

Efficient alcoholysis of furfuryl alcohol to *n*-butyl levulinate catalyzed by 5-sulfosalicylic acid

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Abstract

It is urgent to study the utilization of biomass energy to solve the environmental problems caused by the excessive use of fossil fuels. In this study, a rapid and efficient route for the conversion of furfuryl alcohol (FA) into *n*-butyl levulinate (BL) has been catalyzed by 5-sulfosalicylic acid. The nearly complete conversion of FA and a considerable 99.7% selectivity of BL are obtained under the optimal conditions. Based on the experimental results, a possible mechanism for the alcoholysis of FA is proposed. The present study provided a promising way for alkyl levulinates synthesis over economical and environmentally benign catalysts.

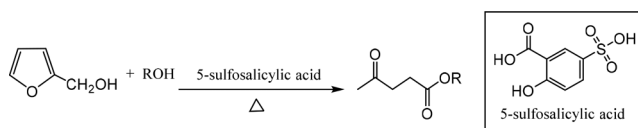
KEYWORDS

5-sulfosalicylic acid, alcoholysis, alkyl levulinates, catalysis, furfuryl alcohol

1 | INTRODUCTION

The gradual depletion of fossil fuel resources has stimulated the global efforts to convert abundant and renewable biomass resources into high value-added chemicals in the last decades.^[1] Alkyl levulinates, which have been identified as one of the top 10 biorefinery candidates, are known to have widespread applications, for example, as plasticizing agents, solvents, odorous substances, and fuel additives.^[2,3] In addition, alkyl levulinates contain two functional groups (a ketone group and an ester group),

which make them versatile building blocks for the synthesis of various chemicals and pharmaceuticals.^[4,5] Generally, alkyl levulinates are mainly obtained by direct esterification of levulinic acid (LA) with the corresponding alkyl alcohol in the presence of acid catalysts.^[6] However, the separation and purification in the production of LA are costly, which made it unsuitable as the raw material for this purpose.^[7] Consequently, efforts were devoted to the development of new methods to produce alkyl levulinates directly from widely available and economical sources such as cellulose,^[8] carbohydrates,^[9–12]



SCHEME 1 Conversion of FA into alkyl levulinates over 5-sulfosalicylic acid

furfural,^[13,14] and furfuryl alcohol (FA).^[15–21] Among them, FA is a preferred raw material due to its easy accessibility from furfural and high reactivity for the alcoholysis reaction to produce alkyl levulinate.^[18] Thus, the development of a feasible and competitive pathway for FA upgrading is strongly demanded.

It was found that FA alcoholysis with alcohol to produce alkyl levulinates is influenced by the acid site density, strength, and accessibility of active sites to reactants.^[19,22] Up to date, various homogenous or heterogeneous catalysts including ion-exchange resins,^[15] organosilica nanotubes,^[16] salts,^[18–20] oxides,^[21,23] ionic liquids,^[7,24] and zeolites^[25,26] have been concretely investigated. For example, Zhang et al. reported several organic–inorganic hybrid solid acids for the alcoholysis of FA and reached a high ethyl levulinate yield of 93%.^[17] Shyam and coworkers studied a sulfonic acid-functionalized hafnium-based MOF, as an efficient solid acid catalyst for the alcoholysis of FA and esterification of LA affording alkyl levulinates.^[1] However, several defects of these above-mentioned catalysts, such as the complex preparation process, the cost, environmental concerns, limited their applications to some extent.^[3] Accordingly, the development of a more cheap, facile, stable, and efficient catalyst system for the alcoholysis of FA to produce alkyl levulinates is still a challenge.

Herein, we wish to present a practical protocol, where a simple aromatic acid, 5-sulfosalicylic acid was selected as a sole catalytic component to promote alcoholysis of FA to alkyl levulinates with excellent conversion and decent selectivities (Scheme 1). The effects of multiple process parameters, including catalyst amount, reaction temperature, alcohol volume, and water content were studied as a function of time to optimize the yield of alkyl levulinates. 5-Sulfosalicylic acid is expected to be a potential candidate for alkyl levulinate production from biomass-derived platform molecules.

2 | RESULTS AND DISCUSSION

2.1 | Substrate screening

Firstly, the alcoholysis of FA was carried out in a variety of solvents in order to explore the scope of this method.

In the case of linear alcohol, with the increase of the carbon length, alkyl levulinates yield increased gradually. (Table 1, entries 1, 2, 3 and 5). This difference could be attributable to the boiling point being the controlling factor. However, with the increase of the molecular volume, the yield of alkyl levulinates significantly decreased from 96.2 to 43.8% with *n*-propanol and isopropanol, respectively (Table 1, entries 3 and 4). In addition, the steric effect was much more obvious when using *n*-butanol, isobutanol, 2-butyl alcohol, or tert-butanol (Table 1, entries 5, 6, 7, and 8). This tendency is consistent with the literature^[7,17,18] and these results suggest that 5-sulfosalicylic acid as the catalyst with optimized conditions was appropriate for the synthesis of linear-alkyl levulinates by carrying out the alcoholysis of FA.

2.2 | Effect of *n*-butanol volume on FA alcoholysis

The concentration of the starting material is a key factor with great influence on most chemical reactions. Thus, the effects of *n*-butanol volume were investigated in different reaction time, and the results are shown in Figure 1. When *n*-butanol volume was 5 ml, the FA conversion increased to 99.3% after 10 hr compared with that obtained at low alcohol volume 3 ml. Consistent with the literature reports, a lower mole ratio between FA to *n*-butanol results in polymerization of FA in the presence of strong acidic catalyst.^[27] However, further increases in the *n*-butanol volume led to a significant decrease in the BL selectivity. The adverse effect of higher volume concentration of *n*-butanol may be caused by lowering the concentration of intermediates.^[12] The intermediate 2-butoxy methyl furan (BMF) is formed quickly by the reaction of FA with *n*-butanol, but the rate of conversion of the BMF to the product is very low. When the reaction is carried out in 7 or 9 ml of *n*-butanol, the content of the BMF is lower than that obtained in 5 ml of *n*-butanol.

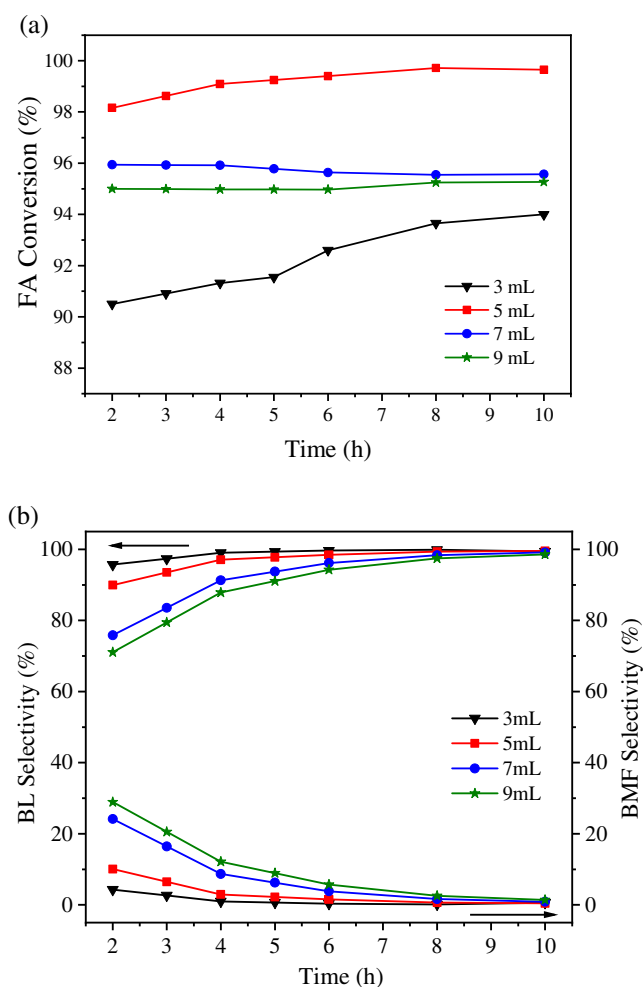
2.3 | Effect of catalyst amount on FA alcoholysis

The amount of catalyst definitely impacts the acidic concentration in the reaction solutions, and correspondingly influences the product distribution. As shown in Figure 2, the amount of 5-sulfosalicylic acid ranges from 1 to 9 wt% based on FA, while the other conditions remain constant. FA conversion increased with the increase of catalyst amount from 1 to 5 wt%, which should be attributable to an increase in the availability and number of catalytically active sites. When the

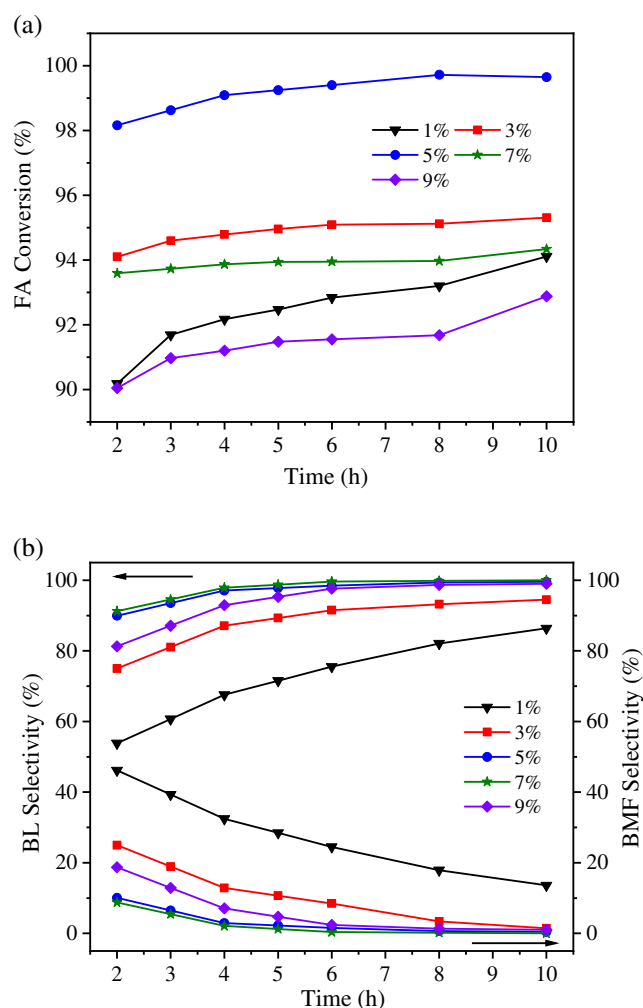
TABLE 1 Impact of substrate on the catalytic yield of alkyl levulinates

Entry	Substrate	Boiling point (°C)	Time (hr)	Conversion (%)	Yield (%)
1	Methanol	65	10	49.0	48.7
2	Ethanol	78	10	67.8	67.8
3	<i>n</i> -propanol	97	10	99.6	96.2
4	Isopropanol	82	10	43.8	43.8
5	<i>n</i> -butanol	118	10	99.7	99.3
6	Isobutanol	92	10	93.6	92.4
7	2-butyl alcohol	100	10	76.9	75.7
8	Tert-butanol	82	10	80.8	60.8

Note: Reaction conditions: 3 mmol FA, 5 ml alcohol, 5 wt% catalyst dosage, reflux temperature.

**FIGURE 1** Effect of *n*-butanol volume (a) FA conversion, (b) BL selectivity and BMF selectivity. Reaction conditions: 3 mmol FA, specified *n*-butanol volume, 5 wt% catalyst dosage, 118°C

reaction was carried out at the catalyst amount of 5 wt%, 99.7% FA conversion, and 99.6% BL selectivity. However, increasing the amount of catalyst further to 9 wt%, the conversion of FA, and the selectivity of BL began to

**FIGURE 2** Effect of catalyst amount on (a) FA conversion, (b) BL selectivity and BMF selectivity. Reaction conditions: 3 mmol FA, 5 ml *n*-butanol, specified catalyst dosage, 118°C

decrease and the color of reaction mixture became darker, indicating that the side reaction about the polymerization of FA to form oligomeric products had increased. From this, it can be judged that higher catalyst

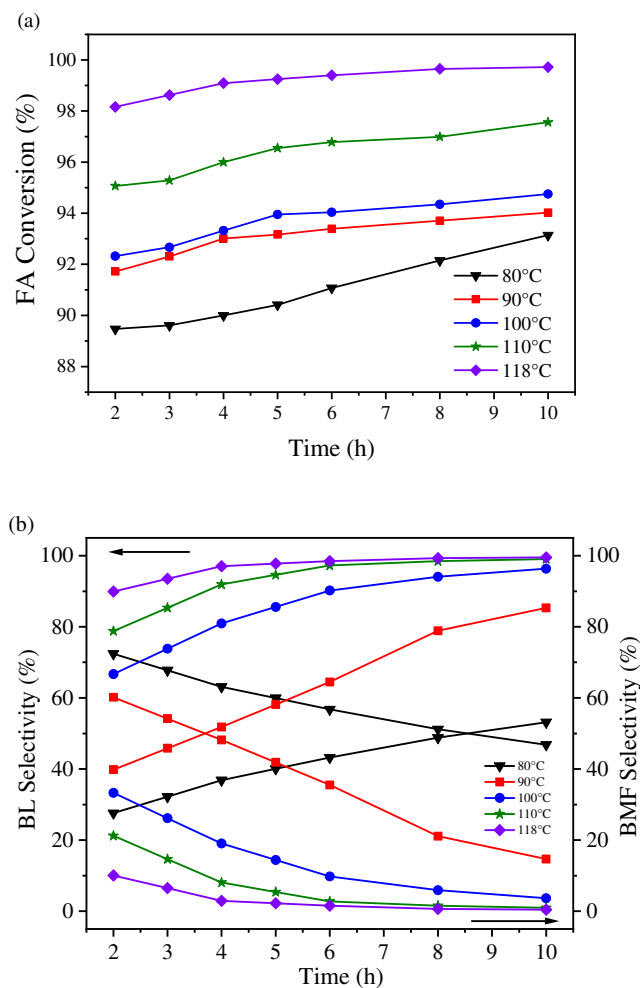


FIGURE 3 Effect of temperature (a) FA conversion, (b) BL selectivity and BMF selectivity. Reaction conditions: 3 mmol FA, 5 ml *n*-butanol, 5 wt% catalyst dosage, specified temperature

amount are less preferable, since such conditions tend to result in the more rapid polymerization of FA. The most reasonable catalyst amount for use in further investigation can be set at 5 wt%.

2.4 | Effect of reaction temperature on FA alcoholysis

Temperature appears to have a profound effect on both the reaction rate and the product selectivity. Therefore, the reaction temperature which ranged from 80 to 118°C was tested in the FA alcoholysis reaction and the results are depicted in Figure 3. When the temperature was increased from 80 to 110°C for the same reaction time, the selectivity of BL within 10 hr increased sharply, from 53.2 to 99.6%. At the lowest temperatures such as 80°C, the conversion of FA and selectivity of BL improved smoothly with reaction time, which may have been because the

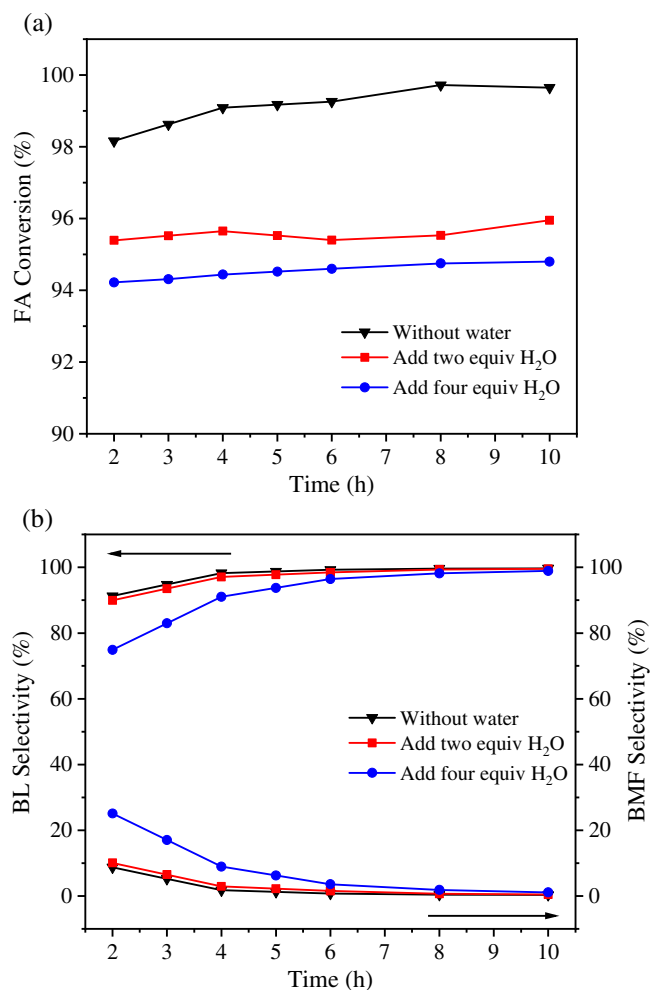
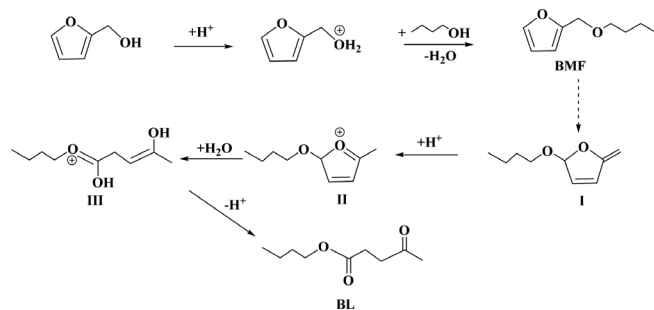


FIGURE 4 Effect of water content on (a) FA conversion, (b) BL selectivity and BMF selectivity. Reaction conditions: 3 mmol FA, 5 ml *n*-butanol, 5 wt% catalyst dosage, 118°C, specified water content

reaction needed more time to reach the equilibrium conversion. About 99.7% FA conversion and 99.6% BL selectivity could be achieved when the reaction temperature was further increased to 118°C. These observations suggest that high temperature was able to accelerate the rate of chemical reaction as well as enhance the selectivity of BL. The optimized results showed that a reasonable temperature of 118°C was necessary to accomplish full conversion of the FA and get the highest selectivity of BL.

2.5 | Effect of water content on FA alcoholysis

Subsequently, the effect of the water content was also studied and the results are shown in Figure 4. With the water content increased from without water to two equivalents, the conversion of FA gradually decreased from



SCHEME 2 Proposed mechanism of the conversion of FA to BL over 5-sulfosalicylic acid

99.7 to 94.8% after 10 hr, and part of FA had probably been reacting with the water to form LA. When the amount of water added four equivalents, FA conversion and BL selectivity were noticeably decreased. This effect was inconsistent with the results from Zhang et al.,^[17] who proved that the addition of water has a positive effect on the conversions of FA and 2-butoxymethylfuran to butyl levulinate. Our results indicate that in this case of high water content in the *n*-butanol medium, the reaction of FA became subject to the competing processes of alcoholysis and hydrolysis.

2.6 | Proposed mechanism for FA alcoholysis

In order to further identify the structure of the intermediate product in the reaction process, the reaction solution was eluted with a ratio of ethyl acetate: petroleum ether = 1:6 to separate the product. NMR analysis and identification confirmed that the main intermediate product was BMF (Figure S1). Additionally, BMF ($m/z = 154$) (Figure S2), the intermediate I ($m/z = 154$) and III ($m/z = 173$) during the reaction process were also identified by GC-MS techniques (Figure S3). According to the above results and that of previously reported literature,^[28,29] the mechanism of alcoholysis of furfuryl alcohol to *n*-butyl levulinate was proposed in the presence of 5-sulfosalicylic acid catalyst. This mechanism involves three consecutive processes (Scheme 2). In the first step, the FA molecules are activated by 5-sulfosalicylic, and the activated FA molecules are attacked by *n*-butanol molecules to form BMF and water molecules. Next, the BMF undergoes the addition and elimination of the alcohol to form the intermediate I. Subsequently, the protonation of Intermediate I produces the cyclic oxonium (Intermediate II). Then, the intermediate III is formed via the ring-opening reaction owing to water molecules attacking cyclic oxonium obtained by protonation of epoxy groups. Finally, BL is generated by the isomerization from intermediate III.

2.7 | Comparison of 5-sulfosalicylic acid catalyst with previous catalysts

The catalytic activity of the 5-sulfosalicylic acid catalyst was compared with the reported catalysts and presented in Table 2. The temperatures between 110 and 150°C were commonly applied for the synthesis of *n*-butyl levulinate. A moderate temperature of 118°C could meet the demand of reaction for our method catalyzed by 5-sulfosalicylic acid. Interestingly, the use of 5-sulfosalicylic acid required only a small amount of catalyst to achieve the maximum yield of alkyl levulinates than other catalysts. A possible explanation for this appearance is that the active sites of 5-sulfosalicylic acid catalysts are easier to access by the substrate. Comparing with these reported catalysts employed for the synthesis of BL, the present catalyst exhibits high activity without using an excessive amount of alcohols and catalyst. Rate of the reaction and TOF on the acidity of the catalyst are comparable to the reported catalysts. The present 5-sulfosalicylic acid catalyst gave 96.2% of BL yield with complete conversion within 4 hr at 118°C (TOF = 10.74 hr⁻¹, based on the molar amount of -SO₃H). In summary, 5-sulfosalicylic acid is an efficient, economic, and reusable catalyst in this process. Based on these features, our method exhibits a promising prospect for the large-scale synthesis of alkyl levulinates from biomass-derived FA.

3 | EXPERIMENTAL

3.1 | Materials

All of the chemicals and solvents were used directly without further purification. 5-Sulfosalicylic acid (99%) was purchased from Hubei Shengtian Biological Technology Co., Ltd, furfuryl alcohol (99%) was purchased from Beijing Chemical Reagent Factory. All of the alcohols were purchased from Sinopharm Chemical Reagent Co., Ltd.

3.2 | Alcoholysis of furfuryl alcohol

Alcoholysis of FA with various alcohols (e.g., methanol, ethanol, and *n*-butanol) was carried out in a three-necked round-bottomed glass flask fitted with a water-cooled condenser. The reaction was performed under the conditions of alcohol refluxing temperature, atmospheric pressure, 5 wt% of an air-exposed catalyst, 3.0 mmol FA and 5 ml alcohol. At periodic intervals, 0.2 ml of the reaction

TABLE 2 Comparison of our method with previous reports for the synthesis of *n*-butyl levulinate

Entry	Catalyst	Catalyst dosage	Catalyst acidity (mmol/g)	<i>T</i> (°C)	<i>t</i> (hr)	Mole ratio (FA: <i>n</i> -butanol)	BL yield(%)	TOF (hr ⁻¹)	References
1	[(HSO ₃ -p) ₂ im][HSO ₄]	12.3 wt%	4.88	110	2	1:22	93.0	7.75	[7]
2	Amberlyst 39	14.6 wt%	4.80	110	6	1:8	63.0	1.53	[15]
3	Aquivions P87S resin	6.3 mol%	1.15	132	4.3	1:25	82.1	3.04	[30]
4	GC-PTSA-AC	51.0 wt%	3.04	120	4	1:40	91.0	1.50	[31]
5	5-sulfosalicylic acid	5.0 wt%	13.67	118	4	1:18	96.2	10.74	This work

mixture was withdrawn and then diluted with acetonitrile to 5 ml. The diluted suspension was centrifuged and then analyzed. After completion of the reaction, the crude product was obtained after removing solvent under vacuum or extraction. The product is purified by column chromatography on silica gel using ethyl acetate: petroleum ether as the eluent. The catalyst was recovered by rotary evaporation from the eluent, dried in the air, and reused.

3.3 | Analytic methods

The products were analyzed on a gas chromatograph equipped with a flame ionization detector and a HP-5 column (30 m × 0.32 mm × 0.50 μm). The injection port temperature was 250°C, the oven temperature was 190°C, the detector temperature was 280°C, and N₂ as the carrier gas was 1.0 ml/min. In order to calculate the FA conversion and product selectivity accurately, hexane as internal standard was applied. FA conversion, product selectivity, turnover frequency (TOF), and acidity of the catalyst were calculated using the following equations:

$$\text{FA conversion (\%)} = \left(1 - \frac{\text{moles of FA in product}}{\text{initial moles of FA}}\right) \times 100\%.$$

$$\text{BL selectivity (\%)} = \left(\frac{\text{moles of BL in product}}{\text{initial moles of FA} - \text{moles of FA}}\right) \times 100\%.$$

$$\text{BL yield (\%)} = \left(\frac{\text{moles of BL in product}}{\text{initial moles of FA}}\right) \times 100\%.$$

$$\text{Acidity of the catalyst} = \frac{\text{Moles of H}^+ \text{ (mmol)}}{\text{Weight of catalyst (g)}}.$$

4 | CONCLUSIONS

Efficient conversion of FA to BL was experimentally studied using 5-sulfosalicylic acid as catalysts under mild conditions, where the highest yield of 99.3% was obtained when it was employed at 118°C after 10 hr. This approach is green, simple to handle, commercially available starting materials, as well as it does not require hazardous organic solvents, thereby providing an economic, safe and environmentally friendly route to biomass utilization.

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$$\text{TOF} = \frac{\text{Moles of BL (mmol)}}{\text{Weight of catalyst (g)} \times \text{Acidity of the catalyst (mmol/g)}} \times \frac{1}{\text{Reaction Time (hr)}}.$$

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SUPPORTING INFORMATION

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