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TG-FTIR analysis of pecan shells thermal decomposition

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ABSTRACT

The thermal decomposition of pecan shells within the temperature range of 30 °C to 800 °C and at heating rates of 5 to 30 °C/min was studied by the use of TG-FTIR. Friedman's isoconversional method was used for kinetic analysis of the thermal decomposition process. Differential scanning calorimetry was also used to quantify the amount of energy required to thermally degrade pecan shells. The thermal decomposition process was found to compose of four stages—moisture evaporation, hemicelluloses decomposition, cellulose decomposition and lignin degradation. The peak temperatures for hemicelluloses (275 to 315 °C) and cellulose (348 to 385 °C) degradation increased with heating rate. The major gases given off were identified to be carbon dioxide, carbon monoxide, acetic acid and ethanol. The amount of energy required to thermally degrade pecan shells was about 30% of the energy content of the shells.

1. Introduction

Pecan (*Carya illinionensis*) is a tree nut that is grown in most of the southern states of U.S. The nuts of pecan are edible and can be consumed fresh or used as an ingredient during cooking. Preparation of the nuts for consumption requires that pecan be processed via a series of operations (e.g. grading and sizing, cracking, shelling, drying, grading and sorting) that results in pecan shells as byproduct. Some of the current uses for pecan shells include mulching, fire log imitation, glue and soap abrasives, and activated carbon resource [1–3]. Private communication by the authors with pecan shell processors indicate that a substantial amount of the approximately 55 million kilograms of pecan shells (nass.usda.gov) produced annually are however not utilized. This study investigates the potential of using pecan shells as biomass feedstock.

Thermochemical methods are commonly used to convert biomass (such as pecan shells) into value-added products. These methods involve heating of biomass to various temperatures between 200 and 900 °C that result in production of fuels and chemicals (via pyrolysis and gasification), and heat and power (via combustion). Thermogravimetric (TGA) analysis is the most common method for quantifying thermal decomposition of biological materials because the fast and repeatable data obtained enable in-depth analysis of mass loss and determination of kinetic parameters [4,5]. Knowledge of kinetics of thermal decomposition of biomass is needed for design, operation and control of thermochemical conversion equipment and processes [6].

Fourier transform infrared spectroscopy (FTIR) is a versatile tool that is used to obtain the composition of evolved gases as biomass is thermally decomposed in the TGA [7,8]. Information on the type, quantity and time of release of a gas product is essential to the complete understanding of the fundamentals and mechanisms involved in the thermal decomposition process. Gases that are generally evolved during thermal decomposition of organics and bio-polymers such as biomass are carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), ethane (C_2H_4), ammonia (NH_3), hydrocyanic acid (HCN), sulfur dioxide (SO_2) and carbonyl sulfide (COS) [8,9]. Fang et al. [10] found that the following gas products were obtained from thermal decomposition of different biomass types (merbau, cotton straw, birch)—CO_2, CO, H_2O, CH_4, acetic acid (CH_3COOH) and methanol (CH_3OH).

The objectives of this study were to: (a) determine the rate and kinetics of thermal decomposition of pecan shells in nitrogen atmosphere; (b) quantify the composition of gas evolved during thermal decomposition of pecan shells; and (c) quantify the energy required to thermally degrade pecan shells.

2. Materials and methods

2.1. Sample preparation

The pecan shell sample used in this study was obtained from the Louisville Pecan Company, Louisville, AL. The samples were ground in a Wiley mill (to pass through a #40 screen) before use. Heating value, ash, carbon and hydrogen contents of the pecan shell samples were quantified. Heating value of pecan shells was obtained with an IKA C200 calorimeter (IKA Works Inc., Wilmington, NC). Ash content of samples was determined according to the National Renewable Energy Laboratory's (NREL) laboratory analytical procedure [11] for the determination of ash in biomass that involved ashing of samples at 575° ± 25 °C for three hours. Carbon and hydrogen contents were

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Table 1
Heating value, ash, carbon and hydrogen contents of pecan shells and switchgrass.

Property	Pecan shells	Switchgrass*
Heating value (MJ/kg)	20.06[a] (0.03)	19.20[a] (1.21)
Ash (%)	2.49[a] (0.01)	2.96[a] (2.96)
Carbon (%)	46.97[a] (0.39)	48.21[a] (2.21)
Hydrogen (%)	5.42[a] (0.01)	5.58[a] (0.31)

Values are means of duplicate and numbers in parentheses are standard deviation. In each row, values with the same letter are not significantly different ($P<0.05$).
*Fasina [39]

determined using an elemental analyzer (Model 2400 Series II Perkin-Elmer, Shelton, CT).

2.2. Thermogravimetric analysis

Thermal decomposition of the ground sample was carried out in a Pyris 1 TGA—thermogravimetric analyzer (Perkin-Elmer, Shelton, CT). A sample mass of about 5 mg was used for TG analysis. Heating of a sample was conducted at heating rate of 5, 10, 20, and 30 °C/min within the temperature range of 30 °C to 800 °C under nitrogen atmosphere. Before use, the TGA was calibrated for temperature and mass according to the procedure outlined by the manufacturer of the equipment.

2.3. FTIR analysis of gases evolved during thermal decomposition

A Fourier Transform infrared (FTIR) spectrometer (Model 100, Perkin-Elmer, Shelton, CT) was used to quantify the gases evolved when the TGA was used to thermally decompose the pecan shells. A transfer line was used to connect the FTIR to the TGA. The transfer line was heated and maintained at a temperature of 220 °C to prevent the condensation of the volatile gases evolved during the thermal decomposition process [12]. The software provided by the FTIR spectrometer manufacturer was used to obtain spectra of the gas flowing through the measurement cell every 20 s. Quantitative analysis of the series of spectra was then carried out by (a) matching the spectra against those from the library search of a software (QASOFT, Infrared Analysis, Inc., Anaheim, CA) thereby identifying the constituent of the gas at each spectra, and (b) using the software to quantify the concentration of the identified gases.

2.4. Thermal decomposition energy

A differential scanning calorimeter (DSC) was used to quantify the energy required to thermally decompose pecan shells. The DSC (Model Q200, TA Instruments, New Castle, DE) was operated under nitrogen atmosphere at a flow rate of 20 ml/min. Samples (approximately 5 mg) were equilibrated at 30 °C for 2 min, then heated to 550 °C at five different heating rates (5, 10, 20, and 30 °C/min) and then held at 550 °C for 2 min. Temperature (°C), time (min), heat flow (W/g) and sample purge flow (ml/min) were all recorded by the software provided by the manufacturer of the DSC. The equipment was calibrated before use according to manufacturer's specifications.

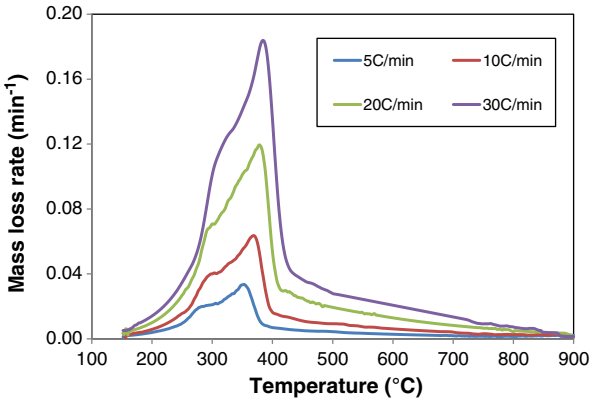

Fig. 2. Mass loss rates from the thermal decomposition of pecan shells at different heating rates.

3. Results and discussion

3.1. Compositional analysis

The compositional data (heating values, ash, hydrogen and carbon contents) for pecan shells is summarized in Table 1. Also shown on the table are the corresponding values for switchgrass—a high yielding perennial grass that has been identified to have potential as a bioenergy crop [13]. The measured values for the parameters for pecan shells were not significantly different from those of switchgrass. This confirms the potential of using pecan shells for bioenergy applications in southeastern part of United States. The heating value, ash, carbon and hydrogen contents of pecan shells were measured to be 20.06 MJ/kg, 2.49%, 46.97% and 5.42% respectively.

3.2. Thermogravimetric analysis

Observed thermal behavior (TG curve) for pecan shells during thermal decomposition is shown in Fig. 1. At each heating rate, there was an initial mass loss (approximately 15% of total weight) that was

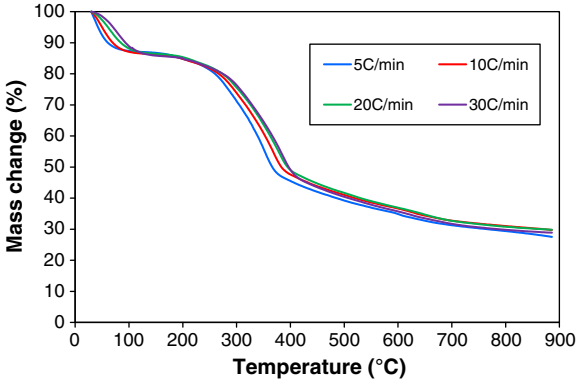

Fig. 1. Mass loss from thermal decomposition of pecan shells at different heating rates.

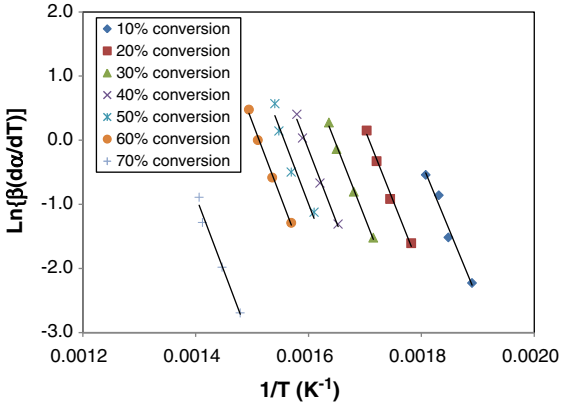

Fig. 3. Isoconversional plots of Ln[β(dα/dT)] versus 1/T.