



Synthesis of 5-hydroxymethyl furfural from cellulose via a two-step process in polar aprotic solvent

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ABSTRACT

The synthesis of 5-hydroxymethyl furfural (HMF) from cellulose via a two-step process was investigated. To optimize reaction conditions, the separate conversion of cellulose and glucose was first performed in tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) via a one-step process using phosphotungstic acid (PHA) as catalyst. The direct conversion of cellulose to HMF was then performed via the two-step process. The first step and the second step were carried out in THF and the mixture solvent composed of THF/DMF, respectively. Cellulose was converted to HMF and glucose in the first step in THF. Both of cellulose and the as-formed glucose were then converted to HMF in the second step. The conversion of cellulose to HMF and glucose were significantly improved by the two-step process, and the total yield of HMF and glucose was elevated from 52.1 to 97.0%. A possible mechanism for the formation of HMF from cellulose via the two-step process was also proposed.

1. Introduction

Renewable resources are widely considered outstanding, viable and pollution-free alternative to conventional fossil sources such as petroleum and coal with a shortage in fossil fuel as well as more and more serious emission of greenhouse gases (Hosseini & Wahid, 2016; Sansaniwal, Rosen, & Tyagi, 2017). Biomass is an important renewable feedstock for fuel and chemical production due to its abundance and relatively low cost (Jiménez-Morales, Teckchandani-Ortiz, Santamaría-González, Maireles-Torres, & Jiménez-López, 2014). In recent years, the conversion of biomass into platform chemicals and potential alternatives to fossil-based feedstock (Rout, Nannaware, Prakash, Kalra, & Rajasekharan, 2016; Zhao, Shen, Ge, Chen, & Yoshikawa, 2014) has attracted significant attention in green and sustainable chemistry (De, Saha, & Luque, 2015; Deuss, Barta, & Vries, 2014).

5-Hydroxymethylfurfural (HMF) is a building block for producing various high-volume organic chemicals and liquid fuels. A variety of bio-based chemicals including 2,5-furandicarboxylic acid, 2,5-dimethylfuran, 2,5-bis(hydroxymethyl)furan, gamma-valerolactone and levulinic acid (LVA) can be derived from HMF (Jiménez-Morales, Teckchandani-Ortiz et al., 2014). These chemicals play important roles both in chemistry and energy fields. For example, 2,5-dimethylfuran is a potential biofuel with a greater energy content than bioethanol. Cellulose is the main component of plant biomass. It is desirable to

produce HMF from cellulose directly due to its abundance, non-food and renewability. Direct conversion of cellulose possesses advantages such as simple technology and ready availability of raw materials. Unfortunately, cellulose is a water-insoluble polymer composed of glucose monomer units, linking together via β -1,4-glycosidic bonds (Deng, Liu, Zhang, Tan, & Wang, 2010), resulting in recalcitrant and heterogeneous nature of cellulose. Therefore, it is difficult to obtain good yield and selectivity in the direct conversion of cellulose.

So far, the direct transformation of cellulose to platform chemicals is still a challenge though it has attracted worldwide attention for decades (Fan, Liao, Fang, Wang, & Song, 2013). It is currently accepted that both glucose and fructose are intermediates for the production of HMF from cellulose directly, in which glucose can be transferred to fructose and then converted to HMF (Daorattanachai, Khemthong, Viriya-Empikul, Laosiripojana, & Faungnawakij, 2012; Peng, Lee, Wu, & Wu, 2012). As a result, the synthesis of HMF from glucose (Saang'onyo, Parkin, & Ladipo, 2018) and fructose (de Carvalho, Rodrigues, Monteiro, Ribas, & da Silva, 2018) is investigated widely. Generally, HMF can be effectively synthesized via the dehydration of saccharides such as glucose and its isomer of fructose in the presence of catalysts, in which mineral acid (Fachri, Abdilla, Bovenkamp, Rasrendra, & Heeres, 2015), Lewis acid (Dumesic, Pagán-Torres, Wang, & Shanks, 2014), heteropolyacid (Jiménez-Morales, Moreno-Recio, Santamaría-González, Maireles-Torres, & Jiménez-López, 2014), supported acid

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(Jiménez-Morales, Teckchandani-Ortiz et al., 2014; Kobayashi, Komanoya, Hara, & Fukuoka, 2010; Jiménez-Morales, Teckchandani-Ortiz et al., 2014) and zeolite (Hu et al., 2014; Otomo, Yokoi, Kondo, & Tatsumi, 2014) are found to be efficient catalysts.

The catalytic transformation of cellulose to HMF is one of the outstanding utilizations of biomass. Most works focused on the synthesis of HMF from cellulose were performed via a one-step method (Abou-Youcef & Hassan, 2014; Abou-Youcef & Steele, 2013; Chiappe et al., 2017; Shirai, Ikeda, & Qian, 2017). The pretreatment was often performed before the conversion of cellulose in the presence of catalyst (Hota, Mori, & Kasuya, 2018; Zhang et al., 2014). In addition, ionic liquids were considered to be efficient reaction media for the direct conversion of cellulose (Anderson, Ding, Welton, & Armstrong, 2002). Ionic liquids such as 1-ethyl-3-methylimidazolium chloride (Abou-Youcef & Hassan, 2014) and 1-butyl-3-methylimidazolium chloride (Xiao, Liu, Wang, Fang, & Zhang, 2014) are widely employed. Bi-functionalized catalyst (Zhang et al., 2014), zeolite (Abou-Youcef & Steele, 2013), co-catalyst composed of ionic liquid and metal salt (Ding et al., 2012), Lewis acid (Su et al., 2009), metal chloride (Abou-Youcef & Hassan, 2014; Zhou et al., 2015) and polymer with acidic site (Rinaldi, Meine, Stein, Palkovits, & Schüth, 2010) have been developed. For example, the conversion of cellulose with 53.2% HMF yield was achieved under microwave irradiation (da Silva Lacerda et al., 2015). Although relatively high yield of HMF was obtained in the presence of ionic liquids, the synthesis of ionic liquids is tedious and non-green with high cost, difficult recovery and reuse, resulting in significant challenges in industrial application. The direct conversion of cellulose to HMF was also performed in other media (Lee, Dutta, & Wu, 2014; Nandiwalé et al., 2014; Ogasawara, Itagaki, Yamaguchi, & Mizuno, 2011; Shirai et al., 2017). In hot compressed water, around 10% HMF yield from cellulose was obtained by acid catalyst (Daorattanachai, Khemthong et al., 2012; Daorattanachai, Namuangruk, Viriya-Empikul, Laosiripojana, & Faungnawakij, 2012). Polar aprotic solvents are also believed to be efficient for the direct conversion of cellulose into HMF. Cellulose conversion catalyzed by H₂SO₄ gave 44% yield of HMF in THF (Weingarten et al., 2014). In biphasic system composed of organic phase and aqueous phase, NaHSO₄-ZnSO₄ displayed excellent performance for the conversion of cellulose into HMF with 53% yield (Shi, Liu, Zhang, Wang, & Ma, 2013). In these works, strong acid catalysts or complex catalytic system are generally required. It may result in the problems of corrosion, treatment of waste liquid and separation. Furthermore, the composition of the reaction mixture is complex due to the formation of by-products including levoglucosan (LGA), levoglucosone, LVA, formic acid and humins. As a result, the total yield of HMF and glucose, another important platform chemical derived from biomass, was relatively poor even in ionic liquid (Su et al., 2009). The development of a more environmentally-benign and simple catalyst is strongly preferred in order to satisfy the requirement of green and sustainable chemistry.

The conversion of cellulose into HMF via a two-step process was also developed (Qi, Watanabe, Aida, & Smith, 2011; Tan, Zhao, & Zhang, 2011), which was generally carried out in ionic liquids in the presence of complex catalytic system. For example, HMF yield of 73% was obtained via the conversion of microcrystalline cellulose using acidic cation exchange resin and CrCl₃ as catalysts for the first step and the second step in 1-ethyl-3-methyl imidazolium chloride (Qi et al., 2011), respectively. Obviously, the reaction mixture needs to be treated after the first step due to different catalysts for both steps. The catalytic system, reaction media and technology are relatively complex.

In this work, a new approach to produce HMF from cellulose catalyzed by green catalyst of phosphotungstic acid (PHA) in mixed polar aprotic solvent composed of tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) via a two-step process was proposed. The conversion of cellulose and glucose to HMF was first performed separately via a one-step process to optimize reaction conditions. Based on the optimized conditions, the conversion of cellulose was then

performed via a two-step process, in which cellulose was initially converted to HMF as well as glucose in THF in the first step. Both the conversion of cellulose and the as-formed glucose were then enhanced in the second step in the mixture of THF/DMF. It was expected to enhance the selective formation of HMF and glucose from cellulose. In addition, PHA was employed as catalyst for both steps. Therefore, no pretreatment was required after the first step. The technology is simple, and the solvent is available as well as easily recovered. A possible mechanism for the production of HMF from cellulose via the two-step process was also proposed based on quantitative and qualitative analysis.

2. Materials and methods

2.1. Materials

Cellulose (average particle size of 90 μm) and HMF (purity of 99%) were of reagent grade and purchased from Sigma. Other reagents and solvents were purchased from Sinopharm Chemical Reagent Co. Ltd (Peking, China) and of analytically pure. All the reagents were utilized without further pretreatment.

2.2. Synthesis of HMF

2.2.1. Synthesis of HMF from cellulose via a one-step process

Typically, 0.5 g cellulose, 0.5 g PHA and 10 ml THF were added into a 100 ml stainless steel autoclave. The autoclave was sealed and the air in it was flushed with 1 MPa nitrogen three times. Then 1 MPa nitrogen was introduced and the mixture was heated at 190 °C for 6 h under magnetic stirring. The autoclave was cooled to room temperature and the pressure in it was gradually released. Solid residues were collected by filtration, washed with THF and the washes were combined with filtrate. The liquid reaction mixture was then centrifuged and analyzed quantitatively.

2.2.2. Synthesis of HMF from glucose

Typically, 0.5 g glucose, 0.5 g PHA and 10 ml DMF were added into a 100 ml stainless steel autoclave. The autoclave was sealed and the air in it was flushed with 1 MPa nitrogen three times. Then 1 MPa nitrogen was introduced and the mixture was heated at 130 °C for 4 h under magnetic stirring. The autoclave was then cooled to room temperature and the pressure in it was gradually released. The reaction mixture was centrifuged and analyzed quantitatively.

2.2.3. Synthesis of HMF from cellulose via a two-step process

In a typical procedure, 0.5 g cellulose, 0.5 g PHA and 10 ml THF were added into a 100 ml stainless steel autoclave. The autoclave was sealed and the air in it was flushed with 1 MPa nitrogen three times. Then 1 MPa nitrogen was introduced and the mixture was heated to 190 °C for 6 h. After cooling to room temperature, 10 ml DMF was added to the autoclave and the mixture was subsequently kept at 130 °C for 4 h under nitrogen atmosphere. The autoclave was cooled to room temperature and the pressure in it was gradually released. Solid residues were collected by filtration, washed with THF and the washes were combined with filtrate. The liquid reaction mixture was then centrifuged and analyzed quantitatively.

2.3. Analysis

The quantitative analysis of HMF was determined by a G2020 gas chromatography (GC) equipped with a HP-1 capillary column (30 m × 0.25 mm × 0.25 μm). The initial temperature was retained at 50 °C for 3 min, then ramped to 230 °C at 10 °C/min, and held at this final temperature for 5 min. The gasification and detector temperatures were 240 and 260 °C, respectively. Glucose content was determined via 3,5-dinitrosalicylic acid (DNS) method using a UV measurement at

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