

Innovative fractionation and separation of bio-crude oil

Abstract

A new approach for the analysis of bio-crude oils (BCOs) has been qualitatively explored. The analytical scheme is based on the fractionation of BCO through precipitation in water, freeze-drying, solid phase extraction (SPE) and combinations of analytical techniques for the analysis of fractions. Monomeric components in BCO were characterised through gas chromatography coupled with mass spectrometer and flame ionisation detector (GC-MS/FID). The molecular mass distribution of oligomers was determined using gel permeation chromatography (GPC). The fractionation procedure appeared to have succeeded to a large extent as evident in the detection of various components along their expected fraction in the GC-MS/FID analysis. However, a quantitative analysis of the multiple components in different fractions appeared difficult owing to the loss of many volatile fractions through the fractionation procedure. And less than 7 wt. % of the sugar-related components in the acetylated polar SPE fraction were identified.

Keywords

Bio-crude oil, sugars, solid phase extraction, pyrolysis, freeze-drying, acetylation

1. Introduction

Biomass is one of the essential forms of stored energy. Its advantages over others include its low cost and long-term availability. Biomass essentially consists of lignocellulose. Specific biomass characteristics like low density (mass/energy) and the extensive distribution in rural areas give it the prime advantage of being considered as an appropriate alternative in the production of liquid fuel for transport and other energy purposes. A vital process to translate this into practice is the fast pyrolysis, a process that converts based on the thermochemical conversion of biomass principally to a bio-crude oil (BCO). BCO is an umbrella term for hundreds of diverse compounds with varying functionality, polarity and degree of polymerisation. This heterogeneity could be seen as a disadvantage, which hinders its direct utilisation as a transport fuel or platform chemical (Meier et al. 1995, Bridgwater et al. 1999, Czernik and Bridgwater 2004, Mohan et al. 2006).

For quite a long time, there have been concerted efforts in the area of developing appropriate analytical methods to address significant challenges of BCO in order to understand its composition and enhance its applications (Elliott 1988). Pyrolysis oil has been studied using Fourier transformation infrared spectroscopy (FTIR), H and C nuclear magnetic resonance spectroscopy (NMR), high performance liquid chromatography (HPLC), gas chromatography-mass spectrometry/flame ionisation detection (GC-MS/FID) and electron-impact mass spectrometry (EIMS) chemical ionization mass spectrometry (CIMS) (Boocock et al. 1983, Ménard et al. 1984, Schirmer et al. 1984, Faix et al. 1990). And new generation analytical techniques such as comprehensive two-dimensional GC have been employed to study even more detailed composition (Marsman et al. 2007, Tessarolo et al. 2013). The International

46 Energy Agency (IEA) has focused on applying improved analytical methods for BCO
47 (Oasmaa and Meier 2005, Oasmaa et al. 2009, Elliott et al. 2012). Almost all these
48 analytical studies have dealt mostly with the volatile fractions of BCO leaving the non-
49 volatile fractions as unidentified most of which are sugar-derived products.

50 One analytical route that can bring about a substantial breakthrough in the separation of
51 BCO to specific products is the comprehensive characterisation of holocellulose
52 derived “sugars” which constitute a considerable fraction in BCO. For some reasons
53 analysis of these components is difficult owing to the complexity of the BCO mixture
54 and the non-volatile character of this fraction, which hinders the direct use of GC-MS
55 analysis. And the separation of these components by distillation is impossible due to the
56 thermal instability of this fraction. Under heating, the fraction turns to undesirable
57 products, like char or humin-like substance (Rasrendra et al. 2013b, Rasrendra et al.
58 2013a). A procedure for the characterisation of such carbohydrates by the Brix method
59 has been proposed (Oasmaa and Kuoppala 2008). Also, an application for membrane
60 filtration technology to concentrate and separate sugars from aqueous fractions of bio-
61 oil has been used and the concentration of sugars in the bio-oil determined by HPLC
62 (Hassan et al. 2013). Fractionation methods can help in successful identification of
63 BCO components, but the problem associated with separation steps (liquid-liquid
64 extraction, vacuum distillation etc.) such as their complexity and high cost have also
65 hindered their success in the area of BCO separation (Garcia-Perez et al. 2007, Sipilä et
66 al. 1998, Ba et al. 2004, Oasmaa et al. 2010). The aim of this work, therefore, is to
67 present a more straightforward and quicker procedure for the fractionation of BCO
68 using the solubility of BCO in water as the functional mode of separation. Through the
69 addition of water, the coherence of BCO is lost, and the indissoluble pyrolytic lignin
70 (PL) is precipitated (Radlein and Piskorz 1997, Scholze and Meier 2001).

71 Polarity is another essential characteristic of BCO, and its acidity is well documented
72 (Rasrendra et al. 2011, Meier 1999, Bayerbach and Meier 2009). But relatively little is
73 known about the characterisation of non-volatile polar BCO fraction, which is mostly
74 decomposed sugars (Brodzinski and Meier 2004). Such sugars can be defined as non-
75 volatile monomers and oligomers (MAOs). Their separation is a complex multi-stage
76 process (Garcia-Perez et al. 2007, Sipilä et al. 1998, Ba et al. 2004, Oasmaa et al.
77 2010). However, the application of solid phase extraction (SPE) can be considered to
78 simplify the task. This technique is not commonly in use for characterisation of BCO.
79 Although, the application of SPE as an analytical tool for complex samples has been
80 reported (Albertsson et al. 1995). In this study, a combination of lignin precipitation,
81 SPE and freeze drying is presented as a novel strategy to achieve fractionation of BCO
82 prior to analysis.

83

84 **Material and methods**

85 **1.1. Materials**

86 Samples of BCO employed in this study were obtained from in-house produced BCO
87 from beech wood and another sample from a specific project. Their mode of production
88 and related information are listed in

89

90 Table 1.

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92

93 **Table 1: List of Samples**

	ID	Feed	Product	Capacity	Source	Scale/Technology
1	BE/BS-10	beech	BCO	500g/h	Internal	BS/BFB
2	DYN/BFB-04	hardwood mix	BCO	100t/d	External	CP/BFB

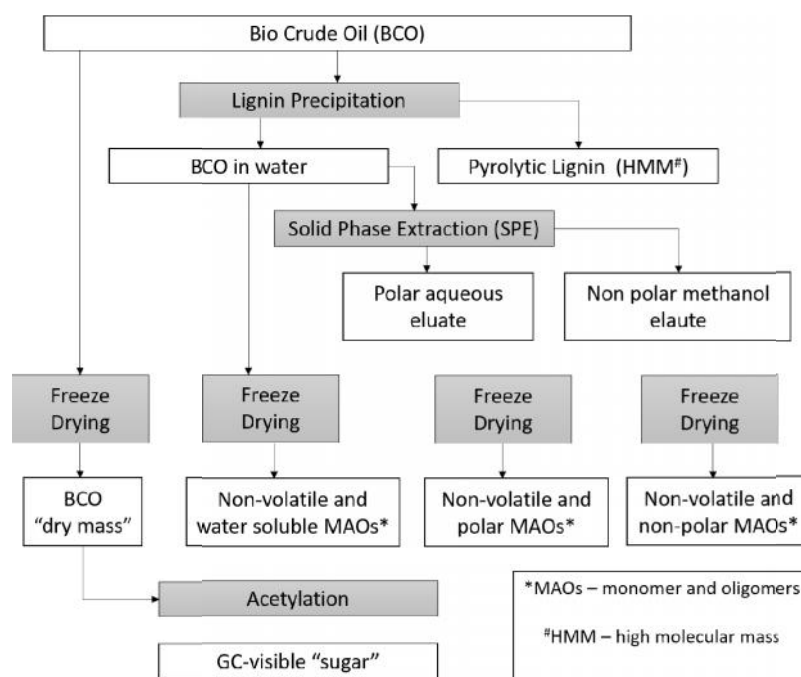
94 CP = commercial plant, BS = bench scale unit, BFB = bubbling fluidised bed

95 Separation methods

96 The samples were analysed as whole samples and as fractions using the analytical
97 scheme shown in

98 Figure 1.

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103 **Figure 1: Scheme of separation methods into fractions**

104 Following the precipitation of the lignin, liquid fraction introduced on silica bonded
105 octadecyl SPE-columns (C18) to obtain a non-polar aqueous eluate. A nearly pure polar
106 MAO-fraction was obtained after removing the water and other volatiles with FD.
107 Through acetylation, these MAOs were further characterised with GC-MS/FID.

108 1.1.1. Lignin precipitation

109 For the lignin precipitation (LP), 1ml was introduced into a mixer containing about
110 500ml distilled water drop-wisely, and the mixing carried out at 22.000 rpm. The
111 obtained oil-in-water emulsion was filtered under vacuum with pre-weighed filter
112 papers (589/3; mesh $\approx 2\mu\text{m}$). Additional 500ml water to further clean the residue.

113 Sticky residues in the mixer were dissolved in ethanol, and the solvent subsequently
114 removed using rotary evaporator. Two fractions were obtained; the water fraction
115 (BCO extract) and the residue (pyrolytic lignin). To obtain a complete mass balance the
116 filter and all used glassware were dried and weighed carefully before and after the
117 procedures.

118 **1.1.2. Solid phase extraction**

119 Reversed phase C18-E columns from Phenomenex were used for the SPE fractionation
120 of pyrolytic water. The columns were placed on Visiprep 5-port Vacuum Manifold. The
121 SPE columns were conditioned with methanol, followed by water. The amount of the
122 used sample was less than 10% (by weight) of the columns bed material (normally
123 500mg/6ml). Polar compounds were not retained on the column. For mass
124 determination, the polar water phase was freeze-dried and the nonpolar fraction eluted
125 with methanol was vacuum dried.

126 **1.1.3. Freeze-Drying**

127 Freeze-drying (FD) of samples were carried out using ALPHA 2-4 LSC Freeze Dryer,
128 Christ, Germany. Samples with high water content (aqueous SPE fractions) were
129 freeze-dried in pre-weighed round bottom flask. Pure BCOs and non-polar organic
130 fractions were mixed with distilled water (v : v/1:10), and the mixture sonicated.

131 **1.2. Analytical methods**

132 **1.2.1. GC-MS**

133 The various bio-oil samples, HDO fractions and other treated samples require adequate
134 and specified GC-MSD methods, as follows:

135 a) Organic fractions

136 About 60 mg of the sample was dissolved in 1 ml acetone, which contained a known
137 amount of fluoranthene as an internal standard for quantification. GC was performed
138 using an Agilent 6890. Injector conditions: split/splitless injector, temperature 250 °C,
139 split ratio 1:15, injection volume 1 µl.

140 Separation was carried out on a 60 m x 0.25 mm VF-1701MS (Varian) fused-silica
141 column, containing 14% cyanopropyl-phenyl-methylpolysiloxane (0.25 µm film
142 thickness). Oven programme was as follows: hold constant at 45°C for 3 min, heat with
143 4°C/min to 280°C and held for 20 min. Helium was used as carrier gas with a constant
144 flow of 2 ml/min. The system was equipped with parallel FID & MS-detection.
145 Electron impact mass spectra were obtained on an HP 5972 MS using 70 eV ionisation
146 energy.

147 b) Aqueous fractions

148 About 950 µl sample was mixed with 50 µl water, which contained a known amount of
149 1,2-dimethoxyethane as an internal standard for quantification. GC was performed
150 using an Agilent 6890. Injector conditions: PTV injector, temperature 250 °C, split
151 ratio 1:15, injection volume 1 µl.

152 Separation was carried out on a 30 m x 0.25 mm VF-WaxMS (Varian) fused-silica
153 column, containing polyethylene glycol (0.25 µm film thickness). Oven programme was
154 as follows: hold constant at 45°C for 3 min, heat with 4°C/min to 280°C and held for

155 20 min. Helium was used as carrier gas with a constant flow of 2 ml/min. The system
156 was equipped with parallel FID & MS-detection. Electron impact mass spectra were
157 obtained on an HP 5972 MS using 70 eV ionisation energy.

158 Samples were determined by comparison with mass spectra of authentic compounds
159 and mass spectra in the NIST library; more details can be found in previous
160 work(Windt et al. 2011)

161 a) Acetylated fractions

162 Acetylated samples were carried out on the same system with split ratio changed to 1:5
163 and the oven programme starts with temperature held at 100°C for 2 min, then heated at
164 1,5°C/min to 200°C, followed by the second ramp of 3°C/min. to 260°C and a third at
165 10°C/min up to the final temperature of 280°C and held for 30 minutes.

166 An Agilent 6890 GC; 5975B inert XL MSD was used for the “Wax-method” (wax),
167 which is designed for polar analytes and samples matrices with high humidity ratio.
168 The sample was introduced in a GC-vial and spiked with a 50µl internal standard
169 solution (diethoxyethane in 1, 2-propanediol approx. 60mg/ml), then filled up with
170 water to a total volume of 1ml. The injection occurred in a quartz liner at -20°C, the
171 desorption were done under the following conditions: Hold 0.5 s, ramp 12°C/s final
172 temperature 260°C. A ZB Innowax (60 m x 0.25 mm, 0.25 µm film) GC column,
173 sample introduction occurs in a split mode (1:10). The carrier gas was He and the
174 system ran in constant flow mode (2 ml/min.). The oven program was: temperature at
175 36 °C held 4 min., ramp 6°C/sec., end temp. 260 °C, held 10 min. The system also was
176 equipped with parallel FID & MS- detection. Electron impact mass spectra were
177 obtained by using 70 eV ionisation energy.

178 1.2.2 Acetylation

179 Derivatisation of polar samples was done with acetylation of water free samples.
180 Around 60mg of analyte was dissolved in dry pyridine and acetic anhydride from
181 Supelco (USA). Both chemicals were applied in a spill-over (500µl each), and the
182 acetylation proceeds over 24 hours by room temperature. Preliminary studies
183 (controlled by GC-MSD) were carried out to ensure that all reactions are finished at
184 these conditions.

185 1.2.3 GPC

186 Gel permeation chromatography (GPC) was carried out on an Agilent 1100 Series
187 equipped with Refractive Index Detector (RI) @ 40 °C and UV-Photometer ($\lambda = 254$
188 nm) and applied to determine the molecular weight distribution. The samples were
189 normalised on same dissolution concentration (1mg/ml) and introduced on two
190 PolarGel-L-columns in series (Varian, 300 x 7,5 ml), Flow 0.8ml/min, Oven 60°C,
191 injection volume 100µl. The used solvent was Dimethylsulfoxide (DMSO) + 1 %
192 Lithium bromide (LiBr). Calibration was carried out with 10 Polyethylenglycol
193 standards in the mass range between 106 to 21030 g/mol, analysis with HP Chemstation
194 GPC add-on (PSS).

195 **2 Results and Discussions**196 **2.2 Separation**

197 The result of the fractionation shown in Table 2 showed that water constitutes about
 198 24% of whole BCO. Following the separation of the pyrolytic lignin from the entire
 199 BCO, the water fraction contains the rest of BCO components. Also, a fraction of the
 200 extractive is also contained in the pyrolytic lignin. Further fractionation of the BCO
 201 water was done with SPE through which the sample was separated into non-polar and
 202 polar fractions. The aliphatic C18-chain structure of the used SPE column retains the
 203 nonpolar components, while the eluent comprises the polar parts. The retained fraction
 204 was subsequently eluted with methanol. These fractions were concentrated and
 205 analysed as described earlier. After the freeze-drying of the water fraction from BCO, a
 206 syrupy product was obtained, and the residue mass was found to be 41.0 ± 0.6 wt. % as
 207 determined for the reference sample BE/BS-10. The SPE polar phase constituted the
 208 highest fraction with about 24 wt % while the SPE nonpolar fraction PL constituted
 209 about 14 wt. % of the whole BCO. It was found out that the use of freeze-drying to
 210 eliminate the water content of the sample or fraction caused loss of some volatiles
 211 thereby making it impossible to recover the entire components in the BCO once freeze-
 212 dried.

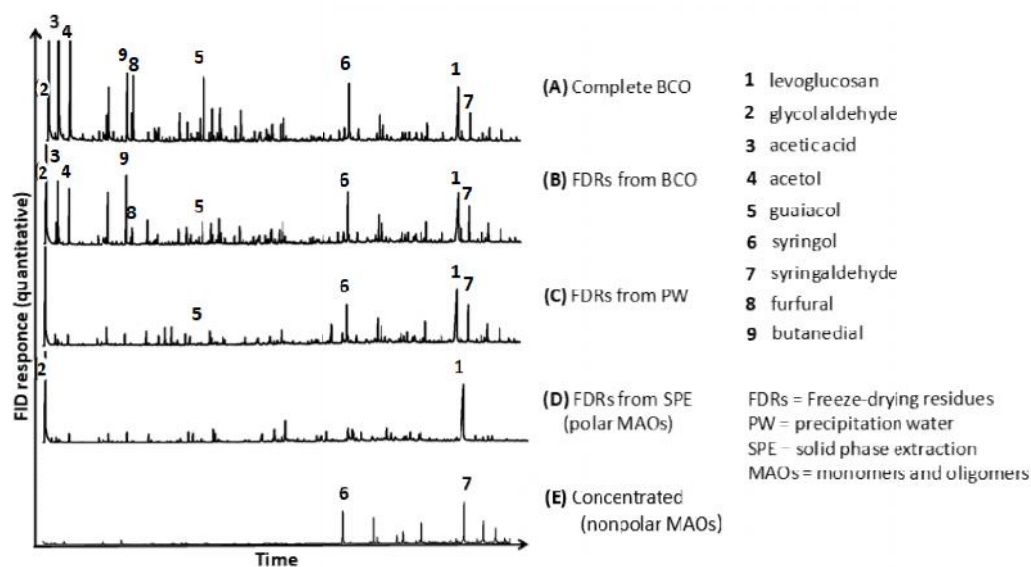
213 **Table 2 Average yields of different BCO fractions**

Fraction	Mass [wt. %]	Range [abs.%]
¹ FDR of BCO	64.4	± 0.5
FDR of ² PW	41.0	± 0.6
SPE polar phase	24.2	± 0.3
SPE non-polar phase	13.8	± 0.9
Py-lignin	14.3	± 1.1

214 ¹FDR = Freeze drying residue; ²PW= precipitation water;215 **2.3 Analysis of fractions**216 **2.3.1 GC-MSD**

217 Chromatograms of different fractions of the samples analysed using GC-FID are shown
 218 as overlays in

219 Figure some non-volatile components but which are Gas Chromatography detectable
 220 (GCDs) can be identified in all samples. The topmost chromatogram (A) is obtained
 221 from whole BCO. The comparison of the freeze-dried BCO chromatogram (B) with the
 222 (A) indicates that a more significant portion of the highly volatile components such as
 223 acetol, acetic acid and furfural were a loss to through the freeze-drying. And the entire
 224 fractions of these components have been lost following the removal of the pyrolytic
 225 lignin from BCO and the separation of the water fraction into polar and non-polar
 226 fractions via SPE. The result indicates the effectiveness of separating procedure but
 227 with poor recovery of the highly volatile components. The non-volatile fraction
 228 especially the monomeric and oligomeric components, mainly consist of decompose
 229 sugar were efficiently recovered and resolved by the procedure. This can be seen in the
 230 prominence of component like levoglucosan in chromatogram D.



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233 **Figure 2 Overlay GC-FID chromatograms of BCO fractions**

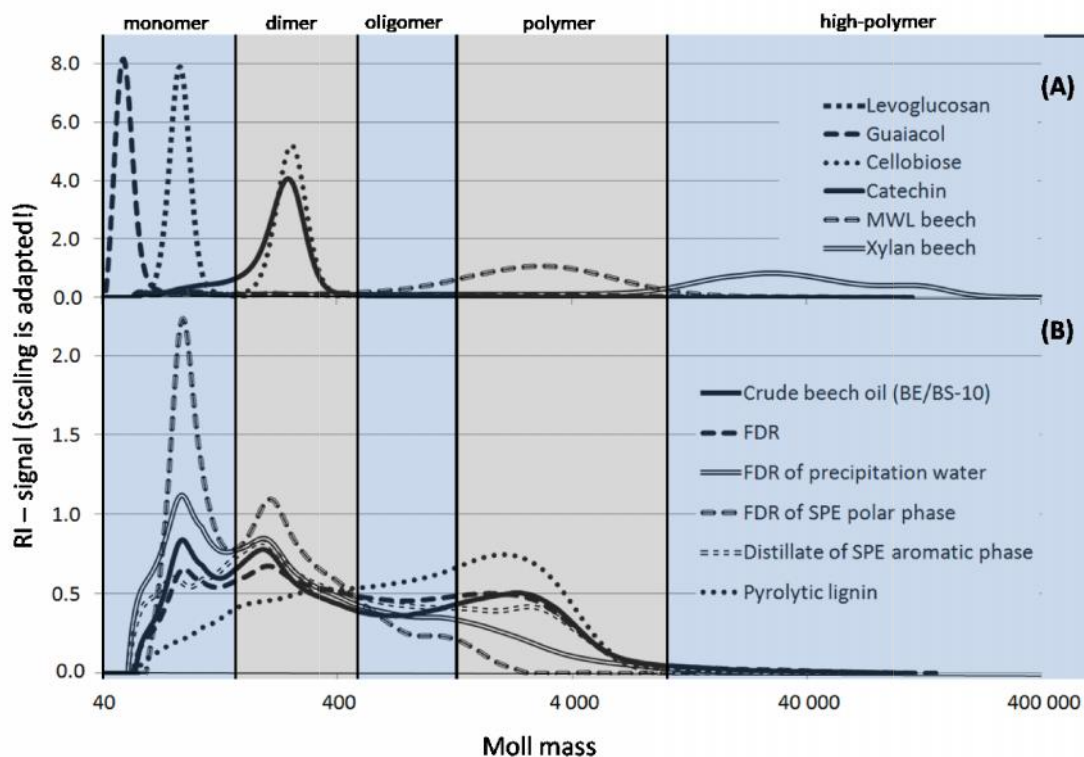
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235 2.3.2 GPC

236 Naturally, associated with lyophilisation is a loss of small size molecules and this
237 predestines it as qualified preparation for GPC analysis. This analytical method is
238 conceived for oligomers and high molecular compounds. So molecular masses below
239 150 were not calibrated for this chromatography. Reference materials, listed in

240 Figure (A), were used to create a draft classification scale (e.g. monomer, dimer, trimer
241 and polymer). GPC analyses of BCO (BE/BS-10) and the respective fractions are
242 compared in

243 Figure (B). The untreated BCO shows components distribution; relevant peaks are
244 observable in the monomer, dimer and also in higher molecular sections. The GPC
245 graph of the FDR is nearly similar, but with a slight disproportional increase in
246 molecule sizes. Pyrolytic lignin (PYL) shows the highest values; only a minor
247 decomposition can be observed by comparing with milled wood beech lignin (MWL)
248 as a reference for the former lignin structure (Björkmann 1956).



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251 **Figure 3 Summary of GPC-chromatograms**

252 (*BCO* = bio-crude oil; *SPE* = solid phase extraction; *FDR* = Freeze-drying residue;

253 2.3.3 GC-MS/FID of acetylated fractions

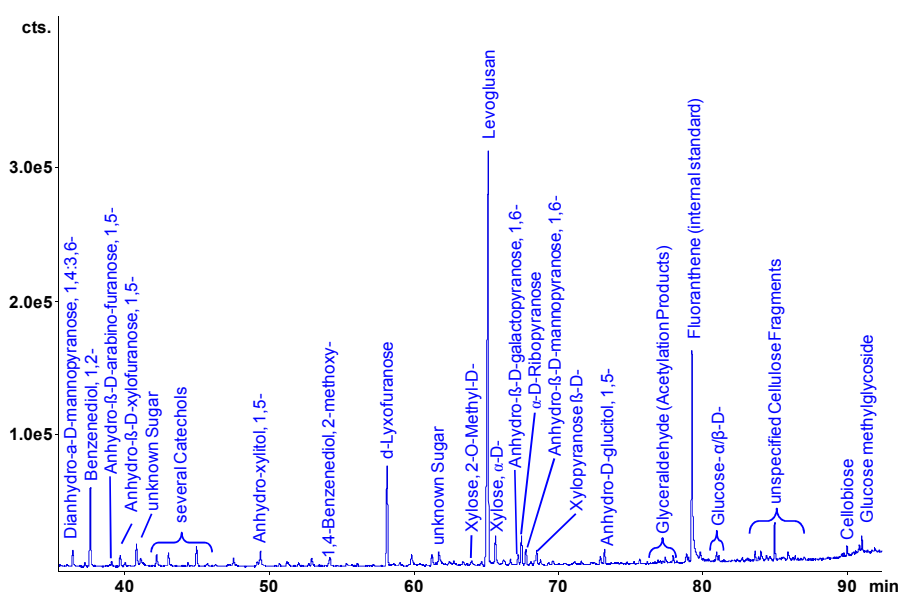
254 The result of the sugar-related fraction, i.e. the SPE polar fraction of the BCO is shown
255 in Table 3 and Figure 4. It is evident from the result that levoglucosan remained the
256 dominant sugar product in the fraction, constituting about 3 wt. %. This component is
257 an anhydrosugar of glucopyranose. The analysis revealed the presence of analogous
258 anhydro-compound of other sugar such as Anhydro- β -D-arabinofuranose, 1,5-,
259 Anhydro- β -D-xylofuranose, 1,5-, Anhydro- β -D-mannopyranose, 1,6-, Anhydro- β -D-
260 galactopyranose, 1,6- etc. Some of these components have hitherto been classified as
261 unknown sugar prior to this fractionation and analysis. They are thought to have formed
262 from their respective hemicellulose in the manner similar to the formation of
263 levoglucosan from cellulose. However, the presence of pure sugar such as Xylose, α -D-
264 and Glucose, α -D- in the chromatogram was not envisaged in the fraction bearing in
265 mind the nature of the conversion process through which the BCO produced. In all, the
266 total amount of quantifiable sugar was far below 7 wt. % of the BCO.

267 **Table 3 Characterisation of various acetylated “sugars” from beech BCO.**

RT	Acetate from:	FID Area	RRF	wt. %
36.4	Dianhydro- α -D-mannopyranose, 1,4:3,6-	619 877	2	0.09
37.6	Catechol, Benzenediol, 1,2-	3 044 410	1	0.23
39.1	Anhydro- β -D-arabino-furanose, 1,5-	130 248	2	0.02
39.7	Anhydro- β -D-xylofuranose, 1,5-	440 569	2	0.07
40.8	unknown sugar	1 006 746	1	0.11
42.2	Hydrochinon, Benzenediol, 1,4-	501 736	1	0.04
43.0	Benzenediol, methyl-	533 909	1.5	0.06
44.4	unknown sugar	155 694	1	0.02
45.0	Benzenediol, ethyl,	883 871	1	0.07

49.4	Anhydro-xylitol, 1,5-	600 234	2	0.09
54.2	1,4-Benzenediol, 2-methoxy-,	417 074	1	0.03
58.2	d-Lyxofuranose	4 270 707	1	0.32
61.7	unknown sugar	925 800	1	0.10
64.0	Xylose, 2-O-Methyl-D-	248 023	1.3	0.02
65.2	Levoglucosan	22 088 912	1.8	3.04
65.6	Xylose, α -D-	1 306 462	1.3	0.13
67.2	Anhydro- β -D-galactopyranose 1,6-	476 968	2	0.07
67.5	α -D-Ribopyranose	1 211 481	1.3	0.12
67.8	Anhydro- β -D-mannopyranose, 1,6-	669 475	2	0.10
68.5	Xylopyranose, β -D-	596 820	1.3	0.06
73.2	Anhydro-D-glucitol, 1,5-	524 293	1	0.04
79.3	Fluoranthene	8 833 215	1	0.66
81.0	Glucose, α -D-	180 080	1.3	0.02
81.1	Glucose, β -D-	158 683	1.3	0.02
89.0	Cellobiose	288 464	1	0.03
91.0	Glucose methylglycoside	370 012	1.3	0.04

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Figure 4 A section of the chromatogram of SPE acetylated polar fraction

272 3 Conclusions

273 The fractionation procedure was able to achieve the separation of BCO into PYL and
 274 aqueous fractions, which was subsequently separated into polar and non-polar fractions.
 275 However not much success was recorded in the recovery of the components especially
 276 the volatile fractions. The analysis of the acetylated sugars revealed some new sugars
 277 hitherto classified as unknown sugars. However, the number of resolved components
 278 were not significantly large. There is, therefore, a need for a further study on the
 279 fractionation and separation methods in order to quantitative evaluate the analytical
 280 procedure.

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