

# EFFECT OF PROCESS CONDITIONS ON THE YIELD OF PYROLYTIC PRODUCTS FROM SOUTHERN PINE<sup>1</sup>

*Thomas Elder*

Assistant Professor  
Department of Forestry, Alabama Agricultural Experiment Station  
Auburn University, AL 36849

(Received September 1982)

## ABSTRACT

Southern pine samples were subjected to temperatures of 250, 350, 400, 500, and 800 C for 1, 2, and 4 hours in an atmosphere of flowing nitrogen gas at two flow rates. Solid, liquid, and gaseous phases were produced, the yields of which were statistically analyzed and found to be dependent on the pyrolytic conditions. All product yields differed significantly with temperature, but no significant differences with regard to reaction times were detected.

*Keywords:* Pyrolysis, southern pine, temperature, time, flow rate, product yields.

## INTRODUCTION

The thermal degradation of lignocellulosic material involves a large number of complex chemical reactions, which produce a solid charcoal-like material, a tarry liquid, and a gas (Browne 1958; Beall and Eickner 1970; Allan and Mattila 1971; Soltes and Elder 1981). On a broad scale, thermal degradation may be viewed as a continuum of processes that results in a continuum of product yields. At one extreme is carbonization, which predominately produces the solid phase, while gasification yields the gas in major proportion. In between, pyrolysis may produce about equal amounts of all three phases. The yield of each phase is a function of the conditions to which the feedstock is subjected.

There has been considerable interest in reforming wood and biomass by pyrolytic methods for fuels and chemicals. The char has been reported to have energy contents from 11,000–13,000 Btus per pound with virtually no nitrogen or sulfur (Knight et al. 1976). A material with energy contents of this level and low amounts of sulfur and nitrogen may be of use in mixture with high sulfur coals. The energy content of the mixture would not differ markedly from pure coal, but could greatly decrease the levels of sulfur- and nitrogen-based emissions that may arise from the combustion of coal. The tarry liquid has energy contents of 10,000–13,000 Btus per pound, and may contain up to one-third phenolic type compounds (Knight et al. 1976; Lin 1978). The liquid is a complex mixture of chemical compounds that are present in low concentrations, but broad fractionations have shown that the liquid may be used not only as a fuel, but also as a chemical feedstock (Elder and Soltes 1979).

By definition, carbonization and pyrolysis are carried out in the absence of oxygen, while gasification processes involve the use of controlled amounts of oxidizing agents. However, many procedures that are commonly called carbonization or pyrolysis are actually controlled combustions that introduce limited

---

<sup>1</sup> Alabama Agricultural Experiment Station, Journal Series No. 9-83427.

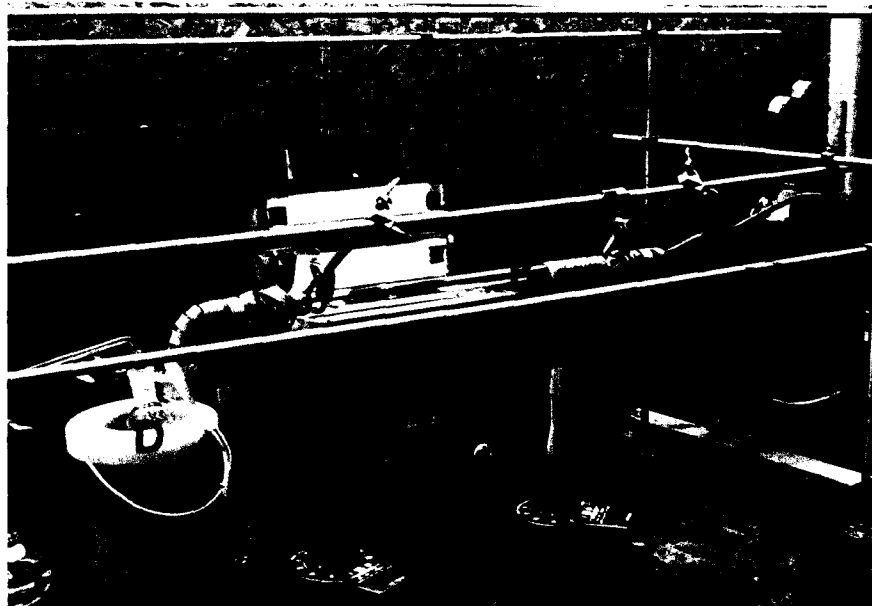


FIG. 1. Pyrolytic reactor used in this study (A is the nitrogen gas source, B is the temperature-resistant reactor tubing, C is the split-tube furnace, D is the liquid nitrogen trap, E is the distilled water scrubber).

amounts of air or oxygen. This study is concerned with variability in the yields of products resulting from alteration of pyrolytic reaction conditions in a flowing nitrogen atmosphere.

The reaction conditions that are commonly discussed in the literature are: temperature, heating rate, particle size, and the residence time of the evolved volatiles in the reaction zone. In general, it has been found that low temperatures and slow heating rates will maximize char production; gases are predominately produced at temperatures above 600 C and by long residence times that promote the formation of gases by cracking of the tars (Soltes et al. 1981). Yields of liquid are optimized at temperatures of 450–600 C, with rapid heating rates and short residence times (Soltes et al. 1981). Barnes et al. (1979) found that for a given residence time and heating rate, char production decreased with temperature to 500 C where it leveled off. In the same study, it was found that furfural production in the liquid phase increased with temperature to 500 C where it too became constant. Blankenhorn et al. (1978) found that porosity of the char increased with temperatures to 700 C and then decreased at higher temperatures. The pyrolysis of lignin was found to result in yields that were somewhat dependent on the method used to isolate the lignin (Vorher and Schweers 1975).

Many of the trends associated with yields of pyrolytic products and reaction conditions are intuitive in nature. It is the intent of the current study to quantify these trends by evaluation of the yields of pyrolytic products as a function of process parameters, including temperatures of 250, 350, 400, 500 and 800 C, reaction times of 1, 2 and 4 hours, and purge gas flow rates of 135 and 405 milliliters per minute.

TABLE 1. *Yields of each phase by temperature, flow rate and time of heating (each value is a percentage of the original oven-dry sample).*

Temperature (degrees centigrade)	Flow rate (ml/minute)	Time (hours)	Char %	Tar %	Trap %	Nonrecovered %
250	135	1	54.99	10.61	0.47	24.93
250	135	2	47.20	23.93	0.27	28.60
250	135	4	41.34	21.74	0.36	36.56
250	405	1	50.98	11.95	2.03	35.04
250	405	2	46.91	10.38	2.52	40.19
250	405	4	39.72	15.17	2.93	42.18
350	135	1	27.82	29.36	0.58	42.24
350	135	2	27.29	32.45	0.78	39.48
350	135	4	28.69	27.16	0.74	43.41
350	405	1	29.06	24.61	3.31	43.02
350	405	2	27.58	20.63	5.11	46.68
350	405	4	27.60	23.97	4.37	44.06
400	135	1	24.29	31.56	0.36	43.79
400	135	2	24.46	34.99	0.42	40.13
400	135	4	22.87	27.56	0.78	48.79
400	405	1	23.95	28.25	4.52	43.28
400	405	2	23.90	31.06	2.52	42.52
400	405	4	24.24	24.19	4.38	47.19
500	135	1	21.73	35.35	0.46	42.46
500	135	2	22.25	34.11	0.69	42.95
500	135	4	20.75	35.20	0.62	43.43
500	405	1	20.62	34.57	2.01	42.80
500	405	2	21.42	26.67	2.54	49.37
500	405	4	20.59	26.30	3.94	49.17
800	135	1	16.47	43.04	0.79	39.70
800	135	2	16.78	29.95	0.32	52.95
800	135	4	20.75	44.17	1.62	33.46
800	405	1	17.24	27.27	2.52	52.97
800	405	2	16.79	29.41	2.05	51.75
800	405	4	15.85	29.12	3.35	51.68

## METHODS AND MATERIALS

In this study, pyrolysis runs have been carried out with a bench scale reactor (Fig. 1). The reactor body is made of temperature-resistant glass tubing connected to a nitrogen gas source and a series of traps. The heat source for the reaction is a split-tube furnace. The first trap is immersed in liquid nitrogen, and the second trap is a water scrubber, held at room temperature, through which the uncondensed effluent stream is bubbled. The nitrogen gas provides a positive pressure towards the traps, and the flow rate of the gas is varied to alter the residence time of the evolved volatiles. The rate of heating was not controlled; rather the furnace was preheated to the target temperature and raised into position around the reaction tube for the prescribed length of time. The rate of temperature increase has been controlled in previous studies (Barnes et al. 1979; Blankenhorn et al. 1978), but introduces variation in total time of heating between runs. Samples that were exposed to higher target temperatures were subjected to longer reaction times than those which employ lower target temperatures. Control of reaction time by preheating to the target temperature eliminates this source of variation.

TABLE 2. Summary of results for Duncan's multiple range test for each phase and parameter. (Values with the same letter do not differ significantly at the 5% level.)

		Temperature C (mean % yield)		Flow rate ml/minute (mean % yield)		Time hours (mean % yield)
Char	A	250 (46.857)	A	135 (27.845)	A	1 (28.715)
	B	350 (28.007)	A	405 (27.097)	A	2 (27.458)
	C	400 (23.952)				
	C	500 (21.227)				
	D	800 (17.313)			A	4 (26.240)
Tar	A	800 (33.827)	A	135 (31.345)	A	1 (28.557)
	A	500 (32.033)			A	2 (27.458)
	B A	400 (29.602)	B	405 (24.237)	A	4 (27.350)
	B	350 (26.363)				
	B	250 (17.130)				
Scrubber	A	350 (2.482)	A	405 (3.207)	A	4 (2.309)
	B A	400 (2.163)			A	2 (1.722)
	B A	800 (1.775)	B	135 (0.617)	A	1 (1.705)
	B A	500 (1.710)				
	B	250 (1.430)				
Nonrecovered	A	800 (47.085)	A	405 (45.460)	A	4 (43.993)
	A	500 (45.030)			A	2 (43.462)
	A	400 (44.283)	B	135 (40.192)	A	1 (41.023)
	A	350 (43.148)				
	B	250 (34.583)				

Oven-dry southern pine specimens ( $0.5 \times 0.5 \times 6.0$  cm) were used for each run. The pyrolytic conditions employed were temperatures of 250, 350, 400, 500 and 800 C; times of 1, 2, and 4 hours; and nitrogen gas flow rate of 135 and 405 milliliters per minute. All combinations of time, temperature, and flow rate were used, resulting in 30 different combinations of conditions and samples. The samples were placed in porcelain combustion boats, which were then centered in the reactor such that the samples were in the middle of the heated zone of the furnace. The reactor was flushed with nitrogen gas, the flow rate was adjusted, and the preheated furnace was raised into position around the reactor for the specified length of time. Upon completion of a run, the furnace was removed and the reactor was allowed to cool with maintenance of gas flow. The char was removed and weighed, and the tar was rinsed out of the first trap and reaction tube with acetone. The tar is very viscous and virtually completely acetone-soluble, which facilitates its collection. This solution was evaporated under reduced pressure to remove the acetone, and the resultant oil was weighed. The amount of material collected in the water scrubber was determined by evaporation of the water and subsequent weighing. The weight of nonrecovered materials was determined by subtracting the weights of all recovered components from the original weight of an oven-dry sample.

The results from each phase were statistically examined by analysis of variance, Duncan's multiple range test, and regression techniques.

#### RESULTS AND DISCUSSION

The percentage yields of char, liquid, material collected in the scrubber and nonrecovered substances on an oven-dry basis are reported in Table 1.

Analysis of variance procedures indicated that significant differences in char yields are present and the results of Duncan's multiple range test are reported in Table 2. The only condition that differed significantly with respect to char yield was temperature. As the temperature increased, the char yield decreased with each increment. The time and flow rate variations showed no impact on char yield percentage.

Levels of tar were also found to differ significantly with variation in conditions (Table 2). Significant differences in tar yields were detected between temperature and flow rate. Tar yields increased with increasing temperature to the 400–500 C range, at which point they leveled off. Contrary to conventional thinking, the tar yields were significantly higher at the lower flow rates. Variation in time had no effect on tar yield.

Results of Duncan's multiple range test for the material collected in the scrubber are reported in Table 2, and are somewhat mixed. In contrast to the data for the char and tar, which showed definite trends with temperature, there seemed to be little pattern in the scrubber data with respect to temperature. Interestingly, the impact of variation in flow rate was just the opposite of the relationship found for the tar percentages; the higher flow rates resulted in more material collected in the scrubber. As in the other analyses, time was not a significant factor. The amounts of nonrecovered products (Table 2) showed a general increase with temperature, but the only significant difference was detected between 250 C and all other temperatures. The higher flow rate resulted in a higher percentage of nonrecovered products, while time, again, had no effect.

Regression analyses were performed on the percent yield data of char, liquid (or tar), material trapped in the scrubber and nonrecovered substances. After sorting by flow rate, the yield of each product was used in regressions that used temperature as the independent variable in simple linear, quadratic and logarithmic models (Figs. 2–9). Since analysis of variance results indicated that reaction time did not significantly influence yields, that variable was not included in the regressions.

Linear equations for char and tar percentages at 135 milliliters per minute were statistically significant with R-squared values of 0.55 and 0.62, respectively. The material collected in the water trap and the nonrecovered amounts based on runs at 135 milliliters per minute did not give significant linear relationships and had low R-squared values. Significant linear relationships were detected for yields of char, tar, and nonrecovered material at the 405 milliliter flow rate. This is reflected in R-squared values of up to 0.72 for the nonrecovered portion.

Sorting the data by flow rate, and by the use of quadratic and logarithmic transformation of the temperature, had a noticeable effect on the fits of both char and tar data. As may be seen in the figures, the quadratic model gives somewhat higher R-squared values than the logarithmic model. The results from these analyses are interesting and somewhat surprising. It is of importance that the time factor does not result in significant differences in yields of products. The yields of the three major products are, therefore, apparently complete after a relatively short time, and an increase in reaction time did not improve their production. This is not to say, however, that the composition and properties of a given phase may not be time-dependent.

It is surprising that the lower flow rate of purge gas resulted in higher yields of the liquid phase. This is the direct opposite of the anticipated results. It has been

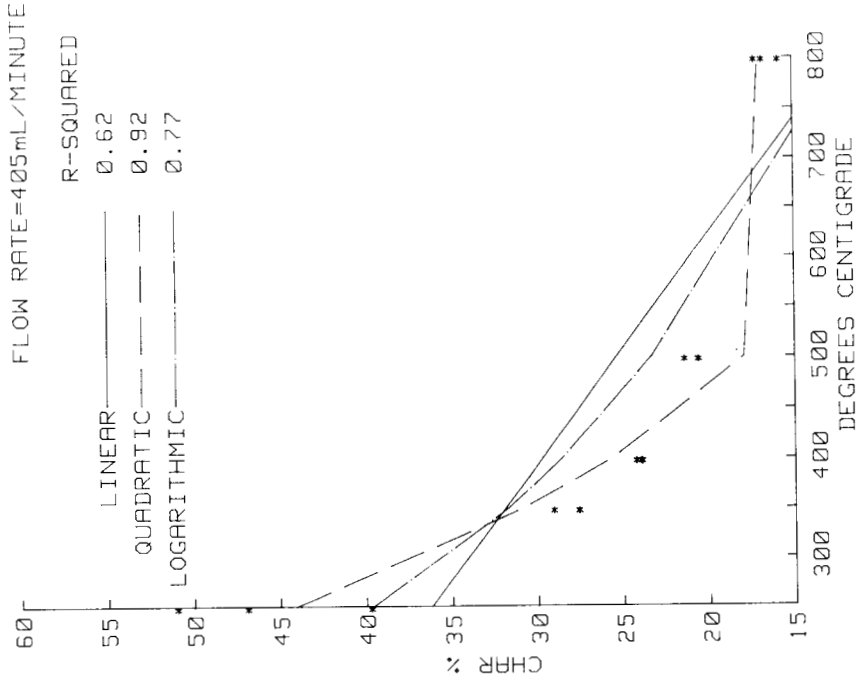


FIG. 3. Char yield percentage vs. temperature at a nitrogen flow rate of 405 ml/minute (\* = data points).

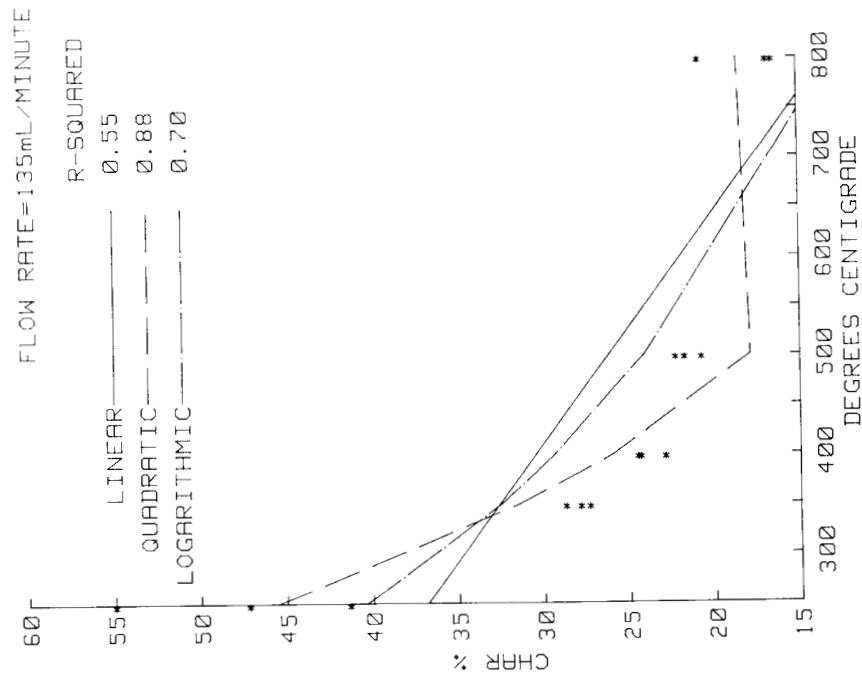


FIG. 2. Char yield percentage vs. time, at nitrogen flow rate of 135 ml/minute (\* = data points).

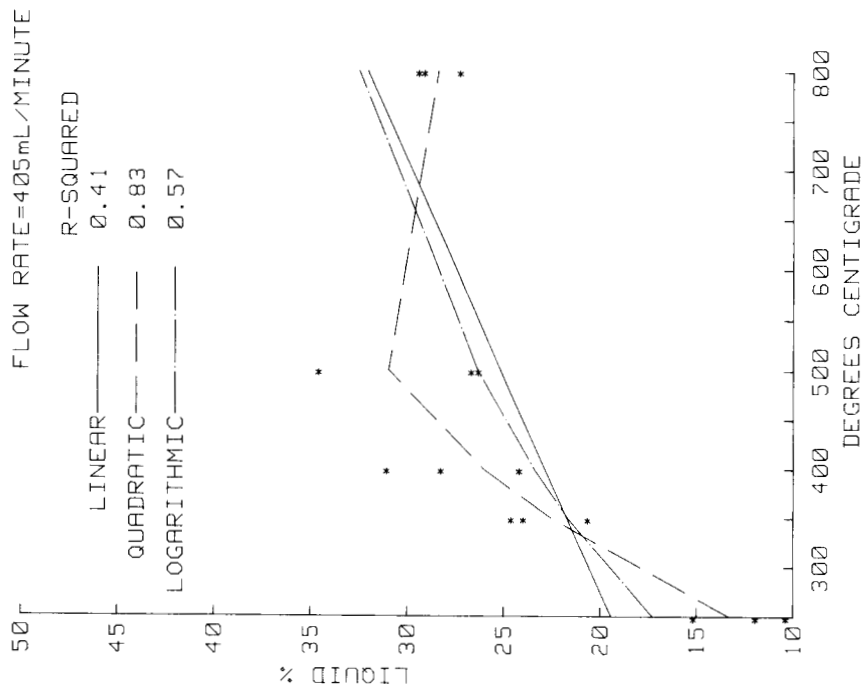


Fig. 5. Liquid yield percentage vs. temperature at a nitrogen flow rate of 405 ml/minute (\* = data points).

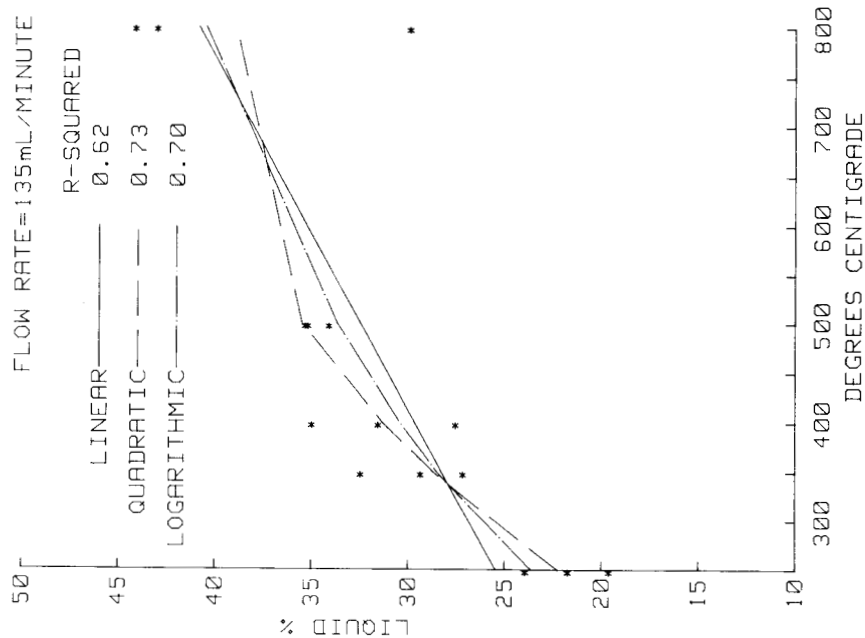


Fig. 4. Liquid yield percentage vs. temperature at nitrogen flow rate of 135 ml/minute (\* = data points).

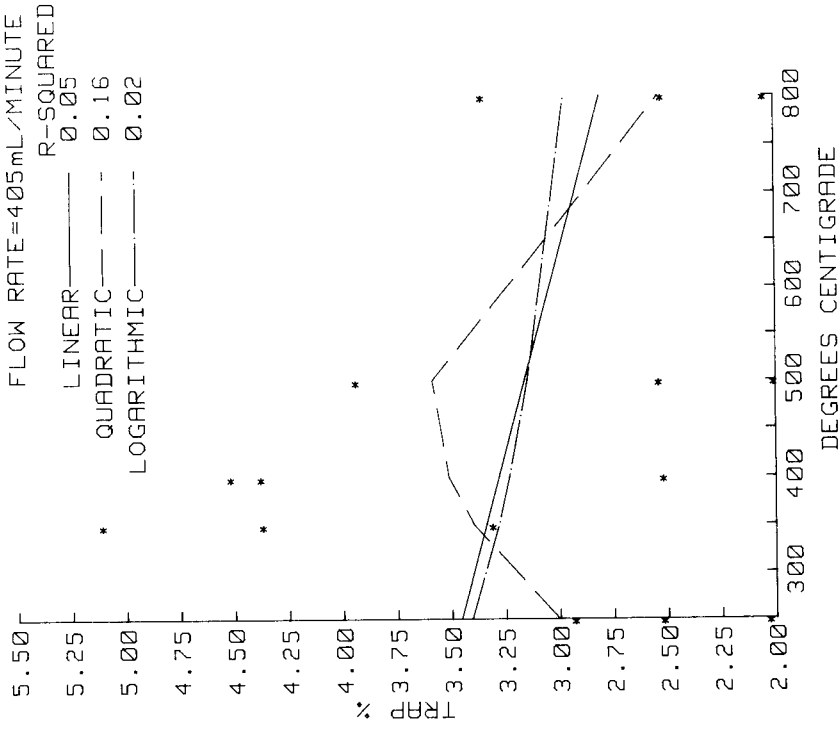


Fig. 7. Percentage of material trapped in water scrubber vs. temperature at a nitrogen flow rate of 405 ml/minute (\* = data points).

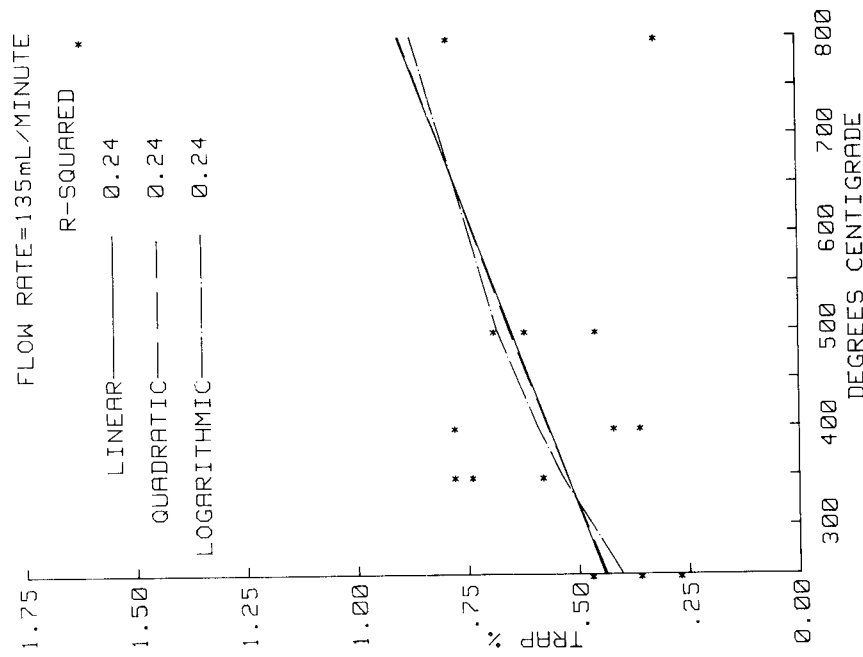


Fig. 6. Percentage of material trapped in water scrubber vs. temperature at nitrogen flow rate of 135 ml/minute (\* = data points).



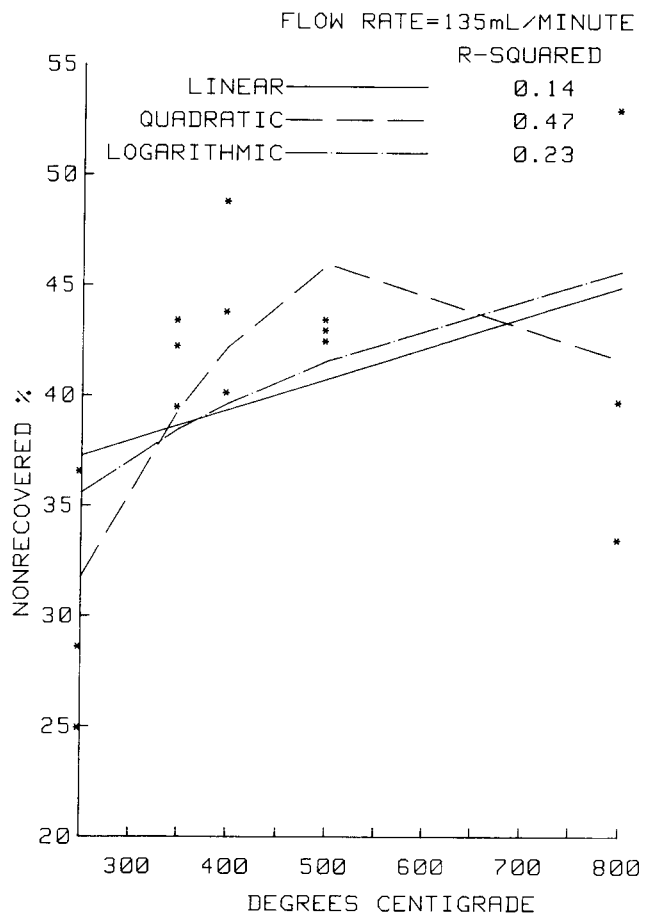


FIG. 8. Percentage of nonrecovered material vs. temperature at a nitrogen flow rate of 135 ml/minute (\* = data points).

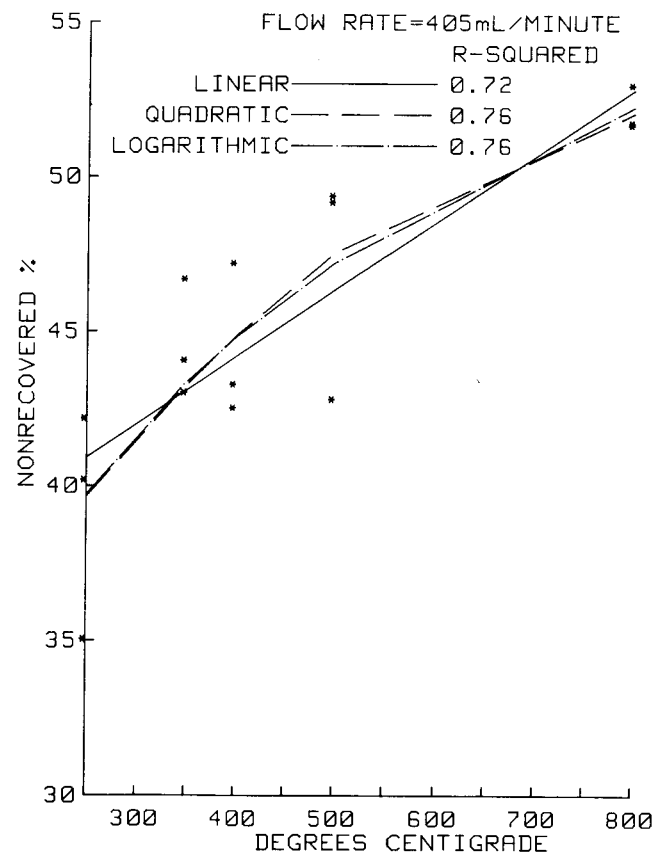


FIG. 9. Percentage of nonrecovered material vs. temperature at a nitrogen flow rate of 405 ml/minute (\* = data points).

thought that the condensible volatiles that form the liquid phase should be maximized by rapid removal from the reaction zone, thus decreasing the possibility of secondary reactions that may involve cracking to form lower molecular weight compounds or repolymerization to form char. Two possible explanations for this reversal in trends have been considered. The first is that the higher flow rate is removing substances before they have adequate time to form condensible compounds. The second possibility involves the construction of this particular reactor. The trap that is immersed in liquid nitrogen is a 100-milliliter, two-necked, round bottom flask. At the higher flow rates, perhaps some of the marginally condensible substances are swept out before they can be cooled to their condensation point. This explanation may be reinforced based on the yields from the scrubber, and the levels of nonrecovered components that are significantly increased at the higher flow rate. Modifications to the reactor are being studied in an attempt to increase the residence time of the effluent in the cold trap while maintaining the same flow rates in the reactor.

There were no real surprises with regard to temperature on the yield of products. Increasing temperature resulted in reduced char yields, and increased levels of tar and nonrecovered materials. It is interesting to note, however, that the yield of tar does not differ significantly between 400 and 800 C, or with time from one hour to four hours. These data indicate that from a strictly gravimetric standpoint, the original wood may be processed at 400 C for one hour or at 800 C for four hours with no significant change in yield.

These results raise additional questions that need to be explored: Is the reactor design a significant factor in the yields that are reported? What is the impact of process variables on within phase properties? Could the time be further decreased without impacting significantly on the levels of products or their properties? and would different species or the pyrolysis of nonwood components result in different yields and products?

#### REFERENCES

- ALLAN, G. G., AND TAPIO MATTILA. 1971. High energy degradation in K. V. Sarkanen and C. H. Ludwig, eds. *Lignins: Occurrence, structure and reactions*. Wiley Interscience, New York.
- BARNES, D. P., P. R. BLANKENHORN, AND W. K. MURPHEY. 1979. GLC analysis of temperature effects on furfural production during pyrolysis of black cherry. *Wood Sci.* 12(2):122-128.
- BEALL, F. C., AND H. W. EICKNER. 1970. Thermal degradation of wood components: A review of the literature. U.S.D.A. Forest Service. Research Paper FPL 130. Madison, WI.
- BLANKENHORN, P. R., D. P. BARNES, D. E. KLINE, AND W. K. MURPHEY. 1978. Porosity and pore size distribution of black cherry carbonized in an inert atmosphere. *Wood Sci.* 11(1):23-29.
- BROWNE, F. L. 1958. Theories of the combustion of wood and its control. FPL Report 2136. Madison, WI.
- ELDER, T. J., AND E. J. SOLTES. 1979. Pyrolysis of lignocellulosic materials. Phenolic constituents of a wood pyrolytic oil. *Wood Fiber* 12(4):217-226.
- KNIGHT, J. A., M. D. BOWEN, AND K. R. PURDY. 1976. Pyrolysis—a method for conversion of forestry wastes to useful fuels. Presented at conference on energy and wood products industry. Forest Products Research Society. Madison, WI.
- LIN, S.-C. 1978. Volatile constituents in a wood pyrolysis oil. Master's thesis, Texas A&M University, College Station, Texas.
- SOLTES, E. J., AND T. J. ELDER. 1981. Pyrolysis in I. S. Goldstein, ed. *Organic chemicals from biomass*. CRC Press, Boca Raton, Florida.

- , A. T. WILEY, AND S.-C. LIN. 1981. Biomass pyrolysis—towards an understanding of its complexity, versatility and potentials. *Biotechnology and Bioengineering Symposium No. 11*: 125–136.
- VORHER, W., AND W. H. M. SCHWEERS. 1975. Utilization of phenol lignin. *Applied Polymer Symposium No. 28*:277–284.