

# Conversion of Cellulose Into 5-Hydroxymethylfurfural (HMF) In a H<sub>2</sub>O/Tetrahydrofuran/Cyclohexane Biphasic System With Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> As Catalyst

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## Research Article

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## Abstract

A simple and efficient biphasic system consisting of H<sub>2</sub>O, tetrahydrofuran (THF), cyclohexane (CHX) and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was employed to convert cellulose into 5-hydroxymethylfurfural (HMF) with high yield of 71.2%. The real volumes of organic phase ( $V_{\text{org}}$ ) and aqueous phase ( $V_{\text{aque}}$ ) of the biphasic system at reaction temperature were measured to found out that over 80% of the added H<sub>2</sub>O was dissolved into the organic phase at reaction temperature, leading to high  $V_{\text{org}}/V_{\text{aque}}$  (over 44/1) and high concentration of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (over 0.34 g/mL) in aqueous phase. The high concentration of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in aqueous phase could efficiently catalyze the conversion of cellulose into HMF, while the high  $V_{\text{org}}/V_{\text{aque}}$  could protect the formed HMF from rehydration, all of which are responsible for the high efficiency of the system on conversion of cellulose into HMF. The addition of CHX into reaction mixture could decrease the solubility of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and H<sub>2</sub>O in the organic phase, which could improve the stability of HMF in the reaction system, resulting higher yield of HMF from cellulose. Because of the high  $V_{\text{org}}/V_{\text{aque}}$  of the reaction system, one microemulsion-like system and liquid film catalytic model are proposed for the cellulose-to-HMF process.

## Introduction

The increasingly problems of resource shortage and global climate change are driving human society to develop green and renewable resources for energy and materials production. Biomass is cheap, widespread and renewable, which is regarded as one promising candidate for energy and fuels production. Efficient production of platform chemical 5-hydroxymethylfurfural (HMF) from biomass provides sustainable routes for the utilization of natural renewable resources because HMF could be used to produce liquid fuels, materials and fine chemicals (Hu et al., 2020; Xu et al., 2020; Zhao et al., 2021). Nowadays, excellent HMF yield have be achievable from glucose and fructose, but the high price of these monosaccharides hinders the production of HMF with these monosaccharides as starting material. Compared with glucose and fructose, cellulose could be obtained from lignocellulosic biomass through the pulping process, thus using cellulose as the starting substrate is more attractive for HMF sustainable production. However, the robust structure of cellulose and instability of HMF under harsh reaction condition make the direct production of HMF from cellulose one challenge.

Conversion of cellulose into HMF involves the steps of hydrolysis of cellulose into glucose, isomerization of glucose into fructose and dehydration of fructose into HMF (Binder & Raines, 2009; Zhao et al., 2007). Some researchers proposed that glucose could also generate HMF with 3-deoxyglucosone as reaction intermediates instead of fructose (Jadhav et al., 2011). The levulinic acid and humin type polymer are the main byproducts formed during the synthesis of HMF from hexose (Hu et al., 2020). Generally, levulinic acid and humin type polymers are all proposed to be formed by hydrolytic ring-opening of HMF. The 2,5-dioxohex-3-enal formed by hydrolytic ring-opening of HMF is proposed to be the key intermediate for levulinic acid formation (Horvat et al., 1985), while the 2,5-dioxo-6-hydroxy-hexanal formed by hydrolytic ring-opening of HMF is proposed to be the key precursor for humins formation (Horvat et al., 1985; Patil et al., 2012; Patil & Lund, 2011). Therefore, suppressing the hydrolytic ring-opening reaction of HMF is crucial for improve the yield of HMF during the preparation of HMF.

In order to suppress the formation of levulinic acid and humin type polymer during the synthesis of HMF, most of the studies employ organic solvents as reaction medium for HMF production, which could be roughly divided into three species of S-contained organic solvents (such as DMSO) (Jin et al., 2021; Rasrendra et al., 2012), N-contained organic solvents (including amide derivatives and the imidazolium ionic liquids) (Binder & Raines, 2009; Zhang et al., 2017), and O-contained organic solvents (tetrahydrofuran (THF), methyl isobutyl ketone (MIBK), butanol,  $\gamma$ -valerolactone (GVL), etc.). Compared with other organic solvents, the O-contained organic solvents have several advantages of renewable, easy recyclable and low environmental pollution, so these O-contained organic solvents show potential application in HMF production process. The biphasic solvent systems consisting of water, O-contained organic solvents and inorganic salts could extract the formed HMF from aqueous phase into organic phase to protect its further degradation, and have been proved to be promising on large scale production of HMF. Especially, the H<sub>2</sub>O-THF consisted biphasic system is frequently employed as reaction media for conversion of cellulose with impressive HMF yields (Cao et al., 2019; Jing et al., 2018; Shen et al., 2020; Shi et al., 2013; Yang et al., 2012). Compared with other O-contained organic solvents, the boiling point of THF was only 66 °C, so THF could be easily separated with products for recycling (Li et al., 2020). Besides, THF can be synthesized from biomass-based derivatives, such as furfural and

1,4-butanediol(Lange & Wadman, 2020), thus is a promising renewable and green solvent. Because the THF is miscible with H<sub>2</sub>O, NaCl is often added into THF-H<sub>2</sub>O mixture for promoting solvent partitioning into two phases, with the aqueous phase saturated by 20%-35% of NaCl(Jing et al., 2018; Shen et al., 2020; Yang et al., 2012). It should be mentioned that the high concentration of NaCl solvents could also cause corrosion. Thus, avoiding the use of NaCl in THF-H<sub>2</sub>O mixture could be favored for HMF production. However, only very few studies tried to convert cellulose in H<sub>2</sub>O-THF co-solvents without the addition of NaCl(Fang et al., 2018; Shi et al., 2013). Besides, it is well-known that the temperature could influence the liquid-liquid phase equilibrium of polycomponent system(García-Flores et al., 2015), so the real V<sub>org</sub> and V<sub>aque</sub> of the biphasic system at reaction temperature should be quite different with those measured at room temperature. However, to the best of our knowledge, no previous literature reported the real V<sub>org</sub> and V<sub>aque</sub> of the biphasic system at reaction temperature for cellulose conversion.

Another research topic for HMF synthesis is the catalyst development. Liquid mineral acids, acidic ionic liquids ([2-PhIm-SO<sub>3</sub>H][CF<sub>3</sub>SO<sub>3</sub>], [PSMIM]HSO<sub>4</sub>, etc.) (Kumar et al., 2021; Xuan et al., 2016), water soluble acidic metal salts (AlCl<sub>3</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, FeCl<sub>3</sub>, CuCl<sub>2</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, SnCl<sub>4</sub>, NaHSO<sub>4</sub>, etc.) (Shen et al., 2020; Shi et al., 2013; Yang et al., 2012), and solid acids (γ-AlOOH, Amberlyst-15, Nafion-H, ZrPO<sub>3</sub>, FePO<sub>4</sub>, MnPO<sub>4</sub>, Nb/C, HfO(PO<sub>4</sub>)<sub>2</sub>, phosphated TiO<sub>2</sub>, etc.) (Cao et al., 2019; Jin et al., 2021; Li et al., 2018a; Tang & Su, 2019; Xia et al., 2016; Xu et al., 2018) are developed for HMF production. Kumar reported that Brønsted acidic ionic liquid [2-PhIm-SO<sub>3</sub>H][CF<sub>3</sub>SO<sub>3</sub>] could catalyze the conversion of cellulose to yield 70% of HMF in H<sub>2</sub>O-MIBK consisted biphasic system(Kumar et al., 2021). Lai et al. reported one temperature-responsive catalysts Ch<sub>n</sub>H<sub>5-n</sub>CeW<sub>12</sub>O<sub>40</sub> (n = 1 ~ 5), which could efficiently catalyze the conversion of cellulose to yield 67.5% HMF in H<sub>2</sub>O/DMSO/MIBK biphasic system, and they owned the excellent performance to the homogeneous catalysis at high temperature, the strong Brønsted acidity of [H<sub>5-n</sub>CeW<sub>12</sub>O<sub>40</sub>]<sup>n-</sup>, and the appropriate Lewis acidity from Ce(III) (Lai et al., 2020). With phosphated TiO<sub>2</sub> as a catalyst, Atanda et al. reported significant HMF yield of 86% by catalytic conversion of cellulose pretreated by ball milling and acid-impregnated in biphasic system containing H<sub>2</sub>O, THF and N-methyl-2-pyrrolidone(Atanda et al., 2015). Cao et al. reported the excellent HMF yield of 69.8% from cellulose in NaCl-H<sub>2</sub>O/THF biphasic system, with HfO(PO<sub>4</sub>)<sub>2</sub> as catalyst(Cao et al., 2019). Despite some reported heterogeneous catalysts have showed the ability to efficiently catalyze the conversion of cellulose with impressive HMF yield, the high cost for the catalyst preparation, the complicated catalyst preparation process and the longish reaction time for the heterogeneous catalysis process still hampered their industrial application in HMF production. Compared with the solid catalysts, the acidic salts possess several appealing advantages such as commercial availability, easy handling, inexpensiveness, and environmental benignity, and previous literatures have reported that satisfactory HMF yields could be achieved from cellulose with some acidic salts(Li et al., 2018b; Shen et al., 2020; Shi et al., 2013; Yang et al., 2012). Yang et al. reported that AlCl<sub>3</sub> could catalyze the conversion of cellulose in H<sub>2</sub>O-NaCl/THF biphasic system to yield 37% of HMF(Yang et al., 2012). Shen et al. reported that Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> could catalyze the conversion of cellulose in H<sub>2</sub>O-NaCl/GVL biphasic system to produce HMF with high yield of 43.5%(Shen et al., 2020). Previously, we reported that NaHSO<sub>4</sub>-ZnSO<sub>4</sub> could convert the cellulose in H<sub>2</sub>O-THF consisted biphasic system to yield 53% of HMF(Shi et al., 2013). We found that because of the dissolving of H<sub>2</sub>O into THF, the V<sub>aque</sub> was quite lower than the volume of the added H<sub>2</sub>O, resulting high V<sub>org</sub>/V<sub>aque</sub> (over 40/1), and relatively high catalyst concentration in the aqueous phase, all of which are proposed to be responsible for the high efficiency on conversion of cellulose into HMF.

Herein, we studied the conversion of cellulose into HMF in a biphasic system consisting of water, THF and cyclohexane (CHX), with Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> as catalyst. The dissolving of H<sub>2</sub>O and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> into organic phase was carefully studied to found that over 80% of the added H<sub>2</sub>O was dissolved into the organic phase, but the presence of H<sub>2</sub>O in organic phase with H<sub>2</sub>O content below 17% could not cause obvious degradation of HMF in the reaction system. The addition of CHX could suppress the transferring of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> into organic phase, and high HMF yield of 71.2 % was obtained under optimized condition. The actual volume of each phase of the biphasic system at reaction temperature was measured to found that the increasing of reaction temperature could lead to the increasing of solubility of H<sub>2</sub>O in the organic phase, resulting the V<sub>org</sub>/V<sub>aque</sub> reached over 44/1, and the Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> concentration in aqueous phase reached over 0.34 g/mL. The high concentration of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in the aqueous phase, high V<sub>org</sub>/V<sub>aque</sub> and the low solubility of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in organic phase were proposed to be the main reason for the high efficiency on conversion of cellulose into HMF.

## Experimental Section

### 2.1 Materials

The cellulose (50  $\mu\text{m}$ ), glucose monohydrate, THF (99.5%), CHX (99.7%), and HMF (99%) were all purchased from Aladdin Reagents company. The metal salts  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ,  $\text{AlCl}_3$ ,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  used in this study were all analytically pure grade. All reagents were used without further purification.

### 2.2 Conversion of cellulose into HMF

The catalytic conversion of cellulose was carried out in a 50 mL Stainless steel reactor. In a typical process, 1.0 g cellulose, 0.4 g  $\text{Al}_2(\text{SO}_4)_3$ , 3 mL  $\text{H}_2\text{O}$ , 16 mL THF and 3 mL CHX were added into the reactor, then the reactor was heated to 180 °C and kept at the reaction temperature for an hour to carry out the reaction process. After the reaction, the reaction mixture was taken out from the reactor, the  $V_{\text{org}}$  and  $V_{\text{aque}}$  were measured by measuring cylinder, and 1 mL organic phase was taken out and diluted by THF for 10 times and further diluted by  $\text{H}_2\text{O}$  for 20 times before HPLC analysis. All the aqueous phase was diluted to 10 mL and further diluted for 20 times before HPLC analysis. Then the reaction mixture was filtrated and the collected solid residue was washed by pure water and ethanol, dried at 80 °C and weighted for calculating the conversion of cellulose.

The HMF concentration in the organic phase was analyzed by means of high-performance liquid chromatography (HPLC) equipped with an UV detector (with the wavelength of 254 nm) and a Zorbax SB-C18 column, using water–methanol (30:70, v/v) as the mobile phase at a flow rate of 0.5 mL/min and a column temperature of 30 °C. Quantification of products was determined by an external standard method based on the average peak area.

### 2.3 Determination of the distribution of $\text{Al}_2(\text{SO}_4)_3$ in aqueous and organic phase under room temperature.

A certain amount of  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{H}_2\text{O}$ , THF and CHX were added into a test tube, and the  $V_{\text{org}}$  and  $V_{\text{aque}}$  were measured by measuring cylinder after the  $\text{Al}_2(\text{SO}_4)_3$  was totally dissolved. Then the organic phase and aqueous phase were separated and dried at 110 °C to move all solvents, and the collected  $\text{Al}_2(\text{SO}_4)_3$  was weighted by electronic scales.

### 2.4 Observation of the real state of the biphasic system at room temperature and reaction temperature.

One 35 mL transparent pressure tubular vessel made of high borosilicate glass (external diameter 20 mm, inner diameter 10 mm, length 50 cm) was used for direct observation of the real state of the biphasic system. A certain amount of  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{H}_2\text{O}$  were successively put into the transparent pressure tubular vessel and stirred until the  $\text{Al}_2(\text{SO}_4)_3$  was totally dissolved. Then THF and CHX were added into the mixture and further stirred for 10 min, and the  $V_{\text{org}}$  and  $V_{\text{aque}}$  of the mixture at room temperature were read. After that, the tubular vessel was put into one transparent silicone tube protective cover, then put into an oven and heated at 180 °C for around an hour. Then the transparent pressure vessel was taken out from the oven and the  $V_{\text{org}}$  and  $V_{\text{aque}}$  were determined by comparing with the standard curve.

## Results And Discussion

### 3.1 The conversion of cellulose into HMF in biphasic system consisting of $\text{H}_2\text{O}/\text{THF}$

Because the aluminium salts such as  $\text{AlCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  have been reported to show impressive activity on catalyzing the conversion of polysaccharides into platform chemicals (Chen et al., 2019; Huang et al., 2018; Li et al., 2014; Shen et al., 2020; Yang et al., 2017; Yang et al., 2012; Zhang et al., 2016), here we employed  $\text{Al}_2(\text{SO}_4)_3$  as the catalyst for cellulose-to-HMF process. In the beginning, we studied the conversion of cellulose with  $\text{H}_2\text{O}/\text{THF}$  volume ratio as 2/20 because that the high

$V_{\text{org}}/V_{\text{aque}}$  could efficiently protect the formed HMF from further degradation. As shown in Table 1, with the addition of  $\text{Al}_2(\text{SO}_4)_3$ , the cellulose conversion sharply increased from only 14.9% without catalyst to 95.9%, accompanied with HMF yield increased from only 1.6% to 56.3 %, suggesting that the  $\text{Al}_2(\text{SO}_4)_3$  could efficiently convert cellulose into HMF. The excellent performance of the reaction system here was ascribed to the high  $V_{\text{org}}/V_{\text{aque}}$ , high concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase and the special catalytic performance of  $\text{Al}_2(\text{SO}_4)_3$  on conversion of cellulose. As shown in Table 1, only around 0.4 mL amount of aqueous phase was formed, indicating that around 80% of the added water were dissolved into the organic phase, and the  $V_{\text{org}}/V_{\text{aque}}$  was as high as 43.2/1. Besides, considerable amount of the added  $\text{Al}_2(\text{SO}_4)_3$  was precipitated out from the aqueous phase, suggesting that the aqueous phase was saturated by  $\text{Al}_2(\text{SO}_4)_3$ . As has been reported previously (Choudhary et al., 2013; Huang et al., 2018; Tang et al., 2015; Yang et al., 2017), the  $\text{Al}_2(\text{SO}_4)_3$  in the aqueous phase could undergo hydrolysis to form  $[\text{Al}(\text{OH})_2]^+$  and  $\text{H}^+$  in aqueous phase, in which  $[\text{Al}(\text{OH})_2]^+$  is efficient on isomerization of glucose into fructose, while  $\text{H}^+$  is responsible for hydrolysis of cellulose into glucose and dehydration of fructose into HMF. Thus, the high concentration of  $\text{Al}_2(\text{SO}_4)_3$  in the aqueous phase could efficiently catalyze the conversion of cellulose into HMF, while the high  $V_{\text{org}}/V_{\text{aque}}$  could guarantee the efficiency on extraction of the formed HMF into the organic phase to prevent its further degradation.

Table 1  
The results of conversion of cellulose into HMF in  $\text{H}_2\text{O}$ -THF mixture <sup>[a]</sup>

Entry	Solvent (mL)		$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ dosage (g)	$V_{\text{aque}}$	$\text{H}_2\text{O}$ content in organic phase (wt.%)	$\text{Al}_2(\text{SO}_4)_3$ distributed in organic phase (%)	Concen- $\text{Al}_2(\text{SO}_4)_3$ - aque (g/mL)	$V_{\text{org}}/V_{\text{aque}}$	Cellulose conversion (%)	HMF yield (%)
	$\text{H}_2\text{O}$	THF								
1	2.0	20.0	0.0	0	10.1	0	-	-	14.9	1.6
2	2.0	20.0	0.4	0.4	8.7	1.6	Saturated <sup>[b]</sup>	43	95.9	56.3
3	3.0	19.0	0.4	0.6	12.5	1.7	0.35	36	97.6.	59.3
4	4.0	18.0	0.4	0.8	16.7	4.1	0.26	27	98.2	61.1
5	6.0	16.0	0.4	0.9	26.4	6.7	0.23	23	71.1	43.8
6	8.0	14.0	0.4	1.2	35.4	13.4	0.17	17	64.9	32.5
7 <sup>[c]</sup>	2.0	20.0	0.4	1.1	4.8	0.8	0.19	19	58.2	32.2
8 <sup>[c]</sup>	4.0	18.0	0.4	3.3	4.2	0.7	0.06	6	32.7	25.5

<sup>[a]</sup> Reaction condition: 1 g cellulose, 0.4 g  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , 180°C, 1 h. <sup>[b]</sup> Considerable  $\text{Al}_2(\text{SO}_4)_3$  was precipitated out from the solvents. <sup>[c]</sup> 35% of NaCl was added (based on the mass of added water)

We further studied the conversion of cellulose with higher  $\text{H}_2\text{O}$ /THF volume ratio. With the increasing of  $\text{H}_2\text{O}$ /THF volume ratio from 2/20 to 3/19 and 4/18, the HMF yield slightly increased from 56.3 % to 59.3% and 61.1%, respectively. The increase of HMF yield was ascribed to that the increasing water content could adjust the  $V_{\text{aque}}$  and the concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase to proper values for HMF production. It should note that the  $\text{H}_2\text{O}$  content in the organic phase increased from 8.7–16.7% with the increase of  $\text{H}_2\text{O}$ /THF volume ratio from 2/20 to 4/18 but the HMF yield didn't decrease, indicating that the presence of 16.7% of  $\text{H}_2\text{O}$  in the organic phase show very little impact on the stability of HMF in the organic phase. However, further increasing the  $\text{H}_2\text{O}$  content by increasing the  $\text{H}_2\text{O}$ /THF volume ratio to 6/16 and 8/14 resulted in a clear decrease in HMF yield to 43.8 % and 35.3%, respectively, accompanied with the decreasing of cellulose conversion to below 75%. The decreasing of efficiency on cellulose-to-HMF process with the increasing of  $\text{H}_2\text{O}$ /THF volume ratio was ascribed to the decrease of  $V_{\text{org}}/V_{\text{aque}}$ , the decrease of concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase and the increase of concentration of  $\text{Al}_2(\text{SO}_4)_3$  and content of  $\text{H}_2\text{O}$  in organic phase (Yang et al., 2017). As shown in Table 1, with the increase of  $\text{H}_2\text{O}$ /THF volume ratio from 4/18

to 8/14, the volume of aqueous phase increased from 0.8 mL to 1.2 mL, leading to the  $V_{\text{org}}/V_{\text{aque}}$  decreased from 26.8/1 to 16.9/1. Besides, the  $\text{H}_2\text{O}$  content and the solubility of  $\text{Al}_2(\text{SO}_4)_3$  in the organic phase all increased with the increase of  $\text{H}_2\text{O}/\text{THF}$  ratio. With the increase of  $\text{H}_2\text{O}/\text{THF}$  volume ratio from 4/18 to 8/14, the  $\text{H}_2\text{O}$  content in the organic phase increased from 16.7–35.4%, while the amount of  $\text{Al}_2(\text{SO}_4)_3$  distributed in the organic phase increased from 4.1 % to 13.4%, all of which could decrease the stability of HMF in the organic phase. On the other hand, the increase of  $V_{\text{aque}}$  and the transferring of  $\text{Al}_2(\text{SO}_4)_3$  into the organic phase all lead to the decreasing of concentration of  $\text{Al}_2(\text{SO}_4)_3$  in the aqueous phase from saturated to 0.17 g/mL, resulting the decreasing of the efficiency on hydrolysis of cellulose. In brief, the decreasing concentration of  $\text{Al}_2(\text{SO}_4)_3$  in the aqueous phase and the increasing content of  $\text{H}_2\text{O}$  and  $\text{Al}_2(\text{SO}_4)_3$  in organic phase lead to the decreasing of efficiency on conversion of cellulose into HMF with high  $\text{H}_2\text{O}/\text{THF}$  volume ratio.

To further confirm that the dissolving of  $\text{H}_2\text{O}$  and  $\text{Al}_2(\text{SO}_4)_3$  into organic phase could decrease the stability of HMF in the reaction system, we studied the stability of HMF with various  $\text{H}_2\text{O}/\text{THF}$  volume ratio. As shown in Fig. 1(a), after the same reaction time, the remained HMF with the  $\text{H}_2\text{O}/\text{THF}$  volume ratio of 8/14 was always lower than that with the  $\text{H}_2\text{O}/\text{THF}$  volume ratio of 4/18, clearly confirming that the stability of HMF decreased with the dissolving of  $\text{H}_2\text{O}$  and  $\text{Al}_2(\text{SO}_4)_3$  into organic phase.

The HMF yield obtained here was obviously higher than that of 43.5% reported by Shen et al., who also employed  $\text{Al}_2(\text{SO}_4)_3$  to catalyze the conversion of cellulose pretreated by  $\text{Al}_2(\text{SO}_4)_3$ -assisted ball milling in biphasic system consisted by  $\text{H}_2\text{O}$  and  $\gamma$ -valerolactone (GVL) (Shen et al., 2020). In Shen's work, 20% of NaCl (based on the mass of added water) was added into the reaction mixture to prevent the inter-miscible of  $\text{H}_2\text{O}$  and GVL. Here we also studied the influence of the addition of NaCl on conversion of cellulose into HMF in  $\text{H}_2\text{O}$ -THF biphasic system, and the results clearly showed that the addition of NaCl could sharply decrease the efficiency on conversion of cellulose into HMF (Table 1, entry 7–8). When 35% of NaCl (based on the usage of water) was added, the cellulose conversion decreased from over 95 % to below 60 %, accompanied with HMF yield decreased from over 56 % to below 35% (Table 1, entry 2–4 and 7–8), suggesting that the addition of NaCl is against the conversion of cellulose into HMF in the biphasic system. Further study found that the addition of NaCl could increase the  $V_{\text{aque}}$  of the reaction system because that the NaCl could suppress the dissolving of  $\text{H}_2\text{O}$  into the organic phase. Thus, for the reaction systems with the addition of NaCl, the concentrations of the  $\text{Al}_2(\text{SO}_4)_3$  in the aqueous phase were much lower than those reaction systems without NaCl, and the  $V_{\text{org}}/V_{\text{aque}}$  were also much lower than those conditions without NaCl, all of which were against for the conversion of cellulose into HMF. The result was not accord with Yang's work (Yang et al., 2017), who found that the addition of NaCl could slightly improve the yield of furfural from xylan with  $\text{Al}_2(\text{SO}_4)_3$  as catalyst. We propose that the difference was caused by the fact that the hydrolysis of cellulose was much difficult than that of xylan, which presented as the rate-determining step for cellulose-to-HMF process (Shi et al., 2013) and need high concentration of  $\text{Al}_2(\text{SO}_4)_3$  in the aqueous phase to execute this reaction. Therefore, we proposed that NaCl should not be added into the  $\text{H}_2\text{O}$ -THF biphasic system for preparation of HMF from cellulose.

## 3.2 Influence of CHX on the conversion of cellulose into HMF in biphasic system

As shown above, the dissolving of  $\text{Al}_2(\text{SO}_4)_3$  into the organic phase could decrease the catalytic efficiency on the conversion of cellulose into HMF. Thus, suppressing the dissolving of  $\text{Al}_2(\text{SO}_4)_3$  into the organic phase by addition of some non-polar solvent into organic phase may improve the HMF yield. CHX is one common and cheap non-polar solvent, and it is intersoluble with THF in any proportion but insoluble in water, so we studied the effect of addition of CHX into the reaction mixture on preparation of HMF from cellulose. Unexpectedly, the addition of CHX into the reaction mixture efficiently increased the HMF yield (Table 2). Change the reaction mixture from  $V_{\text{H}_2\text{O}}:V_{\text{THF}} = 2:20$  to  $V_{\text{H}_2\text{O}}:V_{\text{THF}}:V_{\text{CHX}} = 1:20:1$ , the HMF yield increased from 56.1–62.5%, and even higher HMF yield of 64.1% and 67.2 % could be achieved with  $V_{\text{H}_2\text{O}}:V_{\text{THF}}:V_{\text{CHX}} = 2:18:2$  and 3:16:3, respectively (Table 2, entry 1–3). Further study proved that the addition of CHX into reaction mixture could decrease the solubility of  $\text{Al}_2(\text{SO}_4)_3$  in the organic phase. Only less than 1% of  $\text{Al}_2(\text{SO}_4)_3$  was transferred into the organic phase with the

addition of CHX, and over 99% of  $\text{Al}_2(\text{SO}_4)_3$  was remained in the organic phase. Obviously, the suppressing of solubility of  $\text{Al}_2(\text{SO}_4)_3$  in organic phase could increase the stability of HMF in organic phase (Fig. 1(b)), thus improved the efficiency on conversion of cellulose into HMF.

Table 2  
The results of conversion of cellulose into HMF in  $\text{H}_2\text{O}$ -THF-CHX mixture <sup>[a]</sup>

Entry	Solvent (mL)			$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ dosage (g)	$V_{\text{aque}}$ (mL)	$\text{Al}_2(\text{SO}_4)_3$ distributed in organic phase (%)	Concen- $\text{Al}_2(\text{SO}_4)_3^-$ aque (g/mL)	$V_{\text{org}}/V_{\text{aque}}$	Cellulose conversion (%)	HMF yield (%)
	$\text{H}_2\text{O}$	THF	CHX							
1	1.0	20.0	1.0	0.4	-	0.3	Saturated <sup>[b]</sup>	-	77.4	62.5
2	2.0	18.0	2.0	0.4	0.6	0.4	0.34	34	92.3	64.1
3	3.0	16.0	3.0	0.4	2.8	0.7	0.07	6	96.9	67.2
4	4.0	14.0	4.0	0.4	4.8	0.6	0.04	4	85.9	49.8
5	5.0	12.0	5.0	0.4	5.7	0.4	0.04	3	82.9	36.6
6	6.0	10.0	6.0	0.4	7.1	0.4	0.03	2	77.3	25.3

<sup>[a]</sup> Reaction condition: 1 g cellulose, 0.4 g  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , 180°C, 1 h. <sup>[b]</sup> Great amount of  $\text{Al}_2(\text{SO}_4)_3$  was precipitated out from the solvents.

Some previous studies also reported that addition of organic phase modifier into the reaction could minimize HMF degradation by suppressing the humins formation (Atanda et al., 2015; Roman-Leshkov et al., 2006). Atanda et al. reported that addition of N-methyl-2-pyrrolidone (NMP) into  $\text{H}_2\text{O}$ /THF biphasic system could increase the HMF yield from 60–80%. They proposed that NMP acts as an aqueous phase modifier that can suppress humin formation in water and simultaneously enhance partitioning of HMF into the organic layer (Atanda et al., 2015). Here we proposed that the effect of CHX on the efficiency of cellulose-to-HMF process was ascribed to that CHX could suppress the dissolution of acidic salts  $\text{Al}_2(\text{SO}_4)_3$  into organic phase, leading to higher stability of HMF in organic phase. We also studied the stability of HMF in the reaction mixture at 180°C, and the results were shown in Fig. 1(b). As shown, over 75% of the HMF were remained after 60 min, clearly confirmed that the addition of CHX into the reaction system improved the stability of HMF in the reaction mixture.

Further increase the  $\text{H}_2\text{O}$  and CHX content (for the conditions of  $V_{\text{H}_2\text{O}}:V_{\text{THF}}:V_{\text{CHX}} = 4:14:4$ ,  $5:12:5$  and  $6:10:6$ ) lead to sharp decrease of HMF yield to below 50% (Table 2, entry 4–6). The sharp decreasing of HMF yield with the increase of  $\text{H}_2\text{O}$  and CHX content was ascribed to that the increasing of  $\text{H}_2\text{O}$  and CHX content could increase the  $V_{\text{aque}}$  of the reaction system, leading to relatively low  $\text{Al}_2(\text{SO}_4)_3$  concentration in the aqueous phase and low  $V_{\text{org}}/V_{\text{aque}}$ . As shown in Table 2, for the conditions of  $V_{\text{H}_2\text{O}}:V_{\text{THF}}:V_{\text{CHX}} = 4:14:4$ ,  $5:12:5$  and  $6:10:6$ , the  $V_{\text{org}}/V_{\text{aque}}$  have decreased to below 5:1, and the  $\text{Al}_2(\text{SO}_4)_3$  concentration in the aqueous phase have decreased to below 0.04 g/mL, all of which are against for conversion of cellulose into HMF.

It was noted that for the condition of  $\text{H}_2\text{O}$ /THF/CHX volume ratio as 3:16:3, the concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase was only 0.07 g/mL and the  $V_{\text{org}}/V_{\text{aque}}$  was only 6.4:1, all of which were much lower than those without the addition of CHX, but the cellulose conversion (96.9 %) and HMF yield (67.2%) were all higher than those conditions without CHX. The high cellulose conversion suggested that the  $\text{Al}_2(\text{SO}_4)_3$  concentration in the aqueous phase at reaction temperature should be much higher than that measured at room temperature. Because the temperature could influence the liquid-liquid phase equilibrium of polycomponent system (García-Flores et al., 2015), the real  $V_{\text{org}}/V_{\text{aque}}$  and the concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase at reaction temperature should be different with those measured at room temperature. Thus, we tried to measure the actual  $V_{\text{org}}$  and  $V_{\text{aque}}$  of the reaction mixture, and the results were shown in the next section.

### 3.3 The real state of the biphasic system at reaction temperature

Table 3 showed the  $V_{\text{org}}$  and  $V_{\text{aque}}$  of the reaction system under the room temperature and 180°C. Because  $\text{H}_2\text{O}$  and THF are complete intersoluble, only one phase was formed at both room temperature and reaction temperature with the absence of CHX and  $\text{Al}_2(\text{SO}_4)_3$ . Aqueous phase was formed when  $\text{Al}_2(\text{SO}_4)_3$  was added into mixture of  $\text{H}_2\text{O}$ /THF, but the  $V_{\text{aque}}$  was always much lower than that of the added  $\text{H}_2\text{O}$ , indicating that considerable added  $\text{H}_2\text{O}$  was dissolved into organic phase. For the condition of  $\text{H}_2\text{O}$ /THF/ $\text{Al}_2(\text{SO}_4)_3$  as 2/20/0.4 and 4/18/0.4, only 0.4 mL and 0.8 mL of aqueous phase were formed at room temperature, respectively, which sharply decreased to only 0.2 mL and 0.4 mL at 180 °C, respectively. The decreasing of  $V_{\text{aque}}$  with the increase of temperature was ascribed to the increased solubility of  $\text{H}_2\text{O}$  in THF with the increase of temperature. Further increasing of  $\text{H}_2\text{O}$ /THF volume ratio to 6/16 and 8/14 slightly increased the  $V_{\text{aque}}$  to 0.9 mL and 1.2 mL at room temperature, respectively, and increase of temperature to 180 °C only slightly decrease the  $V_{\text{aque}}$  to 0.8 mL and 1.1 mL, respectively, suggesting that the affinity between  $\text{H}_2\text{O}$  and THF become insensitive with temperature when the  $\text{H}_2\text{O}$  content in organic phase reached over 26%.

Table 3  
The real state of the biphasic system at room temperature and 180 °C

Composition of the biphasic system		Biphasic system at room temperature				Biphasic system at 180 °C			
Solvent H <sub>2</sub> O (mL)	Salts (g)	V <sub>org</sub> (mL)	V <sub>aque</sub> (mL)	Concen- Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> <sup>-</sup> Aque (g/mL)	V <sub>org</sub> /V <sub>aque</sub>	V <sub>org</sub> (mL)	V <sub>aque</sub> (mL)	Concen- Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> <sup>-</sup> Aque (g/mL)	V <sub>org</sub> /V <sub>aque</sub>
H <sub>2</sub> O/THF = 2/20	0	22.0	0	0	-	27.7	0	0	-
H <sub>2</sub> O/THF = 4/18	0	22.0	0	0	-	27.4	0	0	-
H <sub>2</sub> O/THF = 6/16	0	22.0	0	0	-	27.1	0	0	-
H <sub>2</sub> O/THF = 8/14	0	22.0	0	0	-	26.8	0	0	-
H <sub>2</sub> O/THF = 2/20	0.4g Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	21.6	0.4	Saturated	54	27.4	0.2	1.03	137
H <sub>2</sub> O/THF = 4/18	0.4g Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	21.4	0.8	0.26	27	26.9	0.4	0.51	68
H <sub>2</sub> O/THF = 6/16	0.4g Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	21.1	0.9	0.23	23	26.3	0.8	0.26	33
H <sub>2</sub> O/THF = 8/14	0.4g Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	20.3	1.2	0.17	17	25.7	1.1	0.19	23
H <sub>2</sub> O/THF/CHX = 1/20/1	0	22.0	0	0	-	27.8	0	0	-
H <sub>2</sub> O/THF/CHX = 2/18/2	0	22.0	0	0	-	27.6	0	0.	-
H <sub>2</sub> O/THF/CHX = 3/16/3	0	19.2	2.8	0	7	27.4	0	0	-
H <sub>2</sub> O/THF/CHX = 4/14/4	0	17.4	4.6	0	4	25.8	1.5	0	17
H <sub>2</sub> O/THF/CHX = 1/20/1	0.4g Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	21.6	0.4	Saturated	54	27.6	0.2	1.03	138
H <sub>2</sub> O/THF/CHX = 2/18/2	0.4g Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	21.4	0.6	0.34	36	27.4	0.3	0.68	91
H <sub>2</sub> O/THF/CHX = 3/16/3	0.4g Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	19.2	2.8	0.07	7	26.8	0.6	0.34	45
H <sub>2</sub> O/THF/CHX = 4/14/4	0.4g Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	17.3	4.8	0.04	4	25.3	1.9	0.11	13
H <sub>2</sub> O/THF/CHX = 5/12/5	0.4g Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	16.3	5.7	0.04	3	23.2	3.8	0.05	6
H <sub>2</sub> O/THF/CHX = 6/10/6	0.4g Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	14.8	7.1	0.03	2	20.4	6.5	0.03	3

When CHX was added into H<sub>2</sub>O-THF mixture, only monophasic system was formed when the H<sub>2</sub>O/THF/CHX volume ratio was 1:20:1 and 2:18:2, while further increase the H<sub>2</sub>O and CHX content lead to the generation of biphasic system. For the condition of H<sub>2</sub>O/THF/CHX volume ratio as 3:16:3, biphasic system was formed at room temperature but only one phase was observed at 180 °C. However, for the condition of H<sub>2</sub>O/THF/CHX volume ratio as 4:14:4, biphasic system was formed at both room temperature and at 180 °C. The phase behavior could be explained by the H<sub>2</sub>O-THF-CHX phase diagram shown in Fig. 2. It is well-known that THF is completely miscible with H<sub>2</sub>O and CHX, while the H<sub>2</sub>O and CHX are almost immiscible, so the H<sub>2</sub>O-THF-CHX phase diagram could be divided into two regions of monophasic region and biphasic region (García-Flores et al., 2015). Besides, increasing of temperature could enlarge the monophasic region of the phase diagram of H<sub>2</sub>O-THF-CHX, indicating that a certain biphasic region at room temperature could become monophasic state at high temperature. Thus, the H<sub>2</sub>O-THF-CHX phase diagram at different temperature could be divided into three regions of monophasic region, biphasic region and transition region, as shown in Fig. 2 (García-Flores et al., 2015). In the monophasic region, the H<sub>2</sub>O/THF/CHX mixture presented as monophasic at both room temperature and 180 °C. In the transition region, the H<sub>2</sub>O/THF/CHX mixture presented as biphasic at room temperature but became monophasic at 180 °C. In the biphasic region, H<sub>2</sub>O/THF/CHX mixture presented as biphasic at both room temperature and 180 °C. Obviously, the plots of H<sub>2</sub>O/THF/CHX volume ratio as 1:20:1 and 2:18:2 are presented in the monophasic region of the H<sub>2</sub>O-THF-CHX phase diagram, the plot of H<sub>2</sub>O/THF/CHX volume ratio as 3:16:3 is presented in the transition region, while the plots of H<sub>2</sub>O/THF/CHX ratio = 4:14:4 is presented in the biphasic region.

For most of the biphasic systems, the  $V_{aque}$  at 180 °C were lower than the  $V_{aque}$  at room temperature. For example, the  $V_{aque}$  at room temperature was 0.8 mL for the condition of H<sub>2</sub>O/THF/Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> ratio (mL/mL/g) as 4/18/0.4, which decreased to only 0.2 mL at 180 °C. What is more exaggerated, for the condition of the H<sub>2</sub>O/THF/CHX/Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> ratio (mL/mL/mL/g) as 3/16/3/0.4, the  $V_{aque}$  sharply decreased from 2.8 mL at room temperature to only 0.6 mL at 180 °C. The variation of  $V_{aque}$  with the increasing of temperature could be described by the following equation:

$$\Delta m_{aque} = V_{aque} \times \Delta C_{THF \rightarrow aque} - V_{org} \times \Delta C_{H_2O \rightarrow org}$$

Where the  $\Delta m_{aque}$  denotes the change of the mass of aqueous phase,  $V_{aque}$  and  $V_{org}$  denote the volume of aqueous phase and organic phase at room temperature, respectively, while  $\Delta C_{THF \rightarrow aque}$  and  $\Delta C_{H_2O \rightarrow org}$  denote the variable quantity of solubility of THF in aqueous phase and the variable quantity of solubility of H<sub>2</sub>O in organic phase with the increase of temperature, respectively. Because the  $V_{org}$  was much higher than  $V_{aque}$  in the biphasic system in this study, so the above equation could be simplified as follows:

$$\Delta m_{aque} \approx -V_{org} \times \Delta C_{H_2O \rightarrow org}$$

Thus, the  $\Delta m_{aque}$  should decrease with the increase of temperature for most conditions in this study.

Be different from the aqueous phase, the  $V_{org}$  measured at 180 °C were all higher than those measured at room temperature, which was caused by the volume expansion of the organic solvents and the transferring of H<sub>2</sub>O from aqueous phase to organic phase. The increasing of  $V_{org}$  and decreasing of  $V_{aque}$  with the increase of temperature jointly lead to the  $V_{org}/V_{aque}$  ratios at 180 °C be higher than those at room temperature. For the conditions of H<sub>2</sub>O/THF/Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> as 2/20/0.4 and 4/18/0.4, the  $V_{org}/V_{aque}$  ratios at 180 °C all reached as high as over 60/1, while for the conditions of H<sub>2</sub>O/THF/Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> as 6/16/0.4 and 8/14/0.4, the  $V_{org}/V_{aque}$  ratios were all below 33/1. The difference of the  $V_{org}/V_{aque}$  and the concentration of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in aqueous phase should be one main reason for the excellent performance of the former reaction systems and poor performance of the later reaction systems.

The decreasing of  $V_{\text{aque}}$  with the increase of temperature could increase the  $\text{Al}_2(\text{SO}_4)_3$  concentration in the aqueous phase, which could also influence the cellulose-to-HMF process. Assuming that the distribution of  $\text{Al}_2(\text{SO}_4)_3$  in the biphasic system at high temperature was the same as that at room temperature, we could calculate the  $\text{Al}_2(\text{SO}_4)_3$  concentration in the aqueous phase at 180 °C, and the results were also shown in Table 3. Due to the decrease of  $V_{\text{aque}}$  with the increase of temperature, the concentrations of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase at 180 °C were all much higher than those at room temperature. For cases of  $\text{H}_2\text{O}/\text{THF}/\text{Al}_2(\text{SO}_4)_3$  as 4/18/0.4, the concentrations of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase at 180 °C was 1.03 g/mL, much higher than that of 0.26 g/mL at room temperature. What's more exaggerated, for the condition of  $\text{H}_2\text{O}/\text{THF}/\text{CHX}/\text{Al}_2(\text{SO}_4)_3$  as 3/16/3/0.4, the concentrations of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase increased from 0.07 g/mL to 0.34 g/mL. The high concentrations of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase at 180 °C of the reaction system should also be responsible for the high efficiency on cellulose conversion.

The excellent performance of the reaction system of  $\text{H}_2\text{O}/\text{THF}/\text{CHX}/\text{Al}_2(\text{SO}_4)_3$  as 3/16/3/0.4 could be explained by the relatively high  $V_{\text{org}}/V_{\text{aque}}$  (44.6/1) and high concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase (0.34 g/mL) at reaction temperature. As shown in Table 3, with the increase of temperature from room temperature to 180 °C, the  $V_{\text{aque}}$  sharply decreased from 2.8 mL to 0.6 mL. The sharp decrease of  $V_{\text{aque}}$  could be explained by the  $\text{H}_2\text{O}$ -THF-CHX phase diagram shown in Fig. 2. The plot  $\text{H}_2\text{O}/\text{THF}/\text{CHX} = 3/16/3$  was in the transition region of the phase diagram, so the mixture presented as biphasic at room temperature to generate 2.8 mL of aqueous phase. However, the mixture of  $\text{H}_2\text{O}/\text{THF}/\text{CHX} = 3/16/3$  present as monophasic at 180°C, so no aqueous phase could be observed with the absence of  $\text{Al}_2(\text{SO}_4)_3$ . When  $\text{Al}_2(\text{SO}_4)_3$  was added into the  $\text{H}_2\text{O}/\text{THF}/\text{CHX}$  mixture at 180 °C,  $\text{Al}_2(\text{SO}_4)_3$  could capture  $\text{H}_2\text{O}$  from the organic phase to generate aqueous phase, leading to the formation of 0.6 mL aqueous phase at 180 °C. The sharp decrease of  $V_{\text{aque}}$  leading to the  $V_{\text{org}}/V_{\text{aque}}$  sharply increased from 6.9/1 at room temperature to 44.6/1 at 180 °C, and the concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase increased from 0.07 g/mL to 0.34 g/mL, which are responsible for the excellent efficiency of the reaction system. The changeable  $V_{\text{aque}}$  for the conditions of  $\text{H}_2\text{O}/\text{THF}/\text{CHX}/\text{Al}_2(\text{SO}_4)_3$  as 3/16/3/0.4 shows some advantages for cellulose-to-HMF process. The  $V_{\text{aque}}$  was low at reaction temperature, so the high  $V_{\text{org}}/V_{\text{aque}}$  ratio and high concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase could guarantee the high efficiency on converting cellulose into HMF. However, the  $V_{\text{aque}}$  was high at room temperature, thus the catalyst could be extracted to the aqueous phase and recycled easily.

The above results showed that the reaction mixture of  $\text{H}_2\text{O}/\text{THF}/\text{CHX}/\text{Al}_2(\text{SO}_4)_3$  as 3/16/3/0.4 was much more efficient than that of 4/14/4/0.4, which could be explained by the difference of  $V_{\text{org}}/V_{\text{aque}}$  and the concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase at 180 °C. For the condition of  $\text{H}_2\text{O}/\text{THF}/\text{CHX}/\text{Al}_2(\text{SO}_4)_3$  as 3/16/3/0.4, the  $V_{\text{org}}/V_{\text{aque}}$  and the concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase were 44.6/1 and 0.34 g/mL, but for the condition of  $\text{H}_2\text{O}/\text{THF}/\text{CHX}/\text{Al}_2(\text{SO}_4)_3$  as 4/14/4/0.4, the  $V_{\text{org}}/V_{\text{aque}}$  and the concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase were only 16/1 and 0.13 g/mL. Obviously, the relatively lower  $V_{\text{org}}/V_{\text{aque}}$  and the concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase should be responsible for the poor performance of the condition of  $\text{H}_2\text{O}/\text{THF}/\text{CHX}/\text{Al}_2(\text{SO}_4)_3$  as 4/14/4/0.4. Combining the catalytic performance and the real state of the reaction system, we could found that the concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase and the  $V_{\text{org}}/V_{\text{aque}}$  ratio shows obvious influence on the conversion of cellulose into HMF. It seems that when the concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase was higher than 0.34 g/mL and the  $V_{\text{org}}/V_{\text{aque}}$  was higher than 44.6/1, the reaction mixture was quite efficient on conversion of cellulose into HMF. However, the efficiency of cellulose-to-HMF process decreased with the decrease of concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase and  $V_{\text{org}}/V_{\text{aque}}$  ratio when the concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase were below 0.34 g/mL and  $V_{\text{org}}/V_{\text{aque}}$  ratio were below 44.6/1.

In brief, because of the increased solubility of  $\text{H}_2\text{O}$  in the organic phase with the increase of temperature, the  $V_{\text{org}}/V_{\text{aque}}$  and the concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase at reaction temperature were all much higher than that measured at room temperature. For the mixture of  $\text{H}_2\text{O}/\text{THF}/\text{CHX}/\text{Al}_2(\text{SO}_4)_3$  as 3/16/3/0.4, the concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase increased from 0.07 g/mL at room temperature to 0.34 g/mL at 180 °C, while the  $V_{\text{org}}/V_{\text{aque}}$  increased from 6.9/1 at room temperature to 44.6/1 at reaction temperature, which were responsible for the excellent performance of the reaction system.

Combining the real state of the biphasic system and the reaction performance on cellulose-to-HMF process, we found that the reaction systems with  $\text{Al}_2(\text{SO}_4)_3$  concentration in the aqueous phase over 0.34 g/mL,  $V_{\text{org}}/V_{\text{aque}}$  ratio over 44/1 and  $\text{H}_2\text{O}$  content in organic phase below 17% all showed excellent performance on conversion of cellulose into HMF.

### 3.4 The microemulsion-like systems and liquid film catalytic processes

It should be mentioned that because the  $V_{\text{aque}}$  at 180 °C was quite low (below 0.6 mL for all the conditions with excellent performance), the aqueous phase even could not wet the surface of cellulose. Thus, we proposed that the reaction system should be the so-called microemulsion-like system instead of the biphasic system (Fig. 3). Under stirring, the organic phase acts as the dispersion medium, while the cellulose particles and the aqueous phase are dispersed in the organic phase. Because of the hydrophilic property of the cellulose particles (Shi et al., 2013), the aqueous phase covers on the surface of the cellulose particles to generate one acidic liquid film, which could efficiently catalyze the hydrolysis of cellulose and isomerization-dehydration of hexose, while the formed HMF is efficiently extracted into the organic phase to suppress its further degradation. The CHX in the organic phase decreased the solubility of  $\text{Al}_2(\text{SO}_4)_3$ , thus improved the selectivity of HMF from cellulose and suppressed the formation of humins.

### 3.5 Screening of acidic metal salts for cellulose conversion

In order to further improve the efficiency on cellulose-to-HMF process, a variety of other acidic metal salt catalysts were tested for the conversion of cellulose in the  $\text{H}_2\text{O}/\text{THF}/\text{CHX}$  biphasic system, and the results were shown in Fig. 4. The cellulose conversions were lower than 65% with  $\text{ZrOCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{ErCl}_2$  as catalyst, suggesting that the catalytic activity on hydrolysis of cellulose of these catalyst were relatively low. The low catalytic activities of these catalysts were ascribed to the relatively lower acid strength of the aqueous phase generated by hydrolysis of these metal salts (Yang et al., 2017). Although  $\text{HfO}(\text{PO}_4)_2 \cdot 0$  is reported to be excellent on conversion of cellulose into HMF as one solid acid (Cao et al., 2019), here we found that  $\text{HfCl}_4$  is also not efficient on conversion of cellulose in biphasic system, which is similar with previous report (Zhang et al., 2012). The  $\text{ErCl}_2$  also showed low efficient on conversion of cellulose, which could be due that the  $\text{ErCl}_2$  is more favor for conversion of cellulose into lactic acid (Lei et al., 2014). The  $\text{AlCl}_3$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{SnCl}_4 \cdot \text{H}_2\text{O}$  all showed moderate activity on conversion of cellulose into HMF, and moderate HMF yield of over 40% was obtained from these three catalysts. For the same metal cations of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ , the chlorine salts all showed lower efficiency than the sulfates on the cellulose-to-HMF process. Yang et al. reported similar phenomenon on xylan-to-furfural process (Yang et al., 2017). The lower efficiency of the chlorine salts was proposed to be caused by the higher solubility of the chlorine salts in the organic phase than that of the sulfates (Yang et al., 2017).

Obviously, the catalytic activity of these explored salts were all lower than  $\text{Al}_2(\text{SO}_4)_3$ , clearly showing that the  $\text{Al}_2(\text{SO}_4)_3$  should be one promising candidate for large-scale producing HMF from cellulose.

### 3.6 Influence of catalyst usage, reaction temperature, reaction time and cellulose dosage on HMF production

The influence of catalyst usage, reaction temperature, reaction time and cellulose dosage was studied with  $\text{H}_2\text{O}/\text{THF}/\text{CHX}$  volume ratio as 3/16/3. As shown in Fig. 5(a), increase the  $\text{Al}_2(\text{SO}_4)_3$  dosage to 0.05 g and 0.3 g, the HMF yield sharply increased to 34.3% and 62.3%, but further increase the dosage of  $\text{Al}_2(\text{SO}_4)_3$  from 0.3 g to 0.5 g only lead to slight increase of HMF yield from 62.3% to 71.2%. The increased HMF yield with the increase of  $\text{Al}_2(\text{SO}_4)_3$  dosage was ascribed to that the increase of  $\text{Al}_2(\text{SO}_4)_3$  in reaction system could increase the concentration of  $\text{Al}_2(\text{SO}_4)_3$  in the aqueous phase, which could accelerate the hydrolysis of cellulose and dehydration of hexose. Further increasing the  $\text{Al}_2(\text{SO}_4)_3$  to 0.6 g lead to the decrease of HMF yield, which was ascribed to that the excessive  $\text{Al}_2(\text{SO}_4)_3$  loading accelerated the side reactions (e.g., rehydration or condensation of HMF) (Yang et al., 2017).

As shown in Fig. 5(b), the cellulose conversion was low at low reaction temperature of 160°C and 170°C, suggesting that the temperature below 170°C was not enough for  $\text{Al}_2(\text{SO}_4)_3$  to catalyze the conversion of cellulose. As the reaction temperature

was increased, the conversion of cellulose and yield of HMF gradually increased and reached a plateau at 180 °C and 190 °C, indicating that the reaction rates increased with the increasing of reaction temperature. However, at temperatures above 200 °C, the HMF yields decreased to below 40%, indicating that the formed HMF became unstable with reaction temperature of 200 °C. The temperature could influence the cellulose-to-HMF process through two main routes. On one hand, the increase of temperature could accelerate the hydrolysis of cellulose and dehydration of glucose, thus accelerate the cellulose-to-HMF process. On the other hand, the increase of temperature could further decrease the  $V_{\text{aque}}$  of the system, resulting higher  $V_{\text{org}}/V_{\text{aque}}$  and higher concentration of  $\text{Al}_2(\text{SO}_4)_3$  in aqueous phase, which could also accelerate the reaction process.

The influence of reaction time on the yield of HMF showed similar trend (Fig. 5(c)). Low cellulose conversion of 75.3% was achieved within 30 min, accompanied with HMF yield of 52.7%. Prolonging the reaction time to 60 min leads to the increasing of HMF yield to 71.2%, but further increasing of reaction time to 90 min lead to decreasing of the HMF yield to only 54.1%, which was also ascribed to the degradation of the formed HMF into humin type polymer (Shi et al., 2020; Shi et al., 2013).

We further studied the influence of cellulose/solvent ratio on HMF yield from cellulose because that the high cellulose/solvent ratio is favored for HMF production in large scale. Not surprisingly, the cellulose conversion and HMF yield all decreased with the increase of cellulose/solvent ratio. With the increase of cellulose/solvent ratio (g/mL) from 1:22 to 2:22, 4:22 and 5:22, the HMF yield decreased from 71.2–58.7%, 49.8% and 40.3%, while the HMF concentration in organic phase increased from 28.5 g/L to 49.2 g/L, 64.6 g/L and 63.4 g/L, respectively (Fig. 5(d)). The decrease of HMF yield with the increase of cellulose/solvent ratio was ascribed to the accelerated condensation/polymerization of HMF with the increase of HMF concentration in the reaction system, which has been reported by previous literatures (Fang et al., 2018; Shi et al., 2013). Many literatures employed extremely low cellulose/solvent ratio (below 1:50) to obtain relatively high HMF yield (Li et al., 2018a), which could result in quite low HMF concentration in the reaction mixture. Cao et al. reported high HMF yield of 69.8% from cellulose with  $\text{HfO}(\text{PO}_4)_2$  as catalyst, but the cellulose/solvent ratio was 1/50 (g/mL), leading to HMF concentration in the reaction mixture only 1.1 g/mL (Cao et al., 2019). Lai et al. achieved an excellent HMF yield of 67.5% from cellulose with  $\text{ChH}_4\text{CeW}_{12}\text{O}_{40}$  as catalyst, but the cellulose/solvent ratio was 1/70 (g/mL), also leading to HMF concentration below 0.75 g/mL (Lai et al., 2020). Some other literatures even conducted the cellulose-to-HMF process with cellulose/solvent below 1/80 (g/mL) (Li et al., 2018a; Li et al., 2018b), leading to extremely low concentration of HMF in the reaction mixture. In this study, acceptable HMF yield and high HMF concentration in organic phase could be obtained with high cellulose/solvent ratio, indicated that the reaction system has great prospects for industrialization.

## Conclusions

High HMF yield of 71.2% was obtained from cellulose in  $\text{H}_2\text{O}/\text{THF}/\text{CHX}$  consisted biphasic system, with  $\text{Al}_2(\text{SO}_4)_3$  as catalyst. Under the reaction temperature, over 90% of the added water was dissolved into the organic phase, resulting the  $V_{\text{org}}/V_{\text{aque}}$  of the reaction system reached as high as 44.7/1 and the concentration of  $\text{Al}_2(\text{SO}_4)_3$  in the aqueous phase reached as high as 0.34 g/mL. The addition of CHX into the reaction mixture could suppress the dissolving of  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{H}_2\text{O}$  into the organic phase, resulting higher stability of HMF in the organic phase and higher selectivity of HMF from cellulose. The high concentration of  $\text{Al}_2(\text{SO}_4)_3$  in the aqueous phase, high  $V_{\text{org}}/V_{\text{aque}}$  and low concentration of  $\text{Al}_2(\text{SO}_4)_3$  in the organic phase are responsible for high efficiency of the reaction system for conversion of cellulose into HMF.

## Declarations

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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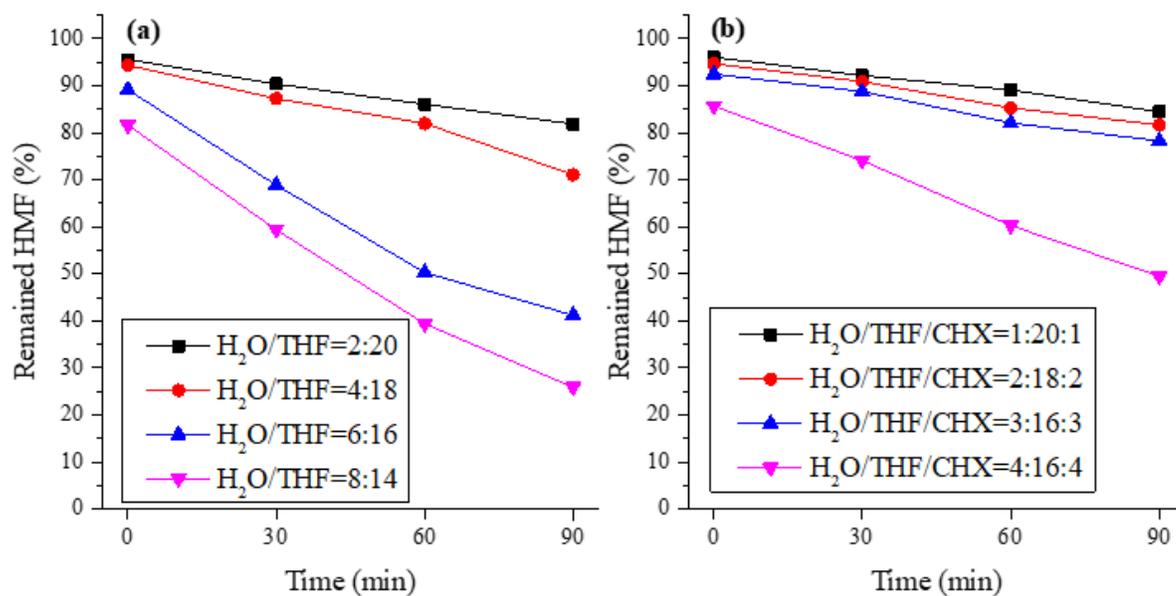
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## Figures



**Figure 1**

The stability of HMF in (a) H<sub>2</sub>O/THF and (b) H<sub>2</sub>O/THF/CHX mixture Reaction conditions: 0.5g HMF, 22 mL solvents, 0.4g Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 180 °C.

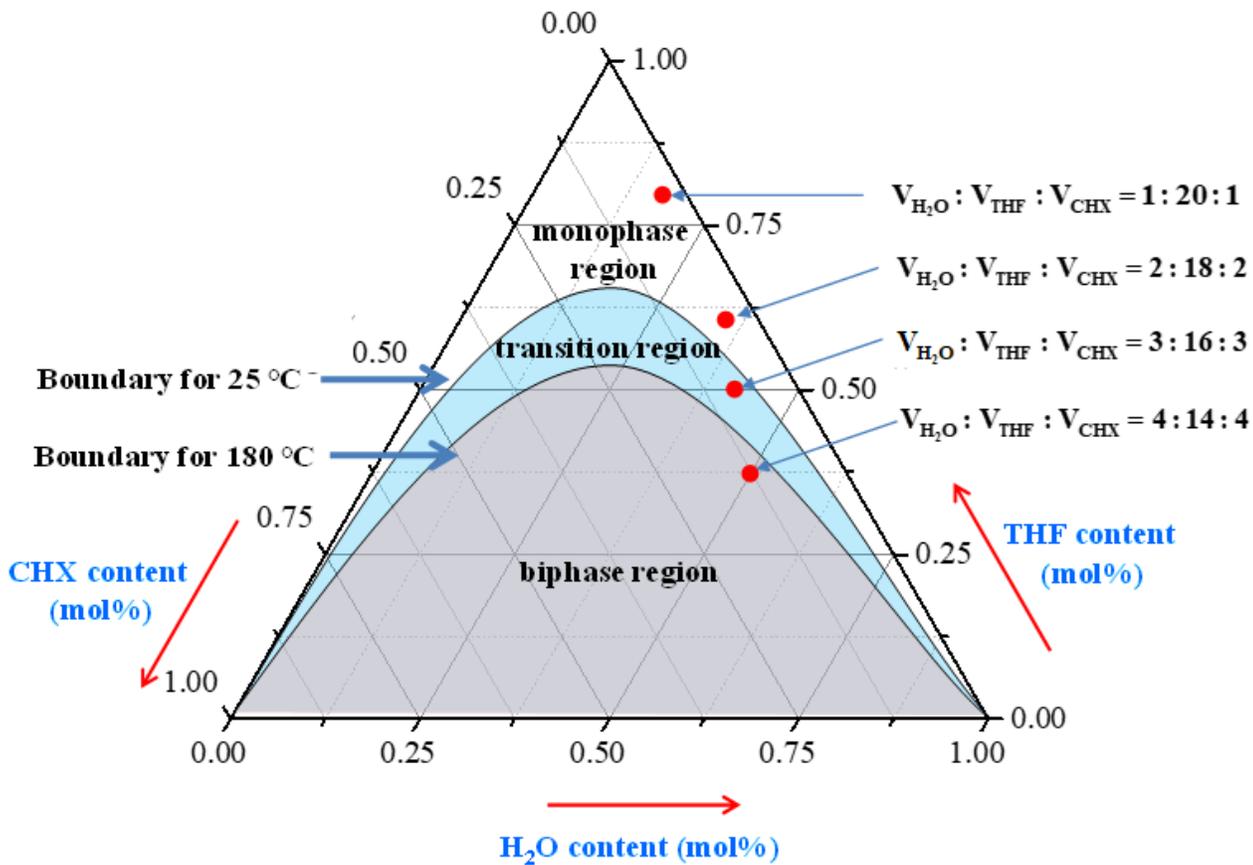


Figure 2

Schematic illustration of liquid-liquid phase equilibrium diagram of H<sub>2</sub>O/THF/CHX mixture at different temperature

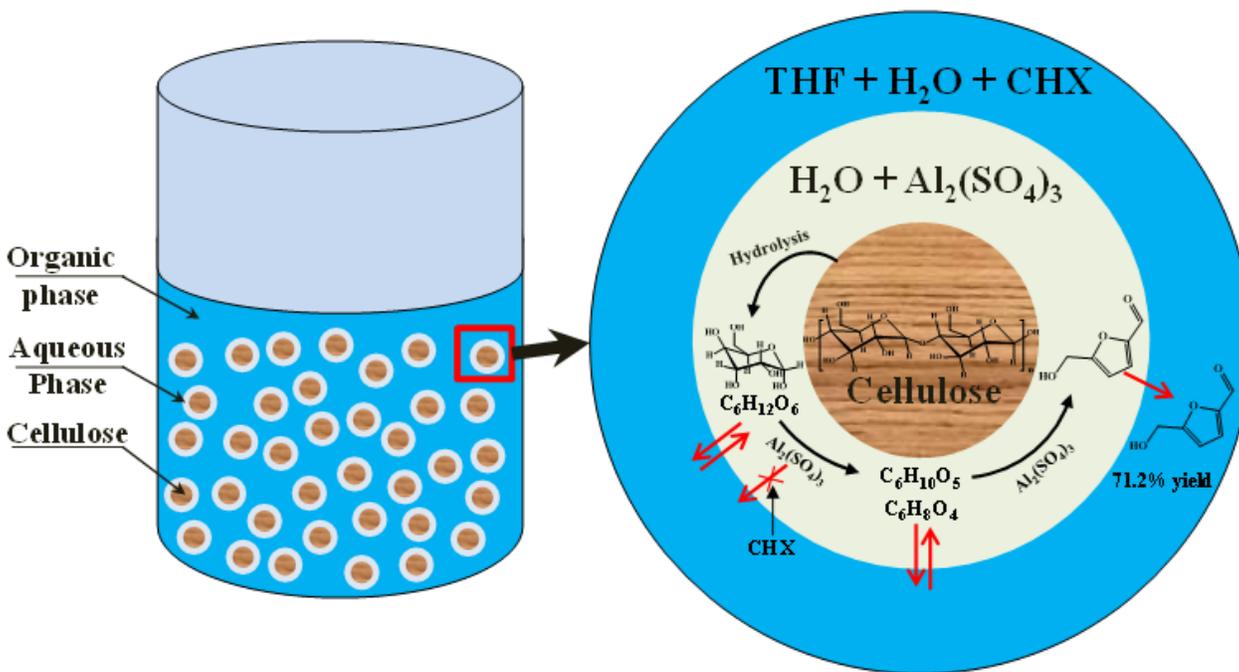
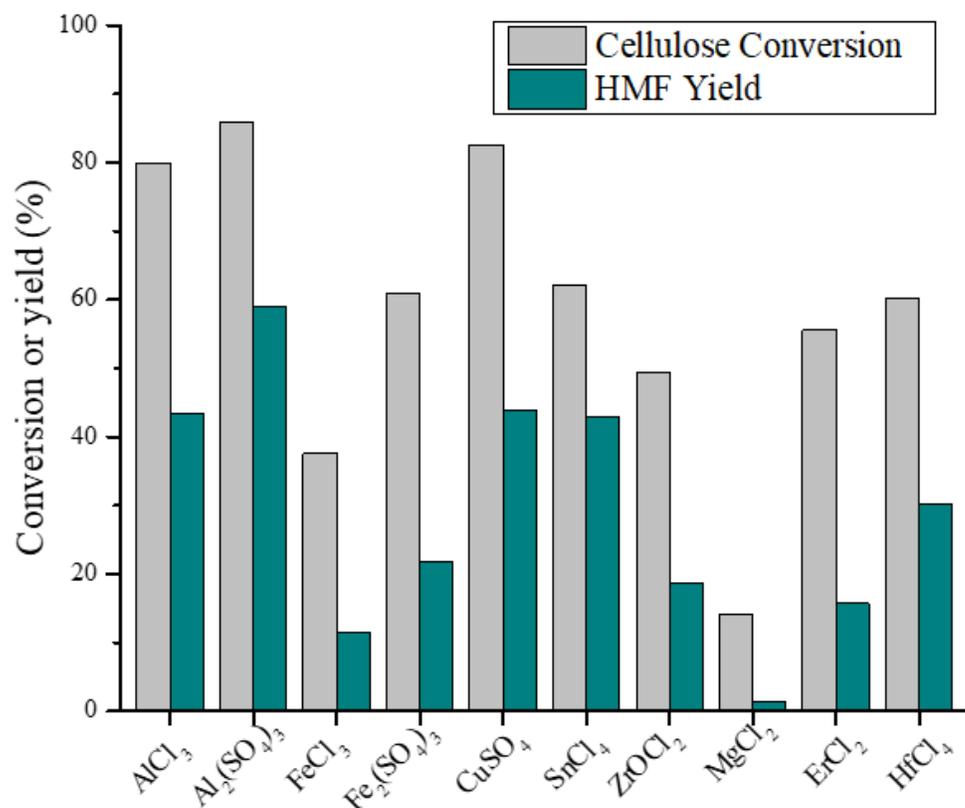


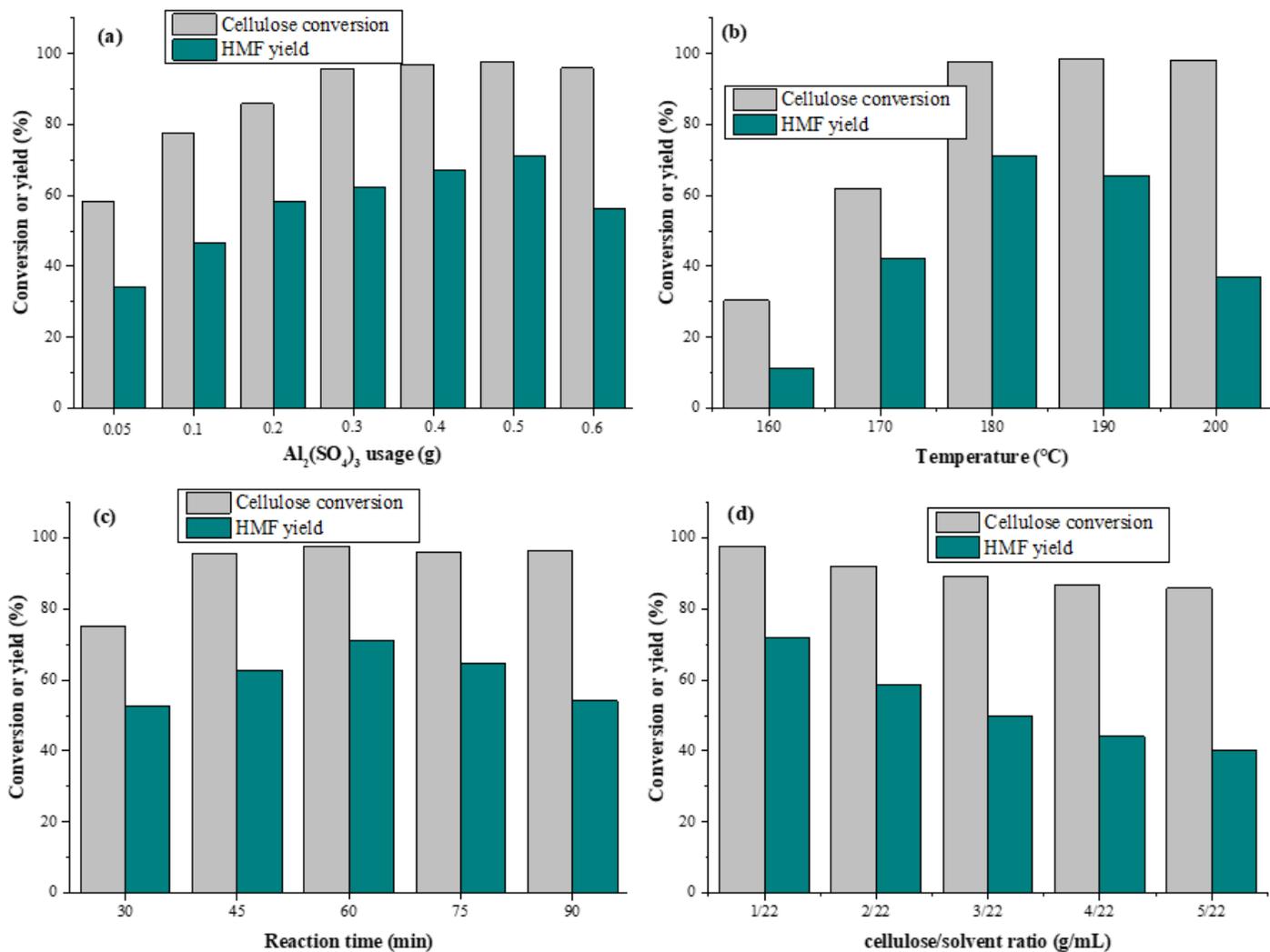
Figure 3

Proposed schematic illustration of conversion of cellulose into HMF in H<sub>2</sub>O/THF/CHX biphasic system



**Figure 4**

Screen of acidic salts on conversion of cellulose into HMF Reaction condition: 1 g cellulose, 3 mL H<sub>2</sub>O, 16 mL THF, 3 mL CHX, 180 °C, 1 h, 0.2 g catalyst.



**Figure 5**

Conversion of cellulose with  $Al_2(SO_4)_3$  with catalyst loading (a), different temperature (b), different time (c) and cellulose/solvent ratio (d). All reaction conditions were kept identical except for the one that was varied when necessary: 1 g cellulose, 3 mL H<sub>2</sub>O, 16 mL THF, 3 mL CHX, 180 °C, 1 h, 0.5 g catalyst.