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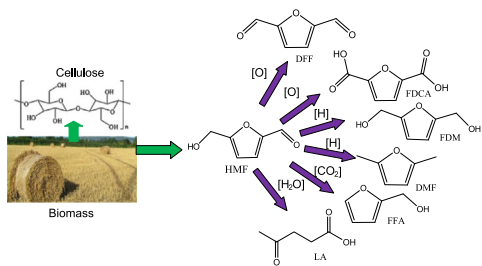
## Review

## Synthesis of hydroxymethylfurfural from cellulose using green processes: A promising biochemical and biofuel feedstock

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## GRAPHICAL ABSTRACT

Synthesis of cellulose derives industrially important compounds through HMF.



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## ABSTRACT

Inedible, lignocellulosic biomass has been recognized as most promising renewable resource for the production of high value bio-chemicals. The pretreated biomass or isolated cellulose is a biopolymer of glucose used as a starting material for the synthesis of 5-hydroxymethylfurfural (HMF). HMF is listed among the top 10 bio-based chemicals by USA Department of Energy and it acts as feedstock for deriving a number of commodity products (Bonzell and Petersen, 2010, Green Chem. 12, 539). In present review, we have systematically summarized the catalytic reaction for the synthesis of HMF from pretreated biomass/isolated cellulose using green processes. Further, through catalytic approach, HMF is translated into industrial important chemicals (2,5-diformylfuran, furan-2,5-dicarboxylic acid, 2,5-furandimethanol, furfuralalcohol, etc) or high calorific value biofuel (2,5-dimethylfuran, 2,5-dimethyltetrahydrofuran, 2,5-bis(alkoxymethyl)furans, etc). In the profitable scale of HMF production, levulinic acid (LA) is generated as a major byproduct. Besides HMF, this review also outlines the catalytic strategy for the conversion of LA to industrially important chemicals along with the biofuel additives. Finally, the bio-toxicity of synthesized chemicals, which connected into different functional groups have been summarized to meet the criteria of the green technology for commercialization.

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## 1. Introduction: Why renewable resources?

Environment pollutions, energy shortages, demand/supply ratio of crude oil and insufficient commodity products are the major global issues of today's world. To overcome these challenges, there is a need of utilizing most abundant and underutilized lignocellulosic biomass for the production of designed molecules (Kamm et al., 2006). Now-a-days depleting fossil feedstock has been continuously used by various chemical industries to produce numerous important products such as fuel, lubricants, fine chemicals, synthetic fiber, plastics, detergents, pesticides, fertilizers, pharmaceutical products, solvent, coke, waxes, asphalt, etc. (Rout et al., 2014a). In order to overcome this global challenge, valorization of cellulosic biomass to commodity chemicals has come up as most promising alternative and for this purpose cellulose derived 5-hydroxymethylfurfural (HMF) is a key chemical identified by USA Department of Energy (Bonzell and Petersen, 2010). In recent years, the development of green catalytic technology for the production of HMF from cellulosic biomass has shown tremendous research interest in the laboratory scale.

HMF is a resourceful intermediate linking the biomass based carbohydrate chemistry with conventional petroleum based industrial chemical technology (Zhao et al., 2007). HMF and its derivatives could potentially replace voluminously consumed petroleum-based building blocks, which are currently used to make plastics and fine chemicals. Huber et al. (2005) reported that HMF is a key intermediate to produce liquid alkanes from renewable biomass resources. Similarly, HMF was catalytically reduced to 2,5-dimethylfuran (DMF) and later compound was used as a high calorific (31.5 MJ/L)

biofuel (Somers et al., 2013). Currently, the high production cost of HMF limits its availability in plenty for industrial applications. A process to produce pure HMF from abundant renewable carbohydrates in high yield at low energy input must be developed before a biorefinery platform can be built on the basis of this substrate. Current processes to produce HMF involve the use of acid catalysts and are mainly limited to fructose as feed. A drawback with acid catalysts is that they promote various side reactions, significantly increasing the cost of product purification. Similarly, fructose is an expensive chemical and it equally contributed the cost of HMF production in commercial scale (Kazi et al., 2011). Therefore, we limit our discussion to the biomass derived non-food carbohydrate such as cellulose for production of HMF with a glimpse of pretreatment methods and effective processes for isolation of major biopolymers.

## 2. Pre-treatment of the biomass (agricultural residues)

Presently, the overall quantity of plant biomass accessible per annum in the world is around  $1 \times 10^{11}$  ton (Zhang and Zhao, 2010). Out of which only  $6 \times 10^9$  ton is used for foodstuff and other commercial applications, alternatively the remaining material might be explored as a feedstock for cellulosic biorefinery. Biomass based technology will require tremendous research effort for developing new systems that include production, conversion and utilization of bio-products in a sustainable manner (Rout et al., 2014a). For that, the feedstock supply is a foremost step in the biorefinery, which is one of the key obstacles for cost-effective production of cellulosic

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