

Gasification of Iowa Coal in the SYNTHANE PDU Gasifier

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Introduction

Vast deposits of high sulfur caking coals found in the eastern and midwestern United States can be converted to clean gaseous energy by gasification. In the 1980's many coal gasification plants are expected to be constructed in the United States to produce a high-Btu gas as a supplement to the dwindling supply of natural gas. One important consideration in the development of a coal gasification process is the acceptability of various coal feedstocks. The SYNTHANE process is one such process for the manufacture of high-Btu gas from coal. This report demonstrates the capability of using the SYNTHANE process for the gasification of the mildly caking high sulfur₉ coal from Iowa. This coal is not only present in substantial reserves (7.2×10^7 tons) (1) but is also convenient to the large energy markets of the Midwest. The Iowa coal for this study is from the Iowa Coal Project Demonstration Mine #1 of Iowa State University. This coal bed is located in the southwest corner of Mahaska County and is part of the Cherokee Group.

Experimental Equipment

A schematic flow diagram of the SYNTHANE PDU gasification system is shown in figure 1. This system combines the steps of fluidized-bed pretreatment, free-fall carbonization and fluidized-bed gasification. The pretreater is an 8-foot long, 3/4-inch diameter pipe with a 2-1/2-foot long, 1-inch diameter expanded zone. Both sections of pipe are schedule 80 and made of 304 stainless steel. The pretreater is enclosed by four individually controlled heaters that supply heat for startup and to counter radiation losses. The carbonizer is a 6-foot long, 10-inch diameter schedule 40 pipe made of 304 stainless steel located directly above the gasifier. Electric heaters surrounding the carbonizer maintain the temperature at 1000° F. The gasifier is a 6-foot long, 4-inch diameter schedule 40 pipe made of 310 stainless steel. Surrounding the gasifier is a 10-inch schedule 40 pipe made of 304 stainless steel which acts as a pressure shell. In the annulus three individually controlled electric heaters, wrapped in a 2-inch thick blanket of insulation, supply heat for startup and to counter radiation loss during operation. A 1/8-inch pipe entering the base of the gasifier serves as the gas distributor. A thermowell made of 3/8-inch pipe located in the center of the gasifier extends from 1-inch above the gas distributor to the top of the carbonizer. Twelve thermocouples inserted into the thermowell detect internal temperatures from the base of the gasifier to the top of the carbonizer. A variable speed extractor screw located at the base of the gasifier maintains the bed height by removing reacted char. The raw product gas leaving the top of the gasifier is filtered to remove fine particles and cooled in a series of two water-jacketed condensers. Effluent water and tar are collected in a receiver. The dry gas is then analyzed by mass spectrometric and chromatographic methods prior to metering the flow rate.

Experimental Procedure

The caking Iowa coal (analysis shown in table 1) was crushed and sized to an average size of 240 microns with a U.S. Standard mesh range of 20 X 0. The pulverized coal was fed to the base of the pretreater under pressure (40 atm) at a rate of about 20 lb/hr. The coal then moved through the pretreater in a fluidized state with nitrogen

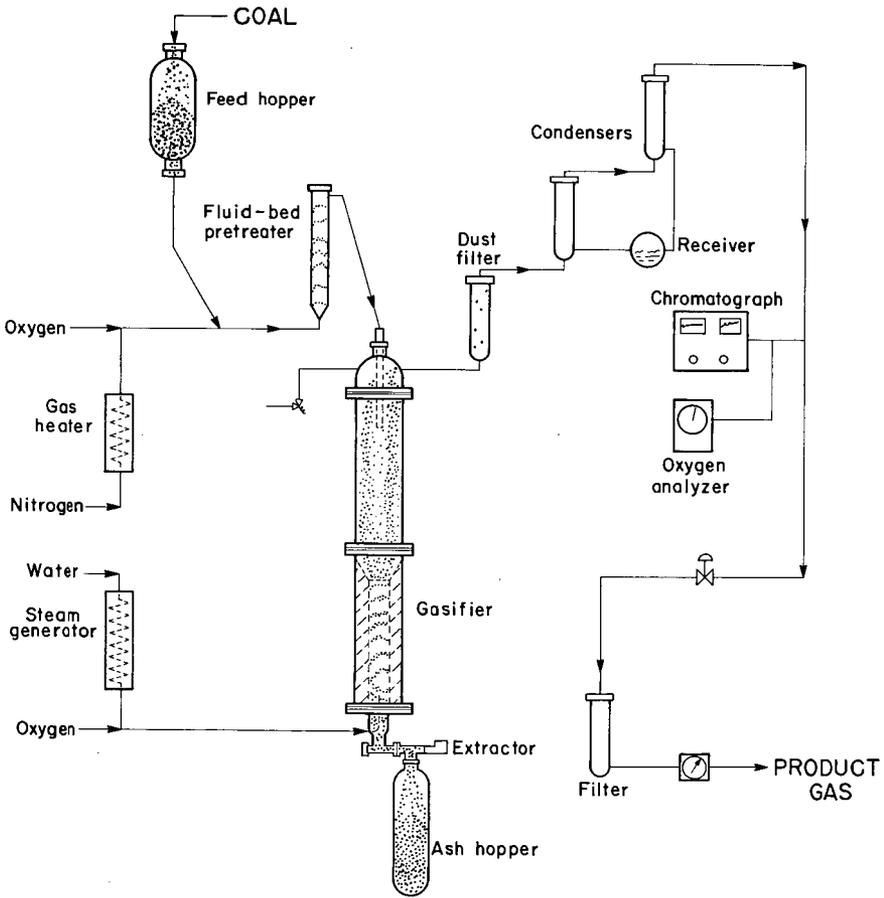


Figure 1-SYNTHANE PDU GASIFIER.

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and oxygen. The pretreating conditions were the same as those developed for the pretreatment of Illinois No. 6 coal as reported by Gasior (2). The decaked coal emptied from the top of the pretreater and was gravity fed into the gasifier through the carbonizer, countercurrent to the exiting product gas. A mixture of steam and oxygen entering the base of the gasifier provided both the reactant and fluidizing gases. Gasifier temperatures were maintained by varying the flow rate of oxygen to the reactor. A fluidized-bed height of about 68 inches was maintained by adjusting the char extraction rate to coincide with the coal feed and gasification rates.

Discussion and Results

The operating conditions and results for the three experimental gasification tests are shown in table 2. Coal feed rates for these tests ranged from 17.6 to 19.9 lb/hr, which are equivalent to coal throughputs of 37.4 to 42.4 lb/hr ft³ of gasifier volume. Average gas inputs of 0.35 lb oxygen/lb coal and 1.8 lb steam/lb coal resulted in a superficial gas velocity of 0.29 ft/sec at 40 atmospheres pressure in the 4-inch gasifier. No difficulty was experienced in maintaining temperature control in the fluidized-bed with the average of the maximum gasifier temperatures ranging from 1761° to 1832° F, and no slag-sintering problems occurred at peak gasifier temperatures of 1850° F.

The results of the three tests showed that carbon conversions ranged from 77.0 to 80.2 percent and steam conversions or decomposition ranged from 14.3 to 16.9 percent. Raw gas analysis showed that the hydrogen sulfide yield was 0.77 SCF/lb coal, maf, for the 8 percent sulfur coal, while product gas yields ($H_2 + CO + CH_4 + C_2H_6$) averaged 13.6 SCF/lb coal, maf, with equivalent methane yields ($CH_4 + C_2H_6$) ranging from 3.45 to 3.60 SCF/lb coal, maf.

Comparing test results using Iowa coal to similar test results using Illinois No. 6 coal, as reported by Forney (3), the Iowa coal results showed higher carbon conversions (78.6 vs. 71.8 percent), lower product gas yields (13.6 vs 14.9 SCF/lb coal, maf) and higher hydrogen sulfide yields (0.77 vs. 0.36 SCF/lb coal, maf). The higher temperature accounted for the high carbon conversion while the high sulfur content of the coal resulted in high hydrogen sulfide yields and slightly lower hydrogen yields. The high steam to coal ratio (1.8/1) resulted in a high hydrogen to carbon monoxide ratio (3.3/1). Calculations indicate that shift equilibrium for all tests is achieved between the average temperature and the temperature at the top of the bed. The high hydrogen to carbon monoxide ratio would eliminate the need for a shift reactor and can be controlled to give the desired ratio for methanation (~3.05/1) by adjusting the steam to coal ratio.

Table 3 shows the distribution of sulfur forms in the coal and char. Sulfur forms are determined by extraction of the coal and char samples with hydrochloric and nitric acids. The analysis and a weight balance between the coal fed and char produced indicates that most of the sulfur in the coal is converted to hydrogen sulfide and trace sulfur compounds in the gas and tar. About 0.7 weight percent of the sulfate sulfur, 0.3 weight percent of pyritic sulfur and 26.9 percent of the organic sulfur found in the coal remain in the char after gasification. Pyritic sulfur is easily removed by its reaction with hydrogen. (4) The sulfate sulfur is also converted to hydrogen sulfide.

As shown in table 4, there are a number of trace sulfur compounds in addition to the large quantities of hydrogen, carbon monoxide, carbon dioxide, methane, ethane and hydrogen sulfide produced in the gasifier. These trace compounds are separated from the product gas by cryogenic distillation and by measured mass spectrometric analysis. The product gas contains 3.2 volume percent sulfur compounds and would require a sulfur clean up prior to methanation.

The analysis and fusibility of ash for Iowa coal and char are shown in table 5. Certain compounds contained in the ash of coals undoubtedly contribute to the carbon conversion, gasification rates, the quantity and the quality of gas produced. (2, 5, 6) According to Grossman (7) and Ely (8) iron is the major contributor in lowering the fusion temperature of coal ash under reducing conditions. Gasior (2) also found that coals having the greatest percentage of calcium and magnesium compounds have the lowest sintering temperature. Results of these Iowa coal gasification tests appear to confirm these findings since no sintering was observed.

The major effluent problem associated with the steam-oxygen gasification of Iowa coal is the unreacted steam leaving the gasifier as contaminated water condensate. The analysis of this water is shown in table 6 along with a coke plant water analysis for comparison. The amounts of the contaminants vary greatly, but the cyanide and thiocyanate content of the gasification effluent is much smaller than in the coke plant effluent while the phenol and COD content are greater. It is believed that the high steam partial pressure in the SYNTHANE gasifier causes conversion of nitrogen compounds to ammonia. Coke plant water pollution has been alleviated to some extent (9), but some problems still remain. The Iowa coal effluent water analysis shows no significant difference from other reported analyses of SYNTHANE effluent waters. (10)

A coal tar byproduct is also produced from the gasification of Iowa coal. This tar leaves the gasifier as a vapor with the unreacted steam and is easily separated from the effluent water condensate by decanting. The tar is heavier than water and negligible amounts of a lighter-than-water phase are produced. Table 7 shows the analysis and physical properties of the tar produced. For the gasification of Iowa coal, tar yields averaged 7.3 percent of the coal fed, compared to 4.0 percent for Illinois No. 6 coal. Gasior (2) and Nakles (11) have found that feeding the coal below the top of the fluidized-bed can significantly reduce the tar yield. A simulated ASTM distillation of this tar shows that less than 50 percent of the tar boils below 940° F. The high percentage of sulfur (3.2%), however, could drastically limit the direct use of these tars as a fuel. With an effective desulfurization process, the desulfurized tar could be used as a nonpolluting boiler fuel or an oil refinery feedstock.

Conclusions

Overall results from an exploratory study to gasify a mildly caking, high sulfur Iowa coal in the SYNTHANE PDU gasifier have shown that carbon conversions of 80 percent and steam conversions of 16 percent can be achieved at average maximum gasifier temperatures of 1832° F and coal throughputs of 40 lb/hr ft². These results confirm published findings that coals having the largest amount of calcium and magnesium compounds have the lowest sintering temperatures and that the amount of sulfur in the tar and gaseous products is generally related to the amount of sulfur in the coal. The effluent water shows no significant difference from other SYNTHANE gasifier condensates, and is generally similar to coke-oven byproduct water.

Acknowledgment

We especially thank F.R. Schmidt, Metallurgist of ERDA's Ames Laboratory, Iowa State University, Ames, Iowa who provided the coal used in these experiments and performed the coal and char analyses required for the material balance calculations.

Table 1. - Analysis and free-swelling index of Iowa coal

Class	High-Volatile C
Analysis (as received), %	
Moisture	2.9
Volatile Matter	36.2
Fixed carbon	41.2
Ash	19.7
Hydrogen	4.4
Carbon	59.2
Nitrogen	0.8
Oxygen	8.0
Sulfur	7.9
Free-swelling index	1.5

Table 2. - Operating conditions and results for Iowa coal gasification tests in a fluidized-bed at 40 atmospheres pressure

Test No.	209	210	211
Operating time, hrs.	6.0	6.0	6.0
Coal feed rate, lb/hr	17.6	19.5	19.9
lb/hr ft ³ gasifier	37.4	67.0	68.0
Bed height, in.	68.4	67.9	68.0
Steam rate, lb/hr	35.3	35.1	35.3
Oxygen rate, SCFH	75.5	81.5	76.9
Temperature, °F			
peak	1844	1850	1850
average maximum	1761	1832	1832
average	1664	1691	1702
top of bed	1572	1576	1601
Superficial gas velocity at avg. max. temp., ft/sec	0.28	0.29	0.29
Yields and conversions			
Carbon conversion, weight percent	80.2	77.0	78.6
Steam decomposition, weight percent	14.3	15.4	16.9
Product gas ^{1/} yield, SCF/lb coal, maf	13.7	13.5	13.6
Equivalent methane ^{2/} yield, SCF/lb coal, maf	3.60	3.53	3.45
Tar yield, % of coal ^{3/} fed	7.6	7.0	7.4
Product gas analysis, dry, N ₂ free (%)			
H ₂	33.6	33.2	33.7
CO	9.2	10.3	10.7
CH ₄	11.9	12.1	11.9
CO ₂	40.7	39.8	39.1
C ₂ H ₆	1.4	1.4	1.4
H ₂ S	3.2	3.2	3.2

^{1/}H₂ + CO + CH₄ + C₂H₆.

^{2/}CH₄ + C₂H₆.

^{3/}As received after air drying.

Table 3. - Distribution of sulfur forms in Iowa coal and char and the sulfur conversion

	<u>Sulfate</u>	<u>Pyritic</u>	<u>Organic</u>
% S in Coal	0.41	5.18	2.35
% S in Char	0.01	0.05	2.55
lb char/lb coal	0.29	0.28	0.26
% Converted	99.3	99.7	73.1

Table 4. - Trace components in dry product gas^{1/} from the fluidized-bed gasification of Iowa coal with steam and oxygen at 40 atmospheres pressure

Test No.	209	210
Hydrogen Sulfide	11,040	12,000
Carbonyl sulfide	250	250
Methyl mercaptan	<5	<5
Thiophene	<5	<5
Sulfur dioxide	-	-
Benzene	100	N.D. ^{2/}
Toluene	100	N.D. ^{2/}
Xylene	-	-

^{1/}All values in ppm by volume.

^{2/}Not determined.

Table 5. - Analysis and fusibility of ash^{1/} of Iowa coal and char

<u>Major Elements in Ash</u>	<u>Coal, %</u>	<u>Char, %</u>
SiO ₂	35.4	34.1
Al ₂ O ₃	14.0	14.7
Fe ₂ O ₃	39.5	44.0
TiO ₂	0.8	0.6
CaO	3.6	2.8
MgO	0.4	0.3
Na ₂ O	1.3	0.4
K ₂ O	0.9	0.7
SO ₃	1.5	0.1
Fusibility of ash, °F		
Initial deformation temp.	1900	1930
Softening temperature	1950	1980
Fluid temperature	2040	2030

^{1/}Staff, Office Director of Coal Research Methods of Analyzing and Testing Coke and Coal, BuMines Bull. 638, 1967, 82 pp.

Table 6. - Effluent water analysis^{1/} from the fluidized-bed gasification of Iowa coal with steam, and oxygen at 40 atmospheres pressure^{2/}

Test No.	209	210	211	Coke Plant
pH	9.0	9.2	9.1	9.0
Suspended solids	6	16	15	50
Phenol	2060	2340	2180	2000
COD	14500	17400	16800	7000
TOC	4600	4970	4850	N.D. ^{3/}
Thiocyanate	108	129	135	1000
Cyanide	0.029	0.027	0.122	100
Chloride	22	40	118	N.D. ^{3/}
Ammonia	N.D. ^{3/}	N.D. ^{3/}	N.D. ^{3/}	5000

^{1/}Standard method for the examination of water and waste water according to the American Public Health Association; American Water and Waste Water Association, and Water Pollution Control Federation, 13th Edition, 1971.

^{2/}All values in ppm except pH.

^{3/}Not determined.

Table 7. - Product tar analysis and physical properties of dewatered tar from the fluidized-bed gasification of Iowa coal with steam and oxygen at 40 atmospheres

Test No.	210	211
Ultimate analysis of tar, ^{1/} weight percent		
C	83.7	83.8
H ₂	6.6	6.4
N ₂	0.9	1.0
S	3.2	3.2
O	5.6	5.6
Benzene insolubles, weight percent	0.8	1.1
Viscosity, SSU @ 180° F ^{2/}	132	152
Specific Gravity @ 60/60° F ^{3/}	1.151	1.150
ASTM Distillation, weight percent boiling/°F	48.8/940°	40.2/928°

^{1/}ASTM D271.

^{2/}ASTM D88.

^{3/}ASTM D70.

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CHEMICAL BOND CLEAVAGE DURING ASPHALTENE FORMATION¹

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An important question arising from experiments involving coal liquefaction processes is "which bonds are broken when solid coal is converted to liquids, or to soluble oils, asphaltenes, and preasphaltenes?" In earlier work² it was proposed that ether linkages were cleaved and hydrogenolysis occurred during treatment of coal with hydrogen-donor solvents at elevated temperatures. Thus, a limited number of model ether structures were shown to break in the presence of tetrahydroquinoline at 309°. It was also reported^{2,3} that solubilization could not be due to cleavage of single methylene bridges in coal. However, structures containing one methylene group in the bridge, such as diphenylmethane, are stable under the above conditions.

We presented data in a recent manuscript⁴ showing that other structure types undergo thermolysis under the conditions of asphaltene formation. A variety of diaryl- and triarylethanes and ethylenes were found to cleave at the central C-C bond; the derived products were characterized. Certain ethers were found to cleave accompanied by the formation of water.

We have now investigated a large variety of compounds containing structural linkages chosen, partly, from coal models suggested by Given,⁵ Weiser,⁶ and Hill and Lyon.⁷ Some bond types appear to cleave rapidly, others with difficulty, and some not at all. These compounds are arranged in groups and their relation to coal liquefaction is considered. Examples of bonds which break easily are those attaching large groups to the aromatic nucleus of phenols and phenol ethers. Parabenzylphenol is rapidly converted, principally, to toluene and phenol with a little benzene and *p*-cresol. Several products are produced from phenylethyl ether; benzene, toluene, ethylbenzene, phenol, ethane, ethylene, and water.

Implicit in a portion of the above discussion is another important question relating to the structural units in coal. For example, "does it contain any isolated, nonaromatic double bonds?" Hydrogen nmr does not show olefinic structure and carbon nmr is ambiguous. Our solution is based on the stitching and riveting reactions developed by H. C. Brown.⁸ Vitrinite, or a pyridine-soluble fraction of it, was reacted with diborane. Then the hydroborated coal was converted to a trialkylborane derivative by treating it with ethylene gas. Any trialkylborane formed within the coal structure was finally converted to a radioactive-labeled ketone by treatment with radioactive carbon monoxide, or with labeled cyanide ion, followed by hydrolysis. A determination of the specific carbon-14 activity enabled us to calculate the number of double bonds originally present. We are presently applying the above technique to other coal-derived materials. A summary of our data follows:

<u>Sample</u>	<u>Radio. Equiv., Wt.</u>	<u>No. of Carbons Per Double Bond</u>
Vitrinite (Ill. #6)	7300 g.	498
Pyridine-soluble Vitrinite	1500 g.	102
Blank	61000 g.	

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ISOPROPYL ALCOHOL AS A COAL LIQUEFACTION AGENT

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The use of Tetralin and similar H-donor solvents in the hydroconversion of coal to liquid fuels is well known (1), and is important in large-scale coal conversion processes (2). We present here evidence that isopropyl alcohol can act as an H-donor solvent, yielding products similar to those generated in Tetralin-based systems. Contrary to the case for Tetralin, it appears that the action of the isopropyl alcohol can be promoted by the presence of bases. This report presents initial data from a research program still in progress; a full account of the work will be presented in a subsequent manuscript.

EXPERIMENTAL PROCEDURES

The experiments described here were carried out in a 300-ml MagneDrive, stainless steel autoclave from Autoclave Engineers. The substrate was beneficiated Illinois No. 6 coal supplied by Pennsylvania State University (PSOC 26), and ground under nitrogen in a ball mill to -60 mesh. In each run, 5-g samples of the coal were used, in addition to 75 to 150 g of alcohol solvent. These experiments were run at 335°C for 90 min, with typically 45 min heat-up and 60 min cool-down periods. No hydrogen was used in any of the experiments described, and the pressures are those generated by the solvents themselves. The reaction temperature of 335°C was above the critical temperatures of the alcohols used.

In these experiments the product mixture was filtered, the residue washed with more solvent until the washings were colorless, and the filtrate recovered by evaporation of the solvent under vacuum. For those cases in which alkoxide salts were used, all fractions were appropriately neutralized with concentrated HCl. Both the filtrate and residue were then dried to constant weight at 110°C under < 1 torr pressure. Mass balances were generally greater than 95%. In all cases the isolated filtrate was found to be fully pyridine-soluble. Pyridine solubilities of the residues were determined at room temperature, with 0.5 g of a product coal fraction stirred for 1 hr in 50 ml pyridine. The pyridine solubilities of the residues were established for all cases and recorded as the fraction of the residue soluble in pyridine. For some cases, it was convenient to refer to the composite pyridine solubilities and elemental composition values, that is, these values for the entire coal sample. In these instances the individual values for both the filtrates and residues were appropriately summed and recorded.

H_{al}/H_{ar} ratios were obtained from the proton NMR spectra, which were run on a Varian EM 360 spectrometer using nearly saturated solutions of sample in pyridine- d_5 or CS_2 /pyridine- d_5 mixtures. The SRC used was supplied by Catalytic, Inc., Wilsonville, Alabama, sample number 16573, derived from an Illinois No. 6 coal and processed to K109 SRC specification.

RESULTS AND DISCUSSION

Autoclave Experiments

The results of a series of experiments run at 335°C with a number of solvents are summarized in Table 1. The figures for the pyridine solubilities and elemental analyses are composite values, calculated from the respective values for both the filtrate and residue from each run.

Table 1
TREATMENT OF BENEFICIATED ILLINOIS NO. 6 COAL
AT 335°C FOR 90 MINUTES^a

Run No.	Conditions ^b	Pyridine ^c Solubility (%)	Elemental Analyses ^d			
			H/C (molar)	O/C (molar)	N (%)	S (%)
-	Untreated coal	17	0.79	0.117	1.58	2.20 ^e
21	iPrOH ($\rho = 0.5$)	50	0.81	0.086	1.63	1.82
53	iPrOH + Al(OiPr) ₃ ^f ($\rho = 0.3$)	61	0.87	0.073	1.64	1.81
54	iPrOH + K(OiPr) ^g ($\rho = 0.3$)	97	0.95	0.090	1.69	0.11
62	iPrOH + K(OiPr) ^g ($\rho = 0.3$)	89	0.83	-	1.33	-
36	tBuOH ($\rho = 0.2$)	13	-	-	-	-
61	tBuOH + K(OtBu) ^f ($\rho = 0.5$)	12	-	-	-	-
48	Tetralin ^h	48	0.81	0.079	1.58	1.83

^aNo hydrogen is added to the system; the pressure during a run is in the range of 2000 psi, and due only to the vapor pressure of the medium. The starting coal has been beneficiated to about 2% ash.

^bSince 335°C is above the T_c of both alcohols, the amount of solvent present is expressed as ρ , the number of g of alcohol per ml of reactor volume (285 ml).

^cSolubility of recovered material in pyridine, based on ash free weight of the starting coal. Composite values, as discussed in the text.

^dAsh-free basis. Composite values, as discussed in the text.

^eThis value represents the organic sulfur in the starting coal.

^f1 g metal alkoxide/5 g coal was used.

^g0.5 g potassium salt/5 g coal was used.

^hThe critical temperature of Tetralin is $484 \pm 32^\circ C$. Thus the medium here was subcritical.

The table shows that the untreated coal has a pyridine solubility of 17%. In Run 21, in which the coal is treated with isopropyl alcohol, the resulting product coal displays a solubility in pyridine of 50%. This result is clearly significant, and is comparable to the results for a similar experiment with Tetralin, Run 48,

where the resultant coal product shows a 47% pyridine solubility. The surprising similarity of the elemental analyses for the products in both cases leads us to conclude that, like Tetralin, isopropyl alcohol acts as an H-donor under these conditions.

An alternative possibility is the introduction of isopropoxy groups to the coal, which would possibly increase both the solubility and the H/C ratio. This route is most likely ruled out for Run 21, however, on the basis of the decrease in the O/C ratio with respect to the starting coal.

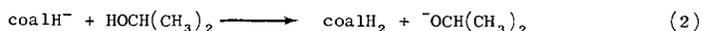
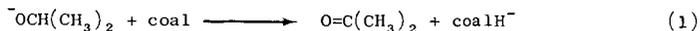
This point is confirmed by the results of Run 36, where t-butyl alcohol was used. The structural differences between isopropyl and t-butyl alcohols are insignificant for work at these temperatures, and if alkoxylation were important, it would take place with both alcohols. The pyridine solubility of the product coal from the t-butyl alcohol experiment, however, is somewhat less than that of the starting coal, and significantly less than the results for Runs 21 and 48. These data thus support our contention that for the isopropyl alcohol case no incorporation of solvent into the coal has taken place. On the other hand only the isopropyl alcohol can provide hydrogen, perhaps as hydride, as discussed below. The large difference in the results is thus consistent with H-donation by isopropyl alcohol.

These results suggest a similarity in general mechanism to the known Meerwein-Ponдорff reduction of carbonyl groups with isopropoxide salts, most commonly aluminum isopropoxide in isopropyl alcohol (3). In this reaction hydride ion from the oxygen-bearing carbon in the alcohol is transferred to a carbonyl group, thereby reducing it. To test this possible mode of reaction, aluminum isopropoxide was added to the reaction mixture in Run 53 and potassium isopropoxide was added in Run 54.

For Run 53, the product is 61% soluble in pyridine, somewhat enhanced relative to the value for isopropyl alcohol alone. For the potassium isopropoxide case the result is striking. The product coal is essentially fully pyridine-soluble, and additionally, the organic sulfur in the coal has been reduced to the low value of 0.41%.

While these data strongly support a hydride transfer process, it might be proposed that the results were due to some kind of base-promoted dissolution. This possibility was eliminated by the data from Run 61, in which potassium t-butoxide in t-butyl alcohol was used. Here the result is little different from that for t-butyl alcohol alone.

Thus it can be concluded that isopropyl alcohol can act as an H-donor solvent for coal conversion in a process involving hydride transfer from the alcohol, or alkoxide salt, to the coal. The net transfer of H₂ to the coal could involve a chain process, such as



in which the alkoxide ion is regenerated with each cycle, H_2 has been transferred to the coal, and acetone is formed. The formation of acetone has in fact been confirmed qualitatively, and experiments are currently under way to assess the quantitative nature of the process.

Product Characterization

While we have written reaction (2) with the notation $\text{coal}H_2$, we do not wish to imply that simple hydroaddition to multiple bonds has necessarily occurred. The question of the specific site of hydrogen reaction remains open, and it is of interest to establish the degrees to which hydroaddition and hydrocracking have taken place.

Accordingly, it is convenient to look at our product data in more detail, namely in terms of the separated fractions of the product coal. Table 2 presents data for the fraction of the starting coal isolated from the solvent after reaction, the H/C and H_{al}/H_{ar} ratios for that fraction, the H/C ratio of the residue, and the solubility of the residue in pyridine. Also given are H_{al}/H_{ar} for the starting coal, for the residue from the potassium isopropoxide experiment, and for an Illinois No. 6 SRC. The values for pyridine solubility of the residue are given as the fraction of the residue soluble in pyridine. For example for Run 21, of the starting 5 g of coal, 1.0 g, or 20%, was recovered from solution in isopropyl alcohol at the end of the run. Of the remaining 4.0 g of residue, 1.5 g, or 37.5% was soluble in pyridine.

Table 2
ILLINOIS NO. 6 COAL WITH VARIOUS MEDIA
AT 335° FOR 90 MINUTES

Run No.	Medium	Filtrate ^a			Residue		
		Fraction of Starting Coal ^b (%)	H/C	$\frac{H_{al}}{H_{ar}}$	H/C	$\frac{H_{al}}{H_{ar}}$	Pyridine Solubility ^c (%)
Untreated coal	-	-	-	-	0.79	5.2 ^d	17.0
25	Heptane	1.7	1.20	3.2	0.79	-	6.9
48	Tetralin	17.5	0.95	2.2	0.79	-	35.8
21	i-Propyl alcohol	20.0	0.95	2.1	0.78	-	37.5
54	KO _i Pr/ i-propyl alcohol	40.0	1.08	3.4	0.87	1.8	95.0
SRC	-	-	-	-	0.75	1.2	99.0 ⁺

^aThe solubilities of the untreated coal in the media are $\leq 1\%$ for all cases.

^bThese values represent the solubilities of the resultant coal products in the respective media. The filtrates were found to be completely pyridine soluble in all cases.

^cThese values represent the fraction of the isolated residue soluble in pyridine.

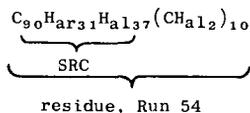
^dG. Hill, H. Hariri, R. Reed, and L. Anderson, *Advances in Chemistry Series 55*, 427 (1966).

Results for an experiment with heptane (Run 25) are presented in the table for comparison. Clearly the heptane run did not result in much coal dissolution, nor did the residue display any unusual behavior.

For Runs 48 and 21, however, with Tetralin and isopropyl alcohol, respectively, about a fifth of the starting coal is converted to material soluble in the media themselves, and the H/C ratios are enhanced. The residues for both cases have also undergone chemical change. For both the Tetralin and the alcohol experiments the residues are 35-40% pyridine-soluble. The H/C values for these fractions, however, are essentially the same as that for the starting coal. Thus it would appear that, for both solvents, a chemical process is taking place that (1) adds hydrogen to some fraction of the coal, converting it to material soluble in the respective media, and (2) generates a residue with a large pyridine solubility, but with no significant increase in hydrogen content.

The results for Run 54 with potassium isopropoxide show that 40% of the starting coal is converted to a product soluble in the reaction medium. That fraction is considerably enriched in hydrogen, and a substantial fraction of the added hydrogen is aliphatic, comparable to the small quantity of material isolated from the filtrate of the heptane experiment. The residue in this case is essentially fully pyridine-soluble and, in contrast to those for Runs 21 and 48, has been enriched in hydrogen. The H/C and H_{al}/H_{ar} data are reasonably similar to those shown in the table for SRC, although it is clear that our product has more overall aliphatic character than the SRC. Both are also considerably more aromatic in character than the starting coal, although the H_{al}/H_{ar} value for the coal is for an "average coal" and is probably only a rough, semiquantitative value of the ratio for our starting coal.

If just the hydrogen and carbon contents are considered, the values for both the Run 54 residue and the SRC permit the calculation of an average molecule for both. Interestingly, the data for both can be accommodated by



This result includes number average molecular weight data in the range 1000-1300, which we have obtained for both materials. It appears that the two may be simply related, with additional polymethylene bridges, or hydroaromatic components, present in our product. The implications of this result await further study.

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HYDRODESULFURIZATION IN THE SOLVENT REFINED COAL PROCESS

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The Solvent Refined Coal (SRC) process is currently recognized as one of the more promising processes for producing an environmentally acceptable boiler fuel from coal. In the SRC process, coal is liquefied to allow removal of entrained mineral matter by physical separation methods and reacted with hydrogen to remove chemically part of its organic sulfur. Liquefaction of coal has been shown to occur almost instantaneously upon reaching reaction temperatures while in the presence of a hydrogen-donor solvent, the overall rate limiting step in liquefaction being rehydrogenation of process solvent - which may be performed separately in the recycle stream - to replenish hydrogen-donor species (1,2). Based on data collected in this laboratory hydrodesulfurization (HDS) of coal, on the other hand, appears to be a much slower reaction. As a result, the kinetics of HDS will be a primary, if not the controlling factor in the design and operation of the dissolver/reactor in the SRC process.

In the present work, an experimental evaluation is made of the feasibility for accelerating HDS of coal by simply varying reaction conditions and utilizing coal mineral matter and/or other cheap regenerable catalysts. The rate data reported were all obtained in a batch system; and, except for one series of experiments, only one coal type, a bituminous Kentucky No. 9/14, was used. Experimental methods and materials are given in (2), except as noted herein. A reaction model was developed that gives an excellent fit to the experimental data. The model, as well as other results of the comparative studies performed, is intended to assist in predicting and interpreting results from pilot studies of the SRC process, such as those at Wilsonville, Alabama, and Tacoma, Washington. The model provides also a useful design tool; but, for a reaction system as complex as the one dealt with here, it would be presumptuous to suggest that it represents the true mechanism.

In a previously reported catalyst screening study (5), several minerals indigenous to coal were shown to have a catalytic effect on the HDS of creosote oil. Of particular interest was the observation that in the presence of reduced metallic iron the HDS rate of the oil was significantly higher than that resulting when no mineral was present; whereas, in the presence of pyrite the HDS rate was about the same as it was when no mineral was present. These observations were surprising in that both reduced iron and pyrite are converted into the sulfide form (pyrrhotite) within the first fifteen to twenty minutes of reaction. Based on these observations, to further examine the practicality of coal mineral catalysis, a series of experiments was performed to ascertain whether the acceleration of the HDS rate in the presence of iron was predominantly thermodynamic or catalytic in nature. It is possible that iron, by removing H_2S , promotes HDS by Le Chatelier's principle, or simply prevents the H_2S from reducing the activity of catalytic sulfides by preferential adsorption.

Basic Nature of Reactions

The influent coal/oil slurry to the reactor/dissolver in the SRC process includes a wide variety of sulfur-containing compounds; thiols, disulfides, sulfides, thioethers, γ -thioopyrone, thiophenes, dibenzothiophenes, and other heterocyclic sulfur compounds. In general, thiols, disulfides, sulfides, thioethers, and γ -thioopyrone are very reactive - undergoing hydrogenolysis at an appreciable rate, forming H_2S and hydrogenated compounds, without the aid of a catalyst; whereas, heterocyclic sulfur compounds are much less reactive - requiring a catalyst to achieve an acceptable HDS rate. As a result of the large difference in reactivity of these two groups of sulfur-containing

compounds and to simplify analysis, the HDS reactions involving individual compounds in each of these two groups sometimes are lumped together; and HDS of a coal/oil slurry is often treated as if there were only two reactive compounds (3,4).

In addition to HDS reactions, under reaction conditions used in the SRC process, hydrocracking (i.e., breaking of C-C bonds) and hydrogenation reactions also occur. It is by means of these reactions - particularly cracking reactions - that coal solids are converted into lower molecular weight components that are soluble in SRC process solvent, allowing removal of entrained mineral matter by subsequent physical separation methods. These reactions take on importance, other than liquefaction of coal solids, by consuming hydrogen in the process without removing sulfur. Only that amount of hydrogenation, or cracking, required to liquefy coal solids and allow mineral matter removal is desired. Any excess hydrogenation beyond this amount, such as in the formation of C₁ - C₄ gases, etc., results in inefficient use of hydrogen, thus higher operating costs. This should be avoided as much as possible. Actually SRC product contains a slightly lower hydrogen/carbon ratio (H/C = 0.75) than the feed coal itself (H/C = 0.8). Furthermore, the stoichiometric amount of hydrogen required solely for removal of an acceptable amount of sulfur as H₂S in the SRC process is an order-of-magnitude less than the total amount of hydrogen currently consumed (two weight per cent of MAF coal feed) at the Wilsonville, Alabama, and the Tacoma, Washington, SRC pilot plants. Excess hydrogenation therefore accounts for most of the hydrogen consumed in producing solvent refined coal.

The rate of noncatalytic (except for mineral matter) HDS, unlike that of hydrogenation, appears to be relatively insensitive to hydrogen concentration, in the form of either dissolved molecular hydrogen or readily transferable hydrogen such as that attached to donor species (e.g., tetralin) contained in the process solvent. Variation, for example, in initial hydrogen partial pressure from 1000 to 2600 psig at reaction temperature had no significant effect on the final organic sulfur content of a coal/creosote-oil reaction mixture, even after two hours of reaction (Table 1). Also, as shown in Table 2, the reduction in total sulfur content of the coal was essentially the same after fifteen minutes of reaction when slurried with creosote oil - which contained only trace amounts of tetralin and other known hydrogen-donor species - as when slurried with pre-hydrogenated creosote oil - which, like the SRC recycle oil used, contained significant amounts of tetralin and 9,10 dihydrophenanthrene. The rate of liquefaction, on the other hand, was significantly higher when the coal was extracted in prehydrogenated creosote oil. When reacted in an inert nitrogen atmosphere, the cresol-soluble yield was almost twice that obtained when the coal was extracted with untreated oil. The high sensitivity of the rate of liquefaction, as opposed to the relative insensitivity of HDS to hydrogen concentration is further evidenced in that the cresol-soluble yield was significantly higher when the coal was reacted in an initial 2000 psi hydrogen atmosphere, both when slurried with creosote oil and also when slurried with pre-hydrogenated creosote oil. Also, solvent-to-coal ratio had no significant effect on HDS rate relative to that of liquefaction (Table 3).

The rate limiting step in liquefaction has been shown to be the reaction of dissolved molecular hydrogen with the donor solvent, with the transfer of hydrogen from the donor solvent to coal solids occurring rapidly (1,2). In fact, when extracted in a highly active hydrogen donor solvent such as hydrogenated creosote oil, coal solids have been observed to liquefy almost instantaneously upon reaching reaction temperature (1). Thus the observed sensitivity of the rate of liquefaction to hydrogen concentration should be expected. Furthermore, as long as solvent quality (i.e., a sufficiently high hydrogen-donor concentration) is maintained - which can be done independently by hydrogenating the recycled process

solvent as is done in the Exxon process - with liquefaction occurring almost instantly. HDS should be the controlling factor in the design and operation of the dissolver/reactor. HDS kinetics thus take on a special importance for the commercialization and development of the SRC process.

Coal Mineral Catalysis

A limited experimental evaluation of process advantages and disadvantages of coal mineral catalysis was presented in an earlier work (5). As part of this evaluation, twelve different coal minerals and, also, actual SRC mineral residue as well as coal ash were individually screened to rate their catalytic activity on the HDS rate and hydrogenation of creosote oil relative to that of a commercial Co-Mo-Al catalyst. Some results of this earlier work are given in Table 4 and in Figures 1 and 2. Reduced iron, reduced pyrite (presumably pyrrhotite), and pyrite had decreasing effects on sulfur removal during hydrogenation/hydrodesulfurization of creosote oil at 425°C, with reduced iron being second only to Co-Mo-Al in catalytic activity for HDS and with pyrite, despite its pronounced effect on hydrogenation, having essentially no apparent catalytic activity for HDS. The relatively insignificant effect of pyrite on HDS rate was further evidenced in that the rate of organic sulfur removal from coal slurried in creosote oil remained essentially the same even after about seventy-five per cent of its pyritic content had been removed physically by magnetic separation prior to reaction (Figure 3). Reduced iron, on the other hand, was found to have a significant effect on HDS reactions when present in only trace amounts (Table 5).

The stable form of iron in the presence of hydrogen and hydrogen sulfide in the temperature range of 400 to 500°C is pyrrhotite (6,7). As shown in Figure 4, pyrite is reduced to the sulfide (presumably pyrrhotite) within about fifteen minutes of reaction at 425°C. Rapid reduction of pyrite coal minerals has also been observed to occur in the dissolver/reactor at the Wilsonville SRC pilot plant (8). H₂S product from the reduction of pyrite is thus generated in the early stages of HDS. H₂S is known to inhibit catalytic HDS of petroleum feedstocks; thus, since some of the same sulfur-containing components in petroleum feedstocks exist also in coal/oil slurries, H₂S may inhibit HDS of coal/oil slurries, or possibly react with previously desulfurized components. Therefore, since reduced iron acts as an H₂S scavenger, instead of an H₂S producer as does pyrite, one possible reason for the differences in catalytic activities of reduced iron, reduced pyrite, and pyrite could be the different amounts of H₂S present during HDS as is shown in Table 4. In fact, the H₂S partial pressure was increased by a magnitude of two to three by the reduction of pyrite; whereas no traceable amount of H₂S product was present during the reduced iron run. Also, when different weight percentages of iron were charged with creosote oil (Table 5), no H₂S product was detected until less than one per cent by weight of iron was present. Interestingly enough, when iron was present in higher weight percentages (2.4 to 20%), the amount of sulfur removed during reaction was only slightly different, and when present in lower percentages (1.0 to 0.5%), it decreased in proportion to the amount of iron present, with trace amounts of iron being as effective as 0.5 weight percent. The retarding effect of H₂S on HDS is further evidenced in that when H₂S was added prior to reaction the amount of sulfur removed was less during hydrogenation/HDS of both a bituminous Kentucky No. 9/14 mixture coal and a sub-bituminous (Wyodak) coal (Table 10).

When iron gauze was used to scrub out any H₂S product formed during hydrodesulfurization of creosote oil, while being mounted in the top of the reactor above the oil, the amount of sulfur removal was about 20% higher than that obtained without any scavenger agents present; that is, the final sulfur content of the oil was 0.39% as opposed to 0.50%, a decrease equivalent to that obtained when one

weight percent of iron was present. Apparently then, H₂S does have a retarding effect on HDS as might be expected from thermodynamics.

When five weight percent iron and a sufficient amount of H₂S (to prevent its complete removal by reaction) were present during HDS of creosote oil, the amount of sulfur removal was only the same as that when either a trace amount or a half weight percent of iron was present (Table 5). Apparently H₂S retards the effectiveness of iron sulfide as a catalyst, with trace amounts of iron sulfide having about the same catalytic effect on HDS rates as larger amounts when an appreciable H₂S atmosphere exists. Since H₂S does have a thermodynamic effect on the HDS reactions; however, the severity of its catalytic inhibition effect is not completely defined.

In summary then, reduced iron appears to favor HDS by scavenging H₂S product, preventing any reverse reactions and by catalyzing HDS reactions. Unfortunately, as shown in Table 6, reduced iron, like most HDS catalysts, also accelerates hydrogenation; as a result its use as a catalytic agent in the SRC process could contribute to excess hydrogenation. Because of its potential as an inexpensive HDS catalyst, however, further experiments are now in progress to better evaluate its role in accelerating HDS reactions and its selectivity for HDS versus hydrogenation.

Hydrodesulfurization Kinetics in the SRC Process

As shown in Figure 5, the variation of organic sulfur content of a coal/creosote-oil reaction mixture with time follows a path close to that expected for an overdamped second order dependence of rate on organic sulfur content. This kinetic behavior is consistent with the basic nature of HDS reactions as described in the foregoing discussion, in that it can be modelled by considering the reaction mixture to contain only two hypothetical sulfur-containing compounds with significantly different rate constants. The desulfurization reaction of each of the two hypothetical components is assumed to follow first-order kinetics. A test as to whether this assumed kinetic model is representative is the difference in magnitude of the experimental rate constants, for the actual two groups of lumped sulfur components are known to react at two widely differing rates. The large difference in slope of the two lines in Figure 6 indicates that the experimental rate constants are indeed significantly different, attesting that the model is representative.

The high sensitivity of HDS rate to reaction temperature and its low sensitivity to hydrogen concentration suggested that the HDS reactions were chemically controlled and pseudo-homogeneous kinetics were thus used in modeling. Furthermore, since the retarding effect of H₂S and the catalytic effect of pyrite coal minerals apparently either offset each other or exist to such an extent that the effect on HDS rate is insignificant - as a first-hand approximation-no kinetic terms were used to represent the reverse reaction by H₂S product. The rate equation was thus written as:

$$r_{\text{HDS}} = -k_1 S_1 - k_2 S_2 \quad (1)$$

where: S₁, and S₂ are the organic sulfur concentration (g/cc) present in the form of the two hypothetical sulfur-containing components, respectively. For a batch reactor,

$$S = S_{10} e^{-k_1 t} + S_{20} e^{-k_2 t} \quad (2)$$

The adjustable parameters S_{10} , S_{20} , K_1 and K_2 were determined empirically, using a nonlinear minimum sum-of-the-squares numerical search routine. The Arrhenius relationship was assumed, and rate data for three different reaction temperatures were used in determining empirical values for the four adjustable parameters. A list of these values is given in Table 7; and a comparison between predicted HDS paths and rate data is made in Figure 5, showing good agreement. Also, the Arrhenius plots of the empirical rate coefficients are given in Figure 6. The rate coefficients for the two hypothetical components differ by two orders of magnitude (Table 8), in consistency with the large difference in slopes of the two straight lines in Figure 6. In addition, the high activation energy (Table 8) for the reactive sulfur-containing component provides further evidence that the desulfurization reactions are chemically, rather than mass transfer controlled. Note that there is no catalyst present, except for the indigenous coal mineral matter. Finally, as shown in Table 9, the energies and enthalpies of activation are indicative of chemical rate processes, rather than transport processes. The high activation energy and low entropy of activation for the fast reaction are indicative of a homogeneous reaction; the lower values for the slow reaction indicate a possible catalytic effect, perhaps due to coal mineral matter. Here again, however, since the exact reaction mechanism is unknown, one must exercise caution when attaching significance to these numerical values.

Conclusions

Hydrodesulfurization reactions occur, under reaction conditions used in the SRC process, at a rate that is practically independent of hydrogen concentration. Reduced iron has a catalytic effect on HDS reactions; in fact, it exhibits a significant memory effect. Because of additional H_2S product, pyrite has only a slight catalytic effect on HDS reactions. The retardation of HDS reactions by H_2S product is due to catalytic inhibition as well as thermodynamic effects. HDS reactions can be modeled as two first-order reactions occurring in parallel, with two widely different rate constants.

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Table 1
 NETS AND ORGANIC SULFUR
 IN REACTOR MIXTURE

Reacting Temp., °C.	Reaction Time Min.	2600 PSI		7000 PSI		1000 PSI		Average Total Organic
		Total Organic						
385	15	.85	.82	.94	.81	.95	.82	.95
410	15	.88	.75	.89	.76	.81	.73	.82
435	15	.81	.68	.81	.69	.84	.71	.82
385	30	.89	.76	.90	.77	.89	.76	.89
410	30	.81	.68	.83	.70	.86	.73	.89
435	30	.73	.63	.73	.68	.89	.67	.89
385	60	.81	.70	.87	.74	.89	.76	.86
410	60	.75	.68	.81	.72	.86	.73	.86
435	60	.73	.60	.74	.61	.73	.60	.73
385	120	.81	.68	.87	.74	.89	.76	.89
410	120	.75	.61	.75	.63	.86	.73	.86
435	120	.65	.53	.66	.53	.69	.56	.67

Table 2. Effect on Gaseous Hydrogen and Solvent Type on Liquefaction and Hydrodesulfurization of Coal

Solvent Type	Atmosphere (atm)	Conversion (Based on Cresol Solubles) %	Total Sulfur in Reaction Mixture	Total Sulfur in Solvent (±)	Total Sulfur in Total Solvent (±)
Cresote Oil	2000 psi H ₂	42.1	.90 ± .02	.5	2.0
Hydrogenated Cresote Oil	2000 psi H ₂	83.1	.49 ± .03	trace	2.0
Psycyle Oil (Sample No. 16171)	2600 psi H ₂	70.9	.73 ± .01	.25	2.1
Cresote Oil	2000 psi H ₂	61.0	.91 ± .05	.5	2.1
Hydrogenated Cresote Oil	2000 psi H ₂	90.7	.51 ± .03	trace	2.0
Psycyle Oil (Sample No. 16171)	2000 psi H ₂	85.8	.75 ± .02	.26	2.2

NOTE: Reaction Time = 15 min.
 Solvent-to-Coal Ratio = 3/1
 Reaction Temperature = 410°C

Table 3
Effect of Solvent/Coal Ratio on Hydrodesulfurization and Liquefaction

Solvent-to-Coal Ratio	Temperature (°C)	Conversion based on Cresol Solubles	Residual Organic Sulfur
1.5/1	410	84.5	1.45
2/1	410	85.3	1.39
3/1	410	90.7	1.55
3/1	385	80.4	1.66
4/1	385	83.6	1.81

Operating Conditions: 2,000 rpm
2,000 psig H₂

Reaction Time = 15 min.

Initial organic sulfur = 1.63

Table 4
CATALYST SCREENING RUNS:
LIQUID S SULFUR, TOTAL PRESSURE, AND FINAL GAS COMPOSITION

MINERAL	% S	TOTAL PRESSURE (10 ⁻³ PSI)	PARTIAL PRESSURES (PSI)				
			H ₂ (10 ⁻³)	H ₂ S	CO ₂	CH ₄	C ₂ -C ₅
NONE	0.52	2.40	2.13	10.	2.5	64.	18.
NONE	0.46	2.42	2.23	7.1	2.0	62.	24.
MUSCOVITE (-80)	0.39	2.18	1.94	8.5	1.0	51.	20.
PYRITE (-80, + 150)	0.41	1.99	1.54	230.	1.1	99.	36.
IRON (-325)	0.27	1.98	1.75	<1.	12.	16.	20.
REDUCED PYRITE	0.36	1.96	1.85	17.	0.4	61.	18.
COAL ASH	0.23	1.92	1.72	<1.	1.4	57.	15.3
SIDERITE	0.34	1.81	1.61	<1.	67.	93.	29.
SRC SOLIDS (-325)	0.32	1.73	1.48	13.	24.	85.	30.
PYRITE (-325)	0.55	1.63	1.22	196.	7.3	133.	71.
Co-Mo-AL (-80, + 150)	0.02	1.12	0.92	<1.	1.9	128.	74.
Co-Mo-AL (-325)	0.02	1.02	0.73	1.7	1.3	138.	79.

Table 5. Effect of Iron Concentration On Hydrodesulfurization of Cresote Oil

Iron Concentration (weight percent)	Final H ₂ S Partial Pressure (Pst)	Residual Sulfur (percent)
20.	0.	.34
20.	0.	.34
13.	0.	.35
13.	0.	.36
13.	0.	.35
4.7	0.	.35
2.4	0.	.38
0.99	8.	.40
0.49	66.	.43
trace (memory effect)	63.	.42
trace (memory effect)	--	.45
0	36.	.50
0	67.	.50

Reaction Conditions:

Temperature = 425°C
H₂ Pressure = 3000 psig @ 425°C
Agitation Rate = 1000 rpm
Initial Sulfur Concentration = 0.64 percent
Reaction Time = 2 hours

Table 7

Hydrodesulfurization Model Parameters

S ₁₀	1.53 x 10 ⁻³ g/cc
S ₂₀	6.51 x 10 ⁻³ g/cc
K ₁ (385°C)	1.69 x 10 ⁻² min ⁻¹
K ₁ (410°C)	5.30 x 10 ⁻² min ⁻¹
K ₁ (435°C)	15.32 x 10 ⁻² min ⁻¹
K ₂ (385°C)	8.15 x 10 ⁻⁴ min ⁻¹
K ₂ (410°C)	13.89 x 10 ⁻⁴ min ⁻¹
K ₂ (435°C)	22.74 x 10 ⁻⁴ min ⁻¹

Table 8

Arrhenius Constants

ln K ₁₀	27.11	min ⁻¹
ln K ₂₀	7.417	min ⁻¹
ΔE ₁	40.78	kcal
ΔE ₂	18.99	kcal

Table 9

Comparison of Energies, Enthalpies, and Entropies of Activation of Hydrodesulfurization with Data for Hydrodesulfurization of Coal Tar over WS₂ Catalyst.*

	HDS Model		Coal Tar*	kcal/mole
	Reaction 1	Reaction 2		
ΔE	40.7	38.9	11	kcal/mole
ΔH	39.2	15.8	9	kcal/mole
ΔS	-16.8	-58.2	-50	E.U.

*S. A. Quader, W. H. Wiser, G. R. Hill

I. & E.C. Process Design and Development

Vol. 7, No. 3, 395, July, 1968

Table 6: Comparison of Hydrogenation and Hydrodesulfurization of Cresote Oil in the Presence of Iron Catalyst

Wt. % Fe	(H/H ₀)AVG	(S _F /S ₀)AVG
0	0.80	0.78
0.5	0.71	0.63
1.0	0.74	0.62
2.4	0.74	0.58
4.7	----	0.55
13.0	0.69	0.56
20.0	0.64	0.52

Table 10: Effect of H₂S on Rate of Hydrodesulfurization of Kentucky and Wyodak Coals

Atmosphere	Coal Type	Solvent Type	Solvent-to-Coal Ratio	Cresol Soluble Yield (%)	Total % Sulfur Before	Total % Sulfur After	% Sulfur Liquid Fraction	% Sulfur Solid Fraction
H ₂	Wyodak	Recycle	3:1	76.0	0.52	0.41	0.35	1.15
H ₂ + H ₂ S	Wyodak	Recycle	3:1	76.6	0.52	0.72	0.62	2.04
H ₂	Kentucky 9/14	Recycle	2:1	86.4	1.10	0.80	0.52	2.86
H ₂ + H ₂ S	Kentucky 9/14	Recycle	2:1	88.9	1.10	0.98	0.60	3.58

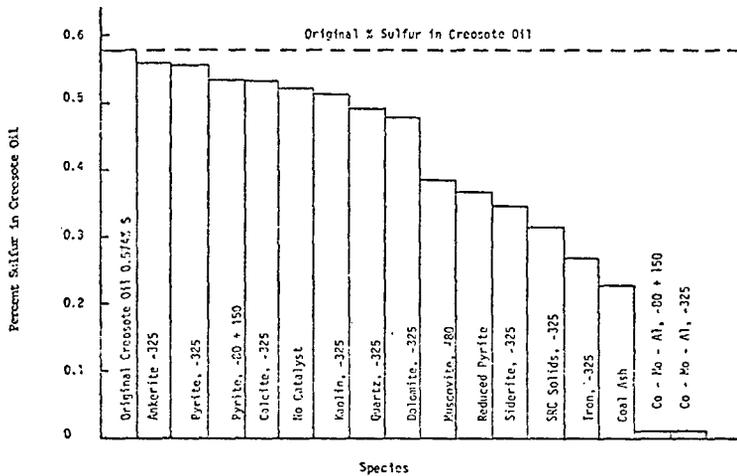


Figure 1. COMPARISON OF DESULFURIZATION ACTIVITY OF CATALYST

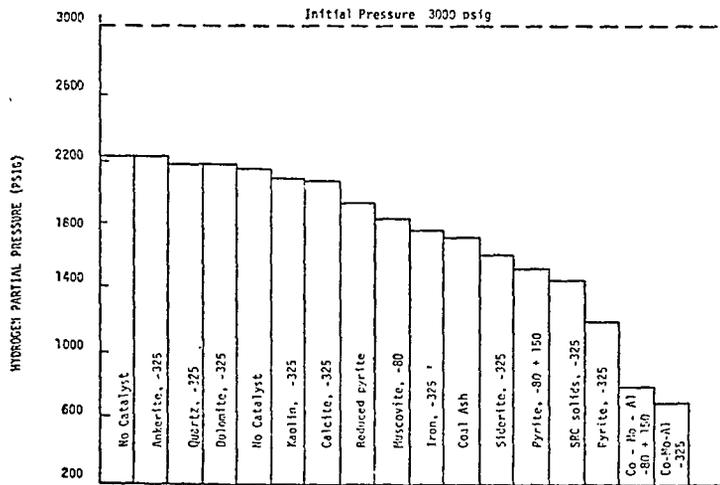
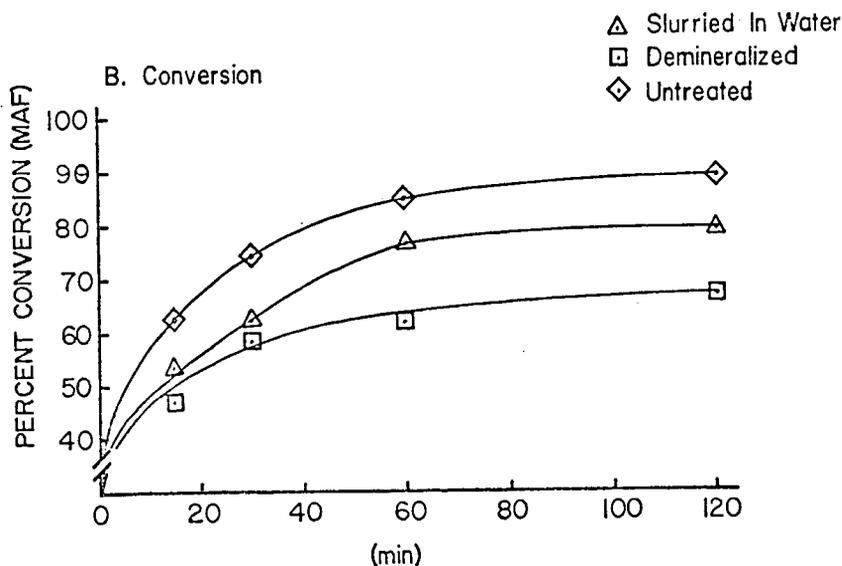
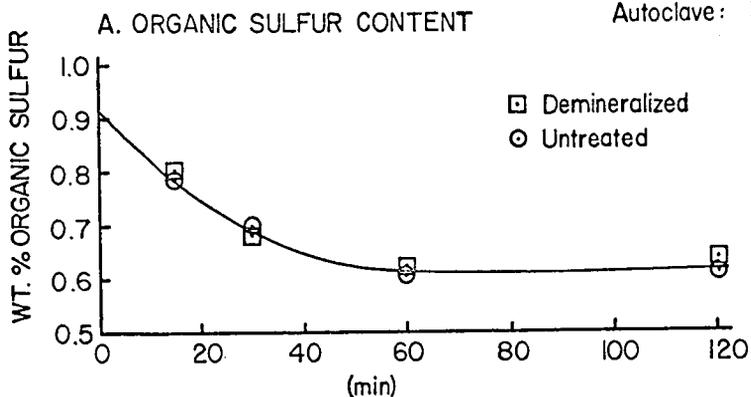


Figure 2. COMPARISON OF HYDROGENATION ACTIVITY OF CATALYST

Figure 3. Effect of Demineralizing Coal Feed and Slurrying Coal Feed with Water on Conversion

Temperature: 410° C
 H₂ Pressure: 2000psig @ 410°C
 Agitation Rate: 1000 rpm
 Autoclave: 300 cc



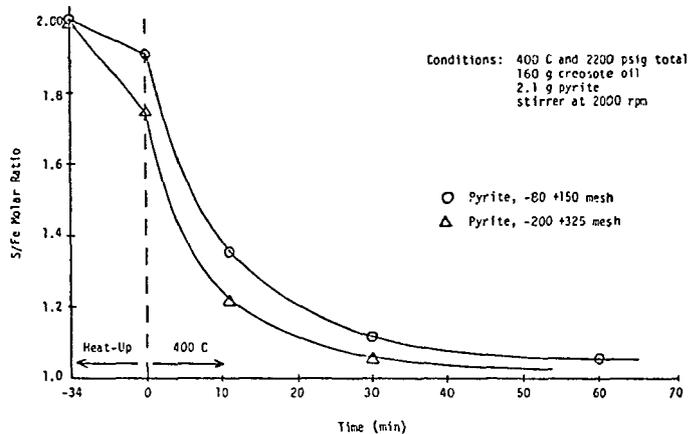


FIG. 4. PYRITE REDUCTION AS A FUNCTION OF TIME

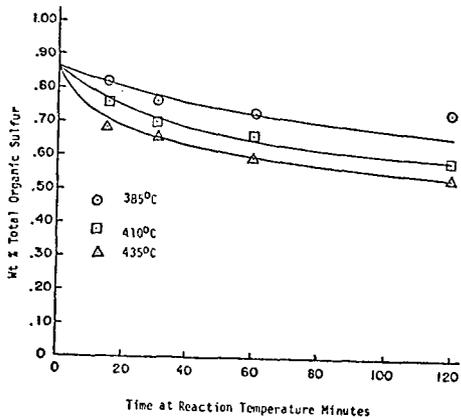


Figure 5. Effect of Reaction Temperature on Organic Sulfur Concentration

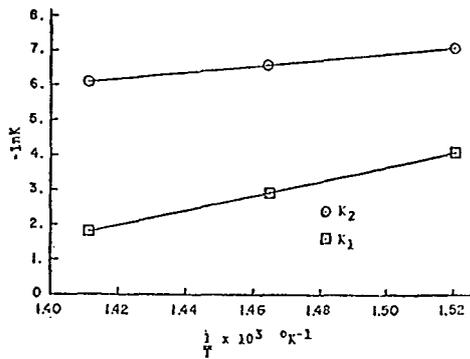


Figure 6. Arrhenius plot for hydrodesulfurization

PREPARATIVE GPC SEPARATIONS OF SOLVENT REFINED COALS. W. M. Coleman, D. L. Wooton, H. C. Dorn and L. T. Taylor, Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

A preparative quantitative separation of the THF soluble portion of several solvent refined coals (Pittsburg #8, Amax, etc.) has been demonstrated employing gel permeation chromatographic techniques utilizing three column packings: (1) a styrene-divinyl benzene packing (BioBeads S-X4), (2) a cross linked poly(N-acryloylmorpholine) polymer (Enzacryl Gel K1), and (3) a modified alkylated dextran (Sephadex LH-20). Each packing material will be evaluated based on the extent and time of separation as well as the cost of materials. Fractional weight distributions within each SRC separation are determined and their average molecular weights compared. Weight distributions for common fractions of different SRC solid products derived from various feed coals will also be discussed.

MINOR AND TRACE METAL ANALYSIS OF SOLVENT REFINED COALS BY FLAMELESS ATOMIC ABSORPTION. W. M. Coleman, P. Szabo, D. L. Wooton, H. C. Dorn, L. T. Taylor, Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA. 24061.

Several solvent refined coals differing in the raw feed coal used, their THF insoluble fraction, their THF soluble fraction and their sized separated fractions have been analyzed for twelve metallic elements (Mg, Al, K, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cl, Pb) via flameless atomic absorption spectroscopy. Prior to analysis each sample was wet ashed with equal quantities of concentrated H_2SO_4 and 30% H_2O_2 . Matrix effects were compensated for by the method of standard additions and deuterium arc background correction. Metal analysis on a National Bureau of Standards Coal employing the same ashing and analysis scheme were determined and compared with certified values.

AGING CHARACTERISTICS OF COAL LIQUIDS

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INTRODUCTION

Materials handling and storage is an important part of any chemical process. The SYNTHOIL process (1), which converts coal to a low-ash, low-sulfur fuel oil, requires careful storage to control the viscosity of the product. The economics of this process requires a light hydrogenation of coal, and therefore any chemical changes during storage that may increase the viscosity of the product to a level at which it becomes a handling problem must be avoided. Recommended handling procedures can be determined by laboratory studies. Previous studies (2,3) give a brief resume of the changes in viscosity of SYNTHOIL samples during ambient storage for times up to 120 days. The present report, also based on viscosity measurements, covers a variety of storage conditions which include storage temperatures of 30°-61°C, atmospheres of nitrogen, air and oxygen, both stirred and unstirred samples and ambient light versus darkness. Further studies of these samples based on chemical and instrumental analyses will be reported.

EXPERIMENTAL

Aging tests were made on three coal liquids from SYNTHOIL run FB-53. Run FB-53 was made with a West Virginia coal, (Pittsburgh Seam, hvAb) and operated at 4000 psig H₂ and 450°C. Pelleted CoO-MoO₃-SiO₂-Al₂O₃ catalyst was used in the reactor. The samples investigated were from Batches 1, 21, and 50 which were obtained after 4, 84, and 200 hours, respectively, of operation of the coal liquefaction reactor.

The most comprehensive aging tests were made on the Batch 1 sample. After an initial viscosity measurement, a 200 ml sample of this batch was transferred to each of fifteen one-liter containers. Each sample was simultaneously connected to the aging apparatus and there subjected to a particular combination of the aging factors. Periodically ~10 g samples were removed from the aging containers and viscosity measurements made. All viscosity measurements were made with a Brookfield viscometer which permitted measurements at various temperatures. Thus, viscosity measurements were made at two temperatures, 30°C and 61°C, by circulating water from the aging baths through the heating jacket of the viscometer.

Similar, though less extensive, aging tests were performed on samples from Batches 21 and 50 from run FB-53. Data accumulation was limited because of the high initial viscosities of these samples and their rapid rate of change.

RESULTS AND DISCUSSION

The results of the aging tests are presented in Figures 1-3. The graphs represent the change in viscosity that occurs with aging time; infrared spectra in the figures were obtained on thin films of representative samples.

Figure 1 shows the changes in viscosity that occur when Batch 1 samples are stored at 61°C, stirred, exposed to light and subjected to one of the three

test gases, oxygen, air or nitrogen. In this and all subsequent figures, exposure to oxygen had the most pronounced impact upon the increase in viscosity; exposure to air had the next strongest impact. A small change was noted for the samples exposed to nitrogen. Also included in Figure 1 are the results for Batch 50 samples aged at the same conditions, i.e., 61°C, exposed to light and exposed to oxygen, air or nitrogen. As the figure shows, the initial viscosity of these samples is much greater than that for Batch 1 which was obtained early in the run. The much more rapid increase in viscosity of these Batch 50 samples confirms previous work (2).

The most significant viscosity increases occurred in samples exposed to oxygen. Hydrocarbon oxidation is confirmed by the infrared spectra shown in Figure 2. The spectrum obtained from the fresh reactor oil and spectra from oils exposed to different gases differ at 1690 cm^{-1} which has been assigned to carbonyls that have been formed during aging. That the formation of this band is progressive (continues throughout the aging process) can be shown by the gradual increase of the carbonyl absorption. There are many ways in which this light oxidation of SYNTHOIL may cause the observed viscosity increase. The formation of carbonyls represents a small increase in molecular weight. Carbonyls might combine with phenols as hydrogen bonded molecules or as polymers, or oxidation may proceed by way of peroxide formation and a free-radical mechanism. The ultimate objective of this work is the identification of an appropriate mechanism and the development of an inhibitor. Lin (4) has made some helpful observations.

The observed increase in viscosity for a sample stored under nitrogen may be explained in several ways. There may be a physical agglomeration similar to the crystallization of a solid from a supernatant liquid. There may be a chemical interaction between the acidic and basic components which are known to be present in SYNTHOIL (5). Further, there may be a volatilization of the lighter components under the influence of heat and stirring. Volatility effects were minimized by using a slow gas input and covered containers.

Figure 3 shows the results for samples exposed to the same gases, but aged at 45°C. The same ordering of increased viscosity of samples relative to the exposure gas as noted for the samples stored at 61°C is found; i.e., oxygen > air > nitrogen. Figure 3 also contains data for Batch 21 stored at 45°C. As noted previously, these results show that faster rates of increase in viscosity occur for samples with higher initial viscosities.

Viscosity data were obtained at 30°C for the nine samples aged in the three gases and at three temperatures. Similar relationships to those found for the viscosity measurements at 61°C are apparent. One distinction is that the changes noted for the samples exposed to nitrogen and air appear more severe. This is undoubtedly due to the substantially higher initial viscosity occasioned by the lowering of the temperature at which the viscosities were measured. An examination of the melting points of typical benzenoid molecules makes it apparent that there will be wide variations of viscosity with temperature.

The effects of not stirring the sample and not exposing the samples to ambient light were observed. A significant reduction in the aging of the samples exposed to either oxygen or air occurs when the particular sample is not stirred; the sample exposed to nitrogen shows no change. This obviously indicates that stirring merely exposes new sample constantly to the oxygen in the gaseous environment; i.e., there is no intrinsic effect due to mechanical agitation of

the sample. In addition, these results also indicate that the ambient light of the laboratory has essentially no impact on the aging properties of these samples. Further study of sunlight or other UV sources would be necessary.

Solvent separations made using the original sample, a sample after 35 days storage at 61°C under nitrogen, and a sample after 28 days storage at 61°C under oxygen gave the following data:

	Oil	Yield, Percent by Weight		Ash
		Asphaltene	Benzene Insol.	
Original	73	20	7	3
N ₂ Storage	75	18	7	3
O ₂ Storage	62	20	18	3

For this table Oil is defined as benzene soluble, pentane soluble materials and Asphaltene as benzene soluble, pentane insoluble materials. As the data indicate, no changes in component distribution occurred for the sample stored under N₂, while the sample stored under O₂ showed a decrease in oil and a corresponding increase in benzene insoluble materials. This increase in benzene insoluble material may indicate polymer formation.

CONCLUSION

These data provide some insight into the effects of time, heat, light, mechanical agitation, and gaseous environment on SYNTHOIL aging. Further analyses underway include solvent and chromatographic separations and spectral identification of the aging products. These should help to establish a mechanism for aging and perhaps suggest inhibitors which will improve the storage characteristics of SYNTHOIL.

ACKNOWLEDGMENT

SYNTHOIL samples were provided by Exploratory Engineering, PERC, Dr. Paul M. Yavorsky, Supervisor. Solvent extraction data were provided by Dr. Frank K. Schweighardt, Spectro-Physics, PERC.

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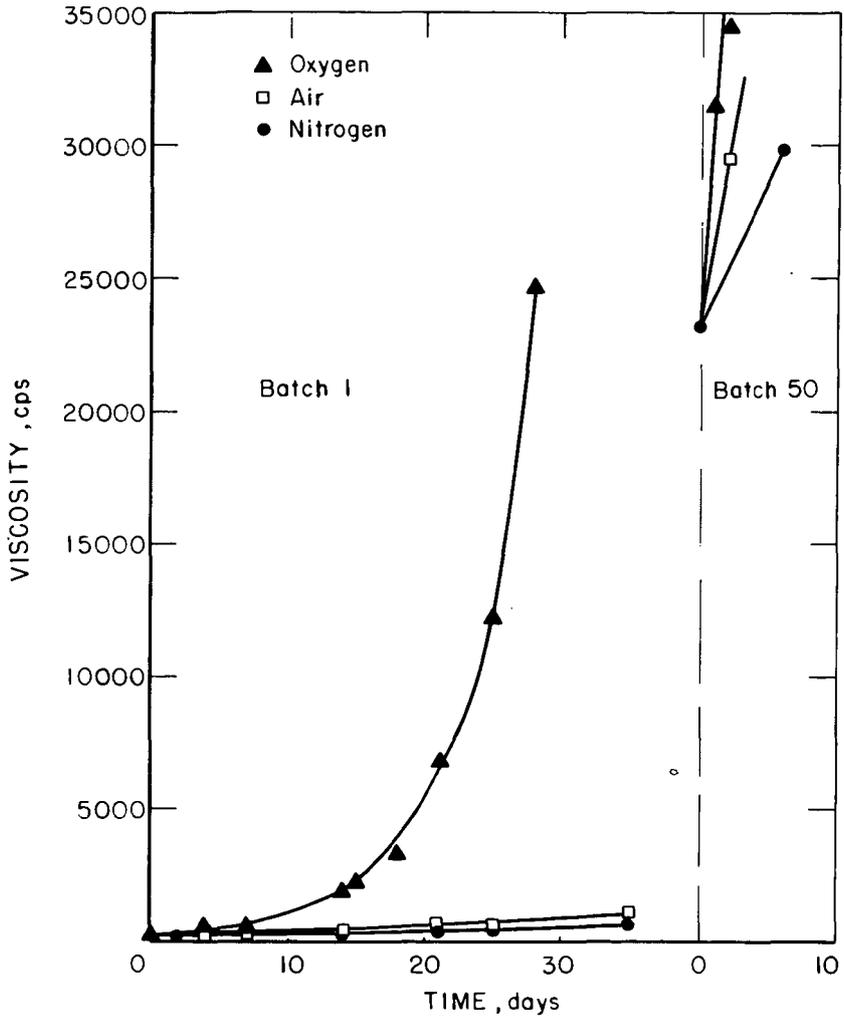


Figure 1 -Viscosity change with storage time Storage at 61°C, viscosity at 61°C .

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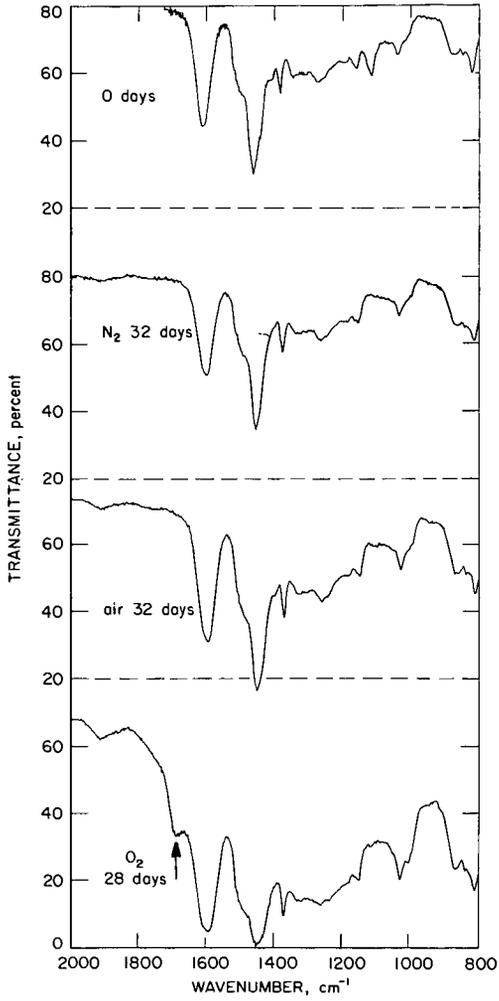


Figure 2 - Infrared spectra showing the increase of C=O during SYNTHOIL storage in various gases.

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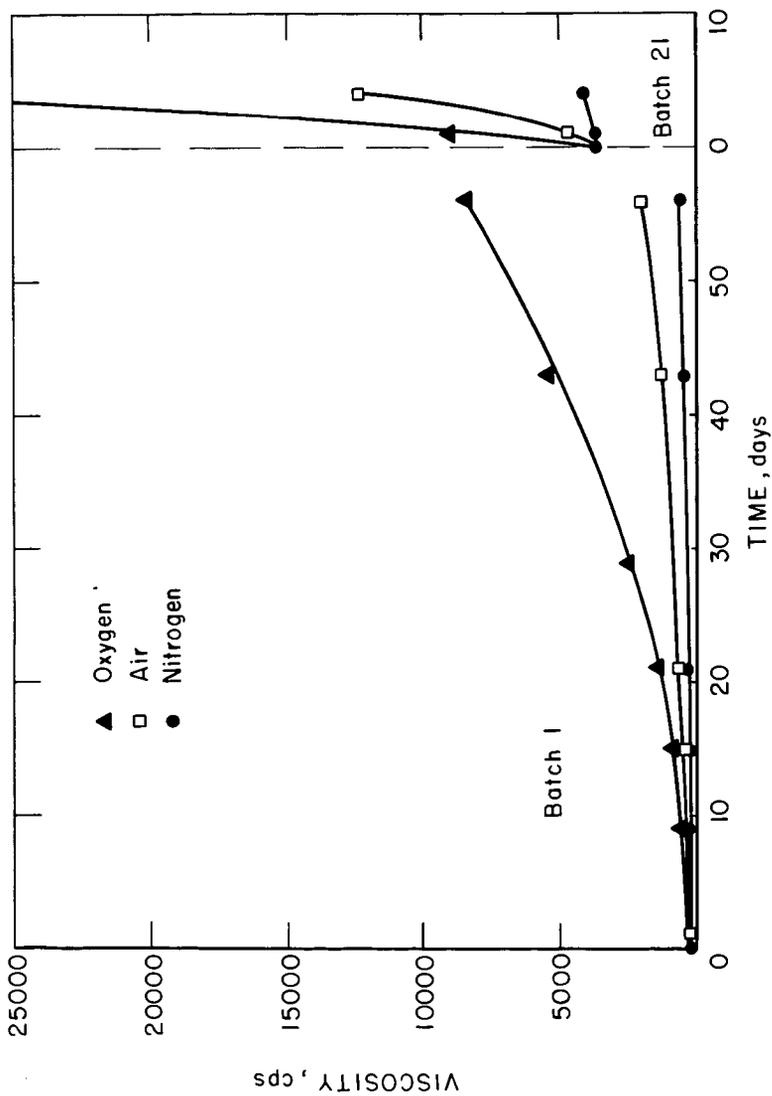


Figure 3 - Viscosity change with storage time Storage at 45°C, viscosity at 61°C

6-23-76 L-14935

THE TOSCOAL PROCESS - PYROLYSIS OF WESTERN COALS
AND LIGNITES FOR CHAR AND OIL PRODUCTION

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INTRODUCTION

Western coals and lignites generally have high moisture and organic-bound oxygen contents compared to Eastern coals. Arkansas lignites contain as much as 52% moisture (1), and Powder River subbituminous coals contain from 21 to 30% moisture (2). Pennsylvania bituminous and anthracitic coals contain only 3-6% moisture (3). To the extent that coal contains organically-bound oxygen, it has already been "burned" and its heating value has suffered accordingly. The oxygen values of coals vary inversely with coal ranking. Anthracites contain about 3% oxygen, on a moisture and ash free basis. Corresponding values for lignites are 20-30% (4).

The disadvantage of high oxygen and moisture contents in Western coals is offset by their low sulfur contents, and large volumes of Western coals are being shipped to the East despite freight rates which are very high when calculated on a heating value basis.

Any technique which effects selective removal of moisture and combined oxygen, primarily as carbon dioxide and water, will be of interest unless the cost is too high or an offsetting quality disadvantage results.

Removal of moisture has been widely discussed and examined (5,6,7). Lignites and subbituminous coals have been dried on a very large scale (5). Shipment, handling and storage problems were circumvented, and successful utility burning tests were run. While drying reduces shipping weight and increases the heating value of the solid fuel, it does not produce oil and high Btu gas coproducts.

Low temperature pyrolysis, i.e., to 800-900°F, removes any moisture remaining after the usual preheating steps and, more significantly, produces valuable oil and gas products while eliminating much of the organically-bound carbon dioxide and water. Both carbon dioxide and water are easily removed, if desired, from the gaseous and liquid hydrocarbon products.

The char product produced from low temperature carbonization can be used as a utility boiler fuel, potentially as the major component in the manufacture of formcoke and as a feedstock to gasification which would make a synthesis gas free of hydrocarbons and tars.

The oil product may be used as a fuel oil and as a source of chemicals. It may be converted to pitch binders for carbon and to metallurgical coke.

Previous reports have been given on the TOSCOAL process (8,9,10). Since these initial reports, we have continued our development efforts and have successfully

extended our pilot plant test work to coals having caking properties and have found the char to be an attractive feed to gasification.

DESCRIPTION OF THE TOSCOAL PROCESS

Tosco Corporation has investigated oil shale retorting by the TOSCO II process at the pilot plant and semi-works scale since the late 1950's. Operations at our 1,000 ton/day Parachute Creek semi-works were terminated by Tosco Corporation and its partners in 1972, after total expenditures of more than 50 million dollars. In 1969 and 1970 we were successful in retorting subbituminous coal in our 25-ton per day oil shale pilot plant located near Denver, without significant changes in process conditions normally designed for oil shale. We have chosen the name TOSCOAL to designate the process which involves the application of our oil shale retorting technology to the low temperature pyrolysis of coal.

A diagram of the TOSCOAL process is shown in Figure 1. Coal is fed to a surge hopper and dried and preheated by dilute phase fluid bed techniques. This step may be modified, as required, to effect deagglomeration (decaking). The preheated feed is then transported to a pyrolysis drum where it is contacted with heated ceramic balls. The char product leaves the pyrolysis drum at 800-1000°F, passes through the trommel screen and is subsequently cooled and sent to storage. The cooled ceramic balls, being larger than the coal, pass over the trommel screen into a separate compartment and are returned to the ball heater by means of an elevator. Pyrolysis vapors are condensed and fractionated. Uncondensed gas, having a heating value of 500-1000 Btu/lb, may be utilized as a ball heater fuel or processed and sold after sulfur removal. Removal of contained carbon dioxide would raise the heating value of the gas to even higher levels.

The TOSCO II oil shale process produces essentially 100% of the oil yield measured by Fischer assay or about 0.8 barrel barrel of oil from a ton of oil shale having a Fischer assay of 35 gal/ton. TOSCOAL processing of coal also produces about 100% of the oil predicted by Fischer assay. Subbituminous coals yield 0.3 to 0.6 barrels of oil per ton of raw coal. Oil yields from bituminous coals are greater.

TOSCOAL processing offers several advantages:

1. The use of an indirect heat source results in the production of gas having a high heating value.
2. The process is continuous.
3. The process operates with a high throughput of solid product per unit volume of retort and with good heat transfer and moderate mixing.
4. Pollution control is much better than for conventional coke ovens used in high temperature carbonization.

Previously reported pilot plant runs with a non-caking Wyoming subbituminous coal have now been augmented by successful operations with coals having Free Swelling Indices (FSI) of 1 and 3.5. Prior deagglomeration, by fluid bed treatment with steam and air, was needed before processing the coal having the FSI of 3.5.

We have used the Tosco Material Balance Assay (TMBA) technique (11) to determine a product slate and to provide sufficient product for property determinations. Data obtained provide a useful benchmark with which to compare pilot plant retorting results. The TMBA procedure requires only 100 grams of representative coal. The apparatus used for TMBA is illustrated in Figure 2. The method is basically the well known Fischer assay procedure with provision for collecting all of the product gas for later analysis by gas chromatography. Coal is placed in the steel retort and the head is bolted on to assure no loss of vapors. The contents of the retort are heated to a terminal temperature of 930-950^oF using a prescribed temperature-time profile. Oil and water are collected in the centrifuge tube which is immersed in ice water. The gas product passes through a pressure activated solenoid valve and is collected in the glass container shown. Good material balances are obtained on a routine basis.

PILOT PLANT RESULTS WITH COAL

1. Subbituminous Coal

Our initial pilot plant work was carried out on several hundred tons of subbituminous coal obtained from the Wyodak mine located near Gillette, Wyoming. A typical analysis of this coal, as received, is shown in Table 1.

It is our observation, in the pilot plant retorting of this coal, that the mechanical handling of the solid and liquid products was very similar to that experienced in extensive prior operations with oil shale.

Pilot plant retorting was conducted at three retorting temperatures with the results given in Table 2. TMBA data are included for comparison. The char yield decreased with increased retorting temperature, and the oil yield increased. The water yield was not defined accurately in the pilot plant since some steam was used in the process. Accordingly, the water yield was calculated from the moisture of the coal and from Fischer assay data. The compositions of the coal feeds to these four test runs were not identical, although each coal was from the Wyodak mine.

Product char properties are listed in Table 3 and plotted in Figure 3. The char volatile matter values decreased, and the heating values increased as the retort temperature was raised. The general range of heating values obtained is excellent for boiler fuel application and represents about a 50% increase over the heating value of the corresponding raw coal.

The properties of the oil products are given in Table 4. The oil properties change only slightly with increased retort temperature. The low sulfur values are to be noted. The oils are rich in potential chemical values. In particular, the IBP to 446^oF portion of the tar produced in Run C-3 contained 65 weight percent of phenols, cresols, and cresylic acids.

The retort gas yields are given in Table 2. The product gases gave the analyses shown in Table 5. It is to be noted that the mixture obtained has a high heating value, and the heating value obtained after removal of acid gases is in the natural gas range. Removal of the butane and heavier components for other use would tend to slightly reduce the reported heating values.

FIGURE 1. TOSCOAL Process

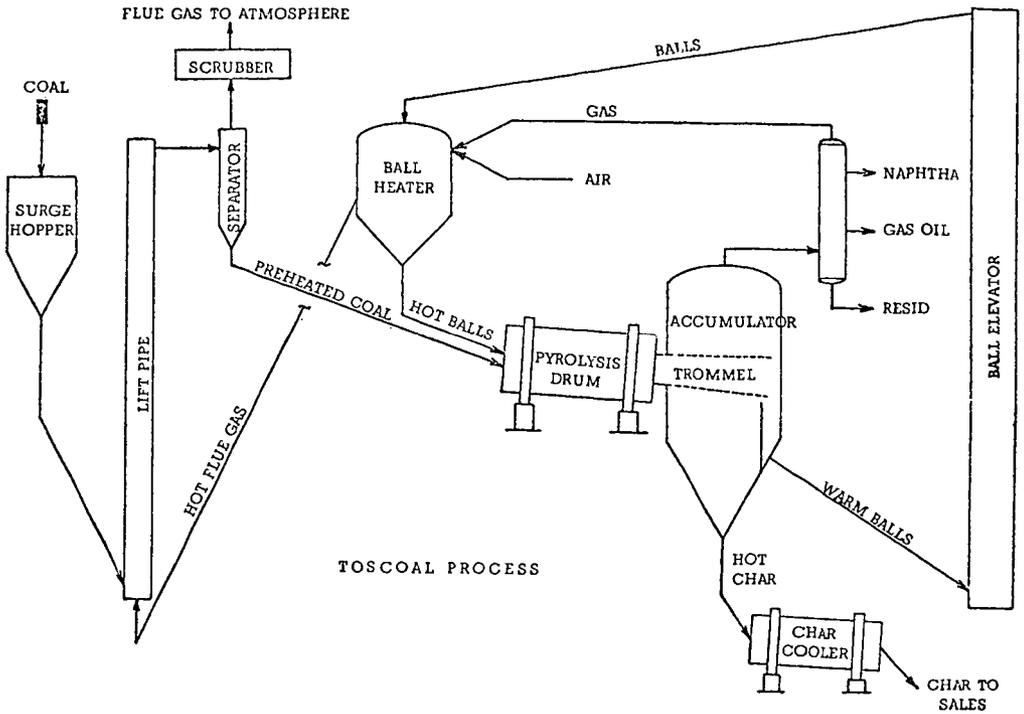


FIGURE 2. Product Collection Assembly - Tosco Material Balance Assay

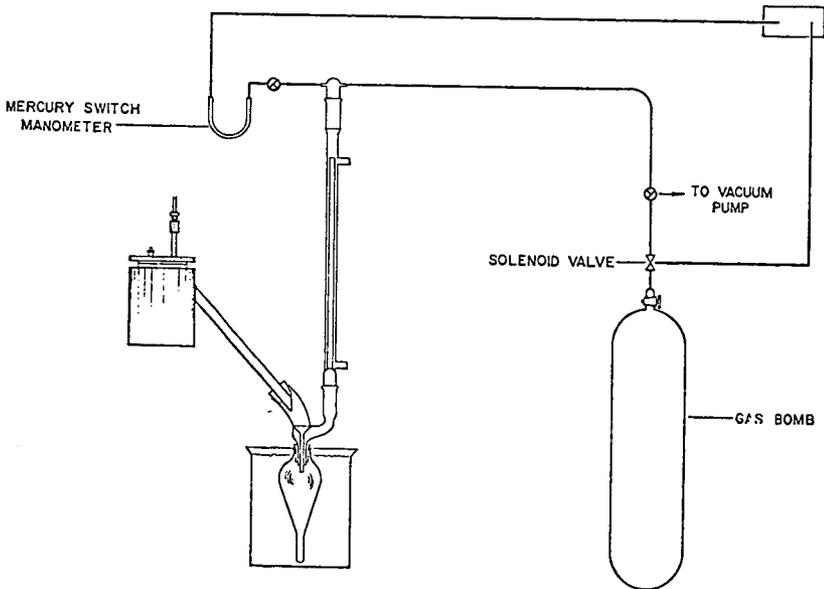


TABLE 1
WYODAK COAL ASSAY
(Samples 120-8, 120-10)

<u>Proximate (wt %)</u>		<u>Ultimate (wt %)</u>	
Moisture	30.0	Carbon	46.4
Ash	5.3	Hydrogen	2.8
Volatile Matter	30.7	Oxygen	14.7
Fixed Carbon	<u>34.0</u>	Nitrogen	0.7
Total	100.0	Sulfur	0.3
Heating Values,		Moisture	30.0
Gross, Btu/lb	8,139	Ash	<u>5.3</u>
Net, Btu/lb	7,570	Total	100.2

Other Data

Free Swelling Index	0
Hardgrove Grindability	56
Lb SO ₂ /MM Btu	0.74

TABLE 2
TOSCOAL RETORTING OF WYODAK COAL
Product Yields (lb/ton of as-mined coal)

Retort Temperature	Pilot Plant			TMBA
	800°F	900°F	970°F	935°F
Run No.	C-8	C-2	C-3	3383
Char	1049.0	1011.7	968.7	989.7
Gas (C ₃ and lighter)	119.0	156.7	126.0	156.5
(SCF/ton)	(1250.0)	(1777.0)	(1624.9)	(1876)
Oil (C ₄ and heavier)	114.0	143.0	186.2	157.8
(gal/ton)	(13.2)	(17.4)	(21.7)	(19.8)
Water	<u>702.0*</u>	<u>702.0*</u>	<u>702.0*</u>	<u>702.0</u>
Totals (lb)	1984.0	2013.4	1982.9	2006
Recovery (%)	99.2	100.7	99.1	100.3

* Value assumed from Fischer assay and moisture content. The addition of steam to the process prevented accurate measurement of water produced in retorting.

TMBA Tosco Material Balance Assay, No. 3383

TABLE 3
TOSCOAL CHAR PROPERTIES

<u>Retort Temperature</u>	<u>Pilot Plant</u>			<u>TMBA</u>
	<u>800°F</u>	<u>900°F</u>	<u>970°F</u>	<u>935°F</u>
Run No.	C-8*	C-2	C-3	3383
<u>Proximate (wt %)</u>				
Moisture	0.0	0.0	0.0	0.0
Ash	12.4	10.0	9.8	8.9
Volatile Matter	25.3	19.7	15.9	15.8
Fixed Carbon	<u>62.3</u>	<u>70.3</u>	<u>74.3</u>	<u>75.3</u>
Total	100.0	100.0	100.0	100.0
<u>Ultimate (wt %)</u>				
Carbon	68.8	74.7	77.5	76.5
Hydrogen	3.4	3.0	2.9	3.0
Oxygen	13.3	11.8	8.3	7.8
Sulfur	0.5	0.2	0.3	0.4
<u>Other Data</u>	1.0	1.2	1.3	
Equilibrium Moisture (wt %)	10.0	10.8	9.9	ND
Hardgrove Grindability	59.5	49.1	45.6	ND
<u>Heating Values</u>				
Gross, Btu/lb	11,826	12,560	12,963	13,155
Lb SO ₂ /MM Btu	0.85	0.32	0.46	0.61

* Feed Wyodak coal was different from that used in runs C-2 and C-3.

ND Not determined

TMBA Tosco Material Balance Assay, No. 3383

TABLE 4
TOSCOAL OIL PROPERTIES

<u>Retort Temperature</u>	<u>Pilot Plant</u>			<u>TMBA</u>
	<u>800°F</u>	<u>900°F</u>	<u>970°F</u>	<u>935°F</u>
Run No.	C-8*	C-2	C-3	3383
<u>Ultimate (wt%)</u>				
Carbon	81.4	80.7	80.9	81.4
Hydrogen	9.3	9.1	8.7	9.4
Oxygen	8.3	9.4	9.3	7.0
Nitrogen	0.5	0.7	0.7	0.6
Sulfur	<u>0.4</u>	<u>0.2</u>	<u>0.2</u>	<u>0.2</u>
Total	99.9	100.1	99.8	98.6
Heating Value (Gross, Btu/lb)	16,590	16,217	15,964	16,465
API Gravity	7.9	4.5	1.9	12.8
Pour Point (°F)	90	100	95	ND
Conradson Carbon (wt%)	7.6	9.9	11.4	ND
<u>Distillation** (vol%)</u>				
2.5	413°F	420°F	390°F	ND
10	490	475	405	
20	575	550	455	
30	645	625	545	
40	710	700	640	
50	765	775	725	
<u>Viscosity (SUS)</u>				
180°F	122	123	128	ND
210°F	63	66	69	ND

* Feed Wyodak coal was different from that used in Runs C-2 and C-3.

** Combination of TBP and D-1160 distillations.

TMBA Tosco Material Balance Assay, No. 3383 ND Not Determined

TABLE 5

TOSCOAL GAS ANALYSES

Retort Temperature	Pilot Plant			TMBA
	800°F	900°F	970°F	935°F
Run No.	C-8*	C-2	C-3	3383
<u>Component (mole %)</u>				
H ₂	0.8	1.0	7.8	5.6
CO	18.0	17.3	18.4	15.1
CO ₂	51.1	42.3	36.4	44.7
H ₂ S	1.7	1.3	0.3	0.8
CH ₄	16.9	22.0	24.9	22.4
C ₂ H ₆	3.6	4.7	4.4	4.6
C ₂ H ₄	1.9	1.9	2.4	2.3
C ₃ H ₈	1.3	2.2	1.2	1.2
C ₃ H ₆	1.6	3.7	1.6	1.4
iC ₄ H ₁₀	0.1	0.1	0.0	0.1
C ₄ 's (other)	0.3	2.0	1.1	1.0
C ₅ 's	1.0	1.8	0.7	0.5
C ₆ 's	0.7	0.6	0.4	0.5
C ₇ 's	0.5	0.1	0.3	0.0
C ₈ ⁺	<u>0.2</u>	<u>0.0</u>	<u>0.1</u>	<u>0.0</u>
Total	99.7	101.0	100.0	100.2
Average Molecular Weight	35.9	35.0	30.6	32.3
Weight Percent Carbon	40.5	45.9	44.7	42.0
<u>Heating Values (Calculated)</u>				
Gross, Btu/SCF	534	717	630	552
Net, Btu/SCF	494	663	580	508
Calculated with CO ₂ and H ₂ S removed				
Gross, Btu/SCF	1,113	1,234	995	998
Net, Btu/SCF	1,029	1,138	920	919

* Feed Wyodak coal was different from that used in Runs C-2 and C-3.

2. Higher Rank Coals

The successful operation of the TOSCOAL pilot plant with sub-bituminous coal was encouraging and suggested access to most of the Western coals and lignites. However, some Western coals and most of the Eastern coals are of higher rank and have an FSI ranging from 1 to 9. The feasibility of retorting with heated ceramic balls was in question since caking coals fuse below the retorting temperature range of 800-1100°F. Some short process tests with Illinois No. 5 coal (FSI-4) confirmed that the retort mix became "sticky" and resistant to flow.

We first processed six tons of coal from the Plateau Mine (Price, Utah) which had an FSI of 1, i.e., only a slight tendency to swell on heating. Coal assays are listed in Table 6 and pilot plant product yields and properties are given in Table 7, along with comparative TMBA results. No problems were encountered with this coal and no pretreatments, other than the usual drying and preheating, proved to be necessary.

Processing of Illinois No. 6 coal, having an FSI of 3.5, required pre-treatment with steam and air at 570°F in a fluid bed before retorting. Pilot plant operability was good after this deagglomeration.

Assay data for the raw and pretreated coal are given in Table 6. The effect of deagglomeration was to decrease the TMBA oil yield and to increase the char yield. Deagglomeration presumably involves uptake of oxygen by the coal since subsequent pyrolysis (TMBA) shows an increase in product carbon dioxide in the gas. The raw coal yielded 11 pounds of CO₂ per ton of coal, and the corresponding value for coal treated with steam and air was 31 pounds.

Pilot plant processing of three tons of the deagglomerated coal was carried out to produce the results given in Table 7. Due to the short run length, material balances were not attempted at each of the two conditions.

LABORATORY RETORTING

It is not always possible to obtain sufficient test coal for pilot plant operations. As described above, we have used the TMBA procedure to investigate retorting of small quantities of coal. Although TMBA is a batch operation and TOSCOAL processing is continuous, we have found the product yields and product properties to be sufficiently similar to encourage wider use of this relatively simple laboratory procedure.

An excellent application of the use of low temperature carbonization as an assay technique for coal was reported by Landers in 1961 (12). Data, similar to those produced using TMBA, were reported on 220 domestic and foreign coals.

The Tosco Fischer assay procedure has been applied to a number of Western coals and lignites. Five examples, other than those discussed above, are described in Table 8. The assays of the coals and product chars are shown. The increase in the heating value of the char, as compared to the raw coal, is to be noted. In examination of product yields, it is apparent that low temperature carbonization of the materials shown produces about a 50% yield of char, based on the as-mined raw coal or lignite. Gas, oil and water yields vary with the source of the coal and with the retorting conditions.

TABLE 6
ASSAYS OF PLATEAU COAL, ILLINOIS NO. 6 COAL
AND DEAGGLOMERATED ILLINOIS NO. 6 COAL

	<u>Plateau Coal</u>	<u>Illinois No. 6 Coal</u>	
		<u>As Received</u>	<u>Deagglomerated</u>
Proximate (wt%)			
Moisture	10.0	8.8	0.7
Ash	13.0	6.7	8.3
Volatile Matter	34.1	32.0	31.6
Fixed Carbon	<u>42.9</u>	<u>52.5</u>	<u>59.4</u>
Total	100.0	100.0	100.0
Sulfur	0.9	0.7	0.7
Free Swelling Index (FSI)	1.0	3.5	1.5
Heating Value (Gross, Btu/lb) (Dry Basis)	11,906	13,293	13,071
TMBA Results (Dry Coal Basis)			
TMBA No.	1252	1340	1341
TMBA Temp. (°F)	970	932	932
Oil, lb/ton	358.3	245.9	166.6
(gal/ton)	(45.6)	(27.9)	(19.0)
(API)	(18.6)	(2.2)	(2.7)
Char, lb/ton	1,417.9	1,603.6	1,675.2
Gas, lb/ton	140.1	79.1	103.8
(SCF/ton)	(2,039)	(1,360.8)	(1,630.7)
(Btu/SCF)	(945)	(1025)	(857)
Water, lb/ton	<u>76.5</u>	<u>39.9</u>	<u>40.8</u>
Total lb/ton	1,992.8	1,968.5	1,986.4

TABLE 7

TOSCOAL PROCESSING OF HIGHER RANK COALS
PLATEAU COAL AND DEAGGLOMERATED ILLINOIS NO. 6 COAL

	<u>Plateau Mine, Price, Utah</u>		<u>Inland Mine No. 1 - Illinois No. 6 Coal</u> <u>Sesser, Illinois - Pilot Plant**</u>			
	<u>Tosco Material</u>		<u>Pilot Plant</u>		<u>Tosco Material</u>	
	<u>No 1252</u>	<u>Balance Assay</u>	<u>Low Temp.</u>	<u>High Temp.</u>	<u>Balance Assay</u>	
Retorting Temp (°F)	960	970	945	1075	932	
<u>Products (lb/ton, dry coal basis)</u>						
Char	1399	1418	ND	ND	1469	
Oil	308	358	ND	ND	167	
Gas	216	140	93	171	131	
Water	77*	77	ND	ND	41*	
Total Material	2000	1993			1748***	
Total Hydrocarbon as Oil & Gas (includes CO & H ₂)	436	437			236	
<u>PRODUCT PROPERTIES</u>						
Char, Volatile Matter (wt%)	14.0	ND	13.9	9.7	ND	
Oil, API	14.3	18.6	ND	ND	2.7	
Gas						
SCF/ton	2448	2039	1395	3088	1631	
Btu/SCF	1173	945	944	852	857	

* Value from TMBA was used

** Prior to retorting, the coal was deagglomerated by treatment with steam and air in a fluid bed.

*** Material balance closure was not good due to small amount of total feed to the pilot plant.

ND Not Determined

TABLE 8

FISHER ASSAY PRODUCT YIELDS AND PROPERTIES

Coal	(Fischer Assay Temperature - 950°F)				
	Big Horn (1)	Big Sky (2)	Savage (3)	Arkansas Lignite (4)	Elkol (5)
Proximate (wt %)					
Moisture	22.0	21.9	33.2	24.2	19.5
Ash	4.8	9.5	6.0	10.8	3.0
Volatile Matter	34.8	29.6	29.5	ND	30.6
Fixed Carbon	38.4	39.0	31.3	ND	46.9
Total	100.0	100.0	100.0		100.0
Heating Value, Btu/lb	9,578	8,948	7,230	ND	10,484
Product Yields (lb/ton of as-mined coal)					
Char (Volatile Matter, wt%) (Heating Value, Btu/lb)	1,023.3 (13.2)	1,144.6 (15.0)	879.1 (13.0)	899.6 (ND)	1,143.0 (15.4)
Gas (C ₃ & lighter) (SCF/ton) (Btu/SCF)	136.6 (1,940.4) (617)	118.9 (1,674.9) (613)	155.7 (1,886.7) (451)	155.2 (1,875.1) (500)	131.8 (1,933) (693)
Oil (C ₄ & heavier) (gal/ton)	222.2 (27.5)	162.7 (20.5)	126.9 (15.8)	295.9 (37.8)	187.0 (22.9)
Water	617.2	568.5	807.3	650.2	535
Total (lb)	1,999.3	1,994.7	1,969.0	2,000.9	1,996.8
Recovery (%)	100.0	99.7	98.5	100.0	99.8

(1) Big Horn Coal Company, Sheridan, Wyoming

(2) Peabody Coal Company, Big Sky Mine, Colstrip, Montana

(3) Knife River Coal Mining Company, Savage, Montana

(4) Fischer Assay No 1258

(5) Kemmerer Coal Company, Elkol Mine, Frontier, Wyoming

ND - Not Determined

Using the type of data given in Table 8 it is feasible to estimate the yields and product properties to be obtained from commercial operations at any desired scale.

UTILIZATION OF PRODUCT CHAR

Utility Boiler Fuel

Important characteristics of solid fuels include the temperature of ignition, the temperature at the maximum rate of ignition, and the temperature at which complete burnout occurs. In most cases higher volatile matter and higher surface area are reflected in improved ignition characteristics. Chars from lower rank coals, such as lignite and subbituminous, generally ignite and burn rapidly due to the large surface area.

Laboratory tests have been conducted on TOSCOAL chars by three major boiler manufacturers. One found that the ignition characteristics were satisfactory and concluded that the char could be burned readily in a conventional, horizontally-fired boiler. Babcock and Wilcox personnel conducted burning profile tests on char in comparison to other solid fuels using the procedure published by Wagoner and Duzy (13). The results are illustrated in Figure 4. The "C-4 TOSCO" char was produced in our pilot plant from Wyodak coal by retorting at 800°F. The Tosco char ignited more readily and burned out completely at a lower temperature than did bituminous coals.

Another boiler firm conducted small scale firing tests with char from the C-3 pilot plant run. They concluded that this low VM char (16%) burned in a similar fashion to Pennsylvania low volatile bituminous coal.

Commonwealth Edison (Chicago) and others have extensively investigated the utility boiler firing of partially dried lignite (5). Improvements over firing raw lignite were observed.

Texas lignite has been used as a boiler fuel after both charring and drying (14). The current practice of Texas Utilities is to burn dried lignite at their Rockdale mine facility.

Formcoke

There is currently great interest in finding a substitute for the conventional blast furnace coke used in making iron for subsequent conversion to steel. The coke is made from expensive coking coals, and the manufacturing process involves substantial air pollution. The use of non-coking coals, such as those found in the Western United States would be attractive since they are cheap and the supply is virtually limitless. Much of the technology currently being investigated for manufacturing synthetic coke (formcoke) involves pyrolysis of non-coking coals and subsequent production of calcined briquettes or pellets from the char (15, 16, 17, 18). The addition of a pitch binder and sometimes some coking coal and other solids is required. Our judgment is that the TOSCOAL process can produce a satisfactory char and, after further oil processing, the pitch binder in an efficient and environmentally clean manner.

Feed to Gasification

One of the major problems encountered in coal gasification is handling the tars produced along with the primary gas product. These tars may cause

FIGURE 3

EFFECT OF TOSCOAL PROCESSING TEMPERATURE
ON CHAR VOLATILE MATTER AND GROSS HEATING VALUE
(Pilot Plant Results)

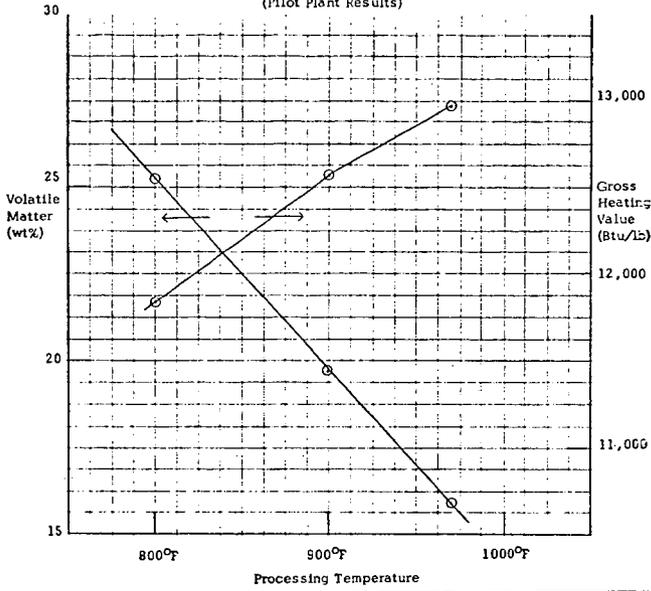
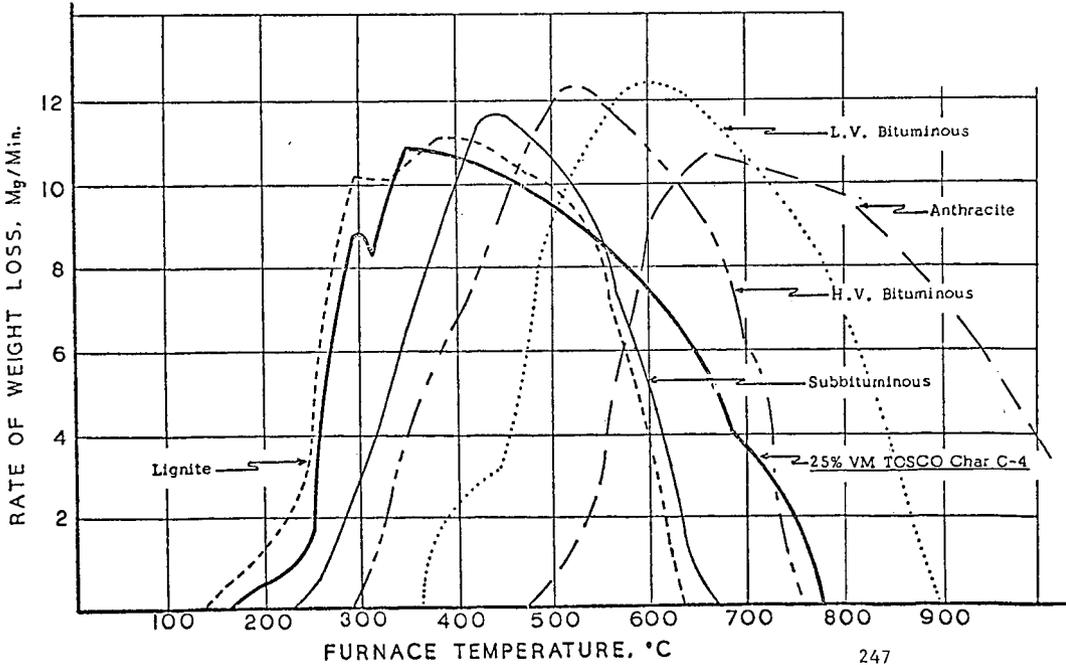


FIGURE 4

DTGA BURNING PROFILE



problems in heat recovery, in recovery of particulate solids and in water purification. Gasification of TOSCOAL char produces a synthesis gas free of tars and very low in methane, as illustrated in Table 9. Such a gas can be converted to high purity hydrogen or used as synthesis gas feed for methanol production.

Gasification of char has been investigated previously by FMC and others in the consortium called COGAS Development Company (19,20,21).

TABLE 9

GASIFICATION OF TOSCOAL CHAR
FROM ILLINOIS NO. 6 COAL

Conditions

Reactor Temperature (°F)	1525
Fluidizing Gas	Steam (no air or O ₂)

Product Gas Composition (Mole %)

H ₂	59.5
CO	18.3
CO ₂	19.9
H ₂ S	0.1
CH ₄	<u>2.3</u>
Total	100.1

UTILIZATION OF OIL

Oil from low temperature carbonization, 800-1000°F, of coal differs from that produced in a coke oven (1600°F) in that it contains a larger amount of oxygen and hydrogen and lower levels of pure compounds such as benzene and naphthalene.

Use of oil from TOSCOAL processing as a fuel oil is reasonable. Oils from Western coals and lignites generally have low-sulfur contents.

The oil from Run C-3, 970°F retorting of Wyodak coal (Table 4) yielded, by distillation, an IBP to 446°F fraction having a cresylic acid content of 65 volume percent. These acids are used in the manufacture of phenolic resins and phosphate ester plasticizers.

Oils from low temperature carbonization have been hydrogenated to a synthetic crude oil which has then been evaluated as a refinery charge stock (22), and as a carbon black feedstock (23).

After thermal treatment, oil from low temperature carbonization of lignite can be used as electrode pitch (24) and for the manufacture of coke (25).

Pitch, to be used in formcoke manufacture, can be made by air blowing the liquid product from low temperature carbonization (26).

ECONOMICS

The cost of a potential commercial TOSCOAL processing plant, using a subbituminous coal of the Big Horn type has been estimated. The design plant capacity yields are:

1) Feed rate, ton/day of "as mined" coal	7,230
2) Dry char product, ton/day	3,910
3) Oil product, bbl/day	4,130
4) Net product gas, MM Btu/day	2,261
5) Net gas, oil and dry char HHV values as a percent of wet feed HHV	94.7

Part of the hydrocarbon product mix is used internally as process fuel.

The plant envisioned is based on a maximum size single pyrolysis train operating at a retort temperature of 900^oF. Operation at 800^oF would increase plant capacity, but would produce somewhat less liquid product per ton of feed coal.

The investment, in June 1976 dollars, would be \$73 million for the pyrolysis battery limits. The investment cost does not include the mine, feed preparation, product storage, land, buildings, rail siding and loading facilities and offsite utilities. Equipment for sulfur dioxide removal is also not included but may not be necessary.

Components of the operating cost are:

- 1) A total of 28 shift workers
- 2) Maintenance cost of \$2.8 MM/year
- 3) Operating supplies of \$0.5 MM/year
- 4) Power requirement of 37 MM KWH/year

Expenditure of these estimated investment and operating costs would produce a superior solid fuel which would offer cost savings in utility power generation. A recent study (27) compared investment costs and operating parameters for a 500 megawatt P.C. (pulverized coal) fired boiler to be fired, on the one hand, with Gillette, Wyoming coal and North Dakota lignite and, on the other hand, with chars from these coals. In the Gillette coal case an investment savings of nine dollars per installed KW can be realized, for the boiler island, in changing fuels from raw coal to char. These savings are mainly in reduced requirements for pulverizers and for boiler furnace size. Further, boiler efficiency would improve by 5.3% and internal power consumption, mainly for fans and pulverizers, would decrease by 2,500 KW.

Corresponding savings in the North Dakota lignite case were higher. The investment would be reduced by \$17.5 per installed KW. Boiler efficiency would improve by 6.8%, and internal power consumption would decrease by 6,300 KW.

In addition to savings in power generation, an advantage of char over moist, "as mined" coal and lignite would be in lowered freight costs. Assuming a freight cost of 12 mills/ton mile, the cost of shipping a ton of Wyodak coal (Table 1) 1,000 miles would be \$12.00 or \$.74/MM Btu. On the same basis, the cost of shipping one ton of Wyodak char (C-8 run, Table 3) would be only \$.51/MM Btu. This saving assumes there would be no offsetting cost in handling the more pyrophoric and dusty char.

Covered hopper cars have been manufactured by Thrall Car Manufacturing Company (Chicago Heights, Illinois) and perhaps could be used to haul char produced from low temperature carbonization. Currently, the "flip top" cars are being used to ship "as mined" lignite across North Dakota to the Big Stone Power project at Big Stone City, South Dakota. The covered car was needed to reduce dust loss and to prevent freezing during the winter.

SUMMATION

TOSCOAL processing of coal is based on technology acquired in twenty years of continuous work on the TOSCO II oil shale retorting process. Coals of low rank can be used directly. Those of higher rank may be retorted after treatment with air and steam to effect decaking.

Processing of Western coals and lignites is of interest in reducing the large freight costs currently involved in transporting moisture and non-combustible components. Use of chars rather than coal as utility boiler fuels offers investment and operating cost advantages. Chars produced may also be used in the manufacture of formcoke and as an improved feedstock in gasification.

Liquid products may be used as a fuel, and as a source of chemicals, coke and pitch binders.

High heating value gas is produced as a coproduct.

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