Effect of Autohydrolysis of Waste Fiber Palm Lignocellulosic From of the Production Chain of Biodiesel

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ABSTRACT

The palm waste generated in the production chain of palm oil biodiesel was of about 38% of lignocellulosic waste formed normally empty bunches of fibers. The fundamental characterization of pretreated empty bunches of fibers with liquid hot water. This material with average size of 80 mesh was composed of cellulose 14,4%, hemicellulose 16%, insoluble lignin acid 29,4%, lignin-soluble acid 3,2%, extractives 28,2% and total ash 5,2%. The time and temperature of liquid pretreatment with hot water were 30 and 60 min and 100° C. The characterization of these materials was made by SEM, EDS and infrared spectrometry and HPLC extractives. These analyzes showed modification of the morphology the fibers of empty clusters of oil palm with the appearance of porosity and increase of pulp crystallization rate by the solubility of amorphous cellulose, hemicellulose and lignin as shown by the results of FT-IR. After the hydrothermal treatment, the product of the hydrolysis reaction analyzed by HPLC. The increasing the pretreatment time confirms that the auto-hydrolysis process occurs causing an expansion of the fibers, exposing the crystalline cellulose and probably partial leaching of the hemicellulose and lignin. The products were identified: glucose, xylose, and acetic acid. Therefore, under the conditions of the pretreatment was not observed the formation of furfural.

Keywords: Biomass, Auto-Hydrolysis, Fibers

I. INTRODUCTION

In recent years there has arisen great interest worldwide for greener technologies that enable the use of raw materials that have the least environmental impact. Lignocellulosic biomass has been used as renewable resources for producing biofuels. (Ko et al., 2015).

In this context the use of biomass waste generated in agribusiness and forestry has made it possible to use lignocellulosic materials as a feedstock for the generation of new products by chemical or biotechnological route, and in the formulation of biodegradable materials.

 The interest in vegetable fibers is due to the advantages it presents compared to synthetic fibers because they have low density, biodegradability, reactivity, high strength and specific modulus as well as their low cost.

Also have potential for the production of biofuel because of the presence of cellulose, hemicellulose and lignin.

Biomass waste production forecasts in Brazil are present in the National Energy Plan. According to the table, the potential of agricultural waste, agro-industrial and energy forests will increase by the year 2030 and should be used, contributing to the energy matrix. In the case of this sector, the amount refers only to sugarcane bagasse, and research necessary to increase this sector recovering waste from other crops such as soybeans and corn among others.

TABLE I.

ESTIMATED PRODUCTION AND SUPPLY OF BIOMASS WASTE AS A PRIMARY ENERGY SOURCE FOR THE PRODUCTION OF FUELS (106 T. YR-1) (MME, 2007).

|	2005	2010	2020	2030
Agricultural Waste	**478**	**633**	**904**	**1196**
Soy	185	251	359	482
Corn	176	251	361	485
Rice Straw	57	59	66	69
Cane Straw Sugar	60	73	119	160
Agroindustrial Waste	**80**	**98**	**154**	**207**
Bagasse Sugar Cane	58	70	115	154
Rice Husk	2	2	3	3
Leaches	13	17	25	34
Wood	6	8	12	16
Energy Forests	**13**	**30**	**43**	**46**
Surplus Wood	13	30	43	46

Agricultural waste accounts for about 85% of the total. While the soybean and corn is around 65% of the total and sugarcane straw around approximately 11%. The rest stands out sugarcane bagasse produced in sugar and ethanol manufacturing process, which is approximately 10%.

The development prospect of an agro-energy program using palm oil as the main source of biodiesel production causes concern regarding the allocation to be given to by-products and waste generated by this agricultural industry, since the management of this waste involves costs and care pollution (Furlan, 2006). Narrowing of environmental legislation and the need for companies to reduce waste have forced the palm oil industry and research institutions to seek viable alternatives for the use of the production chain by-products.

Palm oil known as oil palm is a monocot family of Arecaceae. This palm tree of African origin with economic life of 25 years for the agroindustrial holding features well-distributed production during all months of the year and was introduced in Brazil by slaves in Rio de Janeiro and Bahia. The species was included in the Brazilian Amazon in 1942 through seeds from Bahia. Although less productive in oil, this has better quality, as well as having the lowest growth rate in height - making it easy to harvest and extends the production cycle - and resistance to some pests and diseases that occur in African species.

Palm oil is rich in carotenoids (pigments found in plants and animals), which derives its intense red color (Poku, 2002). In its processing can be obtained two types of oil: palm oil (as is known in the international market), which is extracted from mesocarp, and palm kernel oil (palm kernel oil) is extracted from endosperm. Palm oil can be fractionated from the crystallization and simple separation process in which solid fractions are obtained (stearin) and liquid (olein) (Ravigadevi et al, 2000).

The palm waste generated in the production chain of palm oil biodiesel. During the production of this biofuel's production of about 38% of lignocellulosic waste formed normally empty bunches of fibers, leaves and stem (Figure1).
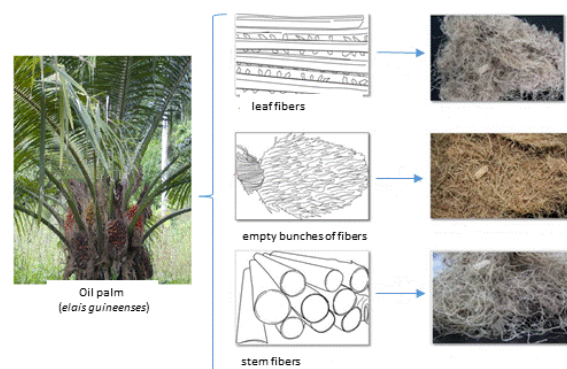
Figure 1: Palm Biomass

In general, the lignocellulosic materials are basically comprised of about 40-60% cellulose, 20-40% hemicellulose and 10-25% lignin and minor constituents (inorganic and organic) (Murphy and McCarthy, 2005).

Comparisons of the composition of the different plant fibers are presented in Table II. In general correlation is observed between the composition values of the fibers, which is dependent on the constitution of the soil, the method of planting, the crop, the climatic conditions and also infections and the age of the plant. So lots of different fibers may differ properties (Annunciado et.al., 2005).

Normally can be observed similarity of values of the ash content of oil palm fiber in the ashes content sisal; the moisture content of palm fiber with the moisture content of the loofah. It was also observed that the lignin present palm fiber similar to those observed for the coconut fiber and bagasse in the range from 22.7 to 29.7% (Silva et al., 2007) while the content of palm fiber cellulose is

comprised in the range found in coconut fiber (36-43%) and sugarcane bagasse (26.6 to 54.3%) (Corma et al., 2006).

TABLE II.
AVERAGE CHEMICAL COMPOSITION OF SEVERAL VEGETABLE FIBERS. (ADAPTED FROM ANNUNCIADO ET AL., 2005; BALAT ET AL., 2008; RADOMSKI, 2009).

Composition (%)	Cotton	coconut fiber	palm fiber	Sisal
ashes	0,6	2,22	3,0	3,1
humidity	8,0	12,0	6,93	6,0
extractives	---	6,8	24,26	6,2
Hemicellulose	5,7	0,25	5,6	10,1
Cellulose	82,7	36-43	37,9	65,8
Lignin	1,0	17,8	22,31	12,0

The hemicellulose content of oil palm fiber is equal to the content found in cotton. However, it was found that the extractives content of oil palm fiber was higher compared to the values obtained for the plant fibers shown in Table II, but was similar to the extractives content of the straw of corn, the value was 28.53 % (Salazar et al. 2005).

Oil palm (*Elaeis guineensis*) has a high content of cellulose, lignin and hemicellulose, essential substances for the production of bioenergy. The production of palm oil is fast compared to other agricultural crops. At the end of the third year after planting, it begins commercial production with six to eight tons of grapes per hectare being produced. However, in the eighth year, the production reaches 20 to 30 tons of grapes, reaching 35 tons per hectare. These values then fall slightly each year until the end of the productive life of oil palm, to 25 years. The yield of palm oil and palm kernel is respectively 22% and 3% by weight of the bunches. Despite the palm fibers are not present in Table II it is noteworthy that residual biomass from the biodiesel production chain, which corresponds to 39% and their productivity is 4000 kg oil/ha$^/$year. In addition, it meets the sustainability criteria of the Kyoto Protocol and especially the National Program of Production and Use of Biodiesel in Brazil, setting the man in the field, through family farming, developing sustainable practices in previously degraded areas in the Amazon, generating employment, income and electricity for isolated community.

For use in bioprocesses, the lignocellulosic material to be treated to break the structure formed by the lignin and hydrolyze hemicellulose and cellulose, releasing fermentable sugars. (Camassola and Dillon, 2009). The pre-treatment is considered one of the most relevant process steps in the conversion of biomass to fermentable sugars; because influence the cost of the process steps. Therefore, this step deserves special attention in the research and development process due to its potential to improve efficiency and lower the cost. This is considered effective to meet several criteria, such as avoiding the need to reduce the size of biomass particles, limiting the formation of degradation products that inhibit the growth of fermentation microorganisms, minimize demand power.

According to Wei et al., 2009, pretreatment of lignocellulosic material involves physical, chemical, biological and even operations for cleaning and reduce the size of the feedstock by promoting the separation of cellulose, hemicellulose and lignin.

To achieve the proper development of the second generation bioethanol obtaining process should dominate the process of expanding biomass fibers by acid hydrolysis process of lignocellulosic material by chemical route, which is environmentally friendly by not using sulfuric acid. The proposal of this phase research work aims to obtain sugars (glucose, maltose, arabinose, xylose, galactose ...) obtained by auto-hydrolysis.

It is noteworthy that there is still little research on the use of this raw material for the production of bio-ethanol and other chemical inputs. As with other lignocellulosic materials, its use requires a pretreatment of the fibers to expand, so as to facilitate access to cellulose, or by biotechnological route, either by chemical route.

Typically, the pretreatment of lignocellulosic fibers can be carried out by steam explosion treatment process used is the acid hydrolysis in the presence of H_2SO_4. This process is usually carried out in batch in a stainless steel reactor, with time presents problems of corrosion. Thus, this study sought to characterize and verify the behavior of palm fibers, subjected to an expansion of the fiber process, auto-hydrolysis in different weather conditions and reaction temperature. The work aims at the

realization of hydrolysis of lignocellulosic from the production chain of palm biodiesel.

The methodology used to determine the components of the material is based on documents from the National Renewable Energy Laboratory (NREL). The first step is the preparation of the apparatus for carrying out the extraction. The second stage is the Extractive Determination of Biomass; then is the use of Carbohydrate Determination protocols and Lignin in Biomass, and ending with the methodology of Ash Determination in Biomass.

II. METHODS AND MATERIAL

Preparation of Biomass

The empty bunches of palm oil, the Tenera type are from Embrapa experimental field in Urubu, located in Rio Preto da Eva, State of Amazonas. These clusters initially autoclaved for 20 minutes at 1 atm (121 °C) were dried at room temperature, threshed and packed in plastic, transparent bags separated into fruit, stem fibers and tenon. These spikes of empty clusters were then crushed in a Wiley mill and subsequently in the mill balls and sieved to give fibers of approximately 80 mesh.

Determination of extractives Biomass - Extraction with Water And Ethanol (95 ° Gl)

The extraction employed a Soxhlet apparatus, which was placed in a cellulose capsule containing about 3.0 grams of sample and 150 ml of water. After this extraction step with water, the residue was used in this new biomass extraction using ethanol as solvent. The extraction time was also 6 hours.

Content of the determination of carbohydrates and lignin in biomass

The mass of 300 mg of biomass was placed in a pressure tube, to which was added an aliquot of 3.0 ml of 72% sulfuric acid under stirring over 1 minute. The pressure tube was then placed in a water bath at 30 ° C for sixty minutes and stirred for 10minutes intervals. Then they were added 84 ml of deionized water. The analysis of the sugar solution obtained was performed using the set of recovery rules sugars (NRA). In these sugars were considered the following: D (+) glucose, D (+) xylose, D (+) galactose, L (+) arabinose, D (+) mannose. In this procedure, the required amounts were weighed of each sugar and added 10.0 mL of deionized water. Then was added 348 mL of 72% sulfuric acid, and then transferred this NRA to a pressure tube which was immediately capped. These tubes were placed in a rack which was placed in an autoclave at 121 °C for one hour. Under the same conditions were put recovery patterns of sugars, used as reference.

Figure 2. Empty bunch of fibers of palm (own collection of Catalysis Group - IME).

Analysis of Lignin Insoluble

The autoclave withdrawn solutions were filtered on Gooch crucible previously subjected to thermal treatment in a muffle oven at 575 °C for four hours, and then registering the weight (tare). The filtrate was collected and used in Lignin analysis procedure Soluble. The solids remaining in the crucible were washed with 50 mL of deionized water. Then, these were dried at 105 °C. After drying, they were allowed to stand in a desiccator under vacuum for one hour and then determined their weight.

Analysis of the Lignin Solubility in Acid Medium

An aliquot of the solution obtained was analyzed at a wavelength of 240 nm suitable for a UV-Visible spectrophotometer using the equipment Evolution 201, Thermo Scientific. From the results obtained it was calculated.

Analysis of Structural Carbohydrates

In a 50mL Erlenmeyer flask was transferred about 20 mL of vacuum filtration of the hydrolysed solution, and then be neutralized with calcium carbonate. After neutralizing the solution and independent calibration verification standards (PVCI) were analyzed by high-performance liquid chromatography (HPLC Water

Alliance). The column used in this analysis was the HPX-87H BioradAminex coupled to a protective column.

Standards (PVCI) cellobiose, glucose, xylose, galactose, furfural, arabinose and mannose were prepared in the ranges of concentrations shown in Table III. In this preparation was used in a concentration range shown to remain, so that it was validated calibration curve.

TABLE III.
CALIBRATION STANDARDS

Compounds	Compounds Concentration (mg /ml)
D-cellobiose	0,1 – 4,0
D (+) glucose	0,1 – 4,0
D (+) xylose	0,1 – 4,0
D (+) galactose	0,1 – 4,0
D (+) arabinose	0,1 – 4,0
D (+) mannose	0,1 – 4,0
furfural	0,1 – 4,0
Acetic Acid	0,1 – 4,0
PVCI	Half linear range of the concentration is equal to a calibration point.

(Source: adapted from. NREL, 2008)

Energy Dispersive X-Ray Spectroscopy (EDS or EDX) is a chemical microanalysis technique used in conjunction with scanning electron microscopy (SEM).

The morphology of the fibers before and after the hydrolysis process was analyzed by in a Inspect microscope FEI Quanta FEG model 250. Before analyzing the materials were subjected to gold plating. The EDS x-ray detector measures the relative abundance of emitted x-rays versus their energy.

Hydrolysisof Biomass

The hydrolysis reaction was performed in a Parr reactor temperature of 100 °C and 170 °C for 30 to 60 minutes. The mass of biomass was 7 g and the volume of distilled water 70 ml.

Analysis of Hydrolysis Products

The producers of the hydrolysis were analyzed by high-performance liquid chromatography (HPLC) using

chromatograph, Waters brand model Alliance 2695, with refractive index detector (RID) at 80 °C. For the analysis of the products used an Aminex HPX-87H column from BioradAminex at 80 °C and degassed water as the mobile phase. The injection volume 10 ml and the flow rate of 0.7ml / min. All tests were assessed in triplicate and the data processed using the arithmetic mean

III. RESULTS AND DISCUSSION

In the characterization of empty clusters palm to compare the work of Radomski (2009), it appears that there is great variation between the percentage amount of cellulose, hemicellulose and lignin insoluble. Already the work of De Souza (2014) the percentage amount of pulp was well below what has been determined in this work and Radomski, but the amount of hemicellulose was compared to two papers. However, in this study we obtained a total closure of the nearest carbon to 100% with a standard deviation acceptable. (Table IV)

TABLE IV.
PALM BUNCH COMPOSITION WITH AND WITHOUT EXTRACTIVES

FRACTION	COMPOSITION (% m/m)		
	YOGUIM (2015)	RADOMSKI (2009)	SOUZA (2014)*
Cellulose	14,43 ± 0,33	37,9	4,6
Hemicellulose	16,12 ± 0,68	5,6	37,5
Lignin acid insoluble	29,49 ± 0,39	16	29
Lignin-soluble acid	3,19 ± 0,07	6,31	1,5
Extractives	28,24 ± 0,43	24,26	17,8
Total ash	5,16 ± 0,05	3	4,5
Total	**96,6 ± 1,95**	**93,07**	**94,5**

* biomass from oil palm mesocarp fibers

It is observed that the fibers obtained at the ears of the clusters have about 50% less than the cellulose fibers obtained from the base of the cluster, used by Radomski (2009). The cellulose present in the mesocarp fibers was only about 5%. Comparing the hemicellulose values it appears that the higher content is found in the mesocarp fibers which is around 38%.

## Morphological analysis by SEM/EDS

The residual biomass palm subjected to hydrotreating in Parr batch reactor, where hydrolysis occurred at 100 °C for 30 min, it was practically the same morphology (Figure 3).
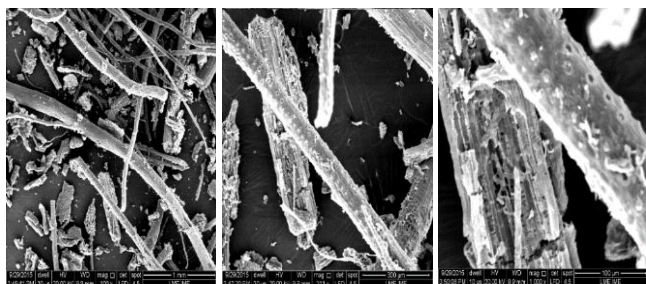
Figure 3. Photomicrograph of lignocellulosic waste palm submitted to hydrotreating a 100ºC for 30min.

However, the cell walls have been changed. this fractionation is observed probably due to the presence of the autogenous pressure generated in the system. The approximate composition was determined by EDS. This biomass after hydrothermal process of autohydrolysis has about 73% C, 17% O, 0.8% K expressed in atomic percentage. The presence of the platinum coating must be performed on the sample of biomass and Cu and Zn, the sample holder used.

This lignocellulosic material was subjected to the same procedure for 60 minutes. Note the change in cell walls that present roughness and the appearance of sponge-like cavities, generating high porosity. Yet it appears that the expansion of the fiber allows the exposure of the pulp. According to the literature can be solubilized hemicellulose, cleaved acetyl groups and small changes are caused in the pulp and lignin (WITHERS, Dominguez, Parajó, 1999) (Figure 4)
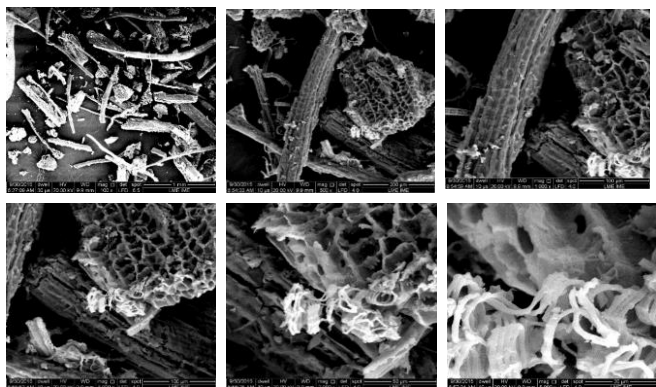
Figure 4. Photomicrograph of lignocellulosic residue submitted to pretreatment palm a100ºC for 60 minutes in increments of 100, 500, 1000, 2000 and 5000 times

In the micrograph of this fiber subjected to hydrotreating by 60 min (Figure 7) is verified by SDS, which has a certain heterogeneity in average composition, expressed in atomic percent, about 68% C; 20% O; 0.5% Si; 0.8% K; 0.03% S and 0.5% Ca.
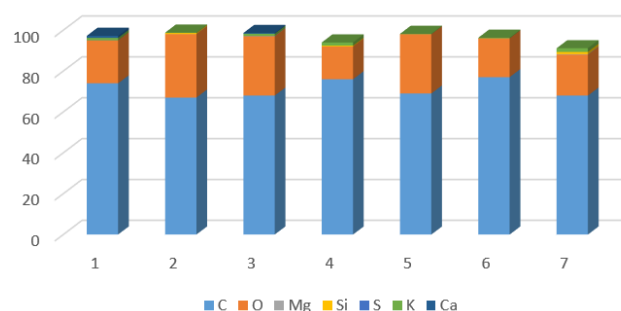
Figure 5. Fiber composition referred to the hydrotreating process to 100 °C for 60 min.

## Espectrometria de Infravermelho – Indíce de Cristalinidade Total

A comparison of infrared spectra of oil palm fiber in nature with the fibers subjected to hydrotreating temperature of 100 °C for 30 to 60 minutes is shown in figura 6

Analysis of the spectra shows that the band at 3420 cm^{-1} characteristic of OH, which is more intense for palm residue in nature. The extension of this band is associated with the bonds of inter and intramolecular hydrogen bonds. The other observed in the region of 3000 – 2800 cm^{-1}, are attributed to the symmetric and asymmetric stretch of CH and methyl groups present in the methylene celulose. Note the decrease in intensity with increasing hydrotreating time, indicating a reduction in binding due to hydrogen bonding, probably due to disruption of hydrogen bonding of the cellulose.

The band at 1642 cm^{-1} is associated with the adsorbed water in the cellulose. Bands to 1430, 1370.1335 and 1320 are attributed to symmetrical bending of CH$_2$, CH bending, OH in the plan, CH$_2$ rocking vibration, and the bands at 1162, 1111, 1057, 1033, 898 cm^{-1} are assingned to asymmetric COC bridge stretching, the any on glucose in asymetric stretching, stretching CO, CH in

plane deformation, CH deformation of cellulose, respectivamente. Still was observed the peaks is xylan from hemicelluloses are derived from molecular vibrations in the uronic acids at 1730 and 1600 cm^{-1}.

The total crystalline index (TCI) is proportional to the degree of crystallinity is a relationship between the heights of the bands 1372 and 200 cm^{-1} in infrared (Garrote et all, 2014). The cellulose has two regions, one at 1430 cm^{-1} associated with the amount of crystalline structure and another band at 898 cm^{-1} related to amorphous region.
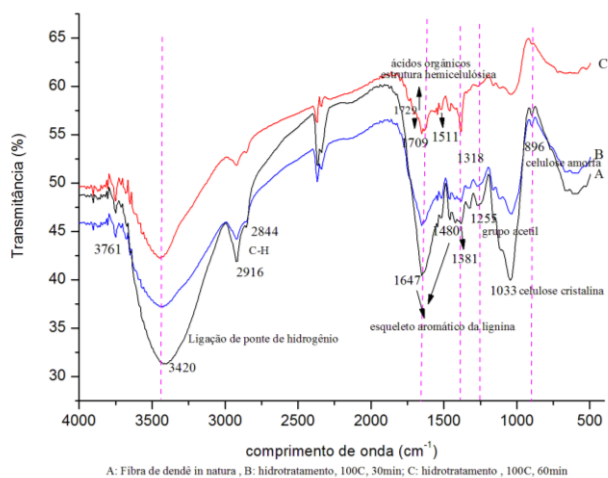
Figure 6. Comparison of the IR spectra of palm biomass residue before and after pretreatment. A: palm fiber in nature; B: Hydrotreating at 100 °C, 30 min; and C: Hydrotreating at 100 °C, 60 min.

The analysis of these spectra shows that the self-hydrolysis of empty biomass palm bunches temperature of 100 ° C, indicates a decrease of some characteristic peaks of hydrogen bridge bonds, cellulose and hemicellulose.

The relationship between the heights of the bands at 1372 and 2900 cm^{-1} is used to assess crystallinity. According to Nelson and O'Connor this ratio gives the total crystallinity index (TCI), which is proportional to the degree of crystallinity of cellulose. Thus, this ratio was determined for the biomass waste (in nature) before and after hydrolysis for 30 and 60 minutes, with values of 0.3; 0.5 and 0.8, respectively. To prove this trend was carried out the hydrolysis reaction also at 100 °C for 24h and analyzed by SEM and infrared spectrometry as shown in figure 7.
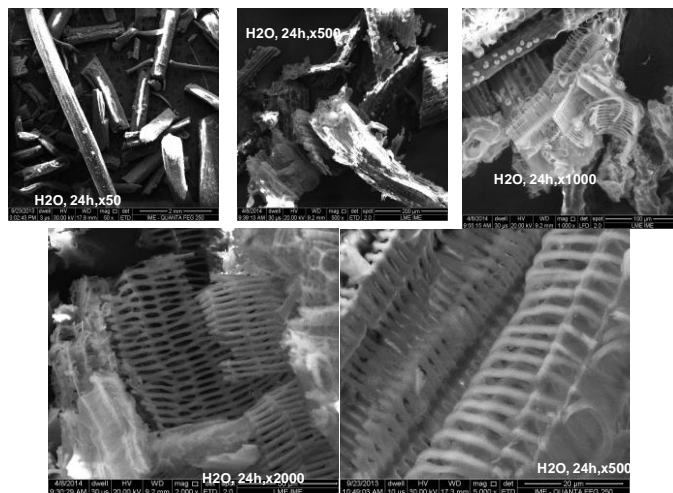
Figure 7. Photomicrograph of waste fibers from palm production chain of biodiesel oil palm hydrolyzed in deionized water at 100 ° C for 24 hours in increments of 500, 2000 and 5000 times.

Comparison of the photomicrographs indicates that the increase in hydrotreating time of 30, 60 minutes to 24 hours favored the hydrolysis process of self shown by the appearance of porosity and by exposing the crystalline cellulose. Furthermore, it was found that the total crystallinity index after 24 hours was increased by 87% when compared with the hydrolysis reaction carried out at 100 °C for 1h. The figure 8 shows a comparison of the total crystallinity index.
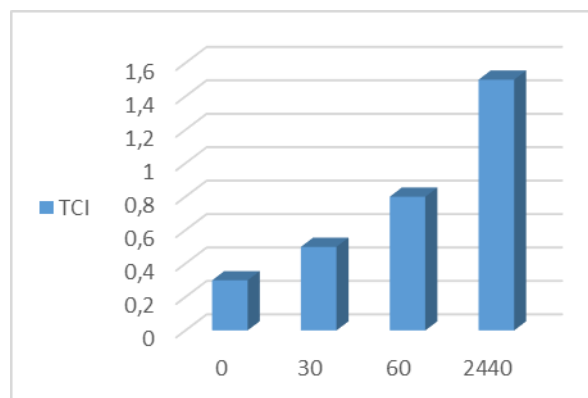
Figure 8. Comparison of crystallization index (TCI) in the palm natural fibers of cluster (0) and after hydrolysis treatment at different times (min).

The increasing the pretreatment time confirms that the auto-hydrolysis process occurs causing an expansion of the fibers, exposing the crystalline cellulose and probably partial leaching of hemicellulose and lignin.

According to the literature during the hydrothermal process only part of the ester groups is removed. The temperature and time are important variables in the self-hydrolysis process. Through these variables can

determine the process severity factor, which has a direct effect on the acidification of the medium due to cleavage of the acetyl groups generated from the degradation products of sugars and degree of polymerization of XOs (Garrote, Domingez, Parajó, 1999).

After the hydrothermal treatment, the product of the hydrolysis reaction medium analyzed by HPLC. The products were identified: glucose, xylose, and acetic acid. Forming furfural was observed, indicating that there was a xylose dehydration reaction (Table V).
Therefore, this reaction is catalytic species of acetic acid generated by the acetyl groups present in the hemicellulose. Even the presence of fermentation inhibitors depends on the chemical composition of plant fiber, as well as the process of fertilization, fertilization and disease.

TABLE V. PRODUCTS OF THE HYDROLYSIS REACTION DETECTED BY HPLC.

T (°C)	t (min)	Glicose (g/L)	Xilose g/L	Acetic Acid
MONOSSACCHARIDE				
100	30	1,0	0,3	0,04
	60	1,0	0,3	0,06
OLIGOSSACCHARIDE				
100	30	0,1	0,03	0,2
	60	0,2	0,04	0,2

Therefore, it is observed that the reaction of auto-hydrolysis of lignocellulosic waste palm appears as fermentation inhibitor of furfural. Only acetic acid is produced. Probably due to the absence of acid catalysts, which would be responsible for the dehydration of xylose. Certain fibers may have different amounts of inhibitors, such as derivatives of furans (furfural and HMF) derived from weak acids (acetic acid, formic acid and levulinic) and lignin derivatives (phenols) as compared to other fibers. Quantitation of fermentation inhibitors produced during pretreatment by acid hydrolysis of some lignocellulosic materials is shown in the Table VII.

TABLE VI. INHIBITOR CONCENTRATIONS DETECTED IN VARIOUS HYDROLYSATES BIOMASSES (CHANDEL, ADAPTED, 2011).

Lignocellulosic Material	Inhibition Profile		References
	Compounds	C(g/L)	
Sugarcane Bagasse	Furans	1.89	Chandel et al., 2007
	Phenolic	2.75	
	Acetic Acid	5.45	
Wheat Straw	Furfural	0.15	Nigam, 2001
	Acetic Acid	2.70	
Rice Straw	Acetate	1.43	Baek &Kwon, 2007
	HMF	0.15	
	Furfural	0.25	
Corn Straw	Acetic Acid	1.48	Cao et al., 2009
	Furans	0.56	
	Phenolic	0.08	
Eucalyptus globulus	Furfural	0.26	Villarreal et al., 2006
	HMF	0.07	
	Acetic Acid	3.41	
	Phenolic	2.23	
Wood Light	Acetic Acid	5.3	Qian et al., 2003
	Furfural	2.2	

Wyman et al., 2005, in their studies show that dilute acids (0.5-1.0% sulfuric acid) at moderate temperatures (140-190 ºC) efficiently removes and recovers most of the hemicellulose to soluble sugars, and the yield of pulp increases with the removal of hemicellulose. However, he noted that to increase the hemicellulose hydrolyzate fermentability is necessary to reduce the concentration, or totally eliminate the middle, the toxic compounds generated.

IV. CONCLUSION

The increasing the pretreatment time confirms that the auto-hydrolysis process occurs causing an expansion of the fibers, exposing the crystalline cellulose and probably partial leaching of the hemicellulose and lignin. This process low cost will enable the use of the waste generated during the production of biodiesel, which corresponds to 38% (m/m) which is considered environmental liabilities. Furthermore, the expanded fibers of empty clusters likely to facilitate the accessibility of enzymes for the production of biofuels from waste biomass.

The products after pretreatment were identified: glucose, xylose, and acetic acid. Therefore, under the conditions of the pretreatment was detected only acetic acid.

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