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Effective conversion sucrose into 5-hydroxymethylfurfural by tyrosine in [Emim]Br

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ABSTRACT

In this study, the synthesis of 5-hydroxymethylfurfural (5-HMF) from sucrose was carried out in ionic liquids 1-ethyl-3-methylimidazolium bromide ([Emim]Br) catalyzed by amino acids, and tyrosine displays the best activity. Under the optimal reaction conditions, 76.0% yield of 5-HMF from sucrose was obtained at 160 °C for 4 h. The uniquely effective activity of tyrosine for sucrose conversion into 5-HMF in [Emim]Br is mainly attributed to its two types of active sites, free base NH_2 and dissociated H^+ sites. The former one plays a crucial role in the isomerization of glucose to fructose, and the latter one is active in the hydrolysis of sucrose into monosaccharides and dehydration of generated fructose to 5-HMF. Furthermore, the presence of acidic phenol group in tyrosine also has the synergic catalytic effect on sucrose conversion. In addition, with the use of tyrosine catalyst, other carbohydrates to form 5-HMF were also tested, and the effects of solvent, reaction temperature and reaction time on sucrose conversion into 5-HMF were investigated in detail. A possible mechanism for this catalytic process has been proposed.

1. Introduction

5-hydroxymethylfurfural (5-HMF) and its derivatives obtained from renewable biomass resources have the potential to serve as substitutes for the petroleum-based building blocks that are currently used in the production of plastics and fine chemicals [1–4]. Up until now, different feedstocks have been used to produce 5-HMF, including fructose [1,3,4], glucose [3–5], maltose [6], sucrose [6–8], cellobiose [7–9], inulin [6–8], starch [6,7], cellulose [5,6,9,10] and raw lignocellulosic biomass [5,9–11]. However, only fructose can be well converted into 5-HMF by acid catalyzed dehydration [4,12]. There is no doubt that the direct use of abundantly available sucrose for the large-scale production of 5-HMF would be a better ideal.

Generally, conversion of sucrose to 5-HMF involves two steps, namely, sucrose rapidly hydrolyze to monosaccharide glucose and fructose followed by the dehydration of fructose and glucose to give 5-HMF [4]. The dehydration of fructose can be well catalyzed by strong acids, such as mineral acids and organic acids [1,9,13,14], salts [5,15], acidic ionic liquid [16–19], strong acid cation exchange resins [1,10,20,21], zeolites [19,22] and supported heteropolyacids [13]. However, those acid catalysts have low activity in glucose conversion to 5-HMF because they are unfavorable of glucose insomerization into fructose.

The catalysts of Bronsted bases or Lewis acids are commonly used for glucose isomerization to fructose [23–27]. However, inorganic bases can reduce stability of monosaccharides and typically lead to side reaction [5]. Chun et al. [28] produced 5-HMF efficiently (82 ± 3.9 wt%) from sucrose using [omim][Cl] as a reaction solvent with HCl and chromium catalyst. When zinc chloride/HCl as a catalyst, 5-HMF yield only reached 58 ± 2.7%. Han et al. [9] screened a number of metal chlorides for the conversion of sucrose, and they identified tin chloride as a potentially interesting catalyst. Compared with fructose, sucrose are more difficult to convert into 5-HMF, but only potentially toxic metals (Cr chlorides) resulted in a better catalytic performance. Therefore, the development of a non-toxic and efficient catalytic systems for the conversion of sucrose to 5-HMF has become a challenge topic.

Amino acids are well-known acid–base bifunctional compounds, and ionic liquids (ILs) have been proven to be excellent solvents for carbohydrate conversion [4,5]. Herein, we used acid–base bifunctional amino acid as green catalyst to convert sucrose to 5-HMF in ionic liquid [Emim]Br, and the sucrose conversion process via tyrosine was well studied.

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2. Experimental

2.1. Materials

Sucrose (99%), 5-HMF, N,N-dimethylformamide (DMF), N-ethyl bromide(>99%), 1-methylimidazole (>99%), morpholine, pyridine, $SnCl_4$, $TiCl_4$, $CrCl_2$, $CrCl_3$, benzenesulfonic acid, leucine, tyrosine, tryptophan, proline and the rest of amino acids were purchased with analysis reagents degree.

2.2. Preparation of the ionic liquids (ILs) and catalyst

[Emim]Br was synthesized from the reaction of 1-methylimidazole with ethyl bromide at 25 °C for 24 h. The synthesis [Emim]Br was purified by acetonitrile and ethyl acetate to wipe off the residual ethyl chloride and 1-methylimidazole, and the purified [Emim]Br was dried in vacuum drying oven at 70 °C for 24 h. [Bmim]Br synthesis from n-butyl bromide and 1-methylimidazole, [Emor]Br synthesis from ethyl bromide and morpholine and [EPy]Br synthesis from ethyl bromide and pyridine followed above process.

H_2SO_4/ZrO_2 and H_2SO_4/Al_2O_3 solid acid catalysts were prepared by impregnation method. The active component H_2SO_4 was introduced by impregnation of the supports with aqueous solutions of H_2SO_4 (1 mol/L). The impregnation lasted for 24 h, and then catalysts were dried at 120 °C in air for 4 h, and further calcined at 550 °C in air for 4 h.

2.3. Typical experimental procedure

The catalytic experiments were performed in the 20 mL flask. In a typical experiment, 0.9 g sucrose and 0.49 mmol catalysts were added into 5 mL solvent. After reaction system had been purged with nitrogen, the reaction mixture was heated in an oil-bath at 160 °C for 4 h. After the desired reaction time elapsed, reaction mixture was cooled to room temperature immediately.

2.4. HMF yield characterization

All reaction products were analyzed by the high performance liquid chromatograph (Waters1525 equipped with UV and a 996 photodiode array detector) and quantified with 1-chloronaphthalene as interior standard (or calibration curves generated from commercially available standards). Following a typical reaction, the product mixture was diluted with 50 mL CH_3OH, centrifuged to sediment insoluble products, and 0.05 mol 1-chloronaphthalene was added into the product solution to analyze. The concentrations of products were calculated from HPLC-peak integrations. 5-HMF yield was based on sucrose loading, and 1-chloronaphthalene was used as interior standard to calculate 5-HMF molar yields.

$$\text{5-HMF yield (mol\%)} = \frac{\text{moles of 5-HMF}}{2\,\text{moles of sucrose}} \times 100\%$$

3. Results and discussion

3.1. Catalytic conversion of sucrose into 5-HMF over various amino acid catalysts

The various amino acids were used to catalyze sucrose conversion to 5-HMF at 160 °C, and results were summarized in Table 1. Among the used amino acids, tyrosine effectively promoted 5-HMF synthesis from sucrose, and 5-HMF yield achieved 76.0%. Although isoleucine and leucine are isomer, leucine displayed high activity in sucrose conversion into 5-HMF, however, only 4.6% 5-HMF yield was obtained over isoleucine. The biggest difference between leucine and isoleucine was their inequable steric hindrance. Therefore the low catalytic activity of isoleucine might be attributed to its high steric hindrance. The hydrolysis of sucrose into monosaccharide and the dehydration of fructose to 5-HMF can be well catalyzed by acid groups, but acidic glutamic acid showed near no activity for 5-HMF synthesis although it contains two carboxylic acids, however, alkaline lysine can display well activity for sucrose conversion into 5-HMF.

Table 1
Catalytic conversion of sucrose into 5-HMF over various amino acid catalysts.

Amino acid	Isoelectric points	5-HMF yield (mol%)
Glycine	5.97	20.6
Alanine	6.02	19.1
Valine	5.97	30.7
Leucine	5.98	33.5
Isoleucine	6.02	4.55
Proline	6.3	2.86
Glutamine	5.70	43.6
Lysine	9.74	38.7
Glutamic acid	3.22	3.45
Cysteine	5.02	25.6
Methionine	5.06	42.4
Serine	5.68	30.8
Tyrosine	5.67	76.0
Tryptophan	5.88	28.4

Conditions: 0.9 g sucrose, 0.49 mmol catalyst, 5 mL [EMIM] Br, 160 °C, 4 h.

In order to explore the different catalysis of the weak acid tyrosine, acidic glutamic acid and alkaline lysine in the hydrolysis of sucrose into glucose and fructose, isomerization of glucose to fructose and conversion of fructose to 5-HMF, the different ionic forms of three amino acids in [Emim]Br solution were studied. In neutral [Emim]Br solution, the weak acid tyrosine was ionized into $HOPhCH_2CH(NH_2)COO^-$ and dissociated H^+, but glutamic acid mainly existed in $HOOCCH(NH_3^+)CH_2CH_2COO^-$ form, which is due to [Emim]Br pH (6.8–7.1) > p*I* (the isoelectric point of tyrosine and glutamic acid). Alkaline lysine changed into $H_3N^+(CH_2)_4CH(NH_2)COO^-$ in [Emim]Br because of [Emim]Br pH < p*I* (the isoelectric point of alkaline lysine). Those results indicated the uniquely effective activity of tyrosine for sucrose conversion into 5-HMF in [Emim]Br is mainly attributed to its two types of active sites, free base NH_2 and dissociated H^+ sites. The former one plays a crucial role in the isomerization of glucose to fructose, and the latter one is active in the hydrolysis of sucrose into monosaccharides and dehydration of generated fructose to 5-HMF. Furthermore, the presence of acidic phenol group in tyrosine also has the synergic catalytic effect on sucrose conversion.

3.2. Catalytic conversion of sucrose to 5-HMF over various amino acid at different temperature in [Emim]Br

Here, catalytic conversion of sucrose to 5-HMF over various amino acid at different temperature in [Emim]Br was well tested (Fig. 1). Reactions were carried out at different temperature which ranges from 80 to 180 °C, and the optimized temperature for sucrose conversion to 5-HMF is from 140 to 160 °C. 80 °C is an unsuitable temperature for sucrose conversion because at this temperature the rate of sucrose hydrolysis and fructose dehydration is very slow. Tyrosine can well catalyze 5-HMF synthesis from sucrose at 120–180 °C, and 5-HMF yield achieved maximum 76.0% at 160 °C for 4 h. As for all the used amino acid catalysts, 5-HMF yield significantly declined at 180 °C. In addition, valine and glycine can also show better activity at low temperature (100–120 °C).

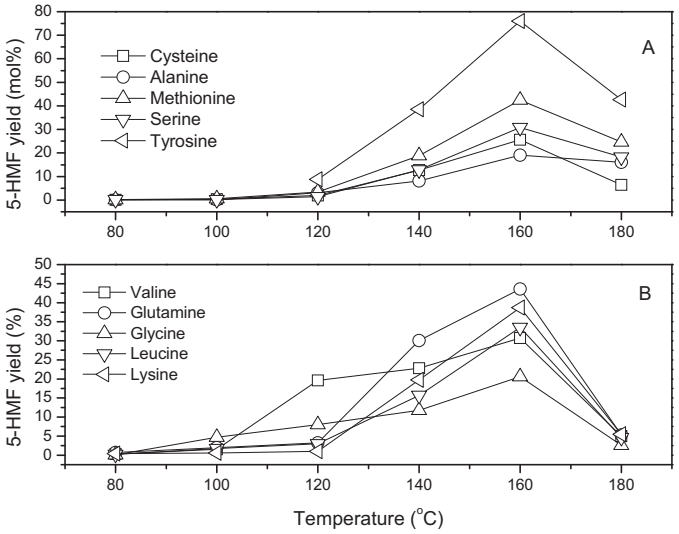


Fig. 1. 5-HMF yield from sucrose catalyzed by different amino acid catalysts in [Emim]Br at various temperature (conditions: 0.9 g sucrose; 0.49 mmol catalyst; 5 mL [Emim]Br solvent; 160 °C, 4 h).

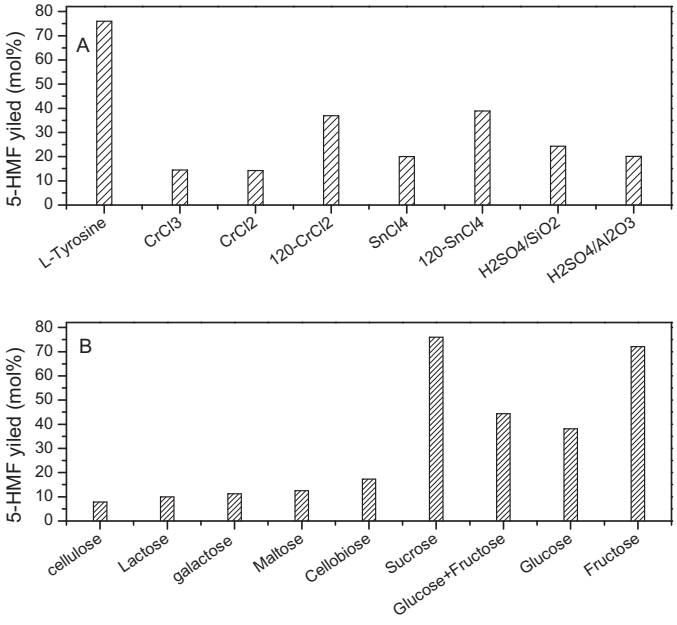


Fig. 2. (A) 5-HMF yield from sucrose over different catalysts in [EMIM] Br (conditions: 0.9 g sucrose, 0.49 mmol catalyst, 5 mL [EMIM] Br, 160 °C, 4 h); (B) 5-HMF yield from different substrates over L-tyrosine in [EMIM] Br (conditions: 0.9 g substrate, 0.49 mmol catalyst, 5 mL [EMIM] Br, 160 °C, 4 h). 120 indicated 120 °C reactions.

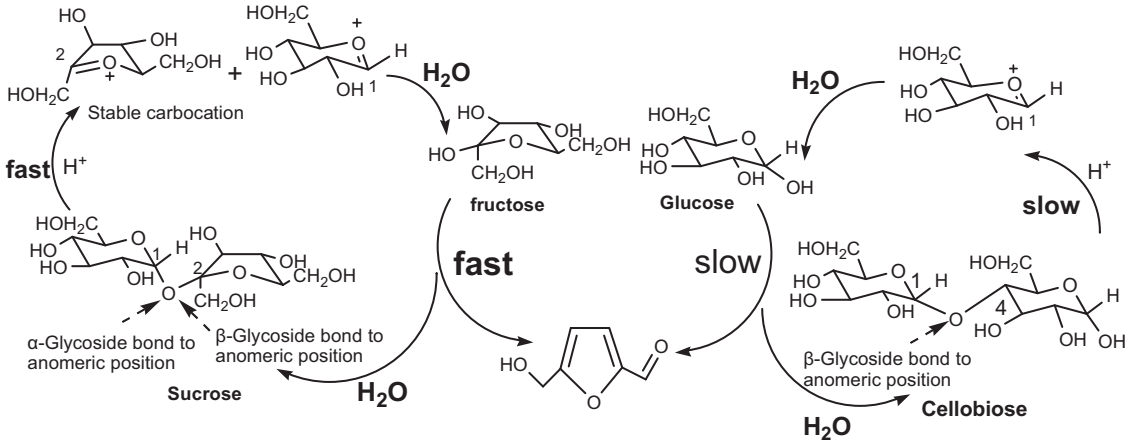
3.3. Catalytic conversion of different carbohydrates to 5-HMF over various catalysts

Tyrosine, metal chlorides and supported acids et al. were used to catalyze sucrose conversion to 5-HMF at 160 °C (Fig. 2A). 5-HMF yields catalyzed by $CrCl_2$ and $SnCl_4$ were less than 25% at 160 °C, and those can be improved to 36.9% and 38.9% by the decline of reaction temperature to 120 °C because $CrCl_2$ and $SnCl_4$ can catalyze 5-HMF degradation into levulinic acid at high temperature. Although $SO_4^{2-}/ZrO_2–Al_2O_3$ catalyst was found to act as a bifunctional catalyst with high activity for both hydrolysis and dehydration of starch [29], low 5-HMF yields of 24.3% and 20.1% were obtained over H_2SO_4/ZrO_2 and H_2SO_4/Al_2O_3, respectively. Among the used catalysts, only tyrosine can effectively catalyze 5-HMF synthesis from sucrose under same conditions.

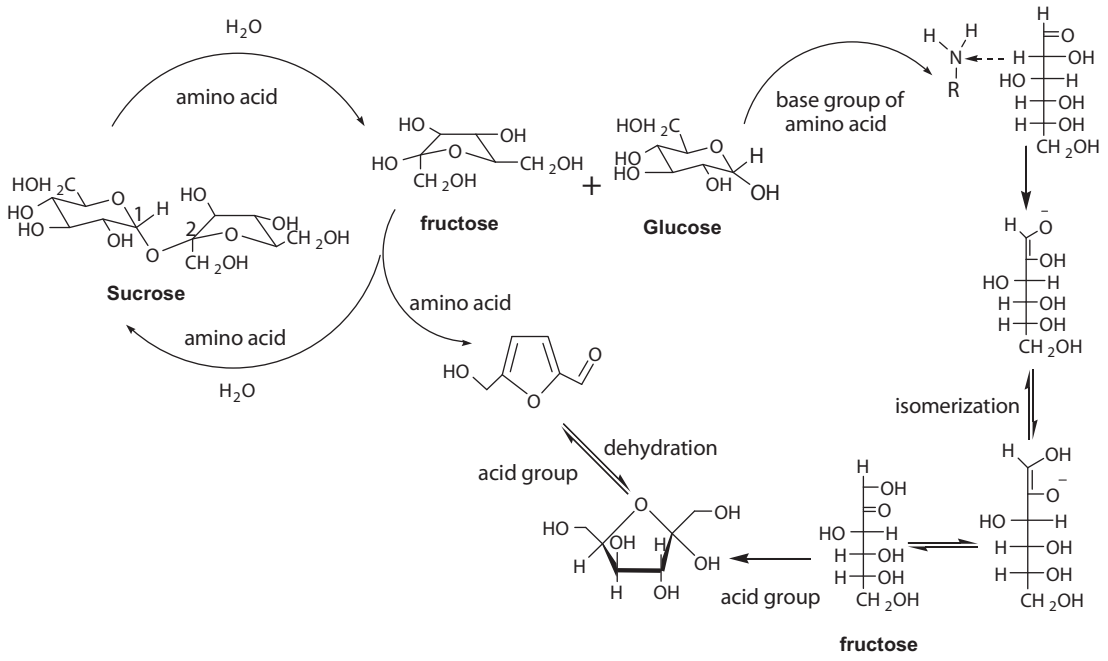
We also tested tyrosine catalyst for catalyzing other carbohydrates to form 5-HMF (Fig. 2B), and results demonstrated that tyrosine was uniquely effective to convert sucrose into 5-HMF while it showed less activity to convert cellulose, cellobiose, lactose and maltose to 5-HMF even at 160 °C, which was attributed to the difference structure of various carbohydrates. In maltose, cellobiose, galctose and cellulose, the monosaccharide units are joined by 1,4-glycosidic bond which was rather more difficult hydrolysis than that of 1,2-glycosidic bond. The reasons for that is the glycoside hydrolysis of disaccharide and polysaccharide to monosaccharide units via the carbocation are reversible (Scheme 1) and the high stability of carbocation intermediate of furanose rings (glucose rings was less stability) is responsible for sucrose 1,2-glycosidic bond easy cleavage [30,31].

The dehydration of fructose and glucose was also studied by using tyrosine catalyst in [Emim]Br system. It can be seen that 72.1% yield of 5-HMF was obtained from the dehydration of fructose, while the yield of 5-HMF from the dehydration of glucose is only 38.1% because glucose isomerization is a crucial step [32]. This results suggested that amino group play a crucial role in the isomerization of glucose to fructose and Brønsted COOH acid groups can well catalyze fructose dehydration to 5-HMF (Scheme 2).

5-HMF yield directing from sucrose achieved 76.0%, but this result was much better than 5-HMF yield from the mixture of fructose and glucose (1:1 mol) under same conditions. On the



Scheme 1. 5-HMF synthesis process from sucrose and cellobiose in presence of bifunctional catalyst [31,32].



Scheme 2. Sucrose cleavage and glucose isomerization in presence amino acid catalyst.

basis of those results one can hypothesize that there must exist the synergistic effects between glycosidic bond hydrolysis and monosaccharide dehydration. Namely, the glycosidic bond cleavage reaction was initiated by the trace water in ionic liquid, and then fructose and glucose were dehydrated to give H_2O. A part of H_2O was subsequently consumed by the glycosidic bond hydrolysis, which kept 5-HMF yield decline from loss to levulinic acid by minimizing 5-HMF exposure to H_2O at elevated temperatures (Scheme 2).

3.4. Effect of solvent on sucrose conversion to 5-HMF

Experiments conducted in different solvents (Fig. 3) offer insight about the role of solvents in converting sucrose into 5-HMF. The conversion of sucrose into 5-HMF was demonstrated in many solvents including [Emim]Br, [Bmim]Br, DMSO, DMF, [Emor]Br and [EPy]Br. For basic solvent DMF, low 5-HMF yield 27.7% was obtained. It seems that the basic solvent inhibited the formation of 5-HMF, which should be probably due to the neutralization of the acid sites in tyrosine the by the basic DMF. DMSO is another better solvent for 5-HMF synthesis, and 5-HMF yield increased to 59.0%. Among [Emim]Br, [Bmim]Br, [Emor]Br and [EPy]Br, [Emim]Br is the best solvent for sucrose conversion, and 5-HMF yield achieved 76.0%, but [Emor]Br and [EPy]Br are unfavorable of 5-HMF synthesis at high temperature due to their low decomposition temperature. Although [Bmim]Br was a homologue of [Emim]Br, much lower 5-HMF was obtain in [Bmim]Br because the ILs with a shorter-chain cation have a larger dissolving ability than those with a longer-chain cation when their anions are identical. These results are consistent with those reported in the literature [33–35]. In addition, the trace of 1-methylimidazole excision in ionic liquid will deteriorate 5-HMF synthesis.

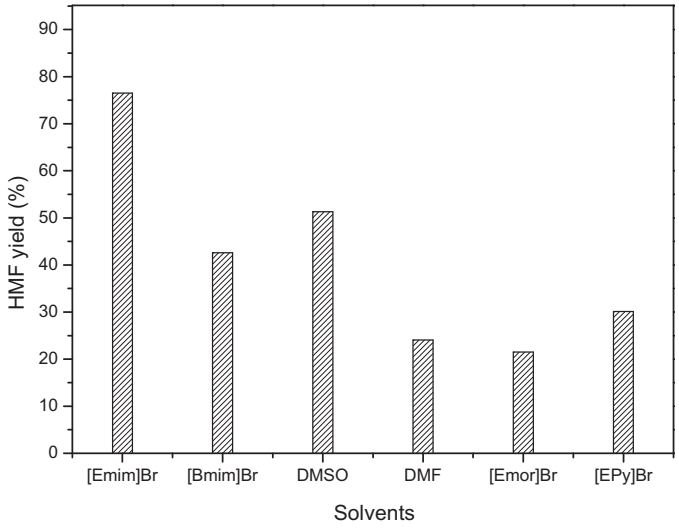


Fig. 3. 5-HMF yield from sucrose catalyzed by tyrosine in various solvent (conditions: 0.9 g sucrose, 0.49 mmol catalyst, 5 mL solvent, 160 °C, 4 h).

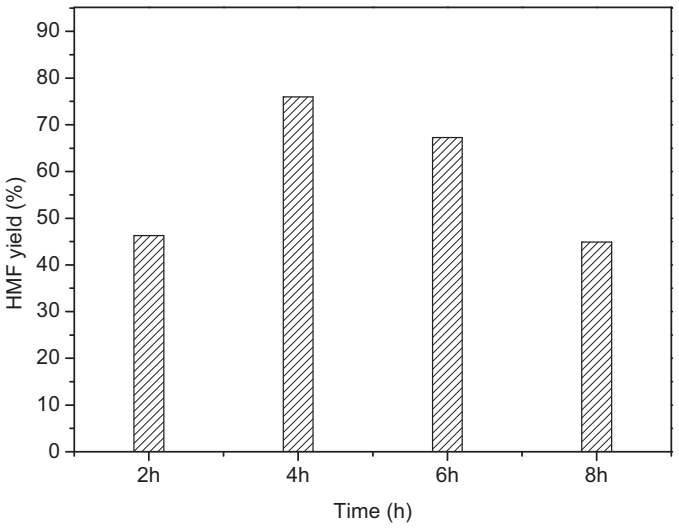


Fig. 4. 5-HMF yield from sucrose catalyzed by tyrosine in various time (conditions: 0.9 g sucrose, 0.49 mmol catalyst, 5 mL [Emim]Br solvent, 160 °C).

3.5. The effect of reaction time on the conversion of sucrose to 5-HMF

Fig. 4 shows the effect of reaction time on the sucrose conversion to 5-HMF. 5-HMF yield increased from 53.3% to 76.0% as reaction time increasing from 2 h to 4 h. By prolonging the reaction time to 8 h, 5-HMF yield declined deeply, so the longer reaction time is detrimental to the enhancement of 5-HMF yield. 5-HMF yield decline is mainly caused by rehydration of 5-HMF into levulinic acid. However, nearly no side-reactions of polymerization of 5-HMF or cross-polymerization of 5-HMF with carbohydrate were detected.

4. Conclusions

Tyrosine shows the uniquely effective activity for sucrose conversion into 5-HMF, and 5-HMF yield from sucrose achieved 76.0%. The optimized temperature for sucrose conversion to 5-HMF by amino acids ranges from 140 to 160 °C, and the high effective activity of tyrosine is mainly attributed to its free NH_2, dissociated H^+ and the presence of acid phenol group. Base NH_2 group plays a great role in glucose isomerization to fructose, and Brønsted COOH acid group catalyze sucrose hydrolysis and fructose dehydration. 1,2-glycosidic bond is more easily hydrolyzed than 1,4-glycosidic bond, which results in tyrosine showing higher activity in sucrose conversion into 5-HMF. In the sucrose conversion to 5-HMF, a part of H_2O formed from fructose and glucose dehydration was subsequently consumed by the glycosidic bond hydrolysis, which keeps 5-HMF yield decline from loss to levulinic acid by minimizing 5-HMF exposure to H_2O at elevated temperatures. The basic solvent inhibits the formation of 5-HMF due to the neutralization of the acid sites by basic solvent, and neutral [Emim]Br is the best solvent for sucrose conversion into 5-HMF.

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