

## THE EFFECT OF MILD OXIDATION ON THE THERMAL DESULFURIZATION AND HYDRODESULFURIZATION OF TWO ILLINOIS BITUMINOUS COALS IN A FLUIDIZED BED REACTOR

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### ABSTRACT

Two high sulfur Illinois No. 6 coals were desulfurized in a fluidized bed reactor (FBR) to less than one percent sulfur by a thermal and chemical approach which included pyrolysis followed by char hydrodesulfurization. Chars were prepared for hydrodesulfurization by three different procedures; pyrolysis only, oxidation prior to pyrolysis and oxidation after pyrolysis. Pre-oxidizing conditions reduced agglomeration during pyrolysis and for one coal, which was physically cleaned, it led to significantly increased overall sulfur removal compared to the non-oxidized char. Oxidation after pyrolysis had no obvious beneficial effects. Under the best conditions tested, chars were produced having sulfur contents less than one percent for both coals.

### INTRODUCTION

Efforts to abate the deleterious impact of burning high sulfur coals are easily classified into three approaches. Post-combustion desulfurization, which includes wet limestone scrubbing, is being utilized by electric utilities but is beset by high capital and operating costs. The second category, desulfurization during combustion, includes fluidized bed combustion. This method of sulfur dioxide control is quite promising, but has not yet gained widespread usage by electric utilities. The third classification is precombustion desulfurization which includes physical and chemical coal cleaning. As yet, only physical cleaning is used commercially but it is limited to inorganic sulfur removal.

One approach to removing sulfur, including organic sulfur, is to first pyrolyze the coal and follow this step with high temperature hydrodesulfurization. This combination of steps is quite effective in removing a significant amount of the total sulfur from high sulfur coals. The products of these two steps include up to one barrel of pyrolysis oil per ton of coal, a low to medium Btu gas, coal char and elemental sulfur [1]. The relative amounts of each product depend on the coal feed and on the conditions used for the pyrolysis and hydrodesulfurization steps.

In the work described here, two Illinois basin coals were pyrolyzed in a fluidized bed reactor under a variety of conditions and then subjected to hydrodesulfurization. Three pyrolysis treatments were employed. The first treatment, denoted as pre-oxidized, consisted of a mild oxidation prior to pyrolysis, followed by pyrolysis under nitrogen. The second treatment, denoted as non-oxidized, was pyrolysis under a nitrogen atmosphere. The third treatment, denoted as post-oxidized was identical to the second or non-oxidized treatment, except that a mild oxidation occurred after the pyrolysis step. Thus, three chars were produced, pre-oxidized, non-oxidized, and post-oxidized, and these were used as hydrodesulfurization feeds.

While preoxidation is effective in decaking highly agglomerating coals [2], it does lower the yield of pyrolysis oil and is undesirable for this reason alone. However, preoxidation apparently leads to larger pores in an otherwise microporous char [3]. This tends to increase both the rate and the extent of hydrodesulfurization [4]. Since pre-oxidation has been effective in producing chars which are more reactive towards hydrogen, it was hypothesized that an oxidation of the char after removal of the volatile matter might also be effective. This processing sequence would permit maximum conversion of coal to pyrolysis oil. Agglomeration would be averted in some other way such as multistaged heating.

## EXPERIMENTAL

Coal samples - Two Illinois No. 6 coals were used in this study. The samples were obtained from the Illinois Basin Coal Sample Program (IBCSP) and are referred to as the IBCSP-1 and IBCSP-4 samples [5]. The IBCSP-1 coal is a mine-washed sample containing 4.62% total sulfur of which 3.35% is organic sulfur. The IBCSP-4 sample is a Run-of-Mine sample containing 34% ash and 4.2% total sulfur (equivalent to 9.87 lbs SO<sub>2</sub>/MMBtu). In order to reduce the mineral matter and pyritic sulfur content, two types of physically cleaned coal were prepared from the IBCSP-4. A "deslimed" coal was prepared by slurring and agitating the sample and then sieving it over a 235 mesh screen. The step effectively reduced the clay content of the sample, but retained much of the coarser pyrite and other mineral matter. The sample after treatment had 14.8% ash, 3.05% pyrite and 6.28% total sulfur on a dry ash free (daf) basis. A 28x200 mesh fraction was prepared from the deslimed coal utilizing a staged crushing and screening technique to ensure that the size fraction was representative of the starting material.

A second sample of physically cleaned IBCSP-4 was prepared using a gravity concentrating table in order to reject liberated coarse pyrite grains and other mineral matter. The sample was also deslimed using the above procedure to reject any clays that reported to the coal fraction. Following this treatment, the "tabled" coal had 4.18% total sulfur of which 1.22% sulfur was pyritic. Analyses of the 28x200 mesh fractions of both tabled and deslimed coal appear in Table 1.

Char production - Chars for hydrodesulfurization experiments were prepared in bulk using a 2-inch, batch, fluidized bed reactor. The description of this apparatus appears elsewhere [6]. Basically, 200-gm batches of coal were pyrolyzed in this system and when appropriate, reacted with gaseous streams of dilute oxygen. The reactor was constructed of type 304 stainless steel and was heated externally by a 3-inch, tube furnace. A microprocessor was used to control the bed temperature via a type K thermocouple immersed in the center of the bed.

The three different types of chars prepared here are designated as pre-oxidized, non-oxidized, and post-oxidized. Several batch runs at each treatment regime were necessary to provide kilogram-quantities of each type of char for hydrodesulfurization tests. After combining the appropriate batches, the chars were then riffled into 25-gm portions, and stored under inert conditions in sample bottles which were sealed with paraffin.

Pre-oxidized chars were prepared by heating a 200-gm charge of coal to 250°C in the 2-inch FBR using nitrogen as a fluidizing gas. Once at 250°C, the fluidizing gas was switched to five percent oxygen in nitrogen. The coal was fluidized under these conditions for 30 min. at which time the fluidizing gas was switched back to nitrogen. The temperature was raised to 850°C and held there for 15 min. The reactor was cooled to ambient conditions under a purge of nitrogen.

Non-oxidized chars were prepared using heating schedules similar to those used by the FMC Char Oil Energy Development (COED) process [7]. Multistaged or slow heating of our coals was necessary to avoid agglomeration. For IBCSP-4 coal, four soak temperatures were used, 350, 375, 400, and 425°C. For IBCSP-1 coal, a heating rate of 1.7°C/min was employed without any isothermal soak periods. Agglomeration did not occur. Once the temperature reached 850°C, the char was held for 15 min. before cooling to ambient conditions under a purge of nitrogen.

The post-oxidized samples were prepared in the same way as the non-oxidized samples with one exception. During the cool down period, the bed temperature was allowed to reach 450°C for IBCSP-1 coal or 250°C for IBCSP-4 coal and then held at that temperature while five percent oxygen was admitted as a fluidizing gas. The temperature was lowered to 250°C for the second coal because this temperature was preferable for a comparison of pre-oxidization with post-oxidation. The post-oxidative treatment was continued for 15 min. (IBCSP-1) or 30 min. (IBCSP-4) after which the fluidizing gas was switched back to nitrogen. The reactor was then cooled to ambient conditions.

Hydrodesulfurization - A 1-inch batch fluidized bed hydrodesulfurizer was used for char hydrodesulfurization tests. The reactor was constructed from a 24-inch length of type 446 stainless steel, schedule 40 pipe. A distributor plate of porous Hastelloy-X stainless steel (average pore size of 10 microns) was located nine inches from the bottom of the pipe. The space below the plate was filled with 1/4-inch ceramic Raschig rings which served as a gas preheater. Type 446 stainless steel caps were used at both ends of the reactor and were fitted to accept 1/4-inch tube fittings.

For each hydrodesulfurization (HDS) experiment, approximately 10 grams of char was accurately weighed and charged to the reactor. The sample was heated rapidly to the reaction temperature under a nitrogen flow which generally took about 45 min. Once the system reached the designated reaction temperature ( $\pm 1^\circ\text{C}$ ), nitrogen was shut off and hydrogen was introduced to the reactor for a period of 90 minutes except where noted. When the desired treatment time had elapsed, hydrogen was turned off and nitrogen was once again introduced to the reactor. The reactor system was allowed to cool to near room temperature and the desulfurized char was removed, weighed and analyzed.

## RESULTS AND DISCUSSION

Hydrodesulfurization of IBCSP-1 coal - Three chars were prepared from IBCSP-1 coal (pre-oxidation, non-oxidation, and post-oxidation). As shown in Figure 1, it can be seen that after pyrolysis, the post-oxidized char had the lowest sulfur content, approximately 2.4%. The non-oxidized char contained roughly 2.7% sulfur while the pre-oxidized char was marginally higher at 2.8% sulfur. Table 2 shows that hydrodesulfurized chars were produced having sulfur contents of 0.9% sulfur (an average of four combinations of temperature and hydrogen flow rate) from pre-oxidized coal compared to 1.2% average sulfur for the same array of conditions for the post-oxidized sample. By taking an average over the four sets of conditions, the effect of oxidation is measured over a wide range of conditions.

Examination of the percent initial char sulfur remaining after hydrodesulfurization reveals that hydrodesulfurization removed the most sulfur from the pre-oxidized sample. On average, only 27.4% of the sulfur initially present in the HDS sample remained after treatment. For the non-oxidized sample, 34.7%, on average, of the char's sulfur remained after hydrodesulfurization while 42.6%

remained for the post-oxidized char. Apparently, pre-oxidized chars are the most reactive towards hydrogen.

The final sulfur contents of the chars do not show appreciable differences between the treatments. Thus, there is no apparent advantage to post-oxidation as a part of a multi-step process which includes pyrolysis and hydrodesulfurization. As can be seen in Figure 1, sulfur is removed during the post-oxidation. The amount is relatively small but it is presumably converted to sulfur dioxide. Also, the amount of sulfur removed during hydrodesulfurization, the sulfur being removed as hydrogen sulfide, is the least of all three treatments. When considering product differences with regard to ease of gas cleanup, the post-oxidation treatment would be the most troublesome if it produced dilute sulfur dioxide that had to be removed from the gas stream. Mild pre-oxidation is not expected to yield appreciable sulfur dioxide. As there was no overall improvement in desulfurization when post-oxidized chars were used, this treatment was not investigated further with this particular coal.

Hydrodesulfurization of deslimed IBCSP-4 coal - As shown in Figure 2, the sulfur content of post-oxidized chars, non-oxidized chars and pre-oxidized chars produced from this coal with higher pyrite content were all similar. As shown in Table 3, all three types of hydrodesulfurized chars, on average, were similar in sulfur content. Although there is some scatter among the data, there is no treatment that is clearly superior. As with IBCSP-1, the post-oxidation treatment is of dubious merit and was not investigated further.

Pre-oxidation is quite effective in controlling agglomeration although pyrolysis oil yields are usually reduced. For the case of IBCSP-1 and IBCSP-4 (deslimed) coals, the sulfur content of the hydrodesulfurization products were not appreciably affected by pre-oxidation. However, due to its extreme effectiveness in handling caking coals, it was investigated further.

Effect of physical cleaning of IBCSP-4 coal - If a coal contains an appreciable quantity of pyritic sulfur, it is desirable to physically remove as much as possible before any processing. This is due to the thermodynamic limitations imposed by the unfavorable reaction between ferrous sulfide and hydrogen. Pyrite is converted to ferrous sulfide during pyrolysis and in order to remove this remaining inorganic sulfur, high hydrogen space velocities are required [8]. In the case of IBCSP-4, where the pyritic sulfur content was 3.05%, as compared to 1.34% pyritic sulfur in the IBCSP-1 coal, it seemed logical to remove additional pyrite by tabling. This step alone lowered the pyritic sulfur content to 1.22% or roughly that of the IBCSP-1 coal.

Removing pyritic sulfur from the tabled coal resulted in a vastly more effective hydrodesulfurization step. This is clearly demonstrated in the data shown in Table 4. Data in this table are organized in eight sets of two experiments. For each set, the only difference between the experiments is the level of physical cleaning. For the first set, lines one and two, the sulfur content in the product is 2.99% for the deslimed and 2.01% for the tabled coal. This same trend can be seen in each succeeding set of runs. On average the tabled coal resulted in a hydrodesulfurized product which was 1.25 percent lower in sulfur content.

A close inspection of the data in Table 4 reveals a synergistic effect between physical cleaning and oxidation. In lines 1 and 3, all factors remain constant except for oxidation. This is also true for lines 2 and 4, 5 and 7, 6 and 8, etc. For deslimed coal, the effect of oxidation on desulfurization is generally

quite small or nonexistent. However for tabled coal, desulfurization is significantly increased for all cases in which pre-oxidized chars were used. Thus, with this particular cleaned coal, pre-oxidation is quite effective in aiding hydrodesulfurization. The relative merit of a pre-oxidation step compared to no oxidation depends on technical and economic considerations. Pre-oxidation would permit coals to be pyrolyzed faster than by staged heating resulting in a cost savings. However, the decreased oil yields would impact negatively on the economics.

Concluding remarks - A combination of pyrolysis and char hydrodesulfurization is an effective method to reduce the total sulfur content of high sulfur coals to less than one percent. Oxidation, both before and after pyrolysis, generally had little effect on the overall level of desulfurization for two Illinois basin coals, although pre-oxidation markedly increased the extent of desulfurization for physically cleaned IBCSP-4. In fact, the only appreciably desulfurized IBCSP-4 chars had been pre-oxidized and physically cleaned.

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Table 1. Analysis of feed coals.

Analysis	IBCSP-1	IBCSP-4	IBCSP-4	
			Deslimed	Tabled
<u>Proximate, wt% as received</u>				
Moisture	14.1	10.2	3.5	1.5
Volatile matter	37.9	27.4	36.6	38.3
Fixed carbon	39.2	28.2	45.1	50.4
Ash	8.8	34.2	14.8	9.8
<u>Ultimate, wt% daf</u>				
Hydrogen	5.42	5.25	5.26	4.64
Carbon	75.41	69.86	77.91	81.66
Nitrogen	1.32	1.22	1.57	1.90
Oxygen	12.96	11.29	8.97	7.61
Sulfur	4.75	6.37	6.28	4.18
pyritic	1.34	3.54	3.05	1.22
organic	3.34	2.67	3.23	2.86
sulfatic	0.07	0.15	tr	0.10
Calorific value, Btu/lb	12,606	8,492	11,554	12,556
Specific sulfur content, lbs SO <sub>2</sub> /MMBtu	5.81	9.87	8.88	5.91

Table 2. Hydrodesulfurization of char from IBCSP-1 coal<sup>a</sup>.

Oxidation	Experimental Conditions		Sulfur in HDS char %	Initial char S left in HDS char %	
	Temp °C	Flow cc/min			
Pre	800	500	0.91	27.6	
Pre	850	500	1.00	30.5	
Pre	800	1000	0.92	28.0	
Pre	850	1000	0.83	23.3	
			Average	0.92	27.4
Non	800	500	1.33	42.9	
Non	850	500	1.13	35.2	
Non	800	1000	0.88	27.8	
Non	850	1000	1.06	32.8	
			Average	1.10	34.7
Post	800	500	1.27	47.2	
Post	850	500	1.24	43.8	
Post	800	1000	1.03	35.5	
Post	850	1000	1.24	44.0	
			Average	1.20	42.6

<sup>a</sup>Time, 90 minutes

Table 3. Hydrodesulfurization of char from deslimed IBCSP-4<sup>a</sup>.

Oxidation	Sulfur in HDS char wt %	SO <sub>2</sub> from burning HDS char lbs/MMBtu	Initial char S left in HDS char %
Pre	1.84	3.23	45.2
Pre	1.95	3.36	45.5
	Avg 1.89	3.30	45.3
Non	1.95	3.44	40.0
Non	1.67	2.80	38.4
Non	2.04	3.50	46.2
	Avg 1.89	3.25	41.5
Post	1.90	3.34	43.7
Post	2.27	3.97	52.1
	Avg 2.09	3.66	47.9

<sup>a</sup>Temperature, 850°C; time, 90 minutes; H<sub>2</sub> flow rate, 1000 cc/min.

Table 4. Hydrodesulfurization of char from tabled and deslimed IBCSP-4<sup>a</sup>.

No.	Experimental Conditions				Sulfur in HDS char wt %	SO <sub>2</sub> from burning HDS char lbs/MMBtu	Initial char S left in HDS char %
	Coal Type	Pre-Oxi- dized	Temp °C	Time min.			
1	Deslimed	No	750	45	2.99	5.25	70.05
2	Tabled	No	750	45	2.01	3.30	66.40
3	Deslimed	Yes	750	45	3.40	5.88	86.00
4	Tabled	Yes	750	45	1.50	2.42	54.30
5	Deslimed	No	850	45	2.57	4.53	59.40
6	Tabled	No	850	45	1.62	2.65	52.30
7	Deslimed	Yes	850	45	2.51	4.30	58.85
8	Tabled	Yes	850	45	1.22	1.97	43.70
9	Deslimed	No	750	90	2.77	4.88	64.55
10	Tabled	No	750	90	1.76	2.85	57.25
11	Deslimed	Yes	750	90	2.64	4.49	63.10
12	Tabled	Yes	750	90	1.14	1.82	40.95
13	Deslimed	No	850	90	2.24	3.99	51.20
14	Tabled	No	850	90	1.41	2.31	45.60
15	Deslimed	Yes	850	90	2.28	3.86	53.05
16	Tabled	Yes	850	90	0.77	1.24	27.15

<sup>a</sup>Hydrogen flow rate, 750 cc/min.

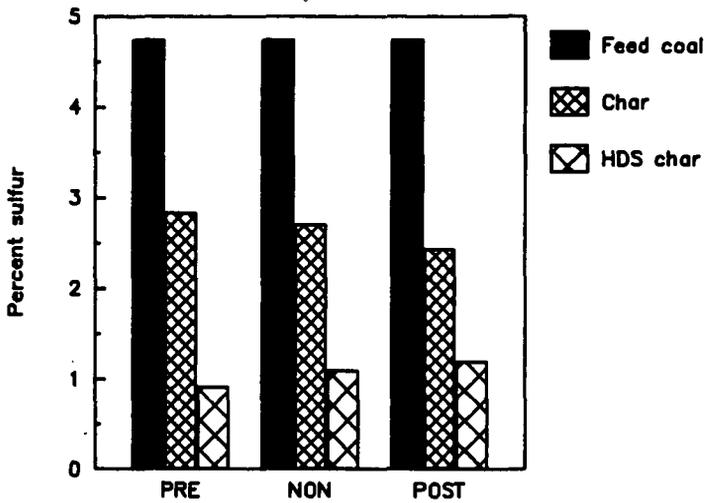


Figure 1. Desulfurization of IBCSP-1.

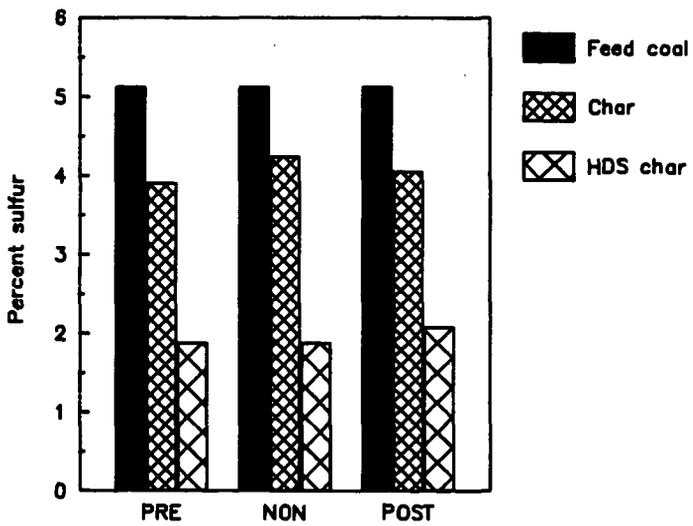


Figure 2. Desulfurization of IBCSP-4.