Bioresource Technology 183 (2015) 101–110

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Comparison of different pretreatments for the production of bioethanol and biomethane from corn stover and switchgrass

G. Papa [a,d], S. Rodriguez [c,d], A. George [c,d], A. Schievano [b], V. Orzi [b], K.L. Sale [c,d], S. Singh [c,d], F. Adani [b,*], B.A. Simmons [c,d]

[a] *University of California, Berkeley, 5885 Hollis St., Emeryville, CA, USA*
[b] *Gruppo Ricicla-DiSAA, Università degli Studi di Milano, via Celoria 20100, Milan, Italy*
[c] *Sandia National Laboratories, 7011 East Avenue, Livermore, CA, USA*
[d] *Joint BioEnergy Institute, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA, USA*

HIGHLIGHTS

- Second biofuel generation can be produced from non-food crop and crop residues.
- Lignocellulose needs pretreatment reducing plant recalcitrance.
- Ionic liquids – IL-are a promising method to reduce biomass recalcitrance.
- The integrated production of bioethanol and biogas can improve total energetic yield.

ARTICLE INFO

Article history:
Received 26 December 2014
Received in revised form 26 January 2015
Accepted 28 January 2015
Available online 11 February 2015

Keywords:
Ionic liquid pretreatment
Pressurized hot water pretreatment
Bioethanol
Biomethane
Biomass pretreatment

ABSTRACT

In this study the efficiency of mild ionic liquid (IL) pretreatment and pressurized hot water (PHW) is evaluated and compared in terms of bioethanol and biomethane yields, with corn stover (CS) and switchgrass (SG) as model bioenergy crops. Both feedstocks pretreated with the IL 1-ethyl-3-methylimidazolium acetate $[C_2C_1Im][OAc]$ at 100 °C for 3 h exhibited lower glucose yield that those treated with harsher pretreatment conditions previously used. Compared to PHW, IL pretreatment demonstrated higher bioethanol yields; moreover IL pretreatment enhanced biomethane production. Taking into consideration both bioethanol and biomethane productions, results indicated that when using IL pretreatment, the total energy produced per kg of total solids was higher compared to untreated biomasses. Specifically energy produced from CS and SG was +18.6% and +34.5% respectively, as compared to those obtained by hot water treatment, i.e. +2.3% and +23.4% for CS and SG, respectively.

1. Introduction

Biofuels based on the conversion of sustainable non-food lignocellulosic biomass are one of the primary cornerstones in the global effort to replace fossil fuels with renewable sources and has the potential to generate about one quarter of the world's energy production by 2035 (Kopetz, 2013). The investments in second generation bioethanol and biomethane have been increasing in response to global policies aiming to achieve GHG emission reduction targets and diversify energy sources. In this context, the production of multiple types of biofuels and energy products from a commercial biorefinery represents a compelling alternative to petroleum to maximize the energy value of available biomass resources. The development of biorefineries related to the production of biofuels utilizing lignocellulosic feedstocks, such as agriculture and forestry residues, municipal solid wastes, woody and herbaceous energy crops, is still in the early commercial stage and many technical and economic challenges must be overcome before a renewable energy industry can become a successful and commercially viable enterprise (Kaparaju et al., 2009).

For either anaerobic digestion to biogas or fermentation to ethanol routes, the pretreatment and subsequent enzymatic hydrolysis (i.e. saccharification) of lignocellulosic biomass is a key process because it reduces the long structural carbohydrates chains of cell

---

* Corresponding author.
E-mail addresses: fabrizio.adani@unimi.it (F. Adani), basimmons@lbl.gov (B.A. Simmons).

http://dx.doi.org/10.1016/j.biortech.2015.01.121
0960-8524/© 2015 Elsevier Ltd. All rights reserved.

wall to smaller, fermentable monomeric sugars that can be fermented into biofuels (Wyman et al., 2005). This biomass deconstruction process, identified as a key rate-limiting step, poses a technical and economic bottleneck because of the complex and recalcitrant structure of lignocellulosic plant cell walls that limits accessibility to hydrolytic enzymes that generate fermentable sugars (Adani et al., 2011). Pretreatments are employed to reduce the effects of biomass recalcitrance and enhance the accessibility of cell wall polysaccharides to enzymes, thus making the conversion rates of polysaccharides to monomeric sugars more efficient (Wyman et al., 2005). Research and development on efficient pretreatments is ongoing to obtain the best energy gain possible. In particular recent reviews summarize current approaches and describe in detail trends, major challenges and perspective on this topic (Baeyens et al., 2015; Kang et al., 2014). Moreover, robust comparative studies around different pretreatment techniques provide detailed information and highlight the importance of quantify and tracking the individual components present in both the original biomass sample, during pretreatment and saccharification to fermentable sugars (Garlock et al., 2011) and finished products.

Among the numerous pretreatment approaches investigated over the years, certain ionic liquids ILs (e.g. 1-ethyl-3-methylimidazolium acetate, abbreviated as [C_2C_1Im][OAc]) are effective at disrupting the structures of plant cell walls of lignocellulose, disrupting the hydrogen bond network of cellulose and enable its dissolution with its easy recovery upon anti-solvent addition (Singh et al., 2009). Therefore they have been identified as a promising method to reduce biomass recalcitrance for downstream microbial and enzymatic processing during cellulosic ethanol production (Singh et al., 2009).

Currently, the perceived costs of the ionic liquid conversion technology are prohibitive for commercial deployment and further discoveries are needed in order to minimize costs and enhance sustainability in terms of energy efficiency. Typically, IL pretreatment is performed at temperature of 160 °C a residence time of 3 h and with a biomass loading ratio of 4–5% (w/w) (Luo et al., 2013). Different studies (Li et al., 2013) suggest different biomass loadings or temperatures and times, as options to be used instead, as the amount of energy required is also an important aspect to be considered. Severe pretreatment conditions (e.g. high temperature) have an impact from an economic perspective on IL costs; in addition it has been recently reported for well characterized catalytic systems that temperatures of 120 °C or lower are preferred to enhance biomass hydrolysis (Barr et al., 2014).

Promising results are emerging from studies on route for integrated production of bioethanol and biogas (Kaparaju et al., 2009; Bondesson et al., 2013) and new concepts of industrial symbiosis and integrated unite operations are receiving significant attention (Martin et al., 2014), with the objective to investigate whether combined processes could significantly improve energy production efficiency (Dererie et al., 2011; Rabelo et al., 2011) and reduce the costs of biomass pretreatment. To date, no studies have been conducted using ionic liquids as pretreatment strategies toward the perspective for the production of bioethanol and biomethane. While the effect of certain ILs on fermentable sugar yields from lignocellulosic material is known (Singh et al., 2009), no reports are known that report on this effect on anaerobic digestion (AD).

Pretreatment prior to anaerobic digestion (AD) has been shown to have benefits on increasing the hydrolysis yield and reducing digestion time and therefore generate positive impacts on total methane yield for crop residues. Physical, chemical, physicochemical, and biological treatments have been proposed as effective ways to improve the rate-limiting hydrolysis in biogas production. More information about advantages of current applied pretreatments techniques, can be found in an excellent recent review (Appels et al., 2008).

Data recently published by Gao et al. (2013a,b), indicated that harsh IL pretreatment can increase total biogas production on a relative basis (Sdm^3 kg dry matter – dm), although no complete mass balances were performed in terms of both biomass weight and biogas produced before and after pretreatment.

In the current report, we compare and contrast the impacts on ionic liquid pretreatment on bioethanol and biogas production. This work represents the first known report in studying the applicability of mild IL pretreatment as a strategy to guarantee good glucose recovery from the biomass and optimizing the total energy production by combining bioethanol and biogas production. The results of this work can be used for subsequent in-depth economic studies elucidating the advantages of mild biomass pretreatment for the combined production of bio-methane and bioethanol.

2. Methods

2.1. Biomass samples

Two lignocellulosic biomass feedstocks, corn (*Zea mays* L.) stover (CS) and switchgrass (SG) (*Panicum virgatum* L.), were chosen as representative of two important and promising bioenergy crops. Switchgrass was provided by the laboratory of Dr. Ken Vogel at the US Department of Agriculture, Lincoln, NE, USA. The corn stover (CS) used in this study contains corncobs without grain (NK brand N33-J4) and was provided by Prof. Bruce Dale at Michigan State University. The biomass was size reduced in a conventional laboratory blender (a Thomas-Wiley Mini Mill, City State) and followed by sieving to obtain fraction within 850–425 μm. All samples were stored at 4 °C until further use.

2.2. Pretreatment

The selection of pretreatment conditions used in this study were based on reducing biomass pretreatment cost and energy, recovering high yields of glucose to produce bioethanol, and combining bioethanol production with biogas/biomethane by using residues from the pretreatment and saccharification processes (Rabelo et al., 2011).

2.2.1. Ionic liquid pretreatment

A previous study on IL pretreatment presented the benefits of both gentle process conditions and high solids loading (Li et al., 2013). In this work moderate biomass solid loading levels, i.e. 5–10% (w/w) and lower temperature (100 °C) which is preferred due to less energy consumption. A Parr reactor system used to perform pretreatment worked at a volume of 1 L with a biomass loading of approximately 50–80 g. Corn stover and switchgrass were treated with the ionic liquid 1-ethyl-3-methylimidazolium acetate [C_2C_1Im][OAc] (Basionics™ BC-01, BASF, Florham Park, NJ) at biomass loadings of 5% (w/w) and 10% (w/w), respectively. Ionic liquid pretreatment was carried out at a temperature of 100 °C for 3 h in the Parr reactor. After 3 h incubation the biomass plus IL slurry was transferred into a 5 L plastic-container, water was added as the anti-solvent, and stirred with a blender to recover the solubilized cellulose. A precipitate formed and a basket strainer was used as a filter to remove liquid fraction. The precipitate was washed five times with deionized water (1 L each time) in order to ensure that IL had been removed, and the solid cake was freeze-dried and the weights recorded. The pretreated materials were then stored at room temperature for further analyses.

2.2.2. Pressurized hot water pretreatment

Pressurized hot water pretreatment (PHW) was performed as comparative mild-treatment of IL. Doing so the PHW was performed