

NOVEL APPROACH TO COAL LIQUEFACTION
UTILIZING HYDROGEN SULFIDE AND CARBON MONOXIDE

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INTRODUCTION

All coal liquefaction processes involve thermal cracking of weak bonds in coal to form radical fragments which are stabilized by abstracting hydrogen atoms from a donor solvent. The activity of the hydrogen donor solvent is maintained by further hydrogenation of a recycled fraction. Thus, the costs of hydrogen comprise a major expense in any liquefaction process especially if pure H_2 is used. Hydrogen sulfide, a by-product of a negative value from the cleaning of natural gas, crude oil or coal, has been demonstrated to be a potential hydrogen source for a few chemical processes, such as selective reduction of NO_x to hydroxyl amine [1] and reduction of nitroaromatics to amines [2]. The effect of H_2S on coal liquefaction in the presence of hydrogen donor solvents and under H_2 atmosphere has been reported to increase the coal conversion to soluble products [3,4]. Hydrogen sulfide in these latter cases was not the main source of hydrogen but acted as a promoter in the presence of hydrogen donors and elemental H_2 . In order to utilize the inherent hydrogen value of hydrogen sulfide, we studied the effect of H_2S and CO on coal liquefaction in the absence of other hydrogen sources. A more detailed study of this chemistry was achieved by the use of coal tar, a material that contains many of the basic structural features of coal itself. The objective of this study has been to utilize low grade industrial hydrogen streams, particularly those produced via coal gasification which contain a large variety of impurities including H_2S , CO, CO_2 , COS and NH_3 . Utilization of the H_2S/CO from such dirty streams in the first stage of coal liquefaction will alleviate a number of expensive process steps in the cleaning of syngas.

EXPERIMENTAL

1. The coal liquefaction experiments were carried out in a 316 SS, 300 mL Magnedrive, packless, stirred autoclave (Autoclave Engineer, Inc.), fitted with a 1200 watt heating jacket. The coal was pulverized to -60 mesh and dried under nitrogen in a vacuum oven at 100°C. The coal sample (20 g), solvent (80 g of 1-methylnaphthalene or tetralin) and a catalyst (2 g), if required, were charged into the autoclave. The autoclave was flushed and pressure tested with nitrogen, then charged with 1655 kPa of H_2S (about 4.5 g) and to 6894 kPa with CO. The reaction was carried out at 400°C for 2 hours while stirring, then quenched utilizing a cold water cooling coil. The contents of the reactor were transferred into an extraction thimble and extracted with ethyl acetate for 24 hours. The thimble was dried in a vacuum oven and the weight of the residue

was determined. Conversion is defined as the percentage of the organic matter in coal that was converted to ethyl acetate-solubles and gases on a dry ash-free basis. The extract was stripped of ethyl acetate and the asphaltenes were precipitated by adding 800 mL of pentane. The sulfur contents of the asphaltenes were determined by Eschka method (ASTM D-271).

2. Coal tar treatment with H_2S and CO was carried out in the same manner as the coal liquefaction but without any solvents to avoid complications with the analytical procedure. Coal tar (80 g) was mixed with 5% presulfided Harshaw HT-400E catalyst ($Co-Mo-\gamma Al_2O_3$) and loaded into the autoclave prior to charging with H_2S (1655 kPa) and CO (6894 kPa). The autoclave was then heated at 400°C for 2 hours while stirring. Small aliquots of the product mixture were dissolved in $CDCl_3$, filtered, then subjected to both 1H -nmr and ^{13}C -nmr analysis. One experiment was carried out using 60% enriched ^{13}CO in a microreactor consisting of a 30 mL stainless steel vessel (Hoke) connected to a manifold and fitted with a magnetic stirrer and a heating jacket. The reaction was carried out at 350°C, 1655 kPa of H_2S and 5515 kPa of ^{13}CO for 6 hours. The contents of the vessel were extracted with $CDCl_3$, filtered and subjected to ^{13}C nmr. During the course of the coal tar treatment any hydrogen-containing solvents were carefully excluded.

3. Catalyst Preparation. A commercial sample of 13% MoO_3 and 3% CoO on γ -alumina was obtained from The Harshaw Chemical Company, Beachwood, Ohio. The pellets were ground to -60 mesh, heated to 500°C in a nitrogen stream, and then sulfided at 400°C with a 40% stream of H_2S in N_2 for one hour.

RESULTS

Utilization of the waste components from a coal cleaning process in the liquefaction of coal can only be achieved if H_2S , with other components, hydrogenates or serves as a radical trap during coal pyrolysis. The inherent hydrogen in hydrogen sulfide has now been shown to be capable of supplying the main source of hydrogen necessary for coal liquefaction. The coals were dried to avoid water that may act as a hydrogen source through the water-gas shift reaction. 1-Methylnaphthalene was used as a non-hydrogen donor dispersing medium. Catalysts used with certain runs were sulfided samples of $Co-Mo$ on $\gamma-Al_2O_3$ (Harshaw HT-400E). Liquefaction results of Illinois No. 6 Dean Mitchell coal are shown in Table 1. A comparison of the blank run in which coal was heated in 1-methylnaphthalene under nitrogen at 400°C and with H_2S treatment showed slight increase in conversion to ethyl acetate soluble products of 18% vs. 12.5% for the blank run indicating partial liquefaction using only H_2S . The sulfur content of the asphaltene fraction increased from 3.36% for the reaction under nitrogen to 6.34% when H_2S was used. The use of a mixture of H_2S and CO caused a threefold increase in conversion from 12.5% (Run 1) to 38.2% (Run 3). Sulfur content showed only a slight increase from 3.36% to 4.33%. Although the use of catalysts such as

sulfided Co-Mo on γ - Al_2O_3 (Run 4) or ammonium molybdate (impregnated on the coal, Run 5) did not cause significant change in conversion, it did decrease the sulfur content slightly. When a large excess of H_2S was used with the same amount of CO, a higher conversion was achieved with a slight increase in the sulfur content (Run 7).

Liquefaction of coal has been studied with mixtures of CO and H_2O by several groups with the main effort now involved in the COSTEAM process [5]. A comparison of $\text{H}_2\text{S}/\text{CO}$ versus $\text{H}_2\text{O}/\text{CO}$ was carried out. In the absence of a hydrogen donor solvent, $\text{H}_2\text{S}/\text{CO}$ was found to be more effective for coal liquefaction (38.2%) than $\text{H}_2\text{O}/\text{CO}$ (28%) under the same conditions (Runs 3 and 8).

The results of liquefying Illinois No. 6 Delta Mine coal in the presence of either an inert solvent (1-methylnaphthalene) or a hydrogen donor solvent (tetralin) are shown in Table 2. In agreement with previous data, the liquefaction in the presence of H_2S and CO in an inert solvent increased the conversion to 59.5% (Run 10) relative to a blank experiment (38.5% conversion, Run 9). The use of catalyst did not influence the conversion or the sulfur content. This indicated that the reaction of $\text{H}_2\text{S}/\text{CO}$ was either noncatalytic or catalyzed by the inorganic minerals in coal. The use of a hydrogen donor solvent gave a higher conversion and slightly lower sulfur content than the use of an inert solvent (Run 12 vs. Run 9). Furthermore, the use of $\text{H}_2\text{S}/\text{CO}$ enhanced the coal liquefaction in the presence of a hydrogen donor as evident from the results in Table 2.

Coal tar was used as a coal-like material in order to examine the nature of $\text{H}_2\text{S}/\text{CO}$ interaction on coal linkages. Although we do not imply that coal tar is a model for coal, it does contain many of the structural components in the original coal and has the added advantage of greater solubility in chloroform.

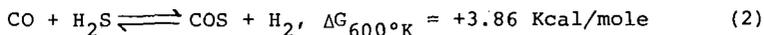
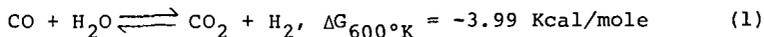
Coal tar samples were treated with $\text{H}_2\text{S}/\text{CO}$ in the presence of sulfided Co-Mo on Al_2O_3 catalysts under similar liquefaction conditions. Both ^1H and ^{13}C -nmr were used to evaluate the gross change in hydrogen and carbon distribution in coal tar as a result of $\text{H}_2\text{S}/\text{CO}$ treatment. Examination of the results in Table 3 demonstrated a substantial increase in the content of the aliphatic protons from 5.3% for the tar heated under nitrogen to 15.9% for the tar treated with $\text{H}_2\text{S}/\text{CO}$. A similar increase in the aliphatic carbon content from 4.4% to 6.6% was observed. The ^1H -nmr spectra of both nitrogen- and $\text{H}_2\text{S}/\text{CO}$ -treated coal indicated that the major change in the aliphatic hydrogen was due to functional aryl-methyl groups (singlets at δ 2.33-2.5 ppm) and the generation of ethylenic linkages between aromatic rings (singlets at δ 3.3 ppm) such as acenaphthene or dihydrophenanthrene structures. The appearance of aryl-methyl groups was quite intriguing since it indicated the possibility of methylating coal tar or coal using a mixture of $\text{H}_2\text{S}/\text{CO}$. The ^{13}C -nmr has substantiated this observation by indicating the appearance of singlet peaks around δ 22.0 and 30.3 ppm due to aryl-methyl and dihydrophenanthrene structures. The use of ^{13}CO and H_2S clearly showed the incorporation of $^{13}\text{CH}_3$ groups

as evident from the substantial increase in the aliphatic carbon, from 6.6% to 12.1% when CO or ^{13}C O was used respectively. The ^{13}C -nmr also indicated a major increase in the region of $\delta 18.5\text{-}22$ ppm indicative of aryl-methyl groups as a result of treating coal tar with ^{13}C O/ H_2S .

DISCUSSION

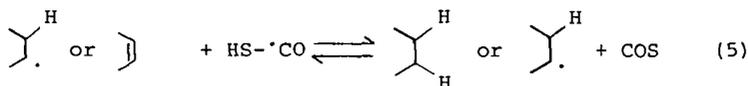
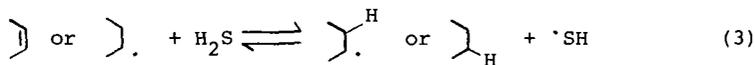
The above results show that the presence of CO with H_2S is required to achieve substantial hydrogenation and/or methylation of coal with H_2S . Hydrogen transfer to coal may involve nascent hydrogen or other similar intermediates that have been considered in CO/ H_2O reduction of coal. The weaker bond energy of H-S bonds in H_2S versus H-O bonds in H_2O undoubtedly provides one advantage for hydrogen transfer from H_2S . One must also consider a shift type reaction which can occur with H_2S /CO over sulfided catalysts to produce elemental H_2 [6].

While H_2S has a much lower heat of formation than water, a shift reaction for H_2S /CO is highly unfavorable as compared to the shift reaction for H_2O /CO.



A more likely mechanism for hydrogen transfer involves splitting of H_2S to give a hydrogen atom or abstraction of hydrogen atom from H_2S by the coal radical fragments followed by trapping the thiyl radical with CO to form a thioformyl radical. The latter is a better hydrogen donor than H_2S itself resulting in the formation of COS.

Scheme I



The ability of H_2S /CO to methylate aromatics only in the presence of a sulfided catalyst surface may also involve a thioformyl intermediate. We currently feel that thioformyl cations or radicals on an active metal sulfide surface attack aromatic rings which are electron rich. Subsequent hydrogenation of the thioformyl group appears to lead to the aryl-methyl product in a coal or coal tar. While methylation with H_2S /CO probably bears

resemblance to the formate mechanisms proposed earlier by Friedman, et al [7], further investigation of this area is necessary to make any accurate conclusions.

CONCLUSIONS

This investigation has shown that treatment of coal with a mixture of H₂S and CO allows the liquefaction of coal to an ethyl acetate soluble material. The interaction of H₂S/CO with coal results in both hydrogenation and methylation of coal fragments. While the mechanism has not been fully established, the ability of this reagent to solubilize coal in the absence of hydrogen and/or a donor solvent will allow reduction in the raw material cost of hydrogen in future liquefaction processes.

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TABLE 1. Dean Mitchell Coal Solubilization with H₂S, CO at 400°C for 2 hours

Run	Solvent	Reactants, Catalyst	Conversion (% daf)	Sulfur ^(a)
1	1-methylnaphthalene	N ₂	12.5	3.36
2	"	H ₂ S/N ₂	18.0	6.34
3	"	H ₂ S/CO	38.2	4.33
4	"	H ₂ S/CO, Co/Mo ^(b)	37.1	3.86
5	"	H ₂ S/CO, (NH ₄) ₂ MoO ₄ ^(c)	41.8	3.92
6	"	H ₂ S/CO, Co/Mo/K ₂ CO ₃ ^(b)	32.5	4.4
7	"	H ₂ S(25 g)/CO, Co/Mo ^(b)	46.6	4.85
8	"	H ₂ O/CO ^(d)	28.0	4.03

(a) Total sulfur in asphaltene.

(b) Sulfided Harshaw HT-400E. 3% Co, 12% Mo oxides on Al₂O₃.

(c) Wet impregnated on the coal followed by vacuum drying.

(d) H₂O quantity was 2.4 g, to provide same molar quantity as 4.25 g of H₂S. Pressure at ambient temperature was brought to 6894 kPa with CO.

TABLE 2. Delta Mine, Illinois No. 6 Coal Solubilization at 400°C for 2 hours

Run	Solvent	Reactants, Catalyst	Conversion (% daf)	Sulfur ^(a)
9	1-methylnaphthalene	N ₂	38.5	2.73
10	"	H ₂ S/CO	59.5	2.78
11	"	H ₂ S/CO, Co/Mo/K ₂ CO ₃ ^(b)	58.5	2.70
12	tetralin	N ₂	73.5	2.53
13	"	H ₂ S/CO, Co/Mo/K ₂ CO ₃ ^(b)	83.0	2.48

(a) Total sulfur in asphaltene.

(b) Sulfided Harshaw HT-400E. 3% Co, 12% Mo oxides on Al₂O₃.

TABLE 3. NMR Data of Coal Tar Reaction with
H₂S/CO

<u>Reactants</u>	<u>Aliphatic</u>		<u>Aromatic</u>	
	<u>H</u>	<u>C</u>	<u>H</u>	<u>C</u>
Coal tar, N ₂ (a)	5.3	4.4	94.74	95.6
Coal tar, H ₂ S, CO (a)	15.9	6.6	84.09	93.4
Coal tar, H ₂ S, ¹³ CO (b)	12.7	12.1	87.17	87.9

(a) Reaction was carried out in 300 mL autoclave at 400°C, 6894 kPa ambient pressure for 2 hours in the presence of 5% Harshaw HT-400E sulfided catalyst.

(b) Reaction was carried out in 30 mL microreactor at 400°C, 5515 kPa ambient pressure for 6 hours in the presence of 5% Harshaw HT-400E sulfided catalyst.