

THERMAL CRACKING OF LOW-TEMPERATURE LIGNITE PITCH. PART II.

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Thermal cracking of pitch from the carbonization of Texas lignite at low temperature has been under investigation as a means of producing aggregate and a binder that could be used to fabricate carbon metallurgical electrodes. A previous report on this subject covered preliminary tests on the thermal cracking of lignite pitch at 1,450° F in a 2-1/2 inch diameter reactor and showed that a variety of products could be obtained (1). In this work, a 4-inch diameter reactor was utilized to evaluate oil, coke, and gas quality and yields as a function of pitch feed rate temperature between 1,200° and 1,450° F.

EQUIPMENT AND MATERIALS

Figure 1 is a flowsheet of the system. The cracking unit consisted of a 93-inch length of 4-inch schedule 40, type 304, stainless-steel pipe, heated electrically. Total heating capacity of the cracker was 13.74 kw. A 1-inch pipe extended up through the center to within about 2-1/2 feet of the top and was perforated with 1/4-inch openings to allow withdrawal of gas and oil vapors from the reaction zone.

Pitch utilized as feed material was prepared by distilling crude low-temperature lignite tar under vacuum to an atmospheric boiling point of 660° F. The pitch yield was about 45% of the tar. Ultimate analysis and physical properties of the pitch are summarized in Table 1.

PROCEDURE

Pitch heated to 400° F was pumped from the feed tank by a gear pump through electrically heated lines into the top of the thermal cracker. Pitch utilized in all the runs came from the same source and was analyzed each time for C and H content. No significant difference was found. A flow of purge gas (11% CO₂, 88% N₂) swept products from the reaction zone. Cracked pitch was collected in the receiver and the oil was condensed and separated. Gas was passed through the scrubber and gas meter, then sampled and vented. After each run, which lasted 1-1/2 hours, the pitch flow was stopped and the pump was flushed with tar distillate fraction (from tank) to keep the pump from freezing during shutdown. It is not likely that true steady state was achieved owing to change in reactor geometry by build-up of coke. Also, heat transfer changed for the same reason. Steady state conditions are believed to have been approached, however.

After the cracking unit cooled, it was opened at the top and bottom and the coke was removed from the walls. Cracked pitch was removed from the receiver and oil was drained from the condenser and knockout. Each of the three products was weighed to the nearest one-tenth pound. The oil was distilled under vacuum to an atmospheric boiling point of 752° F, giving about 20 to 30% distillate and 70

to 80% residue. This residue was tested for carbon and hydrogen content and for softening point. If the test results were in the desired range, the residue was used as an electrode binder. The distillate was oxidized to phthalic and maleic anhydrides or separated into acids, bases, and neutral oils. The neutral oils were separated into n-olefins, paraffins, and aromatics.

Gas produced by the thermal cracking was analyzed by gas chromatography.

RESULTS AND DISCUSSION

Thermal cracking was carried out at temperatures from 1,200° to 1,450° F and pitch feed rates varying from 5.5 to 9.5 lb/hr.

A residence time (liquid basis) of nearly 0.70 second was found necessary to crack the pitch. In initial tests with a 5-foot-long cracker, the residence time was only slightly more than 0.55 second and cracking was not effected. Addition of a 2-1/2 foot length of pipe to the cracker increased the residence time to 0.68 second, an increase sufficient to crack the pitch.

Figure 2 shows the coke yield for three different feed rates at the temperatures investigated. Highest coke yields were obtained at the lowest feed rate, indicating that the lower space velocity (gas basis) led to a greater percentage of the pitch coming into contact with the hot wall of the cracker. The higher cracking temperatures also produced more coke. In the 2-1/2 inch diameter reactor that had been used before, coke yields were lower and cracked pitch yields were higher.

The oil yield, shown in Figure 3, was higher at the 5.5 lb/hr pitch rate, but a yield inversion occurred between 7.0 and 9.5 lb/hr. Thus, the oil yield decreased with increase in feed rate to a certain point, then increased. Possibly, the oil is derived by two means during the cracking process: (1) distillation of feed pitch, and (2) cracking, with the latter predominant at low rates and giving way to distillation at high rates. This seems to be verified by the decrease in carbon-hydrogen ratio of the oil residue with increase in feed rate, as shown in Figure 4. Figure 4 also shows that the carbon-hydrogen ratio of the oil residue increases with increasing temperature, this indicating the greater cracking effect of higher temperatures.

Gas yields, Figure 5, appear to have been less affected by feed rate until 1,300° F when the yields leveled out at different percentages, the leveling plateau being higher at lower feed rates. This indicates that higher cracking temperatures and longer residence time both tend to produce more gas due to the greater amount of cracking that occurs.

Typical material balances are given in Table 2. Product recovery was generally greater than 90 percent. Some losses were incurred in removing the coke from the reactor and the cracked pitch from the receiver. Material balances had been established for the system in previous experiments and were published (1). In these earlier tests, material balances ranged from 91.6 to 99.1 percent.

TABLE 2. - Material Balance for Thermal Cracking of
 Low-Temperature Lignite Pitch

Crude pitch rate, pph	Coke rate, pph	Oil rate, pph	Cracked			Total, pph	Loss, pph	Loss, pct
			pitch rate, pph	Gas rate, pph	Loss, pct			
9.0	2.5	2.5	0.8	2.6	8.4	0.6	6.7	
7.0	1.9	1.6	0.9	2.0	6.4	0.6	8.6	
9.2	2.5	2.6	0.9	2.6	8.6	0.6	6.5	
6.7	1.8	1.8	0.7	2.2	6.5	0.2	3.0	
9.5	2.7	2.7	0.9	2.7	9.0	0.5	5.2	
5.6	1.6	1.6	0.2	1.7	5.1	0.5	9.0	

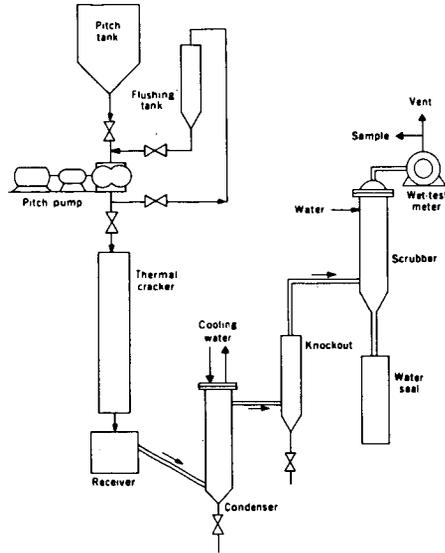


FIGURE 1. - Thermal Cracking System.

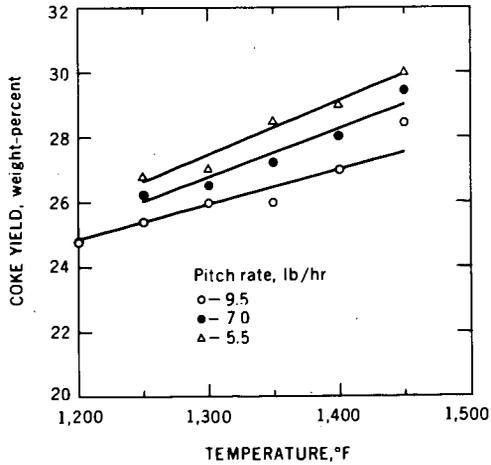


FIGURE 2. - Coke Yield as a Function of Pitch Rate and Temperature.

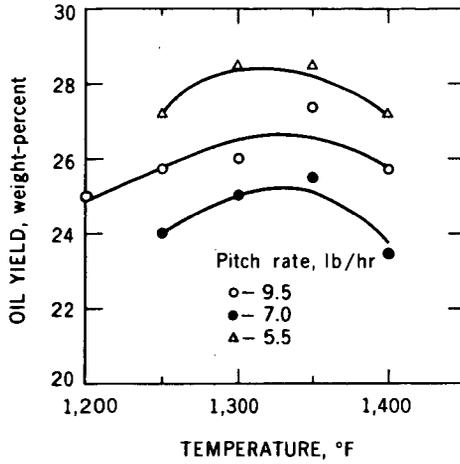


FIGURE 3. - Effect of Pitch Rate and Temperature on Oil Yield.

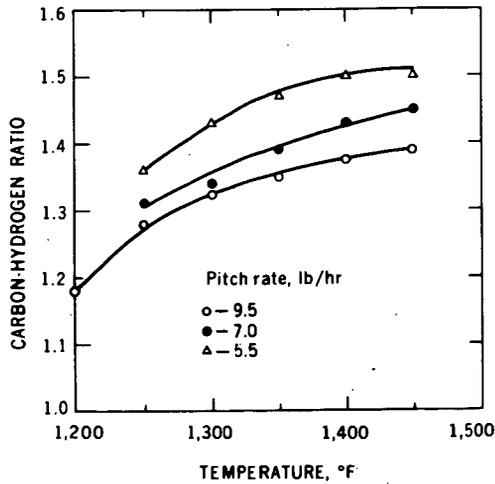


FIGURE 4. - Carbon-Hydrogen Ratio of Oil Residue.

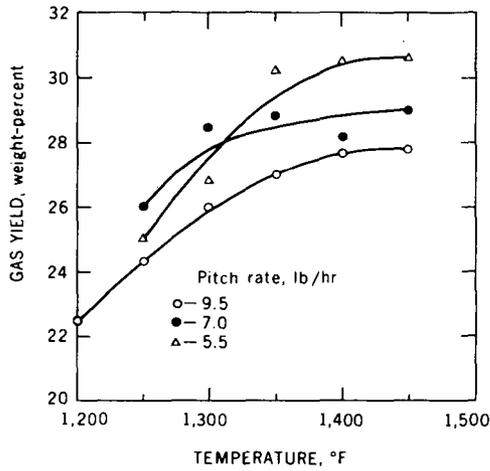


FIGURE 5. - Effect of Pitch Rate and Temperature on Gas Yield.

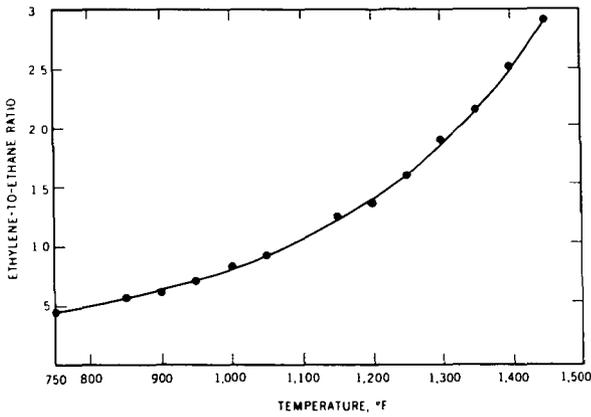


FIGURE 6. - Ethylene-to-Ethane Ratio Versus Temperature.

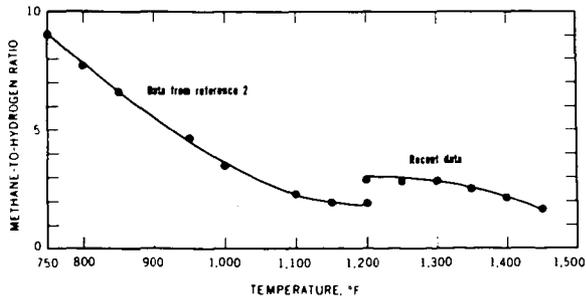


FIGURE 7. - Methane-to-Hydrogen Ratio Versus Temperature.