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Yield and Product Properties of Wood Chips and Particles Torrefied in a Crucible Furnace Retort

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ABSTRACT: Biomass preprocessing by torrefaction improves feedstock consistency and thereby improves the efficiency of biofuels operations, including pyrolysis, gasification, and combustion. A crucible furnace retort was fabricated of sufficient size to handle a commercially available wood chip feedstock. Varying the torrefaction times and temperatures provided an array of samples exhibiting various degrees of thermal degradation. Subsamples of the wood chip feedstock were also dried or ground to smaller particles prior to torrefaction to determine if such pretreatments would affect yields. Principal component analysis (PCA) was performed on Fourier transform infrared (FTIR) spectroscopic data from the samples. The PCA scores and loadings plot clearly demonstrated the various degrees of polysaccharide degradation for the different torrefaction temperatures used.

KEYWORDS: Biofuels, Biomass, Drying, Particle Size, Principal Component Analysis

1 INTRODUCTION

Torrefaction conditions are typically anaerobic, under atmospheric pressure, and use temperatures ranging from 200 to 300°C [1,2]; this differs from so-called wet torrefaction, a hydrothermal process utilizing pressurized water at similar temperatures [3,4]. Property enhancements include greater resistance to moisture uptake, reduced microbial degradation, higher carbon density, and easier grinding [5-7]. Torrefaction is not always beneficial for biofuel upgrading by pelletization because of greater friction in the pellet mill and lower compression strength of the resultant pellets [8].

During torrefaction of biomass, chemical changes occur unevenly among the cell wall polymers (hemicelluloses, cellulose, and lignin). Specifically, the hemicelluloses soften at temperatures below 200°C and undergo deacetylation, dehydration, and depolymerization reactions between 200 and 300°C [2]. Among the hemicelluloses, the xylans have been suggested to be particularly reactive [9,10]. Thus, greater presence of xylans in hardwoods compared to softwoods has been used to explain higher reactivity of willow and birch wood samples, both being hardwoods, compared to that of larch, a softwood [9,10]. With temperatures approaching 250°C, the other cell wall polymers, cellulose and lignin, are still largely unchanged [6,11]. As temperature is further raised upwards of 300°C, all the cell wall polymers are degraded, with disproportionation reactions ultimately leading to highly condensed aromatic polymer structures [11], in part from the polymerization of levoglucosan derived from cellulose pyrolysis [12].

Although numerous studies have been conducted on torrefaction of various types of biomass, more research is needed to better understand the impact of processing large particles [2]. Indeed, only a few studies have investigated the effect of particle size on wood torrefaction [13,14]. In the present study, we assess the utility of a crucible furnace fitted with a retort specifically fabricated for laboratory-scale torrefactions of a commercially available wood chip feedstock. The impact of feedstock drying and grinding on torrefactions carried out in this equipment was also of particular interest. Fourier transform infrared (FTIR) spectroscopy, coupled with multivariate analyses, has been used to assess the effect of temperature and duration during torrefaction of woody biomass [15,16]. Because our research has shown the utility of mid-infrared spectroscopic data [17], here we briefly present our efforts to conduct principal component analysis (PCA).

2 MATERIALS AND METHODS

2.1 WOOD FEEDSTOCK

Pulp-grade southern yellow pine wood chips were obtained from a local chip mill (Winnfield, LA). A subsample of the wood chips was ground in an electric chipper shredder (Echo, Inc., Model SH-5000; Lake Zurich, IL) and then

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screened by hand to give particles passing through an 8 mesh (2.4-mm openings) sieve and retained on a 20 mesh (0.85-mm openings) sieve; particles were mostly slivers ranging from 2 to 20 mm in length. The moisture content (MC) of each feedstock (wood chips, ground wood) was determined by drying subsamples in an oven (103 ± 2°C).

2.2 TORREFACTION

Wood chips/particles were then torrefied in a crucible furnace retort fabricated by Thermal Product Solutions (Williamsport, PA). Details regarding the features of the crucible furnace retort and its operation were previously reported [18]. Figure 1 shows the retort placed in a cooling stand, next to the crucible furnace.

Figure 1: *Crucible furnace and retort.*

A schematic of the retort (Figure 2) shows how the cover was installed, with specific attention given to placement of the outlet purge tube (c), aligning past the side of the crucible. The retort was equipped with a thermocouple (a), purge gas inlet (b), and cover sealed to the vessel with a rubber O-ring seal (d). Hanging on the front of the retort (Figure 1) is a disconnected thermocouple that was inserted into the purge gas inlet to assess temperature gradients within the retort.

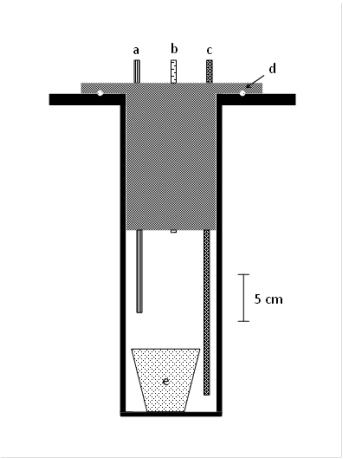

Figure 2: *Schematic of retort.*

Wood samples (ca. 50 g, air-dry chips, oven-dry chips, air-dry particles) were contained within a high-form porcelain crucible (250 mL) placed in the bottom of the retort. Under a constant purge of N_2 (1 L min^{-1}), the retort was heated from ambient temperature to the targeted operating temperatures of 230, 260, and 290°C. Total run times ranged from 2 to 4 h, including 1 h needed to reach operating temperature [18]. When the torrefaction run was complete, the retort was removed from the furnace and placed in a stand to cool (1.5 h) before stopping the flow of N_2 and removing the sample-containing crucible. Yields of torrefied wood were based on dry weights of the torrefied wood and the feedstock. Torrefied wood samples were ground in a large Wiley mill (Thomas Scientific, Model 4; Swedesboro, NJ) equipped with a 4-mm screen. Subsamples used for FTIR spectroscopy required further grinding in a small Wiley mill equipped with a 0.85-mm screen.

2.3 FTIR SPECTROSCOPY AND PRINCIPAL COMPONENT ANALYSIS

Mid-IR spectra of the samples were collected using a Nexus 670 FTIR spectrometer (Thermo Nicolet Instruments, Madison, WI) equipped with a Golden Gate MKII Single Reflection ATR accessory. Ground wood samples were applied directly to the diamond window. Three spectra were collected for each sample. Principal component analysis of the spectral data were performed using Unscrambler (version 8.0) software (CAMO, Woodbridge, NJ).

3 RESULTS AND DISCUSSION

3.1 RETORT CALIBRATION

The crucible furnace retort used in the current study was fabricated to allow for torrefaction of wood chip feedstocks and to generate sufficient material for future application assessments; the design allowed the retort to be lifted from the furnace and placed in a stand for faster cooling. Maintaining a continuous purge of N_2 removed the possibility of sample oxidation during cooling. Results from cooling temperature monitoring were previously reported [18]; briefly, by removing the retort from the furnace and placing it in the cooling stand near a fan, time to reach 100°C from 260°C was only 10 min. Using a flexible thermocouple inserted through the air inlet and down to the bottom of the crucible, temperature was shown to decrease at a slightly faster rate than at the higher location of the fixed internal thermocouple.

Initial operation of the crucible furnace retort revealed a temperature gradient; the temperature at the fixed internal thermocouple (Figure 3) was 75°C lower than that at the external controller thermocouple. Temperature monitoring with a flexible thermocouple inserted through the retort air inlet port demonstrated that the temperature at the bottom of the retort was about 35°C lower. Given the temperature

differences within the retort, a calibration was conducted to give a better representation of the temperature the feedstock would experience. For each temperature setting programmed, steady-state temperatures were recorded at the fixed internal thermocouple and at the bottom of the crucible placed in the retort, the latter monitored with the flexible thermocouple. Plotting these values showed linear relationships ($R^2 > 0.99$) for both thermocouples (Figure 3). The higher temperature setting programmed into the controller to achieve the target temperature for the feedstock was calculated using the equation determined from the flexible thermocouple temperature readings. For example, heating the feedstock/crucible to a target temperature of 260°C required the controller to be programmed to a temperature of 305°C. The simple caveat here is that the programmed temperature is not always the true temperature for some retort designs.

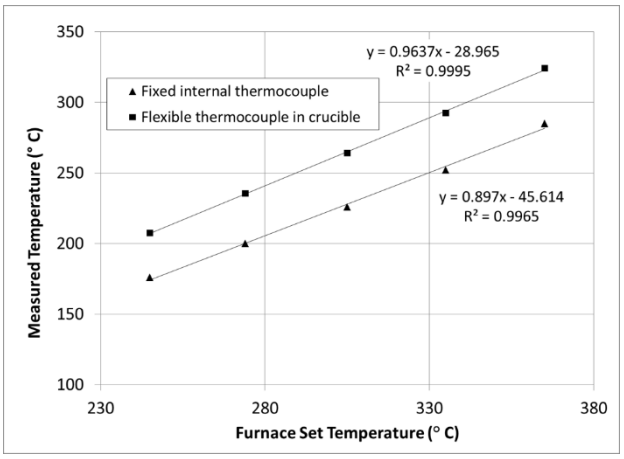

Figure 3: *Temperature calibrations at thermocouples.*

3.2 TORREFACTION

3.2.1 Air-dry chips

Torrefaction of air-dry (9.6% MC) wood chips gave the expected increasingly darker coloration with increasing time and temperature; the most dramatic difference in color change was with increasing temperature for a given time (Figure 4).

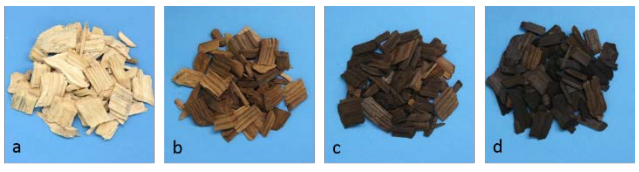

Figure 4: *Wood chips (a) before and after 3 h of torrefaction at (b) 230, (c) 260, and (d) 290°C.*

This observation was readily apparent in the data, with yields being impacted to a greater extent by temperature as opposed to time (Table 1). The wide range of yields would appear to reflect a wide spectrum of chemical changes (e.g., hemicellulose deacetylation, dehydration, etc.) resulting from the torrefaction conditions. Thus, high yields for the lowest temperature (230°C) likely represent torrefied woods for which decomposition most likely occurred primarily amongst the hemicelluloses. At the highest temperature applied (290°C), some of the cellulose and lignin was undoubtedly degraded.

Table 1: *Percentage yields of torrefied product for different temperature and time conditions.*

	Time	Yield (%) at three target torrefaction temperatures		
	(h)	230°C	260°C	290°C
Air-dry wood chips	2	95.64 ± 0.25	85.30 ± 1.88	67.36 ± 1.13
	3	92.95 ± 0.76	82.01 ± 1.47	61.61 ± 0.45
	4	91.53 ± 0.39	78.41 ± 0.01	51.24 ± 1.27
Oven-dry wood chips	2	93.23 ± 1.36	82.46 ± 0.17	60.18 ± 1.10
	3	91.06 ± 0.12	79.40 ± 0.47	54.01 ± 1.39
	4	90.33 ± 0.38	78.07 ± 0.69	51.29 ± 1.24
Air-dry 8-20 mesh wood particles	2	92.60 ± 0.09	80.29 ± 0.28	55.05 ± 0.62
	3	90.21 ± 0.05	77.09 ± 1.01	51.93 ± 1.32
	4	88.77 ± 0.26	75.03 ± 0.11	49.91 ± 0.82

Temperature readings for the fixed internal thermocouple were monitored because they provided an indication of conditions within the retort, albeit those not specifically experienced by the feedstock. During heating cycles with an empty crucible, the fixed internal thermocouple showed that temperature stabilized after about 50 min (Figure 5). This was similarly observed from the flexible thermocouple.

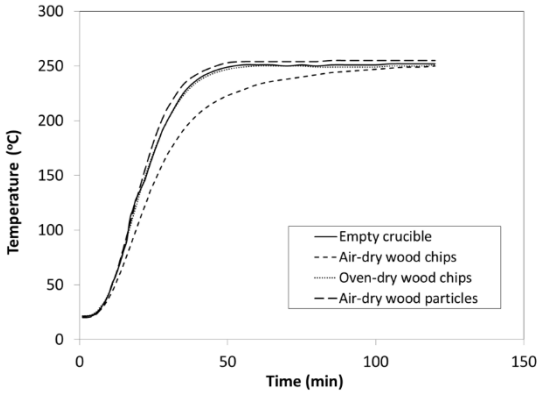

Figure 5: *Temperatures at internal retort thermocouple during the first 2 h of heating cycle with and without feedstocks in crucible.*

Upon the inclusion of air-dry wood chips, it took 2 h for the temperature at the fixed internal thermocouple to match that for when the crucible was empty. Moisture content of air-dry chips averaged 9.6%. The response of the retort to relatively small amounts of water suggests that the temperature within the retort would be significantly impacted if wet biomass (i.e., above equilibrium moisture content) were to be used as feedstock.

3.2.2 Oven-dry chips

Given the results with air-dry wood chips, we hypothesized that use of oven-dry wood chips would remove the lag in temperature increase and thereby result in greater residence time at elevated temperatures, thus affording lower yields (i.e., higher thermal degradation). Indeed, plotting temperatures for experiments with oven-dry wood chips paralleled those obtained with an empty crucible (Figure 4). In most cases, yields were lower with oven-dry wood chips than with air-dry wood chips (Table 1). The exceptions were at extreme conditions (4 h at both 260 and 290°C) whereby the extended time compensated for the lag in temperature increase during the heating phase of the process. Water present in wood subjected to thermal processing releases acetyl groups from the hemicelluloses, thereby affording acetic acid as a catalyst for carbohydrate depolymerization [19]. Yield data (Table 1) show that under the torrefaction conditions used in the current study, the lag in temperature increase more than offsets any augmentation of wood depolymerization imparted by the presence of moisture.

3.2.3 Air-dry wood particles

One design advantage for this retort was the ability to torrefy large particles. Indeed, in their review, Ciolkosz and Wallace [2] specified that the study of large particle torrefaction was a research need, the rationale being that torrefaction yields/products from a given feedstock are a function of time, temperature, and particle size. Torrefaction of air-dry (8.3% MC) wood particles (8-20 mesh) from the wood chips gave lower yields (i.e., higher thermal degradation) than for intact air- and oven-dry wood chips. The greatest difference was at a temperature of 290°C and a total treatment time of 2 h; yields for air-dry wood chips and air-dry wood particles were 67% and 55%, respectively. Monitoring temperature at the fixed internal thermocouple gave a surprising result in that the temperature increase in the retort paralleled those for both the empty crucible and the air-dry wood particles (Figure 5). These results suggest that slower temperature increases in the retort, resulting from the presence of moisture in the feedstock, are negated by particle size reduction. Thus, although heat transfer into a large particle may impact torrefaction yields, the present results suggest that a greater factor may be slower losses of moisture as a function of increasing particle size.

3.3 FTIR SPECTROSCOPY AND PRINCIPAL COMPONENT ANALYSIS

FTIR spectra were also collected from the complete set of ground torrefied wood samples. The application of PCA to the spectra transforms the original coordinate system of spectral data into a new coordinate system of principal components (e.g., PC1, PC2), from which the data can be displayed as a scores plot (Figure 6). The samples appear to cluster according to treatment temperature with those exposed to the lowest treatment temperatures (230 and 260°C) located on the negative side of PC1, and those with the highest temperature (290°C) located on the positive side; PC1 accounts for 96% of the total variance. The samples treated at 290°C show much greater variation along PC1 than those at the lower temperatures.

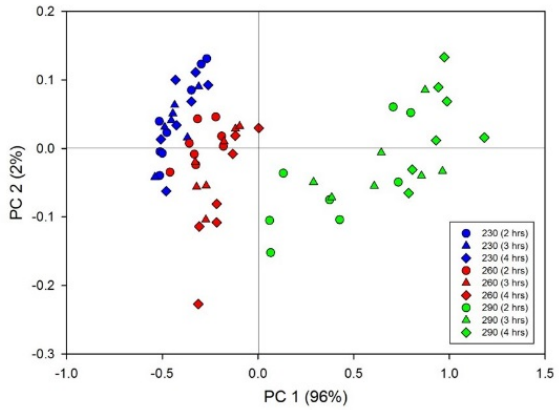

Figure 6: *PCA scores plot (PC2 vs PC1) of torrefied wood from all feedstocks.*

Figure 7 shows the PC1 loadings plot for Figure 6, displaying which wavenumbers contributed most to the separation along PC1. As would be expected for thermal degradation of wood, the carbohydrate bands at 1184 and 1024 cm^{-1} are the most predominant in the plot.

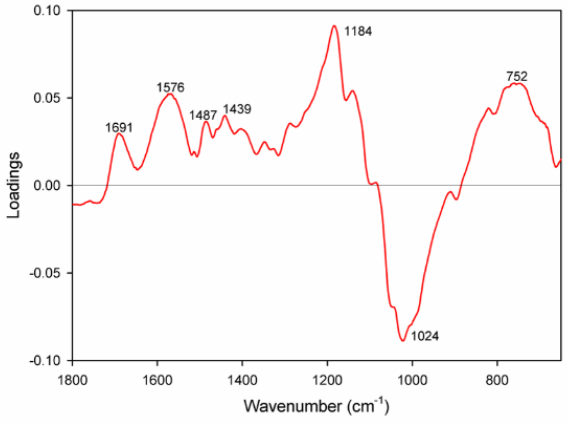

Figure 7: *PCA loadings plot for PC1.*

4 CONCLUSIONS

Yields of torrefied wood were impacted more by difference in temperature than time of treatment. Moisture in the feedstock resulted in slower temperature increases in the retort, affording higher yield (i.e., lower thermal degradation). Grinding of the feedstock negated this effect. The PCA scores and loadings plot clearly demonstrated the various degrees of carbohydrate degradation for the three torrefaction temperatures used.

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