

HOT VAPOR TREATMENT OF GULF PROVINCE LIGNITES

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INTRODUCTION

Fluidized steam beds are used in Germany (1, 2), Australia (3), Hungary (4) and more recently in The United States (5) for the drying of low rank coal. The technologies developed for this process can be carried out on a continuous mode, and provides an economical alternative to dewatering the fuel before, or during, the combustion operation. Fuels which contain sulfur do produce sulfurous effluent gases under steam drying conditions. It has long been known that treatment of coals with hot hydrogen produces hydrogen sulfide, and sulfur dioxide with hot oxygen. In fact, sulfurous fumes are sometimes noted when sulfur-containing coals are heated in air at temperatures below 200 °C. The present work is to study conditions under which this effect could be enhanced. The possibility of achieving significant desulfurization under the comparatively mild thermal conditions in a fluidized steam bed - typically 160 °C. with a wide range of residence times - prompted a search for vapor phase reagents that would induce chemical desulfurization of coal under hot vapor conditions.

Studies of chemical reagents for coal desulfurization are of several types. Chemicals of promise to us are the redox reagents, studied in water solution. Notable examples of these include the CO/H₂O water gas shift couple (6), numerous mineral acids (7, 8), alkali bases (9, 10), transition metal cations (11), peroxy radical generators (12, 13), and the HBr/Br₂ redox couple (14). Perchloroethylene is a reagent that has demonstrated desulfurization potential (15), and can be vaporized. EPRI has in fact sponsored research into the behavior of coals under hot vapor treatment (16). For our initial experiments, nitrous oxide, trimethylamine and dimethyl ether were selected. All three are well-documented electron transfer reagents.

Two reactors were constructed for the study (17). A fixed bed reactor was made from stainless steel tubing. The reactor is fed with premixed hot vapor, heated continuously, and monitored for temperature and pressure. It is the results of these experiments that will be discussed here. A fluidized bed was made from a section of tubing seven cm. in diameter, to study the process under more realistic conditions. Three typical Gulf province lignites were used. The hot vapor reagents consisted of nitrogen or air mixed with 0.2 % steam and 15 to 30 % of the reagent.

EXPERIMENTAL

Reactors A fixed bed reactor was fabricated from stainless steel tubing 1.9 cm. in diameter by 15.2 cm. long. Sintered stainless steel plates threaded at the bottom (100 um. pores) and top (90 um. pores) of the unit contain the sample and the fines that are generated. Line connections leading to and from the reactor are 1.27 cm. in diameter. Figure 1 is a diagram of the apparatus. Close to the entrance and exit ports to the reactor are thermal wells for thermocouples, and ports for the differential flow meter probes. The reactor is wrapped with heating tape. Gases are led through flowmeters into a section of 3/4" stainless steel tubing wrapped with heating tape. Water is also metered into this preheater. The heated vapors are led into the bottom of the reactor.

A fluidized bed system was made from a stainless steel tube 7 cm. in diameter and 12 inches high, fitted at the bottom with a removable distributor plate of sintered stainless steel. A 90 um. pore filter at the exit contained the fines. This unit takes a much larger gas volume than the fixed bed unit. The preheater is a series of parallel tubes positioned inside of a Lindberg tubular furnace. The reactor itself is heated by a tubular furnace as well.

Lignites Yegua sequence lignite was a polydisperse run-of-mine sample from the Texas Municipal Power Authority generating plant at Gibbon Creek. Particals as large as 7 mm. are present with intermediate and fine particals. Wilcox sequence lignites were also provided by TMPA, from their mines in Freestone County and Martin Lake. These two lignites were sieved to 16 X 30 mesh and 30 X 200 mesh respectively, and deslimed. Table 1 lists the properties of these lignite samples.

Reagents Nitrous oxide was obtained from the Nitrous Oxide Corporation. Trimethylamine and dimethyl ether were supplied by the Aldrich Chemical Company. The gas mixtures consist of nitrous oxide in moist air, trimethylamine in moist nitrogen, and dimethyl ether in moist nitrogen. The composition of the gases is given in Table 2.

Hot Vapor Treatment Temperatures under which the lignites were treated are shown in Table 3. Also shown here are the sulfur contents and calorific values of the untreated, nitrogen control, and treated lignites. Treated samples were sealed under nitrogen until their analyses.

Analysis Proximate analysis were done on all samples, with analysis for total sulfur. In selected experiments, samples of the effluent gases were analysed by gc-ms.

RESULTS AND DISCUSSION

Results from the gas mixtures in Table 2, at the temperatures listed in Table 3, for the three lignites treated in the fixed bed reactor, are listed in Table 3. Here is listed the total sulfur content, calorific value and the sulfur emissions parameter. Although none of these experiments show significant desulfurization, some aspects of the data deserve note. None of the Gibbon Creek samples show a change in their calorific value, but both the Freestone County and Martin Lake samples increase in calorific value by 15 to 20%.

Analysis of selected samples of the effluent gases (Freestone County, N_2 ; Martin Lake, NMe_3 and Martin Lake Me_2O) showed that hydrogen sulfide is evolved. The apparent increase in the sulfur content of the treated lignites indicates that mass loss is occurring. The volatile matter yield of the treated samples is never more than 3 to 4% higher than the values given in Table 1. Tar does collect in the effluent gas tubing. All this suggests that mass loss from the samples, by decarboxylation or resin devolatilization, is larger than any desulfurization effect.

When heated at 110 °C. for an hour, all the treated samples show an increase in mass, typically from 2 to 5%. The treatment of Martin Lake lignite in the fluidized bed at 110 °C. results in the formation of dust, which is not present in the original lignite.

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Table 1: Properties of the Lignites Studied.

Lignite	H ₂ O % Whole	S _{tot} % Dry	Ash Yield % Dry	Volatile Matter % DAF	Calorific Value Btu/#
Gibbon Creek	30.5	1.45	37.0	58.7	7630
Freestone County	12.2	0.73	9.2	50.0	9421
Martin Lake	11.8	1.79	10.7	51.0	9219

Table 2: Hot Vapor Treatment Conditions. Temperatures are listed in Table 3.

Label	Treatment	Vapor Composition	Residence Time, Min.
UN	Untreated Lignite	-	-
N ₂	Wet Nitrogen Control	N ₂ /H ₂ O = 99.8/0.2	20
N ₂ O	Nitrous Oxide	N ₂ O/Air/H ₂ O = 24.8/75.0/0.2	20
NMe ₃	Trimethyl Amine	NMe ₃ /N ₂ /H ₂ O = 19.2/80.6/0.2	20
Me ₂ O	Dimethyl Ether	Me ₂ O/N ₂ /H ₂ O = 23.9/75.9/0.2	20

Table 3: Treatment temperatures, Sulfur contents and calorific values for the untreated lignites (UN), wet nitrogen controls (N₂), and representative samples of the treated lignites.

Lignite	Treatment (Table 2)	Temp. °C.	S _{tot} % Dry	Calorific Value, BTU/#	#SO ₂ MBTU
Gibbon Creek	UN	-	1.45	7630	3.8
	N ₂	220	1.33	7666	3.5
	N ₂ O	220	-	-	-
	NMe ₃	130	1.36	7666	3.6
	Me ₂ O	220	1.44	7623	3.8
Freestone County	UN	-	0.73	9421	1.6
	N ₂	220	1.00	11335	1.8
	N ₂ O	220	1.27	11466	2.2
	NMe ₃	130	0.91	11063	1.7
	Me ₂ O	220	0.93	11213	1.7
Martin Lake	UN	-	1.79	9219	3.9
	N ₂	120	2.15	10909	3.9
	N ₂ O	110	2.39	10784	4.4
	NMe ₃	110	2.29	10837	4.2
	Me ₂ O	120	2.09	10919	3.8

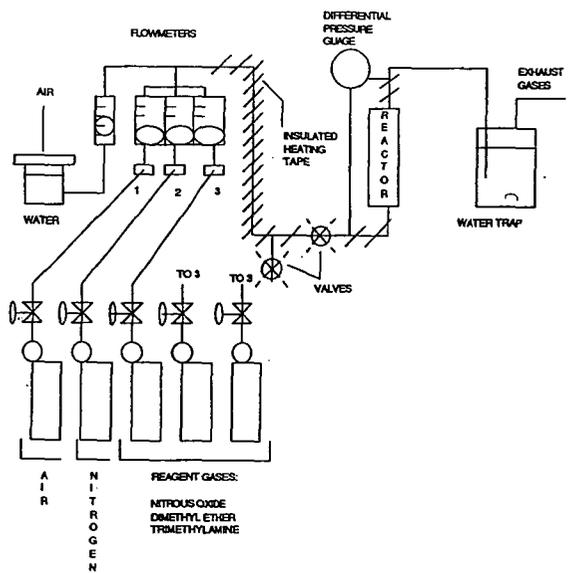


Figure 1: Diagram of the Fixed Bed Reactor. In the Fluidized Bed Reactor, the preheater and Reactor are heated by Lindberg tubular furnaces.