EFFECT OF TREE SPECIES ON THE DEVOLATILIZATION OF OVEN-DRY WOOD

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ABSTRACT

This study investigates the devolatilization of oven-dry wood chips from the branches and stems of six hardwood and two softwood tree species. Six hardwood species, covering a wide range of wood specific gravity were examined: cottonwood, Kentucky coffeetree, red oak, honey locust, black locust, and Osage-orange. The softwood species were ponderosa pine and eastern red cedar. Devolatilization curves (histories) along with the time for complete devolatilization (terminal time) and the corresponding terminal char yield were obtained from experiments with each tree species in a tubular furnace at 800°C. Graphical relationships were established between the terminal char yield and the ash content, and the terminal char yield and the wood specific gravity.

The results reveal that the terminal time and the terminal char yield are affected by tree species. An increasing trend between terminal char yield and wood specific gravity was roughly approximated.

Keywords: Devolatilization, cottonwood, Kentucky coffeetree, red oak, honey locust, black locust, Osage-orange, ponderosa pine, eastern red cedar.

INTRODUCTION

Previously we have evaluated biomass properties and gasification behavior for several broadleaf tree species grown in the Central Great Plains. Specifically, we have reported on Siberian elm (Geyer et al. 1987), black locust (Geyer and Walawender 1994), silver maple (Geyer and Walawender 1997), catalpa (Geyer and Walawender 1999), and populus clones (Geyer et al. 2000). Biomass properties included biomass yield, calorific value, ash content, specific gravity, and fiber length. Gasification behavior consisted of gas composition, gas heating value, and gas yield along with char yield. In this work we examine the influence of tree species on the first step in the gasification process, devolatilization. Six hardwood species covering a wide range of specific gravity were investigated: cottonwood, Kentucky coffeetree, red oak, honey locust, black locust, and Osage-orange. In addition two soft woods, ponderosa pine and eastern red cedar, were also examined.

One of the most popular forms of wood conversion to energy is air gasification. The first step in air-blown gasification is pyrolysis or devolatilization. When heated, wood undergoes pyrolysis to form solid char and combustible volatiles. The volatiles then mix with oxygen in an air-blown gasifier to produce a combustible mixture, which undergoes partial combustion and releases energy to provide the heat necessary to support the pyrolysis. In the char gasification step, the resultant char is subsequently reduced by reaction with the hot gas components (CO and H_2O) to produce additional gas. Pyrolysis is the dominant step in the overall process since 80–90% of the wood mass is converted to volatiles during this step.

Pyrolysis is not a single reaction but a complex series of competing reactions that take place in parallel and/or in series. Temperature, heating rate, and feedstock properties can influence the course of these reactions. While the effects of temperature and heating rate on the pyrolysis of wood are well understood (Shafizadeh 1982), the effects of the chemical composition (i.e., ash content) and physical properties (i.e., specific gravity) are less understood. Wood is a variable substance in terms of these properties both within and between tree species. Systematic studies to compare the devolatilization behavior of a wide variety of tree species have not been conducted previously.

This study investigates the pyrolysis of oven-dry wood chips from six hardwood and two softwood tree species. Devolatilization curves, the terminal time (the time for complete pyrolysis), and the corresponding char yield were established by experiment. Graphical relationships between the char yield and ash content and char yield and specific gravity were established.

EXPERIMENTAL FACILITIES AND PROCEDURES

Experiments were conducted to establish weight fraction of solid remaining versus time curves for each tree species. Weighed dry wood chips were immersed in a fluidized bed for varying lengths of time, and the residual weights were determined. Also measured for each tree species were the ash content and the wood specific gravity.

Fluidized-bed description

The fluidized bed used in this study is illustrated in Fig. 1. It contained four zones: the disengaging, fluidized-bed, packed-bed, and gas inlet zones. The inlet, packed and fluidized zones were constructed from a schedule 40 pipe of inconel 600 alloy (10.16-cm I.D. by 55-cm length); a second section of pipe (15.24-cm ID, by 20-cm length) formed the disengaging zone. The inlet section was 7.62 cm in height and allowed the fluidizing gas to uniformly enter the packed- and fluidized-bed zones. The inlet and packed-bed zones and the packed- and fluidized-bed zones were each separated by 60-mesh 316 stainless steel screens. The packed-bed zone was filled with 5-mm aluminum oxide balls. The fluidized-bed material was a mixture of 80%–20% sand-limestone with a 500-μm average diameter. The limestone was added to prevent agglomeration, which typically occurs in a bed composed only of silica sand (Walawender et al. 1981). The reactor was externally heated by two pairs of semi-cylindrical electric resistance heaters with each pair capable of delivering up to 1250 watts of power for a maximum sustained operating temperature of 1200°C. More details on the fluidized bed are given in Boateng et al. 1991.

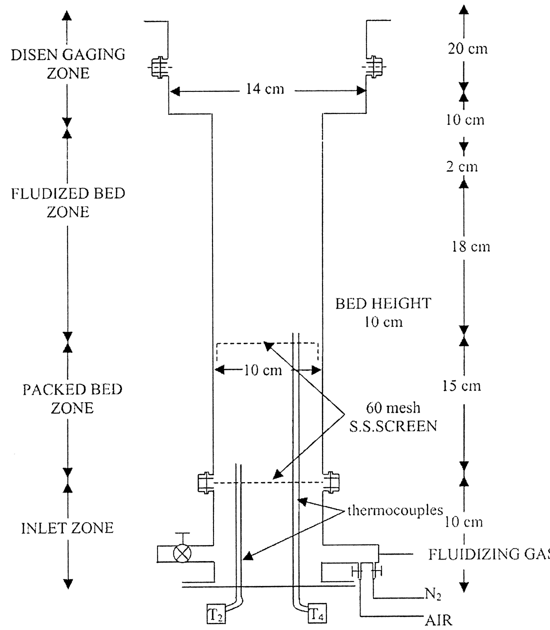


FIG. 1. Fluidized-bed reactor.

TABLE 1. *Characteristics of the wood sources.*

Species	Common name	Tree age (years)	Chip source	Diameter (cm)
BL	Black locust	7–10	Branches	5–8
CW	Cottonwood	7–10	Stems	8–10
HL	Honey locust	7–10	Stems	5–8
KC	Kentucky coffeetree	7–10	Stems	5–8
OO	Osage-orange	20	Branches	2–5
PP	Ponderosa pine	25	Branches	8–10
RC	Eastern red ceder	2–3	Stems	2–5
RO	Red oak	25+	Branches	8–10

Tree species

The tree species investigated were six hardwoods: cottonwood (*Populus deltoides* Bartr.), Kentucky coffeetree (*Gymnocladus dioicus* (L.) K. Koch), red oak (*Quercus rubra* L.), honey locust (*Gleditsia triacanthos* L.), black locust (*Robinia pseudoacacia* L.), and Osage-orange (*Maclura pomifera* (Raf.) Schneid.); and two softwoods: ponderosa pine (*Pinus ponderosa* Laws.) and eastern red cedar (*Juniperus virginiana* L.). The abbreviations used to designate these tree species are listed in Table 1.

Wood chip preparation

All of the wood chips used in the experiments came from freshly cut stems or branches. The ages and the diameters of the sources are listed in Table 1. The wood was cut one day before performing the set of experimental runs on each tree species. The stems or branches were chipped within 1 to 3 h after cutting. The chip sizes were fairly uniform and set by the chipper. The average thickness was 1.5 to 2 mm. Approximately 100 bark-free chips of the nearly same size were hand-selected for each species. This was done to insure a fairly consistent initial size since the extent of devolatilization depends on particle size (Chern et al. 1991). Hand selection was also used to insure that the chips were not fragmented due to the stresses caused by the chipper. The chips were then oven-dried at 105°C for a minimum of 24 h and stored in a desiccator.

Procedures

The reactor heaters were turned on about 3 to 4 h before starting an experiment. Air served as the fluidizing agent during the heat-up period. Just before beginning an experiment, the fluidizing-air flow was replaced by nitrogen. The reactor temperature and fluidization velocity were maintained at 800°C and 9.5 m/s, respectively, for all of the experiments.

A wood chip was randomly selected from the desiccator, weighed to the nearest one-tenth of a milligram, and placed into a cylinder made from 60-mesh stainless steel gauze. The devolatilization studies were conducted by placing the cylinder into the bubbling, fluidized bed. Each chip was immersed for different lengths of time ranging from 2 to 50 s. After a prespecified period of time, the cylinder was quickly withdrawn, placed in a jar, and quenched by a cool stream of nitrogen. The cool char was then carefully removed from the cylinder and weighed. The resulting data were used to generate a weight fraction remaining-time curve for each tree species well into the region where the terminal char yield (complete pyrolysis) was clearly established. Three replications were conducted for each devolatilization time.

Chemical and physical analyses

The properties determined for each tree species consisted of the ash content and the wood specific gravity (dry basis). The ash content was determined by following the procedure described in ASTM STANDARD D 1102-56 (1981). The specific gravity was determined from the weight and dry volume of a smooth, dry wood cylinder machined from unchipped branches/stems.

METHODS OF DATA ANALYSIS

The devolatilization curve for each tree species was obtained by plotting the weight fraction remaining versus time in order to determine the mean terminal time (mean time for complete pyrolysis). The weight fraction remaining was calculated from the ratio of the

TABLE 2. *Statistical comparison of mean terminal times for oven-dry hardwoods and softwoods.*

Species	Mean terminal time (s)	$(n)^{+}$	S.D.*
CW	14.0^{a}	(3)	0.000
PP	14.0^{a}	(3)	2.00
RC	14.0^{a}	(3)	2.00
KC	15.0^{a}	(3)	1.15
RO	16.0^{ab}	(3)	0.000
HL	18.0^{bc}	(3)	0.000
OO	20.0^{cd}	(3)	2.00
BL	21.0^{d}	(3)	2.31

$^{+}$ Number of determinations.
* Standard deviation.
^{abcd} Means with the same superscript are similar at $P < 0.05$.

TABLE 3. *Statistical comparison of mean terminal char yields for oven-dry hardwoods and softwoods.*

Species	Mean terminal char yields (%)	$(n)^{+}$	S.D.*
OO	14.08^{a}	(36)	0.65
KC	13.23^{ab}	(55)	0.30
HL	12.53^{bc}	(36)	0.34
BL	12.07^{cd}	(43)	0.46
RO	11.69^{cde}	(37)	0.34
PP	11.38^{de}	(48)	0.57
RC	11.04^{ef}	(42)	0.57
CW	10.17^{f}	(58)	0.37

$^{+}$ Number of determinations.
* Standard deviation.
^{abcdef} Means with the same superscript are similar at $P < 0.05$.

weight of the resultant char and the initial weight of the dry wood chip. For times in excess of the terminal time, the weight fraction remaining was constant. This constant weight fraction was termed the terminal char yield.

In order to properly compare the terminal char yields of the different tree species, the weight fraction remaining was adjusted for the ash content. The relation for the adjusted weight fraction remaining relation is given below.

$$WFR = \frac{W_{char}}{W_{chip}(1 - AC)} - \frac{AC}{(1 - AC)} \quad (1)$$

where

- WFR = adjusted weight fraction remaining
- W_{char} = weight of the char at time t
- W_{chip} = initial weight of the dry wood chip
- AC = fractional ash content of dry wood

Equation (1) is equivalent to the weight of ash-free char divided by the weight of ash-free wood. The adjusted weight fraction remaining-time data were fitted by nonlinear regression to the following empirical equation:

$$WFR = \frac{2(1 - C)}{1 + \exp[b(t^{N})]} + C \quad (2)$$

where

- t = time (s)
- C = terminal fractional char yield (ash free)

and

- b, N = constants determined by regression

Equation (2) is strictly empirical; it has no physical significance. It simply provides a good representation of the devolatilization curves.

In order to graphically compare the progress of pyrolysis of the different tree species on a common basis, the adjusted devolatilization histories were plotted in terms of a dimensionless time. The dimensionless time was defined as the ratio of the actual time to the terminal time (time for completion of pyrolysis).

STATISTICAL ANALYSIS

In order to compare the mean terminal times and char yields, statistical methods were employed. All of the statistical analyses were conducted with the SAS (Statistical Analysis System) software package. The data were analyzed as a completely randomized design. The LSD (Least Significant Difference) procedure (see, Peterson 1985) was used to test for significant differences between all tree species combinations.

RESULTS

Tables 2 and 3, respectively, show the statistical comparison of the mean values of the terminal times and char yields for each tree

TABLE 4. *Parameters fit by nonlinear regression for Eq. (2).*

Species	N	b
BL	2.5	3.35 × 10-3
CW	2.5	9.88 × 10-3
HL	2.7	3.30 × 10-3
KC	2.5	7.23 × 10-3
RC	2.0	2.37 × 10-3
RO	2.4	7.06 × 10-3
OO	3.0	8.68 × 10-4
PP	2.6	3.78 × 10-2

species. All comparisons were made at a significance level of 0.05 (i.e., 95% confidence). The standard deviations are also given in the tables. Table 4 lists the parameters, b and N, for Eq. (2).

Tables 5 and 6 summarize the ash contents and specific gravities for each tree species, respectively. Means and standard deviations are included in the tables.

Figure 2 displays a typical fit of Eq. (2) to the adjusted weight fraction remaining-dimensional time data. The progress of pyrolysis, as a function of dimensionless time, is compared in Fig. 3 for the six hardwood and two softwood tree species. Figure 4 shows the graphical relationship between the mean terminal time and wood specific gravity for all eight tree species. Figures 5 and 6 illustrate the relationships between the mean terminal char yield and the ash content, and the mean terminal char yield and wood specific gravity, respectively.

TABLE 5. *Wood ash content.*

Species	Ash (%) Mean	(n)⁺	S.D.*
BL	0.75	(3)	0.001
CW	0.75	(3)	0.037
HL	0.86	(3)	0.012
KC	1.2	(3)	0.057
RC	0.98	(3)	0.017
RO	0.78	(3)	0.038
OO	1.3	(3)	0.017
PP	0.42	(3)	0.017

⁺ Number of determinations.
* Standard deviation.

TABLE 6. *Wood specific gravity.*

Species	Specific gravity Mean	(n)⁺	S.D.#
BL	0.79	(3)	0.0014
CW	0.40	(3)	0.0071
HL	0.75	(2)	0.0063
KC	0.71	(3)	0.029
PP	0.44	(3)	0.025
RC	0.53	(3)	0.015
RO	0.73	(2)	0.0028
OO	0.80	(1)	—

⁺ Number of determinations.
Standard deviation.

DISCUSSION

Inspection of Table 2 reveals that pyrolysis was complete for all eight species at terminal times ranging from 14 to 21 s. Figure 3 suggests an approximate correlation of the devolatilization data when it is plotted in dimensionless time; with the possible exception of ponderosa pine, the individual curves are relatively close to each other. Figure 4 suggests that the mean terminal time for all eight tree species increases with respect to increasing specific gravity.

The terminal char yield appears to be related to the wood's chemical and physical prop-

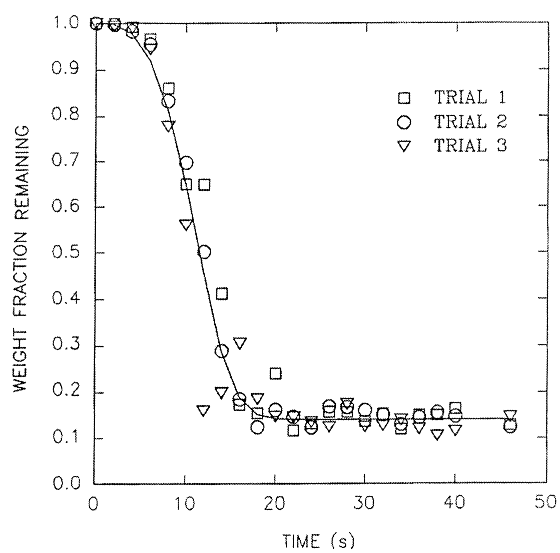
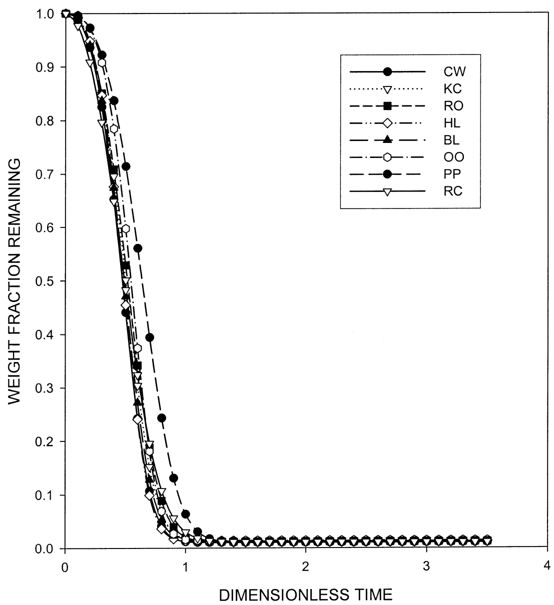


FIG. 2. Fit of Eq. (2) to adjusted oven-dry data for Osage-orange.



FIF. 3. Comparison of devolatillization histories for all species.

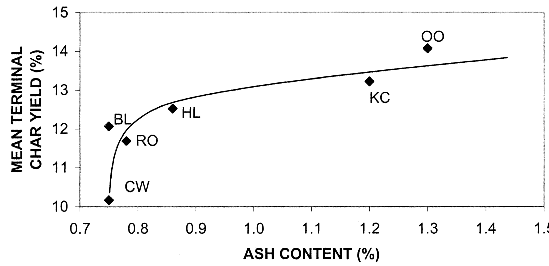


FIG. 5. Relationship between mean terminal char yield and ash content for the hardwoods.

erties. The mean values for the adjusted terminal char yield ranged between 10.17% for cottonwood and 14.08% for Osage-orange. It is evident from Table 3 that statistically significant differences in the mean terminal char yield exist between most of the tree species. Thus, the possible influences of the chemical and physical properties on the terminal char yield were examined.

Grey et al. (1985) and Scott et al. (1985) both have attributed increasing char yield to increasing ash content. Figure 5 is in general agreement with the reported behavior for the hard wood species. The soft woods deviate significantly from the curve shown in Fig. 5 and are not included in the figure. Although the char yields are comparable—11.04 for cedar and 11.38 for pine—the ash contents differ by about a factor of 2 (0.98% for cedar and 0.42% for pine). This may be a consequence of age (2–3 years for cedar and 25 years for pine).

Since the specific gravity is a measure of how much wood substance is present in a unit volume, it is intuitive that it is directly related to the pore volume of the wood. Generally, woods with lower specific gravity contain more pores which, unless blocked, should allow volatiles to escape more readily than in higher specific gravity wood. Therefore, it is expected that the terminal char yield should increase with increasing specific gravity. However, Fig. 6 shows that the expected behavior

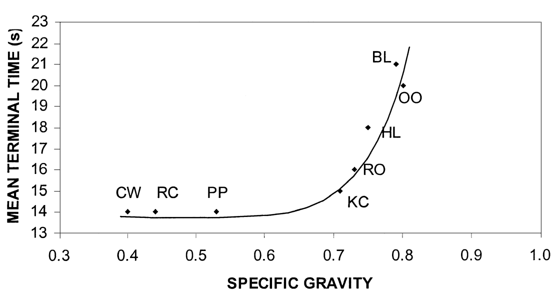


FIG. 4. Relationship between mean terminal time and specific gravity for all species.

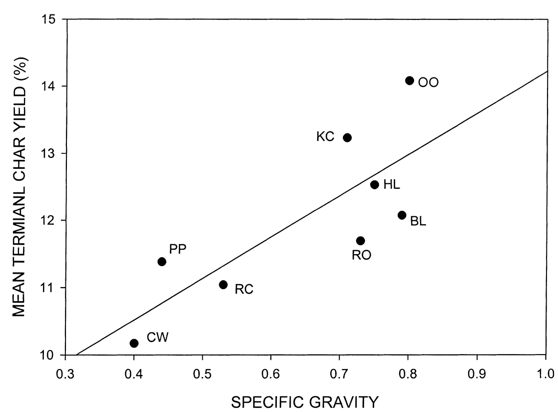


FIG. 6. Relationship between mean terminal char yield and ash content for all species.

is only roughly approximated. Although char yield tends to increase, it is not a simple direct proportion to specific gravity. This may be an indication that some yet to be identified factors may be important in determining char yield.

CONCLUSIONS

This paper has presented a study of the influence of six hardwood and two softwood tree species on wood devolatilization. The results indicate that the terminal time and char yield are affected by tree species. An increasing trend between the mean terminal char yield and specific gravity was only roughly approximated. These observations suggest that other factors may be involved in determining char yield.

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REFERENCES

AMERICAN SOCIETY FOR TESTING MATERIALS (ASTM). 1981. Standard test method for ash in wood, ASTM D 1102-56, Philadelphia, PA.

BOATENG, A. A., L. T. FAN, W. P. WALAWENDER, AND C. S. CHEE. 1991. Morphological development of rice-hull-derived charcoal in a fluidized-bed reactor. Fuel 70: 995–1000.

CHERN, S. M., W. P. WALAWENDER, AND L. T. FAN. 1991. A kinetic model of single particle biomass pyrolysis in a downdraft gasifier. Pages 701–726 *in* D. L. Klass, ed. Energy from Biomass and Wastes XIV. Institute of Gas Technology. Chicago, IL.

GEYER, W. A., AND W. P. WALAWENDER. 1994. Biomass properties and gasification behavior of young black locust. Wood Fiber Sci. 26(3):354–359.

———, AND ———. 1997. Biomass properties and gasification behavior of young silver maple trees. Wood Fiber Sci. 29(1):85–90.

———, AND ———. 1999. Biomass and gasification properties of young catalpa trees. Wood Fiber Sci. 31(1):95–100.

———, R. M. ARGENT, AND W. P. WALAWENDER. 1987. Biomass properties and gasification behavior of 7-year-old Siberian elm. Wood Fiber Sci. 19(2):176–182.

———, JON DEWYKE, AND W. P. WALAWENDER. 2000. Biomass and gasification properties of young populus clones. Wood Fiber Sci. 32(3):375–384.

GREY, M. R., W. H. CORCORAN, AND G. R. GAVALAS. 1985. Pyrolysis of a wood-derived material. Effects of moisture and ash content. Ind. Eng. Chem. Process Des. Dev. 646–651.

PETERSON, R. G. 1985. Design and analysis of experiments. Marcel Dekker, Inc., New York, NY. Pp. 73–77.

SCOTT, D. S., J. PISKORZ, AND D. RADLEIN. 1985. Liquid products from the continuous flash pyrolysis of Biomass. Ind. Eng. Chem. Process Des. Dev. 24:581–588.

SHAFIZEDEH, F. 1982. Pyrolytic reactions and products of biomass. Fundamentals of Thermochemical Biomass Conversion. Elsevier, New York, NY. Pp. 183–217.

WALAWENDER, W. P., S. GANESAN, AND L. T. FAN. 1981. Steam gasification of manure in a fluid bed influence of limestone as a bed additive. Energy from Biomass and Wastes V. Institute of Gas Technology. Pp. 517–527.