



## Review article

# Porous nanomaterials as green catalyst for the conversion of biomass to bioenergy



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## HIGHLIGHTS

- Liquid fuels from biomass via HMF.
- HMF, furfural and 2,5-furandicarboxylic acid (FDCA) from biomass via catalytic processes.
- Bioresources such as glucose, fructose, sucrose and polymeric carbohydrates for preparing liquid energy fuels.
- Porous resin/carbons, zeolites, mesoporous metal oxides, porous organic polymers as efficient catalysts for the conversion of biomass to bioenergy.

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## ABSTRACT

Natural fossil fuel is the prime resource of energy and with the rapid technological development its reserve is depleting at an alarming rate. To overcome this concern bio-refinery is the most emerging and necessary approach, where liquid fuels and related demanding fine chemicals can be derived very effectively from biomass via platform chemical 5-hydroxymethylfurfural (HMF). HMF, furfural and 2,5-furandicarboxylic acid (FDCA) can be derived from biomass via several catalytic processes. Thus the objective of this review is to summarize various catalytic methods to produce 5-hydroxymethylfurfural (HMF) the precursor of 2,5-dimethylfuran (DMF) from a variety of monomeric bioresources such as glucose, fructose, dimeric (sucrose) and also polymeric carbohydrates like starch, cellulose and biomass derived carbohydrates (raw biomass). High surface acidity and porous nanostructures (high surface area) of the nanomaterials play crucial role in these heterogeneous catalytic processes. Several nanoporous solid acid catalysts like porous resin, micro/mesoporous carbons, microporous zeolites, mesoporous metal oxides, functionalized mesoporous silicas and porous organic polymers employed in the selective biomass conversion reactions are discussed in detail in this review. Bifunctional catalysts, MOFs and metal phosphonates with functionalised surfaces in comparison to those of the conventional solid acid catalysts are also discussed in-depth.

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## 1. Introduction

In past few decades technological advancement of the mankind is mostly dependent on oil as it is the primary source of energy. With the exponential economical growth of the developed and developing countries like India and China, the demand is likely to be increased more and more in the forthcoming years. Rapid utilization of natural fossil fuels as a greater part of energy sources at the advent of massive civilization and industrialization resulted depletion of these reserves [1,2]. A new recyclable and renewable resource needs to be focused to balance this crisis. Increased CO<sub>2</sub> emission from the natural resource also found to be a major contributing factor of global warming and this has a devastating effect on earth's eco-system. Owing to these serious concerns a constant effort has been devoted by the researchers to seek for an alternative source of energy in the near future [3]. In recent times, there is an increased interest for the biobased chemicals as non-conventional energy resources such as carbohydrates, non-food biomass, lignocellulosic compounds, and bioethanol. High oxygen content in the molecular structure of carbohydrates is a limitation in this context [4]. Oxygen content can be lowered by using three main pathways. Firstly, by the removal of the highly oxidized carbon molecules such as CO<sub>2</sub>, formic acid or formaldehyde. Formation of ethanol, butanol and CO<sub>2</sub> is an example of fermentative conversion of carbohydrates. Removal of oxygen from the molecule by hydrogenolysis is another method which typically removes oxygen to form water combining with one molecule of hydrogen. Typical example of hydrogenolysis is one-pot conversion of cellulose into polyols, which are very important intermediates for the production of perfumes, beer, polyesters, polyethers, polyurethanes, pharmaceuticals, etc. [5]. The third option is the dehydration of carbohydrates to furans and levulinic acid (LA). Although bioethanol serves as a fuel supplement when mixed with gasoline, it can act as a long term renewable fossil fuel alternative. In large quantities it is currently produced from grains such as corn and this is a major concern as this directly competes with the food supply [6]. Although bioethanol can be produced from biomass sources like

straw and cob in good yields but its relatively low energy density (18.2 MJ/L) and high CO<sub>2</sub> release on ignition, which make its ecologically less attractive. To produce more economical and sustainable alternative with lesser drawbacks lignocellulosic compounds have shown promising results for future perspectives [7]. In 1951, Newth et al. first published an article on furan production from carbohydrate [8]. Since then researcher's interest for the production of bioenergy from biomass through catalytic processes has grown gradually [9]. In 1980s HMF production from carbohydrates were mainly based on aqueous mineral acid catalyzed systems. The history of HMF synthesis and its real field application have been reported by Lewkowsky's furan chemistry review in 2001 [10]. Ionic liquids are used as eco-friendly solvents by Lima [11] and Stark [12], and immobilized on silica supports [13] for selective sugar dehydration. Many researchers experimented HMF as an introductory compound to produce highly demanding chemicals such as promising next generation polyester building block monomers (2,5-furandicarboxylic acid (FDCA) [14,15], 2,5-bis(hydroxymethyl)furan (BHMF) [16,17], 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTF) [18,19] and potential biofuel candidates (2,5 dimethylfuran (DMF) [20,21], 5-ethoxymethylfurfural (EMF) [22], ethyl levulinate (EL) [23] and  $\gamma$ -valerolactone (GVL)) [24] (Fig. 1) directly from biomass via green catalytic processes.

Lignocellulosic compounds have versatile uses and they have abundant supply mainly from agricultural industry and paper producing plants. The major constituents of these compounds are 40–50% cellulose, 16–33% hemicelluloses and 15–30% lignin, and these are available in several industrial waste streams [25–27]. As, cellulose is the primary component, it has gained more attraction for the biomass conversion processes. Several methods are implicated for the hydrolysis of cellulose using various types of catalysts and solvents such as mesoporous carbon functionalized with metal [28–30] or acid groups [31], ionic liquids [32,33], supercritical water [34,35], and sulfonated ion exchange resins [36]. Degradation of cellulose breaking  $\beta$ -1,4-glycosidic bonds is a complicated procedure. To overcome this complication ionic liquids have been introduced to obtain a homogeneous solution prior to hydrolysis.

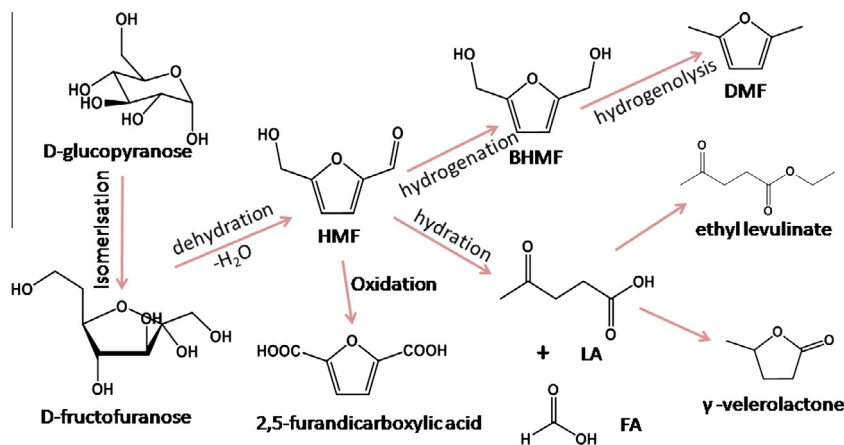


Fig. 1. Possible reaction products for the acid catalyzed dehydration and subsequent rehydration of fructose and related compounds.

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