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Green hydrolysis of corncob cellulose into 5-hydroxymethylfurfural using hydrophobic imidazole ionic liquids with a recyclable, magnetic metalloporphyrin catalyst

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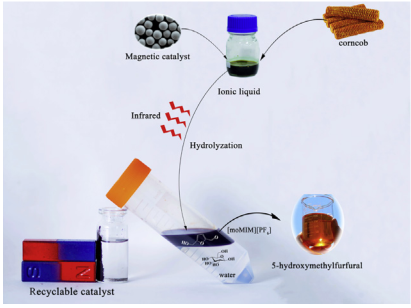
HIGHLIGHTS

- A magnetic metalloporphyrin (MCMP-M) was prepared via nucleophilic addition.
- A biphasic ionic liquid couple with mixed MCMP-M enable hydrolyzing of corncob cellulose.
- MCMP-M and ionic liquid can easily recycle and reuse.
- Infrared radiation as heat source showed superior 5-HMF formation than traditional measure.

GRAPHICAL ABSTRACT



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ABSTRACT

Ionic liquids (ILs) with catalysts have been widely investigated in the production of 5-hydroxymethylfurfural (5-HMF) from biomass, in particular those which are high in cellulose. In this study, a series of hydrophobic imidazolium ionic liquids and magnetic-chitosan metallo-porphyrin particles (MCMP-M) were designed and their abilities to convert 5-hydroxymethylfurfural (5-HMF) and total reducing sugars (TRS) from the corncob were evaluated. The results showed that [moMIM][PF_6] and MCMP-Al were suitable solvents and both the catalysts were effective for the 5-HMF and TRS conversion (52.47 and 31.06, respectively). The mixed catalysts (MCMP-Al, Cr and Mg) coupled with [moMIM][PF_6] could increase the conversion yield of 5-HMF and TRS (66.58% and 43.68% in 50 min, respectively) with infrared radiation heating during distillation under reduced pressure for a short time (50 min). More importantly, the products could be separately recovered through the aqueous phase and the ILs and catalysts could be reused up to 40 times despite the slight loss of its catalytic activity. Moreover, the catalyst system also could be used for other carbon sources to produce the 5-HMF.

1. Introduction

Over the past century, the use of petroleum derived fuels has increased significantly all over the world and has become a major factor which has driven industrial development. The world has become increasingly dependent on fossil resource, however, fossil fuels are non-renewable resources which are gradually becoming expended [1,2]. Although society requires more energy and production chemical, fossil fuel reserves are shrinking gradually and so alternative energy sources are urgently needed. In addition, the associated environmental and energy conservation problems including global climate change and uncertain petroleum sources

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exceed the benefits of fossil fuels. Based on the above factors, many studies have been motivated to develop sustainable alternative resources to fuel and chemicals [3].

Biomass is a novel renewable energy resource which is a sustainable and alternative energy resource being developed as an alternative energy source in most countries [4]. Biomass is the only carbon source widely available apart from fossil fuels [5]. In industry, biomass can be transformed into value-added chemical products and liquid fuels [6,7]. Lingo-cellulosic is a major biomass resources that has been used to produce many chemical products including 5-hydroxymethylfurfural which is an important intermediate product in the chemical industry [8,9]. Biomass is a new source of 5-HMF and fructose that can be efficiently converted to 5-HMF through acid catalyzed dehydration with excellent yields above 70%. Cellulose has become a new source of 5-HMF in recent years [10,11]. With the development of the fine chemical industry, 5-HMF has become an intermediate for other 2,5-disubstituted furan derivatives, which could subsequently be used in the production of fine chemicals, pharmaceuticals and polymers [12–14].

However, approximately 60–90% (wt) of cellulose is found in the plant and the structure is highly crystalline which is caused by the presence of extensive intra- and inter-molecular hydrogen bonds and Van der Waals interactions [15]. Due to these inert structural characteristics, cellulose is considered to be difficult to be accessed by common reagents such as water, ethyl alcohol and other organic reagents [16,17]. Many chemical methods, including acid hydrolysis, hydro-thermal or alkaline treatments, or subcritical and supercritical fluids have been used in the treatment of lingo-cellulosic biomass. However, this treatment method has many problems: it has environmental consequences as the cellulose dissolution or catalyst is strongly oxidative, is a corrosive acid and a toxic solvent. The process can also cause secondary pollution and is not in accordance with the demand for green chemistry [18]. On the other hand, the conversion product is difficult to be separated from other by-products when the reaction is complete and the high cost of fructose restricts its large-scale application Table 1.

The common solution method uses ILs as environmentally friendly solvents that have been applied in the wood and biomass industries, particularly for cellulose dissolution [19]. ILs have been shown to be good solvents for the dissolution of cellulose due to the hydrogen bond acceptor strength and high polarity [20]. Some reports have shown ILs as solvents or catalysts for the dehydration of carbohydrates can increase the yield of 5-HMF as high as 70% under mild operating conditions [21]. Some studies have reported that metal salts can increase the efficiency of 5-HMF as catalysts for the conversion of cellulose or glucose (cellulose hydrolysis product) in ILs [20,22]. Synthetic metalloporphyrins have been used as biomimetic catalysts models and their potentiality in biomass production e.g., lignin degradation, has been previously investigated [23]. In addition, metalloporphyrin usage might be more selective because of its simulation of cytochrome P450 [24]. Metalloporphyrins have been mentioned in the catalyst field, and considered as possible biomimetic systems for biomass production.

Table 1
The fitting results of first-order and Arrhenius plot.

Item	No.	Standard cure equation	R^2
Time-ln$C_{5\text{-}HMF}$	1	y = 0.0069x − 0.8448	0.9668
	2	y = 0.0095x − 0.8160	0.9259
	3	y = 0.0099x − 0.8361	0.9399
	4	y = 0.0132x − 0.8622	0.9953
	5	y = 0.0154x − 0.8482	0.9755
Time-lnC_{TRS}	1	y = −0.0044x − 0.1205	0.9808
	2	y = −0.0057x − 0.1569	0.9822
	3	y = −0.0071x − 0.1363	0.9882
	4	y = −0.0076x − 0.1535	0.9336
	5	y = −0.0129x − 0.0729	0.9633
T-lnk 5-HMF		y = −1.6352x + 0.0131	0.9645
T-lnk TRS		y = −2.0419x + 0.0131	0.9157

Despite the inherent advantages of ILs and metal catalysts, there are some limitations associated with their use, in particular the requirement for a highconcentration of 5-HMF, which is a catalysts inhibitor [25]. High concentrations of 5-HMF could reduce the catalytic activity of ILs and catalysts. Given the environment protection implications and cost of production, another limitation is recovery of solvents (ILs) and catalysts after the hydrolyzation. To solve these problems, a liquid-liquid biphasic and magnetic recovery capability system will be built in this study and the efficiency of this system in the hydrolytic process of cellulose was evaluated. To the best of our knowledge, 5-HMF is a relatively hydrophobic material which is expected to be easily removed from the aqueous phase and transferred to the hydrophobic phase (ILs). In this way, the ILs will also be easily recovered and reduce the toxic action for the catalyst.

There are many limitations in the use of conventional biocatalysts, in particular difficulties associated with recycling of a biocatalyst. Magnetic separation is an effective tool and an attractive method for recycling that has been reported in some studies [26–28]. Several investigations have synthesized magnetically separable metalloporphyrin and the core is Fe_3O_4 [24,29,30]. The stability of the magnetic metalloporphyrin depends on the strength of bonding force between the metallopohyrin and the magnetic nanoparticles. Jing et al. synthesized a magnetical Fe(III) porphine chloride nanoparticles via covalent bonding [24]. Chitosan is a linear copolymer which has rich chemical groups in its structure resulting in excellent ability to bridge during the process of polymer synthesis. Chitosan also shows hydrophobic properties and has a stable structure.

In this study, we designed a magnetic metalloporphyrin which was wrapped with chitosan to improve stability. Due to advantages of ILs and magnetic metalloporphyrin, a novel biphasic IL system and catalyst were designed and used in this study. A series of hydrophobic ILs, 1-Methyl-3-amylimidazolium- hexafluorophosphate([maMIM][PF_6]), 1-Methyl-3-n-octylimidazolium- hexafluorophosphate([moMIM][PF_6]), 1,2-Dimethyl-3-amylimidazolium-hexafluorophoshpate ([dmaMIM][PF_6]), and 1, 2-Dimethyl-3-n-octylimidazolium-hexafluorphosphate ([dmoMIM][PF_6]) were synthesized. A metalloporphyrin polymer was used in the metalloporphyrin as the monomer and linked with chitosan-Fe_3O_4 nanoparticle. The hydrolysis of cellulose from corncob, recovery of glucose in the aqueous phase and more importantly, separation of 5-HMF from the aqueous phase to the IL phase, were realized. Moreover, evaluation of the hydrolysis conditions in the heating model, catalyst and ionic liquid dosage, reaction temperature and reaction time were also investigated.

2. Material and methods

2.1. Materials

5-HMF standard, trioctylphosphine was purchased from Sigma Reagent Company. Microcrystalline cellulose (MCC), 1,2-Dimethylimidazole, trioctylphosphine and other reagents which are mentioned in this study were all purchased from Aladdin Bio-Chem Technology Co., Ltd., Shanghai, China.

2.2. Synthesis of ionic liquids

1-Methylimidazole (42.5 g) and 1-Bromopentane (60.2 g) were slowly added to trichloroethane (50 mL) under an argon