Available online at www.sciencedirect.com
SciVerse ScienceDirect
http://www.elsevier.com/locate/biombioe
BIOMASS & BIOENERGY

Review

Advances in biomass transformation to 5-hydroxymethylfurfural and mechanistic aspects

Saikat Dutta [a,**], Sudipta De [b], Basudeb Saha [b,*]

[a] Department of Chemistry, University of Florida, Gainesville, FL 32611, USA
[b] Laboratory of Catalysis, Department of Chemistry, University of Delhi, Delhi 110 007, India

ARTICLE INFO

Article history:
Received 25 October 2011
Received in revised form
30 January 2013
Accepted 3 February 2013
Available online 26 March 2013

Keywords:
Biomass
Cellulose
Lignocellulosics
Dehydration mechanism
Sustainable chemistry

ABSTRACT

Biomass-derived 5-hydroxymethylfurfural (HMF) has been emerged as a key platform chemical for the production of fine chemicals and liquid fuels. The direct transformation of cellulose and lignocellulosic biomass into HMF in ionic liquids and organic solvents is most desired in terms of process economics and sustainability. The focus of this review is purely on the HMF production from cellulose and lignocelluloses and mechanistic aspects of HMF formation in order to bridge the gap in understanding the factors responsible for selective conversion and selection of catalyst. Additionally, present review is devoted exclusively to the latest developments, namely microwave-assisted degradation of cellulose to HMF, application of solid acid and ionic-liquid catalysis to address their effectiveness for HMF production. Approaches for the cellulose transformation into HMF are especially emphasized in order to explore newer avenues of biomass as renewable feedstock for energy and chemicals.

1. Introduction

The ever increasing global demand for energy coupled with a finite oil supply not only dramatically volatilizes the oil prices but also challenges economic and industrial security worldwide [1,2]. Continued reliance on petroleum feedstock will lead to an unacceptable amount of greenhouse gas emissions which has been the major concern [3]. Since the global consumption of the liquid petroleum tripled in the ensuing years [4], researchers and policy-makers have given priority to explore alternative feedstock to avoid the most unfortunate scenarios of energy crisis in future. Much of this attention has been directed at liquid biofuels and in particular, biomass feedstock which has been utilized as source for liquid biofuels and hydrocarbons [5]. In this context, biomass-derived biofuels feature tremendous potentials as renewable energy. Biomass represents an abundant carbon-neutral renewable resource and its enhanced use would address several challenges. Advances in process chemistry leading to a new manufacturing concept for converting renewable biomass-derived carbohydrates and biomasses into valuable chemicals and liquid fuels, offers the total sustainability that will lead to a new manufacturing paradigm [6].

It is estimated that after about 15 years, up to 30% of raw materials for the chemical industry will be produced from renewable biomass [7]. The products from renewable resources (fiber composite materials, starch- and protein-derived products) are already available in the market [8]. Current chemical

* Corresponding author. Tel.: +91 011 2766 6646; fax: +91 011 2766 7794.
** Corresponding author.
E-mail address: bsaha@chemistry.du.ac.in (B. Saha).
0961-9534/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biombioe.2013.02.008

research is focused on the production of scalable quantity of platform chemicals to convert them into chemical building blocks [9]. The platform chemicals can be produced from carbohydrates and biomass chemically or biologically. The building-block chemicals can subsequently be converted into multitude of high-value added bio-based chemicals (molecules with multiple functional groups). HMF is an aromatic aldehyde that exists naturally in coffee, honey, dried fruits, fruit juices and flavoring agents. The concentration of HMF in food products varies widely, for example levels of HMF in wine, spirits and fruit juices have been found to be as high as 200 mg dm^{-3} [10]. HMF has been considered as feedstock of bioenergy, building-block chemical, and medicine. Among the burgeoning chemical technologies for alternatives, controlled elimination of water from biomass-derived carbohydrates (catalytic dehydration) has been extensively studied in the recent years to access HMF [11]. In the past, HMF was produced preferentially from a biopolymer, inulin by acid-catalyzed intramolecular dehydration [12]. HMF holds special promise since the carbon skeletons are identical to those obtained in cellulose and hemicelluloses and can serve as a sustainable feedstock for liquid fuels and chemicals as shown in Fig. 1. Common polyester building-block 2,5-furandicarboxylic acid (FDCA) (1) can be derived from HMF [13,14]. FDCA can be used as a replacement for terephthalic acid in the production of polyethyleneterephthalate and polybutyleneterephthalate [15]. Furthermore, the reduction of HMF can lead to products such as 2,5-bis(hydroxymethyl)furan (2), and 2,5-bis(hydroxymethyl) tetrahydrofuran (3) (Fig. 1) which serve as alcohol components in the production of polyesters, providing completely biomass-derived polymers when combined with FDCA.

In addition, HMF is a precursor for the 2,5-dimethylfuran (4) and 2-methylfuran (5) (Fig. 1) which are promising liquid transportation fuels [16–18]. Moreover, HMF can serve as a precursor in the synthesis of liquid alkanes for their use in diesel fuel [19]. Moreover, HMF also successfully functions as an anti-sickling agent that specifically binds to intracellular sickle hemoglobin (Hbs) without inhibition by plasma and tissue proteins or other undesirable sequences [20]. Deriving HMF from biomass (cellulose, lignocellulose) would bridge the growing gap between the supply and demand of energy and chemicals. Doing so requires efficient chemical catalysts to directly convert biomass into HMF selectively. In the production process of HMF, degradation is associated and evidences in support of both the open-chain and the cyclic fructofuranosyl intermediate pathways suggest that HMF degradation occurs by fragmentation, condensation, rehydration, reversion, and/or additional dehydration processes (Fig. 2) [21,22]. Unfortunately, the industrial use of HMF as a chemical intermediate is currently impeded by high production costs [12]. HMF could be produced in high yields from sugars using high-boiling organic solvents including DMSO, DMF, and mixture of polyethyleneglycol with water over various catalysts, including sulfuric acid and sulfonic acid resins which make the process energy-intensive including tedious isolation procedures [23–26]. In pure water, biomass conversion is generally nonselective, leading to many by-products such as levulinic acid, formic acid, and humins [27]. Application of biphasic water-immiscible organic solvent to extract HMF continuously from the aqueous phase resulted poor HMF partitioning into the organic streams which consumes large volume of solvents leading to high expenditure to purify the HMF product [21,28].

Dumesic et al. introduced a modified biphasic system to address limitations of HMF production by the acid-catalyzed dehydration of 30–50% fructose (by mass fraction) feed with

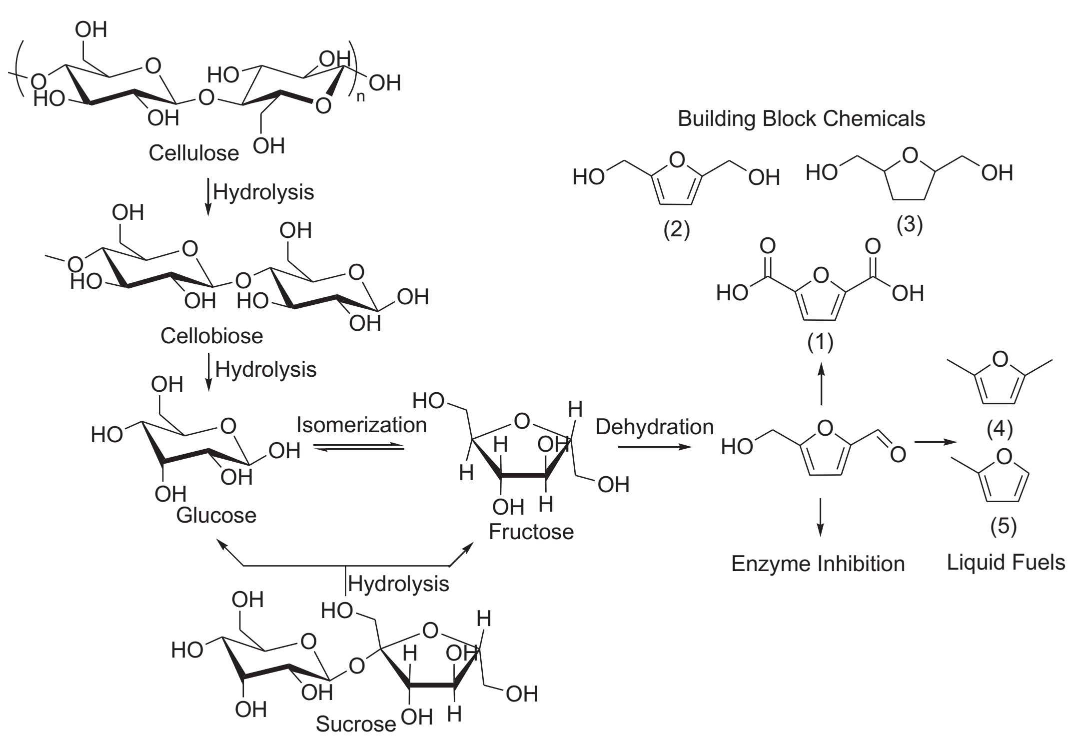

Fig. 1 – Production of HMF, from cellulose and carbohydrates, serves as feedstock for a range of chemicals and liquid fuels.