Assessment of hydrothermal pretreatment of various lignocellulosic biomass with CO_2 catalyst for enhanced methane and hydrogen production

Cigdem Eskicioglu [a, b, *], Florian Monlau [c], Abdellatif Barakat [c, f], Ivet Ferrer [d], Prasad Kaparaju [b, e], Eric Trably [b], Hélène Carrère [b]

[a] UBC Bioreactor Technology Group, School of Engineering, The University of British Columbia, Okanagan Campus, 3333 University Way, Kelowna, BC V1V 1V7, Canada
[b] LBE, INRA, 11100, Narbonne, France
[c] IATE, CIRAD, Montpellier SupAgro, INRA, Université de Montpelier, 34060, Montpellier, France
[d] GEMMA — Group of Environmental Engineering and Microbiology, Department of Civil and Environmental Engineering, Universitat Politècnica de Catalunya Barcelona Tech, c/Jordi Girona 1-3, Building D1, E-08034, Barcelona, Spain
[e] Griffith School of Engineering, Nathan Campus, Griffith University, 170 Kessels Road, QLD 4111, Australia
[f] Materials Science and Nano-engineering Department, Mohamed 6 Polytechnic University, Lot 660, Hay Moulay Rachid, 43150, Benguerir, Morocco

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ABSTRACT

Hydrothermal pretreatment of five lignocellulosic substrates (i.e. wheat straw, rice straw, biomass sorghum, corn stover and Douglas fir bark) were conducted in the presence of CO_2 as a catalyst. To maximize disintegration and conversion into bioenergy (methane and hydrogen), pretreatment temperatures and subsequent pressures varied with a range of 26—175 °C, and 25—102 bars, respectively. Among lignin, cellulose and hemicelluloses, hydrothermal pretreatment caused the highest reduction (23—42%) in hemicelluloses while delignification was limited to only 0—12%. These reductions in structural integrity resulted in 20—30% faster hydrolysis rates during anaerobic digestion for the pretreated substrates of straws, sorghum, and corn stover while Douglas fir bark yielded 172% faster hydrolysis/digestion due to its highly refractory nature in the control. Furans and phenolic compounds formed in the pretreated hydrolyzates were below the inhibitory levels for methane and hydrogen production which had a range of 98—340 ml CH_4/g volatile solids (VS) and 5—26 ml H_2/g VS, respectively. Results indicated that hydrothermal pretreatment is able to accelerate the rate of biodegradation without generating high levels of inhibitory compounds while showing no discernible effect on ultimate biodegradation.

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1. Introduction

As energy sustainability concerns are increasing globally, alternatives to renewable energy sources are being brought to the forefront. Among these renewable sources is the development of an energy efficient biomass-to-biofuel process which can replace fossil fuel use and reduce greenhouse gas emissions. In particular, lignocellulosic agricultural residues have a very significant unutilized energy potential. For example, lignocellulosic biomass is abundant all year round and often after the remaining portion is used as animal feed it is burnt in an open environment which can further cause environmental concerns (Palacious-Orueta et al., 2005; Bhatia et al., 2012). Another advantage of using lignocellulosic waste for bioenergy is that it does not compete with land use for food production.

Anaerobic digestion and dark fermentation have been extensively studied for their ability to convert a wide variety of lignocellulosic biomass to methane (Sawatdeenarunat et al., 2015) and biohydrogen (Singh et al., 2015), respectively. However, the complex structure of lignocellulosic biomass, comprised of cellulose, hemicelluloses and lignin, does not provide easy access for the biodegradable organics in bioreactors. Such limited accessibility causes significantly lower methane/hydrogen yields than the theoretical estimations based on

biomass compositional/structural features (Monlau et al., 2012a; Carrere et al., 2016). A review by Monlau et al. (2013a) states that the amount of lignin is the most important factor when determining the biodegradability of lignocellulosic biomass along with other factors, such as cellulose crystallinity and accessible surface area. Therefore, research has focused on various pretreatment technologies utilizing mechanical (Sharma et al., 1988; Palmowski and Muller, 2000), chemical (Sun et al., 2001; Zhu et al., 2010; Monlau et al., 2013b), thermal (Kumar et al., 2009), and biological (Rouches et al., 2016) methods or combinations (Monlau et al., 2013c) to dissolve lignin (delignification), and to reduce cellulose crystallinity for increasing surface area and accessibility for better enzymatic hydrolysis/microbial degradation. Following pretreatment, chemical methods may have a high impact on downstream processes or the environment and limited chemical recovery potential which may require further pH neutralization before digestion. For example, high sodium may jeopardize digestate land application or inhibit methanogens in digesters (Antonopoulou and Lyberatos, 2013; Carrere et al., 2016). For enzymatic methods, typically, polysaccharides hiding under the lignin limit the enzymatic activity, therefore are at times combined with other types of pretreatment (Sun and Cheng, 2002). Furthermore, depending on the type/intensity of the pretreatment applied (i.e. dilute-acid, high temperature/pressure, steam explosion and thermo-alkaline pretreatments), some of the inhibitory by-products of pretreatment, such as furfural, 5-hydroxymethylfurfural (5-HMF) and phenolic compounds, to hydrogen and/or methane formers have also been reported (Palmqvist and Hahn-Hagerdal, 2000; Horn et al., 2011; Monlau et al., 2013c). Therefore, the chosen pretreatment method should reduce energy demand, minimize use of chemicals and formation of inhibitory by-products, and allow for reuse of co-products in a feasible biorefinery concept (Cherubini, 2010).

Hydrothermal pretreatment of lignocellulosic biomass at elevated temperatures/pressures (150–300 °C, initial pressure of 0–60 bar, 2–40 min) has garnered consideration for the production of methane, hydrogen and bioethanol from lignocellulosic substrate as it eliminates chemical addition and corrosion resistant material requirements for hydrolysis reactors (Chandra et al., 2012; He et al., 2016). It has been traditionally applied in pulp industries (Kubikova et al., 1996) and is considered more environmentally friendly compared to other methods with higher sugar recovery in a relatively short period of time and little to no inhibitor production (Kaparaju and Felby, 2010). It has been postulated that when optimized the results are comparable to dilute-acid pretreatment, but without chemical addition/post-neutralization. The use of CO_2 in hydrothermal pretreatment has been shown to further enhance hydrolysis of various types of biomass, such as Eucalyptus bark (Matsushita et al., 2010), corn stover (van Walsum and Shi, 2004), wheat straw (Relvas et al., 2015), and various polysaccharides (Miyazawa and Funazukuri, 2005). Carbonic acids generated in situ from water and added CO_2 can lower the pH of the solution and act as an environmentally friendly acid catalyst accelerating hydrolytic organic reactions at high-temperatures (Relvas et al., 2015). At the end of the pretreatment process, CO_2 can be easily removed by depressurizing the reactor to atmospheric pressure, avoiding the need of a subsequent treatment. The availability of CO_2 as a component in the fermentation processes (i.e. bioethanol or biogas) makes this a potentially cost-effective option for biomass pretreatment.

Although hydrothermal pretreatment with CO_2 pressurization is viewed as a promising technology, the existing literature is limited to the aforementioned studies focusing only on either the hydrolysis phase (van Walsum and Shi, 2004; Miyazawa and Funazukuri, 2005; Matsushita et al., 2010; Relvas et al., 2015), or enhancement of methane yield from sewage sludge (Spooner et al., 2007) and

hydrogen yield from starch (Orozco et al., 2012). However, no sufficient insight has been provided on the levels/effect of inhibitory compounds on methane/hydrogen yields from common lignocellulosic biomass including energy crops. Therefore, the objective of this study was to evaluate the entire impact of hydrothermal pretreatment with CO_2 pressurization not only on the compositional structure of various lignocellulosic substrates but also on the enhancement of methane and hydrogen yields in anaerobic digestion and dark fermentation, respectively. The yields were estimated from batch biochemical methane potential (BMP) and biochemical hydrogen potential (BHP) assays. Additionally, potentially inhibitory compounds after pretreatment were quantified.

2. Materials and methods

2.1. Lignocellulosic substrates

The substrates tested included wheat straw (WS), biomass sorghum (B140) (S), rice straw (RS), corn stover (CS), and Douglas fir bark (DFB) containing different solids (Table 1) and compositional structure (cellulose, hemicellulose and Klason lignin). Wheat straw (*Triticum aestivum*), grown in France (latitude: 48°50′18″N, longitude: 4°13′54.5″E), was first processed using a cutting mill. It was further sieved to have a particle size range of 400 μm - 1 mm. Sorghum (B140) was produced at a site (latitude: 43.6491994, longitude: 3.874161111) in Montpellier Lavalette (France) in 2012. It was milled to pass a 1 mm screen. Rice straw was provided by RIZ Camargue CANAVERE (a local farm in Saint-Gilles Languedoc-Roussillon region, south of France). It was first cut by a mill equipped with a 6 mm sieve followed by a 1 mm sieve (SM200, Retsch, GE). Corn stover was provided by INRA Versailles (Paris region, France). The sample was coarsely cut to less than 2 mm by knife milling (SM200, Retsch, GE). Douglas fir bark was supplied by Brassac Industries sawmill (Tarn region, France). It was a heterogeneous size material (chips of 5–20 cm length and 1 mm–3 cm thickness) produced from the debarking of 50 years old Douglas fir trees harvested in April 2013. Douglas fir bark chips were first dried in an oven at 40 °C overnight to reach a moisture content of 8.87%. Knife milling was then performed in a Retsch SM 100 system with a 6 mm and 2 mm size sieve at a speed of 1500 rpm.

2.2. Hydrothermal pretreatment

Hydrothermal pretreatment of substrates was conducted in a PARR 5500 High Pressure Compact Reactor equipped with mechanical mixer, heater, and controller. The reactor had an effective volume of 450 ml and was capable of achieving a maximum temperature and pressure of 350 °C and 200 bar, respectively. Upon addition of substrate (15 g) and distilled water (300 g), the reactor was sealed and pressurized to the desired levels by a CO_2 line from a cylinder/regulator. After pressurization the CO_2 line was disconnected and the temperature/pressure increase in the reactor was recorded with respect to heating time while the reactor content was being mixed at 140 rpm. The PARR reactor controller allowed the pretreatment to be programed based on different ramping rates (temperature increased per unit heating time). In this research, the heating duration was kept constant (30 min) and at the end of the 30 min, the heater and mixer were turned off and the vessel was immersed in an ice bath. When the temperature levels dropped below 40 °C, the vessel was slowly depressurized to atmospheric levels by turning on a pressure release valve found on the reactor. The lid was opened and pretreated slurry was recovered. The solid fraction was separated from the liquid fraction (hydrolyzate) via a mesh sieve with 150 μm pore size (Fig. 1). The use of the 150 μm sieve resulted in loss of 2.2–8.3% of TS in substrates pretreated