

# Acid Liquefaction of Potato (*Solanum tuberosum*) and Sweet Potato (*Ipomoea batatas*) Cultivars Peels – Pre-Screening of Antioxidant Activity/Total Phenolic and Sugar Contents

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In the present study, the liquefaction of both regular and sweet potato peels was conducted to investigate the bio-oil produced, the sugar and total phenolic content, and antioxidant activity. Initially, the bio-oil obtained after liquefaction was partitioned into two different fractions, a hydrophilic fraction and the other consisted of the portion that contained the apolar compounds. Afterward, the samples of the whole bio-oil, aqueous extract, and organic phase of both cultivars were analyzed by attenuated total reflection- Fourier Transform infrared (ATR-FTIR) spectroscopy, hydroxyl number, and acid value. This was done in combination with assessment of the sugar and total phenolic contents and antioxidant activity. The samples demonstrated a considerable content of phenolic moieties in their composition. The antioxidant activity, which was assessed by the 2,2-diphenyl-1-picrylhydrazyl radical method, revealed that the antioxidants of the liquefied products and its extracts were generally better than that of butylated hydroxytoluene. Glucose, sucrose, and maltose were identified and quantified within all of the samples.

*Keywords:* Potato; Sweet potato; Peel; Liquefaction; Antioxidant activity; Total phenolic content; ATR-FTIR

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## INTRODUCTION

Scientists are focused on finding solutions for the use of wastes with no value to produce value-added products. The utilization of waste residues as raw materials has been attempted many times over the years. In general, these raw materials (*e.g.*, agricultural residues, wood, municipal solid waste, dedicated energy crops, industrial wastes, *etc.*) are categorized as feedstock classified biomass (Arapoglou *et al.* 2010). In this work, the authors concentrated on, and allocated resources to, finding a solution to mitigate potato peel waste (PPW). According to the data of the Food and Agriculture Organization of the United Nations (FAO), more than 300 million tons of PPW was produced in 2014, and that amount has continued to increase annually (Food and Agriculture Organization 2016). The waste residues resulting from the potato industry represents approximately 27% of the weight produced. Composed mostly of its peel, this waste residue causes a remarkable problem in its management, and it is necessary to find a solution to decrease its

environmental impact (Schieber *et al.* 2001; Guechi and Hamdaoui 2016). The potato industries are extensively supporting research and development activities focused on environmentally friendly and sustainable solutions. Because PPW is prone to rapid microbial spoilage, it is usually used for feeding livestock. (Maske and Satyanarayan 2012). This waste is described as having a broad range of biological properties, such as antioxidant, antibacterial, apoptotic, chemopreventive, and anti-inflammatory properties (Wu 2016). To use this waste as only livestock feed leads to the loss of raw material with considerable economic potential (Wu 2016). The main components of PPW are usually water, starch, cellulose, hemicellulose, fermentable sugars, lignin, proteins, polyphenols, and alkaloids (Izmirliloglu and Demirci 2012; Khawla *et al.* 2014; Liang and McDonald 2014; Liang *et al.* 2014; Chintagunta *et al.* 2016; Guechi and Hamdaoui 2016). Thus, this residue can potentially be utilized as feedstock for biorefineries and for the production of value-added products. In fact, due to the higher content of sugars, potato peels can be used as a substrate to produce via enzymatic hydrolysis to produce, for instance, ethanol (Arapoglou *et al.* 2010) or acetic acid (Betiku and Adesina 2013).

Several studies have researched the antioxidant activity of potatoes (Wu 2016). In fact, its skin contains up to ten times more antioxidants than in its pith (Fig. 1) (Singh *et al.* 2011; Wu *et al.* 2012; Albishi *et al.* 2013). The mixture of phenolic compounds identified in potatoes consists of free phenolic molecules and phenolic molecules that are esterified or bonded to other moieties. Chlorogenic, caffeic, *p*-coumaric, and ferulic acids are some of the antioxidant compounds (Farvin *et al.* 2012; Albishi *et al.* 2013).

The liquefaction of biomass, such as lignocellulosic residues (residues containing cellulose and lignin), is a process that has been widely investigated, and is used in the depolymerization and solubilization of biomass at moderate temperatures (120 °C to 180 °C) in polyhydric alcohols, which usually resorts to acid catalysts (Balat 2008; Jasiukaityte *et al.* 2009; Jasiukaitytė-Grojzdek *et al.* 2012; Kunaver *et al.* 2012; Briones *et al.* 2012; Hu and Li 2014; Hu *et al.* 2014).

Succinctly, the natural antioxidant properties of potato peel combined with its high carbohydrate content make it suitable for liquefaction. The purpose of this research was to study the products produced from such a process and determine if it is a suitable source of antioxidants that can be used in chemical reactions to replace synthetic ones like BHT, BHA, TROLOX, *etc.* Moreover, the liquefied products can be refined into chemical building blocks with high economic value.

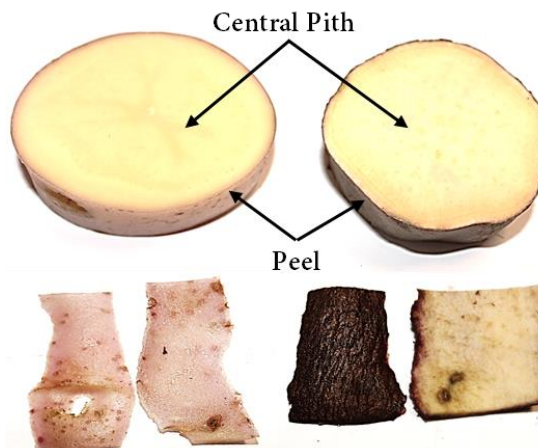


Fig. 1. Morphology of potatoes (left) and sweet potatoes (right)

In this paper, the authors decided to investigate the direct liquefaction of regular potato (*Solanum tuberosum*) peels and sweet potato (*Ipomoea batatas*) peels catalyzed by acids. Despite the differences between potatoes and sweet potatoes, they are both rich in carbohydrates, antioxidants, and fibers. (Liang and McDonald 2014; Salawu *et al.* 2015) The thermochemical direct liquefaction of the sweet potato peel and potato peel was conducted to access the respective liquefied products. The total phenolic content and antioxidant activity were determined for the hydrophobic (organic) and hydrophilic (aqueous) extracts from the liquefied products. The glucose, sucrose, and fructose content were also screened.

## EXPERIMENTAL

### Materials

The studied potato peel and sweet potato peel, which both contained an average of 80% water, were collected from cultivars purchased in a local Portuguese market. Subsequently, the material was minced and frozen. 2-Ethylhexanol, diethylene glycol, *p*-toluenesulfonic acid, tetrahydrofuran, methanol, acetone, potassium hydroxide (0.5 M and 0.1 M in ethanol, titration solutions) used were of chemical grade (Sigma-Aldrich, Sintra, Portugal). The maltose, sucrose, and D-glucose quantification kit (Cat. No. 1111395003 was purchased to R-Biopharm (Darmstadt, Germany). The chemical products used in this work for antioxidant characterization, such as 2,2-diphenyl-1-picrylhydrazyl (DPPH•) and gallic acid, were acquired from Sigma-Aldrich (Sintra, Portugal). Folin-Ciocalteu reagent, sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), and methanol were obtained from Merck (Oeiras, Portugal).

### Methods

The present study was divided into three phases, which corresponded to the workflow depicted below (Fig. 2).

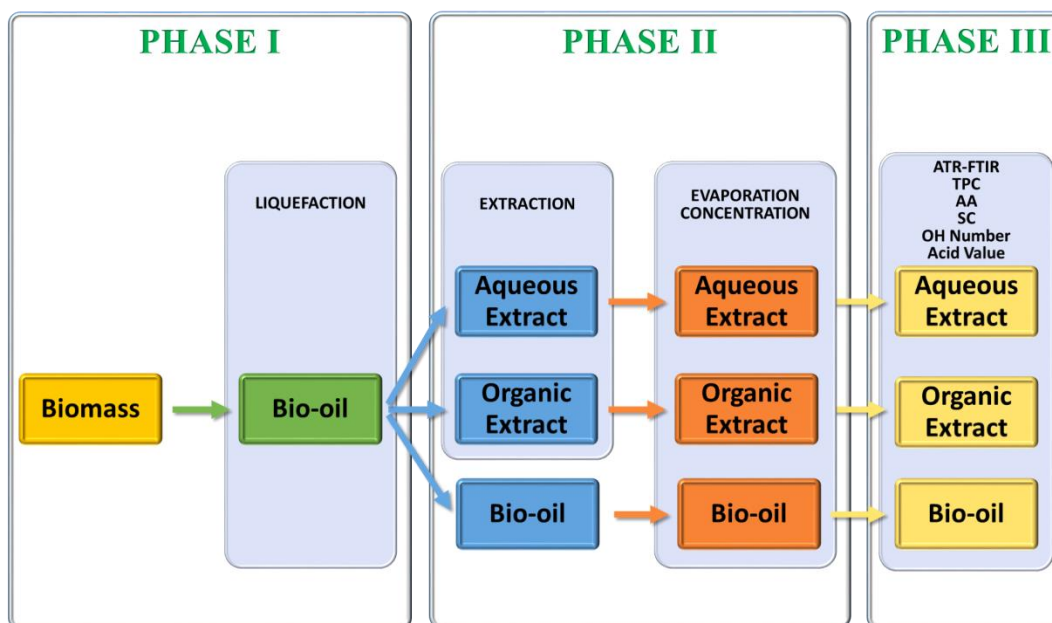


Fig. 2. Workflow established for this study

Phase I consisted of the liquefaction of potato and sweet potato peels. During Phase II, the samples of the bio-oil obtained were used for the separation of the hydrophilic components *via* aqueous extraction. The aqueous and organic phases, along with the samples of the bio-oil, were subsequently concentrated under a vacuum. Phase III, characterized the samples by ATR-FTIR, hydroxyl number, acid number, antioxidant activity (AA), TPC, and sugar content (SC).

#### *Liquefaction procedure*

The liquefaction was conducted according to Ventura *et al.* (2016). A reactor was loaded with a mixture of solvents (2-ethylhexanol:diethylene glycol = 2:1, w/w), 3% w/w of *p*-toluene sulfonic acid, and 10% w/w of biomass (both based on the solvent mixture, the weight of the potato peel was based on its dried weight). After the potato peel was added, the mixture was then stirred, and the temperature was set to 160 °C. Concerning the sweet potato peel, the process was investigated with three temperatures, which were 120, 140, and 160 °C. For both types of potato peels, the reaction was performed during several reaction times. The water content of the loaded sample, as well as that of the mixture formed during the reaction, was distilled during the reaction. The reactions were performed until no peel was visually distinguishable, and then the reaction was studied at different reaction times. After liquefaction, the reactor was allowed to cool to room temperature. Afterward, the mixture was filtered. A sample of the bio-oil was collected and extracted with distilled water several times until the water came out clear. The combined aqueous fractions were evaporated under reduced pressure, which produced a light brown syrup. The organic phase was also dried on a rotary evaporator under reduced pressure and was then dried over anhydrous magnesium sulfate to remove any residual moisture. A brown oil was obtained from this process.

#### *Measurement of liquefaction extent*

The conversion was gravimetrically evaluated by the residue content (unreacted raw material). The filtered residue was washed with acetone and methanol. The obtained solid residue was then oven-dried at 120 °C until no change in the weight was observed. The liquefaction yield was calculated according to Eq. 1,

$$\text{Liquefaction Yield (\%)} = \left(1 - \frac{M_r}{M_i}\right) \times 100 \quad (1)$$

where  $M_i$  is the initial mass of the biomass (grams), and  $M_r$  is the mass of the obtained residue (grams).

#### *Hydroxyl number and acid value determination*

The methodology adopted to determine the hydroxyl number and acid value was the same as described by Mateus *et al.* (2015).

The acid number was determined according to ASTM D4662-08 (2008) standard. The number of milligrams of KOH required to neutralize the acid of one gram of sample was calculated using Eq. 2,

$$\text{acid number } \left(\frac{\text{mg}_{\text{KOH}}}{\text{g}_{\text{polyol}}}\right) = \frac{[(A - B) \times 56.1 \times N]}{W} \quad (2)$$

where “A” denotes the volume of KOH solution required for titration of the sample (mL); “B” is the volume of KOH solution required for titration of the blank (mL); “N” is the normality of the KOH solution; and “W” represents the weight of the sample (g).

Regarding the hydroxyl number, it was determined according to ASTM D4274-05 (2005) standard. The hydroxyl number was corrected and calculated applying the Eq 3:

$$\text{hydroxyl number } \left( \frac{\text{mg}_{\text{KOH}}}{\text{g}_{\text{polyol}}} \right) = \frac{[(B - A) \times 56.1 \times N]}{W} + C \quad (3)$$

where “A” represents the volume of KOH solution used for titration of the sample (mL); “B” is the volume of KOH solution required the blank (mL); “N” is the normality of the KOH solution; “W” is the weight of the sample (g); and “C” denotes the acid number of the sample.

#### *Scavenging effect on 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical*

The antioxidant capacity of the samples was determined by the DPPH radical (DPPH•) method. This is a simple colorimetric method that is fast and highly sensitive. The DPPH• is characterized by its purple color, which shows strong absorption in the ultraviolet-visible (UV-Vis) region at 517 nm.

This method is based on the DPPH•’s capacity to be reduced by antioxidants. The reduction of DPPH• is easily noticeable because the colors change from purple to yellow, which causes a decrease in absorbance.

The scavenging effect on the DPPH• was performed in two phases. First, the decrease in absorbance as a function of time was monitored at intervals of 5 min at 517 nm to determine the inhibition time, so that the radical inhibition curves could be outlined. Then, in the second stage, the absorbance was measured at 517 nm, using methanol as a blank. After that, the reaction mixture was kept in the dark for 40 min, and the radical inhibition was determined for different concentrations of the extract. The inhibition percentage was plotted against the extract concentration, and a linear equation was properly fitted to derive the half-maximal inhibitory concentration ( $IC_{50}$ ). The results were expressed as  $\mu\text{g}$  of extract per mL of the reaction mixture ( $\mu\text{g}/\text{mL}$ ).

#### *Determination of total phenolic content (TPC)*

The total phenolic content (TPC) of the samples was determined through the Folin-Ciocalteu reagent method. This is the most attractive spectroscopic method for determining the TPC due to its sensitivity, fast response, reproducibility, and accuracy compared to other methods.

The Folin-Ciocalteu method has a yellow color and is comprised of a mixture of phosphomolibdenum acid and phosphotungstic acid. This method is based on the ability of phenolic compounds to reduce complexes of phosphomolibdenum/phosphotungstic acid and form blue-colored chromophores that absorb at a maximum wavelength of 765 nm.

Approximately 250  $\mu\text{L}$  of Folin-Ciocalteu reagent was added to 3.70 mL of water and 50  $\mu\text{L}$  of rice extract and the solution was reacted for 5 min. Then, the solution was neutralized with 1 mL of 15% (m/v)  $\text{Na}_2\text{CO}_3$ , and incubated for 30 min at 40 °C in a water bath. After the incubation time, the solution was left to cool at room temperature for 10 min, and the absorbance was measured at 760 nm against a blank with the same conditions.

Gallic acid (GA) was used as a standard, and TPC was expressed as mg of GA equivalent per g of sample. The working range was 10 to 200  $\mu\text{g/mL}$ , and the linear equation had a correlation coefficient greater than 0.9997.

#### *Maltose, sucrose, and D-glucose determination*

The amount of sugars (maltose, sucrose, and D-glucose) was determined using an enzymatic kit (Cat. No. 1111395003 from R-Biopharm). This kit was based on enzymatic hydrolysis using  $\alpha$ -glucosidase (maltase) and  $\beta$ -fructosidase (invertase).

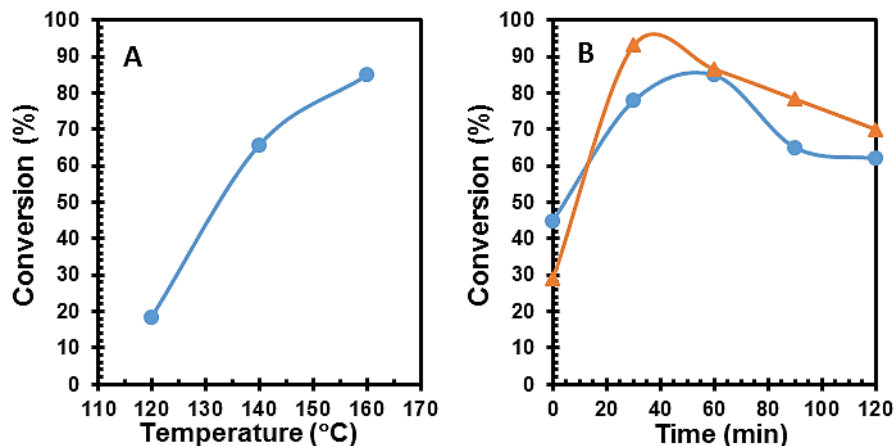
The amount of nicotinamide adenine dinucleotide phosphate (NADPH) formed in those reactions was stoichiometric to the amount of sucrose, and D-glucose, and half of the amount of maltose. The increase in NADPH was measured *via* its light absorbance at 340 nm.

#### *Attenuated Total Reflection- Fourier Transform Infrared (ATR-FTIR) Spectroscopy*

In this study, the ATR-FTIR spectra were obtained using an ATR accessory. The spectra were recorded on a Thermo Nicolet Nexus instrument (Oeiras, Portugal) with 128 scans at a resolution of  $4\text{ cm}^{-1}$ .

## RESULTS AND DISCUSSION

The liquefaction reaction of sweet potato peel proceeded smoothly. The conversion yield increased with the higher temperatures, being highest conversion achieved at  $160\text{ }^\circ\text{C}$  (Fig. 3). After the temperature of the reactional medium reached  $160\text{ }^\circ\text{C}$ , the liquefaction process was screened for different reaction times. For both types of waste, the conversion yields were calculated for time periods ranging from 0 to 120 min, and similar reaction profiles were obtained. After reaching a maximum conversion, the solid residue started to increase, which led to a decrease in the conversion yields. For longer reactions, tar-type and humins content appeared and resulted in a considerable reduction of the liquefaction product yield (Fig. 3). This phenomenon is already well-described for these types of processes, and are commonly associated with recondensation reactions or decomposition products (Hassan and Shukry 2008; Pan *et al.* 2012; Dos Santos *et al.* 2015). The highest conversion yields were 93% and 85% for potato peel and sweet potato peel, respectively.



**Fig. 3.** Effect of temperature (A) on the acid-liquefaction of sweet potato peel, and the effect of time (B) on the acid liquefaction of sweet potato peel (●), and potato peel (▲)

The characterization *via* ATR-FTIR of the liquefied potato and sweet potato peel, and of their organic extract (Figs. 4 and 5) was conducted. These experiments were performed to explain the chemical nature of each extract. Because the chemical composition of potato and sweet potato peels are similar, the spectra of their products were very similar, which was expected. The representative bands indicated the presence of lignin, cellulose, and hemicellulose depolymerization products.

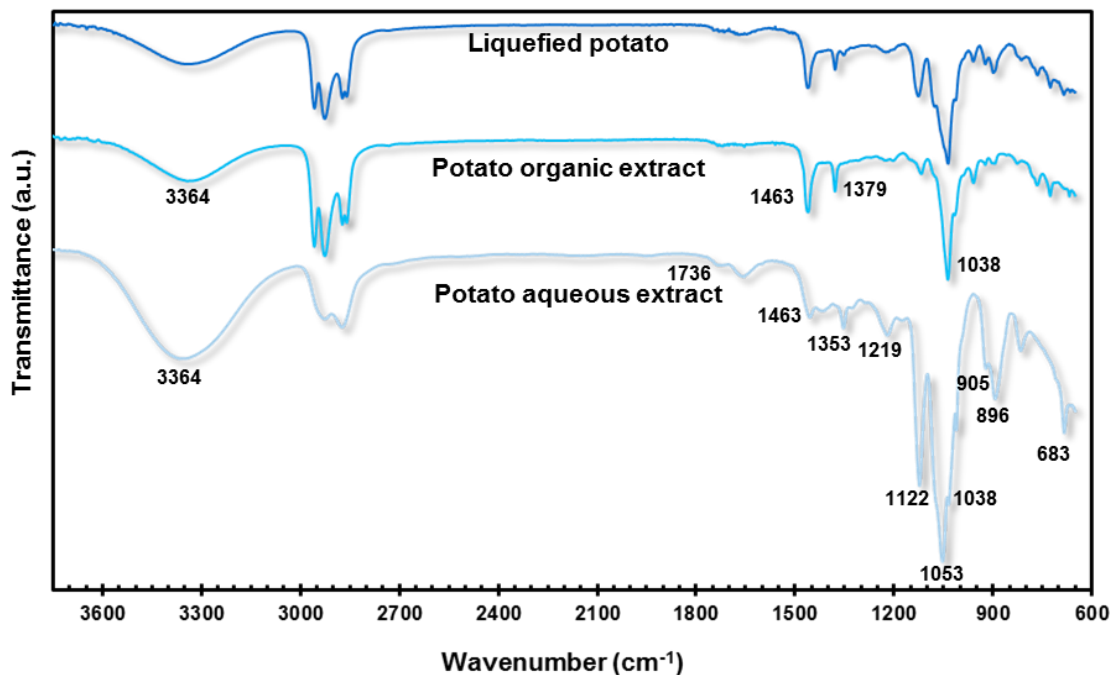


Fig. 4. The ATR-FTIR spectra of the liquefied products from potato peel

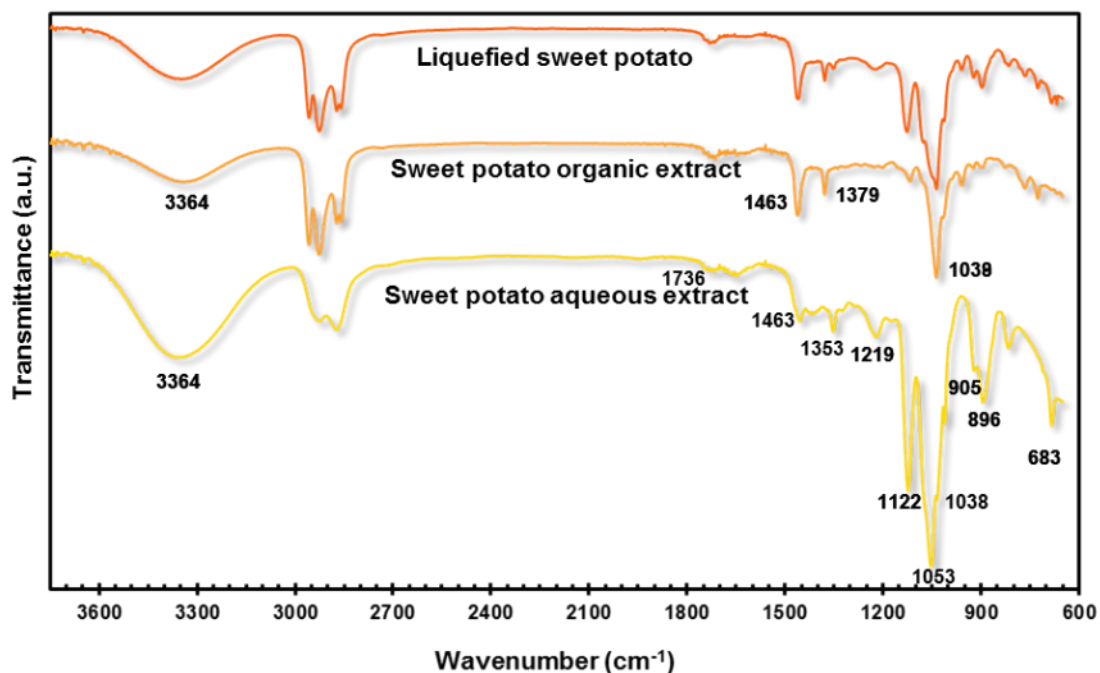


Fig. 5. The ATR-FTIR spectra of the liquefied products from sweet potato peel

An intense band at 1038  $\text{cm}^{-1}$  was the result of the aromatic C-H in-plane deformation for guaiacyl-type material found in lignin (Xiao *et al.* 2001). Characteristic bands of benzene rings were found at 1463  $\text{cm}^{-1}$ , which were present also in the lignin (Hoareau *et al.* 2004; Zhou *et al.* 2011). Lastly, a third band related to the syringyl rings appeared at 1379  $\text{cm}^{-1}$ , which provided corroborating evidence that the lignin was depolymerized (Zhou *et al.* 2011). These three bands appeared more sharply in the organic phase, which explained the higher phenolic content when compared to that of the aqueous extract. In contrast, the spectra of the aqueous extract of both cultivars exhibited the carbohydrate fingerprint region (683 to 1220  $\text{cm}^{-1}$ ). The band at 683  $\text{cm}^{-1}$  and the sharp peak at 1053  $\text{cm}^{-1}$ , which are characteristic of carbohydrates, were assigned to C-H bend and C-O-C stretch signals, respectively (Tipson *et al.* 1959; Monde *et al.* 2004; Ardejani *et al.* 2008; Yona *et al.* 2014). The  $\text{CH}_2\text{OH}$  side chain that is related to the C-O-H bending mode, and related to carbohydrates, was clearly observed at 1219  $\text{cm}^{-1}$  (Tipson *et al.* 1959; Nikonenko *et al.* 2000; Kizil *et al.* 2002). A discrete peak at 1122  $\text{cm}^{-1}$ , that is characteristic of the ring structure, was attributed to the stretching vibrations of the C-O-C bonds (Sekkal *et al.* 1995; Nikonenko *et al.* 2000; Mohebbi 2008; Yona *et al.* 2014). The 1 $\rightarrow$ 4 glycosidic linkage found amongst cellulose, hemicellulose derivatives, and di- and polysaccharides was assigned to a peak at 905  $\text{cm}^{-1}$  (Sekkal *et al.* 1995; Kizil *et al.* 2002). Furthermore, the anti-symmetric out-of-phase ring stretch attributed to a C-H equatorial deformation vibration band, which was found within the  $\alpha$ - and  $\beta$ -pyranoses spectra, appeared at 896  $\text{cm}^{-1}$  (Sekkal *et al.* 1995; Yona *et al.* 2014).

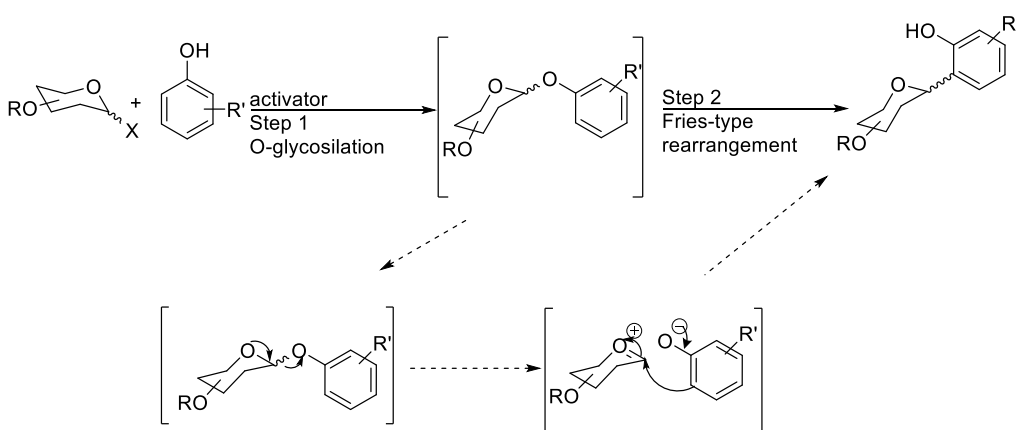
**Table 1.** ATR-FTIR Bands Assignment (Characteristic Bands)

$\bar{\nu}$ ( $\text{cm}^{-1}$ )	Band Assignment	Potential Compounds
3364	O-H stretch	Hydroxyl groups
1736	C=O stretch	Carboxylic acids, esters
1463	C-H deformations and aromatic ring vibrations	Benzene rings
1379	Aromatic C-H deformation	Syringyl rings (from lignin)
1353	Carboxylate ( $\text{COO}^-$ ) symmetric stretching vibration	Carboxylic acid deprotonated
1219	C-O-H bend	$\text{CH}_2\text{OH}$ (side chain) D-glucose
1122	C-O-C stretch	Cyclic ethers- pyranoses moieties
1053	C-O-C stretch	Cyclic ethers, carbohydrates
1038	Aromatic C-H in-plane deformation	Guaiacyl moieties (from lignin) phenolic moieties
905	(1 $\rightarrow$ 4) Bond C-O and the C-C stretch	Cellulose, glycosidic linkages
896	C-H bend (anomeric) $\beta$ -(1 $\rightarrow$ 4) bond symmetric stretching mode	$\alpha$ - and $\beta$ -pyranoses, cellulose
815	Asymmetric ring stretching vibration (tetrahydropyran ring)	Carbohydrates
683	C-H bend	Carbohydrates

In addition, potato peel, whether of the regular or sweet variety, is also known for possessing several antioxidants in its chemical composition. These compounds appeared mostly as polar molecules with phenolic acid moieties (*e.g.*, chlorogenic, caffeic, *p*-coumaric, and ferulic acids) (Dos Santos *et al.* 2016a). Such compounds are highly prone



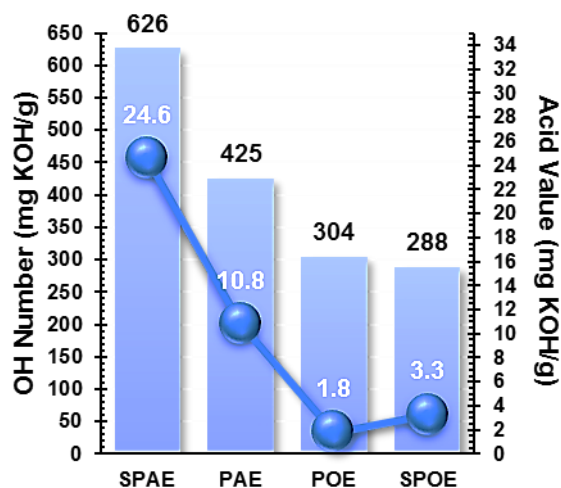
to migrate to the water extract, and more so, if carboxylic acids are present in the carboxylate form. The centered peak at  $1353\text{ cm}^{-1}$  was assigned to a carboxylate group (Hadžija and Špoljar 1995). Moreover, in acidic mediums, the reactions between the hydroxyl groups and phenolic molecules could occur. For instance, Fries-type reactions, which involve a phenolic scaffold and sugar, form a glycoside during an early stage. Afterward, and *via* intra-molecular arrangement, this leads to C-glycosylated compounds (Dos Santos *et al.* 2011; Dos Santos *et al.* 2013). These types of compounds are supposed to have more affinity with the aqueous phase. Therefore, it was not entirely unexpected that the bands as  $1463$  and  $1038\text{ cm}^{-1}$ , which were detectable in the organic phase and related to the phenolic compounds resulting from lignin depolymerization, were also found within the spectrum of the aqueous phase. The very discrete and weak C=O stretching band centered at  $1736\text{ cm}^{-1}$  was observed in the aqueous extract spectrum.



**Fig. 6.** Fries-type rearrangement reaction mechanism

To some extent, the determination of the hydroxyl number, along with the acid value (Fig. 7), supported the assumptions presumed in the ATR-FTIR analysis. The values for both the hydroxyl number and acidity were clearly superior in the aqueous phase rather than in the organic extract. These results validated the assumption that the hydrophilic extracts were more enriched with hydroxyl groups when compared to the apolar ones. With regards to the determination of the acid value for both wastes, a higher concentration of acid was observed in the aqueous extracts than in the organic extracts of the liquefied products. This difference between the organic and aqueous phases was also verified in similar studies, where the liquefied bio-oils were extracted with water (Dos Santos *et al.* 2016b).

The values obtained were in accordance with other liquefied products already described and used for the formulation of value-added products. For instance, the acid value and hydroxyl number obtained for the sweet potato aqueous extract were similar to those obtained from other depolymerization products that were used to produce polyurethane foams. Thus, a possible use for the liquefied products obtained is for the production of polyurethane foams (Mehmet *et al.* 2003; Pan *et al.* 2012; Hu and Li 2014). In contrast, one of the many applications that could be envisaged for the extracts with the lower acidic nature and hydroxyl number is for use as a biofuel (Xiu and Shahbazi 2012; Seljak *et al.* 2014; Dos Santos *et al.* 2016c; Mateus *et al.* 2016).



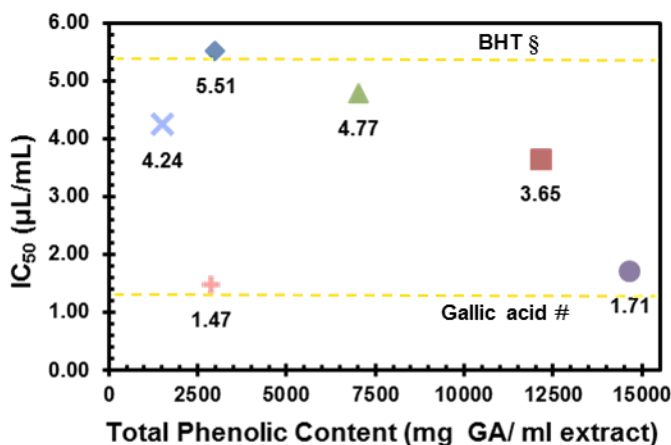
**Fig. 7.** Hydroxyl number and acid value: SPAE- sweet potato aqueous extract, PAE- potato aqueous extract, POE- potato organic extract, and SPOE- sweet potato aqueous extract

### Antioxidant Activity

As previously mentioned, the antioxidant activity of the extracts was analyzed by the scavenging effect on the DPPH radical and by the Folin-Ciocalteu method. The results of both of these tests are presented in Fig. 8.

The concentration of extract required to inhibit 50% of the DPPH radical was obtained *via* interpolation from a linear regression analysis of antioxidant activity *vs.* extract concentration. For a clear analysis of the results, it is important to note that a lower  $IC_{50}$ -value is associated with a higher antioxidant capacity. The same test with the same conditions was applied to the natural antioxidant GA, for comparison purposes.

From Fig. 8, it was determined that all of the samples in the study had an  $IC_{50}$  higher than the GA, which meant that the antioxidant capacity of the potato and sweet potato extracts was lower ( $5.51 \leq IC_{50} \leq 1.47$ ). However, Božin *et al.* (2012) applied the same test to the synthetic antioxidant BHT, which had an  $IC_{50}$  higher than all of the extracts with the exception of the liquefied potato. These results showed that it was possible to use natural resources, which are undervalued, in the place of synthetic options.



**Fig. 8.** The TPC and antioxidant capacity of the liquefied products (◆- liquefied potato, ■- organic extract of liquefied potato, ×- aqueous extract of liquefied potato, ▲- liquefied sweet potato, ●- organic extract of liquefied sweet potato, + - aqueous extract of liquefied sweet potato); § means  $IC_{50} = 5.37 \mu\text{L/mL}$  (Božin *et al.* 2012), and # means  $IC_{50} = 1.33 \mu\text{L/mL}$

The organic extracts were those with highest phenolic contents (SPOE: 14648 mg GA/L; POE: 12145 mg GA/L), and the aqueous extracts had the lowest contents (SPAEE: 2868 mg GA/L; PAE: 1498 mg GA/L). From the phenolic content screening, it was expected that the sweet potato would have a TPC higher than the potato, which was verified in this study. The sweet potato had a TPC of 0.074 mg AG/g and the potato had a TPC of 0.070 mg AG/g (Scalbert *et al.* 2016).

From the analysis of Fig. 8, it appeared that there might have been a relationship between the TPC and antioxidant capacity. To obtain a more precise conclusion, the linear correlation coefficient was determined using the linear correlation of Spearman. If the antioxidant capacity was greater and the  $IC_{50}$  value was smaller, then a relationship between the two would be confirmed. A negative correlation between the  $IC_{50}$  and the total phenolics was expected.

For the analysis of the Spearman's coefficient, there was no correlation ( $\rho = -0.1$ ,  $p > 0.05$ ), but when the samples from the aqueous phase of both matrices were excluded, a correlation was verified ( $\rho = -1$ ,  $p < 0.05$ ).

**Table 2.** Sugar Content of Aqueous Extract of Liquefied Potato and Sweet Potato

Sugar	Extract	SC (g/L)	SD (g/L)	CV (%)
Glucose	PAE	32.29	1.63	5
	SAE	24.60	a)	a)
Sucrose	PAE	64.99	0.39	1
	SAE	85.65	a)	a)
Maltose	PAE	55.05	0.61	1
	SAE	43.91	0.01	0

SC- Sugar content, SD- Standard deviation, CV- Coefficient of variation, PAE- Potato peel aqueous extract, SAE- Sweet potato peel aqueous extract; the measurements were conducted in duplicates. a) Only one measurement was considered because operational errors were detected, and as such the value was considered an outlier.

Among the sugars tested, sucrose, glucose, and maltose made up 42.48% to 55.56%, 15.96% to 21.20%, and 28.48% to 36.14% of the total sugars, respectively. The total sugar contents were 152.33 g/L and 154.16 g/L in potato and sweet potato, respectively.

The SAE had the highest level of total sugars. In the present study, it was found that sucrose was the dominant sugar in both extracts, which was in agreement with the Portuguese food composition database (Instituto Nacional de Saúde 2016).

## CONCLUSIONS

1. The liquefaction of the potato and sweet potato peel were conducted successfully and produced good yields of the desired bio-oil. Although, for the sweet potato peel, longer reaction times increased the solid residues and reduced the conversion yields.
2. The TPC was analyzed and the organic phase of the sweet potato contained the highest TPC, which was almost double the amount found in the liquefied sweet potato. In the potato, the same finding was verified, but the difference was larger, with three times more TPC found in the organic extract.

3. The antioxidant activity was assessed by the DPPH radical method of the liquefied products, and generally, its extracts were better than that of the synthetic antioxidant BHT. In particular, the aqueous extract of the liquefied sweet potato contained an antioxidant activity that was approximately 3.5 times higher than that of the BHT, which was nearly as good as that of the GA.
4. Glucose, sucrose, and maltose were identified in the aqueous extracts of both of the PPWs.
5. The chemical characterization of the products demonstrated that they may be suitable for the formulation of value-added goods (chemicals or materials) and/or for use as fuels, anti-oxidant additives or sugar platform for fermentation processes.

## ACKNOWLEDGMENTS

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## REFERENCES CITED

- Albishi, T., John, J. A., Al-Khalifa, A. S., and Shahidi, F. (2013). "Phenolic content and antioxidant activities of selected potato varieties and their processing by-products," *J. Funct. Foods* 5(2), 590-600. DOI: 10.1016/j.jff.2012.11.019
- ASTM D4662-08 (2008). "Standard test methods for polyurethane raw materials: Determination of acid and alkalinity numbers of polyols," ASTM International, West Conshohocken, PA.
- ASTM D4274-05 (2005). "Standard test methods for testing polyurethane raw materials: Determination of hydroxyl numbers of polyols," ASTM International, West Conshohocken, PA.
- Arapoglou, D., Varzakas, T., Vlyssides, A., and Israilides, C. (2010). "Ethanol production from potato peel waste (PPW)," *Waste Manage.* 30(10), 1898-1902. DOI: 10.1016/j.wasman.2010.04.017
- Ardejani, F. D., Badii, K., Limaee, N. Y., Shafaei, S. Z., and Mirhabibi, A. R. (2008). "Adsorption of direct red 80 dye from aqueous solution onto almond shells: Effect of pH, initial concentration, and shell type," *J. Hazard. Mater.* 151(2-3), 730-737. DOI: 10.1016/j.jhazmat.2007.06.048
- Balat, M. (2008). "Mechanisms of thermochemical biomass conversion processes. Part 3: Reactions of liquefaction," *Energ. Source Part A* 30(7), 649-659. DOI: 10.1080/10407780600817592
- Betiku, E., Adesina, O., (2013). "Statistical approach to the optimization of citric acid production using filamentous fungus *Aspergillus niger* grown on sweet potato starch hydrolyzate," *Biomass and Bioenergy*, 55, 350-354. DOI: 10.1016/j.biombioe.2013.02.034.
- Božin, B., Lakić, N., Čonić, B. S., Kladar, N., Orčić, D., and Mimica-Dukić, N. (2012). "Antioxidant and antimicrobial properties of a new chemotype of woodland sage (*Salvia nemorosa* L. subsp. *nemorosa*, *Lamiaceae*) essential oil," *Biologia Serbica* 34(1-2), 51-60.

- Briones, R., Serrano, L., and Labidi, J. (2012). "Valorization of some lignocellulosic agro-industrial residues to obtain biopolymers," *J. Chem. Technol. Biotechnol.* 87(2), 244–249. DOI: 10.1002/jctb.2706
- Chintagunta, A. D., Jacob, S., and Banerjee, R. (2016). "Integrated bioethanol and biomanure production from potato waste," *Waste Manage.* 49, 320-325. DOI: 10.1016/j.wasman.2015.08.010
- Dos Santos, R. G., Jesus, A. R., Caio, J. M., and Rauter, A. P. (2011). "Fries-type reactions for the C-glycosylation of phenols," *Curr. Org. Chem.* 15(1), 128-148. DOI: 10.2174/138527211793797855
- Dos Santos, R. G., Xavier, N. M., Bordado, J. C., and Rauter, A. P. (2013). "Efficient and first regio- and stereoselective direct C-glycosylation of a flavanone catalysed by Pr(OTf)<sub>3</sub> under conventional heating or ultrasound irradiation," *Eur. J. Org. Chem.* 2013(8), 1441-1447. DOI: 10.1002/ejoc.201201518
- Dos Santos, R. G., Bordado, J. C., and Mateus, M. M. (2015). "Microwave-assisted liquefaction of cork- From an industrial waste to sustainable chemicals," *J. Ind. Eng. Manage.* 4(4), 173-177. DOI: 10.4172/2169-0316.1000173
- Dos Santos, R. G., Ventura, P., Bordado, J. C., and Mateus, M. M. (2016a). "Valorizing potato peel waste: An overview of the latest publications," *Rev. in Environ. Sci. Bio/Technol.* 15(4), 585-592. DOI: 10.1007/s11157-016-9409-7
- Dos Santos, R. G., Carvalho, R., Silva, E. R., Bordado, J. C., Cardoso, A. C., Do Rosário Costa, M., and Mateus, M. M. (2016b). "Natural polymeric water-based adhesive from cork liquefaction," *Ind. Crop. Prod.* 84, 314-319. DOI: 10.1016/j.indcrop.2016.02.020
- Dos Santos, R. G., Bordado, J. C., and Mateus, M. M. (2016c). "Potential biofuels from liquefied industrial wastes- Preliminary evaluation of heats of combustion and van Krevelen correlations," *J. Clean. Prod.* 137, 195-199. DOI: 10.1016/j.jclepro.2016.07.082
- Farvin, K. H. S., Grejsen, H. D., and Jacobsen, C. (2012). "Potato peel extract as a natural antioxidant in chilled storage of minced horse mackerel (*Trachurus trachurus*): Effect on lipid and protein oxidation," *Food Chem.* 131(3), 843-851. DOI: 10.1016/j.foodchem.2011.09.056
- Food and Agriculture Organization (2016). "Food and Agriculture Organization of the United Nations- Statistics division," (<http://faostat3.fao.org/browse/Q/QC/E>), Accessed 20 May 2016.
- Guechi, E. -K., and Hamdaoui, O. (2016). "Biosorption of methylene blue from aqueous solution by potato (*Solanum tuberosum*) peel: Equilibrium modelling, kinetic, and thermodynamic studies," *Desalination and Water Treatment* 57(22), 10270-10285. DOI: 10.1080/19443994.2015.1035338
- Hadžija, O., and Špoljar, B. (1995). "Quantitative determination of carboxylate by infrared spectroscopy: Application to humic acids," *Fresen. J. Anal. Chem.* 351(7), 692-693. DOI: 10.1007/BF00323352
- Hassan, E. M., and Shukry, N. (2008). "Polyhydric alcohol liquefaction of some lignocellulosic agricultural residues," *Ind. Crop. Prod.* 27(1), 33-38. DOI: 10.1016/j.indcrop.2007.07.004
- Hoareau, W., Trindade, W. G., Siegmund, B., Castellan, A., and Frollini, E. (2004). "Sugar cane bagasse and curaua lignins oxidized by chlorine dioxide and reacted with furfuryl alcohol: Characterization and stability," *Polym. Degrad. Stabil.* 86(3), 567-576. DOI: 10.1016/j.polymdegradstab.2004.07.005

- Hu, S., and Li, Y. (2014). "Polyols and polyurethane foams from acid-catalyzed biomass liquefaction by crude glycerol: Effects of crude glycerol impurities," *J. Appl. Polym. Sci.* 131(18). DOI: 10.1002/app.40739
- Instituto Nacional de Saúde. (2016). "PortFIR," (<http://portfir.insa.pt/foodcomp/search?searchString=batata&comparisonOperator=0>), Accessed 31 October 2016.
- Izmirliloglu, G., and Demirci, A. (2012). "Ethanol production from waste potato mash by using *Saccharomyces cerevisiae*," *Appl. Sci.* 2(4), 738. DOI: 10.3390/app2040738
- Jasiukaityte, E., Kunaver, M., and Strlic, M. (2009). "Cellulose liquefaction in acidified ethylene glycol," *Cellulose* 16(3), 393-405. DOI: 10.1007/s10570-009-9288-y
- Jasiukaitytė-Grojzdek, E., Kunaver, M., and Crestini, C. (2012). "Lignin structural changes during liquefaction in acidified ethylene glycol," *J. Wood Chem. Technol.* 32(4), 342-360. DOI: 10.1080/02773813.2012.698690
- Khawla, B. J., Sameh, M., Imen, G., Donyes, F., Dhouha, G., Raoudha, E. G., and Oumèma, N. -E. (2014). "Potato peel as feedstock for bioethanol production: A comparison of acidic and enzymatic hydrolysis," *Ind. Crop. Prod.* 52, 144-149. DOI: 10.1016/j.indcrop.2013.10.025
- Kizil, R., Irudayaraj, J., and Seetharaman, K. (2002). "Characterization of irradiated starches by using FT-Raman and FTIR spectroscopy," *J. Agr. Food Chem.* 50(14), 3912-3918. DOI: 10.1021/jf011652p
- Kunaver, M., Jasiukaitytė, E., and Čuk, N. (2012). "Ultrasonically assisted liquefaction of lignocellulosic materials," *Bioresour. Technol.* 103(1), 360-366. DOI: <http://dx.doi.org/10.1016/j.biortech.2011.09.051>
- Liang, S., and McDonald, A. G. (2014). "Chemical and thermal characterization of potato peel waste and its fermentation residue as potential resources for biofuel and bioproducts production," *J. Agr. Food Chem.* 62(33), 8421-8429. DOI: 10.1021/jf5019406
- Liang, S., McDonald, A. G., and Coats, E. R. (2014). "Lactic acid production with undefined mixed culture fermentation of potato peel waste," *Waste Manage.* 34(11), 2022-2027. DOI: 10.1016/j.wasman.2014.07.009
- Maske, N., and Satyanarayan, S., (2012). "Effect of special fish feed prepared using potato peels on fresh water fish *Labeo rohita*," *J. Ind. Pollut. Contr.* 29(1), 33-38.
- Mateus, M. M., Acero, N. F., Bordado, J. C., and Dos Santos, R. G. (2015). "Sonication as a foremost tool to improve cork liquefaction," *Ind. Crop. Prod.* 74, 9-13. DOI: 10.1016/j.indcrop.2015.04.063
- Mateus, M. M., Bordado, J. C., and Dos Santos, R. G. (2016). "Potential biofuel from liquefied cork - Higher heating value comparison," *Fuel* 174, 114-117. DOI: 10.1016/j.fuel.2016.01.081
- Mehmet, A., Basturk, M. A., and Diğrak, M. (2003). "New polyurethane-type rigid foams from liquified wood powders," *J. Mater. Sci. Lett.* 22(17), 1225-1228. DOI: 10.1023/A:1025356702660
- Mohebbi, B. (2008). "Application of ATR infrared spectroscopy in wood acetylation," *J. Agr. Sci. Technol.* 10(3), 253-259.
- Monde, K., Taniguchi, T., Miura, N., and Nishimura, S. -I. (2004). "Specific band observed in VCD predicts the anomeric configuration of carbohydrates," *J. Am. Chem. Soc.* 126(31), 9496-9497. DOI: 10.1021/ja048446t
- Nikonenko, N. A., Buslov, D. K., Sushko, N. I., and Zhibankov, R. G. (2000). "Investigation of stretching vibrations of glycosidic linkages in disaccharides and

- polysaccharides with use of IR spectra deconvolution,” *Biopolymers* 57(4), 257-262. DOI: 10.1002/1097-0282(2000)57:4<257::AID-BIP7>3.0.CO;2-3
- Pan, H., Zheng, Z., and Hse, C. Y. (2012). “Microwave-assisted liquefaction of wood with polyhydric alcohols and its application in preparation of polyurethane (PU) foams,” *Eur. J. Wood Prod.* 70(4), 461-470. DOI: 10.1007/s00107-011-0567-6
- Scalbert, A., Du Chaffaut, L., Neveu, V., Vos, F., Perez-Jiminez, J., Crespy, V., Andres-Lacueva, C., Urpis-Sarda, M., Rothwell, J., Boto-Ordoñez, M., *et al.* (2016). “Phenol explorer,” (<http://phenolexplorer.eu/search?utf8=%E2%9C%93&query=potato&button=>), Accessed 31 October 2016.
- Salawu, S. O., Udi, E., Akindahunsi, A. A., Boligon, A. A., and Athayde, M. L. (2015). “Antioxidant potential, phenolic profile, and nutrient composition of flesh and peels from Nigerian white and purple skinned sweet potato (*Ipomea batatas L.*),” *Asian J. Plant Sci. Res.* 5(5), 14-23.
- Schieber, A., Stintzing, F. C., and Carle, R. (2001). “By-products of plant food processing as a source of functional compounds - Recent developments,” *Trends Food Sci. Tech.* 12(11), 401-413. DOI: 10.1016/S0924-2244(02)00012-2
- Sekkal, M., Dincq, V., Legrand, P., and Huvenne, J. P. (1995). “Investigation of the glycosidic linkages in several oligosaccharides using FT-IR and FT Raman spectroscopies,” *J. Mol. Struct.* 349, 349-352. DOI: 10.1016/0022-2860(95)08781-P
- Seljak, T., Kunaver, M., and Kตราšnik, T. (2014). “Emission evaluation of different types of liquefied wood,” *J. Mech. Eng.* 60(4) 221-231. DOI: 10.5545/sv-jme.2013.1242
- Singh, A., Sabally, K., Kubow, S., Donnelly, D. J., Gariepy, Y., Orsat, V., and Raghavan, G. S. V. (2011). “Microwave-assisted extraction of phenolic antioxidants from potato peels,” *Molecules* 16(3), 2218-2232. DOI: 10.3390/molecules16032218
- Tipson, R. S., Isbell, H. S., and Stewart, J. E. (1959). “Infrared absorption spectra of some cyclic acetals of sugars,” *J. Res. Nat. Bur. Stand.* 62(6). DOI: 10.6028/jres.062.041
- Ventura, P., Bordado, J. C., Mateus, M. M., and Dos Santos, R. G. (2016). “Upcycling potato peel waste- Data of the pre-screening of the acid-catalyzed liquefaction,” *Data in Brief* 7, 1455-1457. DOI: 10.1016/j.dib.2016.04.032
- Wu, D. (2016). “Recycle technology for potato peel waste processing: A review,” *Proc. Environ. Sci.* 31, 103-107. DOI: 10.1016/j.proenv.2016.02.014
- Wu, Z. -G., Xu, H. -Y., Ma, Q., Cao, Y., Ma, J. -N., and Ma, C. -M. (2012). “Isolation, identification, and quantification of unsaturated fatty acids, amides, phenolic compounds, and glycoalkaloids from potato peel,” *Food Chem.* 135(4), 2425-2429. DOI: 10.1016/j.foodchem.2012.07.019
- Xiao, B., Sun, X. F., and Sun, R. (2001). “Chemical, structural, and thermal characterizations of alkali-soluble lignins and hemicelluloses, and cellulose from maize stems, rye straw, and rice straw,” *Polym. Degrad. Stabil.* 74(2), 307-319. DOI: 10.1016/S0141-3910(01)00163-X
- Xiu, S., and Shahbazi, A. (2012). “Bio-oil production and upgrading research: A review,” *Renew. Sust. Energ. Rev.* 16(7), 4406-4414. DOI: 10.1016/j.rser.2012.04.028
- Yona, A. M. C., Budija, F., Kričej, B., Kutnar, A., Pavlič, M., Pori, P., Tavzes, Č., and Petrič, M. (2014). “Production of biomaterials from cork: Liquefaction in polyhydric alcohols at moderate temperatures,” *Ind. Crop. Prod.* 54, 296-301. DOI: 10.1016/j.indcrop.2014.01.027

Zhou, G., Taylor, G., and Polle, A. (2011). “FTIR-ATR-based prediction and modelling of lignin and energy contents reveals independent intra-specific variation of these traits in bioenergy poplars,” *Plant Methods* 7(9), 1-10. DOI: 10.1186/1746-4811-7-9

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