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Levulinic acid production from *Cicer arietinum*, cotton, *Pinus radiata* and sugarcane bagasse†

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Levulinic acid is a key platform chemical. Even gasoline range chemicals could be produced from levulinic acid making it a strategically significant compound. Producing levulinic acid from biomass is attractive from economic as well as environmental aspects. An acid catalyzed hydrothermal process for converting biomass to levulinic acid is reported. The effect of biomass type, acid (HCl) concentration, and reaction temperature of hydrothermal treatment on the conversion of biomass and yield of levulinic acid were studied. Widely available cellulosic biomass and agricultural wastes, namely, *Cicer arietinum*, cotton, *Pinus radiata* and sugarcane bagasse were successfully converted to levulinic acid. Although HPCL analysis could not be performed, qualitative and quantitative analysis of levulinic acid was conducted using ^{13}C and ^{1}H NMR spectroscopy. Under optimal reaction conditions (423 K, 1 M HCl, 2 h) the yields of levulinic acid obtained from *Cicer arietinum*, cotton, *Pinus radiata* and sugarcane bagasse were 32.6, 44.0, 19.0 and 36.5 wt%.

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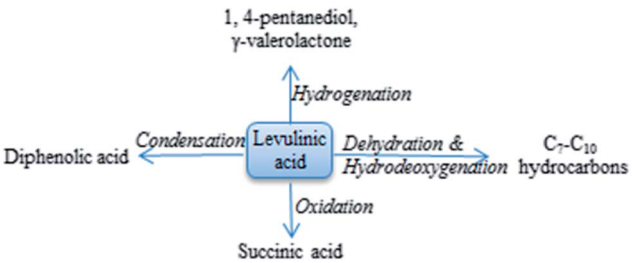
1. Introduction

Levulinic acid ($CH_3COCH_2CH_2COOH$) is a valuable bulk chemical. The key factor that makes levulinic acid important is the presence of two reactive functionalities, namely, the carboxylic acid (–COOH) and the ketone (=CO) groups in the same molecule. This structural advantage facilitates the transformation of levulinic acid to various other chemicals (Scheme 1).[1]

In addition, levulinic acid is designated by FDS as generally recognized as safe (GRAS) for specific uses in foods. Moreover, the antibacterial activity of levulinic acid in combination with sodium dodecyl sulfate is revealed recently.[13] Levulinic acid is a potential sanitizer for large-scale food processing facilities.



Scheme 1 Reactivity of levulinic acid making it a key platform chemical.[2–12]

The current market price of levulinic acid is 3.2 $ per kg.[4] The production of levulinic acid from saccharose was first reported by Mulder.[14] As new applications of levulinic acid are being explored, the demand for levulinic acid is also expected to grow. To meet the growing demand for levulinic acid and to keep its price in control newer feedstocks and strategies are being explored as exemplified in Table 1.

Several patents were granted for levulinic acid production processes owing to the commercial importance of this chemical.[22–24]

Currently, the only semi-commercial levulinic acid production unit is based on Biofine process using tobacco bagasse and paper mill sludge with H_2SO_4 as catalyst.[20,25] In spite of the use of efficient reactors as well as the polymerization inhibitors to reduce char formation, in the two stage biomass conversion in Biofine process the maximum levulinic acid yield is 70–80 wt% of the theoretical maximum of 71.6 wt% from cellulose. This corresponds to the conversion of nearly 50% by mass of C-6 sugars to levulinic acid, 20% to formic acid and 30% to tars.[26] Effective separation of levulinic acid and the recovery of sulphuric acid are the major drawbacks of the Biofine process.[25]

Moreover, due to the availability in the close proximity to the industry, tobacco bagasse and paper mill sludge were employed as feedstocks. These feedstocks alone cannot make the levulinic acid production process sustainable. Thus the objective of the current work is to evaluate a variety of potential cellulosic feedstocks, *Cicer arietinum* (CA), cotton, pine cones from *Pinus*

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Table 1 Strategies for levulinic (LV) acid production

Feed stock	Strategy	LV acid yield (wt%)	Reference
Bagasse & paddy straw	Hydrothermal process in a cylindrical pressurized steel reactor (220 °C, 45 min), HCl, 4.45 wt%	22.8 & 23.7 wt% for bagasse and paddy straw respectively	15
Galactose (*Gelidium amansi*)	Hydrothermal process in a stainless steel tubular reactor at 180 °C for 48.22 min, H_2SO_4 (3 wt%)	42.88%	16
Sugar cane bagasse	Hydrothermal reactor, 150 °C, 6 h, stainless steel floor stand reactor, H_2SO_4 (0.55 M)	19.4 wt%	17
Rice husk	Hydrothermal reaction in a stainless steel autoclave at 170 °C, 56 bar, 60 min, HCl, (4.5 wt%)	59.4 wt%	18
Carbohydrates of plant and animal origin	Microwave irradiation at 110–190 °C for 10–50 min, HCl or H_2SO_4 (2 M)	31.8 wt% from D-fructose	19
Tomato plant wastes (TPW), cellulose and chitosan	Microwave assisted flash hydrolysis at 225 °C and 40 bar N_2 pressure, HCl (1 M)	63, 90 and 95 wt% from TPW, cellulose and chitosan	20
Sweet sorghum	Microwave irradiation at 160 °C for 30 min, H_2SO_4 (2 M)	31.4 wt% yield	21

radiata (PR) and sugar cane bagasse (SCB), that could make the levulinic acid production process sustainable.

2. Experimental

Materials used

The biomass used as cellulosic feedstocks for levulinic acid production are shown in Fig. 1. *Cicer arietinum* (CA) is obtained from the agricultural fields of Israel after the harvest. Cotton (D50) and sugar cane bagasse (SCB) were supplied by Milouban Cotton Linters Pulp, MCP Ltd., Israel. Pine cones fallen from the trees were collected from the Eli Cohen park near Bar Ilan University, Israel. CA, SCB and PR were grounded by a mechanical blunder and sieved with a USA standard testing sieve to a mesh size of 250 μm and used subsequently. Cotton is used as received.

Fig. 1 Cellulosic feedstocks used for levulinic acid production.

Experimental methods

The biomass conversion involving hydrolysis, dehydration and rehydration reactions yielding levulinic acid, were carried out in a cylindrical stainless steel reactor with polytetrafluoroethylene lined inside to resist corrosion by the acid catalyst. The dimensions (thickness × internal diameter × depth) of the stainless steel reactor are (8 × 42 × 70 mm) and that of the internal PTFE lining are (3 × 32 × 40 mm) and the volume of the reactor is 32 mL. Typical batch process comprise of taking 1.0 g of biomass in 20 mL of HCl (1–5 M) in the reactor. A preheated air oven is used for heating the reactor to the desired temperature (393 and 423 K). The reaction was quenched by immersing the reactor in a cool water bath after the desired reaction time. The reaction product was collected and separated from the unreacted residual biomass by filtration through a Whatman® (150 MM Φ) filter paper. The residue is washed with excess distilled water and dried overnight at 373 K and weighed. The difference between the initial and final weight of the biomass is a measure of the amount of biomass converted to the reaction products.[27] The yield of levulinic acid (wt%) is calculated from the following equation based on the weight of the raw material.[16]

$$\text{Yield of levulinic acid (wt\%)} = [\text{levulinic acid content after reaction (g)/Initial biomass content (g)}] \times 100.$$

Analysis of reaction products

Even though HPCL analysis could not be conducted, the potential of ^{13}C and ^{1}H NMR spectroscopy was exploited for the identification and estimation of levulinic acid. Reaction products from the biomass were analyzed by ^{13}C NMR spectroscopy

for the confirmation of levulinic acid formation and identification of other by products. ^{1}H NMR spectroscopy is used for the quantification of levulinic acid using pyrogallol as internal standard.[21] D_2O was employed as solvent. Typical sample for analysis comprise of 400 μL of the analyte and 200 μL of the solvent and known amount of pyrogallol. Spectral analysis was carried out at room temperature. ^{13}C and ^{1}H NMR spectra were recorded on Bruker Avance DPX 300.

3. Results and discussion

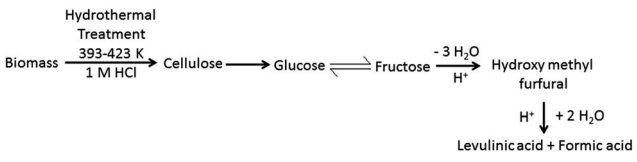
Girisuta *et al.*, investigated the kinetics as well as the sequence of reactions involved in the conversion of glucose to levulinic acid.[28] Acid hydrolysis of lignocellulosic biomass leads to the conversion of the cellulose component to glucose. The glucose generated isomerizes to fructose which is dehydrated *in situ* to form the intermediate product, hydroxyl methyl furfural, which subsequently undergoes hydration to form the decomposition products, levulinic acid and formic acid.[19,29,30] A series of hydrolysis, dehydration and rehydration reactions involved in the conversion of biomass to levulinic acid in the presence of an acid catalyst are shown sequentially in Scheme 2.

Levulinic acid formation through HMF intermediate is always accompanied by the formation of formic acid as a byproduct, which is unavoidable imposing a theoretical limit of 64.4 wt% yield of levulinic acid from glucose.

HCl is used as acid catalyst for the conversion of different biomass, namely, *Cicer arietinum* (CA), cotton, *Pinus radiata* (PR) and sugar cane bagasse. Use of HCl is based on the reports of Bevilaqua *et al.*, 2013 and Tabasso *et al.*, 2014. HCl was reported to be more efficient than H_2SO_4 for levulinic acid production.[18] Among various mineral, acids based on the reactivity and volatile nature, HCl is preferred.[20] Solid acid catalysts are also being vigorously investigated as possible alternative to mineral acids for making the process environmentally friendly which is outside the scope of the present study.[27,31]

Initially, the suitability of various biomasses for producing levulinic acid is tested under mild hydrothermal reaction conditions (393 K, 1 M HCl, 1 h). The values of conversion of biomass, yield of levulinic and formic acids are depicted in Fig. 2. The nature of the biomass was found to have significant effect on the conversion and levulinic acid yield. A sharp contrast is observed in the conversion of cotton compared to other biomasses, CA, PR and bagasse. The lowest value of conversion (7.1 wt%) of cotton is due to the structural rigidity.

The mild conditions used for the hydrolysis could not convert cotton effectively even though relatively higher values of



Scheme 2 Schematic representation of conversion of biomass to levulinic acid.

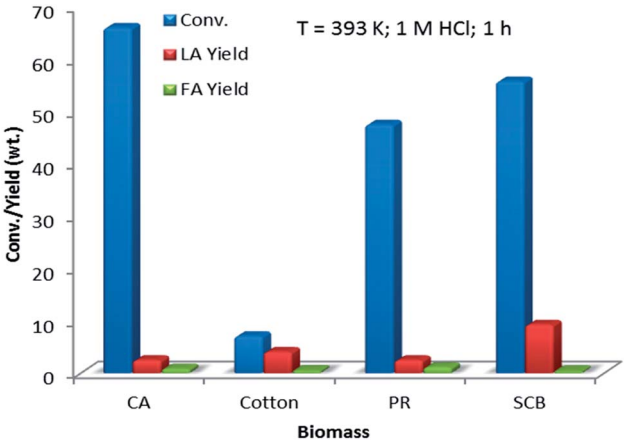


Fig. 2 Effect of nature of biomass on the hydrolysis reaction (393 K; 1 M HCl; 1 h).

conversion are achieved in the case of CA (66%), PR (47.5%) and bagasse (55.8%). In spite of the high conversion values, the yields of levulinic acid are low. Hydrolysis at 393 K with 1 M HCl yielded monosaccharides as major product. The presence of monosaccharides in the hydrolyzate is shown in the ^{13}C NMR spectra (Fig. S1†). Jeong *et al.*, observed minimum production of levulinic acid under the optimum conditions (139.4 °C, 3% H_2SO_4, 15 min) for sugars and major amount of levulinic acid production at higher reaction temperature (160 °C) from *Gelidium amansi*.[32]

To improve the reactivity of cotton and optimize the reaction conditions for levulinic acid, production the concentration of HCl is varied from 1 to 5 M with other conditions being the same (393 K, 1 h). The effect of concentration of HCl on the conversion of cotton and the yield of levulinic and formic acids is shown in Fig. 3. Even the poorly reactive cotton showed a steep raise in the conversion from 7.1 to 56.3 wt% as the HCl concentration is increased from 1 to 5 M. Proportionately, the

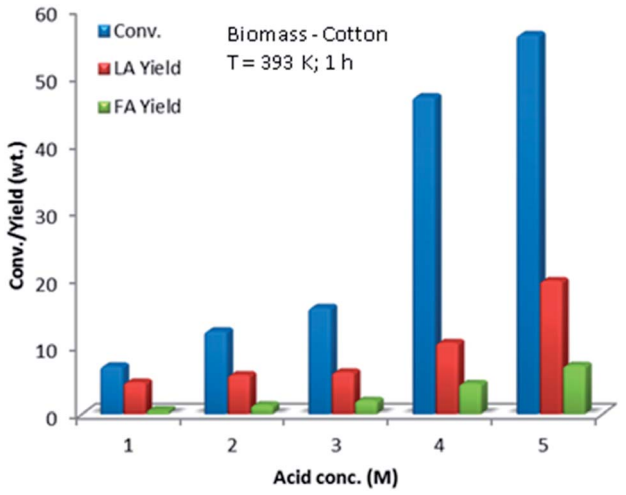


Fig. 3 Effect of concentration of acid on the conversion of cotton and yields of levulinic and formic acids.

yields of levulinic acid also increased from 4.7 to 19.8 wt%. Even though there is an 8 fold increase in the cotton conversion, the yield of levulinic acid is enhanced only by 4 fold with 5 M HCl. This different is attributed to the unreacted glucose in the solution along with levulinic and formic acids. The presence of glucose was observed in the ^{13}C NMR spectrum of the hydrolyzate.

Even though the use of higher acid concentration improved the conversion of cotton and yield of levulinic acid, corrosion of industrial installations may limit the practical utility of the process. Alternately, the path way of increasing the reaction temperature for improving the levulinic acid yield has also been evaluated.

The variation in the conversion of different biomasses and the yields of levulinic and fomic acids in the hydrolysis process carried out at 423 K is shown in Fig. 4.

A steep increase in the levulinic acid yields is achieved by raising the reaction temperature from 393 to 423 K (Fig. 2 & 4). Cotton which has been poorly reactive at 393 K showed a conversion value of 78.7 wt% at 423 K and a levulinic acid yield of 44 wt%. This indicates that the reaction temperature has a more significant effect on biomass conversion rather than the acid concentration. The effect of reaction temperature on rate of chemical reactions is well studied and it is known that for every 10 °C raise in temperature the reaction rate is doubled. The enhancement in the conversion of biomass as a function of temperature could be due to reduced hydrogen bonding interactions that facilitate easy accessibility of acidic protons to the, reaction site β-(1 → 4)-glycosidic bonds. In fact, the extensive inter and intra molecular bonding hydrogen as well as the type of linking of the D-anhydro-glucopyranose prevailing in the cellulose structure makes the hydrolysis of cellulose nearly 2 orders of magnitude tougher than starch hydrolysis.

The levulinic acid yields from *Cicer arietinum* (CA), *Pinus radiata* (PR) and sugar cane bagasse (SCB) are 32.6, 19 and 36.5 wt%, respectively, which are lower than the yield obtained from cotton (44 wt%). Even though sugar cane bagasse was widely investigated as feedstock for levulinic acid production, there have been no reports on the feasibility of conversion of stalks of *Cicer arietinum*, cotton, and pine cones from *Pinus radiata* to levulinic acid. In principle the ratio (wt/wt%) of levulinic and formic acids in the product hydrolyzate should be 2.5 as only one molecule of formic acid is formed per each glucose molecule that is converted to levulinic acid. In the present context, the ratio (wt/wt%) of levulinic to formic acids is observed to be in the range of 2.7–4.7 which is greater than the expected ratio. This indicates the possibility of additional pathways being operative for the formation of formic acid from the biomass. In particular, the hemicellulose (polymer of C5 sugars) yields xylose whose decomposition yields formic acid.[28] The excess formic acid in the product than the usual equimolar product distribution of levulinic and formic acid could be attributed to the xylose degradation. To substantiate this, pure xylose was subjected to acid hydrolysis under identical conditions and formic acid formation as a by product in addition to the main dehydration product furfural is noticed.

The formation of levulinic and formic acids as a result of the hydrothermal treatment of biomass (423 K, 1 M HCl, 2 h) is revealed from the ^{13}C NMR spectra shown in Fig. 5.

Signals typical of levulinic acid are observed in the reaction products from the biomasses tested. The peaks corresponding to levulinic acid are indicated and assigned to particular carbon nuclei in the levulinic acid structure from which the signal is originating (Fig. 5).

Signals characteristic of the two methylene groups one adjacent to the carbonyl and the other adjacent to the carboxyl are observed at 28.3 and 38.2 ppm. Signals typical of the methyl group and the carboxyl groups are observed at 29.6 and 177.8 ppm. Peak corresponding to the carboxyl carbon of levulinic acid that appeared at 214.2 ppm is not included in the presented region of the spectra. The ^{13}C NMR spectra of the levulinic acid produced from biomass matched well with the standard spectrum of levulinic acid (Spectral Database for Organic Compounds, SDBS, National Institute of Advanced Industrial Science and Technology, Japan). Further, the ^{13}C NMR spectrum of the levulinic acid sample procured from

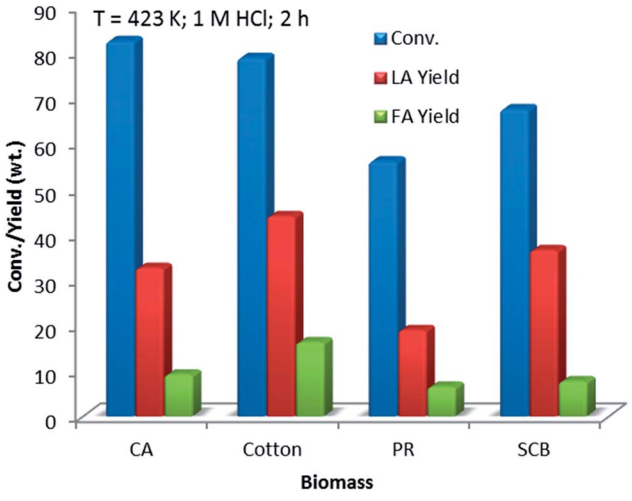


Fig. 4 Conversion of biomass and yield of levulinic and formic acids at 423 K.

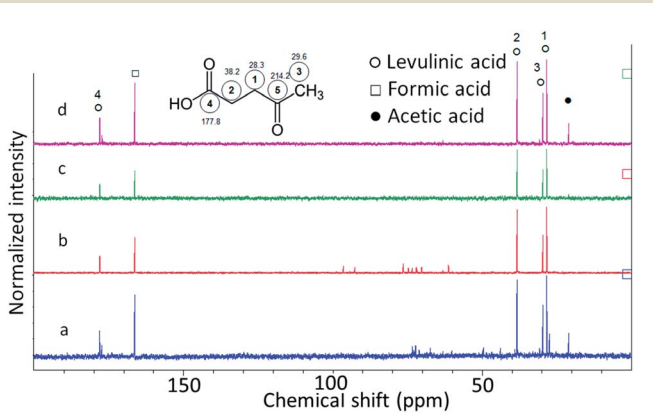


Fig. 5 ^{13} C NMR spectra of hydrolyzate from, (a) *Cicer arietinum* (b) cotton and (c) *Pinus radiata*, (d) sugar cane bagasse at 423 K using 1 M HCL for 2 h.

Sigma Aldrich is recorded and shown in Fig. S2.† The ^{13}C NMR signals of the levulinic acid produced from different biomass are in accordance with the signals of commercial LA. This indicates that the biomass tested are potential sources of levulinic acid with varying yields.

In addition to the peaks typical of levulinic acid, signals characteristic of formic acid (166.3 ppm) and acetic acid (21 ppm) are also observed. The formic acid formation is due to the decomposition reaction of glucose produced from biomass to levulinic acid and formic acid in accordance with Scheme 2. The source of acetic acid is the hemicellulose component that is present in the lignocellulosic biomasses, *Cicer arietinum*, *Pinus radiata* and sugar cane bagasse. Rackemann *et al.*, 2014 and Dussan *et al.*, 2013 reported hemicellulose as the origin of formation of acetic acid in biomass conversion.[25,33] Moreover, the acetic acid (21 ppm) peak is absent in the reaction product obtained from cotton which is pure cellulose and devoid of hemicellulose. This further authenticate that the acetic acid by product is originating from the hemicellulose component in the conversion of lignocellulosic biomass. In the case of *Cicer arietinum* and cotton additional signals in the range of 60–100 ppm attributable to undegraded glucose are observed (Fig. 5(a) and (b)).

Levulinic acid produced from biomass is further confirmed from ^{1}H NMR analysis (Fig. 6). The appearance of a singlet signal at 2.2 ppm (3H, s), two triplets at 2.38 (2H, t) and 2.65 (2H, t) ppm confirm the presence of levulinic acid. For comparison the ^{1}H NMR spectrum of the authentic sample of levulinic acid procured from Sigma Aldrich is shown in Fig. S3† which matched well with the spectra of levulinic acid produced from biomass (Fig. 6). Complementary to the presence of a peak at 21 ppm in the ^{13}C NMR spectra (Fig. 5) a signal at 1.9 ppm is evident in the ^{1}H NMR spectra of the reaction product from biomass (Fig. 6). This peak corresponds to the formation of acetic acid as by product. Moreover, the peak at 1.9 ppm is only present in the product obtained from lignocellulosic biomasses (*Cicer arietinum*, *Pinus radiata* and sugar cane bagasse) and is absent in the hydrolyzate from cotton which is pure cellulose.

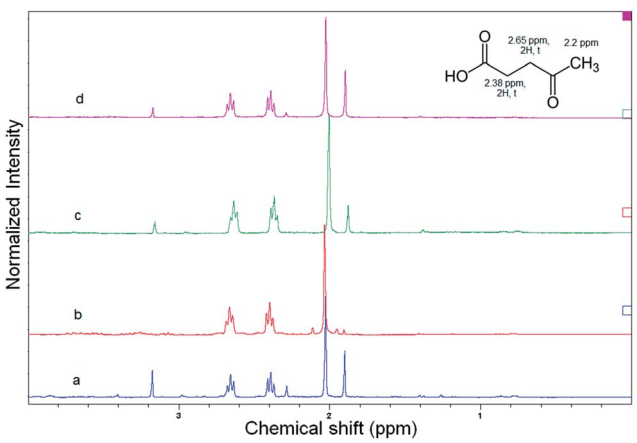


Fig. 6 ^{1}H NMR spectra of hydrolyzate from, (a) *Cicer arietinum* (b) cotton and (c) *Pinus radiata*, (d) sugar cane bagasse at 423 K using 1 M HCl for 2 h.

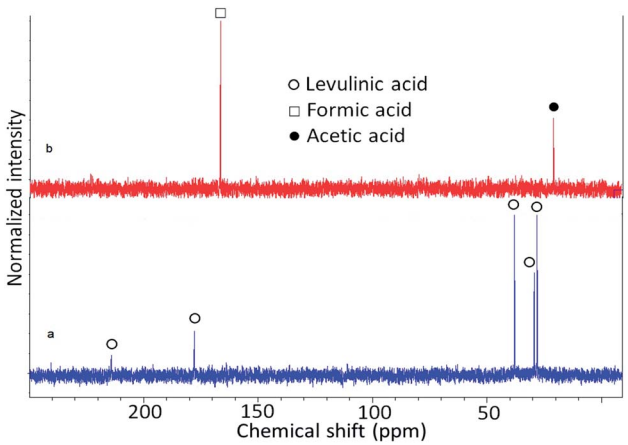


Fig. 7 ^{13}C NMR spectra of (a) residue and (b) distillate separated from the hydrolyzate obtained from sugar cane bagasse using rotoevaporation.

Levulinic acid in pure form could be isolated from the product mixture containing the reaction by products based on the difference in the boiling points using rotoevaporation (evaporation under reduced pressure) technique. The high boiling point of levulinic acid (245 °C) facilitates easy evaporation of low boiling point by products (formic and acetic acids).

The reaction product obtained from the hydrolysis of sugar cane bagasse is subjected to rotoevaporation (Laborota 4000-efficient) at 70 °C for 1 h. Reaction byproducts as well as water were completely removed from the container leaving behind levulinic acid.

The product after the rotoevaporation as well as the distillate obtained were analyzed using ^{13}C NMR to evaluate the effectiveness of isolation of levulinic acid (Fig. 7). Exclusive presence of levulinic acid is observed in the residue when the hydrolyzate is subjected to rotoevaporation (Fig. 7(a)). The distillate contained acetic acid and formic acid (Fig. 7(b)).

Rotoevaporation is thus a simple method for the isolation of levulinic acid from the hydrolyzate of biomass.

4. Conclusion

The feasibility of levulinic acid production from *Cicer arietinum*, cotton, *Pinus radiata* and sugar cane bagasse is demonstrated. Among various biomasses studied, cotton showed highest yield (44 wt%) of levulinic acid under modest reaction conditions. Widely available agricultural wastes *Cicer arietinum* and sugarcane bagasse were economically viable and environmentally benign feedstock yielding 32.6 and 36.5 wt% levulinic acid respectively. Reaction temperature was found to be a crucial parameter compared to the concentration of acid in the conversion of biomass. Levulinic acid could be easily separated from the product mixture comprising the reaction by products formic and acetic acids using rotary evaporation. Hydrothermal method offered a simple means for the production of levulinic acid from biomass.

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