International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.2, pp 704-710, 2015

Review on production of 5-Hydroxymethylfurfural from carbohydrate rich biomass

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Abstract: Hydroxymethylfurfural (HMF) is an organic compound obtained from sugars like fructose, cellulose, inulin and starch. In recent days of bio refinery, HMF plays an important role in the production of fuels and other value added chemicals. HMF is present in day to day foods like milk, coffee, roasted nuts and sliced bread. Fructose, fast dehydrating sugar, is the preferred raw material for the maximum production of HMF (95.5%). Production is carried out in the presence of solvents and catalysts. Dimethyl Sulfoxide (DMSO) and 1-butyl-3-methyl imidazolium tetra fluoroborate together increases the yield of HMF to 80%. The catalysts used can also be recycled back for about six runs from which 58.4% of HMF is obtained.

Introduction

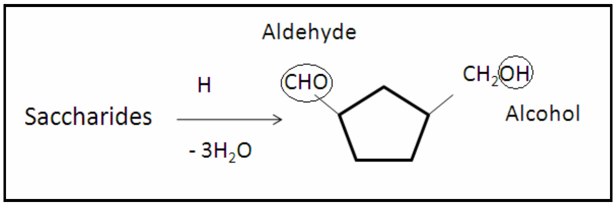
Fossil resources containing oil, natural gas, coal, etc. have a vital role in the global energy market. The World Energy Outlook (WEO) stated that the demand for fossil fuels will increase up to 84% in 2030 (1). Apart from this, global warming and environmental pollution contribute to demand in energy. In order to overcome these energy crises, scientists have been focused on renewable biomass feedstock (2). Biomass-derived carbohydrates are the best and promising alternatives for the production of fuels (3). 5-Hydroxymethylfurfural (HMF) is a water-soluble, heterocyclic organic compound derived from sugars. HMF is the versatile intermediate which as this can be further transformed into various high-performance fuels such as 2, 5-dimethylfuran (DMF) and other forms such as, 5-hydroxy-4-keto-2,pentenoic acid, 2,5-furandicarboxylic acid, 2,5-diformylfuran, dihydroxymethylfuran, levulinic acid (5). HMF contains both aldehyde and alcoholic groups. HMF is also present in some natural foods like milk, honey, fruit juices, spirits and bread. In bio refinery, 5-HMF (5-Hydroxymethylfurfural) is one of the primary renewable building blocks. According to the "*Top value Added Chemicals",* 5-HMF is one of the top building block chemicals (4). HMF can be produced from various carbohydrate sources like glucose, sucrose, cellulose, and inulin. Fructose is the preferred raw material for the maximum yield of HMF (6).

HMF in Day to Day Cooking

5-Hydroxymethylfurfural is generated when food stuffs are cooked. It was estimated that 30-150 mg of HMF is consumed daily by a single human through foods (7). Milk, which is highly concentrated with lactose and proteins, undergoes isomerization and lactose degradation when it is heated. This leads to the formation of HMF. Browning of sliced bread is also the result of HMF formation. Roasting of crushed hazelnuts produced 8.0 mg/kg of HMF, whereas roasting of defatted crushed hazelnuts produced only 2.2 mg/kg (8)

HMF Production

Production of HMF is done by acid-catalyzed dehydration which can be symbolically represented as,



Production is usually done using homogenous and hetero acids. But, the mostly preferred is the latter one.

Table 1: Comparison between homogenous and heterogeneous acids.

S. No	Homogenous acids	Heterogeneous acids
1.	High toxicity.	Comparatively low.
2.	Highly corrosive.	Low corrosive property.
3.	High catalytic waste.	Easy recycling of catalysts.
4.	Difficult separation from the reactants.	Easy separation from the reactants.
5.	Need of large amount of catalyst.	Has higher selectivity.

Dehydration of six carbon sugars results in the synthesis of HMF. Fructose, because of its rapid dehydration rate, considered as the most preferred feedstock. But the major drawback is its high cost. In case of glucose, dehydration is quite a tedious process, as it should be isomerized to fructose before dehydration (9).

Biomass

Biomass resources include industrial wastes such as forest residues, pulp process wastes, sawdust, hog fuel agricultural pruning and clean wood waste from landfills (10). Various biomasses were used for the production of HMF. Few are;

Wheat Straw

Wheat straw contains hemicellulose (25%), cellulose (35%), and lignin (25%). Here, HMF production includes two steps: hydrolysis to break the cellulosic fibres and hemicellulose to monomeric carbons followed by a dehydration step to form furfural from the sugars.

Girasol Tubers and Potato Tubers

50-60% of inulin (dry weight) is present in Girasol tubers which is oligofructose polymer. In general potato tubers contains 65% of starch (dry weight) and this is the homopolymer containing units of glucose. This process involves two steps: acid-extraction and thermal dehydration (11).

Jerusalem Artichoke

Jerusalem artichoke's tuber stores sugar as a fructose-based polymer (12). It contains high content of inulin (>75%). Inulin contains glucose and fructose which can be further converted to HMF. This hydrolysis is conducted either by enzymatic or acidic conditions (13). The basic solution to use is a co-solvent system *i.e.* water and an organic solvent. This promotes the dehydration (12).

Starch

This is the cheapest and abundantly available renewable carbohydrate source. Dehydration in this process involves the following steps: 1) Glucose to fructose isomerization; 2) dehydrating the sugars to HMF (14).

Cellulose

Cellulose is used widely as it is inexpensive and abundantly available resource. In this process, HMF yield is about 89% (15).

Catalysts and Solvents

Solvents

DMSO: It lowers the water concentration and retards rehydration pathway of Hydroxymethylfurfural to levulinic and formic acids. It also inhibits the acyclic reaction which stops the undesired by-products. When DMSO is used as a solvent for dehydration, the process should be carried under vaccum (0.97×10^5 Pa) for continuous water extraction.

Methylisobutylketone (MIBK): This is used as a co-solvent because it does not support the complete separation of product (HMF), as the separation is from the aqueous phase. This can be solved by adding 2-butanol to MIBK. This is termed as bi-phasic system as amberlyst is also used as catalysts and the overall yield is 77% of HMF.

1-Butyl-3-Methyl Imidazolium Tetrafluoroborate: This gives a product of about 50% when amberlyst 15 is used as a catalyst. But when DMSO is used as co-solvent the yield has increased upto 80%.

Catalysts

Recently, the use of catalysts has been broadly classified into 3 groups:

1. Cation-exchange resins
2. Microporous materials
3. Macroporous materials

Cation Exchange Resins

In general, for the production of HMF, solvents and catalysts were used. Cation exchange resins are one of those catalysts. Most widely used ion exchange resin in the production of HMF is Amberlyst sulfonic ion exchange resin. Researchers obtained very low yields of HMF when water is used as a solvent alone. By adding amberlyst as a catalyst, high yields of HMF were obtained. This is because of the active HMF rehydration to formic and levulinic acids. Amberlyst particles of size 0.15 – 0.053 mm was recorded in which the HMF yield is 100%.

Overall Catalytic Activity System

The catalytic activity system for some catalysts was by Ordomsky et al.

MOR zeolite < γ-Al_2O_3 < Amberlyst-15 < $ZrPo_4$ < Nb_2O_5

Microporous Acid- Catalysts

1. Zeolites were first used for the production of HMF from xylose by Moreau et al.,
2. Lessard et al., compared the production of HMF by using different zeolites like SM-25, mordenite 13/20 and faujasite. Mordenite 13 catalyst gives 99% conversion of xylose.
3. Kim et al., tested various zeolites in DMSO, Toluene, water and found that water has the lowest rate of conversion.

Mesoporous Acid- Catalysts

The most widely used catalysts were metal oxides. In that broad classification, ZrO_2 and TiO_2 were the most important samples.

1. Yang et al. studied the SO_4^{2-}/ ZrO_2 – Al_2O_3 catalyst system with DMSO/water solvent system with significant yield of HMF.
2. Yamaguchi et al. used Tin and Tungsten oxide mixtures along with Lewis acid content with a yield of 48% of HMF.
3. Carlini et al. reported the significance of Lewis and bronsted sites on phosphate salts of niobium by achieving high selectivity of HMF with low conversion of fructose.
4. Carlini et al. also reported Vanadyl phosphate based catalysts. In which they increased the HMF selectivity by 90% by the partial exchange of VO^{3-} sites by Fe.

Examples of Catalysts

1.	Mineral acids	:	H_2So_4, HCl & H_3Po_4
2.	Organic acids	:	Maleic acid, levulinic acid, Oxalic acid, p-toluene sulfonic acid
3.	Lewis acids	:	$ZnCl_2$, $AlCl_3$ & BF_3
4.	Salts	:	Pyridine/$(Po_4)_3^-$, NH_4So_4/So_3, pyridine/ HCl & Thorium, Aluminium,Zirconium, lanthanide ions
5.	Solid Catalysts	:	Ion exchange resins, zeolites & metal (IV) phosphates

Advantages of solids as catalysts

1. Dehydration
2. Isomerization
3. Polymerization
4. Alkylation

Advantages of Aqueous solvents

1. Cheap
2. Non-toxic
3. Non-inflammable
4. Clean solvent
5. Increased economic feasibility

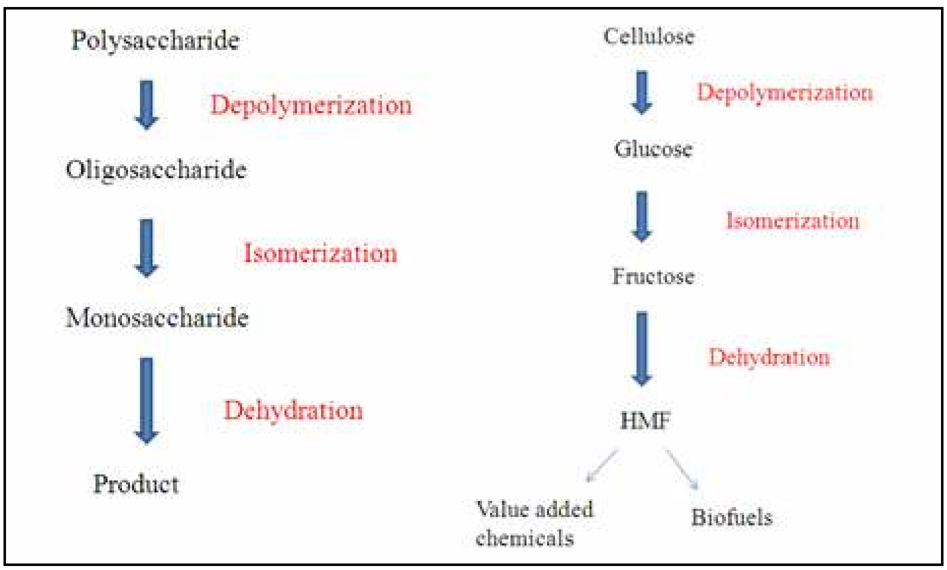
Table 2: Overview of the HMF yield from different biomass using solvents and catalysts in literature.

S.No	Saccharides	Solvent	Catalyst	Time	Temperature	Yield	Reference
1.	Hexoses	DMSO	Zrp	3h	140^o C	81%	(16)
2.	Cellulose	Ionic liquids	Zeolite & $CrCl_2$		120^{o}C	47.5%	(15)
3.	Fructose	DMSO	[CMIm] Cl	120 min	120^{o}C	90.8%	(3)
		DMA				94.5%	
		Ethanol				6.7%	
		NMP				91.2%	
		DMF				77.5%	
4.	Cellobiose	DMSO	[CMIm] Cl + ZrO Cl_2. 8H2O	420 min	120^{o}C	46.1%	
5.	Inulin	DMSO	[CMIm] Cl	180 min	120^{o}C	88.4%	
6.	Glucose	DMSO	[CMIm] Cl + ZrO Cl_2. $8H_2O$	420 min	120^{o}C	50.6%	
7.	Sucrose	DMSO	[CMIm] Cl + ZrO Cl_2. $8H_2O$	420 min	120^{o}C	73.4%	
8.	Glucose	[EMIm] Cl + $CrCl_2$				68 - 70%	(17)
9.	Glucose	DMSO	1-(1-propylsulfonic) – 3-methylimidazolium chloride	600 min	150^{o}C	15.7%	(3)
10.	Fructose	DMSO	$[C_6(mpy)_2]2Br^-$	60min	110^{o}C	91%	(10)
			$[C_6(Mpy)_2][NiCl_4]^2$	60min	110^{o}C	95.5%	
			$[C_6(Mpy)_2][CoCl_4]^{2-}$	60min	110^{o}C	77.9%	

			$[C_{10}(Epy)_2]2Br$	60min	110°C	83%	
			[BMIm]Cl	6h	100°C	83%	
11.	Fructose	DMSO	$[BMIm]BF_4$ &$[BMIm]PF_6$	3h	80°C	50%	(18)
12.	Fructose	DMSO	1-H-3-methylimidazolium chloride [HMIm]Cl	15-45 min	90°C	90%	(18)
13.	Fructose		[EMIm]Cl + $CrCl_2$			83%	(19)
14.	Fructose		[EMIm]Cl + $CrCl_2$			70%	(19)

{[EMIm] Cl-1-Ethyl-3-methylimidazolium chloride; [BMIm] PF_6 - 1-Butyl-3-methylimidazolium hexafluoro phosphate; [BMIm] BF_4-1-Butyl-3-methylimidazolium tetra fluoroborate; [BMIm]Cl-1-Butyl-3-methyl imidazolium chloride; $[C_{10}(Epy)_2]2Br$-1, 10-decane-1,10-diylbis(3-ethylpyridinium)dibromide; $[C_6(Mpy)_2][NiCl_4]^{2-}$- 1,10-hexane-1,6-diylbis (3-methylpyridinium) tetrachloro- nickelate (II) ; $[C_6(Mpy)_2][CoCl_4]^{2-}$-1,10-hexane-1,6-diylbis (3-methylpyridinium) tetrachloride; [CMIm] Cl - 1-butyl-3-methylimidazolium chloride ; $CrCl_2$ - Chromium(II) chloride}

Overall Production Pathway for HMF:



Effect of Reaction Temperature

P. Daorattanachai et al. implemented the reaction tests at various temperatures ranging from 200-270°C with phosphoric acid as the catalyst. They found that below the temperature of 200°C HMF is the main product along with other byproducts like levulinic acid and anhydroglucose (AHG).

At high temperatures above 200°C, other products like acetaldehyde, acetic acid, formic acid, glycolaldehyde, propenoic acid, phenol, and solid precipitate were generated.

But after 230°C, the yield of HMF is decreased gradually.

Catalyst Reusability

Catalyst reusability plays a vital role in Green engineering and important application in large scale industries.

Acidic ion-exchange resins can be recycled at 75°C for about 20 min after the extraction of HMF by ethyl acetate. The reaction mixture which is heated to 60°C in vaccum oven for about 24h for the removal of ethyl acetate and water. The catalyst can be reused for the next run. Maximum of seven runs can be done using the same resin.

Ionic liquids and DMSO can be used for about six times without any loss in its activity. The 58.4% of HMF can be yielded even after six runs.

Conclusion

Fructose is the important commercial source for the production of HMF with high yield of 95.5%. DMSO is the widely used solvent. HMF yield is very high at the temperature of about 230^o C, after which degradation of HMF takes place. Catalyst recycle can also be done for about 6 runs without reduction in its catalytic activity.

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