

Facile and Efficient Conversion of Furfuryl Alcohol into *n*-Butyl Levulinate Catalyzed by Extremely Low Acid Concentration

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Alkyl levulinates have been identified as promising chemicals with various industrial applications. Here, a catalytic process for the synthesis in an *n*-butanol medium of *n*-butyl levulinate *via* the alcoholysis of biomass-derived furfuryl alcohol was performed using an extremely low concentration of sulfuric acid (≤ 0.01 M) as the catalyst. A study was conducted that was designed to optimize the process variables, which include acid concentration, reaction temperature, initial substrate concentration, and water content, as a function of time. The optimum conditions resulted in a furfuryl alcohol conversion of nearly 100% and a high *n*-butyl levulinate yield of up to 97%, which was confirmed by isolated yield. An advantage of this catalyst system is that negligible undesired oligomeric products were formed from the side reaction for the polymerization of furfuryl alcohol, the catalyst cost is low, and less solid waste was discharged from the neutralization of spent acid. Overall, this catalytic strategy is a facile, efficient, and economical approach to the conversion of biomass-derived furfuryl alcohol into alkyl levulinates.

Keywords: Furfuryl alcohol; Alkyl Levulinates; Extremely low acid; *n*-Butanol

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INTRODUCTION

Given the gradual depletion of fossil fuel resources and the progressive decline in the health of the environment, much effort has been devoted to the development of attractive chemical or biological means for converting the abundant renewable biomass into transportation fuels and industrial chemicals that can serve as replacements for petroleum-based products. Among these efforts, the preparation of alkyl levulinates has recently attracted attention (Peng *et al.* 2012a; Su *et al.* 2013). The synthesis of alkyl levulinates from lignocellulosic biomass can be accomplished using the hexoses in cellulose and the pentoses in hemicelluloses and processing *via* various catalytic routes. The production of alkyl levulinates from hexoses is an integrated process involving either a series of acid-catalyzed alcoholysis reactions, or involving acid hydrolysis followed by esterification of the resulting acid using an alcohol (Peng *et al.* 2011; Yadav and Yadav 2014). In contrast, production from pentose begins with a dehydration reaction that produces furfural, followed by hydrogenation to form furfuryl alcohol, which is then converted into alkyl levulinates through acid-catalyzed alcoholysis (Le Van Mao *et al.* 2011; Neves *et al.* 2013). Alkyl levulinates are known to have widespread applications in the fragrance and the flavor industries and as additives for diesel and biodiesel transportation fuels (Hayes 2009; Windom *et al.* 2011; Wang *et al.* 2012). Additionally,

alkyl levulinates are a class of versatile building blocks that can be used for the synthesis of different chemicals and drugs *via* chemical reactions at the ester and keto groups (Shen *et al.* 2009; Yang *et al.* 2013).

Hemicellulose, the second most abundant type of polysaccharides in nature, constitutes about 20 to 35% of the lignocellulosic biomass. During the production of alkyl levulinates from hemicelluloses, one of the key steps is the conversion of furfuryl alcohol to alkyl levulinates (Mamman *et al.* 2008; Neves *et al.* 2013). To develop an economically feasible process for future industrial applications, the identification of a proper acid catalyst for the conversion of furfuryl alcohol to alkyl levulinates is of great importance and has become one of the focuses of study. Traditionally, dilute mineral acids such as H₂SO₄ and HCl (0.1 to 0.5 M) have been employed as effective catalysts in this reaction. However, it was found that furfuryl alcohol readily polymerizes to form oligomeric products in the presence of dilute mineral acids, thus giving rise only to a moderate yield of alkyl levulinates. Besides, the use of dilute mineral acids usually leads to objectionable corrosion of the equipment and environmental pollution (Van De Graaf and Lange 2007; Bertarione *et al.* 2009).

Recently, several novel heterogeneous catalysts were successively developed. For instance, the study of Lange *et al.* (2009) reported the possibility to convert furfuryl alcohol to ethyl levulinate using various acidic ion-exchange resins and zeolites by slowly feeding the furfuryl alcohol to the reaction medium. It was found that macroporous resins are more active in producing ethyl levulinate, and acidic zeolites such as H-ZSM-5 also catalyze this reaction but with a lower activity. Several authors (Zhang *et al.* 2011; Hengne *et al.* 2013; Wang *et al.* 2014; Demma Carà *et al.* 2014) presented efficient catalytic strategies for the conversion of furfuryl alcohol into alkyl levulinates using solid acid catalysts such as organic-inorganic hybrid material, sulfonic acid functionalized ionic liquids, and propylsulfonic acid-functionalized mesoporous silica. It should be pointed out that these catalysts are costly due to their complex synthetic technique. Neves *et al.* (2013) and Zhao *et al.* (2014) studied the catalytic performance of several commercial and as-synthesized solid acid catalysts in the reaction of furfuryl alcohol with ethanol, and the optimized yields of ethyl levulinate in 80% and 74.6% could be obtained over porous aluminosilicate and sulfated oxides, respectively. In a practical application, the recycling of solid acid catalyst must be considered. Although it can be easily separated from the reaction products, the catalytic activity of a recovered catalyst of this type is usually reduced significantly if it goes untreated before repeated use due to the adsorption of formed oligomeric products on the solid acid surface and the gradual loss of acid sites.

In recent years, the concept of an extremely low acid concentration (≤ 0.01 M) has attracted considerable interest for its potential application in the process of degrading lignocellulosic biomass with the goal of producing sugar or other fine chemicals, where it offers the advantages of relatively less corrosion to equipment (Peng *et al.* 2012b), minimal environmental impact as less solid waste formed from the subsequent neutralization of spent acid, and low cost of the catalyst (Kim *et al.* 2001; Ojumu *et al.* 2003; Zhuang *et al.* 2010). Thus, the use of extremely low concentrations of acid also qualifies as a “green technology.” The aim of this study was to investigate the possibility of using an extremely low sulfuric acid concentration to catalyze the conversion of biomass-derived furfuryl alcohol into alkyl levulinates. Here, *n*-butanol was selected as the reaction medium for the synthesis of *n*-butyl levulinate. The composition of the

reaction products was identified by GC-MS, and the reaction pathway for the alcoholysis of furfuryl alcohol was thus considered. The effects of multiple process parameters, including acid concentration, reaction temperature, initial substrate concentration, and water content, on catalytic performance were studied as a function of time to optimize the yield of *n*-butyl levulinate. Finally, the obtained *n*-butyl levulinate was isolated from the resulting product mixture for the alcoholysis of furfuryl alcohol.

EXPERIMENTAL

Materials and Chemicals

Furfuryl alcohol (98% purity) and *n*-butyl levulinate (98% purity) were purchased from Aladdin Reagent (Shanghai, China), and methyl levulinate (99% purity) was purchased from Alfa Aesar (Tianjin, China). Ethanol (99.9% purity), *n*-butanol (99.5% purity), and sulfuric acid (98% purity) were obtained from Merck KGaA (Darmstadt, Germany), Sichuan Xilong Chemical Industry Co., Ltd. (Chengdu, China), and Chengdu Kelong Chemical Co., Ltd. (Chengdu, China), respectively. All chemicals were directly used without further purification or treatment.

Experimental Procedure

Furfuryl alcohol was used as the starting material in this study. Either *n*-butanol or a mixture of water and *n*-butanol was employed as the reaction medium, and an extremely low concentration of sulfuric acid (≤ 0.01 M) was selected as the catalyst. For each experiment, selected amounts of furfuryl alcohol, *n*-butanol solution of H₂SO₄, and water were mixed into a 100-mL round-bottom flask equipped with a reflux condenser. The above mixture was then brought to the desired temperature *via* oil-bath heating and was continuously stirred at 800 rpm with a magnetic stirrer. The experiments were conducted within a sulfuric acid concentration range of 0.001 to 0.01 M, within a temperature range of 90 to 120 °C, within an initial furfuryl alcohol concentration range of 0.1 to 2.0 M, within a water content range of 0 to 10%, and within a reaction time range of 0 to 8 h. After running the reaction for a desired duration, the sample (0.5 mL) was withdrawn by the intermittent sampler, diluted with an ethanol solution containing the internal standard of methyl levulinate (1 g/L), and then analyzed.

Products Analysis

The composition of liquid-phase products was analyzed using a GC-MS (Agilent 6890 GC system coupled with an Agilent 5975 mass detector) with a DB-5 capillary column (30.0 m \times 320 μ m \times 0.25 μ m) and a flame-ionization detector (FID) operating at 250 °C. The injection port temperature was 250 °C. The oven temperature was programmed from 60 °C to 90 °C (6 min) at a heating rate of 5 °C/min, then to 190 °C (5 min) at a heating rate of 20 °C/min. The reactant and products were quantified by GC data, based on the internal standard method. The amounts of furfuryl alcohol and *n*-butyl levulinate were determined using calibration curves obtained by analyzing their standard solutions with a known amount. The 2-(butoxymethyl)furan identified by GC-MS is not commercially available, and its amount was calculated using calibration data of *n*-butyl levulinate while assuming a similar carbon response factor. *n*-Butyl levulinate yield was defined as the M of *n*-butyl levulinate obtained per M of furfuryl alcohol in the feed.

RESULTS AND DISCUSSION

Reaction Products and Pathway

The liquid-phase composition that was produced by the reaction was analyzed using GC and GC-MS, and a typical example of a GC chromatogram is given in Fig. 1a. Several distinct substances were detected in the liquid-phase, namely ethanol, *n*-butanol, furfuryl alcohol, methyl levulinate, 2-(butoxymethyl)furan, and *n*-butyl levulinate. Among these, 2-(butoxymethyl)furan and *n*-butyl levulinate were the two major products from the alcoholysis of furfuryl alcohol. The furfuryl alcohol and *n*-butanol were unreacted reactants. The ethanol and methyl levulinate acted as the diluting agent and internal standard, respectively, for analysis. Figure 1b shows a typical concentration profile of reactants and products as a function of the reaction time. One can observe that the concentration of furfuryl alcohol dropped swiftly, and it was almost more than 98% consumed within the relatively short time of 3 h. The amount of 2-(butoxymethyl)furan was slightly higher during the initial stage of the reaction, but later decreased. With the prolonging of reaction time, the concentration of *n*-butyl levulinate gradually increased.

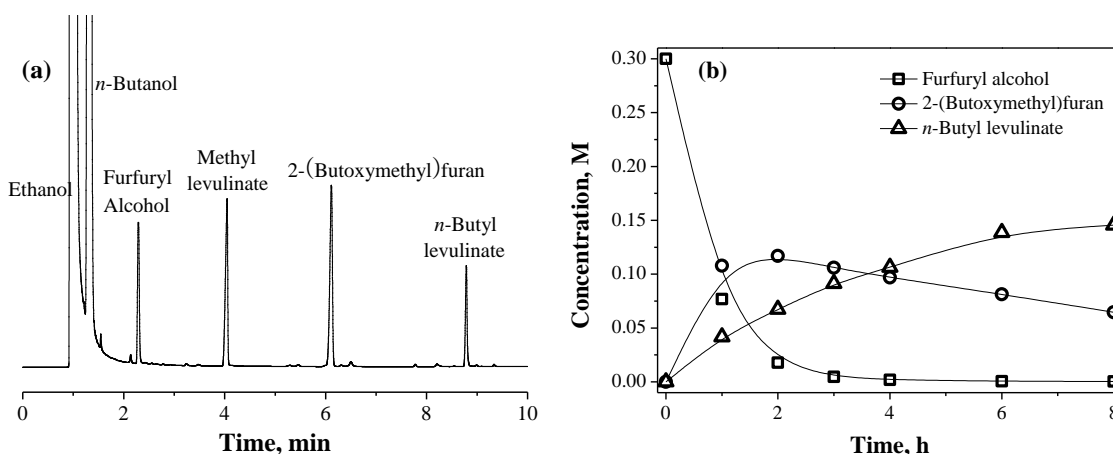
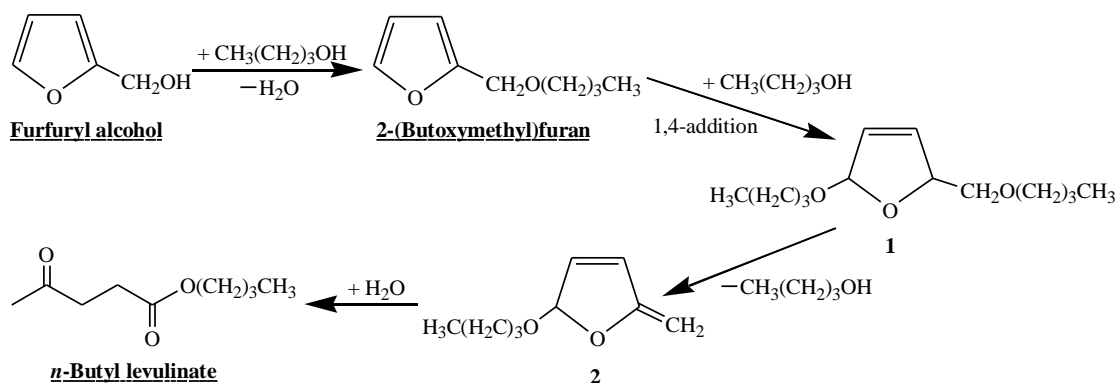


Fig. 1. Typical gas chromatogram (a) and concentration profile (b) for the conversion of furfuryl alcohol under extremely low sulfuric acid. Reaction conditions: furfuryl alcohol concentration, 0.3 M; sulfuric acid concentration, 0.005 M; temperature, 110 °C

There have been several reports on the mechanism of furfuryl alcohol alcoholysis into alkyl levulinates. Zhang *et al.* (2011) maintain that the reaction of furfuryl alcohol with alcohols to form alkoxyethylfuran is an important step for the possible reaction pathway. The further investigation of Maldonado *et al.* (2012) indicates that conversion of furfuryl alcohol to alkyl levulinates takes place by multiple pathways. The primary pathway involves solvent-assisted transfer of a water molecule from the partially detached protonated hydroxyl group of furfuryl alcohol to a ring carbon, followed by intra-molecular hydrogen shift. In our present study, 2-(butoxymethyl)furan was found to be a key intermediate during the conversion of furfuryl alcohol to *n*-butyl levulinate, which is compatible with the results of Zhang *et al.* (2011). Here, a simplified possible reaction pathway is given in Scheme 1. In the initial step, furfuryl alcohol reacts with *n*-butanol by means of intermolecular dehydration to form the key intermediate 2-(butoxymethyl)furan. Then, the intermediate 1 is generated via a 1,4-addition.

Subsequently, the discharge of *n*-butanol results in the next intermediate 2, which can be further dehydrated to *n*-butyl levulinate under the reaction conditions. Regarding this pathway, the findings from Fig. 1b also imply that the conversion of the key intermediate 2-(butoxymethyl)furan to *n*-butyl levulinate is more arduous and complex than the conversion of furfuryl alcohol to 2-(butoxymethyl)furan. It could be concluded that the decomposition of 2-(butoxymethyl)furan is crucial to the final yield of *n*-butyl levulinate. During the experiments, dark-brown insoluble substances known as oligomeric products, which result from side-reactions of the acid-catalyzed alcoholysis of furfuryl alcohol, were observed. Fortunately, however, the quantity of the oligomeric products was relatively low, indicating that the polymerization of furfuryl alcohol can be inhibited to some extent in the presence of an extremely low acid concentration.



Scheme 1. Possible reaction pathway for the conversion of furfuryl alcohol into *n*-butyl levulinate under extremely low sulfuric acid concentrations

Effect of Acid Concentration

An extremely low concentration of sulfuric acid (≤ 0.01 M) was applied as an acid catalyst for the conversion of furfuryl alcohol to *n*-butyl levulinate. The comparison was carried out using 0.1 M of dilute sulfuric acid as the catalyst. Figure 2a illustrates the effects of sulfuric acid concentrations ranging from 0.001 to 0.1 M on the yield of *n*-butyl levulinate given various different reaction times while the temperature was held constant at 110 °C. As can be seen from extremely low concentration of sulfuric acid, the yield of *n*-butyl levulinate was increased when higher acid concentrations were employed. This influence was remarkable, and after 8 h the yield of *n*-butyl levulinate had increased from 45 to 78% with the increase in acid concentration from 0.001 to 0.005 M. When the sulfuric acid concentration was 0.001 M, the yield increased almost linearly but gently with the extension of the reaction time. This implied that an acid concentration of 0.001 M did not offer enough acid sites for the synthesis of *n*-butyl levulinate during a short reaction time, which gave rise to a low reaction rate. When the acid concentration was further increased to 0.01 M, the conversion took place at a faster rate, but the final yield of *n*-butyl levulinate was slightly higher compared with that for 0.005 M sulfuric acid. Similar results have also been observed for cellulose hydrolysis (Zhuang *et al.* 2010) and for the alcoholysis of glucose into methyl levulinate (Peng *et al.* 2012b) using extremely low concentrations of acid. When the sulfuric acid concentration of 0.1 M, the yield of *n*-butyl levulinate grew significantly with reaction time, and the equilibrium point was reached in 1 h. However, the equilibrium yield seems to be lower than that with the

extremely low concentration of sulfuric acid, and the color of reaction mixture became darker with brownish black, indicating that the side reaction about the polymerization of furfuryl alcohol to form oligomeric products had increased. From this it can be judged higher acid concentrations are less preferable, since such conditions tend to result in the more rapid polymerization of furfuryl alcohol and the greater consumption of base for subsequent neutralization. The most reasonable sulfuric acid concentration for use in further investigation can be set at around 0.005 M.

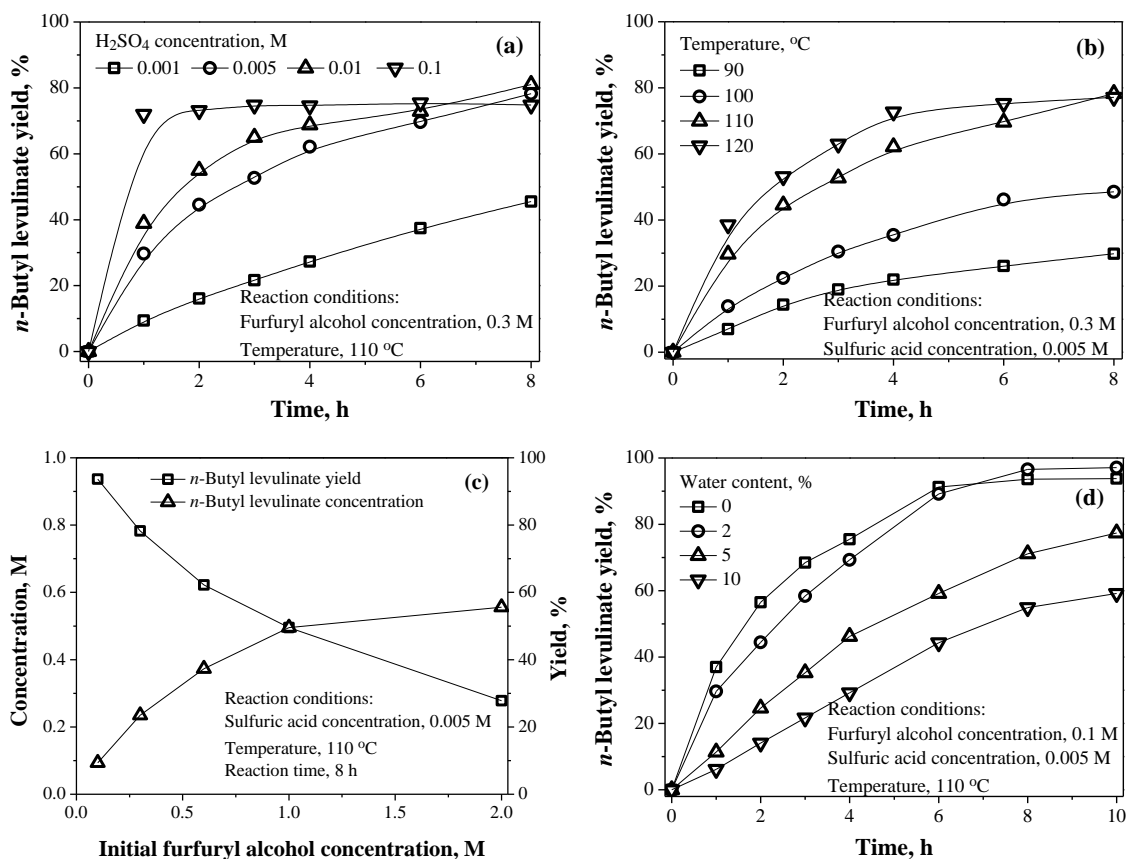


Fig. 2. Effects of sulfuric acid concentration (a), reaction temperature (b), initial furfuryl alcohol concentration (c), and water content (d) on the conversion of furfuryl alcohol into *n*-butyl levulinate

Effects of Reaction Temperature

The effects of reaction temperature as a function of reaction time on the yield of *n*-butyl levulinate were investigated with the aim of finding the optimum conditions. The experiments were carried out at 90, 100, 110, and 120 °C, respectively. It can be observed from Fig. 2b that temperature played an important role in the reaction process. High temperature was able to accelerate the rate of chemical reaction as well as enhance the yield of *n*-butyl levulinate. When the temperature was increased from 90 to 110 °C for the same reaction time, the yield of *n*-butyl levulinate grew significantly. The yield was observed to rise slightly over 110 °C after 8 h of reaction time. At lower temperatures such as 90 and 100 °C, the yield of *n*-butyl levulinate improved smoothly with reaction time, which may have been because the reaction needed more time to reach the equilibrium conversion. When the temperature was increased to 110 °C, the yield of *n*-

butyl levulinate increased very rapidly at the beginning of the reaction, and the equilibrium point had almost been reached by 8 h of reaction, with an *n*-butyl levulinate yield of around 80%. When the temperature was further increased to 120 °C, the production took place at a faster rate, but the final yield of *n*-butyl levulinate did not change substantially compared with that for 110 °C. The impact of temperature was thus similar to that of acid concentration.

Effects of Initial Substrate Concentration

The optimal concentration of substrate is crucial for the efficient use of furfuryl alcohol material and for the final concentration of *n*-butyl levulinate. Figure 2c shows the effects of initial furfuryl alcohol concentration, ranging between 0.1 and 2 M, on the concentration and yield of *n*-butyl levulinate. It was found that the yield of *n*-butyl levulinate dropped significantly with the increase in initial furfuryl alcohol concentration, implying that the substrate inhibited kinetics substantially. The production rate and selectivity of *n*-butyl levulinate decreased as the initial furfuryl alcohol concentration was increased. When the initial furfuryl alcohol concentration was 0.1 M, the yield of *n*-butyl levulinate reached a maximum of 94% within 8 h. However, the concentration of *n*-butyl levulinate in the reaction system was fairly low, at about 0.09 M. In practical applications a higher concentration is desired not only because it can enhance the production efficiency of *n*-butyl levulinate, but also because it can cut down on the energy consumption that occurs during the purification of the product. When the initial furfuryl alcohol concentration was increased from 0.1 to 1.0 M, the concentration of *n*-butyl levulinate rose significantly, from 0.09 to 0.5 M, but the yield of *n*-butyl levulinate was found to decrease. When the furfuryl alcohol concentration was further increased to 2.0 M, only a slight increase in *n*-butyl levulinate concentration was observed, indicating that furfuryl alcohol was not fully utilized. The reason for this incomplete utilization was probably due to product feedback inhibition and reactivity diminution. Therefore, compromises have to be made with regards to the concentration and yield of *n*-butyl levulinate for practical usage to reduce production cost. Higher and lower substrate concentrations are unfavorable conditions for the application of this technology.

Effect of Water Content

Because the reaction of furfuryl alcohol with *n*-butanol to form the intermediate 2-(butoxymethyl)furan is the first step in the process, minimal water can be produced during this reaction. Moreover, the right amount of water is also required for the conversion of the intermediate into *n*-butyl levulinate, as shown in Scheme 1. It was proposed that water might have some effect on the alcoholysis of furfuryl alcohol. Therefore, a control experiment was conducted by varying the volume percentage of water in the reaction system, the results of which are plotted in Fig. 2d. When the water content of the system was 2%, the reaction rate, when observed at the early stage of 4 h, was slightly slower than that for the reaction system without added water. However, it was interesting to observe that after the completion of the reaction at 8 h, a slightly higher yield of *n*-butyl levulinate, up to 97%, was obtained for the 2% water condition, in comparison to that of 94% achieved without water. One explanation for why that amount of water at the early stage of the reaction was enough, or even more than enough, for the production of *n*-butyl levulinate is that the conversion of furfuryl alcohol to the intermediate is a rapid process, and the addition of a moderate amount of water can

promote the degradation of the intermediate to *n*-butyl levulinate at the latter stage because water is gradually consumed as the reaction progresses. When water was added in excess of 5%, the yield of *n*-butyl levulinate was noticeably decreased, and part of furfuryl alcohol had probably been reacting with the water to form levulinic acid. Thus, the product mixture was analyzed by ion chromatography (IC) equipped with an IonPac AS11-HC analytical column and a conductivity detector. Results showed that the yield of levulinic acid for the water content of 5% and 10% were ca. 8% and 23%, respectively. In this case of high water content in the *n*-butanol medium, the reaction of furfuryl alcohol became subject to the competing processes of alcoholysis and hydrolysis.

Isolation of *n*-Butyl Levulinate

Under the optimum conditions of furfuryl alcohol concentration 0.1 M, sulfuric acid concentration 0.005 M, water content 2%, reaction temperature 110 °C, and time 8 h, a small-scale experiment with the total volume of 1000 mL was conducted in the production of *n*-butyl levulinate from the alcoholysis of furfuryl alcohol. It was found that the yield of *n*-butyl levulinate determined by GC was consistent with the above optimized yield of around 97%. Further, the obtained *n*-butyl levulinate was isolated from the resulting product mixture. The mixture was neutralized and dehydrated firstly with calcium oxide, then filtered to separate the liquid and solid samples. It is clear that the only a small amount of calcium oxide was required, and less solid waste was generated for per unit volume of reaction mixture during this process. Based on their distinctly different boiling temperatures, the liquid sample was isolated by a distillation technique that combines an atmospheric distillation with a vacuum distillation. Low boiling substances (mainly *n*-butanol) was separated out firstly by atmospheric distillation at 120 °C. Next, the residual component was isolated by vacuum distillation at 190 °C while the fraction of 9.5 g was collected. The fraction contained *n*-butyl levulinate of about 98% by GC analysis, the corresponding isolated yield of *n*-butyl levulinate in ca. 95% was obtained, which can provide a valid support for the GC yield reported in this work.

CONCLUSIONS

1. 2-(Butoxymethyl)furan was found to be a key intermediate during the conversion of furfuryl alcohol to *n*-butyl levulinate, and the transformation of the intermediate to *n*-butyl levulinate is much slower and more difficult than that of furfuryl alcohol to the intermediate.
2. An acid concentration of 0.005 M was able to offer enough acid sites for the completion of the reaction. The formation of *n*-butyl levulinate was favored in the initial dilute furfuryl alcohol concentration at a moderate temperature. The addition of a small amount of water was able to slightly promote the production of *n*-butyl levulinate. Under the optimal conditions, a high *n*-butyl levulinate yield of 97% was achieved, which was also confirmed by isolated yield.
3. The optimum yield of alkyl levulinates using extremely low concentration of sulfuric acid was equal to or even surpassed those previously obtained by dilute mineral acid and solid acid catalysts. Moreover, this catalytic strategy presents several advantages including the formation of negligible undesired oligomeric products from the

polymerization of furfuryl alcohol, low catalyst cost, and the discharge of less solid waste due to minimization of subsequent neutralization of spent acid.

ACKNOWLEDGEMENTS

The authors are grateful to the financial support from the Applied Basic Research Program of Yunnan Province (2013FD007), the Natural Science Foundation and Analysis Testing Foundation of Kunming University of Science and Technology (KKSJ201305021, 20140816), the State Key Laboratory Open Foundation of Pulp and Paper Engineering of China (201225), and the kind support from the Committee of the 4th Conference on Biorefinery towards Bioenergy (ICBB2013) in Xiamen, China.

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Article submitted: January 6, 2014; Peer review completed: April 12, 2014; Revised version received and accepted: May 3, 2014; Published: May 8, 2014.