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# Benefits of weakening in thermogravimetric signals of hemicellulose and lignin for producing briquettes from soybean crop residue

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ABSTRACT

Thermogravimetric signals of hemicellulose and lignin were found to subside due to the binderless briquetting of soybean crop residue. Minor but distinct thermogravimetric signals of secondary charring reactions were observed in raw crop residue and its briquetted biofuel. The bio-component related kinetics was evaluated using the Kissinger method. Activation energy level of intrinsic cellulosic biopolymer was found higher in briquette than that level in crop residue. The activation energy profile with respect to conversion fraction for raw residue and its briquette was analyzed by the Kissinger–Akahira–Sunose method. The activation energy profile of briquette was superior to raw residue of soybean crop showing the better thermal stability in briquetted biofuel, highlighting the benefits of briquetting process. In addition to the physico-chemical transformations occurred in lignin, the hemicellulose and cellulose related transitions were also expected to play positive role for briquetting.



## 1. Introduction

Briquette is the compact solid fuel made from the loose crop residues [1–5]. The formation of briquettes is positive toward better utilization of loose CR (crop residues) for energy generation [4–7]. The briquettes are used as an alternate to wood in combustion and gasification devices. The crop residues are available in a huge quantity after the harvest of the crop [8,9] which can be utilized as a substantial and sustainable renewable energy source. The major constraint in utilization of crop residues as energy source is their low bulk densities [2,4,5,9–11] which vary from 100 to 200 kg/m$^3$. The low bulk density poses problems in handling, transportation and storage of crop residues. Due to less density, the energy density of crop residues is low and the CR also requires a lot of space for the transportation. The biomass based energy generation systems need the biofuel with better flow ability. The fuel having uniform size and shape has better flow ability. Better flow ability of fuel in bio-reactors reduces the chocking and blockage in the bio-energy systems. The easy flow property of crop residues in the bio-energy reactors is poor due to their light weight and irregular shape and size. To deal with these constrains, it is better to convert the crop residues into high density uniform solid biofuel, i.e. briquettes. Briquetting [1–7,9–20] is the process to compress the crop residues to make uniformly sized compact solid pieces of high density, which can be effectively used as fuel. Briquettes can be produced from the loose biomass until the density of 1200 kg/m$^3$. These can cleanly be burnt and therefore are eco-friendly. In India, briquettes are mostly manufactured from saw dust, bagasse, mustard stalk, groundnut shell, cotton stalk and pigeon pea stalks, etc. Basically, almost all lignocellulosic crop residues can be briquetted by using the optimum process parameters of the briquetting [2–7,10]. Mainly, three types of commercial briquetting systems are in use for generation of briquettes which are; i) Screw-press type, ii) Piston-press (die-punch) type and iii) Rotary dies and roller type [1–7,9–20].

In piston-press type systems, a die exists. The raw bio-material is pressed by the piston (ram) through a die, putting very heavy pressure on bio-materials. The raw biomaterial is heated due to high pressure, and its temperature goes up. The inner biomatrix changes and a compact briquette comes out of the system. In screw press type briquetting machine, a conveyer screw conveys the raw material to the die. The conveyer screw is designed in a manner to exert heavy pressure to raw bio-material when the bio-material reaches to the die. The die in the screw press type systems are basically an opening to allow the densified extruded briquettes, out of the machine. A difference in the piston-press and screw-press type briquetting machines is that the first exert pressure in

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regular pulses, whereas in second the pressure is exerted continuously. At present, both types of system are in use to briquette the bio-materials. The energy consumption per unit output is less in piston-press briquetting system [2–5,10].

Briquetting process can be done using the binder or without binder. Binderless briquetting process demands high pressure as well as high temperature as compared to the briquetting with binder. The binders are materials that facilitate the binding of the bio-particles when subjected to relatively low pressure and temperature. The need of binder depends on the bio-material being briquetted. The use of binders increases the production cost of briquettes. Binder may also hinder in the burning process of briquettes. Almost all lignocellulosic material can be briquetted without binder. Cellulose, hemicellulose, lignin are the main components of CR. In briquetting, the raw CR is compressed at high pressures, and temperatures exceeding 200–250 °C are expected in die-region to relax and melt the lignin which fuses the CR particles into briquettes of designed shape and size [2,10]. Lignin works like a binding agent. This is basically a change in the inner bio-matrix due to high pressure and temperature exerted on the bio-material during the briquetting. This can be studied using the TGA (thermogravimetric analysis) wherein a bio-material is subjected to heat in precisely monitored chamber. The thermal degradation of different constituents of bio-material can be identified using TGA for a specific bio-material. Thermal degradation of bio-materials can be assumed to happen in the stages of moisture release, hemicellulose degradation, cellulose degradation and lignin degradation as stated by Vasile et al. [21]. Caballero et al. [22] explained the thermal degradation of lignocellulosic bio-materials as the summation of the independent degradations of their main components. López-González et al. [23] also stated that the devolatilization curve of bio-materials could be taken as the sum of the corresponding individual components contributions. Leadakowicz and Stolarek [24] mentioned that the evolution of each volatile could be considered as a single first order reaction assuming that the constituents of bio-material were evolved by independent parallel reactions. According to Sanchez-Silva et al. [25] hemicellulose had a random and amorphous structure with low strength whereas cellulose had a strong crystalline structure. They also mentioned that lignin showed the highest thermal stability, decomposing in the broader temperature range (200–700 °C), studied and the DTG (differential thermogram) profile of lignin segment was the flattest [25]. Thermal degradation of lignin was very complex as it was heavily cross-linked highly-branched intrinsic biopolymer.

Using thermogravimetric data, the raw SCR (soybean crop residue) and its briquetted biofuel (SB) were compared to investigate about thermal stability of various specific bioconstituents. During briquetting, the crop residues undergoes through stresses due to high temperature and pressure in a semi-confined environment making internal changes in different components of bio-material. There are various methods for determination of kinetics [4,5,21–40] of thermal degradation, like Friedman method, Coats–Redfern method, Kissinger, Kissinger–Akahira–Sunose (KAS) method, and Ozawa–Flynn–wall (OFW), etc. The KAS, OFW and Coats–Redfern methods are integral isoconversional methods whereas Friedman is differential method [4,5,26,27,29]. Kissinger method is basically not an isoconversional method. This method is used to find the kinetics of different biocomponents based of the temperature-location corresponding to maximum degradation rate associated with a specific bioconstituent. In Kissinger method also, studies at the different β are required to find the activation energies related to different components of the biomaterials. At the other end, Kissinger–Akahira–Sunose (KAS) method has ability to scan the kinetics in relation to conversion fraction of mass during thermal degradation. Kinetics is needed for designing of the energy devices to use the raw biomaterials and their briquettes as biofuel. This article presents comparative thermogravimetric kinetics of soybean crop residue and its briquette. Thermogravimetric changes occurring due to briquetting stresses in the biomaterial were explained on the basis of activation energy profiles of SCR and SB.

## 2. Materials and methods

The residues of soybean crop were taken for study. Thermogravimetric analyses of crushed biomaterial of SCR and crushed biomaterial of the briquettes (made from SCR) were done to understand the internal physico-chemical transformations, affecting the thermal stability of the different biocomponents, occurred during the briquetting process. Thermogravimetric analyzer (Model: pyris-6; Make: Perkin Elmer) was used. Thermogravimetry provided the information about the weight loss (%) of biomaterial with respect to the temperature or time (thermogram) during the thermal degradation process. The first order derivative (degradation rate profile) plot of the thermogram gave the weight loss rate *versus* temperature or time, i.e., about the degradation rate, %/min. Degradation rate profile is termed as "DTG (differential thermogram)".

For analysis, the exactly same thermogravimetric heating method was taken for both types of materials. The heating method was to maintain the TGA temperature at 35 °C for two minutes and then to raise the temperature at different heating rates (β) from 35 °C to 1000 °C in the nitrogen (flow rate 30 ml/min) environment. Four β (10, 20, 30 and 40 °C/min) were used for TGA experiments. For TG-analysis, raw SCR were crushed and then crushed material was briquetted. The briquettes were again crushed for TG analysis. The sieve analysis was done for crushed raw SCR and crushed SB. The particle distributions of crushed biomaterials from both (i.e., SB and SCR) were done in the size ranges of >0.2 mm, 0.2–0.4 mm, 0.4–0.7 mm, 0.70–1.4 mm, 1.4–1.7 mm and <1.7 mm. The specimens for TG-experiments were taken from the size range (0.4–0.7 mm) which gave the highest portion of crushed material (38–40% of total crushed biomaterial) in sieve analysis. Therefore, the particle size selected for TG-experiment was 400–700 μm for biomaterials obtained by crushing the SB and SCR. Hence, for TG-analysis, the samples were drawn from the crushed form of the SCR and SB, having similar particle size and similar masses. The masses taken for repetitive TGA runs for SCR and SB were 10 ± 2 mg. The pyris-6 thermogravimetric analyzer used the exactly same crucibles for all runs. As the particle size for TG-samples taken from biomaterial of SB and SCR was same (400–700 μm), the effects of bulk density and porosity, especially during TG-experiments, were minimized. Therefore, the present paper essentially presents the changes occurring in the intrinsic biopolymeric components due to briquetting stresses.

The bulk densities of soybean crop residues, brought from the farmer's fields, were 120 ± 20 kg/m$^3$ (ar). The SCR was crushed and the bulk density of crushed SCR was 245 ± 5 kg/m$^3$. For forming the

**Table 1**
Characterization of crushed SCR and SB, used for TG-analysis.

| | Proximate analysis % (db) | | | Ultimate analysis % (db) | | | | Density (kg/m$^3$) |
|---|---|---|---|---|---|---|---|---|
| | Moisture | Volatiles | Ash | C | H | N | S | |
| Crushed SCR (400–700 μm) | 9 ± 3 | 72 ± 3 | 4.0 ± 0.3 | 39 | 7 | 2 | 0.5 | 245 ± 5 |
| Crushed SB (400–700 μm) | 7 ± 3 | 70 ± 3 | 6.5 ± 0.3 | 40 | 6 | 2 | 0.5 | 250 ± 5 |

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