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Pretreatment and fractionation of barley straw using steam explosion at low severity factor

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ABSTRACT

Agricultural residues represent an abundant, readily available, and inexpensive source of renewable lignocellulosic biomass. However, biomass has complex structural formation that binds cellulose and hemicellulose. This necessitates the initial breakdown of the lignocellulosic matrix. Steam explosion pretreatment was performed on barley straw grind to assist in the deconstruction and disaggregation of the matrix, so as to have access to the cellulose and hemicellulose. The following process and material variables were used: temperature (140–180 °C), corresponding saturated pressure (500–1100 kPa), retention time (5–10 min), and mass fraction of water 8–50%. The effect of the pretreatment was assessed through chemical composition analysis. The severity factor R_0 , which combines the temperature and time of the hydrolytic process into a single reaction ordinate was determined. To further provide detailed chemical composition of the steam exploded and non-treated biomass, ultimate analysis was performed to quantify the elemental components. Data show that steam explosion resulted in the breakdown of biomass matrix with increase in acid soluble lignin. However, there was a considerable thermal degradation of cellulose and hemicellulose with increase in acid insoluble lignin content. The high degradation of the hemicellulose can be accounted for by its amorphous nature which is easily disrupted by external influences unlike the well-arranged crystalline cellulose. The carbon content of the solid steam exploded product increased at higher temperature and longer residence time, while the hydrogen and oxygen content decreased, and the higher heating value (HHV) increased.

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1. Introduction

The depleting fossil fuel resources along with global warming associated with greenhouse gas (GHG) emission has been a

serious concern to the global community. Presently, this has necessitated looking for a renewable, sustainable, and environmentally friendly energy. Lignocellulosic biomass has been identified as one of the renewable, near carbon neutral,

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and local fuel sources to complement fossil fuels and to contribute to energy security [1]. It is estimated that the worldwide annual production of lignocellulosic biomass (agricultural and forest resources) is approximately 200 Gt [1]. However, there are some challenges associated with the use of lignocellulosic biomass. Lignocellulosic biomass is a complex formation of cellulose, hemicellulose, and lignin. The lignin acts as an external crosslink binding the hemicellulose and cellulose with cellulose positioned at the inner core of the structure [2,3]. This nature of lignocellulosic biomass matrix makes it naturally resistant to the microbial and enzymatic degradation needed for biochemical conversion. Hence, the goal for the biofuel industry is to make the process technically feasible and economically attractive. Many pretreatment technologies have been applied in the past decades to deconstruct and fractionate a complex lignocellulose structure to its simpler molecules.

Canada has a large agricultural sector with barley production as the second largest crop behind wheat [4]. This implies that Canada will play a very significant role in the development of the biorefinery sector because of its contribution as a predominant supplier or source of biomass feedstock. Barley straw has a higher mass fraction of cellulose (40%) than wheat straw (30%), although wheat straw has a higher mass fraction of hemicellulose (50%) than barley straw (20%), with both substrates having similar mass fraction of lignin (15%) [5,6]. Perusal of the literature shows that a lot of research has been done on wheat straw; therefore, there is a need to explore the potential of barley straw for the biofuel industries. Hence, for these reasons as well as its higher cellulose content than wheat straw, barley straw was chosen for this work.

1.1. Steam explosion

Steam explosion is operated by introducing the feedstock into the reactor and heating under steam pressure (2000–5000 kPa; 200–260 °C) for a few minutes [7]. Steam explosion induces chemical effects because water itself acts as an acid at high temperatures [8]. In the course of the process, hemicellulose is hydrolyzed by acetic acid and other acids, and the hemicellulose eventually becomes water-soluble [7,8]. Cellulose is slightly depolymerized, lignin softens and is eventually depolymerized. The reaction is instantaneously interrupted by sudden opening of the reactor to depressurize the treated material which is discharged through a nozzle into a collection vessel [7]. The sudden decompression rapidly decreases the temperature and quenches the reaction at the end of the pretreatment. The rapid thermal expansion involved in the termination of the reaction opens up the particulate structure of the biomass [8]. However, at excessive conditions (high temperatures and pressures), there is degradation of xylose (a hemicellulose) to furfural and glucose (a cellulose monomer) to 5-hydroxymethyl furfural [7,9]. Furfural is an undesirable compound in a fermentation process because it inhibits microbial growth and activity [7,9]. Chornet and Overend [10] reported that the severity of thermal pretreatment depends on the combined effects of temperature and moisture particularly in the amorphous compounds in biomass. In the present study, we hypothesized that using higher biomass initial

moisture content and lower temperature could damp the severe steam explosion pretreatment conditions and lead to reduction in the degradation of the xylose and glucose. Chemical consequences of thermal treatment of lignocellulosics either in a suspension (large amount of liquids present) or in steaming processes (low amount of free water present) was summarized by Chornet and Overend [10] as follows: “the extent of disaggregation of lignin-carbohydrates complexes is a function of the severity of the treatment, and the degree of depolymerization of hemicellulose and cellulose polymers and the rupture of glycosidic bonds”.

1.2. Severity factor

Due to the different types of available lignocellulosic biomass, a severity factor has been developed to combine and normalize the process parameters of steam explosion so as to facilitate comparisons [10]. Effort has been in progress to minimize product degradation resulting from pretreatment conditions. The rate constant of the severity factor, according to Chornet and Overend [10] can be described by the Arrhenius model:

$$k = Ae^{-\frac{E_a}{RT}} \quad (1)$$

k = rate constant; A = Arrhenius frequency factor; E_a = activation energy ($\text{kJ kg}^{-1} \text{mol}^{-1}$); R = universal gas constant ($8.314 \text{ kJ kg}^{-1} \text{mol}^{-1} \text{K}^{-1}$); T = absolute temperature (K).

The reaction ordinate was developed as:

$$R_o = \int_0^t \exp\left[\frac{(T_r - T_b)}{14.75}\right] dt \quad (2)$$

R_o = reaction ordinate; t = residence time (min); T_r = reaction temperature (°C); T_b = base temperature at 100 °C; (14.75 is the conventional energy of activation assuming that the overall process is hydrolytic and the overall conversion is first order), therefore;

$$R_o = t \exp\left[\frac{(T_r - 100)}{14.75}\right] \quad (3)$$

The log value of the reaction ordinate gives the severity factor which is used to map the effects of steam explosion pretreatment on lignocellulosic biomass.

$$\text{Severity} = \log_{10}(R_o) \quad (4)$$

Heitz et al. [11] reported that it is possible to directly translate results obtained from laboratory steam explosion pretreatment processes into industrial practice by employing the concept of a severity factor. This is similar to those used in pulping industry which integrates temperature and retention time into a single measure for the purpose of controlling the process [12].

Chum et al. [13] investigated the effect of acid catalyzed pretreatment on aspen (*Populus tremuloides*). These authors included a pH term to equation (7) above to compensate for the contribution of the added acid. Severity parameter that reflects acidity or alkalinity functions can be very useful tool in the planning of experiments for pretreatment process that requires the addition of catalyst (acid/base) [13]. However, it

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