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THE USE OF COMPRESSED FLUIDS TO OBTAIN BIOCOMPOSITES FROM PALM OIL FIBER (*ELAEIS* SP.)

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Abstract - Empty fruit bunch fiber (EFBF) is a lignocellulosic waste generated by the palm oil agribusiness. The amount of EFBF produced is equal to the oil obtained, and it can be used as raw material to obtain biocomposites. The objective of this work is to fragment the EFBF employing pressurized fluids in a semi-continuous system to obtain different biocomposites. For this, pure water and a mixture of water/carbon dioxide were employed as solvent to obtain sugar monomers and a mixture of compressed water/ethanol (1:1 vol.) to obtain crystalline cellulose. The experiments were conducted in the temperature range of 120 to 240 ºC, using reaction times between 5 and 15 min at 60 bar, and solvent flow rate of 0.75 mL.min^{-1}. A maximum of 30.47 mg.mL^{-1} of xylose was obtained at 210 ºC for 15 min of reaction with pure water as solvent. The best condition to obtain crystalline cellulose was 240 ºC for 30 minutes of reaction, obtaining 38.2% of cellulose from palm oil EFBF.

Keywords: Palm oil waste, Biocomposites, Pressurized fluids.

INTRODUCTION

The different effects of the use and depletion of fossil fuels, such as environmental pollution and dependence on petrochemicals, are a matter of concern worldwide. Alternative technologies and sustainable solutions for converting biomass and obtain biocomposites and biofuels are being increasingly designed and developed (Nel e Cooper, 2009; Zakaria *et al*., 2015).

Lignocellulosic biomass is a heterogeneous polymer composed of carbohydrates and lignin. Its use can be entire or by deconstruction into its constituent polymers: cellulose, hemicellulose and lignin. In the bio-refinery concept, the use of lignocellulosic biomass happens by a different process, optimized and integrated aiming to produce several products, such as carbohydrates, oils, lignin, carotenoids among others. This range of products can also be transformed into fuels and biocomposites with aggregate values (Vaz Jr., 2012; Carvalheiro *et al*., 2008; Mood *et al*., 2013; García *et al*., 2014).

Several vegetable sources can be used to substitute fossil fuels, for example, wastes of the palm oil agro industry. In Brazil, the area planted in 2013 was 122.000 hectares, with a total of 1.34 million tons of harvested bunches and 335.000 tons of oil produced (BRASIL, 2015).

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The different solid wastes generated, such as leave, mesocarp, the empty fruit bunch fiber (EFBF), and endocarp are mostly used as energy sources in boilers of the extractor plants. However, it is logical to think of different ways to use this waste as a renewable biocomposites/biofuels source. EFBF, the structure supporting the fruits, represents around 20% of the total weight of the bunch. This amount is equal to the percentage of oil extracted, being a residue of high availability (Chiesa e Gnansounou, 2014).

Among different processes to convert biomass, the most used routes nowadays and the most promising are physical-chemical processes. However, most technologies (acid, alkaline or enzymatic hydrolysis) demand a significant quantity of chemical products and catalysts, as highlighted by Lachos-Perez et al. (2016). As an alternative to these processes, pressurized fluids such as sub/supercritical water and mixtures of water with ethanol or carbon dioxide (green solvents) have been applied in different biomass conversion processes, obtaining high recovery levels of different bioproducts (Oliveira et al., 2017; Lachos-Perez et al., 2016; Saldaña and Valdivieso-Ramírez, 2015; Relvas et al., 2015; Alvarez et al., 2014).

Another advantage of the pressurized fluids is the possibility to easily manipulate certain characteristic of the solvent such as density, polarity, viscosity and dielectric constant by changing the system temperature and pressure. This characteristic allows control of the solubility and fragmentation power of different compounds aiming to maximize the production of specific phytochemicals from a variety of biomasses; in addition, high yields are achieved without the use of catalyst (Kurnin et al., 2016; Wen et al., 2009; Saldana and Valdivieso-Ramírez, 2015). The fluids to be used must have critical pressure and temperature adequate for the process, good solubility for the solute, be inert and easily separated from the obtained product and have low cost (Toor et al., 2011).

Continuous or semi-continuous processes have been reported in the literature as an alternative to batch ones for obtaining products of interest from biomass, for example, bio-oil (Oliveira et al., 2017), sugars (Lachos-Perez et al., 2016) and phytochemicals such as phenolics and antioxidant (Alvarez et al., 2014). The main advantage of these processes is the possibility to control independently all the process variables. Recently our group proposed a semi-continuous unit for biomass liquefaction that, different from the other processes for hydrothermal liquefaction (HTL), dispenses the use of biomass slurries, since a pure or a mixture of solvents is pumped through a reactor that contains the biomass (Oliveira et al., 2017). A similar apparatus for subcritical water hydrolysis (SWH) was also described by Lachos-Perez et al. (2016).

In this sense, this study has the objective to fragment empty palm oil bunch fiber through pressurized fluid technology to obtain different biocomposites employing the apparatus described previously with a small modification.

EXPERIMENTAL

Empty fruit bunch fiber (EFBF) from palm oil (variety Dura) was provided by Empresa Baiana de Desenvolvimento Agrário – EBDA. The EFBF was dried in the sun for two days, manually cut, crushed in a slicer, and classified with Tyler series sieves in the range of 32-60 mesh. The raw fiber was stored in glass containers. All the experiments were performed using the same lot of EFBF. The CHN (carbon, hydrogen and nitrogen) content of the EFBF was measured in a CHN analyzer (Perkin-Elmer, model 2400 XP) and the moisture content was determined by titration using the Karl Fischer reagent in an automatic titrator (Methrom, 870 KF titrino plus).

Lignocellulosic characterization

For lignocellulosic characterization of the empty fiber bunch fiber the methodology developed by National Renewable Energy Laboratory - NREL/TP-510-42618 (NREL, 2008) was followed. First, the EFBF water/ethanol soluble portion was removed through Soxhlet extraction. In sequence, the material was hydrolyzed in 72% sulfuric acid at 30 ºC for 60 min. After this, the hydrolyzed mixture was diluted to 4% in water, autoclaved at 121 ºC for 1 hour, and filtered in porous baffle crucibles. The solid residual waste was considered to be Klason lignin.

UV-VIS spectrophotometry was used to determine the soluble lignin in the hydrolyzed liquid, at a wavelength of 280 nm. The sugar content was determined through the concentration of cellobiose, glucose, xylose, mannose, galactose and arabinose employing High Performance Liquid Chromatography – HPLC (Shimadzu Prominence, model LC10AD), with a refraction ratio detector (RID-10A) and SPD-M20A of the DAD type (Diode Array Detector) for spectrophotometry in the ultraviolet. Analyses were realized in a Supelcogel Pb column at 85 ºC, preceded by a Supelguard Pb guard column, eluted with ultrapure water with a constant flow rate of 0.6 $mL.min^{-1}$.

To determine the degradation products hydroxyl--methyl-furfural (HMF) and furfural the same equipment described above was employed with ultraviolet detector and an Aminex Bio-Rad HPX-87H column at 65 ºC, equipped with a guard column, eluted with a solution of H_2SO_4 (5 μM) at a constant flow rate of 0.6 $mL.min^{-1}$.

Thermogravimetric analyses (TG)

The thermal behavior of the empty fiber bunch fiber (EFBF) was studied in a differential thermogravimetric analyzer (Shimadzu, DTG-60H). The samples were heated from room temperature up to 800 ºC at a heating rate of 20 $ºC.min^{-1}$. High purity nitrogen (99.99%, White Martins) was used as purge gas (flow rate of 50 $cm^3.min^{-1}$) to provide an inert atmosphere around the sample during analyses. The sample mass lost due to heating (TG) and its first derivative (DTG) were continuously collected with the aid of a specific software.

EFBF Fragmentation

For the EFBF fragmentation process, a semi-continuous biomass thermoconversion unit (Figure 1) was employed. The main difference of this apparatus to that described previously (Oliveira et al., 2017) is the possibility of operation with pressurized liquid and gas solvents simultaneously employing a HPLC pump (Fischer Scientific, Series III) and a syringe pump (Isco, model 260D) connected with a thermostatic bath kept at 7 ºC to maintain the carbon dioxide (CO_2) in the liquid state at 100 bar, allowing one to calculate the solvent density (0.9374 $g.cm^{-3}$ - NIST, 2017). These pumps move the liquid and gaseous solvent, respectively, in the whole system line. The oven (Jung) can operate at temperatures up to 1000 ºC. The reactor is a stainless steel tube (Swagelok), with 30 cm of length and external diameter of 3/8". The reactor outlet has a condenser and a zero volume pressure transducer (NOVUS, model TP-691) connected to an universal indicator used to monitoring the system pressure. A needle valve located at the end of the line is employed for adjustment/control of the system pressure. Two thermocouples, one connected at the inlet and another at the outlet of the reactor, were used to measure the temperature inside the oven.

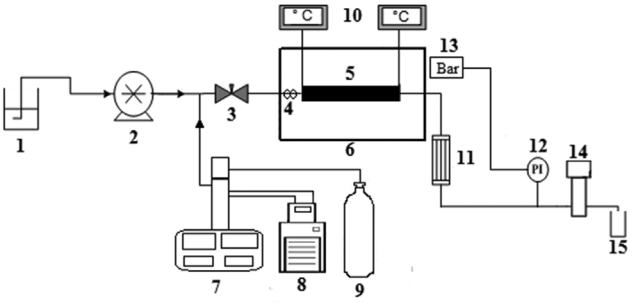

Figure 1: Biomass thermoconversion unit, with capacity to operate with pressurized liquid and/or gaseous solvents in semi-continuous flow. 1- solvent reservoir; 2- isocratic pump; 3- micrometric valve; 4- pre-heater zone; 5- reactor; 6- oven; 7- syringe pump; 8- batch; 9- CO_2; 10- inlet and outlet temperature indicators; 11- cold zone; 12- pressure transducer; 13- pressure indicator; 14- back pressure regulator and 15- sample flask.

At each experimental run the reactor was loaded with about 1g of EFBF and connected to the system. Then, the solvent or the mixture of solvents was pumped to fill the line and set at the desired pressure. The oven is turned on with a heating rate of 20 $ºC.min^{-1}$ up to the programmed temperature. When the working temperature and pressure are reached, the liquid fraction is collected during a defined time (according to Table 1) at constant flow rate (0.75 $mL.min^{-1}$). After the fragmentation the oven was shut down and the extract was collected for 5 more minutes to ensure the recuperation of all fragmented products inside the reactor and outlet lines. After this time, the solvent flow was interrupted and the system was depressurized. The biomass (EFBF) remaining in the reactor was removed and dried in an oven at 40 ºC until constant weight. All the experiments were performed in duplicate from where the errors were calculated and presented in the form of an error bar in the graphs. The percentage of consumed/fragmented biomass was calculated by Equation 1.

$$\%\ mass\ consumption = \frac{(initial\ mass\ (g) - final\ mass\ (g))}{initial\ mass\ (g)} 100 \qquad (1)$$

The fragmentation runs were performed, first, employing pure water as solvent (with a constant flow rate of 0.75 $mL.min^{-1}$ and pressure of 60 bar) aiming to extract xylose from EFBF. The experimental conditions adopted for these tests are summarized in Table 1.

Table 1: Experimental conditions for palm oil EFBF fragmentation employing pure water and water/ethanol (1:1 vol.) as solvent.

Run	Temperature (°C)	Time (min)
1	120	5
2	150	5
3	180	5
4	210	5
5	240	5
6	120	15
7	150	15
8	180	15
9	210	15
10	240	15
11	120	30
12	150	30
13	180	30
14	210	30
15	240	30

For the best condition found in the fragmentation process by pressurized water, a certain amount of carbon dioxide (CO_2) was added as co-solvent aiming to increase xylose yield by medium acidification. The amount of CO_2 present in the water during the experiments was calculated based on the study of Duan and Sun (2003), which shows that, at a pressure of 100 bar, the maximum solubility of CO_2 in water is approximately 0.7 mol of CO_2 per kg of water, in the temperature range studied in this step (180-240 °C). The volumetric ratio of each solvent was calculated considering the density of each one at the pressure of 100 bar for each temperature. To ensure that the maximum solubility of CO_2 in water was attained, the CO_2 was added with an excess of 1.5 fold, considering a total flow rate of 1.0 mL.min^{-1}. The values of flow rates calculated for each solvent are shown in Table 2.

Table 2: Solvent flow rate (mL.min^{-1}) for the EFBF fragmentation employing water/CO_2 as solvent.

Temp. (°C)	Water	CO_2
180	0.75	0.25
210	0.74	0.26
240	0.74	0.26

In a second set of experiments a mixture of water/ethanol (1:1 vol.) was employed as fragmentation solvent aiming to obtain cellulose from EFBF. The experimental conditions evaluated were the same presented in Table 1. All the fragmentations were performed in duplicate with a constant flow of 0.75 mL.min^{-1} and pressure of 60 bar.

Characterization of the liquid extract obtained from the fragmentation with pressurized water and pressurized water + carbon dioxide

The composition in sugars and products of degradation of liqueurs obtained from the fragmentation was performed following the methodology described by NREL/TP-510-42623, using the same equipment and chromatographic conditions described previously.

Characterization of the solid products obtained from the fragmentation by pressurized water/ethanol (1:1 vol.) mixture

The solid wastes remaining from the best fragmentation conditions were analyzed by Fourier Transform Infrared Spectroscopy - FT-IR (Agilent Technologies, Model Cary 630 FT-IR). The samples were evaluated in the spectral range of 4000 to 650 cm^{-1} and each spectrum presented is an average of 16 scans. For X-Ray Diffraction - X-RD analysis a Empyrean diffractometer (PANalytical) with radiation CU-Kα (1º= 1.5406 Å) was employed. All the data were collected in a continuous way in Bragg-Brentano geometry with a range of 2θ from 10º to 50º according to Hassan *et al*. (2013) and a step size of 0.01º. Both analyses were compared with the spectrum and the diffractogram of standard cellulose (Sigma Aldrich, U.S – C6288) to identify the best experimental condition to obtain cellulose of greater quality and crystallinity.

RESULTS AND DISCUSSION

The lignocellulosic characterization of the empty fiber bunch fiber (EFBF) performed according to NREL/TP-510-42618 and the elemental composition are presented at Table 3. The results of lignocellulosic characterization suggested that the palm oil EFBF employed in this work is similar to that reported by Hassan *et al*. (2013) and Chiesa and Gnansounou (2014), with a total content of holocellulose (cellulose + hemicellulose) and lignin close to 50% and 25%, respectively. The elemental composition analysis of EFBF indicates high content of carbon and oxygen in the biomass, and the values are in agreement with those reported in the literature (Chang, 2014).

Table 3: Lignocellulosic characterization and elemental composition of the empty fiber bunch fiber (EFBF).

	Content (%)
Cellulose	33.9
Hemicellulose	15.0
Lignin	28.1
Moisture	7.6
Extractive	15.3
Ashes	7.6
Carbon	40.5
Hydrogen	5.9
Nitrogen	0.0
Oxygen*	53.6

*Calculated by diference.

Thermogravimetric analyses (TG)

The thermogravimetric analyses performed at temperatures up to 800 ºC indicate a mass loss of palm oil EFBF of approximately 70%, as can be seen in Figure 2. Initially, a loss around 10% was observed in the temperature range from 100 to 225 ºC, attributed to the water and smaller chain compounds present in the sample. The most significant mass loss was observed between 225 and 340 ºC, as evidenced by the DTG curve, being approximately 35%. This loss can be related to holocellulose degradation (Lin *et al*., 2015). However, a bigger mass loss was expected in this temperature range, because the holocellulose content in the sample is close to 50%, but it should be emphasized that other factors, such as cellulose crystallinity, may influence the degradation process (Hassan *et al*., 2013). Above 340 ºC up to the final temperature the mass loss happens slowly. In this temperature range the loss was close to 25% of the total mass, and can be attributed to the degradation of the remaining holocellulose and lignin (Lin *et al*., 2015). The high ash content (7.6%), allied to charcoal formation, contributes to a lesser total mass loss.

Fragmentation of palm oil EFBF by pressurized water

The fragmentation profile of palm oil EFBF by pressurized water can be seen in Figure 3. As one can note, the error bars that indicate the reproducibility of the apparatus are smaller than the symbols for most of the conditions presented in Figures 3 and 4. Time variation from 5 to 30 min at temperatures of 120 and 150 ºC does not causes a significant difference on the extracted mass. At this condition the mass consumption was close to 15%, being in accordance with reported values of extractive compounds determined in this work by the NREL/TP-510-42618 test. When the fragmentation temperature was 180 ºC the same behavior was observed at 5 and 15 minutes. Similar yield was observed by Chiesa *et al*. (2014) performing an acid treatment of palm oil EFBF using sulfuric acid (0.05 vol%) at 140 ºC for 10.5 minutes, the mass extracted being close to 15%. After 30 minutes of fragmentation at 180 ºC approximately 33% of the EFBF loaded in the reactor was fragmented.

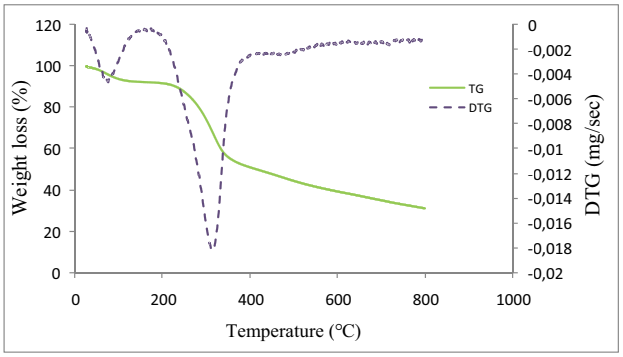

Figure 2: Palm oil EFBF TG and DTG curve.

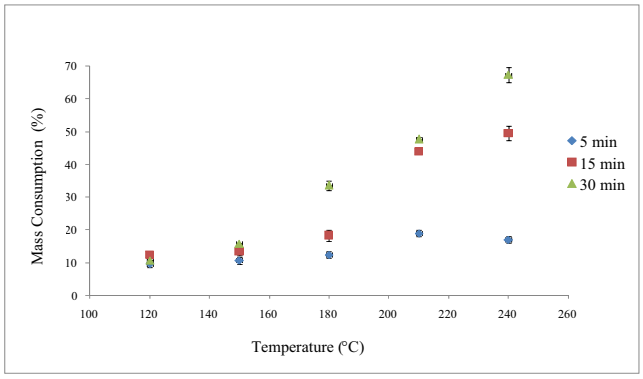

Figure 3: Fragmentation profile of palm oil EFBF using pressurized water as solvent at 60 bar.

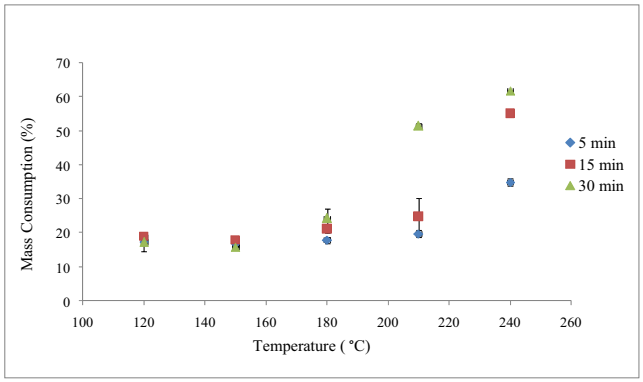

Figure 4: Palm oil EFBF fragmentation profile using pressurized water/ethanol mixture (1:1 vol.) at 60 bar.

At 210 ºC one can observe a drastic increment in the EFBF consumption from 5 to 15 min of fragmentation where the mass consumption increases from 19% to 44%. However, this percentage was only raised 3.7% in 30 minutes of extraction, reaching a maximum of 47.6% of mass consumption.

The highest fragmentation was achieved at 240 ºC with 30 minutes of reaction, reaching a maximum of consumed mass of 67.3%. Chiesa *et al.* (2014) obtained similar results (66.5% of mass consumption) at 210 ºC in 20 minutes employing an acid treatment (1.02 %vol of sulfuric acid).

The mass consumption with 15 min at 240 ºC (49.5%) is similar to those obtained with 30 min of extraction at 210 ºC. In 5 minutes of extraction at 240 ºC there was no EFBF fragmentation, only extraction of soluble compounds.

As one can note in Figure 3, the best conditions for palm oil EFBF fragmentation using pure water as solvent are at temperatures above 180 ºC with fragmentation/reaction time above 15 min. So, for these conditions, the effect of carbon dioxide (CO_2) on the mass consumption was evaluated. The CO_2/water ratios employed are summarized in Table 2. Table 3 present a comparison between the experimental runs with and without CO_2. The addition of CO_2 in the fragmentation process represented a small gain in fragmentation yield of the EFBF only at 180 °C with 30 min of reaction. On the other hand, at 210 °C with 15 min of fragmentation the mass consumption decreased in the presence of CO_2. For all the other experimental conditions the injection of CO_2 did not significantly change the mass consumption.

The chemical characterization regarding the content of sugars monomers and degradation products presents in the liqueurs obtained from fragmentation of palm oil EFBF by pure water is presented in Table 5. For this process the product of interest is xylose. The low glucose value is indicative that the cellulose was preserved.

Table 4: Consumed mass percentage of EFBF fragmentation using H_2O and H_2O/CO_2 for the respective experimental conditions.

	Reaction time (minutes)			
	15		30	
Temp (°C)	H_2O	H_2O/CO_2	H_2O	H_2O/CO_2
180	-	-	33.6±1.4	39.0±0.3
210	44.0±0.7	36.7±1.5	47.6±0.6	49.0±4.2
240	49.5±2.2	52.1±5.3	67.3±2.4	62.5±2.7

Table 5: Sugar monomers and degradation product concentrations (mg.mL^{-1}) from liqueurs obtained from EFBF fragmentation using pressurized water at distinct experimental conditions.

Run	Experimental Conditions		Glucose	Xylose	Arabinose	HMF	Furfural
	Temperature (°C)	Time (min)					
1	120	5	0.39	0.22	0.28	0.01	0.01
2	120	15	0.31	0.17	0.15	0.02	0.02
3	120	30	0.23	0.15	0.07	0.01	0.01
4	150	5	0.57	0.27	0.30	0.02	0.02
5	150	15	0.45	0.28	0.32	0.02	0.03
6	150	30	0.39	0.50	0.44	0.02	0.02
7	180	5	0.46	0.28	0.18	0.05	0.05
8	180	15	0.74	2.14	1.38	0.03	0.03
9	180	30	0.89	12.81	1.58	0.04	0.04
10	210	5	1.24	6.66	1.60	0.03	0.03
11	210	15	2.08	30.47	2.23	0.08	0.09
12	210	30	1.23	21.83	1.37	0.06	0.06
13	240	5	0.42	0.36	0.18	3.20	3.95
14	240	15	0.54	5.84	0.38	5.87	3.94
15	240	30	0.44	3.85	0.28	6.38	3.93

As can be seen, the concentration of sugar monomers and degradation products in the liqueurs is low for experiments performed at the lowest temperatures 120–150 ºC (runs 1-6). At 180 ºC and fragmentation time above 15 min the sugars concentration in the liqueur increases considerably, indicating the beginning of fractionation.

The liquor with highest concentration in sugar monomers was obtained at 210 ºC/15 minutes. As one can note, xylose was the sugar most formed (30.47 $mg.mL^{-1}$) in the palm oil EFBF fragmentation employing pressurized water as solvent. The concentration of glucose and arabinose remains always below 2.08 and 2.23 $mg.mL^{-1}$, respectively, and the presence of degradation products in the liquor is very low (<0.09 $mg.mL^{-1}$). The high content of xylose in the liqueurs can be attributed to two main factors: first, palm oil EFBF is composed of 24% xylene, a polymer constituted of xylose, which composes hemicellulose (Wyman, 1994) and, second, the temperature and reaction time evaluated were not enough to break up the cellulose due to its high crystallinity. Hassan *et al*. (2013) claim that the severity of the treatment should be adequately controlled to ensure the maximum recuperation of sugars of interest. This shows that the palm oil EFBF fragmentation with pressurized water is a very selective process to obtain xylose.

When the reaction time and temperature are increased (run 12-15) the concentration of sugar monomers formed decreased. This fact can be related with sugars degradation, since the concentration of degradation products increased, mainly at 240 ºC. According to previous work (Lachos-Perez et al., 2016), high temperatures promote organic acid formation and, consequently, the pH of the hydrolysate decreases, leading to xylose degradation and an increase in hydroxyl methyl-furfural (HMF) concentration.

However, in this work the formation of degradation products was not proportional to sugars degradation. This fact can be related to the formation of intermediate compounds from the sugar breakdowns, which were not quantified/identified. The addition of CO_2 to the water did not cause alterations in chemical composition.

Fragmentation of EFBF by pressurized water/ethanol mixture

The main objective in this section is to obtain cellulose with high purity from palm oil EFBF. For this, a pressurized mixture of water/ethanol (1:1 vol.) was employed as solvent to remove hemicellulose and lignin from EFBF. In this sense, cellulose is the solid portion of EFBF that remains in the reactor after the fragmentation. The aqueous phase (liquor) obtained in this section was not characterized.

Figure 4 shows the palm oil EFBF fragmentation profile employing pressurized water/ethanol mixture at different temperatures and reaction times at 60 bar. The results showed similar behavior to those observed in the fragmentation with pure water, where temperature variation from 120 to 180 ºC, using the mixture water/ethanol as solvent, had a small effect on the EFBF fragmentation. In this temperature range the percentage of mass consumption was around 18%, and can be attributed to the EFBF soluble portion.

When the temperature increased to 210 ºC with 30 minutes of reaction time, the mass consumption increased twice compared to the reaction time of 15 min at the same temperature, reaching a value close to 50%. The maximum consumption (61.7%) was obtained at the highest temperature and reaction time (240 ºC/30 min), and was close to the best condition obtained with pure water as solvent (67.3%) for the same experimental conditions.

The solid remaining in the reactor after the fragmentation/extraction process in the best experimental conditions (210 ºC/30 min and 240 ºC/5/15/30 min) was analyzed by FT-IR and X-RD to check whether the remaining solid is in fact cellulose and to determine the quality and crystallization of the product obtained. All the samples were compared to standard cellulose.

Figure 5 presents a set of FT-IR spectra collected from the different samples compared with standard cellulose. Various absorption bands can be empirically assigned to structural groups of cellulose based on the results obtained from standard cellulose. All samples present these characteristic bands, so one can confirm that the solid obtained from palm oil EFBF after the treatment with pressurized water/ethanol mixture is composed mainly of cellulose.

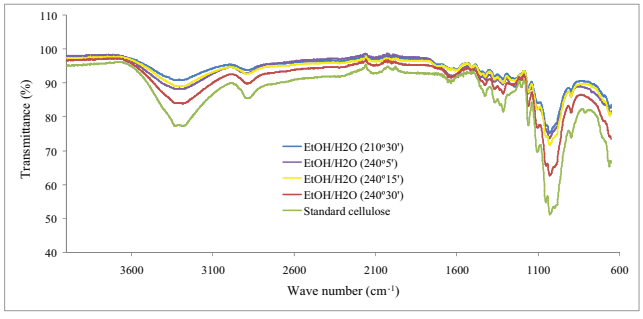

Figure 5: FT-IR spectra from solid wastes of the palm oil EFBF obtained after the treatment with water/ethanol mixture (1:1 vol.) at different experimental conditions and standard cellulose.

The sample with highest similarity with standard cellulose was obtained at 240 ºC for 30 min of reaction. Considering that all remaining solid in the reactor is composed of cellulose, the yield obtained for this experimental condition, as a function of the initial biomass and the mass consumed in the fragmentation process, was approximately 38.2% of cellulose. The result is slightly larger than that reported in the lignocellulosic characterization in Table 3 (33.9%). It should be emphasized that the cellulose obtained in this work was not submitted to any purification process after the fragmentation step. Thus, some fragments of other compounds that were not isolated from the reactor can be present at the cellulose sample. These fragments can also lead to a displacement of the spectral baseline due to the rise of the transmittance value.

Analyzing the X-RD diffractograms presented in Figure 6, it is possible to see the characteristic peaks of cellulose at 15°, 22° and 35° 2θ in all the samples obtained under different experimental conditions. These peaks correspond to crystallographic planes (101), (002) and (040), respectively, and are intrinsic of lignocellulosic fibers (Guimarães *et al*., 2010). The most pronounced peak (close to 26° 2θ) for the cellulose samples obtained in this work correspond to silicon dioxide, found typically in wood surfaces (Yoon and Kin, 2008).

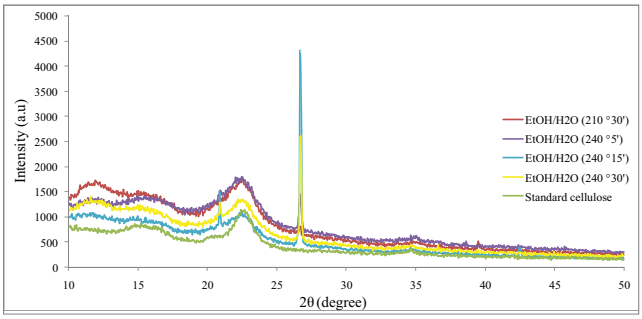

Figure 6: Palm oil EFBF X-RD diffratograms after fragmentation with water/ethanol mixture (1:1 vol.) at different experimental conditions and standard cellulose.

One can note that the intensity of the cellulose samples obtained were above that of the standard cellulose, indicating a higher crystallization index. However, the cellulose obtained at 240 ºC and 30 min of reaction, has a crystallinity lower than the others obtained at temperatures of 210 ºC and 240 ºC with 5 min of reaction time, which has intensities above 1500 (a.u), still, this cellulose has an intensity higher than the standard one.

According to Ass *et al*. (2006), the cellulose obtained from palm oil EFBF is type I, displaying a peak at $22° \leq 2\theta \leq 23°$, referring to the crystalline fraction and at $18° \leq 2\theta \leq 19°$, regarding the amorphous fraction, whereas type II cellulose presents a peak at $18° \leq 2\theta \leq 22°$ for the crystalline region and $13° \leq 2\theta \leq 15°$ for the amorphous region.

CONCLUSIONS

The fragmentation of palm oil EFBF with pressurized water is shown to be an efficient method to obtain xylose. The addition of CO_2 to this process did not represent gains to the fragmentation or sugars yield under the conditions studied here. The cellulose obtained after EFBF fragmentation with a water/ethanol mixture (1:1 vol.) was similar to the standard cellulose in terms of purity and crystallinity.

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