Microwave-assisted Conversion of Carbohydrates into 5-Hydroxymethylfurfural Catalyzed by $ZnCl_2$

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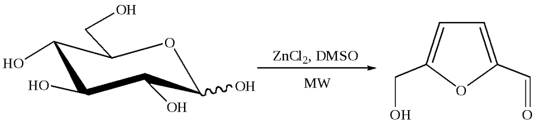
A convenient system for producing 5-hydroxymethylfurfural (HMF) through dehydration of carbohydrates by microwave heating in the presence of $ZnCl_2$ was studied. The use of $ZnCl_2$ gave higher selectivity than other metal salts in the conversion of glucose. With $ZnCl_2$ as catalyst, sucrose could be utilized effectively. Under the conditions of microwave irradiation (300 W, 8 min), HMF yields were 54.6, 55.1, and 80.6 % from glucose, fructose and sucrose, whereas upon conventional oil bath heating ($0.11\ g\,mL^{-1}$ sugar solution, weight ratio of $ZnCl_2$ to substrate = 1 : 4, 189 °C, 60 min) HMF yields from glucose, fructose and sucrose were only up to 37.7, 42.7, and 57.7 %, respectively.

Key words: Microwave-assisted Reaction, Degradation of Carbohydrate, 5-Hydroxymethylfurfural (HMF), Zinc Chloride

Introduction

With the diminishing fossil fuel reserves and growing concerns about global warming effects, utilization of renewable resources instead of fossil fuel will be very essential in the near future [1 – 4]. Abundant biomass resources represented by carbohydrates are a promising alternative for the sustainable supply of fuel and valuable chemicals. It is known that the direct production of useful organic compounds from carbohydrates is difficult. 5-Hydroxymethylfurfural (HMF) obtained from carbohydrates (*e. g.* fructose, sucrose and glucose) by dehydration, is an important "bridge" for the efficient use of carbohydrates. HMF is a so-called "sleeping giant" and holds a key position in biomass-derived intermediates. It is expected to become a novel platform for chemicals based on biomass resources [5, 6].

In the conversion of sugars into HMF, the tested catalyst species have exceeded hundreds, which were divided into five groups: organic acids, inorganic acids, salts, Lewis acids, and others [7]. Solvents used as reaction media included supercritical fluids [6, 8], subcritical fluid/carbon dioxide [9, 10], ionic liquids [11 – 17], single-phase [18], and two-phase [19 – 21] reaction systems. Nowadays the preparation of HMF is still limited to small-batch production, because most of the systems have various drawbacks: high pressure/high temperature, high cost of ionic liquids, and difficulties in the separation of the products. Moreover most of the systems appear not to convert glucose and sucrose, which are the more stable and abundant sugar sources, into HMF as efficiently as fructose.



(1)

Recently microwave irradiation is an increasingly popular method of heating. Under microwave irradiation Watanabe and coworkers have converted fructose into HMF with ZrO_2, TiO_2 and ion-exchange resin as catalysts [22 – 24], but they did not succeed in converting glucose. In the present study we explored an efficient catalyst, $ZnCl_2$, for the conversion of glucose into HMF under microwave irradiation (Eq. 1). The microwave irradiation conditions were optimized, and the catalyst $ZnCl_2$ was also used for the dehydration of sucrose and fructose. Compared with conventional oil bath heating, higher HMF yields were achieved.

Results and Discussion

Catalyst screening experiments

There are competing reaction pathways that lead to formation of by-products in the conversion of glu-

Table 1. Conversion of glucose into HMF catalyzed by various metal salts[a].

Entry	Catalyst	HMF yield (%)
1	$Sr(OAc)_2$	–
2	$NiSO_4$	8.7
3	$MnSO_4$	0.8
4	$MgSO_4$	1.5
5	LiBr	1.2
6	$ZrCl_4$	12.4
7	$CoCl_2$	20.5
8	$CaCl_2$	4.8
9	$ZnCl_2$	54.6
10	Py·HCl	11.2
11	$CrCl_3$	36.5
12	$CuCl_2$	3.6
13	$FeCl_2$	6.6
14	$FeCl_3$	2.7

[a] Conditions of microwave irradiation: 300 W, 8 min.

cose. One is that dehydration forms non-furan cyclic ethers, the other is that C–C bond scission occurs through reverse aldol condensation. To obtain high HMF yields from glucose thus requires effective catalysts. Initially, screening experiments of metal salt catalysts for the dehydration of glucose were performed (Table 1). The microwave irradiation conditions were set at a microwave power of 300 W and an irradiation time of 8 min. It was found that most of the metal salts were not efficient in producing HMF. Especially with salts of Sr, Mg, Mn, Cu, Ca, and Fe, HMF was obtained in very low yields. Moreover, the catalytic effects of those metal salt catalysts, which trigger the formation of HMF with conventional heating such as Cr and Zr [9, 13, 14], did not remarkably improve. With salts of Cr, Co, and Zr as catalysts, HMF yields were 36.5, 20.5, and 12.4 %, respectively. Apparently, under different reaction conditions the catalytic effects of metal salts vary considerably. Han has reported that $ZnCl_2$ did not have a catalytic effect on the conversion of fructose into HMF [16]. On the contrary, in Williams' and Amarasekara's work with cellulose as substrate, $ZnCl_2$ showed a similar effect as some other salts, but the yields of HMF only reached 8 – 9 % [25, 26]. In our own work, the Lewis acid $ZnCl_2$ favored a higher selectivity for the formation of HMF (54.6 % yield). Therefore, $ZnCl_2$ was selected as the catalyst for carbohydrate dehydration.

Effects of microwave power and irradiation time on HMF yields with $ZnCl_2$ as catalyst

With glucose as raw material and $ZnCl_2$ as catalyst, both irradiation power and time had large effects on the HMF selectivity (Fig. 1). The irradiation power was varied from 100 W to 500 W. The yield of HMF reached the maximum (54.6 %) at 300 W. At 500 W, the color of the solution became gradually darker, because side reactions increased forming humins and polymers. Fig. 1b shows the influence of irradiation time with respect to the HMF yields at an irradiation power of 300 W. For the dehydration of glucose, the yield of HMF reached the maximum after 8 min, and decreased strongly at longer irradiation times. Again, the reason was that side reactions increased when the reaction time was prolonged excessively.

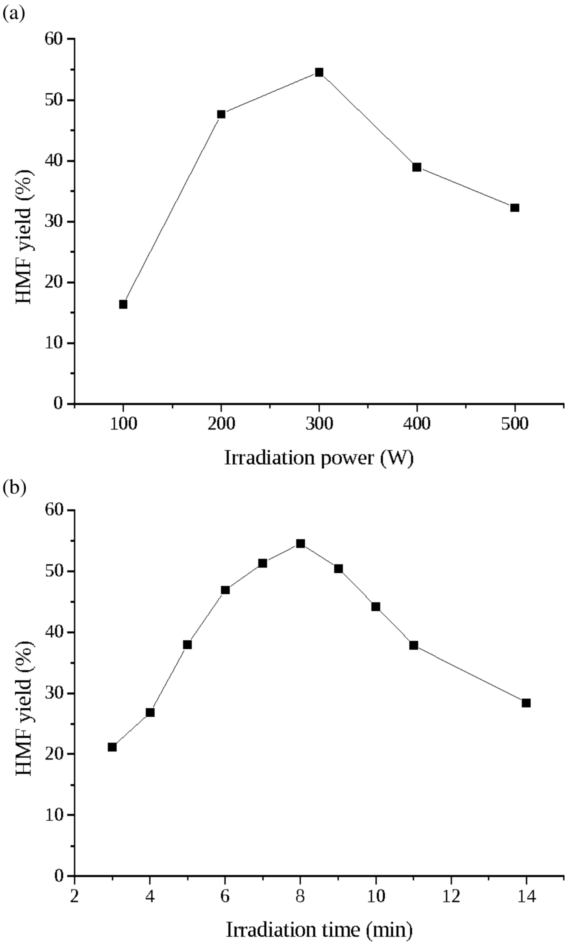


Fig. 1. Influence of microwave irradiation power and time on HMF yields; conditions of microwave irradiation: (a) $ZnCl_2$, 8 min; (b) $ZnCl_2$, 300 W.

Conversion of sucrose into HMF catalyzed by $ZnCl_2$ with oil bath heating

Because the furanosyl structure of fructose is beneficial to the conversion into HMF, fructose was used

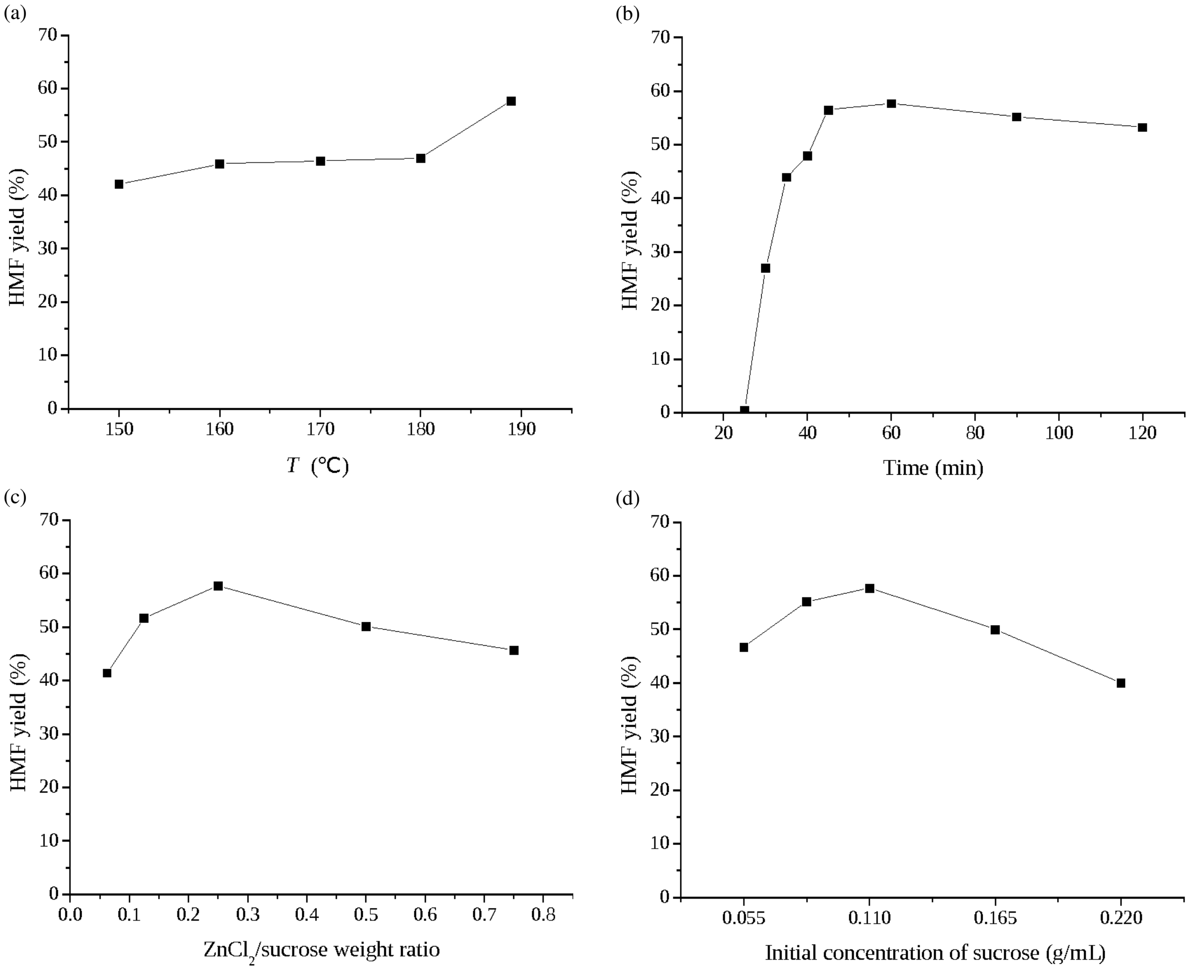


Fig. 2. Effects of (a) reaction temperature, (b) reaction time, (c) weight ratio of $ZnCl_2$ to sucrose, and (d) initial concentration of sucrose on HMF yields from sucrose. Default conditions unless otherwise noted: 0.11 $g\,mL^{-1}$ sucrose, weight ratio of $ZnCl_2$ to sucrose = 1 : 4, 189 °C (reflux), 60 min.

as substrate in many reaction systems. Even when sucrose was used as raw material, the part effectively utilized is the fructofuranosyl ring [5]. From the above-mentioned experiments, the Lewis acid $ZnCl_2$ was found to have a favorable catalytic effect on the conversion of glucose into HMF. Therefore with $ZnCl_2$ as catalyst, both the glucosyl part and the fructosyl part of sucrose was expected to be utilized effectively.

The dehydration of sucrose under oil bath heating with $ZnCl_2$ as catalyst was studied by varying the parameters temperature, reaction time, weight ratio of $ZnCl_2$ to sucrose, and the initial concentration of sucrose (Fig. 2). With increasing reaction temperature, HMF yields rose accordingly (Fig. 2a). At the boiling point of DMSO (189 °C), HMF was obtained in the highest yield of 57.7 %.

The influence of the reaction time on the HMF yield is shown in Fig. 2b. The reaction seemed to set in when a reaction temperature of 180 °C was reached (after 25 min of heating). The highest yield was achieved after 45 min of heating to 189 °C (56.5 %), followed by a decline at longer reaction time. Although the HMF yields diminished after 60 min, HMF was more stable under the conditions of oil bath heating as compared to microwave irradiation.

The weight ratio of $ZnCl_2$ to sucrose also had an important influence on the HMF yields (Fig. 2c). The best yield was achieved at the weight ratio of 1 : 4. The initial concentration of substrate sucrose also had an influence on HMF yields (Fig. 2d). At the initial sucrose concentration of 0.11 g mL^{-1}, the best HMF yield was achieved. Higher initial concentration of sucrose did not lead to a more effective conversion into HMF.

Differences of HMF yields from glucose, fructose, and sucrose in both microwave irradiation and oil bath heating

With glucose, fructose and sucrose as raw material, HMF yields in both microwave irradiation and oil bath heating are shown in Fig. 3. In other work, HMF yields from glucose were generally lower than from fructose. With sucrose as substrate instead of fructose, HMF yields were determined based on the fructofuranosyl ring [5]. In our reaction system, HMF yields from glucose catalyzed by ZnCl$_2$ were close to those from fructose. HMF yields using sucrose as raw material were higher than those using fructose and glucose as raw material. Due to the lower price of sucrose as compared to glucose and fructose, the higher HMF yields from sucrose offer an advantage for the large scale production of HMF.

A possible reason for the higher yields under microwave irradiation is that “specific” or “nonthermal” microwave effects cause a decrease in activation energy or an increase in the pre-exponential factor [22, 23]. However, as no temperature monitoring was done in our experiments, no conclusion can be drawn with regard to the reaction kinetics as yet.

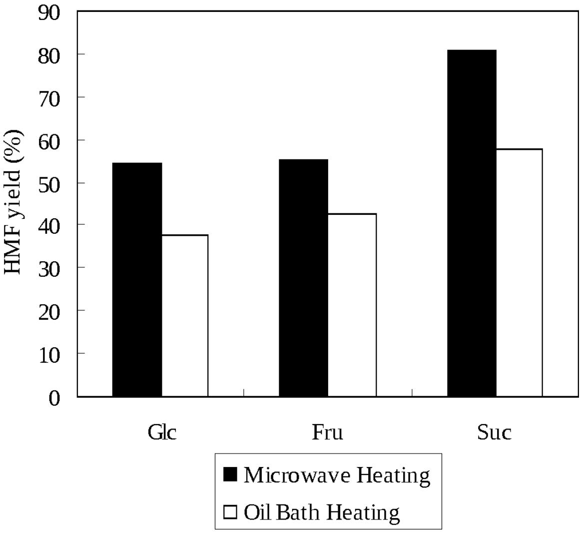


Fig. 3. Conversion of glucose, fructose, and sucrose into HMF; conditions: (■) ZnCl$_2$, DMSO, 300 W, 8 min; (□) 0.11 g mL^{-1} substrate, weight ratio of ZnCl$_2$ to substrate = 1 : 4, DMSO, 189 °C, 60 min.

Conclusion

We have reported a convenient catalytic system for producing 5-hydroxymethylfurfural (HMF) through the dehydration of carbohydrates by microwave heating in the presence of ZnCl$_2$. Not only was the yield from glucose close to that from fructose (54.6 and 55.1 %, respectively), but also higher yields (80.6 %) were obtained by dehydration of sucrose in our system. Some advantages of this system are easy work-up, improved yields, and clean reaction conditions.

Experimental Section

Microwave-assisted experiments were carried out with a WBFY-201 Microwave Reactor Apparatus (Gongyi City Yuhua Instruments Co., Ltd). The ^{1}H NMR spectra were recorded on a Bruker DRX-500 spectrometer. ESI-MS spectra were obtained on a TSQ Quantum-LC/MS/MS mass spectrometer (Finnigan). Samples were analyzed on a LC-100 High Performance Liquid Chromatograph (Shanghai Wufeng Scientific Instruments Co., Ltd). Glucose, fructose, dimethylsulfoxide (DMSO), furfural, 5-hydroxymethylfurfural, and all metal salts were of analytical purity and were used without further purification. Pyridine hydrochloride was prepared in our own laboratory [27].

General procedure for conversion of carbohydrates into HMF under microwave irradiation

To a mixture of sugar (0.5 g) and DMSO (10 mL) in a 50 mL single-necked flask equipped with a reflux condenser, the catalyst (0.75 mmol) was added. This assembly was placed into the microwave oven. The microwave irradiation power and time were set at the experimental conditions given above. When microwave irradiation started, the solvent DMSO began to reflux within one minute. After the microwave reactor was turned off, the solutions were allowed to cool to r. t.

General procedure for the conversion of carbohydrates into HMF with oil bath heating

To a mixture of sugar and DMSO (10 mL) in a 50 mL three-necked flask equipped with a reflux condenser and a thermometer, ZnCl$_2$ was added. The reaction mixture was heated to the temperatures given above through an oil bath. The timing was started with the beginning of the heating. After the reactions were complete, the mixtures were allowed to cool to r. t.

General procedure for analysis and separation of HMF

Samples were taken periodically from the reactor, filtered and analyzed by HPLC. Analyses were performed using an ultraviolet fluorescence LC-UV100 detector, which was set at 284 nm. The column used was an Arcus C18 (5 μm, 4.6×150 mm). The eluent was water/methanol (v/v = 8 : 2) at a flow rate of 0.8 mL min^{-1}. With furfural as internal standard of HPLC [28], HMF yield (mol-%) was evaluated on a carbon basis by:

$$\text{Yield} = \frac{\text{moles of carbon in HMF}}{\text{moles of carbon loaded as substrate}} \times 100 \ (\%)$$

To obtain the product, the HMF mixture was evaporated to dryness under high vacuum and separated by silica gel column chromatography (ethyl acetate/petroleum ether = 1 : 4 to 1 : 1, v/v). *5-Hydroxymethylfurfural*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.71 (br, s, 1H, OH), 4.72 (s, 2H, CH_2OH), 6.52 (d, J = 3.4 Hz, 1H, 4-H-furyl), 7.22 (d, J = 3.6 Hz, 1H, 3-H-furyl), 9.59 (s, 1H, CHO). – MS (ESI): *m/z* = 127.10 $[M+H]^+$.

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