



Original Research Paper

Process analysis of superheated steam pre-treatment of wheat straw and its relative effect on ethanol selling price

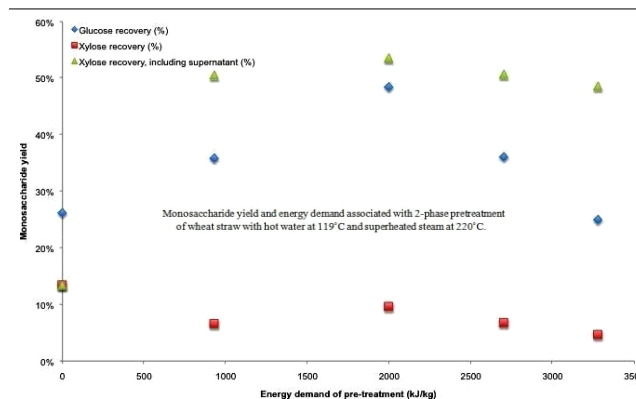
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HIGHLIGHTS

- Examined superheated steam as a method of pre-treatment for lignocellulosic wheat straw.
- Glucose yield from material pre-treated with superheated steam was measured at 47%.
- Preliminary economic evaluation of the pre-treatment method showed that using superheated steam would produce ethanol as economically as if steam explosion was used.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 7 October 2014
 Received in revised form 13 November 2014
 Accepted 26 November 2014
 Available online 1 December 2014

Keywords:

Superheated steam
 Bioethanol
 Lignocellulose
 Wheat straw
 Pre-treatment

ABSTRACT

Existing bioethanol operations rely on starch-based substrates, which have been criticized for their need to displace food crops in order to be produced. As an alternative to these first generation biofuels, the use of agricultural residues is being considered to create more environmentally-benign second generation, or cellulosic biofuels. Recalcitrance of these substrates to fermentation requires extensive pre-treatment processes, which often consume more energy than can be extracted from the ethanol that they produce, so one of the priorities in developing cellulosic ethanol is an effective and efficient pre-treatment method. This study examines the use of superheated steam (SS) as a process medium by which wheat straw lignocellulosic material is pre-treated. Following enzymatic hydrolysis, it was found that 47% of the total glucose could be liberated from the substrate, and the optimal conditions for pre-treatment were 15 min in hot water (193 kPa, 119°C) followed by 2 min in SS. Furthermore, a preliminary relative economic analysis showed that the minimum ethanol selling price (MESP) was comparable to that obtained from steam explosion, a similar process, while energy consumption was 22% less. The conclusion of the study is that SS treatment stands to be a competitive pre-treatment technology to steam explosion.

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1. Introduction

Growing concern surrounding the scarcity of fossil fuels has spurred research into alternative renewable sources for high energy density liquid fuels, such as biologically-derived ethanol. Existing operations rely heavily

on sugar- and starch-based ethanol production from dedicated crops such as corn in the United States and sugarcane in Brazil, though the former has been criticized in terms of the net energy balance achieved by the conversion

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Abbreviation	Definition
AOAC	Association of Official Agricultural Chemists
AFFCO	Association of American Feed Control Officials
HPLC	High performance liquid chromatography
MESP	Minimum ethanol selling price
NREL	National Renewable Energy Laboratory
SS	Superheated steam

process (Shapouri et al., 2002). Increasingly, development of biologically-derived fuels has encountered resistance due to the 'food versus fuel' debate, proponents of which state that displacing food crops for the purpose of cultivating fuel crops is ethically questionable (Pimental, 2003). Among the manifestations of these concerns is the shift from sugar and starch substrates (referred to as 1st generation biofuels) to cellulosic substrates (2nd generation biofuels), obtained from agricultural residues and byproducts, forgoing the need to displace existing food crops for the purpose of fuel production.

Lignocellulosic agricultural residues such as wheat straw represent a promising resource in terms of abundance, feedstock cost, and environmentally benign production (Saha et al., 2005; Brodeur et al., 2011), and can be successfully hydrolyzed and subsequently fermented into ethanol by a variety of organisms (Lynd et al., 2005). While initially attractive, one drawback inherent in the utilization of wheat straw is its relatively high lignin content when compared to corn or sugarcane (Kaparaju and Felby, 2010). Lignin is problematic in that it renders the substrate recalcitrant to hydrolysis and fermentation, resulting in low yields from raw material. Consequently, intensive pre-treatment prior to hydrolysis is required to achieve yields suitable for economical large-scale fuel production (Mosier, et al., 2005). As the pre-treatment can represent a large proportion of the overall conversion cost, it is currently a barrier to widespread adoption in industry (Wyman, 2007).

Several effective pre-treatment technologies have been developed, with varying effectiveness across a variety of substrates. These include, among others, physical, liquid hot water, steam explosion, acid hydrolysis, lime, and wet oxidation pretreatment. A summary of the effects and conditions of various pre-treatment methods are shown in Table 1 (Talebna et al., 2010). The energy-intensive nature of these pre-treatment methods contributes substantially to their prohibitive costs (Egeman and Elander, 2005). In addition to the process economics, the large energy expenditures involved in the pre-treatment shift the energy balance more unfavorably for lignocellulosic feedstocks (von Blottnitz and Curran, 2007). The overall conversion process stands to benefit greatly from improvements in the pre-treatment component.

Table 1.
Effects of pre-treatment methods on sugar yields from wheat straw.

Pre-treatment	Condition	Effect
Physical		
Ball milling	Hammer milling at 11.4 kWh/t, 2 hours	Degree of saccharification increased from 17.7% to 61.1% ^a
Thermal		
Liquid hot water	80°C, 5-10 mins followed by 195°C, 6-12 min	Increased recovery of hemicellulose and cellulose to 70% and 93%, respectively ^b
Steam explosion	230°C, 1 min	Increased recovery of hemicellulose and cellulose to 83.7% and 93.5%, respectively ^c
Chemical		
Acid hydrolysis	170°C, sulfuric acid	98% of theoretical glucose yield following enzymatic hydrolysis ^d
Lime	50°C -135°C, 1 - 24h	Reducing sugar yield increased by factor of 10 ^e
Oxidative		
Wet oxidation	10 bar pressure, 170°C	Enzymatic convertibility of cellulose increased to 85% ^f

^a Pedersen and Meyer, 2009

^b Perez et al., 2008

^c Beltrame et al., 1992

^d Kootstra et al., 2009

^e Chang et al., 1998

^f Bjerre et al., 1996

This study examines the use of superheated steam (SS) as a means of pre-treating wheat straw prior to enzymatic hydrolysis without the use of chemical catalysts and at a potentially reduced energy expenditure. Superheated steam has been successfully implemented into industrial processes such as food processing and drying and biomass decontamination and has led to substantial increases in energy efficiency due to high penetration and energy delivery (Cenkowski et al., 2007; Pronyk et al., 2004). Thermal processes such as steam explosion have been used successfully for pre-treatment of lignocellulosic biomass, though in addition to generation of toxic by-products, it requires the addition of acid catalyst for best results (Alvira et al., 2010). Pretreatment with SS could provide a more energy efficient process, without the need for acid catalysis or the generation of inhibitory compounds.

Economic feasibility of producing ethanol from lignocellulosic substrates has been hampered by the intensive nature of the pre-treatment processes, and the pursuit of more efficient pre-treatment technologies is an important factor (Wyman, 2007).

The objectives addressed in this paper are the effectiveness of SS pre-treatment of lignocellulosic wheat straw in terms of glucose yield from enzymatic hydrolysis, and a relative analysis of the effect that using this pre-treatment method would have on the selling price of ethanol produced.

2. Thermal pre-treatment

Typical thermal pre-treatments targeting delignification of lignocellulosic substrates such as steam explosion operate at temperatures of 180 to 230°C (Talebna et al., 2010). Additionally, depolymerization of lignin occurs at approximately 180°C, and thermal pre-treatments resulting in increased digestibility have been shown to be effective at temperatures ranging from 170 to 270°C (Agbor et al., 2011). The primary goal of an ideal pre-treatment process is to render 100% of the fermentable material accessible to the microorganisms for conversion. The 6-carbon sugars are left intact in the biomass, while the more thermosensitive 5-carbon sugars are recovered from the supernatant (Alvira et al., 2010).

Increased yield has been shown to correlate with the severity of the pre-treatment process (Li et al., 2007), often represented in terms of severity factor, S_o , a function of time and temperature (Overend and Chornet, 1987). However, increasing the pre-treatment temperature can also lead to deleterious effects, such as sugar degradation (decreasing the total theoretical yield), and generation of inhibitory compounds (impeding microbial conversion) (Jönsson et al., 2013). For this reason, the temperature selected for pre-treatment with SS in this study was 220°C.

2.1. Pre-treatment methodology

The raw biomass, wheat straw, was obtained from Biovalco Inc. The theoretical yields of cellulose and hemicellulose from the raw biomass were 0.437 g/g and 0.240 g/g, respectively. A compositional analysis of the raw biomass prior to pre-treatment is shown in Table 2. The analysis was performed by the University of Saskatchewan College of Agriculture and Bioresources in accordance with Association of Official Agricultural Chemists (AOAC, 2011) and Association of American Feed Control Officials (AFFCO, 2009) standards.

Table 2.
Compositional analysis of raw biomass.

Parameter	Composition (%)	Method
Moisture	4.82	AOAC 930.15
Dry matter	95.18	AOAC 930.15
Lignin	10.63	AOAC 973.18
ADF*	54.37	AOAC 973.18
NDF**	78.4	AOAC 2002.04
Cellulose	43.74	cellulose = ADF - lignin
Hemicellulose	24.03	hemicellulose = NDF - ADF

* ADF = acid detergent fibre

** NDF = neutral detergent fibre

Initial tests indicated that the effect of SS pre-treatment was enhanced by the use of hot water prior to exposure to SS. Biomass treated using only SS did not show significant improvement in glucose or xylose yields. For this analysis, the samples were subjected to 15 min of hot water treatment followed by 2, 5, or 10 min of SS treatment, using the following steps:

- 1) Prior to pre-treatment, the raw biomass samples were ground and sieved to <355 μm .
- 2) Samples were then boiled in pressurized hot water (193 kPa, 119°C) for 15 min using a Lagostina 3L pressure cooker.
- 3) Following hot water treatment, the samples were placed into the steam chamber where SS at atmospheric pressure was passed through them for the prescribed duration of time in a batch process.

Temperature stability occurred at 217°C, and this was the temperature used for the calculation of the severity factor of each treatment. Following the pre-treatment, the samples were subjected to enzymatic hydrolysis to verify the degree to which the celluloses and hemicelluloses had been rendered accessible for saccharification. The degree to which the sugars were converted is indicative of the potential for fermentation. Hydrolysis was carried out in accordance with the laboratory analytical procedure released by the National Renewable Energy Laboratory (NREL) for the enzymatic saccharification of lignocellulosic biomass (Selig et al., 2008). The enzymes used were lyophilized powder cellulase (from *Aspergillus niger*, 1.3 FPU/mg) and β -glucosidase (from *Prunus amygdalus*, 7.4 pNPGU/mg) supplied by Sigma-Aldrich. Incubation was carried out at 50°C \pm 1°C for a duration of 96 h followed by high performance liquid chromatography (HPLC) analysis for the presence of glucose and xylose. In addition to the hydrolysate, the supernatant from the hot water phase of the treatment was similarly analyzed. The model of HPLC used was the Breeze 2 system from Waters (Mississauga, ON). The system consisted of an HPX-87H column from Biorad (Hercules, CA) with Micro-guard Cation H+ guard column, and a 2414 refractive index detector. The HPLC system used 5 mM sulfuric acid as the mobile phase at a flow rate of 0.6 mL/min and a column temperature of 45°C.

3. Effect on economy of processing

Proper assessment of a pre-treatment technology must include an economic analysis in order to evaluate its feasibility. Existing literature generally evaluates economic viability on the basis of a minimum ethanol selling price (MESP) resulting from production costs to compare different technologies (Eggeman and Elander, 2005). While this is a useful tool for evaluation, it is susceptible to uncertainties arising from the proprietary nature of ethanol corporate cost data, as well as the economies of scale (Gallagher et al., 2005). Being a thermal process, SS pre-treatment of wheat straw will be compared to steam explosion, a well-developed technology for pre-treatment of lignocellulose. The main differences between the two processes are a) an acid catalyst is used in the first phase of steam explosion processing, b) SS pre-treatment occurs at atmospheric pressure, and c) steam is passed through the biomass during SS pre-treatment as opposed to the explosive decompression of steam and biomass used in steam explosion.

3.1. Methodology

An equation specific to the economics of cellulosic ethanol was proposed to calculate the cost of ethyl alcohol production (Soloman et al., 2007) and is expressed as follows (Eq. 1):

$$C_A = C_B/95 + C_K + C_L + C_E + C_M + C_O - P_P \quad \text{Eq. 1}$$

Where

- C_A = cost of ethanol production (\$/gal)
- C_B = cost of biomass feedstock (\$/dry short ton)
- C_K = cost of capital investment
- C_L = cost of labor
- C_E = cost of energy
- C_M = cost of raw materials
- C_O = other costs
- P_P = price of excess electric power byproduct to be sold

The following assumptions were made in order to employ this equation:

Estimates pertaining to the cost of raw material are generally inconsistent, and are in the range of \$10/Mg to \$25/Mg (Kaylen et al., 2000; Walsh, 1997). An extensive study of lignocellulosic biomass harvest systems concluded that, depending on crop yield, the cost of raw wheat straw can be estimated as being between \$11.26 and \$14.01 per Mg, which is the assumption made for this study (Thorsell et al., 2004). An average sized (50 Mgal/year) ethanol plant typically requires approximately \$65-\$100 million in capital costs and \$45-\$60 million in annual operating costs (Urbanchuk, 2006). These costs are assumed to encompass the cost of labor and raw materials for this evaluation, and be similar between the two processes. The effect on MESP discussed is in the context of modifying the pre-treatment procedure while keeping all other parameters constant.

Energy costs associated with SS processing are generally evaluated based on the moisture removed from the biomass during the treatment (Berghel and Renstrom, 2002). Processing of wet, pressed agricultural pulps requires approximately 2900 kJ/kg of water removed (Mujumdar, 2006), and the assumption made for this study was that this is an appropriate number to use for the pre-treatment of wheat straw, for the moisture content prior to SS processing is 70-80%. Table 3 shows the energy consumed during the SS processing for each of the treatments. Steam explosion, by contrast, consumes approximately 1800 kJ/kg of biomass (Zhu et al., 2010; Zhu and Pan, 2010).

Table 3.
Energy demand associated with SS treatment.

Treatment	Change in moisture content (kg/kg)	Corresponding energy demand* (kJ/kg)
15 min. HW	0	0
15 min. HW + 2 min. SS	0.368	1068
15 min. HW + 5 min. SS	0.611	1772
15 min. HW + 10 min. SS	0.809	2348

HW = hot water treatment

*due to SS processing

Similarly to the methodology used in SS processing, steam explosion occurs in 2 steps, the first being an acid impregnation to catalyze delignification. In order to achieve 80% of theoretical ethanol conversion from wheat straw, the raw material was soaked in 0.9% w/w H_2SO_4 at 45°C for 18 h prior to steam explosion (Ballesteros et al., 2006). The corresponding step in SS pre-treatment is soaking in hot water at 193 kPa (119°C) for 15 min.

In order to develop an estimate for comparison of the magnitude of energy consumption associated with these thermal processes, the severity factor for each shall be considered. The severity factor is expressed as follows (Eq. 2) (Overend and Chornet, 1987):

$$\log R_O = \log [t \times \exp((T - 100)/14.75)] \quad \text{Eq. 2}$$

Where

$\log R_O$ = severity factor

t = time (min)

T = temperature (°C)

The ratio of severity factors between acid impregnation and hot water prior to SS to steam explosion are 0.42 and 0.52, respectively, so for the purposes of evaluation, it is assumed that the energy expenditure for the treatments are 760 kJ/kg and 930 kJ/kg, respectively.

Power generation from the combustion of excess biomass is assumed to generate energy based on a lower heating value of wheat straw of 16 MJ/kg (Jenkins et al., 1998) and an electrical conversion efficiency of 25% (Energy and environmental analysis, 2008) and sold back to the grid at 0.04\$/kWh (Eggeman and Elander, 2005).

4. Results and discussion

HPLC analysis of the hydrolyzed samples showed that the glucose yields increased significantly as a result of SS pre-treatment. Xylose however, was shown to decrease following pre-treatment, likely due to being solubilized during the hot water phase of the treatment (Brodeur et al., 2011). Furthermore, glucose yield decreased with increasing time subjected to SS

treatment, indicating the possibility of glucose degradation, or the formation of inhibitory compounds (Talebnaet al., 2010). The greatest degree to which the celluloses were hydrolyzed occurred with a treatment of 15 min hot water and 2 min of SS. The glucose and xylose conversion as a result of treatment with SS are shown in Figure 1. The conversion was calculated based on the observed glucose and xylose contents in the hydrolysate compared to the theoretical yield of glucose and xylose from the cellulose and hemicellulose, respectively.

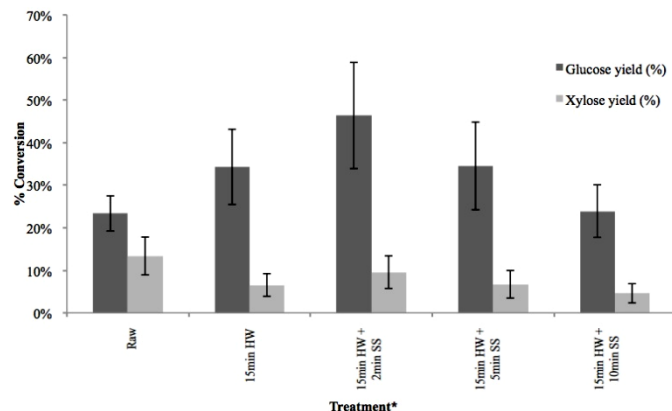


Fig.1. Glucose and xylose conversion as a result of enzymatic hydrolysis.
*HW indicates treatment in hot water at 193 kPa, 119°C, SS indicates treatment in superheated steam at 220°C.

While the treatment was successful in increasing the glucose yield from the substrate, there was a marked decrease in the xylose production. In order to ascertain the total xylose that could potentially be recovered from the substrate, the water used in the hot water phase of the pre-treatment was analyzed with the HPLC for the presence of glucose, xylose, and cellobiose that could potentially have been solubilized during that phase of the process.

Results of the analysis showed that in the treatment water, there was an average concentration of 16.6 mM of xylose present, representing a yield of 43.9%. No glucose was detected, and only trace amounts of cellobiose. Taking this into account, the yield of xylose as a result of the combined hot water and SS treatment is shown in Figure 2.

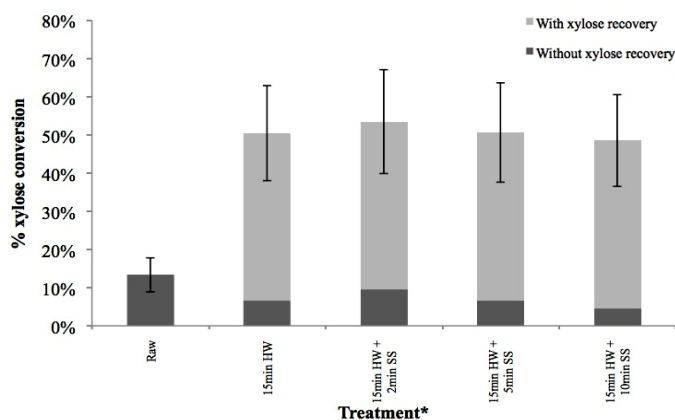


Fig.2. Xylose conversion with and without recovery from hot water.
*HW indicates treatment in hot water at 193 kPa, 119°C, SS indicates treatment in superheated steam at 220°C.

There was a substantial increase in xylose recovery if the fraction solubilized in the hot water phase of the treatment was accounted for. This would significantly improve the total yield of sugars of the overall treatment.

The trend observed was that glucose yield tended to increase up to 2 min of SS pre-treatment, after which it declined. Xylose yield came primarily from

the hot water phase of the treatment. The purpose of the pre-treatment process was to maximize the total sugar yield, so based on the results obtained, the optimal configuration of SS pre-treatment was 15 min in hot water followed by 2 min in SS. This corresponds to a theoretical ethanol production of approximately 0.103g ethanol/g biomass, or 0.136g ethanol/g biomass with xylose recovery.

Referring back to Eq. 1, and operating under the assumptions listed above, an estimate can be put forth for the MESP of ethanol derived from wheat straw using SS and steam explosion for pre-treatment. The assumed price of H₂SO₄ is \$100/ton (\$0.11/kg) (Bout and Shewchuk, 2013). Table 4 shows the cost breakdown of the conversion of wheat straw to ethanol using steam explosion and SS pre-treatment based on the assumptions listed above. All costs are adjusted per unit volume of ethanol produced. Introduction of xylose recovery is assumed to increase the capital and operating costs by 3%.

Table 4.
Cost breakdown of ethanol production.

Pre-treatment method	Steam explosion	Superheated steam	Superheated steam with xylose recovery
Raw materials	\$0.06	\$0.10	\$0.07
Capital cost	\$0.44	\$0.44	\$0.45
Operating cost	\$0.28	\$0.28	\$0.29
Energy cost*	\$0.22	\$0.30	\$0.22
Other cost**	\$0.01	\$0.00	\$0.00
Energy revenue	\$0.20	\$0.34	\$0.26
MESP	\$0.80	\$0.77	\$0.78

* energy cost is assumed to be \$0.07 / kWh

** cost of H₂SO₄

While the MESP of ethanol produced with SS pre-treatment is lower than that using steam explosion, a significant portion is due to the increased revenue associated with the energy generated from excess biomass combustion, a result of the lower glucose conversion efficiency, and consequently, more excess biomass. However, if the efficiency of the pre-treatment increases, under the same assumptions, the MESP would decrease, shown in Figure 3.

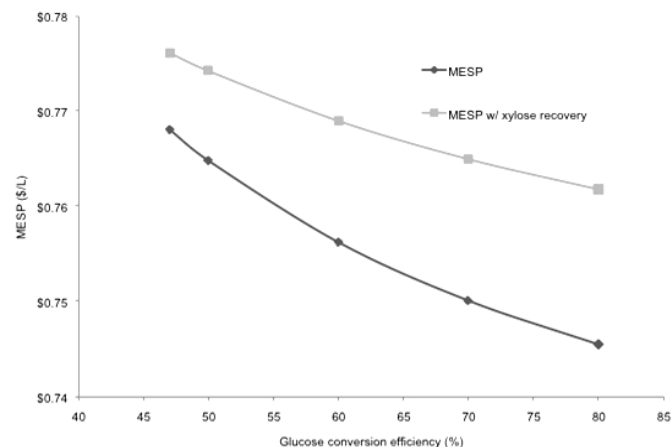


Fig.3. Effect of glucose conversion efficiency on MESP of wheat straw pre-treated with SS.

As the goal of this study was not to conduct a comprehensive economic evaluation of the production of cellulosic ethanol using SS pre-treated wheat straw, the preceding analysis yields a MESP not representative of values found in existing literature (Eggeman and Elander, 2005; Tao, et al., 2011). The MESP developed were meant to be used in relative terms, and not absolute. The results are, however, conclusive in that they indicate that pre-treatment with SS is not only technically feasible, but produces a similar result in terms of economic viability to existing pre-treatment technologies. More importantly, SS pre-treatment stands to improve the energy efficiency of the pre-treatment process, as it was shown to consume only 78% of the energy of steam explosion pre-treatment per kg of biomass.

4. Conclusion

Pre-treatment of lignocellulosic wheat straw using SS has similar performance characteristics to developed technologies such as steam explosion in terms of economic viability. Furthermore, it is a promising technology in that it consumes less energy than steam explosion, reducing the energy requirements of the pre-treatment step, which is critical to developing viable cellulosic ethanol biorefineries at an industrial scale. Improvements can be made to the SS pre-treatment in order to improve the overall yield from the biomass, which is still comparatively low with regards to other pre-treatment technologies (Conde-Mejia et al., 2012). Hypothetically, increasing the process efficiency to 80% through optimization and addition of catalysts could further decrease the energy consumption by approximately 38%, with only a modest increase in process cost associated with catalyst (0.01\$/L ethanol) if the chemical demand is similar to steam explosion. The conclusion drawn from this study is that pre-treatment of wheat straw using a SS process stands to be competitive with existing technology from a technical and economic standpoint, and can be improved upon through optimization.

5. Acknowledgments

The authors would like to acknowledge the support of BioFuelNet Canada in the preparation of this work.

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