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REPORT ON GRANT NO. ET-78-G-01-3425

by

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Title: Coal Liquefaction Research

Work on this project began in November 1978 with one graduate student (W. McKee) and the assistance of Professor A. T. Bell (faculty advisor).

The first objective was to confirm earlier work by the principal investigator and his colleagues indicating that the presence of liquid water added to a SiO_2-Al_2O_3 catalyst permitted cracking of paraffin hydrocarbons at low temperatures at which no cracking occurred in the absence of water. It had also been observed that the catalyst remained white during cracking in the presence of water, while it turned dark (coke deposition?) in the absence of water.

Two types of equipment were initially used to test the cracking of n-hexadecane as a typical hydrocarbon. In one case, a round-bottom flask, containing the catalyst and hydrocarbon and a magnetic stirrer was connected by a short neck to a condenser and traps (distillation operation). In the other case, the flask was connected to a reflux condenser.

Catalysts used were Mobil Durabead A (containing zeolite) after crushing and Davison Chemical Co. silica-alumina (35% Al_2O_3-65% SiO_2) fluid bed catalyst. All catalysts were calcined in dry air at 500°C and if water was to be added, 10% water (on catalyst weight) was added dropwise while shaking the flask and was then permitted to equilibrate in an inert atmosphere for 24 hours at room temperature. N-hexadecane was then added.

The flask containing all ingredients was heated to 250°C in an oil bath and maintained at temperature for 1 hour while stirring.

In the case of the distillation set-up, a few drops of condensate were collected, when water was present in the flask. These consisted of water and light hydrocarbons (C_2-C_{14}). The catalyst stayed white. If no water was present in the flask, no overhead was obtained and the catalyst darkened. Results for the silica-alumina and the zeolite catalyst were equivalent.

When total reflux was employed, the contents of the flask were sampled and analysed. It was found that considerably more cracking (by a factor of 5-10) occurred even at the low temperature of 250°C, in the absence than in the presence of water. This is in contrast to the preliminary findings, which had all been carried out in a distillation set-up and may have been misinterpreted because in the presence of water some cracked hydrocarbons are steam distilled, which cannot occur in the absence of water.

Gaschromatographic analysis of the cracked hydrocarbons showed, however, a very unexpected result. The cracked product distribution of runs in the presence or absence of water varied considerably. The paraffin-olefin ratio in particular appears much higher when water is present than in its absence. This interesting and novel finding is now being explored.

PULPING OF COAL

Report to DOE - Fossil Fuels under
Grant No. ET-78-G-01-3425

by

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On the basis of verbal approval by Dr. Paul Scott of DOE, a brief (one month) study was undertaken with the help of Dr. James Sinclair (Postdoctural). This was based on the idea that our present picture of coal molecules[1,2] indicates that a large fraction of coal consists of polymerized lignine molecules. Since separation of lignine from cellulose is the prime reaction in the "pulping" of wood, it was thought possible that appreciable fractions of coal could be brought into aqueous solution by "pulping" with alkaline sulfites. No reference to such work were found in the literature. In case of success, an analysis of the aqueous solution would provide valuable information on the structure of the sulphonated coal molecules and one could foresee technilogical fall out.

The work undertaken was carried out with a lignite supplied by the Grand Forks Energy Technology Center, since liquite is closer to wood than subbituminous or bituminous coals. Results described in the attached memo by Dr. Sinclair indicate that the mild sulfonation of lignite did not succeed in solubilizing appreciable amounts of coal, probably because depolymerization is too difficult under the mild conditions used.

No further work on this subject is planned.

PULPING OF LIGNITE

by

James Sinclair

University of California

Berkeley, California

INTRODUCTION:

The sulfite pulping process for the delignification of wood is one of the oldest pulping processes known. Discovered in 1866 the process utilizes the reaction of a mixture of bisulfite and excess aqueous sulfur dioxide with the lignins in the wood to sulfonate these nonfiberous components rendering them water soluable.[1;2;3] It was felt that a similar sulfonation reaction might occur in coal (lignite) to solubilize various components present in the coal.

RESULTS AND DISCUSSION:

In general the results from this study of the sulfonation of coal in order to soluablize it in aqueous media were consistantly disappointing. No significant solubilities were achieved utilizing similar conditions to those in the wood pulping industry.

Two different sulfonating agents were explored for solubilization of a lignite (see Table 1). Sodium bisulfite and a sulfite cooking liquor prepared from calcium carbonate and excess sulfur dioxide in water. Prior to sulfonating the coal a blank experiment was performed in order to determine the percentage of recovery should no reaction occur. This experiment would correct for standard moisture loss on drying (the coal received was 32-64% moisture) and any components of the coal which might be water soluable without sulfonation. The blank experiment was performed by refluxing a sample of

coal in the correct proportion of water and working it up and drying under the conditions used in sulfonation reactions. A recovery of 88.2% (based on starting weight) was obtained.

The reaction of the coal with sodium bisulfite was performed three times (Table 2). In the first experiment a sample of coal was refluxed for 27½ hr. in a sodium bisulfite solution (calculated to be 6% in SO_2). Work up gave a 73.4% recovery. The second reaction utilized harsher sulfonating conditions, a sodium bisulfite solution 10% in SO_2 and refluxing for 65 hr. After work up a 68.2% recovery was obtained. The third experiment utilized higher temperatures and pressure. The reaction was run in a pressure bottle at 140°C and 45 psi for 16 hr., conditions close to those used in wood pulping. After washing and drying the residual coal, 70.9% was obtained.

The attempted sulfonation of the coal utilizing a calcium based cooking acid were performed using pressures and temperatures simulating the wood pulping process. The calcium bisulfite cooking acid was prepared and standardized according to the procedures of Casey[1] (pg. 140). A ratio of five parts cooking acid to one part dry (discounting the 32.64% moisture) coal was used. The experiments were performed by placing the coal in a pressure bottle fitted with a stainless steel gauge, introducing the appropriate amount of cooking acid and heating. In the first experiment the mixture was heated to 140°C (45 psi) for only ∿2 hr. before a malfunction of the hot plate caused the temperature to rise to 180°C (95 psi) for approximately one hour at which time the reaction was shut down. Work up gave a 79.9% recovery. This high recovery could be due to greater amounts of sulfonation due to the higher pressures and temperatures, or

precipitation of calcium salts by washing only with water. When the coal was dried, a small amount of white crust formed on the side of the vessel.

The second calcium bisulfite experiment was run very closely to wood pulping conditions except that a longer cooking time at 140°C was used. In wood pulping a temperature of 140°C and a time of only 8-10 hr. are used in order to avoid attacking the cellulose. In our experiments we wished to attack and solubilize as much of the coal structure as possible so the reaction was run at 140°C for 17 hr. On cooling crystals were observed in the reactor. It is known that calcium bisulfite precipitates if the concentration of free SO_2 in the solution drops. Consequently, the reaction was washed with a solution of SO_2 in H_2O and then with distilled water. Drying gave 70.8% recovery.

The results from these experiments indicate that little, if any, sulfonation to soluble portions of the coal was occurring. However, the general structure of coal contains many functional groups which should sulfonate readily. It is suspected that some sulfonation and solubilization of the coal was occurring (the mother liquors were brown in most cases) with concomitant sulfonation of the condensed nonsolubilizable coal structure.

These two factors combine to give the appearance of no reaction by balancing the weight loss due to soluabilization with weight gain by sulfonation of the coal backbone. The extent of these reactions cannot be determined by the experiments performed but is probably less than ten percent.

It was noted in Casey[1] (Pg. 183-184 that: "Wood which has been heated to high initial temperatures in the absence of free sulfurous acid (or sulfites) cannot be deliqnified in sulfite liquor." Since coal is formed by heat and pressure it is probable that sulfonation reactions to solubilize portions of the coal fail for the same reason they do in preheated wood.

CONCLUSION:

It is apparent from the table that no appreciable reaction to solubilize the coal occurred. Since it was desired to solubilize significant percentages of the coal in these experiments it must be concluded that the experiment to sulfonate and solubilize coal under wood pulping conditions was not successful.

This work was supported by the U.S. Department of Energy under Contract W-7405-ENG-48.

Table 1

Lignite from DOE,

Grand Forks Energy Technology Center*

Analysis:

13.44%	ash
32.64%	moisture
53.92%	carbonaceous material

Ash Composition:

27.63%	SiO_2
13.96%	AkO_3
14.17%	Fe_2O_3
0.61%	TiO_2
0.21%	P_2O_5
14.48%	CaO
3.90%	MgO
5.54%	Na_2O
0.41%	K_2O
19.09%	SO_3

* Analysis supplied by Grand Forks Energy Technology Center.

Table 2

Sulfonation of Coal

Sulfonating Agent	Temperature C	Pressure	Time (hr)	Percent Recovery*
NONE	100°	ATM.	20	68.2
$NaHSO_3$	100°	ATM.	27½	73.4
$NaHSO_3$	100°	ATM.	65	68.2
$NaHSO_3$	140°	45psi	16	70.9
$CaHSO_3/SO_2$	140-180°	45-95psi	3	79.9
$CaHSO_3/SO_2$	140°	45psi	17	70.8

* The percent recovery is the weight of dried material recovered divided by the starting weight of moist coal.

TREATMENT WITH WATER:

In a 250 ml round bottom flast fitted with a condenser was placed 39.45 qm of coal and 150 ml of water. The mixture was refluxed for 20 hr., cooled and transferred to two 250 ml centrifuge bottles. The mixture was centrifuged (2500 rpm ∿2 hr.) to give a cloudy solution. The supernatant was decanted the solid slurried with H_2O (∿300 ml) and centrifuged again to give a plae, but cloudy solution. The wash was repeated a third time to give a still slightly cloudy solution. The remaining coal was dried on a vac line to give 26.89 qm on 68.2% based on starting weight.

TREATMENT WITH $NaHSO_3$:

In a 100 ml round bottom flask, fitted with a condenser and magnetic stirring bar was palced 7.770 gm of coal and 50 ml of a $NaHSO_3$ solution 6% in SO_2 (prepared by diluting 51-3 gm of Mallencrodt $NaHSO_3$, 58.5% SO_2 assay, to 500 ml with water). The mixture was heated at reflux under N_2 for 27½ hr. After cooling the mixture was filtered through a tared fine sintered glass funnel, washed twice with ∿75 ml H_2O and dried to a constant weight in a vacuum dessicator on a vac-line. There was recovered 5.74 gm of black powder (73.4% based on starting coal).

The mother liquors were evaporated to give 6.84 gm of a pale brown solid.

TREATMENT WITH $NaHSO_3$:

In a 500 ml round bottom flask fitted as before was placed 88.6 gm of coal, 300 ml of H_2O and 51.7 gm of $NaHSO_3$ (10% SO_2/300 ml H_2O). The mixture was heated to reflux under N_2 for 65 hr. The mixture was cooled and poured into two 250 ml centrifuge bottles and

and centrifuged (2200 rpm s hr.) to give a yellow brown cloudy solution. The mother liquor was decanted and the residue slurred in ∿300 ml H_2O (∿150 ml each bottle) centrifuged and the cloudy brown liquor decanted. Filtering the supernatant through a fine frit failed to retain significant amounts of material and the filtrate was still cloudy. The washing procedure was repeated three more times, each time the supernatant was cloudy. The last wash ∿300 ml was diluted to 300 ml and 100 ml evaporated to give 0.89 gm black residue (or 2.67 gm/300 ml).

The well washed coal was dried 3 days on a vac line to constant weight to give 65.47 gm or 68.2% based on original weight.

TREATMENT WITH $NaHSO_3$ UNDER PRESSURE

In a pressure bottle was placed 39.34 gms of powdered coal, 140 ml of water, and 24.13 gm of sodium bisulfite. The bottle was sealed, heated to 100°C for 1 hr. and then to 140°C and 45 psi for 16 hr. The mixture was cooled and allowed to settle overnignt to give a clean brown solution over a black solid. The supernatant was decanted and the residue transfered to two centrifuge bottles and washed three times with ∿300 ml of water to give cloudy supernatants and a black solid. The solid was dried on a vacuum pump for 2½ days to give 27.91 gm (70.9%) of a free flowing black powder.

TREATMENT WITH $CaHSO_3/SO_2$ 180°C

A calcium sulfite cooking liquor was prepared by placing 81.9 gm powdered $CaCO_3$ in 3ℓ H_2O and bubbling in SO_2 until after all the $CaCO_3$ disolved. The solution was allowed to stand overnight and then titrated according to Cascy (pg 140) for total and free SO_2. The solution contained 6.1% total SO_2 and 4.5% free leaving 1.6% combined. This corresponds to a strong sulfite pulping liquor.

In a pressure bottle with gauge was placed 46.17 gm of coal and 160 ml of the sulfite liquor. The mixture was heated to 100° for 1 hr. and then to 135-140° (45 psi) for 2-3 hr. at which time the hot plate went beserk and stayed and stayed on heating the mixture to 180° (95 psi) when it was turned off. The mixture settled overnight and most of the brown clear liquor was decanted. The residue was slurried in H_2O and split between two centrifuge bottles. Centrifuging completely settled the particulate material. The pale yellow supernatant was decanted and the residue washed twice more with water (total ~1200 ml). The residue was dried 3 days on a vac line to give 36.87 gm, 79.9% (based on starting coal).

TREATMENT WITH $CaHSO_3/SO_2$ 140°

In a pressure bottle was placed 43.6 gm coal and 150 ml of the sulfite cooking liquor. The mixture was heated to 100° for 1 hr. then brought to 140° over 1½ hr. and heated at 140° 17 hr. (45 psi). The mixture was cooled and decanted to two centrifuge bottles. After centrifuging the clear brown sulfite cooking liquor was decanted and the residue washed in the normal manner first with 3 portions of an SO_2-H_2O solution ($CaHSO_3$ precipitates when the SO_2 concentration is too low) followed by 3 water washes. The residue was dried 3 days on a vac line to give 30-89 gm (70.8%) of black solid powder.

REFERENCES

1. J.P. Casey, Pulp and Paper Technology, Vol II, Interscience 1960. Other related general referenced.

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