

# Chemical Engineering Technology in Forest Products Processing

Barbara Crowell  
(editor)

American Institute of Chemical Engineers  
Forest Products Division

Volume 2, 1988

TS  
1171  
.C47  
1988  
v.2

# CO/CO<sub>2</sub> RATIO OF KRAFT CHAR BURNING

Gregg W. Aiken and John H. Cameron ♦ The Institute of Paper Chemistry, Appleton, WI 54912

A study of kraft black liquor char burning was carried out in a laboratory reactor with a laminar O<sub>2</sub>/N<sub>2</sub> jet impinging vertically on the char for two experimental arrangements. With sulfate as the oxygen source, the CO/CO<sub>2</sub> ratio was a linear function of the elemental C/O ratio. At 1033 to 1113°K, temperature did not affect the CO/CO<sub>2</sub> ratio. With air as the oxygen source, the CO/CO<sub>2</sub> ratio was principally CO with a CO/CO<sub>2</sub> ratio of 4 to 24 at 1000 to 1150°K and 2.1 to 10.5% O<sub>2</sub>. The results were consistent with the sulfate/sulfide cycle theory of char burning.

## INTRODUCTION

Black liquor burning in recovery boilers is a complex process due to several factors. First of all, the water content of the liquor is typically 30 to 35%. Secondly, the black liquor has a high inorganic salt content. Thirdly, the inorganic salts flowing out of the recovery boiler as smelt must be obtained in a useful form, since the pulping chemicals are regenerated from this smelt.

The char bed is in the hearth zone of a kraft recovery boiler. Char bed temperatures of up to 1422°K (2100°F) have been measured (1); its molten salt content makes the char bed corrosive; the region is also fairly inaccessible. Due to these adverse conditions, char bed sampling surveys reported in the literature are quite limited.

Char burning is the final stage in black liquor combustion where the char residue of pyrolysis is converted to combustion gases and smelt, the remaining inorganic salts. A simplified composition of the char residue and the smelt given in Table 1 was developed by Grace from elemental and inorganic salt analyses of kraft chars (2). The fixed-carbon concentration of the char, the carbon not in the carbonate form, is the dominant char species. Char reactions can broadly be defined as either being involved in the reduction of sodium sulfate to sodium sulfide or involved

in the gasification of the fixed-carbon content of the char.

Table 1. Simplified char and smelt compositions (moles/mole Na<sub>2</sub>).

	Char	Smelt
Na <sub>2</sub> S	1/6	19/60
Na <sub>2</sub> SO <sub>4</sub>	1/6	1/60
Na <sub>2</sub> CO <sub>3</sub>	2/3	2/3
C	3	1/12
H	1	--

Grace suggested that the sulfate/sulfide cycle was the primary means of fixed-carbon combustion (3). Oxygen in the combustion air reacts with the sulfide content of the char to form sulfate. The sulfate is then reduced by carbon to form sulfide and CO and/or CO<sub>2</sub> as the product gas. The sulfate/sulfide cycle was suggested in two types of char burning experiments. In the smelt pool reactor studies, char burning was quantified for the reaction of limited amounts of char in an inorganic salt pool. In the single particle reactor studies, a black liquor pellet was burned in a convective O<sub>2</sub>/N<sub>2</sub> stream. One of the objectives of this current study was to determine

whether the sulfate/sulfide cycle adequately describes char pile burning, where oxygen access to the char carbon is restricted, i.e., for conditions where the carbon/oxygen ratio is much greater than in these previous studies.

The rates of the two sulfate/sulfide cycle reactions were studied by Cameron in a smelt pool reactor (4). He found that the rate of the sulfide oxidation reaction was limited only by the rate of oxygen supply to the reactor. The rate of the carbon-sulfate reaction, on the other hand, is a strong function of temperature in the 1033 and 1367°K range (5,6).

Cameron also found that the kinetics of the carbon-sulfate reaction were very dependent upon the carbon source (5). Kraft char, soda char and carbon rods were the carbon sources used. He reported that the CO/CO<sub>2</sub> ratio was at most 0.1. Thorman used activated carbon as the carbon source for his studies of the sulfate reduction by carbon reaction (6). He reported a CO/CO<sub>2</sub> product ranging from 1 to 11. The results of our investigation will show that this difference in CO/CO<sub>2</sub> ratios was due to the difference in oxygen contents of the systems.

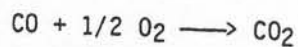
The CO/CO<sub>2</sub> ratio of the carbon-sulfate reaction has a significant effect on the endothermic nature of the reaction, as shown in Table 2.

Table 2. Heats of reaction of the carbon-sulfate reaction.

	$\Delta H_r$ : kJ/kg Na <sub>2</sub> SO <sub>4</sub>	
	1000°K	1300°K
Na <sub>2</sub> SO <sub>4</sub> + 2 C → Na <sub>2</sub> S + 2 CO <sub>2</sub>	1261	1177
Na <sub>2</sub> SO <sub>4</sub> + 4 C → Na <sub>2</sub> S + 4 CO	3667	3539

The reaction is approximately three times as endothermic with CO as the carbonaceous gas product than with CO<sub>2</sub> as the product. The CO/CO<sub>2</sub> ratio also dictates the air supply required during burning. Twice as much oxygen is required if CO<sub>2</sub> is the combustion product, as opposed to CO.

One reaction that complicates CO/CO<sub>2</sub> ratio determinations for studies involving the oxidation of carbon-containing fuels, is the gas-phase oxidation of CO:



It is difficult to determine whether CO<sub>2</sub> in the exhaust gases is a product of this gas-phase reaction or the product of a char pile reaction. Our investigation was able to quantify the contribution of this reaction to the CO<sub>2</sub> in the exhaust gases.

The objectives of this investigation were to determine

- The factors affecting the CO/CO<sub>2</sub> ratio of the carbon-sulfate reaction, with sulfate as the oxygen source for combustion.
- The factors affecting the CO/CO<sub>2</sub> ratio of char burning, with oxygen in the supply gases as the oxygen source for combustion.
- Whether the sulfate-sulfide cycle theory adequately describes char pile burning.

A fixed-bed char reactor with an impingement geometry for the supply gases was chosen for this study because it is somewhat analogous to char bed conditions.

## EXPERIMENTAL

### Apparatus

A schematic of the fixed-bed char reactor apparatus is shown in Figure 1. The induction furnace temperature controller compares the temperature of the outside surface of the stainless steel retort, measured by the optical pyrometer, to the set point and adjusts the current supplied to the induction furnace coil accordingly.

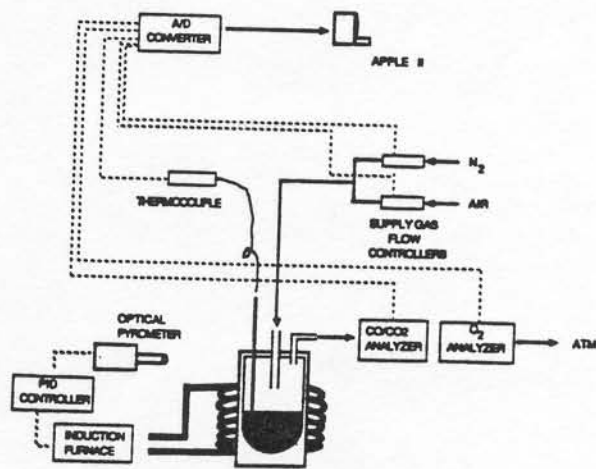


Figure 1. Experimental apparatus.

For most experiments, the stainless steel retort contained an alumina crucible in which the char was placed. For the pyrolysis portion of char preparation, a Hastelloy retort was used without the alumina crucible.

Ports in the reactor head allowed for the insertion of a supply gas tube, for the insertion of thermocouples and for the removal of the gases to the gas analyzers.  $O_2$  and  $N_2$  were metered into the reactor using mass flow meters. The supply gas tube was made of 4.8-mm stainless steel tubing and centered 20 mm above the char surface at the beginning of the experiment.

For the carbon-sulfate experiments, one 3.2-mm, Type K thermocouple was inserted into the reactor and positioned in the char/salt mixture at the base of the crucible. For the air-termination experiments, two 1.6-mm, Type K thermocouples were inserted into the reactor. One was located at a radial position near the crucible wall. Both were positioned 0 to 2 mm above the char surface at the beginning of the experiment. The measured temperature of the char and the temperature measured by the thermocouples positioned just above the char surface were found to be approximately equal.

Exhaust gas composition was measured using a  $CO/CO_2$  analyzer and an  $O_2$  analyzer. These gas analyzers were calibrated before each experiment with standard calibration gases and checked afterward to ensure the accuracy of the data.

Temperature measurements, supply gas flow rates and exhaust gas composition data were collected by a data acquisition system attached to a microcomputer.

#### Char Preparation Procedure

A commercial 51%-solids kraft hardwood liquor was dried in a vacuum oven at 423°K and 1.67 kPa for at least 16 hours with a slight nitrogen purge. The dry black liquor solids were coarsely ground and placed in the induction furnace reactor, approximately 80 grams in a 1-liter Hastelloy reactor. The reactor temperature was then increased to 1223°K and held for 10 minutes at this temperature. A nitrogen purge rate of about 0.30 mL/min was maintained throughout the pyrolysis and cool-down stages. The char remaining was then ground until it could pass through a 10-mesh standard sieve.

The fixed-carbon concentration of the kraft char was determined by burning a 1 gram

sample of the char in the induction furnace reactor and integrating the amount of  $CO$  and  $CO_2$  in the exhaust gases. The carbon concentration measured was  $23.4 \pm 1.0\%$ . The total sulfur was determined by Schoniger flask oxidation followed by an ion chromatograph sulfate determination. The total sulfur measured was 6.8%.

#### Procedure for the Carbon-Sulfate Experiments

For the carbon-sulfate experiments, kraft char, sodium carbonate and sodium sulfate were ground together with a fixed-carbon:sulfate ratio of approximately 2, 4, and six. An initial sulfidity of 33% was maintained for all runs. Ten grams of sample were charged to the reactor for each experiment. A nitrogen flow rate of about 0.9 L/min was purged through the reactor for the duration of each experiment. The reactor temperature was rapidly raised to 1077°K and controlled at that target for most experiments. Experiments were also run at 1033 and 1113°K. The  $CO$  and  $CO_2$  concentrations in the exhaust gases were monitored until either the concentrations were negligible or had leveled at low values (less than 0.5%  $CO$  or  $CO_2$ ).

The amounts of carbon and sulfate in the mixture dropped as the reaction proceeded. The relative amounts of carbon and sulfate were monitored as the elemental fixed-carbon to oxygen ratio, the  $C/O$  ratio. The  $C/O$  ratio was chosen rather than the  $C/SO_4$  because the sulfate added was not the only oxygen source. Oxygen sorbed by the char was also present. The  $C/O$  level in the mixture at any time during the run was calculated by subtraction of the total moles of  $C$  and  $O$  evolved in the exhaust gases up to that time (as  $CO$  and  $CO_2$ ) from the initial moles of  $C$  and  $O$ , then dividing the moles of  $C$  by the moles of  $O$ .

The initial mass of fixed-carbon was obtained by multiplying the mass of the char by the fixed-carbon concentration. Computation of the initial mass of oxygen was complicated by the fact that kraft char readily sorbs oxygen. Both the oxygen content of the sulfate and the oxygen content of the char were taken into account. The initial moles of oxygen were back-calculated by integrating the total amount of oxygen in the  $CO$  and  $CO_2$  generated during the sulfate-limited experiments. These were the experiments with initial  $C/SO_4$  ratios of 4 and 6. Since sulfate was the limiting reactant, all the oxygen present in the mixture should have evolved upon heating. The ratio of the oxygen

Figure 3 shows the effects of cutting the air flow at the 21.92-minute mark with 4.2% O<sub>2</sub> at 1022°K. Prior to the termination of air flow, the CO, CO<sub>2</sub> and O<sub>2</sub> concentrations are fairly constant at 2.1, 1.1, and 1.6%, respectively. After the air flow is cut, the CO<sub>2</sub> and O<sub>2</sub> concentrations drop rapidly. The CO concentration, on the other hand, increases before decreasing slowly with time. The drop in oxygen concentration reduces the amount of gas-phase oxidation of CO to CO<sub>2</sub>. The char pile reactions are initially less affected by the termination of oxygen in the supply gases than the gas-phase reaction. The termination of air flow therefore results in an increase in CO initially due to the combined effect of the sudden drop in the CO-consuming, gas-phase oxidation reaction and the buffering capacity of the CO-generating char pile reactions. When these char pile reactions eventually respond to the lack of oxygen in the supply gases, the CO concentration gradually decreases with time.

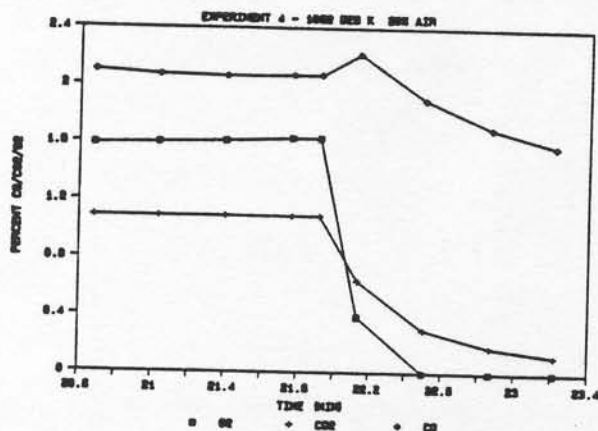


Figure 3. Kraft char combustion 1022°K, 4.2% O<sub>2</sub>.

The CO/(CO + CO<sub>2</sub>) ratio measured at the 22.5-minute mark of Figure 3 should be representative of the gaseous product of the char pile reactions without the complications of the gas-phase oxidation of CO. The CO/(CO + CO<sub>2</sub>) just prior to the cutting of air flow was 0.66. The CO/(CO + CO<sub>2</sub>) measured at the 22.5-minute mark, after air flow termination, was 0.86.

Figure 4 shows that cutting the air flow at the 9.1-minute mark with 10.5% O<sub>2</sub> at 1083°K results in a dramatic flip-flop in CO and CO<sub>2</sub> concentrations. This is solid evidence supporting the hypothesis that the rapid drop in CO<sub>2</sub> upon air flow termination is due to the stopping of the gas-phase oxidation of CO. If the CO<sub>2</sub> and CO both dropped after air-flow

termination, but at different rates, one could argue that two parallel heterogeneous reactions are responsible for the CO and CO<sub>2</sub> generated. Perhaps the carbon-sulfate reaction produced the CO while direct carbon oxidation produced the CO<sub>2</sub>. The fact that the CO increases upon air flow termination refutes this hypothesis. It is difficult to conceive of a plausible mechanism whereby the rate of a heterogeneous oxidation reaction will increase upon the termination of air flow.

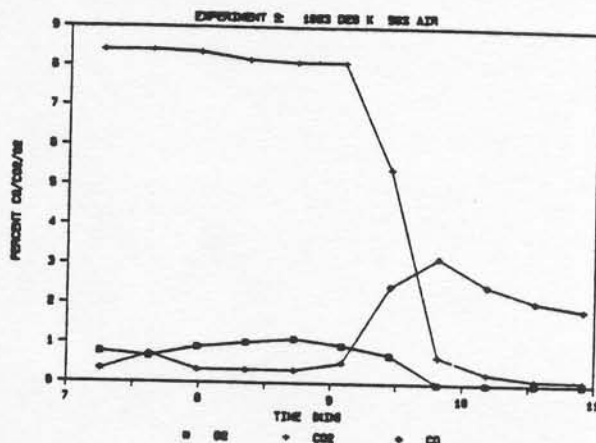


Figure 4. Kraft char combustion 1083°K, 10.5% O<sub>2</sub>.

The CO/(CO + CO<sub>2</sub>) ratio measured in the exhaust gases just prior to air flow termination was 0.06. The off char pile CO/(CO + CO<sub>2</sub>) calculated at the 9.8-minute mark was 0.82. The amount of gas-phase oxidation of CO to CO<sub>2</sub> was quite substantial in this instance.

The results of all the kraft char combustion experiments are listed in Table 3. The CO/(CO + CO<sub>2</sub>) ratio recorded just prior to cutting the air flow is given as "exhaust gas." The CO/(CO + CO<sub>2</sub>) ratio recorded after air flow termination, when the measured O<sub>2</sub> concentration was less than 0.15%, is listed as "off char pile." The ranges listed for each "CO/(CO + CO<sub>2</sub>)" and "Temperature" entry represent the range of values recorded for the four to six times during each experimental run that the air flow was cut.

The data given in Table 3 suggest that:

- CO is the primary char pile combustion product for all experimental conditions studied.
- There is no apparent temperature dependence, time dependence or supply gas oxygen concentration dependence to the off char pile CO/(CO + CO<sub>2</sub>) ratio.

- The amount of gas-phase oxidation of CO to CO<sub>2</sub> can be quite significant.

Table 3. Kraft char combustion results.

Temperature, °K	Percent O <sub>2</sub>	CO/(CO + CO <sub>2</sub> )	
		Exhaust Gas	Off Char Pile
1004-1012	2.1	0.78-0.92	0.88-0.92
1019-1024	4.2	0.65-0.79	0.86-0.90
1049-1083	10.5	0.06-0.71	0.80-0.86
1089-1093	2.1	0.74-0.78	0.83-0.94
1076-1082	4.2	0.77-0.84	0.87-0.90
1097-1100	10.5	0.72-0.80	0.81-0.90
1098-1111	2.1	0.83-0.88	0.96
1108-1116	4.2	0.78-0.82	0.84-0.91
1141-1154	10.5	0.74-0.82	0.83-0.90

The results of the carbon-sulfate studies suggest that a high CO/CO<sub>2</sub> ratio would result only if the C/O ratio is high. Previous research indicated that sulfate reduction by carbon is probably one of the controlling reactions in kraft char burning via the sulfite/sulfide cycle (3). The kraft char combustion experiments, included in this current study, revealed that the CO/(CO + CO<sub>2</sub>) ratio of the char pile reactions ranged from 0.80 to 0.96 for all conditions studied. This is equivalent to a CO/CO<sub>2</sub> ratio ranging from 4 to 24. The C/O ratio required to attain this CO/CO<sub>2</sub> ratio range, according to the empirical expression derived in the carbon-sulfate studies is 9.9 to 6.0.

This C/O ratio can be used to estimate the reduction ratio in the char, the ratio of sulfide to sulfide plus sulfate, assuming all the oxygen present in the char is in the sulfate form.

The reduction ratio calculated using the measured fixed carbon/oxygen ratio of 3.44, ranges from 0.91 to 0.98. So even for relatively low temperature, high supply gas oxygen concentration conditions where low reduction ratios might be anticipated, high reduction ratios were calculated.

## CONCLUSIONS

The CO/CO<sub>2</sub> ratio of sulfate reduction by kraft char carbon is a function of the fixed-carbon:oxygen ratio in the source material. The following empirical expression describes that relationship:

$$CO/CO_2 = 0.403 C/O$$

The air-termination series of kraft char burning experiments revealed that the CO/CO<sub>2</sub> ranged from 4 to 24 for all conditions studied.

These data were used to estimate reduction ratios ranging from 0.91 to 0.98 for the char burning experiments. These are much higher values than anticipated for the low temperature conditions employed.

## ACKNOWLEDGMENT

Portions of this work were used by GWA as partial fulfillment of the requirements for the Ph.D. degree at The Institute of Paper Chemistry.

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