One-pot Synthesis of 5-Hydroxymethylfurfural Using a Homogeneous Aqueous Solution of Cellulose (Cellulose-LiBr-H₂O) and Combined Metal (II)- Surfactant Catalyst

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One-pot synthesis of 5-hydroxymethylfurfural (HMF) from cellulose or glucose through employing a concentrated solution of LiBr as solvent together with a combined metal (II) and surfactant catalyst was studied. First, cellulose was dissolved in the solvent, and then it was hydrolyzed with hydrogen bromide (HBr) under moderate conditions before the solution was neutralized. The next step toward HMF synthesis was performed at 140 °C for 3 h with the addition of the abovementioned catalyst at a 10 mol% level of the substrate. Metal (II) chlorides that could serve as a Lewis acid (*i.e.*, catalysts), or combined metal (II) and surfactant catalysts, were adopted for converting glucose to HMF. The yield of HMF reached 30.5% from glucose, and 33.8% from cellulose when tin (II) dodecylsulfate was used as a Lewis acid catalyst. The catalyst containing tin (II) yielded better results than those that contained zinc (II) or copper (II).

Keywords: 5-hydroxymethylfurfural (HMF); Glucose; Cellulose; Metal (II) chloride; Surfactant

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INTRODUCTION

Due to the recent increase in environmental concerns, the production of fuels and raw materials from renewable biomass has become the focus of an increasing number of studies (Chheda *et al.* 2007; Corma *et al.* 2007). These studies include attempts to produce 5-hydroxymethylfurfural (HMF) from carbohydrates in good yields, where HMF is expected to serve as an industrial chemical after being synthesized from biomass *via* simple reactions. It is expected to be used for making polymers, such as polyesters (Moore and Kelly 1978; Gandini *et al.* 2009), polyamides (Gharbi and Gandini 1999), polyurethanes (Boufi *et al.* 1995), and poly(vinylfurans) (Yoshida *et al.* 2008), for preparing bio-fuels (Román-Leshkov *et al.* 2007). While high yields of HMF can be obtained from fructose, sucrose, and inulin, the yields from glucose and cellulose are relatively low. Various conditions have been adopted for synthesizing HMF, *e.g.*, an immiscible two-phase (water/organic) reacting system employing a Brønsted acid as catalyst (Román-Leshkov *et al.* 2006; Teng *et al.* 2016), ionic liquids as a solvent (Zhao *et al.* 2007; Su *et al.* 2009) with Lewis acid catalysts (such as chromium chloride, various metal chlorides (Tyrlik *et al.* 1995; Ishida and Seri 1996), or its triflates) (Wang *et al.* 2011; Rasrendra *et al.* 2012), solid acid (Shimizu *et al.* 2009; Dou *et al.* 2018) and base

catalysts (Ohara *et al.* 2010), and combinations of zeolite and a Lewis acid (Otomo *et al.* 2014). However, challenges still exist in producing HMF from cellulose in industrially large volumes.

In this study, the authors aimed to examine whether the combination of Lewis acid and surfactant catalysts can effectively catalyze the reaction of the creation of HMF from glucose. The combined acid and surfactant catalysts were first developed by Kobayashi *et al.* (1997, 2002) in an attempt to promote aldol condensation between silylenols and aldehydes in an aqueous medium. These combined acid and surfactant catalysts are expected to catalyze reactions in water without the severe degradation of the Lewis acid to Brønsted acid (Kobayashi *et al.* 2002). In addition, the authors also expect the surfactant portion of the catalyst to protect the product from further degradation in acidic water. For enabling one-pot synthesis of HMF from cellulose, the authors will use a concentrated solution of aqueous LiBr ($\leq$ 60 wt%), a recently developed solvent for cellulose (Yan *et al.* 2014) (Fig. 1).

The dissolved cellulose will then be acid-hydrolyzed into glucose in this solvent and neutralization of the mixture will follow. Next, a further hydrothermal treatment that leads to HMF synthesis will be performed after adding the abovementioned combined Lewis acid and surfactant catalyst to this mixture once neutralization occurs.
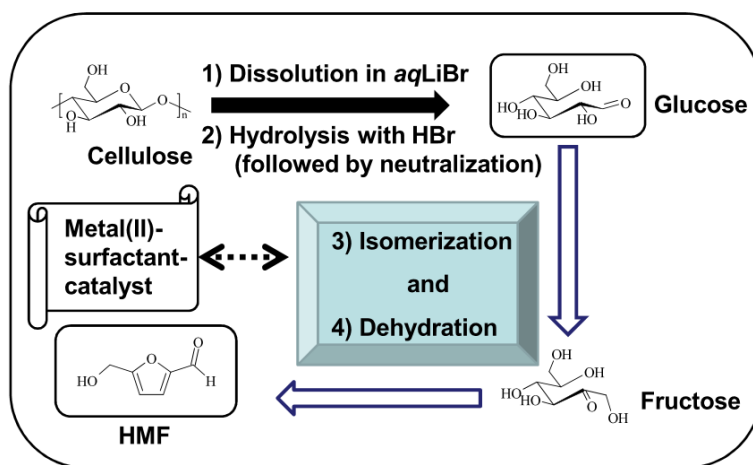

Fig. 1. Schematic for the synthesis of HMF from cellulose

EXPERIMENTAL

Materials

Microcrystalline cellulose (Funacel®(II), Funakoshi, Tokyo, Japan) was used as the original cellulose sample. Hydrobromic acid (47 wt% to 49 wt%), lithium bromide monohydrate, zinc (II) chloride, copper (II) chloride, tin (II) chloride dehydrate, and sodium dodecyl sulfate were supplied by Wako (Wako Pure Chemicals Industries, Tokyo, Japan).

All of the other chemicals were purchased from Wako or TCI (Tokyo Chemical Industries, Tokyo, Japan). All of the chemicals obtained were reagent grade and used as received.

Methods

Instrumentation

Gas-liquid chromatographic (GLC) analysis for determining the glucose content was performed using a GC353B (GL Science, Tokyo, Japan) equipped with a flame-ion detector. The capillary column used for the determinations was a 30QC2/BPX70 (SGE, Melbourne, Australia, 30 m × I.D. 0.22 mm). The temperatures for the injector and the detector were 250 °C and 280 °C, respectively. The temperature of the oven was programmed as follows: 190 °C for 1 min (initial), increased at a rate of 3 °C/min, and then kept at 260 °C for 2 min (final).

A gas chromatography/mass spectrometry (GC/MS) analysis for the determination of HMF content was performed using a GC-17A (Shimadzu, Kyoto, Japan) equipped with a GCMS-QP5000 device (Shimadzu, Kyoto, Japan) as a MS detector, employing an electron impact ionization method. The capillary column used was a CP-Sil 8CB (VARIAN Medical Systems, Palo Alto, CA, USA; 30 m × I.D. 0.25 mm). The injector and detector temperatures were 250 °C and 280 °C, respectively. The oven temperature was programmed as follows: 130 °C for 3 min (initial), increased at a rate of 2 °C/min, and then kept at 260 °C for 2 min (final).

All of the measurements in this study were accomplished in duplicate, and the averaged data was used.

Hydrolysis of cellulose in aqueous lithium bromide (LiBr) solution, and the determination of glucose content in the solution to monitor hydrolysis

To make a cellulose/LiBr/ H_2O solution, cellulose was added in an aqueous solution of LiBr (60 wt% of LiBr concentration, 2 mL) at a resulting cellulose concentration of 6.0 wt% in the mixture in a glass tube. Then, the tube was set within a stainless-steel autoclave before being heated in an oil bath at 120 °C for 1 h to perfectly dissolve the cellulose.

Hydrobromic acid (47–49%) was added into the obtained solution, so that the resulting acid concentration was 1.2 wt% or 2.0 wt%. The hydrolysis of cellulose was performed in a water bath at 80 °C for either 15 min or 30 min. After these durations, the mixture was cooled and neutralized using an aqueous sodium hydroxide before filtration.

The filtrate was transferred to a 25-mL volumetric flask and diluted with deionized water by filling up to the marked line. Then, *myo*-inositol (10 mg), as an internal standard, was added to a small aliquot (1 mL) of the abovementioned solution. The dissolved substance in this solution (most of which was glucose) was reduced using sodium borohydride in a water bath at 40 °C for 90 min. After the reaction, acetic acid (0.5 mL) was added to make the remaining sodium borohydride ineffective. Then, acetic anhydride (9 mL) and 1-methylimidazolium (0.9 mL) were added to the solution, and acetylation was carried out at room temperature for 10 min. Deionized water (15 mL) was added to stop the reaction. Lastly, dichloromethane (2 mL) was added to extract the acetylated substances, and then GLC analysis was performed.

Synthesis of combined Metal (II) - Surfactant catalysts (Deleersnyder et al. 2008)

Sodium dodecyl sulfate (Na(DOS)) (2.8971 g, 10.05 mmol) was dissolved in deionized water (70 mL) in a water bath at 70 °C. To this solution, a solution of $ZnCl_2$ (0.6766 g, 4.96 mmol) in deionized water (5 mL), pre-heated at 70 °C, was added. The mixture was then cooled and allowed to remain in a refrigerator for three days. The precipitate was filtered by a glass crucible (G1) and dried using a vacuum oven at 40 °C

overnight. By similar operations, Cu(DOS)$_2$ and Sn(DOS)$_2$·2H$_2$O were prepared from Na(DOS) (2.8855 g, 10.01 mmol) and CuCl$_2$ (0.6616 g, 4.92 mmol) and from Na(DOS) (2.8935 g, 10.03 mmol) and SnCl$_2$·2H$_2$O (1.1228 g, 4.98 mmol), respectively. The yields were as follows: 83.0% for Zn(DOS)$_2$, 95.6% for Cu(DOS)$_2$, and 49.1% for Sn(DOS)$_2$·2H$_2$O. The elementary analyses for the obtained catalysts were conducted as follows: metal contents were measured by a chelate titration method using ethylenediaminetetraacetic acid. Sulfur and chloride contents were measured by an oxygen flask combustion method. Carbon and hydrogen contents were analyzed by a CHN corder. The analysis calculated for Zn(DOS)$_2$ (=C$_{24}$H$_{50}$O$_8$S$_2$Zn): C, 48.35%; H, 8.45%; S, 10.76%; Zn, 10.97%. The following were found: C, 46.20%; H, 8.71%; S, 10.54%; Zn, 6.47%. The analysis calculated for Cu(DOS)$_2$ (=C$_{24}$H$_{50}$O$_8$S$_2$Cu): C, 48.50%; H, 8.48%; S, 10.79%; Cu, 10.69%. The following were found: C, 45.36%; H, 8.82%; S, 10.49%; Cu, 7.13%. The analysis calculated for Sn(DOS)$_2$·2H$_2$O (=C$_{24}$H$_{54}$O$_{10}$S$_2$Sn): C, 42.05%; H, 7.94%; S, 9.35%; Sn, 17.32%. The following were found: C, 39.79%; H, 7.21%; S, 9.68%; Sn, 5.53%.

Procedure for conversion of monosaccharide to HMF

A 60 wt% aqueous solution of LiBr (2 mL) containing glucose at a concentration of 6.0 wt% (which is a model solution of cellulose hydrolysate in our study for one-pot synthesis of HMF), or the exact solution of cellulose hydrolysate mentioned above, was added to the prepared catalyst (10 mol%). The mixture in a glass tube was then set in a stainless-steel autoclave and sealed. The mixture was heated in an oil bath at either 120 °C or 140 °C, for 3 h. After the reaction, the mixture was neutralized using an aqueous solution of sodium hydroxide and filtered.

The filtrate was transferred to a 25-mL volumetric flask and diluted with deionized water by filling up to the marked line. An aliquot (10 mL) of the solution was then concentrated to a syrup using a rotary evaporator under 50 °C at a pressure below 30 hPa before repeated extraction with methyl isobutyl ketone (MIBK) (30 mL, 5 times) and ethyl acetate (EA) (30 mL, twice). Vanillin (20 mg) was added to the combined solvents used for the extraction (MIBK/ EA) as a reference. The resulting solution was concentrated to a volume of *ca* 5 mL. The HMF content was analyzed *via* GC/MS and the remaining unreacted glucose content was analyzed *via* GC.

Calculation of the yield, conversion, and selectivity of HMF

The yield, conversion, and selectivity of HMF were defined and calculated based on the results of GC and GC/MS following the work of Román-Leshkov *et al.* (2009). The yield of HMF was the percentage of moles of obtained HMF divided by the moles of initial glucose. The conversion was the percentage of the moles of consumed glucose divided by the initial moles of glucose present. Lastly, the selectivity was the percentage of the mole of obtained HMF divided by the moles of consumed glucose. The equations are shown below.

Yield (%) = 100×(moles of HMF produced)/(moles of glucose initial)　　　(1)

Conversion (%) = 100×(moles of glucose reacted)/(moles of glucose initial)　　(2)

Selectivity (%) = 100×(moles of HMF produced)/(moles of glucose reacted)　　(3)

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RESULTS AND DISCUSSION

The acid hydrolysis of cellulose with HBr in an aqueous solution of LiBr under various conditions in terms of the yields of glucose and the rates of residual solid was estimated. The results under the typical four conditions (H-1–H-4) are listed in Table 1. At shorter durations, higher yields of glucose (H-1 > H-2 and H-3 > H-4) and lower residual mass rates (H-1 < H-2 and H-3 < H-4) were obtained, as can be seen from the comparison between H-1 and H-2 and between H-3 and H-4. It was considered that at longer durations, glucose created during hydrolysis underwent further degradation, resulting in the formation of more humic residual substance. Furthermore, higher glucose yields were obtained at higher concentrations of the acid (H-1 and H-2). This may have been a result of insufficient acid hydrolysis of cellulose in a solution with a lower acid concentration (H-3 and H-4), which suggested the existence of water-soluble oligomeric saccharides. An even higher acid content (3.0 wt%) and higher temperature (120 °C) were examined, but both led to poorer yields of glucose ($\leq$ 7.2%) and higher residual mass rates ($\leq$ 50.1%). Therefore, H-1 was selected as the condition for the experiments. Because one-step production of HMF from cellulose was expected, the HMF content along with the remaining glucose content was expected, but HMF was not detected under the conditions mentioned above. Instead, quite mild hydrolysis conditions of cellulose were detected, wherein the reaction proceeded in a very short duration.

Table 1. Acid (HBr) Hydrolysis of Cellulose in LiBr/H_2O Solution

Conditions	H-1	H-2	H-3	H-4
Aq HBr (wt%)	2.0	2.0	1.2	1.2
Duration (min)	15	30	15	30
Temperature (°C)	80	80	80	80
Yield of glucose (%)	94.9	90.7	87.1	82.3
Residual mass (%)	2.0	3.9	1.3	2.0

Conversion of Glucose to HMF

The conversion of glucose to HMF was studied as the next step. The yield of HMF and the conversion of glucose and its selectivity, obtained by using metal (II) chloride (= Lewis acid) without the surfactant or by using the metal (II) combined with the surfactant, are listed in Table 2. The reaction medium used was a 60 wt% aqueous solution of LiBr with the aim of achieving one-pot synthesis of HMF from cellulose. Concerning glucose conversion, better results were obtained at 140 °C than that at 120 °C, in most cases. Glucose conversion for $CuCl_2$ and $SnCl_2 \cdot 2H_2O$ was almost perfect at 140 °C under this condition, while the yield of HMF was 0% for $CuCl_2$ and 28.9% for $SnCl_2 \cdot 2H_2O$, respectively. The highest yield of HMF obtained using $SnCl_2 \cdot 2H_2O$ was in accordance with the results of Chen and Lin (2010), indicating that the Lewis acid catalyst containing tin was effective in promoting the isomerization of glucose to fructose (Enslow and Bell 2015; Nguyen *et al.* 2016), which is regarded as an intermediate compound in the transformation from glucose to HMF. Sn^{2+} might have promoted an intramolecular hydride shift in glucose forming metal complex as Sn^{4+} did in previous work (Román-Leshkov *et al.* 2010). In addition, HMF was created without the Lewis acid, and better results were obtained under the L-2 condition than under L-4 and L-6 conditions. The exact reason for the poorer HMF yields for L-4 and L-6 is unsure. However, it can be reasoned that the HMF created in the reaction was further transformed

into other substances, such as levulinic acid and formic acid. Alternatively, glucose could have been transformed (*e.g.*, epimerized or isomerized) to substances other than fructose (*e.g.*, mannose and sorbose) that do not lead to the creation of HMF in the presence of metal chlorides (Nguyen *et al.* 2016).

Table 2. Yield of HMF, Glucose Conversion, and its Selectivity

Entry	Catalyst	Temp. (°C)	HMF Yield (%)	Glucose Conversion (%)	Selectivity (%)
L-1	– *	120	3.8	62.3	6.1
L-2		140	12.3	68.0	18.1
L-3	$ZnCl_2$	120	0	51.4	0
L-4		140	8.4	50.3	16.6
L-5	$CuCl_2$	120	0	65.0	0
L-6		140	0	100	0
L-7	$SnCl_2 \cdot 2H_2O$	120	0	66.0	0
L-8		140	28.9	98.6	29.3
LS-1	Na(DOS)	120	10.7	71.3	15.0
LS-2		140	6.8	83.8	8.2
LS-3	$Zn(DOS)_2$	120	6.2	72.0	8.6
LS-4		140	0	100	0
LS-5	$Cu(DOS)_2$	120	4.4	74.7	5.9
LS-6		140	0	94.2	0
LS-7	$Sn(DOS)_2 \cdot 2H_2O$	120	0	63.7	0
LS-8		140	30.5	92.6	33.0

* Without any metal chloride or surfactant

The effect of the surfactant that could form a complex with the metal was also estimated. The results are presented in Table 2 (LS-1 through LS-8). In those cases, a temperature of 120 °C seemed to be more favorable for all cases except for $Sn(DOS)_2$, which showed the highest yield of HMF and selectivity (LS-8). The lower yields of HMF and selectivity at 140 °C were attributed by the transformation of HMF to the other compounds, while the higher yield of HMF with $Sn(DOS)_2$ at 140 °C may have been caused by the rate of HMF creation exceeding the rate of transformation of HMF to other substances. The HMF yield of 30.5% and its selectivity of 33.0% with LS-8 were the highest figures obtained in this research, indicating the positive effect of the combined catalyst of metal (II) and surfactant.

Creation of HMF from Cellulose by Using a Combined Catalyst of Lewis Acid and Surfactant

Following an acid hydrolysis of cellulose in a 60 wt% aqueous LiBr solution (cellulose wt% = 6.0%), the procedure for preparing HMF by using the combined catalyst of Lewis acid and surfactant ($Sn(DOS)_2 \cdot 2H_2O$) mentioned above was executed at 140 °C for 15 min. The process comprised of more than three steps, including the acid hydrolysis of cellulose, neutralization of the solution, and creation of HMF from the resultant glucose, including the transformation of glucose to fructose and dehydration of fructose. Those steps were performed in one pot. The resulting HMF yield from cellulose was estimated as 33.8%, and its selectivity was 33.8%. Those values corresponded well with the values obtained from glucose.

The yield obtained was slightly lower than that reported by Caes *et al.* (2013), who treated cellulose in an ionic liquid (EMIM-C) with catalytic additives such as

Brønsted acid, alkaline earth metal chloride, and boronic acid derivatives (maximum 41%). However, the yield was comparable with the yields reported by Daorattanachai *et al.* (2012), who treated cellulose using alkaline earth metal phosphates in an aqueous medium ($\leq$ 34%), and by Kuo *et al.* (2013) using mesoporous zirconinia nanocatalyst in an ionic liquid system (EMIM-C) (< 30%). Meanwhile, the value was higher than that obtained in a work in which the cellulose was treated in an aqueous medium with Sn(IV) (dos Santos *et al.* 2013).

CONCLUSIONS

1. The HMF was synthesized from cellulose in a one-pot procedure, which employed a concentrated solution of LiBr as a solvent along with a combined metal (II) surfactant catalyst. The maximum yield of HMF from cellulose (33.8%) was attained when tin(II)-dodecylsulfate catalyst was used at 140 °C for 3 h.

2. The effect of surfactant was not obvious in the other cases; whereas, tin (II) with the surfactant resulted in a higher yield of HMF compared to that without the surfactant.

3. Acid hydrolysis of cellulose in the first step completed promptly in a short time (15 min) at 80 °C produced high yield glucose (94.9%); however, HMF was not detected in the condition.

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