Biomass pyrolysis and combustion integral and differential reaction heats with temperatures using thermogravimetric analysis/differential scanning calorimetry

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Jiacheng Shen [1], C. Igathinathane *, Manlu Yu, Anand Kumar Pothula

Department of Agricultural and Biosystems Engineering, North Dakota State University, 1221 Albrecht Boulevard, Fargo, ND 58102, USA

HIGHLIGHTS

- Concept of biomass iso-conversion reaction heats pyrolysis and combustion developed.
- Biomass pyrolysis and combustion integral and differential reaction heats determined.
- Developed the reaction heat models from TGA/DSC characteristics.
- Evaluated heat capacities of switchgrass, big bluestem, and corn stalks.

GRAPHICAL ABSTRACT
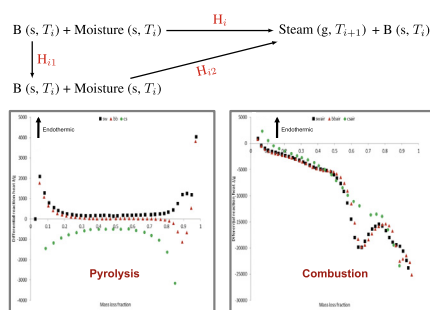
ABSTRACT

Integral reaction heats of switchgrass, big bluestem, and corn stalks were determined using thermogravimetric analysis/differential scanning calorimetry (TGA/DSC). Iso-conversion differential reaction heats using TGA/DSC pyrolysis and combustion of biomass were not available, despite reports available on heats required and released. A concept of iso-conversion differential reaction heats was used to determine the differential reaction heats of each thermal characteristics segment of these materials. Results showed that the integral reaction heats were endothermic from 30 to 700 °C for pyrolysis of switchgrass and big bluestem, but they were exothermic for corn stalks prior to 587 °C. However, the integral reaction heats for combustion of the materials followed an endothermic to exothermic transition. The differential reaction heats of switchgrass pyrolysis were predominantly endothermic in the fraction of mass loss (0.0536–0.975), and were exothermic for corn stalks (0.0885–0.850) and big bluestem (0.736–0.919). Study results provided better insight into biomass thermal mechanism.

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1. Introduction

Biomass pyrolysis and combustion are considered as major and direct routes to derive energy from lignocellulosic materials. Reaction heats with temperatures during biomass pyrolysis and combustion form important tools to decide whether the pyrolysis is capable of maintaining self-energy balance and to evaluate efficiency of combustion process. Thermal analysis systems enable to subject samples to different temperature profiles and gaseous environment in a controlled manner for mass and heat measurements.

Thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) analyzer measures sample mass loss and heat flow simultaneously, and the heats required or released during pyrolysis and combustion can be calculated by integrating the heat flow with respect to time. Therefore, TGA/DSC provides a simple approach to estimate the heats required or released for biomass

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* Corresponding author. Tel.: +1 701 667 3011; fax: +1 701 667 3054.

E-mail address: Igathinathane.Cannayen@ndsu.edu (C. Igathinathane).

[1] Present address: Department of Biological and Agricultural Engineering, 203 Engineering Hall, University of Arkansas, Fayetteville, AR 72701, USA.

pyrolysis and combustion in a wide temperature range. Two terminologies for caloric measurement of biomass pyrolysis and combustion were used in literature: heats required or released (J g^{-1} residual biomass) and reaction heat (J g^{-1} reacted biomass).

The early investigation on heat requirements using a TGA/DSC was about pyrolysis of four Finnish peats conducted by Aho et al. (1989) Recently, using the TGA/DSC analyzers, heats required or released from some biomass pyrolysis and combustion have been reported. Buryan and Staff (2008) found that the heats required for pyrolysis varied from around 180 to 700 kJ kg^{-1} for amaranth, barley chaff, cocoa peelings, maize chaff, sorrel, rood, and peanut peelings. The heat requirements of pyrolysis also were dependent on the heating rate of the TGA/DSC used in the experiments. He et al. (2006) investigated the caloric requirements of pyrolysis of pine, peanut shell, cotton stalk, and wheat straw. Manyà et al. (2013) studied the heat required during pyrolysis of two-phase olive mill waste. Both investigations showed the pyrolysis reactions were either endothermic or exothermic, depending on the reaction temperatures. Chen et al. (2012) applied TG-DSC to study drying characteristics and heat requirements of cotton stalk at four temperatures (60, 80, 100 and 120 °C). They showed that the heat requirements of cotton stalk during drying ranged from 189 to 406 kJ kg^{-1}. On the other hand, the reaction heats of cellulosic materials with temperatures using TGA/DSC also were investigated. Rogers and Ohlemiller (1980) investigated thermal and oxidation decomposition of cellulosic insulation materials, and reported that the cumulative heats of oxidation of waste paper ranged from −2958 to −9535 J g^{-1} (reacted) in a reacted percentage 60–100%. Rath et al. (2003) reported that the heats of the primary pyrolysis of beech and spruce were between 41.9 and 387.3 J g^{-1}, respectively. He et al. (2009) measured the heats of smoldering combustion in straws and stalks using simultaneous thermal analysis. They concluded that the reaction heats of the agro-stalks in oxidative polymer degradation stage were more than 6920 J g^{-1}, and in char oxidative stage were around 23,000 J g^{-1}.

The characteristics produced by TGA/DSC analyzer can represent two types of heat flow curves: (1) original heat flow (W), and (2) normalized heat flow (original heat flow divided by the residual mass of biomass, W g^{-1} residual biomass) with respect to time or temperature. Integration of original heat flow with respect to time produces the heat required by the process (J), and integration of normalized heat flow produces the heat requirement per residual biomass mass (J g^{-1} residual biomass). The reaction heat per unit mass is defined as the absorbed or released heat divided by the reacted (de-volatized) mass (J g^{-1} reacted biomass) (Smith et al., 2005). Furthermore, it is well known that biomass mainly consists of three biopolymers: hemicellulose, cellulose, and lignin. The fourth major non-biopolymer component generally found in biomass is ash. Cellulose is a glucose polysaccharide, hemicellulose is polysaccharides with a backbone of different hexoses and pentoses, and lignin is a complex network of different phenyl propane units. Each component in biomass has a range of decomposing temperature, and these temperature ranges are overlap (Cheng et al., 2012). Thus, the reaction heats of biomass pyrolysis and combustion vary with temperatures (or conversion or mass percentages) because each component reaction absorbs (defined as positive) or releases (defined as negative) different heats. This character of biomass, consisting of many different components, creates issues in studying its decomposition kinetics because it is often difficult to identify the decomposed products and the biomass component sources these products are derived from. Thus, the biomass components conversion cannot be readily calculated. A concept of iso-conversion has been applied to the decomposition kinetics of biomass to produce iso-conversion kinetic parameters and to overcome the analytical difficulty (Aboyade et al., 2011; Chandrasekaran and Hopke, 2012; Ma et al., 2013; Chen et al., 2013). In this method, the biomass conversion was even divided, for example 10%, for each segment to produce iso-conversion kinetic parameters, and thus to overcome the analytical difficulty. Such a concept also can be applied to the reaction heats to produce the iso-conversion differential reaction heat or the differential reaction heat when each conversion parts is not equal. To the authors' best knowledge, no reports on the iso-conversion differential reaction heats of biomass with temperatures were found in literature.

Therefore, for this research effort three major crop based biomass feedstocks were selected. Herbaceous plants such as switchgrass (Panicum virgatum), and big bluestem (Andropogon chrysocomus), and crop residues such as corn stalks (Zea mays) can form good biomass feedstocks for pyrolysis and combustion. Switchgrass has several advantages than other biomasses: high productivity in long-term (>10 years) across many environments, suitability for marginal land, relatively low water and nutrient requirements, and positive environmental benefits (Sanderson et al., 2006). Big bluestem is the dominant grass species of the Midwestern tall grass, and has the similar benefits as those of switchgrass. Corn stalk is a commonly available agricultural biomass residue in areas of large amounts of corn production. It was estimated that the US produced about 75 million dry tonnes in 2005 (Shen and Wyman, 2011).

In this study, the objectives were to: (1) measure thermogravimetric (TG), differential thermogravimetric (DTG), and DSC characteristics of three biomass materials (switchgrass, big bluestem, and corn stalks) during pyrolysis and combustion using a TGA/DSC analyzer; (2) determine kinetic parameters in the primary decomposition stage for both pyrolysis and combustion; (3) determine the integral and differential reaction heats with temperatures; (4) develop mathematical models of integral and differential reaction heats with respect to temperatures using a polynomial function of temperatures; and (5) to calculate the heat capacities of the selected biomass materials with temperatures in the first stage of pyrolysis and combustion.

2. Methods

Switchgrass, big bluestem, and corn stalks were harvested from the experimental plots of Northern Great Plains Research Laboratory, Agricultural Research Service, USDA, Mandan, ND in the 2012 harvest season. They were first dried at room temperature, and then ground to the particle size less than 0.5 mm using a Wiley knife mill (Model 4, Thermo Scientific, Ashville, NC, USA) fitted with a 0.5 mm circular opening screen. The grind particles were dried at 103 °C for 24 h prior to the experiments to obtain bone dry condition of the samples following the standard procedure (ASABE Standards, 2012). Biomass pyrolysis and combustion experiments were conducted in the TGA/DSC (Model: Mettler Toledo, TGA/DSC 1 STARe System, Columbus, OH, USA) equipped with STARe software, with nitrogen (for pyrolysis) and air (for combustion) at flow rates of 50 mL min^{-1}. The samples of 10.0 ± 0.1 mg for switchgrass and big bluestem and 3 ± 0.1 mg for corn stalk (because of its light density) were held in 70 µL alumina crucible for the experiments. The experimental temperature ranged from 30 to 700 °C, and the heating rate was controlled at 10 °C min^{-1}. Following the operations handbook of TGA/DSC manufacturer, a blank with an empty crucible was first run, and the heat flow with the blank was separated from the heat flow with the sample to produce the actual heat flow.

2.1. Kinetic model

Biomass pyrolysis can be generally classified as three stages: moisture removal in the first stage; the hemicellulose and cellulose