# Levoglucosenone, furfural and levomannosan from mannan-rich feedstock: a proof-of-principle with ivory nut

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# Abstract

This work pioneers the thermocatalytic conversion of tagua seeds (or ivory nut) from the palm Phytelephas aequatorialis into key chemical building blocks, being levoglucosenone, furfural and levomannosan. Annually, ca. 100,000 metric ton of those seeds are produced in Ecuador. Mannan (a mannose-polymer similar to cellulose) is the main constituent in tagua. Thermocatalytic conversions were first explored on analytical scale to see if -and to which extent- e.g., levoglucosenone, was obtained from tagua, using catalysts with proven activity for cellulose conversion, being  $H_3PO_4$  or  $ZnCl_2$ . Non-catalytic fast pyrolysis led to levomannosan as main product (33.89 wt.%  $\pm$  0.24 wt.%), much like levoglucosan is the main product from cellulose pyrolysis. Catalytic fast pyrolsysis using H<sub>3</sub>PO<sub>4</sub> or ZnCl<sub>2</sub> resulted in value-added levoglucosenone (max 6.64 wt.%  $\pm$  0.27 wt.%) and furfural (max 13.17 wt.%  $\pm$  0.66 wt.%) at the expense of levomannosan (between 12 wt.%-14 wt.%). Validation experiments with a continuous fast pyrolysis auger reactor were successful and led to pyrolysis liquids with e.g., 3.69 wt.% levoglucosenone, using H<sub>3</sub>PO<sub>4</sub>-infused ivory nut. Although further optimization should follow this work, the results showcased a fundamental "mannan to levoglucosenone and furfural" conversion and therefore the potential of mannan-rich feedstock for biorefining. Moreover, these results can be translated to other mannan-rich

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agricultural residues, like açaí seeds, which are a major residue in Brazil (1.1 million metric ton annually).

*Keywords:* fast pyrolysis, thermocatalytic conversion, levoglucosenone, biorefinery, ivory nut mannan

# 1 1. Introduction

<sup>2</sup> The transition from a fossil-based economy to a bio-based economy remains key for sustainable

<sup>3</sup> development. This in part entails the decarbonisation of the energy landscape. Yet, the

<sup>4</sup> production and refining of commodity and specialty chemicals inherently remains carbon-dependent.

<sup>5</sup> It is therefore critical to substitute fossil-based chemical building blocks by renewable-based

<sup>6</sup> building blocks. In other words, the development and facilitation of biorefineries, which

7 convert bioresources into key chemical intermediates is most opportune. These intermediates

<sup>8</sup> can be drop-in molecules, like *e.g.*, benzene or phenol from lignin [1], or new-to-industry

<sup>9</sup> molecules, like *e.g.*, Cyrene from cellulose as green solvent alternative for dimethylformamide

10 (DMF) and N-methyl-2-pyrrolidone [2].

<sup>11</sup> Effective biorefining goes in tandem with a meticulous selection of conversion processes

and the applied bioresources. Indeed, the conversion processes should be sustainable, simple

<sup>13</sup> and flexible. On the other hand, the bioresource should render biorefining in a techno-economically

<sup>14</sup> feasible manner. This means that the bioresource (i) has an advantageous composition, (ii)

<sup>15</sup> is preferably available in a concentrated area in sufficient quantities and (iii) constitutes

<sup>16</sup> an agricultural residue or by-product from an existing economy, for which no additional

17 land-use is required.

<sup>18</sup> In this work, we present for the first time a unique process & bioresource combination that

<sup>19</sup> ticks off the above conditions and ultimately converts local agricultural residues into value-added

<sup>20</sup> biorefinery building blocks such as levoglucosenone, furfural and levomannosan.

<sup>21</sup> The bioresource we focused on is the seed from the fruit of the *Phytelephas aequatorialis* 

palm tree (Fig. 1). This seed, also called "tagua", "jarina seed" or "ivory nut" has a particularly

<sup>23</sup> hard white endosperm (hence the name ivory nut). The palm is indigenous to the Amazon

region, where the tagua seeds are used to cast buttons, disks and ornaments from it, leaving

- <sup>25</sup> cutting residues, corresponding to between 65-88 wt.% of the original tagua mass [3]. Valorisation
- <sup>26</sup> of these local tagua residues in a biorefinery can therefore be considered as a simultaneous
- <sup>27</sup> waste management strategy as well. Tagua cultivation is concentrated in Ecuador, more
- specifically in the Manibí province, where annually ca. 100,000 metric ton tagua is produced [4].
- <sup>29</sup> The major constituent of tagua are carbohydrates (*ca.* 70 wt.% mannan A and B and *ca.* 7.5
- wt.% cellulose). Mannan encompasses  $\beta(1-4)$  linked mannose units, very similar to cellulose, which comprises of  $\beta(1-4)$  linked glucose units.



Figure 1: Left: tagua seeds, middle: cut out disks, right: cutting residues.

The insight that tagua essentially is a very pure source of mannan opens doors to its valorisation 32 into various anhydrosugars (levomannosan, levoglucosenone and furfural) that ought to 33 be the basic building blocks for near-future biorefineries [5, 6, 7]. The production of these 34 could be established through fast pyrolysis, which entails the temperature-driven depolymerisation 35 and dehydration of carbohydrates. Upon fast pyrolysis, condensable aerosols, viz., pyrolysis 36 liquids, are obtained which contain the aforementioned anhydrosugars [8]. 37 The specific composition of tagua gives an extra positive dimension from a biorefinery 38 point-of-view. Starting from lignocellulosic biomass would required either extensive fractionation 39 of cellulose prior to pyrolysis or extensive purification. Moreover, the inherently low mineral 40 content of tagua (0.95 wt.% d.b.) [8] is very beneficial for pyrolytic depolymerisation and 41 dehydration. These metals could catalyse the undesired ring opening of anhydrosugars [9] 42 to e.g., acetic acid, hydroxyacetaldehyde, ect. 43 Despite the advantageous composition and availability of tagua, its valorisation potential 44

- <sup>45</sup> remains largely underexplored. Early work of Furneau *et al.* [10] and Knauf *et al.* [11]
- <sup>46</sup> showed that pyrolytic depolymerisation and dehydration of tagua primary yields levomannosan

(1,6-anhydro- $\beta$ -D-mannopyranose). Levomannosan is the mannan-analogue of levoglucosan 47 (1,6-anhydro- $\beta$ -D-glucopyranose) from cellulose pyrolysis; it only differs by one stereocenter. 48 Recently, our research group revisited this bioresource and demonstrated larger-scale pyrolysis 49 in a fully controlled, continuously operated, lab-scale reactor [8]. Pyrolysis liquids were 50 obtained with a yield between 58-60 wt.% and were rich in levomannosan. 51 Since levoglucosan is considered an important platform molecule [7], it can be anticipated 52 that levomannosan could fulfill that role as well. However, other carbohydrate derivatives, 53 like levoglucosenone (1,6-anhydro-3,4-dideoxy- $\beta$ -D-pyranosen-2-one) and furfural are 54 considered one tier higher in terms of their current value as platform chemicals [12, 6, 13, 55 5]. One promising application of levoglucosenone is its use as starting product for Cyrene, 56 a bio-based solvent (vide supra) obtained by the Furacell process. For furfural, a plethora of 57 applications are possible [5]. Levoglucosenone results from acid-catalyzed dehydration of 58 cellulose or levoglucosan [14]. Often in literature, phosphoric acid is used as catalyst [15, 59 16, 17, 18, 19], as well as in the patent of the Circa group [20], that developed the Furacell 60 process. Furfural on the other hand is typically obtained upon dehydration of C5 carbohydrates, 61 like xylose using e.g.,  $ZnCl_2$  as catalyst [21, 22, 23, 24] 62 A highly relevant research question is therefore if tagua could *directly* yield levoglucosenone 63 or furfural, like cellulose does, in appreciable quantities upon thermocatalytic conversion. A 64 proof-of-principle in this regard has not been the subject of any scientific research so far. 65 Yet, a positive answer could mean a game-changer, in terms of how to provide key chemical 66 building blocks from low-cost tagua waste, using simple process schemes (*i.e.*, without 67 extensive fractionation or purification, otherwise required for lignocellulosic biomass). 68 These results can moreover be translated to other similar bioresources, such as acaí seeds 69 from the Euterpe oleracea Mart. palm. These seeds also contain ca. 62 wt.% C6 carbohydrates 70 (ca., 53 wt.% being mannan) and present a major source of waste in Brazil (1.1 million 71 metric ton annually) [25]. The production of açaí berries, from which these seeds are by-products, 72 is increasing fast, given its status as "super food". 73

#### 74 2. Materials and Methods

#### 75 2.1. Tagua samples

The ivory nut samples were ground ( $\phi < 2$ mm) and dried at 105 °C overnight before use for catalyst-free micropyrolysis experiments.

# 78 2.2. Infusion of tagua for in-situ catalysis

Tagua was infused with either phosphoric acid or zinc chloride, depending on the product 79 of interest. As starting point to demonstrate the "mannan to levoglucosenone" conversion in 80 this proof-of-principle, H<sub>3</sub>PO<sub>4</sub> was used a catalyst. Two stock solutions of phosphoric acid 81 (Phosphoric acid 85% a.r., ChemLab Belgium) in demineralized water were prepared of 3 82 wt.% H<sub>3</sub>PO<sub>4</sub> and 6 wt.% H<sub>3</sub>PO<sub>4</sub>. These concentrations were chosen, based on earlier work 83 of Meng *et al.* [15]. Two grams ground tagua ( $\phi < 2$ mm) was added to 100 mL of each 84 of the two H<sub>3</sub>PO<sub>4</sub> stock solutions. The suspensions were stirred at room temperature for 2 85 hours, filtered over a Buchner filter and dried (105 °C, 3 hours). 86 Like  $H_3PO_4$  for levoglucosenone,  $ZnCl_2$  was used as default catalyst to test furfural "mannan 87 to furfural" option [21, 22, 23, 24]. Five grams ground tagua ( $\phi < 2$ mm) was added to 88

- <sup>89</sup> 50 mL ZnCl<sub>2</sub> stock solutions, containing 1 or 1.5 wt.% ZnCl<sub>2</sub> ( $\geq$  97%, VWR chemicals,
- <sup>90</sup> Belgium). The suspensions were stirred at room temperature for 2 hours and evaporated

91 (105 °C, 3 hours). The two ZnCl<sub>2</sub>-infused tagua samples had *ca*. 9 wt.% ZnCl<sub>2</sub> and 13 wt.%

 $_{92}$  ZnCl<sub>2</sub>, respectively.

## 93 2.3. Analysis of (infused) tagua

<sup>94</sup> The elemental composition of the tagua seeds was  $C_6H_{11}O_5N_{0.3}$  [8]. To obtain the phosphorus

<sup>95</sup> content after infusion, microwave destruction and spectrophotometry were performed. First,

- $_{96}$  0.44 g infused tagua was digested with 4 mL HNO<sub>3</sub> and 1 mL H<sub>2</sub>O<sub>2</sub> in a microwave (program:
- <sup>97</sup> from room temperature to 200 °C in 20 minutes and holding time of 10 minutes). The phosphorous
- $_{98}$  content was then determined via the Hach Lange testkit LCK350 6-60 mg/L PO<sub>4</sub><sup>3-</sup>.

# 99 2.4. Analytical catalytic fast pyrolysis (Py-GC-MS/FID)

To demonstrate the principal conversion of tagua to levoglucosenone and furfural, using 100  $H_3PO_4$  and  $ZnCl_2$ , micro-scale fast pyrolysis was performed in duplicate using a tandem 101 micro reactor (TMR) unit. A mass of *ca*. 300  $\mu$ g of tagua or catalyst-infused tagua was 102 loaded in a deactivated stainless steel sample cup. The sample cup was dropped into a pre-heated 103 pyrolysis tube. The sample was consequently heated rapidly to the set pyrolysis temperature 104 of 350 °C at a rate of ca. 2000 °C/s (this heating rate is claimed by the manufacturer). The 105 secondary reactor for ex-situ catalytic vapor-phase upgrading remained empty at 350 °C. 106 The TMR (Rx-3050TR, Frontier Laboratories Ltd.) was coupled to a gas chromatograph 107 followed by a mass spectrometer (Thermo Fisher Scientific Trace GC Ultra and Thermo 108 ISQ MS) and a flame ionisation detector (FID). A restrictor capillary tube and an open split 109 interface are attached before the head of the column to keep the GC column flow rate stable 110 due to the pressure conditions. A flow controller unit monitored the pressure of the reactor 111 (0.4 MPa) and column inlet (0.14 MPa) independently. A scheme for the Py-GC-MS/FID is 112 shown in Fig 2. 113

The carrier gas (high-purity Helium) flow inside the TMR was 50 ml/min. The inlet temperature 114 of the GC was 280 °C and the split ratio in the interface was 1:50. The pyrolysis products 115 were separated in the GC using a Restek capillary column (Rtx-1707, 60 m × 0.25 mm × 116 0.25  $\mu$ m) with a stationary phase consisting of a crossbond 14% cyanopropylphenyl and 117 86% dimethyl polysiloxane. The GC oven temperature was set as follows: 3 min hold at 40 118 °C followed by heating to 270 °C at 4.1 °C/min and the final temperature was held constant 119 for 1 min. The MS transfer line temperature was 280 °C, the ion source temperature was 120 kept at 250 °C and the electron ionisation energy was 70 eV (scanning range: m/z 29-300). 121 The carrier gas and volatiles leaving the GC column were directed to a 3-way splitter, which 122 separates the gas flow in a close ratio of 50/50 towards the MS and FID. The FID operated 123 at a base temperature of 250 °C and an ignition threshold of 0.5 pA. The flow of air, hydrogen 124 and nitrogen (reference gas) used in the FID were 350, 35 and 30 ml/min respectively. 125 Peak identification was based on retention times, manual inspection of the fragmentation 126 pattern and the result from the NIST Mass Spectral Search Program (Version 2.3). Quantification 127



Figure 2: Set-up for micropyrolysis, coupled to a gas chromatograph, mass spectrometer and flame ionization detector.

of specific compounds was based on the FID intensity and the calibration curves for those
 compounds.

#### 130 2.5. Validation in a continuous auger fast pyrolysis reactor

Gram-scale experiments were conducted to further explore and validate the results from 131 analytical pyrolysis. About 40 g ivory nut were used, be it raw or infused with a 3 wt.% 132 H<sub>3</sub>PO<sub>4</sub> solution under the same conditions as for microscale experiments. Since little differences 133 were observed between micropyrolysis of ivory nut treated with 3 wt.% or 6 wt.% H<sub>3</sub>PO<sub>4</sub> 134 (vide infra), infused ivory nut with 3 wt.% H<sub>3</sub>PO<sub>4</sub> was used for larger-scale experiments. 135 The experiments were performed in a fully controlled, continuously operated, pyrolysis 136 reactor (Fig. 3), previously described by Ghysels et al. [8], which was operated at 350 °C. 137 The condensed liquids in the electrostatic precipitator and liquid collection vessel were 138 collected and analyzed by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR. These spectra were recorded at 400 139 MHz and 100.6 MHz, resp. on a Bruker Avance III spectrometer, equipped with 1H/BB 140



Figure 3: Scheme of lab-scale pyrolysis reactor. (1) biomass hopper; (2) sand hopper; (3) sand conveyor; (4) biomass conveyor; (5) reactor conveyor or auger screw with cooling jacket; (6) in situ reactor; (7) pistons; (8) solid collection vessel; (9) knock-out vessel; (10) second knock-out vessel; (11) electrostatic precipitator); (12) liquid collection vessel; (13) glass condenser; (14) cotton wool filter; (15) gas meter; (16) exhaust system; (17) micro-GC sample line [8].

z-gradient probe (BBO, 5 mm). Tetramethylsilane (TMS) was used as an internal chemical

shift standard. All spectra were processed using TOPSPIN 3.6.2. The chemical shift as

 $_{143}$   $\delta$ -value was reported in ppm. A portion of the recovered pyrolysis liquids (0.9 g) was diluted

with 0.9 g deuterated dimethyl sulfoxide (DMSO-D6) to obtain a 1:1 mass ratio for the

NMR analysis. To render quantitative <sup>1</sup>H-NMR analysis, fumaric acid was added to a concentration
 of 0.05 wt.%.

# 147 **3. Results and Discussion**

# 148 3.1. Qualitative analysis of whole pyrograms

Representative pyrograms (*i.e.*, FID-chromatograms of volatiles emitted from micropyrolysis)
 for raw and catalyst-infused tagua are in Fig. 4. The pyrograms are annotated with the seven
 most abundant compounds, and for which therefore calibration curves were set-up. The

- detailed peak list can be consulted in Supplementary Information. The first important observation
- is that catalytic pyrolysis dramatically simplifies the composition of the pyrolysis vapors;
- the number of peaks decreased significantly for  $H_3PO_4$ -infused tagua in particular and for
- <sup>155</sup> ZnCl<sub>2</sub>-infused tagua to a lesser, yet meaningful, extent (Fig. 4). This brings positive perspectives for purification and downstream processing.



Figure 4: Representative pyrograms for non-catalytic pyrolysis of tagua (top), catalytic pyrolysis with H<sub>3</sub>PO<sub>4</sub> (middle) and catalytic pyrolysis, using ZnCl<sub>2</sub> (bottom).

<sup>157</sup> Upon non-catalytic pyrolysis of tagua, the relative peak area for levomannosan corresponded

- to *ca.* 31.61%  $\pm$  0.32%, for levoglucosenone 0.81%  $\pm$  0.04% and for furfural 5.88%  $\pm$
- <sup>159</sup> 0.04%. Pyrolysis of tagua, infused with 3 wt.% H<sub>3</sub>PO<sub>4</sub>, gave rise to a predominant levoglucosenone
- peak, with a relative peak area 50.66%  $\pm$  0.67%. This is a unique and unprecedented result;
- <sup>161</sup> it confirms that catalytic fast pyrolsis of tagua *directly* results levoglucosenone as key chemical
- <sup>162</sup> building block. The relative peak areas for levomannosan and furfural were  $7.04\% \pm 0.91\%$

and 7.75%  $\pm$  0.06%, respectively. In other words, the compound of interest, being levoglucosenone, 163 covered ca. half of the vapor composition on FID-area basis. Doubling the H<sub>3</sub>PO<sub>4</sub> concentration 164 only modestly increased the levoglucosenone contribution (52.79%  $\pm$  0.11%). Catalytic 165 pyrolysis of cellulose leads to 1,4:3,6-Dianhydro- $\alpha$ -D-glucopyranose [26] with relative 166 peak areas between 5-15% [15]. DGP is considered an undesired by-product for levoglucosenone 167 production, as it currently has no meaningful applications. Here, DGP (and its mannan-analogue) 168 remained a minor compound  $(1.49\% \pm 0.13\%)$ , which is considered positive. 169 Further by-products from pyrolysis of tagua, infused with  $H_3PO_4$ , are furfural (relative 170 peak area of 7.75%  $\pm 0.06\%$  for 3 wt.% H<sub>3</sub>PO<sub>4</sub> and 7.99%  $\pm 0.28\%$  for 6 wt.% H<sub>3</sub>PO<sub>4</sub>) 171 and 2(5H)-furanone (relative peak area of  $6.26\% \pm 0.29\%$  for 3 wt.% H<sub>3</sub>PO<sub>4</sub> and  $5.27\% \pm$ 172 0.05% for 6 wt.% H<sub>3</sub>PO<sub>4</sub>). While applications for furfural have been addressed before (vide 173 infra), 2(5H)-furanone is being studied as scaffold for anticancer agents [27, 28]. 174 Upon catalytic pyrolysis of ZnCl<sub>2</sub>-infused tagua, furfural became the predominant peak 175 (Fig. 4). This result is unprecedented as well. The relative peak area for furfural was 29.36% 176  $\pm$  0.15% for infusion with 1 wt.% ZnCl<sub>2</sub>, while 28.50%  $\pm$  2.81% for infusion with 1.5 177 wt.% ZnCl<sub>2</sub>. The relative peak area for levoglucosenone, the second largest peak for ZnCl<sub>2</sub> 178 infusion, was 10.82%  $\pm$  0.34% for infusion with 1 wt.% ZnCl<sub>2</sub>, while 16.27%  $\pm$  1.75% 179 for infusion with 1.5 wt.% ZnCl<sub>2</sub>. While the relative contribution of furfural in the pyrolysis 180 vapors remained stable in tandem with the ZnCl<sub>2</sub> content, the contribution of levoglucosenone 181 increased. 182

# 183 3.2. Quantitative analysis of target compounds

Quantitative data are presented in Fig. 5. Calibration of these compounds was successful, as the average coefficient of determination  $R^2$  for the seven five-point calibration curves was 0.995. The yields are expressed on absolute basis (mass compound per mass -infusedtagua). By comparing to other scholarly reports, "yield" was found to be ambiguously reported; sometimes on liquid basis, sometimes on biomass basis and sometimes, peak areas from chromatography were reported as yields [29]. This often obscures direct comparison. The herein obtained absolute yield in levomannosan and levoglucosan upon catalyst-free



Figure 5: Yields for major compounds upon non-catalytic and catalytic fast pyrolysis of tagua. The wt.% numbers signify the catalyst concentration in stock solution.

pyrolysis of plain tagua were 33.89 wt.%  $\pm$  0.24 wt.% and 2.43 wt.%  $\pm$  0.15 wt.%, respectively. 19 The combined yield in both anhydrosugars neatly aligns with expected yields for levoglucosan 192 from pyrolysis of analytical-grade cellulose of many previous reports [30]. Furfural had 193 a yield of 9.13 wt.%  $\pm$  0.23 wt.%, which is more than what is expected from cellulose 194 pyrolysis [31]. Infusing with zinc chloride led to higher furfural yields: 12.92 wt.%  $\pm$  0.91 195 wt.% after infusion in 0.1 wt.% stock solution and 13.17 wt.%  $\pm$  0.66 wt.% after infusion in 196 the 0.15 wt.% stock solution. Like pyrolysis of pure tagua, pyrolysis of ZnCl<sub>2</sub>-infused tagua 197 led to hydroxyacetone (indicative for undesired ring-opening fragmentation of anhydrosugars) 198 and 5-hydroxymethylfurfural. However, modest yields in levoglucosenone were observed as 199 well, upon pyrolysis of ZnCl<sub>2</sub>-infused tagua: 1.65 wt.%  $\pm$  0.05 wt.% and 2.09 wt.%  $\pm$  0.19 200 wt.% for infusion with 0.10 wt.% and 0.15 wt.% ZnCl<sub>2</sub>, respectively. 201 The largest levoglucosenone yield was observed for pyrolysis of  $H_3PO_4$ -infused tagua, 202 being 6.32 wt.%  $\pm$  0.34 wt.% for infusion with 3 wt.% H<sub>3</sub>PO<sub>4</sub> and 6.64 wt.%  $\pm$  0.27 wt.% 203

for infusion with 6 wt.%  $H_3PO_4$  at the expense of levomannosan. The lowest  $H_3PO_4$  level

 $_{205}$  led to virtually the same yield as the highest  $H_3PO_4$  level for infusion. These yields align

within the lower-to-medium range of literature on cellulose/wood with -engineered- catalysts; 206 some report lower yields [16, 32, 33], other report higher yields [34, 35, 36, 37]. Furfural 207 was another compound with a high absolute yield; their yield (9.42 wt. $\% \pm 9.31$  wt.% for 208 infusion with 3 wt.%  $H_3PO_4$  and 10.06 wt.%  $\pm$  9.72 wt.% for infusion with 6 wt.%  $H_3PO_4$ ) 209 fall within that for pure tagua and that of  $ZnCl_2$ -infused tagua. Although 2(5H)-furanone 210 constitutes a valuable compound as well, its absolute yield remains modest, being ca. 1.2 211 wt.%. In catalytic pyrolysis with ZnCl<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub>, yields between 12 wt.% to 14 wt.% for 212 levomannosan/levoglucosan were observed. This is significant as well, provided their future 213 value as platform chemicals. 214

215 3.3. Mechanistic insights

Phosphoric acid is acknowledged as very good catalyst for levoglucosenone production 216 from cellulose [15, 16, 17, 18, 19, 20]. The herein highest observed yield in levoglucosenone 217 from mannan-rich ivory nut, being 6.64 wt.%  $\pm$  0.27 wt.%, is however lower than cellulose-based 218 phosphoric acid-mediated pyrolysis. Nevertheless, it can be expected that other catalysts, 219 tailored for mannan, could increase the yield in levoglucosenone. Indeed, Fig. 6 shows how 220 the different stereocenter in cellulose and mannan could affect catalytic dehydration towards 221 levoglucosenone. The top row in Fig.6 shows a cellulose chain with a levoglucosan-end; the 222 bottom shows mannan with a levomannosan end. The hydrogen (position 2) and hydroxyl 223 group (position 3) that participate in dehydration are highlighted in blue. Upon catalytic 224 dehydration of the levoglucosan-end with H<sub>3</sub>PO<sub>4</sub>, it is clear that both the participating hydrogen 225 and hydroxyl moieties point in the same upward direction. This is not the case for mannan, 226 where both participating groups point in opposite directions. This steric hindrance (i.e., less 227 accessibility for  $H_3PO_4$ ) could explain why mannan-rich ivory nut yields less levoglucosenone, 228 compared to cellulose and why screening for new catalysts could be an opportune next step 229 to optimize levoglucosenone yields from mannan-rich feedstock. After this key dehydration 230 step, the carbon at the 2nd position has a  $sp^2$  hybridisation and therefore is no longer a 231 stereocenter. From this mutual enol intermediate, levoglucosenone production follows, 232 according to Lu et al., [38] and Hu et al. [19]. 233





Figure 6: Mechanism put forth for the production of levoglucosenone from cellulose and mannan.

# 234 3.4. Levoglucosenone from continuous auger fast pyrolysis reactor pyrolysis

Fast pyrolysis of untreated ivory nut, infused with 3 wt.% H<sub>3</sub>PO<sub>4</sub>, at 350 °C in the continuous 235 auger fast pyrolysis reactor (Fig. 3) resulted in  $68.9 \pm 1.3$  wt.% pyrolysis liquids. the phophorous 236 content on the infused ivory nut was 0.040 g  $H_3PO_4$  per g infused sample. <sup>13</sup>C-NMR analysis 237 of the as-obtained liquids is shown in Fig. 7, which unambiguously underpins the predominant 238 presence of levomannosan, rather than levoglucosan, in the pyrolysis liquids. The yield in 239 pyrolysis liquids, obtained from infused ivory nut with 3 wt.%  $H_3PO_4$  was 49.5 wt.%  $\pm$  3.8 240 wt.%. Similarly, <sup>13</sup>C-NMR analysis underpinned the presence of majorly levoglucosenone 24 and levomannosan. By spiking fumaric acid, the concentration of levoglucosenone was 242 determined from the <sup>1</sup>H-NMR spectrum as 3.69 wt.% in the pyrolysis liquids. This corresponds 243 to an absolute yield in levoglucosenone of 1.8 wt.%. This yield is -expectedly- lower than 244 those from analytical pyrolysis, given the prolonged hot-vapor residence time in the continuous 245 auger fast pyrolysis reactor. This indeed prompts further secondary cracking of e.g., levoglucosenone 246 into non-condensable gases, like CO and CO<sub>1</sub>. Although these exploratory experiments 247 in the continuous auger pyrolysis reactor show potential, higher yields are expected from 248 further optimization of the catalyst and operating parameters (vide supra). 249

#### 250 4. Conclusions

<sup>251</sup> Catalytic pyrolysis of tagua ameliorates the product portfolio by generating desired added-value <sup>252</sup> chemical building blocks, like levoglucosenone (max 6.64 wt.%  $\pm$  0.27 wt.%), furfural



Figure 7: top: <sup>13</sup>C-NMR of pyrolysis liquids, obtained without catalysts, at 350 °C and compared to levomannosan and levoglucosan standards. bottom: <sup>13</sup>C-NMR of pyrolysis liquids, obtained from ivory nut infused with 3 wt.%  $H_3PO_4$ , at 350 °C and compared to levoglucosenone and levomannosan standards.

(max 13.17 wt.%  $\pm$  0.66 wt.%) and levomannosan (max non-catalytic 33.89 wt.%  $\pm$  0.24 253 wt.%; max catalytic 13.13 wt.%  $\pm$  1.63 wt.%). The complexity of evolved products upon 254 catalytic fast pyrolysis decreased, which brings positive prospects for downstream processing 255 and purification. Moreover, no fractionation or carbohydrate-separation was required to 256 obtain these yields, which brings a techno-economic advantage over cellulose-based processes. 257 Overall, this work demonstrates the direct valorisation of local agricultural residues into 258 key chemical intermediates for biorefining at analytical and reactor scale. Future work 259 could encompass the validation of these results on larger scale and/or optimisation of the 260

<sup>261</sup> catalysts/process conditions.

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#### 266 Appendix A. Supplementary information

Supplementary information associated with this article can be found, in the online version,at doi.

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