Ultrasonic Pretreatment of Cowpea Bean Pod with K₃PO₄: Effect on Bio-Oil Yield and Phenolic Compounds Content

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Ultrasonic pretreatment of cowpea bean pod biomass with addition of tripotassium phosphate (K₃PO₄) was used to induce the production of bio-oil enriched in phenolic compounds. An ultrasound bath operating at 40 kHz, 154 W power, and constant biomass:K₃PO₄ ratio of 5:1 (m/m) was used for pretreatments with different durations: 0.5, 1.5, 3, 6, 8, and 12 h. After the pretreatment, the biomass was pyrolyzed in a fixed bed reactor at 600 °C, under a flow of N₂ at 5 mL min⁻¹. The pyrolysis results indicated that the use of K₃PO₄ reduced the bio-oil yield, when compared to non-catalytic pyrolysis, and that the use of ultrasound caused increased biomass devolatilization, increasing the gas yield and reducing the formation of biochar. Gas chromatography mass spectrometry (GC-MS) analysis of the bio-oils indicated that pretreatment of the biomass led to significant increases of the phenolics contents, as well as alteration of the chemical profile of these compounds. The highest phenolics content of 8.12% m/m was obtained for the biomass submitted to 1.5 h of ultrasonic pretreatment, compared to 4.89% m/m for the untreated biomass.

Keywords: biomass, pretreatment, ultrasound, phenolic compounds, K₃PO₄

Introduction

The growing energy demand and limited global resources for clean energy production has led to an intensified search for alternative and renewable energy sources. The use of biomass as a substitute for fossil fuels has gained prominence in recent years, mainly because it is a renewable resource with wide availability and low pollution potential. It can make a valuable contribution to mitigating problems associated with increasing levels of atmospheric greenhouse gases generated as byproducts of fossil fuel combustion. Biomass can be understood as all organic material of non-fossil origin, derived from diverse sources such as agricultural residues, wastes from forestry activities, dedicated cultivations, livestock residues such as animal fat and manures, microalgae, and other types of wastesc. Approximately 450 gigatons of carbon worldwide are estimated to be in the form of plant biomass. Lignocellulosic biomass can be highlighted as a sustainable energy source, given its abundance and absence of competition with food production, since it is available in the form of wastes, such as those originating from agricultural or forestry activities. In addition to energy production, the applications of biomass include biomaterials and inputs for the chemical industry.

A wide range of conversion processes can be used to release energy from biomass, including direct burning for heat production, thermochemical processes such as pyrolysis, carbonization, gasification, or catalytic liquefaction, and biochemical processes such as anaerobic fermentation and ethanol fermentation. Pyrolysis, the most promising technology to exploit this potential, consists of the thermal decomposition of biomass in an oxygen-free atmosphere, generating gases, solids, and liquids that can be used as fuels or as feedstocks for chemicals of high commercial value. The yields of these three products compete, mainly determined by the composition of the biomass, but also influenced by the process conditions such as temperature, heating rate, and residence time. In general, low heating rates and long vapor retention times favor the formation of biochar, while high heating rates and short retention times favor the production of bio-oil. High heating rates and long vapor retention times favor the gas yield, due to secondary reactions that decompose compounds present in the pyrolytic vapor, forming non-condensable compounds.

The pyrolysis of biomass material usually leads to bio-oil as the main product, together with a complex mixture...
of organic compounds that may include carboxylic acids, esters, aldehydes, ketones, alcohols, sugars, phenolic compounds, and hydrocarbons, which can be used as raw materials in the chemical and fuel industries.\textsuperscript{2,11,12} Bio-oils rich in phenolic compounds are of interest to these industries, since they can replace phenol of petrochemical origin as raw materials for the production of phenolformaldehyde resins such as novolak and resole resins, other high-quality resins,\textsuperscript{13,14} and materials based on epoxy or polyurethane.\textsuperscript{15-17}

The use of catalysts to improve the production of bio-oils has been highlighted, due to the difficulty and cost of isolating bio-oil components using techniques based on vacuum distillation,\textsuperscript{18,19} absorbent resins,\textsuperscript{20,21} liquid-liquid extraction,\textsuperscript{22,23} or supercritical fluids.\textsuperscript{24,25} These catalysts can be used during pyrolysis in \textit{in situ} processes, when the catalyst is added together with the biomass in the reactor,\textsuperscript{26,27} or \textit{ex situ},\textsuperscript{28} by passing the pyrolytic vapors through a catalytic bed after leaving the reactor. These processes favor selective product yields, reducing costs in the purification of compounds and improving the quality of bio-oils by eliminating components such as carboxylic acids, aldehydes, and ketones. The use of catalysts also favors the formation of products of greater commercial interest, such as hydrocarbons and alkylphenols.\textsuperscript{29-31}

Chen \textit{et al.}\textsuperscript{32} in a study of the effect of the catalyst on the conversion of bamboo wastes, obtained an increase of the phenolics content in bio-oil from 47 to 80\%, using an N-doped biochar catalyst.

Durak\textsuperscript{33} in a study of the effects of boron catalysts and pyrolysis parameters on product types and yields, obtained an increase of the yield of liquid products from 20.12 to 27.97\%, using 10 \textit{wt.}\% Colemanite at 550 °C, together with a substantial increase from 3.54 to 26.18\% in the content of identified phenolic compounds.

The use of pretreatments to reduce the recalcitrance of biomass, increasing its susceptibility to pyrolytic reactions, is also an essential tool for optimization of yields.\textsuperscript{7,34} Ultrasonic pretreatment is an economical and environmentally appealing option, among the available pretreatment methods involving chemical, physical, and biological processes (or their combinations).\textsuperscript{15,36} This pretreatment causes depolymerization and cleavage of structural components of the biomass, without generating toxic waste that would require appropriate treatment and disposal.\textsuperscript{37}

Pretreatment using ultrasound is based on the formation of cavitation bubbles by the propagation of ultrasonic waves in a liquid medium. When the bubbles collapse, they release large amounts of energy, causing the homolytic breakdown of solvent molecules and the generation of free radicals that promote depolymerization of the biomass. The formation of microjets and acoustic currents may lead to increased porosity, erosion, and fragmentation of biomass particles, in addition to increasing mass transfer in the medium.\textsuperscript{36-38} Ultrasonic pretreatment can also cause the breakdown of lignin-hemicellulose bonds, as well as homolytic cleavage of the β-O-4 and α-O-4 bonds in the macromolecular structure of lignin. Macromolecules such as lignin and hemicellulose are less likely to move along with the solvent, when submitted to an acoustic field, consequently leading to the rupture of bonds.\textsuperscript{38}

The present study investigates the effect of ultrasonic treatment in association with the use of K\textsubscript{3}PO\textsubscript{4} as a catalyst, as well as the influence of the pretreatment time, on the enrichment of bio-oil produced by the pyrolysis of cowpea bean pod biomass.

\textbf{Experimental}

\textbf{Materials}

The biomass used in the experiments was cowpea (\textit{Vigna unguiculata}) bean pods, obtained in a local market in the city of Aracaju ( Sergipe State, northeastern Brazil). After removal of the grains, the pods were manually selected, washed in tap water to remove residues, and dried for 24 h at 60 °C in an air convection oven, in order to obtain biomass with moisture content lower than 10\%. After drying, the biomass was crushed and sieved to obtain particles sized between 40 and 60 mesh, which were stored in sealed bottles for later use.

\textbf{Ultrasound pretreatment of the biomass}

The biomass without ultrasonic pretreatment was labeled as raw biomass, while the pretreated biomass was labeled according to each ultrasonic pretreatment time. The pretreatment was performed at 40 °C in an ultrasonic bath (USC-2800A, UNIQUE, Indaiatuba, Brazil) operated using 40 kHz frequency and 154 W power in all the experiments. A mass of 5 g of tripotassium phosphate (K\textsubscript{3}PO\textsubscript{4}) ( Dinâmica, Indaiatuba, Brazil) was dissolved in 350 mL of deionized water and was added to 25 g of raw biomass, corresponding to 20 \textit{wt.}\% of catalyst in the biomass. This proportion was based on the work of Zhang \textit{et al.},\textsuperscript{39} who studied the effect of the quantity of catalyst used in the pyrolysis process. The suspension was ultrasonicated, under mechanical stirring at 500 rpm, for times of 0.5, 1.5, 3, 6, 8, and 12 h. After the pretreatments, the samples were frozen at −80 °C and lyophilized for the removal of water.
Biomass characterization

Proximate and ultimate analyses

The analyses of the raw and pretreated biomasses were performed in the Department of Chemistry of the Federal University of Sergipe. The moisture and ash contents were determined according to the protocols of the National Renewable Energy Laboratory. The moisture content was determined by drying the samples at 105 °C until reaching constant weight. The ash contents were determined by placing the samples in crucibles and heating in a muffle furnace at 575 °C for 6 h, after which they were transferred to a desiccator and allowed to cool to ambient temperature, followed by weighing. This procedure was repeated until a constant weight was reached. The volatile matter content was determined by heating the samples at 950 °C in an inert atmosphere (to avoid oxidation by air), with correction for the moisture content. The fixed carbon content was obtained by difference, according to equation 1.

\[
\text{Fixed carbon (\%) } = 100 - (\text{ash + volatile matter + moisture})
\]

Ultimate analysis of the samples employed a CHN/O elemental analyzer (CHN628, LECO, Rio de Janeiro, Brazil), with all the values calculated on a moisture-free and ash-free basis. The higher heating value (HHV) was estimated from the elemental composition, considering the main elements, as proposed by Sheng and Azevedo (equation 2).

\[
\text{HHV (MJ kg}^{-1}\text{) } = (0.3137 \, \text{C}) + (0.7009 \, \text{H}) + (0.0318 \, \text{O}) - 1.3675
\]

Thermogravimetric analysis

Thermogravimetric (TGA) analyses were performed using a simultaneous DTA-TGA instrument (model DTA-50, Shimadzu, Kyoto, Japan), with the temperature increased from 30 to 1000 °C, at a heating rate of 10 °C min⁻¹, under an atmosphere of nitrogen gas supplied at a flow rate of 100 mL min⁻¹. These analyses used approximately 5 mg of sample in an alumina crucible.

Pyrolysis of the biomass

The pyrolysis employed a laboratory-scale pyrolyzer (Figure 1) constructed of stainless steel, with an internal diameter of 5.3 cm and length of 30 cm, externally heated by an electric furnace, as described by Santos et al. In this system, the vapor outlet was connected to a metal pipe cooled with ice water (0 °C) and the vapors were collected in four jacketed flasks maintained at approximately −10 °C by circulating ethylene glycol.

The raw and pretreated biomass samples were analyzed (in triplicate) using the same temperature (600 °C), amount of sample (8.0 g), and flow rate (5 mL min⁻¹) of N₂ used to provide an inert atmosphere. The temperature chosen was based on the TGA procedure described in a previous study by our group, where raw biomass showed a mass loss of up to 72.7% at 600 °C. With the reactor preheated to 600 °C, the samples were introduced through the upper opening and heated for 60 min to ensure that the pyrolysis reactions were completed. During this time, the bio-oil was collected in the condenser bottles connected in series to the outlet of the reactor. Control experiments were performed under the same conditions, using biomass without pretreatment (raw biomass) and biomass without the ultrasonic pretreatment, but with the addition of K₃PO₄. The other experiments were performed using biomass samples pretreated for the times described above.

Collection of pyrolysis products

The bio-oil produced was recovered by washing the condensation system with dichloromethane (Synth, Diadema, São Paulo). The aqueous fraction was separated, extracted using dichloromethane, and solvent-soluble compounds were incorporated into the bio-oil. The solvent was subsequently removed using a rotary evaporator, in order to calculate the bio-oil yield.

Characterization of the bio-oil

A preliminary derivatization step with BSTFA (N,O-bis(trimethylsilyl) trifluoroacetamide) was performed for quantification of the phenolic compounds in the bio-oil samples. BSTFA, a silylation reagent, replaces the hydrogens from phenolic hydroxyls with silyl groups, resulting in molecules with higher volatility and thermal resistance. A mass of approximately 10 mg of each
bio-oil was transferred to a 1.5 mL vial, together with 50 μL of pyridine (Sigma-Aldrich, São Paulo, Brazil) and 50 μL of BSTFA (Sigma-Aldrich, São Paulo, Brazil). Dichloromethane was added to make up to a final volume of 1 mL. The solution was subsequently homogenized and the sealed vial was heated at ca. 60 °C for 30 min in a sand bath. An aliquot of 100 μL of this sample was transferred and diluted to 1 mL, with the addition of methyl hexanoate (50 mg L⁻¹) (Sigma-Aldrich, São Paulo, Brazil) as internal standard for the gas chromatography mass spectrometry (GC-MS) analysis. The GC-MS analyses were performed using a QP2010 Plus chromatograph (Shimadzu, Kyoto, Japan) equipped with a ZB-5MS column (60 m × 0.25 mm internal diameter (i.d.), 5% phenyl-95% dimethylpolysiloxane, 0.25 μm film thickness) (Phenomenex, California, USA). The quadrupole analyzer was operated in SIM mode, with ionization at 70 eV. Helium was used as the carrier gas, at a flow rate of 1.7 mL min⁻¹, and 1 μL volumes of samples were injected using a split ratio of 1:30. The injector and detector temperatures were 280 and 300 °C, respectively. The GC oven temperature program was as follows: initial temperature of 100 °C for 2 min, ramp from 100 to 160 °C at 2 °C min⁻¹, ramp from 160 to 280 °C at 15 °C min⁻¹, and maintaining the final temperature for 10 min. The amounts of 11 compounds were monitored to identify the effect of pretreatment on the production of phenolics: phenol, o-cresol, p-cresol, m-cresol, 4-ethylphenol, 3,5-dimethylphenol, guaiacol, 2,5-dimethylphenol, o-catechol, 4-methylcatechol, and 2,6-dimethoxyphenol (Sigma-Aldrich, São Paulo, Brazil). These compounds were identified and quantified by the internal standard method. The samples were analyzed in triplicate.

## Results and Discussion

### Chemical characterization of the biomass

#### Proximate and ultimate analyses

The results of the elemental and proximate analyses are shown in Table 1. All the samples presented moisture content lower than 9%. Moisture content below 10% favors the pyrolysis process by facilitating heat transfer to the biomass particles. Higher ash contents were observed for the pretreated samples, due to the addition of potassium phosphate during the treatment. High ash content can negatively influence the biomass pyrolysis process, since the ash acts as a heat sink, hindering heat transfer. In addition, depending on its composition, ash can have a significant influence on the yield and distribution of pyrolysis products. However, the most noticeable difference for the samples submitted to pretreatment was the decreased fixed carbon content, especially for the samples submitted to 1.5, 8, and 12 h of pretreatment. A reduction in fixed carbon content means an increase in volatile matter content, leading to higher bio-oil yields.

The chemical composition of the raw biomass influences the formation and characteristics of the pyrolysis products. The lignocellulosic components of the cowpea bean pod biomass were described in a previous study by Santos et al., reporting the contents of cellulose (30.0%), hemicellulose (24.3%), lignin (7.3%), and extractives and minerals (38.4%).

### Thermogravimetric analysis

The TGA and derivative thermogravimetric (DTG) curves are presented in Figure 2. The TGA results for

### Table 1. Proximate and ultimate analyses of the raw and pretreated biomass samples

| Analysis          | Raw biomass | Pretreated biomass |
|-------------------|-------------|--------------------|
|                   | 0.5 h       | 1.5 h   | 3 h     | 6 h     | 8 h     | 12 h    |
| Moisture / wt.%   | 8.9         | 7.5     | 6.7     | 7.8     | 6.8     | 7.7     | 6.6     |
| Volatile matter   | 70.4        | 65.5    | 71.7    | 64.4    | 67.2    | 72.2    | 72.2    |
| Fixed carbon      | 16.3        | 7.7     | 2.1     | 8.5     | 6.7     | 0.3     | 1.5     |
| Ash / wt.%        | 4.4         | 19.2    | 19.4    | 19.3    | 19.3    | 19.8    | 19.6    |

| Analysis          | Raw biomass | Pretreated biomass |
|-------------------|-------------|--------------------|
|                   | Carbon      | 42.0               | 35.5 | 35.9 | 35.3 | 35.7 | 35.4 | 35.5 |
|                   | Hydrogen    | 5.9                | 5.2  | 5.2  | 5.2  | 5.1  | 5.3  | 5.0  |
|                   | Oxygen      | 37.5               | 31.8 | 31.0 | 32.2 | 30.9 | 32.2 | 31.5 |
|                   | Nitrogen    | 1.4                | 1.2  | 1.1  | 1.1  | 1.1  | 1.2  | 1.1  |
|                   | HHV / (MJ kg⁻¹) | 17.1               | 14.4 | 14.5 | 14.4 | 14.4 | 14.5 | 14.3 |

HHV: higher heating value.
the raw and pretreated biomasses showed similarities in behavior, such as the presence of three stages of thermal decomposition. The first stage was predominantly due to the volatilization of free water. According to El Abbari et al., the second stage could be attributed to the decomposition of holocellulose (predominantly hemicellulose), which decomposes at low temperatures near 200 °C, extending to approximately 315 °C. The third stage involved the decomposition of cellulose, which decomposes at higher temperatures, due to its crystallinity and the existence of hydrogen bonds between the molecules. At temperatures above 400 °C, almost all the cellulose had already been decomposed. Lignin, the most thermally stable among the three structural components of this biomass, due to its highly aromatic and polymerized structure, decomposes slowly over the temperature range from 300 to 1000 °C, resulting in a higher residual content, compared to cellulose.

The DTG curves showed that for the pretreated samples, the third event, corresponding to the decomposition of cellulose, was shifted to a lower temperature range, compared to the curve for the raw biomass. In a study of the effect of potassium salts on tobacco leaf pyrolysis, Ding et al. reported that the presence of potassium ions resulted in a decomposition route with lower activation energy, compared to pure cellulose, consequently accelerating the pyrolysis rate.

The TGA curve for the raw biomass showed that significant mass loss (61.75%) occurred up to 400 °C, with maximum decomposition rate between 220 and 380 °C. The loss of mass decreased and stabilized above 400 °C, leaving a residue of approximately 20.7%. The samples submitted to pretreatment showed behavior similar to that of the raw biomass below 400 °C. However, the mass loss was smaller (approximately 15%, according to the analysis of ash content), which could be explained by the increase in inorganic matter content caused by the addition of tribasic potassium phosphate during the pretreatment. After reaching 500 °C, the curves started to acquire more pronounced decomposition patterns, compared to the curve for the raw biomass, with the biomasses submitted to 1.5, 8, and 12 h of pretreatment presenting final residue contents comparable to that for the raw biomass (21.52, 20.01, and 21.12%, respectively), despite the increase in the inorganic load. These results indicated that the pretreatment facilitated volatilization of the biomass and caused a decrease of the residual biochar. This biochar decrease could be attributed to the rupture, depolymerization, and degradation of the biomass components, when submitted to the ultrasonic treatment. Different regions of macromolecules such as lignin and cellulose cannot uniformly follow the movement of the medium caused by the propagation of ultrasonic waves in the liquid, leading to the homolytic breaking of bonds and the formation of macroradicals. Zhang et al. reported that the collapse of cavitation bubbles on the surfaces of cellulose fibers made them shorter and reduced their crystallinity, so the biomass became more susceptible to thermal degradation, favoring its volatilization and reduction of the biochar content. This could explain the observed shift of the peak corresponding to cellulose degradation towards a lower temperature range, compared to the raw sample, due to the loss of crystallinity of the cellulose, which became more amorphous and degraded at lower temperatures.

Suliman et al. reported that lignin presents an optimal treatment time, when lignocellulosic biomass is submitted to ultrasonic treatment. After this time, its content gradually increases, due to the repolymerization of radicals formed during the degradation process. This behavior, which has also been observed elsewhere, could provide an explanation for the low residue content observed for the biomass submitted to 1.5 h of pretreatment, as well as the sudden increases of the contents for the samples submitted

![Figure 2](image-url)
to 3 and 6 h of treatment. The samples submitted to 8 and 12 h of treatment could subsequently undergo a new phase of degradation.

**Pyrolysis yields**

Different times of ultrasonication of the cowpea bean pod biomass, in the presence of K$_3$PO$_4$, were used in order to evaluate the effects on the yields of pyrolysis products and the concentration of phenols in the final bio-oil. The temperature chosen was based on the results of the TGA analyses. The raw biomass sample showed 72.7% mass loss up to 600 °C, followed by a mass loss of only 6.5% at higher temperatures. Considering the energy expenditure for heating the reactor and the low increase in yield above 600 °C, this temperature was chosen for all the samples. The yields of the pyrolysis products obtained after pretreatment of the biomasses are presented in Figure 3.

![Figure 3](image)

**Figure 3.** Pyrolysis yields of biomass samples submitted to pretreatment for different times.

The yields of products from pyrolysis of the cowpea bean pods were 25.3, 28.3, and 46.4% for the liquid, solid, and gas products, respectively. A previous study of adzuki bean residue pyrolysis found yields of approximately 30, 46, and 29% for liquid, solid, and gas pyrolysis products, respectively. Different yields are obtained depending on the biomass composition, reactor type, and pyrolysis conditions. The high content of a component such as holocellulose (54.3%) in the bean pods favored the gaseous product yield.

The results showed that the addition of K$_3$PO$_4$ to the biomass caused decreases of the bio-oil and biochar yields, with a proportional increase in the gas yield. The gas yield was increased by between 11 and 30%. This behavior could be explained by the decomposition of organic components such as linear aldehydes, furans, and anhydrous sugars, due to the catalytic action of potassium, as described by Zhang et al. and Lu et al. The findings indicated that the pretreatment attacked the structures of lignin and holocellulose, promoting the pyrolysis process.

The biochar yields showed small differences. However, as mentioned previously, for the biomasses submitted to pretreatment, the addition of potassium phosphate caused an increase of the ash content, from 4.38% (for the raw biomass) to approximately 19.5%. As a result, the biochar content resulting from pyrolysis with the addition of potassium phosphate was lower than for pyrolysis of the raw biomass.

The biomass sample pretreated with K$_3$PO$_4$ and ultrasonication for 0.5 h showed a similar bio-oil yield as the sample pretreated only with K$_3$PO$_4$. However, there was a reduction of biochar formation, while the gas yield increased, which could be attributed to the effect of the ultrasonic treatment on the lignocellulosic structure.

During the ultrasonic pretreatment, different regions of the lignin macromolecule move at different speeds. This leads to (i) homolytic cleavages between the β-O-4 and α-O-4 bonds and their forming units, and (ii) the removal of side chains, due to collisions with solvent molecules, reducing their recalcitrance and facilitating their devolatilization. No clear reduction of the bio-oil yield was observed for samples submitted to longer pretreatment times.

**Chemical analysis of the bio-oil**

Figure 4 shows the total contents of the phenolic compounds (phenol, o-cresol, p-cresol, m-cresol, 4-ethylphenol, 3,5-dimethylphenol, guaiacol, 2,5-dimethylphenol, o-catechol, 4-methylcatechol, and 2,6-dimethoxyphenol) monitored by GC-MS in the bio-oil samples.

![Figure 4](image)

**Figure 4.** Contents (mg g$^{-1}$) of total phenolic compounds analyzed in the bio-oil samples.
samples from the raw biomass, the biomass with K<sub>3</sub>PO<sub>4</sub>, and the biomass treated with ultrasonication and K<sub>3</sub>PO<sub>4</sub>. The addition of K<sub>3</sub>PO<sub>4</sub> to the biomass, without ultrasonic pretreatment before the pyrolysis, resulted in a 23.2% increase of the concentration of phenolic compounds in the bio-oil, compared to the raw biomass, reflecting the catalytic effect of K<sub>3</sub>PO<sub>4</sub> in the selective production of phenolic compounds.

Lignin is subject to various reactions during the pyrolysis process, including cleavage of the β-O-4 type bonds between the forming units, together with decarboxylation and dehydration reactions, resulting in a wide range of phenolic compounds that possess side chains remaining from the lignin structure. The presence of basic catalysts such as K<sub>3</sub>PO<sub>4</sub> during pyrolysis can facilitate hydrogen transfer, promoting demethylation, demethylation, decarboxylation, and other reactions of lignin-derived phenolics, such as guaiacol. In a study of the effects of hydrogen donor compounds on guaiacol pyrolysis, Zhou et al. reported that the presence of hydrogen donor groups, in particular methanol, provided a higher phenolics content. This was attributed to inhibition of the formation of aromatic hydrocarbons such as benzene and toluene by stabilization of the hydroxyl group, consequently favoring the formation of phenolic compounds, especially phenol. In the biomass pyrolysis environment, the presence of autogenous methanol and holocellulose itself ensures a source of hydrogen for these reactions. Zhang et al. observed that the addition of K<sub>3</sub>PO<sub>4</sub> changed the reaction pathways during the pyrolysis process, significantly modifying the phenolics distribution and concentration. In addition, the presence of K<sub>3</sub>PO<sub>4</sub> inhibits the formation of some classes of compounds, such as linear aldehydes, anhydrous sugars, and furans, from the decomposition of holocellulose.

According to Zhang et al., potassium has a catalytic action on anhydrous sugars from the decomposition of cellulose and hemicellulose, promoting dehydration reactions that lead to phenol and methylated and methoxylated derivatives, contributing to increase of the phenolics content in the bio-oil.

The catalytic effect of K<sub>3</sub>PO<sub>4</sub> on the concentration of phenolics in the bio-oil was potentiated in the samples that received ultrasonic pretreatment, with the highest concentration reached using 1.5 h of pretreatment, which resulted in a 66% increase, compared to the bio-oil obtained from the raw biomass (without treatment). This could be attributed to the effect of ultrasonication on the structural components of the lignocellulosic biomass (lignin, cellulose, and hemicellulose). As reported by Sul’man et al., these components undergo decomposition under the effect of ultrasonic treatment, resulting in low molecular mass fragments. These fragments would be more subject to volatilization during the pyrolysis process and, in the case of lignin, would contribute to a higher concentration of phenolic compounds.

However, with continuing ultrasonic treatment, the fragments formed by lignin decomposition would be subject to polymerization reactions, forming molecules of greater mass that are increasingly difficult to volatilize, which provides an explanation for the decreased contents of phenolics in the samples submitted to 3 and 6 h of treatment. With further ultrasonic treatment and increased de-structuring of the biomass, more internal regions of the lignocellulosic structure would be exposed, facilitating its decomposition and the formation of lignin fragments, contributing to increase of the phenolics content.

The performance of biomass pretreated by ultrasound depends on parameters such as power, frequency, temperature, type of ultrasonication system (ultrasonic bath or a horn), and solvent. Zhang et al. evaluated the effect of ultrasonic pretreatment of poplar wood for 12 h with potassium salts in an aqueous solution, observing phenolics concentration increases of up to 174% when using high concentrations of salt (60% m/m). However, long ultrasonic pretreatment times can make the process economically unviable.

In a study of ultrasonic depolymerization of organosolv lignin, Liu et al. showed that the ultrasonic treatment caused the ary1-ether bonds in the lignin molecule to be broken, forming monomeric phenol units. However, after the optimal treatment time, continuation of the treatment caused the repolymerization of these phenolic monomers. This effect was also observed by Gilic et al. during the ultrasonic treatment of lignin, where different simultaneous processes caused alternating depolymerization, by the cleavage of side chains, and repolymerization of the lignin monomers.

Table 2 shows the distributions of the monitored compounds in the bio-oil samples. The data showed that unlike the quantified phenolic compounds, there were reductions of 1,2-dihydroxybenzene (o-catechol) and 4-methyl-1,2-dihydroxybenzene (4-methylcatechol) in the samples that received K<sub>3</sub>PO<sub>4</sub>. Compounds such as 4-ethylphenol and 3,5-dimethylphenol, which did not appear in the bio-oil obtained from the raw biomass, were present in the bio-oil samples obtained with the addition of K<sub>3</sub>PO<sub>4</sub>. This could be attributed to stabilization of the hydroxyl groups by the presence of K<sub>3</sub>PO<sub>4</sub>, preventing dehydroxylation to aromatic hydrocarbons such as ethylbenzene and 1,3-dimethylbenzene.

The addition of K<sub>3</sub>PO<sub>4</sub> alters the pathways of lignin decomposition, inhibiting the demethylation reactions
of methoxymethylenic compounds such as guaiacol or 2,6-dimethoxyphenol, but without having any apparent effect on demethoxylation reactions, which could explain the decreases of o-catechol and 4-methylcatechol in the bio-oils, while phenol and guaiacol increased. A high concentration of methoxyphenolic compounds in the bio-oil is undesirable, because the bio-oil becomes unstable as a result of the tendency to repolymerize to lignin, with higher viscosity and lower reactivity for the formation of phenol resins. The isolation of phenols (alkyl phenols) and their subsequent chemical modification by methylolation, phenolation, or demethylation reactions can improve their reactivity, enabling their use in the production of phenolic resins.

The concentration of alkyl phenols (phenol, methyl phenols, and ethyl phenol) increased from 26.8 mg g⁻¹ (raw biomass) to 60.9 mg g⁻¹ (biomass with 1.5 h of ultrasound pretreatment). However, the production of methoxyphenols (catechols and guaicols) showed stability during the pyrolysis processes, with maximum concentrations of 22.9 mg g⁻¹ for the raw biomass and 22.7 mg g⁻¹ for the biomass with 0.5 h ultrasound pretreatment.

The ultrasound treatment potentiated the effect of K₃PO₄ on the content of phenolic compounds in the bio-oil, increasing the content by between 12.3 and 118%, compared to the bio-oil obtained from the biomass with addition of K₃PO₄ but without sonication. The levels of phenolic compounds were between 40 and 215% higher in the samples obtained from the biomass submitted to the ultrasound pretreatment, compared to the bio-oil from the biomass without pretreatment and without the addition of K₃PO₄.

### Conclusions

The use of ultrasonic pretreatment associated with K₃PO₄ was effective in increasing the phenolic compound contents in the bio-oils produced from the biomasses. The pyrolysis results indicated that the use of K₃PO₄ reduced the bio-oil yield, compared to the non-catalytic pyrolysis, but increased the concentration of the quantified phenolic compounds by between 12.3 and 118%. The use of ultrasound potentiated the effect of K₃PO₄, causing increased devolatilization of the biomass, contributing to higher gas yield and lower formation of biochar. Analysis of the bio-oils by GC-MS indicated that the ultrasound pretreatment led to significant increases of the phenolics contents in the oils, as well as alteration of the phenolic compound profile. The best result was obtained for the biomass submitted to 1.5 h of pretreatment, which showed between 40 and 215% higher levels of phenolic compounds, compared to the bio-oils from samples that were untreated or without the addition of K₃PO₄.

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### References

1. Kumar, R.; Strezov, V.; Weldekiidan, H.; He, J.; Singh, S.; Kan, T.; Dastjerdi, B.; Renewable Sustainable Energy Rev. 2020, 123, 109763.
2. Choo, M. Y.; Oi, L. E.; Show, P. L.; Chang, J. S.; Ling, T. C.; Ng, E. P.; Phang, S. M.; Juan, J. C.; J. Taiwan Inst. Chem. Eng. 2017, 79, 116.

3. He, C.; Tang, C.; Li, C.; Yuan, J.; Tran, K. Q.; Bach, Q. V.; Qiu, R.; Yang, Y.; Renewable Sustainable Energy Rev. 2018, 91, 259.

4. Bilgili, F.; Koçak, E.; Bulut, Ü.; Kasıkaya, S.; Renewable Sustainable Energy Rev. 2017, 71, 830.

5. Bar-On, Y. M.; Phillips, R.; Milo, R.; Proc. Natl. Acad. Sci. U. S. A. 2018, 115, 6506.

6. Olatunji, O.; Akinlabi, S.; Madushele, N. In Valorization of Biomass to Value-Added Commodities; Daramola, M. O.; Ayeni, A. O., eds.; Green Energy and Technology; Springer International Publishing: Cham, 2020.

7. Rabemanolontsoa, H.; Saka, S.; Bioresour. Technol. 2016, 199, 83.

8. Mussana, H.; Yang, X.; Tessima, M.; Han, F.; Iqbal, N.; Liu, L.; Ind. Crops Prod. 2018, 113, 225.

9. Adams, P.; Bridgwater, T.; Lea-Langton, A.; Watson, I. In Greenhouse Gases Balances of Bioenergy Systems; Thornley, P.; Adams, P., eds.; Academic Press: city, 2018, p. 107.

10. Zabaniotou, A.; Rosvas, D.; Delivand, M. K.; Francavilla, M.; Libutti, A.; Cammerino, R.; Monteleone, M.; Sustainable Energy Technol. Assess. 2017, 23, 33.

11. Krause, M. C.; Mointhinho, A. C.; Ferreira, L. F. R.; de Souza, R. L.; Krause, L. C.; Caramão, E. B.; J. Braz. Chem. Soc. 2019, 30, 1608.

12. Lyu, G.; Wu, S.; Zhang, H.; Front. Energy Res. 2015, 3, 28.

13. Cui, Y.; Hou, X.; Wang, W.; Chang, J.; Materials 2017, 10, 668.

14. Vithanage, A. E.; Chowdhury, E.; Alejo, L. D.; Pomeroy, P. C.; DeSisto, W. J.; Frederick, B. G.; Gramlich, W. M.; J. Appl. Polym. Sci. 2017, 134, 44827.

15. Celikbag, Y.; Meadows, S.; Barde, M.; Adhikari, S.; Buschle-Diller, G.; Auad, M. L.; Via, B. K.; Ind. Eng. Chem. Res. 2017, 56, 9389.

16. Barde, M.; Adhikari, S.; Via, B. K.; Auad, M. L.; Green Mater. 2018, 6, 76.

17. Noreen, A.; Zia, K. M.; Zuber, M.; Tabasum, S.; Zahoor, A. F.; Prag. Org. Coat. 2016, 91, 25.

18. Rahman, S.; Helleur, R.; MacQuarrie, S.; Papari, S.; Hawboldt, K.; Sep. Purif. Technol. 2018, 194, 123.

19. Nam, H.; Choi, J.; Capareda, S. C.; Algal Res. 2016, 17, 87.

20. Stanford, J. P.; Hall, P. H.; Rover, M. R.; Smith, R. G.; Brown, R. C.; Sep. Purif. Technol. 2018, 194, 170.

21. Gomes, E. D.; Mota, M. I.; Rodrigues, A. E.; Sep. Purif. Technol. 2018, 194, 256.

22. Kanaujia, P. K.; Naik, D. V.; Tripathi, D.; Singh, R.; Poddar, M. K.; Siva Kumar Konathala, L. N.; Sharma, Y. K.; J. Anal. Appl. Pyrolysis 2016, 118, 202.

23. Hu, H. S.; Wu, Y. L.; Yang, M.-D.; Biomass Bioenergy 2018, 108, 487.
47. Guedes, R. E.; Luna, A. S.; Torres, A. R.; J. Anal. Appl. Pyrolysis 2018, 129, 134.
48. Gogoi, S.; Bhuyan, N.; Sut, D.; Narzari, R.; Gogoi, L.; Kataki, R. In Energy Recovery Processes from Wastes; Ghosh, S. K., ed.; Springer Singapore: Singapore, 2020, ch. 10.
49. El Abbari, H.; Bentahar, S.; El Marouani, M.; Taibi, M.; Zeriouh, A.; Sebbahi, S.; Kifani-Sahban, F.; J. Therm. Anal. Calorim. 2019, 137, 1485.
50. Shen, D.; Jin, W.; Hu, J.; Xiao, R.; Luo, K.; Renewable Sustainable Energy Rev. 2015, 51, 761.
51. Ding, M.; Wei, B.; Zhang, Z.; She, S.; Huang, L.; Ge, S.; Sheng, L.; J. Therm. Anal. Calorim. 2017, 129, 975.
52. Gilca, I. A.; Popa, V. I.; Crestini, C.; Ultrason. Sonochem. 2015, 23, 369.
53. Zhang, M. F.; Qin, Y. H.; Ma, J. Y.; Yang, L.; Wu, Z. K.; Wang, T. L.; Wang, W. G.; Wang, C. W.; Ultrason. Sonochem. 2016, 31, 404.
54. Hideno, A.; BioResources 2016, 11, 6309.
55. Liu, B.; Du, B.; Sun, Y.; Zhu, M.; Yang, Y.; Wang, X.; Zhou, J.; Fuel Process. Technol. 2020, 203, 106387.
56. Mohammed, I. Y.; Abakr, Y. A.; Mokaya, R.; Biomass Convers. Biorefin. 2018, 8, 699.
57. Lu, Q.; Zhang, Z. B.; Yang, X. C.; Dong, C. Q.; Zhu, X. F.; J. Anal. Appl. Pyrolysis 2013, 104, 139.
58. Lévêque, J.-M.; Cravotto, G.; Delattre, F.; Cintas, P. In Ultrasonics Sonochemistry; Daramola, M. O.; Ayeni, A. O., eds.; Springer Cham: Cham, Switzerland, 2018, ch. 4.
59. Subhadar, P. B.; Ray, P.; Gogate, P. R.; Ultrason. Sonochem. 2018, 40, 140.
60. Zhang, Z.-X.; Li, K.; Ma, S.-w.; Cui, M.-s.; Lu, Q.; Yang, Y.-p.; Ind. Crops Prod. 2019, 137, 495.
61. Wu, Z.; Zhu, X.; Guo, H.; Jiang, Y.; Gu, X.; Catal. Today 2019, 226.
62. Zhou, J.; Jin, W.; Shen, D.; Gu, S.; J. Anal. Appl. Pyrolysis 2018, 134, 143.
63. Sarika, P. R.; Nancarrow, P.; Khansaheb, A.; Ibrahim, T.; Polymers 2020, 12, 2237.
64. Cheng, Y.; Sui, G.; Liu, H.; Wang, X.; Yang, X.; Wang, Z.; J. Appl. Polym. Sci. 2019, 136, 2.

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