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# Recycling of post-use starch-based plastic bags through pyrolysis to produce sulfonated catalysts and chemicals

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**KEYWORDS.** Starch-based plastic bags; pyrolysis; heterogeneous acid catalyst; building blocks; chemical recycling

**ABSTRACT.** Pyrolysis was explored as a technology for depolymerizing and charring starch-based plastic bags in a novel valorization perspective based on a chemical recycling strategy, alternative to anaerobic digestion or composting. The char obtained from the thermal treatment (420°C for 15 h) was sulfonated to give a highly active and recyclable heterogeneous acid catalyst (10 wt% yield based on starch-based plastic bags subjected to pyrolysis), comparable in terms of catalytic activity and reusability to the analog catalyst prepared from potato starch and tested on a model esterification reaction. From pyrolysis liquid of starch-based plastic bags,

highly pure terephthalic acid (4 wt% yield) was isolated through self-precipitation, whereas the remaining pyrolysis liquid produced (21 wt%) was solvent-fractionated to give a polar fraction (7 wt% yield) enriched in levoglucosan, and a less polar fraction (14 wt% yield) enriched in monobutenyl adipate and terephthalate.

## 1. INTRODUCTION

Starch-based plastics have a pivotal role in today's bioeconomy, especially for the development of novel biomaterials able to conjugate both mechanical and environmental performances. Thermoplastic starch (TPS) is the mainly used starch-derivative in this field, industrially achievable by treating native starch with plasticizers (e.g. glycerol, ethylene glycol) in an extrusion process. TPS is used alone or blended with other (fossil-based or renewable) less biodegradable polymers for improving TPS mechanical properties and, at the same time, increasing the biodegradability of the other polymer counterpart. TPS-blends available on the market comprise aliphatic polyesters (e.g. poly- $\epsilon$ -caprolactone PCL, and polylactic acid PLA), polyvinyl alcohol (PVA), aromatic-aliphatic co-polyesters (e.g. polybutylene adipate terephthalate PBAT), and cellulose derivatives; they represent about 21% of the yearly global bioplastic production, with an expected production of almost 0.5 Mt in 2024 ([www.european-bioplastics.org](http://www.european-bioplastics.org)). Applications of starch-based materials include foams and fillers (mainly TPS on its own), agricultural films, compostable bags for organic and yard waste collection, and products for short-life applications like shopping bags. [1]

The end-of-life management of starch-based plastics by composting and anaerobic digestion is recognized as an appropriate strategy of disposal to reduce the amount of waste sent to landfill and the associated environmental impacts, [2] and produce energy (biogas) and/or soil

amendment (compost or digestate). [3] Even if quaternary recycling (energy recovery) or biological approaches are among the best strategies for treating starch-based plastic waste, neither primary recycling (re-extrusion of starch-blends to produce similar goods), nor secondary recycling (mechanical size reduction into pellets, flakes, or powders), nor tertiary recycling (chemical treatment for producing small molecules suitable as feedstock for the production of new chemicals and plastics) has been demonstrated so far. [4] Hydrolysis, pyrolysis, hydrocracking, and gasification are among the most promising technologies proposed for the chemical recycling of plastics and could help to meet circular economy targets, allowing to manage mixed and contaminated plastic waste streams. In particular, thermal cracking at high temperature (e.g. pyrolysis) produces liquid oil and gaseous intermediates (chlorine- and heavy metal-free) [4] from a large variety of fossil-based plastic waste (e.g. polyethylene, polypropylene, polystyrene, polyethylene terephthalate, polyamides), providing additional material input for petro-refineries. Pyrolysis is particularly efficient on polyolefins, [5,6,7] since the liquid oil produced can be used as fuel thanks to high heating values (HHV, around 40 MJ kg<sup>-1</sup>) similar to diesel and gasoline. The quite high processing costs and energy requirements are still debated and must be solved for an industrial implementation to avoid limiting pyrolytic treatments to small-scale or big industrial-scale projects under very strict conditions. [4]

The main aim of the present work is to propose a novel route for valorizing post-use starch-based plastic bags (hereafter named SBP-bags) through pyrolysis. [8] To the best of our knowledge, this is the first time that pyrolysis has been applied to this kind of waste, usually treated through composting. Two specific targets are here foreseen to valorize both the solid residue and liquid fraction produced from pyrolysis:

- the production of novel SO<sub>3</sub>H-containing catalyst by sulfonation of the solid residue (char), useful as heterogeneous catalyst. Starch and polysaccharide-containing materials are among the best precursors for producing sulfonated carbons, [9] and SBP-bags on the market contain a relevant percentage of TPS for increasing their biodegradability and compostability;
- the recovery of valuable intermediates (dicarboxylic acids and polyols) for the chemical industry by fractionating pyrolysis liquid; this target relies on the fact that SBP-bags here used are a blend of TPS (a potential source of anhydrosugars) and PBAT (a potential source of terephthalic acid and adipic acid, and their derivatives). Terephthalic acid and adipic acid are two building blocks whose industrial synthesis involves harsh oxidation processes mediated by strong oxidants on fossil platform chemicals (p-xylene and benzene, respectively); for this reason, possible alternative production of these dicarboxylic acids from waste like SBP-bags is particularly appealing in terms of overall economics, sustainability, and avoidance of consumption of non-renewable raw materials and harmful chemicals.

## 2. MATERIALS AND METHODS

*2.1 Chemicals.* All solvents and chemicals used in this study were obtained from Sigma Aldrich and used without purification. Post-use starch-based plastic bags (SBP-bags) were got from a local supermarket (Ravenna, Italy).

*2.2 Preparation of chars from SBP-bags and potato starch.* In a typical procedure, SBP-bags (4 g, cut in pieces of about 1 cm<sup>2</sup>) or potato starch (3 g) were subjected to bench-scale pyrolysis,

using an apparatus consisted of a sliding sample carrier placed in a heated quartz tube connected to ice traps and a settling chamber (Figure 1). The quartz tube was heated by a cylindrical co-axial furnace and purged by  $1.5 \text{ L min}^{-1}$   $\text{N}_2$  flow. Samples were moved into the heated zone of the quartz tube and heated for 15 h at  $420^\circ\text{C}$  (measured temperature) under  $\text{N}_2$  flow. The resulting char was collected and ground to powder in a mortar, whereas pyrolysis liquid was collected in an ice trap and dissolved in ethyl acetate. The yields of chars from SBP-bags and potato starch were  $10.8 \pm 0.2$  and  $14.8 \pm 0.6$  wt%, respectively.

*2.3 Preparation of  $\text{SO}_3\text{H}$ -catalysts from SBP-bags and potato starch.* Chars from SBP-bags and potato starch (about 1 g) were poured into concentrated  $\text{H}_2\text{SO}_4$  (100 mL) and heated at  $150^\circ\text{C}$  for 15 h under  $\text{N}_2$  atmosphere to sulfonate the material. After sulfonation, the suspension was cooled to rt and diluted with distilled  $\text{H}_2\text{O}$  (500 mL); then the catalysts were collected by filtration and washed several times with hot distilled  $\text{H}_2\text{O}$  ( $> 80^\circ\text{C}$ , 100 mL each time). The resulting  $\text{SO}_3\text{H}$ -catalysts were dried at  $70^\circ\text{C}$  for 48 h under vacuum to remove water.

*2.4 Elemental analysis.* The elemental composition of all the precursors, chars and  $\text{SO}_3\text{H}$ -catalysts was determined using an elemental analyzer (Thermo Scientific, Flash 2000, Organic Elemental Analyzer) through the flash combustion technique. Ash content was determined by weight upon calcinations for 5 h at  $550^\circ\text{C}$ .

*2.5 Determination of total acid sites and  $\text{SO}_3\text{H}$ -sites.* The total number of acid sites of  $\text{SO}_3\text{H}$ -catalysts (phenolic C-OH, C-COOH, and C- $\text{SO}_3\text{H}$  groups) was estimated by titration; an aqueous NaOH solution (0.01 M, 10 mL) was added to each material (25-30 mg). The mixture was stirred

for 60 min at rt under ultrasonic vibration. After centrifugal separation, the supernatant solution was titrated by an aqueous HCl solution (0.01 M) using phenolphthalein as the indicator. The number of strong acid sites (C-SO<sub>3</sub>H groups) was also estimated by titration; an aqueous NaCl solution (0.01 M, 10 mL) was added to each material (40-45 mg). The mixture was stirred for 60 min at rt under ultrasonic vibration. After centrifugal separation, the supernatant solution was titrated by an aqueous NaOH solution (0.01 M) using phenolphthalein as the indicator.

*2.6 Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Brunauer–Emmett–Teller (BET) analysis.* SEM images were collected using a HRSEM (ULTRA Plus, Zeiss, Oberkochen, Germany or LEO, Zeiss, Oberkochen, Germany) after coating the samples with 3 nm of gold (Figure 1S in ESI). XRD measurements were performed with a PanAnalytical X'Pert Pro diffractometer equipped with X'Celerator detector with Cu K $\alpha$  radiation in the range 20-70° 2 $\theta$ , step size 0.0501 2 $\theta$  and counting time 40 sec per step. The specific surface area of the chars from SBP-bags and potato starch was determined by the multiple BET (Micromeritics, Gemini) method using liquid nitrogen. Before analysis, the chars were pretreated at 120°C under vacuum to remove all adsorbed moisture from the carbon surface.

*2.7 Catalytic activity of SO<sub>3</sub>H-catalysts from SBP-bags and potato starch.* The esterification of dodecanoic (lauric) acid (1.25 mmol, 250 mg) with methanol (12.5 mmol) at 80°C by using 10 wt% of SO<sub>3</sub>H-catalyst (25 mg) compared to lauric acid, was used as a model reaction. After 3 h, H<sub>2</sub>O (2 mL) was added, the solution was centrifuged (3.000 rpm for 10 min) and methyl laurate separated as a well-distinct layer on the top of the solution. Methyl laurate was collected and weighted, an aliquot was withdrawn, diluted, and analyzed by GC-MS to determine the



conversion as described below. An aliquot was also analyzed by  $^1\text{H}$  NMR to detect the presence of any small polyarens domain derived from the catalyst (Figures 2S and 3S in ESI). The  $\text{H}_2\text{O}$ -MeOH solution, containing  $\text{SO}_3\text{H}$ -catalyst, was dried under  $\text{N}_2$  at  $25^\circ\text{C}$  for 15 h and  $80^\circ\text{C}$  for 24 h under vacuum; then the  $\text{SO}_3\text{H}$ -catalyst was reused under the experimental conditions described above without any further purification.

*2.8 Fractionation and analysis of pyrolysis liquid.* Once SBP-bags-pyrolysis liquid was collected in an ice trap and dissolved in ethyl acetate, a white solid precipitated from the solution. This solid was collected, washed with ethyl acetate, and weighted ( $4.5\pm0.4$  wt% yield based on the amount of pyrolyzed SBP-bags). An aliquot (1-2 mg) was withdrawn, silylated for 30 min at  $70^\circ\text{C}$  (with 0.1 mL ethyl acetate, 0.08 mL bis(trimethylsilyl)trifluoroacetamide containing 1% of trimethylchlorosilane, and 0.04 mL of pyridine) and then analyzed by GC-MS as described below. Another aliquot (about 10 mg) was withdrawn and analyzed by  $^1\text{H}$  NMR to determine the purity by the integration of proton signals compared to an internal standard. To this purpose, spectral data have been acquired in deuterated DMSO with a known amount of dimethyl malonic acid (DMMA) as an internal standard and a delay time between successive scans of 20 s to ensure complete proton relaxation and therefore quantitative integration. Spectrum (Figure 4S in ESI) was recorded using a 5 mm probe on a VARIAN Mercury 400 spectrometer; all chemical shifts have been quoted relative to deuterated solvent signals with chemical shifts ( $\delta$ ) given in ppm and coupling constants (J) values given in Hz.

SBP-bags- and starch-pyrolysis liquids were dried under  $\text{N}_2$  to remove ethyl acetate, weighted (yield of  $25.4\pm0.4$  and  $29\pm0.6$  wt%, respectively) and then analyzed by GC-MS after silylation as described below.

*2.9 GC-MS analysis.* GC-MS analyses were performed by using a 6850 Agilent HP gas chromatograph connected to a 5975 Agilent HP quadrupole mass spectrometer. The injection port temperature was 280°C. Analytes were separated by a HP-5 fused-silica capillary column (stationary phase, poly[5% diphenyl/95% dimethyl]siloxane, 30 m, 0.25 mm i.d., 0.25 µm film thickness), with helium as the carrier gas (at constant pressure, 33 cm s<sup>-1</sup> linear velocity at 200°C). Mass spectra were recorded under electron ionization (70 eV) at a frequency of 1 scan per second within the range 12-600 m/z.

The following thermal program was used for monitoring the esterification of lauric acid through SO<sub>3</sub>H-catalysts from SBP-bags and potato starch: from 50 to 180°C at 50°C min<sup>-1</sup> and then from 180 to 300°C at 5°C min<sup>-1</sup>; methyl laurate yield was calculated by using a calibration curve (50-500 ppm) prepared with methyl palmitate, assuming a unitary response factor.

The following thermal program was used for analyzing pyrolysis liquid composition: from 50°C (5 min) to 325°C (3 min) at 5°C min<sup>-1</sup> and then 325°C for 10 min. Compounds were identified by comparison with NIST database.

### 3. RESULTS AND DISCUSSION

#### *3.1 SO<sub>3</sub>H-containing catalyst from SBP-bags*

##### *3.1.1 Preparation of char from SBP-bags*

Applying the pyrolysis followed by a sulfonation procedure, a wide variety of SO<sub>3</sub>H-containing catalysts has been produced from inexpensive carbon sources like pure carbohydrates (e.g. starch), lignocelluloses, agricultural and industrial wastes, but not plastic waste. These materials are characterized by a flexible amorphous carbonaceous framework covalently functionalized

with SO<sub>3</sub>H-groups, bearing hydrophilic-oxyphilic properties and strong Brønsted acidity. [10] In particular, long-time pyrolysis (15 h) seemed fundamental for producing more robust and reusable SO<sub>3</sub>H-catalysts. [11,12,13] To this purpose, SBP-bags (about 5 g of material cut in 1 cm<sup>2</sup> piece) were subjected to a pyrolytic treatment at 420°C for 15 h, and the same treatment was applied to potato starch as comparison. Despite the total length of the overall thermal treatment was 15 h, the process applied to both SPB-bags and potato starch can be seen as the combination of two distinct thermal steps: intermediate pyrolysis of 20-30 min at 420°C that depolymerized the feedstock and produced the liquid and gaseous fractions, followed by a “charring” phase at the same temperature that graphitized the chars for the following 15 h, creating stable backbones that were further sulfonated to provide the SO<sub>3</sub>H-catalysts.

The initial carbon content of SBP-bags (54.5 wt%, entry 1, Table 1), higher than that of potato starch (37.5 wt%, entry 2), reflects the co-presence of polybutylene adipate terephthalate (PBAT) in starch-based plastic bags here used. [14] According to the elemental analysis, a content of 70% of PBAT in the blend could be estimated. The yield of char produced after pyrolysis of SBP-bags (10.8±0.2 wt%) was in between the typical yield of chars from fossil-based plastics [5] and that obtained here from potato starch (14.8±0.6 wt%), in line with the inhibition of polymerization and cross-linking reactions involved in the formation of char observed for co-pyrolysis of plastics and biomass. [15,16,17] The H/C molar ratio for SBP-bags-char (0.46, entry 3, Table 1) was slightly higher than that of potato starch-char (0.41, entry 4); this could imply the formation of smaller polyarenes having a relatively higher number of “peripheral” hydrogen atoms which could be substituted through electrophilic aromatic substitution with SO<sub>3</sub>H groups. X-ray powder diffraction (XRD) revealed that SBP-bags-char contained rutile TiO<sub>2</sub> and CaCO<sub>3</sub>, and a very low quantity of amorphous material; rutile (diffraction peaks pattern marked with “R”

in Figure 2) is one of the most used white pigment in the plastics industry, [18] whereas calcium carbonate (diffraction peaks pattern marked with “C” in Figure 2) has the role of filler in a wide range of polymer resins for enhancing optical and mechanical properties, durability, smoothness and ink adsorption. [19] Both  $\text{TiO}_2$  and  $\text{CaCO}_3$  presence was confirmed by SEM images (Figure 1S in ESI) in which aggregates of submicron/micron particles were visible on an amorphous structure; a wide distributed porosity (100 nm diameter) was also observed, probably associated with the production of specific volatile compounds during pyrolysis. The char from potato starch was completely amorphous, and no clear diffraction pattern was detectable (Figure 2).

The Brunauer-Emmett-Teller (BET) surface areas of the chars from SBP-bags and potato starch were  $51.4 \pm 0.1$  and  $115.7 \pm 0.2 \text{ m}^2 \text{ g}^{-1}$ , respectively. The ashes amount (3.8 wt%) could explain the two-times lower value found for SBP-bags than potato starch, since the number of inorganic materials is reported to be inversely correlated with the surface area. As reported in the literature, the feedstock subjected to pyrolysis and the pyrolysis conditions strongly influence the surface area of the resulting chars: the highest porosity is achieved when woody feedstocks are treated at 500-900°C, whereas the number of inorganic materials (e.g. ashes) and long residence times have a decreasing effect. The low BET surface area values here found are in line with what was reported in the literature if pyrolysis temperature below 500°C is applied to feedstocks with no lignin at all, like in the present case. [20,21] It is worth mentioning that a further decreasing effect of the porosity of the final  $\text{SO}_3\text{H}$ -containing catalysts is associated to the liquid-phase sulfonation with concentrated  $\text{H}_2\text{SO}_4$ , reported causing a deterioration/collapse of the pore structure [10], especially true in the case of polysaccharide-derived materials (surface area  $< 2 \text{ m}^2 \text{ g}^{-1}$  for  $\text{SO}_3\text{H}$ -catalysts prepared from starch- or cellulose-chars). [12,22]

### 3.1.2 Preparation of $\text{SO}_3\text{H}$ -catalyst from SBP-bags

After pyrolysis, SBP-bags-char was subjected to a sulfonation procedure with concentrated  $\text{H}_2\text{SO}_4$  at  $150^\circ\text{C}$  for 15 h; the same treatment was applied to potato starch char [12] to produce an analogous sulfonated material, whose characteristics and catalytic activity were compared to those of SBP-bags-catalyst. After sulfonation, the introduction of  $\text{SO}_3\text{H}$  groups on the chars from SBP-bags and potato starch was testified by both elemental analysis (S amount of 3 and 1.6 wt%, respectively; entries 5 and 6, Table 1) and titration:  $\text{SO}_3\text{H}$  density was in both cases below  $1 \text{ mmol g}^{-1}$  ( $0.8$  and  $0.4 \text{ mmol g}^{-1}$ , respectively) as reported for a large variety of sulfonated hydrochars, biochars, or semicarbonized matter derived from lignocellulosic or polymeric materials. [10]  $\text{SO}_3\text{H}$  groups were 31% of the total acid density in the catalysts from SBP-bags and 23% of the total acid density in the catalyst from potato starch, proving the presence of weaker acid sites ( $\text{COOH}$ , phenolic  $-\text{OH}$  groups) on the surface of these carbon frameworks that can confer hydrophilic/oxyphilic properties, increase the adsorption of hydrophilic molecules, and promote synergic catalytic activities. [10] XRD confirmed that the  $\text{SO}_3\text{H}$ -catalyst from SBP-bags had an amorphous structure and still contained rutile  $\text{TiO}_2$ , even if in a lower amount than the char precursor ( $\text{TiO}_2$  is soluble in hot concentrated  $\text{H}_2\text{SO}_4$  and was probably leached); the diffraction pattern of  $\text{CaCO}_3$  was no-more visible, presumably because of its transformation during the sulfonation treatment. The  $\text{SO}_3\text{H}$ -catalyst from potato starch was completely amorphous, with two visible broad shoulders between  $15^\circ$ - $30^\circ$  and  $40^\circ$ - $45^\circ$  already observed for sulfonated carbons. [10] SEM images of  $\text{SO}_3\text{H}$ -catalyst from SBP-bags (Figure 1S in ESI) confirmed the presence of an amorphous structure with a certain porosity, whereas  $\text{TiO}_2$  structures were no more visible; on the other hand,  $\text{SO}_3\text{H}$ -catalyst from potato starch was mainly

characterized by smooth amorphous areas with some nanostructures (average dimensions of 200 nm), and aggregates of nanoparticles with 20-30 nm diameter.

### *3.1.3 Catalytic activity of SO<sub>3</sub>H-catalyst from SBP-bags*

Both SO<sub>3</sub>H-catalysts prepared from SBP-bags and potato starch were tested in the esterification of fatty acids with alcohols, a typical liquid-phase transformation known to be catalyzed by sulfonated carbons [11,12,23,24]. The reaction was performed on lauric acid and methanol (10 eq.) at 80°C in 3 h; methyl laurate yields were between 87-93% over 7 cycles with catalyst from SBP-bags, and between 81-87% with catalyst from potato starch (Figure 3). The excellent reactivity, common for these catalysts, has been attributed to the swelling or pore enlargement in alcoholic media, which can favor the adsorption of bulky hydrophobic substrates (like fatty acids) on the hydrophilic surface of the catalysts. [10] The excellent long-term stability and recyclability observed seem to exclude the presence of small polycyclic aromatic hydrocarbon domains containing SO<sub>3</sub>H-groups that can be leached during the reaction workup (with the consequent need to regenerate the catalyst with relevant amounts of H<sub>2</sub>SO<sub>4</sub>, procedure claimed to be less convenient and less environmental friendly than the direct use of minimal quantities of homogeneous acids). This was a further confirmation of what was already observed in the literature: i) a prolonged thermal treatment (15 h) is fundamental to graphitize the chars and provide robust carbonaceous precursors of highly active and recyclable catalysts; ii) 420°C is an optimal temperature for obtaining a relevant density of SO<sub>3</sub>H groups on the catalyst surface (a temperature below 400°C could give a too soft material rather than a rigid structure, readily leachable, whereas a temperature higher than 450°C could create a too rigid structure, less flexible and less prone to sulfonation). [11,12,13]

### 3.2 Chemicals from SBP-bags pyrolysis liquid

The depolymerization of condensation polymers such as polylactic acid (PLA), PET, and polyurethane (PU) is usually achieved through catalytic hydrolysis or glycolysis, rather than thermal treatments; [4] in fact, liquid fractions obtained from pyrolysis of condensation polymers are often enriched in oxygenated monomers (like benzoic acid from PET) that decrease HHV (e.g. 28 MJ kg<sup>-1</sup> for PET-pyrolysis liquid), making these oils unsuitable for energy purpose. [5] On the other hand, these monomers can be reused to synthesize the original polymers or exploitable as building blocks. SBP-bags here used contained a relevant percentage of PBAT (almost 70%), a condensation polymer made by terephthalic acid and adipic acid, which could be recovered by depolymerization. Actually, during the first 10 minutes of pyrolysis, a white powder (4.5±0.4 wt% yield based on SBP-bags subjected to pyrolysis) self-precipitated from the condensed pyrolysis vapors that were collected in ethyl acetate (Figure 4a): this solid proved to be terephthalic acid (TA), with a purity of 96.5% by <sup>1</sup>H NMR (Figure 4S in ESI). Traces (< 1%) of an additional compound, tentatively identified as 4-((but-3-en-1-yloxy)carbonyl)benzoic acid (BTA, the monobutenyl ester of terephthalic acid), were also detected by GC-MS analysis. The yield of pyrolysis liquid here achieved was 21.4±0.4 wt% based on SBP-bags subjected to pyrolysis; as a comparison the yield of pyrolysis liquid from potato starch was 29 wt%. The chemical compounds identifiable by GC-MS after silylation in the pyrolysis liquids from SBP-bags and potato starch have been listed in Table 2; the pyrolysis liquid from SBP-bags mainly contained starch pyrolysis products like levoglucosan (LG) and other anhydrosugars/sugars (S) (28 and 6%, respectively), and PBAT pyrolysis products like BTA (28%), adipic acid (AA, 12.5%), 6-(but-3-en-1-yloxy)-6-oxohexanoic acid (BAA, the monobutenyl ester of adipic acid,

11%), and terephthalic acid (TA) (5%) (Table 2 and Figure 4b). As expected, the GC-MS spectra of pyrolysis liquid from potato starch was almost exclusively characterized by levoglucosan (LG) and other anhydrosugars/sugars (S) (78 and 12%, respectively), with lower amounts of hydroxymethylfuraldehyde (0.8%) and ascopyrone P (2.7%) (Table 2 and Figure 5S in ESI).

When ethyl acetate was partially removed under nitrogen from SBP-bags-pyrolysis liquid, a second white precipitate (0.75 wt% yield based on initial SBP-bags subjected to pyrolysis) was collected; this precipitate was enriched in TA and a minor amount of all the other compounds reported in Table 2 (data not shown). The brownish syrup that was recovered after complete removal of ethyl acetate was then partitioned between ethyl acetate and water to give (Table 3):

- a water-soluble fraction (32% of pyrolysis liquid, corresponding to a yield of 6.7 wt% based on SBP-bags subjected to pyrolysis) containing LG (the main component with a relative abundance of 46%), other sugars/anhydrosugars (32%), and minor amounts of AA (9%) and lactic acid LA (5%);
- an ethyl acetate-soluble fraction (68% of pyrolysis liquid, corresponding to a yield of 14.3 wt% based on SBP-bags subjected to pyrolysis) enriched in monobutenyl dicarboxylic acids (BTA and BAA with relative abundances of 28 and 17%, respectively) and adipic acid (13%). Minor amounts of dibutenyl adipate (DBAA, 2.5%) and dibutenyl terephthalate (DBTA, 4%) were also detected.

Thus, by exploiting the different solubility of SBP-bags-pyrolysis products in ethyl acetate, it was possible to recover highly pure terephthalic acid, a polar fraction enriched in levoglucosan, and a less polar fraction enriched in monobutenyl esters and adipic acid (Figure 5). Both terephthalic acid and adipic acid (and their butenyl esters) can be used as drop-in monomers to



produce new condensation polymers in the plastic industry, whereas levoglucosan has a high potential as a chiral synthon in organic synthesis and intermediate for biodegradable surfactants and pharmaceuticals. [25] Contrarily to what reported in the literature when PET is subjected to pyrolysis, almost no benzoic acid was here detected (< 1%); [5] this finding could be a consequence of the pyrolytic behavior of PBAT (no data on pyrolysis of PBAT are reported in the literature) or to the specific pyrolysis conditions here applied.

#### 4. CONCLUSION

A novel valorization route is here proposed for the treatment of post-use starch-based plastic bags, as a possible useful alternative to composting; this approach relies on pyrolysis as an attractive technique for both depolymerizing and charring the constituents of SBP-bags, mainly starch and PBAT, to produce chemicals and catalysts. The overall valorization process produces:

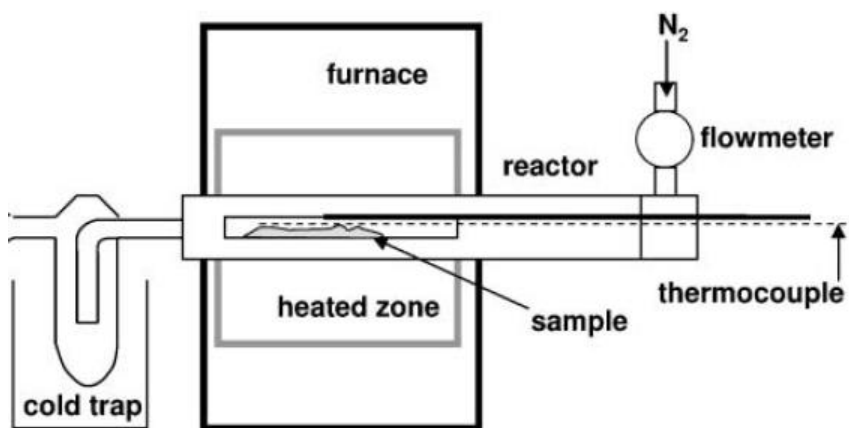
- $\text{SO}_3\text{H}$ -containing heterogeneous catalyst (10 wt%), highly stable and active in the promotion of the esterification of fatty acids; the performance of this catalyst resulted comparable to that of  $\text{SO}_3\text{H}$ -catalyst prepared from potato starch, confirming the possibility of synthesizing these materials from inexpensive every-day life plastic waste or agro-industrial/lignocellulosic waste instead of purified feedstocks (e.g. polysaccharides);
- highly pure terephthalic acid (4 wt%, 98.5% purity), usable as a monomer in polyester synthesis, in a circular economy perspective. This finding is peculiar of the feedstock (SBP-bags) here used: to the best of our knowledge, there are no other pyrolytic treatments applied to any waste (e.g. lignocelluloses, agricultural waste, or other industrial waste) that can provide an isolated and highly pure chemical compound directly exploitable as a building block in the chemical industry;

- pyrolysis liquid (21 wt%), enriched in levoglucosan, adipic acid, and monoesterified dicarboxylic acids, that can be further fractionated and provide intermediates exploitable in the polymer and chemical industry.

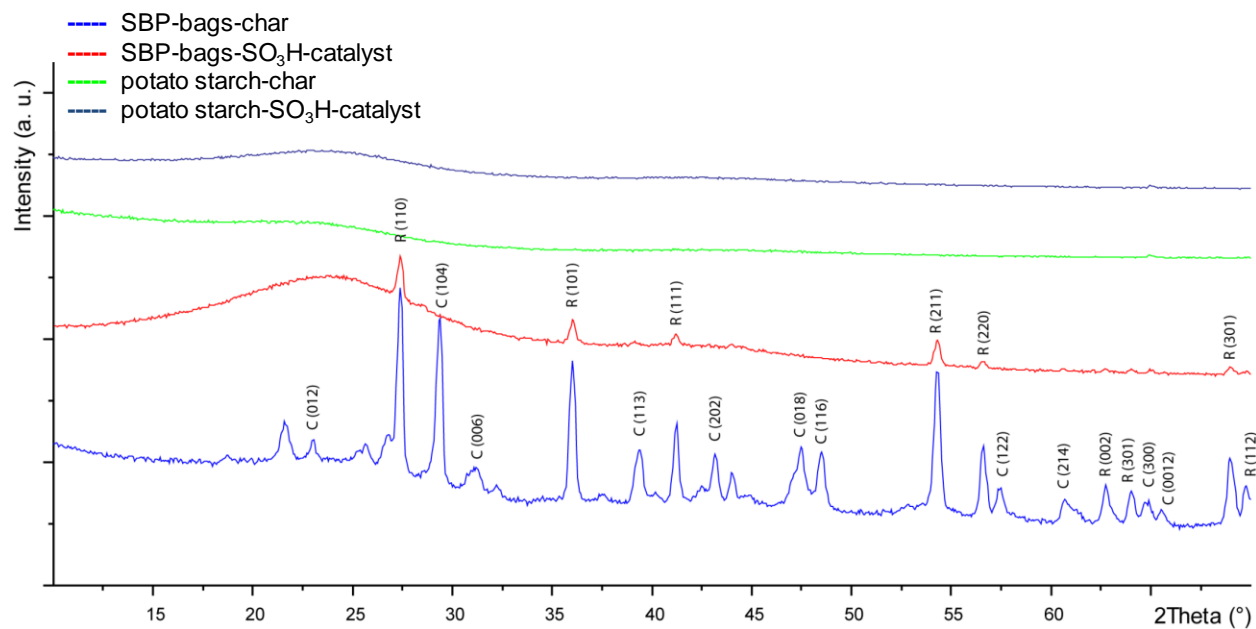
This approach can be in principle applied to other industrial starch-based plastic blends, to produce solid acid catalysts from the starch fraction, and chemicals from the condensation polymer fraction. It is worth mentioning that the tuning of pyrolysis conditions could increase the production of SBP-bags-chars (e.g. lower heating rate and longer residence time), or maximize SBP-bags-derived chemicals (e.g. higher heating rate), according to the request, attesting the versatility of pyrolytic approach for chemical recycling of plastics.

## FIGURES

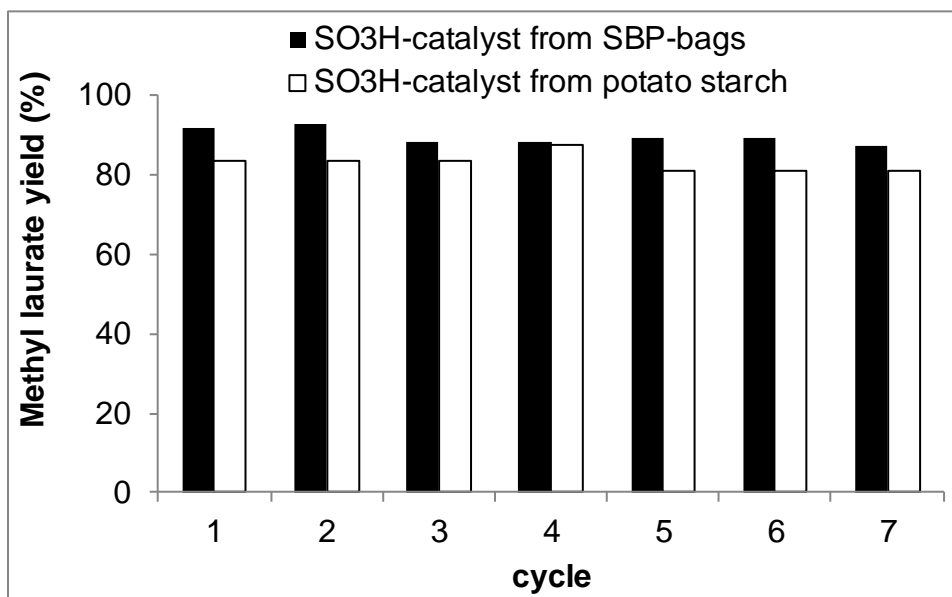
**Figure 1.** Bench-scale pyrolysis apparatus used for pyrolyzing SBP-bags and potato starch.



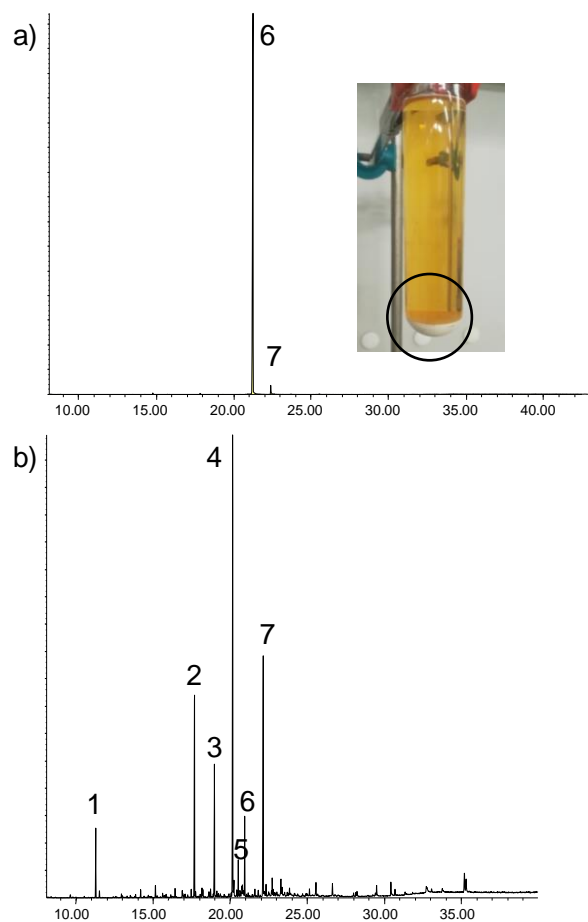
**Figure 2.** Diffraction pattern of chars and SO<sub>3</sub>H-catalysts from SBP-bags and potato starch.



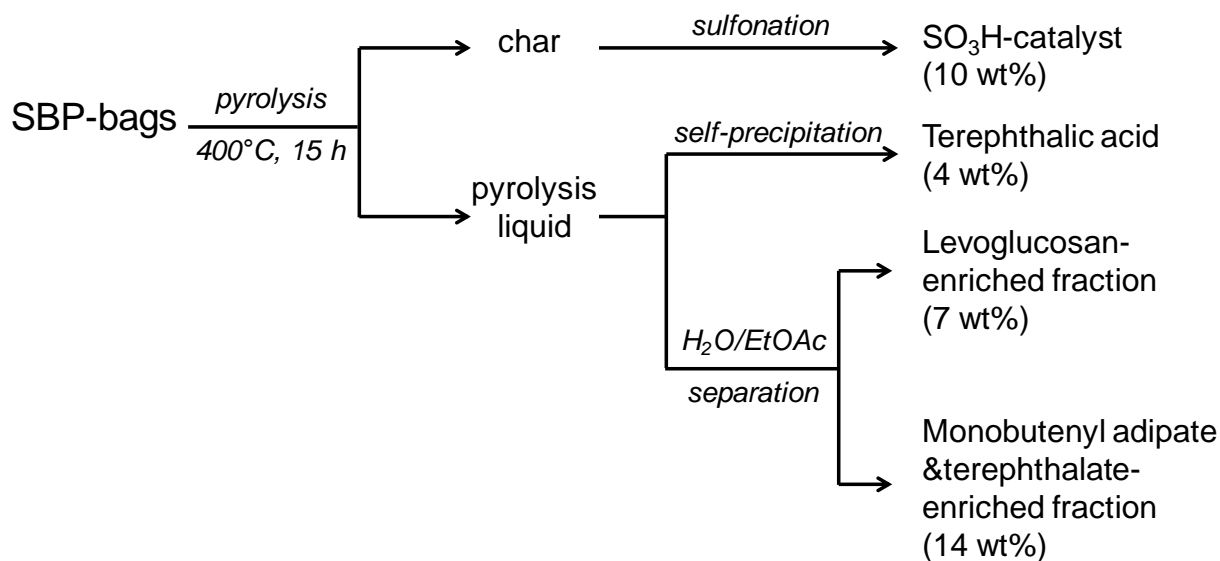
**Figure 3.** Activity and recyclability of SO<sub>3</sub>H-catalysts from SBP-bags and potato starch (10 wt%) in the esterification of lauric acid with methanol (10 eq.) (3 h, 80°C).



**Figure 4.** Chromatograms of a) terephthalic acid that self-precipitated from a solution of SBP-bags pyrolysis liquid in ethyl acetate; b) SBP-bags pyrolysis liquid. (Main identified peaks: 1 lactic acid; 2 adipic acid AA; 3 monobutenyl adipate BAA; 4 levoglucosan LG; 5 sugar S; 6 terephthalic acid TA; 7 monobutenyl terephthalate BTA).



**Figure 5.** The overall scheme of SBP-bags valorization through pyrolysis to produce SO<sub>3</sub>H-catalyst, terephthalic acid, and fractions enriched in levoglucosan and monobutenyl esters of adipic acid and terephthalic acid.



# TABLES

**Table 1.** Elemental composition (wt%), H/C ratio, and acid density (total and related to SO<sub>3</sub>H groups) of SBP-bags and starch, and their chars before and after sulfonation (mean ± standard error).

Entry		N	C	H	S	Ashes	H/C ratio	Total acid density (mmol g <sup>-1</sup> ) <sup>a</sup>	SO <sub>3</sub> H density (mmol g <sup>-1</sup> ) <sup>b</sup>
1	SBP-bags	0.2±0.01	54.5±0.4	6.7±0.07	-	3.8	1.5	-	-
2	Potato starch	-	37.5±0.7	6.4±0.1	-	-	2.0	-	-
3	SBP-bags char	0.4±0.04	62.3±0.4	2.4±0.2	-	0.4	0.46	nd	-
4	Potato starch char	-	82.8±0.3	2.8±0.1	-	0.5	0.41	nd	-
5	SBP-bags SO <sub>3</sub> H-catalyst	0.3±0.01	59.5±0.7	2.1±0.09	3.0±0.3	-	0.42	2.6±0.04	0.8±0.01
6	Potato starch SO <sub>3</sub> H-catalyst	0.1±0.02	67.7±1.6	2.3±0.1	1.6±0.04	-	0.41	1.7±0.02	0.4±0.01

<sup>a</sup> the total acidity density is referred to as total acid sites (-SO<sub>3</sub>H, COOH, phenolic -OH groups) determined by titration with NaOH;

<sup>b</sup> determined by titration with NaCl; nd: not determined.

**Table 2.** Relative distribution of chemical compounds in SBP-bags-pyrolysis liquid and potato starch-pyrolysis liquid determined by GC-MS after sample silylation.

Compound	Relative abundance (%)	
	SBP-bags	Potato starch
Benzoic acid (BA)	0.9±0.4	-
Adipic acid (AA)	12.5±1.4	-
6-(but-3-en-1-yloxy)-6-oxohexanoic acid (BAA)	10.6±0.8	-
di(but-3-en-1-yl) adipate (DBAA)	1.2±0.7	-
Levogluconan (LG)	27.7±1.5	77.8±0.1
Other sugars and anhydrosugars (S)	5.6±0.5	11.6±1.2
Terephthalic acid (TA)	5.4±0.7	-
4-((but-3-en-1-yloxy)carbonyl)benzoic acid (BTA)	27.9±2.0	-
di(but-3-en-1-yl) terephthalate (DBTA)	1.7±0.5	-
Lactic acid (LA)	4.0±0.4	-
Other (unidentified and oligomers)	2.5±0.6	10.6±0.3

**Table 3.** Relative distribution of chemical compounds in SBP-bags-pyrolysis liquid after H<sub>2</sub>O/EtOAc fractionation determined by GC-MS after sample silylation.

Compound	Relative abundance (%)	
	H <sub>2</sub> O-soluble fraction	EtOAc-soluble fraction
Benzoic acid (BA)	-	0.9
Adipic acid (AA)	8.9	12.8
6-(but-3-en-1-yloxy)-6-oxohexanoic acid (BAA)	-	17.2
di(but-3-en-1-yl) adipate (DBAA)	-	2.5
Levogluconan (LG)	46.4	1.8
Other sugars and anhydrosugars (S)	32.5	-
Terephthalic acid (TA)	-	4.9
4-((but-3-en-1-yloxy)carbonyl)benzoic acid (BTA)	-	27.7
di(but-3-en-1-yl) terephthalate (DBTA)	-	4.0
Lactic acid (LA)	4.8	1.2
Other (unidentified and oligomers)	7.4	27.0



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## REFERENCE

- 1 C. Bastioli, Properties and applications of Mater-Bi starch-based materials, *Polym. Degrad. Stab.* 59 (1998) 263–272. DOI: 10.1016/S0141-3910(97)00156-0
- 2 M. R. Yates, C. Y. Barlow, Life cycle assessments of biodegradable, commercial biopolymers - A critical review, *Resour. Conserv. Recycl.* 78 (2013) 54–66. DOI: 10.1016/j.resconrec.2013.06.010
- 3 J. H. Song, R. J. Murphy, R. Narayan, G. B. H. Davies, Biodegradable and compostable alternatives to conventional plastics, *Philos. Trans. R. Soc. B Biol. Sci.* 364 (2009) 2127–2139. DOI: 10.1098/rstb.2008.0289.
- 4 I. A. Ignatyev, W. Thielemans, B. Vander Beke, Recycling of Polymers: A Review. *ChemSusChem* 7 (2014) 1579–1593. DOI: 10.1002/cssc.201300898.
- 5 S. D. Anuar Sharuddin, F. Abnisa, W. M. A. Wan Daud, M. K. A Aroua, Review on pyrolysis of plastic wastes. *Energy Convers. Manag.* 115 (2016) 308–326. DOI: 10.1016/j.enconman.2016.02.037
- 6 Muhammad Saad Qureshi, Anja Oasmaa, Hanna Pihkola, Ivan Deviatkin, Anna Tenhunen, Juha Mannila, Hannu Minkkinen, Maija Pohjakallio, JuttaLaine-Ylijoki, Pyrolysis of plastic waste: Opportunities and challenges. *JAAP* (2020) 104804. DOI: 10.1016/j.jaap.2020.104804

- 7 A. K. Panda, R. K. Singh, D. K. Mishra, Thermolysis of waste plastics to liquid fuel. A suitable method for plastic waste management and manufacture of value-added products - A world prospective, *Renew. Sustain. Energy Rev.* 14 (2010) 233–248. DOI: 10.1016/j.rser.2009.07.005
- 8 C. Samorì, P. Galletti, E. Tagliavini, A. Parodi, “Valorizzazione di materiali plastici a base di amido mediante pirolisi”, Pat. Pend. 102020000024754, University of Bologna (IT), 20/10/2020.
- 9 M. Toda, A. Takagaki, M. Okamura, J. N. Kondo, S. Hayashi, K. Domen, M. Hara, Biodiesel made with sugar catalyst, *Nature* 438 (2005) 178. DOI: 10.1038/438178a
- 10 L. J. Konwar, P. Mäki-Arvela, J. P. Mikkola, SO<sub>3</sub>H-Containing Functional Carbon Materials: Synthesis, Structure, and Acid Catalysis, *Chem. Rev.* 119 (2019) 11576–11630. DOI: 10.1021/acs.chemrev.9b00199
- 11 X. Mo, E. Lotero, C. Lu, Y. Liu, J. G. Goodwin, A Novel Sulfonated Carbon Composite Solid Acid Catalyst for Biodiesel Synthesis, *Catal. Letters* 123 (2008) 1–6. DOI: 10.1007/s10562-008-9456-y
- 12 C. Samorì, C. Torri, D. Fabbri, G. Falini, C. Faraloni, P. Galletti, S. Spera, E. Tagliavini, G. Torzillo, *ChemSusChem* (2012) 1501–1512. DOI:10.1002/cssc.201100822.
- 13 J. Howard, D. W. Rackemann, J. P. Bartley, C. Samori, W. O. S. Doherty, Conversion of sugar cane molasses to 5-Hydroxymethylfurfural using molasses and bagasse-derived catalysts, *ACS Sus. Chem. Eng.* 6 (2018) 4531–4538. DOI:10.1021/acssuschemeng.7b02746.
- 14 K. E. Borchani, C. Carrot, M. Jaziri, Biocomposites of Alfa fibers dispersed in the Mater-Bi type bioplastic: Morphology, mechanical and thermal properties, *Composites: Part A*. 78 (2015) 371–379. DOI. 10.1016/j.compositesa.2015.08.023.

- 15 M. Brebu, S. Ucar, C. Vasile, J. Yanik, Co-pyrolysis of pinecone with synthetic polymers, *Fuel* 89 (2010) 1911–1918. DOI: 10.1016/j.fuel.2010.01.029.
- 16 X. Zhang, H. Lei, S. Chen, J. Wu, Catalytic co-pyrolysis of lignocellulosic biomass with polymers: a critical review, *Green Chem.*, 18 (2016) 4145–4169. DOI: 10.1039/c6gc00911e.
- 17 V. I. Sharypov, N. Marin, N. G. Beregovtsova, S. V. Baryshnikov, B. N. Kuznetsov, V. L. Cebolla, J. V. Weber, Co-pyrolysis of wood biomass and synthetic polymer mixtures. Part I: influence of experimental conditions on the evolution of solids, liquids and gases, *J. Anal. Appl. Pyrolysis*, 64 (2002) 15–28. DOI: 10.1016/S0165-2370(01)00167-X.
- 18 S. A Farrokhpay, review of polymeric dispersant stabilisation of titania pigment, *Adv. Colloid Interface Sci.* 151 (2009) 24–32. DOI:10.1016/j.cis.2009.07.004.
- 19 O. A. Jimoh, K. S. Ariffin, A. E. Bin Hussin Temitope, Synthesis of precipitated calcium carbonate: a review, *Carbonates and Evaporites*, 33 (2018) 331–346. DOI: 10.1007/s13146-017-0341-x.
- 20 M. Uchimiya, L. H. Wartelle, K. T. Klasson, C. A. Fortier, I. M. Lima, Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil, *J. Agric. Food Chem.*, 59 (2011) 2501–2510. DOI: 10.1021/jf104206c.
- 21 F. Ronsse, S. Van Hecke, D. Dickinson, W. Prins, Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions, *GCB Bioenergy*, 5 (2013) 104–115, DOI: 10.1111/gcbb.12018.
- 22 K. Nakajima, M. Hara, Amorphous carbon with SO<sub>3</sub>H groups as a solid Brønsted acid catalyst, *ACS Catal.*, 2012 (2) 1296–1304, DOI: 10.1021/cs300103k.

- 23 L. H. Chin, A. Z. Abdullah, B. H. Hameed Sugar cane bagasse as solid catalyst for synthesis of methyl esters from palm fatty acid distillate, Chem. Eng. J. 183 (2012) 104-107. DOI: 10.1016/j.cej.2011.12.028.
- 24 I. M. Lokman, M. Goto, U. Rashid, Y. HinTaufiq-Yap, Sub- and supercritical esterification of palm fatty acid distillate with carbohydrate-derived solid acid catalyst, Chem. Eng. J. 284 (2016) 872-878. DOI: 10.1016/j.cej.2015.08.102.
- 25 I. J. Itabaiana, M. Avelar do Nascimento, R. O. Mendonça Alves de Souza, A. Dufour, R. Wojcieszak, Levoglucosan: a promising platform molecule? Green Chem (2020) DOI: 10.1039/D0GC01490G.