Anaerobic digestion of lignocellulosic wastes pre-treated with ionic liquids

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Abstract

This study assessed the hydrolysis of lignocellulosic biomass (LB) with ionic liquids (IL) as a pre-treatment to increase their biomethane potential (BMP). The pre-treatment was conducted for grape stem (GS), wheat straw (WS) and barley straw (BS) at 120 ºC during 120 min, using dissolutions of 1-ethyl-3-methylimidazolium acetate (EminAc) in deionized water of 5, 15, and 25% v/v. The hydrolysis with IL significantly disrupted the lignocellulose matrix of treated biomasses into soluble sugars, which were recovered from the reaction medium (IL + water) by means of extraction with isopropanol. GS showed the highest sugar production yield followed by WS (175.3 ± 2.3 and 158.2 ± 5.2 mg glucose g^{-1} biomass, respectively), while BS was slightly hydrolysed (51.1 ± 3.1 mg glucose g^{-1} biomass). Likewise, the pre-treatment significantly reduced the cellulose crystallinity index of the resulting solid fraction of GS by 21.5 % and WS by 15.7 % at the highest IL concentration, but slightly affecting the cellulose crystallinity of BS (5.3 %). Thus, BMP tests were only carried out for untreated, hydrothermally and EmimAc 25% pre-treated GS and WS. The untreated GS and WS showed methane yields of 211 ± 10 and 354 ± 1 mL CH_4 g^{-1} VS, respectively. Methane yield of solid fraction obtained after 25 % IL pre-treatment slightly increased (of 3.7 % in the case of WS), although the concentration of sugars present in the liquid fraction would increase the final energy recovery by assuming a methane yield of 118 and 106 mL CH_4 for GS and WS, respectively.

Introduction

Lignocellulosic biomass (LB) is the fourth largest energy source (after coal, oil, and natural gas), and one the most important renewable energy option today for the biogas industry. However, the anaerobic digestion (AD) of LB is limited due the low anaerobic biodegradability of its lignocellulosic structure, composed of lignin, cellulose and hemicellulose, entangled in such a way that they become inaccessible for hydrolysis, and successive AD stages. However, some studies have already revealed that ionic liquids (ILs) can easily dissolve carbohydrates, wood, lignin, and other biologically occurring polymers by their interaction with the hydroxyl groups of cellulose breaking the hydrogen bonds, which link cellulose, hemicellulose and lignin. Therefore, ILs can be considered as a promising method for lignocellulosic biomass pre-treatment for fermentation or biofuel production (Papa et al., 2015).

Material and Methods

The IL used for LB pretreatment was 1-ethyl-3-metil imidazolium acetate (Emim-Ac). The substrates used were wheat straw (GS) and barley straw (BS) collected from an agricultural farm in Madrid Community, and grape stem (GS) from Alvinesa (Daimiel, Ciudad Real). The substrates were grinded and sieved to a particle size < 25 µm and their characteristics are showed in Table 1.

Table 1. Solids characterization of lignocellulosic biomass studied: wheat straw, barley straw and grape stem.

	BS	WS	GS
TS (g kg^{-1})	963 ± 0.7	964 ± 0.6	962 ± 0.4
VS (g kg^{-1})	897 ± 1.2	896 ± 2.0	897 ± 0.1

The pretreatment was carried out at 120 ºC for 120 min in a thermoreactor equipped with 200 mL glass tubes, each one was loaded with 2 g biomass and 40 mL of a solution of EmimAc in deionized water (DW) (5, 15 and 25 % v/v), which account for substrate to IL ratios of 1:1, 1:3 y 1:5, respectively. Moreover, a hydrothermal pretreatment (HT) (same operating conditions but using only DW) was conducted to discard any possible hydrolytic effect of the water. The treated LB were separated by filtration, generating an amber-coloured liquid fraction used for determining the soluble sugars and subsequently the sugars yield (mg glucose g^{-1} biomass) after hydrothermal and IL pretreatments. The solid fractions were washed with DW and oven-dried overnight to determine cellulose crystallinity index using X-ray powder diffraction (XRD). Finally, the IL was recovered from the liquid fraction using isopropanol.

A BMP test was conducted for untreated (raw), hydrothermally treated, and 25% EmimAc treated wheat straw (WS, WSHT, and WS IL 25%, respectively) and grape stem (GS, GSHT, and GS IL 25%, respectively). The inoculum used was a granular anaerobic sludge from an industrial digester processing brewery wastewater. The BMP was carried out under mesophilic conditions (35 ºC) using 120 mL glass serum vials. The initial inoculum concentration was set at 15 g VS L^{-1} and the inoculum-to-substrate ratio (ISR) at 2:1 on a VS basis. The test lasted 50 d, moreover, theoretical methane yield from the sugar contained in the liquid fraction was calculated taking into account the theoretical chemical oxygen demand (COD) of glucose (1.067 g O_2 g^{-1}).

Results and Discussion

As we can see in Table 2 the pre-treatment significantly reduced the cellulose crystallinity index of GS (21.5 %) and WS (15.7 %) at the highest IL concentration, while slightly influenced the cellulose crystallinity of BS (5.3 %). Therefore, GS and WS were selected for AD experiments of solid fraction.

Table 2. Cellulose crystallinity (raw) and index reduction (%) after hydrothermal and IL pretreatments

	raw	HT (%)	EmimAc 5% (%)	EmimAc 15% (%)	EmimAc 25% (%)
Grape stem	23.3	18.5	15.5	19.3	21.5
Wheat straw	49.7	9.1	8.0	15.5	15.7
Barley straw	43.1	1.9	0	4.4	5.3

Cumulative methane yields of raw materials and solid fractions of GS and WS after hydrothermal and IL 25% pretreatments are showed in Figure 1. As can be seen, the methane yield obtained for the raw and pretreated materials are similar, although the final yield are much higher for WS than for GS (360 ± 10 and 208 ± 11 and mL CH_4 g^{-1} VS, respectively), this is related with the higher, twofold, initial cellulose crystallinity of wheat straw.

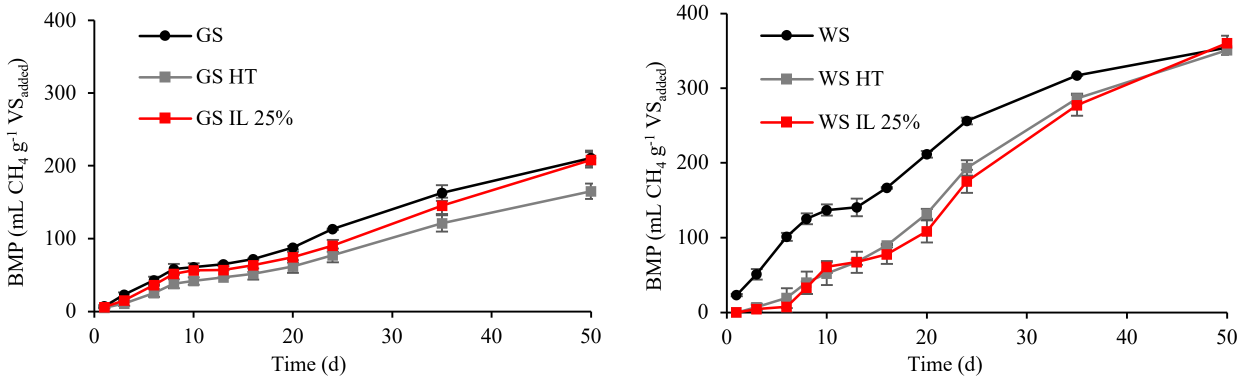

Figure 1. Cumulative methane yield of raw GS and WS and of the solid fractions after HT and IL pretreatments.

WS showed a high conversion of sugars not only after IL 25%, but also after HT pretreatment (158.2 and 123.4 mg glucose g^{-1} biomass, respectively) (Table 3). However, GS shows a remarkable response to the IL pretreatment, increasing the sugar yield of hydrothermal pretreatment from 47.8 to 175.3 mg glucose g^{-1} biomass. This considerable increase shows the effectiveness of EmimAc to weaken the lignocellulosic structure of GS. Therefore, if the theoretical methane yield achieved from the liquid fraction obtained after IL 25% pretreatment of GS and WS (Table 3), was taking into account, the whole methane yield (solid fraction + liquid fraction) would be considerably improved.

Table 3. Theoretical methane yield from the liquid fractions after hydrothermal and IL pretreatments

	HT		EmimAc 25%	
	Sugar yield (mg glucose g^{-1} biomass)	Methane yield (mL CH_4)	Sugar yield (mg glucose g^{-1} biomass)	Methane yield (mL CH_4)
Grape stem	47.8 ± 0.6	32.1 ± 0.4	175.3 ± 2.3	117.8 ± 1.8
Wheat straw	123.4 ± 1.1	83.0 ± 0.8	158.2 ± 5.0	106.3 ± 3.4

Conclusions

The pretreatment with 25% EmimAc reduced the crystallinity of the wheat straw by 15.7% and released a sugar yield of 158.2 mg glucose g^{-1} biomass. The methane yield obtained from raw and solid fraction of wheat straw 25% EmimAc pretreated were similar (≈ 360 ± 5 mL CH_4 g^{-1} VS). Although, if solid and liquid fraction obtained after the IL pretreatment of wheat straw were digested, the net energy recovered compared with the obtained for the raw material would be considerably improved due to the significant methane yield (106.3 mL CH_4) of the sugar released,.

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