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## Integrating bio-oil and carbohydrate valorization on the fractionation of sugarcane bagasse via Organosolv process using Mo<sub>2</sub>C-based catalysts

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1        **Integrating bio-oil and carbohydrate valorization on**  
2        **the fractionation of sugarcane bagasse via *Organosolv***  
3        **process using Mo<sub>2</sub>C-based catalysts**

4  
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27 **Abstract**

28 This work studied the fractionation of sugarcane bagasse via *Organosolv* treatment  
29 using isopropanol/water in the presence of Raney-Ni and molybdenum carbide catalysts  
30 (Bulk Mo<sub>2</sub>C and Mo<sub>2</sub>C supported on activated carbon (AC) or Al<sub>2</sub>O<sub>3</sub>). The degree of  
31 delignification, the bio-oil and solid residue composition depended on the type of  
32 catalyst. A partial extraction of hemicellulose occurred followed by depolymerization,  
33 resulting in a product distribution that depended on the catalyst. Raney-Ni catalyst  
34 promoted the formation of diols and triols, while xylose, furfural, and furan were  
35 mainly produced by Mo<sub>2</sub>C based-catalysts. The *Organosolv* treatment without catalyst  
36 and in the presence of bulk Mo<sub>2</sub>C produced a bio-oil containing mainly 2,3-  
37 dihydrobenzofuran. Mo<sub>2</sub>C/AC and Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> are promising catalysts for the  
38 fractionation of sugarcane bagasse that produced a bio-oil with higher yield to  
39 substituted methoxyphenols and a solid residue more easily hydrolyzed by cellulases,  
40 producing higher yield to glucose than Raney-Ni catalyst.

41

42 **Keywords:** bio-oil; *Organosolv*; biomass fragmentation; reductive catalytic  
43 fractionation; Raney-Ni; Mo<sub>2</sub>C

44

## 45 **1. Introduction**

46 Lignocellulosic biomass is a sustainable resource for the production of fuels and  
47 chemicals. However, the fractionation of lignocellulose into its major constituents  
48 (cellulose, hemicellulose and lignin) and the complete utilization of each separated  
49 fraction is still a challenge that reduces the competitiveness of the process using this  
50 feedstock. From the industrial point of view, the fractionation of lignocellulosic biomass  
51 still has issues. For instance, considering the second-generation ethanol (2G ethanol)  
52 plants that started their production in the last decade, only few of them are still under  
53 operation [1]. The delay on the technology development is partially associated with the  
54 pretreatment of biomass that was once considered a simple step of production, but it  
55 was not the reality for the large-scale operation of biorefineries [1,2]. Therefore, the  
56 search for an efficient method of fractionation of the lignocellulosic biomass is  
57 fundamental to overcome the barriers faced by a biorefinery.

58 Currently, large progresses have been made on the valorization of carbohydrate  
59 fractions (cellulose and hemicellulose), whereas the use of isolated lignin remains less  
60 explored, being mostly burned for energy generation [3]. However, the success of a  
61 biorefinery also requires the valorization of the lignin fraction.

62 Lignin, a complex and water-insoluble aromatic polymer, is derived primarily  
63 from methoxylated hydroxycinnamyl alcohol building blocks. Unlike cellulose, with a  
64 well-defined sequence of monomeric units that are linked by regular  $\beta$ -1,4-glycosidic  
65 bonds, lignin is characterized by a variety of distinct and chemically different bonds,  
66 each one demanding different condition for cleavage when selective depolymerization is  
67 targeted. Although structurally more complex, the higher carbon content and lower  
68 oxygen content of lignin, relative to the holocellulose fraction, renders it an attractive  
69 feedstock for the production of biofuels and chemicals [4]. In spite of the large

70 production of lignin by the Kraft process of the pulp and paper industry, there are no  
71 commercial process for the valorization of Kraft lignin into fuels or chemicals. This is  
72 partially due to its recalcitrant and complex chemical nature [5].

73 One alternative delignification technology is the so-called *Organosolv* process  
74 that uses different organic solvents/water mixtures. The solvent polarity not only affects  
75 the delignification degree, but also the fragmentation of the lignin oligomers to mono-  
76 and dimers [6]. The polarity of the solvent enhances the swelling of the lignocellulosic  
77 matrix, making it more accessible. However, the solubility of lignin oligomers (small  
78 lignin fragments with molecular weight between 100 – 400 Da) [4] significantly  
79 decreases in too polar solvents such as pure water, but water is important for the  
80 solubilization of holocellulose [7]. The combination of both counteracting effects  
81 provides a synergistic effect resulting in an increased biomass extraction and  
82 fragmentation [8].

83 Recently, solvents with hydrogen donor capabilities such as 2-propanol  
84 (isopropanol) have also been used on the treatment of lignocellulosic biomass [9-13] as  
85 well as on the hydrodeoxygenation of bio-oil produced [14-16]. The hydrogen donor  
86 solvents can produce *in situ* H<sub>2</sub> by catalytic decomposition, enhancing the solvolytic  
87 process of  $\alpha$ -O-4 and  $\beta$ -O-4 ether bonds of the lignin structure and thus, promoting the  
88 fractionation of the biomass [5, 17]. The *Organosolv* process using hydrogen donor  
89 solvents has been used mostly on the fractionation of different types of wood. There are  
90 only few works about the *Organosolv* treatment of sugarcane bagasse using ethanol as  
91 solvent [12,13]. Although there are no studies about the fractionation of sugarcane  
92 bagasse using isopropanol as hydrogen donor solvent, the performance of both alcohols  
93 were similar in the fractionation of birch wood using Pd/C catalyst at 200 °C and 30 bar  
94 of H<sub>2</sub> for 3 h [6].

95           Despite the advantages of the *Organosolv* process, the repolymerization of lignin  
96 on the surface of the residual biomass can occur during the fractionation process,  
97 decreasing the efficiency of the subsequent downstream processing [18]. This is because  
98 this repolymerized lignin is characterized by very strong, highly recalcitrant C—C  
99 bonds [4]. This leads to a decrease in the efficiency of delignification, reducing the  
100 complete utilization of biomass fractions.

101           Recently, a new strategy for biomass fractionation has been proposed to avoid or  
102 reduce the repolymerization of lignin, the so-called reductive catalytic fractionation  
103 (RCF), in which biomass fractionation and lignin depolymerization occurs  
104 simultaneously in the presence of a heterogeneous catalyst [5,19, 20]. The role of the  
105 catalyst is to avoid repolymerization reactions by hydrogenating unsaturated lignin  
106 intermediates to monophenolic compounds. Other advantages of this catalytic  
107 fractionation process are: (i) the use of native lignin that exhibits high reactivity in  
108 comparison to isolated lignin, which is more condensed and recalcitrant; (ii) the lignin  
109 oil obtained can be upgraded under less severe conditions; (iii) the carbohydrate fraction  
110 (holocellulose) remains in the solid, whereas the lignin fraction is kept in the liquid  
111 phase, containing a high amount of aromatic compounds; and (iv) the decrease on the  
112 operational steps.

113           Since 2008, the number of papers about RCF has been steadily increasing but  
114 only a limited number of catalysts have been used. Most of these studies performed the  
115 fractionation in the presence of a catalyst containing noble metals such as Pd [6], Pt  
116 [21], Ru [22] or Rh [22] and transition metals such as Ni [19,20] supported on carbon or  
117 an unsupported catalyst (e.g., Raney Ni) [10,23].

118           Transition metal carbides are cheaper than noble metal catalysts, but exhibit  
119 similar catalytic behavior. They have been tested in a variety of reactions such as

120 hydrodesulfurization, hydrodenitrogenation and hydrodeoxygenation of bio-oil and  
121 model compounds representative of the lignin fraction of lignocellulose biomass [24-  
122 26] and deoxygenation of wood pyrolysis vapors [26]. Transition metal carbides have  
123 also demonstrated great potential for the conversion of lignin, exhibiting high selectivity  
124 for the cleavage of  $\beta$ -O-4,  $\alpha$ -O-4,  $\beta$ - $\beta$  and 4-O-5 bonds [25].

125         There are different works in the literature that reported the use of metal carbides  
126 (mainly molybdenum and tungsten) for the depolymerization of isolated lignin [27,28].  
127 However, the catalytic fractionation of lignocellulosic biomass is much more complex,  
128 involving delignification, depolymerization and/or repolymerization of lignin fragments  
129 simultaneously. Only one work investigated the performance of metal carbide catalysts  
130 for the fractionation of lignocellulosic biomass [29]. In this work, Li *et al.* [29] reported  
131 the direct catalytic conversion of raw woody biomass into two groups of chemicals over  
132 a carbon supported Ni-W<sub>2</sub>C catalyst. The carbohydrate fraction was converted to diols  
133 with a yield of 75.6 % (based on the amount of cellulose and hemicellulose), while the  
134 lignin component was converted selectively into monophenols with a yield of 46.5 %  
135 (based on lignin). Therefore, the metal carbide catalyst favored not only the conversion  
136 of carbohydrate fractions, but also the depolymerization of lignin, which makes it  
137 competitive when compared to noble metal catalysts.

138         It is also important to notice that most of the works on RCF used different types  
139 of wood (hardwoods and softwoods) [30] but only one work studied the fractionation of  
140 a grass (*Miscanthus*) using methanol and Ni/C catalyst [31]. Typical lignin structures in  
141 grasses contain ferulate, *p*-coumarate and triclin units that are not usually present in  
142 hardwoods and softwoods. Therefore, the depolymerization of lignin from grasses will  
143 produce different phenolic monomers than the ones obtained from woods.

144           Therefore, the goal of this work was to study the fractionation of sugarcane  
145 bagasse (grass) via *Organosolv* treatment using isopropanol as solvent and source of  
146 hydrogen (*in situ*) in the presence of different catalysts. Bulk Mo<sub>2</sub>C and Mo<sub>2</sub>C  
147 supported on activated carbon (AC) or  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> containing 20 % (m/m) of molybdenum  
148 carbide were evaluated. Raney-Ni commercial catalyst was used as reference. The  
149 characterization of the bio-oil and residual biomass was carried out by GC $\times$ GC-TOFMS  
150 and confocal microscopy, respectively. Both techniques provide important information  
151 about the composition of the bio-oil and morphology of the residue, and they are  
152 scarcely used in the literature on the biomass fractionation studies. The approach used in  
153 this work allows the full transformation of the fractionated biomass into biofuels and  
154 green chemicals through the integration of both lignin valorization and carbohydrate  
155 upgrading. The enzymatic hydrolysis of the solid residue containing carbohydrate  
156 fraction integrates the production of second-generation ethanol and the lignin extraction  
157 for the bio-oil production.

158



## 159 **2. Experimental**

### 160 **2.1. Catalyst synthesis**

161 The bulk Mo<sub>2</sub>C was prepared by temperature-programmed carburization (TPC)  
162 of molybdenum oxide (MoO<sub>3</sub>, Sigma-Aldrich). The sample was heated under a 20 %  
163 CH<sub>4</sub>/H<sub>2</sub> (v/v) mixture (200 mL min<sup>-1</sup>.g<sub>oxide</sub><sup>-1</sup>) at a heating rate of 2.5 °C min<sup>-1</sup> from 25 to  
164 650 °C, remaining at this temperature for 2 h. After synthesis, it was changed the gas  
165 feed to He (200 mL min<sup>-1</sup>) and the system was cooled to room temperature. Since the  
166 transition metal carbides are pyrophoric, the reactor was flooded internally with  
167 isopropanol after carburization and the catalyst was removed and stored in isopropanol  
168 until its use in the reaction.

169 Mo<sub>2</sub>C/AC and Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> catalysts containing 20 % (m/m) of molybdenum  
170 carbide were prepared by incipient wetness impregnation of the supports, activated  
171 carbon (AC – Merck) and γ-Al<sub>2</sub>O<sub>3</sub> (BASF), with an aqueous solution containing  
172 ammonium heptamolybdate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O, Merck). After impregnation, the  
173 materials were dried at 100 °C for 12 h. Then, the Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> catalyst precursor was  
174 calcined at 500 °C for 5 h. Finally, the carburization of both samples followed the  
175 procedure previously described for the bulk Mo<sub>2</sub>C catalyst.

176 The nickel catalyst used was a commercial Raney-Ni 2800 slurry (Sigma-  
177 Aldrich), an active catalyst stored in water, containing Ni (≥ 89 %) and Al (6-9 %), and  
178 20-60 μm particle size.

179

### 180 **2.2. Catalyst Characterization**

181 Specific surface areas of the samples were measured on a Micromeritics ASAP  
182 2020 analyzer by N<sub>2</sub> adsorption at -196 °C.

183 Temperature-programmed carburization (TPC) experiments were performed in a  
184 homemade apparatus. The sample (100 mg) previously loaded into a quartz U-tube  
185 micro reactor was heated under a 20 % (v/v) CH<sub>4</sub>/H<sub>2</sub> mixture (100 mL min<sup>-1</sup>) at a  
186 heating rate of 2.5 °C min<sup>-1</sup> from 25 to 650 °C, remaining at this temperature for 2 h.  
187 The gases coming out from the reactor were analyzed continuously by online mass  
188 spectrometry (Pfeiffer Vacuum QME 200) monitoring the ion signals *m/z* 16 (CH<sub>4</sub>), *m/z*  
189 18 (H<sub>2</sub>O) and *m/z* 28 (CO).

190 Powder XRD patterns were recorded in a Bruker D8 diffractometer. The spectra  
191 were recorded in Bragg angles between 10° and 90°, with a step size of 0.02° and an  
192 acquisition time of 1 s. The crystalline phases of the samples were identified using the  
193 ICCD data base. For this characterization, the precursor oxide was *ex situ* treated by  
194 TPC and passivated at room temperature, under a mixture of 0.5 % O<sub>2</sub>/He (30 mL min<sup>-1</sup>  
195 1) for 12 h.

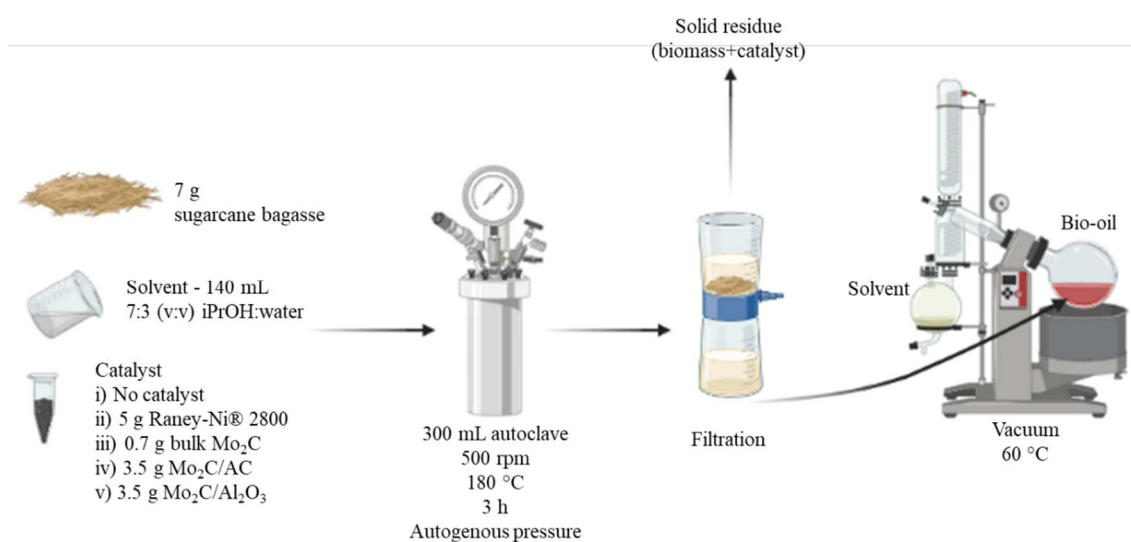
196 CO chemisorption technique was carried out in order to measure the dispersion  
197 of the catalysts. The samples were activated under the same conditions previously  
198 described for the TPC experiment. Then, the samples were cooled to 30 °C and pulses  
199 of CO were injected until saturation. The dispersion was calculated assuming that one  
200 CO molecule is chemisorbed at each metal site.

201

### 202 **2.3. Sugarcane bagasse fractionation**

203 The delignification of sugarcane bagasse (from Iacanga plant, São Paulo -  
204 Brazil) was performed through the *Organosolv* treatment using isopropanol (iPrOH,  
205 Vetec) and water as solvents. 7 g of sugarcane bagasse and 140 mL of solvent were  
206 used. The reaction was conducted in a 300 mL autoclave (Parr reactor) at 180 °C for 3  
207 h, under mechanical stirring at 500 rpm and autogenous pressure (Scheme 1). The

208 reactor was then cooled to room temperature in an ice bath. The liquor was separated  
 209 from the pretreated bagasse by filtration. The pretreated bagasse retained on the filter  
 210 was washed with iPrOH to remove all the compounds adsorbed thereon and then dried  
 211 at 40 °C. The liquor and the washing permeate of the pretreated bagasse were mixed  
 212 and placed into a rotary evaporator under vacuum at 60 °C for removal of the solvents.  
 213 The bio-oil and the pretreated bagasse were kept under refrigeration for the  
 214 characterization analyzes. The catalytic method was carried out similarly as  
 215 *Organosolv*. 5 g of the nickel catalyst (Raney-Ni® 2800, Sigma Aldrich) was used. For  
 216 the carbide catalysts, it was used 0.7 g of bulk Mo<sub>2</sub>C, and 3.5 g of Mo<sub>2</sub>C/AC and  
 217 Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> catalysts, in order to keep the same amount of active phase.  
 218



219  
 220 **Scheme 1.** Schematic diagram of experimental procedure of sugarcane bagasse  
 221 fractionation.

222

#### 223 2.4. Characterization of biomass

224 The chemical compositional analyses of biomass (e.g. lignin and sugars) were  
 225 performed following NREL (National Renewable Energy Laboratory, USA) analytical

226 procedures [32]. The degree of delignification ( $D_{lig}$ ) and the fraction of sugar in the  
 227 pretreated bagasse ( $R$ ) recovered were calculated using Eqs. 1 and 2.

228

$$229 \quad D_{lig}(\%) = \frac{(f_{lignin\ total,0} - f_{lignin\ insol,f}) \cdot f_{sol.recup}}{f_{lignin\ total,0}} \cdot 100 \quad (1)$$

$$230 \quad R(\%) = \frac{f_{sugar\ recup} \cdot f_{sol.recup}}{f_{sugar,0}} \cdot 100, \quad \text{where,} \quad f_{sol.recup} = \frac{m_{bagasse,f}}{m_{bagasse,0}} \quad (2)$$

231

232 where  $f_{lignin\ total,0}$  is the fraction of total lignin (acid soluble and insoluble lignin) present  
 233 in the bagasse before treatment and  $f_{lignin\ insol,f}$  is the acid insoluble lignin fraction present  
 234 in the pretreated bagasse recovered after treatment.  $f_{sugar\ recup}$  is the sugar fraction in the  
 235 pretreated bagasse after treatment and  $f_{sugar,0}$  is the sugar fraction in the bagasse before  
 236 treatment.  $f_{sol.recup}$  is the fraction of solid residue recovered after the reaction (unreacted  
 237 bagasse),  $m_{bagasse,f}$  is the mass of unreacted bagasse,  $m_{bagasse,0}$  is the mass of initial  
 238 bagasse loaded into the reactor. The fraction of bio-oil formed is calculated in the same  
 239 way as  $f_{sol.recup}$ , but considering the mass of bio-oil recovered after the rotary evaporator  
 240 process.

241 Thermogravimetric analyzes evaluated the thermal stability of untreated and  
 242 pretreated bagasse. They were run on a Hitachi STA7300, at a heating rate of  $5\text{ }^{\circ}\text{C min}^{-1}$   
 243 from room temperature to  $700\text{ }^{\circ}\text{C}$  under  $\text{N}_2$  flow at  $80\text{ mL min}^{-1}$ .

244 Confocal fluorescence imaging was carried out using a Zeiss LSM 710 confocal  
 245 microscope. Untreated and pretreated bagasse samples were stained with Safranin O and  
 246 Congo Red. The residues were stained with 0.1 % Safranin O for 5 min, then destained  
 247 by washing in aqueous solution of 50 % ethanol at  $30\text{ }^{\circ}\text{C}$  for 3 min until the washing  
 248 solution is translucent. Then, the residues were stained with 1 % Congo Red under the  
 249 same conditions as Safranin O and then washed. After staining procedure, slides were

250 mounted with Fluoromount-G<sup>®</sup>. Sections stained were excited at 488 nm wavelength.  
251 The confocal microscopy images of cellulose and lignin were collected in the 497-544  
252 nm and 561-603 nm spectral regions, respectively. Samples were observed using an LD  
253 Plan-Neofluar 40x/0.6 Korr M27 and LD Plan-Neofluar 20x/0.6 Korr M27 objective,  
254 and each 1 mm thick image series was rendered as a maximum projection (2D) image  
255 from the Z-stack) with an image size of 1024 × 1024 pixels. Images were treated using  
256 Image J software v. 1.52e.

257

## 258 ***2.5. Characterization of bio-oil***

259 Thermogravimetric analyzes of bio-oils were performed on a Hitachi STA7300,  
260 using the same conditions previously described for the biomass. TGA experiments of  
261 the liquid product, performed under an inert atmosphere, were used for estimating the  
262 fraction of volatile compounds at the injector temperature of the chromatograph [10].

263 In order to analyze the bio-oils via GC×GC-TOFMS, approximately 13.0 mg of  
264 each bio-oil sample were weighed using an analytical balance and dissolved with 2.0  
265 mL of methanol solvent. Then, the solutions were filtered in 0.2 μm syringe filters and  
266 dried in a N<sub>2</sub> stream. The samples were resolubilized with 0.5 mL of the standard  
267 mixture followed by the chromatographic analysis. Standard mixture was composed of  
268 deuterated internal standards, used for identification and semi-quantification, were  
269 obtained from CDN Isotopes (Quebec, Canada) and have purity greater than 97 %:  
270 toluene-D<sub>8</sub>, 1-heptanol-D<sub>15</sub>, hexanoic acid-D<sub>11</sub>, phenol-D<sub>6</sub>, decalin-D<sub>18</sub>, hexadecane-D<sub>34</sub>  
271 and 5α-cholestane-D<sub>6</sub>.

272 The GC×GC-TOFMS system used was a Pegasus 4D (Leco, St. Joseph, MI,  
273 USA), which includes an Agilent Technologies 7890 GC (Palo Alto, CA, USA)  
274 equipped with a secondary oven, a non- moving quad-jet dual-stage modulator, and a

275 Pegasus H11 (Leco, St. Joseph, MI, USA) time-of-flight mass spectrometer. The GC  
276 columns consisted of a DB-5 (Agilent Technologies, Palo Alto, CA, USA) with 5 %-  
277 phenyl–95 %-methylsiloxane (30 m × 0.25 mm i.d., 0.25 μm df) as the first dimension  
278 column (<sup>1</sup>D) and a DB-17 (Agilent Technologies, Palo Alto, CA, USA) with 50 %-  
279 phenyl–50 %-methylsiloxane (1.2 m × 0.1 mm i.d., 0.1 μm df) as the second dimension  
280 column (<sup>2</sup>D). The <sup>2</sup>D column was connected to the TOFMS via a 0.5 m × 0.25 mm i.d.  
281 empty deactivated fused silica capillary using SGE mini-unions and SilTite™ metal  
282 ferrules 0.1–0.25 mm i.d. (Ringwood, VIC, Australia). The injections were performed  
283 in a splitless mode of 1 μL at 300 °C using a purge time of 60 s and a purge flow of 5  
284 mL min<sup>-1</sup>. Helium (99.9999 % purity) was used as carrier gas at a constant flow rate of  
285 1.0 mL min<sup>-1</sup>. The chromatographic conditions were optimized. The primary oven  
286 temperature program was 40 °C for 5 min and ramped up to 320 °C at 5 °C min<sup>-1</sup>. The  
287 temperature of the secondary oven was 5 °C higher than that of the primary oven.  
288 Modulation period was 5 s, with a 1.5 s hot-pulse and 1.0 s cool-pulse duration, with  
289 modulator temperature 30 °C higher than the primary oven temperature. The MS  
290 transfer line was maintained at 300 °C, and the TOFMS was operated in the electron  
291 ionization mode with a collected mass range of *m/z* 35–600. The ion source temperature  
292 was 230 °C, the detector was operated at –1400 V, with electron energy 70 eV, and an  
293 acquisition rate of 100 spectra s<sup>-1</sup>.

294 GC×GC-TOFMS data acquisition and processing were performed using  
295 ChromaTOF® software version 4.5 (Leco, St. Joseph, MI, USA). Samples were  
296 submitted to a data-processing method for which the individual peaks were  
297 automatically detected based on a 500:1 signal-to-noise ratio. The areas of individual  
298 peaks were acquired using the base peak of each spectrum, generating a list of all  
299 detected peaks. The relative area was calculated by peak area/total area of compounds

300 detected with signal-to-noise ratio higher than 500:1, excluding the solvent area.  
301 Identification was performed by comparing the deconvoluted mass spectrum obtained  
302 with the NIST Mass Spectral Library software (NIST 08, Software Version: 2.0) for  
303 correct matching, in addition to the retention times and elution order of the authentic  
304 standards. After comparison, only peaks with similarities greater than 80 % were  
305 identified.

306

## 307 ***2.6. Enzymatic hydrolysis of untreated and pretreated bagasse samples***

308 Enzymatic hydrolysis of untreated and pretreated bagasses samples were carried  
309 out with the commercial enzymes Celluclast 1.5L and Novozyme 188. The activity of  
310 the enzymes was measured as previously described in the literature [33]. A unit of  $\beta$ -  
311 glucosidase (BGU) was defined as the amount of enzyme that converted 1  $\mu\text{mol}$  of  
312 cellobiose to glucose in 1 min and a unit of FPase (FPU) corresponds to the release of 1  
313  $\mu\text{mol}$  of glucose per minute at 50 °C.

314 Enzymatic hydrolysis was performed in duplicate assays using 0.5 g biomass  
315 (dry weight) in 50 mL glass vials flasks containing sodium citrate buffer (0.05 M), at  
316 pH 4.8 and enzymes, in an assay of 10 g (total mass), reaching solids content of 5 %  
317 (m/m). In these assays, a mixture of commercial enzymes Celluclast 1.5L and  
318 Novozyme 188 at FPU:BGU ratio of 1:3 was used as sources of cellulases and beta-  
319 glucosidase, respectively. The cellulase (Celluclast) dosage for enzymatic hydrolysis  
320 was 20 FPU  $\text{g}^{-1}$  of glucans. Sodium azide (0.01 g) was added to prevent the growth of  
321 microorganisms.

322 The flasks were sealed and kept in a rotary incubator maintained at 50 °C and  
323 200 rpm. Samples were collected at 2, 4, 6, 24, 48 and 72 h, and only 10 % of the initial  
324 total volume was withdrawn. Each aliquot was transferred to tubes which were kept in a

325 boiling water bath for 5 min in order to denature the enzyme pool. Subsequently they  
326 were centrifuged and the supernatants were submitted for glucose quantification in the  
327 biochemical analyzer (YSI 2700 Select TM, Marshall Scientific).

328 The glucose yield was calculated according to Eq. 3.

329

330 
$$Y_{\text{glucose}} = \frac{(C_{\text{glucose}} - C_{\text{glucose},0})}{1.111 \left( \frac{w_t}{V_{h0}} \right) F_{\text{ins},0} \cdot F_{\text{glucan}}} \cdot 100 \quad (3)$$

331

332 where  $C_{\text{glucose}}$  is the concentration of glucose in the hydrolysate ( $\text{g L}^{-1}$ ),  $C_{\text{glucose},0}$  is the  
333 initial glucose concentration in the hydrolysis assay,  $w_t$  is the total mass of the  
334 hydrolysis assay (g),  $V_{h0}$  is the initial volume of liquid (L),  $w_t$  corresponds to the initial  
335 mass of liquid added to the hydrolysis assay,  $F_{\text{ins},0}$  is the initial mass fraction insoluble  
336 in the total hydrolysis assay,  $F_{\text{glucan}}$  is the initial mass fraction of glucans in the solid  
337 insoluble.

338



### 3. Results and discussion

#### 3.1. Catalyst Characterization

The BET surface areas of the catalysts increased from 25 m<sup>2</sup> g<sup>-1</sup> for the bulk Mo<sub>2</sub>C to 540 m<sup>2</sup> g<sup>-1</sup> and 165 m<sup>2</sup> g<sup>-1</sup> for Mo<sub>2</sub>C/AC and Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub>, respectively.

Fig. 1 shows the profiles of different products formed during treatment under 20 % CH<sub>4</sub>/H<sub>2</sub> (v/v) mixture: *m/z* 18 (H<sub>2</sub>O); *m/z* 28 (CO) and *m/z* 16 (CH<sub>4</sub>). For the bulk Mo<sub>2</sub>C, the curve corresponding to water shows a shoulder at 625 °C and a peak at 640 °C. However, there is only one peak at 650 °C on the curves of the *m/z* 28 and 16 signals. This result indicates that the first peak in the curve of *m/z* 18 corresponds to the reduction of MoO<sub>3</sub> to MoO<sub>2</sub> with water formation (Eq. 4). The second peak in the *m/z* 18 curve is followed by the consumption of methane and the formation of CO, suggesting the formation of Mo carbide (Eq. 5). The same results are reported in the literature [34].

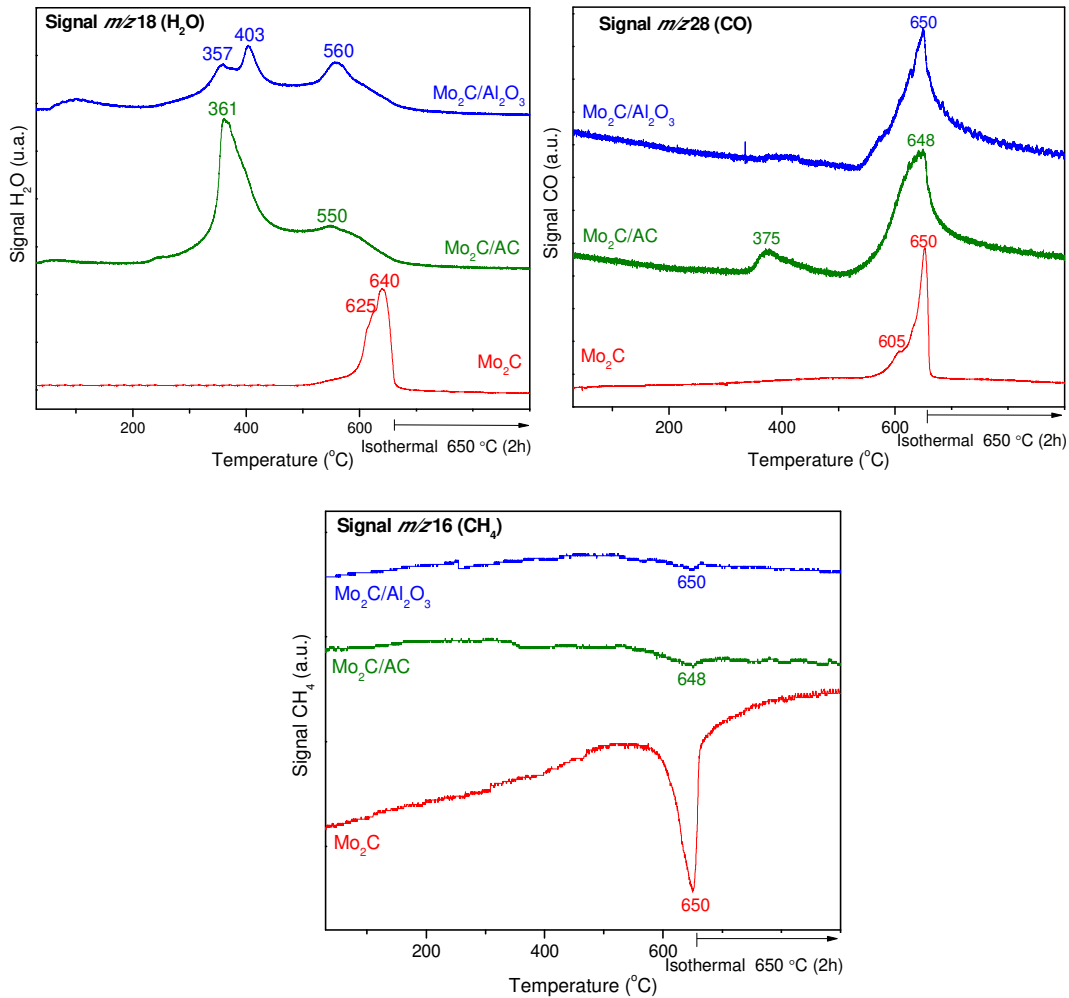
352



355

For the supported samples, the profiles corresponding to water are more complex than that one for bulk sample. Mo<sub>2</sub>C/AC exhibited peaks at 361 and 550 °C while three peaks are observed on the profile of Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> catalyst at 357, 403 and 560 °C. It is observed the formation of CO above 500 °C, with a peak at around 650 °C, which is followed by a peak with weak intensity corresponding to the consumption of methane. Therefore, the region at low temperature in the profile of water formation could be attributed to the reduction of MoO<sub>3</sub> to MoO<sub>2</sub> with different particle size, whereas the water formation at high temperature (above 500 °C) is likely due to the formation of Mo

364 carbide. Then, the TPC experiments suggests that Mo carbide was formed after  
 365 treatment at 650 °C for 2h under 20 % CH<sub>4</sub>/H<sub>2</sub> (v/v) mixture for all samples. XRD  
 366 experiments after TPC were carried out to confirm the formation of Mo carbide phase  
 367 and the results will be presented next.  
 368



369

370

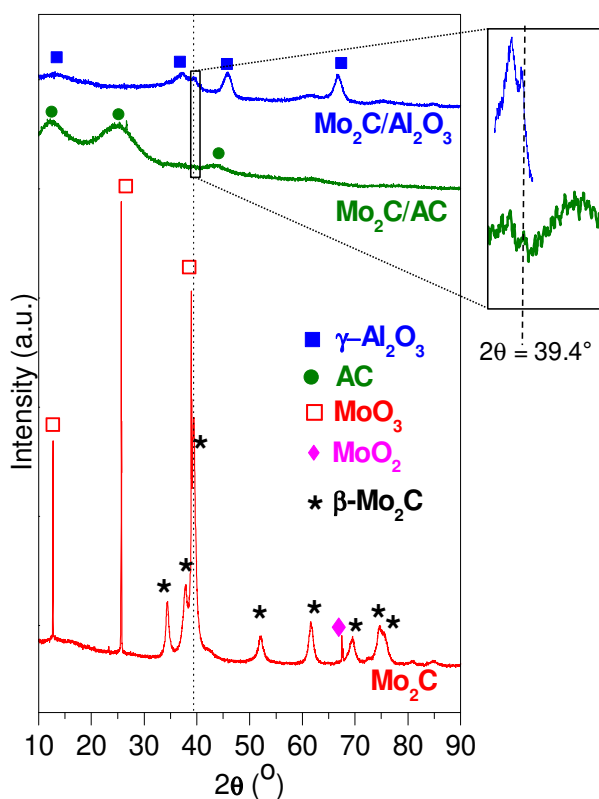
371 **Figure 1.** Signals of the products formed during the TPC up to 650 °C (2.5 °C min<sup>-1</sup>)  
 372 under 20 % CH<sub>4</sub>/H<sub>2</sub> (v/v) mixture.  $m/z$  18 (H<sub>2</sub>O);  $m/z$  28 (CO); and  $m/z$  16 (CH<sub>4</sub>).  
 373

374 Fig. 2 shows the diffractograms of Mo-based catalysts after carburization. The  
 375 diffractogram of bulk Mo<sub>2</sub>C exhibits the lines characteristic of  $\beta$ -Mo<sub>2</sub>C phase (ICDD  
 376 35-0787) at  $2\theta = 34.4, 37.9, 39.4, 52.0, 61.7, 69.5, 72.4, 74.6$  and  $75.5^\circ$ . However, the

377 lines corresponding to  $\text{MoO}_3$  ( $2\theta = 12.8, 25.7, 39.0^\circ$ ) phase are also observed,  
378 suggesting that the Mo carbide was partially oxidized when the sample was exposed to  
379 air after TPC. However, this phase is not expected during the catalytic experiment  
380 because the catalyst was in situ reduced before the reaction.

381 For both supported catalysts, the diffractograms revealed the presence of the  
382 main diffraction line of  $\beta\text{-Mo}_2\text{C}$  phase at  $2\theta = 39.4^\circ$ , which agrees well with the TPC  
383 results that revealed the formation of carbide phase.

384



385

386 **Figure 2.** X-ray diffractograms of  $\text{Mo}_2\text{C}$ ,  $\text{Mo}_2\text{C}/\text{AC}$  and  $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$  samples. Dotted  
387 line corresponds to the most intense diffraction line of  $\beta\text{-Mo}_2\text{C}$  phase ( $2\theta = 39.4^\circ$ ).

388

389 It has been observed that the type of support influences the formation of  
390 molybdenum carbide phase. Han *et al.* [34] reported the formation of the molybdenum

391 carbide phase on carbon nanotube (CNT) at lower temperature than over activated  
392 carbon support.

393 The amount of CO chemisorbed and the calculated dispersion are reported in  
394 Table 1. Both supported Mo<sub>2</sub>C catalysts have approximately the same dispersion around  
395 14-15 %, which is in agreement with other works in the literature [24,35].

396

397 **Table 1.** CO chemisorption and carbide dispersion (D).

Catalyst	Chemisorption ( $\mu\text{mol}_{\text{CO}} \cdot \text{g}_{\text{catalyst}}^{-1}$ )	D (%)
Mo <sub>2</sub> C	68	-
Mo <sub>2</sub> C/AC	141	14.4
Mo <sub>2</sub> C/Al <sub>2</sub> O <sub>3</sub>	150	15.3

398

### 399 **3.2. Catalytic fractionation of sugarcane bagasse**

400 First, the delignification of sugarcane bagasse was performed using the  
401 *Organosolv* treatment in an aqueous solution containing 2-propanol (iPrOH:H<sub>2</sub>O, 70 %  
402 v/v) at 180 °C for 3 h. 2-Propanol was used as a solvent as well as a hydrogen-donor.  
403 The aim of this procedure is to retain the holocellulose (cellulose and hemicellulose)  
404 fraction as a solid residue and to keep the lignin in the liquid phase.

405 After treatment with aqueous solution of isopropanol (iPrOH), 30 % of the initial  
406 biomass produced the bio-oil and 70 % was recovered as the solid residue (pretreated  
407 bagasse) (Table 2). The relative content of cellulose in the pretreated bagasse increased  
408 from 39.9 % (untreated bagasse) to 52.8 % (pretreated bagasse), while the hemicellulose  
409 fraction remained unchanged around 25 % (Table S1). Based on the initial content, this  
410 treatment retained a considerable part of the sugars in the solid residue with high

411 recovery of cellulose (93 %) while hemicellulose was partially recovered (69 %) (Table  
 412 2). However, the insoluble lignin content decreased considerably from 22.5 to 13.1%  
 413 (Table S1), resulting in 59 % of delignification of sugarcane bagasse (Table 2).

414

415 **Table 2.** Degree of delignification and recovered fraction (%) after *Organosolv* reaction  
 416 with isopropanol solution in the absence of catalyst (iPrOH) and in the presence of  
 417 Raney-Ni (Ni+iPrOH), Mo<sub>2</sub>C (Mo<sub>2</sub>C+iPrOH), Mo<sub>2</sub>C/AC (Mo<sub>2</sub>C/AC+iPrOH) and  
 418 Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> (Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub>+iPrOH) catalysts.

	iPrOH	Ni+iPrOH	Mo <sub>2</sub> C+iPrOH	Mo <sub>2</sub> C/AC+iPrOH	Mo <sub>2</sub> C/Al <sub>2</sub> O <sub>3</sub> +iPrOH
Bio-oil fraction	30	23	49	34	45
Solid fraction	70	69	44	36	47
Fraction sum	100	92	92	70	92
Delignification	59	62	80	14	14
<b>Recovered fraction in pretreated bagasse in comparison to the initial biomass *(%, m/m)</b>					
Cellulose	93	93	73	31	28
Hemicellulose	69	74	28	15	31

\* Untreated bagasse consisted of 39.90 % cellulose, 25.69 % hemicellulose, 22.54 % total lignin, 4.96 % extractives and 0.93 % ash (Table S1).

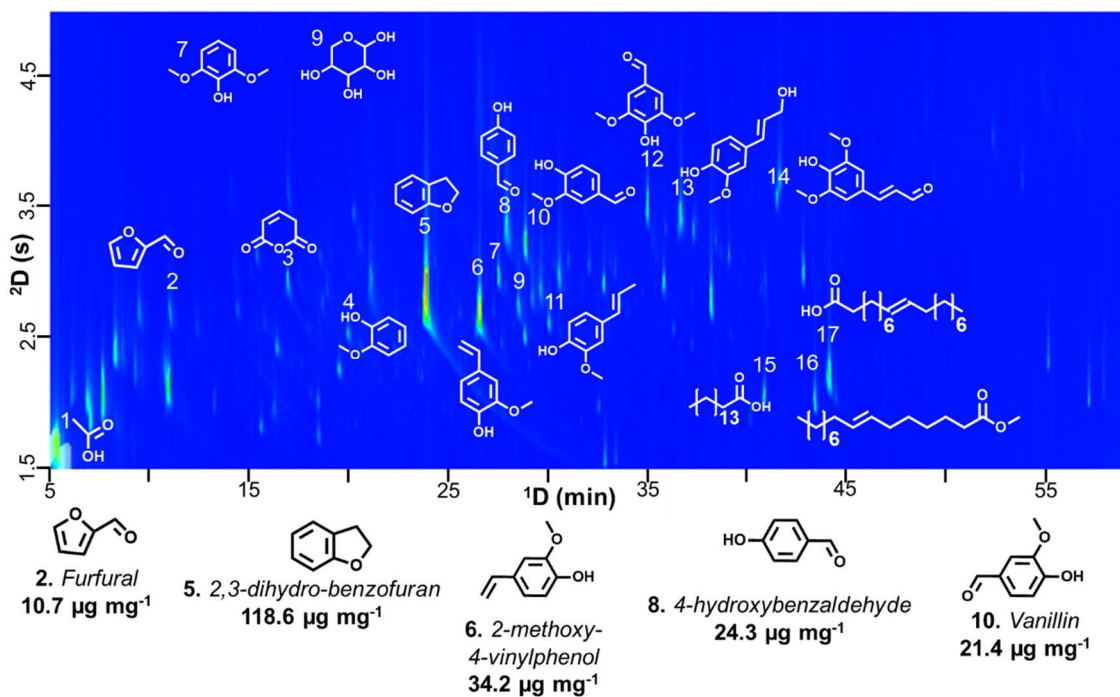
419

420 A similar result was reported by Novo *et al.* [36] for *Organosolv* fractionation of  
 421 sugarcane bagasse with an aqueous solution containing 80 % of glycerol. The authors  
 422 recovered 93 % of cellulose, a value similar to the one obtained in our work with iPrOH  
 423 reaction, and approximately 80 % of delignification was achieved at 190 °C and 4 h.  
 424 The lower degree of delignification of our work is likely due to the type of solvent and  
 425 the lower reaction temperature used (2-propanol, 180 °C). Ferrini and Rinaldi [10] used  
 426 the *Organosolv* method for the delignification of poplar wood under the same  
 427 conditions of our work (reaction temperature and solvent) and obtained 77 % of

428 delignification. This result reveals the effect of the composition of lignocellulosic  
429 biomass on the delignification degree. Lignin from grasses, such as sugarcane bagasse,  
430 is less susceptible to delignification than lignin from hardwood (poplar). The reactivity  
431 of lignin depends on the composition of reactive functional groups within monomer  
432 units [37]. Lignin is composed by three fundamental monomers: *p*-coumaryl alcohol (*p*-  
433 hydroxyphenol - H), coniferyl alcohol (guaiacyl - G), and sinapyl alcohol (syringyl - S).  
434 In softwood lignins, the dominant monomer is guaiacyl (G), while hardwood lignins  
435 consists of both guaiacyl (G) and syringyl (S) units. Grasses have large quantities of all  
436 three phenylpropylenes [38].

437         Van den Bosch *et al.* [39] performed the catalytic fractionation of different  
438 lignocellulosic feedstocks (birch, poplar, a pine-spruce mixture and *Miscanthus*) using  
439 the *Organosolv* method with methanol and H<sub>2</sub> for 3 h and a Ru/C catalyst. The  
440 hardwoods (birch and poplar) exhibited both the highest degree of delignification (93 %  
441 and 86 %, respectively), and the highest yields of monomers and dimers. On the other  
442 hand, the softwood samples (pine and spruce mixture) led to a moderate degree of  
443 delignification (56 %) and a low yield of phenolic monomers. *Miscanthus* samples,  
444 which belongs to the family of grasses as sugarcane bagasse, presented an intermediate  
445 degree of delignification (63 %), as well as an intermediate monomer yield. Therefore,  
446 these results indicate that the lignin building block composition will influence in its  
447 tendency to depolymerization into phenolic monomers and dimers compounds.

448         Fig. 3 shows a two-dimensional gas chromatography (GC×GC-TOFMS) image  
449 corresponding to the bio-oil obtained by the *Organosolv* treatment of sugarcane bagasse  
450 without catalyst, highlighting the main detected and identified species.



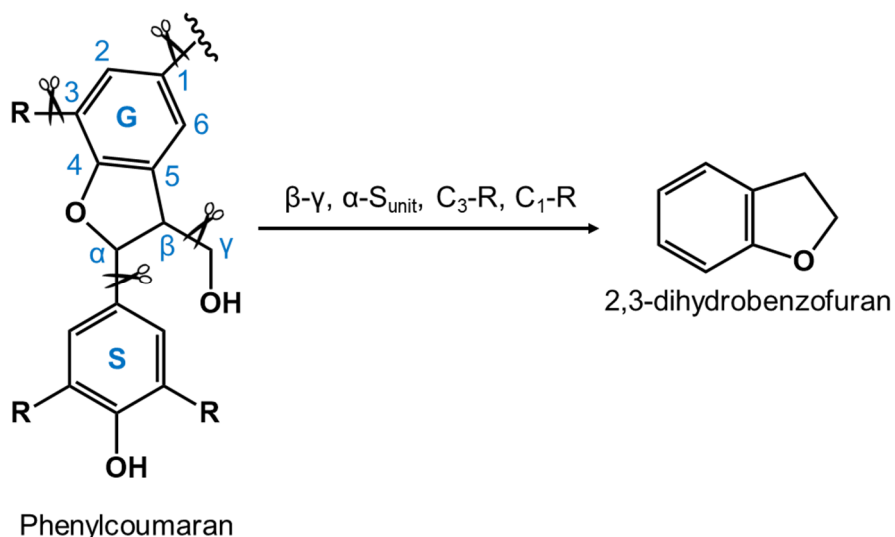
451

452 **Figure 3.** GCxGC-TOFMS chromatogram of bio-oil sample from iPrOH *Organosolv*  
 453 treatment. The main analytes are highlighted under the chromatogram.

454

455 2,3-dihydrobenzofuran is the main component of the bio-oil ( $118.6 \mu\text{g mg}^{-1}$ ) that  
 456 also contains significant amounts of substituted methoxyphenols (2-methoxy-4-  
 457 vinylphenol, vanillin, 4-hydroxy-benzaldehyde). 2,3-dihydrobenzofuran and substituted  
 458 methoxyphenols are obtained from the decomposition of lignin structure [40,41].  
 459 Phenylcoumaran structures formed by  $\beta$ -5' coupling are one of the main structures  
 460 present in the lignin of sugarcane bagasse as identified in the NMR (Nuclear Magnetic  
 461 Resonance) spectra [42]. The depolymerization of this structure led to the formation of  
 462 2,3-dihydrobenzofuran (Fig. 4), which has pharmaceutical, industrial, and medical  
 463 applications. Several biologically active natural and synthetic compounds are based on  
 464 the 2,3-dihydrobenzofuran core. For instance, 2,3-dihydrobenzofurans have  
 465 antitubercular, anti-HIV, anticancer, antiprotozoal and cytotoxic activities [43].

466



467

468 **Figure 4.** Depolymerization of phenylcoumaran structures and formation of 2,3-  
 469 dihydrobenzofurans, where, G: guaiacyl and S: syringyl units; C<sub>1</sub> and C<sub>3</sub> are the carbons  
 470 in position 1 and 3, respectively, of the guaiacyl units.

471

472 GCxGC images of the bio-oil obtained by *Organosolv* treatment of poplar wood  
 473 under the same reaction conditions used in our work (180 °C, iPrOH/H<sub>2</sub>O (7:3, v/v))  
 474 [10] did not reveal the presence of 2,3-dihydrobenzofuran, which also demonstrate that  
 475 this compound is typical of depolymerization of lignin derived from grasses.

476 Table 3 reports the concentration of the main classes of compounds present in  
 477 the bio-oil. Substituted phenols and methoxyphenols stood out as a class of compounds  
 478 identified in the bio-oil (44.7 %) and they are derived from lignin. Table S2 lists the  
 479 main constituents of the bio-oil obtained without catalyst and their respective  
 480 concentrations. Substituted methoxyphenols such as 2-methoxy-4-vinylphenol (analyte  
 481 6, Fig. 3) was detected. This compound has application as flavoring agent in foods and  
 482 beverages [44]. Additionally, a considerable amount of vanillin was quantified, which is  
 483 a lignin oxidation product applied as flavoring agent for foods [45].

484



485 **Table 3.** Concentration ( $\mu\text{g mg}_{\text{biooil-volatilized}}^{-1}$ ) and percentage of the identified classes in  
 486 the bio-oils obtained by Semi-quantification via GC $\times$ GC-TOFMS. Fraction of volatiles  
 487 at 300 °C obtained by thermogravimetric analysis of bio-oils.

Group**	Concentration ( $\mu\text{g mg}_{\text{biooil-volatilized}}^{-1}$ / %)									
	iPrOH		Ni+iPrOH		Mo <sub>2</sub> C+iPrOH		Mo <sub>2</sub> C/AC+iPrOH		Mo <sub>2</sub> C/Al <sub>2</sub> O <sub>3</sub> +iPrOH	
<b>Carbohydrates derived-compounds</b>										
Acids	5.5	/1.9	21.2	/2.7	12.4	/4.1	19.1	/3.9	9.0	/2.8
Alcohols and sugars	7.0	/2.5	73.7	/9.5	13.9	/4.5	23.4	/4.8	11.6	/3.7
Ketones	0.6	/0.2	0.5	/0.1	2.5	/0.8	5.7	/1.2	7.0	/2.2
Esthers	2.0	/0.7	1.0	/0.1	4.7	/1.5	26.2	/5.3	2.8	/0.9
Furanics derived	18.8	/6.6	237.2	/30.6	45.9	/15.0	76.4	/15.6	109.7	/34.7
<b>Lignin derived-compounds</b>										
Substituted phenols and methoxyphenols	126.8	/44.7	146.3	/18.9	107.2	/35.0	208.1	/42.4	129.0	/40.8
2,3-Dihydrobenzofuran	118.6	/41.8	3.6	/0.5	118.2	/38.6	121.8	/24.8	1.2	/0.4
Others lignin derived-compounds	3.5	/1.2	289.8	/37.4	1.6	/0.5	9.8	/2.0	45.8	/14.5
Hydrocarbons	0.9	/0.3	2.5	/0.3	0.1	/0.0	0.0	/0.0	0.3	/0.1
<b>Total</b>	283.7		776.2		306.5		490.5		316.3	
<b>Fraction volatiles 300 °C (%)</b>	54		76		39		48		54	

\* Concentration: semi-quantified analyte mass relative to bio-oil volatilized mass at 300 °C

\*\* Aldehydes and ethers were found in traces in the bio-oil samples

488

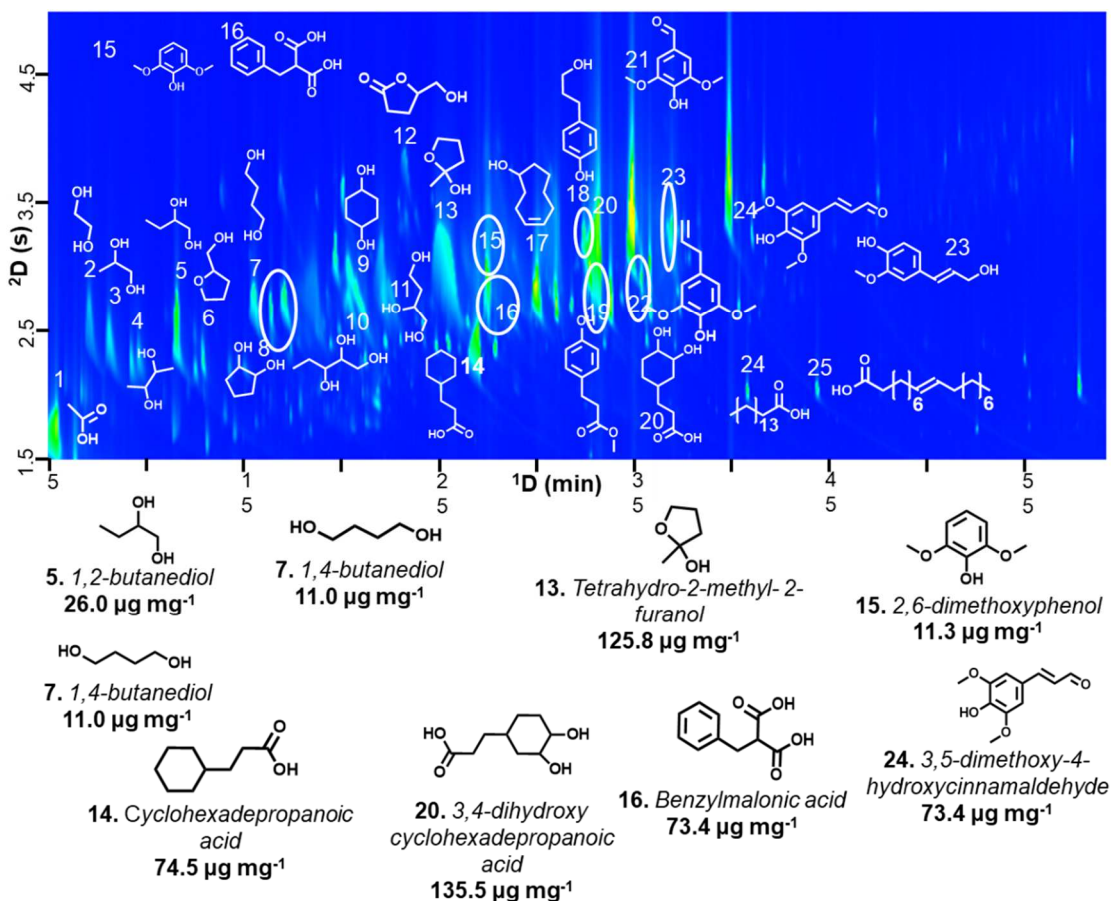
489 The *Organosolv* treatment was also evaluated in the presence of Raney-Ni  
 490 commercial catalyst, used as reference, in comparison to molybdenum carbide catalysts,  
 491 proposed in our study as alternative catalyst. The addition of Raney-Ni catalyst did not

492 produce significant changes in the delignification degree (62 %) or in the fraction of  
493 recovered cellulose (93 %) and hemicellulose (74 %) in the solid residue (Table 2) in  
494 comparison to the *Organosolv* treatment without catalyst. The variations in the relative  
495 content of cellulose, hemicellulose and lignin in the solid residue were also quite close  
496 to the ones observed in the absence of catalyst (Table S1).

497 Van den Bosch *et al.* [19] reported similar results with the *Organosolv* treatment  
498 of birch sawdust using methanol and Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, reaching delignification degrees  
499 of 84 and 87 % without and with catalyst, respectively. According to the authors, the  
500 solvent was responsible for the extraction of lignin and its subsequent depolymerization  
501 by solvolytic cleavage of the β-O-4 bonds. It was suggested that the catalyst stabilized  
502 the products generated from lignin, preventing the repolymerization. The ability of  
503 organic solvents to dissolve lignin facilitates its depolymerization especially because of  
504 the increase in mass transfer between the catalyst and solubilized substrate [6]. In  
505 contrast, for the wood poplar, Ferrini and Rinaldi [10] reported a decrease in the  
506 delignification degree on the treatments in the presence of Raney-Ni catalyst (77 to 63  
507 %).

508 The chromatogram of the bio-oil produced in the presence of Raney-Ni catalyst  
509 is displayed in Fig. 5. The presence of acetic acid and diols corresponds to the  
510 depolymerization of cellulose and hemicellulose. In addition, Fig. S1 shows that at least  
511 76 % of the compounds present in the Ni+iPrOH bio-oil are volatilized at 300 °C  
512 (temperature of chromatograph injector), and therefore analyzed. It is important to take  
513 into account that this was the bio-oil sample with the highest fraction of volatiles, with  
514 775.8 µg of analytes identified for each mg of volatilized bio-oil (at 300 °C, Table 3).

515



529 coronavirus disease 2019 (COVID 19) [46]. Acetic acid is likely due to sugars  
530 degradation and acetyl bond cleavage in the xylans [47].

531 The main lignin-derived products formed were 3,4-dihydroxy-  
532 cyclohexanepropanoic acid (135.3  $\mu\text{g}/\text{mg}$ ), 3-(4-hydroxy-3,5-dimethoxyphenyl)-prop-2-  
533 enal (72.4  $\mu\text{g}/\text{mg}$ ), cyclohexanepropanoic acid (74.5  $\mu\text{g}/\text{mg}$ ), and benzylmalonic acid  
534 (73.4  $\mu\text{g}/\text{mg}$ ). Curiously, only a low concentration of 2,3-dihydrobenzofuran was  
535 detected in the bio-oil obtained in the presence of Raney-Ni (3.6  $\mu\text{g}/\text{mg}$ ).  
536 Benzylmalonic acid was not produced in the absence of the catalyst and 3-(4-hydroxy-  
537 3,5-dimethoxyphenyl)-prop-2-enal was produced in low concentration, indicating that  
538 Raney-Ni participated on the depolymerization of lignin and then, changed the product  
539 distribution. 3,5-Dimethoxy-4-hydroxycinnamaldehyde (sinapaldehyde) is an  
540 intermediate in the synthesis pathway of native lignin monomer precursor sinapyl  
541 alcohol [4].

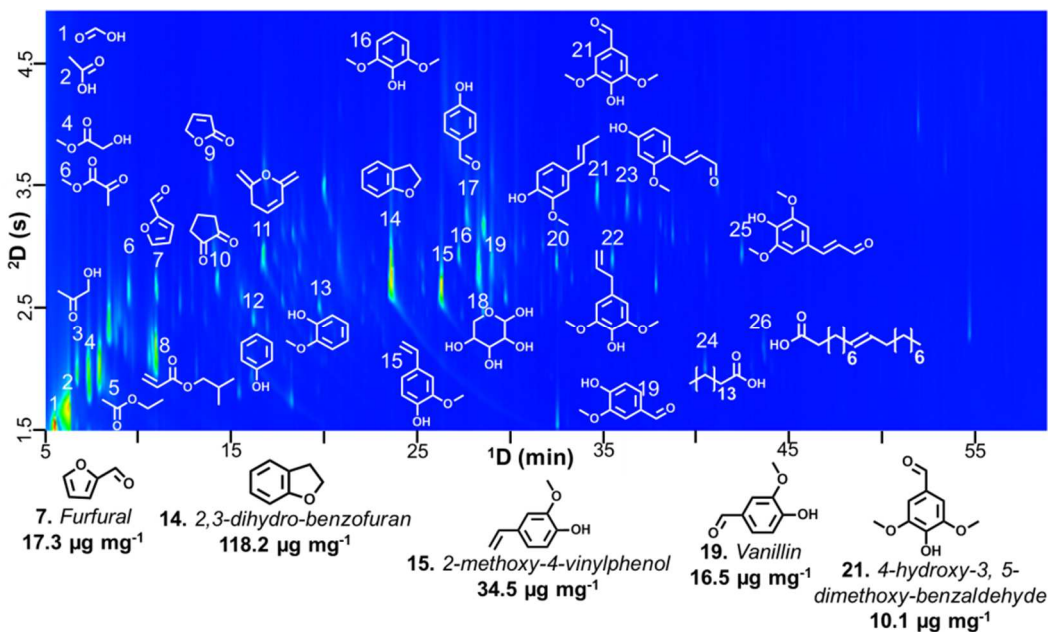
542 Comparing the Ni+iPrOH bio-oil from sugarcane bagasse with that from wood  
543 [10], both exhibited high content of alcohols from hydrogenolysis of hemicellulose  
544 sugars [47]. Analyzing qualitatively, the bio-oil obtained from the treatment of wood  
545 with Raney-Ni catalyst presented mostly methoxyphenols similar to the ones presented  
546 in the sugarcane bio-oil, such as eugenol, 2,6-dimethoxyphenol, 2,6-dimethoxy-4-(2-  
547 propenyl)-phenol. However, the bio-oil from sugarcane differ from that of wood by the  
548 presence of phenol and methoxyphenols substituted by acid groups (analytes 14, 16 and  
549 20, Fig. 5).

550 *Organosolv* treatment of bagasse was also evaluated in the presence of  
551 molybdenum carbide catalysts (bulk  $\text{Mo}_2\text{C}$  or  $\text{Mo}_2\text{C}$  supported on activated carbon  
552 (AC) or  $\gamma\text{-Al}_2\text{O}_3$ ).

553 The treatment with the bulk Mo<sub>2</sub>C catalyst (Mo<sub>2</sub>C+iPrOH) produced a larger  
554 amount of bio-oil and, consequently, a decrease in the solid fraction was observed,  
555 when compared to the reactions with only iPrOH or Ni+iPrOH (Table 2). This is likely  
556 due to the higher delignification degree (80 %) as well as to the larger extent of  
557 cellulose and hemicellulose depolymerization. At this condition, only 28 % of the  
558 hemicellulose of the untreated bagasse was retained in the solid residue. This affected  
559 the bio-oil composition that contained acetic acid (11.8 µg/mg), xylose (9.3 µg/mg),  
560 furfural (17.3 µg/mg) and furan (7.9 µg/mg), all hemicellulose-derived products (Table  
561 S2). However, diols and triols were not formed.

562 Fig. 6 shows the chromatogram of the bio-oil produced in the treatment with the  
563 bulk Mo<sub>2</sub>C catalyst. There was practically no formation of diols in the bio-oil produced  
564 by bulk Mo<sub>2</sub>C that also exhibited a lower formation of acetic acid than Raney-Ni (Table  
565 S2). On the other hand, xylose, furfural and furan were preferentially formed on the  
566 carbide-based catalyst (Table S2). The concentration of substituted phenols and  
567 methoxyphenols (107.2 µg/mg) was lower than on Raney-Ni (Table 3). The main  
568 compound in the bio-oil obtained from the treatment with Mo<sub>2</sub>C was 2,3-  
569 dihydrobenzofuran (118.2 µg/mg), as observed for the *Organosolv* reaction without  
570 catalyst. Moreover, 2-methoxy-4-vinylphenol (34.5 µg/mg), 4-hydroxybenzaldehyde  
571 (19.3 µg/mg), vanillin (16.5 µg/mg), and 4-hydroxy-3,5-dimethoxybenzaldehyde (10.1  
572 µg/mg) were also detected (Table S2).

573



574

575 **Figure 6.** GCxGC-TOFMS chromatogram of bio-oil sample from bulk Mo<sub>2</sub>C catalyzed  
 576 iPrOH *Organosolv* treatment. The main analytes are highlighted under the  
 577 chromatogram.

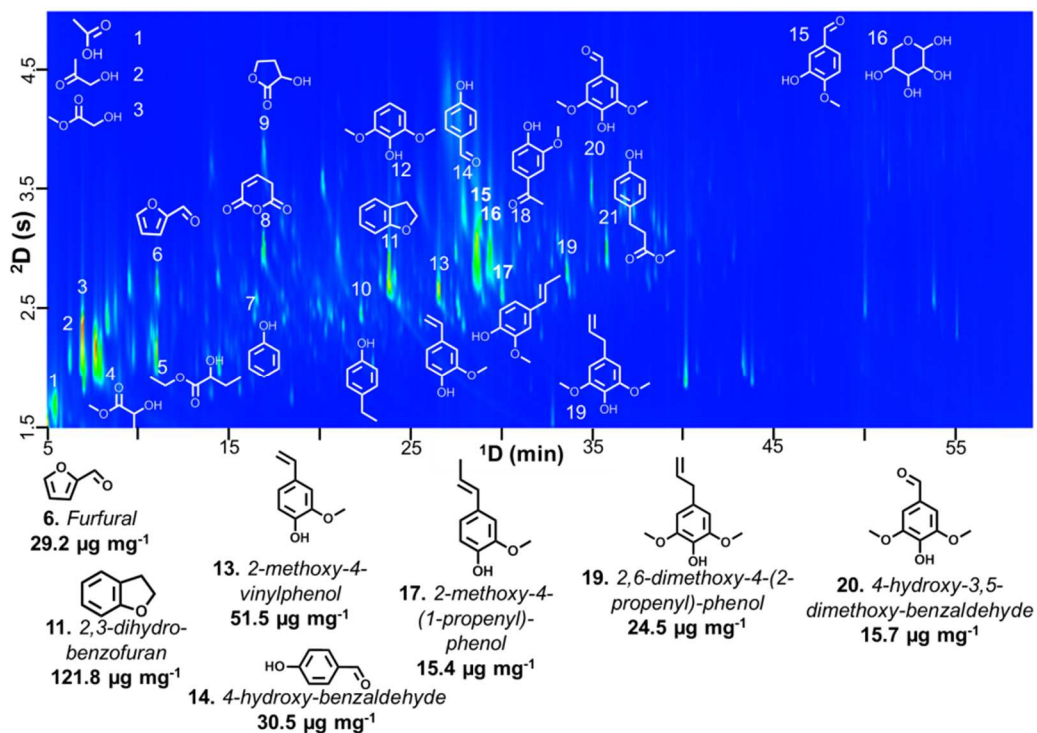
578

579 It is also important to notice that only 39 % of the bio-oil obtained on the  
 580 treatment with bulk Mo<sub>2</sub>C was volatilized at 300 °C (temperature of chromatograph  
 581 injector) as shown by the TGA experiments (Fig. S1), which may explain the apparent  
 582 decrease in the total amount of compounds in this bio-oil, when compared with the bio-  
 583 oil from Ni+iPrOH catalyzed system.

584 In comparison to the reaction with bulk Mo<sub>2</sub>C reaction, the use of Mo<sub>2</sub>C  
 585 supported in AC or Al<sub>2</sub>O<sub>3</sub> resulted in low delignification (14 %) and high cellulose and  
 586 hemicellulose extraction. For instance, it was observed a retention of only 31 and 15 %  
 587 of the initial cellulose and hemicellulose content, respectively, in the solid residue  
 588 recovered after the reaction with Mo<sub>2</sub>C/AC (Table 2). These results agree with the  
 589 considerable amount of acetic acid, xylose, furfural and lactones in the bio-oils from  
 590 reactions catalyzed by Mo<sub>2</sub>C supported catalysts (Table S2).

591 The bio-oil produced in the treatment with Mo<sub>2</sub>C/AC (Fig. 7) contained  
592 considerable amounts of acetic acid (18.7 μg/mg), xylose (18.2 μg/mg) and furfural  
593 (29.2 μg/mg) (Table S2). These results show a significant depolymerization of  
594 hemicellulose in the presence of Mo<sub>2</sub>C/AC catalyst. 2,3-Dihydrobenzofuran was the  
595 main lignin derived product (121.8 μg/mg) as observed for the bulk Mo<sub>2</sub>C catalyst.  
596 Considering the substituted phenols and methoxyphenols, there was significant  
597 formation of 2-methoxy-4-vinylphenol (51.5 μg/mg), 4-hydroxy-benzaldehyde (30.5  
598 μg/mg), 2,6-dimethoxy-4-(2-propenyl)-phenol (24.5 μg/mg), 4-hydroxy-3,5-dimethoxy-  
599 benzaldehyde (15.7 μg mg<sup>-1</sup>) and 2-methoxy-4-(1-propenyl)-phenol (15.4 μg mg<sup>-1</sup>). The  
600 Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub>+iPrOH bio-oil (Fig. 8) contained a significant amount of lactones such as  
601 2-hydroxy-γ-butyrolactone and substituted methoxyphenols such as 3-hydroxy-4-  
602 methoxy-benzaldehyde. As observed for Raney-Ni catalyst, 2,3-dihydrobenzofuran was  
603 not formed in the reaction using Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> catalyst. The tests with Mo<sub>2</sub>C/AC and  
604 Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> catalysts exhibited the highest yield to substituted methoxyphenols (24 %),  
605 which, in general, are good octane components of gasoline.

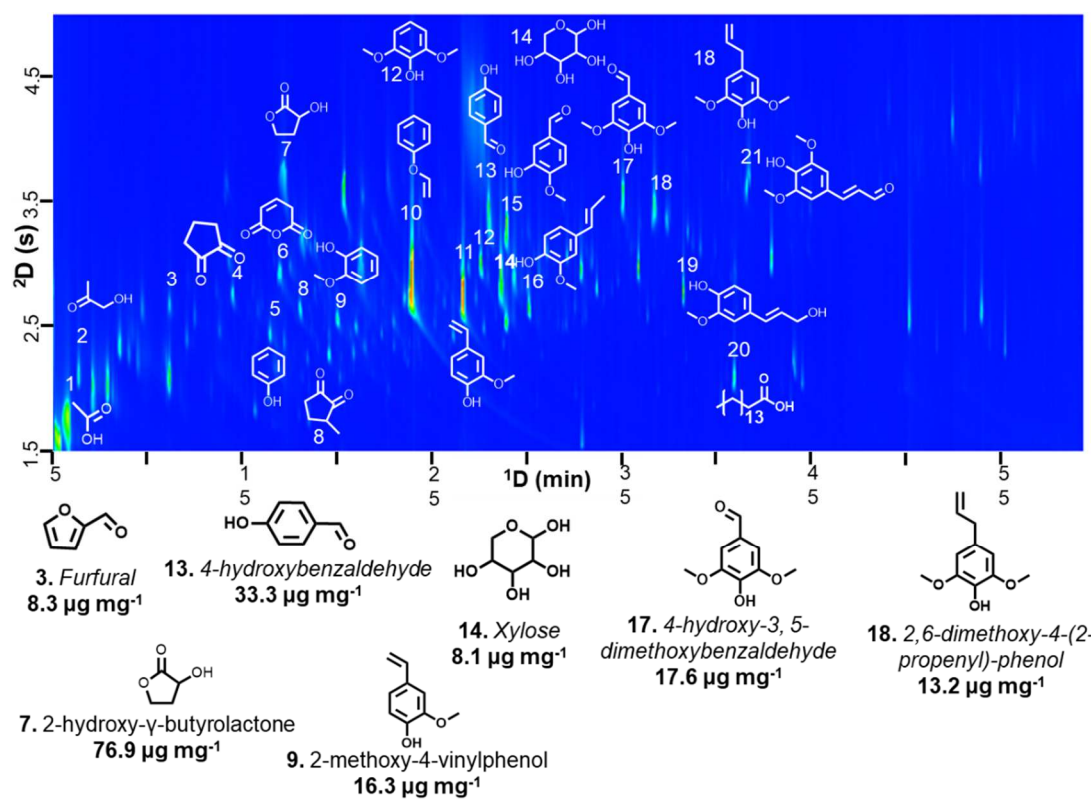
606



607

608 **Figure 7.** GCxGC-TOFMS chromatogram of bio-oil sample from Mo<sub>2</sub>C/AC catalyzed  
 609 iPrOH *Organosolv* treatment. The main analytes are highlighted under the  
 610 chromatogram.





611

612 **Figure 8.** GCxGC-TOFMS chromatogram of bio-oil sample from  $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$   
 613 catalyzed *iPrOH Organosolv* treatment. The main analytes are highlighted under the  
 614 chromatogram.

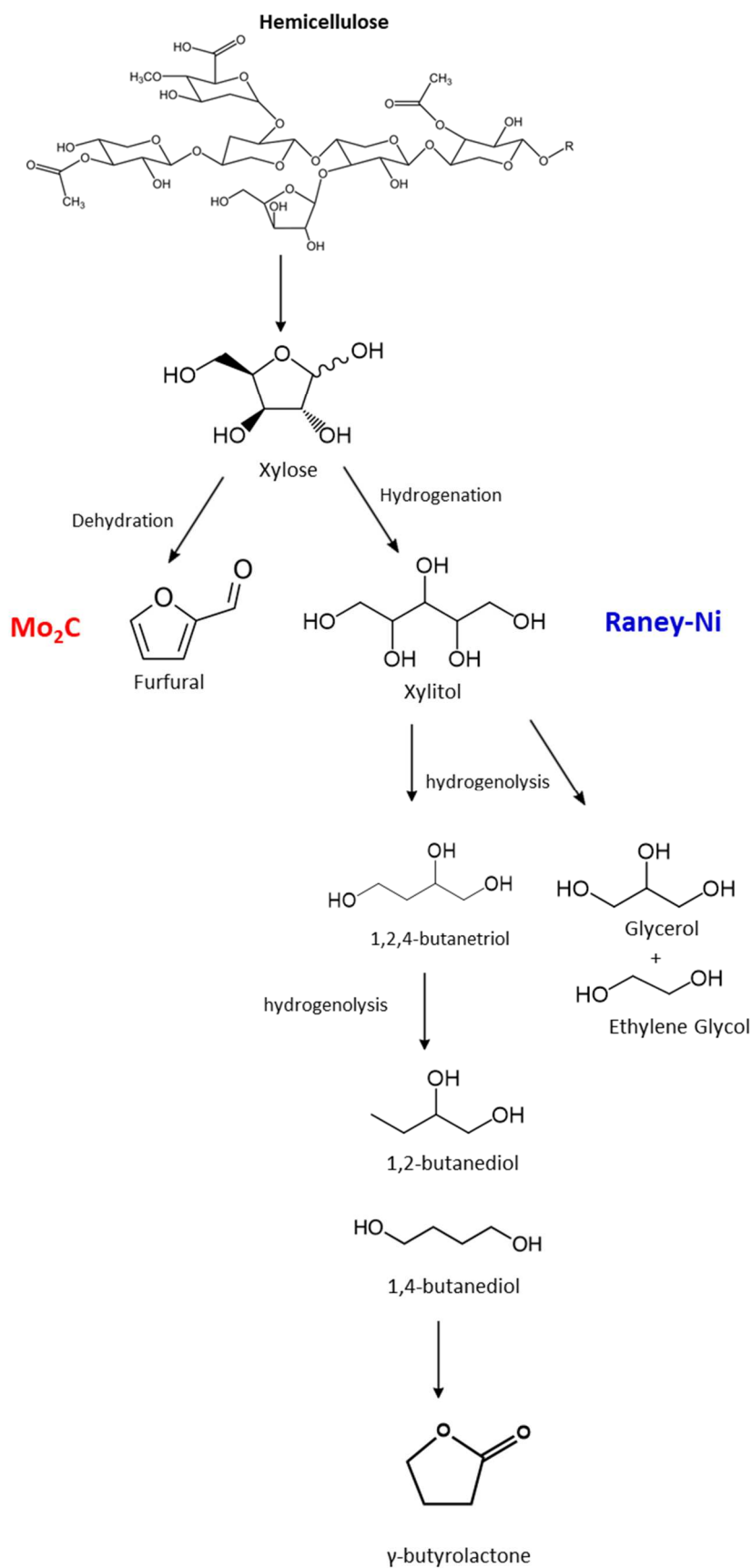
### 615 3.3. Effect of the type of metal phase

616 The fractionation of sugarcane bagasse caused a partial extraction of  
 617 hemicellulose from the biomass through the solvolysis performed by the  
 618 isopropanol/water mixture, whereas the cellulose fraction remained in the solid residue  
 619 practically untouched. The addition of Raney-Ni did not change significantly the  
 620 fraction of cellulose and hemicellulose recovered in the solid residue in comparison the  
 621 *Organosolv* treatment of bagasse. However, in the presence of Raney-Ni catalyst, the  
 622 solvolytic extraction of hemicellulose was accompanied by its catalytic  
 623 depolymerization and the formation of large quantities of diols (1,2-butanediol, 1,4-  
 624 butanediol), triols (glycerol, 1,2,4-butanetriol), furans (tetrahydro-2-methyl-2-furanol)  
 625 and lactones (2-hydroxy- $\gamma$ -butyrolactone and 5-hydroxymethyldihydrofuran-2-one). The

626 carbide phase also favored the depolymerization of hemicellulose, but the main products  
627 obtained were xylose and furfural.

628 Hemicelluloses are linear polymers of  $\beta$ -D-xylopyranosyl units linked by (1 $\rightarrow$ 4)  
629 glycosidic bonds (xylose), with many of the xylose units substituted at position 2 or 3  
630 by 4-O-methyl- $\alpha$ -D-glucuronopyranosyl acid. Hemicelluloses may also have a high rate  
631 of substitution by acetyl groups. In the presence of catalysts, the amount of acetic acid,  
632 diols, xylose, furfural and lactones in the bio-oil significantly increased (Table S2).  
633 These results indicates that they catalyzed the removal of the acetyl groups and the  
634 acetic acid released likely promoted the cleavage of  $\beta$ -(1,4) glycosidic bonds of  
635 hemicellulose. The xylose formed is isomerized and dehydrated to furfural [48], or it is  
636 hydrogenated to xylitol [49] (Scheme 2). The dehydration is promoted by the acid sites  
637 of the supported Mo<sub>2</sub>C catalysts represented by the Lewis acid sites of the support  
638 (alumina) and of the Mo<sub>2</sub>C phase. This explains the higher fraction of furfural on the  
639 bio-oil of Mo<sub>2</sub>C based catalysts. On the other hand, Raney-Ni does not contain acidity  
640 and then, this reaction pathway is not relevant. However, this catalyst has high  
641 hydrogenation and hydrogenolysis activity. Therefore, glucose and xylose are  
642 preferentially hydrogenated to sorbitol and xylitol, respectively. The hydrogenolysis of  
643 sorbitol and xylitol leads to the production of glycerol, ethylene glycol and 1,2,3-  
644 butanetriol that is further converted to 1,2-butanediol or 1,4-butanediol [50]. The  
645 dehydrogenation of 1,4-butanediol may produce  $\gamma$ -butyrolactone and its derivatives.  
646 Therefore, the active phase (metallic Ni or Mo<sub>2</sub>C) and the type of support strongly  
647 affects the product distribution of the bio-oil.

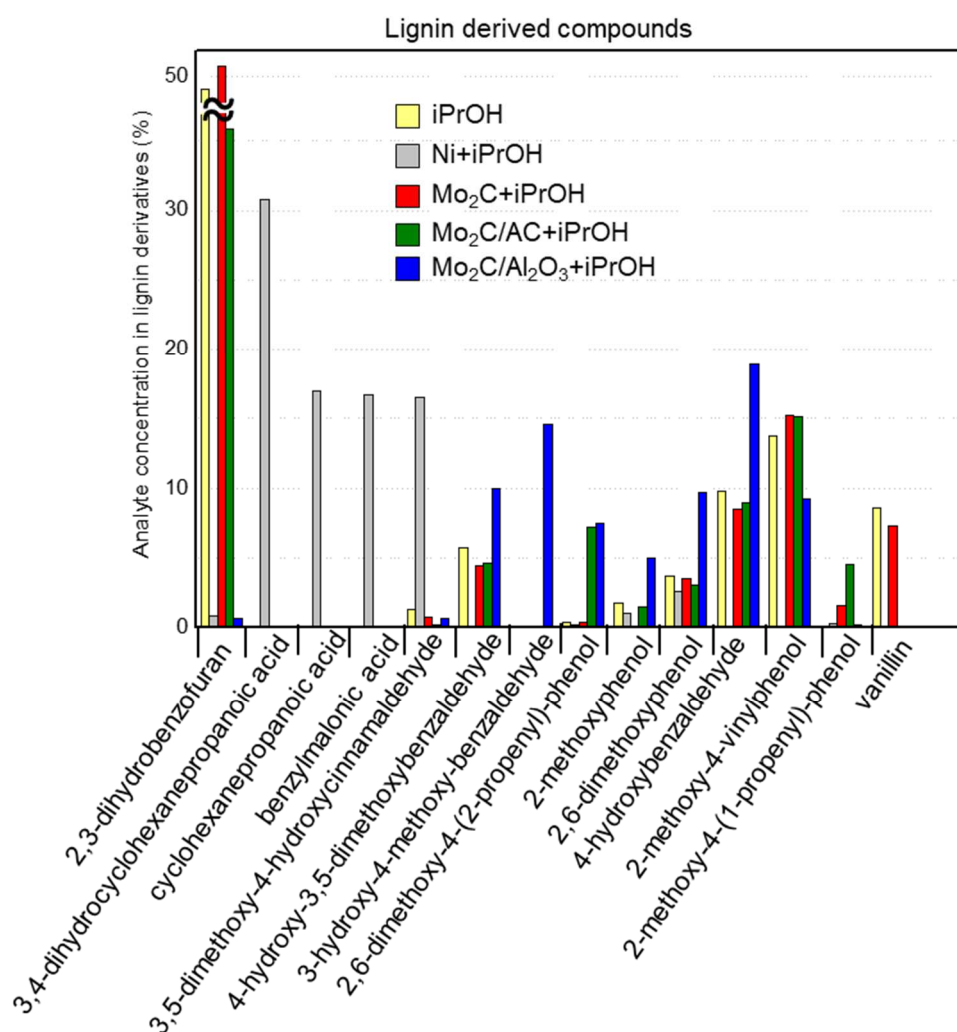
648



649

650 **Scheme 2.** Reaction pathways for the production of the main hemicellulose-derived  
 651 products observed in this work on Raney-Ni and Mo<sub>2</sub>C-based catalysts.

652 The addition of catalyst also affected the product distribution obtained from  
 653 lignin depolymerization, which depended on the active phase (Fig. 9). For *Organosolv*  
 654 treatment, 2,3-dihydrobenzofuran was the main product formed, while Raney-Ni  
 655 catalyst favored the formation of 3,4-dihydroxy-cyclohexanepropanoic acid,  
 656 cyclohexanepropanoic acid and benzylmalonic acid, substituted methoxyphenols that  
 657 were only formed on this catalyst.  
 658



659  
 660 **Figure 9.** Distribution of the concentration of main identified analytes derived from  
 661 lignin. Percentage calculated in relation to the total products derived from lignin.

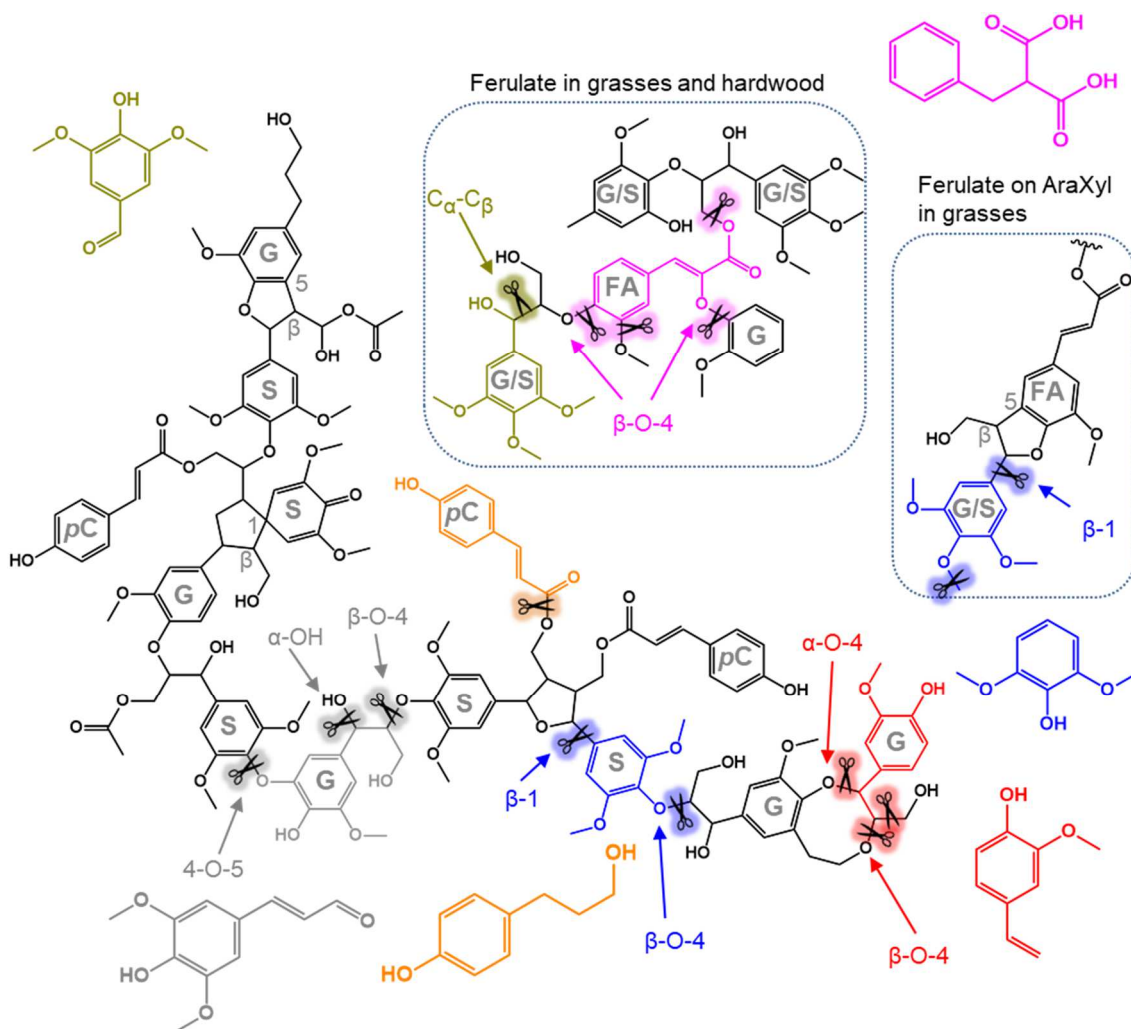
662

663 For the bulk Mo<sub>2</sub>C catalyst, the product distribution and the percentage of lignin-  
664 derived compounds was quite similar to that for *Organosolv* treatment without catalyst.  
665 However, the percentage of each lignin-derived compounds varied on the supported  
666 carbide phase in comparison to the *Organosolv* treatment without catalyst. For instance,  
667 3-hydroxy-4-methoxybenzaldehyde and 2,6-dimethoxy-4-(2-propenyl)-phenol were  
668 formed over Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> catalyst, but they were not observed in the bio-oil of the  
669 *Organosolv* treatment without catalyst. For Mo<sub>2</sub>C/AC catalyst, 2,6-dimethoxy-4-(2-  
670 propenyl)-phenol, and 2-methoxy-4-(1-propenyl)-phenol were formed whereas only  
671 trace amounts were detected in the *Organosolv* treatment without catalyst. These results  
672 revealed that the type of support also plays a role in the reaction since the carbide phase  
673 was the same, regardless the catalyst.

674 Scheme 3 shows the main lignin structures containing different units for grasses  
675 with inter-unit bonding such as ferulate or triclin units [42]. This Scheme also displays  
676 the main compounds formed in the bio-oil obtained with the Raney-Ni and Mo<sub>2</sub>C  
677 catalysts, representing the cleavage of different C-O and C-C bonds. For Raney-Ni,  
678 benzylmalonic acid is obtained by the cleavage of β-O-4 bonds of the ferulate unit while  
679 3-(4-hydroxy-3,5-dimethoxyphenyl)-prop-2-enal (sinapaldehyde) is produced by  
680 breaking β-O-4 and 4-O-5 bonds of a guaiacyl unit. 3-(p-hydroxyphenyl)-1-propanol is  
681 produced from *p*-coumarate unit. In the case of Mo<sub>2</sub>C/AC catalyst, 2-methoxy-4-  
682 vinylphenol is formed through the cleavage of β-O-4 and α-O-4 bonds between two  
683 guaiacyl units. 2,6-Dimethoxyphenol may be obtained by the cleavage of β-1 bond  
684 between a guaiacyl/syringyl unit and phenylcoumaran unit of a ferulate structure. The  
685 cleavage of β-1 bond may occur depending on the reaction conditions and catalyst used  
686 as demonstrated by the reactions using lignin model compounds [5]. Therefore, the type

687 of the active phase promoted the cleavage of specific C-O and C-C bonds, originating  
 688 different substituted methoxyphenols.

689



690

691 **Scheme 3.** Monomers formed in the reactions and suggested precursor structure. G:  
 692 guaiacyl and S: syringyl units; pC: p-coumarate; FA: ferulate.

693

694 Since transition metal carbide catalysts, like the Mo<sub>2</sub>C type catalysts presented  
 695 in this work, have catalytic activity similar to noble metal catalysts [24-29], we can  
 696 make a parallel with the results obtained by Ru/C catalyst used by Lv *et al.* [51]. These  
 697 authors suggested a reaction mechanism for the depolymerization of a hydrolyzed  
 698 residue of cornstalk chips in an aqueous solution of ethyl acetate and Ru/C catalyst.  
 699 They proposed that the  $\beta-O-4$ ,  $\alpha-O-4$ ,  $\beta-5$  and  $4-O-5$  linkages as well as the bonds in the

700 side chain of phenylpropane (e.g.,  $\alpha$ - $\beta$ ,  $\alpha$ -OH,  $\beta$ -OH and  $\gamma$ -OH) could be greatly  
701 cleaved, indicating that these linkages and side chain bonds were fractured under mild  
702 conditions. For instance, the  $\beta$ -O-4 linkages and  $\alpha$ - $\beta$  side chain bond in oligomer could  
703 be broken to form dimer, and then the  $\alpha$ -O-4 linkage and the side chain  $\alpha$ -OH and  $\beta$ -OH  
704 bonds in dimer might be fractured to obtain monomers. The  $\alpha$ -O-4 and  $\beta$ -5 linkages of  
705 dimers as well as  $\alpha$ -OH or/and  $\beta$ -OH of side chain bonds, might be cleaved to obtain the  
706 monomers.

707         Considering the yields of substituted methoxyphenols, Yan *et al.* [21] reported  
708 the results obtained for the fractionation of birch wood sawdust in water at 200 °C and  
709 40 bar of H<sub>2</sub> using active carbon supported Ru, Pd, Pt and Rh catalysts. The main  
710 monomer formed for each catalyst were: Pt/C (guaiacylpropanol); Pd/C  
711 (syringylpropanol); Rh/C (guaiacylpropanol); and Ru/C (syringylpropanol). The sum of  
712 the yields of the main monomers formed followed the order: Pt/C (33.6 %) > Pd/C (25.5  
713 %) > Rh/C (19.7 %) >> Ru/C (4.6 %). These results revealed that the type of the metal  
714 plays a key role on the distribution of products derived from lignin depolymerization.

715         Li *et al.* [29] investigated the fractionation of birch wood at 235 °C and 60 bar of  
716 H<sub>2</sub> in water using carbon supported W<sub>2</sub>C promoted by Ni, Ir, Pd, Pt and Ru catalysts and  
717 obtained monomers yield of 36.9, 30.6, 28.4, 26.7 and 0.00 %, respectively. In addition,  
718 the distribution of phenolic products varied significantly depending on the catalyst. For  
719 Pd-W<sub>2</sub>C/AC, the main phenolic monomers were guaiacylpropanol and  
720 syringylpropanol. On the other hand, Ni-W<sub>2</sub>C/AC, Pt-W<sub>2</sub>C/AC and Ir-W<sub>2</sub>C/AC favored  
721 the formation of guaiacylpropane and syringylpropane, which were probably produced  
722 from the hydrogenolysis of guaiacylpropanol and syringylpropanol, respectively. These  
723 results suggested that Pd-based catalyst favored the lignin hydrogenation preferentially  
724 to hydroxyl group, while Ni-W<sub>2</sub>C/AC and other catalysts facilitated the dehydroxylation

725 reaction. In addition, a significant formation of diols (ethylene glycol, 1,2-propylene  
726 glycol, 1,2-butylene glycol) was observed for all catalysts, which was attributed to the  
727 depolymerization of cellulose and hemicellulose. The yields of diols were higher than  
728 that obtained for substituted methoxyphenols and followed the order: Ni-W<sub>2</sub>C/C (70.6  
729 %) > Pd-W<sub>2</sub>C/C (47.4 %) > Pt-W<sub>2</sub>C/AC (35.6 %) > Ir-W<sub>2</sub>C/AC (25.2 %) > Ru-  
730 W<sub>2</sub>C/AC (0.0 %). Li *et al.* [29] also carried out the fractionation of sugarcane bagasse at  
731 235 °C and 60 bar of H<sub>2</sub> on water using Ni-W<sub>2</sub>C/C, which was the catalyst that exhibited  
732 the highest yield to substituted methoxyphenols for the treatment of birch wood (36.9  
733 %). The yield to substituted methoxyphenols significantly decreased to 23.4 % for the  
734 treatment of sugarcane bagasse, which reveals the important effect of the biomass type  
735 on the yield of substituted methoxyphenols. Furthermore, a high yield of diols was also  
736 observed (59.6 %).

737 In our work, the yields of substituted methoxyphenols obtained in the  
738 *Organosolv* treatment with our Mo<sub>2</sub>C-based catalysts (bulk Mo<sub>2</sub>C – 18 %; Mo<sub>2</sub>C/AC -  
739 24 %; Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> - 24 %) (Tab. S3) were higher than that ones for the treatment  
740 without catalyst (13 %) and Raney-Ni (13 %). Considering the total yield of monomer  
741 in our work, the following values were obtained for the carbide catalysts: bulk Mo<sub>2</sub>C –  
742 49 %, Mo<sub>2</sub>C/AC - 51 %; Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> - 35 % (Tab. S3), which are comparable with the  
743 data from literature for catalytic fractionation of hardwood and softwood. However, the  
744 yield to monomers reported in the literature vary significantly because of the different  
745 reaction conditions (temperature, pressure, solvent), catalysts and type of biomass used  
746 [30], which makes the comparison of our results quite hard. In particular with sugarcane  
747 bagasse, there is only the work of Li *et al.* [29] who also used supported carbide  
748 catalysts. In this case, the yield to substituted methoxyphenols on both works was  
749 approximately the same (23 and 24 %) but Li *et al.* [29] used more severe reaction



750 conditions (235 °C and 60 bar of H<sub>2</sub>) than our work (180 °C and autogenous pressure).  
751 In addition, a lower formation of diols was observed in our work.

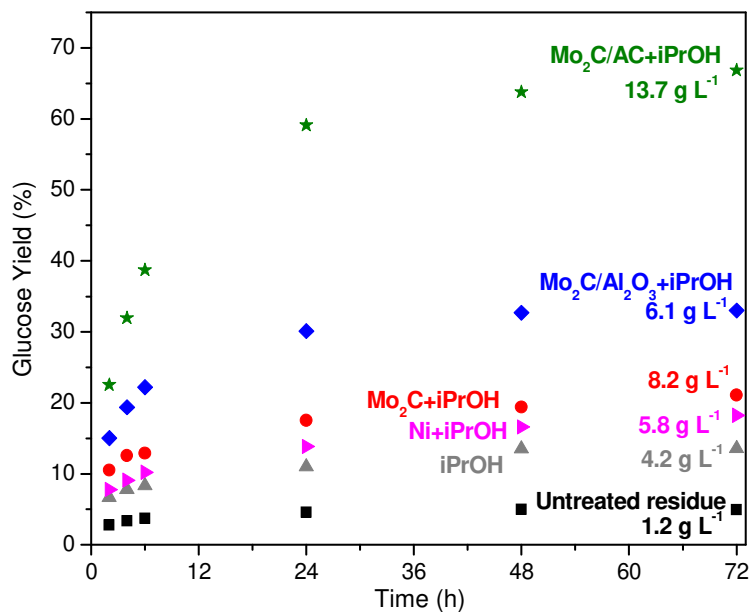
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### 753 ***3.4. Enzymatic hydrolysis and characterization of the Organosolv pretreated bagasse***

754 Pretreatment is one of the most expensive stages in second-generation  
755 technologies, however, it is crucial for ensuring good ultimate yields of sugars from  
756 both polysaccharides [48]. Initially, this operation has been considered a simple step,  
757 but commercial scale 2G ethanol plants presented difficulties in the treatment processes  
758 of lignocellulosic biomass [52]. Addressing this issue is fundamental for the success of  
759 the biorefinery, which allows the use of all fractions of the lignocellulosic biomass [53-  
760 55]. Therefore, it is important that both the bio-oil formed and the pretreated bagasse  
761 exhibits high quality. In this context, the enzymatic hydrolysis using cellulases of the  
762 *Organosolv* pretreated bagasse (solid residue) was performed for gaining insights into  
763 its potential as feedstock for cellulosic ethanol production.

764 Fig. 10 shows the glucose yield as a function of time during the enzymatic  
765 hydrolysis of the untreated and the pretreated bagasse samples obtained after the  
766 treatments with different catalysts. As expected, the untreated bagasse hydrolysis  
767 resulted in the lowest glucose yield (~ 5 %, 72 h), because cellulose in the intact plant  
768 cell walls is not promptly available for the cellulases attack. However, the hydrolysis of  
769 pretreated bagasse from the iPrOH and Ni+iPrOH treatments also achieved low glucose  
770 yields of 12 and 16 % respectively, suggesting that the modification of the cell wall  
771 structure at these conditions did not improve the exposure of cellulose for the enzymatic  
772 attack.

773



774

775 **Figure 10.** Glucose yield obtained on the enzymatic hydrolysis of untreated and  
 776 pretreated sugarcane bagasse after *Organosolv* treatment using isopropanol  
 777 (iPrOH):water solution in the absence or in the presence of different catalysts. The  
 778 values in  $g L^{-1}$  refer to glucose concentration at 72 h.

779

780 Nonetheless, improved glucose yields were obtained with the pretreated biomass  
 781 from carbide-based catalysts treatments, corresponding to approximately 20 %, 67 %  
 782 and 35 % for  $Mo_2C$ ,  $Mo_2C/AC$  and  $Mo_2C/Al_2O_3$  treated samples, respectively.  
 783 Considering these catalysts, the highest delignification degree was obtained by the  
 784 treatment using  $Mo_2C+iPrOH$ , but the glucose yield was the lowest, showing that there  
 785 was not a direct correlation between delignification and the exposure of cellulose for the  
 786 enzymatic attack. This is a reasonable result, as enzymatic hydrolysis effectiveness can  
 787 be affected by different parameters other than lignin content, such as cellulose degree of  
 788 polymerization, crystallinity and hemicellulose content. For instance, the yield of  
 789 glucose in the enzymatic hydrolysis followed the order  $Mo_2C/AC > Mo_2C/Al_2O_3 >$   
 790  $Mo_2C > Raney-Ni \approx iPrOH$ , which corresponded to the reverse order to the amount of  
 791 hemicellulose in the biomass that was hydrolyzed (Tab. S1).

792 Galkin *et al.* [56] performed the enzymatic hydrolysis of the pulp obtained in the  
793 treatment of different hardwoods using a Pd/C catalyst. The glucose yield for the  
794 *Organosolv* treatment without catalyst after 2 h was higher than the ones obtained for  
795 all hardwoods in the presence of Pd/C catalyst. These results indicate that the pulp  
796 obtained by the catalytic fractionation has lower susceptibility to enzymatic hydrolysis  
797 than *Organosolv* treatment and depended on the type of biomass. The glucose yield  
798 followed the order: *Organosolv* > Sweden Birch wood > Finish Birch wood > Poplar. In  
799 our work, the glucose yield obtained on the enzymatic hydrolysis of the pulp obtained  
800 by the catalytic fractionation was higher than that for *Organosolv* treatment, regardless  
801 of the catalyst.

802 Comparing the glucose yield and concentration obtained for the hydrolysis of  
803 Mo<sub>2</sub>C+iPrOH pretreated bagasse with that one for Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> pretreated bagasse, it is  
804 observed that the hydrolysis of the solid residue obtained with alumina supported  
805 catalyst resulted in a higher yield, but in a lower concentration of glucose generated.  
806 The higher yield occurred because the Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> residue was more accessible to  
807 cellulases action. However, from Table 2, it is observed that a large part of the  
808 polysaccharides was removed during the *Organosolv* reaction. Thus, in the pretreated  
809 bagasse recovered after the Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub>-*Organosolv* treatment, a lower cellulose  
810 content was available in the pretreated bagasse to be converted by the enzymes, leading  
811 to a lower glucose concentration value (6.1 g L<sup>-1</sup>).

812 Therefore, the treatments may have impacted the cellulose structure. Figure S2  
813 depicts the thermogravimetric curves (TG) and their first derivative curves (DTG) of  
814 pretreated bagasse obtained under different treatments. The thermal degradation of  
815 hemicellulose and cellulose occurs at temperatures close to 330 °C for untreated  
816 residues [57]. Lignin and hemicellulose initiate degradation at lower temperatures than

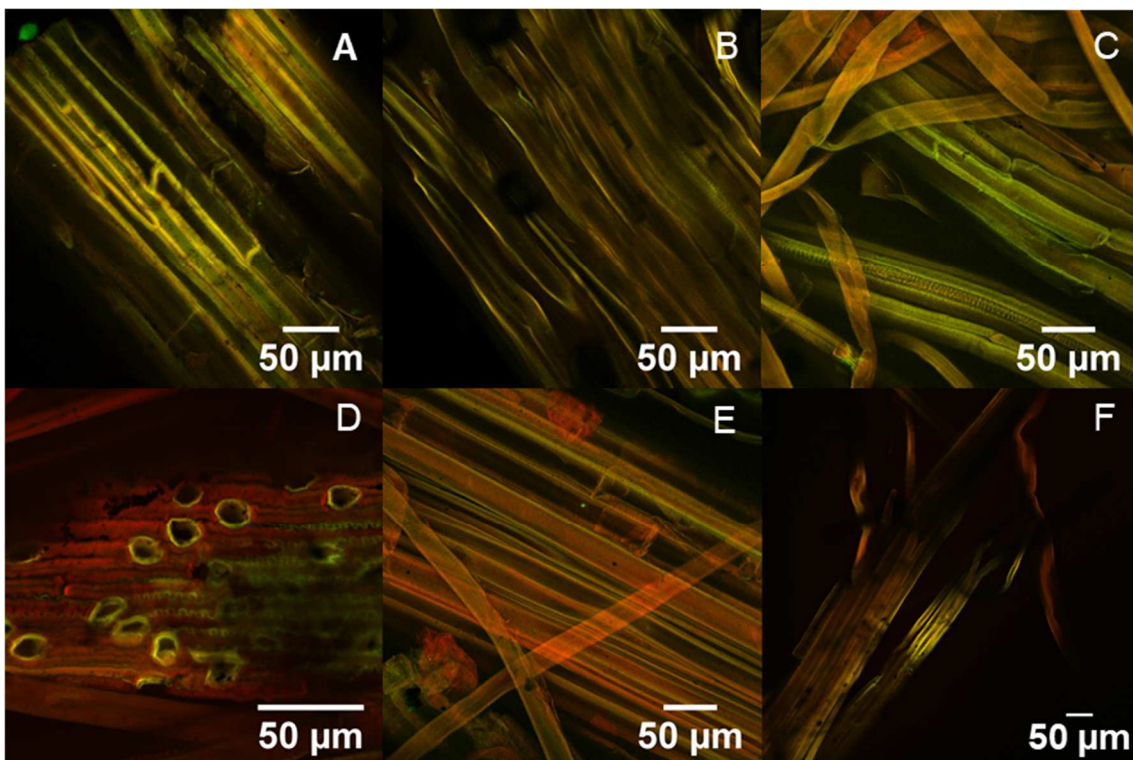
817 cellulose. Lignin has a wide range of degradation, close to 237-510 °C. Cellulose,  
818 however, degrades between 374-425 °C and hemicellulose between 288-382 °C, which  
819 can be observed as a shoulder in the DTG of untreated bagasse. This shoulder is also a  
820 result of lower molecular weight components such as extractives [57].

821 DTG curves revealed that the impact of the treatment on cellulose was higher for  
822 samples treated with Mo<sub>2</sub>C catalysts, since there is considerable variation in the  
823 maximum temperature peak. The Mo<sub>2</sub>C type catalysts presented a decrease in the  
824 maximum temperature in the DTG, which may be related to a facilitated degradation of  
825 cellulose due to structural modifications affecting its stability [58], when compared to  
826 iPrOH treatment and in the presence of Raney-Ni catalyst. It should also be considered  
827 that the exposure of the cellulose favored the enzymatic action and consequently, the  
828 increase in the glucose yield of the pretreated samples, consistent with results presented  
829 in Fig. 10.

830 Aiming at getting further insights regarding lignin distribution and cellulose  
831 exposure in the pretreated bagasse samples, confocal microscopy analysis was  
832 performed (Fig. 11). The images were treated with the software using the histogram  
833 stretching mode to provide greater contrast between the structures. Images were  
834 obtained in different spectral regions for lignin and cellulose observation; thus Fig. 11  
835 shows the overlay of both images. The original microscopy images without histogram  
836 stretching are provided in Fig. S3. It could be observed that the lignin (red color) and  
837 cellulose (green color) structures are practically intact on the untreated bagasse,  
838 showing intact cell walls. After treatment, fibrous and porous surfaces are observed,  
839 except for the Ni+iPrOH residue because it had a more compact surface. Furthermore,  
840 the unprocessed images (Fig. S3) reveal that the surface of the residues are covered by  
841 the lignin structure (red), except for the Mo<sub>2</sub>C/AC+iPrOH pretreated bagasse that

842 exposes the cellulose structure (green). In Fig. S3 (E) it is possible to see that this is the  
843 only sample in which cellulose is clearly exposed in its surface, correlating well with  
844 the improved enzymatic hydrolysis yields obtained for this residue. In particular, as  
845 show in Table 2, the treatment with Mo<sub>2</sub>C/AC+iPrOH resulted in an increased removal  
846 of cellulose and hemicellulose, but the remaining polysaccharides became more  
847 accessible to the hydrolysis.

848



849

850 **Figure 11.** Confocal micrographs of the distribution of cellulose and lignin in pretreated  
851 bagasse samples processed with the software in histogram stretching mode. Red  
852 fluorescent signs identify the lignin structure and green signal identifies the structure of  
853 the cellulose. Residues: A) untreated bagasse, B) iPrOH, C) Ni+iPrOH, D)  
854 Mo<sub>2</sub>C+iPrOH, E) Mo<sub>2</sub>C/AC+iPrOH, F) Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub>+iPrOH.

855

856 Additionally, by correlating these observations with the data presented in Table  
857 S1, it is possible to conclude that the samples derived from conditions with high lignin

858 content presented an intense red color (Fig. 11, E and F). However, for conditions that  
859 resulted in low lignin content in the bagasse residue (Fig. 11, C and D), the  
860 predominance of red color in some areas could also be observed.

861 This observation could also be partially related to a possible condensation and/or  
862 repolymerization of the previously depolymerized smaller fragments formed followed  
863 by their deposition on the surface of the solid residue. This repolymerized lignin is  
864 characterized by very strong C—C bonds that are highly recalcitrant in relation to the  
865 C—O bonds characteristic of native lignin, making this material less susceptible to  
866 enzymatic attack. In the reaction, the solvent extracts lignin from the lignocellulosic  
867 matrix and breaks the  $\alpha$ -O-4 ether bonds, resulting in the formation of unsaturated  
868 phenolic intermediates. During Organosolv treatment,  $\alpha$ -O-4 bonds in the lignin  
869 structure are cleaved predominantly, and the  $\beta$ -O-4 linkages remains unreacted due to  
870 the lower activation energy for cleavage of  $\alpha$ -O-4 bonds [59]. The catalyst in turn is  
871 responsible for the hydrogenation of the reactive unsaturated side chains of the lignin  
872 intermediates that have been solubilized, leading to the formation of stable phenolic  
873 monomers and avoiding undesirable reactions of repolymerization [19]. By correlating  
874 the confocal images and the enzymatic hydrolysis results, it is suggested that the  
875 Mo<sub>2</sub>C/AC could be a better hydrogenation catalyst thus avoiding the lignin  
876 repolymerization on the surface of the pretreated bagasse and, consequently favoring the  
877 enzymatic hydrolysis. Therefore, this indicates that not only the content, but also the  
878 lignin distribution affects the cell wall recalcitrance to the enzymatic depolymerization.

879 A similar result was reported by Santo *et al.* [60]. These authors evaluated the  
880 compositional and structural changes on sugarcane bagasse caused by hydrothermal  
881 and/or *Organosolv* (ethanol) treatments. They found that the treatments resulted in

882 lignin degradation, rearrangement and inhomogeneous deposition of significant  
883 amounts of lignin on the surface of the treated residue.

884 Despite of the apparent low delignification, the hydrolysis of the bagasse treated  
885 by Mo<sub>2</sub>C/AC+iPrOH achieved 67 % glucose yield (13.7 g L<sup>-1</sup> glucose). This is a  
886 promising result, showing that the production of bio-oil from bagasse could be  
887 associated with production of cellulosic ethanol, giving a proper use to distinct biomass  
888 fractions.

889

#### 890 **4. Conclusion**

891 The *Organosolv* treatment of sugarcane bagasse caused a partial extraction  
892 of hemicellulose from the pretreated bagasse through the solvolysis performed by  
893 the isopropanol/water mixture. The extent of hemicellulose extraction from the  
894 pretreated bagasse varied in the following order: without catalyst  $\approx$  Raney-Ni  $\ll$   
895 bulk Mo<sub>2</sub>C  $\approx$  Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub>  $<$  Mo<sub>2</sub>C/AC. High recovery of cellulose in the solid  
896 residue was achieved in the absence of catalyst and with Raney-Ni but the  
897 recovered fraction of cellulose decreased on Mo<sub>2</sub>C-based catalysts. After  
898 solvolytic extraction, hemicellulose was depolymerized and product distribution  
899 obtained depended on the type of active phase. Raney-Ni catalyst promoted the  
900 formation of diols (1,2-butanediol, 1,4-butanediol) and triols (glycerol, 1,2,4-  
901 butanetriol), while xylose, furfural, and furan were mainly produced by Mo<sub>2</sub>C  
902 based-catalysts.

903 The catalyst also influenced the product distribution obtained from lignin  
904 depolymerization, which depended on the active phase. The *Organosolv*  
905 treatment without catalyst and in the presence of bulk Mo<sub>2</sub>C and Mo<sub>2</sub>C/AC  
906 catalysts produced significant amount of 2,3-dihydrobenzofuran, whereas this

907 compound was detected in trace amounts in the bio-oil obtained from Raney-Ni  
908 and  $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ . This product stem from the depolymerization of  
909 phenylcoumaran structures characteristic of lignin from grasses such as sugarcane  
910 bagasse and it is not formed on the catalytic fractionation of hardwoods and  
911 softwoods.

912  $\text{Mo}_2\text{C}$ -based catalysts favored the formation of substituted  
913 methoxyphenols but product distribution depended on the active phase.  
914 Cyclohexanepropanoic acid, 3,4-dihydroxycyclohexanepropanoic acid and  
915 benzylmalonic acid were only formed on Raney-Ni catalyst, whereas substituted  
916 methoxyphenols such as 3-hydroxy-4-methoxybenzaldehyde and 2,6-dimethoxy-  
917 4-(2-propenyl)-phenol were formed over  $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$  catalyst. These results  
918 were likely due to the capacity of the active phase to promote the cleavage of  
919 specific C-O and C-C bonds, originating different substituted methoxyphenols.  
920 For Raney-Ni, benzylmalonic acid is obtained by the cleavage of  $\beta$ -O-4 bonds of  
921 the ferulate unit, while 3,5-dimethoxy-4-hydroxycinnamaldehyde  
922 (sinapaldehyde) is produced by breaking  $\beta$ -O-4 and  $\alpha$ -O-5 bonds of a guaiacyl  
923 unit. The  $\text{Mo}_2\text{C}/\text{AC}$  and  $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$  catalysts exhibited the highest yield to  
924 substituted methoxyphenols ( $\sim 24\%$ ), which is similar to the values reported in  
925 the literature for bio-oil from catalytic fractionation of sugarcane bagasse but at  
926 less severe reaction conditions.

927 The enzymatic hydrolysis of the solid residue obtained from the  
928 *Organosolv* treatment of sugarcane bagasse without catalyst and with Raney-Ni  
929 resulted in very low glucose concentration and yield. The fractionation with  $\text{Mo}_2\text{C}/\text{AC}$   
930 generated a pretreated bagasse that was readily hydrolyzed by cellulases, producing  
931 glucose yield and concentration of 67 % and  $13.7 \text{ g L}^{-1}$ , respectively. TG experiments



932 revealed that the cellulose structure was differently affected by the treatment depending  
933 on the catalyst. DTG curves showed lower stability of cellulose treated with Mo<sub>2</sub>C  
934 catalysts, which is likely due to structural modifications that occurred during  
935 fractionation. Confocal microscopy analysis confirmed that cellulose structure is  
936 more exposed after treatment with Mo<sub>2</sub>C/AC catalyst, which favored the  
937 enzymatic action and consequently, the highest glucose yield obtained for this  
938 residue.

939 Therefore, Mo<sub>2</sub>C/AC and Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> are promising catalysts for the  
940 fractionation of sugarcane bagasse that produced a bio-oil with higher yield to  
941 substituted methoxyphenols and a solid residue more easily hydrolyzed by  
942 cellulases, producing higher yield to glucose than Raney-Ni catalyst.

943

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# Graphical Abstract

