Advances in Production of 5-Hydroxymethylfurfural from Starch

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Abstract: 5-hydroxymethylfurfural (5-HMF) is an important platform compound which can be synthesized from renewable biomass. 5-HMF can be used as intermediates of many reactions and it has potentiality of resolving the crisis of resources and energy. This paper reviews the methods and research progresses of synthesis of 5-HMF from starch in the last decade: starch can be hydrolyzed into glucose under acidic conditions, glucose can be isomerized to fructose by solid base, then solid acid can be used for dehydration of fructose to 5-HMF. pH determines the formation of 5-HMF, the lower of pH, the easier 5-HMF is formed and fewer humic matters are produced. Finally, the application of 5-HMF is summarized.

Keywords: 5-HMF; starch; glucose; synthesis mechanism; effect factors

1 Introduction

Currently, with the shortage of petroleum, natural gas and other fossil fuels over our globe, people are trying to find a new kind of alternative material. Biomass is a renewable and cheap resource with huge amount, abundant biomass resources are the main sources which can take place of fuels and valuable chemicals in the post-fossil era of human.

5-HMF is one of the monomers of highly representative biomass-based material. 5-HMF contains active groups-aldehyde and hydroxymethyl, so the chemical properties of 5-HMF is active, it can be used as intermediates of many reactions, materials of synthesis of macrocyclic compounds, monomers of synthesis of polymer. Many high value-added products can be produced by oxidizing 5-HMF, such as: laevulic acid, 2, 5-dimethylfuran, 2, 5-furan dicarboxylic acid and so on. Now, the preparation of 5-HMF is produced by dehydration of carbohydrates: under the acidic conditions, hexose is formed by hydrolysis of sugar, and then further dehydrated to 5-HMF. But the common problems are the low conversion efficiency; the extent of reaction is under poor control and so many by-products.

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2 Preparation of 5-HMF

The structure of 5-HMF is shown in Figure 1:

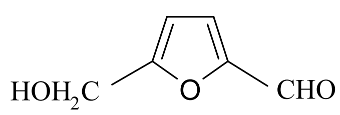

Figure 1: Structure of 5-HMF

Five-ring compound 5-HMF is one of the most concerned bio-based platform chemicals. The conventional methods of preparing 5-HMF have high demands for raw materials, at present, the preparation of 5-HMF from fructose is more common[1]. Nowadays, there are many reports on preparation of 5-HMF at home and abroad, Xinhua Qi[2]and others have researched fructose dehydration for preparing 5-HMF by sulfated zirconia solid acid and found that: under the conditions that: the reaction happened at 180℃ in acetone-dimethyl sulfoxide (DMSO) for 20 minutes, the conversion efficiency of fructose up to 93.6%, the production rate of 5-HMF was 72.8%. Clement Lansalot-Matras[3] who studied the preparation of 5-HMF by ionic liquids from fructose pointed out: When the reaction was carried out in 1-butyl 3-methyl imidazolium tetrafluoroborate（$BMIM^+BF_4^-$） as sovent and Amberlyst-15 as catalyst, the yield of 5-HMF up to 50%. When the reaction was carried out in 1-butyl 3-methyl imidazolium tetrafluoroborate($BMIM^+BF_4^-$) and 1-butyl 3-methyl imidazolium hexafluorophosphate($BMIM^+PF_6^-$) as solvents, DMSO was used as a co-solvent and Amberlyst-15 as catalyst, the yield of 5-HMF was nearly 80%. However, at present, the reports of preparation of 5-HMF from starch are extremely trifling. In the past decade, the research of solid acid catalyst glucose to 5-HMF received much development, it provides basis for starch hydrolyzes to glucose in acidic conditions by heating and further transforms to 5-HMF.

2.1 Synthesis mechanism of preparation of 5-HMF from hexose

The synthesis mechanism of preparation of 5-HMF from hexose is shown in Figure 2[4]:

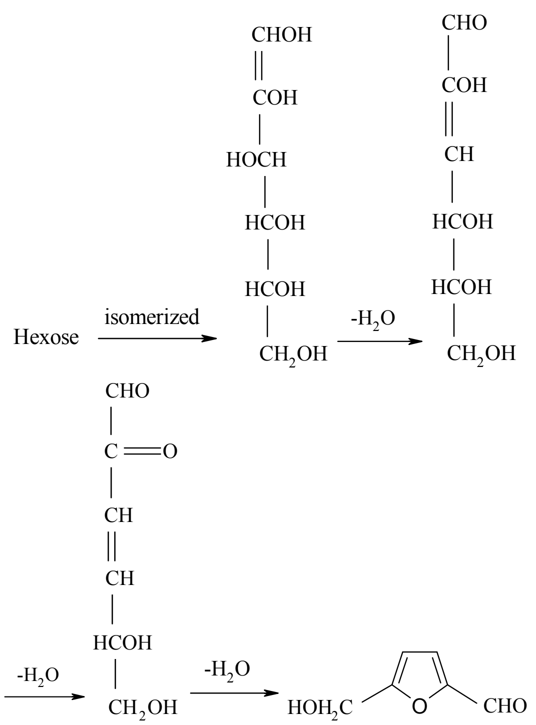

Figure 2: Preparation of 5-HMF of hexose dehydration in acidic conditions

Hexose is isomerized to 1, 2-enediol in solution, enol structure is considered to be the key for preparing 5-HMF. Then, 1, 2-enediol transformes into 3-deoxy-hexose, further it dehydrates to 5-HMF. Besides 5-HMF, during the reaction process, it is also prone to aggregation, resulting in soluble polymer and insoluble materials, such as humic matter, levulinic acid, formic acid and other by-products, these have significantly effects on the yield of 5-HMF[5]. Therefore, we should select the appropriate reaction conditions to prepare 5-HMF for improving its yield.

2.2 Synthesis mechanism of preparation of 5-HMF from starch

Starch and cellulose can be hydrolyzed into glucose under acidic conditions or enzymatic conditions. Starch hydrolyzes into glucose in hot water at 453-513K, and also produces 5-HMF, maltose and fructose. Hydrolyzate glucose is the most abundant monosaccharide, the reaction of glucose dehydration is an important and attractive chemical reaction, because it produces two valuable derivatives, anhydroglucose and 5-HMF[6]. During these anhydroglucoses, 1, 6–anhydro–β–D- glucopyranose and 1, 6-anhydro-β-D-glucofuranose, are very valuable chemicals, 1, 6–anhydro–β–D- glucopyranose, also known as levoglucosan, can be used as intermediate for biodegradable surfactants, stereoregular polysaccharides, macromolecular polymers and drug[7,8]. These anhydroglucoses are formed by dehydration of one water molecule from 1,6-β-D-glucopyranose and 1,6-β-D-glucofuranose, and the pyranose and furanose forms are under tautomeric equilibrium respectively. 5-HMF as the derivative of furan, is obtained by dehydration of three water molecules from hexose, which can be used as intermediates of plastics, polymers and fuels[9]. The reaction mechanism of selective dehydration of glucose to produce anhydroglucose and 5-HMF is shown in Figure 3:

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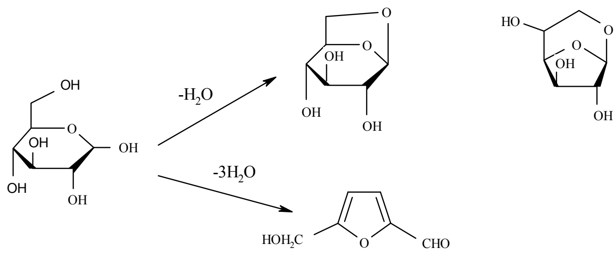

Figure 3: Reaction mechanism of selective dehydration of glucose

It is always a research focus that how to improve the selectivity of dehydration reaction of glucose and make products easier separation and purification. It is found that $ZnCl_2$ as catalyst has higher selectivity than other metal salts during the hydrolysis reaction of glucose, the yield of 5-HMF is 54.6%[10]. Xinhua Qi[11]and others have researched the reaction of catalytical conversion of fructose and glucose into 5-HMF in hot compressed water by microwave heating and found that: ZrO_2 promotes isomerization of glucose into fructose, the selectivity of isomerization of glucose into fructose was higher than 60%, and about 50% of glucose conversion occurred after 1 minute.

2.3 Kinetics of reparation of 5-HMF from glucose

The initial concentration of 5-HMF depends on the pH of original solution, heating the solution after the system of its pH 3.8 has set up, the initial concentration of 5-HMF is high to 12.38±1.8ppm. When pH down to 3.8 from 5.1 of the heating solution, the average initial concentration of 5-HMF is 2.03±0.74ppm. Therefore, pH determines the formation of 5-HMF, the lower of pH, the easier to form furan compounds[12].

The concentration and reaction time of 5-HMF present linear relationship, and the formation of 5-HMF followed apparent zero-order kinetics: $[HMF]_t=[HMF]_o+kt$[13]. Jing Qi[14]has studied the kinetics of non-catalyzed decomposition of glucose in high-temperature liquid water and pointed that during the decomposition of glucose, there were 5-HMF, two unidentified compounds and insoluble humic matter produced. The first order kinetic model of glucose decomposition in high-temperature liquid water is shown in Figure 4:

glucose $\xrightarrow{k_1}$ 5-HMF $\xrightarrow{k_3}$ LA $\xrightarrow{k_5}$ decomposition product

glucose $\xrightarrow{k_2}$ humic matter

5-HMF $\xrightarrow{k_4}$ unidentified soluble products

Figure 4: The first kinetic modle of glucose decomposition in high-temperature liquid water

So, how to control the extent of this reaction has become the critical issue to improve the yield of 5-HMF.

3 Effects on preparation of 5-HMF

3.1 Reaction medium

3.1.1 Water phase system

Water is the best solvent, is also the ideal green, sustainable solvent, but is not ideal for the dehydration of hexose, water leads low selectivity and yield of preparing 5-HMF from hexose[15]. 5-HMF formed in the water phase system is easily hydrate with water and produce by-products levulinic acid and formic acid and so on, seriously affecting the yield of 5-HMF. Taku Michael Aida[16], who studied the dehydration of D-glucose at 80Mpa in high-temperature water, the results shown that: in water phase, high temperature and pressure are helpful to raise the yield of furan compounds.

Glucose can dehydrate to 5-HMF and other furan compounds in $MgCl_2$ and $MgSO_4$ saturated solution. The formation of 5-HMF in sulfate solution may relate to the participate of hydration hydroxyl groups[17]. However, dehydration of glucose is a selective reaction in water with low conversion rate, aqueous solution of sulfate and chloride have different effects on dehydration of glucose[18].

3.1.2 Non-aqueous medium

Organic solvents are always selected as non-aqueous media. In order to improve the yield of 5-HMF, we can improve the aqueous reaction medium, such as using DMSO and 1-methyl-2-pyrrolidinone as the reaction medium. It is found that: DMSO, dimethylformamide (DMF), acetonitrile and polyethylene glycol and other organic solvents can improve the selectivity of sugar conversion reaction, and these organic solvents with high boiling point can shorten reaction time and restrain the formation of humic matter[19]. Because of low solubility of hexose in organic solvents, many people begin to research the water-organic solvents biphasic system[20]. Chheda JN[21]has studied the dehydration of fructose, glucose and xylose to 5-HMF and furan compounds in the biphasic system, the reactive aqueous phase is modified with DMSO, methyl isobutyl ketone or dichloromethane as organic phase. The biphasic system allowed us to identify preferred DMSO and pH levels for each sugar to maximize the 5-HMF selectivity at high sugar conversions, results shown that: selectivities of 89%, 91% and 53% for dehydration of fructose, xylose and glucose respectively. The conditions of leading dehydration of monosaccharides are also suitable to polysaccharides, such as: starch, cellulose, sucrose and so on and have high selectivity and conversion rate. It is reported that: when the dehydration of carbohydrates happened in ethyl acetate/ionic liquid biphasic system, the yield of 5-HMF and reaction selectivity are higher than 90%, and this condition helps separation of products[22].

3.1.3 Other reaction medium

In recent years, many efforts are applied to biomass hydrolysis and decomposition in critical or subcritical water, it is studied that sugar (monosaccharides, polysaccharides) can convert to 5-HMF in critical or subcritical water. At present, there are a few reports on glucose in the supercritical fluid into 5-HMF at home and abroad, Feridoun Salak Asghari[23]has studied the dehydration of fructose to 5-HMF in sub-critical water over heterogeneous zirconium phosphate catalysts and found: about 80% of fructose was decomposed in sub-critical water at 240℃ after 120s, and the selectivity of the dehydration reaction of fructose to 5-HMF rose to 61%. Also found that the zirconium phosphate solid acids were stable under sub-critical water conditions, and they can easily be recovered without changing their catalytic properties. Besides, it is pointed out that sub-critical and supercritical acetone/water biphasic system can raise the yield of 5-HMF, reaction selectivity of 77%, conversion rate of 99%[24].

3.2 Types of catalysts

Catalyst is the core of preparing 5-HMF, people selected mineral acid as catalyst in the early time, then with further research, Lewis acid and organic acid are popular. Now, solid acid and ionic liquid as new catalyst are widely used.

3.2.1 Catalyst of mineral acid

The mineral acid has been widely used in preparation of 5-HMF, it can effectively improve the yield of 5-HMF and the conversion rate of hexose. The reaction of HCl, H_2SO_4 and H_3PO_4 catalyze glucose dehydration to 5-HMF has been researched, results shown that: low acidity was helpful to form 5-HMF, increasing acidity would promote 5-HMF convert to levulinic acid[25].

3.2.2 Catalyst of Lewis acid

$SnCl_4$ as a common Lewis acid can effectively convert glucose to 5-HMF, the formation of the five-membered-ring chelate complex of Sn atom and glucose may play a key role for the formation of 5-HMF[26]. Lanthanides (Ⅲ) ions in aqueous solution are also possess Lewis acid activity, Hitoshi Ishida[27]has found that lanthanide (Ⅲ) metal can effectively catalyze D-glucose to 5-HMF, under the conditions that at 140 ℃, 10 atmospheres, it increased the yield of 5-HMF.

3.2.3 New catalysts

The traditional method of mineral acid catalyzes hexose to 5-HMF is simple, easy operation, low investment, but there are serious problems of equipment corrosion, waste pollutes environment, so many by-products and so on. The development of solid acid which is a new environmentally friendly catalyst provides new possibilities for green preparation of 5-HMF.

3.2.3.1 Catalyst of solid acid

Solid acid can catalyze glucose dehydrate selectively to 5-HMF. Mika Ohara[28]and others have studied the syntheses of 5-HMF and levoglucosan by selective dehydration of glucose using solid acid and base catalysts, the results showed that: using a combination of solid acid and base catalysts afforded selective formation of 5-HMF. Hydrotalcite solid base was used for isomerization of glucose to fructose, and Amberlyst-15 was used as the acid catalyst for dehydration of fructose to 5-HMF. This catalytic system greatly increased the yield of 5-HMF and reaction selectivity under mild conditions(below 100℃). In addition, SO_4^{2-}/ZrO_2, $SO_4^{2-}/ZrO_2\text{-}Al_2O_3$ solid acid catalysts are proved to increase the yield of 5-HMF from glucose, the best yield of 5-HMF was 47.6% under the conditions that: at 403K for 4 h over $SO_4^{2-}/ZrO_2\text{-}Al_2O_3$ with Zr-Al mole ratio of 1:1. The catalyst with higher acidity and moderate basicity was more favorable for the formation of the target product[29]. Masaru Watanabe[30]has researched the degradation reactions of glucose with acid and base solid acid at 473 K in hot water and found that: TiO_2 solid acid promoted the formation of 5-HMF, and ZrO_2 solid base promoted the isomerization of glucose to fructose.

Besides, the molecular sieving is also a kind of solid acid with high acidity and catalytic activity. Molecular sieving can promote glucose into oxygenation hydrocarbon[31]. Khavinet Lourvanij[32]has studied the dehydration of glucose catalyzed by Y-form zeolites under low temperature, the results showed that: the conversion rate was 100% at 160℃ for 8 h. It is possible that: the particles on the surface of Y-form zeolites promote this reaction.

3.2.3.2 Ionic liquid

Ionic liquid consist of nitrogen or phosphorus cations and large organic or mineral anions, it is not just a kind of green solvent, and its ionic characteristics make it different from molecular sieving but has special catalytic effects. Ionic liquid is a new kind of catalyst which is more friendly, more extensive usage. It has better catalytic ability and can be easier separated and retrieved than homogeneous catalyst[33]. It has been researched the direct conversion of glucose and cellulose to 5-HMF in ionic liquid [C_4MIM]Cl under microwave. The yield of 5-HMF from glucose was 90%, much higher than the reaction took place in oil bath at 100℃ for1 h.

4 Application of 5-HMF

In recent years, attentions have been paid on the use of biomass conversion to high added value chemicals[34]. 5-HMF which has been produced by dehydration of glucose, fructose, cellulose and so on is considered to be a potential oil reserves of fine chemicals, belongs to the renewable platform compound of furans[35]. 5-HMF can be converted into large-scale industrial agents, for example: furan, tetrahydro-furfural, furfural alcohol and a variety of green bio-based polymers[36]. Also, many chemical substances which are transformed by 5-HMF have much greater potential applications[37].

5 Conclusion

It is promising that preparation of 5-HMF from biomass, but, unfortunately, it has not yet industrialized for producing 5-HMF from carbohydrates, especially starch, cellulose polymers. However, we believe that with the deepening of researches and technology developments, the reaction mechanism of preparing high yield of 5-HMF from sugar will eventually be clarified.

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