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The Effect of Carbonization Heating Rate on Charcoal and Active Carbon Yields

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ABSTRACT

The thermal decomposition of white oak chips was investigated by pyrolyzing 1-k samples at atmospheric pressure in an electrically-heated batch reactor using five carbonization heating rates from 0.98 to 9.44°C/min, and a maximum temperature of 490°C. The resulting charcoals were then activated with steam in a second batch reactor. Iodine number was used as a measure of the sorptive capacity of the active carbon. Charcoal yields decreased as the carbonization heating rate increased, particularly for rates less than about 4°C/min. Active carbon yields decreased and iodine numbers increased as the severity of gasification increased. For carbonization heating rates greater than about 4°C/min, the active carbon yield for a given iodine number was essentially independent of the heating rate.

Index Entries: Carbonization heating rate; white oak chips; pyrolysis products; iodine number; activated carbon.

INTRODUCTION

This investigation was conducted in support of a site-specific feasibility study of an updraft, packed-bed, vertical-shaft, char-recirculation gasification system that would produce active carbon, electricity, and process steam from chipped hardwood wastes. It is an extension of an earlier study of the pyrolysis of mixed hardwood chips (*1*). Its principal

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goal was to develop an empirical model of the product yields for the pyrolytic decomposition of paper-grade white oak chips and the subsequent gasification/activation of the resulting charcoal chips.

White oak is the dominant hardwood species in the region. Since the area sawmills are too geographically isolated to economically dispose of their slabs and end cuttings, these materials present a solid waste disposal problem. The gasification system being studied would take this waste as paper-grade chips, dry it, and convert it into active charcoal and combustible gases and vapors. On leaving the gasifier, the gases and vapors would be burned, and the thermal energy of the resulting combustion products would be used to generate process steam and electricity. Details of the char-recirculation gasification process are given by Martin (2).

In order to model the gasifier, either thermodynamically or kinetically, empirical relationships are needed for the pyrolysis product yields. Also, for modeling the gasification process, a relationship between the carbon activity, or gasification level, and the active carbon yield is needed. Since it was too expensive to construct and operate steady-state, continuous-flow reactors, it was necessary to use batch reactors to simulate the actual pyrolysis and gasification processes.

Such studies for mixed-hardwood chips (*1*) have shown that the pyrolysis product yields are functions of the maximum temperature to which the charcoal is heated. Therefore, the initial goals of this research were:

1. To determine the yields of pyrolysis products as functions of the maximum charcoal temperature; and
2. To determine the iodine number of the resulting steam-gasified charcoal as a function of its yield.

In pursuit of the first goal, it was found that the decomposition product yields were sensitive to the carbonization heating rate as well as the maximum temperature. Therefore, the research goals were extended to include:

3. The determination of the yields of pyrolysis products as a function of the rate of heating for a single maximum charcoal temperature; and
4. The determination of the iodine number of the resulting steam-gasified charcoal as a function of its yield.

This paper addresses the last two goals. Complete results are given by Martin (2).

METHODS

Experimental Systems

Pyrolysis System

The pyrolysis reactor was essentially the same as that described by Purdy et al. (*1*). However, for the present studies, the reactor furnace was

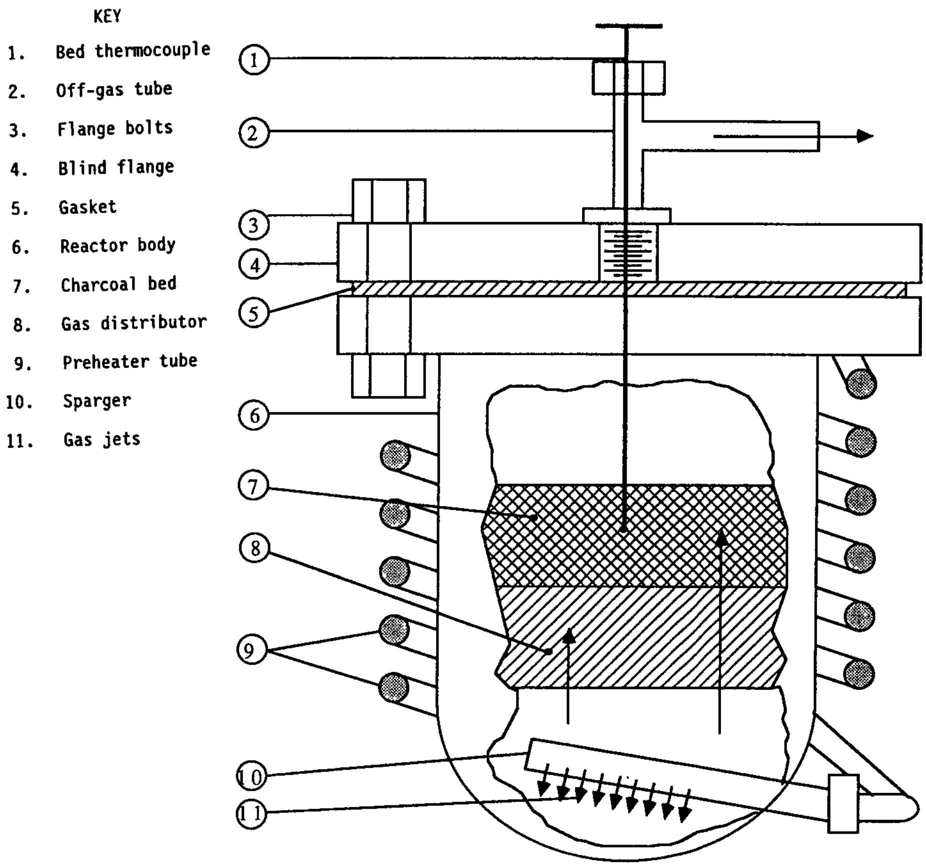

Fig. 1. Gasification reactor.

controlled with a Lindberg-Eurotherm 818P programmer-controller. The programmer operated interactively with the furnace, using the reactor-wall temperature as the controlled variable. Thus, the temperature of the inside wall of the reactor was ramped at a specific rate to a specific final temperature. Also, a Chromalox coil heater was used to preheat the nitrogen purge gas prior to its injection at the base of the reactor. This permitted hot-nitrogen purges of the reactor during drying, at the end of the exothermic pyrolysis process, and at the end of the run.

Gasification System

Figure 1 shows the gasification reactor. Details of its construction are given in ref. 2. The reactor was suspended in a Fisher 497 programmable ashing furnace. Steam and nitrogen were injected into a plenum at the base of the reactor, where they were uniformly distributed over the reactor cross section before they flowed upward through the charcoal bed. The resulting product gases, carbon monoxide and hydrogen, exited the reactor and furnace and were flared immediately using an open-flame Bunsen burner.

KEY

1. Pressure regulator
2. Nitrogen tank
3. Flow meter
4. Top-loading balance
5. Flask
6. Water tubing
7. Peristaltic pump
8. Flow-control valves
9. Boiler
10. Bunsen burner
11. Bed thermocouple
12. Gas thermocouple
13. Gasifier
14. Furnace
15. Reactor off-gas tube
16. Bunsen burner

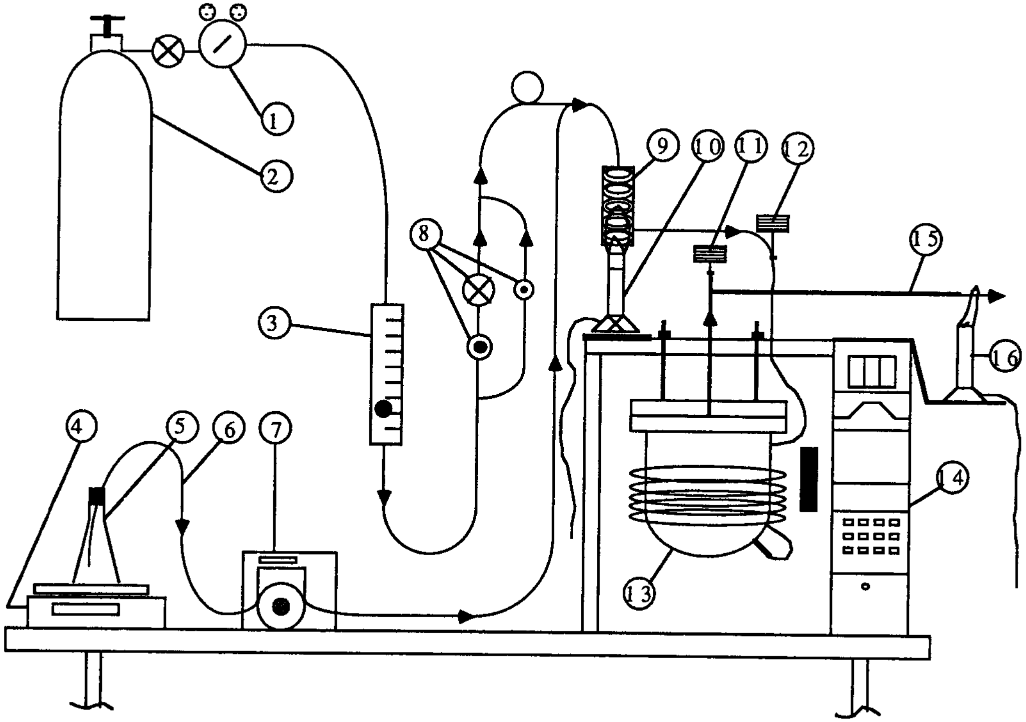

Fig. 2. Charcoal activation system.

The overall system is shown in Fig. 2. Nitrogen flowed from the regulated supply through a dynamic flow meter at a rate of about 1 ft^3/h. Water was drawn from a 500-mL flask (supported by an electronic balance) by a microprocessor-controlled peristaltic pump that discharged it to the nitrogen line. From this juncture, the nitrogen-water mixture flowed through a boiler where the water was vaporized and superheated. The mixture then entered the furnace where it was heated further before entering the reactor.

Experimental Procedures

Pyrolysis System

The headspace heater and the furnace were turned on to bring the temperature of the chips to 120°C and hold them there for two hours. During this drying period, 150°C nitrogen was injected at the base of the reactor at a rate of about 2 scfh. The resulting evaporated free moisture from the chips was collected and the nitrogen was vented to the exhaust hood. At the end of this purge, the nitrogen was turned off and a gas collection bag was connected to the system.

Constant-rate heating then occurred until the maximum temperature of 490°C was reached. Near the end of the exothermic portion of the decomposition process, 370°C nitrogen was injected at the base of the reactor at a rate of about 10 scfh to a total of one cubic foot. This flow purged the organic vapors from the reactor, thereby minimizing their "loss" by secondary chemical reactions. The maximum temperature was held for one hour, and then another 370°C-nitrogen purge was used to transport the residual gases from the reactor.

At this point, the furnace was turned off and the cooling process was begun. Nitrogen was periodically added to the reactor to maintain an inert environment at pressures slightly above ambient. Once the reactor was sealed, the condensation train was disassembled (*1*).

Gasification System

This procedure was initiated by selecting a 100-g sample of charcoal chips, counting the chips, and placing them on the screen at the top of the bed of alumina beads, which serves as the gas distributor (Fig. 1). This amount of charcoal gave a bed depth of about 6 cm. At this point, the reactor was sealed and placed in the furnace. Next, the gas lines were connected to the reactor, distilled water was added to the flask, the water tubing was filled, and the balance was tared.

The nitrogen was then turned on at about 0.5 scfh, and the boiler and off-gas-flare Bunsen burners were lighted to preheat the nitrogen going to the reactor and to burn any off-gases from the system, respectively. Finally, the furnace-temperature program and the computer datalogger were started.

The furnace took about 4 h to reach the desired activation temperature of 900°C. At this time, the water was turned on at 50 mL/h, a rate of about 1.5 times the actual steam/carbon reaction rate.

Once the estimated water consumption was reached, the pump and furnace were turned off, the water line was clamped at the tee, and the background flow of nitrogen was left on to prevent ambient air from entering the reactor during the cool-down period. The off-gas flare was turned off only after all combustible gas had been purged from the reactor.

The system was allowed to cool overnight. Then the nitrogen was turned off, the active carbon was removed from the reactor and weighed, and the chips were counted before being placed in airtight storage cans. Samples of this carbon were milled and then ground and dried at 105°C in preparation for a determination of the iodine number (2).

RESULTS AND DISCUSSION

Carbonization Heating-Rate Study

Five runs were made with heating rates of 0.98 to 9.44°C/min and the same maximum charcoal temperature of 490°C. The results are given in Table 1 and Figs. 3, 4, and 5.

The pyrolysis product yields as a function of the heating rate are shown in Fig. 3 with the data points connected for clarity. Apparent scatter in the gas- and water-yield data made trends difficult to interpret. The water yield appears to be decreasing slightly with increasing rate, but the gas rate appears to be essentially "constant." However, it is very clear that the charcoal yield is decreasing and the condensible organics yield is increasing with increasing heating rates.

Analysis of the charcoal for its volatile matter, fixed carbon, and ash contents showed a well-ordered behavior as evidenced by Fig. 4. The charcoal yield drops sharply at low heating rates and then decreases more slowly for rates above about 4°C/min. It is interesting that the fixed carbon appears to plateau above this rate.

The importance of this behavior to the prediction of the performance of a pyrolysis system is evident, especially if the ultimate goal is to produce active carbon. From the reactor-wall- and centerline-temperature profiles for these runs, it was seen that the initial decomposition process was exothermic. Therefore, to achieve the low heating rates, it was necessary to cool the chip bed during this process, a condition that would not normally be possible in an updraft, packed-bed, vertical-shaft reactor. (The thermal capacity of the reactor vessel itself served as the energy sink for the low rate runs.)

As the heating rate was increased, it appeared that the decomposition process would occur adiabatically at a rate of about 6°C/min. To

Table 1
Summary of Product Yield Data
for Pyrolysis Runs Using Paper-Grade White Oak Chips

Run Number	070389	071089	071789	081589	082989
Maximum temperature, °C	487	490	488	490	492
Heating rate, °C/min	4.14	2.90	0.98	9.44	7.32
Charcoal					
Dry yields, g/kg dry feed					
Fixed carbon	239.6	246.0	266.7	231.1	233.9
Volatile matter	52.7	60.6	66.0	44.4	46.9
Ash	4.6	5.6	6.1	7.3	5.7
Total char	296.9	312.2	338.8	282.8	286.5
Water of pyrolysis					
Yield, g/kg dry feed	240.2	227.5	234.1	226.5	221.6
Condensible organics					
Dry yields, g/kg dry feed					
Light oil	217.7	211.2	178.1	240.0	237.4
Heavy oil	66.9	82.6	75.6	82.8	64.3
Total oil	284.6	293.8	253.7	322.8	301.7
Gas and light organics					
Dry yield (by difference), g/kg dry feed	178.3	166.5	173.4	167.9	190.2

achieve rates greater than this, heating of the chip bed appeared to be necessary. (If the initial thermal decomposition of the wood chips is to be controlled, it will be necessary to have a process that can control the thermal energy exchange between the decomposing solids and the upward flowing "hot" gases.)

The condensible organics were separated into light-oil and heavy-oil fractions for each of the runs. These data are presented in Table 1 and Fig. 5. The heavy-oil yield appears to be independent of the heating rate, but the light-oil yield clearly increases with heating rate. Individual gas component data were obtained for these runs, and they may be found in ref. 2.

Gasification Study

Each of the five charcoals was gasified to at least two different levels of activity to determine the relationship between the iodine number and the yield of active carbon. The results are given in Table 2 and Fig. 6.

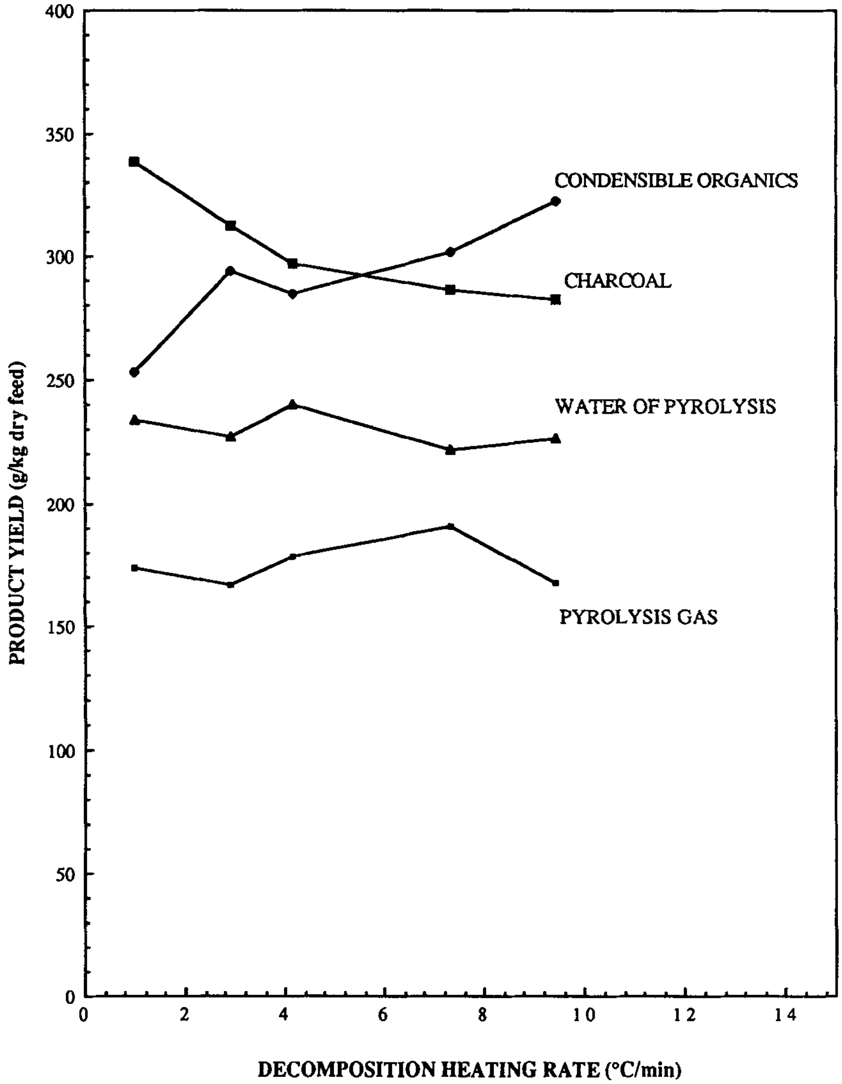

Fig. 3. Product yield vs decomposition heating rate for pyrolysis of paper-grade white oak chips to a maximum temperature of 490°C.

The gasification process practiced in this study consisted of first heating 100-g samples of each charcoal product to 900°C in a nitrogen atmosphere, thereby devolatilizing it before reacting it with steam. Therefore, the material to be gasified consisted of fixed carbon and ash.

From the results shown in Fig. 4 for charcoal and its components, it appears that whereas the charcoal yield decreases with increasing heating rate, the sum of the fixed-carbon and the ash components is essentially independent of this rate for rates greater than about 4°C/min. Since the gasification/activation process is one of the reacting steam with the fixed

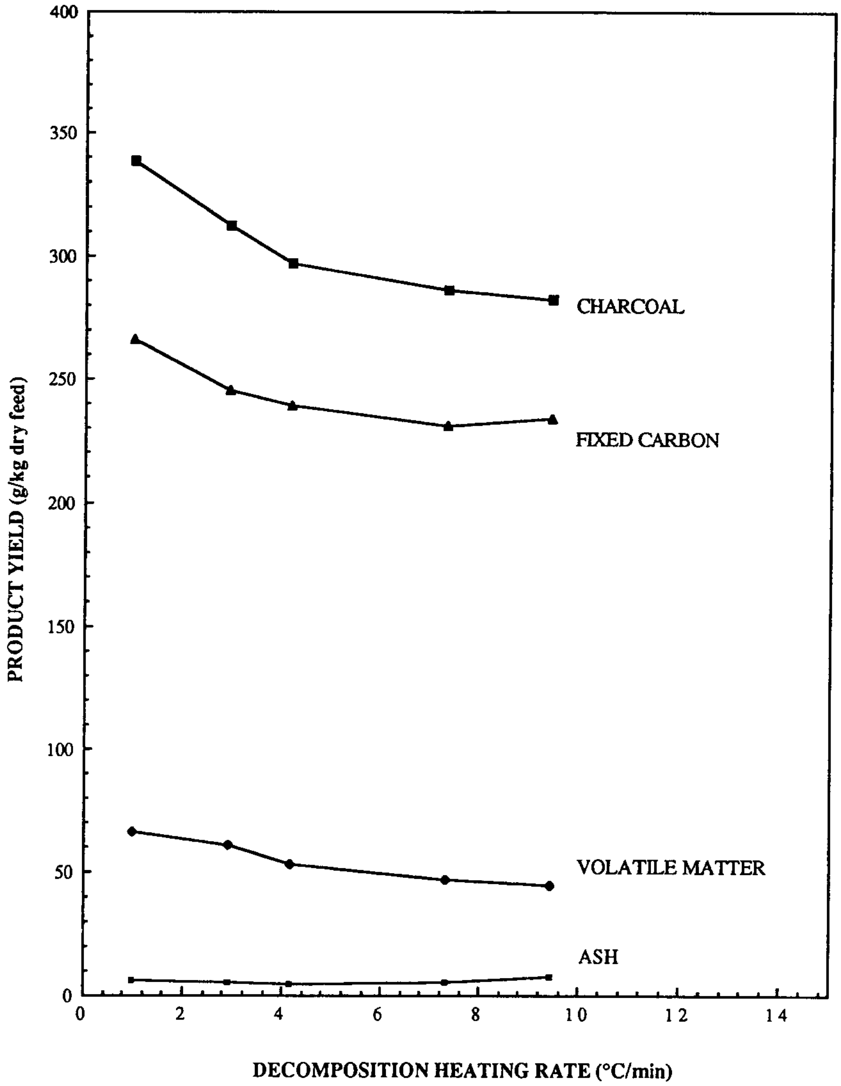

Fig. 4. Yields of charcoal and its components vs decomposition heating rate for pyrolysis of paper-grade white oak chips to a maximum temperature of 490°C.

carbon throughout the internal structure of the devolatilized charcoal chips, it might be expected that the yield of active carbon (kg active carbon per kg dry feed/wood chips) for a given level of activity (e.g., internal surface area or iodine number) would only be dependent on the heating rate for charcoals produced at rates less than about 4°C/min.

This expectation is borne out by the active carbon data given in Table 2 and shown in Fig. 6. For a given level of activity (iodine number), the active carbon yields are significantly higher for the carbons produced

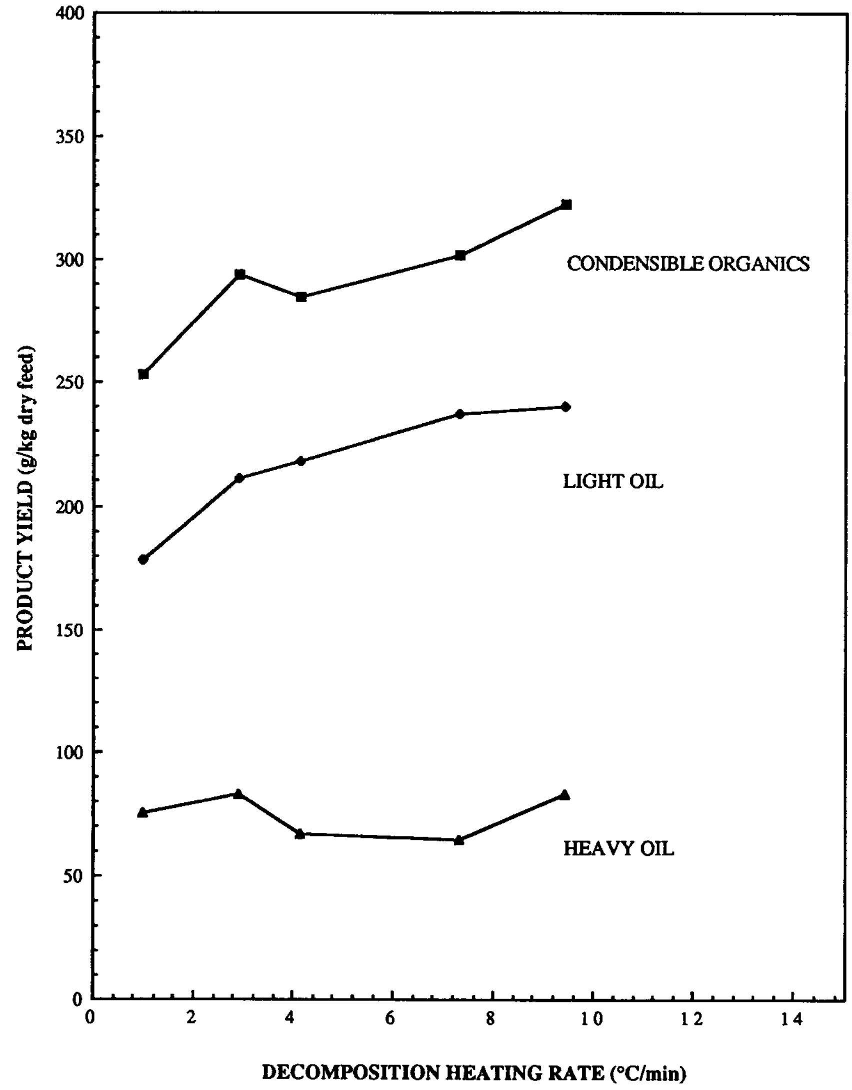

Fig. 5. Yields of condensible organics and its components vs decomposition heating rate for pyrolysis of paper-grade white oak chips to a maximum temperature of 490 °C.

from the 0.98 °C/min (071789) and 2.90 °C/min (071089) charcoals. Those active carbons produced from the other three charcoals have practically the same iodine-number-yield relationships.

From these results, it appears that cooling the solids during the initial exothermic decomposition process increases the production of fixed carbon which, in turn, increases the yield of active carbon for a given level of activity. (This research did not explore advantages other than yield that might accrue from such cooling.)

Table 2
Active Carbon Data

Pyrolysis run number	Activation run number	Water consumption, g/kg dry feed	Active carbon yield, g/kg dry feed	Iodine Number, mg I/g carbon
070389	092689	610	148	902
070389	101289	243	201	658
070389	101789	637	136	988
071089	122889	272	219	695
071089	010290	626	155	978
071789	101989	411	208	780
071789	102489	229	253	566
071789	102689	620	190	847
072489	120590	628	227	553
072489	121989	602	140	934
081589	110289	514	151	885
081589	110989	268	180	765

CONCLUSIONS

Based on the results of this study, the following conclusions were drawn:

1. There exists an operating window through which wood chips can be carbonized, such that the initial exothermic pyrolysis process is practically adiabatic.
2. Excursions from this adiabatic process, involving modest cooling or heating of the chips, seemingly have no practical influence on the charcoals' fixed-carbon yields, or on the yields of active carbon produced from these charcoals.
3. In order to use this operating window in an updraft, packed-bed, vertical-shaft reactor, a means must be provided to control the energy exchange between the gas stream and the bed solids. (A char-recirculation gasifier has this capability.)

ACKNOWLEDGMENTS

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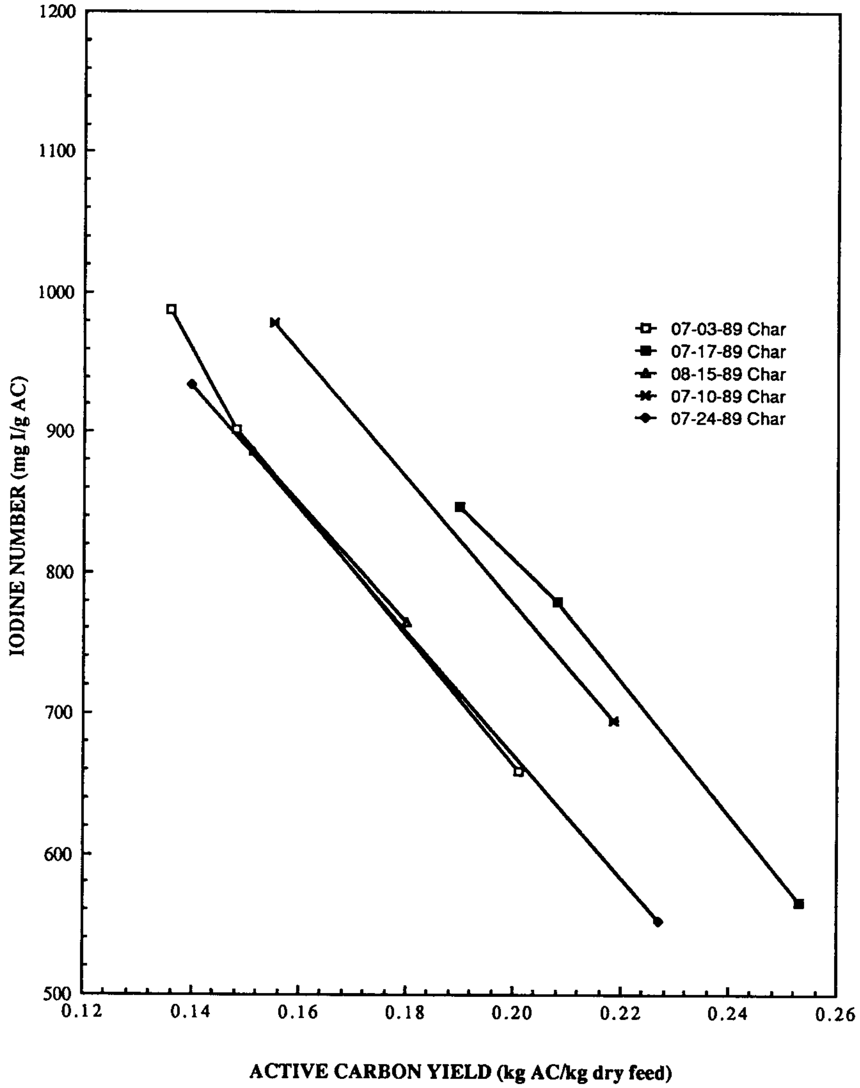

Fig. 6. Iodine number vs active carbon yield for steam activation of charcoals produced from paper-grade white oak chips that had been heated at various rates to a maximum temperature of 490°C.

and the Center for Electric Power, the Manufacturing Center, and the Departments of Chemical and Mechanical Engineering at Tennessee Tech.

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