Energy Conversion and Management 145 (2017) 255–264

Contents lists available at ScienceDirect

Energy Conversion and Management

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

Bioethanol production from paperboard mill sludge using acid-catalyzed bio-derived choline acetate ionic liquid pretreatment followed by fermentation process

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ARTICLE INFO

Article history:
Received 2 February 2017
Received in revised form 30 March 2017
Accepted 2 May 2017

Keywords:
Lignocellulosic waste
Choline acetate ionic liquid
Enzymatic saccharification
Furans compound
Ethanol production

ABSTRACT

Paperboard mill sludge (PMS) composed of cellulose, hemicellulose, lignin and ash contents of 36.72 ± 2.81, 32.91 ± 1.75, 22.89 ± 0.56, and 7.48 ± 0.39%, respectively. Enzymatic hydrolysis process followed by fermentation of native PMS provided an ethanol yield of 0.36 ± 0.01 g/L which equivalent to net gain energy of −0.84 ± 0.03 kJ/g_{PMS}. Choline acetate ionic liquid [Cho][OAc] IL was extensively used as a solvent for PMS to upgrade the performance. Pretreatment with [Cho][OAc] IL/PMS ratio of 10% (w/w) for 1.0 h, at a temperature of 120 °C exhibited hemicellulose and lignin removal efficiency of 5.05 ± 0.52 and 14.71 ± 1.22%, respectively with 89.19 ± 5.62% cellulose recovery. This corresponded to net gain energy of 0.60 ± 0.04 kJ/g_{PMS} based on ethanol yield from enzymatic saccharification process which was quite low due to a limited hemicellulose removal and glucose yield of 24.1 ± 1.4 g/L. [Cho][OAc] IL/PMS ratio of 10% (w/w) supplemented with 1% (v/v) HCl substantially improved the removal efficiency of hemicellulose (36.38 ± 4.51%), lignin (17.42 ± 1.19%) and cellulose (82.17 ± 4.28%) which provided the maximum net energy of 5.36 ± 0.30 kJ/g_{PMS}.

1. Introduction

Lignocellulosic biomass is considered the most abundant and renewable carbon source for energy production which mainly comprised of cellulose, hemicellulose and lignin. The cluster of lignin connected together by covalent and non-covalent bonds providing the complex and rigid structure of lignocellulosic materials [1]. Approximately, 30–90 million tons per year paper mill sludge (PMS) is globally produced from paperboard industries [2]. 3.0 million cubic meters of PMS are annually generated in Egypt and unfortunately dumped directly into the desert causing a severe ground water pollution [3,4]. Bioethanol production from PMS is a promising approach where the organic content of bio-waste could be converted into useful biofuel to reduce the continuous crude oil utilization [5–8]. However, the presence of lignin, the crystallinity of cellulose and covalent cross-linkages between lignin and hemicelluloses of PMS would be strong barrier for ethanol fermentation process [9,10]. Therefore, pretreatment of PMS is an essential step for sugar production, reducing the hemicellulose and lignin contents prior to fermentation bioprocess [11]. Several pretreatment techniques for lignocellulosic wastes have been previously investigated such as mechanical methods for size reduction [12], classical thermal, biological, ultrasonication, acid and alkaline process [13,14]. A combination of chemical-biological [15], microwave-alkali-acid [16] and mechanical-sodium hydroxide pretreatment [17] exhibited better performance surpassed the sole pretreatment methods. However, compared to other pretreatment techniques, the digestibilities of lignocellulosic wastes can be significantly improved in combination with higher glucose yield using ionic liquids (ILs). The latter are groups of organic salts with melting point below 100 °C and undoubtedly are considered 'eco-friendly' due to negligible vapor pressure, non-flammability, high thermal, chemical stability [18] and recoverable solvent [19]. Baral and Shah [20] weighed the eco-footprint of using different types of

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http://dx.doi.org/10.1016/j.enconman.2017.05.004
0196-8904/

Nomenclature

PMS	paperboard mill sludge	FPU	filter paper unit
ILs	ionic liquids	DNS	dinitro-salicylic acid
5-HMF	5-hydroxymethylfurfural	HPLC	high performance liquid chromatography
[Cho][OAc] IL	choline acetate ionic liquid	LOI	lateral order index
PTEF	polytetrafluoroethylene	HBI	hydrogen bond index
TRS	total reducing sugar	GPC	gel permeation chromatography
DMF	dimethylformamide	SEM	scanning electron microscope
XRD	X-ray powder diffraction	LOI	lateral order index
CrI	crystallinity index	HBI	hydrogen bond index
GPC	gel permeation chromatography		
M_n	number-average molecular weight		
M_w	average molecular weight		

IL as a pretreatment tool for lignocellulose materials and found that IL is the most environmental and sustainable sugar production method for bio-refineries. Recently, ILs containing ions bio-derived from naturally occurring bases and acids have been received considerable attention as promising solvents for recalcitrant wastes. Natural ILs have a powerful ability to disrupt the three-dimensional structure of lignocellulosic wastes and increases the lignin conversion, thereby providing more accessible cellulose to enzyme [21] and reduces the cellulose crystallinity [22]. However, the capability of an ILs to dissolve lignocellulosic wastes essentially depends on the type of anions, cations, waste type, contact time and IL/waste ratio. Ichiura et al. [23] found that addition of 1-butyl-3-methylimidazolium chloride improved the degradation of PMS into organic and inorganic fractions at contact time of 6.0 h. The maximum total reducing sugar (TRS) of 27.54 g/L was harvested from rice straw using 1-ethyl-3-methylimidazolium acetate [24]. However, the imidazolium cations of the IL had an inhibitory effect on the subsequent enzymatic saccharification process [25]. Cholinium ILs were tested and found to be less inhibitory to enzymes and fermentative microorganisms as compared to imidazolium ones [26]. The anions of halogens, formate and acetate are an excellent for lignocellulosic solubility [27,28]. Acetate anion has high hydrogen bond basicity and efficiently disrupting the inter- and intra-molecular of biopolymers compared to chlorides. Furthermore, acetate anion IL has a (β) Kamlet-Traft parameter of 1.2 as compared β of 0.83 for chloride. ILs with β > 1.0 provides a high potential of sugar yield from lignocellulosic wastes [1]. Accordingly, choline acetate [Cho][OAc] IL has been selected for the pretreatment of PMS in the present study. [Cho][OAc] IL provided complete cellulose conversion of Kenaf powder after 48 h [29]. Ninomiya et al. [25] found that pretreatment of bagasse using [Cho][OAc] IL provided sugar recovery and saccharification ratio of 79.6 and 95% respectively. However, 50% of lignin remained unaffected after the fractionation process and no experimental procedures have been conducted for hemicellulose hydrolysis. In this context, acid pretreatment solubilizes the hemicellulose and thereby disrupts the lignocellulosic structure, which linked via van der Waals forces [9]. However, formation of fermentation inhibitors such as furans is the main demerits of acid pretreatment. Moreover, lignin remains on the surface of crystalline cellulose after acid pretreatment, which subsequently blocks the enzyme accessibility [9]. Simultaneous supplementation of IL by dilute acid would overcome such adverse and negative effects. Wang et al. [30] found that the saccharification ratio reached 89.9% using imidazolium IL in combination with dilute HCl. However, the deterioration ability of IL was occurred due to water existence, as well as the hazardous effect of imidazolium ILs [35,36]. The use of [Cho][OAc] IL supplemented with dilute HCl will certainly achieve dual benefits of high sugar yield and low fermentation inhibitors production from paper mill sludge. In addition, Liu et al. [32] stated that combination of IL and diluted acid is acceptable from environmental point of view where the remaining portions of residual acids are negligible in the products. Ninomiya et al. [25] found that the percentage of [Cho][OAc] recovery was approximately 90–100% after 5th of recovery cycles. Furthermore, two pretreatment process connected in series is preferable where precipitation of cellulose would be occurred in the 1st step using IL followed by lignin precipitation via acid supplementation to the liquor [39,40]. The hypothesis relied on the powerful dissolution and delignification ability of IL along with hemicellulose hydrolysis using dilute HCl. Therefore, the study focused on (1) assessment of the single effect of [Cho][OAc] IL on the dissolution and delignification of PMS (2) studying the effect of dilute acid supplementation to [Cho][OAc] IL for hemicellulose hydrolysis and sugar production (3) investigating the production of fermentation inhibitors in terms of furfural and 5-hydroxymethylfurfural (5-HMF) during the pretreatment process (4) conducting the enzymatic saccharification of the undissolved carbohydrates in the regenerated PMS, and (5) calculating the net gain energy harvested from PMS based on bioethanol production.

2. Materials and methods

2.1. Paperboard mill sludge (PMS) and reagents

PMS was sampled from collection sink (3 m width × 3 m depth) of Aldar Albydaa factory, Alexandria, Egypt. The recycled paper wastes after de-inking is used a primary raw material for manufacturing process. The PMS was transported to the experimental laboratory, dried at a temperature of 70 °C, and ground to be ranged from 500 to1000 μm. The cellulose, hemicellulose, lignin, and ash contents of PMS were 36.72 ± 2.81, 32.91 ± 1.75, 22.89 ± 0.56 and 7.48 ± 0.39%, respectively. Choline acetate (>95%(T), 2-Hydroxye thyl-trimethylammonium acetate, COL Acetate, was purchased from Sigma-Aldrich company.

2.2. Experimental setup

2.2.1. PMS pretreatment using [ChO][OAc] IL

The effect of [ChO][OAc] IL on delignification of PMS and total reducing sugar production was investigated at different IL/PMS ratios in the 1st set of experiments (Fig. 1). The dried PMS (500–1000 μm) was used for the experiments. 0.5 g of PMS was mixed with 0.5, 1.5, 2.5, 5, and 7.5 g of [Cho][OAc] IL in 45 mL PTFE centrifuge tubes resulting IL/PMS ratios of 1, 3, 5, 10, and 15% (w/w), respectively. The reactants were continuously stirred at a temperature of 120 °C in oil bath (AS ONE EO-1) for a period of 0.5, 1.0, 2.0, and 4.0 h. The mixtures were allowed to be cooled at