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LABORATORY SCALE CARBONIZATION OF NORTH DAKOTA LIGNITE: INFLUENCE OF TEMPERATURE AND ATMOSPHERE ON PRODUCT DISTRIBUTION AND ACTIVITY

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INTRODUCTION

The purpose of this investigation has been to study the effect of temperature and atmosphere on carbonization characteristics of lignite. An objective has been to produce a char with minimum sulfur and maximum reactivity toward air, with minimum loss of heating value. Research in carbonization has been extensive on higher rank solid fuels, including efforts to reduce sulfur and control reactivity of chars and cokes (1, 2). For North Dakota lignite, previous attention has been focused upon yield and composition of byproducts.

The considerable influence of atmosphere and temperature on the proportion of sulfur volatilized during carbonization of coal from Illinois and Indiana has been reported by Snow (3) and Mangelsdorf and Broughton (4). Significant differences in sulfur removal were found, depending upon atmosphere during carbonization. More recently, Draycott (5), of the University of Sydney, Australia, reported studies of desulfurization of metallurgical coke in a variety of atmospheres. Best desulfurization occurred at 1,000°C in oil gas with intermittent blasts of steam. Ninety-two percent of the sulfur was removed with a coke loss of about forty percent.

CARBONIZATION EQUIPMENT

The test apparatus was essentially a tube furnace with three separately controlled electric heaters to provide a reproducible and uniform temperature distribution within the unit during carbonization. The carbonization tube was constructed of 1-1/2-inch, schedule 40, stainless steel pipe. Three thermocouples were mounted in the 14-1/2-inch length which held the sample, a fourth in an end heater section, and a fifth was imbedded in the sample; these provided for temperature measurement and control. The tube was charged externally and then placed in the furnace.

The arrangement of the carbonization equipment, including the modifications for various atmospheres, is shown in figure 1. A collection train was provided for the byproduct tar, water, hydrogen sulfide, ammonia, light hydrocarbons, and gas.

PROCEDURE

Each charge consisted of 200 grams (0.441 lb) of lignite, sized 4 x 8 mesh, from the Kincaid mine, Burke County, North Dakota. Nitrogen was passed through the carbonization tube at the rate of 0.6 cubic feet per hour. In the tests in which carbonization gas was recycled, its flow was regulated to give a superficial space velocity of one-half foot per second, and in the tests in which carbonization was done in a steam atmosphere, steam was injected at the rate of about 500 grams (1.102 lb) per hour. The average heating rate was 400°F per hour, and the sample was held at temperature for 2 hours.

All products except gas were weighed. Gas volume was measured, the gas analyzed, and the weight of the nitrogen-free gas calculated. The condensate contained most of the tar and water and part of the ammonia and hydrogen sulfide product. These components were separated, and their weights were added to those collected in the remainder of the product collection train.

In nitrogen and carbonization gas atmospheres, the test temperatures were 500°, 800°, 900°, 1,000°, 1,300°, and 1,700°F. Three individual tests were performed at each temperature for material balance plus one test to produce char for reactivity measurements.

For carbonization in steam, similar tests were performed at a lower range of temperatures, 500° to 1,100°F, at 100°F intervals because of the significant gasification that occurred at higher temperatures. Char for reactivity measurements was made at 1,200° and 1,300°F in steam, and for comparison purposes, in nitrogen atmosphere at 800°, 900°, and 1,000°F, using the same lignite feed sample.

LIGNITE FEED SAMPLES

Three different batches of lignite from the Kincaid mine were used in these tests. Feed number 1 was used for the nitrogen atmosphere material balance tests. Feed number 2 was used for the nitrogen atmosphere char production tests, and all of the tests in recycled carbonization gas atmosphere. Feed number 3 was used for steam atmosphere tests, and the three comparison tests that were made in nitrogen atmosphere. Analyses of these feeds are shown in table 1. The much higher sulfur content of feed number 3 is of special interest.

TABLE 1. - Analyses of lignite feed for carbonization experiments[1/]

Feed number	1	2	3
Proximate analysis, percent:			
Moisture	31.9	26.9	32.3
Volatile matter	26.6	29.5	29.6
Fixed carbon	32.2	34.7	30.6
Ash	9.3	8.9	7.5
Ultimate analysis, percent:			
Hydrogen	6.5	5.9	6.7
Carbon	42.7	46.7	44.2
Nitrogen	.4	.8	.7
Oxygen	40.7	37.3	38.8
Sulfur	.4	.4	2.1
Ash	9.3	8.9	7.5
Heating value, Btu/lb	7,200	7,780	7,660

1/ Kincaid lignite "as-charged."

PRODUCT YIELDS

The product yields obtained by carbonizing in nitrogen and carbonization gas atmospheres were very similar. As carbonization temperature increased, yields of gas, tar, and water product increased at the expense of the char; the rate of increase became less as temperature advanced. Product yields as a function of carbonization temperature are shown in figures 2 and 3.

The product yields obtained from steam carbonization, as shown in figure 4, were similar to the others below 900°F. Above this temperature the yield of char product continued to decline steeply with advancing temperature, and the yield of gas product increased very rapidly. Figure 5 compares the char yields obtained from nitrogen and steam carbonization to illustrate the effect of gasification.

TESTS OF CHARS

Crossing-Point Temperature

The reactivity of each char in air was determined in a crossing-point-temperature apparatus. The apparatus was constructed of a length of 1/2-inch stainless steel pipe placed in a small vertical tube furnace. A 1-1/2-inch deep charge sized 40 x 60 mesh was supported on a screen in the middle of the tube. The wall temperature and the temperature at the center of the charge were recorded. The wall temperature was increased at a rate of 27°F per minute, while air was diffused through the sample at the rate of 0.45 cubic feet per hour. The crossing-point temperature was defined as the temperature at which the inside temperature overtook the wall temperature which means the lower the crossing-point temperature the more reactive the char towards air.

The crossing-point temperatures for chars are shown in figure 6. The lowest crossing-point temperatures were found for the chars carbonized in the 800° to 1,000°F region. Both recycled carbonization gas and steam decrease char activity toward air. Char produced from feed number 3 gave higher crossing points than char produced from feed number 2 under similar conditions.

Acetic Acid Adsorption

The chars produced in steam atmosphere were tested for their ability to adsorb acetic acid. After evidence of soluble alkali in the chars was found, each char was treated in a Soxhlet extractor with water for 60 hours and then dried. The acetic acid adsorption test procedure was to mix a half gram of 40 x 60-mesh soluble-alkali-free char with 50 milliliters of 5 millinormal acetic acid in a closed container and shake mechanically for 2 hours. The final acid strength was determined, and an adsorption constant calculated. This constant was the ratio of acid concentration in the char to that in the liquid at equilibrium.

Figure 7 shows the acetic acid adsorption constants of the chars tested as functions of the carbonization temperatures. Activity shows a rapid increase as the carbonization temperature increases from 1,000°F.

Low crossing-point temperatures and low acetic acid adsorption constants occur in the same carbonization temperature region. These two types of activity seem to be quite distinct. The opposite trends of the two char activities with carbonization temperature were confirmed by a statistical rank test.

Sulfur Removal Relationships

The criteria used for a well desulfurized char was low sulfur and high heating value. The sulfur content of the chars was therefore compared in this report on the basis of pounds of sulfur per million Btu. Figure 8 shows the sulfur contents of the various chars on this basis as a function of carbonization atmosphere and temperature.

The chars carbonized in nitrogen show the lowest sulfur content at 900°F carbonization temperature. The chars carbonized in recycled carbonization gas were similar except that the 900°F char was higher in sulfur than the 800° or 1,000°F chars.

The sulfur contents of the chars carbonized in steam were different: increasing from 500° to 700°F, dropping to 1,000°F, holding fairly constant to 1,200°F, and rising rapidly to 1,300°F. The higher sulfur in feed number 3 is reflected in the chars produced from it.

The criterion used for a good desulfurization process was a high ratio of sulfur loss to heating value loss. This function, the loss ratio, was obtained by dividing the percentage sulfur lost by the percentage Btu lost, and it depends upon the sulfur content and heating value of the feed, the char yield, and the sulfur content and heating value of the char produced.

The loss ratios as functions of carbonization atmosphere and temperature are shown in figure 9. The highest loss ratios were at 900°F for chars produced in nitrogen atmospheres and best at 800°F for chars produced in recycled carbonization gas. For chars produced in steam, two peaks were found, the highest loss ratio was at 500°F, and the second highest was at 1,000°F.

SUMMATION

The highest reactivities of chars toward air were found in chars produced by carbonizing in the region of 800° to 1,000°F. Carbonization in either recycled carbonization gas or steam produced chars less reactive than those carbonized in nitrogen.

The reactivity measured by acetic acid adsorption was not the same reactivity as that measured by crossing-point temperature. The acetic acid adsorption value varies with carbonization temperature in the opposite manner as compared to crossing-point values for the chars that were produced by carbonization in steam.

The lowest char sulfur content and highest loss ratio occurred at 900°F when carbonizing in a nitrogen atmosphere. For carbonization in recycled carbonization gas, the lowest sulfur content occurred at 1,000°F and the highest loss ratio at 800°F. The desulfurization by carbonizing in steam was quite different. The lowest sulfur content occurred at 1,200°F, the highest loss ratio was found at 500°F, and the next best at 1,000°F. Differences in lignite feed were reflected in the char produced, both in reactivity toward air and in sulfur removal.

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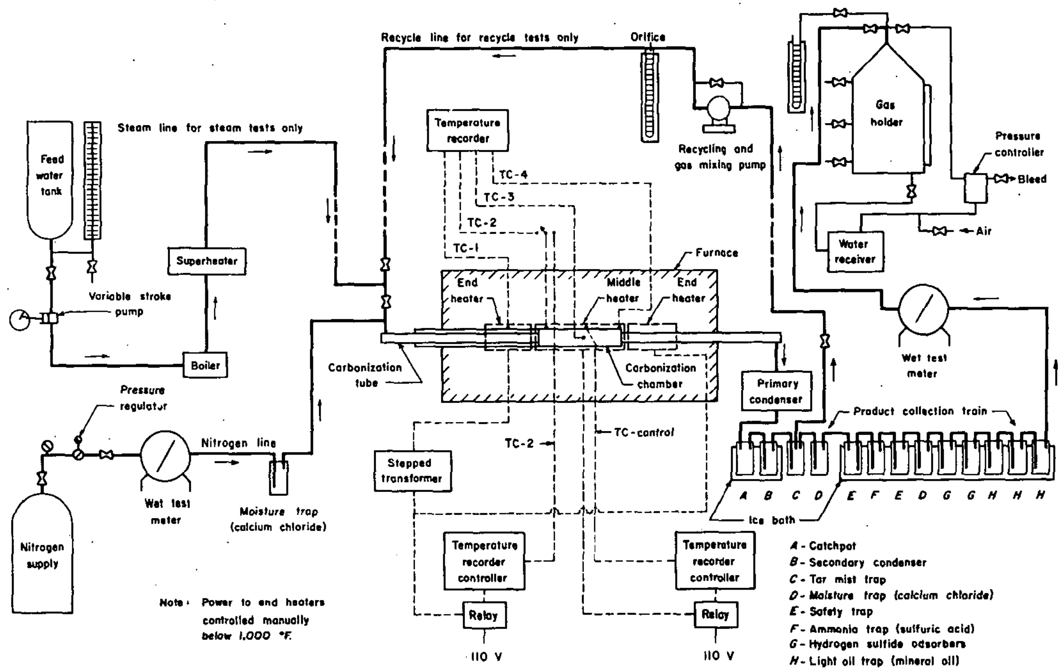

Fig I Flow sheet, carbonizer and auxiliary equipment.

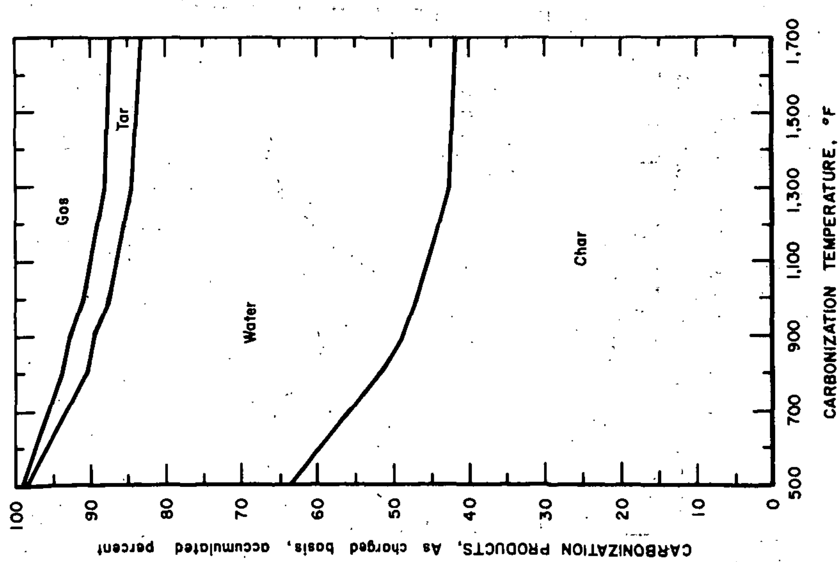

Fig 2 Product yields, carbonization in nitrogen atmosphere.

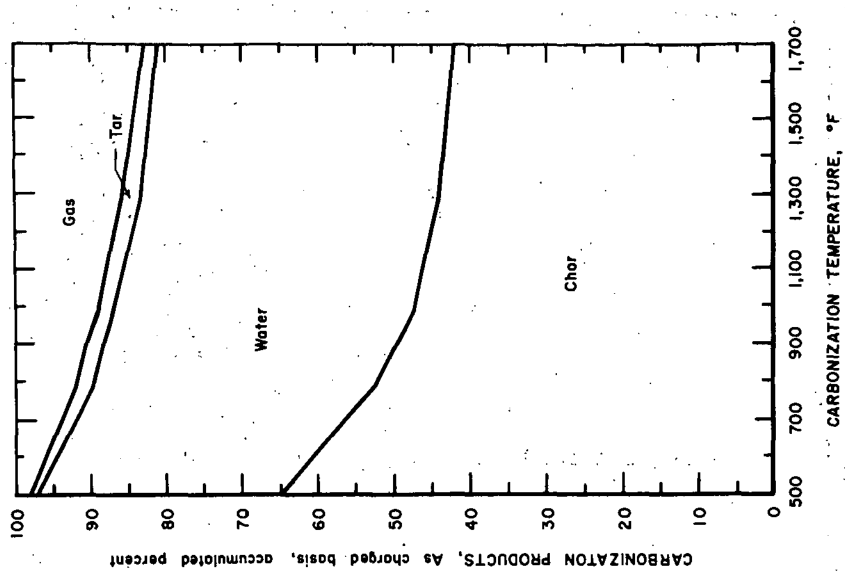

Fig 3 Product yields, carbonization in recycled carbonization gas atmosphere.

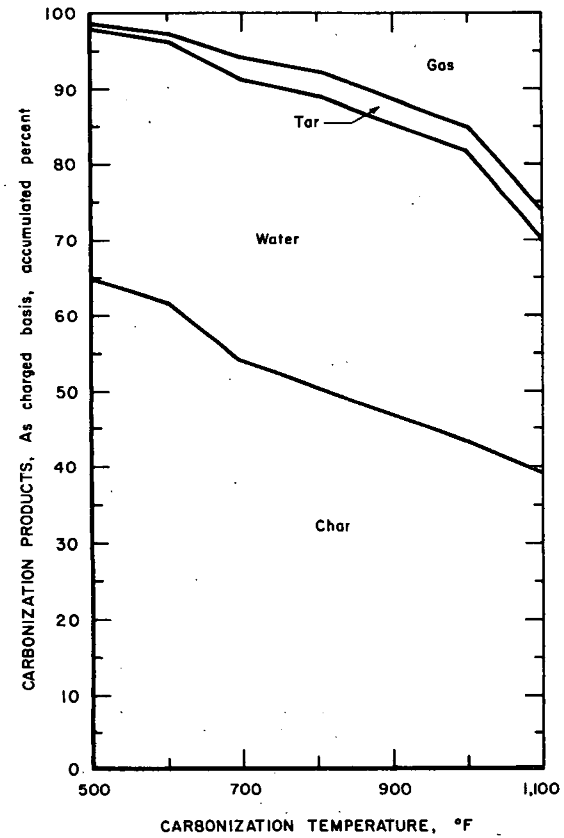

Fig. 4 Product yields, carbonization in steam atmosphere.

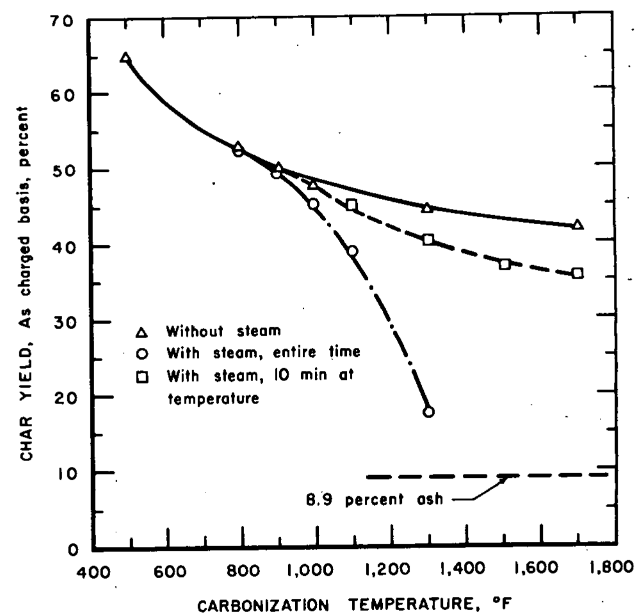

Fig 5 Effect of steam on char yield.

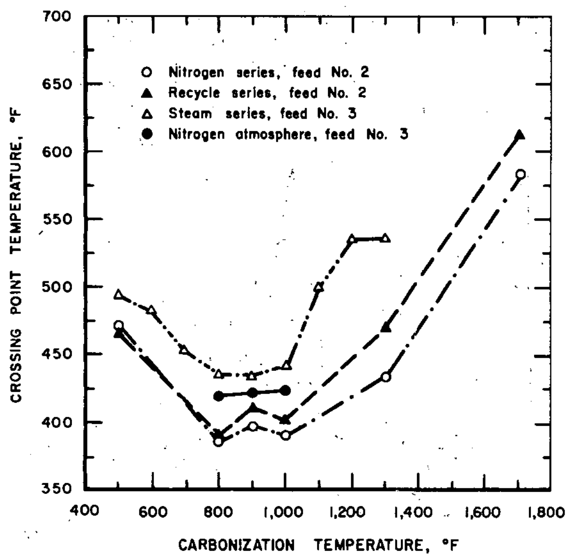

Fig 6 Crossing-point temperatures or chars as a function of carbonization temperature and atmosphere.

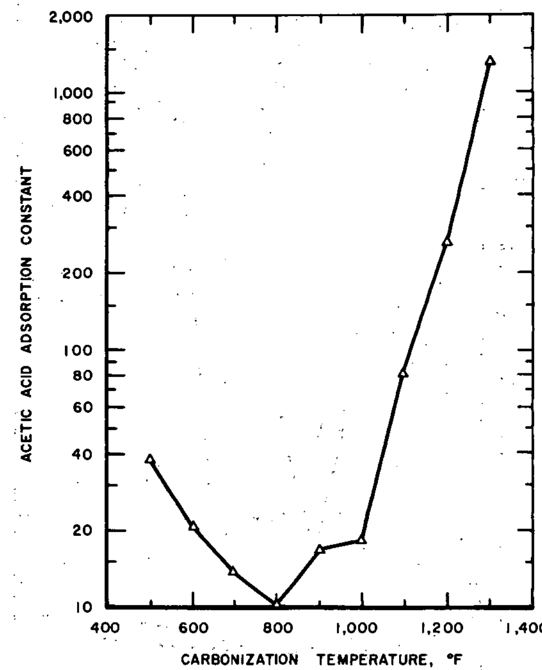

Fig 7 Acetic acid adsorption of chars as a function of carbonization temperature in steam atmosphere.

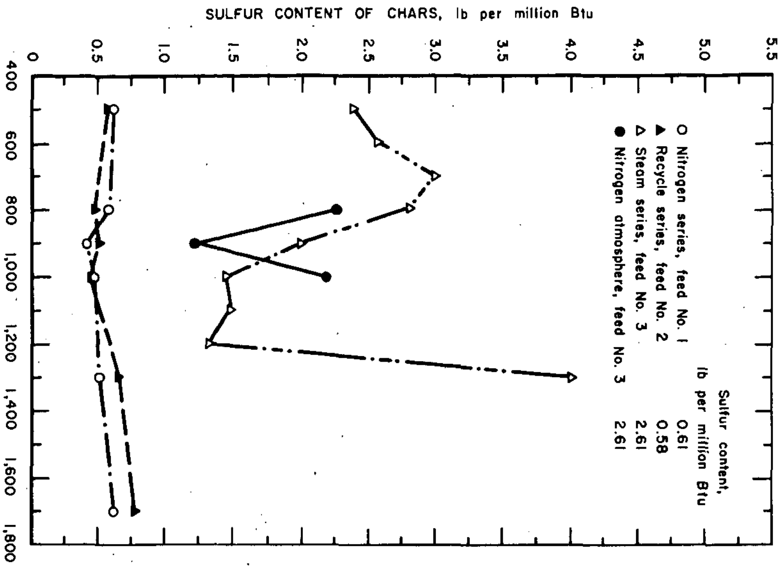

Fig 8 Sulfur contents of chars as a function of carbonization temperature and atmosphere.

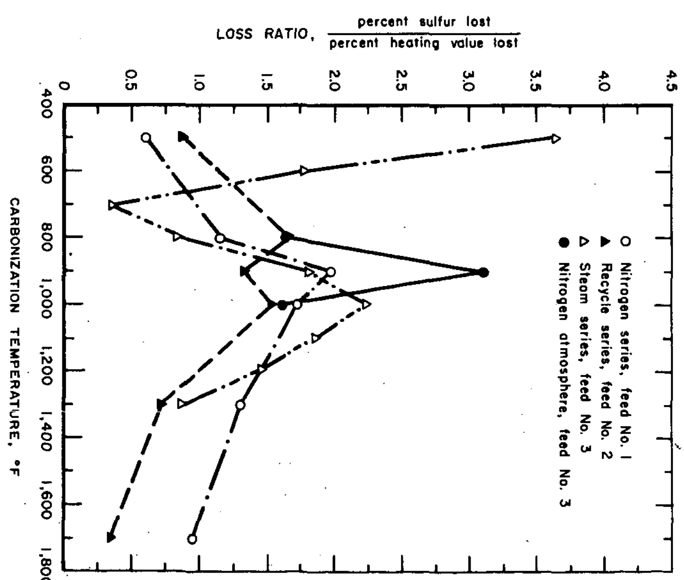

Fig 9 Sulfur-heating value loss ratio as a function of carbonization temperature and atmosphere.