



Efficient conversion of carbohydrates into 5-hydroxymethylfurfural using choline chloride-based deep eutectic solvents

Dung Kim Thi Ngo^a, Trinh Hao Nguyen^{b,c}, Phat Ngoc Nguyen^{b,c},
Hai Truong Nguyen^{b,c}, Trinh Ngoc Thi Huynh^a, Ha Bich Phan^{b,c,d}, Phuong
Hoang Tran^{b,c,*}

^a Faculty of General Sciences, Tra Vinh University, Tra Vinh City, Tra Vinh Province, Viet Nam

^b Department of Organic Chemistry, Faculty of Chemistry, University of Science, Ho Chi Minh City, Viet Nam

^c Vietnam National University, Ho Chi Minh City, Viet Nam

^d Institute of Public Health, Ho Chi Minh City, Viet Nam

ARTICLE INFO

Keywords:

Deep eutectic solvents
5-Hydroxymethylfurfural
Fructose
Choline chloride

ABSTRACT

In this study, the conversion of monosaccharides to 5-hydroxymethylfurfural (5-HMF) using different deep eutectic solvents (DESS) was investigated in various conditions. Among all the investigated DESS, [ChCl][trichloroacetic acid], based on choline chloride and trichloroacetic acid with the ratio 1:1, showed the highest catalytic activity. A maximum 5-HMF yield was 82 % for 1 h at 100 °C using [ChCl][trichloroacetic acid] as a catalyst from fructose. [ChCl][trichloroacetic acid] could be recovered and reused three times with a slight loss in activity. Our work demonstrated the low-cost and effective method for the synthesis of 5-HMF from carbohydrates.

1. Introduction

The utilization of renewable biomass as a source for energy, fuel, and various chemical compounds has garnered significant interest [1]. Recently, the development of the sustainable pathway for conversion of biomass into 5-HMF has attracted considerable attention and deep eutectic solvents were emerging as prominent candidates [2,3]. The main feedstocks for 5-HMF manufacturing were fructose and glucose [4–7]. The dehydration of saccharides such as sucrose, glucose, and fructose (1) results in the production of 5-HMF (2), which was an important precursor for the utilization of carbohydrates (Scheme 1) [8,9]. Through oxidation, hydrogenation, or aldol condensation, 5-HMF can be transformed into a variety of useful products, including 2,5-furandicarboxylic acid (3), 2,5-dihydroxymethylfuran (4), dimethylfuran (5), 2,5 bis(hydroxymethyl)tetrahydrofuran (6) [10,11]. These building blocks, including 3, 4, 6, have been used in the production of polyesters, and dimethylfuran has significant promise for use as a liquid fuel in transportation [6, 12–15]. 5-HMF is a versatile industrial precursor with several potential uses in the pharmaceutical, fuel, additive, and material industries [16,17].

Extensive research has been conducted on the conversion of carbohydrates into 5-HMF, with a particular focus on the utilization of

* Corresponding author. Department of Organic Chemistry, Faculty of Chemistry, University of Science, Ho Chi Minh City, Viet Nam.
E-mail address: thphuong@hcmus.edu.vn (P.H. Tran).

<https://doi.org/10.1016/j.heliyon.2023.e21274>

Received 1 May 2023; Received in revised form 11 October 2023; Accepted 18 October 2023

Available online 30 October 2023

2405-8440/© 2023 Published by Elsevier Ltd.

This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

a highly sulfonated polyaniline-based organocatalyst (S-A-PAN-H) for the synthesis of 5-HMF from fructose [18]. The conversion of carbohydrates into 5-HMF used tandem catalysis in a heterogeneous catalytic system [19]. The use of tungstophosphoric acid-encased dendritic fibrous mesoporous silica catalyzed for the synthesis of 5-HMF from carbohydrates under microwave irradiation [20]. The solvents used in a catalytic system are an essential component, and they directly influence the amount of 5-HMF produced and subsequent purification [21]. A wide variety of solvents, such as water, organic solvents, water-organic solvents, ionic liquids (ILs), and DESs, have been used as solvents for the reaction [22].

The DESs were formed by combining in the proper molar proportions, a new class of sustainably derived solvents that had melting temperatures that were lower than any individual component [2,3,23–27]. Because of their nature of renewability and global availability, carbohydrates, the main ingredient of lignocellulosic biomass (~75 %), have been considered one of the most promising feedstocks for producing carbon-based chemicals and fuel [5,28–31]. Nowadays, there is more and more attention on the conversion of carbohydrates into 5-HMF using DESs. Zang et al. developed a combination of choline chloride (ChCl), ethylene glycol (EG), and maleic acid for the synthesis of 5-HMF from fructose with 87 % yield [32]. Salvatore Marullo et al. reported the fructose and sucrose metabolism using Amberlyst-15 catalyst in DES; the 5-HMF yields were obtained about 76 % for fructose and 69 % for sucrose [33]. Phan et al. described a pathway for combining CrCl₃·6H₂O salt in [DMSO][CholineCl] deep eutectic solvent for the conversion of glucose and fructose into 5-HMF [17]. However, along with the development of scientific research, the requirement for a simple 5-HMF preparation process, easy product isolation, and high yield and selectivity in a short time has attracted much attention.

In this work, we present an efficient method for the preparation of 5-HMF from fructose utilizing DES as a green catalyst. The high yield of 5-HMF was obtained in 82 % from fructose at 100 °C for 1 h using [ChCl][trichloroacetic acid] as a catalyst. Interestingly, the 5-HMF was extracted by ethyl acetate and the catalyst can be recovered and reused with just a minor loss in activity. Our research proved the efficient method for converting carbohydrates into 5-HMF.

2. Experimental and computational section

2.1. Chemicals and instrumentation

2.1.1. Chemicals and supplies

Choline chloride (99 %, HiMedia Lab), dimethyl sulfoxide (99 %, Sigma–Aldrich), iron (III) chloride (99 %, Sigma–Aldrich), chromium (III) chloride hexahydrate (99 %, Sigma–Aldrich), D-glucose (99 %, Sigma–Aldrich), D-fructose (99 %, Sigma–Aldrich), formic acid (>98 %, Merck), furfural (99.5 %, Merck), 5-hydroxymethylfurfural (99.5 %, Merck), 2,5-furandicarboxaldehyde (99.5 %, Sigma–Aldrich).

2.1.2. Instrumentation

The reaction was carried out on a magnetic hotplate stirrer (DLab MS7-H550) or ultrasonic bath (Derui Ultrasonic DS-20, 37 KHz, 140 W). A Q-500 thermal gravimetric analyzer was utilized to conduct thermal gravimetric analysis (TGA) under controlled airflow conditions. The temperature was gradually increased at a rate of 5 °C per minute. The Fourier transform infrared (FT-IR) spectra were obtained by conducting measurements on a Bruker E400, employing KBr pellets as the sample medium. Nuclear magnetic resonance (NMR) spectra were acquired using a Bruker Avance-500 MHz spectrometer.

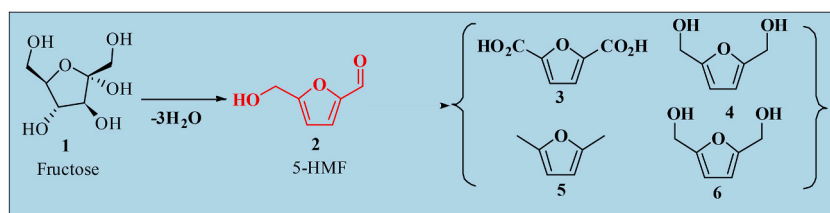
Fructose analysis was conducted using a Shimadzu UFCL-XR instrument with PRP-X 100 column. The SCIEX-QTRAP®5500 L C/MS/MS, operating in the negative ion mode with electrospray ionization, was utilized for the analysis. Acetonitrile (A) and water (B) were employed as the mobile phases in this experiment. The composition of the mobile phase was as follows: 5 % B for the first 1 min, 50 % B for the subsequent 10 min, and then a return to 5 % B from 10.1 to 15 min. The column temperature was maintained at 25 °C at all times.

The reaction products were able to be measured (285 nm) using an Agilent HPLC equipped with an InertSustain C18 column with a particle size of 5 μm and a dimension of 4.6 × 150 mm and a DAD detector at 30 °C. As the eluent, using methanol and sulfuric acid (2.5 mM), the flow rate was 0.7 mL min⁻¹. The formulas to calculate 5-HMF were presented as follows (1):

$$\text{5-HMF yield (\%)} = (\text{moles of 5-HMF}/\text{moles of initial fructose}) \times 100 \quad (1)$$

$$\text{Fructose conversion (\%)} = [1 - (\text{mass of fructose}/\text{mass of initial fructose})] \times 100 \quad (2)$$

$$\text{5-HMF selectivity (\%)} = (\text{5-HMF yield}/\text{fructose conversion}) \times 100 \quad (3)$$



Scheme 1. Conversion of fructose to 5-HMF.

2.2. Preparation of deep eutectic solvents

The DESs were synthesized utilizing a well-documented methodology outlined in the scientific literature [34]. Each DES was made by heating the corresponding pure components with the ratio of mole as follows [ChCl][Oxalic acid] (choline chloride/oxalic acid = 1/1), [ChCl][*p*-TsOH] (choline chloride/*p*-TsOH = 1/1), [ChCl][CrCl₃·6H₂O] (choline chloride/CrCl₃·6H₂O = 1/2), [ChCl][trichloroacetic acid] (choline chloride/trichloroacetic acid = 1/1), and [ChCl][FeCl₃] (choline chloride/FeCl₃ = 1/2) at 80 °C while stirring until a colourless solution was formed. Scheme 2 depicted the structures of the DESs.

2.3. Typical process for conversion carbohydrate to 5-HMF using DES

In a conventional experimental procedure, fructose (1 mmol, 0.180 g) and DES (5 mmol) were put into conventional heating or sonication. The mixture was heated to different temperatures, including room temperature, 60 °C, 80 °C, 100 °C, 120 °C, and 130 °C for some time (1, 1.5, 2, 2.5, 3, 3.5, 4, and 4.5 h) with two methods such as conventional heating and sonication to choose the optimal reaction conditions. Aliquots of the reaction mixture were taken at a variety of time intervals, after which they were diluted with water (1 × 10 mL) and subjected to centrifugation at a speed of 4000 rpm for 3 min. After passing the resultant supernatant through a membrane with a pore size of 0.45 μm, the filtrate was collected and placed in a vial for later use. HPLC-DAD method was used to determine the yield of 5-HMF.

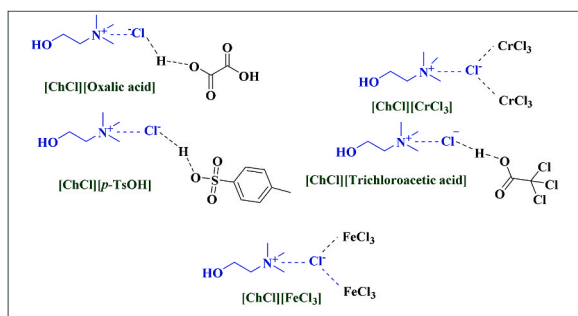
2.4. Recycling of DES

When the reaction was finished, DES was washed several times with ethyl acetate (10 × 5 mL) to separate 5-HMF from the reaction mixture. DES was dried at 80 °C for 3 h. After that, 1 mmol fructose was added and heated under optimal conditions. The recovered [ChCl][trichloroacetic acid] was reused three times without considerable loss in catalytic activity.

3. Results and discussion

3.1. Characterization of DESs

Fourier transforms infrared (FT-IR) spectroscopy determined choline chloride-based deep eutectic solvents, shown in Fig. 1, and the detail of DESs was depicted in Figs. S2–3 (Supporting information). The FT-IR spectra of pure choline chloride showed the absorption peak at 3500–3000 cm⁻¹, demonstrating the hydroxyl group. The signal at 2960 and 1400 cm⁻¹ indicated the presence of alkyl groups. A comparison between the DES spectrum and each of its component parts was presented in Fig. 1. As seen in [ChCl][Oxalic acid], the signal at 3420 cm⁻¹ demonstrated the –OH stretching, which was associated with the –OH group of oxalic acid. The FT-IR of [ChCl][Oxalic acid] showed the signal at 3342 cm⁻¹. This result indicated the signal of the –OH group. The signals at 1726 cm⁻¹, 1643 cm⁻¹, and 1199 cm⁻¹ were assigned to the C=O, C–C, and C–O groups, respectively [35]. As seen in FT-IR spectrum of [ChCl][*p*-TsOH], the frequency at 3377 cm⁻¹ was assigned to the OH stretching frequency associated with the –OH group. Peaks at 1172 cm⁻¹ and 1120 cm⁻¹ (the asymmetric stretching vibration of the O=S=O), 1008 cm⁻¹ (the symmetrical stretching vibration of O=S=O), and 682 cm⁻¹ (extending the C–S stretching vibration peak), respectively, were assigned to the SO₃H group [36]. The FT-IR spectrum of [ChCl][CrCl₃·6H₂O] and choline chloride showed the –OH group shifted between 3500 and 3000 cm⁻¹ due to the formation of hydrogen bondings [37]. The spectra of choline chloride, trichloroacetic acid, and the [ChCl][trichloroacetic acid] produced from choline chloride and trichloroacetic acid at a 1:1 M ratio were shown in the FT-IR spectra. It is possible to notice a change in the O–H stretching in the DES (3348 cm⁻¹) and trichloroacetic acid (3395 cm⁻¹). Additionally, there was a shift in the carboxylic group from 1750 cm⁻¹ to 1645 cm⁻¹ [38]. In the structure of pure choline chloride, the vibrations associated with the O–H and C–N bonds were in the range of 3250 and 1092 cm⁻¹, respectively. The [ChCl][FeCl₃] spectrum provided the same signal as the reported literature [39].



Scheme 2. Structures of the DESs.

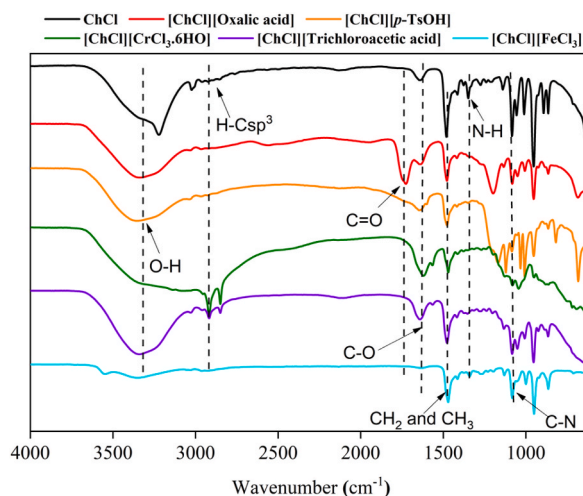


Fig. 1. FT-IR spectra of DESs.

Thermogravimetric analysis (TGA) was employed to examine the thermal stability of DESs. The gravimetric analysis of all studied DESs is shown in Figs. S2–4 (please see Supporting information). Fig. 2 displayed the thermal weight loss curves for [ChCl][trichloroacetic acid] and its components. The sample presented a weight loss (about 15 %) below 150 °C, which was mainly due to the loss of a small amount of absorbed water. [ChCl][trichloroacetic acid] gradually started weight loss at 200 °C and completely decomposed at about 320 °C. Therefore, [ChCl][trichloroacetic acid] remained thermally stable in the studied temperature range from 60 °C to 130 °C.

Finally, the Raman spectra of [ChCl][CrCl₃·6H₂O] and [ChCl][FeCl₃] have been collected in Fig. 3. For [ChCl][CrCl₃·6H₂O], the strong bands at 320–370 cm⁻¹ in the Raman spectrum can be seen, illuminating the Cr–Cl bond (Fig. 3-left) [40]. The Fe–Cl bond was assigned to the peak at 370 cm⁻¹ (Fig. 3-right) [41].

3.2. The influence of temperature on the converting of fructose to 5-hydroxymethylfurfural

In the survey of reaction conditions, the temperature plays the most crucial role in the yield of the reaction. Fig. 4 displayed fructose conversion to 5-HMF that affected temperature at various temperatures for 3 h. At room temperature, the low yield of 5-HMF was obtained in the reaction (Fig. 4a–e). [ChCl][Oxalic acid] afforded the highest yield at 100 °C, which provided 29 % yield of 5-HMF (Fig. 4a), while at ambient temperature, and the productivity was under 5 %. At a certain temperature, the 5-HMF yield was 24 %, 15 %, 11 %, and 9 % at 60 °C, 80 °C, 120 °C, and 130 °C, respectively. The findings of comparing [ChCl][p-TsOH], [ChCl][CrCl₃·6H₂O], and [ChCl][FeCl₃] produced low 5-HMF at all the temperatures that were explored for this research, with the difference in yield being around 5 % for each survey. After 3 h of reaction at 100 °C, [ChCl][trichloroacetic acid] produced an excellent 5-HMF yield of approximately 70 % (Fig. 4d). However, the 5-HMF effectiveness was reduced with increasing temperature, which could be

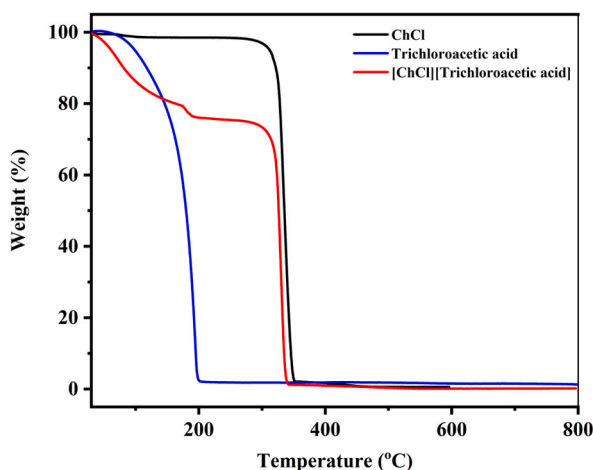


Fig. 2. TGA of choline chloride (ChCl), trichloroacetic acid, and [ChCl][trichloroacetic acid].

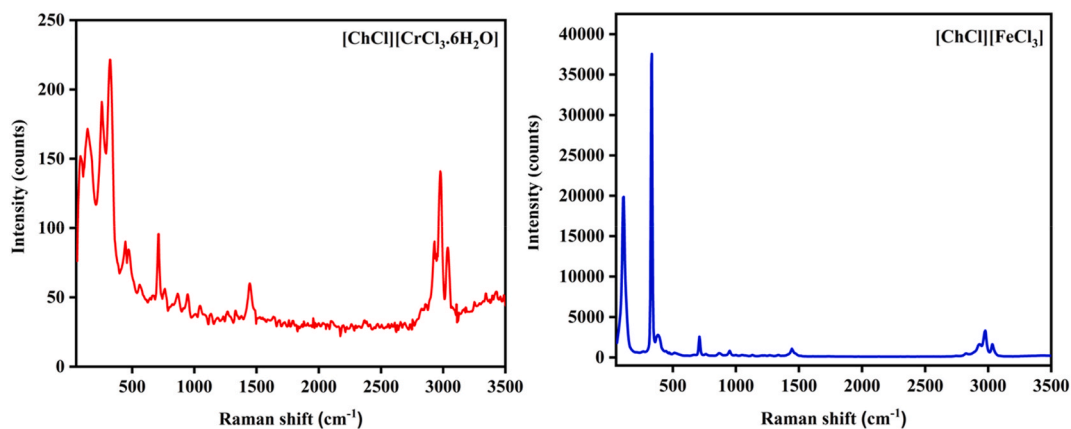


Fig. 3. Raman spectra of $[\text{ChCl}][\text{CrCl}_3 \cdot 6\text{H}_2\text{O}]$ (left) and $[\text{ChCl}][\text{FeCl}_3]$ (right).

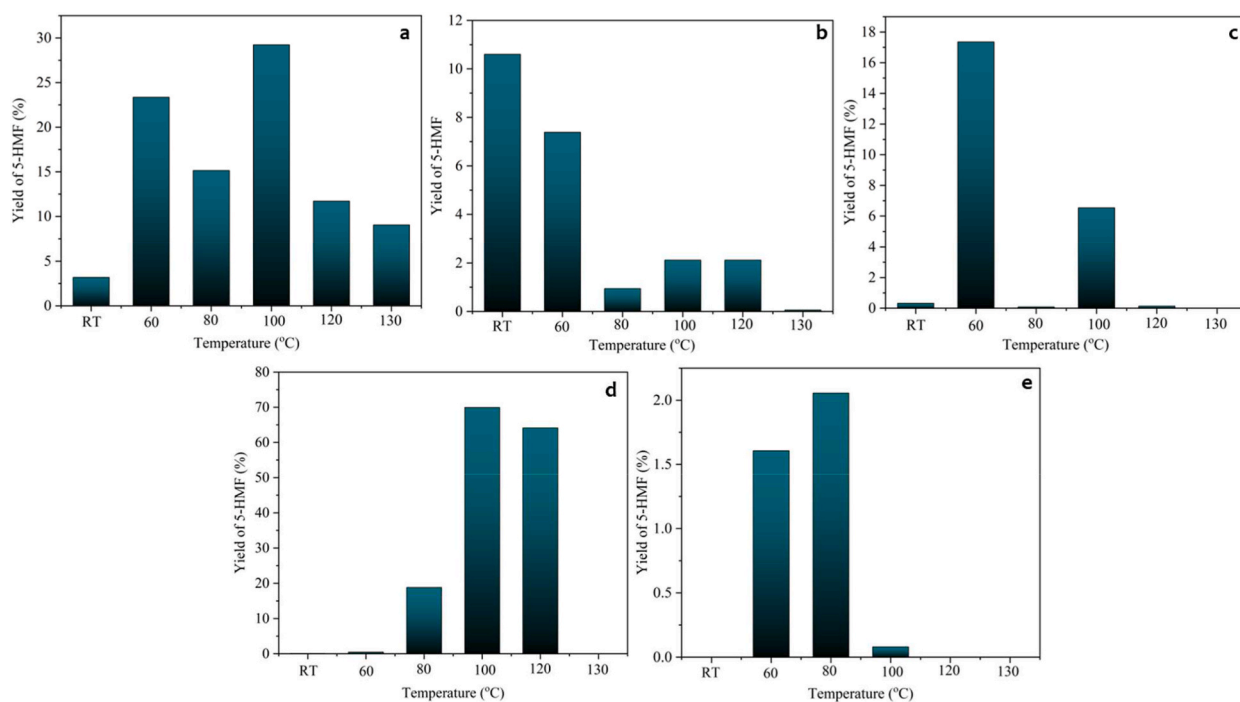


Fig. 4. The effect of temperature on 5-HMF yields. Reaction conditions: Fructose (180 mg, 1 mmol), DES (5 mmol), with various temperatures for 3 h. (A) $[\text{ChCl}][\text{oxalic acid}]$, (B) $[\text{ChCl}][p\text{-TsOH}]$, (C) $[\text{ChCl}][\text{CrCl}_3 \cdot 6\text{H}_2\text{O}]$, (D) $[\text{ChCl}][\text{trichloroacetic acid}]$, (E) $[\text{ChCl}][\text{FeCl}_3]$.

explained by the formation of humins at high temperatures [42]. These findings agree with those of Lee et al. [43]. The yield of reaction by-products was more remarkable at a temperature of 100 °C than 80 °C. It suggested that an increase in temperature produced the side reaction.

3.3. The effect of time on the formation of 5-HMF

Next, the reaction time survey for five DESs was studied with different time intervals depicted in Fig. 5. With $[\text{ChCl}][\text{Oxalic acid}]$, 5-HMF was obtained in 40 % for 2 h (Fig. 5a). As the reaction time increases, the 5-HMF efficiency tended to decrease for $[\text{ChCl}][\text{oxalic acid}]$, $[\text{ChCl}][p\text{-TsOH}]$, $[\text{ChCl}][\text{CrCl}_3 \cdot 6\text{H}_2\text{O}]$, and $[\text{ChCl}][\text{FeCl}_3]$ slightly, with an insignificant decrease in efficiency ranging around 5 %. Meanwhile, $[\text{ChCl}][\text{trichloroacetic acid}]$ gave a remarkable yield of 5-HMF, which resulted in approximately 85 % for 2 h. There was a tendency to decrease the yield of the reaction, which could be explained by the formation of by-products. In addition, $[\text{ChCl}][\text{CrCl}_3 \cdot 6\text{H}_2\text{O}]$ and $[\text{ChCl}][\text{FeCl}_3]$ gave low yields of less than 10 % for 1 h (Fig. 5c and e). Lewis acidic DESs were not effective when compared with Brønsted acid ($[\text{ChCl}][\text{oxalic acid}]$ and $[\text{ChCl}][p\text{-TsOH}]$ and $[\text{ChCl}][\text{trichloroacetic acid}]$) (Fig. 5a, b and d). Based on

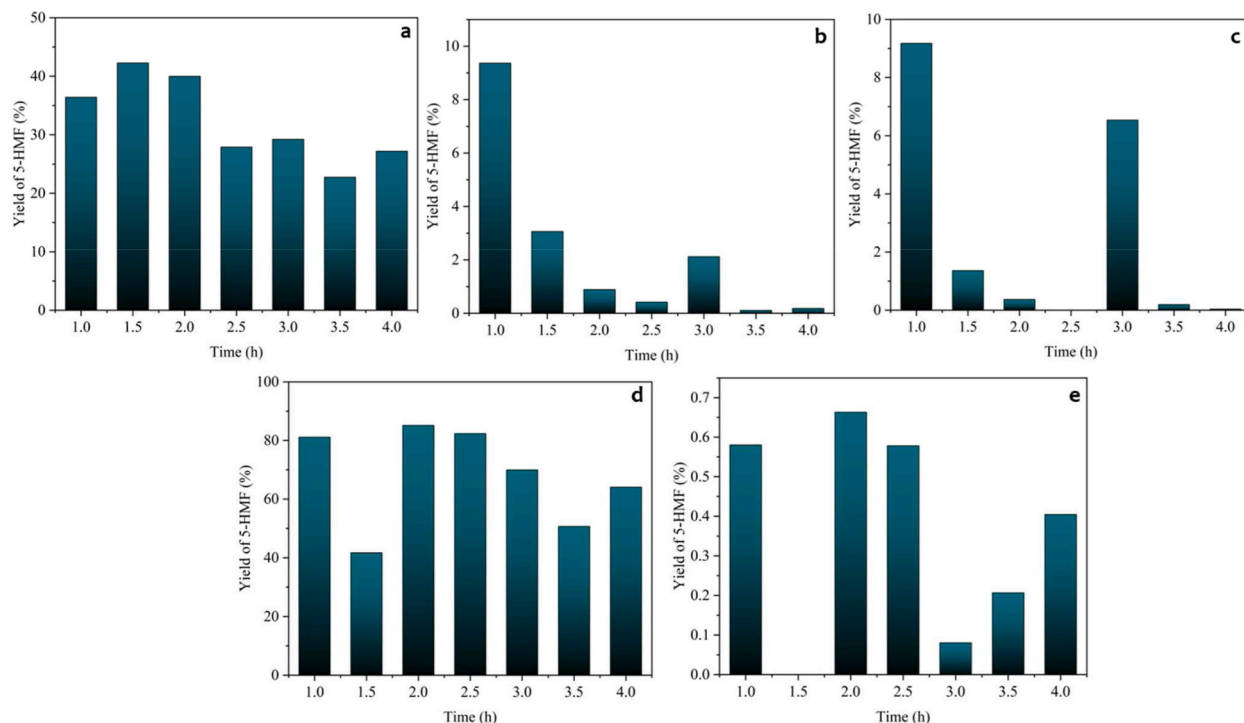


Fig. 5. The investigation of reaction time for the formation of 5-HMF using various DESs. Reaction conditions: Fructose (180 mg, 1 mmol), DES (5 mmol) at different times at 100 °C. (A) [ChCl][Oxalic acid], (B) [ChCl][p-TsOH], (C) [ChCl][CrCl₃·6H₂O], (D) [ChCl][Trichloroacetic acid], (E) [ChCl][FeCl₃].

our findings, it was determined that a reaction duration of 2 h proved to be an optimal reaction time for the conversion of fructose into 5-HMF, employing DES as a catalyst.

3.4. The effect of sonication on the converting of fructose to 5-hydroxymethylfurfural

Recently, the method for the reaction is gaining more attention from the researcher because they want to find a new method with mild conditions. Therefore, in this part, we have investigated the method for the formation of 5-HMF. The reactions were tested with fructose (180 mg, 1 mmol), DES (5 mmol), at 100 °C with different reaction times (Fig. 6). The yields of 5-HMF in [ChCl][Oxalic acid] gave 7–10 % from 1 to 2 h (Fig. 6a). The yield of 5-HMF was 32 % for 1 h using [ChCl][p-TsOH] (Fig. 6b). Among these, [ChCl][FeCl₃] gave the best yield of 5-HMF conversion efficiency of about 45 % (Fig. 6e). Since the ultrasonic temperature is not high enough to convert fructose into 5-HMF, the ultrasonic approach has a lower conversion efficiency than the traditional heating method. Therefore, for the sonication method, it is important to increase the temperature to speed up the conversion of fructose or prolong the reaction time.

3.5. The effect of the heating method for the preparation of 5-HMF

In this work, the impact of several techniques, such as sonication and traditional heating, are compared for the purpose of achieving an effective generation of 5-HMF. The comparison of the form is illustrated in Fig. 7. Fructose was chosen as a representative substrate. Depending on the process, 5-HMF was obtained in moderate to good yields; for example, [ChCl][FeCl₃] gave the lowest yield, which accounted for under 5 % in conventional heating, while the yield of 5-HMF was the highest rate in the sonication method. The formation of humins may occur when 5-HMF combines with fructose and then undergoes cross-polymerization during the fructose dehydration process. Gomes et al. prove that a higher glucose concentration is associated with decreased 5-HMF production [44].

3.6. Recycling of deep eutectic solvents

After completion of the reaction, the process of extracting 5-HMF from the reaction and conducting research on the recovery and reuse of the system was tested with fructose (180 mg, 1 mmol), [ChCl][trichloroacetic acid] (5 mmol) at 100 °C for 1 h. The 5-HMF was extracted by using ethyl acetate (10 × 5 mL). The recycling of other DESs was shown in Figs. S2–5 (Supporting information). The recovered [ChCl][trichloroacetic acid] was reused three times, with the performance after each not significantly reduced (Fig. 8-left). [ChCl][trichloroacetic acid] gave about 76 %, 72 %, and 55 % of 5-HMF yields after three times. The FT-IR spectrum of the recovered

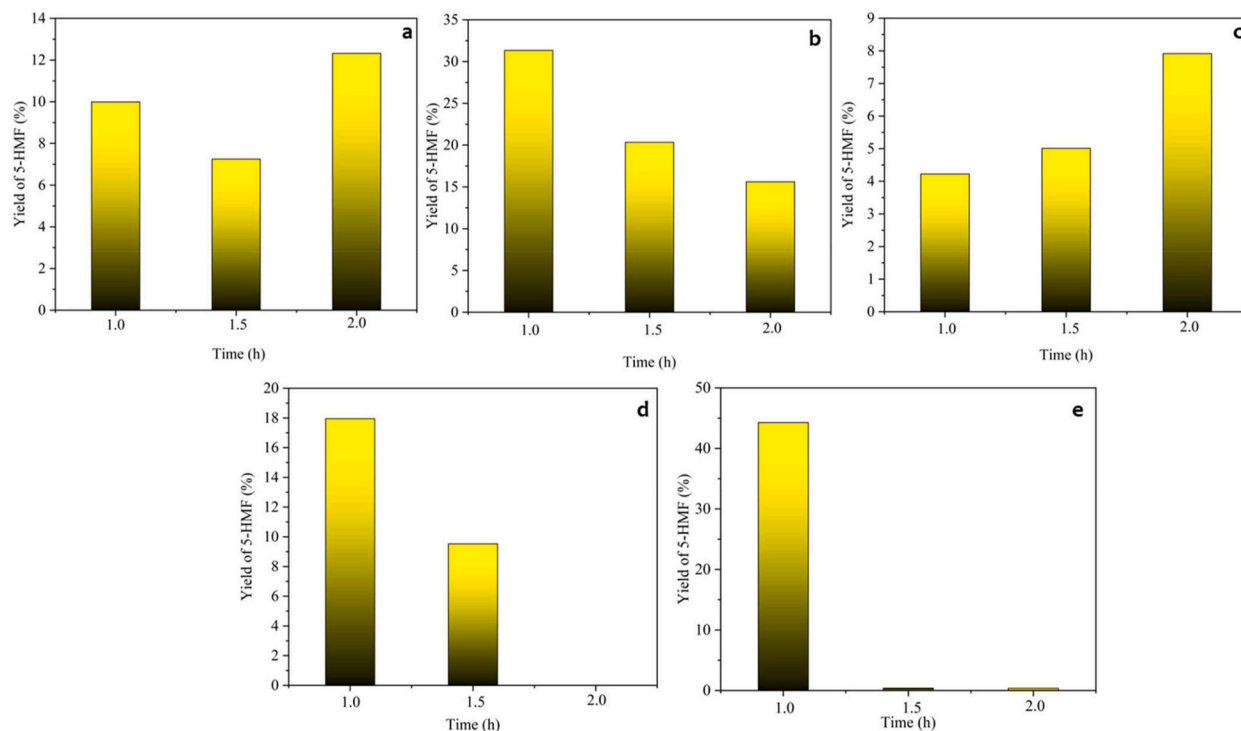


Fig. 6. Investigation of reaction time for the preparation of 5-HMF under sonication. Reaction conditions: Fructose (180 mg, 1 mmol), DES (5 mmol) with 1, 1.5 and 2 h. (A) [ChCl][oxalic acid], (B) [ChCl][p-TsOH], (C) [ChCl][CrCl₃·6H₂O], (D) [ChCl][trichloroacetic acid], (E) [ChCl][FeCl₃].

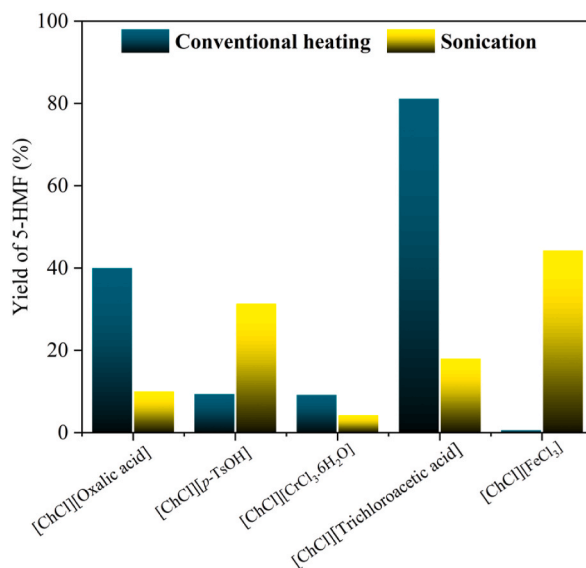


Fig. 7. The effect of the heating method on the synthesis of 5-HMF.

[ChCl][trichloroacetic acid] catalyst demonstrated that the structure of the catalyst remained unchanged primarily (Fig. 8-right).

3.7. Comparison of the various catalysts for fructose conversion

Fructose (180 mg, 1 mmol), catalyst (10 mol%), DMSO (3 mL), 1 h at 120 °C with various catalysts including oxalic acid, p-TsOH, CrCl₃·6H₂O, trichloroacetic acid, and FeCl₃ were carried out under optimized conditions (Fig. 9-right). The yield of 5-HMF was 30 %,

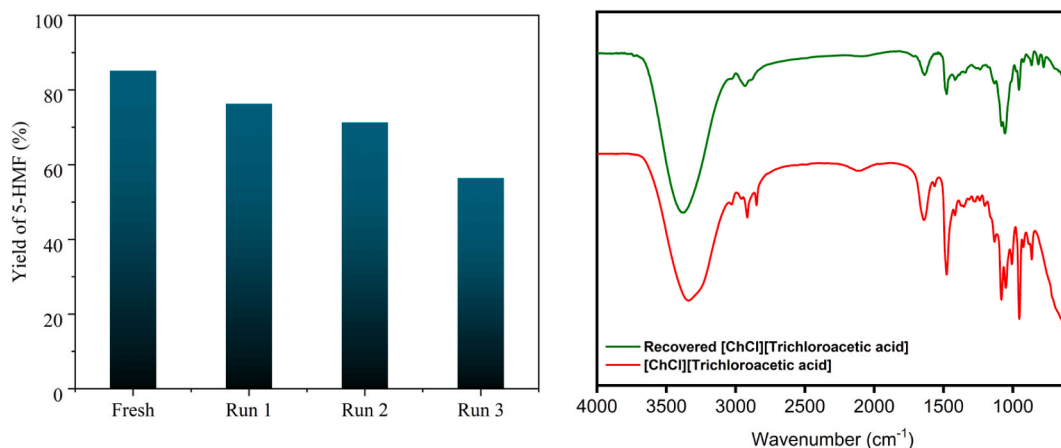


Fig. 8. Recycling of [ChCl][trichloroacetic acid] (left) and FT-IR spectra of DES fresh and recovered DES (right).

50 %, 44 %, 47 %, and 46 % when using oxalic acid, *p*-TsOH, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, trichloroacetic acid, and FeCl_3 . Generally, the yield of reaction using the catalyst and DMSO was obtained higher yield than DES. Besides, in this work, we have successfully investigated the catalyst system for the preparation of 5-HMF from fructose, which accounted for 82 % in 1 h, using [ChCl][trichloroacetic acid]. Meanwhile, the combination of trichloroacetic acid and DMSO gave 46 % 5-HMF in 1 h at 100 °C. The 5-HMF selectivity and fructose conversion were shown in Fig. 9-left. The conversion of fructose reached approximately 100 % within 1 h. However, although the conversion efficiency reached 100 %, the 5-HMF efficiency was not high, which was explained by the formation of by-products during the reaction [45].

3.8. Comparison of differences between previous reports and this work

Table 1 compared our work to existing literature. Fructose dehydration with [ChCl][trichloroacetic acid] produced the required product with high selectivity and allowed the separation of 5-HMF easily (Table 1, entry 6). Our work employed a low temperature for the preparation of 5-HMF from fructose. It then exhibits industrial uses and catalyst system recovery and reuse. The dehydration of fructose also yields a significant amount of 5-HMF, albeit under elevated reaction temperatures and volatile organic solvents. Additionally, these processes resulted in the formation of by-products, thereby complicating the isolation of 5-HMF (Table 1, entries 1–4). Although the reaction time was extended to 2 h, the prominent of the current method did not produce the side-products such as 2,5-furandicarboxaldehyde, 2,5-furandicarboxylic acid, levulinic acid, and formic acid [46–48]. Our study provided a simple and efficient preparation for the synthesis of 5-HMF from fructose.

4. Conclusions

In conclusion, we have effectively engineered five distinct varieties of DESs for the purpose of synthesizing 5-HMF from fructose. In

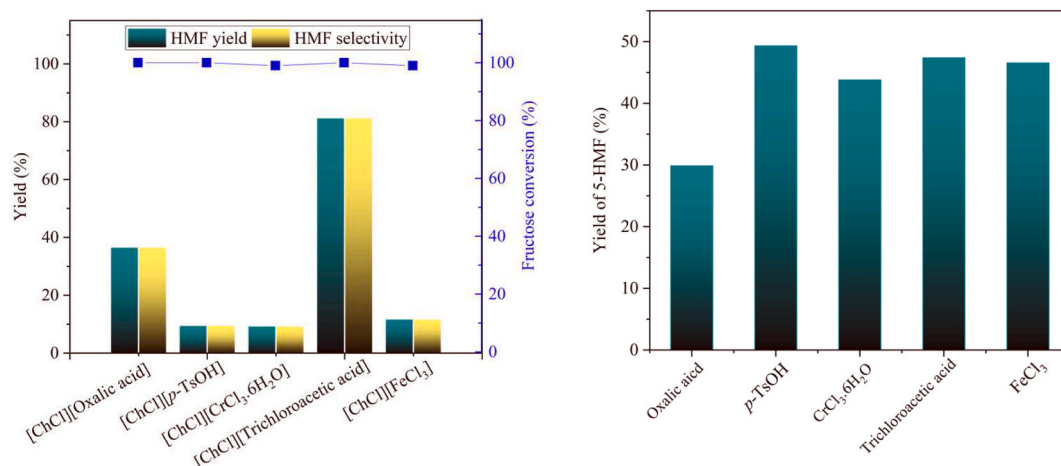


Fig. 9. Fructose conversion (left) and the comparison of the other catalyst system (right).

Table 1

Comparison of other reports with the present work in the synthesis of 5-HMF from fructose.

Entry	Catalyst system	Reaction condition	5-HMF (%) ^a
1	BHC/malic acid/H ₂ O [49]	11 min/140 °C/Microwave	94
2	MeSAPOs, DMSO-MIBK-butanol [50]	2.5 h/170 °C/Stirring	65
3	Tetraethyl ammonium chloride:CrCl ₃ [51]	3.64 min/150 °C/Flow continuous	42
4	CrCl ₃ /[DMSO][CholineCl] [17]	1 h/100 °C/Stirring	93
5	Au@PTh–PThO [11]	1.5 h/Reflux/Stirring	72.6
6	<i>This work</i> : [ChCl][trichloroacetic acid] (5 mmol)	1 h/100 °C/Stirring	82

^a HPLC yield.

general, [ChCl][trichloroacetic acid] gave the best performance compared to the other DESs with an efficiency of about 82 % for 1 h of reaction at 100 °C under conventional heating. The DES has been tested for recovery and reuse. Overall, the study provided an overview of the research on converting fructose to 5-HMF using DES as both solvent and catalyst. The current method can be applied to industrial processes to reduce costs and prevent environmental pollution.

Data availability statement

Data will be made available on request.

CRedit authorship contribution statement

Dung Kim Thi Ngo: Conceptualization, Investigation, Methodology. **Trinh Hao Nguyen**: Conceptualization, Investigation, Methodology. **Phat Ngoc Nguyen**: Conceptualization, Investigation, Methodology. **Hai Truong Nguyen**: Conceptualization, Investigation, Methodology. **Trinh Ngoc Thi Huynh**: Data curation, Formal analysis. **Ha Bich Phan**: Data curation, Formal analysis. **Phuong Hoang Tran**: Funding acquisition, Project administration, Writing – original draft, Writing – review & editing.

Declaration of competing interest

There are no conflicts of interest to declare.

Acknowledgment

This research was fully supported by Tra Vinh University under grant contract number 305/2020/HD.HĐKH-ĐHTV.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2023.e21274>.

References

- [1] S.K. Maity, Opportunities, recent trends and challenges of integrated biorefinery: Part I, *Renewable Sustainable Energy Rev.* 43 (2015) 1427–1445.
- [2] C. Florindo, F.S. Oliveira, L.P.N. Rebelo, A.M. Fernandes, I.M. Marrucho, Insights into the synthesis and properties of deep eutectic solvents based on cholinium chloride and carboxylic acids, *ACS Sustainable Chem. Eng.* 2 (2014) 2416–2425.
- [3] W. Tang, Y. An, K.H. Row, Emerging applications of (micro) extraction phase from hydrophilic to hydrophobic deep eutectic solvents: opportunities and trends, *Trends Anal. Chem.* 136 (2021), 116187.
- [4] Y. Feng, M. Zuo, T. Wang, W. Jia, X. Zhao, X. Zeng, Y. Sun, X. Tang, T. Lei, L. Lin, Efficient synthesis of glucose into 5-hydroxymethylfurfural with SO₄²⁻/ZrO₂ modified H⁺ zeolites in different solvent systems, *J. Taiwan Inst. Chem. Eng.* 96 (2019) 431–438.
- [5] C. García-Sancho, I. Fúnez-Núñez, R. Moreno-Tost, J. Santamaría-González, E. Pérez-Inestrosa, J. Fierro, P. Maireles-Torres, Beneficial effects of calcium chloride on glucose dehydration to 5-hydroxymethylfurfural in the presence of alumina as catalyst, *Appl. Catal.* 206 (2017) 617–625.
- [6] V.P. Kashparova, D.V. Chernysheva, V.A. Klushin, V.E. Andreeva, O.A. Kravchenko, N.V. Smirnova, Furan monomers and polymers from renewable plant biomass, *Russ. Chem. Rev.* 90 (2021) 750.
- [7] T.H. Nguyen, D.A.L. Nguyen, D.D. Le, P.C. Huynh, T.P. Nguyen, N.M. Nguyen, H.B. Phan, P.H. Tran, Highly efficient, rapid, and practical conversion of carbohydrate into 5-hydroxymethylfurfural using a continuous-flow reactor with 1-(4-sulfobutyl)-3-methylimidazolium bromide ionic liquid as a catalyst, *Fuel* 354 (2023), 129399.
- [8] H. Zhao, J.E. Holladay, H. Brown, Z.C. Zhang, Metal chlorides in ionic liquid solvents convert sugars to 5-hydroxymethylfurfural, *Science* 316 (2007) 1597–1600.
- [9] M. Bicker, J. Hirth, H. Vogel, Dehydration of fructose to 5-hydroxymethylfurfural in sub- and supercritical acetone, *Green Chem.* 5 (2003) 280–284.
- [10] G.W. Huber, J.N. Chheda, C.J. Barrett, J.A. Dumesic, Production of liquid alkanes by aqueous-phase processing of biomass-derived carbohydrates, *Science* 308 (2005) 1446–1450.
- [11] X. Guo, J. Tang, B. Xiang, L. Zhu, H. Yang, C. Hu, Catalytic dehydration of fructose into 5-hydroxymethylfurfural by a DMSO-like polymeric solid organocatalyst, *ChemCatChem* 9 (2017) 3218–3225.
- [12] Z. Ding, X. Luo, Y. Ma, H. Chen, S. Qiu, G. Sun, W. Zhang, C. Yu, Z. Wu, J. Zhang, Eco-friendly synthesis of 5-hydroxymethylfurfural (HMF) and its application to the Ferrier-rearrangement reaction, *J. Carbohydr. Chem.* 37 (2018) 81–93.

- [13] D.A. Giannakoudakis, J.C. Colmenares, D. Tsiplakides, K.S. Triantafyllidis, Nanoengineered electrodes for biomass-derived 5-hydroxymethylfurfural electrocatalytic oxidation to 2, 5-furandicarboxylic acid, *ACS Sustainable Chem. Eng.* 9 (2021) 1970–1993.
- [14] H.N. Anchan, S. Dutta, Recent Advances in the Production and Value Addition of Selected Hydrophobic Analogs of Biomass-Derived 5-(hydroxymethyl) Furfural, *Biomass Convers. Biorefin.*, 2021, pp. 1–23.
- [15] Y. Román-Leshkov, C.J. Barrett, Z.Y. Liu, J.A. Dumesic, Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates, *Nature* 447 (2007) 982–985.
- [16] X. Kong, Y. Zhu, Z. Fang, J.A. Kozinski, I.S. Butler, L. Xu, H. Song, X. Wei, Catalytic conversion of 5-hydroxymethylfurfural to some value-added derivatives, *Green Chem.* 20 (2018) 3657–3682.
- [17] H.B. Phan, C.M. Luong, T.H. Nguyen, L.D. Nguyen, K.N. Tran, H.-T.T. Nguyen, P.H. Tran, A facile and practical conversion of carbohydrates into HMF using metal chlorides in [DMSO][CholineCl] deep eutectic solvent, *Biomass Bioenergy* 174 (2023), 106855.
- [18] Z. Liu, L. Zhu, C. Hu, High-efficiency synthesis of 5-hydroxymethylfurfural from fructose over highly sulfonated organocatalyst, *Ind. Eng. Chem. Res.* 59 (2020) 17218–17227.
- [19] Y. Nie, Q. Hou, C. Bai, H. Qian, X. Bai, M. Ju, Transformation of carbohydrates to 5-hydroxymethylfurfural with high efficiency by tandem catalysis, *J. Clean. Prod.* 274 (2020), 123023.
- [20] S.V. Vasudevan, X. Kong, M. Cao, M. Wang, H. Mao, Q. Bu, Microwave-assisted liquefaction of carbohydrates for 5-hydroxymethylfurfural using tungstophosphoric acid encapsulated dendritic fibrous mesoporous silica as a catalyst, *Sci. Total Environ.* 760 (2021), 143379.
- [21] M. Zuo, X. Wang, Q. Wang, X. Zeng, L. Lin, Aqueous-Natural deep eutectic solvent-enhanced 5-hydroxymethylfurfural production from glucose, starch, and food wastes, *ChemSusChem* 15 (2022), e202101889.
- [22] A. Krishnan, K.P. Gopinath, D.-V.N. Vo, R. Malolan, V.M. Nagarajan, J. Arun, Ionic liquids, deep eutectic solvents and liquid polymers as green solvents in carbon capture technologies: a review, *Environ. Chem. Lett.* 18 (2020) 2031–2054.
- [23] F.M. Perna, P. Vitale, V. Capriati, Deep eutectic solvents and their applications as green solvents, *Curr. Opin. Green Sustainable Chem.* 21 (2020) 27–33.
- [24] I. Wazeer, M. Hayyan, M.K. Hadj-Kali, Deep eutectic solvents: designer fluids for chemical processes, *J. Chem. Technol. Biotechnol.* 93 (2018) 945–958.
- [25] J. Huang, X. Guo, T. Xu, L. Fan, X. Zhou, S. Wu, Ionic deep eutectic solvents for the extraction and separation of natural products, *J. Chromatogr. A* 1598 (2019) 1–19.
- [26] J. Wu, Q. Liang, X. Yu, Q.F. Lü, L. Ma, X. Qin, G. Chen, B. Li, Deep eutectic solvents for boosting electrochemical energy storage and conversion: a review and perspective, *Adv. Funct. Mater.* 31 (2021), 2011102.
- [27] Z. Yang, Natural Deep Eutectic Solvents and Their Applications in Biotechnology, 2018.
- [28] S. Sun, L. Zhao, J. Yang, X. Wang, X. Qin, X. Qi, F. Shen, Eco-friendly synthesis of SO₃H-containing solid acid via mechanochemistry for the conversion of carbohydrates to 5-hydroxymethylfurfural, *ACS Sustainable Chem. Eng.* 8 (2020) 7059–7067.
- [29] D. Steinbach, A. Kruse, J. Sauer, P. Vetter, Sucrose is a promising feedstock for the synthesis of the platform chemical hydroxymethylfurfural, *Energies* 11 (2018) 645.
- [30] L.T. Mika, E. Csefalvai, A. Nemeth, Catalytic conversion of carbohydrates to initial platform chemicals: chemistry and sustainability, *Chem. Rev.* 118 (2018) 505–613.
- [31] Y. Jing, Y. Guo, Q. Xia, X. Liu, Y. Wang, Catalytic production of value-added chemicals and liquid fuels from lignocellulosic biomass, *Chem* 5 (2019) 2520–2546.
- [32] X. Zhang, H. Lu, M. Zhang, H. Han, R. Tian, K. Wu, Y. Liu, Y. Zhu, B. Liang, Low-temperature production of 5-hydroxymethylfurfural from fructose using choline chloride-ethylene glycol-maleic acid ternary deep eutectic solvents, *Ind. Eng. Chem. Res.* 62 (2023) 6093–6102.
- [33] S. Marullo, C. Rizzo, F. D'Anna, Activity of a heterogeneous catalyst in deep eutectic solvents: the case of carbohydrate conversion into 5-hydroxymethylfurfural, *ACS Sustain. Chem. Eng.* 7 (2019) 13359–13368.
- [34] G. García, S. Aparicio, R. Ullah, M. Atilhan, Deep eutectic solvents: physicochemical properties and gas separation applications, *ENFUEM* 29 (2015) 2616–2644.
- [35] S.K. Saha, S. Dey, R. Chakraborty, Effect of choline chloride-oxalic acid based deep eutectic solvent on the ultrasonic assisted extraction of polyphenols from *Aegle marmelos*, *J. Mol. Liq.* 287 (2019), 110956.
- [36] A. Gutiérrez-Hernández, A. Richaud, L. Chacón-García, C.J. Cortés-García, F. Méndez, C.A. Contreras-Celedón, Deep eutectic solvent choline chloride/p-toluenesulfonic acid and water favor the enthalpy-driven binding of arylamines to maleimide in aza-michael addition, *J. Org. Chem.* 86 (2021) 223–234.
- [37] G. Qiu, B. Chen, N. Liu, C. Huang, Hafnium-tin composite oxides as effective synergistic catalysts for the conversion of glucose into 5-hydroxymethylfurfural, *Fuel* 311 (2022), 122628.
- [38] S.K. Tnah, T.Y. Wu, D.C.C. Ting, H.K. Chow, K.P.Y. Shak, W. Subramonian, A. Procentese, C.K. Cheng, W.H. Teoh, J. Md Jahim, Effect of chlorine atoms in choline chloride-monocarboxylic acid for the pretreatment of oil palm fronds and enzymatic hydrolysis, *Renew. Energy* 182 (2022) 285–295.
- [39] F. Zhu, R.X. Deng, Q.H. Jiang, Effects of water on electrochemical behavior of ZnCl₂ and FeCl₃ in deep eutectic solvent composed of choline chloride and urea, *Russ. J. Electrochem.* 58 (2022) 617–625.
- [40] R.J.H. Clark, C.S. Williams, The far-infrared spectra of metal-halide complexes of pyridine and related ligands, *Inorg. Chem.* 4 (1965) 350–357.
- [41] G.A. Voyiatzis, A.G. Kalampounias, G.N. Papatheodorou, The structure of molten mixtures of iron(III) chloride with caesium chloride, *Phys. Chem. Chem. Phys.* 1 (1999) 4797–4803.
- [42] Y. Hu, H. Li, P. Hu, L. Li, D. Wu, Z. Xue, L. Zhu, C. Hu, Probing the effects of fructose concentration on the evolution of humins during fructose dehydration, *React. Chem. Eng.* 8 (2022) 175–183.
- [43] C.B.T.L. Lee, T.Y. Wu, C.H. Ting, J.K. Tan, L.F. Siow, C.K. Cheng, J. Md Jahim, A.W. Mohammad, One-pot furfural production using choline chloride-dicarboxylic acid based deep eutectic solvents under mild conditions, *Bioresour. Technol.* 278 (2019) 486–489.
- [44] F. Gomes, L. Pereira, N. Ribeiro, M. Souza, Production of 5-hydroxymethylfurfural (HMF) via fructose dehydration: effect of solvent and salting-out, *Braz. J. Chem. Eng.* 32 (2015) 119–126.
- [45] T.S. Hansen, J.M. Woodley, A. Riisager, Efficient microwave-assisted synthesis of 5-hydroxymethylfurfural from concentrated aqueous fructose, *Carbohydr. Res.* 344 (2009) 2568–2572.
- [46] C. Vidal, J. García-Álvarez, A. Hernán-Gómez, A.R. Kennedy, E. Hevia, Exploiting deep eutectic solvents and organolithium reagent partnerships: chemoselective ultrafast addition to imines and quinolines under aerobic ambient temperature conditions, *Angew. Chem.* 55 (2016) 16145–16148.
- [47] B. Girisuta, L.P.B.M. Janssen, H.J. Heeres, A kinetic study on the decomposition of 5-hydroxymethylfurfural into levulinic acid, *Green Chem.* 8 (2006) 701–709.
- [48] Y. Román-Leshkov, J.N. Chheda, J.A. Dumesic, Phase modifiers promote efficient production of hydroxymethylfurfural from fructose, *Science* 312 (2006) 1933–1937.
- [49] G.R. Gomes, J.C. Pastre, Microwave-assisted HMF production from water-soluble sugars using betaine-based natural deep eutectic solvents (NADES), *Sustain. Energy Fuels* 4 (2020) 1891–1898.
- [50] X. Sun, J. Wang, J. Chen, J. Zheng, H. Shao, C. Huang, Dehydration of fructose to 5-hydroxymethylfurfural over MeSAPOs synthesized from bauxite, *Microporous Mesoporous Mater.* 259 (2018) 238–243.
- [51] H. Zhang, Z. Yu, T. Gu, L. Xiang, M. Shang, C. Shen, Y. Su, Continuous synthesis of 5-hydroxymethylfurfural using deep eutectic solvents and its kinetic study in microreactors, *J. Chem. Eng.* 391 (2020), 123580.