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Highly selective synthesis of biomass-based 1,4-butanediol monomer by alcoholysis of 1,4-diacetoxybutane derived from furan

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ABSTRACT

Biomass-based 1,4-butanediol (BD) was produced with high selectivity from diacetoxybutane (DAB) and alcohol using a $KHSO_4$ catalyst, which could be recycled. The DAB used in this reaction could be produced from furan, which, in turn, can be easily produced from furfural. The conversion of furfural to BD was carried out under mild conditions such as low H_2 pressure (0.69 MPa). These processes produce not only tetrahydrofuran (THF) but also alkyl esters, which are industrial important chemicals. Alkyl esters are alternatives to benzene, toluene and xylene (BTX) solvents. It was confirmed that the BD synthesized in this paper was entirely biobased because its biobased carbon content was 99.63%, as determined by accelerator mass spectrometry based on ASTM D6866.

1. Introduction

The production of chemicals from biomass resources is a very important element of the effort to switch away from petroleum consumption. Decreasing petroleum consumption is desirable for conserving limited resources and preventing global warming. In addition, the diversification of supply sources and the development of renewable resources are expected to contribute to a more sustainable human economy and society.

Chemicals such as monomers for many kinds of polymers are produced from naphtha, which is derived from petroleum. Many chemicals (C4 families) are produced from key materials such as succinic acid or 1,4-butanediol (BD) that is obtained from butadiene in petrochemical industries. BD is a monomer of poly(butylene terephthalate), which is an engineering plastic, and also of poly(-butylene succinate), which is a biodegradable plastic [1–3]. BD is used entirely as a precursor for other C4 chemicals such as monomers and solvents. Its principal derivatives are tetrahydrofuran (THF), butyrolactone, and pyrrolidinone, which are very useful solvents. THF can be polymerized to poly(tetra methylene ether glycol) (PTMEG).

Currently, the price of C4 fossil-based chemicals such as butadiene is increasing due to increased demand for synthetic rubber in developing countries. In addition, the conversion of ethylene derived from the cracking of naphtha, which produces butane and butadiene as by-products to shale- or off-gas, is doing globally. Therefore, the resource diversification of C4 monomers such as BD becomes important. The production of biomass-based BD has already been studied. Genomatica (San Diego, USA) used genetically engineered *E. coli* to metabolize sugar into BD [4]. Genomatica expects the first commercial-scale BD plant in Europe to produce approximately 40 million pounds of BD per year using fermentation processes. The production of biomass-based BD by the hydrogenolysis of erythritol that is fermented from glucose has also been studied [5]. The maximum selectivities for 1,4- and 1,3-BDs from erythritol on Ir-ReO_x/SiO_2 catalyst reached 33% and 12%, respectively at 74% conversion.

We have previously studied the syntheses of C4 chemicals such as succinic acid and BD from furfural [3]. In that work, we reported the production of the first fully biomass-based poly(-butylene succinate) from furfural. Furfural is derived from a variety of agricultural by-products or wastes, including corncobs, oat, wheat bran, and sawdust. For crop residue feedstocks, about 10% of the mass of the original plant matter can be recovered as furfural [6]. The formation of BD from furfural proceeds via the formation of fumaric acid, as indicated in Scheme 1 [3]. However,

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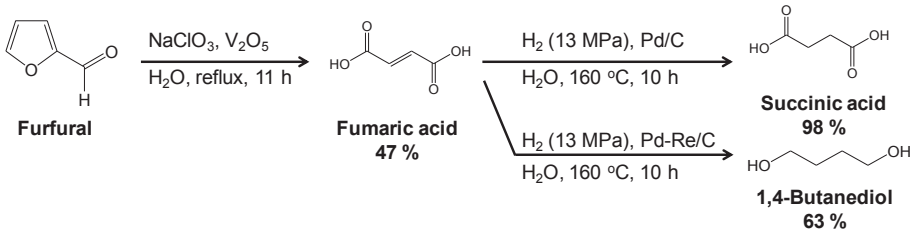
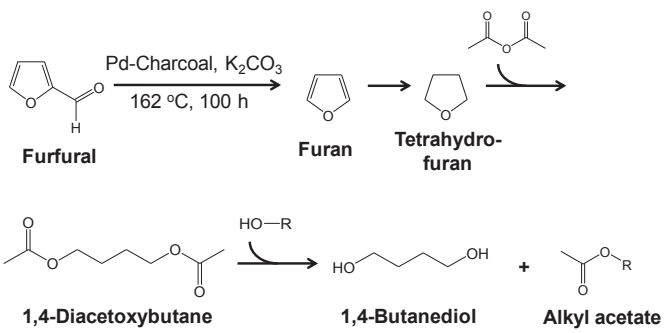


Scheme 1. Succinic acid and 1,4-butanediol (BD) as biomass monomers synthesized via fumaric acid from furfural [3].

some reaction conditions shown in this scheme need to be improved. For example, the very high pressure of hydrogen (13 MPa) that is required for the reaction hinders the commercialization of this reaction due to the higher operation costs and safety issues involving the reaction facilities. In addition, some researches have been studied from furan to biobased BD or other chemicals [7,8].

In this paper, a series of chemical reactions from furfural to BD occurring at mild conditions with higher yields have been studied (Scheme 2). Crucially, there are no chemical reactions in this reaction scheme that requires high hydrogen pressure. Biobased furan was used as received from Wako Pure Chemical Industries (Osaka, Japan). We confirmed that this furan was biobased according to standard ASTM D6866 (American Society for Testing and Materials), as explained below [9]. The conversion from furfural to furan is a simple reaction [10,11]. In this paper, the chemical reaction pathway from 1,4-diacetoxybutane (DAB) to BD using a new alcoholysis process has been studied in detail to obtain a higher yield of BD with useful by-products such as the environmentally friendly solvent, alkyl acetate.

This alcoholysis process co-produces alkyl acetates such as ethyl acetate, propyl acetate or butyl acetate depending on the type of alcohol reacted. These alkyl acetates can act as BTX solvent (benzene-toluene-xylene) substitutes. There are some established industrial processes for the synthesis of BD from petroleum [12]. The Mitsubishi Chemical Company uses hydrolysis in the presence of a solid acid catalyst to convert DAB to THF with the formation of BD as a by-product, as indicated in Scheme 3. However, the specific yield of BD in these processes is not so high being 50–90% [13]. In the case of the yield over 70%, much amount of water (25–50 times to DAB) should be added to the reaction system, then the production cost of BD becomes to be high due to the bigger reactor size. In this process, DAB is hydrolyzed to BD and 1-acetoxy-4-hydroxybutane (AB) in the presence of a solid acid catalyst. Then, AB is converted to THF, which is a useful industrial chemical. In addition, the ratio of BD to AB can be controlled by reaction conditions to obtain the desired amount of BD and THF.



Scheme 2. BD synthesized via tetrahydrofuran (THF) from furfural as described in this paper.

However, this hydrolysis process is not suitable for our conversion process of DAB to BD. This is because THF formed as a by-product during DAB production in this reaction represents waste; however, THF is formed as an intermediate in our process as indicated in Scheme 2.

The comparison of biomass-based products with fossil-based products is very important for the obtained chemicals in this paper. In some cases, a synthesized molecule can comprise both biomass- and fossil-based units. The biobased carbon content can be estimated from the concentration of carbon-14 as measured by accelerator mass spectrometry (AMS) based on ASTM D6866 [14–18].

In this paper, biomass-based BD has been produced from furan that is derived from furfural. This process produces THF and alkyl acetate as by-products, both of which are important industrial chemicals. In addition, the biobased carbon content of the obtained BD was confirmed based on the ASTM D6866 method.

2. Experimental section

2.1. Materials

Furfural and furan were purchased from Wako Pure Chemical Industries (Osaka, Japan) and used after distillation under reduced pressure and N_2 atmosphere. This furan was confirmed to be completely biobased as indicated in Table 3 [18]. Other chemicals were reagent grade and were used without further purification.

2.2. Hydrogenation of furan to THF

Furan (39.6 g, 0.58 mol) was hydrogenated by palladium oxide (1.1 g, 8.9 mmol) to THF under 0.69 MPa H_2 pressure (Hydrogen generator, H_2PEM-100, Perker) in a 200 mL stainless autoclave at 25–45 °C for 16 h [19]. A transparent liquid was obtained after removing the catalyst by filtration. The yield of THF from furan was 80.9% as determined by GC. Purified THF was obtained from the reactant liquid by distillation under N_2 atmosphere.

2.3. Synthesis of DAB from THF and acetic anhydride

Sulfuric acid (34.1 g, 0.35 mol) was added to acetic anhydride (108 g, 1.06 mol) in a 4-neck 200 mL glass round-bottle flask equipped with a dropping funnel, thermometer, and condenser. The solution was continuously stirred by a Teflon stirrer bar at 20–22 °C [20]. Then, THF (25.1 g, 0.348 mol) was added to the reactant, and the mixture was maintained at 20–22 °C for 20 min. The reaction was carried out with stirring at 21–23 °C for 20 h. The obtained reactant liquid was added to 500 mL of deionized water. DAB was extracted from this aqueous solution using 500 mL of chloroform and dried by the addition of anhydrous sodium sulfate. Purified DAB (51.34 g, 0.30 mol) was obtained from dried chloroform solution by distillation under reduced pressure. The yield of DAB from THF was 84.8%.

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