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Short Communication

Sequential extrusion-microwave pretreatment of switchgrass and big bluestem

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HIGHLIGHTS

- Sequential pretreatment enhanced sugar recovery for switchgrass and big bluestem.
- Similar to extrusion, no potential fermentation inhibitors found in sequential pretreatment.
- No effluent production therefore no disposal cost associated with this sequential pretreatment.

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ABSTRACT

Developing an effective and economical biomass pretreatment method is a significant roadblock to meeting the ever growing demand for transportation fuels. Earlier studies with different feedstocks revealed that in the absence of chemicals, neither extrusion nor microwave could be standalone pretreatments. However, there is potential that the advantages of these individual methods can be harnessed in a sequential pretreatment process. Accordingly, switchgrass and big bluestem were extruded and then subject to microwave pretreatment, under optimal conditions that had been separately determined in prior studies. Pretreated biomass was then subject to enzymatic hydrolysis to understand the effectiveness of the sequential pretreatment on sugar recovery and generation of fermentation inhibitors. Statistical analysis confirmed that moisture content, microwave power level, and exposure time (and their interactions) had significant influence on sugar recovery. Sequential pretreatment of switchgrass (25% moisture, 450 W and 2.5 min) resulted in a maximum glucose, xylose, and total sugar recovery of 52.6%, 75.5%, and 59.2%, respectively. This was higher by 1.27 and 2.71, 1.21 and 4.60, and 1.25 and 2.87 times compared to extrusion alone and the unpretreated control, respectively. The same sequential pretreatment conditions achieved maximum glucose, xylose, and total sugar recovery of 83.2%, 92.1%, and 68.1%, respectively, for big bluestem. This was 1.14 and 4.1, 1.18 and 2.7, and 1.20 and 3.0 times higher than extrusion alone and the unpretreated control, respectively. This sequential pretreatment process did not aggravate acetic acid formation over levels observed with the individual pretreatments. Furthermore, furfural, HMF, and formic acid were not detected in any of the treatments. Although the sequential pretreatment process enhanced sugar recovery without increasing the levels of potential fermentation inhibitors, the increased energy input for the microwave treatment may not be economical.

1. Introduction

To meet the ever growing demand for transportation fuels, alternative renewable energy resources have been explored for the past three decades. A variety of biomass resources have been investigated due to their abundance, low cost, and renewable nature. Unfortunately, biomass has a recalcitrant and complex structure, requiring more intensive pretreatment compared to the grinding and hydrolysis steps used in corn-ethanol production. Scientists have investigated a variety of physical, chemical, and biological pretreatment processes to increase biomass susceptibility to enzymatic hydrolysis. Most of the leading pretreatment technologies have their merits and demerits; hence the search for an effective and economical pretreatment process continues.

Extrusion is a continuous, scalable, and effective pretreatment process that minimizes production of fermentation inhibitors (saving detoxification costs), generates no effluent (saving treatment costs), and requires no feedstock washing (saving water and treatment costs). It is a well-established technology in plastic

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and food sectors, and is safe to operate. Sugar recovery from several feedstocks subjected to extrusion alone (without any chemical treatment) has ranged from 50% to 75% (Karunanithy and Muthukumarappan, 2012; Karunanithy et al., 2012). Therefore, it is possible that combining extrusion with another pretreatment approach may further enhance subsequent hydrolysis.

Heat is used to enhance disruption of biomass structure in most pretreatments processes (e.g., dilute acid, ammonia fiber expansion, steam and steam explosion, extrusion). Earlier studies revealed that microwave heating is better than conventional heating (Hu and Wen, 2008) and sand bath heating (Shi et al., 2011); requires less energy (Vani et al., 2012) and reduces pretreatment time (Binod et al., 2012). Moreover, microwave heating is volumetric heating that can have an explosion effect similar to popcorn. Although microwave pretreatment (without any chemicals) reduces the recalcitrance of biomass, subsequent hydrolysis yields (20–60%) are not sufficient for commercialization (Hu and Wen, 2008; Ma et al., 2009).

As noted, neither extrusion nor microwave pretreatment can be a standalone method, however they can be easily combined in a sequential process. First, size reduced feedstock can be moistened to an appropriate level and then processed through an extruder. Feedstock from the extruder die section can be easily channelized onto a moving conveyor where microwave heating can be applied. Prior microwave pretreatment research has shown that microwave power level, exposure time, feedstock particle size, feedstock moisture content, and chemical concentration are important variables that affect microwave. Literature review reveals that there was no previous study where the combination of extrusion and microwave for any of the feedstock including switchgrass and big bluestem. Considering the proposed sequential extrusion-microwave pretreatment, moisture content, microwave power level, and exposure time are the most relevant independent variables. Therefore, the objective of the present study is to investigate the effect of these variables on sugar recovery and fermentation inhibitor production from optimally extruded switchgrass and big bluestem.

2. Methods

2.1. Biomass preparation

Matured switchgrass and big bluestem obtained from local farm were ground in a hammer mill (Speedy Jr., Winona Attrition Mill Co., MN) using 8 mm sieve and stored in an airtight container at room temperature until further pretreatment. Geometrical mean diameter of ground switchgrass and big bluestem was 0.64 and 0.40 mm, respectively (ASAE S319.4, 2008). The particle size distribution peaked between 0.3 and 1.2 mm for switchgrass and 0.4–0.8 for big bluestem. Moisture content of the biomass samples was determined as described in NREL/TP-51-42621.

2.2. Extrusion-microwave pretreatment

The sequential pretreatments are shown in Fig. 1. A laboratory scale microwave oven (Advantium 120 model SCA 1001KSS02, GE Appliances, Louisville, KY, USA) with a maximum of 900 W and it had provision to vary the power levels from 10% to 100% was used in the present study. Each experiment was carried out in duplicate by placing 100 g of extruded and moisture balanced feedstock on a Petri dish. Temperature measurement after microwave pretreatment ranged between 50 and 85 °C depending upon the conditions accordingly the final weight ranged between 20 and 75 g.

2.3. Enzymatic hydrolysis

Enzymatic hydrolysis of pretreated samples (0.3 g in 10 ml hydrolysis volume) was carried out using 0.1 M, pH 4.8 sodium citrate buffer for 72 h at 50 °C and 150 rpm as described in NREL/TP-510-42629. Based on the previous studies, the cellulase (activity 70 FPU/g) dosage at 15 FPU/g dry matter and the ratio of cellulase to β-glucosidase (activity 250 CBU/g) was maintained at 1:4 (Karunanithy and Muthukumarappan, 2012). After hydrolysis, samples were kept in boiling water for 10 min to inactivate enzymes, then centrifuged at 13,000 rpm for 15 min. The supernatant was frozen twice with an intermediate centrifugation to remove precipitates prior to injection into the HPLC.

2.4. Sample analysis

Soluble sugars and byproducts were quantified using an HPLC (Agilent Technologies, Santa Clara, CA; Bio-Rad Aminex 87H column, Hercules, CA) as mentioned in NREL/TP-510-42623. Ground switchgrass and big bluestem were also subjected to enzymatic hydrolysis and analyzed as the control. The sugar concentration obtained from each chromatogram was divided by dry weight of biomass taken for enzymatic hydrolysis to calculate the percentage of different sugars. Sugar recovery was calculated using Eqs. (1) and (2) given below. The sugar recovery reported in this paper was after the enzymatic hydrolysis of the pretreated samples. Acetic acid was the only byproduct found in the pretreated samples and their concentration was reported in gram per litre:

$$Y_{\mathrm{i}} = \frac{S_{\mathrm{ip}}}{S_{\mathrm{ir}}} * 100 \tag{1}$$

$$Y_{\mathrm{c}} = \frac{\sum S_{\mathrm{ip}}}{\sum S_{\mathrm{ir}}} * 100 \tag{2}$$

Y_{i} – individual sugar recovery (%), Y_{c} – combined sugar recovery (%), S_{ip} – individual sugar obtained in hydrolysate of pretreated samples after enzymatic hydrolysis through HPLC, S_{ir} – individual sugar from raw material.

2.5. Statistical analysis

Extruded switchgrass and big bluestem when subjected to microwave pretreatment resulted in a full factorial design of 54 treatment combinations per feedstock (3 moisture content × 3 microwave power level × 3 exposure time × 2 replication = 54). The data were analyzed with GLM procedure to determine the main, interaction and treatment combination effect in SAS 9.1 (SAS Institute, Cary, NC) using a type I error (α) of 0.05.

3. Results and discussion

3.1. Main effect of moisture content, microwave power and exposure time on sugar recovery

The effects of independent variables on sugar recovery from both feedstocks are shown in Fig. 2. As noted from Fig. 2, extrusion significantly increased sugar recovery compared to control. When the extruded material was then adjusted to 25% moisture and subjected to microwave treatment at a power level of 180–720 W and for 2.5–10 min (Fig. 2), glucose, xylose, and total sugar recoveries increased by 11.9%, 13.0%, and 15.8%, respectively, for switchgrass. Similar improvements of 11.5%, 9.2%, and 14.7%, respectively, were observed for extruded and microwave pretreated big bluestem.

As can be seen in Fig. 2, increasing moisture content from 25% to 75% either had no effect on or decreased glucose, xylose, and total