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# Catalytic conversion of carbohydrates to 5-hydroxymethylfurfural from the waste liquid of acid hydrolysis NCC

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ABSTRACT

The principal goal of this work was to reuse the carbohydrates and recycle sulfuric acid in the waste liquid of acid hydrolysis nanocrystalline cellulose (NCC). Therefore, in this work, the optimizations of further hydrolysis of waste liquid of acid hydrolysis NCC and catalytic conversion of $L_4$ to 5-hydroxymethylfurfural (5-HMF) were studied. Sulfuric acid was separated by spiral wound diffusion dialysis (SWDD). The results revealed that cellulose can be hydrolyze to glucose absolutely under the condition of temperature 35 °C, 3 h, and sulfuric acid's concentration 62 wt%. And 78.3% sulfuric acid was recovered by SWDD. The yield of 5-HMF was highest in aqueous solution under the optimal condition was as follows, temperature 160 °C, 3 h, and sulfuric acid's concentration 12 wt%.

Then the effect of biphasic solvent systems catalytic conversion and inorganic salt as additives were still examined. The results showed that both of them contributed to prepare 5-HMF. The yield and selectivity of 5-HMF was up to 21.0% and 31.4%, respectively.



## 1. Introduction

5-Hydroxymethylfurfural (5-HMF), a versatile platform chemical, is expected to play a key role as a petroleum replacement precursor for renewable chemicals and biofuels (Alam, De, Singh, Saha, & Abu-Omar, 2014). It can be transformed to a variety of valuable chemicals such as 5-hydroxymethylfuran-2-carboxylic acid, 5-formyl-2-carboxylic acid, 2,5-furandicarboxylic acid, 2,5-furan dimethanol, 5-ethoxymethyl-2-furfural, 2,5-diformylfuran, maleic anhydride and levulinic acid via oxidation (Lilga, Hallen, & Gray, 2010), etherification (Balakrishnan, Sacia, & Bell, 2012), oxidative cleavage (Du, Ma, Wang, Liu, & Xu, 2011), and deformylation (Antonyraj et al., 2013; Maldonado, Assary, Dumesic, & Curtiss, 2012). Therefore, 5-HMF's existence plays an important role in the chemical field.

Due to economic and application value, how to prepare 5-HMF becomes important. There were many methods have been found, such as inorganic acid, organic acid, inorganic salt, ionic acid as catalyst and biphasic systems catalytic conversion. For example, Morales et al. used a biphasic water/methyl isobutyl ketone (MIBK) as reaction medium and 30 wt% 10Al-MCM catalyst with respect to the substrate weight (glucose), 87% of glucose conversion and 36% of HMF yield were achieved at 195 °C after 150 min reaction time (Jimenez-Morales, Moreno-Recio, Santamaria-Gonzalez, Maireles-Torres, & Jimenez-Lopez, 2014). Zhang et al. showed when niobium phosphate catalyst contains both Brönsted acid and Lewis acid sites, glucose-unit carbohydrate can be transformed to HMF successfully, which can combine the isomerization process with the dehydration step in one-pot reaction system without adding any other acid catalysts. And the yield of HMF can be slightly increased to 39.3% in a biphasic water/MIBK medium (Zhang et al., 2015).

As reported in the literature, there are still many kinds of materials to prepare 5-HMF, such as glucose, fructose, sucrose, cellobiose, starch and cellulose. For example, Su et al. used cellulosic biomass as feedstock for the large-scale production of 5-HMF depends critically on the development of effective low temperature processes. They reported a single-step catalytic process where cellulose as the feed is rapidly depolymerized and the resulting glucose is converted to HMF under mild conditions (Su et al., 2009). Jadhav et al. used dicationic room temperature ionic liquids, with short oligo ethylene glycol linkers to be highly active catalyst for the selective dehydration of fructose and sucrose into 5-HMF. As a result, 92.3% of HMF yield was obtained from fructose in 40 min with one equivalent of $[TetraEG(mim)_2][OMs]_2$ at 120 °C. While, 67.2% of HMF was achieved from dehydration of sucrose at 120 °C in 150 min using two equivalents of $[TetraEG(mim)_2][OMs]_2$ (Jadhav, Kim, & Wang, 2012). Even though there were such kinds of materials, the use of fructose and other materials as substrate are not economical

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because of their slow availability and high cost. Glucose which is the main component of biomass has been considered more desirable substrate (Jain, Shore, Jonnalagadda, Ramanujachary, & Mugweru, 2015). How to apply glucose to 5-HMF needs to be discussed.

Cellulose fibrils consist of different hierarchical microstructures commonly known as nano-sized microfibrils. These nano-sized fibrils are again made up of a combined crystalline and amorphous parts and this crystalline region is named nanocellulose or nanowhisker in the literatures (Klemm, Heublein, Fink, & Bohn, 2005). Nanocrystalline cellulose (NCC) is obtained by the acid hydrolysis of cellulose under conditions where the amorphous regions are selectively hydrolyzed (Kaboorani et al., 2012). The amorphous regions will be hydrolyzed to glucose and oligosaccharides. The common method to prepare NCC is hydrolysis of cellulose by mineral acids, including sulfuric acid (Tang, Yang, Zhang, & Zhang, 2014), hydrochloric acid (Yu et al., 2013), phosphoric acid (Espinosa, Kuhnt, Foster, & Weder, 2013), and their mixtures (Liu et al., 2014). However, a lot of waste including a large amount of acid, glucose and oligosaccharides are produced during the process of acid hydrolysis. If discarded into the nature directly, the waste will cause environmental contamination and result in huge cost of living resources. So it is definitely necessary to recycle and reuse acid, obligation and waste liquid.

As mentioned above, there are lots of valuable materials in the waste water of acid hydrolysis NCC, then how to make full use of them becomes especially necessary. And as discussed before, glucose can be used to prepare 5-HMF by acidic catalyzer and biphasic system. In this article, the main idea was that the waste liquid of sulfuric acid hydrolysis was reprocessed to produce glucose to a full extent, and the sulfuric acid was filtered out by spiral wound diffusion dialysis (SWDD) membrane module, then the glucose was catalyzed to 5-HMF with acid catalyzer and inorganic salt in biphasic system. Sulfuric acid could be removed from the second hydrolysis liquid through SWDD membrane twice, and the recycling sulfuric acid could be used to prepare NCC again. Thus the waste water could be fully reused without causing any environmental contamination and has certain economic value.

## 2. Experimental

### 2.1. Materials

Sulfuric acid (AR), sodium hydroxide (AR), calcium carbonate (AR), glucose (SP), NaCl (AR), LiCl (AR), $MgSO_4$ (AR) were purchased from Tianjin No. 1 Chemical Reagent factory, China. 5-(hydroxymethyl) furfural (5-HMF, SP) and levulinic acid (LA, SP) were purchased from Shanghai Civi Chemical Technology Co., Ltd., China. Bleached hardwood dissolving pulp was provided by Shandong Papermaking Co., Ltd., China. N,N-dimethylformamide (AR), dimethyl sulfoxide (AR), acetonitrile (AR) were purchased from Tianjin Yongda Chemical Technology Co., Ltd., China.

Suspensions of waste water of acid hydrolysis NCC were prepared as follows: hydrolysis was carried out using 60 wt% sulfuric acid at 40 °C for 4 h with constant stirring. Mass ratio of bleached hardwood dissolving pulp and acid was 1:10. Immediately following the acid hydrolysis, the suspension was diluted with deionized water to stop the reaction prior to remove NCC from this suspension. The resulting mixture was centrifuged (8000 rpm) for 10 min at 10 °C. Afterwards, the obtained supernatant ($L_1$) was material we needed. The precipitation, NCC, was sent to other applications.

As listed in Table 1, the main components were 40.69 wt% sulfuric acid, 7.75 g/L glucose and 0.0368 g/L 5-HMF. Actually, there still were many polymers such as NCC whiskers and oligo-sugar. However, it was hard to determine their concentration due to the high concentration of sulfuric acid. Therefore, their concentrations were expressed by glucose's improvement in later hydrolyzation process. Evidently, the concentration of sulfuric acid was too high. Therefore, it should be removed. While, the existence of NCC whiskers and oligo-sugar would block SWDD's pore. So further hydrolyzation was necessary.

**Table 1**
The contents of glucose and 5-HMF in each stage.

| Liquid | Sulfuric acid (wt%) | Glucose (g/L) | 5-HMF (g/L) |
|---|---|---|---|
| Original waste liquid | 40.69 | 7.75 | 0.0368 |
| Secondary hydrolyzate ($L_2$) | 61.54 | 6.44 | 0.440 |
| Before membrane separation (add water) ($L_3$) | 40.09 | 3.75 | 0.030 |
| After the membrane process ($L_4$) | 8.7 | 3.31 | – |

### 2.2. Further hydrolysis of waste liquor and recovery of acid

In order to get better hydrolysis, the effects of sulfuric acid concentration, time and temperature on the hydrolysis experiment were investigated. The impact of dosage on the sulfuric acid was studied by varying its concentration in the solution (e.g., 60 wt%, 62 wt%, 65 wt%, 67 wt%, 70 wt%, 75 wt% and 80 wt%) at the constant condition temperature (35 °C) and time (3 h). To investigate the effect of temperature, the hydrolysis experiment was conducted at a temperature range of 25–42 °C, while the time and sulfuric acid were 62 wt% and 3 h, respectively. The kinetic of hydrolysis was studied using sulfuric acid concentration of 65 wt% at 35 °C but at different hydrolysis time intervals (0–4 h). All the above further hydrolysis experiments' concentration of glucose and 5-HMF of were detected 3 times and the average values are presented in this paper.

After further hydrolysis, there were lots of sulfuric acid in the second hydrolysis solution ($L_2$). The concentration was too high so that it had negative impact to catalysis. Therefore, SWDD membrane module (Li, Zhang, Huang, Zhu, & Wang, 2012; Zhang, Li, Wang, & Xu, 2011) was used to recover sulfuric acid. $L_2$ was diluted so that sulfuric acid concentration in this solution ($L_3$) was suitable for SWDD membrane module. Import and export flow velocity of $L_3$ was controlled at 4–6 mL/min through SWDD membrane. At the same time the diffusate flow (deionized water) rate intensity was also kept constant at 4–6 mL/min, too. After twice separation, the solution ($L_4$) with low concentration of sulfuric acid was obtained. The recovered sulfuric acid was recycled to prepare NCC. Glucose and sulfuric acid in every stage was measured.

### 2.3. Analysis of glucose and 5-HMF

The content of glucose in waste water samples before and after the hydrolysis experiment, and at the each stage of separation was determined using SBA-40C biosensor analyzer (Castillo, Gaspar, Sakharov, & Csoregi, 2003). Each sample pH value was adjusted between 4 and 8. And they were diluted in the deionized water to make sure that glucose concentration was between 20 mg/dL and 80 mg/dL. Analyses were performed in triplicate and the average values are presented in this paper.

5-HMF content was detected through absorption values at a wavelength of 284 nm by UV2550 UV spectrophotometry (Zappala, Fallico, Arena, & Verzera, 2005). A calibration curve of UV absorbency at 284 nm was measured and the amount of 5-HMF in each sample was determined using the calibration curve. All samples were diluted in the deionized water in order to make sure that absorption value varied from 0.200 to 0.800. Analyses were performed in triplicate and the average values are presented in this paper.