

COMBUSTION PROPERTIES OF ILLINOIS COAL-CHAR BLENDS

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INTRODUCTION AND BACKGROUND

The principal product (about 60-70 percent by weight) of mild gasification (MG) processes is a partially devolatilized coal (herein referred to as char) that must be effectively utilized to help the overall economics of the process. The loss of volatile matter (VM) indicates loss of hydrocarbon materials from the coal that are desirable for ignition, carbon burn-out and flame stability. In addition, the chars produced from processing high-sulfur Illinois coals still contain a high residual sulfur content which, when burned directly, would exceed the years 1995 and 2000 emissions limits of 2.5 and 1.2 lbs SO₂/MMBtu.

Recent research suggests that MG of a high-sulfur Illinois coal followed by a low temperature oxidation step may produce a low-sulfur char with considerable VM [1-3]. One potential use of a low sulfur-char is as a compliance fuel burned in a boiler designed to burn low-volatile fuels. The char could also be burned in conventional pulverized coal (PC) boilers with or without an auxiliary fuel such as methane or by blending with high-sulfur Illinois coal or low-sulfur Western coal. However, the combustion characteristics of low-sulfur chars have not been researched extensively. Previous results obtained at the Illinois State Geological Survey (ISGS) indicate that the char derived under MG conditions, when mixed with coal to make a 25% VM blend, can be burned with an acceptable combustion efficiency in PC boilers [3]. This paper describes our efforts to prepare a low-sulfur char from Illinois coal, blend this char with the parent coal, and determine the combustion properties of the char and coal-char blends.

EXPERIMENTAL

The chars used in this work were prepared in a continuous-feed rotary tube kiln (RTK) from an Illinois No. 2 hvCb coal, sample IBC-102 of the Illinois Basin Coal Sample Program [4]. Details of experimental methods are given elsewhere [5]. Preoxidation of -48 mesh coal was done at 150°C for 30 min in air using a feed rate of about 0.9 kg/h. The preoxidized coal was fed at 0.5 kg/h and pyrolyzed in N₂ at 600°C for 30 min. Low temperature oxidation (LTO) was done to remove sulfur from the char. Char was fed at 0.4 kg/h and oxidized at 430°C for 10 min in 17% O₂, balance N₂ during LTO.

The feasibility of decreasing SO₂ emissions during combustion tests by blending calcium-based sorbents with coal prior to charring was investigated. The coal was blended with either an ISGS high-surface area hydrated lime (HSAHL) [6, 7] or a commercially available hydrated lime (COMHYD). Coal-hydrated lime blends were prepared with 68% coal and 32% hydrated lime by weight. A continuous feed charring oven (CFCO) was used for char production [5]. The coal-hydrated lime blends were pyrolyzed in the CFCO using a feed rate of about 2 kg/h, a bed depth of 15 mm, a maximum temperature of 600°C and a residence time of about 16 min.

Five different blends were prepared from the available samples. All samples were ground to 70% -200 mesh prior to blending. The samples prepared were: 1) RTK blend - 62% (by weight) coal + 38% of the RTK char; 2) RTK_{HSAHL} blend - 92% RTK blend + 8% HSAHL; 3) CFCO_{HSAHL} blend - 75% coal + 25% CFCO char (prepared from a coal/HSAHL mix); 4) CFCO_{COMHYD} blend - 75% coal + 25% CFCO char (prepared from a coal/COMHYD mix); 5) Coal_{HSAHL} blend - 90% coal + 10% HSAHL.

Combustion tests were done at the U.S. EPA in their Innovative Furnace Reactor (IFR) by maintaining a constant flow rate of primary, secondary and tertiary air and adjusting the fuel feed rate to achieve a constant oxygen level of about 8.0% in the effluent. This fuel feed rate corresponded to a firing rate of about 39,000 to 42,000 Btu/h. Sorbent was added downstream at a constant injection temperature of about 1200°C and at Ca/S molar ratios between 0 and about 2.4.

Selected samples were tested at the University of North Dakota Energy and Environmental Research Center (UNDEERC) in an optical access drop-tube furnace (DTF) to determine deposit growth factors, deposit strengths, and deposit compositions. Initial slagging temperatures were determined using the test conditions described elsewhere [5]. Coal was combusted at 50% excess air using a feed rate corresponding to about 0.007 g/min of ash, until a deposit of 0.6-1.0 cm had grown on the probe. The temperature was increased at 5°C/min until the deposit began to slump and consolidate (initial slagging temperature). Deposit growth factors are the ratio of deposit weight to the weight of ash fed. Fouling tests were done using conditions that simulate the environment in a boiler convective pass. Feed rates and excess air were the same as for slagging conditions. Deposit crushing strengths were determined by measuring the pressure required to crush the main portion of each deposit following removal from the DTF.

RESULTS AND DISCUSSION

Analyses of the -48 mesh samples prepared from IBC-102 in the RTK are shown in Table 1. The only significant difference between the raw coal and the preoxidized coal appears to be the slightly lower hydrogen and higher oxygen content of the preoxidized sample. During preoxidation, two processes occur concurrently, that is the gain of oxygen, and removal of hydrogen, carbon and oxygen from the coal as CO, CO₂ and water. The latter process becomes of increasing importance as the temperature is increased [8].

Table 1. Analyses of samples prepared in the RTK and CFCO (moisture free).

	Preoxidized				CFCO	
	IBC-102	IBC-102	MG char	RTK char	Char _{HSAHL}	Char _{COMHYD}
Moisture	10.96	1.57	0.79	3.42	0.73	0.74
Proximate						
Volatile Matter	40.43	39.47	15.53	19.93	32.29	33.58
Fixed Carbon	53.38	54.39	75.39	69.86	27.18	27.13
H-T Ash	6.19	6.14	9.08	9.49	40.53	39.29
Ultimate						
Carbon	74.42	74.38	80.97	77.77	45.23	46.74
Hydrogen	4.81	3.73	0.99	0.92	2.74	3.37
Nitrogen	1.38	1.33	1.76	1.85	0.97	0.99
Oxygen	9.31	9.57	3.43	7.07	8.46	7.39
Sulfate Sulfur	0.56	0.51	0.07	0.14	---	---
Pyritic Sulfur	1.45	1.48	0.18	0.17	---	---
Organic Sulfur	1.31	1.29	1.85	1.17	---	---
Total Sulfur	3.32	3.28	2.11	1.48	2.08	2.22
Btu/lb	13,330	13,225	13,284	12,499	7,271	7,830
lb SO ₂ /MMBtu	4.98	4.96	3.18	2.37	5.72	5.67

The pyritic sulfur content decreases and the organic sulfur content increases during devolatilization of the preoxidized coal (Table 1). Typically, 30-60% of the organic sulfur is released at pyrolysis temperatures below about 550°C [2, 9, 10]. However, Huang and Pulsifer [11] found that during pyrolysis in the presence of the gases derived from coal, only 25-33% of the organic sulfur is removed. Conditions in the RTK would be similar to those of Huang and Pulsifer because the nitrogen sweep gas flowed counter current to both to the gases released from the coal and the solid sample as it moved through the reactor. It has also been found that a significant amount of the sulfur released during pyrite decomposition can be retained in the char or react with the organic portion of the coal to form carbon-sulfur bonds [2, 11, 12].

After LTO, the VM content of the char is higher than that of the precursor char due to the chemisorption of oxygen, which is also shown by the increase in oxygen content (Table 1). These stable carbon-oxygen complexes evolve at a higher temperature than the inherent VM, and would not be expected to contribute to the flammability characteristics of the chars. The pyritic sulfur content remains constant while the organic sulfur content decreases substantially compared to the precursor char. This is unexpected, as previous researchers have found that LTO removes mainly pyritic sulfur [2, 11, 13]. The decrease in organic sulfur content may be due to the removal of sulfidic and/or elemental sulfur, which is included in the organic sulfur fraction during determination of the forms of sulfur in the char.

The SO₂ emissions of the RTK char are significantly higher than for a similar char prepared in a fluidized bed reactor (FBR) [5]. Smaller particle diameters and better gas-solid contact in the FBR may help explain this trend [5]. In addition, because the gases flowed countercurrent to the solid flow in the RTK, the SO₂ produced during oxidation may have accumulated to the point where the back reaction of SO₂ with Fe and/or the carbonaceous matrix would be thermodynamically favorable. Based on estimates of the SO₂ concentrations in the RTK during LTO, the major iron-containing product of this system would be Fe₂(SO₄)₃, not Fe₂O₃. This would result in lower sulfur removal than in the FBR, where the SO₂ produced is rapidly removed from the system by the fluidizing gas. A recent study found that while using a multi-step process involving oxidation, about 57% and 87% of the sulfur was removed from an Illinois coal in a fixed-bed and a fluidized-bed reactor, respectively [1].

The results of analyses of the chars prepared in the CFCO are shown in Table 1. The samples prepared with the two different hydrated limes are almost identical according to these results. The VM content of the samples includes the decomposition of Ca(OH)₂ and CaCO₃ that were present from the hydrated lime. Methods were developed to discern the portion of VM due to decomposition of calcium compounds and that due to VM remaining from the coal [5]. Overall, the VM content of the chars derived from the original coal fraction is estimated to be about 13% and 14.5% for the HSAHL and COMHYD chars. The HSAHL and COMHYD chars contained 29.9% and 29.4% CaO. Assuming that all of the sulfur released during pyrolysis

was captured by the Ca-based sorbent, the amount of free calcium available in the char/lime blends for sulfur capture during combustion was 17.7% by weight.

Analyses of the coal-char blends prepared are shown in Table 2. The four samples that have Ca-based sorbents added exhibit higher ash contents, as expected. It is unclear why the total sulfur contents of these samples are also higher, but could be due to the formation of either CaSO_4 or CaS and their subsequent decomposition during tests to determine total sulfur contents.

Table 2. Analyses of coal-char blend samples prepared from IBC-102 (moisture free).

	RTK blend	RTK _{HSAHL} blend	CFCO _{HSAHL} blend	CFCO _{COMHYD} blend	Coal _{HSAHL} blend
Moisture	8.95	7.78	10.21	10.61	12.62
Proximate					
Volatile Matter	31.31	33.05	39.28	38.14	40.12
Fixed Carbon	60.80	48.15	39.31	40.63	38.70
H-T Ash	7.89	18.80	21.41	21.23	21.17
Ultimate					
Carbon	76.12	70.25	65.80	66.15	65.16
Hydrogen	4.11	3.91	4.49	4.63	6.59
Nitrogen	1.49	1.39	1.27	1.25	1.20
Oxygen	7.81	3.32	4.01	3.77	2.83
Sulfur	2.59	2.33	3.02	2.96	3.05
Btu/lb	12,894	11,800	11,480	11,647	11,799
lb SO ₂ /MMBtu	4.02	3.95	5.26	5.08	5.17

Combustion Tests

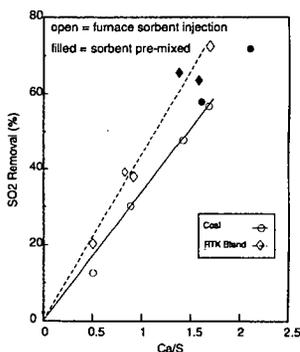


Figure 1. SO₂ removal efficiencies during IFR tests.

The SO₂ removal efficiencies for various Ca/S ratios during combustion of coal and RTK blend samples tested in the IFR are shown in Figure 1. The sorbent (HSAHL) was either physically pre-mixed with the samples or injected about 104 cm downstream (furnace sorbent injection (FSI)) of the fuel injection point. Surprisingly, the method of incorporating sorbent into the furnace does not determine SO₂ removal efficiencies. Similar results were obtained for other fuel and fuel/HSAHL mixtures, but are not shown to allow clarity. Typically, lower temperatures are used during FSI to minimize sintering of the sorbent which would decrease calcium utilization and SO₂ removal. The gas temperature at the FSI point was estimated to be about 1200°C. The temperature at the point of fuel injection was not measured during these tests. However, previous suction pyrometry data 41 cm from the burner tip for tests conducted on a Pittsburgh No. 8 coal at about the same firing rate as the present study indicated a temperature of 1250-1350°C. This suggests that the temperature difference between the two HSAHL injection points is not significant enough to affect SO₂ removal efficiencies.

The SO₂ removal efficiencies for Ca/S of 1.5 were about 52% and 66% for the coal and RTK blend fuels. The result for coal is comparable to the 50% SO₂ removal obtained with FSI of HSAHL in utility boiler tests [6, 7]. Figure 2 shows the general trend for all the samples tested in the IFR. The SO₂ removal efficiencies are greater for fuels which contain char blended with the coal. All types of chars tested enhanced the efficiency of SO₂ removal during tests. It is hypothesized that the presence of char moderates flame temperature, decreasing sintering of the sorbent, which leads to increased sorbent utilization. Ash samples collected downstream during tests using the RTK blend with and without injection of HSAHL contained about 10.8 and 5.5% carbon, respectively. It is difficult to explain the amount of residual carbon in the ash. The calculated residence time of the fuel in the heated zone (>900°C) was about 3.6 seconds with an oxygen concentration of at least 8%. Previous studies by the authors have shown that a char comparable to the RTK char achieved >90% carbon conversion at 1300°C in 6% oxygen for a residence time of 0.8 seconds [3]. The possibility that increased SO₂ removal for coal/char blends was due to incomplete char combustion was accounted for by assuming that the amount of sulfur released from the fuel corresponds directly to the amount of carbon consumed, and calculating the feed rate of fuel based on exhaust gas concentrations. The calculated feed rate was used to determine a predicted concentration of SO₂ in the gas based on analyses of the fuel. The SO₂ removal efficiency was then obtained as the difference between predicted and measured gas concentrations.

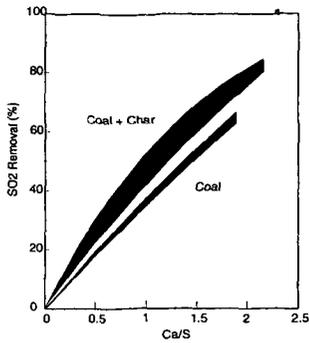


Figure 2. SO₂ removal efficiencies during IFR tests.

Figure 3 shows the emissions produced by combustion of selected fuels in the IFR. The coal produces about 4.4 lbs SO₂/MMBtu with no sorbent added. This is close to that predicted from fuel analyses (Table 1). The CFCO_{HSAHL} and CFCO_{COMHYD} (not shown) blends exhibit emissions similar to that for the parent coal. Due to the presence of sorbent during char preparation, the sulfur released from the coal is retained as CaS and concentrated in a smaller sample (by weight). The total sulfur content of fuels is determined at 1400°C in 100% oxygen, which decomposes the CaS/CaSO₄ present, allowing the entire amount of sulfur in the sample to be determined. However, in the IFR, the lower temperature (1200°C) and much shorter residence time mean that the decomposition of CaSO₄ is much less significant, and that sulfur present as CaS/CaSO₄ is not released. Since SO₂ removal efficiencies are based on total sulfur measurements, the calculated SO₂ removal efficiencies for the CFCO blends are higher than for coal (Figure 2), but because of the increased sulfur content of the blends, the overall emissions are similar.

The RTK blend and coal exhibit emissions of about 1.3 and 2.1 lbs SO₂/MMBtu at a Ca/S of 1.5 (Figure 3). This is true whether FSI is used or the sorbent is physically mixed with the samples prior to combustion. A series of tests was also done by replacing 10% of the higher heating value of the RTK blend with methane. Surprisingly, although the Btu value attributed to the methane would not be expected to have any sulfur associated with it, the RTK blend exhibits the same emissions with or without methane.

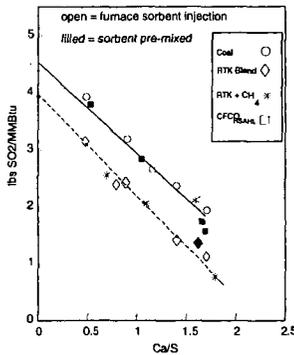


Figure 3. Emissions of fuels in IFR.

The results in Figure 3 suggest that under the conditions present in the IFR, the best method of those studied to reduce the emissions of high-sulfur coals to year 2000 levels of 1.2 lbs SO₂/MMBtu would be to blend the coal with a low-sulfur char, then mix a calcium-based sorbent with the blend at a Ca/S of about 1.5.

Samples tested at UNDEERC for ash deposition characteristics were IBC-102 (coal), the RTK blend and the CFCO_{HSAHL} blend. The initial slagging temperatures (IST) were 1255°C for the coal, 1275°C for the RTK blend, and 1220°C for the CFCO_{HSAHL} blend. The increase in IST for the RTK blend reflects the increased amount of silicon-rich species found in the deposit by scanning electron microscopy point count (SEMP) analysis [14]. The high calcium content of the CFCO_{HSAHL} blend accounts for its low IST. The deposit morphology also shows the CFCO_{HSAHL} blend slagging deposit to be sintered into a nearly amorphous mass, as compared with the coal and RTK blend deposits in which individual ash particles are discernable.

Deposit growth factors for the coal and char blends were determined under both fouling and slagging conditions. Under slagging conditions, growth factors were 0.53, 0.61 and 0.64 for the coal, CFCO_{HSAHL} blend and RTK blend. Under fouling conditions, growth factors were 0.46, 0.53 and 0.61 for the coal, CFCO_{HSAHL} blend and RTK blend. Both blends form deposits more rapidly than the parent coal. Crush strengths of fouling deposits were 10, 29, and 0.2 psi for the coal, CFCO_{HSAHL} blend and RTK blend, respectively. The high calcium content of the CFCO_{HSAHL} blend, which formed a well sintered, dense deposit, accounts for its high crush strength. The RTK blend ash deposit, with more silicon-rich species and higher IST, is less consolidated than either the CFCO_{HSAHL} blend or coal deposits. Although the RTK blend had the highest growth factor, the fouling deposit had a very low crush strength, indicating that it should be easily removed by soot-blowing. Conversely, the CFCO_{HSAHL} blend fouling deposit had a crush strength three times that of the parent coal, indicating that the deposits will be quite consolidated and probably difficult to remove.

Behavior of the three fuels and their resultant deposits was predicted based on chemical composition data. Viscosities of the liquid phases expected to be present in each fouling deposit at 1200°C were calculated from the SEMPC results. The CFCO_{HSAHL} blend deposit contained the greatest proportion of low-viscosity material, indicating a greater tendency to flow at 1200°C. The coal deposit and the RTK blend deposit had similar viscosity distributions, with less low-viscosity material than the CFCO_{HSAHL} blend deposit sample. Thermal chemical equilibrium computational code that is utilized at UNDEERC to predict mineral phases and viscosities based on bulk composition data, was run for the coal and blends. The CFCO_{HSAHL} blend ash exhibited a significantly lower viscosity at lower temperatures than the coal and RTK blend ashes, which are higher and nearly identical in viscosity. However, the predicted weight percentage of liquid phases in the CFCO_{HSAHL} blend ash was very low at these lower temperatures, much lower than that of the coal and

RTK blend ashes. This presented two competing effects: higher-viscosity material present in significant amounts and low-viscosity material present in small amounts. However, the very-low-viscosity material present, coupled with the high ash content of the CFCO_{HSAHL} blend ash, indicated that the deposition behavior would be significantly more severe than for the other two ashes.

Coal composition data were entered into an in-house EERC program that produces a fouling and slagging index. The chars were not evaluated with the program. The coal showed a potential for significant slag formation in the radiant section of a conventional PC boiler similar to that for other Illinois Basin coals. The magnitude of the index (85) is such that it may be controllable using standard remediation techniques, such as wall blowers. Severe slagging coals usually have values of 100-200. One of the main causes for the slagging potential of the ISGS coal is the high pyrite content. However, the potential for slag formation is not as high as it could be. In order to form a good low-viscosity slag, the iron from pyrite requires significant quantities of aluminosilicate clay material present, but the clay content of the IBC-102 coal is fairly low. The potential for high-temperature fouling, such as in the secondary superheater and reheater regions of the convective pass, and low-temperature fouling, such as in the economizer, should be low to nonexistent.

CONCLUSIONS

Based on results presented for the fuels in this study, the RTK blend would be the most attractive boiler feedstock because of its lower slagging and fouling potential and lower sulfur content. The best method to reduce emissions of high-sulfur coals appears to be to blend the coal with a low-sulfur char, then mix a calcium-based sorbent with the coal-char blend prior to combustion. Further studies are necessary to determine if the observed reduction in emissions by physically mixing sorbent prior to combustion is real, or an artifact of the experimental system. The results of that study would have direct implications whether to blend high-volatile, high-sulfur coals with lower-volatile, low-sulfur coals to reduce SO₂ emissions.

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