Efficient conversion of wheat straw into methyl levulinate catalyzed by cheap metal sulfate in a biorefinery concept

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A B S T R A C T

Wheat straw can be converted into biofuel candidate-methyl levulinate with copper sulfate as the cheap catalyst. To take advantage of the whole components of wheat straw, a two-stage pretreatment process was developed in this study. In the first-stage process, the hemicellulose component in wheat straw can be converted into bio-surfactant at the mild conditions, and the lignin component can be extracted as another value added by-product in the second stage. On the basis, the pretreated wheat straw was used as raw material for methyl levulinate production, and a yield of 20.2 wt% can be obtained under the optimum reaction conditions. Meanwhile, the catalyst recycling experiments showed that copper sulfate was stable and can be reused more than five times. The results of mass balances and preliminary economic analysis further indicated that the production of integrated biorefinery processes producing diversified products offers potential for the sustainable valorization of wheat straw.

1. Introduction

Lignocellulosic biomass is considered to be a perfect substitute for fossil resources as one of the renewable resources, and it has attracted extensive attention for the conversion of lignocellulosic biomass into high value-added bio-based products (Isikgor et al., 2015). The carbohydrate fractions of lignocellulosic biomass are cellulose and hemicelluloses which can be converted into different kinds of bio-based products. Among these conversions, direct synthesis of alkyl levulinates in alcohol solvents is considered as a promising conversion route (Chang et al., 2015; Enumula et al., 2017). Alkyl levulinates such as methyl, ethyl, propyl and *n*-butyl levulinates, are short chain fatty esters with numerous applications in medicine, flavouring and fragrance industries. In addition, they can be used as fuel additives to improve petroleum and diesel properties, such as stability, low-temperature fluidity and the flash point (Chuck and Donnelly, 2014; Wang et al., 2016).

In the case of one-pot production of alkyl levulinate, lignocellulose biomass is alcoholysized in a single stage process to convert the carbohydrates fraction to alkyl levulinate. However, yields of alkyl levulinate from lignocellulosic biomass were generally lower, which resulted in the poor economy of the process (Mascal and Nikitin, 2010).The main problem associated with the process is that alkyl levulinate is mainly synthesized from hexose sugars in lignocellulosic biomass, and the pentose sugars are dehydrated to furfural and further degraded or polymerized. This means hemicellulose of lignocellulosic biomass cannot be completely converted in the process. In addition, the lignin fraction in lignocellulosic biomass is partially converted into acid soluble compounds, and acid insoluble lignin fraction is recovered as a mixture together with the humins, which depreciates the application value. Therefore, to add additional cost to the process, it is necessary to fractionate the three major components of lignocellulosic biomass and convert them into more bio-products in a biorefinery concept.

In order to improve the alkyl levulinate production from lignocellulosic biomass, the development of cheap and efficient catalyst is also a hot spot in the field. Mineral acids such as H_2SO_4, HCl are usually economical, frequently-used catalyst in biomass alcoholysis, but they have defects in corrosion equipment and are difficult to recover. Currently, solid catalysts are widely studied for lignocellulosic biomass reactivity in alcohol. Many solid catalysts, such as sulfate metal oxides (Njagi et al., 2015), acidic ionic liquids (Wang et al., 2014), zeolites (Saravanamurugan and Riisager, 2012), resins (Hu et al., 2013), metal salts (Peng et al., 2015) and mixed acid catalyst (Tominaga et al., 2016) have been successively developed to improve the conversion of biomass to alkyl levulinate. Among them, commercially available metal sulfate can be used as the efficient and cheap promising solid catalyst, and has attracted attention due to its efficiency and low cost. For example, Zhou et al. reported that $Al_2(SO_4)_3$ can be used as simple and efficient

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catalyst for the synthesis ML from carbohydrate biomass (Zhou et al., 2014). Tan et al. also reported that one-pot synthesis of ethyl levulinate from cassava in ethanol-water system over $Al_2(SO_4)_3$ as sulfate salt catalyst, and a highest yield of ethyl levulinate was up to 39.27% (Tan et al., 2016). Moreover, metal sulfates were also found to be efficient solid catalysts for the synthesis of butyl levulinate in butanol medium (An et al., 2017; Deng et al., 2017).

Wheat straw represents a valuable source of cellulose, hemicellulose and lignin, which is a potential co-product of agriculture crop. In China, more than 700 million tons of wheat straw could be collected per year, and the utilization of wheat straw has aroused great concern. However, lots of wheat straw are still burned as traditional ways or without utilization yet, resulting in wasting of resources and environmental pollution (Zhong et al., 2015). For utilizing wheat straw efficiently, wheat straw has ever been used as raw materials for the production of levulinate, and a ethyl levulinate yield of 17.91 wt% can be obtained under the optimum conditions (Chang et al., 2012). However, this process still cannot meet the need of commercialization due to its lower economic benefits, and more green and efficient technology should be developed to improve the process.

To the best of our knowledge, there was to date no reports on ML production from wheat straw. Therefore, the objective of this study was to investigate the feasibility of ML production from wheat straw catalyzed by metal sulfates. It was found that commercial copper sulfate was an efficient solid acid catalyst in the process, and its lower cost and recyclable use can make the process more green and economical. Moreover, the conversion of ML from wheat straw was investigated in the context of a biorefinery concept, and the decanol pretreatment and the sodium hydroxide pretreatment were conducted to fractionate the hemicellulose and lignin fraction of wheat straw, yielding diversified high value products. This study provided a practical approach for the high value-added utilization of wheat straw.

2. Methods

2.1. Materials

Wheat straw was collected from a local farm (Zhengzhou, China), and was milled and screened for particles within the size range of 0.18 mm (80 meshes), then oven-dried at 110 °C to constant weight for further use. ML, levulinic acid (LA), methylglucoside (MLG), 5-hydroxymethylfurfural (5-HMF) were purchased from Shanghai Aladdin Industrial Incorporation (Shanghai, China), and 5-methoxymethylfurfural (5-MMF) was purchased from Wujiang win Chemical Co., Ltd (Suzhou, China). Moreover, commercial metal sulfates including $MgSO_4$, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, K_2SO_4, $Ti(SO_4)_2$, $CoSO_4$, $ZnSO_4$, Na_2SO_4 $CuSO_4$, $MnSO_4$, $CaSO_4$ were procured from Luoyang Chemical Reagent Factory (Luoyang, China), and methanol and dichloromethane were procured from Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd. (Tianjin, China).

2.2. Pretreatment of wheat straw

2.2.1. Acidic pretreatment of wheat straw in decanol (first stage)

The first stage has been realized with the aim to convert the hemicelluloses in wheat straw into alkyl pentosides, which is a new kind of bio-based surfactant with good surface activities. The pretreatment was conducted as per the reported procedure (Marinkovic et al., 2011). 50 g of wheat straw was firstly loaded into a 500 mL three-necked flask, then 650 g of decanol containing 0.7 wt% of sulfuric acid and 0.7 wt% of deionized water were added. The reactor was maintained at 109 °C in an oil bath and kept for 2 h with stirring. After that, the reaction mixture was cooled to 40 °C and filtered. The filtrate was distilled to recycle the excess decanol, and residues were recovered as bio-based surfactant. Moreover, the filter cake was washed three times with acetone to remove decanol and dried at 90 °C to constant weight.

The solid can be later processed by the second-stage pretreatment for lignin preparation.

2.2.2. Lignin preparation (second stage)

Lignin was prepared from solid residues obtained from the first stage. The procedure was as follows: the solid and 3.0 wt% NaOH aqueous were added into a three-necked flask equipped with a glass condenser tube, and the mass ratio of solid to liquid was 1:16. Then the mixture was kept at 85 °C for 3 h in a water bath with stirring. After that, the mixture was cooled to room temperature and filtered. Lignin can be extracted from filtrate by adjusting pH to 1.5 with 6 mol/L HCl, and recovered by centrifugation. Then, the filter cake was rinsed with deionized water to neutral, and dried at 60 °C to constant weight for ML production.

2.3. ML production

ML production was conducted in a 100 mL cylindrical pressurized reactor equipped with a magnetic stirring apparatus, in which 4 g of wheat straw or pretreated wheat straw, 36 mL of methanol and solid catalyst were mixed. The ratio of wheat straw to methanol was fixed to 1:9 (mass: volume). After sealing, the reactor was heated to a desired temperature by external electric heating and kept a designed time period under stirring at 600 rpm. The temperature of reactor contents was monitored by a calibrated thermocouple with the accuracy of ± 0.5 °C. The period of reaction time was calculated when achieving the designed temperature. After the reaction, the reactor was cooled by immersing into a water bath to terminate the reaction, and the reaction liquid mixture was filtered with a 0.45 μm syringe filter for GC and HPLC analysis.

The influence of reaction temperature, reaction time and catalyst dosage on ML yield was investigated using response surface methodology (RSM) in this study. A central composite design consist of 17 sets of experiments, including 5 central points was adopted. Table 1 shows the values for all the levels and factors when varying the reaction temperature between 170 and 200 °C, reaction time from 1 to 5 h and the catalyst loading between 0.3 and 0.7 g. The range of the factors was based on the preliminary tests, and the experimental results were fitted to the following second order model (Eq. (1)):

$$Y = a_0 + \sum_{n}^{1} b_i X_{ni} + \sum_{n}^{1} c_i X_{ni}^2 + \sum_{n}^{i=1:j=1} d_i X_{ni} X_{nj} (i > j)$$

(1)

2.4. Catalyst recovery and characterization

After the reaction, the solid residue containing the solid catalyst was firstly separated by centrifugation. After washed with dichloromethane, the collected solid was added into 50 mL deionized water, and stirred for 6 h at 40 °C. Under the conditions, the metal sulfate in the solid residue can be dissolved into water completely. Then, the filtrate contained the dissolved metal sulfate was collected through filtration. After that, the metal sulfate can be recovered by evaporating the water. To recover the catalyst in the reaction liquid, the liquid was filtrated and then distilled by using a rotary evaporator to remove the excess methanol until a dense mixture was formed. Then the mixture was

Table 1
Investigated levels for the three factors.

Factor	Variable	Level		
		−1	0	1
Reaction temperature/°C	X_1	170	180	190
Reaction time/h	X_2	1.0	3.0	5.0
Catalyst dosage/g	X_3	0.3	0.5	0.7