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Mini Review

Chemical Conversion of Molasses for Production of Levulinic Acid and Hydroxymethylfurfural

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Abstract

Molasses, a by-product generated during refining sugarcane or sugar beets into sugars, is composed of more than 50% sugars (e.g., sucrose, glucose and fructose), rendering it a cheap and renewable feedstock for production of platform chemicals such as Levulinic Acid (LA) and 5-Hydroxymethylfurfural (HMF). It was reported that the non-sugar components of molasses were found to deactivate solid acid catalysts, resulting into low product yield and selectivity. However, mineral acid catalysts were not affected by the presence of non-sugar part of molasses, indicating the advantage of mineral acid over solid acid catalyst. However, the corrosive and unrecyclable properties of mineral acid catalysts make them unfavorable for future applications from the point of view of green chemistry. In view of the significantly negative impact of non-sugar part of molasses on solid acid catalyst, research efforts to develop simple and efficient pretreatment methods for removing non-sugar impurities should be encouraged when using solid acid catalyst for catalytic conversion of industrial molasses, in addition to focusing on developing high-activity solid acid catalysts and high-performance reaction solvent systems, Only by making progress in these fields can sustainable production of platform chemicals from molasses be achieved in the near future.

Keywords

Acidic Catalyst; Levulinic Acid; Molasses; Platform Chemicals; HMF

Molasses is an important by-product formed in either cane or beet sugar industry. It is the residue produced from repeated sucrose crystallization during sugar extraction processes when no more sugar can be obtained economically. In general, yield for molasses produced from sugar cane is 3-4%, whilst the beet molasses yield is 4-6%. As a waste product, on the one hand, molasses is a potential pollutant, it could cause severe environmental pollution unless properly disposed of; on the other hand, valorization of cheap and renewable molasses that contains high sugar contents for production of platform chemicals has received consideration attention in recent years in view of sustainability and green chemistry.

Levulinic Acid (LA) and 5-Hydroxymethylfurfural (HMF) are two important platform compounds that can be used to produce a wide variety of chemical products. As early in 2004, LA has been regarded by the United States Department of Energy (DOE) as one of the top green building block chemicals [1]. The presence of ketone and carboxylic acid groups endows LA with high reactivity, making it a versatile precursor for producing a large number of products, including pharmaceuticals, agrochemicals,

flavours and fragrances, personal care products, resins and coatings, plasticisers, solvents, fuel additives, etc. [2]. HMF is another important platform chemical, it was included in the updated version of the United States DOE top 10 value-added bio-based chemicals published in 2010, where furans including HMF, furfural and furan-2,5-dicarboxylic acid were mentioned in the top "10+4" as a revision to the DOE 2004 list [3]. HMF contains aldehyde group as well as an alcohol functional group, allowing it to be subject to structural transformation for production of a large number of end products, such as polymers, pharmaceuticals, fine chemicals, liquid fuels, etc. [4]. Most recently, both LA and HMF are included in the list of top 10 bio-based chemicals where the UK is primed to go from demonstration to large-scale production. These ten green alternatives to fossil-based chemicals were identified by Lignocellulosic Biorefinery Network (LBnet), a UK government-backed organization [5].

The purpose of this paper is to present research advances on conversion of sugarcane or beet molasses for production of LA and HMF, two important green build chemicals, by employing mineral or solid acid catalysts in different reaction solvents under different operational parameters.

Chemical Composition and Application of Molasses

Molasses is a multicomponent system with compositions varying from factory to factory depending on the sugar production processes. Additionally, other factors that contribute to the composition fluctuation include strain of the beet or cane, growing conditions and fertilization, the treatment between harvesting and slicing, etc. [6]. Both sugarcane molasses and beet molasses are characterized by their high sucrose concentration as well as high concentration of reducing sugars, i.e., glucose and fructose. Non-sugar components of molasses mainly include crude protein, bound acids, mineral and trace elements, etc. The typical compositions of sugarcane and beet molasses were shown in table 1 [7].

The high sugar content as well as low-cost availability render molasses attractive in many industries. It is commonly used as feed for livestock. In addition, molasses is also among the most important raw material for fermentation industry. It has been reported to produce a variety of value-added products on commercial scale via microbial fermentation of molasses. These products include bioethanol, yeast, organic acid, acetone/butanol, antibiotics and enzymes, etc. [8,9]. However, due to a decreasing price of corn, the molasses-based fermentation is losing its competitiveness. Moreover, the molasses-based fermentation produces a large amount of wastewater with high Chemical Oxygen Demand (COD) and high salinity. Therefore, developing alternative strategies to efficiently utilize molasses is imperative.

Components	Sugarcane Molasses, % (by weight)	Beet Molasses, % (by weight)
Water	18.82	18.01
Sucrose	36.7	37.5
Glucose	8.82	9.12
Fructose	6.86	7.26
Nonfermentable sugar	4.79	2
Other reduced compounds	4	3
Fat	0.4	0.4
Protein	3.5	6
Organic acids	5	5
SO_2	0.1	0.1
$Ca(OH)_2$	1.01	1.01
Ash	10	10.6

Table 1: Average composition of sugarcane and beet molasses.

Chemical Transformation of Molasses into Levulinic Acid and Hydroxymethylfurfural

Both LA and HMF can be produced from acid catalyzed transformation of hexose sugars (e.g., glucose, fructose) as well as hexose-containing disaccharides (e.g., sucrose) or polysaccharides (e.g., cellulose, starch). HMF is an intermediate during synthesis of LA. Although mineral acids such as HCl and H_2SO_4 have long been used as catalyst, environment-friendly solid acid catalyst is emerging as a competitive alternative to mineral acid due to its easy recover for reuse, no corrosion and no acid waste for disposal [10]. Organic solvents also play multiple important roles in carbohydrate conversion [11,12]: (1) dissolve substrates; (2) extract products from reaction media; (3) interact with substrates, intermediates and products to enhance the thermodynamic equilibrium; (4) act as catalysts. Due to the instability of LA and HMF, it is favorable to use biphasic reaction media containing reaction solvent and extraction solvent in carbohydrate conversion because the extraction solvent can extract LA and HMF from reaction solvent as soon as they are formed. The yields of LA and HMF, therefore, are increased by preventing their

participation in side reactions. Since the research advances with focus on catalyst and reaction solvent for chemical conversion of mono-, di- or poly-saccharides into LA and HMF as well as the reaction mechanisms have been described in detail in previous reviews [12-15]. This paper focuses solely on the research progress on catalytic conversion of molasses for producing LA and HMF.

Although beet and sugarcane molasses have been extensively used as substrate for fermentative production of a range of building block chemicals. There are few reports on chemical transformation of molasses into LA and HMF, two important bio-based building blocks. Table 2 sums up previous literature on LA and HMF production using molasses as feedstock.

Substrate conc.	Molasses pretreatment	Catalyst	Solvent	Conditions	Yield	Reference
27.3% sugar	No	6.5%HCl/1.67% KBr	Water	167°C, 60 min	LA, 45.9%	[16]
42.7% sugar				150 lb./sq.in., 60 min	LA, 31.1%	
10% Sucrose	No	Amberlyst-36	water	140°C, 3 h	LA, 53.2%	[17]
	Ion-exchange				LA, 79.5%	
18.4 % molasses	No	0.2 mol/L H_2SO_4	Water	180°C, 3 h	LA, 30.5% (after 3rd superimposed reaction)	[18]
					LA, 23.9% (after 5th superimposed reaction)	
0.45% molasses	No	$ZnCl_2$/HCl	Tetrahydrofuran/ water (10:1 v/v) saturated with NaCl	180°C, 1 h	HMF, 49.6%	[19]
		$AlCl_3$/HCl			HMF, 43.2%	
6.7% sugar	HCOOH or HCl	Bagasse-derived solid acid catalyst	Water	150°C, 4 h	HMF, about 40%	[20]
3.35% sugar	No	Molasses-derived solid acid catalyst	water	170°C, 3 h	HMF, 64.5%	

Table 2: Molasses as feedstock for LA and HMF production under different reaction conditions.

To the best of our knowledge, the first report on production of LA from cane molasses was published by Rao et al., [16]. They synthesized LA at different pressures for 60 min in a reaction system consisting of 6.5% Hydrochloric Acid (HCl), molasses with total sugars concentration varying from 27.3 to 42.7%. They found that LA yield decreased with an increase of sugar concentration in molasses. A LA yield of up to 45% was obtained when sugar concentration was at 27.3%. While increasing the sugar concentration to 42.7% resulted into a significant decrease of LA to about 30%. Kang and Yu [17] applied a heterogeneous solid acidic cation exchange resin Amberlyst-36™ as catalyst for producing LA from sugar beet molasses in an aqueous media at 140°C. The activity of this solid acid catalyst greatly decreased, most likely due to the presence of non-sugar components in sugar beet molasses such as cations, proteins and alkaline compounds. These impurities deactivated Amberlyst-36 catalyst via either ion exchange with hydrogen ions on/in catalyst or formation of solid deposit on the resin pellet catalyst, which changed the catalyst structure and reduced the available acidic sites for catalysis. In order to keep the catalyst active for repeated reuse, the authors pretreated molasses with ion-exchange pellets for removing some impurities and found that ion-exchanged molasses solution maintained the catalyst active during reaction, thus enabling for multiple rounds of reuse. Notably, the used resin pellets could be conveniently regenerated by washing with deionized water followed by soaking in 10% HCl. Kang et al., [18] investigated the production of concentrated LA from sugar cane molasses in an aqueous reaction mixture consisting of 184.0 g/L sugarcane molasses and 0.2 mol/L H_2SO_4 through a superimposed reaction, in which LA produced from the first round of hexose hydrolysis was further used as solvent

for subsequent rounds of sugar cane molasses hydrolysis to produced concentrated LA. After third and fifth superimposed reactions, LA concentrations obtained in the solution were 148 and 180 g/L, with average yield of 30.5 and 23.9%, respectively. The comparatively low LA yield could be due to the formation of aqueous and solid byproduct formed between LA and other reaction intermediates. Commercial production of LA from sugar industry by-products, including molasses, are going to be realized in the coming years. In 2017, two Italian companies, Bio-on and Sadam Group, announced collaboration on developing and optimizing LA production using co-products from sugar industry as raw material. The project entitled "Industrial eco-sustainable production of LA from sugar industry by-products not intended for human food", with an estimated budget of 6 million Euro, involved building a pilot plant for research and a demo plant with a capacity of 5,000 tonnes of levulinic acid per year [21].

As far as HMF was concerned, Gomes et al., [19] investigated HMF production from glucose, sucrose and sugarcane molasses using a combination of Lewis ($ZnCl_2$ and $AlCl_3$) and Brønsted (HCl) acids in a biphasic system saturated with NaCl. The biphasic reaction system consists of tetrahydrofuran (extraction solvent) and water (reaction solvent). The role of extraction solvent is to immediately extract HMF after its formation in reaction phase. The excessive amount of salt in the biphasic system increases the partition coefficient of HMF in extraction phase (salting-out effect). Therefore, the biphasic system saturated with salt increases HMF yield and selectivity by continuous extraction of HMF into extraction phase from aqueous phase, preventing the occurrence of undesired HMF side reactions in reaction phase. High HMF production was obtained at high temperature (180°C) and high extraction solvent/reaction solvent ratio (10:1) at a short reaction time of 60 min. The authors compared the effect of separate Lewis and Brønsted acids and their combination on catalytic production of HMF from glucose and found that combined catalysts showed better HMF yield than separate Lewis or Brønsted acid catalysts. Their synergistic catalytic effect was explained previously by Choudhary et al., [22], where Lewis acid promotes the isomerization of glucose to fructose, while Brønsted acid plays an important role in dehydration of fructose to HMF. Further experiments were conducted by Gomes et al., [19] and they found that the combined $AlCl_3$/HCl catalytic system showed the maximum HMF yield with glucose as substrate for dehydration. But when sucrose was used for HMF production, $ZnCl_2$/HCl gave the highest HMF yield. The authors attributed this phenomenon to the more acidic systems of $AlCl_3$/HCl than $ZnCl_2$/HCl as well as the weak glycosidic bond of sucrose. Acid hydrolysis of sucrose formed fructofuranosyl cation, which was readily converted to HMF by tautomerization followed by dehydration. The longer exposure of produced HMF to more acidic catalytic system, i.e., $AlCl_3$/HCl, caused side reactions, e.g. condensation reactions between HMF and sugar intermediates and rehydration of HMF to levulinic acid and formic acid, reducing the final HMF yield. Unexpectedly, sugarcane molasses showed almost identical HMF yield compared to synthetic mixture containing the same carbohydrate content as molasses, indicating that the non-sugar components of molasses, such as proteins, organic acids and inorganic salts, had no negative effect on HMF yield using both $AlCl_3$/HCl and $ZnCl_2$/HCl catalytic systems. The HMF yields obtained from $ZnCl_2$/HCl and $AlCl_3$/HCl catalyzed conversion of molasses were 49.6% and 43.2%, respectively, at 180°C for 60 min. Recently, Howard et al., [20] reported the production of HMF from sugar cane molasses using sulfonated carbon-based solid catalyst prepared from sugar cane bagasse and sugar cane molasses in aqueous media using a microwave reactor. In contrast to synthetic molasses solution, hydrolysis of real molasses with sugar cane by-product derived catalysts took place at a very slow rate. The authors attributed the slowing the hydrolysis process to the physical blocking of acidic catalytic sites as well as the saccharide complexes formed between sucrose and inorganic components (e.g., calcium). Additionally, the buffering effect of molasses was also likely to slow the hydrolysis process. Pretreating molasses with mineral acid and increasing the microwave power were found necessary to improve HMF yield for industrial molasses. The beneficial effect of molasses pretreatment with acid (e.g., formic acid, HCl and H_2SO_4) possibly resulted from removal of non-sugar components, a decrease of solution viscosity and increased surface contact between solid catalysts and sugar substrates. A further increase of HMF yield was observed by decreasing the buffering capacity of acid-treated molasses through dilution with water.

Conclusion

LA and HMF are classified as two of top value-added bio-based platform chemicals by the United States DOE and the UK LBNet. They can be used as precursors for producing numerous valuable chemicals and fuels. Molasses with high sugar concentration is an attractive feedstock for production of LA and HMF through either mineral or solid acid-catalyzed reaction. The reported yields of LA and HMF produced from molasses without pretreatment in previous references are not satisfactory (<50%) when using either solid acid or mineral acid as catalyst. The solid acid catalyst exhibited poor activity and selectivity for LA and HMF as a result of the presence of non-sugar part of molasses, indicating the necessity of pretreating molasses for removing certain non-sugar impurities. In strong contrast to solid acid catalyst, non-sugar components

of molasses were reported to show no influence on mineral acid catalyzed production of HMF. The reported low LA or HMF yield from mineral acid catalyzed conversion of molasses in previous literature was most likely due to the use of single aqueous phase as reaction media, instead of biphasic phase consisting of reaction solvent and extraction solvent. In the future study, in addition to design of high-activity solid acid catalysts and search for high-performance biphasic reaction systems, development of simple and efficient pretreatment methods would be also a focus for producing LA and HMF from renewable molasses at high yields and selectivities when environment-friendly solid acids are used as catalysts.

Conflict of Interests

All authors declare no conflicts of interest in this article.

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