

Valorization of cigarette butts for top value-added chemicals: Levulinic Acid

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Research Article

Keywords: CH₃COOH, sludge paper, H₂SO₄, HCl, chemical industry, 5-hydroxymethylfuraldehyde

Posted Date: March 11th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-296494/v1>

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Version of Record: A version of this preprint was published at Scientific Reports on August 4th, 2021. See the published version at <https://doi.org/10.1038/s41598-021-95361-4>.

Abstract

Levulinic acid (LA), one of the top value-added intermediates of chemical industry, can be obtained by thermal hydrolysis (at 200 °C) from cigarette butts (as cellulose feedstock) catalysed by phosphoric acid. The protocol avoids the use of more aggressive H₂SO₄ and HCl, that are generally employed on several cellulose sources (e.g. sludge paper), thus minimizing corrosion phenomena of plants. Neither chemical pre-treatment of butts nor specific purification procedure of LA are required. Notably, by simply modifying acid catalyst (e.g. using CH₃COOH), another top value-added fine chemical such as 5-hydroxymethylfuraldehyde (HMF) is obtained, thus widening the scope of the method. Being cigarette filters a waste available in quantities of megatonnes per year, they represent an unlimited at no cost source of cellulose, thus enabling the up-scale to an industrial level of LA production.

Introduction

The conscious use of the planet's natural resources has become mandatory to ensure the survival of life on earth. To this end, the imperative contribution that the scientific community can provide is to develop new sustainable process and materials, with a significant impact on the social level and with a reduced environmental repercussion. In this context, the tuning of new chemical approaches to exploit the waste has an extreme importance in the realization of the virtuous path that Circular Economy is encouraging, to create environmental and social benefits, in a "Rethinking Progress" approach for sustainable development and sustainability.

Exploiting biomass is the true weapon to face this challenge, the true road for producing energy, fine chemicals and bio-based manufactures in a sustainable manner, thus definitively eliminating the dependence on fossil sources, without loss of soil¹.

Important examples of biomass are wood and energy crops, such as for example soy, useful for producing biofuels but also bio-based chemicals and polymers². Recent years have witnessed a rapid growth in the production of fuels³ and materials entirely deriving from biomasses.⁴ However, this has led to many troubles such as improper exploitation of soils (non-food applications), increase of raw materials price (especially in Third World countries), biodiversity reduction, soil erosion and increased risk of insects and bacteria that destroy crops¹.

Biomass wastes can be the right solution to these problems², constituting a widely available and no cost reservoir of carbohydrates, lipids and proteins, with possible on-site processing, coming from scraps of forests, yards, farms, or municipal waste foods, the proportion of which has been estimated at hundreds of megatonnes (Mt) per year around the world⁵.

Carbohydrates, the main component of these vast reservoir, can be converted via biological or chemical routes into Levulinic Acid (LA)^{6,7}, which is considered one of the twelve most promising industrial bio-intermediates and amongst the most innovative building blocks of chemical industry, due to its

conversion in several high-value bio-based chemicals and materials (Fig. 1)⁶ The main end users of LA are agricultural, pharmaceutical, and cosmetic sectors, although this natural molecule also contributes to the creation of new ecological fuels, fertilizers, and pesticides. It is also used in the biodegradable plastics field and as intermediate element for creating high-performance plastic materials, medicines, and many other new concept "green" products, thus allowing to broaden its scope of application. According to the most recent studies, it is estimated that the world market demand for LA will grow 150-200 times over the next 7-8 years⁷.

The well-known approach to convert lignocellulosic materials (wood, paper, food crops wastes) into levulinic acid is the thermal treatment with strong Brønsted acids (e.g. H₂SO₄) as homogeneous catalysts^{8,9}. To date, a two-step continuous process is used to obviate the deterioration of the plants. Hemicellulose and cellulose fractions of biomass are preliminarily hydrolyzed in a first reactor (at 210 - 230 °C, for few seconds in the presence of 1% - 5% of mineral acid) producing hydroxymethylfurfural (HMF), that is removed in flow feeding continuously a second reactor where it is further hydrolyzed to produce LA (Figure 2)⁹⁻¹²

Despite the high yields, this strategy is difficult to apply at an industrial level, due to the harsh conditions and plants corrosion⁹. To date, only few companies can produce LA at commercial scale directly from biomass^{9,12}. In recent years, much attention has been paid to producing LA by means of milder and more eco-sustainable conditions,¹³ for example employing heterogeneous acid catalysts and green solvents such as water or ionic liquids (ILs)^{7,14}.

As regards the cellulosic starting material, beside agricultural scraps⁹, municipal paper wastes are gaining attention¹⁴. Among these latter, cigarette filters represent a neglected and no cost reservoir of cellulose acetate¹⁵, that is virtually boundless if considering that about 5.5 trillion cigarettes are produced each year¹⁶. Notably, dirty cigarette butts (CBs) are considered a dangerous waste, because of the content of organic and heavy metals contaminants, therefore their use as starting raw materials is rather complex and essentially limited to production of asphalts, mesoporous carbon, and cellulose pulp¹⁶⁻¹⁸. Recently, bioethanol has been produced by fermentation of cellulose obtained by deacetylation of CBs¹⁹, but no attempts have been reported until now on their use to produce LA or other fine chemicals.

Following our ongoing interest in developing green protocols obeying to circular economy principles^{20, 21} we report herein, unprecedented in the literature, a protocol that exploits cigarettes filters as source of Levulinic acid avoiding the strong acidic conditions and extendable at an industrial level.

Results And Discussion

In the proposed procedure the preliminary digestion with strong acids (H₂SO₄) was circumvented using a one-pot procedure involving the less aggressive H₃PO₄²², that preserves fibres structure compared to analogous strong Brønsted acids¹¹. According to most of reported procedures, catalytic hydrolysis

experiments were conducted in a batch reactor processing 250 mg of filters in 15 mL of aqueous H_3PO_4 at different times and temperatures¹² (Table 1). Formation of Levulinic Acid was surveyed by GC/MS and NMR techniques. Both unsmoked and smoked cigarette butts were tested as source of cellulose biomass, whereas acetic and formic acids were formed as by-products together with HMF as an intermediate (Figure 3)^{13,23}.

Blank reaction carried out in the absence of H_3PO_4 led to the complete recovery of unreacted filters, thus confirming that Brønsted acids are true catalysts for the process (Table 1, entry 1). The successive experiments, aimed at evaluating the temperature effect, showed that reaction requires a minimum heating at 180 °C, displaying the maximum yield of 43.9 % in levulinic acid at 240 °C (Table 1, entries 2-6). However, the increase of temperature led also to significant increments of humins by-products (Table 1, entries 5-7).

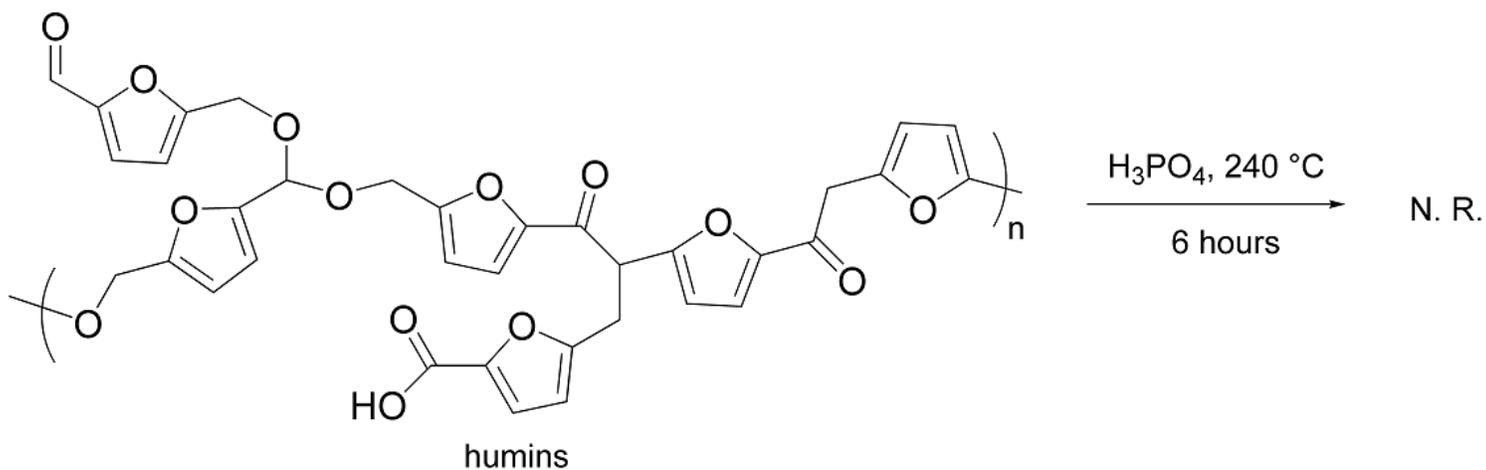
Amount of starting material proved to be a further parameter affecting reaction yield, with 250 mg representing the optimal value (Table 1, entries 5, 8-10). Catalyst loading and reaction time were also investigated. In the former case, the increment of concentration of aqueous H_3PO_4 up to 2.0 M resulted in a neglectable increase of yield in levulinic acid respect to preliminary experiments, thus suggesting that 1.5 M is the best value (Table 1, entries 5, 11-12). In contrast, much prolonged times afforded beneficial effects on reaction yields, allowing to reach a 49.6% of yield in levulinic acid after 6 hours (Table 1, entries 13-14). As expected, no conversion in LA was observed when H_3PO_4 was replaced by a weak acid such as CH_3COOH . Notably, in this case another value-added fine chemical, namely 5-hydroxymethylfuraldehyde (HMF), was observed as unique product, widening the scope of this method (Table 1, entry 15).

Table 1. Synthesis of levulinic acid from cigarette filters.

| Entry | Filters weight (mg) | Catalyst (M) ^b | T (°C) | Time (h) | Levulinic acid yields | |
|-----------|---------------------|--|------------|----------|-----------------------|----------------------------|
| | | | | | (%) ^c | (% filter wt) ^d |
| 1 | 251.24 | — | 200 | 2 | — | — |
| 2 | 253.38 | H ₃ PO ₄ (1.5) | 160 | 2 | — | — |
| 3 | 250.38 | H ₃ PO ₄ (1.5) | 180 | 2 | 22.5 | 10.43 |
| 4 | 252.85 | H ₃ PO ₄ (1.5) | 190 | 2 | 24.7 | 11.42 |
| 5 | 253.19 | H₃PO₄ (1.5) | 200 | 2 | 36.7 | 17.32^e |
| 6 | 250.57 | H₃PO₄ (1.5) | 240 | 2 | 43.9 | 20.28^e |
| 7 | 252.93 | H ₃ PO ₄ (1.5) | 260 | 2 | 35.4 | 16.36 ^f |
| 8 | 101.70 | H ₃ PO ₄ (1.5) | 200 | 2 | 24.3 | 11.28 |
| 9 | 200.80 | H ₃ PO ₄ (1.5) | 200 | 2 | 35.7 | 16.47 |
| 10 | 299.50 | H ₃ PO ₄ (1.5) | 200 | 2 | 30.1 | 13.90 |
| 11 | 251.55 | H ₃ PO ₄ (0.7) | 200 | 2 | 25.2 | 11.46 |
| 12 | 250.96 | H₃PO₄ (2.0) | 200 | 2 | 41.4 | 19.15 |
| 13 | 250.37 | H ₃ PO ₄ (1.5) | 200 | 1 | 17.3 | 8.00 |
| 14 | 251.04 | H₃PO₄ (1.5) | 200 | 6 | 49.6 | 22.94 |
| 15 | 252.52 | CH ₃ COOH (4) | 200 | 2 | — | — ^g |

^a Procedure as reported in experimental section. ^b Volume = 15 mL. ^c Referred to theoretical amount of LA.¹² ^d Referred to the filter weight. ^e Humines= 79 mg (32% w/w). ^e Humines= 173 mg (69% w/w), ^f Humines = 205 mg (82% w/w). ^g 5-hydroxymethylfuraldehyde (HMF) was the main product. (see MS spectrum in Supplemental Information)

Attempts were done to increase the yields of levulinic acid, re-submitting residual humins by-products to the hydrolysis conditions at higher temperatures and prolonged reaction times. The total absence of products indicated that such conditions are not sufficiently hard to give the cleavage of the furan-based polymeric skeleton of humins (eq. 1).



Results in Table 1 showed that the best hydrolysis conditions are 240 °C for 2 hours or 200 °C for 6 hours (Table 1, entries 6 and 14). Nevertheless, in both these cases, greater quantities of solid residue were observed probably due to the higher temperature and the longer times. Therefore, milder conditions of 200 °C for 2 hours were selected for the successive experiments aimed at studying both real waste samples such as the smoked filters and the influence of their pre-treatment (e.g. washing).

At this end, smoked cigarette filters were washed with 100 ml of water at 80°C for three times. The collected water fractions were extracted with ethyl acetate and the organic phase was analysed by GC/MS revealing triacetin (triacylglycerin) as the main product, which is a humectant additive, and trace amounts of phenolic compounds.

As reported in Table 2 (entries 1-2), almost identical results in terms of yields were obtained with washed and unwashed cigarette butts.

Data in Table 2 (entries 4-5) also show that this protocol can favourably compete with analogous ones reported in the literature based on the use of H_2SO_4 and HCl in that very similar yields of levulinic acid can be obtained with a less corrosive acid and toxic H_3PO_4 thus minimizing the corrosion phenomena^{11,22}.

In addition we have also avoided the thermal pre-treatment, which although it increases the yield of levulinic acid, requires a greater expenditure of energy. (entries 3)

Table 2. Synthesis of Levulinic acid from smoked cigarette filters.^a

| entry | Raw material (weight) | Catalyst (M) | T (°C) | Time (h) | LA yields | | Ref. |
|-------|-------------------------------------|---------------------------------------|--------|----------|------------------|----------------------------|-----------|
| | | | | | (%) ^c | (% filter wt) ^d | |
| 1 | Washed filter (251.15 mg) | H ₃ PO ₄ (1.5) | 200 | 2 | 33 | 15.30 | This work |
| 2 | Unwashed filter (251.29 mg) | H ₃ PO ₄ (1.5) | 200 | 2 | 31 | 14.31 | This work |
| 3 | Filter-paper cellulose ^e | H ₃ PO ₄ (0.15) | 200 | 2 | - | 40 | [11] |
| 4 | Paper sludge | H ₂ SO ₄ (0.47) | 200 | 1 | 26.5 | 15.1 | [12] |
| 5 | Paper sludge | HCl (0.47) | 200 | 1 | | 31.4 | [12] |
| | | | | | 55.1 | | |

^a Procedure as reported in experimental section. ^b Volume = 15 mL. ^c Referred to theoretical amount of LA. ^d Referred to the filter weight. ^e The pretreatment temperature and time were set to 50 °C and 24 h.

Moreover, NMR analyses (Figure 4) of crude reaction product of unwashed cigarette butts, revealed that levulinic acid was obtained with the same high degree of purity of that obtained with unsmoked filters (besides a little solvent residue removable *in vacuo*).

These results suggest that that dirt or contaminants of the smoked cigarettes do not interfere with the reaction outcome¹⁷ and that the method is highly selective and doesn't require neither special pre-treatment of the starting waste material nor specific purification procedure of the reaction product.

Further aspects that represent crucial advantages for a plausible industrial application of this method concern: i) the possibility of recycling humins wastes through thermal valorisation (burning) or syn-gas production²⁴, although more recently they have been used for producing macroporous foam-like materials²⁵; ii) the prompt recycle (by distillation) of Ethyl Acetate used for extracting Levulinic acid; iii) the possibility of recovering water phase by eliminating phosphoric acid through precipitation²⁶ and COD by Fenton treatments²⁷.

A complete process diagram of this protocol is listed in Figure 5. In line with Green Chemistry and Circular Economy principles, an E-factor of 19.08 (about 9 with H₃PO₄, but with heat pre-treatment¹¹), very close to that of the pharmaceutical industries and chemical industry²⁸, was calculated taking into account that most of material involved can be recycled and valorized such as in the case of humins that represent a new platform for production of mesoporous carbons.

Conclusion

Unprecedented in the literature, cigarette butts can be used as cellulose feedstock for producing Levulinic acid, one of the top value-added intermediates of chemical industry, by means of thermal hydrolysis (at 200 °C) catalysed by phosphoric acid. The proposed protocol avoids the use of more aggressive H_2SO_4 and HCl, that are generally used for promoting this transformation from other cellulose sources (e.g. sludge paper), thus minimizing corrosion phenomena of plants. Further benefits that enable this method to be suitable for industrial applications are the following:

- reaction doesn't require neither pre-treatment of the starting material nor specific purification procedure of levulinic acid product;
- the possibility of recycling all the process components, ranging from humins by-products (by thermal valorisation), to the extracting solvent Ethyl acetate (by distillation), until to water phase residue (by Fenton COD abatement);
- the opportunity of obtaining, by simply modifying acid catalyst (e.g. using CH_3COOH), another top value-added fine chemical such as 5-hydroxymethylfurfuraldehyde (HMF), thus widening the scope of the protocol.

Further advantages such as the huge amount of cigarette filters (megatonnes per years) that provide a no cost unlimited source of cellulose, suggest that this protocol marks a significant step forward compared to the current literature on this important issue.

Materials And Methods

Materials: Ethyl acetate (>99%) was purchased by Honeywell, Phosphoric acid (85%) and Levulinic acid were purchased from Sigma-Aldrich. All the reagents and solvents were used as received, without any further treatment. GC-MS analyses were run on a Shimadzu GLC 17-A instrument (Shimadzu, MI, Italy) using a SLB-5MS column (30 m x 0.25 mm id, film thickness 0.25 μm). Mass spectra were performed in EI mode (70 eV) and yields of LA were determined via GC-MS by means of a calibration curve. NMR spectra were recorded on a Bruker 500 MHz spectrometer: ^1H NMR (500 MHz) spectra were referenced to residual isotopic impurity of CDCl_3 (7.25 ppm) and ^{13}C -NMR (125 MHz) spectra were referenced to 77.00 ppm.

Attenuated Total Reflectance-Fourier transform infrared spectroscopy (ATR-FTIR).

FTIR analyses were carried out on a Perkin-Elmer UATR Two spectrophotometer equipped with a single reflection diamond ATR crystal (refractive index of 2.4). Spectra were acquired with 32 scans in the range 4000 - 600 cm^{-1} by applying both the baseline and the ATR corrections.

Levulinic acid synthesis

Weighed amounts of cigarette butts (250 mg ca. of "Rizla + ultra slim 5,7 mm") were finely chopped in small pieces and suspended into 15 mL of aqueous H_3PO_4 . Three different concentrations of H_3PO_4 were

explored: 7,5% w/w, 15 % w/w, and 20 % w/w. Each suspension was charged into a 100 mL stainless steel autoclave and heated at temperatures in the range 160 - 260 °C for different times (1 - 6 hours). After cooling, mixture was filtered and/or centrifugated to separate solid "Humins", that were dried and weighed to give from 20% to 80% of yield (depending on the reaction conditions), while supernatant was extracted with ethyl acetate (2 × 20 mL). Combined organic phases were dried and the solvent removed *in vacuo* to give levulinic acid as crude oil.

Optimized procedure was then applied to washed and non-washed smoked cigarette butts recovered in Chemistry Department of Bari University, that were previously disinfected under UV rays and mechanically separated by the surrounding paper. A test was also carried out using unsmoked filter and 15 mL of aqueous CH₃COOH 4M in place of H₃PO₄ as catalyst. Dirty cigarette butts were washed in 3 cycles with 100 mL of water at 80 °C.

Synthesis of Levulinic Acid on grams scale

To validate the protocol, reaction was repeated on grams scale. At this end, 5 g of unwashed smoked filter were treated, in autoclave, with 300 mL of aqueous H₃PO₄ 15% (w:w) for 2 hours. Mixture was filtered and aqueous solution transferred into a separating funnel and extracted with Ethyl Acetate. The combined organic phases were distilled in vacuum to give 0.85 gr of Levulinic acid, while humins fraction was 1.4 g (corresponding to 28 % w/w respect to the starting waste material).

Humins were characterized by ATR-FT /IR²⁵ (see Supplemental Information), while Levulinic acid by ¹H-NMR and ¹³C-NMR and GC/MS. All the spectra agreed with literature²⁹. Levulinic acid (**LA**): colorless liquid, bp 106-110 °C/6 mmHg; ¹HNMR (CDCl₃, 500 MHz): d 2.72 (t, J = 6.5 Hz, 2H), 2.58 (t, J = 6.5 Hz, 2H), 2.16 (s, 3H); ¹³CNMR (CDCl₃, 125 MHz): d 206.6, 178.2, 37.7, 29.7, 27.8, GC/MS (70 eV) m/z (rel. intensity): 116.00 (M+, 2.74), 56.00 (28.82) 43.00 (100).

Calculations and data analysis

Two different yields in Levulinic acid were calculated based on weight of filters and on theoretical amounts of LA. The first one, was calculated with the ratio Levulinic acid (g) obtained after the reaction/cigarette butts(g) x100

The theoretical maximum yield^{11,12} of Levulinic acid is calculated on 250 mg of cigarette butts that contain 245 mg (98% ca.) of cellulose acetate (C.A.).¹⁶ Considering a 2:1 stoichiometric ratio of transformation (a dimeric C.A. unit leads to 2 molecule of Levulinic acid) and that C.A. dimeric unit molecular weight (MW_{C.A.}) is 492.428 mg/mmol., the C.A. millimoles can be calculated as follows:

$$\text{mmol}_{\text{C.A.}} = \text{mg}_{\text{C.A.}} / \text{MW}_{\text{C.A.}} = [245 \text{ mg} / 492.428 \text{ mg/mmol}] = 0.4975 \text{ mmol}$$

Cellulose acetate total conversion leads to 2 moles of L.A. (P.M_{L.A.} = 116.11 mg/mmol) per cellulose acetate dimeric unit.

L.A. maximum millimoles and milligrams are obtained as follows:

$$\text{mmol}_{L.A.} = \text{mmol}_{C.A.} \times 2 = 0.995 \text{ mmol}$$

$$\text{mg}_{L.A.} = \text{mm}_{L.A.} \times \text{PM}_{L.A.} = [0.995 \text{ mmol} \times 116.11 \text{ mg/ mmol}] = 115.54 \text{ mg}$$

Theoretical maximum yield (% W/W) can be calculated as follows:

$$R_{\text{max}} (\%) = (\text{mg}_{L.A.}/250\text{mg}) \times 100 = (115.54 \text{ mg}/250 \text{ mg}) \times 100 = 46.2 \%$$

$$\text{Theoretical yield was calculated as } \text{mm}_{L.Aex.} / \text{mm}_{L.Ath} \times 100$$

*Determination of E-Factor.*⁴

Mass of reactants: 2.2 g of H₃PO₄ (85%) in 15 mL of water (solvent (water) has been excluded from this calculation), Cigarette Filter 0.250 g; total amount of reactants 2.2g+0.250g= 2.45 g

Mass of product : 0.043 g of LA + 0.079 g Humins=0.122

Amount of waste: (2.45-0.122)= 2.38

E-factor= Amount of waste/Amount of product=2.38/0.122= 19.08

Declarations

Acknowledgements: This work is partially supported by funds from European Union-19 FESR “PON Ricerca e Innovazione 2014–2020. Progetto: 20 Energie per l’Ambiente TARANTO-Cod. ARS01_00637”.

Author contributions statement: Conceptualization, A.G. L., V.P. and L. D.; methodology, M.C., A.G.L., O.L., investigation, O.L. A. G. L., M.C., data curation, C.F. A.N.; V.P.; L.D. writing—original draft preparation, A.N. and C. F.; review and editing. All authors have read and agreed to the published version of the manuscript.

Additional Information : Supplemental Information were reported : calibration curve, GC/MS analysis of Reaction with acetic acid, FTIR-ATR Humins

References

1. Pérez, A. P.; Eugenio, N. R. Status of local soil contamination in Europe: Revision of the indicator “Progress in the management Contaminated Sites in Europe, EUR 29124 EN, *Publications Office of the European Union, Luxembourg*, **JRC107508** (2018) doi:10.2760/0938041.
2. Mennino, S. Valorization of Waste: Sustainable Organocatalysts from Renewable Resources. *ChemSusChem* **13**, 439 – 468 (2020) DOI: <https://doi.org/10.1002/cssc.201902500>.
3. Massaro, M. et al. One-pot synthesis of ZnO nanoparticles supported on halloysite nanotubes for catalytic applications. *Clay Sci.* **189**, 105527 (2020) DOI: <https://doi.org/10.1016/j.clay.2020.105527>.

4. Pantone, V. et al. One-Pot Conversion of Epoxidized Soybean Oil (ESO) into Soy-Based Polyurethanes by MoCl₂O₂ Catalysis. *Molecules*, **22**, 333 (2017) DOI: <https://doi.10.3390/molecules220203332017>.
5. Tuck, C.O.; Pérez, E.; Horváth, I.T. Sheldon, R. A. Poliakoff, M. Valorization of Biomass: Deriving More Value from Waste. *Science*, **337**, 695-699 (2012) DOI: <https://doi.10.1126/science.1218930>.
6. Werpy, T.; Petersen, G. Top Value Added Chemicals from Biomass: Results of Screening for Potential Candidates from Sugars and Synthesis Gas. Department of Energy: Washington, DC, USA pp. 1–76 (2004).
7. Badgajara, K. C.; Wilson, L. D.; Bhanagea, B. M. Recent advances for sustainable production of levulinic acid in ionic liquids from biomass: Current scenario, opportunities and challenges *Sustain. Energy Rev.* **102**, 266–284 (2019) DOI: <https://doi.org/10.1016/j.rser.2018.12.007>
8. Signoretto, M., Taghavi, S.; Ghedini, E.; Menegazzo, F. Catalytic Production of Levulinic Acid (LA) from Actual Biomass. *Molecules* **24**, 2760 (2019) DOI: <https://doi.org/10.3390/molecules24152760>.
9. Pileidis, F. D., Titirici, M. M. Levulinic Acid Biorefineries: New Challenges for Efficient Utilization of Biomass. *ChemSusChem* **9**, 562 – 582 (2016) DOI: <http://dx.doi.org/10.1002/cssc.201501405>.
10. Fitzpatrick, S. W. Production Of Levulinic Acid From Carbohydrate-Containing Materials. *US Patent US005608105A* (1997).
11. Muranaka, Y; Suzuki, T.; Sawanishi, H.; Hasegawa, I.; Mae, K. Effective Production of Levulinic Acid from Biomass through Pretreatment Using Phosphoric Acid, Hydrochloric Acid, or Ionic Liquid. *Eng. Chem. Res.* **53**, 11611–11621 (2014) DOI: <dx.doi.org/10.1021/ie501811x>. |
12. Raspolli, Galletti, A.; Antonetti, C.; De Luise, V.; Licursi, D.; Di Nasso, N.N.O. Levulinic Acid from waste biomasses *BioResources*, **7(2)**, 1824–1834 (2012).
13. Raspolli, Galletti, A.; Antonetti, C.; Fulignati, S. Licursi, D. Direct Alcoholysis of Carbohydrate Precursors and Real Cellulosic Biomasses to Alkyl Levulinates: A Critical Review. *Catalysts* **10(10)**, 1221(2020) DOI: <https://doi.org/10.3390/catal10101221>.
14. Dutta, S. Influence of green solvent on levulinic acid production from lignocellulosic paper waste. *Bioresour. Technol*, **298**, 122544 (2020) DOI: <https://doi.org/10.1016/j.biortech.2019.122544>.
15. Marinello, S.; Lolli, F.; Gamberini, R.; Rimini, B. A second life for cigarette butts? A review of recycling solutions. *Hazard. Mater* **384**, 121245 (2020) DOI: <https://doi.org/10.1016/j.jhazmat.2019.121245>.
16. Kurmus, H.; Mohajerani, A. The toxicity and valorization options of cigarette butts. *Waste Management* **104**, 104–118 (2020) DOI: <https://doi.org/10.1016/j.wasman.2020.01.011>.
17. Torkashvand, J.; Farzadkia, M. A systematic review on cigarette butt management as a hazardous waste and prevalent litter: control and recycling. *Environ Sci Pollut Res Int* **26**, 11618–11630 (2019) DOI: <https://doi.org/10.1007/s11356-019-04250-x>.
18. Torkashvand, J.; Farzadkia, M.; Sobhi, H.R.; Esrafil, A. Littered cigarette butt as a well-known hazardous waste: A comprehensive systematic review *Hazard. Mater* **383**, 121242 (2020) DOI: <https://doi.org/10.1016/j.jhazmat.2019.121242>.

19. Shen, F. Deacetylation Processing of Waste Cigarette Butts for High-Titer Bioethanol Production toward a Clean Recycling Process *ACS Sustainable Chem. Eng.* **8**, 11253–11262 (2020) DOI: <https://dx.doi.org/10.1021/acssuschemeng.0c03979>.
20. P. Mastrorilli, A. Monopoli, M. M. Dell'Anna, M. Latronico, P. Cotugno, Nacci A. Ionic Liquids in Palladium-Catalyzed Cross-Coupling Reactions. *Top Organomet Chem* **51**, 237-286 (2015) DOI: 10.1007/3418_2013_64
21. Annese, C., D'Accolti, L., Fusco, C., Licini, G., Zonta, C. Heterolytic (2e) vs Homolytic (1e) Oxidation Reactivity: N–H versus C–H Switch in the Oxidation of Lactams by Dioxirans. *Eur. J.*, **23**, 259–262 (2017) DOI: <https://biblioproxy.cnr.it:2481/10.1002/chem.201604507>.
22. <https://www.materials.sandvik/en/materials-center/corrosion-tables/sulphuric-acid>;
<https://www.materials.sandvik/en/materials-center/corrosion-tables/phosphoric-acid>/
<https://www.materials.sandvik/en/materials-center/corrosion-tables/hydrochloric-acid> (Web data 02/28/2021)
23. Girisuta, B.; Janssen, L. P. B. M.; Heeres H. J. Green Chemicals A Kinetic Study on the Conversion of Glucose to Levulinic Acid. *Eng. Res. Des.*, **84(A5)**, 339–349 (2006) DOI: doi: 10.1205/cherd05038
24. Hoang, T. M. C.; van Eck, E. R. H.; Bula, W. Gardeniers, P. J. G. E.; Lefferts, L. Seshan, K. Humins based by-products from biomass processing as a potential carbonaceous source for synthesis gas production. *Green Chem.*, **17**, 959 (2015) DOI: 10.1039/c4gc01324g
25. Tosi, P. Auto-Crosslinked Rigid Foams Derived from Biorefinery Byproducts. *ChemSusChem* **11**, 2797–2809 (2018) DOI : 10.1002/cssc.201800778.
26. Bunce, J. T.; Ndam, E.; Ofiteru, I. D.; Moore, A.; Graham, D. W. A Review of Phosphorus Removal Technologies and Their Applicability to Small-Scale Domestic Wastewater Treatment Systems. *Environ. Sci.* **6**, 1-15 (2018) DOI: 10.3389/fenvs.2018.00008.
27. Zhang, M.-H.; Dong, H.; Zhao, L.; Wang, D.-x.; Meng, D. Sci. A review on Fenton process for organic wastewater treatment based on optimization perspective *Sci Total Environ.* **670**, 110–121 (2019) DOI: <https://doi.org/10.1016/j.scitotenv.2019.03.180>.
28. Williams, R. T., Williams, T. R. Green Techniques for Organic Synthesis and Medicinal Chemistry. First Edition. Edited by Wei Zhang and Berkeley W. Cue Jr. JohnWiley & Sons, Ltd. Published **2012** by JohnWiley & Sons, Ltd., pp 33-67 ISBN 978-0-470-71151-4 (cloth)
29. Chaudhari, D. A.; Fernandes, R. A. Hypervalent Iodine as a Terminal Oxidant in Wacker-Type Oxidation of Terminal Olefins to Methyl Ketones. *Org. Chem.* **81**, 2113–2121 (2016) DOI: 10.1021/acs.joc.6b00137

Figures

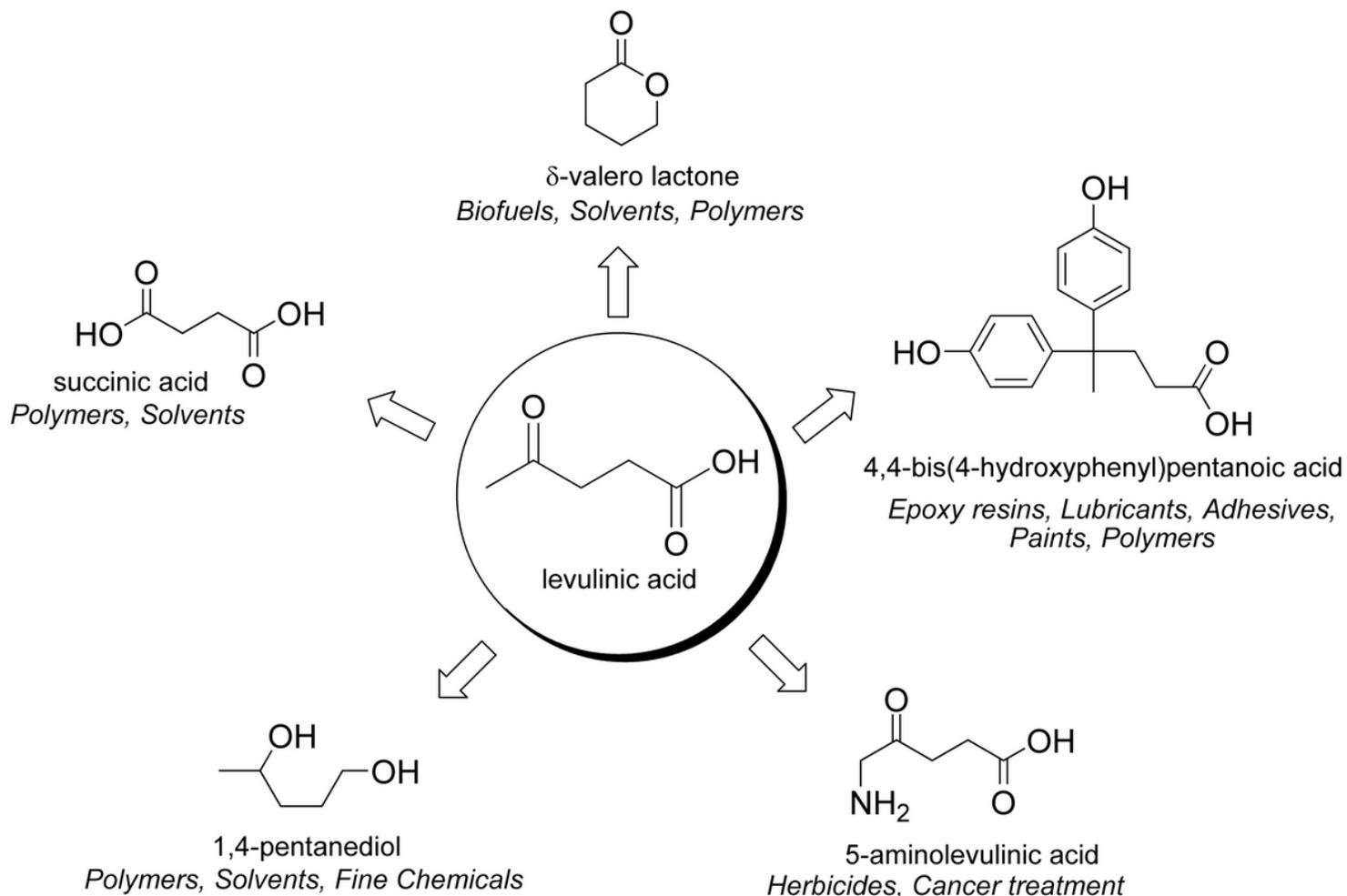


Figure 1

Levulinic acid as a key industrial intermediate.

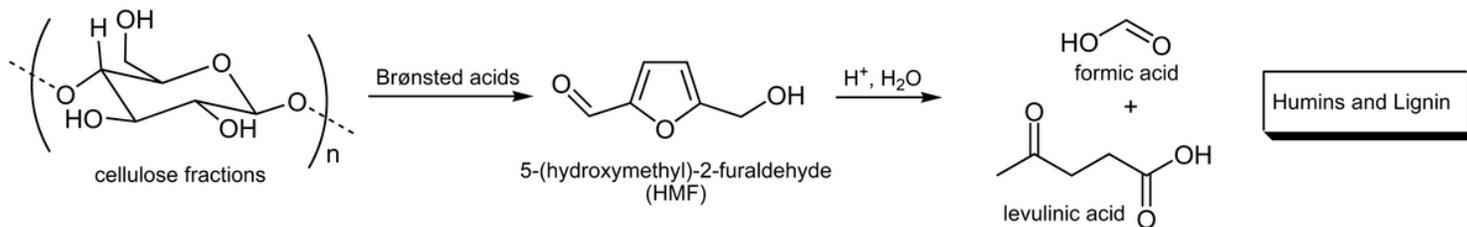


Figure 2

Two-step synthesis of Levulinic Acid.

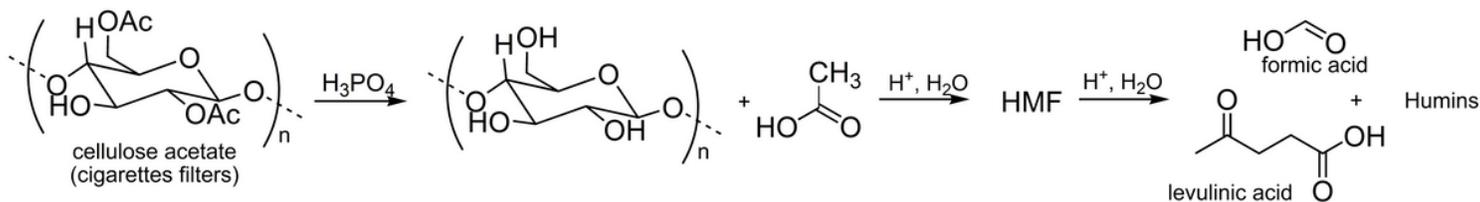
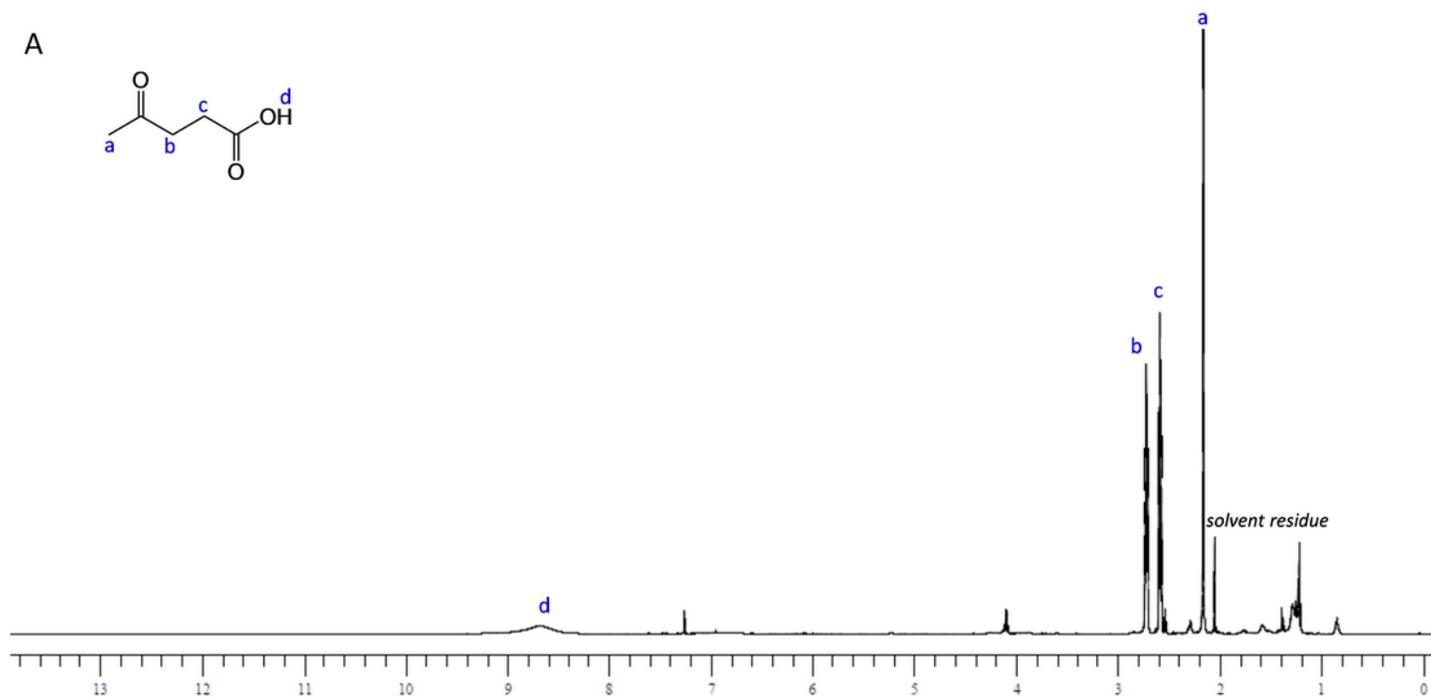
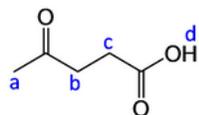


Figure 3

One-step synthesis of Levulinic Acid

A



B

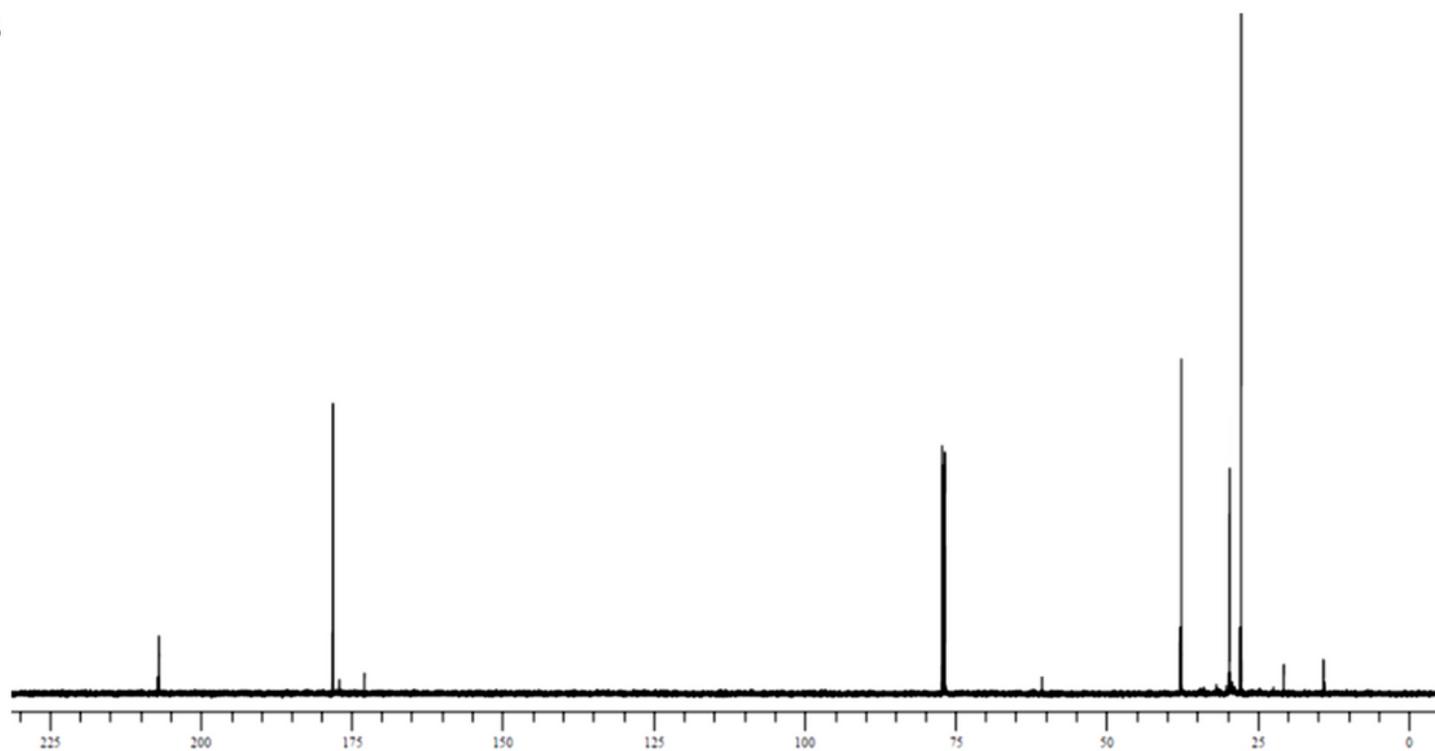


Figure 4

a) ¹H-NMR and b) ¹³C-NMR spectra (CDCl₃) of crude product from smoked unwashed filter.

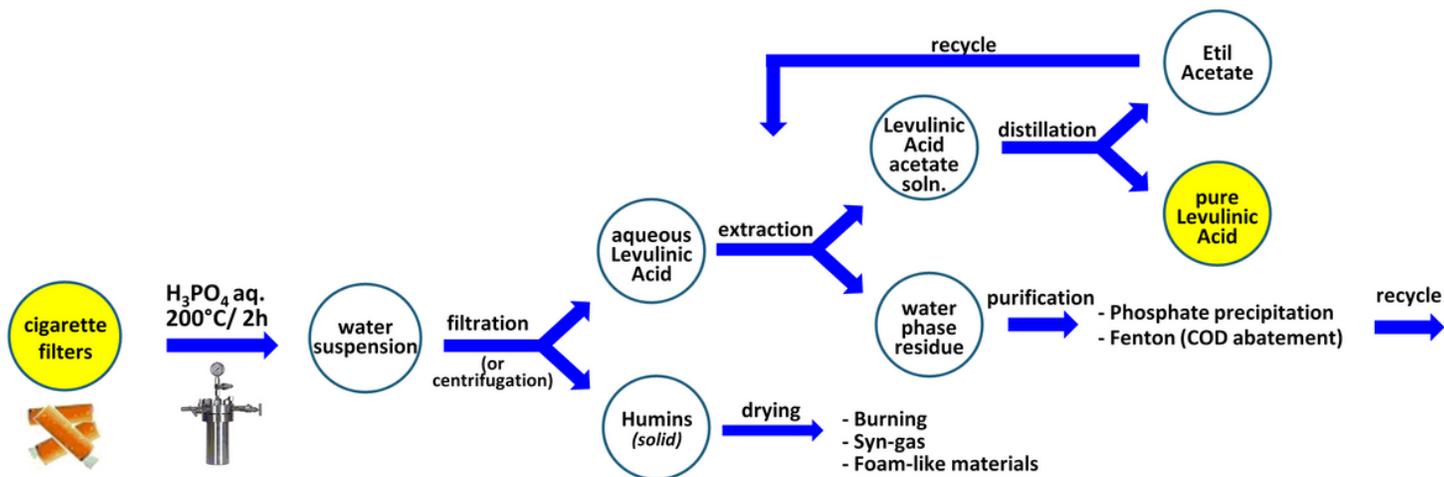


Figure 5

Process diagram of proposed method.

Supplementary Files

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