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Positive transformations in intrinsic bioconstituents due to briquetting of soybean crop residues

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ABSTRACT

Thermogravimetric spectra of binderless briquettes and its raw material, soybean crop residues, were critically analyzed to ascertain the changes occurring in the intrinsic biopolymeric components such as hemicellulose, cellulose and lignin due to briquetting stresses. Transitions of thermogravimetric signals and activation energy levels were analyzed and discussed. The distinct and sharp signals related to the secondary charring process at the high temperature regime in thermogravimetry were noticed in briquettes as compared to these signals in raw residue. Integral isoconversional Friedman kinetics treatment was used to compute the conversion fraction dependent activation energies. Deconvolution analysis of differential thermograms was done to diagnose the internal thermogravimetric transformations. It established the lesser reactivity and better consolidation in case of briquetted biofuel.

Introduction

Conversion of crop residues (CR) to solid compact briquetted fuel (Gangil, 2014a,b, 2015a,b; Chen et al., 2009; Đerčan et al., 2012; Rajkumar and Venkatachalam, 2013; Singh et al., 2007, 2008) is one of the most promising management options to enhance the utility of CR for purpose of energy generation obtaining the energy sustainability in rural areas of developing countries. During briquetting, the stresses are applied on crop residues which change the internal matrix of biomaterial. The physico-chemical transformations occur due to briquetting stresses. In raw form, the handling and storage of CR are difficult during energy generation because of looseness of CR (Gangil, 2014a,b, 2015a, b; Tripathi et al., 1998; Tumuluru et al., 2010; Grover and Mishra, 1996; Purohit et al., 2006; Mythil and Venkatachalam, 2013). Also, CR does not flow properly in the reactors of bioenergy devices due to their irregular shape & size, and light weight. The crop residue based energy and power generation systems need better fuel flow in their bio-reactors which can be obtained using uniform size of biofuels. Uniformity in fuel shape and size avoids the chocking and blockages of fuel in a reactor of bioenergy device. The CR can be used as substitute biofuel against wood chips in the biomass based power generation systems and combustion devices.

The briquettes can be produced from lignocellulosic crop residues (Gangil, 2014a,b, 2015a,b). The raw lignocellulosic material is powdered and fed in a pressing unit for briquetting. The lignocellulosic materials can be briquetted without a binder as the lignin present in these materials can itself act as a binding agent. The briquetting systems available are screw-press type, piston-press (die-punch) type and rotary-die-roller type (Gangil, 2014a,b, 2015a; Tripathi et al., 1998; Tumuluru et al., 2010; Grover and Mishra, 1996). A pressing unit puts compressive stresses on the raw CR in confined and semi-confined environment. In piston-press type systems, the raw bio-material is compressed so that the raw biomaterial can be extruded during compaction through the die. Due to stresses the temperature of biomaterial raises which changes the mutual linkages of biocomponents to form the briquette. In a screw press type briquetting machine, a conveying screw continuously presses the biomaterial through a die. The energy consumed per unit output of briquetting is higher in the case of screw-press type systems as compared to piston press systems.

Major bioconstituents of lignocellulosic crop residues are cellulose, hemicellulose and lignin. During the briquetting, a high pressure is exerted on biomaterials, which raise the temperature of CR. Basically, under the process of briquetting, an intrinsic biopolymeric matrix is placed under the stresses. Therefore, the stresses bring the physico-chemical transformations in each of intrinsic biopolymer. Due to heating of biomaterials in briquetting, some amount of moisture in the loose CR evaporates. Due to densification, biopolymers like, hemicellulose, cellulose and lignin, also pass through positive changes to form the briquetted fuel. When biomaterial is stressed more than 100 MPa or higher raising the temperatures of biomaterial above 200 °C, the softening of lignin occurs, and soft lignin binds the particles of biomaterials, tightly and thus, lignin acts like a binding agent (Gangil, 2014a,b, 2015a,b; Tumuluru et al., 2010). All lignocellulosic crop residues are

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briquettable by choosing the appropriate levels of the process parameters of the briquetting (Fengmin and Mingquan, 2011; Kaliyan and Morey, 2009).

A reliable and in-depth study of internal physico-chemical transformations in intrinsic biopolymers of a biomaterial can be accomplished using the thermogravimetric analysis (TGA) in which the biomaterial is subjected to heat in a precisely monitored and controlled chamber (Slopiecka et al., 2012; Jeguirim et al., 2014). We can also understand the thermal degradation behavior and patterns of different bioconstituents. Thermal degradation of biomaterial occurs broadly in four stages namely in the moisture release, the hemicellulose degradation, the cellulose degradation and the lignin degradation (Vasile et al., 2011). Thermal degradation of lignocellulosic biomaterials is basically addition of the independent degradations of their main components (Caballero et al., 1997). The devolatilization curve of bio-materials obtained in TGA is the sum of the contributions from individual intrinsic biocomponent (López-González et al., 2013). Degradation of each bioconstituent could be assumed as a first order reaction considering the degradation of different intrinsic biocomponents as independent parallel reactions (Ledakowicz and Stolarek, 2002). The structure of hemicellulose is random, amorphous and weak, whereas the structure of cellulose is crystalline and strong (Sanchez-Silva et al., 2012). According to Sanchez-Silva et al. (2012), the lignin was the highest thermally stable component and this biopolymer showed thermogravimetric peaks in the wide range of temperatures (200–700 °C). Also, the peak related to lignin was found the flattest in DTG profile (Sanchez-Silva et al., 2012). Due to heavily cross-linked highly branched complex structure, degradation of lignin has been stated as very difficult (Gangil, 2014a,b, 2015a,b; Sanchez-Silva et al., 2012).

While comparing the thermal degradation of two biomaterials, the signals obtained during TGA may be critically studied. These signals give the information about ease and difficulty during the thermal degradation of specific bioconstituents. Popular isoconversional treatments to execute the kinetics of thermal degradation are Friedman, Coats–Redfern, Kissinger–Akahira–Sunose (KAS), Ozawa–Fynn–Wall (Damartzis et al., 2011; White et al., 2011; Vyazovkin and Sbirrazzuoli, 2006; Janković, 2008; Wang et al., 2012; Sbirrazzuoli et al., 2009; Lu et al., 2009), etc. Friedman is a differential isoconversional treatment (Sbirrazzuoli et al., 2009), whereas Coats–Redfern, Kissinger–Akahira–Sunose (KAS) and Ozawa–Fynn–Wall are integral isoconversional treatments (Sbirrazzuoli et al., 2009). In all these methods, broadly four steps are used to calculate the activation energy. For example, in Friedman method, the first step is to find the Friedman curves. The second step is to extract the Friedman points (kinetics points) at selected isoconversional fractions. Third step is to draw the Friedman kinetics lines with higher coefficients of regression to obtain the slope of these lines. In the last step, the slopes of these kinetics lines are used to compute the activation energies which approximates to −E/R. The similar kinds of steps are conventionally used in the KAS and OFW methods. The major limitation of isoconversional methods is to obtain the high level of regression while fitting the linear equation in kinetics points which is not always possible in the practical situation while analyzing the lignocellulosic biomaterials. As the lignocelluloses have inter-linkages of different kinds of biopolymers, their degradation is a very complex process. Therefore, many a times, isoconversional treatments applied to thermogravimetric data do not yield adequate information while comparing more than one biomaterial. In such cases, a critical investigation of specific biopolymeric TG-signals is needed which can be done by deconvolution analysis. In deconvolution analysis, the DTG is divided in different peaks and the variations of these deconvoluted TG-signals are analyzed.

The present article is a first attempt to apply the deconvolution analysis on the soybean crop residues to study the effects of briquetting stresses. The soybean crop residues and the briquettes made from it were critically analyzed to see the physico-chemical transformations responsible for thermal stability in the case of a briquetted biofuel.

Materials and methods

Soybean crop residues (SS) were gathered from farmer fields. Thermogravimetric analyses (TGA) of powdered SS and its briquettes (SB) were conducted to understand the variations in the internal configuration on the basis of the thermogravimetric signals using a thermogravimetric analyzer (model: pyris-6; by: Perkin Elmer). Thermogravimetry provided the data about the weight loss (%) of bio-material versus temperature or time (thermogram) during the thermal degradation process. Differential thermogram (DTG) was the first order derivative of thermogram that gave information with respect to weight loss rate versus temperature or time, i.e., showing the degradation rate profile (degradation rate, $\%\cdot min^{-1}$). The location (temperature or time values) and amplitude ($d\alpha/dt$ in DTG) of TG-signals are two available parameters that could be compared to diagnose the thermal hardening or softening of a particular component in two kinds of biomaterials under evaluation. Higher amplitude of TG-signals indicated towards the thermal loosening or vice versa. The amplitude was more closely related to the bond energies of molecules of a particular biocompound with other biocompound molecules. The amplitude of the TG-signal is linked with the adhesion of one kind of biocompound with other types. Activation energy can be considered as a combined effect of energy related to the bonds within one kind of biocompound, and the bonds of that particular biocompound with other kinds of biocompounds. Higher activation energy showed the higher thermal stableness or vice versa. Vamvuka et al. (2003) expressed that the peak height was directly proportional to the reactivity. The amplitude was taken as the major consideration in present article.

The recommended sowing period of the soybean crop (*Glycine max* (L.) Merr.) (Mandal et al., 2002; Nevase et al., 2012; Nevase et al., 2013), an important crop in central region (Madhya Pradesh) of the India, was in the last week of June and the crop length is 95–105 days. Normally, combine harvesters were used for harvesting, which left the threshed residues in the field, itself. After harvesting from these machines, the residues (soybean straw (SS)) were taken within one week of the harvesting from the farmers' field. The material brought from the farmers' field was powdered using a hammer mill. In making the briquettes, the powdered SS was pressed in a commercial piston-press briquetting system (rated power 35 kW; rated capacity 500 kg/h). The briquetting plant, shown in earlier writings (Dubey et al., 2009; Gangil, 2015a), is installed at Agricultural Energy and Power Division, Central Institute of Agricultural Engineering, Bhopal, India. The samples of raw powdered SS used for TGA had the particle size distribution values of >0.2 mm (14–16%), 0.2–0.4 mm (15–16%), 0.4–0.7 (37–39%), 0.70–1.4 mm (15–17%), 1.4–1.7 mm (13–15%) and <1.7 mm (0–2%). The temperature during the briquetting at the die-region of briquetting plant reached >200 °C. Gangil (2015a) has highlighted the characteristics of the raw and briquetted material.

In TG analysis, exactly the same thermogravimetric heating method was used for SS and SB. The heating method was to maintain the temperature at 35 °C in TGA for 2 min and then to raise the TGA-temperature at different heating rates (β) from 35 °C to 1000 °C in nitrogen environment. For TGA experiments, four β (10, 20, 30 and 40 °C/min) were used.

Kinetics using the integral isoconversional Friedman method

The Friedman kinetics equation (Sbirrazzuoli et al., 2009) is stated as

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(A) + \ln(f(\alpha)) - \frac{E}{RT} \quad (1)$$

$$\alpha = \frac{w_i - w_t}{w_i - w_t} \quad (2)$$

where; α, conversion fraction; t, reaction time; A, Arrhenius pre-exponential factor; $f(\alpha)$, reaction model; E, activation energy; R,