GC-MS Analysis and Characterization of Bio-Oil from Sweet Potato Peel - A Putative Bio-Fuel

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Abstract: Due to the excessive oil consumption alongside with its possible depletion and the need to find new sources of products with reduced ecological footprint, urges to conduct the research towards to new processes using biomass, especially residues, as sources of raw materials. The acid liquefaction catalyzed by the *p*-toluene sulfonic acid of sweet potato peel waste was conducted under mild conditions leading to a bio-oil with a conversion of 85 %. The products were analyzed by ATR-FTIR, SEM, GC-MS and elemental analysis. The results have demonstrated the liquefaction of sweet potato peel is achievable and affords a high carbon content bio-oil composed mainly by carbohydrate compounds and esters showing that the liquefied products can be envisaged as a chemical platform for several uses, in particular as bio-fuel due to its esters content.

Keywords: Sweet potato peel, liquefaction, bio-fuel, SEM, ATR-FTIR, GC-MS.

INTRODUCTION

The growing concern regarding environmental issues, led to research activities that strive to discover and develop alternatives to petroleum. The need for such alternatives is not only due to the likely lack of sources of fossil raw materials as well as due to the tremendous harmful environmental impact that such sources cause. Scientists are aiming to find solutions that involve the use of waste with no value whatsoever to produce added-value products. The upcycling of residues as raw materials have been attempted over the years [1-3].

Liquefaction of biomass, such as lignocellulosic residues (containing cellulose and lignin in their composition) is a process that has been widely investigated and consists in the depolymerization and solubilization of biomass under mild conditions in polyhydric alcohols. In this last particular case, sometimes it is also referred as biomass solvolysis. Esteves *et al.* (2017) studied the use of raw cork planks from *Quercus suber* for the production of added-value products via polyol liquefaction. The best conditions for higher yields were 160°C for 1h, glycerol-to-PEG400 ratio of 1:9, biomass-to-solvent ratio of 1:6 and 3% of sulfuric acid as catalyst. They found that it was possible to use this liquefied cork in polyurethane foams with

acceptable quality [4]. Briones *et al.* (2011) aimed to assess the feasibility of obtaining polyols from several abundant lignocellulosic agroindustrial residues such as date seed, olive stone, corncob, rapeseed cake and apple pomace, with yields above 90% for almost all resources at 160°C for 1h, weight ratio polyethylene glycol/glycerol/sulphuric acid of 80:20:3, biomass-to-solvent ratio of 0.25. They showed that polyurethanes could be produced using liquefied products obtained from date seeds as a source of polyols. The multifunctional liquids from apple pomace, olive stone, corn cob and rapeseed cake could be used as precursor in polyurethane production and as a partial replacement of the polyhydroxy alcohol in the polyester synthesis, due to the large number of hydroxyl groups available [5]. Jasiukaitytė-Grojzdek *et al.* (2012) used beech *Fagus Sylvatica* milled-wood lignin as a model compound to elucidate lignin structural changes during the liquefaction in ethylene glycol under catalysis of sulphuric acid or p-toluene sulfonic acid monohydrate. They identified 4-hydroxybenzoic acid, vanillic acid, syringic acid, vanillin, coniferyl alcohol, syringaldehyde, sinapyl alcohol, 3,5-dimethoxyphenol, and ferulic acid at the beginning of the lignin liquefaction; and aliphatic, aromatic (syringyl- and guaiacyl-based) esters and acids with the treatment time due to the reaction with ethylene glycol. The simultaneous reactions of degradation and condensation between the degraded fragments of lignin and ethylene glycol gave the final lignin liquefaction product composed of high-molecular mass and low molecular mass fraction [6]. Kunaver *et al.* (2011) did their research on high energy ultrasound

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method for the depolymerization and liquefaction of medium density fiberboard, veneered particleboard, particleboard, oriented strand board, plywood and wheat straw. They demonstrated that the reaction times were shortened by a factor of up to nine with ultrasounds, giving smaller residual particles (wood particles not completely liquefied), without observing any influence on the hydroxyl number of the final products and without any evidence of adhesive or polymeric coatings on the residual particles [7]. Our group has also examined this process but applied to cork [8]. We found that the liquefaction of cork under ultrasounds can be accomplished in a faster way, producing polyhydroxy compounds, a feedstock platform which can be widely used in industry (i.e., polyurethane industry)**.** The work presented herein continues the studies that our research group has been conducting, over the last few years regarding the valorization of wastes towards liquefaction. Our intention is the development of the knowledge of which are the best raw materials from industrial wastes for the production of energy and value-added products, mitigating the harmful effect that the persistent and overuse of petroleum has inflicted to the environment. Aside from cork [9], other natural residues have been considered in our research such as paper sludge**,** swine manure and pinewood sawdust. The elemental analysis of both raw materials and liquefied product allowed to plot the van Krevelen diagram showing that the afforded bio-oils are more closely related to hydrocarbons than to its primitive feedstocks, revealing a strong potential of liquified paper sludge to be used as bio-petroleum [10].

Bio-oil quality and yield is affected by the type of raw material, thermochemical process and operating parameters applied. It is a dark brown and viscous liquid, mainly composed of acids, alcohols, aldehydes, esters, ketones, phenols, and guaiacol. Zhang *et al*. (2019) summarized bio-oil main characteristics in a table, comparing it to heavy petroleum fuel oil.

Sweet potato can be casted as an essential product to solve some of the issues regarding several societal challenges such as food, energy and natural resources. In fact, lately, with the appearance of new cultivar varieties and new uses of this plant, wastes are being generated causing harmful effects in the environment [12].

The chemical composition of sweet potato peel is related to lignocellulosic materials since its primary constituents are cellulose, hemicelluloses, lignin along with other components. Starch and suberin are amongst of some of those compounds which may confer different chemical properties to the resulting oil from the liquefaction of sweet potatoes rind [12-14]. Thus, this residue can be seen as a potential feedstock for biorefineries and for the production of added-valuable products, in particular the compounds resulting from cellulose decomposition which leads to the formation of carbohydrate scaffolds.

Being a local Portuguese product, in the present study we used sweet potato waste as a source of lignocellulosic biomass to evaluate the acid liquefaction in polyhydric alcohol. The liquefied product was characterized by Gas Chromatography/Mass

Table 1: Physical Characteristics of Liquefaction-Derived Bio-Oil and Heavy Petroleum Fuel Oil [11]

Properties	Bio-Oil	Heavy Petroleum Fuel Oil
pH	3.8–4.0	-
Acid value (mgKOH/g)	1.8	-
Density (g/cm^3)	1150–1200 at 40 ˚C	940
Viscosity (cP)	650 at 40 ˚C	180 at 40 ˚C
HHV (MJ/kg)	28.42	40
C (wt.%)	66	85
H (wt.%)	11	11
O (wt.%)	12	1.0
N (wt.%)	9	0.3
S (wt.%)	1	-
Water content (wt.%)	13–12	0.1
Ash content (wt.%)	0.4–0.7	0.1

Spectroscopy (GC-MS), Attenuated Total Reflectance - Fourier Transformed Infrared Spectrometer analysis (ATR-FTIR), elemental analysis, while the morphology of the remained solid residue observed by Scanning Electronic Microscopy (SEM).

MATERIALS AND METHODS

Materials and Chemicals

The sweet potato peel studied was removed from the cultivar with a peeler (Figure **1A** and **1B**). The peel thickness was 1.35 ± 0.21 mm and still containing ca. of 72% of flesh (Figure **1C**). The water content was determined by weight loss. Samples of the peel were minced and placed in an oven at 70 °C; the weight was controlled until no change was observed. The moisture content was determined to be on average 75%. Afterward, sweet potato peel was minced (Figure **1D**) and frozen for further use. The reagents used were chemical grade (Sigma-Aldrich).

Figure 1: Potato peel samples used. **A** – peel (exterior), **B** – peel (interior), **C** – potato peel thickness, **D** – potato peel minced.

Liquefaction Procedure

The procedure was adapted from the work developed previously by Mateus *et al*. regarding the acid-catalyzed liquefaction of lignocellulosic biomass, namely cork [8].

Generally speaking, the experimental apparatus for the liquefaction process comprised, briefly, a reactor, that was equipped with heating and stirring equipment. The reactor unit was embodied with a tailor-made

device, like a Dean-Stark one, to remove, by simultaneous distillation, the water present in biomass as well as that formed during the reaction [10]. The acid liquefaction process was conducted under atmospheric pressure at moderate temperature (160°C).

In this particular case, a 2000 cm^3 reaction reactor loaded with a solvents mixture (2-ethyl hexanol: diethylene glycol = 3:1, w/w), 3 % w/w of p-toluene sulfonic acid and 10% w/w (considering its dry weight) of sweet potato peel both based on the solvent mixture. The whole mixture was subsequently mechanical stirred and heated up to 160°C. After that, the reactional mixture was left to cool until 80ºC and filtered. The remaining solid residue was then washed with methanol and acetone to remove any residual oil still present in the solid residue. Afterward, it was dried in a stove and weighted for the calculation of the conversion ratio.

Measurement of Liquefaction Extent

The conversion yield was gravimetrically evaluated on the basis of the residue content (unreacted raw material) after the liquefaction workup procedure. The weight of the obtained residue, which was dried in an oven set to 120 °C until no change in weight was observed, was used to calculate the conversion rate percentage based on equation **1**.

$$Conversion\ yield\ (\%) = \left(1 - \frac{M_2}{M_1}\right) \times 100 \qquad (1)$$

where M_1 is the initial mass of biomass, M_2 the mass of the insoluble remains at the end of the liquefaction procedure.

Scanning Electron Microscopy Observations

The raw material and the liquefaction residues were micrographed using a Hitachi S-2400 equipment, with a 15 kV beam. The samples were sputtered coated with a thin layer of gold avoiding the electrostatic charging during scanning. The solid residues obtained after the liquefaction process, usually referred to as humin, were micrographed by SEM at a magnification of 25 and 150×, while the raw material was observed at 50 and 250×.

Attenuated Total Reflectance - Fourier Transformed Infrared Spectrometer Analysis

Both potato peel and its liquefied products were analyzed with FT-MIR spectrometer from BOMEM

FTLA2000-100, ABB CANADA, equipped with a light source of SiC and a DTGS detector (Deuterated Triglycine Sulfate). The used accessory was an ATR with single horizontal reflection (HATR) containing a ZnSe crystal of 2mm diameter from PIKE Technologies. The spectra in the range of 600-4000 cm^{-1} were collected with the BOMEM Grams/32 software.

Elemental Analysis

The chemical composition involving the carbon, hydrogen, and nitrogen content was obtained by elemental analysis with a LECO TruSpec CHN analyzer instrument, being sulfur quantified in a LECO CNS2000. The oxygen content was estimated by difference, using the equation 2,

$$O\,(\%) = 100 - (C + H + N + S)\,(\%) \tag{2}$$

Gas Chromatography/Mass Spectroscopy Analysis

GC-MS analysis of the bio-oil was performed in Trace GC-DSQ (MS) Unicam apparatus. The column used is an RTx-5MS capillary column 30 m × 0.25 mm x 0.25 µm film thickness. The injection of 1 µl of bio-oil sample is performed on Splitless mode 1min with Helium as a carrier gas. The injector temperature was maintained at 250 °C. The GC oven temperature was programmed from 60 °C (2 min) to 120 °C at a rate of 30 °C·min^{-1}, 120 °C (2 min) to 300 °C at a rate of 5°C·min^{-1} and held 10 min, 300°C to 320 °C at a rate of 5°C min^{-1} and held 2 min. The transfer interface and the ion source in the mass spectrometer are maintained at 250 °C. Bio-oil sample was dissolved in dichloromethane (10 % w/w) and filtered with a 0.45 µm PTFE filter before analysis. The National Institute of Standards and Technology spectral library was used to identify the compounds.

van Krevelen Correlation

van Krevelen diagrams are graphical plots developed and used to study the difference in chemical composition of kerogen. The van Krevelen diagram thus appears well suited to amplify and expose compositional differences within and between organic products. The diagram was plotted as describes elsewhere [10]. Ethyl levulinate, an ester, was used as a reference compound since it is a purported bio-fuel [15].

RESULTS AND DISCUSSION

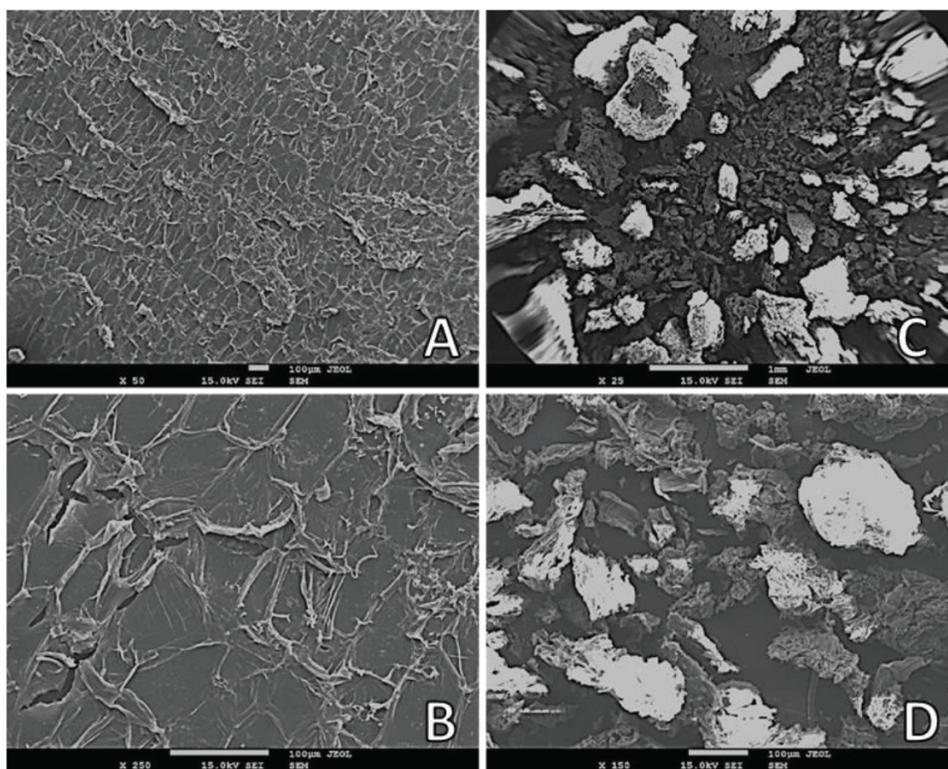The liquefaction process was applied to sweet potato peel waste, raw, without any pretreatment

Figure 2: Micrographs of: **A** – Sweet potato peel (50 ×); **B** - Sweet potato peel (250 ×); **C** – Solid residue from the liquefaction of sweet potato peel (25 ×); **D** – Solid residue from the liquefaction of sweet potato peel (150 ×).
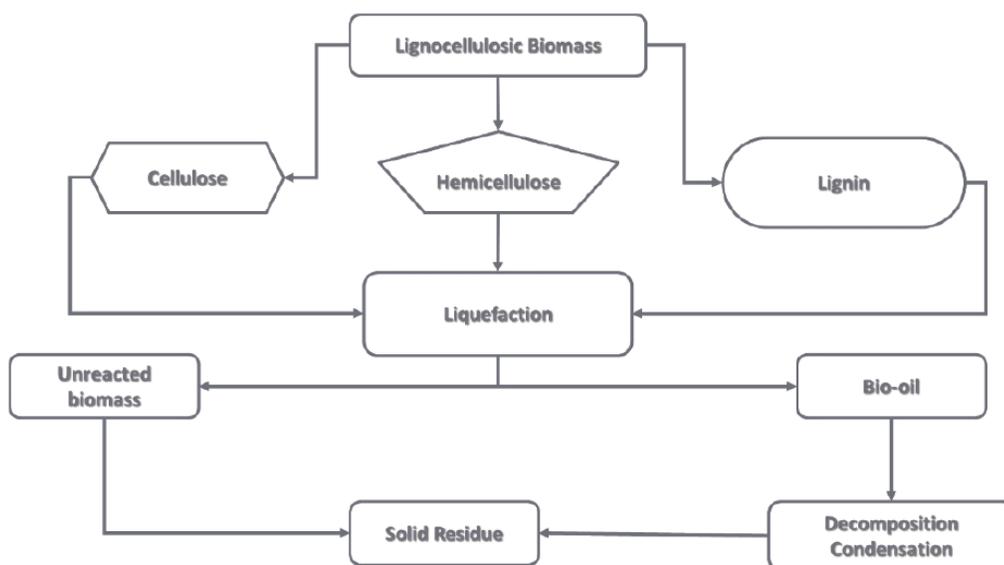
Figure 3: Process diagram of biomass liquefaction.

whatsoever. Previous studies conducted with regular potato have shown that the drying process does not improve the liquefaction yield, in fact, such procedure leads to worst results [16]. In addition, water plays a significant role in the hydrolysis of esters, eters and acetal bonds. Another advantage is that the energy that would be required to dry the feedstock is saved. The water resulting from the dehydration and condensation reactions along with that present in the raw material is removed during the process by destilation. A high conversion yield, 85%, was achieved after 60 minutes at 160 °C. After the workup, the reactional mixture afforded two products: a brownish oil and black solid residue. This later one was used to evaluate the conversion yield and then subject to SEM analysis. The oil was characterized by ATR-FTIR, GC-MS, and elemental analysis.

Figure **2** shows the SEM micrographs of raw materials as well as the liquefied sweet potato peel solid residues resulting from the liquefaction reaction after 60 min at 160 °C.

Figure **2A** and **2B** present the morphology of the sweet potato peel before its liquefaction. A very regular surface, corresponding to the celular structure of the skin of the potato is quite visible. After liquefacion (Figure **2C** and **2D**), it is clear that most of the sample was remarkably disrupted although it can also be observed that a small part of the sample, corresponding to unconverted potato skin, retained the fibrous and regular structure. Moreover, in addition to the structures that results from unreacted biomass a small solid particles, that may result from the

decomposition of the products formed during liquefaction (humin), are also detected, probably resulting from the condensation of biocrude products into insoluble polymer. In general we can suggest that solid residue may result from two sources, unreacted raw material as well as from insoluble products resulting from decomposition/condensation reactions that may occurs in parallel with the depolimerization of the lignocellulosic polymers (Figure **3**).

The afforded brownish bio-oil and the starting feedstock were screened by ATR-FTIR experiments (Figure **4**) to provide the information regarding the chemical composition of the obtained bio oil, a mixture of compounds that result from the innumerous reaction that may occur during the liquefaction process. Table **1** indicates the most relevant bands and the respective assignment.
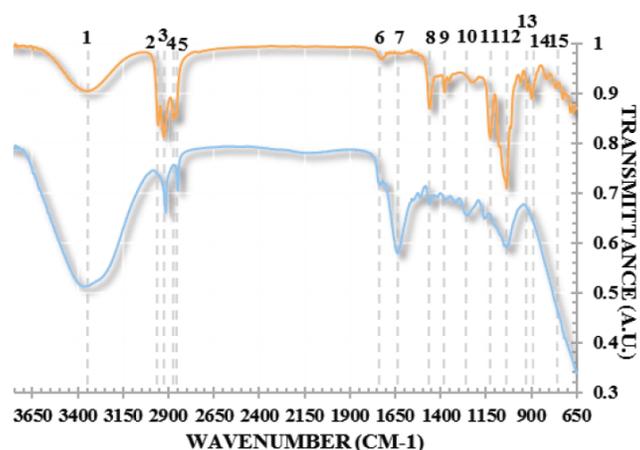

Figure 4: ATR-FTIR spectra: Above – liquefied sweet potato peel, Below – sweetpotato peel.

Table 2:   ATR-FTIR Signals Assignment

Peak Number	$\overline{v}$ (cm^{-1})	Band assignment	Potential compounds	Ref.
1	3334	O-H stretch	hydroxyl groups water	[17]
2	2940	C-H stretch aliphatic chains		[18-20]
3	2920			
4	2862			
5	2856			
6	1734	C=O stretch	carboxylic acids, esters	[21]
7	1635	deformation band	water	---
8	1460	C–H deformations and CH$_2$ symmetric bending	carbohydrates cellulose derivatives	[21-24]
9	1377	aromatic C-H deformation	syringyl rings (from lignin)	[24]
10	1255	C-O-H bend	CH$_2$OH (side chain) D-glucose	[25]
11	1132	C-O-C stretch asym.	Lignin, carbohydrates	[21]
12	1035	aromatic C-H in-plane deformation	guaiacyl moieties (from lignin) phenolic moieties	[23]
13	901	(1→4) bond C-O and the C-C stretch	cellulose, glycosidic linkages, β-glycosidic linkages	[18,26,27]
14	896	C–H bend (anomeric)	carbohydrates, cellulose	[22,26]
15	~800	C–H bend (anomeric)	α-glycosidic linkages	[18]

Concerning the collected vibrational spectra acquired for both samples, a broadband of 3334 cm^{-1} was detected. This signal is related to OH groups, and to water in the case of the sweet potato skin.

Usually, the products derived from the liquefaction of lignocellulosic products, namely from cellulose and hemicellulose, are embodied of polar characteristics with high hydroxyl and acid groups content, although lacking long aliphatic chains. However, the suberin present in the skin of the sweet potato is a relevant component of peel and changes the final composition of liquefied products conferring higher apolar characteristics to obtained bio-oil. On the potato peel spectra, we can observe two bands at 2920 and 2862 cm^{-1} that can be attributed to the stretching vibration of aliphatic C-H group (from cellulose, hemicellulose, lignin, and suberin). A very discrete carbonyl band at 1734 cm^{-1}, can also be found, such signals can be attributed to the ester bonds [19]. The same bands can be found within the liquefied products, which demonstrate that the major components (lignocellulosic derivatives) of potato peels are present in the analyzed sample. Although two additional signals attributed to the C-H group, can be found at 2940 and 2856 cm^{-1},

suffered a slight displacement, probably due to the medium, or to the solvent, 2-ethyl hexanol, which is still present in the sample.

In the sweet potato peel spectrum, a water deformation band at 1635 cm^{-1} is remarkably present. The high intensity of this particular band may hide some of the bands from lignin and suberin. Usually, in these cases, the interpretation of the collected data in absorbance units may enable to detect weaker signals next to strong signals. Although, in this instance, the analysis of the data in such unit does not lead to a different interpretation than that made from transmittance units. Nevertheless, the high intensity of the water bands does not allow to identify some of the bands; the designated ones confirmed the presence of the functional groups that are expected to be found within the sweet potato fresh skin. Between the two spectra, the amount of water content is remarkably different, after the liquefaction procedure the band 1635 cm^{-1}, is almost non-existent, demonstrating that in fact, the bio-oil obtained features a low moisture content.

Within the spectra, it is possible to observe the characteristic of aromatic rings and carbohydrates

bands in the fingerprint region of the spectra. The aromatic bands, typical from lignin derivatives, can be identified at 1460, 1377 and 1035 cm^{-1}, related to benzene rings, syringyl rings, and guaiacyl moieties, respectively, meaning that lignin was liquefied. Regarding the bands corresponding to carbohydrates resulting from the extensive depolymerization of cellulose are also recognized at 1255, 1132, 909, 896, ~800 cm^{-1}.

A sample of the bio-oil was subjected to GC-MS analysis. The major compounds, which were possible to identify within the bio-oil as shown in Table **2**. By GC-MS almost 69% of the sample constituents, excluding solvents, were identified. Those compounds can be grouped as 2-ethyl hexanol esters, carbohydrates derivatives and a small amount of others, 19.5 %, 40.6 % and 8.72 %, respectively.

These results suggest that high content of carbohydrate's macromolecules, namely, starch, cellulose, and hemicellulose led to smaller compounds towards hydrolysis of the anomeric bond, dehydration, oxidations and elimination reactions. The organic acids formed during the liquefaction process, which occurs in acidic medium, promptly react with 2-ethyl hexanol

Table 3:   List of Chemical Compounds Identified in Bio-Oil By GC-MS Analysis

	RT (min)	Compound	Area[a] (%)
1	5.76	2-Ethylhexyl formate	0.23
2	6.09	2-Ethylhexyl acetate	0.16
3	7.46	1,3,4,6-Di-anhydro-α-D-glucopyranose	0.03
4	8.32	2-Ethylhexyl butanoate	0.32
5	8.66	2-Ethylhexyl methoxyacetate	0.12
6	10.72	Di-(2-ethylhexyl) malonate	0.44
7	11.87	2-allyl-5-t-butylhydroquinone	0.91
8	12.6	3-methylamino-1,2,4-triazole	0.32
9	13.26	Di-(2-ethylhexyl) pentanoate	11.89
10	15.45	Di-(2-ethylhexyl) ether	3.96
11	16.44	5-Methylfurfural	2.02
12	16.67	Di-(2-ethylhexyl) glutarate	0.97
13	17.75	Melibiose	0.22
14	18.88	Di-(2-ethylhexyl) maleate	0.52
15	19.8	1-O-(2-ethylhexyl)-glucitol [b]	0.69
16	20.78	6-O-(2-ethylhexyl)-glucitol [b]	0.76
17	21.26	Di-(2-ethylhexyl) oxalate	2.27
18	22.46	Di-(2-ethylhexyl) adipate	2.59
19	24.29	1-O-(2-ethylhexyl)-α-D-glucoside [b]	19.62
20	24.84	Trealose	8.23
21	25.89	Quinic Acid	1.51
22	27.7	1-O-(2-ethylhexyl)-β-D-glucoside [b]	2.07
23	28.21	β-Lactose	0.55
24	28.82	α-Lactose	0.73
25	29.17	D-Mannose	1.28
26	32.29	2,5-Di-O-methyl-D-Ribitol triacetate	0.58
27	32.72	1-O-(2-ethylhexyl)-α-D-mannofuranoside [b]	5.84
		Total of assigned area	68.72

[a]excluding DCM, DEG, and 2-Ethylhexanol peaks.
[b]the prefix "2-ethylhexanoyl" is indicated in place of the prefix "octyl", since is more likely to be a derivative from 2-ethylhexanol rather than n-octanol.

affording the corresponding esters. In addition, some glycosides are also generated by glycosylation of the carbohydrates moieties with 2-ethyl hexanol.

Samples of raw materials and the liquefaction products were subjected to elemental analysis (Figure **5**).
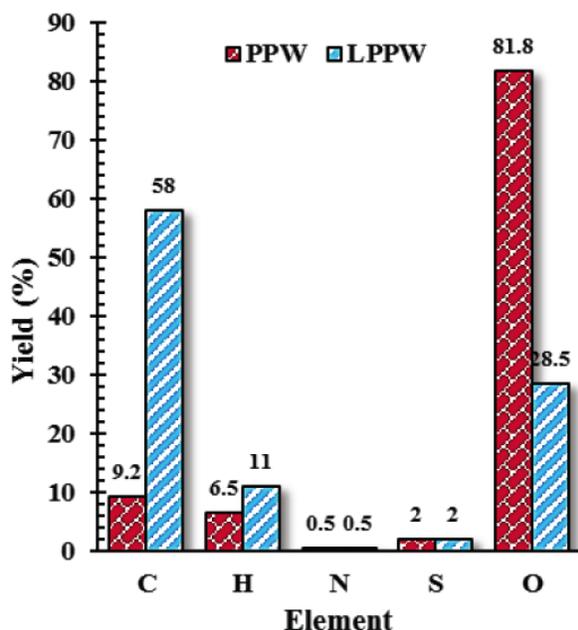

Figure 5: Elemental analysis of potato peel and liquefied potato peel waste.

The high content of oxygen verified on the feedstock is related to the moisture content. On the other hand, within the bio-oil is easily verified a high increase regarding the carbon content, which may be due to the removal of water during the liquefaction process. This reduction in the water content can also be verified in the ATR-FTIR spectrum. The high carbon content may be indicative that these products can be considered to be used as a bio-fuels.

The van Krevelen diagrams indicated that the afforded bio-oil might be embodied with great interest, in particular by its use as bio-fuel, underpinned by its high content of esters.

By observing the van Krevelen diagram, it is possible to see that the bio-oil is closer to the levulinate than to the initial biomass. This observation leads us to conclude, that chemically, there is a greater proximity between levulinic ester and the bio-oil, than between the bio oil and the initial raw material (Figure **6**). The bio-oil obtained in contrast with the primitive has a high carbon content and low levels of moisture, enhancing its properties as bio-fuels.
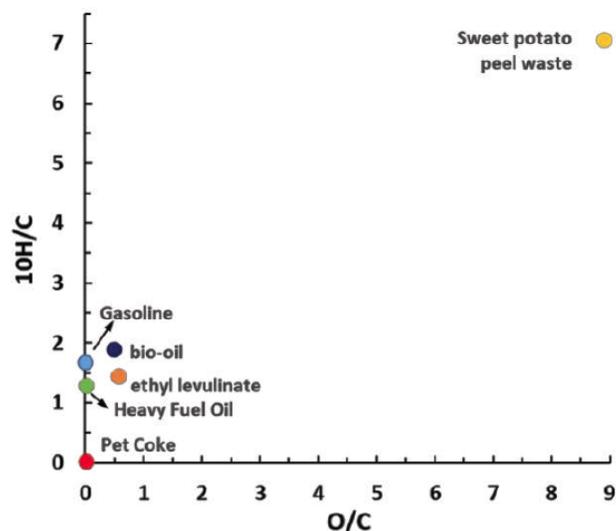

Figure 6: van Krevelen diagram of sweet potato peel and the corresponding liquefied product comparing with some of the market fuels.

CONCLUSIONS

The results have demonstrated that the residue resulting from sweet potato processing industry can be considered a feedstock to be used for acid-catalyzed liquefaction, under mild conditions, affording the targeted bio-oil in high yield. The SEM micrographs clearly indicate the breakdown of the well-defined structure of sweet potato peel. Irregular particles and solid residues resultant from the decomposition of the products generated during the process of liquefaction can be observed in the SEM micrographs. The elemental analysis alongside with the FTIR spectra has demonstrated that spite the high moisture content, the feedstock was, in fact, depolymerized. Such remark can be sustained by the absence of the 1635 cm^{-1} water peak in the infrared spectra as well as the significant decrease of the oxygen content detected in the elemental analysis results. The GC-MS analysis disclosed part of the chemical profile of the bio-oil, indicating that a significant faction is composed by carbohydrate derivatives followed by high amounts of esterified compounds. These later ones confer the afforded bio-oil the potential of use as a bio-fuel. Despite the obtained results, further studies should be conducted to identify other potential uses for the produced bio-oil.

ACKNOWLEDGMENTS

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