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## Review

# Promises in direct conversion of cellulose and lignocellulosic biomass to chemicals and fuels: Combined solvent–nanocatalysis approach for biorefinery

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## ABSTRACT

This review surveys sustainable one-pot conversion methods of cellulose into two very important platform chemicals such as 5-hydroxymethylfurfural and isosorbide retaining applications in many fields. Various new techniques based on such as ionic liquids, acid functionalized mesoporous materials, organic acids, functionalized nanoparticles, and mechanocatalytic depolymerization was discussed in detail for the very important direct conversion of cellulose to 5-hydroxymethylfurfural. More emphasis is given on a comparative analysis of recently developed all successful methods for 5-hydroxymethylfurfural production from cellulose in terms of efficiency, selectivity and cost-effectiveness. The article also complements on the promising extraction methods for the 5-hydroxymethylfurfural using special solvents. The importance of another very interesting platform chemical, i.e. isosorbide is also addressed. Several factors of cellulose to isosorbide transformation including metal nanoparticle size, crystallinity order of the cellulose, and extraction medium which controls the rate of conversion and product distillation have been addressed. The article also surveys the potential discoveries in one-pot conversion of cellulose into biofuels. The strategies of cellulose and lignocellulose conversions to compounds with liquid fuel's features have been discussed focusing on the production of  $\gamma$ -valerolactone as important intermediates to access liquid hydrocarbons and valeric esters. Cellulose value-chain for the direct conversions to liquid fuels (e.g. cellulose to levulinic acid platform to obtain valeric biofuels) by using supported nano-structured metal catalysts are emphasized. Overall an analysis of the main prospects and constraints related to the several conversion routes are presented including the critical thinking on the technical barriers, commercial promise, and environmental issues.

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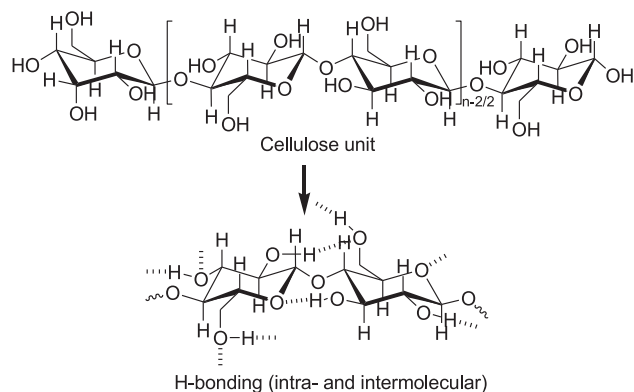
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## 1. Introduction

Adverse effects of the rapid depletion of fossil fuel resources on the global environment and climate change have been already eminent and subject of a major concern worldwide [1,2]. Since the supply of fossil fuels and related petrochemicals may soon be limited, sustainable solutions for the alternative technology for chemicals and fuel production is currently sought on the basis of a surge. Immediate alternative is to develop novel chemical catalysts for the direct and selective conversion of biomass, essentially cellulose and lignocelluloses into platform chemicals such as 5-hydroxymethylfurfural (HMF) [3,4] to utilize as feedstock for the production of fine chemicals [5,6] in particular 2,5-furandicarboxylic acid (FDCA) as polymer building blocks [7,8] and liquid fuels [9,10]. Since cellulose is obtained via biological process from atmospheric CO<sub>2</sub>, water and sunlight, therefore, it is a sustainable feedstock for the production of fuels and fine chemicals with a possible significant reduction in carbon emission via closed carbon cycles, however implementation of complete value chains remain challenging [11,12]. In addition, biomass offers great potential as a renewable feedstock in abundance [13,14]. It is estimated that nearly half of the organic carbon in the biosphere is present in the form of cellulose [14]. The complex chemical composition of cellulosic biomass containing intra- and intermolecular hydrogen bonding in their crystalline form in which chemical environment of the 1,4-β-glycosidic linkages are especially important since they contain dynamically interconverting features [15]. This makes the amorphization of the crystalline domains difficult for depolymerization. Thus, conversion of the cellulose becomes complicated and non-selective for producing target chemical or fuel. Cellulose consists of only anhydrous glucose units within crystalline structure. As a result, the first significant barrier for the direct conversion of cellulose would be the improvement of the reactivity of cellulose for which ball-milling has emerged as an important methodology compared to the acid-catalyzed depolymerization [16]. However, attempts for the conversion of cellulose into chemicals in the aqueous medium was initiated long ago and it is considered as the representative process of lignocellulosic biomass conversion [17].

A cellulose molecule has the generic chemical formula (C<sub>6</sub>H<sub>12</sub>O<sub>5</sub>)<sub>n</sub>. It consists of a skeletal linear polysaccharide, in which glucose monomer units are jointed together through β-1,4-glycosidic linkages in which extensive intramolecular and intermolecular hydrogen bonding networks exists (Fig. 1) [18]. Ultrastructure of cellulose possesses extreme complexity in the form of two crystal phases, namely I<sub>α</sub> and I<sub>β</sub> can be found within the same cellulose sample but also along a given fibril. The chain length of crystalline cellulose consisting of between 2000 and 14000 residues. Accordingly, cellulose has a high average molecular weight (10<sup>6</sup> or more) with number of repeating saccharide monomers is 5000–10000 which is ~150 times higher than that of the hemicellulose [19]. Cellulose exists in the form of a robust crystalline structure in solution or in solid state and it is the principle scaffolding component of all plant cell walls [20]. Such a cell wall polymer is neither soluble in water nor easily digestible in the gastrointestinal



**Fig. 1 – Comparison of the chemical structure of polysaccharides. cellulose with 1,40-β-glycosidic bonds and intra- and inter-chain hydrogen bonding.**

tract of humans. The changes in the types of chemical bonding by the amorphization of crystalline structure in polysaccharides have significant impacts on their physical properties and chemical reactivity [21,22].

Therefore, in terms of both the abundance and availability from bioresources with no impact on food supply, utilization of cellulosic materials as feedstocks is more practicable and sustainable for the production of fuels and commodity chemicals. In this context, the catalytic conversion of cellulose to fuels and chemicals is highly promising than that of any other form of biomass like starch to bioethanol and vegetable oil to biodiesel [23–25]. In biorefinery processes such as fermentation and enzymic catalysis, peculiar enzymes, bacteria and other microorganisms are used to break down 3D network of cellulose (depolymerize) and thus only a few commodity chemicals can be accessible [26]. Nevertheless, such processes generally suffer from low efficiencies, narrow reaction conditions and limited scale of production [27].

Chemocatalytic conversion of cellulose has been developed recently, but it only receives serious attention with the advent of a series of novel reaction routes. However, besides the complexity of biological sources, the inert chemical structure and the compositional ratio of carbon, hydrogen and oxygen in cellulose results additional difficulties in the chemocatalytic conversion to fuels and chemicals. In this context, the development of a new family of highly active and selective catalysts is an essential prerequisite for cellulose conversion to desired products [28].

Fig. 2 lists some typical fine chemicals and fuels which can be produced by chemocatalytic conversion of cellulose from different chemical processes. Clearly, a variety of fuels, including 2,5-dimethylfuran (DMF), 2,5-dimethyltetrahydrofuran (DMTHA), 5-ethoxymethyl-2-furfural (EMF), (Route B) and chemicals such as glucose, fructose, sorbitol, levulinic acid and lactic acid (Route C) can be accessible via depolymerization of cellulose. The series of liquid fuels obtained via route B can also be derived from HMF produced via the path A. In many instances, depolymerization/hydrolysis of cellulose to monomer glucose is regarded as the necessary first step. Then glucose is further converted into HMF via isomerization–dehydration protocol and via

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