STP 1642, 2023 / available online at www.astm.org / doi: 10.1520/STP164220210098

Laura E. Hasburgh[1] and Charles R. Boardman[1]

Measuring the Specific Heat Capacity of Wood during Pyrolysis

Citation

L. E. Hasburgh and C. R. Boardman, "Measuring the Specific Heat Capacity of Wood during Pyrolysis," in *Obtaining Data for Fire Growth Models*, ed. M. C. Bruns and M. L. Janssens (West Conshohocken, PA: ASTM International, 2023), 88–96. http://doi.org/10.1520/STP164220210098[2]

ABSTRACT

Specific heat capacity of red oak and Douglas fir was measured from 0°C to 438°C using differential scanning calorimetry to provide input parameters for fire modeling. Techniques that allow for measurement of the standard heat capacity, excluding the effects of heat of reaction, were explored. Results show the specific heat capacity of wood becomes nearly constant with increasing temperature once pyrolysis starts. Furthermore, for both species of woods, the heat capacity values level out at a higher temperature than leaves, with correspondingly higher final specific heat capacity values.

Keywords

wood, heat capacity, pyrolysis, fire modeling, thermal analysis, differential scanning calorimetry

Introduction

Fire growth models are used to understand and manage both compartment fires and wildland fires. These models rely on various input parameters and changes in

Manuscript received November 2, 2021; accepted for publication March 8, 2022.

[1]Building and Fire Sciences, U.S. Forest Products Laboratory, 1 Gifford Pinchot Dr., Madison, WI 53726, USA

L. E. H. http://orcid.org/0000-0001-6637-2665, C. R. B. http://orcid.org/0000-0002-9571-5601

[2]ASTM 42nd Symposium on *Obtaining Data for Fire Growth Models* held virtually on December 14–15, 2021.

material properties when exposed to high temperatures. One of the fundamental inputs for fire growth models is the specific heat capacity (C_p). Measurement of C_p for biomaterials undergoing thermal degradation, known as pyrolysis, is challenging because multiple physical and chemical processes occur simultaneously.[1] Therefore, better measurements are necessary to improve the results obtained from fire models.

A 2006 comparison by Rein et al. evaluated the ability of three main modeling approaches (analytical, zone, and field) to model accidental compartment fires.[2] They found that geometry dominates in the early stages of a fire and the models agreed on the fire growth. In the later stages of fire, however, there was greater disagreement between the model predictions. This disagreement was partially due to the material properties dominating at later stages and not being considered or accurately represented in the models. Lautenberger provided a thorough review of the capabilities and limitations of pyrolysis models for various materials.[3] He noted the difficulty in obtaining the model input parameters (material properties) and, to circumvent the issue, he developed a generic algorithm-based optimization technique to estimate input parameters from existing laboratory experiments, such as the cone calorimeter. Thermogravimetric analysis (TGA) provides detailed information about a material's decomposition kinetics but cannot obtain other material properties. Alternatively, properties such as the thermal inertia ($k\rho c$), may be estimated from traditional flammability tests, but no procedures exist to obtain individual material properties from fire test data (i.e., thermal inertia and other derived parameters are not explicit material properties and depend on the technique used and environmental conditions).[4–5]

The pyrolysis of wood is often broken down into three main stages: dehydration and slow pyrolysis at temperatures below 200°C, onset of steady pyrolysis up to 300°C, and rapid pyrolysis above 300°C.[6–7] An isotherm of 300°C has become commonly accepted as when wood converts to char.[8] The C_p of wood is inversely related to the charring rate,[9] but the values and behavior of C_p above 200°C are limited. Below 200°C, the C_p of wood exhibits a steady rise with temperature,[10–13] but exploration above 300°C is needed to provide inputs for models. Annex B of EN 1995-1-2 Eurocode 5 does provide C_p up to 1,200°C, but these values were estimated from standard fire exposure and include the heat of vaporization.[13] Recently, C_p for foliar materials was measured up to 434°C using differential scanning calorimetry (DSC) with a sinusoidal patterned energy input added to the standard linear temperature ramp.[15] Calculations using only the sinusoidal energy input and corresponding material temperature response yield a more accurate estimate of C_p during pyrolysis. For all leaves studied, C_p was found to be nearly constant with increasing temperature once pyrolysis started.

We applied the same DSC technique to two species of wood, Douglas fir (*Pseudotsuga menziesii*) and red oak (*Quercus rubra*) to obtain the specific heat of wood for temperatures up to 438°C.

Materials and Methods

MATERIALS

Red oak (RO) and Douglas fir (DF) were obtained and cut down to approximately 5-mm diameter disks with a thickness of 1.25 mm. The final specimens contained both early and latewood but were not further characterized. Three replicates for each wood species were performed. The specimens, between 5 and 15 mg, were placed in aluminum pans with an unsealed lid for specific heat capacity measurement and in open platinum crucibles for mass loss measurement. The initial specimens were exposed to ambient air before measurements, resulting in a range of initial moisture contents between 3% and 12%. Each measurement method included a drying period to reduce the moisture content to zero, and all measurement results are given on a dry basis.

INSTRUMENTATION

To obtain the C_p of DF and RO, the specimens were exposed to a patterned heating sequence up to 438°C using a DSC (TA Instruments Q2000) with 50 mL/min of nitrogen (N_2) purge gas. After an initial drying period, during which time the specimens were fully dried, the DSC was programmed to start a 3.5°C/min temperature ramp at 0°C, which allowed for exploration of C_p measurement up to 438°C. Above this temperature, there is increased risk of damage to the instrument in our configuration. Two separate measurements were made simultaneously: one that uses the total heat flow to calculate C_{total} and another that uses the sinusoidal heat flow to calculate C_p. The total heat flow used to calculate C_{total}, includes all the energy input required to raise the temperature of the specimen. It includes the heat of evaporation, heat of reaction, and energy lost to the environment from the instrument. The temperature ramp of 3.5°C/min allowed for exploration of the full temperature range and calculation of C_{total}, which is based on the full heat flow needed to maintain the temperature ramp. The actual C_p measurement was calculated from the sinusoidal addition to this ramp with an amplitude 0.93°C and period of 100 s. This slow ramp and slow oscillation allow the temperature of the specimen time to follow the applied temperature and were recommended by the instrument manufacturer. The heating rate of 3.5°C/min was chosen to match that needed for accurate C_p measurement. Slower heating rates (between 1°C/min and 5°C/min) are recommended when using the sinusoidal pattern to allow for sufficient modulations during a thermal event and to detect overlapping reactions. Faster heating rates would generate a thermal lag in the material response. This method has a measurement accuracy of approximately 4% when the mass is well known. Further details on this method and associated calibration details can be found in Boardman, Dietenberger, and Weise.[15]

The mass loss that occurred during pyrolysis was measured using a separate TGA (PerkinElmer Pyris 1), which also used N_2 as the purge gas. Two replicates of DF and three replicates of RO were performed. The instrument was calibrated

according to manufacturer specifications for specimen temperature accuracy of 2%. The mass balance has resolution of 0.1 μg and accuracy of 0.02%. The mass fractions at 2°C intervals were applied to adjust the C_p values based on the remaining wood mass as a function of temperature. For comparison, uncorrected C_p values were also computed using the initial dry wood mass. The mass loss data obtained from TGA were required in combination with the DSC results as part of the mass correction process.

To verify the C_p measurement, one specimen of each species was measured on a combination TGA/DSC instrument (Netzsch STA 449 F3). This instrument uses a sinusoidal modulation on a linear temperature ramp and simultaneously measures mass, which improves the mass correction. We specified the same linear ramp rate and sinusoidal period and amplitude as used in the DSC. The instrument manufacturer performed these measurements according to their best practices for accuracy, which we could not verify.

Results and Discussion

OVERVIEW

The sinusoidal C_p calculation method is effective at screening out results specific to the heat of vaporization or heat of reaction. Figure 1*A* shows both the C_{total} and C_p (on a constant mass basis, i.e., using only the initial dry mass and the effect of mass loss not considered) for a DF specimen that was not initially dried. The peak heat flow seen in C_{total} at point A reflects the heat of vaporization in addition to heat capacity, not reflected in C_p, as water evaporates from the specimen. Similarly, the peak in C_{total} at B reflects the heat of reaction screened out by the C_p measurement.

Figure 1*B* plots the mass-corrected C_p values for DF, which includes the best estimate of the mass at each temperature, along with values from the *Wood Handbook* and a comparison with select leaf results.[11,15] The wood C_p continues rising to near 290°C after which pyrolysis starts. In this example, the C_p measurement was affected by the strong heat of reaction, likely from cellulose pyrolysis near 360°C, after which it appears to level out. We speculate that this C_p drop during strong pyrolysis is an artifact of a mismatch between the two time-series measurements needed to calculate C_p—that is, between the heat flow measurement and the mass loss measurement, which were performed on different instruments.

MASS LOSS

Although not the focus of this study, mass loss data are critical to calculation of the specific heat because the mass is changing during pyrolysis. After an initial drying period, during which the moisture content of the specimens was determined, the TGA was programmed to increase temperature at 3.5 K/min, matching the DSC temperature ramp. The mass fraction based on dry mass was then calculated. Figure 2*A* plots that mass fraction versus temperature, and figure 2*B* plots the corresponding mass loss rate.

FIG. 1 (*A*) Heat capacity of DF versus temperature on uncorrected initial dry mass basis and (*B*) mass-corrected C_p compared with the values of C_p for wood from the *Wood Handbook*[11] and leaves from Boardman, Dietenberger, and Weise.[15]

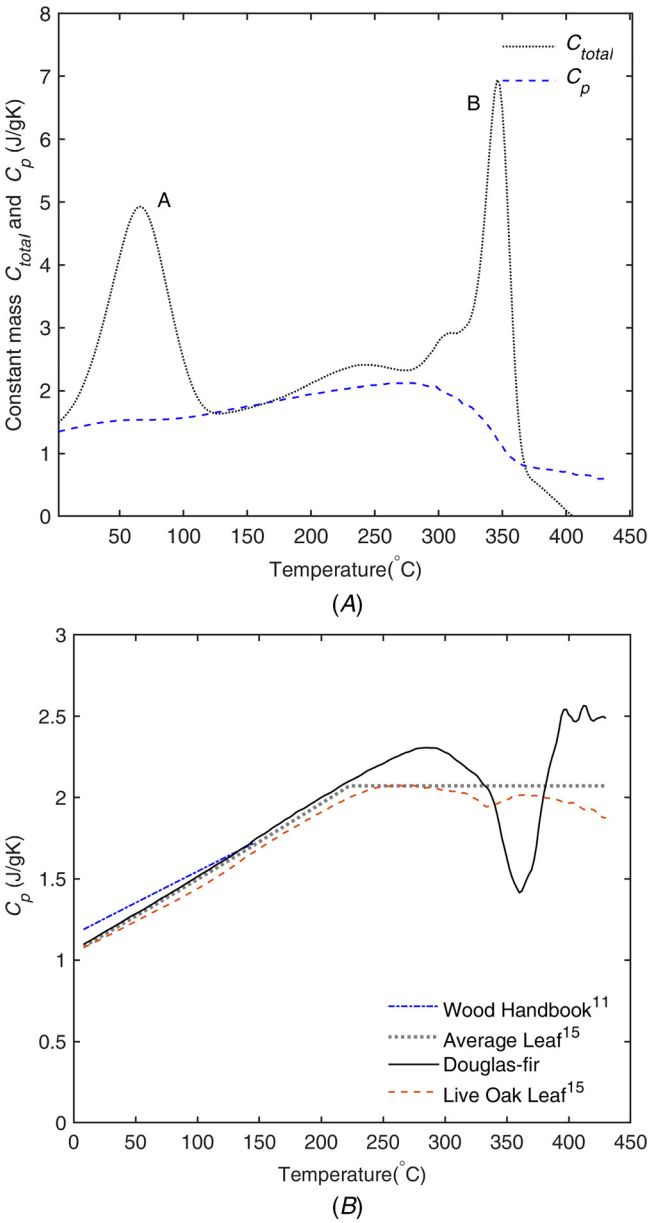
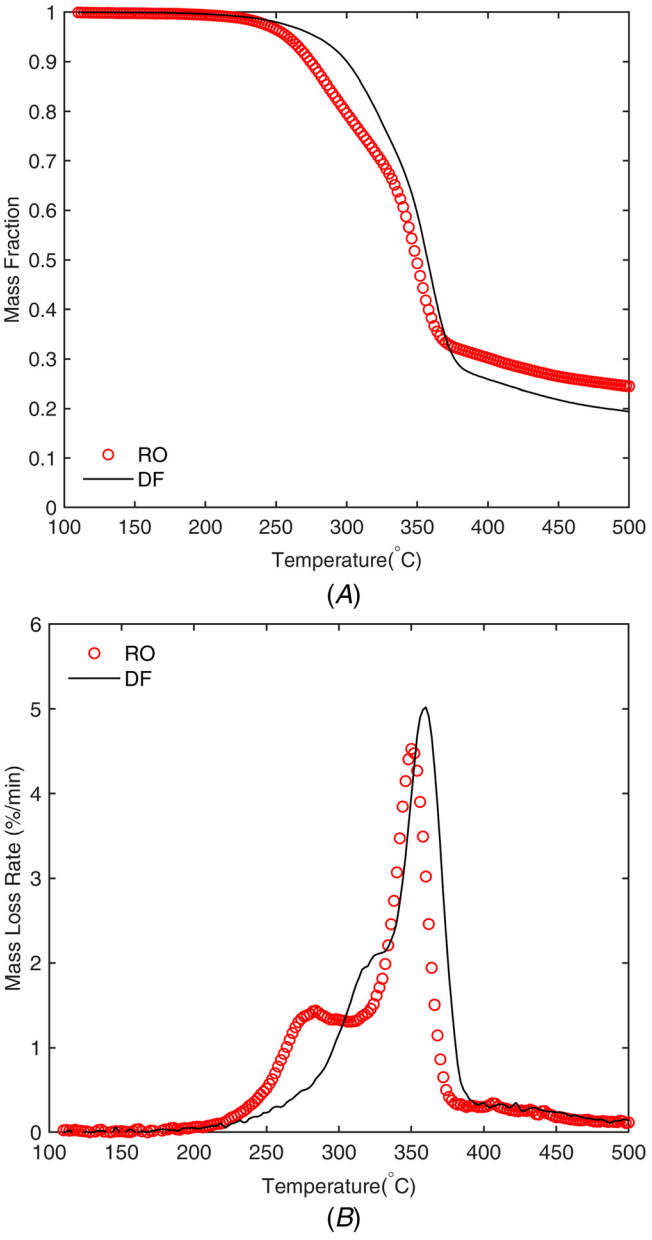


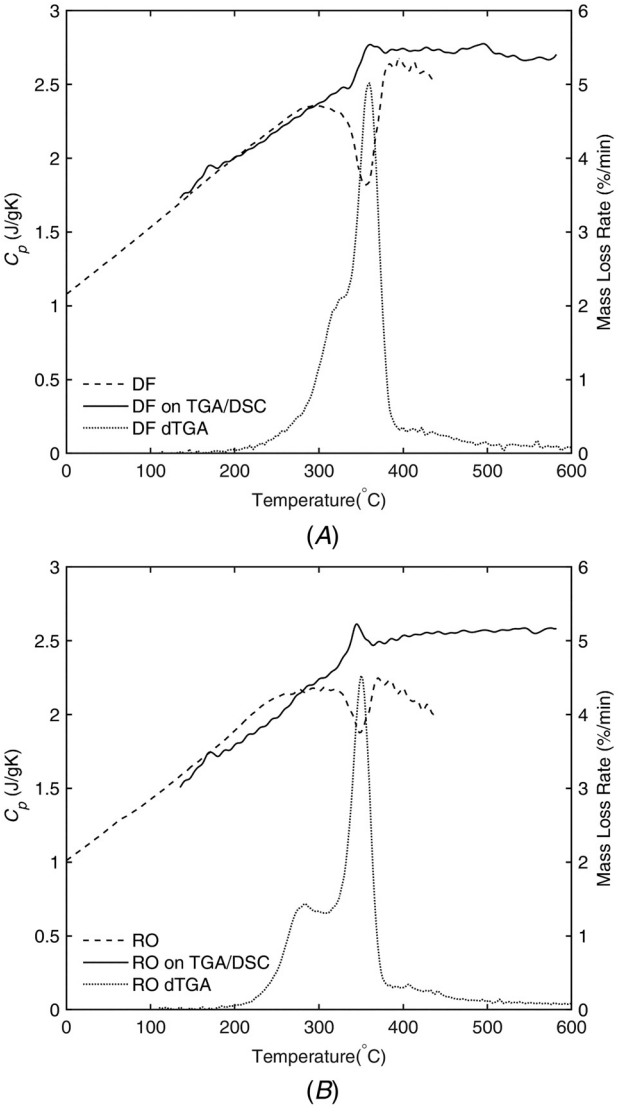
FIG. 2 (*A*) Mass fraction and (*B*) mass loss rate of DF and RO versus temperature on a mass-corrected basis.



HEAT CAPACITY

The averages of three replicates for each wood species from the DSC compared with the results from the combination TGA/DSC instrument are plotted in figure 3. From this plot, the C_p steadily increased from approximately 1 J/gK up to above 2 J/gK at

FIG. 3 Mass-corrected specific heat capacity (C_p) results mass-corrected obtained using separate TGA and DSC methods and a combination TGA/DSC instrument for (*A*) DF and (*B*) RO. The mass loss rates from TGA are included.



temperatures above 250°C. For the specimens measured in the DSC, a dip is observed between 320°C and 375°C and then the C_p appears to decrease. For the specimens measured in the TGA/DSC, at temperatures above 375°C, the C_p appears to level out at approximately 2.7 J/gK for the DF and 2.5 J/gK for the RO.

DISCUSSION

The sinusoidal C_p calculation method first used in the leaf study continued to perform well for these wood specimens. The slight difference in heat capacity between wood species (DF near 6% higher than RO) observed in **figure 3** is larger than the assumed uncertainty of the method. The dip in C_p seen in both specimens between 320°C and 375°C is larger than that in the companion leaf study, indicating that the method was less successful during the rapid mass loss that happens near this temperature (see **fig. 2*B***). Inspection of **figure 3** suggests that this dip is due to the mismatch between the C_p (DSC) and mass loss (TGA) temperature curves, which was eliminated when using the combination TGA/DSC in which case both values could be measured simultaneously. The coefficient of variation between specimens of 3.7% for RO and 8% for DF is small compared with the magnitude of the dip. The RO specimens are less affected by the mass loss mismatch, likely because of the greater presence of complex compounds that degrade across a wider temperature range (see **fig. 2*B***). The earlier degradation of the RO mass loss curve (**fig. 2**) with temperature also indicates the presence of these more easily degraded compounds. The variations in the mass loss rate evident if **figure 2** are likely due to differences in chemical makeup of the cell walls.[16]

The DSC equipment used here had a maximum temperature of 438°C, which limited the exploration using separate TGA and DSC instruments. The combined TGA/DSC equipment, however, was conducted to a maximum temperature of 600°C. Further exploration at higher temperatures (≥1,000°C) would provide material properties for fire models used to explore compartment fires and, at these temperatures, the exploration of C_p would benefit from the use of combined equipment. It remains to be seen how accurate the C_p measurement can get using these combined instruments.

ACKNOWLEDGMENTS

We are grateful for help from several Forest Products Laboratory colleagues. Philip Walsh provided access and support in use of the TGA. Matthew Zurawski helped with specimen preparation. Netzsch instruments ran the specimens on their demonstration machines to show the promise of the combination TGA/DSC instruments.

References

1. L. Shi and M. Y. Chew, "A Review of Thermal Properties of Timber and Char at Elevated Temperatures," *Indoor and Built Environment* (2021), https://doi.org/10.1177/1420326X211035557

2. G. Rein, A. Bar-Ilan, A. C. Fernandez-Pello, and N. Alvares, "A Comparison of Three Models for the Simulation of Accidental Fires," *Journal of Fire Protection Engineering* 16, no. 3 (2006): 183–209.
3. C. Lautenberger, "A Generalized Pyrolysis Model for Combustible Solids" (PhD diss., University of California, Berkeley, 2007).
4. J. Quintiere, "A Simplified Theory for Generalizing Results from a Radiant Panel Rate of Flame Spread Apparatus," *Fire and Materials* 5, no. 2 (1981): 52–60.
5. C. Lautenberger, G. Rein, and C. Fernandez-Pello, "The Application of a Genetic Algorithm to Estimate Material Properties for Fire Modeling from Bench-Scale Fire Test Data," *Fire Safety Journal* 41, no. 3 (2006): 204–214.
6. F. L. Browne, *Theories of the Combustion of Wood and Its Control*, Report no. 2136 (Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, 1958).
7. F. C. Beall, and H. W. Eickner, *Thermal Degradation of Wood Components: A Review of the Literature*, Research Paper no. 130 (Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, 1970).
8. R. H. White, "Charring Rates of Different Wood Species" (PhD diss., University of Wisconsin-Madison, 1988).
9. A. I. Bartlett, R. M. Hadden, and L. A. Bisby, "A Review of Factors Affecting the Burning Behaviour of Wood for Application to Tall Timber Construction," *Fire Technology* 55, no. 1 (2019): 1–49.
10. F. Beall, *Specific Heat of Wood: Further Research Required to Obtain Meaningful Data*, Research Paper no. 184 (Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, 1968).
11. S. Glass and S. Zelinka, "Moisture Relations and Physical Properties of Wood," in *Wood Handbook*, FPL-GTR-282 (Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, 2021): 4-1–4-22.
12. K. Radmanović, I. Đukić, and S. Pervan, "Specific Heat Capacity of Wood," *Wood Industry/Drvna Industrija* 65, no. 2 (2014): 151–157.
13. C. Dupont, R. Chiriac, G. Gauthier, and F. Toche, "Heat Capacity Measurements of Various Biomass Types and Pyrolysis Residues," *Fuel* 115 (2014): 644–651.
14. *Design of Timber Structures—Part 1-2—General—Structural Fire Design*, EN 1995-1-2 Eurocode 5 (Brussels, Belgium: European Committee for Standardization, 2004).
15. C. R. Boardman, M. A. Dietenberger, and D. R. Weise, "Specific Heat Capacity of Wildland Foliar Fuels to 434°C," *Fuel* 292, no. 10 (2021): 120396.
16. R. M. Rowell, *The Chemistry of Solid Wood*, Advances in Chemistry Series (Washington, DC: American Chemical Society, 1984).