The effect of catalyst types and starting materials on furan production in hot compressed water

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Abstract

The catalytic conversion of sugars (glucose and fructose) to furan compounds (HMF and furfural) was studied under hot compressed water (HCW) conditions. The effect of catalyst types (homogeneous acid (H\textsubscript{3}PO\textsubscript{4}) and base (NaOH)), and starting materials (monosaccharide and cellulose) on furan yields was investigated. It was found that at 200 °C, phosphoric acid showed great catalytic activity on the production yield of HMF from dehydration of the sugars, when compared with NaOH. Cellulose is composed of glucose units, and would first be hydrolyzed and then dehydrated to furans. The optimum condition for hydrolysis/dehydration was observed under the acid-catalyzed conditions with the reaction temperature of 230 °C and reaction time of 5 minutes, at which the yields of sugar and furan compounds were achieved at 23.0 and 7.5%, respectively.

Keywords: Hot compressed water; HMF; sugar; cellulose; phosphoric acid

1. Introduction

Nowadays, the shortage of fossil fuels is a serious concern around the globe. Moreover, pollutant emission during their combustion has influenced on the climate change and environmental problems. Utilization of renewable energy from biomass will be one of the solutions to cut-off these problems. Lignocellulosic biomass is one kind of biomasses which refer to plant biomass consisted of biopolymer such as cellulose (40-60\%), hemicellulose (20-40\%), and lignin (10-24\%) \cite{1}. Degradation of the polysaccharide constituents, i.e. cellulose and hemicelluloses results in formation of sugars, e.g. hexose
and pentose which could be used as versatile starting materials for producing a variety of value-added products.

In considering the biomass conversion method, hot compressed water (HCW) is an attractive one for processing of sugars and lignocellulosic feedstocks due to its advantages on environmental friendliness and potential on reaction control through the use of water density [2]. Chemical reactions in HCW can be enhanced by water which acts as solvent, reactant, and catalyst in the systems. HCW has typically been developed for production of various chemicals. Specifically, furan derivatives such as 5-hydroxymethylfurfural (HMF) and furfural, obtained by dehydration of carbohydrates, have been described as key substances that bridge carbohydrate chemistry and petroleum-based industrial chemistry because the wide range of chemical intermediates and end-products can be produced from these compounds. Interestingly, furan compounds can be subsequently converted into diesel fuel additives, biopolymers, and industrial solvents [3]. This versatile chemical platform is considered to play a significant role in biorefinery industry.

In the present work, we aimed at the study of effects of catalyst types on hydration of sugars and the integrative hydrolysis/dehydration of cellulose to produce HMF, furfural, and/or sugars under hot compressed water. Moreover, the influence of reaction temperature and time was investigated to optimize furan yields.

2. Experimental

Glucose, fructose, and sodium hydroxide were commercially obtained from Carlo Erba, whilst cellulose was from Sigma Aldrich. Phosphoric acid was obtained from Ajax Finechem. All are of analytical grade.

The reactions were carried out in an SS316 stainless steel tube reactor with the inner volume of 10 cm³. A typical reaction procedure was as follows: sugar or cellulose (0.1 g) and water (1 cm³) were introduced into the reactor along with 0.1 M H₃PO₄ or 0.1 M NaOH to adjust pH to 2 and 11, respectively. Nitrogen was loaded to raise the reactor pressure to 2.5 MPa. Then, the reactor was heated at desired temperature with a heating rate of 20 °C/min. After reaching the reaction time required, the reaction was stopped instantly by quenching the reactor in an ice-cooling bath.

The samples taken from the reactor were filtered and washed with a portion of deionized water to recover the liquid products. The amount of products in the liquid samples was quantitatively analyzed by a high-performance liquid chromatography (HPLC) after appropriate dilution with pure water. A Shodex RSpak KC811 column with UV detector was employed to detect HMF and furfural compounds. Gel permeation chromatography (GPC) coupled with a Shodex Sugar SP810 column with reflective index (RI) detector was employed to detect the glucose, fructose, and 1,6-anhydroglucose (AHG). The amount of each compound in the liquid products was determined using calibration curves obtained by analyzing standard solutions with known amounts. The HMF or furfural yield, conversion of sugar, and sugar yield were calculated using the following equations:

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\text{HMF or furfural yield (\%) = } \frac{\text{gram of HMF or furfural in product}}{\text{gram of feedstock}} \times 100
\]

\[
\text{Conversion of sugar (\%) = } \frac{(\text{initial sugar mass} - \text{last sugar mass})}{\text{initial sugar mass}} \times 100
\]

\[
\text{Sugar yield (\%) = } \frac{\text{gram of sugar in product}}{\text{gram of initial biomass}} \times 100
\]
3. Result and discussion

3.1 Effect of catalyst type

The effect of catalyst types on dehydration of sugars (glucose and fructose) and hydrolysis/dehydration of cellulose was investigated in detail under HCW condition. Sodium hydroxide and phosphoric acid were chosen as representative base and acid catalysts in these experiments for activity comparison. The results obtained in the absence and presence of the catalysts are shown in Fig. 1. As shown in Fig. 1A, the conversion of glucose was slightly promoted by adding sodium hydroxide and phosphoric acid when compared with blank test without catalyst. However, the HMF yield from glucose dehydration in the presence of phosphoric acid and sodium hydroxide was two times higher than that without catalyst. This result revealed that both base and acid catalysts can effectively enhance glucose dehydration.

![Fig. 1. Effect of catalyst type on the conversion and product yield from dehydration of glucose (A) and fructose (B), and hydrolysis/dehydration of cellulose (C) at 200 °C for 5 min.](image-url)
With or without catalysts, the fructose conversion was nearly comparable at 82-92%. Under the present condition studied, fructose could be rapidly dehydrated to furans, and therefore the addition of sodium hydroxide and phosphoric acid provided a small effect on the fructose conversion. Nonetheless, the HMF yield was highest at 29% over phosphoric acid. The results showed that dehydration reaction of fructose was much easier proceed than that of glucose catalyzed by both sodium hydroxide and phosphoric acid. For glucose transformation, selectivity to furans was highly enhanced with the use of the catalysts. This behavior could be ascribable to their structural change during the reaction. Glucose forms a very stable ring structure, so that the fraction of open chain formed in the solution, and the enolisation rates were consequently slow. On the other hand, less stable ring structures of fructose gave rise to higher open chains, and so the enolisation rates were comparatively high. Strictly speaking, glucose undergoes polymerization to fructose and subsequently fructose is transformed to HMF via dehydration step [4]. The ring-opening step would have a high energy barrier, especially when no catalyst was used, and was presumably considered a rate-determining step in overall glucose transformation to HMF. Using the catalyst would suppress the activation energy required. HMF yield was consequently higher with the use of the catalysts and/or with fructose as the starting material.

Cellulose is polysaccharide which is hydrolyzed and dehydrated to produce sugar and furans, respectively. Glucose, HMF, and furfural, as three main products from cellulose conversion, are depicted in Fig.1C. The catalytic effect of phosphoric acid was much higher than that of without catalyst, and with sodium hydroxide in enhancing the formation of glucose, HMF, and furfural, with a total yield of 10% at 200 °C for 5 min. As it turned out, only phosphoric acid is capable of effective hydrolysis of cellulose, and dehydration of the resultant sugar.

3.2 Effect of reaction temperature

To obtain the highest product yield, it is necessary to optimize the reaction conditions by varying the reaction temperature and time. The reaction tests were implemented at varied temperatures (200-270 °C) in the presence of phosphoric acid.

Fig.2 shows the values of conversion of glucose, fructose, and cellulose, and their product yields. It was clear that temperature had a dramatic effect on the hydrolysis and/or dehydration of glucose, fructose, and cellulose. Glucose conversion was elevated from 43 to 92% when the temperature increased from 200 to 270 °C. HMF yield was gradually incremented as temperature increased, and the yield of ca. 10% was peaked at 220 and 230 °C. At temperature higher than 230 °C, HMF yield gave the opposite results, though the glucose conversion kept slightly increasing. In Fig.2B, fructose conversion showed high values (>85%) for all temperatures studied. HMF yield decreased sharply from 29 to 0% when the temperature increased from 200 to 270 °C, and large amounts of brown insoluble products were formed, presumably to be humins.

The hydrolysis of cellulose is strongly dependent on the temperature (see in Fig.2C). The high temperatures can enhance the transformation of cellulose to glucose. However, degradative side-reactions of glucose could also take place and speed up with the increase of temperature. By increasing the temperature, products yields from cellulose hydrolysis/dehydration were enhanced, reaching a maximum at 230 °C. When the reaction temperature rose above 230 °C, the yield of HMF began to fall, and intermediates such as glucose were not detected. These results were in line with the conversion behaviors of glucose and fructose described above. The higher temperatures thus could accelerate the chemical reactions, meanwhile unwanted side-reactions also appeared at the same time. Under the present conditions investigated, it was found that humins occurred during the reaction at higher temperature. In addition, carboxylic acids and aldehydes were partially detected as confirmed by qualitative analysis of GS-MS.
Fig. 2. Effect of temperature on the conversion and product yield from dehydration of glucose (A) and fructose (B), and hydrolysis/dehydration of cellulose (C) catalyzed by H$_3$PO$_4$ at 200-270 °C for 5 min.

3.3 Effect of reaction time

The effect of reaction time on the hydrolysis and/or dehydration of glucose, fructose and cellulose in the presence of phosphoric acid was studied under hot compressed water conditions at 220, 200, and 230 °C, respectively. As shown in Fig.3A, glucose conversion monotonously increased with increasing reaction time, and was greater than 90% at 30 min. However, HMF production decreased at prolonged time, due to the consecutive decomposition to formic and levulinic acids as confirmed by GC-MS analysis. Fructose conversion showed high values (>90%) at 0-30 min (see in Fig.3B). The HMF yield increased with the prolongation of time from 0 (26%) to 5 min (29%). The yield reached a maximum at 5 min, and then decreased greatly afterward.
Fig. 3C shows the product yields of HMF, furfural, and glucose from hydrolysis/dehydration of cellulose implemented at reaction temperature of 230 °C for 0-10 min. The total yield from hydrolysis/dehydration of cellulose increased from 24 to 31 % when the reaction time increased from 0 to 5 min, respectively. Then it decreased to 16.7 % at a reaction time of 10 min. These results suggested that the increase in the reaction time improved not only the formation of products but also at the same time their decomposition rate. Glucose formation decreased from 23.0 to 6.6 % with increasing reaction time from 5 to 10 min. Sasaki et al (1998) [5] concluded that the glucose decomposition rate is much faster than the hydrolysis rate of cellulose. Thus, even if the hydrolysis products, such as glucose or oligomers, are formed, their further decomposition rapidly takes place and thus a high yield of hydrolysis products cannot be obtained.

![Graphs showing product yields and conversions](image-url)
According to the results in Fig.3C, cellulose was first hydrolyzed into glucose and then dehydrated to furans. The amount of formation of glucose from hydrolysis was more than decomposition of glucose to HMF at initial time of reaction. Then, when glucose was generated more, the HMF yield increased because glucose decomposition rate is much faster than the hydrolysis rate of cellulose (from 3.6 to 7.5% with reaction time at 0 to 5 min, respectively). Moreover, even hydrolysis products at 10 min were formed in higher yield, the amount of glucose decreased because glucose converted to HMF and then HMF could be decomposed to degraded products such as acids or aldehydes.

4. Conclusions

We have studied the effect of catalyst types, reaction temperature, and reaction time on the catalytic conversion of cellulose and sugar to furan compounds in hot compressed water. It was observed that catalyst types, temperature, and reaction time have a great effect on the hydrolysis and dehydration of glucose, fructose, and cellulose. Phosphoric acid shows great catalytic activity for dehydration of glucose and fructose. Moreover, phosphoric acid can promote hydrolysis of cellulose in producing glucose in high yield. Sodium hydroxide as a base catalyst can promote dehydration of glucose in HMF yield, comparable to phosphoric acid. However, sodium hydroxide could not catalyze the cellulose conversion, and there was no significant difference with the HCW without catalyst.

The best reaction condition of glucose, fructose, and cellulose was found at 200-230 °C and 5 min. HMF yield from dehydration of glucose and fructose was 9.6 and 29%, respectively. Sugar and furan compounds from hydrolysis and dehydration of cellulose were achieved at 23.0 and 7.5%, respectively.

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References