has been made to correlate the effectiveness of these solvents with their chemical structure. In group D, percent solubilization of lignite in commercial anthracene oil solvent is reported.

Statistical analysis of reproducibility for solubilization data is made in Appendix D. With the help of standard deviation of differences in solubilities of duplicate runs a significant value for difference in averages of duplicate runs of two solvents is calculated. This difference in the averages of duplicate runs is used to determine if there is any significant difference in solubilization of two solvents. It is found that if the difference in solubilization of two solvents is more than 5 percentage units then there is significant difference in solubilization.

TABLE 7

PERCENT SOLUBILIZATION OF LIGNITE[a] IN ORGANIC SOLVENTS

Run	Solvent	Ease of Filtra-tion	Pressure Max. (psig.)	Solubilization Percent		
				R1	R2	Avg.
A1	Benzene	VE	2180	26.5	30.1	28.3
A2	Phenol	E	2300	29.9	33.3	31.6
A3	o-Cresol	E	2140	42.3	31.0	36.7
A4	n-Butyl amine	E	2400	36.8	37.5	37.2
A5	Cyclohexane	VE	2120	43.7	38.8	41.3
B1	1-Naphthyl amine	D	2200	45.5	40.9	43.2
B2	o-Phenyl phenol	D	2000	45.4	44.6	45.0
B3	Quinoline	VE	2000	45.5	47.4	46.5
B4	Phenanthrene	D	1900	46.5	49.6	48.1
B5	Anthracene	VD	2090	49.1	50.0	49.6
B6	Naphthalene	D	2070	52.3	47.4	49.9
B7	alpha-Naphthol	VD	2200	63.3	62.3	62.8
C1	Tetralin	E	2050	73.0	70.4	71.7
C2	1,2,3,4-Tetrahydro quinoline	VE	2020	93.2	93.5	93.4
D1	Anthracene oil (Distilled)	VD	1900	60.2	65.4	62.8

[a]Lignite: Baukol-Noonan Mine, Burke County, North Dakota.

TABLE 8

PERCENT SOLUBILIZATION OF DIFFERENT
LIGNITES IN TETRALIN

Lignite Source[a]	Solubilization Percent		
	R1	R2	Avg.
(1) Baukol-Noonan, North Dakota	73.0	70.4	71.7
(2) Savage, Montana	72.0	75.8	73.9
(3) Beulah, North Dakota	81.8	82.4	82.1
(4) Velva, North Dakota	82.2	82.3	82.3

[a](1) Baukol-Noonan Mine, Burke County, North Dakota

(2) Breezy Flat Mine, Richland County, Montana

(3) South Beulah Mine, Mercer County, North Dakota

(4) Velva Mine, Ward County, North Dakota

DISCUSSION OF THE RESULTS

Low rank coals are difficult to hydrogenate because of a high-oxygen content and accompanying high degree of cross-linkage. Under depolymerizing conditions oxygen from the lignite results in higher yields of water and carbon dioxide per unit weight of coal substance than do higher rank coals. The two solvents which are known to be good hydrogen donating agents were found to produce the high solubilization of lignite for the solvents investigated, namely tetralin and tetrahydro quinoline.

Different solvents are divided into three groups--A, B and C; the least effective, moderately effective and very effective solvents respectively, depending on their extent of solubilization determined experimentally and are found to have either aliphatic or aromatic (low boiling) structure in group A, polynuclear aromatic structure in group B and hydroaromatic structure in group C solvents.

Solvents in group C, the most effective group, dissolve more than 70 percent of the lignite. Filtration of the reaction mass collected in acetone-benzene mixture is either easy or very easy. It seems that the process of depolymerization and stabilization by hydrogen bonding is almost complete. Both the solvents studied are hydroaromatic

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compounds, and have ability to donate hydrogen. From the study of ease

of filtration it may be said that there are very few colloidal particles

left in the solution and hence the filtration is easy.

The solvents in this group have high boiling points. 1,2,3,4-

tetrahydroquinoline (B.P. 251 degrees C.) dissolved 93 percent of lignite

whereas 1,2,3,4-tetrahydronaphthalene (tetralin, B.P. 206 degrees C.)

gave 71 percent solubilization. It seems that tetrahydroquinoline has

ability to donate hydrogen much more effectively than tetralin. This may

be due to the polarization effect of nitrogen present in hydroaromatic

ring which promotes alternate donation and acceptance of hydrogen by

the hydroaromatic ring to the broken linkages of the coal molecule as

suggested by Franke (6). ⟵

Solvents in group B, the moderately effective group, dissolve 40

to 65 percent of lignite. Filtration of the reaction mass is either diffi-

cult or very difficult, except for quinoline. From the study of extent of

solubilization it can be concluded that there is a significant solution

reaction. Lignite is depolymerized under the operating reaction condi-

tions but some of the depolymerized molecules are of colloidal size.

These colloidal molecules clog the pores of the filter-mat, and make

filtration difficult. Except quinoline, all of these polynuclear com-

pounds have high boiling points. It seems that such a solvent has

ability to act as a hydrogen transfer agent but does not donate its own

hydrogen.

Solvents in group A, the least effective group, dissolve 25 to 40 percent of lignite. Filtration of the reaction mass is either easy or very easy. Lignite is apparently depolymerized under the operating reaction conditions. It appears that the broken linkages of these molecules combine to form a stable structure as the availability of hydrogen for bonding is limited. All of these aliphatic and aromatic compounds have low boiling points. From compressibility calculations it appears that these solvents are in the vapor phase at the operating pressure and temperature conditions. From the ease of filtration it is felt that the resulting reaction mass contains negligible amount of colloidal size particles and hence the filtration is easy. These solvents neither have ability to act in a hydrogen donating capacity nor are they hydrogen transferring agents. These solvents do not contribute appreciably to the solution reaction.

The extent of solubilization with naphthalene and quinoline is not significantly different. Thus in this instance, the polarization effect of nitrogen in naphthalenic ring structure compounds is not significant. This is contrary to the effect of nitrogen in a hydroaromatic ring. The solubilization of lignite with naphthalene and with tetralin is significantly different as is the case with quinoline and tetrahydroquinoline. From this difference in behavior it may be concluded that the hydro-aromatic ring gives significant increase in solubilization. Solubilization with cyclohexane is more than 10 percent better than with benzene.

This may be due to the saturated ring structure of cyclohexane.

The difference is solubilization of lignite with anthracene, naphthalene and phenanthrene is not significant. The solubilization is not increased significantly with the additional condensed benzene ring in the case of naphthalene to anthracene. The effect of angular arrangement of phenanthrene on the extent of solubilization of lignite is not observed. Orchin and coworkers (13) found that phenanthrene dissolved 95 percent of bituminous coal whereas anthracene gave 24 percent solubilization. They observed that phenanthrene dissolved only 23 percent of lignite. This difference in behavior may be attributed to the reduced cross-linkages in the structure of bituminous coal. Thus it may be concluded that the structural arrangement of the coal molecule and the structure of solvent molecule do determine the extent of solubilization.

Solubilization of lignite in phenol and o-cresol is not significantly different. Thus in this case, an additional methyl group has no significant effect on the extent of solubilization.

The solubilization of lignite in alpha-naphthol is significantly greater than with phenol. This difference in behavior may be attributed to the condensed polynuclear structure of alpha-naphthol. Solubilization with o-phenyl phenol was more than o-cresol but was less than alpha-naphthol. Thus a condensed aromatic ring gave significantly higher solubilization than a phenyl ring in this case.

The extent of solubilization of lignite in alpha-naphthol and in 1-naphthyl amine can be compared to predict the relative effectiveness of hydroxyl and amino groups. It appears that the hydroxyl group would significantly increase the solution reaction. The extent of solubilization is not changed significantly with the addition of a third aromatic ring to naphthalene in phenanthrene and anthracene. Thus it may be predicted that an additional number of rings greater than three may not increase solubilization significantly. This conclusion is supported by Orchin et al. (13) in their work on bituminous coal (see Table 1).

The extent of solubilization of Baukol-Noonan, North Dakota, and Savage, Montana, lignite is not significantly different. The extent of solubilization of Beulah and Velva, North Dakota, lignite is comparable and is significantly greater than the first two lignites. No correlation is evident between solubilization and the proximate analysis of lignite. Franke et al. (6) worked on three different lignites from North Dakota, Texas and Washington and found no correlation between the analysis of these lignites and the extent of solubilization. It was noted that the percent solubilization was not related to the heating value of lignite (MAF).

The data obtained by Severson and coworkers (17) show significantly higher solubilization than the present work, although differences between solvents were generally in the same direction. These differences may be a result of difference in design of the two apparatus

used. Secondly, the maximum pressure reached in the autoclave used in this work was appreciably lower for the same starting pressure and final temperature than that used by Severson et al. (19). Also, different methods were employed to determine the extent of solubilization. The data obtained in this work are used primarily to give an indication of the relative effect of different solvents in solution reaction of lignite.

CONCLUSIONS

Solvents have the capacity to act either as hydrogen transferring agents or to donate their own hydrogen in hydrogenation-solution reaction. The most effective solvents are hydroaromatic compounds, which have the capacity to donate their own hydrogen and to transfer hydrogen by alternate acceptance and donation of hydrogen to stabilize the depolymerized coal molecule. The moderately effective group of solvents have polynuclear aromatic structure. The least effective group contains aliphatic and aromatic (low boiling) solvents. The relative ability to solubilize coal may be related to relative ability to transfer hydrogen for these solvents.

In the case of bituminous coal, phenanthrene dissolved 95 percent of coal, and anthracene gave 24 percent solubilization (13). It was found that this difference in behavior was not observed with lignite. The difference in solubilization of lignite with anthracene and phenanthrene was not significant. It is felt that this difference may be caused by different structural arrangement of molecules in lignite and bituminous coal.

In a single case, a hydroxyl group was more effective than an amino group as can be seen from the solubilization with alpha-naphthol

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and 1-naphthylamine. The extent of solubilization with naphthalene and anthracene was not significantly different. It may be predicted that an additional number of rings greater than three may not increase solubilization significantly.

Hydroaromatic solvents were superior to polynuclear solvents in solution reaction. The effectiveness of hydroaromatic solvents was caused by their ability to act as hydrogen donors to coal substances under the depolymerizing conditions.

The extent of solubilization was found to differ significantly, depending on the source of the lignite. There was no evident correlation between the proximate analysis of the lignite and the percent solubilization. Also, the percent solubilization and heating value of lignite showed no conclusive correlation.

SUMMARY

The hydrogenation-solution reaction of lignite was studied in a microautoclave with various organic solvents at reaction conditions of 740 degrees F. and 1500 psig. initial hydrogen pressure. Process variables such as temperature, pressure, time of reaction and particle size of lignite were held constant. Results indicated that the hydro-aromatic compounds are superior in dissolving lignite to any other type of solvents studied. 1,2,3,4-tetrahydroquinoline gave more than 93 percent solubilization. Polynuclear solvents gave moderately good solubilization while aliphatic and aromatic (low boiling) solvents dissolved only 25 to 40 percent of the lignite.

Solvents were classified into three groups--C, very effective (more than 70 percent solubilization); B, moderately effective (40 to 65 percent solubilization); and A, least effective (25 to 40 percent solubilization). It was found that group C solvents were hydroaromatic compounds, group B solvents had polynuclear aromatic structure, and group A solvents were either aliphatic or aromatic (low boiling) compounds.

Four lignites from different mines in the Northern Great Plains Province were hydrogenated with tetralin as solvent to study the effect of lignite composition on the solution reaction. It was noticed from the

results that there was a significant difference in percent solubilization

for some of these lignites. There was no evident correlation between

the extent of solubilization and the proximate analysis. Also, it was

observed that the heating value of lignite and the percent solubilization

showed no correlation in the samples studied.

RECOMMENDATIONS FOR FURTHER WORK

From the results of solubilization with hydroaromatic solvents it is felt that it would be worthwhile to determine solubility of lignite with some more hydroaromatic solvents such as o-cyclohexylphenol and 1,2,3,4-tetrahydro 5-hydroxynaphthalene. These compounds have been found to be very good solvents for bituminous coal. In the case of lignite, probably because of its cross-linked structure, phenanthrene and anthracene gave comparable extent of solubilization. If it is found that o-cyclohexylphenol dissolves considerably lower amount of lignite than 1,2,3,4-tetrahydro 5-hydroxynaphthalene, then it would be more certain that the arrangement of structural rings is a decisive factor in determining the extent of solubilization of lignite.

Another very important contribution would be solubility determination of lignite with mixtures of pure solvents. A mixture of two solvents may give higher solubilization than either of the two solvents alone. It is suggested to determine solubility of lignite with a few more saturated ring compounds under hydrogen pressure. It is recommended to obtain solubility data with high boiling solvents in absence of hydrogen to determine their capacity to donate their own hydrogen.

It is suggested to do some investigation in the direction of treating coal before hydrogenation. It will be an important contribution if a process of partial hydrogenation followed by carbonization to improve the yield of liquid products is developed.

APPENDIX A

SAMPLE CALCULATIONS AND A TYPICAL TEMPERATURE-
PRESSURE HISTORY OF A RUN

Run No.:   C1-R1

Initial Hydrogen Pressure: 1480 psig.

Time: 2 hours

Time in Minutes	Variac Reading	Temperature Degrees F.	Pressure psig.
0	100	375	1600
15	80	690	1800
30	66	740	1850
45	64	740	1900
60	63	725	1940
75	64	735	1960
90	63	735	1980
105	63	735	1990
120	64	735	2000
135	63	740	2000

Complete Sample Calculation: Run No. C1-R1

Weight of weighing bottle + lignite	=	4.8101 gm.
Weight of weighing bottle	=	4.2267 gm.
Weight of lignite	=	0.5834 gm.
Weight of weighing bottle + tetralin	=	29.2623 gm.
Weight of weighing bottle	=	26.6828 gm.
Weight of tetralin	=	2.5795 gm.
Weight of crucible + residue	=	22.7321 gm.
Weight of crucible	=	22.5411 gm.
Weight of residue	=	0.1910 gm.

Moisture (1.107%) = 0.5834 x 1.107/100 = 0.00654 gm.

Ash   (8.356%) = 0.5834 x 8.356/100 = 0.04880 gm.
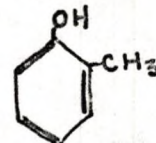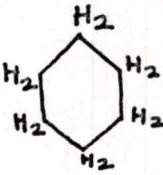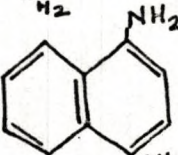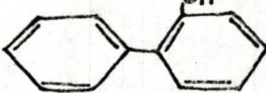
Lignite   (MAF)
$$
\begin{array}{r}
0.5834 \text{ gm.} \\
-0.0065 \text{ gm.} \\
\underline{-0.0488 \text{ gm.}} \\
0.5282 \text{ gm.}
\end{array}
$$

Residue   (MAF)
$$
\begin{array}{r}
0.1910 \text{ gm.} \\
\underline{-0.0488 \text{ gm.}} \\
0.1422 \text{ gm.}
\end{array}
$$
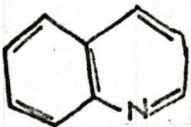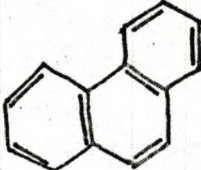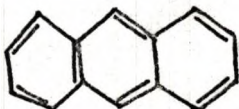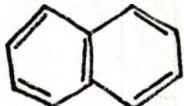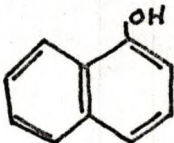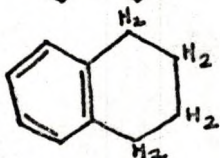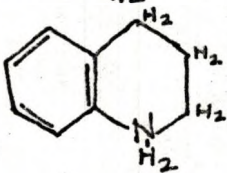
Percent Solubilization = $(1 - \dfrac{\text{Residue (MAF) gm.}}{\text{Lignite (MAF) gm.}})$ x 100 percent

$$= (1 - \frac{0.1422}{0.5282}) \text{ x 100 percent}$$

$$= (1 - 0.2690) \text{ x 100 percent}$$

$$= 73.1 \text{ percent}$$

APPENDIX B

SOURCE, STRUCTURAL FORMULAE, AND BOILING

POINT OF SOLVENTS

Solvent	Formula	Boiling-Point Degrees C.	Source[a]	Grade
Benzene		80	a	Reagent
Phenol		181	b	Reagent
o-Cresol		190	c	Practical
n-Butylamine	$C_2H_5CH_2CH_2NH_2$	77.8	b	Practical
Cyclohexane		80	d	Practical
1-Naphthylamine		300	c	Practical
o-Phenylphenol		275	c	Baker

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APPENDIX B--Continued

Solvent	Formula	Boiling-Point Degrees C.	Source[a]	Grade
Quinoline		236	c	Baker-Reagent
Phenanthrene		340	c	Technical
Anthracene		342	c	Practical
Naphthalene		218	c	Reagent
alpha-Naphthol		278	c	Flakes
Tetralin		206	a	Practical
1,2,3,4-tetrahydro quinoline		251	c	Practical
Anthracene oil	—	300	e	Commercial

[a]Source: a = Matheson Coleman and Bell
            b = Fisher Scientific Company
            c = J. T. Baker Chemical Company
            d = Eastman Organic Chemicals
            e = Reilly Tar and Chemical Corporation

APPENDIX C

PROXIMATE ANALYSIS OF VARIOUS LIGNITES

Lignite Source	Moisture as Received	Heating Value[a] BTU / lb. of Lignite (MAF)	Proximate Analysis, As Run			
			Moisture	Ash	Volatile Matter	Fixed Carbon
Baukol-Noonan, Baukol-Noonan Mine Burke County North Dakota	28.46	12,200	1.11	8.36	38.07	52.46
Velva, Velva Mine Ward County North Dakota	38.84	11,800	1.30	7.03	43.33	48.34
Beulah, South Beulah Mine Mercer County North Dakota	35.56	12,100	0.37	10.80	39.63	49.14
Savage, Breezy Flat Mine Richland County Montana	37.36	11,800	0.86	10.76	41.47	46.91

[a]Heating values are of the samples from the same mines with similar fixed carbon to volatile matter ratio.

APPENDIX D

STATISTICAL INTERPRETATION OF RESULTS

There are two determinations of percent solubilization for each solvent. The difference in solubilization between duplicate runs is caused by unavoidable variations in test conditions. There are a total of 15 different solvents and hence the degrees of freedom are 14. With the help of standard deviation of difference in solubilities of duplicate runs, it is possible to find a significant value for difference in averages of duplicate runs of two solvents (20).

d_i	=	Difference in solubilities of duplicate runs of solvent i
$R_1(i)$	=	Solubility in solvent i in run 1
$R_2(i)$	=	Solubility in solvent i in run 2
Sum $(d_i)^2$	=	Sum of squares of differences
$(\text{Sum } d_i)^2$	=	Square of sum of differences
S^2	=	Variance
S	=	Standard deviation
$\bar{d}$	=	Estimated difference between single runs at 5 percent significance level

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$\overline{D}$ = Estimated difference between average of duplicate runs at 5 percent significance level

N = Number of solvents used for variance calculations

n = Number of runs made with same solvent

di = R1 (i) – R2 (i)

Sum di = 50.0

Sum $(di)^2$ = 279.47

Variance = $\dfrac{N \, (\text{Sum } di^2) \; - \; (\text{Sum } di)^2}{N^2}$

= $\dfrac{15 \times 279.47 \; - \; (50)^2}{225}$

S^2 = 7.52

S = $(7.52)^{0.5}$

= 2.74

From the t-table, at 5 percent significance level and with 14 degrees of freedom,

$$t_{(0.05,\ 14)} = 2.145$$

The difference between single runs at 5 percent significance level is given by:

$$\overline{d} = \pm t_{(0.05,\ 14)} \times S$$

$$\pm \; 2.145 \times 2.74$$

$$\pm \; 5.55$$

In the present case, the average of duplicate runs is to be com-
pared. So:

$$\overline{D} \;=\; \pm\;\frac{\overline{d}}{\sqrt{n}}$$

$$\pm\;\frac{5.55}{\sqrt{2}}$$

$$\pm\;4.17$$

This difference in the averages of duplicate runs may be used to
determine if there is any significant difference in solubilization of two
solvents. Thus, if the difference in solubilization of two different
solvents is more than 5 percentage units, then there is a significant
difference in solubilization.

TABLE 9

SUM OF SQUARES OF DIFFERENCE IN SOLUBILIZATION
OF DUPLICATE RUNS

Run	Difference $di = R1 - R2$	$(di)^2$
A1	3.6	12.96
A2	3.4	11.56
A3	11.3	127.6
A4	0.7	0.49
A5	4.9	24.01
B1	5.5	30.25
B2	0.8	0.64
B3	1.9	3.61
B4	3.1	9.61
B5	0.9	0.81
B6	4.8	23.04
B7	1.0	1.0
C1	2.6	6.76
C2	0.3	0.09
D1	5.2	27.04
	Sum di = 50.0	Sum (di^2) = 279.47

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