

Abstract

The biomass-based production of levulinic acid requires aqueous mineral acid as catalyst. In the present study, the possible reuse of sulfuric acid in the biomass conversion was investigated. The acid can either be reused after extracting the product or before extraction. The results show that both methods are applicable for producing levulinic acid while reducing the sulfuric acid demand of the process. Conversion of D-fructose showed similar results after five recycle steps in both post- and pre-extraction methods. The post-extraction method was successfully repeated four times with cooked tea leaves. The sulfuric acid applied for the conversion of a simulated household waste was successfully recycled eight times with pre-extraction plus once by post-extraction without significant change in the product formation.

Keywords

Levulinic acid, recycle, biomass

1 Introduction

The efficient conversion of biomass-based waste streams to basic chemicals has become a key issue in developing non-fossil-based production of carbon-based consumer chemicals and fuels. Although, it is hard to estimate the depletion of fossil resources or even their price in the future, the valorization of low-cost, readily available and even carbohydrate rich wastes has come into focus of interest [1]. Due to the intensive research activities of biomass conversion, several versatile platform chemicals have been identified and characterized i.e. 5-hydroxymethyl-furfural (5-HMF) [2], levulinic acid (LA) [3], γ -valerolactone (GVL) [4], 2-furfural (FAL) [5], furfuryl alcohol (FOL) [6], just to name a few. Among these molecules, LA and its derivatives including levulinate esters [7] and GVL [4], have several established promising applications (Fig. 1), and therefore, their production and conversion have been well studied.

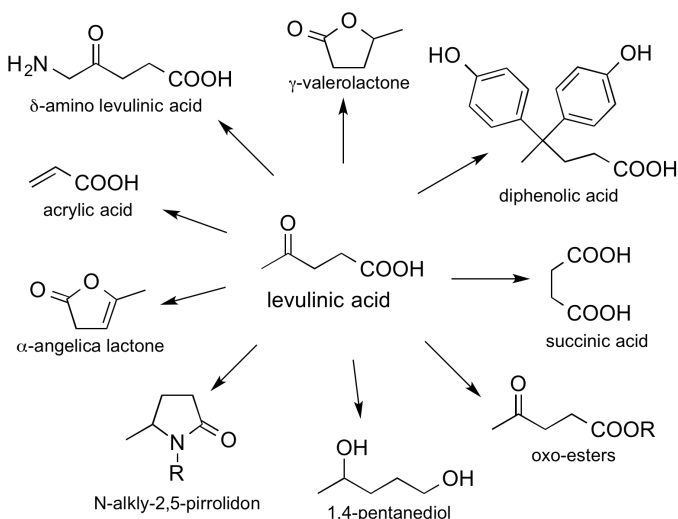


Fig. 1 Levulinic acid based chemicals [8]

1.1 Production of levulinic acid with sulfuric acid as a catalyst

Obviously, the most effective protocol to produce LA from biomass is based on acid catalysed depolymerisation and subsequent dehydration of carbohydrate content of feedstocks (Fig. 2) [9]. Accordingly, several attempts were made

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to produce 5-HMF and/or LA from simple sugar molecules such as D-fructose or D-glucose in the presence of well-designed catalyst species i.e. ionic liquids or organic acids [10]. However, it was established that the transformations could be much more effective by the use of mineral acids preferably hydrochloric or sulfuric acid [11]. Although both of them have significant catalytic activity, the application of aqueous HCl could result in serious environmental concerns. Thus, the utilization of sulfuric acid has been generally preferred. It was shown that the acid acted as a catalyst species in the dehydration of D-fructose as a model substrate to 5-hydroxymethylfurfural and subsequently its rehydration to LA [12]. In addition, depending on the acid content and reaction environment, the product distribution could be dramatically affected. Under aqueous conditions, it was revealed that optimal acid concentration for LA production could be 1.8–2.2 mol×dm⁻³ [11, 13, 14]. It should be noted that the formic acid obtained from rehydration of 5-HMF could also act as a catalyst for the dehydration reactions [15, 16]. Since the reported optimal acid concentration range is much higher than the HCOOH content, only a minor effect of formic acid could be taken into account. Moreover, the water that formed during the dehydration sequence slightly dilutes the reaction medium and therefore could counteract the effect of HCOOH.

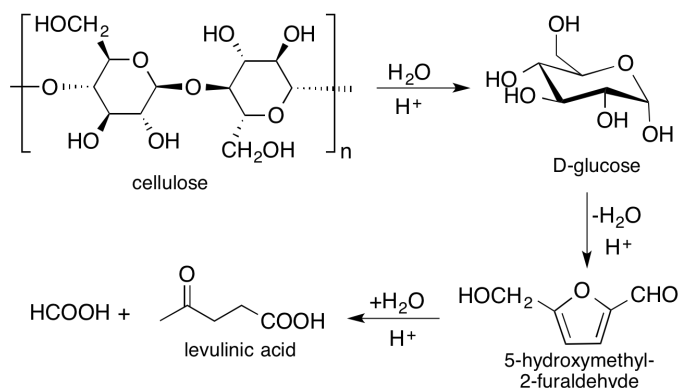


Fig. 2 Acid-catalyzed dehydration of carbohydrates to levulinic acid

While numerous papers have been published on the investigation of acid catalyzed conversion of carbohydrates to LA, little information was provided on mineral acid recycling. In the Biofine technology, in which the sulfuric acid is utilized in a two stage process, its recycling is applied; however, no information on the recycle steps and its effects were provided [17].

Although the extraction could be a convenient separation method and it is widely used for production of 5-HMF applying biphasic conditions [10], only a few studies focused on its application for the isolation of LA [18]. However, to separate LA and the aqueous catalyst phase, the liquid-liquid extraction can obviously be proposed as a robust or even industrially applicable method. We have demonstrated that ethyl acetate, a cheap, biomass-derived, and readily available solvent could be

used for this purpose [11, 13, 14, 19]. Its boiling point (77.1 °C) is much lower than that of LA (245–246 °C). Dumesic showed that alkylphenol solvent combined with GVL could be applied to form a biphasic system for the continuous separation of LA from acidic aqueous phase [20]. Dunlop patented a sulfuric acid recycling method applying a two-step process involving an extraction and a water removal step [21]. It should be noted that the water removal resulting in concentrates sulfuric acid has a significant energy need. Due to their miscibility with water or even high boiling points, other biomass-derived solvents, such as alcohols (methanol, ethanol, etc.) could not be favored. The other possibilities include esters like acetates, from which ethyl acetate has a low boiling point and low miscibility with water. Other organic solvents could have better properties as an extracting agent; however, in the present study our aim was to apply a solvent that can be generated from biomass basis [22, 23].

We report here the investigation of the recycling of sulfuric acid during the conversion of biomass-based wastes to LA under aqueous conditions using ethyl acetate as an extracting agent.

2 Experimental procedure

Sulfuric acid, ethyl acetate and D-fructose were purchased from Molar Chemicals Kft., Budapest, Hungary. The cooked tea leaves applied were gathered from used teabags of Sir Morton Earl Grey tea. A biomass waste mix (BWM) was prepared from different local household wastes, including apple peel, pea pod, potato peel, carrot peel, cooked tea leaves and spent coffee grounds in equal amounts.

Dehydration experiments were performed in an Ace Glass Pressure tube with Ace-Thred PTFE bushing. For the experiments 500 mg of biomass was mixed with 10 mL of 2 M sulfuric acid. The tubes were then heated up to 170 °C by a conventional oil bath and stirred for 8 h by a magnetic stirrer. After the given reaction time, the mixture was cooled to room temperature. The solid phase (humins) from the reaction mixture was filtered on a G3 type glass filter, and the mixture was either extracted or directly reused.

The humin-content is insoluble and therefore its removal would not have negative effects on the yield of LA. The humin formation is the result of aldol condensation between side products of the conversion [24], and may be combusted for heat or energy generation [25].

When the post-extraction route was applied, the aqueous phase was extracted with ethyl acetate (4 x 10 mL) and the solvent was evaporated to gather the final product, while the aqueous phase was reused for further reactions. In the case of pre-extraction routes, the acid was mixed again with 500 mg of the corresponding biomass and was only extracted after multiple steps.

For sample analysis a Shimadzu GCMS-QP2010 SE gas chromatograph equipped with mass spectrometer detector and a Bruker Avance-250 NMR spectrometer was applied.

All of the applied biomass materials were dried at 105 °C for 24 hours and were grinded before mixing. The ash content was determined by published method [19].

The product yields were calculated by mg LA/mg dry biomass. The amount of LA includes amount of the formed ethyl levulinate (EL) in the post-extraction process ($\text{mol}_{\text{product}} = \text{mol}_{\text{LA}} + \text{mol}_{\text{EL}}$, from which the total product is calculated as mg of LA as follows: $\text{mass}_{\text{LA}} = \text{mass}_{\text{product}} \times \text{Molar mass}_{\text{LA}}$).

3 Results

In order to reduce the environmental and economic impact of the biomass conversion, the separation or even recycling of the acid catalyst is fundamentally important and therefore its investigation is highly desired. In addition, the successful acid recycling could also result in lower environmental factor (E-factor) [26] of the process. Accordingly, two different extraction strategies for the recycling of the sulfuric acid containing aqueous phase can be proposed. Fig. 3 shows the steps of producing LA from biomass wastes including the required material streams.

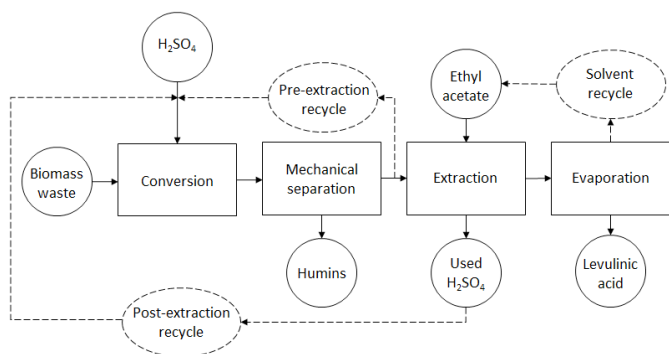


Fig. 3 The basic flowsheet of levulinic acid production with the possible recycle streams

The solvent applied for extraction can easily be reused since ethyl acetate can be condensed after evaporation. For the reuse of sulfuric acid containing phase, two possible routes were proposed and investigated. Firstly, after the catalytic dehydration and subsequent removal of solid residues (humins), the aqueous phase containing LA was directly used in the next run (pre-extraction recycle). The recycling of the liquid phase after removal of solids resulted in an enriched amount of LA in each subsequent step, as expected. Due to the higher final concentration of LA, the extraction could be more efficient. It should be noted that the increased initial amount of solid substrate changes the acid to substrate ratio and significant humin formation would be expected. On the other hand, after the removal of solids, the LA can be separated by an extraction step resulting in LA containing organic phase and sulfuric acid containing aqueous phase. The latter can be used again as a catalyst phase in a subsequent step (post-extraction recycle).

The conversion of several biomass-based wastes to LA by using both conventional and microwave-assisted heating

methods were recently demonstrated. It was revealed that average yields of LA were between 8.16-12.8% for tea leave waste [19]. Thus, we performed the conversion of 500 mg of D-fructose and 500 mg tea leave waste in 10 mL of 2 M sulfuric acid at 170 °C for 8 h using external oil bath resulting in 36.6-37.4 % and 9.2 % of LA yield, respectively. The ash-content of the BWM, which could affect the acid concentration was also determined and found to be 5.9 wt%, while for the cooked tea leaves it was 3.5 wt%. It was in good agreement with published results [13, 19]. Accordingly, the possible pre- and post-extraction methods of sulfuric acid containing phase were firstly investigated by the use of 2.8 mmol D-fructose for each cycle under identical conditions. Comparing the two recycle routes showed no significant change in the conversion rate for five cycles. (Fig. 4). The recycle of the aqueous sulfuric acid solution had expectedly no effect on the conversion itself, since the acid only serves as a catalyst. As we indicated, the maximum yield can be achieved within 1.8–2.2 mol×dm⁻³ acid concentration which is not affected during the procedure.

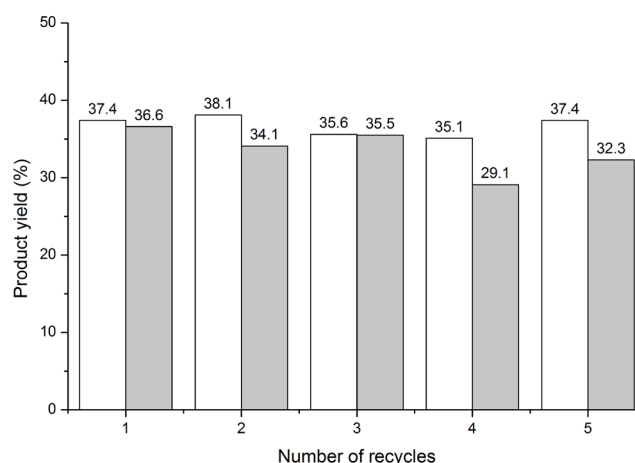


Fig. 4 Product yields from D-fructose by the two acid recycle routes: pre-extraction route (white bars) and post-extraction route (grey bars)

However, by the post-extraction route involving LA removal by ethyl-acetate, ¹H-NMR analysis suggested the formation of ethyl levulinate beside LA after multiple recycle steps, which was confirmed by the GC-MS analysis. The formation of ethyl levulinate is due to the presence of ethyl acetate in the recycled aqueous solution. Under the acidic conditions, the ethyl acetate can decompose to acetic acid and ethanol, which can react with LA under the similar conditions, and form ethyl levulinate.

If the LA content is only extracted after multiple recycles of the sulfuric acid, the formation of ethyl levulinate can be avoided. The ¹H-NMR and GC-MS analysis of these samples showed no presence of ethyl levulinate, only smaller amounts of ethyl acetate could be detected beside the expected compounds.

The post-extraction method was further investigated with a chosen household waste, cooked tea leaves from teabags. In this case, no significant change of product yields was detected for four recycle steps (Fig. 5).

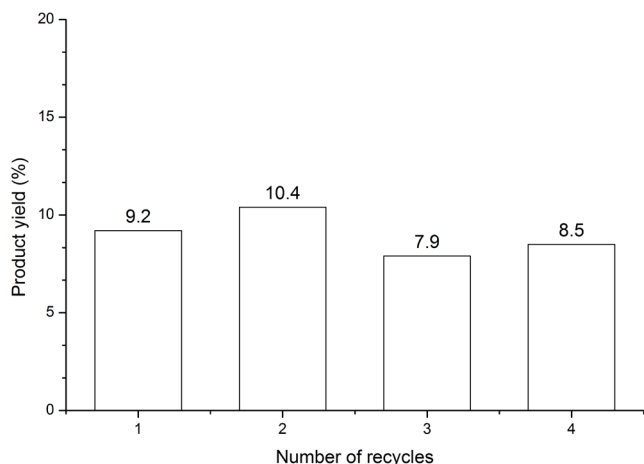


Fig. 5 Product yields from cooked tea leaves by post-extraction recycle

The pre-extraction recycles with biomass waste mix (BWM) were also performed for 3, 6, and 8 times. The results clearly indicate that product yields have not been influenced by the recycling steps, yields varied between 8.5 and 10.5% for each case (Fig. 6).

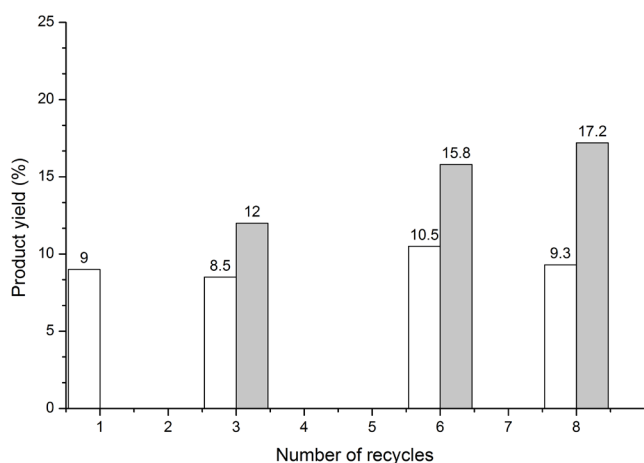


Fig. 6 Product yields from BWM with pre-extraction recycle (white bar) and one additional post-extraction step (grey bar)

After extracting the LA content of the pre-extraction recycle mixtures, the aqueous phases were once again reused in another reaction to monitor whether the acid is still applicable for a consecutive conversion step. In these experiments, the yields (Fig. 6, grey bars) were found to be increased in each case, and expectedly, appearance of ethyl levulinate was observed. The post-extraction yields were higher as the number of recycles increased. The increased yields were probably caused by the incomplete extraction of the product from the previous extraction step. By the pre-extraction recycle routes, soaking the separated solids with extractant showed that less than 5% of the total LA can remain in the solid phases if they are not washed. However, if multiple pre-extraction recycle steps are performed, a greater quantity of LA might be recovered from them. In case of the post-extraction route, the humin was washed with ethyl acetate

during filtration, therefore soaking is not required. Through the reactions with cooked tea leaves and BWM 0.5 g of liquid containing humin was produced by each reaction step.

The environmental factor (E-factor) defined by Sheldon is one of the most important metrics of green chemistry [27] that is a basis of an advanced method developed for analysis of total energy efficiency, land use, and capital and raw material costs for the comparison of chemicals produced by petrochemical- and biomass-based routes [28]. It should be noted that generated waste is a crucial factor for recently defined sustainability metrics [29]. Consequently, by improving a technology the waste can be minimized or even eliminated increasing the sustainability index. For the production of LA E-factor can be easily calculated by dividing the amount of sulfuric acid with the amount of LA and humin, since the ethyl acetate is regenerated by condensation (Eq. (1)); this metric was selected to indicate the improvement in the acid catalyzed dehydration.

$$E = \frac{m_{H_2SO_4}}{(m_{LA} + m_{humin})n} \quad (1)$$

The amount of sulfuric acid required for the reactions is great compared to the two products. If the acid can be reused multiple times, the E factor would decrease significantly, meaning, the conversion becomes more environmentally benign. If the acid is used only once ($n=1$), the E factor is 20.5 by using BWM as biomass and calculating with 9.3% LA yield. However, if the number of reuses is 9, the E-factor decreases to 2.3. It should be noted, that even if the acid cannot be further applied for biomass conversion it might have other applications or with a regenerating process it could be reintroduced to the LA production.

4 Conclusions

The reuse of sulfuric acid was performed multiple times using different biomass types (D-fructose, cooked tea leaves, and a biomass waste mixture). A maximum of 8 reuses was performed without extracting the product in each step, whereas no significant change in the yield was detected. The sulfuric acid was reused after extraction and the conversion showed a slight increase. The reactions with D-fructose showed that the overall yield is similar either by post- or pre-extraction. The reactions with cooked tea leaves and BWM showed that the accumulation of impurities does not affect significantly the reuse of the acid. By reusing sulfuric acid in the process, the amount of waste and therefore the E factor can be reduced from 20.5 to 2.3.

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