

Investigating the alkaline treatment of fiber coconut (*Cocos nucifera* L) for cellulosic ethanol generation

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ABSTRACT: The coconut husk of *Cocos nucifera* L. species has a high potential for use in industry and agriculture, and many studies on the use of this biomass are being developed for the production of biofuels. Sodium hydroxide solution (NaOH) is one of the oldest most and economically viable treatments for reducing the lignin content and improving energy efficiency in biomass. Thus, the objective of this research was to analyze the solubility of the fibers biomass in the mesocarp of *Cocos nucifera* with different concentrations of sodium hydroxide (NaOH). The fibers were separated from the bark, which had their extractives removed, and were subjected to the solubility procedure in 1, 2, 3, and 4% NaOH. The Klason lignin and holocellulose were determined. Changes in functional groups of Klason lignin were observed by infrared spectroscopy (FTIR). There was a decrease in Klason lignin content due to alkaline treatment. Infrared spectra indicated structural changes between the treatments analyzed, especially when the following bands: 3433 cm^{-1} (stretching of OH), 1271 - 1220 cm^{-1} (vibration of the guaiacyl ring with the contribution of the C=O stretch), and 1116 - 1165 cm^{-1} (stretching of CO of acid and/or ester). Coconut fibers treated with 4% NaOH maintained the integrity of holocellulose and presented high lignin degradation.

Investigando o tratamento alcalino da fibra de coco (*Cocos nucifera* L) para geração de etanol celulósico

RESUMO: A casca de coco da espécie *Cocos nucifera* L. apresenta alto potencial para uso na indústria e na agricultura, e diversos estudos sobre a utilização dessa biomassa estão sendo desenvolvidos para a produção de biocombustíveis. A solução de hidróxido de sódio (NaOH) é um dos tratamentos mais antigos e economicamente viáveis para reduzir o teor de lignina e melhorar a eficiência energética da biomassa. Assim, o objetivo desta pesquisa foi analisar a solubilidade da biomassa das fibras no mesocarpo de *Cocos nucifera* com diferentes concentrações de hidróxido de sódio (NaOH). As fibras foram separadas da casca, que tiveram seus extrativos retirados, e foram submetidas ao procedimento de solubilidade em NaOH 1, 2, 3 e 4%. A lignina Klason e a holocelulose foram determinadas. Alterações nos grupos funcionais da lignina Klason foram observadas por espectroscopia de infravermelho (FTIR). Houve uma diminuição no conteúdo de lignina Klason devido ao tratamento alcalino. Os espectros de infravermelho indicaram mudanças estruturais entre os tratamentos analisados, principalmente quando as seguintes bandas: 3433 cm^{-1} (alongamento de OH), 1271 - 1220 cm^{-1} (vibração do anel guaiacil com a contribuição do trecho C = O), e 1116 - 1165 cm^{-1} (estiramento de CO de ácido e / ou éster). As fibras de coco tratadas com NaOH 4% mantiveram a integridade da holocelulose e apresentaram alta degradação da lignina.

Introduction

There is a great concern with the emissions of carbon dioxide in the atmosphere caused by the intense use of fossil fuels. In view of this problem, the incentive of the transport sector and the industrial sector to use renewable and sustainable resources for energy generation grows (Ibarra Gonzalez and Rong 2019; Solarte Toro et al. 2019). Among the existing renewable energy systems, lignocellulosic biomass is considered an abundant resource, with high concentrations of carbon, being able to generate biofuels and chemicals.

Brazil occupies a privileged position in the production of lignocellulosic biomass on the world stage, in 2016 the country had about 7.84 million hectares of planted forests (Inácio et al. 2019; Huang and Lo 2019; Da Silva et al. 2020). In addition, Brazil is a world leader in producing various agricultural products (such as soy, oranges and sugar cane), generating tons of lignocellulosic waste annually (Holla et al. 2022; Pereira et al. 2022). That resources were the object of several types of research to produce bioenergy in a highly sustainable way, mainly for production (Zhu and Pan 2010; Santos et al. 2018; Martins et al. 2019; Pereira et al. 2020; Silva et al. 2021).

Coconut shells are considered an agro-industrial waste source of fiber, with a high content of cellulose and hemicellulose, with about 12 million hectares of the planted area, mainly in Asia and Oceania, is considered one of the 20 most important plant species, which it produces a large amount of residue from the bark (Prades et al. 2016; Freitas et al. 2019). In Brazil, the production of coconut trees covers an estimated area of around 280 thousand hectares, of which 69.25% of the total coconut planted area is represented by *Cocos nucifera*, making the country the fourth-largest producer in the world (Correia 2020). The cultivation of *Cocos nucifera* provides numerous indirect jobs generated along the national production chain, in addition to being an income for many families (Rocha et al. 2022)

However, most of the mature residues of *Cocos nucifera* are commonly used as fuel in boilers and when processed, their fibers are used for carpets, mats and other products (Cardoso and Gonçalves 2016). Due to its high potential for use in industry and agriculture, interest in using *Cocos nucifera* residues as a source of fermentable sugars to obtain biofuels, such as bioethanol, has grown (Putrino et al. 2020). However, to be a viable process, using different treatments, such as oxidation with hydrogen peroxide, ozone, acid treatment and alkaline treatment, can efficiently overcome the inherent recalcitrance of the biomass (Nogueira et al. 2019). There are three stages in bioethanol production: pre-treatment, enzymatic hydrolysis and fermentation. Pre-treatment with sodium hydroxide (NaOH) solution is one of the oldest and most

economically viable treatments for biomass (Esmeraldo et al. 2010), widely used to reduce the lignin content and increase the production of fermentable sugars (Nogueira et al. 2019).

During alkaline treatment, there is a change in the physical structure of the fibers due to the action of alkaline bleaching, favoring biomass delignification (Heggset et al. 2016). It also reduces the diameter and increases the crystallinity of the fibers (Esmeraldo et al., 2010). The success of the alkaline treatment will depend on the concentration of the solution, the reaction time and the time of mechanical agitation of the solution (Di Pietro et al. 2020). Hemicelluloses are highly sensitive to sodium hydroxide's action, which is easily degraded by this base depending on the applied concentration (Sanchez et al. 2010). Lignin is partially removed by alkaline treatment, causing deprotonation reactions of hydroxyls in the structure and facilitating the production of cellulose polymers (Barreto et al. 2010).

Alkaline pre-treatment of lignocellulosic biomass is a challenge to facilitate access of cellulose and hemicellulose to microorganisms for bioethanol production (Putrino et al. 2020). Some references indicate that the alkaline treatment of sugarcane resulted in fibers with a more excellent contact surface, allowing more significant interactions with other materials and enabling bioethanol production (Sanchez et al. 2010). The pre-treatment of *Cocos nucifera* fiber materials have yet to be explored despite the results obtained in work with other raw materials. It is understood that the solubility of lignin is one of the most important factors in defining the best conditions for the yield of the cellulosic product. Thus, the objective of this study was to verify the solubility of the biomass of coconut mesocarp fibers (*Cocos nucifera* L.) with different concentrations of sodium hydroxide (NaOH). Based on the results obtained, we can provide insights into these raw materials use for bioethanol production.

Material and Methods

For this study, thirty green coconuts (*Cocos nucifera* L.) were taken from a settlement located in the municipality of Itaguaí, RJ. In the laboratory, the mesocarp was separated from the endocarp manually, and the epicarp was discarded. The mesocarp was dried outdoors, and after the material was ground in a hammer mill. Then, the fiber and the parenchyma were mechanically separated using a set of sieves and placed in a Becker with distilled water so that the separation occurred by the difference in density (Figure 1). The fibers that remained at the bottom of the becker were removed and dried outdoors.

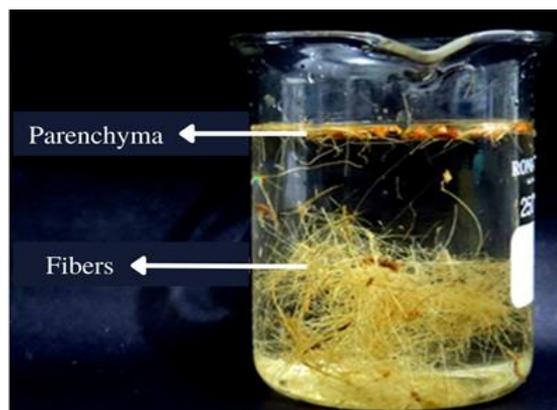


Figure 1. Fibers separated from the parenchyma by density difference in distilled water

Sample preparation free of extractives

To obtain the extractives free material, an extraction cycle using type Soxhlet extractor was performed. The organic solvents were used in increasing polarity: cyclohexane, ethyl acetate, methanol, and distilled water sequentially. The extraction time was 24 hours uninterrupted for each solvent. After this period, the soluble material (extract) in each solvent was concentrated in a rotavapor (Abreu et al. 2006). The extraction cycle was performed in triplicate.

Solubility in a sodium hydroxide (NaOH)

The free extractive fiber samples were submitted to the NaOH solubility procedure, where 1 g of absolutely dry material was placed in an Erlenmeyer flask with 50 ml of 1% sodium hydroxide solution (Abreu et al. 2006). The reaction samples were covered with a watch glass and placed in a 90°C water bath for 60 minutes, shaking every five minutes. After this procedure, the samples were transferred to a sintered Buchner funnel and washed with 100 ml of hot distilled water. Afterward, 25 ml of a 10% acetic acid solution was added remaining 1 minute at rest for the complete neutralization of NaOH. The samples were washed with distilled water until completely free of the acid solution and placed in an oven at $103 \pm 2^\circ\text{C}$ until reaching constant mass. This procedure was repeated with the NaOH solution at concentrations of 2%, 3% and 4%. Each alkaline treatment was performed in the form of triplicate.

Determination of lignin and holocellulose content

Samples previously solubilized in 1, 2, 3, and 4% NaOH, as well as the control sample (not solubilized), were submitted to the Klason lignin determination procedure. Thus, 300 mg of each dehydrated sample (solubilized and control) was treated with 3 ml of 72% sulfuric acid. Samples were homogenized for 1 minute and placed in a water bath for 1 hour at $\pm 30^\circ\text{C}$. They were then washed with 84 ml of distilled water and refluxed for 4 hours.

Afterward, the samples were washed with 500 ml of hot distilled water in a sintered Buchner funnel and, then, taken to the oven at $103 \pm 2^\circ\text{C}$ for 24 hours (Abreu et al. 2006). The determination of Klason lignin for each sample solubilized with NaOH and for the control sample was performed in triplicate.

To determine the holocellulose, 0.5 ml of acetic acid, 1 g of sodium chlorite, and 80 ml of hot distilled water were added to 2.5 g of each sample (solubilized and control samples). The reaction was covered with a watch glass and maintained in a water bath at 70°C. 0.5 ml of acetic acid and 1 g of sodium chlorite were added every hour until complete degradation of the lignin. After this procedure, the samples were kept at rest without adding any reagent for 24 hours (Abreu et al. 2006). The material was washed in with sintered Buchner funnel under a vacuum with deionized water until the yellow color and chlorine odor disappeared. Each sample was oven dried at $103 \pm 2^\circ\text{C}$ for 24 hours. The determination of holocellulose for each sample solubilized with NaOH and the control sample was performed in triplicate.

Fourier Transform Infrared Spectroscopy (FTIR)

For this analysis, samples of Klason lignin solubilized in 1%, 2%, 3%, and 4% NaOH and the control sample (not solubilized) were used. Each sample (2 mg) was mixed in 100 mg of potassium bromide (KBr) in a pelletized condition. The spectra were recorded using a VARIAN 640-IR FT-IR spectrometer in transmittance experimental mode with 4 cm^{-1} of the resolution, 128 scans, and spectral amplitude between $4000 - 400\text{ cm}^{-1}$.

Statistical analysis

The chemical components and the weight loss were subjected to the test of Bartlett and Shapiro-Wilk. Confirming the assumptions of the homogeneity of variance and normality, we proceed to the analysis of variance (ANOVA). When was detected difference between means, the Tukey test was performed. The tests were performed at 5% significance.

Results and discussion

Solubility in alkaline medium

The chemical composition (holocellulose and lignin) of *Cocos nucifera* fiber (Figure 2) was performed to compare the effect of different conditions of pre-treatment with NaOH on the constituents of the material. The average holocellulose values were 63.04% for non-solubilized fibers and 62.76%, 64.48%, 65.04% and 65.36% for fibers treated with 1, 2, 3 and 4% NaOH, respectively. Figure 2 shows that even using different NaOH concentrations, there was no significant difference in the 2, 3 and 4% NaOH treatments and in the untreated material (control) and 1% NaOH. The percentage of holocellulose for

coconut fibers treated with higher concentrations of NaOH showed slightly higher values. A result was similar to that of Tsegaye et al. 2019 for wheat straw, where treatment with NaOH resulted in an increase of about 30% in sugar content (holocellulose). Regarding the lignin contents (Figure 2), it is noted that all percentages were statistically different. The average value of lignin content showed a gradual increase in the solution with 2% NaOH as the concentration of the alkaline solution increased.

However, there was a more substantial decrease in the treatment with 1% NaOH and gradually in higher concentrations. Similar behavior was found by Nogueira et al. 2019 for green coconut fiber, where the percentage of lignin increased from 39 to 21% with the NaOH treatment. The cellulose, hemicellulose and lignin contents of coconut fibers can be affected by alkaline treatments (Muensri et al., 2011).

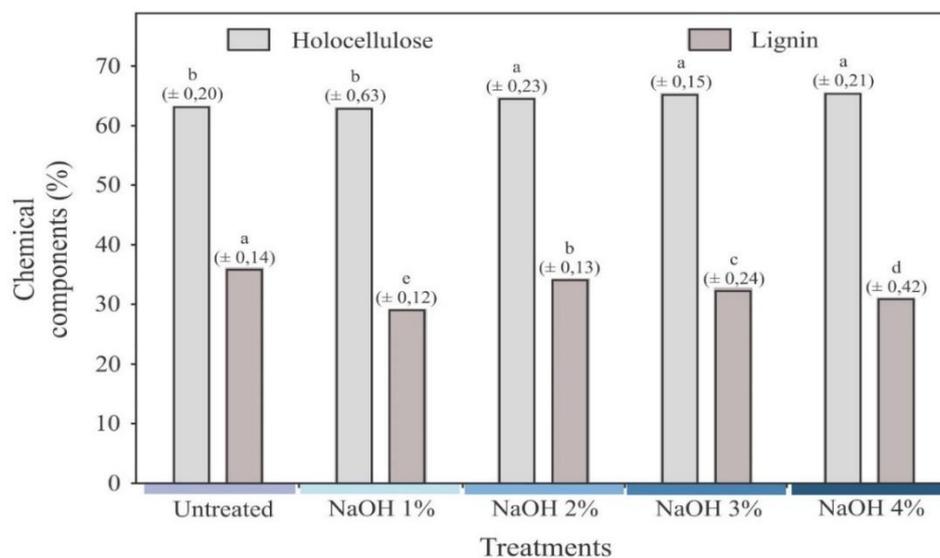


Figure 2. Average lignin content and holocellulose content of samples solubilized in NaOH.

Researchers have reported that NaOH concentration strongly affects the depolymerization of lignocellulosic biomass during alkaline pretreatment (Chu et al., 2018; Martínez-Patiño et al., 2017). In general, the decrease in lignin content is accompanied by an increase in holocellulose content, which aligns with the results obtained in this experiment (Sun et al. 2014). The high cellulose content is essential in biomass conversion to bioethanol to produce concentrated ethanol solutions. Therefore, evaluating the percentage of holocellulose (cellulose + hemicellulose) is crucial for assessing the pretreatment (Xu et al., 2011).

Alkaline pretreatment (NaOH) favors increased cellulose availability since biomass delignification occurs (Huang et al., 2017). Figure 3 shows a proposal for the dissolution mechanism of the polymeric block of lignin that protects cellulose. This scheme (Fig 3) offers that lignin and hemicellulose protect the cellulosic chain. As a hypothesis, it can be suggested that the content of accessible OH in the guaiacyl unit of lignin may represent the key to lignin solubilization in the cell wall (Lapierre et al., 1989). Thus, the composition of a fiber lignin, vessel, parenchyma and lamellae between cells may behave differently in solubility with NaOH. These elements and lamellae have different guaiacyl and syringyl unit ratios. The presence of a syringyl unit in a higher concentration

than a guaiacyl unit represents a lower number of hydroxyl in the free state, unable to be ionized by NaOH (Abreu et al., 1999).

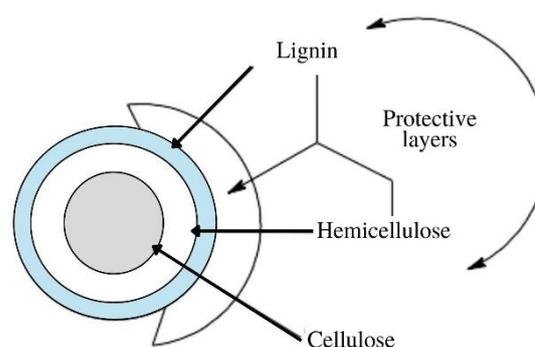


Figure 3. Performance of lignin and hemicellulose as an agent in the protection of cellulose.

The effect of the alkaline treatment on holocellulose is directly correlated with the dissolution, mainly of lignin, since it is from it that it is possible to have access to cellulose (Nogueira et al., 2019). Figure 4 shows the average mass loss of the material (holocellulose and lignin) for each treatment. In this work, the concentrations dissolved it, generating statistically different mass losses (Figure 4). Note that the weight loss was 1.13% for

the material without treatment and 8.23%, 1.52%, 2.79% and 3.81% for treatments with 1, 2, 3 and 4% NaOH. Statistically, the coconut fiber not treated and

treated with 2% NaOH showed no difference, while the other treatments had singularity in their performance (Fig. 4).

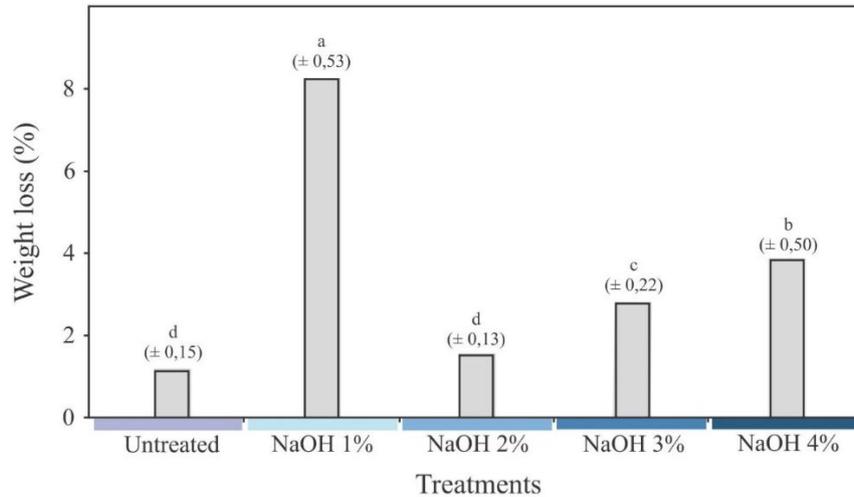


Figure 4. Percentage of mass loss (holocellulose and lignin).

The mass loss (Figure 4) may be directly due to the solubility of NaOH in the hemicelluloses or its degradation under these treatment conditions. As well as the reduction of lignin and the increase of holocellulose, the evaluation of mass loss is essential since, from them, one has subsidies to predict bioethanol yield (Lee et al., 2022). Therefore, the treatment that defines the best solubility conditions should be the one that presented the highest percent for the holocellulose content in concomitance with a moderate mass loss, being the 4% NaOH treatment,

in this case, the one that most corresponds to this purpose.

Infrared Spectroscopy (FTIR) of lignin

FT-IR analysis was performed to investigate Klason lignin chemical and structural changes during alkaline pre-treatment (Figure 5). Table 1 shows the functional groups identified in the material. Studies indicate that chemical modifications, mainly in lignin, are observed in fibers treated with NaOH (Lee et al. 2022).

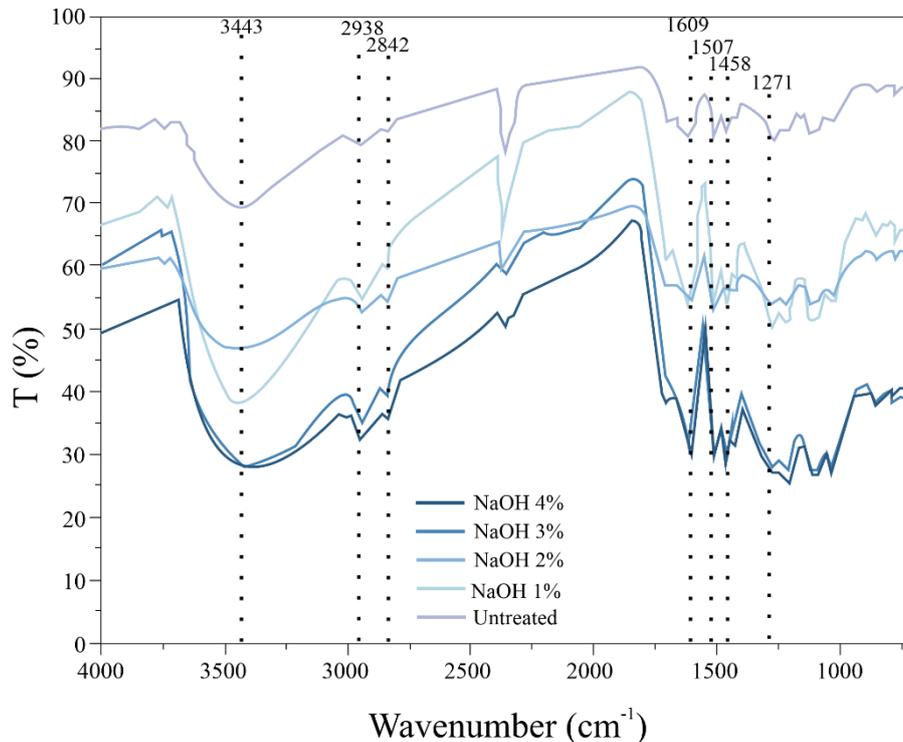


Figure 5. Infrared peaks of the lignin samples obtained from the solubilized materials

Table 1. Assignments of infrared peaks of Klason lignin. Source: (González Pena and Hale 2011; Shi and Li 2012; Poletto and Zattera 2013).

Peaks cm ⁻¹	Peak intensity					Assignments
	Control	NaOH 1%	NaOH 2%	NaOH 3%	NaOH 4%	
1 271	1	4	4	2	2	The vibration of the Guaiacyl ring with the contribution of C=O stretching
1 458	2	5	5	4	4	Asymmetric deformation of -CH ₃ e - CH ₂ -
1 507	5	10	10	10	9	The vibration of the aromatic ring
1 609	4	15	14	15	14	The vibration of an aromatic skeleton with stretching C=O, S > G, G condensed > etherified
2 842	0	1	-	1	1	Stretching of C=O of acid or conjugated ester or conjugated ketone
2 938	1	4	4	5	4	Stretching of C-H methyl and methylene groups
3 443	1	27	19	25	18	Stretching of O-H

The FTIR spectra show that Lignin Klason had changed with the NaOH treatment of *Cocos nucifera* fibers (Figure 5). Note that all identified groups had an increase in band intensity. More evidently, the 3443 cm⁻¹ band (OH stretching), the 1609 cm⁻¹ band (the vibration of an aromatic skeleton with elongation) and 1507cm⁻¹ band (vibration of the aromatic ring) were the ones that most influenced the influence of the alkaline treatment (Table 1). The change in the intensity of the 3443 cm⁻¹ bands may be related to the reduction in the degree of established hydrogen bonding, which is related to the binding of hemicellulose and

lignin, which is in agreement with the result of this work, which higher concentrations of NaOH favor material delignification (Gonçalves et al., 2014).

The increased intensity of bands 1507 cm⁻¹ (vibration of the aromatic ring) and 1609 cm⁻¹ (vibration of an aromatic skeleton with elongation), lignin-related bands indicate the disruption of lignin bonds, corroborating the results of the chemical composition analysis (Gupta and Lee, 2010). To understand the changes in lignin with NaOH treatment, the ratio between the intensity of bands 1609 and 1507 cm⁻¹, which correspond to lignin, was calculated (Table 2).

Table 2. Intensity ratio of lignin bands

Treatments	The vibration of aromatic ring/vibration of aromatic skeleton with stretching C=O, S > G, G condensed > etherified
	1500/1600
NaOH 1%	0,8
NaOH 2%	1,5
NaOH 3%	1,2
NaOH 4%	1,5

Results from the intensity ratio of the 1600 cm⁻¹ to 1500 cm⁻¹ peaks revealed that the structural type of lignin was affected by the action of sodium hydroxide (NaOH), mainly on the etherified (alkyl-aryl) structures of than in the condensed structures. This is because the condensed structures have less free OH in the *Cocos nucifera* fiber than the α and β -O-4 bonds, whose hydroxyls of this bond are impeded by ionization (Heitner et al. 2008). Overall, the FTIR analysis corroborates the results on the chemical composition of the studied material. Coir fiber underwent delignification by reducing steric

hindrance and loosening the bonds between cellulose and lignin.

Conclusions

For the production of bioethanol from coconut fiber, it should be noted that the alkaline treatment is an efficient and economically viable alternative for the delignification of biomass, favoring the availability of holocellulose (sugars), which prevented the process. Among the pre-treatments studied, the coconut fiber observed in the pre-treatment with 4% NaOH was more satisfactory for reducing lignin and having moderate weight loss.

Studies are recommended to analyze the compositional character of lignin (methoxyl content) to define the best experimental conditions to favor greater or lesser solubility of lignocellulosic biomass. With the results obtained, we want to give insights into the potential of coconut fiber for sustainable energy generation.

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