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Production, properties and catalytic hydrogenation of furfural to fuel additives and value-added chemicals

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ABSTRACT

As our high dependence on the supply of diminishing fossil fuel reserves raise great concerns in its environmental, political and economic consequences, utilization of renewable biomass as an alternative resource has become increasingly important. Along this background, furfural as a building block, offers a promising, rich platform for lignocellulosic biofuels and value-added chemicals. These include 2-methylfuran and 2-methyltetrahydrofuran, furfuryl alcohol, tetrahydrofurfuryl alcohol, furan, tetrahydrofuran as well as various cyclo-products (e.g., cyclopentanol, cyclopentanone). The various production routes started from furfural to various fuel additives and chemicals are critically reviewed, and the current technologies for efficient production are identified. Their potential applications as well as the fuel properties of these products are discussed. Challenges and areas that need improvement are also highlighted in the corresponding area. In short, we conduct a comprehensive review of the strategies to produce furfural, new approaches and numerous possibilities to utilize furfural in industrial and laboratory sector for the production of fuel additives and value-added chemicals.

Contents

1. Introduction

Furfural, a sister chemical to 5-hydroxymethylfurfural, is one of the furan derivatives and is regaining attention as a biobased alternative for the production of everything from antacids and

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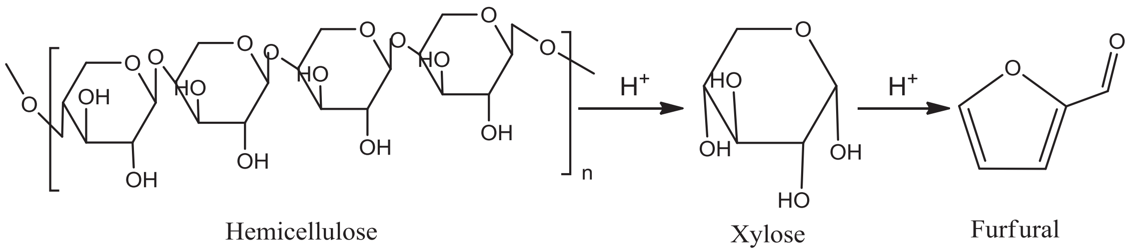

Scheme 1. Production of furfural from hemicellulose.

fertilizers to plastics and paints [1–3]. Recently, it was identified as one of the most promising chemicals for sustainable production of fuels and chemicals in 21st century proposed by Bozell et al. [4]. It is the natural dehydration product of five-carbon sugars (e.g., arabinose and xylose) that are derived from hemicellulose biomass as shown in Scheme 1 [5,6]. The first time furfural produced in relatively large amounts was at the beginning of 1922 in the USA by the Quaker Oats Company, and the consequent development of furfural industry underwent quickly and achieved a relative maturity. As of 2002, the market price of furfural was reported to be ~$1700 per ton [7]. While in the June 2011, the prices were already in the order of $2000 per ton [8]. Apart from being a valuable platform chemical derived from renewable biomass feedstocks [9,10], furfural is also the precursor for many furan-based chemicals and solvents [2,6,11–13]. With a global production of ~300 kton/y, furfural is currently the sole precursor of furyl (e.g., furfurals, furanones and furans) furfuryl (e.g., furfuryl alcohol and furfuryl acetate), furoyl (e.g., 2-furoyl chloride and furoylglycine), and furfurylidene compounds in the chemical industry [14–17]. In addition, furfural along with its sister molecule HMF, can serve as two building blocks for other potential transportation fuels including dimethylfuran and ethyl levulinate [2,6,14].

As the following sections demonstrated, furfural offers enormous prospects for the development of a biorefinery-based feedstock for future fuel additives and chemicals. It is very promising to offer a whole new class of chemicals of the furan family that can be derived from biomass feedstock, with very well established chemistry that has been comprehensively studied. This review leans on invaluable earlier reviews on furfural manufacture and upgrade, starting with the pioneered book from Dunlop and Peters [18], the book from Zeitsch [2] and numerous reviews [19–26]. For the sake of length and cohesion, we focus on our research on the technologies of chemical production and catalytic hydrogenation of furfural to yield various fuel additives and value-added chemicals.

2. Physical and chemical properties

2.1. Physical properties

Furfural, also named as 2-furaldehyde or furfuraldehyde with a molecular formula of $C_5H_4O_2$ and a molecular weight of 96.08, has an aromatic odor reminiscent of almonds [2,3]. Its exceptional physical properties make this heteroaromatic aldehyde as a selective extractant [2,3,14]: (i) to remove aromatics from lubricating oils to improve the relationship of viscosity vs. temperature, (ii) to remove aromatics from diesel fuels to improve the ignition properties and (iii) to form cross-linked polymers [27,28]. Besides, it was also used as an effective fungicide [14]. It has been reported that furfural is particularly effective in inhibiting the growth of wheat smut through killing the fungus when the wheat is soaked for 3 h in a 0.05% aqueous solution of furfural [2,3].

Table 1
General physical property of furfural [2,3].

Molecular weight	96.08
Boiling point (°C)	161.7
Freezing point (°C)	−36.5
Density at 25 °C	1.16
Refractive index, n_D	
20 °C	1.5261
25 °C	1.5235
Critical pressure Pc (MPa)	5.502
Critical temperature T_c (°C)	397
Solubility in water, wt% (25 °C)	8.3
Organic solvent (e.g., diethyl ether)	∞
Dielectric constant at 20 °C	41.9
Heat of vaporization (liquid), (kJ/mol)	42.8
Viscosity, mPa·s, 25 °C	1.49
Heat of combustion at 25 °C (kJ/mol)	234.4
Enthalpy of formation (kJ/mol)	−151
Heat of vaporization (kJ/mol)	42.8
Surface tension at 29.9 °C, (mN/m)	40.7
Explosion limits (in air) (vol%)	2.1–19.3
Flash point (°C), tag closed cup	61.7
Autoignition temperature (°C)	315

The general physical properties of furfural are given in Table 1. Due to its unique and attractive properties, it has been widely utilized as a building block for the synthesis of fine chemicals, the sustainable production of fuel additives and value-added chemicals [2,3,29–31].

2.2. Chemical properties

Furfural holds two powerful and functional groups, an aldehyde (C═O) and a conjugated system (C═C–C═C), making its role as a versatile building block for various applications. The aldehyde group (C═O) of furfural can undergo typical reactions like acetalization, acylation, aldol and Knoevenagel condensations, reduction to alcohols, reductive amination to amines, decarbonylation, oxidation to carboxylic acids, and Grignard reactions [2,9,23,31,32]. The furan ring system (C═C–C═C) can go through alkylation, hydrogenation, oxidation, halogenation, open-ring and nitration reactions [2,24,33,34]. Due to the electron-withdrawing and space effect of carbonyl group, the furan ring of furfural is less accessible to the cleavage of hydrolytic ring.

In this review, we mainly focus on the various well-studied production routes (e.g., dehydration, hydrogenation, oxidation, condensation, open-ring and decarbonyl) from furfural to fuel additives as well as value-added chemicals as shown in Scheme 2. The current technologies for their productions are identified and their potential applications as well as the fuel properties are discussed. Challenges and areas that need improvement are also highlighted.