Evaluation of Torrefaction on the Quality of Bio-Oil Obtained by Pyrolisis of Green Coconut Wastes

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Pyrolysis of green coconut residues is considered a promising source of biomass for transforming energy and generating value-added products from thermochemical processes such as pyrolysis, mainly due to the high volume of this material in the Northeast region. For better pyrolytic results, some pre-treatments of the biomass can be used. In this work, the pre-treatment technique of oxidative and non-oxidative torrefaction was applied, using temperatures of 200 and 250 °C. These torrefied biomasses were subsequently subjected to fast pyrolysis at 700 °C. GC/qMS characterized the bio-oil obtained, and an increase in the content of phenolic compounds was observed in the torrefied biomass samples when compared to the raw biomass, indicating that the process is viable and adds value to the bio-oil obtained by pyrolysis.

Keywords: Torrefaction. Pyrolysis. Bio-Oil. Phenolic Compounds. Chromatography Analyses.

Introduction

The global economy is currently based on the use of fossil sources for both energy generation and products for the chemical industry. However, this source generates polluting gases that disperse into the environment, contributing to increased pollution and climate change impacts. Consequently, there is a need for new sustainable sources of energy generation and products [1].

In this scenario, biomass stands out, defined as any organic matter of animal or plant origin that can generate energy. When biomass is derived from agro-industrial waste, its use helps minimize inappropriate disposal of these materials, reducing environmental impacts [2].

Brazil is one of the world's largest agro-industrial producers, resulting in significant volumes of organic waste. Among the biomass sources derived from these agro-industrial wastes, fiber, and husks of coconut can be highlighted. Brazil ranks fifth in global coconut production, with 1.6 billion fruits produced. The Northeast region concentrates 80.9% of the harvested coconut area and stands out with approximately 73.5% of the national production [3].

One way to utilize these waste materials is through pyrolysis, which is defined as a thermochemical process of biomass degradation under an inert atmosphere, resulting in three products: non-condensable gases, biochar, and bio-oil [4]. Bio-oil, the liquid product of pyrolysis, is a complex mixture of water and organic compounds, including hundreds of oxygenated compounds that give bio-oil acidic characteristics, high viscosity, low calorific value, and high instability [5].

Biomass, mainly derived from agro-industrial waste, presents some disadvantages in its application to pyrolysis, such as high water and oxygen content, which negatively impact thermochemical conversion processes. Therefore, pre-treatment processes aim to improve biomass quality before it is subjected to pyrolysis [6]. Pre-treatment methods such as torrefaction release volatile compounds and modify biomass's physicochemical and structural properties, increasing its energy density and improving its characteristics [7]. Torrefaction occurs at moderate temperatures of 200 to 300 °C under an oxygen-

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free atmosphere. This process can be classified according to the operating temperature ranges: mild (200-235 °C), moderate (235-275 °C), and severe (275-300 °C). Furthermore, it effectively reduces the moisture content in biomass and eliminates volatile oxygenated compounds with lower molecular weight [8,9].

Only hemicellulose is degraded in mild torrefaction, while cellulose and lignin remain unchanged, retaining more biomass mass and energy. Moderate torrefaction leads to partial decomposition of cellulose, resulting in a higher loss of mass and energy than mild conditions. Severe torrefaction causes the depolymerization of lignin, cellulose, and any remaining hemicellulose. This condition results in a greater mass and energy loss but guarantees higher energy density for the biomass [10]. This pre-treatment type destroys biomass's fibrous nature and increases its calorific value. Additionally, it makes the biomass more resistant to water adsorption, thereby increasing its resistance to fungal and bacterial proliferation [11].

Oxidative torrefaction is a process that occurs in an atmosphere containing oxygen at the same temperature range as non-oxidative torrefaction (200-300 °C). The oxidative reactions in this process are generally exothermic, generating heat and reducing the heating demand in torrefaction reactions. Moreover, some studies have suggested that increased oxygen concentration could lead to more significant biomass decomposition, resulting in shorter torrefaction or milder temperatures [12].

Once this biomass undergoes pre-treatment techniques and subsequently undergoes pyrolysis, the generated bio-oil needs to be characterized to propose better applications for it, widely used techniques in various studies include gas chromatography coupled with mass spectrometry (GC/MS).

This study aimed to evaluate a pre-treatment method (torrefaction) for residual coconut biomass to improve the quality of bio-oil produced in pyrolysis, enriching its phenolic compound content. Furthermore, the produced bio-oils were characterized by GC/qMS to assess the potential industrial applications of the identified compounds.

Materials and Methods

Torrefaction Conditions

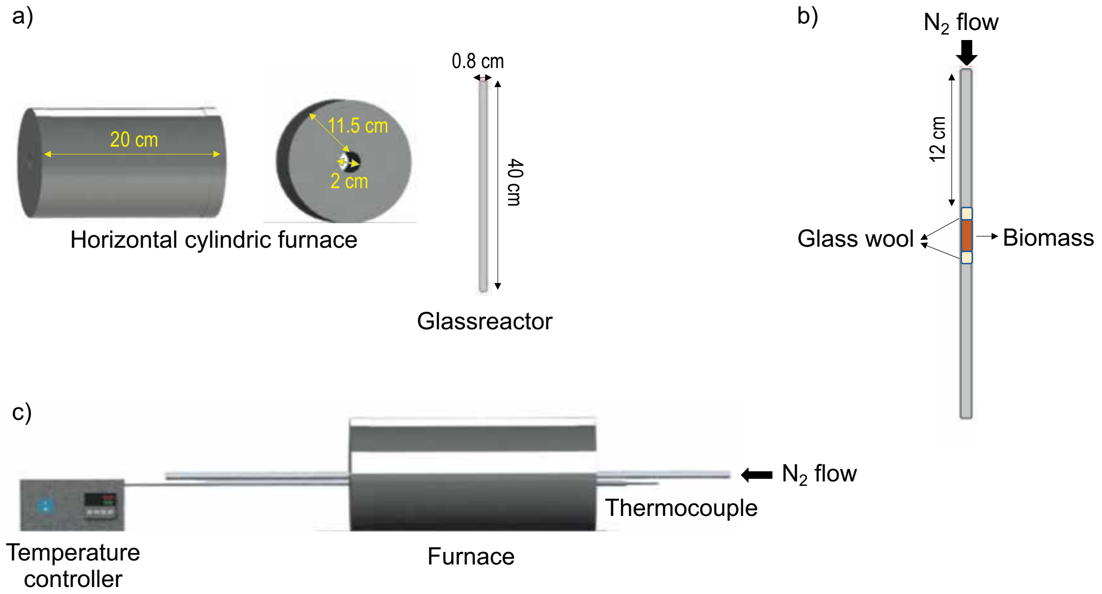
Two types of torrefactions were performed: oxidative and non-oxidative. For non-oxidative torrefaction, a stainless-steel pyrolysis reactor with a diameter of 60 mm and a length of 260 mm was used. It had an upper inlet for biomass addition, a side inlet for injecting inert gas (N_2), and an outlet for removing the gases generated. The detailed system is described in the study by Santos and colleagues, 2020 [13]. The experiment was conducted at 250 °C for 15 minutes, with a nitrogen flow rate of 100 mL min^{-1}, and 3 g of biomass. For oxidative torrefaction, the experiments were conducted in a muffle furnace with dimensions of 81 cm x 76 cm x 64 cm. 3g of biomass were placed in ceramic containers, and the experiments were conducted at 200 °C for 15 minutes. All experiments were performed in triplicate.

Pyrolysis Conditions

Fast pyrolysis experiments were conducted using a system consisting of a circular horizontal furnace with a diameter of 25 cm and a length of 20 cm. The furnace had an internal refractory layer with a thickness of 11.5 cm and a central orifice with a diameter of 2 cm, into which a 40 cm glass reactor was inserted. The glass reactor had an inlet for inert gas (N_2) and a 12.5 cm thermocouple for temperature control. Figure 1 (a, b, c) schematically illustrates the complete system and its detailed parts.

Torrefied and raw biomass samples were pyrolyzed under the same conditions, with a temperature of 700 °C, nitrogen flow rate of 2 mL min^{-1}, and 0.1 g of biomass. The biomass was placed inside the reactor using glass wool at both ends [Figure 1 (b)]. The reactor containing the biomass

Figure 1. Pyrolysis system.



was inserted into the preheated furnace, ensuring that the biomass was centrally positioned for more uniform heating. The reactor was connected to the N_2 flow. The temperature was controlled so that the biomass inside the reactor reached 700 °C and remained at this temperature for 1 minute. Subsequently, the reactor was removed from the furnace, cooled to room temperature, and the formed bio-oil was eluted with 15 mL of acetone.

Chromatographic Analysis – GC/qMS

Chromatographic analyses were performed using the GC/MS-QP-2010-Ultra model equipment (Shimadzu, Japan). The capillary column was a ZB-5, 30 m long, 0.25 mm internal diameter, and 0.25 µm stationary phase thickness. Helium was used as a carrier gas with a flow of 1 mL min^{-1}. In the splitless mode, sample injection (1 µL at a concentration of 5000 ppm) was performed using the AOC-20i automatic injector (Shimadzu, Japan). Injector, interface, and ion source temperatures were kept at 300 °C, and electron impact ionization energy was 70 eV. The system operated in SCAN mode, ranging from 45 to 450 Da. The oven was heated according to the following schedule: from 40 °C to 300 °C at 3 °C min^{-1}, remaining at this temperature for 10 min. Data treatment was performed using the GCMS solution software. The compounds were identified by retention index and mass spectra.

Results and Discussion

The yield obtained from the torrefaction of fresh coconut was 43.5 ± 7.3% for oxidative torrefaction and 70.2 ± 0.3% for non-oxidative torrefaction. Oxygen in the torrefaction atmosphere reduces the mass yield of the process due to biomass carbonization, resulting in rapid mass loss [14]. Table 1 presents the mass yields obtained from pyrolysis of raw and torrefied biomass.

A reduction in bio-oil yield from the raw biomass to the torrefied samples can be observed, especially for the oxidative torrefaction process. In contrast, a considerable increase in the biochar content is observed. Table 2 shows the percentage areas of the compounds identified in each sample.

Figure 2 illustrates the relative areas (%) and number of peaks of the identified compounds in each sample. The data analysis shows that the major

Table 1. Yields of pyrolysis products.

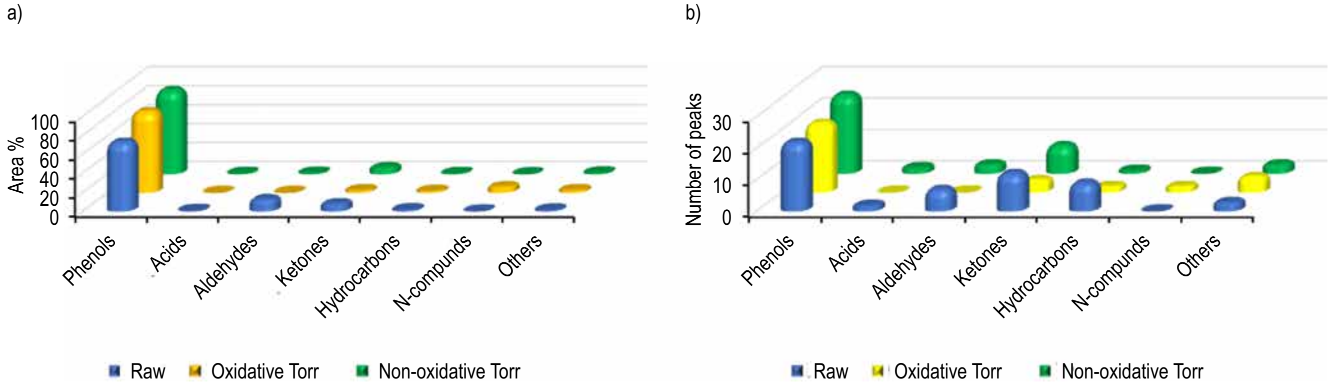
Sample	Bio-oil (%)	Biochar (%)	Gases and Losses
Raw Biomass	21.87	23.06	55.07
Oxidative Torr	4.46	51.63	43.91
Non-oxidative Torr	15.49	37.57	46.94

Table 2. Identification of compound classes regarding the number of peaks and their percentage areas for bio-oil samples.

	Area %			Number of Peaks		
Chemical classes	Raw	Oxidative Torr	Non-oxidative Torr	Raw	Oxidative Torr	Non-oxidative Torr
Acids	1.17	n.d.	0.90	2	n.d.	2
Sugars	n.d	0.87	n.d.	n.d	1	n.d
Alcohols	0.74	n.d.	0.48	1	n.d.	1
Aldehydes	13.22	n.d.	1.19	7	n.d.	3
Ketones	8.49	2.81	7.28	12	4	9
Esters	0.29	0.41	0.52	1	1	1
Ethers	0.73	1.80	0.66	1	3	1
Phenols	73.17	85.50	88.28	22	22	25
Hydrocarbons	2.19	2.00	0.70	9	2	1
N-Compounds	n.d.	6.61	n.d.	n.d.	2	n.d.
Total	100	100	100	55	35	43

n.d. = not detected.

Figure 2. Distribution of percentage areas (a) and total number of peaks (b) of the compounds identified in the samples.



chemical classes found in the raw biomass bio-oil sample were phenols, followed by aldehydes, ketones, and, to a lesser extent, hydrocarbons. Compared to the raw biomass, an increase in the phenolic compound content is also noted in the bio-oils from torrefied biomass. These phenolic compounds are derived from lignin degradation and aromatization reactions of the fragments formed from cellulose decomposition. This behavior can be explained by the degradation of hemicellulose and part of the cellulose during the torrefaction process, increasing the lignin content in the sample, leading to the formation of more aromatic precursors during the pyrolysis process, thus increasing the content of phenolic compounds [14]. The presence of critical phenolic compounds suggests their purification for the acquisition of various high-value chemical products. Phenols are widely used in chemical, pharmaceutical, food, and other industries. Phenol, the primary compound found in all analyzed samples, has well-established industrial applications, high production costs, and is obtained from crude oil.

Conclusion

Based on the results, the implementation of pre-treatment processes on the samples before subjecting them to pyrolysis was justified. This technique improved the bio-oil's quality by increasing higher-value phenolic compounds that can be applied in the chemical industry.

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