PROPERTIES OF CHAR PRODUCED FROM PYROLYSIS OF SOUTHERN PINE[1]

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ABSTRACT

Bench scale pyrolyses were carried out on southern pine at conditions of 250, 350, 400, 500, and 800 C for 1, 2, and 4 hours in a flowing nitrogen atmosphere at flow rates of 135 and 405 milliliters per minute. Data presented in this paper represent work on the properties of the chars produced under these conditions. Results of oxygen bomb calorimetry, density and specific gravity measurements, carbon and hydrogen analyses, and gravimetric yields were statistically analyzed to determine the influence of process conditions on char properties. In general, char yield and percentage of hydrogen and oxygen decreased, while the carbon percentage increased with increasing temperature.

Keywords: Pyrolysis, char, southern pine, material properties.

INTRODUCTION

The pyrolytic processing of wood or other biomass involves the exposure of the material to elevated temperatures in nonoxidizing atmospheres. This type of procedure will result in production of solid, liquid, and gaseous phases in varying proportions. These proportions appear to be somewhat related to the process conditions (Wenzl 1970). Furthermore, the material properties of each phase seem also to be influenced by the reaction conditions. The liquid phase, known as either pyrolytic oil or tar, is a complex mixture of chemical compounds that has been shown to have potential as a chemical feedstock (Elder and Soltes 1979, 1980). The solid phase, char or charcoal, has been the subject of studies relating anatomical changes (Cutter et al. 1980) and material (physical) properties (Blankenhorn et al. 1972, 1978; Kalliat et al. 1983; Moore et al. 1974) to various pyrolytic conditions.

The physical and mechanical properties of char produced at a range of temperatures have been found to undergo inflections of trends in dynamic modulus and external dimensions near 600 C (Blankenhorn et al. 1972, 1978; Moore et al. 1974). Furthermore, it was found that real density decreased, while apparent

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TABLE 1. *Summary of results for Duncan's multiple range test for each property and parameter (values in parentheses are means for the specified condition; m = 6 for temperature, m = 15 for flow rate, and m = 10 for time). (Values followed by the same letter do not differ significantly at the 5% level.)*

	Temperature (degrees centigrade)		Flow rate (milliliters/minute)		Time (Hours)	
Char yield	A	250 (46.857)	A	135 (27.845)	A	1 (28.715)
(mean % yield)	B	350 (28.007)	A	405 (27.097)	A	2 (27.458)
	C	400 (23.952)			A	4 (26.240)
	C	500 (21.227)				
	D	800 (17.313)				
Heat of combustion	A	500 (13,038)	A	405 (12,412)	A	4 (12,521)
(Btus/pound)	A	800 (12,506)	A	135 (12,240)	A	2 (12,272)
	A	350 (12,468)			A	1 (12,184)
	A	400 (12,455)				
	B	250 (11,163)				
Carbon %	A	800 (85.278)	A	135 (78.554)	A	2 (80.690)
	B	500 (84.253)	A	405 (78.515)	A	4 (77.501)
	B	400 (79.305)			B	1 (77.413)
	C	350 (75.552)				
	D	250 (68.285)				
Hydrogen %	A	250 (4.697)	A	405 (3.083)	A	1 (3.135)
	B	350 (3.655)	A	135 (3.069)	AB	2 (3.095)
	C	400 (3.189)			B	4 (2.998)
	D	500 (2.800)				
	E	800 (1.043)				
Oxygen %	A	250 (27.081)	A	405 (18.402)	A	4 (19.501)
	B	350 (20.793)	A	135 (18.377)	A	1 (19.452)
	C	400 (17.510)			B	2 (16.215)
	D	800 (13.678)				
	D	500 (12.947)				
Density (g/cc)	A	800 (1.547)	A	405 (1.403)	A	2 (1.412)
	B	250 (1.368)	A	135 (1.403)	A	4 (1.401)
	B	350 (1.367)			A	1 (1.395)
	B	500 (1.366)				
	B	400 (1.365)				
Specific gravity	A	400 (0.451)	A	135 (0.407)	A	1 (0.433)
	AB	350 (0.429)	A	405 (0.407)	B	4 (0.396)
	AB	500 (0.426)			B	2 (0.392)
	B	250 (0.400)				
	C	800 (0.328)				

density initially decreased and then increased above 600 C. On the other hand, Wenzl (1970) states that the true or real density of charcoal increased steadily with increasing temperature while the apparent density decreases. Anatomically, it has been shown that the cell-wall material and layers coalesce while retaining the identifying pattern of the parent species (Cutter et al. 1980; Knudson and Williamson 1971; McGinnes et al. 1974, 1976). Zicherman and Williamson (1981, 1982) have examined structural characteristics of chars with regard to fissures and their propagation during exposure to elevated temperatures.

The results reported in this paper are part of a larger study on the pyrolysis of wood and quantification of yields, and the properties of the char and other prod-

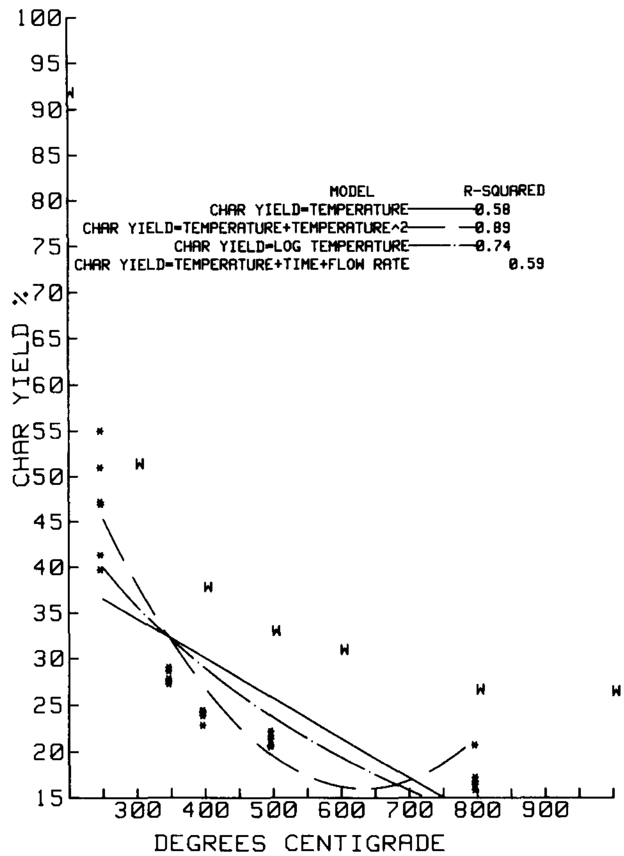

FIG. 1. Char yield percentages vs. temperature, and results of regression analyses (* = data points) (W = data from Wenzl 1970).

ucts. Previous papers (Elder 1984; Elder and Cutter 1983) have dealt with yield data and the properties of the liquid phase. This paper reviews the yield data presented by Elder (1984) and quantifies the char properties as functions of the reaction conditions. The char parameters that will be discussed include yield, heat of combustion, elemental composition, and real and apparent density.

METHODS AND MATERIALS

Pyrolysis runs performed in this study were carried out with a bench scale reactor. As described earlier (Elder 1984), it was constructed of temperature-resistant glass tubing placed in a split-tube furnace and connected to a nitrogen gas source and a series of traps. The nitrogen provided an inert atmosphere for pyrolysis and served to carry the gaseous products into the traps. The flow rate of the gas was altered to vary the residence time of the evolved volatiles in the heated zone. Downstream, the first trap was immersed in liquid nitrogen, while the second trap was simply a water scrubber through which the remaining uncondensed effluent bubbled. Oven-dry southern pine samples, ca. 0.5 × 0.5 × 6.0 cm, were placed in porcelain combustion boats and centered in the heated zone of the furnace.

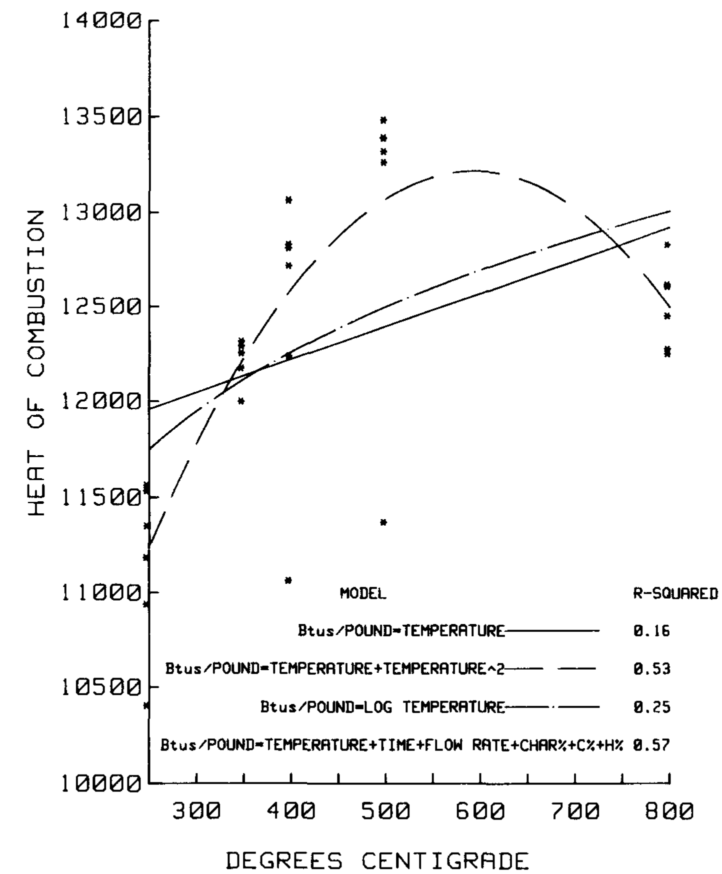

FIG. 2. Heat of combustion (Btus/pound) vs. temperature, and results of regression analyses (* = data points).

The reaction conditions used were as follows: temperature—250, 350, 400, 500, and 800 C; time—1, 2, or 4 hours; purge gas flow rate—135 or 405 ml/min. All combinations of times, temperatures, and flow rates were used in this study resulting in 30 different combinations of conditions and samples. At the start of each run, the flow rate of the nitrogen was adjusted and the furnace preheated to the target temperature. When the conditions were set, the furnace was raised into position around the reaction tubing and closed. At the end of the particular time period, the furnace was removed and the sample was allowed to cool to ambient temperature in flowing nitrogen. The char was then weighed to determine gravimetric yields.

The heat of combustion was determined in a Parr adiabatic oxygen bomb calorimeter by ASTM D 2015-66. Carbon and hydrogen percentages were determined with a Perkin-Elmer elementary analyzer, Model 240, with oxygen used as the combustion gas and helium as the carrier gas. The oxygen content of the samples was then determined by subtraction.

The real or true density of each char sample was determined by flotation of 10

TABLE 2. *Equations for regression models reported in Figs. 1–7.*

Char yield % =	47.2800.043 Temperature
Char yield % =	96.0130.253 Temperature + 0.0002 Temperature^2
Char yield % =	169.786 − 54.128 Log Temperature
Char yield % =	49.882 − 0.043 Temperature − 0.794 Time − 0.003 Flow rate
Heat of combustion =	11,518.863 + 1.754 Temperature
Heat of combustion =	7,309.488 + 19.931 Temperature − 0.017 Temperature^2
Heat of combustion =	5,722.861 + 2,492.358 Log Temperature
Heat of combustion =	13,157.593 + 0.441 Temperature + 62.798 Time + 0.381 Flow rate − 86.122 Char yield % − 0.978 Carbon % + 376.658 Hydrogen %
Carbon % =	65.655 + 0.028 Temperature
Carbon % =	38.614 + 0.145 Temperature − 0.0001 Temperature^2
Carbon % =	−11.669 + 34.308 Log Temperature
Carbon % =	87.550 + 0.010 Temperature − 0.543 Time − 0.001 Flow rate − 0.429 Char yield %
Hydrogen % =	5.6 = 968 − 0.006 Temperature
Hydrogen % =	7.221 − 0.012 Temperature + 5.003 × 10^{-6} Temperature^2
Hydrogen % =	21.733 − 7.096 Log Temperature
Hydrogen % =	4.685 − 0.005 Temperature − 0.024 Time − 0.0001 Flow rate + 0.028 Char yield %
Oxygen % =	28.377 − 0.022 Temperature
Oxygen % =	54.166 − 0.133 Temperature + 0.0001 Temperature^2
Oxygen % =	89.935 − 27.212 Log Temperature
Oxygen % =	7.765 − 0.004 Temperature − 0.567 Time + 0.001 Flow rate + 0.401 Char yield %
Specific gravity =	0.484 − 0.0002 Temperature
Specific gravity =	0.258 + 0.0008 Temperature − 9.035 Temperature^2
Specific gravity =	0.812 − 0.154 Log Temperature
Specific gravity =	0.548 − 0.0002 Temperature − 0.010 Time − 1.481 × 10^{-6} Flow rate
Density =	1.244 + 0.0003 Temperature
Density =	1.501 − 0.0008 Temperature + 1.027 × 10^{-6} Temperature^2
Density =	0.491 + 0.347 Log Temperature
Density =	1.241 + 0.0003 Temperature + 0.001 Time + 4.198 × 10^{-7} Flow rate

to 20 mg of char in a mixture of carbon tetrachloride and benzene at 30 ± 0.1 C (Beall 1972; Stamm 1964). Specific gravity was determined pycnometrically in water (Stamm 1964).

All data were examined statistically using analysis of variance, Duncan's multiple range test, and regression analyses.

RESULTS AND DISCUSSION

The analyses of variance indicated that there were significant differences between reaction conditions. The results of the Duncan's mean separation tests are summarized in Table 1.

The yield of char, as previously reported (Elder 1984), was found to decrease significantly as the reaction temperature increased, but neither reaction time nor gas flow rate had a significant effect. While heat of combustion was significantly lower for the 250 C samples than all other temperature conditions, it was not

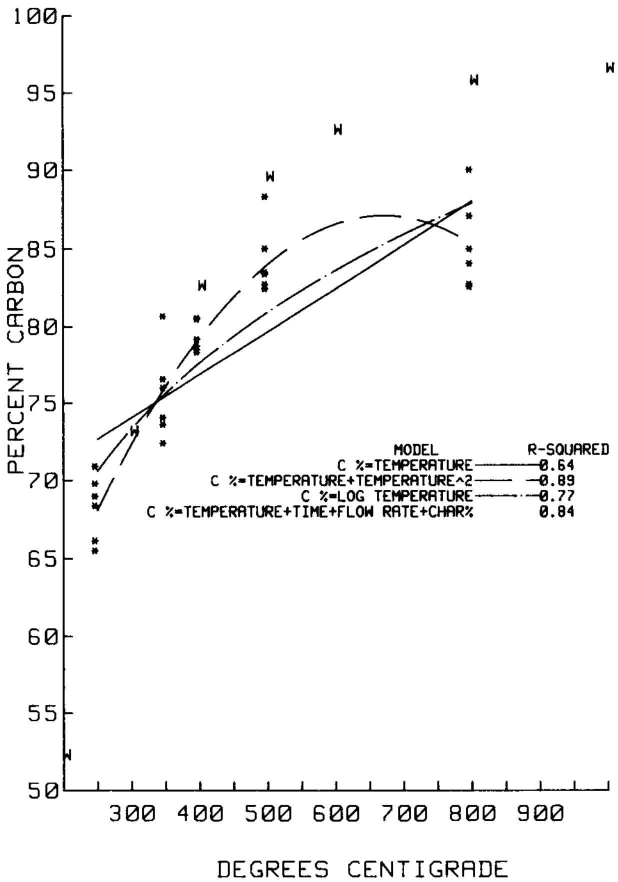

FIG. 3. Carbon percentages vs. temperature, and results of regression analyses (* = data points) (W = data from Wenzl 1970).

affected by the other parameters. The percentages of carbon, hydrogen, and oxygen each differed significantly with both reaction time and temperature. The % C values increased with increasing temperature, while the % H and % O decreased at the higher temperatures. Time patterns for the % O and % C showed reverse trends; the % C was significantly greater for a 2-hour reaction time while the % O was the lowest for this time.

Real density of the char produced at 800 C was significantly higher than at all other temperatures. No other significant differences were found. The trends associated with specific gravity and temperature were reversed from those associated with real density and also were found to be affected by reaction time. The real density of the chars is a measure of the cell wall or char substance itself with no voids, while the specific gravity is the bulk property of the sample and is based on gross volumes. The increase in real density and decrease in apparent density can be interpreted as indicating that the porosity, or internal surface area, of the samples was increasing. Kalliat et al. (1984) have found that the internal

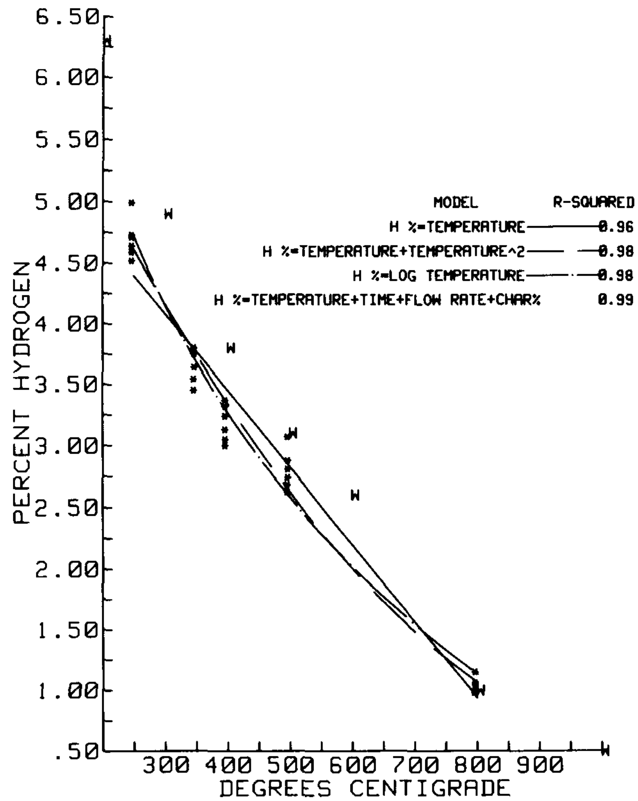

FIG. 4. Hydrogen percentages vs. temperature, and results of regression analyses (* = data points) (W = data from Wenzl 1970).

surface area of southern pine latewood heated to 600 C increased from 1.2 m^2/g to 2.3 m^2/g. Micropore volume increased from 0.06 to 0.13 cm^2/g from 250 to 600 C.

Regression analyses performed on the char yield data showed significant relationships for all models with R-squared values ranging from 0.58 to 0.89 (Fig. 1). The simple linear and the multiple linear models gave the lowest values while marked improvements were noted when either a quadratic or logarithmic model was fitted to the data. Data from Wenzl (1970) are included in this figure as well as in Figs. 3, 4, and 5 for comparative purposes. Table 2 shows coefficients determined for each regression model.

The data for the heats of combustion gave poorer fits, with an 0.16 fraction of explained variance for the simple linear model and 0.57 for the multiple linear model (Fig. 2). The multiple linear model included temperature, time, flow rate, and char yield as process variables. Addition of % C or % H gave no significant improvement in fit of the model. Logarithmic and quadratic fits of heat of combustion vs. temperature yielded R-squared values of 0.25 and 0.53, respectively.

Regressions of % C on several variables gave significant relationships with generally high R-squared values (Fig. 3). Simple linear regression of % C vs.

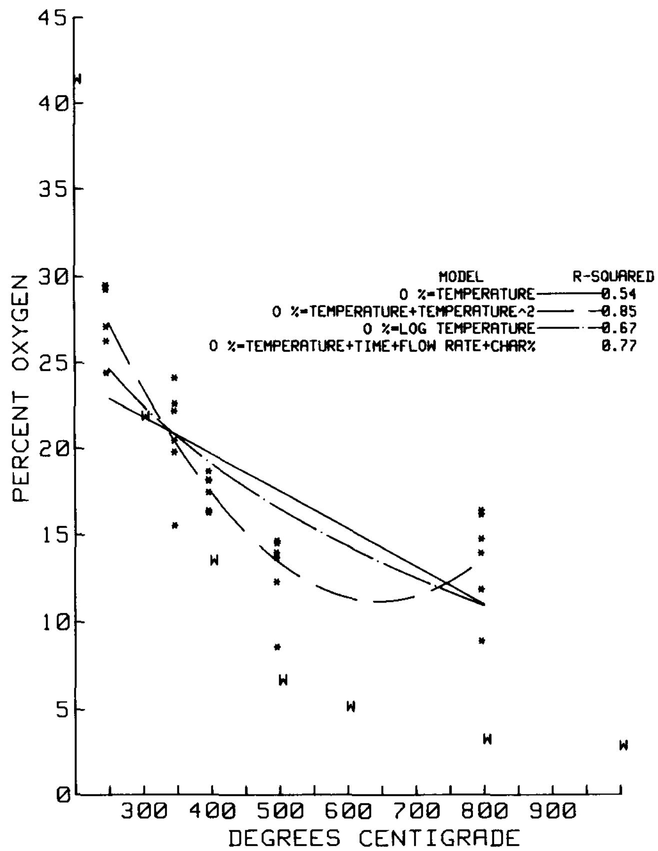

FIG. 5. Oxygen percentages vs. temperature, and results of regression analyses (* = data points) (W = data from Wenzl 1970).

temperature had an R-squared of 0.64 (simple correlation coefficient, r, of 0.8), while the multiple linear model with flow rate, time, and char yield added had a R-squared value of 0.84. As with the yield data, the transformations of the data gave better fits with quadratic fit of % C vs. temperature having a 0.89 R-squared value, and for the logarithmic model, R-squared was equal to 0.77.

Regression of % H on the various parameters gave very high correlation coefficients with R-squared values between 0.96 and 0.99 (Fig. 4). The more complex models were only slightly better fitting than was the simple linear model.

The pattern of R-squared values for the % O (Fig. 5) was similar to the patterns for the % C data. The simple linear model had the lowest R-squared value, 0.54, while the quadratic equation had the highest value, 0.85.

Regression analyses on the specific gravity (Fig. 6) and the real density (Fig. 7) gave significant relationships for all the models tested. Real density fits were as a rule better than the apparent density fits. The simple linear model of real density on temperature had an R-squared value of 0.76, while the addition of the other operating parameters yielded no improvement. The quadratic model had

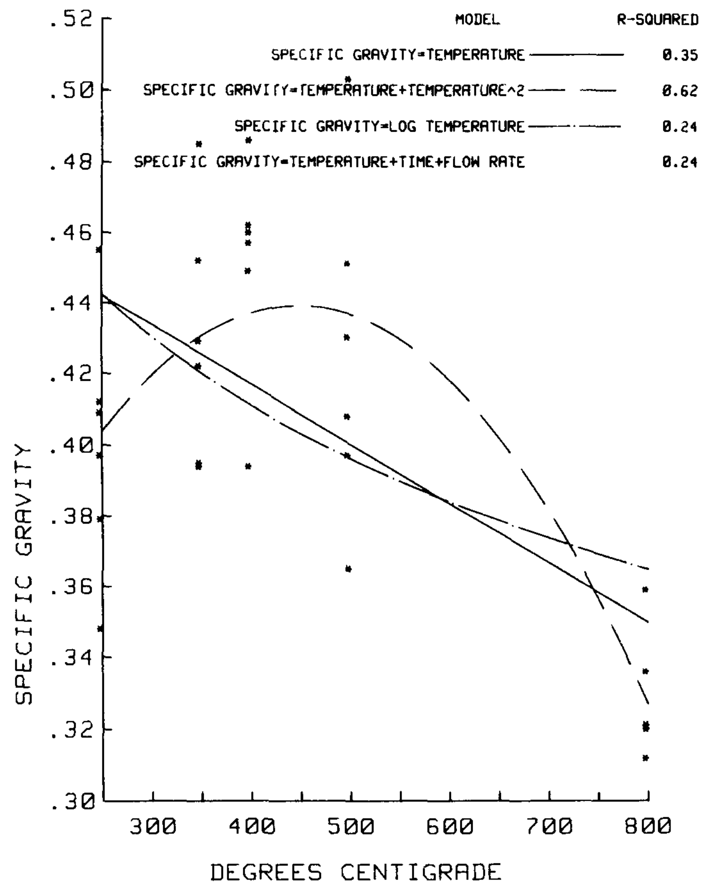

FIG. 6. Specific gravity vs. temperature, and results of regression analyses (* = data points).

the highest value, 0.94.

In comparing our data to that presented by Wenzl, it is important to remember that Wenzl's data included temperatures both below and above the range used in our study. As the plots in Figs. 1, 3, 4, and 5 show, there are definite similarities in trends between the data sets. However, there are divergences at the extremes. It is readily apparent that the specific pyrolysis conditions used exert a marked influence on the results.

In examining the results that were obtained in this study, it is of interest to note that the heat of combustion does not vary significantly for temperatures in excess of 350 C. This, coupled with the yield results, indicates that we may produce a char with a reasonable fuel value without resorting to higher temperatures which produce a lower yield. Furthermore, it has been found that the elemental composition of the chars is significantly related to the reaction conditions. This can be interpreted to mean that the chemical make-up of the chars could be altered predictably to fit the requirements of a particular application.

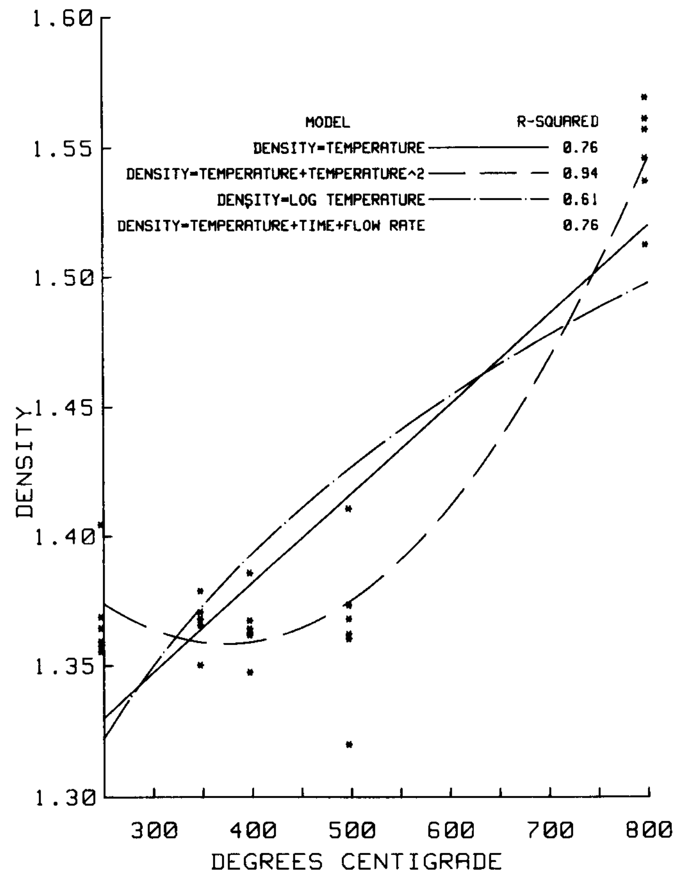

FIG. 7. Density (g/cc) vs. temperature, and results of regression analyses (* = data points).

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