Sustainable Chemistry

Catalytic Conversion of Biomass-Derived Carbohydrates into Levulinic Acid Assisted by a Cationic Surface Active Agent

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Levulinic acid (LA), a bio-renewable chemical building block, has been produced in good isolated yields by treating biomass-derived carbohydrates with aqueous hydrochloric acid in the presence of quaternary ammonium salts as cationic surface-active agent (SAA). Under optimized conditions (120 °C, 3 h, 20.2% HCl), the one-pot process afforded LA in 80% isolated yield from glucose using only 5.77 mol% (10 wt%) of benzyl-tributylammonium chloride (BTBAC) at the SAA. The control reaction (no BTBAC) provided LA in only 64% yield from glucose under identical conditions. The process was optimized on the reaction temperature, loading of BTBAC, and the concentration of HCl. The use of BTBAC led to a nearly 8–17% increase in yield of LA (compared to the control reaction) for all the carbohydrates studied.

Introduction

Transformation of non-food, waste biomass into liquid transportation fuels and value-added chemicals has received worldwide attention from both the academic and industrial communities over the past several years.[1] The chemical-catalytic valorization of biomass is of particular interest since it is fast, selective, biomass agnostic in nature, does not necessitate live organisms, and relatively less energy-intensive.[2] Acid-catalyzed depolymerization and hydrolysis of biomass-derived carbohydrates into levulinic acid (LA) is known for more than a century and a well-documented process.[3] Acid-hydrolysis helps in the selective deoxygenation of highly-oxygenated carbohydrate molecules and reduces the structural complexity significantly while preserving some of the key functional groups.[4] Over the past decades, hundreds of journal publications and patents have been attributed to the production and downstream applications of LA.[5] LA is a synthetically versatile molecule having two highly reactive functionalities, namely ketone & carboxylic acid.[6] LA is at the forefront of

biorefinery research acting as a biorenewable chemical building block for the synthesis of a range of products of commercial interests including fuels and fuel additives,[7] solvents,[8] monomers for polymers,[9] plasticizers,[10] agrochemicals,[11] and pharmaceuticals.[12] LA has been listed as one of the top-ten biorenewable chemicals based on its commercial potential.[13] Various acids such as mineral acids,[14] metal salts,[15] zeolites,[16] ionic liquids,[17] and acidic resins[18] have been exploited as catalysts for the preparation of LA from biomass-derived carbohydrates. Whereas the stronger acids generally work under mild reaction parameters, the weak acids require more demanding conditions. Among several reported processes in producing LA from biomass feedstock, two processes stand out from the rest in terms of high selectivity and isolated yield of LA. The *Biofine* process uses a two-step process where the biomass is first hydrolyzed in aqueous H_2SO_4 into furanic intermediates like furfural and 5-(hydroxymethyl)furfural (HMF) at 220 °C but short residence time. In the second stage, the HMF intermediate is rehydrated into LA at a slightly lower temperature (*ca.* 190 °C) but longer residence time. After the reaction, water is removed by evaporation, and LA is recovered by fractional distillation.[19] In 2008, Mascal *et al.* reported a two-step synthesis of LA where the biomass feedstock is first converted into 5-(chloromethyl)furfural (CMF) within a biphasic batch reactor. In the second step, CMF is rehydrated into LA in nearly quantitative yield. The process provides LA in nearly 80% isolated yield over two steps.[20] There is still significant interest in developing a simple but elegant process that enables producing LA in high selectivity and yield under relatively mild conditions. Even incremental improvement in the process parameters or the yield of LA is of profound importance in this area of research. In this work, the production of LA from biomass-derived carbohydrates using azeotropic hydrochloric acid (20.2% HCl) is reported. The azeotropic hydrochloric acid solution allowed higher temperatures to be achieved without the loss of hydrogen chloride by degassing. The azeotrope also allowed the removal of aqueous hydrochloric acid by distillation without changing the acid composition and subsequent isolation of LA. The reaction was conducted in the presence of quaternary ammonium salts as cationic SAA to study their effect on the selectivity and yield of LA (Scheme 1). The role of SAA has been explored for the preparation of furanics from biomass. The improved yields of furanics in the presence of SAA is attributed to the protective

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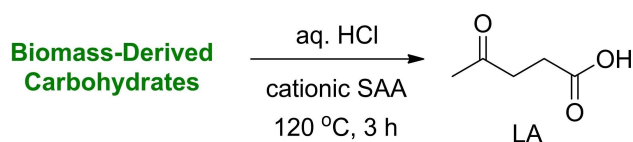
Scheme 1. Preparation of LA from carbohydrates in aqueous hydrochloric acid in the presence of a cationic SAA.
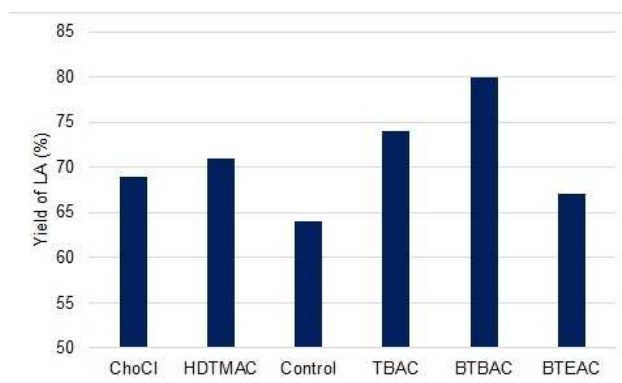

Figure 1. Preparation of LA from glucose using various SAA. Reaction condition: D-glucose (2 g), SAA (5.77 mol%), HCl (20.2% aq., 40 mL), 120 °C, 3 h.

hydrophobic environment created by them around the intermediates and product.[21] The role of SAA has also been investigated before for the direct preparation of LA from carbohydrates. Although the mechanism is not clearly understood, noticeably better yields of LA were obtained using SAA compared to the control reaction. The stabilization of the reactive intermediates by SAA is often cited to explain the improved yield of LA.[22]

The reaction has been optimized on the reaction temperature, duration, the concentration of hydrochloric acid, type of the SAA, and loading of SAA used.

Results and Discussion

Glucose, an inexpensive sugar and the monomer of the most abundant biopolymer cellulose, was chosen as a model substrate for the process optimizations in preparing LA. In a typical reaction, glucose (2 g) was dissolved in 20.2% aqueous hydrochloric acid (40 mL), and BTBAC (0.2 g, 5.77 mol%) was added. The homogeneous solution was taken in a glass pressure reactor and magnetically stirred at 120 °C for 3 h. LA was isolated from the aqueous solution by extracting with ethyl acetate or by distilling out the aqueous acid under reduced pressure. The control reactions were carried out using identical reaction conditions, except no BTBAC was added. All the experiments were performed in triplicate, and the average yield is being reported. The mass balance is the form of insoluble humin was also measured in every reaction. In order to understand the role of SAA on the isolated yield of LA, the experiments were carried out by using six commercially-available quaternary ammonium chlorides with different chain lengths and distribution coefficients (Figure 1). The control reaction without SAA afforded LA in 64% yield. When tetrabutylammonium chloride was used as the SAA, the yield of LA increased significantly to 74%. When hexadecyltrimethylammonium chloride (HDTMAC) and choline chloride (ChoCl) were used as SAA, LA was obtained in 71%, and 69% yield, respectively. BTBAC was found to be the best SAA that afforded LA in 80% isolated yield. The trend can be correlated with the distribution coefficient of the SAA used. With the more non-polar character of the SAA, the yield of LA increases. With shorter alkyl chain length, benzyltriethylammonium chloride (BTEAC) provided LA in 67% yield. After the reaction, the crude LA containing the SAA was chromatographed, and LA was eluted out using diethyl ether. The BTBAC was eluted from the silica gel using 20% methanol in chloroform where 96% of BTBAC was successfully recovered. The effect of the loading of

BTBAC on the yield of LA was studied next. When the loading of BTBAC was decreased to 5 wt% of glucose, LA was isolated in 70% yield, slightly higher than that in the control reaction (Figure 2). A significant increase in the yield of LA was observed by increasing the loading of BTBAC. The yield of LA reached 80% at 10 wt% loading of BTBAC. The trend can be explained by the formation of a protective environment by BTBAC around the reactive intermediates such as 5-(hydroxymethyl)furfural that minimizes side reactions and increases the selectivity towards LA.[23] However, increasing the loading of BTBAC to 20 wt% of glucose did not change the yield of LA appreciably. The optimized reaction on glucose was then applied to other carbohydrate feedstock.

The effect of reaction temperature on the isolated yield of LA was examined. When the reaction was conducted at 130 °C, the yield of LA decreased to 70% (Figure 3). The result can be rationalized by more side reactions and/or decomposition of LA at elevated temperatures. The yield of LA at 100 °C was only 47%, which is attributed to the incomplete conversion of glucose. The yield of LA at 110 °C was found to be 68%.

The effect hydrochloric acid concentration on the yield of LA was studied. The reactions were conducted at 120 °C for 3 h.
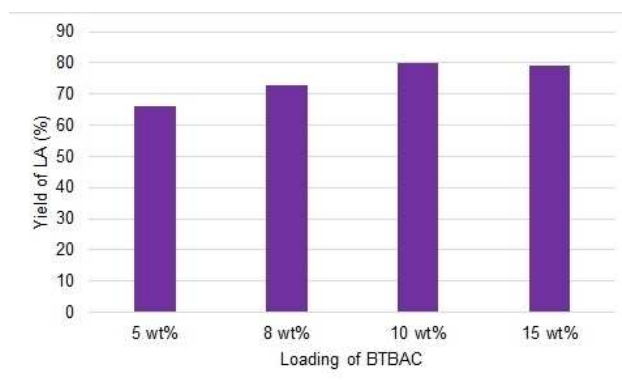

Figure 2. Effect on the loading of BTBAC on the yield of LA. Reaction condition: Glucose (2 g), HCl (20.2%, 40 mL), 120 °C, 3 h.
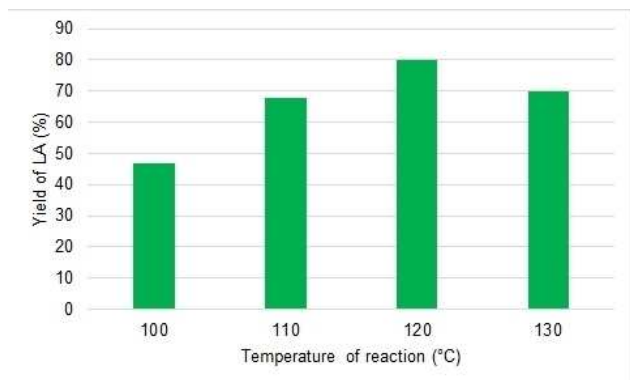
Figure 3. The effect of reaction temperature on the yield of LA. Reaction condition: D-glucose (2 g), BTBAC (0.2 g, 5.77 mol%), HCl (20.2%, 40 mL), 3 h.

Figure 5. Preparation of LA from various carbohydrate feedstock. Reaction condition: Substrate (2 g), BTBAC (0.2 g, 5.77 mol%), HCl (20.2%, 40 mL), 120 °C, 3 h.
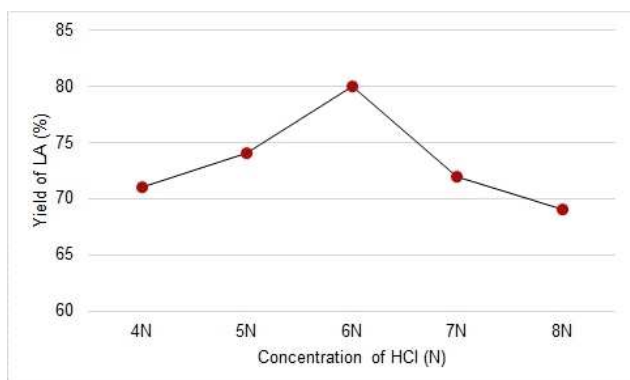

Figure 4. Effect on the hydrochloric acid concentration on the isolated yield of LA. Reaction condition: D-glucose (2 g), BTBAC (0.2 g, 5.77 mol%), aq. HCl (40 mL), 120 °C, 3 h.

Acid concentrations lower than 4 N HCl gave poor yields of LA due to incomplete conversion of the substrate. The HCl concentration was varied between 4–8 N. A higher concentration of HCl was avoided to minimize the evaporative loss of hydrogen chloride gas during workup. As shown in Figure 4, the use of 6 N HCl provided the best yield of LA. Whereas 4 N HCl provided LA in 71% yield, 8 N HCl provided LA in 69% yield. Similarly, the yields of LA at 5 N and 7 N HCl are slightly lower than the yield of LA at 6 N HCl. The lower yield of LA at higher concentrations may be attributed to a higher rate of side reactions and decomposition of LA formed. Lower yields of LA at lower concentrations of HCl may be due to incomplete reactions. The HCl/water system forms an azeotrope at 20.2% ($\sim$6 N) HCl with a constant boiling point of 108.6 °C. The advantages of using the azeotropic mixture include achieving higher reaction temperature without evaporative loss of hydrogen chloride gas. In addition, the diluted solution after reaction can be conveniently concentrated to get back the azeotropic mixture.

The optimpzed reaction was then applied for the production of LA from various biomass-derived carbohydrates. The reactions were carried out at 120 °C for 3 h using 2 g of substrate,
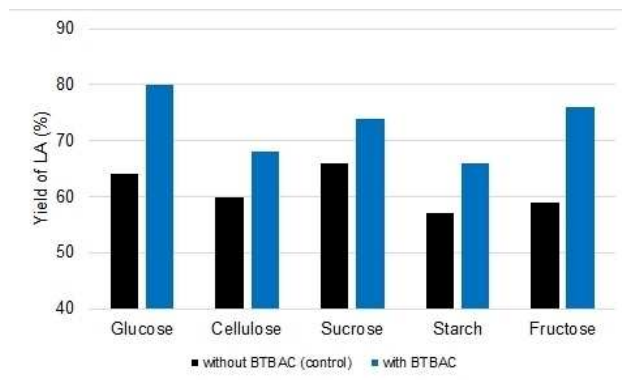
5.77 mol% of BTBAC, and 40 mL of aqueous HCl (6 N) (Figure 5). The control reactions were also carried out under identical conditions, except no BTBAC was added to the reaction mixture. When glucose was used as the substrate, the yield of LA reached 80% using 5.77 mol% of BTBAC, whereas the control reaction provided only 64% of LA. Fructose provided 76% of LA in the presence of BTBAC, whereas the control reaction provided only 59% of LA. When sucrose was used as the substrate, LA was isolated in 74% and 66% yield in the presence and absence of BTBAC, respectively. Polymeric carbohydrates such as starch (soluble) and cellulose (micro-crystalline) provided lower yields of LA compared to the sugars. Cellulose gave 68% yield of LA in the presence of BTBAC, which was otherwise isolated in 60% yield in the control reaction. Starch provided LA in 57% yield in the control reaction that increased up to 66% yield in the presence of 5.77 mol% of BTBAC as a cationic SAA. It was observed that simple sugars like glucose and fructose provided better yields of LA compared to polymeric carbohydrates like starch and cellulose. The results can be explained by the slower kinetics of the depolymerization reaction and the possibility of more side reactions. The effect of SAA was most pronounced in the case of monomeric sugars like glucose and fructose. This may be explained by the fact that the sugars dehydrate immediately into intermediates like HMF, which get protected by the SAA. Presumably, the SAA does not provide much stabilization on the initial depolymerization step of polymeric carbohydrates into mono- and oligosaccharides and the ensuing side reactions such as condensation.

The mass of insoluble humin formed during the reaction was also calculated. After the reaction, the humic matter was filtered under vacuum, washed with excess deionized water, and dried in a hot-air oven at 60 °C till constant weight was obtained. In general, less amount of humic matter was isolated from reactions using BTBAC compared to the control (no BTBAC) reactions (Table 1). The observation indirectly supports the higher yield of LA in reactions using BTBAC as the SAA. The formation of less humic matter in reactions using SAA supports

the hypothesis that they form a protective environment around the reactive intermediates minimizing side reactions.

Conclusion

A one-pot production of LA from biomass-derived carbohydrates has been achieved in 20.2% aqueous hydrochloric acid within a batch-type reactor. The reactions provided a good isolated yield of LA even at high substrate loading (10 wt%) at relatively mild reaction conditions (120 °C, 3 h). The yield of LA improved noticeably by adding an SAA. BTBAC was found to be the most effective SAA that gave 8–17% more yield of LA from all the carbohydrates examined. Both LA and BTBAC were isolated from the aqueous reaction mixture by the removal of aqueous hydrochloric acid by distillation or *via* solvent-solvent extraction.

Supporting Information Summary

The supporting information include details of the materials used, experimental procedure for preparing LA, isolation of insoluble humin, and the recovery of BTBAC.

Conflict of Interest

The authors declare no conflict of interest.

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