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Effects of bio-additives on the physicochemical properties and mechanical behavior of canola hull fuel pellets

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ABSTRACT

Agricultural residues can be converted to value-added products such as fuel pellets. Bio-based additives, including alkali lignin, glycerol and L-proline were used for binding formulation of canola hull fuel pellets. The binding formulation was optimized to produce pellet with the mechanical durability (by drop test) of 99%, relaxed density of 1,110 kg/m^3, and energy density of 18,603 MJ/m^3. L-proline showed the best performance in the enhancement of mechanical properties of pellet when compared with other two amino acids. Comparing with pure glycerol, use of crude glycerol decreased compression energy required for pelletization, but resultant pellet had lower tensile strength. SEM and light microscopy showed the effects of lacking moisture, lignin and L-proline in the formulation. Synchrotron-based computed tomography was used for 3D imaging of fuel pellets yielding estimated porosity values over a range of 1.3–5.7% for different fuel pellets. The effects of pelletization operating conditions were also investigated on the pellets.

1. Introduction

The production of value-added materials from low-value agricultural feedstocks or processing to produce by-products increases the profitability of agro-industries, reduces waste generation and has positive impacts on rural economy. These abundant agricultural feedstocks can be converted to fuel pellets, which have a wide range of applications in power industry as fuel (combustion/co-gasification) and can also be exported to rural areas that rely on solid fuels. Biomass residue is one of the most prospective energy resources to meet the demand of the growing economy. The agricultural wastes are renewable energy resources that can reduce carbon emission when compared to fossil fuels [1,2]. The low bulk density of biomass (<150 kg/m^3), irregular shapes and different sizes limit their transportation, storage and utilization in actual form [3–5]. Densification increases biomass density by 4–10 times which reduces transportation cost and storage space with convenient material handling and less dust formation [3,6]. Densification of biomass into pellets makes the material to uniform shape and sizes for easy handling, which can be directly used for thermochemical processes such as combustion, gasification, pyrolysis or co-firing with coal depending on the ingredients of the fuel pellet [7].

Biomass feedstock used in this study was the material obtained after harvesting and during the screening of canola seed. Although it is termed as canola hull, but this feedstock includes hull, pod, some pieces of leaves, and fine grains, which can pass through combine harvester. In 2016, canola production has been 18.4 and 9.7 million tonnes in Canada and Saskatchewan, respectively [8]. The amount of canola hull collected from harvesting and screening of canola can be estimated at least 10 wt% of the product.

Due to the increasing amount of lignin, glycerol and amino acids obtained, respectively from the pulp and paper industries, biodiesel refineries, and corn wet milling industries, the focus of this research was on the possible application of these bio-based ingredients for the production of biomass fuel pellets. Considering the variety of these bio-additives produced in the chemical industries, two different types of lignin, three different types of amino acids, as well as crude and purified glycerol were used in this study to evaluate their effects on the fuel pellet properties.

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Lignin is well known for its bonding and hydrophobic properties. It is present in the plant cell wall and covalently binds with cellulose and hemicelluloses. After cellulose, lignin is the second most abundant organic polymers on the Earth [9]. Lignin is obtained as a waste or by-product in the production of pulp and bioethanol from biomass precursors [10]. Lignin has a relatively high heating value of 23.3–25.6 MJ/kg, which is nearly 30% greater than that of cellulose and hemicellulose together [11].

Glycerol is another bio-additive used in this project. Worldwide bio-diesel production of 30.1 billion liters in 2015 [12] leads to the production of ~3.0 billion liters of crude glycerol [13,14]. The main by-products of biodiesel refineries are fatty acids, methanol and glycerol [15]. The typical biodiesel-to-glycerol weight ratio is 9:1 in a biodiesel refinery [16]. Canada generates about 43,860 tonnes of crude glycerol from 500 million liters of its annual biodiesel production [17]. Glycerol can act as co-binder [18] and lubricant to reduce the energy required for densification.

From the mechanical point of view, amino acids can be used as a plasticizer in the pellet structure. This property will fortify the mechanical strength and durability of the pellet by increasing its mechanical flexibility. L-Proline is one of the amino acids which has been identified as an effective plasticizer for carbon-based material. It can decrease the glass transition point of carbon materials and has low toxicity compared with other plasticizers [19,20].

The objectives of this study were: (1) to produce fuel pellets from canola hull using bio-additives including binder, lubricant and plasticizer; (2) to optimize the pellet formulation for developing pellets with appropriate density and mechanical strength; and (3) to investigate the effects of ingredients on the chemical and mechanical properties of the fuel pellets.

2. Experimental

2.1. Feedstock

Canola hull was used as the precursor for manufacturing fuel pellets. It was provided by the Milligan Biofuels Inc. (SK, Canada) and was ground using a knife mill (Retsch GmbH, 5657 HAAN, Germany). For pelletization, biomass particle size in the range of 100–1,750 μm was preferred. Grinding of materials was used as an efficient method for making a homogenized batch of feedstock. At the beginning, ~1.0 kg of ground/sieved canola hull was prepared. This biomass batch was thoroughly mixed using a mixer. This batch was used for the pelletization experiments. Before preparation of each formulation, the ground canola hull was dried overnight at 105 °C in an oven (Model 31479, Precision Scientific Co., Chicago, IL, USA), before densification. To ensure the consistent characteristics of feedstock used for preparation of formulations, ash content, moisture content, and ultimate (CHNSO) analysis were performed for feedstock batches. Considering seasonal availability of biomass precursors, these probing techniques are required for any biomass process. However, in this set of experiments, the quality of biomass was consistent which can be because of using only one batch of biomass (received from the provider), grinding/sieving of feedstock, and mixing appropriately. Sawdust was collected from a local sawmill in Saskatoon (SK, Canada) to study the effect of using combined precursor in pelletization.

2.2. Additives

Alkali lignin (low sulphonate content) was procured from Sigma-Aldrich (ON, Canada). De-alkaline Lignin was obtained from TCI America. High purity glycerol (assay: 99.7 wt%) was procured from Fisher Scientific (ON, Canada). L-Proline (assay: ≥ 99 wt%) was obtained from Sigma-Aldrich (ON, Canada). Glycine was obtained from Ward's Scientific (ON, Canada). Nipecotic acid was purchased from Sigma-Aldrich (ON, Canada). Crude glycerol was provided by the Milligan Biofuels Inc. (SK, Canada), and its composition is as follows: glycerol 40, matter organic non-glycerol (MONG) 55, and moisture 5 (all in weight basis). Details of this crude glycerol composition can be found elsewhere [21].

2.3. Preparation of sample and densification

Required amount of solid additives (alkali lignin and amino acid) was added to ~40 g of dry, ground, homogenized canola hull (100–1,750 μm) for each formulation. The mixture was blended using a blade mixer. The glycerol was mixed with required amount of water and the solution was sprayed on the mixture of precursor and solid additives. This mixture was manually homogenized using a spatula for ~10 min. Then, this mixture was kept, in a closed container, for ~72 h at 5 °C in an environmental chamber and was mixed every 12 h.

All samples were densified in a lab scale single-pelleting unit (Instron 5966, Dual Column Tabletop Testing Systems, Instron Corp. Norwood, MA, USA). The densification unit composed of a plunger-die assembly. The internal diameter of a steel cylinder assembled on the Instron testing machine was 6.5 mm and fitted with a 10 kN load cell. The die was surrounded with a dual element heating tape (Cole-Parmer Instrument Company, Vernon Hills, IL, USA) to maintain the desired temperature during densification. The die was positioned on a raised base, which consisted of a sliding gate at the bottom allowing the ejection of the pellet after densification. The plunger was attached to the upper moving crosshead of the testing machine.

Once the die reached the set temperature, a weighed quantity of sample (0.5 ± 0.02 g) was loaded into the die. During the densification process, the initial compressive force of 500 N was applied to the sample. The plunger moved down to the pre-set speed 0.67 mm/s and stopped for 15 s at the applied load of 500 N. This allowed the material to reach the desired set temperature. After 15 s, the plunger moved down with a speed of 0.42 mm/s, and the pre-set final compressive force was applied to densify the sample. Once the pre-set load was attained, the plunger stopped and retained in place for the desired relaxation time. It prevented spring back action of compressed sample [22]. The plunger was withdrawn to release the applied load, and the sliding gate was opened. After 30 s, the plunger moved down to eject the pellet. Industrial pelletization is carried out by using extrusion process. At the first stage, temperature of the particles increases by this process and also by the friction between material and metallic surface of the extruder. In this experiment, heating element around die and 15 s residence time at initial applied load (500 N) were used to provide a uniform elevated temperature distribution in biomass feedstock. The initial compaction in industrial pelletization is for the removal of air trapped between particles and making a packed structure of particles [23]. The initial applied load (500 N) is used for providing this condition. In the next step of pelletization (increase in pelletization load to final set load), particles undergo through different deformation based on their elastic and plastic properties [23].

2.4. Experimental plan

Central composite design (CCD) was used to design the experiments. Four parameters including concentrations of alkali lignin (2–6 wt/wt%), glycerol (4–10 wt/wt%), L-proline (2–6 wt/wt%), and water (11–17 wt/wt%) were considered as the main factors. All concentrations were calculated as the percentage of compound mass with respect to precursor mass. To specify the range of water concentration required for canola hull pelletization, some