1 **A comparison of fast and reactive pyrolysis with in-situ derivatisation of fructose,**

2 **inulin and Jerusalem Artichoke (*Helianthus tuberosus*)**

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7 **ABSTRACT**

8 Reactive pyrolysis is a technique that provides mechanistic information by performing pyrolysis of the

9 substrate in a sealed glass capsule at elevated temperature and pressure for relatively long time. This

10 technique has already shown great potential for the analysis of biomasses, favouring the formation of only

11 the most thermostable compounds. In this work, both fast and reactive pyrolysis with on-line gas

12 chromatography-mass spectrometry analysis (Py-GC/MS) are used to study fructose, inulin and Jerusalem

13 artichoke tubers (*Heliantus tuberosus*). Interesting differences were found between the two systems, and

14 became even more evident as the reaction time was increased. The most striking result was the formation

15 of di-fructose dianhydrides (DFAs), a class of compounds with interesting biological activities. DFAs were

16 obtained in high yields from reactive pyrolysis, but not from fast pyrolysis. Hypotheses on the pyrolysis

17 mechanisms were made based upon the composition of the pyrolysates. This work describes for the first

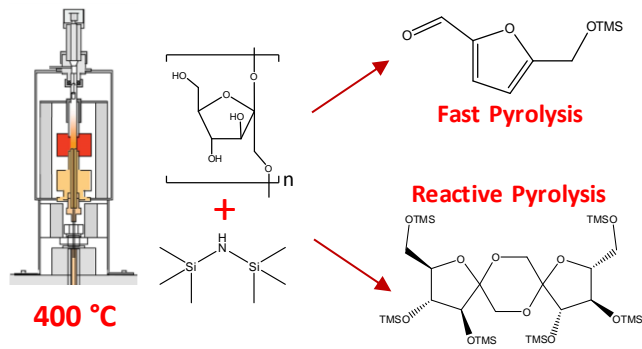18 time the behaviour of fructans under reactive pyrolysis.

19

20 **KEYWORDS**

21 Py-GC/MS; Derivatisation; Fructose; Inulin; Jerusalem artichoke; Di-fructose dianhydrides

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23 **Table of Contents**

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27 **Synopsis**

28 We compared the behaviour of fructans under fast and reactive pyrolysis to unveil new possible strategies

29 for biomass conversion.

30

1. INTRODUCTION

Fructans are oligo- and polysaccharides of fructose. They can be found as energy reserve in many vegetal species [1-4]. Inulin, one of the most common fructans, is a polymer of fructose units connected by β(1,2) bonds. It is usually 30-35 monomers long, and terminates with a glucose molecule [5]. Fructans have a high potential to produce value-added chemicals such as furfural, hydroxymethylfurfural and di-fructose dianhydrides (DFAs) [6-10], and are therefore an important study matter in the field of biomass. DFAs are particularly important for their prebiotic activity: a DFAs-enriched diet has been reported to favour the absorption of calcium and the proliferation of floral bacteria in human and rat intestines [11-13]. Thermal treatment of fructans is a promising strategy to produce DFAs [14].

Analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC/MS) is a powerful and widely diffused technique for the study of biomasses [15-22]. Its main advantages are the use of very small sample quantities and the extensive control over experimental parameters. The chromatographic separation and MS detection can give a full characterisation of the pyrolysate composition. Most of the pyrolysis products of biomasses bear polar functional groups such as hydroxyls and carboxyls, which strongly interact with the stationary phase of common GC columns, producing poorly resolved and asymmetric peaks. Derivatising agents such as tetramethylammonium hydroxide (TMAH) or hexamethyldisilazane (HMDS) can be used to substitute mobile hydrogens with methyl or trimethylsilyl groups, respectively [23, 24]. This reduces the interaction between polar compounds and stationary phase, as well as increasing the volatility of pyrolysis products. However, the formation of partially derivatised compounds is a major issue of derivatisation, since it increases the complexity of the pyrograms without adding information.

Analytical pyrolysis is a constantly improving research field, both from the methods and the instrumentation points of view. Reactive pyrolysis is a recently developed technique which allows to perform on-line Py-GC/MS experiments at prolonged pyrolysis times [25]. The application of reactive pyrolysis to the study of biomasses is still a greatly unexplored field, and very few literature references are available. Kim et al. used reactive pyrolysis to obtain the solvolysis of lignin [26], while Fu et al. compared the results of lignin pyrolysis using both reactive and fast pyrolysis [27]. In a previous work, we demonstrated that increasing the pyrolysis

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57 time of glucose and cellulose in the presence of hexamethyldisilazane (HMDS) favoured the formation of the

58 most thermodynamically stable species and increased the derivatisation degree [28]. This means that long

59 pyrolysis times generate less complex, more reproducible pyrograms.

60 While literature on the pyrolysis of lignin and cellulose is abundant, fructans appear to be less studied [5, 29-

61 31]. In this work, we studied the behaviour of fructose and inulin using both reactive and fast pyrolysis with

62 on-line GC/MS. To improve peak shape and chromatographic resolution, hexamethyldisilazane (HMDS) was

63 used as derivatising agent. The results obtained with the two methods were compared. Hypotheses on the

64 pyrolysis mechanisms in the two cases were made to account for the differences in the pyrolyzate

65 composition. Finally, the results obtained for fructose and inulin were used to study the pyrolysis of

66 Jerusalem artichoke tubers, a vegetal species which is known for its high content in inulin [8, 32, 33].

67

68 **2. MATERIALS AND METHODS**

69 *2.1 Materials:* Hexamethyldisilazane (HMDS, Sigma-Aldrich, USA) was used as derivatising agent. Samples

70 were D(-)-fructose (> 99%, Riedel-de Häen, USA), inulin from *dahlia tubers* (Sigma-Aldrich, USA) and

71 commercially available Jerusalem artichoke tubers (*Helianthus tuberosus*). All samples were dried in oven at

72 60 °C for 8 h before analysis. Jerusalem artichoke tubers were also grinded to a fine powder using a

73 Pulverisette 23 ball mill (Fritsch, Germany) for 5 min at 50 Hz. The inorganic fraction of the samples was

74 evaluated by heating a known quantity of each in a muffle furnace at 700 °C for 2 h. No solid residue was

75 found for fructose, while 2.6% and 12.6% (w/w) inorganic residues were found for inulin and Jerusalem

76 artichoke, respectively.

77 *2.2 Py-GC/MS:* The instrumentation consisted of an EGA/PY-3030D micro furnace pyrolyser (Frontier Lab,

78 Japan) connected to a 6890 gas chromatograph equipped with a split/splitless injector and a 5973 Mass

79 Selective Detector (Agilent Technologies, USA). Experiments were performed both with a regular sample

80 holder and a PY-1050 Micro Reaction Sampler (Frontier Lab, Japan). The structure and functioning of this

81 sampler has already been described in previous publications [25, 28].

82   ***2.3 Sample preparation:*** In fast pyrolysis experiments, approximately 100 µg of sample were directly put

83   inside the sample holder, and 5 µL of HMDS were added. Dispersion of the derivatising agent was aided using

84   a quartz wool plug. The cup was then lowered in the micro-furnace to perform the experiments. In reactive

85   pyrolysis experiments, approximately 50 µg of sample were directly weighted inside the glass capsule, and 3

86   µL of HMDS were added. The glass capsule was then put under a gentle stream of nitrogen to ensure inert

87   atmosphere. Finally, the capsule was flame-sealed and lowered in the micro-furnace to perform the

88   experiments.

89   ***2.4 Experimental parameters:*** All pyrolysis experiments were performed with a furnace temperature of 400

90   °C (preheated) and an interface temperature of 280 °C. The furnace temperature was chosen on the basis of

91   EGA-MS analyses [30]. Injection in the chromatographic system was performed using a 20:1 split ratio.

92   Helium (1 mL/min) was used as carrier gas. Chromatographic separation was achieved using an HP-5MS

93   capillary silica column (30 m x 0.25 mm, film thickness 0.25 µm, Agilent Technologies, USA), connected to a

94   deactivated silica precolumn (2 m x 0.32 mm, Agilent Technologies, USA). The following temperature gradient

95   was used in all experiments: 50 °C isothermal for 1 min; 10 °C/min up to 100 °C; 100 °C isothermal for 2 min;

96   4 °C/min up to 280 °C; 280 °C isothermal for 30 min. The mass spectrometer was operated in EI positive mode

97   (70 eV, m/z range 50-600). The transfer line was kept at 300 °C, while the ion source was kept at 230 °C and

98   the quadrupole at 150 °C. In fast pyrolysis experiments, pyrolysis time was 0.2 min. In reactive pyrolysis

99   experiments, pyrolysis times were 0.2, 0.5, 1, 2, 5, 10, 20, 30 and 60 min. Fast pyrolysis experiments were

100 replicated three times, providing CVs lower than 25%. Reactive pyrolysis experiments were replicated three

101 times at both 0.5 min and 30 min of pyrolysis, providing CVs lower than 20%. CVs were generally lower at

102 long pyrolysis times than at short pyrolysis times.

103 ***2.5 Data interpretation:*** Pyrograms were processed using the Automated Mass spectral Deconvolution and

104 Identification System (AMDIS, version 2.17, NIST, USA). Compound identification was based on comparison

105 with mass spectral libraries (Wiley and NIST/EPA/NIH) and with previous literature data (mass spectra and

106 relative retention order) [19, 20, 23, 30, 34]. In addition, compound identification was performed also using

107 mass spectra interpretation, taking into account the characteristic fragmentation pathways of the most

108 common pyrolysis products of carbohydrates [20, 22, 35].

109

110 **3. RESULTS AND DISCUSSION**

111 *3.1 Identified compounds:* More than 80 pyrolysis products were identified in the pyrograms, and they are

112 reported in Table 1. These products originate from different, competitive thermal degradation pathways. The

113 table also shows a "Match" column, which shows how the identification of each compound was performed.

114 A literature reference indicates that identification was based on published results, while the label "L"

115 indicates that identification was based on the comparison with reference mass spectra libraries. Finally, the

116 label "T" indicates that the structure of the compound was hypothesised. For most of the "T" compounds,

117 hypotheses were not based solely on the mass spectra, but also on the comparison with already identified

118 compounds with similar spectra. For instance, the structures of the four 2-hydroxymethyl-n-hydroxy-2,3-

119 dihydro-(4H)-pyran-4-one (#35, 46, 50 and 54) were hypothesised based on 3,5-dihydroxy-2-methyldihydro-

120 (4H)-pyran-4-one (#39), which is a structural isomer and has a very similar mass spectrum.

121 The most important reaction in carbohydrates pyrolysis, and usually the first one, is the loss of a water

122 molecule [29]. Since carbohydrates have many hydroxyl groups, dehydration can take place in many ways.

123 If dehydration involves a hydroxyl group and a vicinal hydrogen, an aldol-type structure is obtained. This

124 structure can undergo retro-aldol fragmentation, generating 1 to 3-carbon atom products. These small

125 molecules are the first to be eluted by the chromatographic system (#2-9, 13, 23, 25, 31). Small molecules

126 can also be obtained from other reactions, such as elimination, extrusion, rearrangement and Grob

127 fragmentation [36]. If dehydration involves two distant hydroxyl groups, a C-O-C bond is formed. This

128 generates anhydrosugars, which are eluted at high retention times in the chromatograms (#44, 45, 52, 53,

129 55, 58, 62, 64-66). Monosaccharides like fructose generate anhydrosugars from dehydration reactions, while

130 polysaccharides like inulin generate anhydrosugars from cleavage of the glycosidic bond, since their

131 monomers are already dehydrated monosaccharides. Anhydrosugars have been reported as the main

132 pyrolysis products of glucose and cellulose in fast pyrolysis experiments [23].

133   Multiple dehydration can also occur, resulting in the formation of different pyrolysis products. Carbohydrates

134   in their cyclofuran or cyclopyran forms generate furans (#1, 10, 16, 27, 28, 34, 36, 49, 51) and pyrans (#18,

135   19, 32, 35, 39, 42, 46, 47, 50, 54, 60, 63), respectively. On the other hand, C-C bonds can be formed if the

136   dehydration occurs while the carbohydrate is in its linear form. This generates cyclopentenones (#12, 15, 20-

137   22, 26, 30, 37, 38, 40) and hdroxybenzenes (#29, 33, 48, 56). The loss of two water molecules can also

138   generate intermolecular bonds, leading to the formation of DFAs (#71-89). Fructose is known to have a

139   greater tendency than glucose to form dimeric species such as DFAs in a pyrolytic environment [29].

140   All identified pyrolysis products were grouped in categories: small molecules, cyclopentenones, furans,

141   pyrans, hydroxybenzenes, anhydrosugars or dianhydrides. Compounds not belonging to any of these

142   categories were labelled as "others". Table 1 reports the category for each compound. Chromatographic

143   peaks were integrated, and areas of peaks belonging to the same category were added together. Finally, a

144   total yield for each category was expressed as a percentage of the total pyrogram area (Table 2). The

145   comparison of the percentage yields of the pyrolysates provides insight into which mechanisms are favoured

146   or hindered in the different experimental conditions.

147   **3.2 Fructose:** The pyrograms of fructose are reported in Figure 1. The pyrogram obtained from fast pyrolysis

148   is compared to those obtained from reactive pyrolysis at 0.5 and 30 min, which are representative of a short

149   and long pyrolysis time, respectively. The percentage yields of pyrolysis products for fast and reactive

150   pyrolysis at all pyrolysis times are reported in Table 2.

151   Fast pyrolysis gave dihydroxyacetone (#23), hydroxymethylfuraldehyde (HMF, #28), 2,6-anhydro-β-D-

152   fructofuranose (#52, 58), and the δ-lactone of deoxygluconic acid (#61) as main products. These results agree

153   with the literature [30], despite the slight difference in experimental parameters. The other peaks in the

154   pyrogram are mainly due to small molecules (#2, 5), cyclopentenones (#12, 15, 20) and pyrans (#32, 35, 39,

155   46). Furans were the most abundant product category. This is probably due to the fact that fructose

156   molecules are prevalently found in their furanose form.

157   Small molecules accounted for more than 18% of the pyrolysate. Dihydroxyacetone (#23) was the most

158   important product belonging to this category. The formation of this pyrolysis product is much less favoured

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159   in glucose than in fructose [23, 28]. Dihydroxyacetone is formed by cyclic Grob fragmentation with cleavage

160   of C3-C4 bond. As shown in Figure 2, this reaction allows up to two dihydroxyacetone molecules to be

161   obtained in the case of fructose, but not in the case of glucose.

162   A high percentage of anhydrosugars was also obtained. Moreover, the "others" category accounted for 12%

163   of the total area, with deoxygluconic acid (#61) as the main contributor. The formation of anhydrosugars and

164   uronic acids requires minimal degradation of the substrate, since the original carbon skeleton of the

165   carbohydrate remains intact. These results imply that, although small molecules accounted for a high

166   percentage of the total area, a furnace temperature of 400 °C is not sufficient to achieve a complete pyrolysis

167   of fructose. Table 2 also reports the percentage areas of partially derivatised (1+2 TMS) and fully derivatised

168   (3 TMS) anhydrosugars. The two values are very similar, indicating that the derivatisation in fast pyrolysis

169   experiments is far from complete. Partial derivatisation generates multiple peaks for a single compound,

170   increasing the complexity of the pyrogram and the risk of co-elution.

171   Reactive pyrolysis gave different results than fast pyrolysis. 2,3,5-trihydroxy-(4H)-pyran-4-one (#63), which

172   was not detected in the fast pyrolysis chromatogram, was one of the main products alongside HMF and 2,6-

173   anhydrofructofuranose. The most important product categories were furans and pyrans, and the yields for

174   both categories were higher than those obtained from fast pyrolysis.

175   A much lower fragmentation of the substrate was observed, since small molecules accounted for less than

176   5% of the pyrolysate. However, this does not mean that the pyrolysis of the substrate was incomplete. In

177   fact, the total anhydrosugar yield was less than 8%, and the yields of uronic acids were significantly lower

178   than in the case of fast pyrolysis. At the shortest reaction time (0.2 min), the percentage of fully derivatised

179   anhydrosugars was comparable with that of fast pyrolysis.

180   The most striking difference between the chromatographic profiles of fast and reactive pyrolysis is the

181   presence of a cluster of peaks in the range 36-40 min. The peaks in this cluster showed mass spectra with

182   signals at m/z 509, 361, 217 and 204, which are indicative of per-TMS derivatives of DFAs [6, 37]. The

183   formation of DFAs from fructose follows an ionic mechanism involving the reaction between a fructosile

184   cation and a neutral monosaccharide [38]. It is possible that this intermolecular reaction is much more

185 favoured in reactive pyrolysis than in fast pyrolysis, since pyrolysis products have more time to interact with

186 each other inside the glass capsule. It is also interesting to notice that no signal belonging to partially silylated

187 DFAs was found, even at short pyrolysis times.

188 When pyrolysis time was increased, the pyrograms changed drastically. Secondary pyrolysis reactions

189 became more relevant, and the yield of small molecules increased accordingly. These secondary reactions

190 appear to affect mainly furans and pyrans, since their yields were drastically reduced when pyrolysis time

191 was increased. HMF, which was among the main products at short reaction times, could not be identified in

192 the pyrograms at 30 and 60 min. A slight increase in the yield of hydroxybenzenes was also observed. This

193 increase is probably due to the great thermal and chemical stability of the aromatic ring.

194 Cyclopentenones and anhydrosugars maintained relatively constant yields through all the investigated time

195 range. The thermal stability of anhydrosugars in both fast and reactive pyrolysis conditions has already been

196 documented [28, 39]. Moreover, the average derivatisation degree of anhydrosugars quickly rose with the

197 increase of pyrolysis time, and a complete silylation was obtained after 10 min.

198 The yield of di-fructose dianhydrides increased significantly through all the observed time range. After 20

199 min of pyrolysis, DFAs became the most abundant category in the pyrogram, and at 60 min their yield was

200 greater than 50%. This result implies that DFAs are particularly thermostable. The formation of DFAs appears

201 to be kinetically slow, and requires pyrolysis to be performed in a closed system for long reaction times.

202 Overall, the differences between fast and reactive pyrolysis become more evident with the increase of

203 pyrolysis time, meaning that the reaction pathways are different in the two cases. Water molecules released

204 from dehydration reactions of the substrate could play a fundamental role in reactive pyrolysis, promoting

205 different mechanisms than in fast pyrolysis. The catalytic role of water in carbohydrate pyrolysis has already

206 been discussed in the literature [40].

207 *3.3 Inulin:* The pyrograms obtained for inulin are reported in Figure 3. The chromatographic profile obtained

208 from fast pyrolysis was very similar to that obtained for fructose. This means that the depolymerisation of

209 inulin chains is most likely the first reaction that occurs during fast pyrolysis. This result was already observed

210 in fast pyrolysis experiments at 550 °C [30].

211   The yields for each category are reported in Table 2. Since depolymerisation is the first reaction taking place

212   in these conditions, secondary pyrolysis reactions were less favoured for inulin than for fructose. Therefore,

213   a lower yield of small molecules was obtained. The formation of cyclopentenones was also more favoured

214   than for fructose. This could be due to a higher probability of C-C bond formation from inulin monomers

215   during the cleavage of the glycosidic bond. The yields of anhydrosugars, pyrans and furans were similar to

216   those obtained for fructose.

217   As for fructose, the behaviour of inulin in reactive pyrolysis was strikingly different than in fast pyrolysis. In

218   this case, however, the differences were so remarkable that a comparison is difficult. The most evident result

219   is that the formation of DFAs was by far the most favoured reaction. 12 different DFDA peaks were found.

220   After 0.2 min of pyrolysis, DFAs accounted for about 60% of the total composition. The yield in DFAs was

221   higher for inulin than for fructose at all observed pyrolysis times. Moreover, some DFAs were obtained only

222   from fructose (#75, 80, 83, 87), while others were obtained only from inulin (#78, 84, 86). These results imply

223   that the formation of DFAs from inulin does not derive from the intermolecular reactions between

224   monosaccharide units. A partial cleavage of the inulin polysaccharide chain can lead to the formation of

225   disaccharides or other small oligomers, and DFAs can be obtained from the oligomers by intramolecular

226   reactions. The formation of DFAs from oligosaccharides of inulin as a result of glycosidic bond cleavage has

227   already been documented in the literature [41].

228   The yields of all other categories were significantly lower than in fast pyrolysis. The only categories

229   maintaining a yield of more than 10% were furans and anhydrosugars, which were mainly represented by

230   HMF (#28) and 2,6-anhydro-β-D-fructofuranose (#58), respectively.

231   When pyrolysis time was increased, the total yield of DFAs showed an increasing trend, reaching over 84%

232   after 60 min of pyrolysis. However, the number of peaks in the DFA region was reduced, going from 12 to 5

233   (#79, 82, 85, 86, 89). This is evident by the comparison of the pyrograms in Figure 3. The most plausible

234   explanation to this behaviour is that, when given enough time in the pyrolysis chamber, these molecules

235   undergo isomerization reactions to form the most stable isomers. Isomerization of DFAs was already

236 observed in the literature when fructose samples were caramelized in the presence of an acid ion-exchange

237 resin [38].

238 Trends in the yields of the other categories are more difficult to discuss, since their values are small and more

239 subjected to casual error. If the shortest and longest reaction times are compared, cyclopentenones, furans,

240 pyrans, ahydrosugars and other molecules all showed a decreasing trend. However, only a slight yield

241 increase was observed for small molecules. These results show that, as observed for fructose, DFAs can also

242 be obtained from secondary thermal reactions between the primary pyrolysis products of inulin, if enough

243 time is given. Finally, the derivatisation degree of anhydrosugars increased with time, and a complete

244 persilylation was achieved after 10 min of pyrolysis.

245 *3.4 Jerusalem artichoke tubers:* The pyrograms obtained for Jerusalem artichoke are shown in Figure 4.

246 Fast pyrolysis provided similar chromatograms to those obtained for the other substrates. However, the

247 percentage yields of each category were different from those of fructose and inulin. A much lower yield of

248 anhydrosugars was obtained, while small molecules and furans showed very high yields. These differences

249 in the pyrolysate composition are difficult to explain, but the high content of inorganic species in the

250 samples (12.6%) could favour some of the pyrolysis mechanisms over the others. Inorganic salts are known

251 to act as catalysts and alter the pyrolysis mechanisms of carbohydrates and biomasses in general. Fast

252 pyrolysis of biomasses in the presence of inorganic species was shown to increase the yield of specific

253 product categories [42-45].

254 As shown in Table 2, the percentages of partially and totally derivatised anhydrosugars were also comparable

255 with those observed in fructose and inulin. This result shows that the efficiency of HMDS was not altered by

256 the presence of inorganic species.

257 The high yield of small molecules was maintained in reactive pyrolysis experiments. At all pyrolysis times, the

258 chromatograms showed a peak which could be annotated to the persilylated form of the phosphate anion.

259 This peak is marked with an asterisk in Figure 4, and its presence is indicative of the high inorganic content

260 of the samples. The phosphate anion was not observed in the chromatograms obtained from fast pyrolysis,

261 probably because its reaction with the derivatising agent was not favoured.

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262 Compared to fast pyrolysis, a higher yield of anhydrosugars and whole monosaccharides ("others" category)

263 was obtained in reactive pyrolysis. Moreover, the yield of furans was lower. These results show that, under

264 reactive pyrolysis conditions, the catalytic effects of the inorganic species are reduced. This behavior,

265 although counter-intuitive, is extremely interesting, and requires further studies to be understood. The

266 formation of DFAs was observed for Jerusalem artichoke as for fructose and inulin, and a significant yield was

267 obtained even at short reaction times.

268 When pyrolysis time was increased, the yield of furans rapidly decreased, as was observed for fructose and

269 inulin. As expected, a decrease in the yield of whole monosaccharides was also observed. The derivatisation

270 degree of anhydrosugars increased much more quickly, and a complete silylation was already obtained after

271 1 min of pyrolysis. The yield of DFAs increased up to 20 min of pyrolysis, reaching over 64%, but decreased

272 for the two successive pyrolysis times. This could be due to a reduction of the thermal stability of DFAs caused

273 by the inorganic component of the sample. This hypothesis is supported by the increase in the yield of small

274 molecules at 30 and 60 min pyrolysis time. As for inulin, isomerization of DFAs was observed, and at long

275 pyrolysis times only four main peaks (#73, 77, 85, 88) remained.

276

277 **4. CONCLUSIONS**

278 The present work outlines for the first time the behavior of fructans in reactive pyrolysis. The differences

279 between fast and reactive pyrolysis of fructose, inulin and Jerusalem artichoke were investigated. Pyrolysis

280 products were grouped in categories according to their structure, and percentage yields for all categories

281 were obtained from integrated areas for all experiments.

282 Fast pyrolysis gave small molecules, furans and anhydrosugars as the main products, with

283 hydroxymethylfuraldehyde as the most abundant species for all three substrates. Derivatisation of

284 anhydrosugars in fast pyrolysis was partial. For all three substrates, the percentages of partially and fully

285 derivatised anhydrosugars were similar.

286 The product distribution in reactive pyrolysis changed significantly from fast pyrolysis. The increase in

287 pyrolysis time allowed only the most thermostable products to be detected, and favoured isomerization,

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288 conversion and secondary degradation reactions. The most striking difference from fast pyrolysis was the

289 formation of di-fructose dianhydrides, which was surprisingly observed also in the case of fructose.

290 Moreover, the derivatisation degree of anhydrosugars quickly increased with the increase of pyrolysis time,

291 and a complete derivatisation was obtained in all cases after 10 min of pyrolysis. This is an interesting result

292 that could be applied to the study of other substrates by pyrolysis with in situ silylation.

293 Finally, Jerusalem artichoke showed some differences in the trends of pyrolysis products yields. These

294 differences were attributed to the presence of inorganic species in the sample, and require further studies

295 to be fully understood. Although being a more complex system, the high yield of DFAs observed for fructose

296 and inulin was preserved in Jerusalem artichoke. Exploitation of this behavior could be possible in the future

297 to produce DFAs with minimal substrate preparation. Further studies are required to fully understand the

298 role of inorganic components on the pyrolysis mechanisms.

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