

Use of Ionic Liquid-Based Ultrasound Assisted Liquid-Liquid Extraction of Phenols from Aqueous Fractions of Seed Bio-Oil

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The liquid product of the pyrolysis of biomass is a mixture of an organic phase and other aqueous, being the last one rich in phenol monomers which can be used in industrial chemistry as input for plastic and resin production. This work aimed to develop a method for extracting phenols present in the aqueous fraction obtained from the pyrolysis of guava seeds, using ultrasonic assisted liquid-liquid extraction (UALLE) with ethyl acetate and ionic liquids (ILs) as co-solvents (1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide (BMIM.NTF2) and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM.PF6)). The percentage IL, ultrasonic bath potency, temperature, and pH were studied. Quantification of twelve phenol monomers was performed using gas chromatography-mass spectrometry (GC-MS) and the total phenol concentration (TPC) was performed using UV-Vis spectrophotometer. The ionic liquid BMIM.NTF2 was more efficient for phenol extraction than BMIM.PF6. The phenolic extractions were influenced by the pH of the aqueous fraction (higher extraction yields at pH ≤ 7), and thus, presented recoveries above 80% for both ionic liquids.

Keywords: phenols, ionic liquids, ultrasound, aqueous phase, pyrolysis

Introduction

Brazil is one of the largest producers of animal and agricultural industry residues of the world.¹ A viable alternative to this problem is reuse, by conversion with specific thermochemical processes such as pyrolysis coupled to highly consolidated technologies to obtain chemical compounds which have great commercial value, such as phenols.^{2,3}

Through pyrolysis, biomass is converted into three products (solid/bio-char, liquid/bio-oil, and gaseous/biogas) with yields typically dependent on the conditions and biomass used in the pyrolysis process.⁴ The liquid fraction produced by pyrolysis (called bio-oil) consists of an organic phase and an aqueous phase, which come from the natural

moisture of the biomass and the dehydration reactions that occur during pyrolysis.⁵

The aqueous phase may represent as little as 30% of the liquid/bio-oil phase.⁶ The composition of each phase consists of a mixture of more than 300 organic thermal degradation compounds: principally cellulose, hemicellulose, and lignin (which constitute the biomass).⁷ These compounds normally a mixture of hydrocarbons, carboxylic acids, phenols, aldehydes, ketones, sugars, and derivatives of furans, among others,⁸⁻¹¹ can be used in industrial processes for the production of energy, biofuels, or chemical matrix inputs.^{12,13}

Phenolic compounds are often cited for bringing added value when reused as raw material for the chemical industry.^{8,14} Phenolic resins, produced by the condensation of phenols with aldehydes are a prominent application of phenols,¹⁴ being used in a variety of applications such as thermal insulation, adhesives, post moldings, laminated resins, surface coatings, and composites, mainly in

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construction and the automotive industry.¹⁵ Recovery of phenols from the aqueous-phase of bio-oil is important, as they can add value to bio-refinery based in biomass processing.¹⁶

In many studies, liquid-liquid extraction has been used to recover organic compounds from aqueous fractions from the pyrolysis process of biomass.^{9,17-20} Wei *et al.*²⁰ used liquid-liquid extraction to extract organic compounds from the bio-oil aqueous phase, using chloroform, hexane, and petroleum ether. The final extracts contained > 60% phenols and guaiacols, ca. 20% furans, and < 5% ketones and esters, with trace of sugars, acids, and alcohols.

In aqueous matrices, ultrasonic assisted liquid-liquid extraction (UALLE)²¹⁻²⁴ for recovery of organic compounds shows certain advantages. Compared to conventional liquid-liquid extraction, the use of ultrasound in extractions involving two immiscible liquids helps to reduce extraction time and increase phase interactions. When a solvent is exposed to ultrasonic waves, bubbles are formed which then collapse and produce shock waves and jets within the liquid as a result of cavitation. This favors greater mass transfer from the sample to the solvent.²¹

Ionic liquids (ILs) are an alternative to organic solvents for extractions.^{25,26} Their properties, such as chemical and thermal stability, non-flammability, manipulable viscosity; miscibility with water and organic solvents, and their ability to extract organic compounds, make them highly attractive as solvents.²⁵ Due to these characteristics, ionic ILs present a wide range of applications, especially as substitutes for more volatile organic solvents.^{25,27-32}

The present work proposes an extraction method for phenols present in aqueous fractions from guava seed pyrolysis. The effects of ultrasound in partitioning phenolic compounds using organic solvent and adding ionic liquids as co-solvents (1-butyl-3-methylimidazolium hexafluorophosphate-BMIM.PF6, and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide-BMIM.NTF2) was investigated. To date, neither extraction of phenols from guava seed pyrolysis aqueous fractions (when using an ultrasound system), nor the influence of the ionic liquids BMIM.PF6 and BMIM.NTF2 as co-solvents have been reported in the literature.

Experimental

Reagents and standards

The experiments were performed using the solvents: dichloromethane (Dinâmica Química Contemporânea Ltda., Indaiatuba, Brazil), and ethyl acetate (Vetec, Rio de Janeiro, Brazil). The standards used for quantification were

1,1'-biphenyl (internal standard), phenol, 2-methylphenol, 3-methylphenol, 4-methylphenol, 2,5-dimethylphenol, 3,5-dimethylphenol, 2-methoxyphenol, benzene-1,2-diol, 4-methylbenzene-1,2-diol, benzene-1,3-diol, 2,6-dimethoxyphenol, and 2-methoxy-4-prop-2-enylphenol (Sigma-Aldrich, São Paulo, Brazil). For derivatization, trimethylsilyl 2,2,2-trifluoro-*N*-trimethylsilylethanamide (BSTFA) (Sigma-Aldrich, São Paulo, Brazil) and pyridine (Vetec, Rio de Janeiro, Brazil) were used. The ionic liquids: IL-1, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (BMIM.NTF2) (Sigma-Aldrich, São Paulo, Brazil) and IL-2, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM.PF6) were both synthesized at the Laboratory of Medicinal and Technological Chemistry (LaQuiMeT) of the University of Brasília (UnB).

Biomass collection

The guava seeds (*Psidium guajava* L.) used in this work were acquired from the POMAR Fruit Pulp Processing Industry located in the city of Aracaju-SE, Brazil. For storage before the pyrolysis process, the seeds were separated from the pulp residue and washed in running water. They were then dried in an oven at 60 °C for 5 h to ensure a moisture content of below 10% reducing water production during the pyrolysis process and avoiding sample deterioration during the storage period.

Pyrolysis

The pyrolysis process was performed in a system using a vertical oven with a controlled flow of nitrogen, according Bispo *et al.*³³ The collection of the liquid fraction was performed by condensation using a series of seven condensers. The first was directly connected to the reactor, and made of stainless steel, the others (made of glass) were arranged in series and connected in pairs using a bottom collector for the bio-oil. The temperature of the cooling system (1 °C) was maintained by thermostatic bath, Microquímica Equipamentos LTDA, model MQBTC99-20 (Palhoça, Brazil).

The guava seed pyrolysis was performed at 600 °C, using a sample weight of approximately 300 g, in N₂ gas flow (100 mL min⁻¹), and an oven heating rate of 30 °C min⁻¹. After pyrolysis, separation of the aqueous fraction from the bio-oil was performed using a settling funnel. The aqueous fraction used in this work was stored in an amber flask and refrigerated (8 °C) until the extractions.

Effects of power and temperature on ultrasonic-assisted liquid-liquid extraction (UALLE)

The extractions were performed according to the work of Ren *et al.*,³⁴ 1.0 mL of aqueous fraction and 4.0 mL of ethyl acetate were mixed in a sealed Falcon tube. The ultrasonic bath (UNIQUE, model USC-2800A, Indaiatuba, Brazil), utilized a fixed ultrasonic frequency of 40 kHz and the maximum rated power of 154 W. A full factorial design 2² (FFD 2²) combined with a response surface methodology (RSM) was applied to study the effects of independent variables; including temperature (X1), and power (%) (X2), at 10 and 30 min, being taken as the extraction response the total phenols concentration (TPC) as the dependent variable. The assays were performed according to the FFD 2², with four factorial points in duplicate, resulting in eight assays conducted at random. The selection of temperature (30-40 °C), and power (60-100%) levels was performed after preliminary testing, within the experimental limits. The experimental results were analyzed at a 95% confidence level using the online Protimiza Experimental Design software.³⁵

UALLE kinetics

A kinetic curve for UALLE was constructed for optimizing the extraction time for 100% power and at a temperature of 40 °C. The experiments were performed using the aqueous fraction diluted to a 1:5 v/v ratio in distilled water. The extracting solvent used was ethyl acetate (Vetec, Rio de Janeiro, Brazil) at a ratio of 1:4 v/v (aqueous fraction/solvent) placed in a 5 mL Falcon tube with sonication at intervals of 2, 6, 8, 10, 15, 20, 25 and 30 min. Extractions were performed in duplicate (n = 2) and the extracts were analyzed using gas chromatography mass spectrometry (GC-MS).

Ultrasound assisted liquid-liquid extraction with ionic liquids (UALLE-IL)

Extractions were performed using the ILs BMIM.NTF2 and BMIM.PF6. The aqueous fraction was diluted with distilled water (1:5 v:v), and the pH was adjusted according to the factorial design, with NaOH (Diadema, Brazil) 1.0 mol L⁻¹. Table 1 presents the experimental design. 1.0 mL of the diluted aqueous fraction, 4 mL of ethyl acetate, and the IL were added to a 5 mL Falcon tube at 40 °C, and subjected to ultrasonic extraction at 100% power for 25 min. The assays were performed according to the full factorial design (FFD) combined with response surface methodology (RSM) 2², with four factorial points

and three assays at the central points (under identical conditions), all conducted in random order. Selection of IL percentage levels (0.5-1.5%) and pH (4-10) was made considering preliminary tests which were performed within the experimental limits. The experimental results were analyzed at a 95% confidence level using the online Protimiza Experimental Design software.³⁵

Table 1. Full factorial design (FFD) (2²) performed in UALLE for extraction of phenols from the aqueous phase of the pyrolysis of guava seeds. Temperature = 40 °C; ultrasonic power = 100% and extraction time = 25 min

Experiment	IL / %	pH
1	0.5 (-1)	4 (-1)
2	1.5 (+1)	4 (-1)
3	0.5 (-1)	10 (+1)
4	1.5 (+1)	10 (+1)
5	1.0 (0)	7 (0)
6	1.0 (0)	7 (0)
7	1.0 (0)	7 (0)

Coded values in parenthesis. IL: ionic liquid.

Gas chromatography analysis

GC-MS analyses were performed using a gas chromatography/mass spectrometry system, Shimadzu model QP2010 Plus (Kyoto, Japan), using helium (purity 99.999%) as carrier gas at a flow rate of 1 mL min⁻¹, injection volume of 1 µL with split 1:20, using a ZB-5 column-5% phenyl, 95% dimethylpolysiloxane (60 m in length × 0.25 mm internal diameter × 0.25 µm thickness phase) (Phenomenex, California, USA). The oven program of temperature was: 80 °C (2 min), at 2 °C min⁻¹ to 200 °C (1 min), then at 8 °C min⁻¹ to 280 °C (2 min), totaling an analysis time of 75 min. The injector and detector temperature were 280 °C and the ion source temperature was 250 °C. The mass spectrometer operated in SCAN and SIM modes, with 70 eV ionization.

Compound analysis was performed by comparing the fragmentation profiles of the compounds against the NIST 21 and Wiley 08 Libraries, considering peaks with a similarity index above 75% and relative area above 0.10%.

To determine the phenolic compounds extracted from the aqueous fraction, the samples were derivatized as described in Santos *et al.*,³⁶ and adding 20 µL of 1,1'-biphenyl (internal standard) (Sigma-Aldrich, São Paulo, Brazil). Quantification was performed with 12 standards: (phenol, 2-methylphenol, 3-methylphenol, 4-methylphenol, 2,5-dimethylphenol, 3,5-dimethylphenol,

2-methoxyphenol, benzene-1,2-diol, 4-methylbenzene-1,2-diol, benzene-1,3-diol, 2,6-dimethoxyphenol, and 2-methoxy-4-prop-2-enylphenol) in the extracts from the aqueous pyrolysis fraction. Microsoft Excel software was used to generate the bar graphs.³⁷

UV-Vis analysis of TPC in the phenolic extracts

A UV-Vis equipment (Shimadzu, model UV-1800, Kyoto, Japan) was used for the spectrophotometric measurements. After the extraction process, a solution with 40 μL of the extract was diluted to 2 mL with a buffer solution (pH = 10) and this solution was vortexed for 1 min. It was added, under agitation, 2 mL of the 4-aminoantipyrine (Sigma-Aldrich, São Paulo, Brazil,) solution (1.0 g L^{-1}) plus 2 mL of potassium hexacyanoferrate solution ($\text{K}_3[\text{Fe}(\text{CN})_6]$ 8.0 g L^{-1}) (Sigma-Aldrich, São Paulo, Brazil). After 15 min, absorbance was measured for phenolic compounds at 506 nm.³⁸

The TPC in the organic phase was calculated by the equation 1:

$$\text{TPC (\%)} = (\text{CsVs} / \text{CsVs} + \text{CaqVaq}) \times 100 \quad (1)$$

where Cs and Caq are the equilibrium concentration of phenols in the organic phase and the aqueous phase, respectively, while Vs and Vaq are the volumes of the organic phase and the aqueous fraction, respectively.

For the partition coefficient, the calculations were performed using the equation 2:³¹

$$\text{Distribution coefficient, } k = \frac{\text{Concentration of phenol in solvent}}{\text{Concentration of phenol in the aqueous phase}} \quad (2)$$

Results and Discussion

Qualitative GC-MS analysis of the aqueous fraction

The analysis showed more than 100 compounds (Figure S1, Supplementary Information (SI) section) and only 72 compounds were identified, distributed among the various chemical classes: alcohols (16%), acids (4%), phenols (40%), ketones (5%), esters (5%), sugars (7%), hydrocarbons (2%), and others (21%) (compounds with more than one functional group or otherwise were not classified), with the majority class being phenols, identifying 21 compounds.

The phenols presented about 40% (in peak area) of the identified compounds. The twelve analytes evaluated in this work corresponded to approximately 61.5% (in area) of the total phenols identified.

These compounds were derived from the thermodegradation of the lignin, during the pyrolysis process, giving rise to phenolic derivatives of its main monomers being coniferyl, *p*-coumaryl, and sinapyl alcohols.³⁹ Jeenpadiphat *et al.*⁴⁰ explains that benzene-1,2-diol is formed by the breakdown of lignin, and can also be produced from the intermediate 2-methoxyphenol by nucleophilic aromatic substitution reaction in water. 2-Methoxyphenol is not only formed from the breakdown of lignin, but is also produced from the breakdown of the C–C bond of the 4-ethyl-2-methoxyphenol intermediate, which can be derived from cellulose breakdown.

Influence of temperature and power on the UALLE

Initially, the effects of the variables temperature and power were evaluated for UALLE at 10 and 30 min. The sum of the concentrations of the main phenols present in the aqueous fraction of the bio-oil can be seen in Figure 1 for each experimental matrix test.

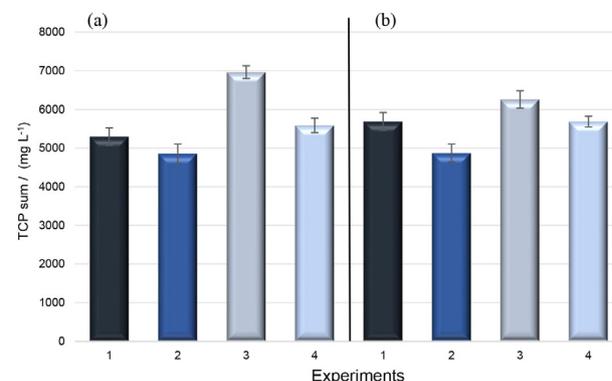


Figure 1. Ultrasonic assisted liquid-liquid extraction of phenols presents in guava seed aqueous pyrolysis fraction, at 10 min (a) and at 30 min (b). Experimental conditions: (1) P (60%), T (30 °C); (2) P (60%), T (40 °C); (3) P (100%), T (30 °C); (4) P (100%), T (40 °C).

The highest phenolic concentration was obtained in experiment 3 at 10 min of extraction with a concentration of $6965.07 \text{ mg L}^{-1}$. Experiment 3 at 30 min presented the second highest concentration. In both cases 100% power was used, being a crucial factor for better extraction.

The ultrasound generates an intense micro-turbulence effect in the medium, and nano size cavitation bubbles can be produced to provide greater interaction between sample compounds and the extracting solvent. This increase in contact surface between solvent and sample provides greater extraction. Higher power (100%) results in increased cavitation forces and promotes greater mass transfer between the liquid phases.⁴¹

The FFD allowed to measure the effects of independent variables temperature (X1) and power (%) (X2) for 10

and 30 min on the UALLE of phenols from the aqueous fraction of the guava seed bio-oil. According to the results, significant variations for temperature (X1) and power (X2) occurred as can be seen in the Pareto diagrams, Figure S2, SI section.

All the independent variables showed to be statistically significant (p -value < 0.05) in the phenol extraction. According to the interaction results, there were no significant variations at the central points, suggesting excellent repeatability. Potency was the most significant factor at 10 min. The highest concentrations of extracted phenolic compounds were reached by increasing potency and decreasing temperature.

For the experiments performed using 30 min of extraction, the interaction effects between variables were different. It was observed that with increasing power and decreasing temperature, better results were achieved, similar to what was observed with a time of 10 min, but the interaction between the variables was not significant, presenting a p -value > 0.05 .

Continuing the statistical analysis, response surface graphs were constructed (Figure 2), having as a response the concentration of phenols in function of the independent power and temperature variables. The times of 10 and 30 min presented linear regressions of 97.27 and 94.60%, respectively.

Figure 2a represents the surface response for extraction temperature *versus* ultrasonic power at 10 min. It can be concluded from Figure 2a that greater responses can be expected at lower temperature values and higher power. Temperature and power present antagonistic effects on the system. Higher power results in increased cavitation forces and promotes greater mass transfer between the liquid phases, but with high temperatures the bubbles implode prematurely decreasing the mass transfer.

Figure 2b presents the surface response for extraction temperature *versus* ultrasonic power at 30 min. In this figure, when the power was adjusted to higher values, the concentration of phenolic compounds extracted increased. Yet with increasing temperature, we noted a decrease on this concentration. Overall, the extractions responded favorably to increased ultrasonic power. The temperature effect is more pronounced at 30 min than 10 min, suggesting the loss of analyte with increasing extraction time.

One strategy to increase the ultrasonic extraction of phenols from the aqueous fraction is to work at high power and lower temperature since these maximize the sonochemical effect. This, considering that better results are obtained in shorter extraction times, makes the method more viable for industrial applications, where time and energy savings are the priority.

Kinetic effect of ultrasound-assisted liquid-liquid extraction

The kinetic effect of UALLE was assessed through the sum of the concentrations of the twelve phenols determined by GC-MS in the aqueous fraction (Figure S3, SI section). Despite being the study of a complex sample, highly heterogeneous and with different compound classes that interfere in the mass transfer mechanism, it was observed that the greatest kinetic velocity was observed at 25 min, mainly due to equilibrium saturation of the phenols in the solvent. However, when the time exceeded 25 min, a decrease in the extraction yield for all studied phenols was observed, probably due to degradation or volatilization. The next experiments were thus performed under the best conditions established: 25 min, 40 °C, 100% power, and 1:4 v/v sample/solvent ratio.

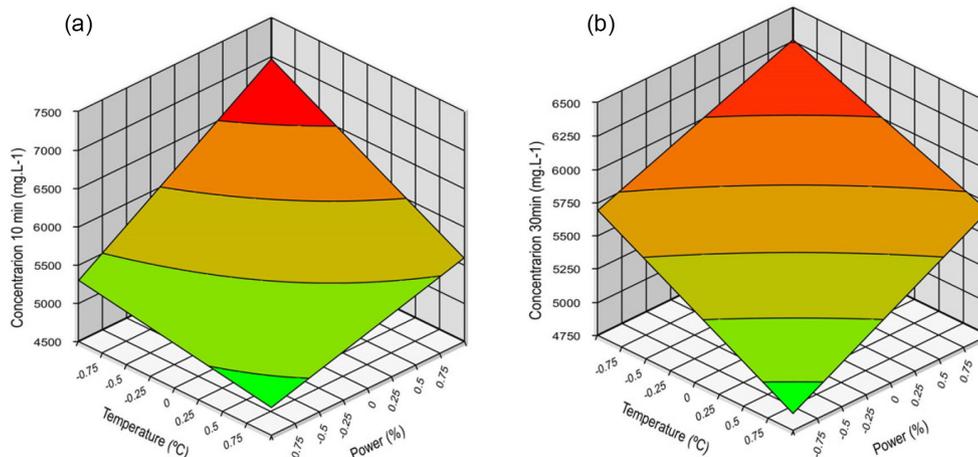


Figure 2. Response surface graphic and contour plots for the extraction of phenols from the aqueous fraction of guava seed bio-oil: (a) temperature (°C) *versus* ultrasound power at 10 min; and (b) extraction temperature (°C) *versus* ultrasound power at 30 min.

Influence of ionic liquids on UALLE-IL

UV-Vis analysis of TPC

The influence of the ILs BMIM.NTF2 and BMIM.PF6 was determined using recovery of TPC by UV-Vis. The effect of the variables, sample pH, and IL percentage on UALLE-IL are shown in Figure 3.

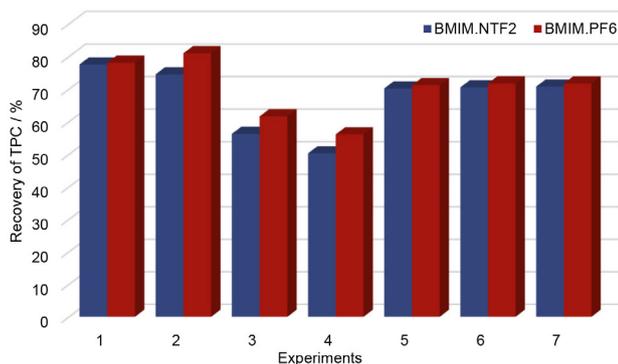


Figure 3. Distribution of TPC in aqueous fraction of guava seed pyrolysis with different conditions of UALLE-IL with ethyl acetate. Conditions: (1) 0.5% (v/v) IL and pH = 4; (2) 1.5% (v/v) IL and pH = 4; (3) 0.5% (v/v) IL and pH = 10; (4) 1.5% (v/v) IL and pH = 10; (5)(6)(7) 1.0% (v/v) IL and pH = 7.

BMIM.PF6 presents yields slightly superior than BMIM.NTF2. For both ILs, the highest extraction occurred at $\text{pH} \leq 7$, which can be explained since in the acid range, the species in aqueous solutions exist in molecular form. The analysis of the influence of pH on extraction shows that to obtain good recovery, the pH of the solution must be lower than the pK_a (between 9.3-10.2).⁴² Thus, an additional increase in the pH of the aqueous phase leads to a corresponding increase in the phenolic fractions, which arrives at 50% when $\text{pH} = \text{pK}_a$.²⁸ This ability of ILs to remove phenolic compounds can be explained either by the interaction between the hydroxyl group of the phenol and hydrogen bonded to the C2 carbon of the imidazolium

ring of the ILs, which has an acidic character, or (even more likely) by interaction between the hydroxyl group of the phenol and the anion of the ionic liquid.^{27,28}

Pareto diagram (Figure S4, SI section), and the response surface graph (Figure 4), show the results of the UALLE ILs. According to these results, pH has a positive effect on the extraction of total phenols. The lower pH experiments obtained higher percentages of phenolic compound extraction. Statistically, (with a p -value < 0.05), the independent variable pH influences positively in the UALLE ILs, in an isolated manner. On the other hand, interactions between the variables IL percentage and pH (X_1, X_2), as well as IL percentage (X_1) alone, were not significant.

Figure 4 presents the response surface graphics and contour graphic, for each ionic liquid, where the percentage of phenols is the response obtained as a function of the independent variables (pH and ILs%). The coefficients of determination (R^2) were equal to 0.9025 and 0.9745 for BMIM.NTF2 and BMIM.PF6, respectively. These values confirm that the established model was well fitted and sufficient to handle variations in around 90.25 and 97.45% of process variables.

Partition coefficients

The partition coefficients of the total phenols with the two ionic liquids using different experimental conditions are shown in Figure 5.

It is known that an important function of a solvent is to contribute to a high partition coefficient without miscibility in the aqueous phase. The partition coefficients reached higher values at $\text{pH} \leq 7$ for both ILs, while at $\text{pH} > 7$ partition coefficients decrease for both. BMIM.PF6 presented better performance in total phenols extraction with a partition coefficient of 4.26, while BMIM.NTF2 achieved a maximum value of 3.45.

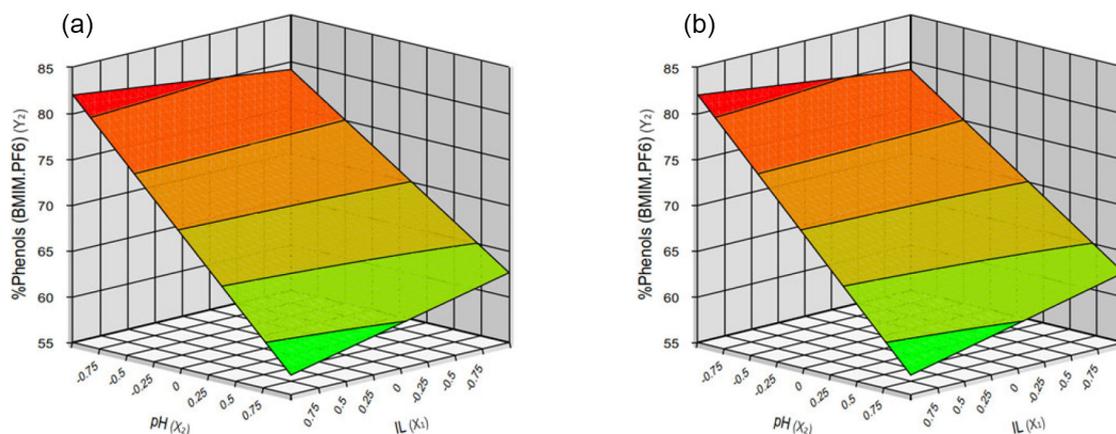


Figure 4. Surface response graphics and contour plots as the response percentage of total phenols extracted by UALLE-IL. (a) pH versus percentage of IL BMIM.NTF2, and (b) pH versus percentage of IL BMIM.PF6.

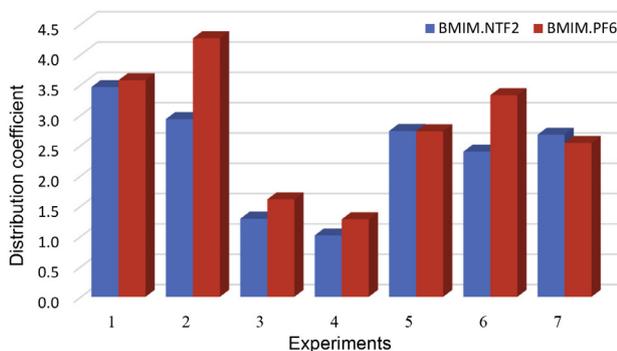


Figure 5. Variation of the distribution coefficient of total phenols with the experimental conditions for extraction with UALLE-ILs. Conditions: (1) 0.5% (v/v) IL and pH = 4; (2) 1.5% (v/v) IL and pH = 4; (3) 0.5% (v/v) IL and pH = 10; (4) 1.5% (v/v) IL and pH = 10; (5)(6)(7) 1.0% (v/v) IL and pH = 7.

Principal main phenols analysis using GC-MS

A comparison of the efficiency of ionic liquids and non-ionic liquids on the UALLE (by GC-MS) for the extraction of the 12 phenols selected, can be viewed in Figure S5, SI section.

The IL BMIM.NTF2 was less efficient for TPC, yet when the compounds were analyzed by GC-MS (sum standard phenols) this IL obtained higher concentrations than BMIM.PF6. This is due to the fact that the spectrophotometric analysis is not selective for phenol monomers, but encompasses smaller molecules from lignin that are not evaluated when using GC-MS.

Interactions between ionic liquids and phenols are dependent on physical properties such as viscosity, saturation, vapor pressure, and surface tension, which affect cavitation. The IL BMIM.PF6 presents a higher viscosity (371 cP at 20 °C) than BMIM.NTF2 (52 cP at 20 °C), this

higher viscosity intensifies molecular interactions, while hindering the mobility of compounds into the solvent phase.⁴¹

The pH of a solution is an important factor in determining its physical and chemical properties, and it can affect the dynamics of cavitation bubbles.⁴³ For the phenols quantified in this experiment, better yields were obtained at pH = 7.

The two ILs used proved to be efficient in UALLE in concentrations above 152% as compared to the experiments performed without the presence of ILs (Table S1, SI section). It was also observed that changes in the pH of the aqueous fraction and the presence of ionic liquids increased the extracted phenols concentration, but the increase in IL percentages did not present differences between the experiments. Table 2 presents the percentage of phenols in relation to the whole in the extraction using BMIM.NTF2.

The concentration of 2-methoxyphenol is higher in relation to the other phenols quantified. The percentage ranged from 33.9 to 41.2%, while for 2,6-dimethoxyphenol it ranged from 25.3 to 34.6%. The highest percentage obtained for 2-methoxyphenol was at pH = 10 (Exp. 3), while more benzene-1,2-diol was extracted at pH = 4 (Exp. 2). The total of alkyl phenols remains around 24%, and most phenols are classified as guaiacols or catechols (around 76%). In the BMIM.PF6 extraction, the percentage values of 2-methoxyphenol were between 36.6 to 41.4%, and 2,6-dimethoxyphenol between 31.1 to 37.2%.

When compared to the UV-Vis analysis, the maximum phenols quantified by GC-MS reached 20.2% for BMIM.NTF2 and 18.1% for BMIM.PF6 (Table S1, SI section). The remainder was formed by fragments of lignin phenols or multifunction compounds (not quantified via GC-MS for lack of reference standards).

Table 2. Percentage of phenols obtained by the sum of peak relative area on GC-MS analysis, for UALLE and IL BMIM.NTF2 extraction

Phenol	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6	Ex 7	Non-IL
Phenol / %	16.2	16.9	14.2	16.0	15.4	16.0	16.5	14.9
2-Methylphenol / %	0.0	0.0	0.7	0.8	0.6	0.7	0.6	0.4
4-Methylphenol / %	0.0	1.3	1.2	1.2	1.3	1.4	1.3	1.1
3-Methylphenol / %	5.9	7.0	6.6	6.1	5.8	6.6	6.6	6.0
3,5-Dimethylphenol / %	0.2	0.0	0.3	0.3	0.2	0.4	0.3	0.2
2-Methoxyphenol / %	37.8	38.5	41.2	37.7	35.0	34.2	33.9	38.9
2,5-Dimethylphenol / %	0.4	0.5	0.0	0.0	0.4	0.4	0.4	0.3
Benzene-1,2-diol / %	4.4	8.6	3.2	3.4	5.0	4.0	3.3	3.5
Benzene-1,3-diol / %	0.0	0.0	0.3	0.3	0.4	0.3	0.2	0.0
4-Methylbenzene-1,2-diol / %	0.8	1.3	1.5	1.4	1.9	2.0	1.7	0.4
2,6-Dimethoxyphenol / %	33.7	25.3	30.3	32.1	33.1	33.3	34.6	33.6
2-Methoxy-4-prop-2-enylphenol / %	0.5	0.6	0.7	0.6	0.8	0.7	0.6	0.8

Detailed experimental conditions: Ex 1: 0.5% (v/v) IL and pH = 4; Ex 2: 1.5% (v/v) IL and pH = 4; Ex 3: 0.5% (v/v) IL and pH = 10; Ex 4: 1.5% (v/v) IL and pH = 10; Ex 5, 6 and 7: 1.0% (v/v) IL and pH = 7, Non-IL: without IL and pH = 4

At pH = 7 the two ILs exhibited similar behavior, and it was thus possible to better quantify the phenol monomers using GC-MS, but the percentages quantified decreased at pH = 4 and at pH = 10, showing that at these pH values there may have been a change in equilibrium in the medium with dimers or other lignin-derived compounds, which was not possible to quantify using GC-MS.

Conclusions

2-Methoxyphenol (guaiacol) and 2,6-dimethoxyphenol (syringol) were the majority compounds in extracts of guava seed bio-oil aqueous fraction. These compounds can be used in bio refineries for the production of phenolic resins, thermal insulation materials, adhesives, post molding, laminated resins, surface coatings, and composites. From analysis of ultrasonic assisted liquid-liquid extraction parameters, the ultrasound potency showed the most significant factor, increasing this parameter, higher concentrations of the extracted phenolic compounds were obtained.

The ionic liquid BMIM.NTF2 was considered an effective co-solvent, allowing greater extractions for the quantified phenols coupled to a conventional organic solvent. The results revealed that phenols extraction by UALLE-IL is highly influenced by the pH of the aqueous fraction, presenting higher yields at pH \leq 7. The phenols quantified by GC-MS reached a maximum of 20.2% of the total phenols. Both ILs presented recoveries above 80% and can be used for extraction of these compounds.

Supplementary Information

Supplementary information (Figures S1-S5 and Table S1) is available free of charge at <http://jbcs.sbc.org.br> as PDF file.

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Author Contributions

Solange C. A. Cerqueira was responsible for formal analysis, investigation and methodology; Laryssa M. Santos for formal analysis; Antonia R. S. Gois for analysis and writing-original draft; Cleide M. F. Soares for data curation and writing review and editing; Brenno A. D. Neto for writing-review and editing and resources;

Lisiane S. Freitas for conceptualization, methodology, resource, supervision, writing-review and editing and resource.

References

- Forster-Carneiro, T.; Berni, M. D.; Dorileo, I. L.; Rostagno, M. A.; *Resour., Conserv. Recycl.* **2013**, *77*, 78. [Crossref]
- Cheng, T.; Han, Y.; Zhang, Y.; Xu C.; *Fuel* **2016**, *172*, 49. [Crossref]
- Bridgwater, A. V.; *Biomass Bioenergy* **2012**, *38*, 68. [Crossref]
- Gouda, N.; Singh, R. K.; Meher, S. N.; Panda, A. K.; *J. Energy Inst.* **2017**, *90*, 265. [Crossref]
- Oasmaa, A.; Czernik, S.; *Energy Fuels* **1999**, *13*, 914. [Crossref]
- Schroeder, P.; do Nascimento, B. P.; Romeiro, G. A.; Figueiredo, M. K.; Veloso, M. C. C.; *J. Anal. Appl. Pyrolysis* **2017**, *124*, 161. [Crossref]
- Maciel, G. P. S.; Machado, M. E.; Barbará, J. A.; Molin, D. D.; Caramão, E. B.; Jacques, R. A.; *Biomass Bioenergy* **2016**, *85*, 198. [Crossref]
- Mukarakate, C.; Evans, R. J.; Deutch, S.; Evans, T.; Starace, A. K.; Dam, J. T.; Watson, M. J.; Magrini, K.; *Energy Fuels* **2017**, *31*, 1600. [Crossref]
- Aysu, T.; *Fuel Process. Technol.* **2015**, *129*, 24. [Crossref]
- Abou-Yousef, H.; Hassan, E. B.; *Fuel* **2014**, *137*, 115. [Crossref]
- Kanaujia, P. K.; Sharma, Y. K.; Garg, M. O.; Tripathi, D.; Singh, R.; *J. Anal. Appl. Pyrolysis* **2014**, *105*, 55. [Crossref]
- Papari, S.; Hawboldt, K.; Helleur, R.; *Ind. Eng. Chem. Res.* **2015**, *54*, 605. [Crossref]
- Mendonça, F. G.; Gomes, J. P. M.; Tristão, J. C.; Ardisson, J. D.; Soares, R. R.; Lago, R. M.; *Fuel* **2016**, *184*, 36. [Crossref]
- Kalam, S.; Chen, N.; Borazjani, H.; Nejad, M.; *Ind. Crops Prod.* **2018**, *125*, 520. [Crossref]
- Ramires, E. C.; Frollini, E.; *Composites, Part B* **2012**, *43*, 2851. [Crossref]
- Mabrouk, A.; Erdocia, X.; Alriols, M. G.; Labidi, J.; *J. Cleaner Prod.* **2018**, *198*, 133. [Crossref]
- Li, X.; Moreno, L. C.; Luque, S. R. G. O.; Rehmann, L.; Kersten, S. R. A.; Schuur, B.; *Bioresour. Technol.* **2016**, *216*, 12. [Crossref]
- dos Santos, W. N. L.; Sauthier, M. C. S.; dos Santos, A. M. P.; Santana, D. A.; Azevedo, R. S. A.; Caldas, J. C.; *Microchem. J.* **2017**, *133*, 583. [Crossref]
- Zhou, M.; Xiao, G.; Wang, K.; Jiang, J.; *Fuel* **2016**, *180*, 749. [Crossref]
- Wei, Y.; Lei, H.; Wang, L.; Zhu, L.; Zhang, X.; Liu, Y.; Chen, S.; Ahring, B.; *Energy Fuels* **2014**, *28*, 1207. [Crossref]
- Khezeli, T.; Daneshfar, A.; *Ultrason. Sonochem.* **2017**, *38*, 590. [Crossref]
- Johna, J. J.; Kuhna, S.; Braekenb, L.; Gervena, T. V.; *Ultrason. Sonochem.* **2018**, *42*, 68. [Crossref]

23. Pradal, D.; Vauchel, P.; Decossin, S.; Dhulster, P.; Dimitrov, K.; *Ultrason. Sonochem.* **2016**, *32*, 137. [Crossref]
24. Ozcan, S.; Tor, A.; Aydin, M. E.; *Water Res.* **2009**, *43*, 4269. [Crossref]
25. García, M. J. S.; Martínez, V. M. O.; Fernández, F. J. H.; Ríos, A. P.; Medina, J. Q.; *J. Hazard. Mater.* **2017**, *321*, 484. [Crossref]
26. Rodriguez-Palmeiro, I.; Rodriguez-Escontrela, I.; Rodriguez, O.; Arce, A.; Soto, A.; *RSC Adv.* **2015**, *5*, 37392. [Crossref]
27. Sas, O. G.; Domínguez, I.; González, B.; Domínguez, Á.; *J. Environ. Manage.* **2018**, *228*, 475. [Crossref]
28. Lakshmi, B. A.; Balasubramanian, A.; Venkatesan, S.; *Clean* **2013**, *41*, 349. [Crossref]
29. Cesari, L.; Canabady-Rochelle, L.; Mutelet, F.; *Sep. Purif. Technol.* **2019**, *209*, 528. [Crossref]
30. Bharti, A.; Banerjee, T.; *Fluid Phase Equilib.* **2015**, *400*, 27. [Crossref]
31. Kim, G.-J.; Kim, J.-H.; *Process Biochem.* **2015**, *50*, 989. [Crossref]
32. Blesic, M.; Lopes, J. N. C.; Gomes, M. F. C.; Rebelo, L. P. N.; *Phys. Chem. Chem. Phys.* **2010**, *12*, 9685. [Crossref]
33. Bispo, M. D.; Barros, J. A. S.; Tomasini, D.; Primaz, C.; Caramão, E. B.; Dariva, C.; Krause, L. C.; *J. Earth Sci. Eng.* **2016**, *6*, 235. [Crossref]
34. Ren, S.; Ye, X. P.; Borole, A. P.; *J. Anal. Appl. Pyrolysis* **2017**, *123*, 30. [Crossref]
35. Rodrigues, M. I.; Costa, P.; *Protimiza Experimental Design*, version 1; Protimiza, Brazil, 2014. [Link] accessed in October 2022
36. Santos, R. M.; Santos, A. O.; Sussuchi, E. M.; Nascimento, J. S.; Lima, Á. S.; Freitas, L. S.; *Bioresour. Technol.* **2015**, *196*, 43. [Crossref]
37. *Microsoft Excel*, version 2016; Microsoft Corporation, USA, 2015.
38. Dolatto, R. G.; Messerschmidt, I.; Pereira, B. F.; Silveira, C. A. P.; Abate, G.; *J. Braz. Chem. Soc.* **2012**, *23*, 970. [Crossref]
39. del Pozo, C.; Bartrolí, J.; Puy, N.; Fàbregas, E.; *Ind. Crops Prod.* **2018**, *125*, 160. [Crossref]
40. Jeenpadiphat, S.; Mongkolpichayarak, I.; Tungasmita, D. N.; *J. Anal. Appl. Pyrolysis* **2016**, *121*, 318. [Crossref]
41. Vernès, L.; Vian, M.; Chemat, F. In *Liquid-Phase Extraction*; Poole, C. F., ed.; Elsevier: Avignon, France, 2020, ch. 12. [Crossref]
42. Fan, J.; Fan, Y.; Pei, F. Y.; Wu, K.; Wang, J.; Fan, M.; *Sep. Purif. Technol.* **2008**, *61*, 324. [Crossref]
43. Sivakumar, M.; Tataka, P. A.; Pandit, A. B.; *Chem. Eng. J.* **2002**, *85*, 327. [Crossref]

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