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Furfural Production from Oil Palm Biomass Using a Biomass-derived Supercritical Ethanol Solvent and Formic Acid Catalyst

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Abstract

This research aimed to produce furfural from oil palm biomass via a biomass-derived solvent (supercritical ethanol) and catalyst (formic acid). The process is 100% biomass-based without the addition of any synthetic chemicals. Ethanol can be produced from biomass through biochemical or thermochemical conversion processes, and formic acid is a by-product of furfural production. Hence, this proposed method is self-sustainable because both can be recycled in the process. Oil palm biomass as a feedstock can address the issue of waste from the palm oil mill industries and turn it into value-added platform chemical such as furfural. In this study, various reaction parameters were evaluated including temperature (240-280°C), reaction time (1-30 min), biomass solid loading (0.4-0.8g), and alcohol: acid ratio (1:1 and 1:2), in a high-pressure and high-temperature batch reactor. The highest furfural yield of 35.8% was obtained in this study, comparable to other commercial and conventional methods. Although the formation of furfural is promoted by formic acid, the reaction temperature significantly impacted the outcome. The significant role of supercritical ethanol as both solvent and reactant may explain the minimal effect of formic acid as a catalyst in the reaction. The high yield of furfural under supercritical ethanol conditions proven in this study illustrates the great potential of this production method.

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1. Introduction

Lignocellulosic biomass has been acknowledged as a realistic alternative bioresource for the production of fuels, various intermediates, and end-product chemicals that are currently derived from non-renewable sources.

The attraction of producing platform chemicals from renewable resources such as biomass has certainly increased with the declining fossil fuel reserves and their increasing price. Cellulose and hemicellulose-derived carbohydrate compounds from biomass can be refined into various value-added products. However, the decomposition/hydrolysis reactions to produce these products are rather challenging due to the high crystallinity of cellulose and the presence of complex lignin polymer networks that formed a sheath of lignin/hemicellulose [1]. Therefore, unravelling the polymer structure of hemicellulose is vital for maximum conversion of the lignocellulosic biomass to platform chemicals.

Furfural has been identified as one of the Top 30 highest value-added bio-based chemicals by the United States Department of Energy in 2004 [2,3]. Furfural, a key compound for the production of various platform and value-added chemical additives can be derived from hemicellulose. Its tremendous potential lies in its value as a competitor with oil derivatives as platform chemicals. It can be used to produce a wide range of non-petroleum derived chemicals such as furan, tetrahydrofuran, and furfuryl alcohol, as well as in areas such as agriculture (herbicides, fungicides, insecticides), food (flavouring agents), medicine (tuberculosis remedies), pharmaceuticals, and plastics, (resins and synthetic fibres) [4]. Furfural is commercially produced through a hydrothermal process using a homogenous acid catalyst that enhances the hydrolysis of hemicellulosic pentosans in the biomass and subsequently the dehydration of the hemicelluloses sugar fragments to produce furfural [5]. In the literature, various types of agricultural residues have been used to produce furfural: olive trees [6], palm pressed fibre [7], birch wood [8], eucalyptus [9], corn cobs [10,11], date-palm trees [12], wheat straw [13], sorghum straw [14], sugar cane bagasse [15], rice husks [16], and rice straw [17]. The versatility of feedstock for furfural production demonstrated its worldwide potential where the choice of feedstocks depends on the geographical availability as well as the policy framework and support by the nation involved.

The vital role of the catalyst in the hydrolysis and dehydration has been previously established. The most widely used process in the industry, the Quaker Oats process, uses sulfuric acid as a catalyst. There are various types of homogenous and heterogeneous catalysts used in furfural production. Homogenous catalysts including mineral acids such as sulfuric acid [12], hydrochloric acid [18], phosphoric acid [14], and nitric acid [19] have been widely reported as efficient catalysts for commercial furfural production. However, these expensive mineral acids catalysts cause the corrosion of pipelines and valves at high temperatures, safety issues, and environmental issues due to hazardous waste effluents. Mineral acids led to undesirable side reactions due to the severe acidity. Therefore, an improvement on the process is needed with the aim to eliminate these complications. Few studies using organic acids to replace mineral acids such as formic acid [13] and acetic acid [15] have been done. Weaker organic acids selectively hydrolyse only the weaker bonds in the hemicellulosic fraction, leaving the cellulose and lignin structures unaltered. In addition, the use of organic acids such as formic acid is an especially attractive and feasible option in an integrated biorefinery because formic acid is one of the by-products during furfural production from the cleavage of the formyl group or the hydrolytic fission of the aldehyde group of furfural. Thus, it is readily available in the process. Formic acid can be recovered from the reaction medium after the reaction via thermal operation, and the waste-producing neutralization of mineral acids can be avoided [20].

Ethanol, a biomass-derived solvent produced from next generation biomass feedstocks through biochemical or thermochemical processes has tremendous potential in furfural production especially under supercritical conditions, as an effective medium in biomass liquefaction [21-24]. The chemical and physical properties of supercritical fluids vary from gas-like to liquid-like by manipulating its temperature and density, which affects its ionic product and dielectric constant has led to increased attention regarding its use as a reaction medium, especially in the gasification and liquefaction of biomass. Ethanol has a critical temperature of 244 °C and critical pressure of 6.38 MPa, considerably lower than other biomass-derived solvents, thereby offering milder conditions for the reaction [25]. Under these conditions, it can dissolve non-polar organic substances. This is extremely advantageous in biomass reactions because supercritical ethanol can readily dissolve and breaks the linkages between lignin and hemicellulose, thus rendering them accessible for acid-catalysed hydrolysis.

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