Bioresource Technology 162 (2014) 358–364

Contents lists available at ScienceDirect

Bioresource Technology

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

Microwave-assisted conversion of microcrystalline cellulose to 5-hydroxymethylfurfural catalyzed by ionic liquids

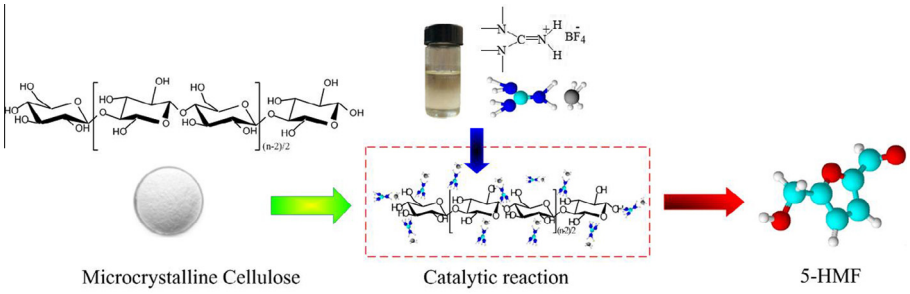
Yongshui Qu [a], Quanyuan Wei [b,c], Hongqiang Li [a], Piotr Oleskowicz-Popiel [d], Chongpin Huang [c], Jian Xu [a,*]

[a] National Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
[b] Beijing Municipal Research Academy of Environmental Protection, Beijing 100037, China
[c] Beijing University of Chemical Technology, Beijing 100029, China
[d] Poznan University of Technology, Faculty of Civil and Environmental Engineering, Institute of Environmental Engineering, Piotrowo 3A, 60-965 Poznan, Poland

HIGHLIGHTS

- Ionic liquid as catalyst to produce 5-HMF from microcrystalline cellulose was tested.
- [TMG]BF_4 was used in 5-HMF production for the first time and confirmed effective.
- Microwave irradiation as heat source showed superior 5-HMF formation than oil bath.
- 5-HMF production was optimized by Response Surface Methodology.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 February 2014
Received in revised form 13 March 2014
Accepted 16 March 2014
Available online 1 April 2014

Keywords:
5-HMF
Ionic liquids
Microwave irradiation
RSM optimization
Microcrystalline cellulose

ABSTRACT

Ionic liquid (IL) has been widely investigated in 5-HMF production from biomass. However, most of studies employed IL as reaction solvent which requires a large amount of IL. In the present study, IL was utilized as catalyst in the conversion of microcrystalline cellulose (MCC) to 5-HMF under microwave irradiation (MI) in N,N-dimethylacetamide (DMAc) containing LiCl. 1,1,3,3-tetramethylguanidine (TMG)-based ILs, including 1,1,3,3-tetramethylguanidine tetrafluoroborate ([TMG][BF_4]) and 1,1,3,3-tetramethylguanidine lactate ([TMG]L) which were commonly used in the absorption of SO_2 and CO_2 from flue gas, were synthesized and applied in the conversion of MCC to 5-HMF for the first time. Of the catalysts employed, [TMG]BF_4 showed high catalytic activity in 5-HMF production from MCC. The condition including the ratio of IL to MCC, temperature and time for MCC conversion was optimized using Central Composite Design (CCD) and Response Surface Methodology (RSM). The highest 5-HMF yield of 28.63% was achieved with the optimal condition.

1. Introduction

The gradual depletion of conventional fossil fuel, environmental pollution and global climate change make it extremely urgent to find alternative resources (Román-Leshkov et al., 2007; Rosatella et al., 2011; Zhang et al., 2013). Biomass has the potential to serve as a sustainable source for producing both energy and organic compounds with many applications, and thus replace products derived from fossil fuels (Zhang et al., 2013). The subject of efficient conversion of cellulose, non-edible components of biomass, into high value-added chemicals is of considerable current interest. As an important intermediate, 5-hydroxymethylfurfural (5-HMF) has been identified as a valuable bio-based multi-purpose building

* Corresponding author. Tel./fax: +86 10 8254 4852.
E-mail addresses: jxu@ipe.ac.cn, super_xujian@yahoo.com (J. Xu).

http://dx.doi.org/10.1016/j.biortech.2014.03.081
0960-8524/

block chemical due to its high reactivity (Wang et al., 2013). A broad range of value added compounds can be synthesized from it, such as 2,5-dimethylfuran (DMF), 2,5-furandicarboxylic acid (FDCA), and levulinic acid (LA) (Kim et al., 2013; Lima et al., 2009; Tong et al., 2010). One of the most important derivatives is DMF, which was envisaged as the promising fuel and can be produced by hydrogenation of 5-HMF.

Ionic liquid (IL) is nonvolatile, nonflammable, highly polar, and easy to separate from reactants and products. These attributes make IL excellent reaction media for the synthesis of organic materials (Liu et al., 2012). Since Zhao et al. (2007) firstly reported the use of $CrCl_2$ as a catalyst in the synthesis of 5-HMF from glucose with 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) as solvent obtaining near 70% yield, the transformation of carbohydrates in metal catalyst/neutral IL systems has been the subject of extensive research. A series of catalysts including mineral acids, H-form zeolites, transition metal ions, strong acid cation exchange resins, etc., have also been employed. So far, the 5-HMF building block has been the only furan derivative obtained from carbohydrates using ILs (Li et al., 2012; Liu et al., 2012; Zakrzewska et al., 2011); however, most of the reported dehydration was mainly focused on the simple hexoses such as fructose and glucose (Zhang and Zhao, 2011a). As the most abundant biopolymer on the earth with longer carbon chains, the conversion of cellulose to 5-HMF has attracted much more attention recently. Binder and Raines (2009) reported the conversion of the purified cellulose in a mixture of N,N-dimethylacetamide (DMAc) containing lithium chloride (LiCl), DMAc-LiCl and [EMIM]Cl. The maximum HMF yield can reach 47% catalyzed by $CrCl_2$ (25 mol%) and HCl (5 mol%) at 140 °C. Zhang and Zhao (2009, 2011b) and Zhang et al. (2011) studied the conversion of a few types of cellulose with different degrees of polymerization (Avicel, Spruce, Sigmacell and α-cellulose) into HMF under microwave irradiation with [BMIM]Cl or [BMIM]Br as solvent and $CrCl_3$ as catalyst. The 5-HMF yields ranging from 53% to 62% were obtained at the same reaction condition. A pair of metal chlorides ($CuCl_2$ and $CrCl_2$) dissolved in [BMIM]Cl were employed to produce 5-HMF from cellulose by Su et al. (2011) and the highest yield of 57% was achieved at 120 °C for 8 h.

It should be noted that most of the reported investigations employed IL as solvent or co-solvent for the conversion of cellulose to 5-HMF, indicating that a large amount of IL is required which makes the whole process not economically feasible. In addition, chromium chloride ($CrCl_2$) was commonly used as the catalyst which would cause the serious environmental pollution since $CrCl_2$ has been considered as one of the main pollutants. A more efficient, economical and environmentally friendly conversion system is therefore required for large scale manufacture of 5-HMF from cellulose. In the previous studies (Qu et al., 2012a,b,c), it has been confirmed effective to produce 5-HMF by dehydration of fructose and glucose employing ionic liquids as catalyst in the presence of normal organic solvent and alkaline ILs has showed high activity for the conversion of fructose to 5-HMF. In order to make this process more industrially feasible, cellulose was utilized as the feedstock in the present study. Although 1,1,3,3-tetramethylguanidine (TMG)-based ILs, for example 1,1,3,3-tetramethylguanidine lactate ([TMG]L), has been proved to have high activity in some Brønsted base-catalyzed reactions such as the Henry condensation reaction (Zhu et al., 2005) and used in the absorption of SO_2 and CO_2 from flue gas (Huang et al., 2006), there have been no reports on TMG-based ILs as catalyst for the conversion of microcrystalline cellulose (MCC) to 5-HMF to the best of our knowledge. In this study, the conversion of cellulose into 5-HMF catalyzed by (TMG)-based ILs, including [TMG]L, 1,1,3,3-tetramethylguanidine tetrafluoroborate ([TMG][BF_4]) and 1,1,3,3-tetramethylguanidine acetate ([TMG]OAc) were investigated with microwave irradiation (MI) as heat source. In addition, Central Composite Design (CCD) was employed to design the experiments. The effect of catalyst loading, reaction temperature and reaction time on the 5-HMF yield was investigated and optimized by response surface methodology (RSM).

2. Experimental

2.1. Materials and catalyst preparation

5-HMF was purchased from Shanghai Jingchun Chemical Reagent Company; toluene, ether, ethanol and N,N-dimethylacetamide (DMAc) containing lithium chloride (LiCl) were purchased from Beijing Chemical Reagent Company. 1,1,3,3-Tetramethylguanidinium, lactic acid, N-methylimidazole were purchased from Beijing Da Tian Feng Tuo Chemical Reagent Company, all reagents were used as received.

Microcrystalline cellulose (MCC), VIVAPUR-105, was purchased from JRS (Rosenberg, Germany). After being sieved, the MCC with 180–200 μm was selected as feedstock.

[TMG]BF_4 was synthesized as follows: tetrafluoroboric acid (40 wt%, 4.39 g, 20 mmol) was added to a solution of 1,1,3,3-tetramethylguanidine (2.30 g, 20 mmol) in ethanol (50 mL). The mixture was stirred vigorously at room temperature for 4 h. The solvent was evaporated to leave the crude [TMG]BF_4 as viscous liquid, which was washed with diethyl ether (3 × 20 mL) and dried at 80 °C for 12 h in vacuum to prepare the pure IL (Berg et al., 2008; Huang et al., 2006). The yield of [TMG]BF_4 was 92.3%. Other [TMG]-based ILs were prepared using similar procedures (Román-Leshkov et al., 2006; Yang et al., 2013). Ethanolamine tetrafluoroborate ([MEA]BF_4) and 1-butyl-3-methylimidazolium acetate ([BMIM]OAc) were synthesized as described by Yuan et al. (2007) and Wu et al. (2013), respectively.

2.2. General procedure for the conversion of MCC to 5-HMF

In a typical reaction, 0.5 g MCC, 0.2 g catalyst and 100 ml LiCl-DMAc (5 wt%) were mixed in a flask equipped with a condenser which was heated to 100–160 °C with microwave irradiation (MI) or oil bath. MCR-3 Microwave Chemical Reactor (Gongyi City Yuhua Instrument Co., Ltd.) was used (Li and Xu, 2013; Peng et al., 2013). Its output power was adjusted to 400 W with proportion integration differentiation (PID) mode according to the difference between set temperature and actual temperature inside. Heat-gathering style magnetism mixer (DF-101s, Changzhou Putian Equipments Co., Ltd.) using dimethicone oil as heating medium was used as oil bath. After the reaction, the liquid fraction was filtered through 0.45 μm pore size membrane and the filtrate was analyzed by HPLC (Agilent 1260, USA) using a C18 column at 35 °C with methanol/water (40/60, v/v) as eluent at a flow rate of 0.6 mL/min. A UV detector was employed.

The yield of 5-HMF (mol%) was evaluated on a carbon basis calculated by Eq. (1):

$$\text{Yield} = \frac{M_{5\text{-HMF}}}{M_{\text{MCC}}} \times 100\% \quad (1)$$

$M_{5\text{-HMF}}$: mole number of 5-HMF.
M_{MCC}: mole number of glucose unit in initial MCC.

2.3. Experimental design

The effect of three independent variables (temperature, reaction time, catalyst loading) on the response (5-HMF yield) was studied using a factorial Central Composite Design (CCD) of Response Surface Methodology (RSM), which is a collection of mathematical and statistical techniques for designing experiments, analyzing the