



Review

# Conversion of biomass to hydroxymethylfurfural: A review of catalytic systems and underlying mechanisms



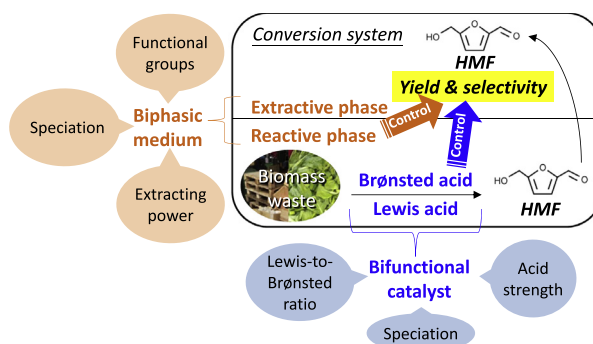
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HIGHLIGHTS

- Biomass conversion to HMF significantly depends on catalysts and solvents.
- Bifunctional catalyst caters for tandem hydrolysis, isomerization, and dehydration.
- Lewis-to-Brønsted acid ratio and acid strength primarily determine HMF selectivity.
- Co-solvents are kinetically and thermodynamically favourable for HMF production.
- Biphasic system enhances HMF selectivity by suppressing side reactions.

GRAPHICAL ABSTRACT



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ABSTRACT

Conversion of biomass waste to hydroxymethylfurfural (HMF), a value-added platform chemical, has captured great research interests driven by the economic and environmental incentives. This review evaluates the recent development of biomass conversion systems for high HMF yield and selectivity, with a focus on the performance of emerging catalysts and solvents from a mechanistic view. We highlight that the ratio and strength of Brønsted and Lewis acid in bifunctional catalyst are critical for maximizing HMF production by selective improvement in the kinetics of desirable reactions (hydrolysis, isomerization, and dehydration) over undesirable reactions (rehydration, polymerization). The characteristics of solvent mixture such as functional groups and speciation govern the reactivity of substrate towards desirable reactions and stability of HMF and intermediates against side reactions. Research efforts to unravel the interactions among co-catalysts/co-solvents and between catalysts and solvents are encouraged, thereby engineering a synergistic conversion system for biomass valorization.

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## 1. Introduction

Biomass waste has exerted significant burdens on the global waste management. For example, lignocellulosic residues of over 340 million tonnes (on a dry mass basis) was produced in United States in 2012 (Ge et al., 2016), whereas in Hong Kong, the daily disposal of biodegradable waste (i.e., food, yard, and paper waste) amounts to 6174 tonnes, contributing to approximately 60% of the municipal solid waste (HK EPD, 2016). Apart from the traditional treatments such as combustion and anaerobic digestion, valorization of the waste to tradable bulk chemicals has attracted immense research interests in recent years driven by the high market incentive (Tuck et al., 2012), thriving bio-based economy, and urge for the petrochemical substitutes (Mohan et al., 2016).

Hydroxymethylfurfural (HMF), a top value-added biomass-derived chemical, appears as a rewarding target product as it can be transformed to various derivatives, for example, ethoxymethylfurfural, 2,5-furandicarboxylic acid, furfuryl alcohol, dimethylfuran, and 2,5-diformylfuran (Dashtban et al., 2014; Mukherjee et al., 2015; Rout et al., 2016). These chemicals serve as the building blocks of diverse commodities including pharmaceuticals, polymers, resins, solvents, fungicides, and biofuels. Such broad versatility has earned HMF a high market value that ranges from USD 2.0 to 300 per kilogram depending on the chemical quality (Yu et al., 2017). Representative reaction schemes can be found in previous studies (Román-Leshkov et al., 2010; Yu et al., 2016). However, current commercial production of HMF predominantly relies on the syrups extracted from energy crops (Kläusli, 2014). Potential use of renewable biomass resources as an alternative feedstock enables more sustainable manufacturing practice.

Cellulose and starch in biomass can be transformed to HMF through a series of chemical reactions: (a) hydrolysis of glucan to glucoses, (b) isomerisation of glucose to fructose, and (c) dehydration of fructose into HMF (Fig. 1). To facilitate the tandem conversion, a wide spectrum of homogeneous and heterogeneous catalysts have been studied, including Brønsted acids (e.g., HCl, H<sub>2</sub>SO<sub>4</sub>, and Amberlyst) that favour hydrolysis and dehydration, as well as Lewis acids (e.g., AlCl<sub>3</sub>, CrCl<sub>3</sub>, and Sn-beta) that promote

isomerization (Mukherjee et al., 2015; Rout et al., 2016). Research efforts have also been made on the use of solvents, including water, polar aprotic solvents (e.g., dimethyl sulfoxide, tetrahydrofuran, and methyl isobutyl ketone) and ionic liquids (i.e., liquid salts), which serve multiple purposes such as dissolution of reactants and extraction of products (Dashtban et al., 2014).

Active investigations into these system components are still underway to address the persisting challenges that hamper the mass production of HMF. For instance, the biomass recalcitrance restricts the one-step conversion, where HMF yield was less than 50% of the cellulose content (Mirzaei and Karimi, 2016; Zhang et al., 2017). In addition, the pronounced off-path reactions that reduce the product selectivity, i.e., rehydration of HMF and polymerization between the sugars and HMF (Fig. 1), still remained as a major hurdle in the latest studies (Kreissl et al., 2016; Moreno-Recio et al., 2016; Yu et al., 2017).

A high-performance conversion system demands critical selection of the catalysts and solvents, which requires a comprehensive understanding on the success factors upfront. It has been remarked that the catalyst characteristics, e.g., active species, active sites, pore size, and surface area, determine the catalytic activity and selectivity towards the desirable intermediates and product (De et al., 2016; Delidovich and Palkovits, 2016). For solvents, properties such as partition coefficient, boiling point, and thermal stability are considered as the indication of performance and recyclability (Saha and Abu-Omar, 2014; Yi et al., 2015). While the recent reviews focus on the technological feasibility from an engineering perspective, there is a missing link between our mechanistic understanding and the performance and physiochemical properties of catalysts and solvents in different catalytic systems. Filling in this knowledge gap can inspire inventions of more productive and selective catalyst-solvent design for biomass valorization.

This review summarizes and scrutinizes the latest experimental and computational studies on the conversion of biomass and carbohydrates employing different catalysts, solvents, and operational parameters (e.g., heating methods, temperature, recycling practices, etc.). Performance of the system components as a function

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