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Original Research Article

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

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

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

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

Material and methods

1.1. Materials

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

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90 Table 1.
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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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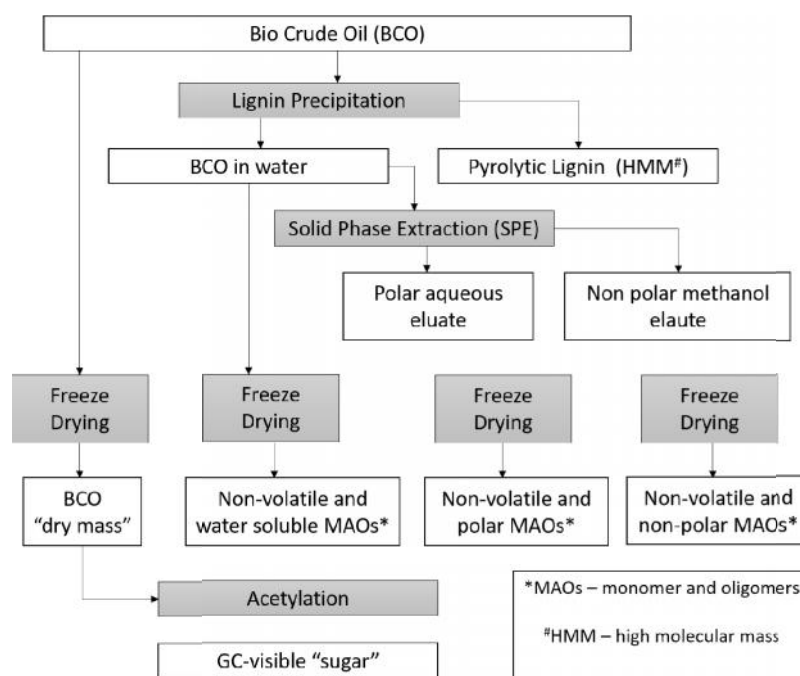

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103 **Figure 1: Scheme of separation methods into fractions**

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 ≈ 2μm). Additional 500ml water to further clean the residue.

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

1.1.2. Solid phase extraction

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

1.1.3. Freeze-Drying

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

1.2. Analytical methods

1.2.1. ~~GC-MS~~

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

a) Organic fractions

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

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

b) Aqueous fractions

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

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

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

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

a) Acetylated fractions

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

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

1.2.2 Acetylation

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

1.2.3 GPC

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

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2 Results and Discussions

2.2 Separation

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

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

[1]FDR = Freeze drying residue; [2]PW= precipitation water;

2.3 Analysis of fractions

2.3.1 GC-MSD

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

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

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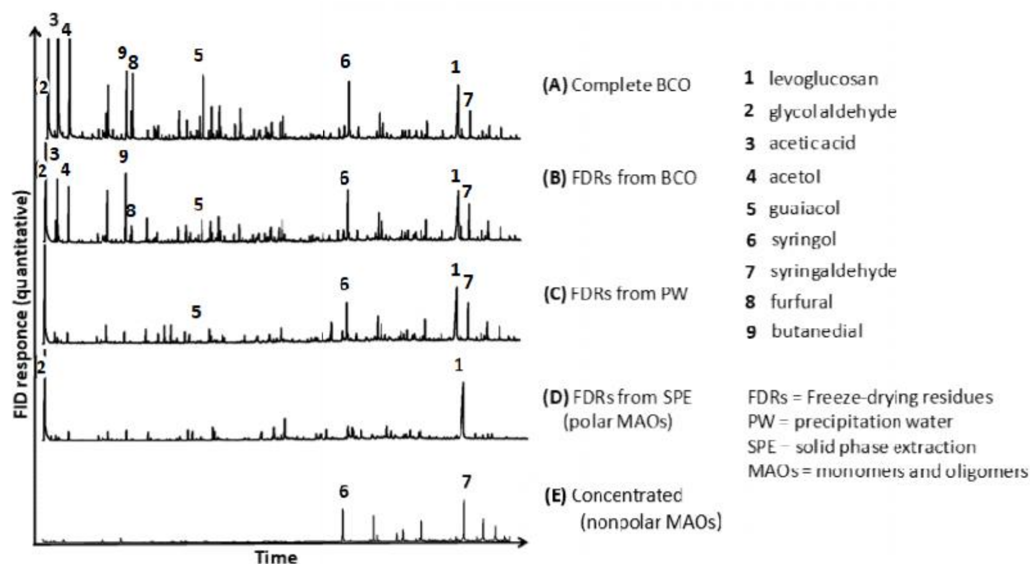

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233 **Figure 2 Overlay GC-FID chromatograms of BCO fractions**

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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 fractions. 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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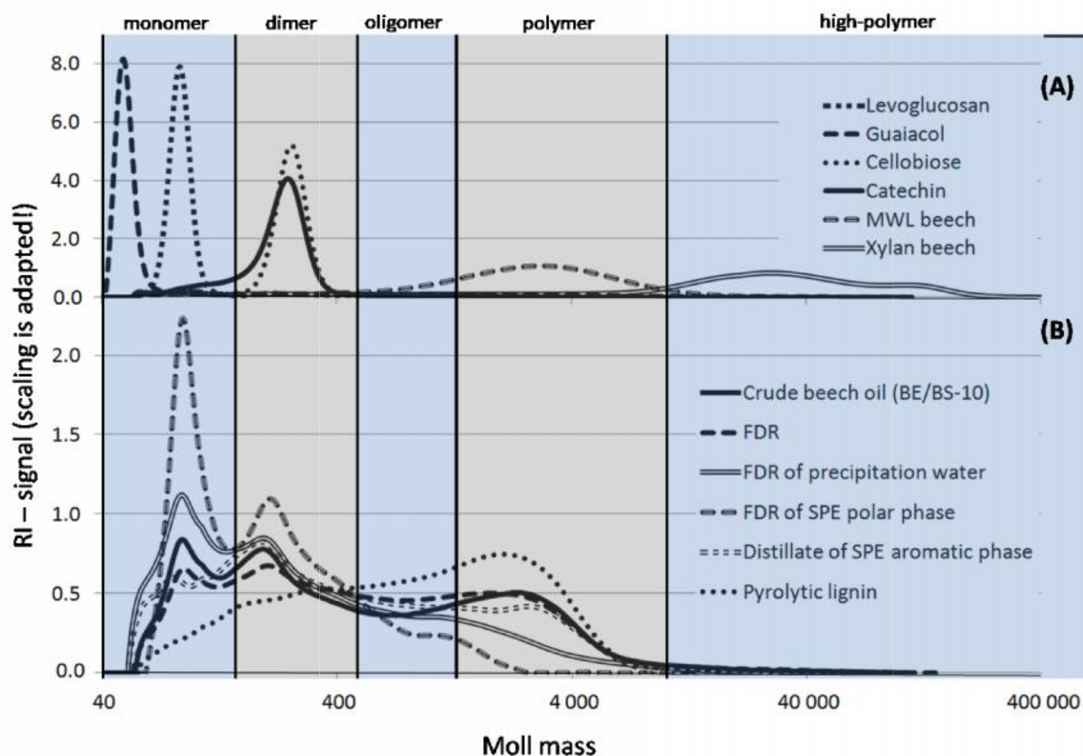

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251 **Figure 3 Summary of GPC-chromatograms**
252 **(***BCO = bio-crude oil; SPE = solid phase extraction; FDR = Freeze-drying residue;*

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-ß-D-arabinofuranose, 1,5-,
259 Anhydro-ß-D-xylofuranose, 1,5-, Anhydro-ß-D-mannopyranose, 1,6-, Anhydro-ß-D-
260 galactopyranose1,6- 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, a-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-ß-D-arabino-furanose, 1,5-	130 248	2	0.02
39.7	Anhydro-ß-D-xylofuranose, 1,5-	440 569	2	0.07
40.8	unknown sugar	1 006 746	1	0.11
42.2	Hydrochinon, Benezenediol, 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

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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, a-D-	1 306 462	1.3	0.13
67.2	Anhydro-ß-D-galactopyranose1,6-	476 968	2	0.07
67.5	á-D-Ribopyranose	1 211 481	1.3	0.12
67,.8	Anhydro-ß-D-mannopyranose, 1,6-	669 475	2	0.10
68.5	Xylopyranose, ß-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, ß-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

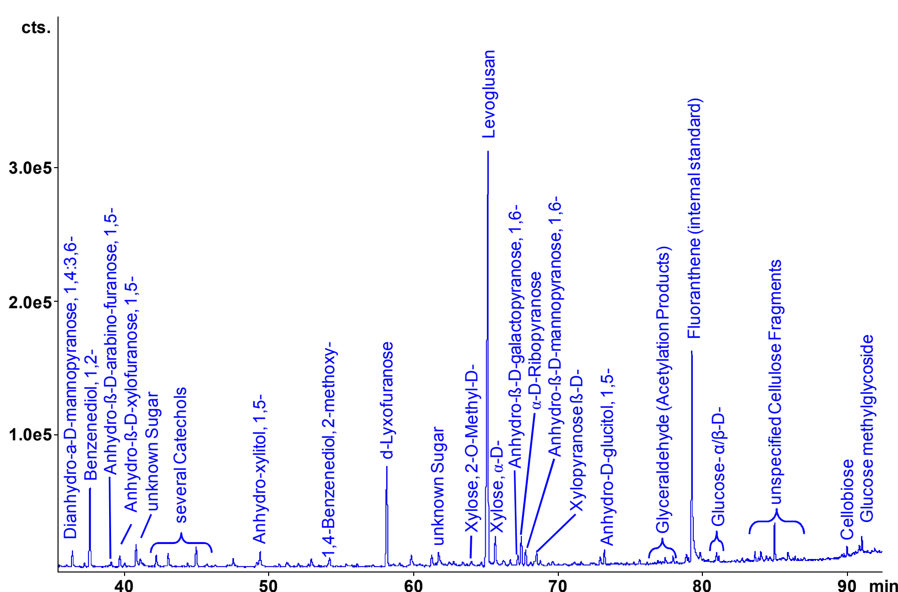

Figure 4 A section of the chromatogram of SPE acetylated polar fraction

3 Conclusions

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

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