



Brisk Method for Fractionating and Separating Bio-Crude Oil

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Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

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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 using 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.*

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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. Fast pyrolysis is a vital process to translate this into practice. This process converts thermochemical conversion of biomass 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 [1].

For a decade, 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 [2]. 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), electron-impact mass spectrometry (EIMS) and chemical ionization mass spectrometry (CIMS) [3]. And new generation analytical techniques such as comprehensive two-dimensional GC have been employed to study even more detailed composition [4]. The International Energy Agency (IEA) has focused on applying improved analytical methods for BCO [5]. 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 have been a challenge mostly due to the complexity of the BCO mixture. In addition, 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 [6]. A procedure for the characterisation of such carbohydrates by the Brix method has been proposed [7]. Also, an application of 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 [8]. Its 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 [9-12]. 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.

Polarity is another essential characteristic of BCO, and its acidity is well documented [13-15]. However, there are limited data on characteristics of non-volatile polar BCO fraction, which is mostly decomposed sugars [16]. Such sugars can be defined as non-volatile monomers and oligomers (MAOs). Their separation is a complex multi-stage process [17]. 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 [18].

Therefore, 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.

2. MATERIALS AND METHODS

2.1 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 Table 1.

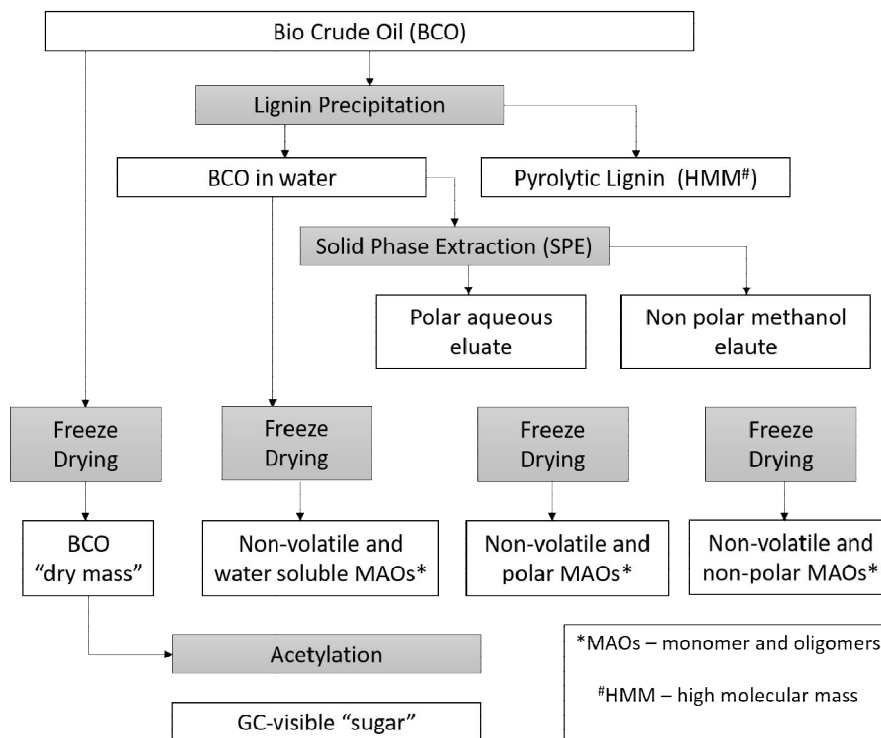
2.2 Separation Methods

The samples were analysed as whole samples and as fractions using the analytical scheme shown in Fig. 1.

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

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

**Fig. 1. Scheme of separation methods into fractions**

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

2.3 Lignin Precipitation

For the lignin precipitation (LP), 1 ml of sample was introduced into a mixer containing about 500ml distilled water drop-wisely, and the mixing carried out at 22,000 rpm. The obtained oil-in-water emulsion was filtered under vacuum with pre-weighed filter papers (589/3; mesh \approx 2 μ m). Additional 500ml water was added to the mixing unit to further clean the residue. 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.

2.3.1 Solid phase extraction

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

2.3.2 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.

2.4 Analytical Methods

2.4.1 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-phenylmethylpolysiloxane (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 polyethylene 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 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 [19].

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 occurred 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 Innwax (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.

2.5 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 applied in a spill-over (500 µl 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.

2.6 GPC

Gel permeation chromatography (GPC) was carried out on an Agilent 1100 Series equipped

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

3. RESULTS AND DISCUSSION

3.1 Separation

The data obtained from the fractionation is presented in Table 2. As shown in Table 2, water constitutes about 24% of whole BCO. This value falls within the range of water content in most BCO [20, 21]. After 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 \pm 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.

3.2 Analysis of Fractions

3.2.1 GC-MSD

Chromatograms of different fractions of the samples analysed using GC-FID are shown as overlays in Fig. 2. 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 topmost chromatogram (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.

Table 2. Average yields of different BCO fractions

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

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

3.2.2 GPC

The lyophilisation of sample is accompanied by a loss of small size molecules, but this has little or no effect on samples being prepared for GPC analysis. GPC is conceived for oligomers and high molecular compounds. So molecular masses below 150 were not calibrated for this chromatography. Reference materials, listed in Fig. 3(A). GPC analyses of BCO (BE/BS-10) and the respective fractions are compared in Fig. 3(B). The untreated BCO shows components distribution; relevant peaks are observable in the monomer, dimer and also in higher molecular sections. The GPC plots of the FDR of precipitation water and FDR of SPE polar fractions are quite similar in distribution, but for a variation in the concentrations of different molecule sizes. Pyrolytic lignin (PYL) plot indicates that the fraction contains the highest polymeric sizes but with some dimers and oligomers. But the plot of milled wood beech lignin (MWL) in 3(A) shows that only polymeric

lignin were found in the sample compared to the PYL, but the concentration of the high molecular size is greater in MWL. This observation correlate with the views of earlier workers that

showed that the average molecular weight of MWL is about ten times larger than that of pyrolytic lignin indicating a severe degree of degradation during pyrolysis [22].

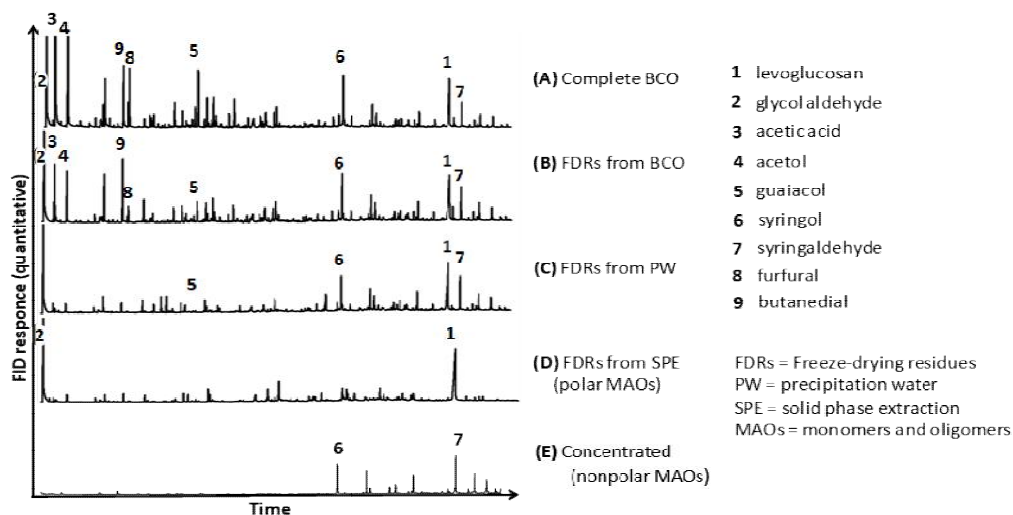


Fig. 2. Overlay GC-FID chromatograms of BCO fractions

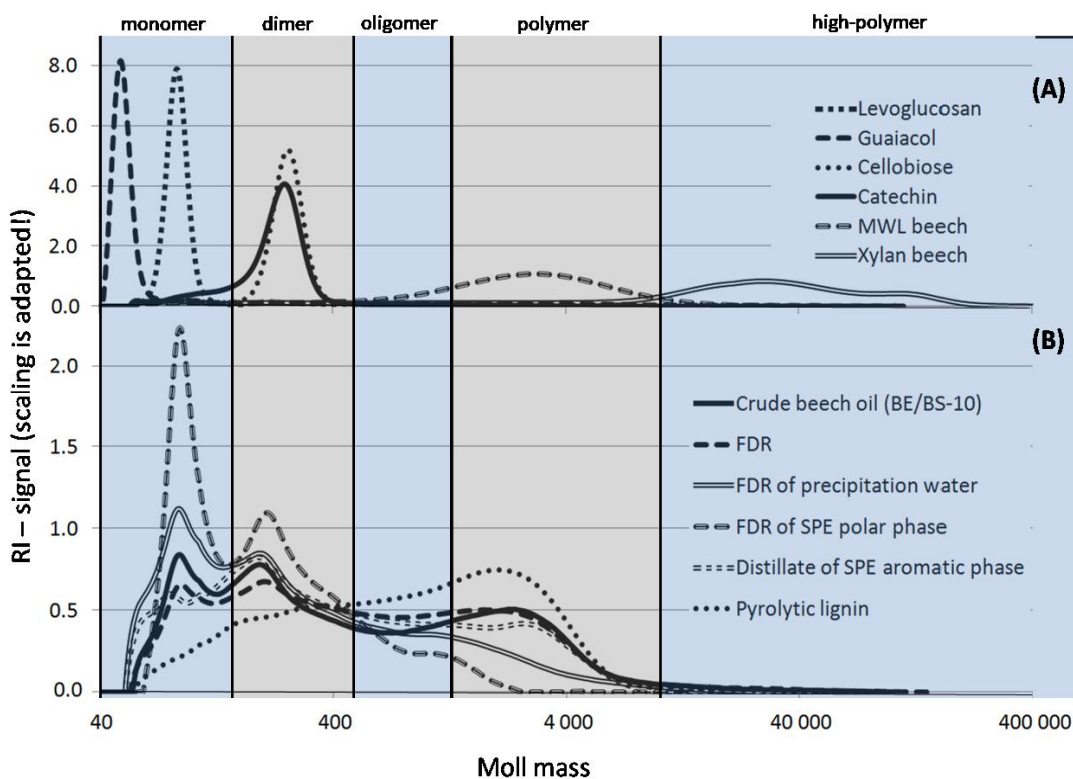


Fig. 3. Summary of GPC-chromatograms

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

3.3.3 GC-MS/FID of acetylated fractions

The result of the sugar-related fraction, i.e. the SPE polar fraction of the BCO is shown in Table

3 and Fig. 4. It is evident from the result that levoglucosan remained the dominant sugar product in the fraction, constituting about 3 wt.%. This component is an anhydrosugar

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

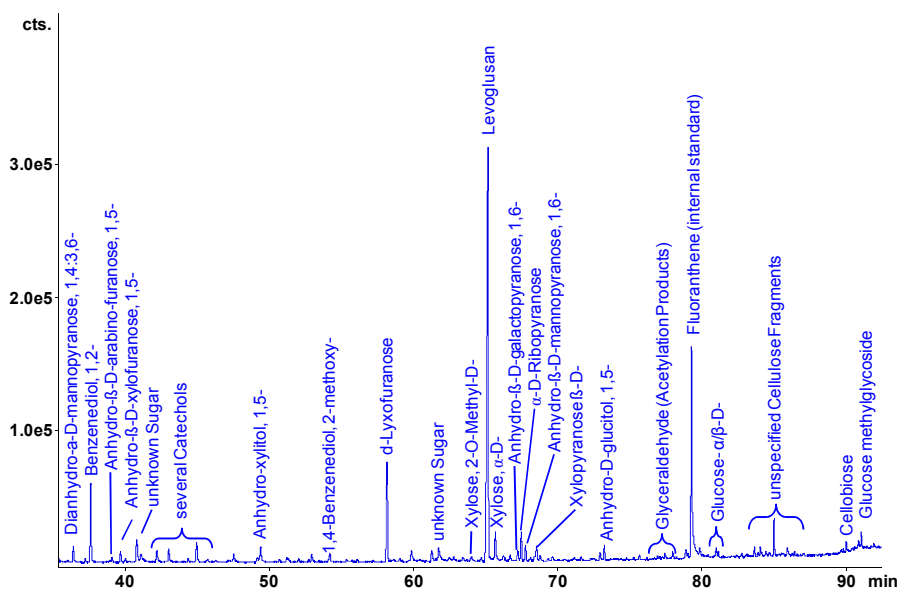


Fig. 4. A section of the chromatogram of SPE acetylated polar fraction

of glucopyranose. The analysis revealed the presence of analogous anhydro-compound of other sugar such as Anhydro-β-D-arabinofuranose, 1,5-, Anhydro-β-D-xylofuranose, 1,5-, Anhydro-β-D-mannopyranose, 1,6-, Anhydro-β-D-galactopyranose1,6- etc. Some of these components have hitherto been classified as unknown sugar prior to this fractionation and analysis. They are thought to have formed from their respective hemicellulose in the manner similar to the formation of levoglucosan from cellulose. However, the presence of pure sugar such as Xylose, α-D- and Glucose, α-D- in the chromatogram was not envisaged in the fraction bearing in mind the nature of the conversion process through which the BCO produced. In all, the total amount of quantifiable sugar was far below 7 wt. % of the BCO.

4. 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. It is evident from the result that levoglucosan remained the dominant sugar product in the fraction, 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 quantitatively evaluate the analytical procedure.

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COMPETING INTERESTS

Author has declared that no competing interests exist.

REFERENCES

1. Bridgwater T. Challenges and Opportunities in Fast Pyrolysis of

Biomass: Part II. Johnson Matthey Technology Review. 2018;62(2):150-60.

2. Jiang Q, Wang L, Hei X, Cheng J, Lu X, Lin Y, Yu G. ARAe-SOM+ BCO: An enhanced artificial raindrop algorithm using self-organizing map and binomial crossover operator. *Neurocomputing*. 2018;275:2716-39.

3. Begnaud F, Chaintreau A. Good quantification practices of flavours and fragrances by mass spectrometry. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*. 2016;374(2079):20150365.

4. Tessarolo NS, dos Santos LR, Silva RS, Azevedo DA. Chemical characterization of bio-oils using comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry. *Journal of Chromatography A*. 2013;1279:68-75.

5. Elliott DC, Meier D, Oasmaa A, van De Beld B, Bridgwater AV, Marklund M. Results of the international energy agency round robin on fast pyrolysis bio-oil production. *Energy & Fuels*. 2017;31(5):5111-9.

6. Rasrendra C, Windt M, Wang Y, Adisasmito S, Makertihartha I, Van Eck E, Meier D, Heeres H. Experimental studies on the pyrolysis of humins from the acid-catalysed dehydration of C6-sugars. *Journal of Analytical and Applied Pyrolysis*. 2013;104:299-307.

7. Oasmaa A, Kuoppala E. Solvent fractionation method with brix for rapid characterization of wood fast pyrolysis liquids. *Energy & Fuels*. 2008;22(6):4245-8.

8. Abou-Yousef H, Steele P. Increasing the efficiency of fast pyrolysis process through sugar yield maximization and separation from aqueous fraction bio-oil. *Fuel processing technology*. 2013;110:65-72.

9. Garcia-Perez M, Chaala A, Pakdel H, Kretschmer D, Roy C. Characterization of bio-oils in chemical families. *Biomass and Bioenergy*. 2007;31(4):222-42.

10. Sipilä K, Kuoppala E, Fagernäs L, Oasmaa A. Characterization of biomass-based flash pyrolysis oils. *Biomass and Bioenergy*. 1998;14(2):103-13.

11. Ba T, Chaala A, Garcia-Perez M, Rodrigue D, Roy C. Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark. Characterization of

- water-soluble and water-insoluble fractions. *Energy & Fuels*. 2004;18(3):704-12.
12. Oasmaa A, Kuoppala E, Ardiyanti A, Venderbosch R, Heeres H. Characterization of hydrotreated fast pyrolysis liquids. *Energy & Fuels*. 2010;24(9):5264-72.
 13. Rasrendra C, Girisuta B, Van de Bovenkamp H, Winkelman J, Leijenhorst E, Venderbosch R, Windt M, Meier D, Heeres H. Recovery of acetic acid from an aqueous pyrolysis oil phase by reactive extraction using tri-n-octylamine. *Chemical Engineering Journal*. 2011;176:244-52.
 14. Meier D. New methods for chemical and physical characterization and round robin testing. *Fast pyrolysis of biomass: a handbook*. 1. Newbury, UK: CPL Press. 1999;92-101.
 15. Bayerbach R, Meier D. Characterization of the water-insoluble fraction from fast pyrolysis liquids (pyrolytic lignin). Part IV: Structure elucidation of oligomeric molecules. *Journal of Analytical and Applied Pyrolysis*. 2009;85(1-2):98-107.
 16. Brodzinski I, Meier D, editors. Development of analytical methods for bio crude oil (BCO). 2nd World Biomass Conference; 2004. Rom.
 17. Schmiedl D, Böringer S, Schweppe R, del Río J, editors. *Kraft Lignin Depolymerisation by Based Catalysed Degradation (BCB)—The Effect of Process Parameters on Conversion Degree and Structural Features of BCD-Fractions*. 13th European Workshop on Lignocellulosics and Pulp; Seville; 2014.
 18. Ötles S, Kartal C. Solid-Phase Extraction (SPE): Principles and applications in food samples. *Acta Scientiarum Polonorum Technologia Alimentaria*. 2016;15(1):5-15.
 19. Windt M, Meier D, Lehnen R. Quantification of polypropylene (PP) in wood plastic composites (WPCs) by analytical pyrolysis (Py) and differential scanning calorimetry (DSC). *Holzforschung*. 2011;65(2):199-207.
 20. Zhang Q, Chang J, Wang T, Xu Y. Review of biomass pyrolysis oil properties and upgrading research. *Energy Conversion and Management*. 2007;48(1):87-92.
 21. Mullen CA, Boateng AA, Goldberg NM, Lima IM, Laird DA, Hicks KB. Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis. *Biomass and Bioenergy*. 2010;34(1):67-74.
 22. Scholze B, Hanser C, Meier D. Characterization of the water-insoluble fraction from fast pyrolysis liquids (pyrolytic lignin): Part II. GPC, carbonyl groups, and ¹³C-NMR. *Journal of Analytical and Applied Pyrolysis*. 2001;58:387-400.

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