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Agricultural palm oil tree residues as raw material for cellulose, lignin and hemicelluloses production by ethylene glycol pulping process

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ABSTRACT

Agricultural crop residues (palm oil empty fruit bunches—EFB) were used as raw material for cellulose, lignin and hemicelluloses obtaining following sustainable criteria. An organosolv pulping process based on ethylene glycol–water mixtures, which allowed an easy recycling of solvents as well as the recovery of generated by-products, was used to induce delignification. Computer simulations using commercial software (Aspen Plus) were made on the whole process in order to design the solvents recovery stages and optimise the operation conditions. Laboratory experiments were carried out with the aim of characterizing raw material, black liquors and released by-products. Considerable high proportion of recycled solvents (91 wt% ethylene glycol and 88 wt% water) was reached with the proposed scheme. This resulted in 70 and 80 wt% reduction of fresh solvent input for ethylene glycol and water respectively, thus reducing the environmental impact of the process. EFB organosolv pulp could be considered an acceptable alternative for producing certain paper qualities with moderate strength requirements while allowing an agricultural residue from a major economic activity (viz. oil palm production) to be exploited.

1. Introduction

The early years of the 21st century are experiencing a considerable increase in public and government concern about the environmental impact of industrial activities. Policies for the conservation of natural resources are becoming more and more restrictive as also environmental legislation is hardening the control of emissions and effluents from the mills [1].

Pulp/paper industry traditional processes may no longer fulfil current environmental demands and competitiveness. Implied energy intense and high water demanding operations have a deep impact on environmental concerns and also represent a considerable operational cost [2]. Effective management of wastewaters is imperative as well [3,4] in order to remove the great quantity of pollutants released during the process (suspended solids, heavy metals, alkali and alkaline earth metals, phenols, cyanide, sulfides, etc.).

The development of organosolv pulping processes allowed overcoming some of the aforementioned drawbacks by using mixtures of water and organic solvents as delignifying agents, which could be recovered by distillation after the pulping process. Moreover, as the whole process was sulfur-free, it was possible to recover by-products from the black liquors easily in a biorefinery sense. Several authors have reported in their studies the pulping effectiveness of different organic solvents such as alcohols, glycols, acids, esters and others, in terms of process yield, pulp quality and optimum operating conditions [5–8]. The great majority of these works sustained the possibility of using these environmentally friendly pulping processes for papermaking.

Furthermore, forest preservation is becoming compulsory for developed countries all around the world and new solutions for reducing CO_2 emissions and deforestation rate are needed. At this point, renewable lignocellulosic feedstock, such as agricultural crop residues, constitutes a suitable option as raw material for pulp and cellulose–fiber based products [9–11]. Apart from alleviating the shortage of natural resources, they already represent the only alternative in deficient forest resources areas and contribute to diminish agriculture residues accumulation [12].

Palm oil (*Elaeis guineensis*) empty fruit bunches (EFB), a lignocellulosic residue generated during oil extraction process, was used as raw material for cellulose, lignin and hemicelluloses production. Huge quantities of these residues are generated and largely unutilized [13]. Only in Malaysia about 15 million tons per year of EFB are obtained and subsequently burned, creating considerable pollution and economical problems [14]. Several studies support the possibility of using EFB as raw material in variety of applications, including power generation [15,16], composites formulation [17,18] and papermaking [13,19–25]. In the latter case, EFB kraft [13,19],

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soda [20,21], potassium hydroxide [22] and organosolv pulping processes have been successfully applied providing good quality pulps. Among organosolv studies, different organic solvents have been used; Sun and Tomkinson [23] cited an ethanol–water process with HCl as catalyst [24], and glycols–water and amines–water mixtures were reported as well [25].

The complex structure of lignin, with a great variety of functional groups and over 10 different types of linkages, depends strongly on the original source and extraction method used [26].

As previously reported elsewhere [27], lignins obtained from sulphite, kraft or organosolv processes present different physico-chemical characteristics. Organosolv methods give rise to low molecular weight (LMW) lignins that are soluble in most common solvents [28]. Their structure presents relatively high amount of phenolic hydroxyl groups and oxidized groups (e.g. Hibbert ketones) that favour their incorporation into polymer formulations and their chemical modification [29]. Hardwood Alcell lignins, extracted through acidic ethanolysis, have been successfully transformed into filament form suitable for carbon fibres without any chemical modification [30] and Alcell lignin/poly(vinyl chloride) composites have been reported to present higher mechanical properties than kraft or sodium lignosulfonate-based materials [31].

Within their ability to undergo chemical modification, organosolv lignins have been found to be an appropriate raw material for producing LMW compounds [32] like vanillin, widely used in cosmetics, simple and hydroxylated aromatics, quinones, aldehydes, aliphatic acids and many others, for which the economic feasibility is being studied [33].

Furthermore, oligomers and monomers hydrolysed from the hemicelluloses as well as the degraded hemicellulosic polymers could be used as a variety of chemicals for industry [34].

In this work, a complete approach for pulp and paper sustainable production based on EFB and ethylene glycol–water organosolv process was developed, in which special focus was put on by-products recovery (lignin and hemicelluloses) and solvents recycling (ethylene glycol and water). Computer simulation with Aspen Plus 12.1 [35] was used to define optimal conditions for valuable chemicals (lignin, hemicelluloses, acetic acid and furfural) obtaining and solvents recovery from spent liquors. Finally, the characterization of isolated by-products, obtained pulp and paper was carried out.

2. Experimental

2.1. EFB characterization

Characterization of original EFB fibres was done according to standard methods. Moisture content (6.6 wt%) was determined after drying the samples at 105 ± 3 °C for 24 h (TAPPI T264 cm-97). Chemical composition, given on an oven dry weight basis, was the following: 2.3 ± 0.7% ash (TAPPI T211 om-93), 15 ± 0.8% aqueous NaOH soluble matter (TAPPI T212 om-98), 3.8 ± 0.6% hot water soluble matter (TAPPI 207 om-93), 2.1 ± 0.4% ethanol–benzene extractives (TAPPI T204 cm-97), 24 ± 0.6% lignin (TAPPI T222 om-98), 60 ± 1.7% holocellulose [36] and 37 ± 1.2% α-cellulose [37].

2.2. Pulping equipment

Organosolv pulping process was carried out at Córdoba University (UCO), Spain, in a 15 L batch cylindrical reactor with temperature and pressure control. Contents were stirred by rotating the reaction vessel via a motor connected through a rotary axle to the control unit. Experimental conditions used were defined as follows: ethylene glycol–water (80/20 w/w) mixture was used as delignifying medium; the experiment was carried out at 180 °C for 150 min, and the liquid/solid ratio was set at 7:1. After cooking, the pulp was washed, separated from uncooked material by screening through a sieve of 1 mm mesh and defibred in a Sprout–Waldron refiner. Black liquors were also collected for subsequent analyses.

Obtained results of pulp and hand sheets were compared with those resulting from traditional soda pulping process (NaOH 15 wt%, 180 °C, 90 min and liquid/solid ratio of 6:1).

2.3. Black liquors characterization

The composition of obtained black liquors was determined using several laboratory techniques. In order to determine lignin content, a precipitation process in which black liquors were diluted in 1.5 volumes of water and later acidified to pH 2 with 1 M HCl [38] was carried out. Precipitated lignin was allowed to settle over a 24-h period, centrifuged at 3500 rpm for 12 min, washed with water twice to remove sugar and other impurities and finally dried in a vacuum oven at 65 °C and −60 cm Hg. Lignin concentration was then calculated gravimetrically, and the isolated lignin sample was stored for subsequent analysis.

After lignin separation, elemental sugars composition of hemicelluloses was quantitatively determined from the supernatant solutions using a Transgenomic CARBOSep CHO682 HPLC column. Before sampling the filtrates were centrifuged once more, in order to avoid interferences of lignin in the chromatograms, and taken to pH 9 with aqueous NaOH to meet column specifications. Experimental conditions included HPLC grade water as the mobile phase, 0.4 mL/min flow, oven temperature 60 °C and injection volume 20 μL.

In another set of experiments, acetic acid and furfural content were obtained from the lignin-free black liquors samples. The former was determined by titration with 0.1N NaOH until the titration end point [39] while the latter was examined by UV spectroscopy by measuring the absorbance at 510 nm [39].

2.4. By-products characterization

Hemicelluloses were extracted from a lignin-free black liquor sample by precipitation in 3 volumes of 95% ethanol at pH 6 [40], with the objective of completing their chemical characterization by Fourier transform infrared spectroscopy (FTIR). Lignin, obtained in previous experiments, was also subjected to FTIR analysis. Measurements were performed in a PerkinElmer 16PC instrument by direct transmittance using KBr pellet technique. Each spectrum was recorded over 20 scans, in the range from 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1}. KBr was previously oven-dried to avoid interferences due to the presence of water, and background spectra were collected before every sampling.

Gel permeation chromatography (GPC) was used to determine lignin molecular weight (MW) and molecular weight distribution (MWD). Lignin samples were subjected to acetylation in order to enhance their solubility in THF, used in this technique as mobile phase. This reaction, which causes the substitution of hydroxyl functions by acetyl groups, was carried out by placing lignin in an acetyl anhydride/acetyl acid mixture (1:1 w/w) containing sodium acetate as a catalyst (0.5 equivalents per mole of acetyl anhydride). The final lignin concentration in the reactive mixture was 20 wt% [41], and the components were allowed to react for 48 h at room temperature and then 1 h under reflux. Resulting product, obtained by precipitation in 1 wt% HCl ice-cold water, was filtered, washed with distilled water and dried. Acetylated lignin sample was examined through THF-eluted GPC technique, using a PerkinElmer instrument equipped with an interface (PE Series 900). Three Waters Styragel columns (HR 1, HR 2 and HR 3) ranging from 100 to 5×10^5 and a refractive index detector (Series 200) were employed, with a flow rate of 1 mL/min. Calibration was made using polystyrene standards.

Glass transition temperature (T_g) of lignin was determined using a Mettler DSC20 differential scanning calorimeter linked to a TC 15 TA processor and medium pressure pans. The scan was run at 10 °C/min under a nitrogen flow rate of 10 mL/min. Before being tested, the sample was extensively dried at 60 °C under vacuum for 24 h in order to eliminate the presence of water. T_g was defined as the mid point of the temperature range at which the change in heat capacity occurs. Finally, the thermal stability of lignin was studied in terms of thermogravimetric analysis (TGA). A dynamic scan from 30 to 800 °C at 10 °C/min was done under helium atmosphere employing a TGA-92 thermobalance from Setaram.

2.5. *Pulp and paper characterization*

Chemical composition of the pulp obtained after organosolv treatment was determined following the same standards used before for original EFB fibres. Furthermore, the following pulp analyses were carried out at Córdoba University (UCO), Spain: pulp yield (gravimetrically), kappa number, viscosity and drainage index (in a Shopper-Riegler apparatus) in accordance with the respective UNE standards (57-034, 57-039 and 57-025). Hand sheets were obtained by using an Enjo-F39.71 sheet former and characterized in terms of breaking length, stretch, burst index and tear index in accordance with the respective UNE standards (57-054, 57-028, 57-058 and 57-033).

3. Results

3.1. *Black liquor characterization*

Black liquors chemical composition is summarized in Table 1.

Black liquor at digester exit presented pH and density values of 5.8 and 0.945 g/cm^3 respectively. Neutral pH liquors opposite to the alkaline ones obtained by traditional soda process favour the subsequent treatment of black liquors in order to recover process by-products. Ash content (11.5 g/L of black liquor, 1.2%) was considerable lower than reported concentrations found in EFB soda black liquors (2.3–8.2%) [42]. This characteristic allows a better use of black liquors either for by-products separation or for energy recovery by burning process.

Table 1
Black liquor composition (g/L of black liquor)

Component	g/L
Ethylene glycol	717
Water	180
Furfural	1.07
Acetic acid	2.20
Ash	11.5
Lignin	25.1
Sugars	
Xylose	3.20
Glucose	2.72
Galactose	1.89
Arabinose	0.083
Mannose	0.40
Total	8.29

3.2. *By-products characterization*

3.2.1. *Chemical structure*

3.2.1.1. Lignin. FTIR absorption spectra of lignin isolated from the black liquor were recorded in the 400–4000 cm^{-1} region (Fig. 1a). A magnification of 500–2000 cm^{-1} region is presented in Fig. 1b. In lignin spectrum the following structures were identified: aromatic phenylpropane skeleton vibrations (1600, 1515 and 1425 cm^{-1}), aromatic and aliphatic hydroxyl groups (3400, 1030 cm^{-1}), C–H aliphatic bonds (2925, 2850 and 1460 cm^{-1}), aromatic methyl group vibrations (1450 cm^{-1}) and ether bridges (1220 and 1080 cm^{-1}). Phenolic hydroxyl groups (1365 cm^{-1}) and non-conjugated carbonyl groups (1715 cm^{-1}) are consequence of the acid hydrolysis of lignin provoked by the acetic acid released from the hemicelluloses of the raw material. In addition to these general bands, the spectrum also showed other signals that may be attributed to syringyl (S) and guaiacyl (G) groups: syringyl ring breathing with C–O stretching (1330 cm^{-1}), syringyl-type aromatic C–H in plane deformations (1118 cm^{-1}), syringyl and guaiacyl ring breathing with C–O stretching (1218 cm^{-1}) and guaiacyl (1265, 1125, 855 and 810 cm^{-1}) units, both characteristic components of lignin. Results were in good agreement with reported data in previous studies [27] where different guaiacyl/syringyl proportions were assigned to non-wood lignins. Some authors [27,43,44] have reported that a high intensity of 1220 cm^{-1} band is related to the presence of C=O groups that are formed after lignin oxidation. The presence in lignin spectrum of a sharp signal at 1650 cm^{-1}, which can be attributed to the oxidation of aromatic rings into quinonic structures, would support the idea that organosolv treatment causes a certain oxidative degradation of lignin.

3.2.1.2. Hemicelluloses. FTIR spectra of hemicelluloses was recorded in the 400–4000 cm^{-1} region (Fig. 2a), showing general bands: 3400 cm^{-1} (characteristic of OH group), 2920 and 1470 cm^{-1} (C–H stretching of methyl or methylene groups). Absorption at 1740 cm^{-1} was attributed to the acetyl and uronic ester groups of the hemicellulosic residue as was previously reported during the fractionation of polysaccharides extracted from EFB fibres [40]. Absorption at 1640 cm^{-1} was associated with the carboxylic C=O stretching of glucuronic acids [45]. A specific band maximum in 1200–1000 cm^{-1} region was related with ring vibrations overlapped with stretching vibrations of (C–OH) side groups and the (C–O–C) glycosidic bond vibration, typical of xylans [40]. A magnification of 900–1500 cm^{-1} region of the spectra is presented in Fig. 2b. This region, which is not perturbed by water, is one of the richest in structural information as it arises from the symmetrical deformations of CH$_2$ groups as well as from C–O stretching bands [45]. Bands at 1470, 1420, 1380, 1255, 1160, 1080 and 1046 cm^{-1} are indicative of hemicelluloses [40,46]. The sharp band at 897 cm^{-1} is characteristic of β-glycosidic linkages between the monosaccharide units, indicating β-linked hemicelluloses [47].

3.2.2. *Lignin molecular weight*

MWD of acetylated lignin sample was analysed through THF-eluted GPC. Fig. 3 shows the GPC chromatogram of EFB lignin. Weight-average MW (M_w) was found to be 3.2×10^3 g/mol, number-average MW (M_n) 1.7×10^3 g/mol and polydispersity (M_w/M_n) presented a value of 1.80.

Lignin chromatogram presented a bimodal curve, showing that two main lignin fractions present in different amounts and with different MW were coexisting. This shape has been previously reported for other organosolv lignin samples, differing from kraft and soda-anthraquinone lignin chromatograms which usually presented normal curves with only a small fraction of LMW oligomers [48,49].

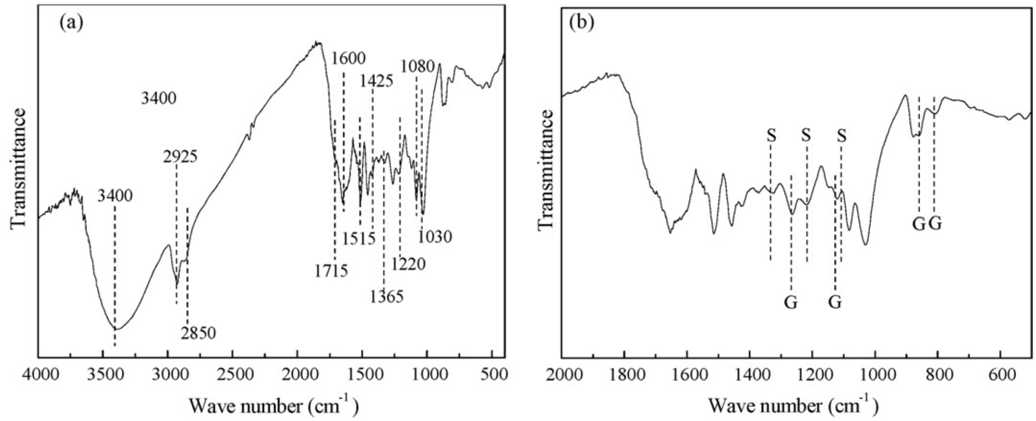

Fig. 1. FT-IR spectra of EFB lignin (a: wave number: 400–4000 cm^{-1} and b: magnification of 500–2000 cm^{-1} region).

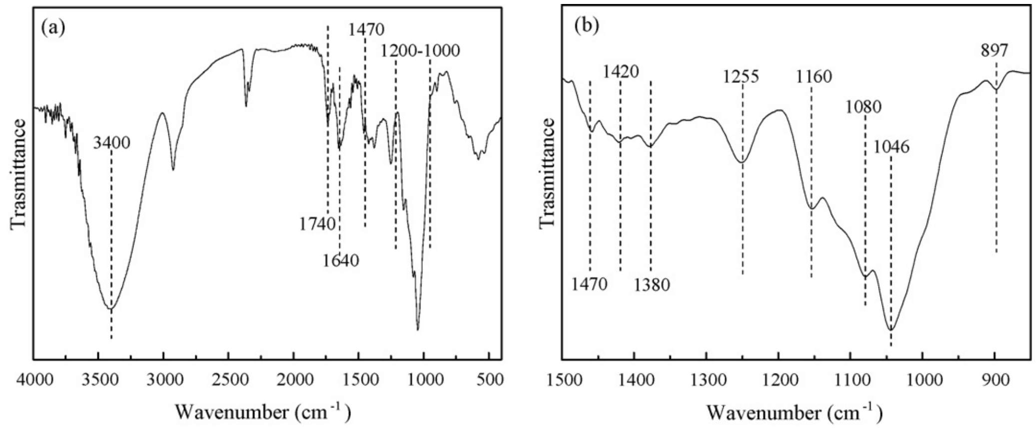

Fig. 2. FT-IR spectra of EFB hemicelluloses (a: wave number: 400–4000 cm^{-1} and b: magnification of 900–1500 cm^{-1} region).

EFB lignin M_w value (3.2×10^3) was relatively low compared to those reported for kraft and soda lignins [27]. It was also in good concordance with other M_w, M_n and M_n/M_w values reported for organosolv lignins [27,28,30,49,50], particularly with those characterizing agricultural residues, such as wheat straw, were M_w values ranging from 3960 to 4340 g/mol were found [51].

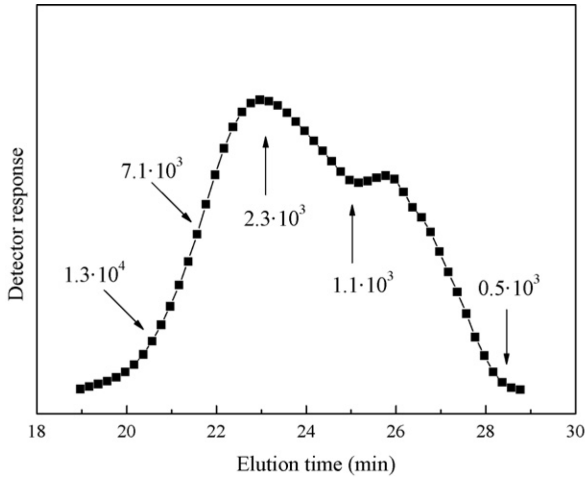

Fig. 3. GPC chromatogram of EFB acetylated lignin sample, showing the M_n of the different fractions.

Lignin MW is closely related to the number of C–C bonds, especially those involving C5 of the aromatic ring, that are linking phenylpropanic units in its structure [52]. Guaiacyl-type units are capable of forming this kind of bonds, but this is not possible in syringyl-type units as they have both C3 and C5 positions substituted by methoxy groups. As these C–C bonds are not cleaved during the pulping of wood due to their higher stability, lignins mostly composed by guaiacyl units are expected to show higher MW than those presenting high contents of syringyl units [27,41]. As it was previously shown by FTIR, both groups are present in the composition of the studied lignin but a low MW suggests higher proportion of syringyl units.

The relatively low polydispersity found indicated the high fraction of LMW present in lignin samples. Lignins with high fractions of LMW molecules have been reported to be adequate as an extender or as a component of phenol–formaldehyde resins because of their high reactivity, in comparison with lignins with high percentages of high molecular weight (HMW) molecules [48,49,53,54].

Organosolv lignins could also be used for improving the properties of the viscous media used for offset inks and paints, in terms of tack and misting reduction [28], as well as for favouring blend capability in polymer formulations [30].

3.2.3. *Thermal behaviour*

3.2.3.1. Differential scanning calorimetry. Glass transition temperature (T_g) was determined by DSC scans after extensively drying the sample (60 °C, 24 h, vacuum-oven dried) in order to release all the moisture content.

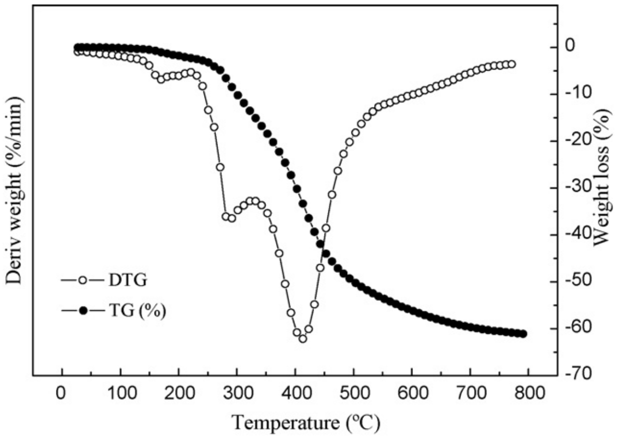

Fig. 4. DTG and TG curves of EFB lignin sample obtained from TGA analysis.

Studied lignin presented good thermal processability, as expected of organosolv lignins, which usually have low inorganic matter contents <0.1%, allowing thermal mobility of lignin molecules. On the contrary, in kraft lignins the presence of ash is significant and inorganic portions must be removed to enable satisfactory thermal processing [29,30].

Lignin T_g was 135 °C, which was slightly higher than those reported of organosolv underivatized lignin preparations: ethanol–water wild tamarind: 100 °C [27]; Alcell: mixed hardwoods: 97 °C, wheat straw: 106–122 °C, reed: 97 °C, kenaf: 66–70 °C [26], hardwood: 97 °C [31]. Higher T_g values were found for kraft and soda lignins: kraft-pine: 144 °C [27], kraft-softwood: 141 °C [31]; soda wheat straw: 160–185 °C [26].

3.2.3.2. Thermogravimetric analysis. Thermal decomposition of EFB organosolv lignin was determined by thermogravimetric analysis (TGA) under helium atmosphere. DTG (rate of weight loss) and TG (weight loss of substances in relation to the temperature of thermal degradation) curves are presented in Fig. 4.

The losses of weight are firstly originated by water, carbon monoxide, carbon dioxide and other pyrolysis products evaporation [55]. The thermogravimetric curve exhibited that weigh loss begins at 135 °C, occurring the most extensive mass loss (30–40% of the original sample) in the temperature range 275–450 °C. $\mathrm{DTG_{max}}$ appeared at 408 °C. Degradation of the complex structure of lignin in this temperature region involved fragmentation of inter-unit linkages between phenolic hydroxyl, carbonyl groups and benzylic hydroxyl, releasing monomeric phenols into the vapour phase [50,55].

Above 450 °C the sample exhibited a gradual mass loss up to 800 °C, related with the decomposition or condensation reactions of aromatic rings [55] resulting in an overall loss of 45–60%. Remaining unvolatilized fraction (56%) was associated with the formation of highly condensed aromatic structures.

Lignin thermogram was in accordance with other works in the literature [27,41,50,51,55].

3.3. Pulp and paper characterization

Table 2 shows the mean value and the standard deviation obtained from three replicate analyses of each parameter for both ethylene glycol and soda pulping processes.

Ethylene glycol pulp chemical characterization showed medium-high percentages of holocellulose, α-cellulose and lignin, high ethanol–benzene extractives and low ash content, which converted it, a priori, in a suitable pulp for paper making. Values were in the range of organosolv non-woody pulps [56–59] as can be seen in Table 3, where chemical composition of different non-woody pulps was included with the aim of comparison. Results obtained for soda pulping process revealed the stronger effect of the traditional pulping process on the fibres, as can be inferred from the higher holocellulose and α-cellulose percentages and lower lignin content. Higher ash content was found as well in soda pulps, which is not desirable.

Pulp and hand sheets characteristics included in Table 2 revealed the following.

Yield: EFB ethylene glycol pulping process presented medium yield value (52%) similar to other results previously reported for ethylene glycol pulping of agricultural residues (cotton stalks and vine shoots [25,57] and alternative raw materials (leucaena [60] and tagasaste: *C. proliferus* [25,59,60]). These references were included in Table 4 with the aim of comparison. Traditional soda process (Table 2) provided lower yield (39%) typical of stronger pulping conditions.

Drainage index for ethylene glycol EFB pulp (10 °SR) was lower than those for ethylene glycol pulp from leucaena [60], tagasaste [25,60], vine shoots [25,57] and cotton stalks [25] but similar to EFB ethanolamine pulps (14–17 °SR) [25], EFB diethylene glycol pulps (9–10 °SR) [25], EFB diethanolamine pulps (12 °SR) [25] and EFB soda pulp (13 °SR) (Table 2). Similar values were reported as well for wheat straw ethanol-acetone pulp [61]. It can be concluded, thus, that this parameter do not depend on the pulping type and it is much more related with the raw material, EFB in this case, which does not provide high swelling capacity and water absorption.

Kappa number (77.9) obtained for EFB ethyleneglycol pulp was lower than leucaena [60], vine shoots and cotton stalks [25], ethylene glycol pulps (120, 149, 148 respectively) and slightly higher than tagasaste ethylene glycol pulp (68.1) [25]. The obtained value is typical of organosolv processes which usually provide pulps with higher kappa number than soda or kraft processes, as corroborates the kappa number of EFB soda pulp (21.8) (Table 2). Nevertheless, high kappa numbers in organosolv pulps do not necessarily mean poor bleaching capability as several studies corroborates where organosolv pulps with higher kappa numbers were easier to bleach than kraft or soda pulps, leading to higher brightness in pulps [62,63]. The high Kappa number of organosolv pulps has been related with the precipitation of the dissolved lignin onto the fibres in the pulping and washing processes and, since organosolv lignin presents lower molecular weight and less cross-linked structures than kraft and soda pulps lignin, it is easier to bleach [63].

Viscosity of analysed pulp (533 mL/g) might be considered a typical medium-high value for an agricultural waste organosolv pulp, as other studies corroborates [25] and slightly lower than obtained result for soda process (610 mL/g), as expected.

Breaking length (1172 m) and stretch (1.18) of ethylene glycol pulp were low, in the range of unrefined pulp from non-wood materials [25,57,60]. These parameters were slightly better for the soda process (Table 2). Nevertheless, both breaking length and stretch have been reported to improve with the degree of refining [22,64]. The strength of paper sheets is higher if the pulp has been well-beaten previously as it provokes the straightening-out of both the long-and-short range crimps and curls that are created in fibres during pulping, pressing, and drying of the pulp [22,64]. Removal of these crimps and kinks in the fibres greatly improves the stress distribution in the sheet.

Finally, the strength-related properties (burst and tear indexes) of ethylene glycol pulp (0.48 kN/g and 0.17 mN m^2/g respectively) were typical of non-wood materials organosolv pulps, slightly lower than soda process pulp properties (0.84 kN/g and 0.21 mN m^2/g respectively) and considerably lower than conventional wooden pulps, as expected. Tearing resistance is a function

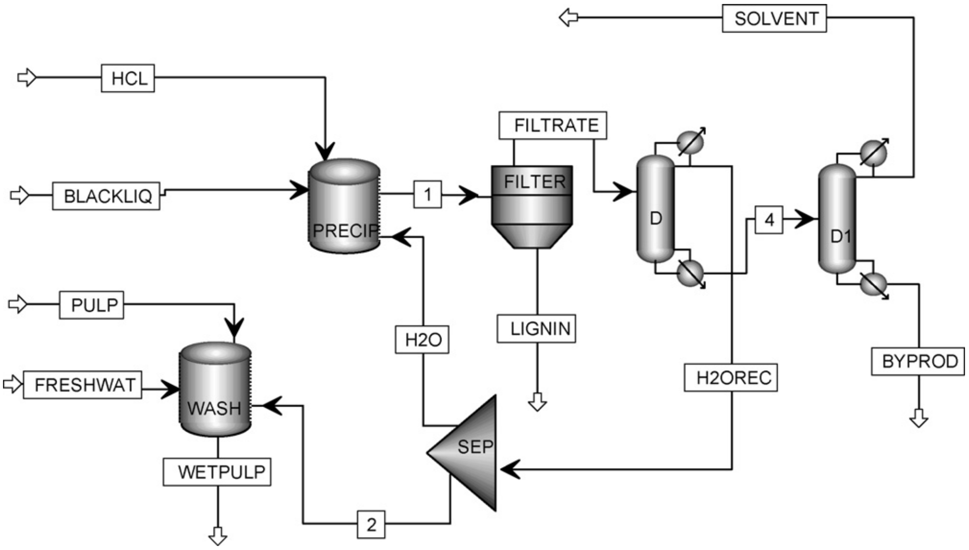

Fig. 5. Flow sheet of solvents and by-products recovery stage of ethylene–water pulping process.

Table 2
Characterization of unbleached pulp samples and hand sheets made from them for EFB ethylene glycol and soda processes

Pulp chemical composition (wt%)			Pulp and hand sheet characterization		
	Ethylene glycol	Soda		Ethylene glycol	Soda
Moisture	7.1 ± 0.5	6.9 (0.2)	Yield (%)	52	39
Ash	1.8 ± 0.03	3.8 (0.06)	Drainage index (°SR)	10	13
Hot water solubility	2.5 ± 0.08	3.8 (0.07)	Kappa number	77.9 ± 0.87	21.8 ± 1.08
1% NaOH solubility	26 ± 1.51	32 (1.00)	Viscosity (mL/g)	533 ± 10	610 ± 13
Ethanol–benzene extractives	7.1 ± 0.09	4.3 (0.04)	Breaking length (m)	1172 ± 52	1675 ± 23
Holocellulose	66 ± 0.15	82 (0.25)	Stretch (%)	1.18 ± 0.11	1.90 ± 0.21
α-Cellulose	62 ± 0.05	67 (0.03)	Burst index (kN/g)	0.48 ± 0.07	0.84 ± 0.06
Lignin	25 ± 0.75	18 (0.30)	Tear index (mN m^2/g)	0.17 ± 0.09	0.21 ± 0.08

Table 3
Chemical characterization of pulp from various agricultural residues

	EFB ethylene glycol, this study	EFB soda, this study	Sunflower stalks–ethanol [56]	Vine shoots–ethylene glycol [57]	Vine shoots–ethanol [57]	Wheat straw–formaldehide [58]	Bagasse–dimethyl formamide [59]
Moisture	7.1	6.9	–	–	–	–	–
Ash	1.8	3.8	–	2.0	2.54	–	1.4
Hot water solubility	2.5	3.8	–	2.76	4.26	–	–
1% NaOH solubility	26	32	–	–	–	–	–
Ethanol–benzene extractives	7.1	4.3	–	4.95	4.35	1.81	–
Holocellulose	66	82	69.2	70	67.1	82	95.8
α-Cellulose	62	67	56	37	53.7	40	83.5
Lignin	25	18	19.5	35	31.9	9	–

of both fibre strength and fibre bonding [64]. Fibre length has been widely considered important in contributing to the tearing strength of paper. In a weakly bonded sheet, since more fibres pull out than break in the tear zone, the tearing resistance is controlled more by the number of bonds that break along the length of the fibres. On the other hand, in a well-bonded sheet, more fibres break than pull out in the tear zone. Consequently, the tearing resistance is controlled more by fibre breaking than by bond breakage [22]. The low

Table 4
Properties of the pulp and paper sheets obtained by ethylene glycol pulping of different non-wood raw materials and agricultural residues

	Yield (%)	Drainage index (°SR)	Kappa number	Viscosity (mL/g)	Breaking length (m)	Stretch (%)	Burst index (kN/g)	Tear index (mN m^2/g)
EFB, this study	52	10	77.9	533	1172	1.18	0.48	0.17
Leucaena [60]	57	41	120.6	383	3481	1.90	1.62	0.26
Tagasaste [60]	57	–	–	–	4794	3.11	2.76	0.35
Vine shoots [25]	78	74.9	149.6	582	2846	1.64	–	–
Cotton stalks [25]	78	68.6	148.8	589	4970	2.58	–	–
Tagasaste [25]	91	50.8	68.1	922	–	3.09	–	–
Cotton stalks [58]	57	–	–	–	4401	2.34	2.13	0.26
Vine shoots [57]	39	16	–	–	267	1.65	0.73	1.47
Tagasaste [58]	63	–	–	–	4644	2.87	2.46	0.33

Table 5
Mass balance (kg/h) for ethylene glycol–water process

Component	Black liquor	1	Filtrate	Lignin	H_2Orec	Fresh wat	H_2O	2	4	Solvent	Byprod
Ethylene glycol	4,792	4,792	4,792	0	0	0	0	0	4,792	4,392	400
Water	1,112	11,034	11,034	0	10,484	1,034	9,922	1,596	550	550	0
Lignin	167	167	50.1	116	0	0	0	0	50.1	0	50
Furfural	25.5	25.5	25.5	0	0	0	0	0	25.5	25.4	0.2
Acetic acid	65.6	65.6	65.6	0	0.6	0	0.5	0.1	65.0	65.0	0
Sugars	81.2	81.2	81.2	0	0	0	0	0	81.2	0	81.2
Others	27.1	27.1	27.1	0	0	0	0	0	27.1	0	27.1
HCl	0	131	131	0	131	0	111	20	0	0	0
Total	6,271	16,325	16,208	116	10,616	1,034	10,034	1,616	5,592	5,033	559

tearing strengths of studies EFB pulp were probably related to the relatively short-fibre material of EFB fibrous strands. However, an appropriate beaten of the pulp, was reported to cause an enormous increase in tearing strength over the unbeaten pulp [22,64]. This tendency may be explained by the shortening effect on fibres in a refining process compensating for increasing resistance promoted by fibrillation and hydration [64].

In conclusion, EFB organosolv pulp could be considered an acceptable alternative for producing certain paper qualities with moderate strength requirements while allowing an agricultural residue from a major economic activity (viz. oil palm production) to be exploited [25,57,58,60]. In any case, refining the pulp can help improve the final properties of the resulting paper sheets [25]. Furthermore, using mixtures of pulp from wood and non-wood materials in different ratios to strengthen the pulp could provide paper sheets with improved physical properties and reduced refining energy costs relative to pure wood pulp [64]. Mixtures of recycled paper with oil palm fibre soda pulp were also studied resulting in an enhancement of strength of recycled fibres due to increase of inter-fibre bonding as a result of adding active virgin fibres [65].

3.4. *Simulation process of solvent recovery and by-products isolation step*

In this work Aspen Plus 12.1 was used for designing and optimising solvent and by-products recovery processes. On the basis of experimental results of black liquors composition, solvent and by-products recovery from these pulping liquors were simulated. Lignin and cellulose were defined by their chemical structures and molecular weights whereas the rest of conventional components were selected from ASPEN PLUS data bank. ELECTNRTL model, based on NRTL electrolyte model and Redlich–Kwong state equation, was used to simulate the thermodynamic properties of solutions. Distillation columns were designed using the rigorous RadFrac column module; the inputs for this model were estimated previously by shortcut model (DSTWU).

Simulation base was 1000 kg/h of dry raw material and solvent input flow rate was 7000 kg/h which correspond to a liquid/solid ratio of 7:1. The scheme proposed (Fig. 5) consisted on one lignin precipitation step and two distillation steps where both ethylene glycol and water were going to be recovered. Black liquors exiting the reactor were diluted with acidified water until pH 2 in order to precipitate and filter a high MW lignin fraction. The ratio between acidified water and black liquor mass flows was set to 1.5/1 in order to precipitate the lignin. After lignin separation, supernatant solutions were subjected to a distillation process in order to recycle solvents and isolate the rest of by-products. Two columns were used in the distillation step. Filtrate stream was fed into the first distillation column (D) from which two different flows exit: a distillate stream (H_2Orec), mostly composed by water, and residue stream (stream 4), which was fed into the second distillation column (D1). Recovered water (H_2Orec) was sent to both precipitating unit (H_2O stream) and pulp washing stage (stream 2).

In the second distillation unit, a solvent fraction rich in ethylene glycol was obtained as distillate (solvent stream); this fraction constituted the solvent recovery stream and was sent back to the reaction step. Solvent stream ethylene glycol and water concentrations were adjusted by mixing them with a fresh stream before feeding them into the reactor again. Aspen Plus design specification tool was used to fix the concentrations. Finally, a stream constituted by the rest of by-products (mainly low MW lignin and sugars) was obtained as a residue (Byprod stream).

This simulation permitted to establish the most convenient conditions for the recovery process. The optimized design of the ethylene glycol–water distillation process included 15 stages for each distillation column, with the feeding in stage 13 for both columns, a reflux ratio of 7.3 for the first column and 7.2 for the second one and a distillate to feed ratio of 0.6 and 0.9 respectively.

Mass balances and compositions of the recovery step streams are summarised in Tables 5 and 6. From these data it is inferred that 91 wt% of the ethylene glycol exiting the digester was recovered (4792 kg/h) and recycled into the pulping reactor. Furthermore, 88 wt% water was obtained and recycled in both lignin precipitation and pulp washing stages. It was reached a reduction of fresh solvents input of 70 wt% for ethylene glycol and 80 wt% for water.

These results were compared with those obtained from other experiments carried out in the lab, in which black liquors filtrates

Table 6
Mass fractions for ethylene glycol–water process

Component	Black liquor	1	Filtrate	Lignin	H_2Orec	Fresh wat	H_2O	2	4	Solvent	Byprod
Ethylene glycol	0.760	0.292	0.296	0	0	0	0	0	0.857	0.872	0.717
Water	0.171	0.674	0.680	0	0.988	1	0.988	0.988	0.098	0.109	0
Lignin	0.017	0.010	0.003	1	0	0	0	0	0.009	0	0.089
Furfural	0.003	0.002	0.002	0	0	0	0	0	0.004	0.005	0
Acetic acid	0.010	0.004	0.004	0	0	0	0	0	0.013	0.013	0
Sugars	0.010	0.005	0.005	0	0	0	0	0	0.014	0	0.146
Others	0.029	0.002	0.002	0	0	0	0	0	0.005	0	0.048
HCl	0	0.011	0.008	0	0.012	0	0.012	0.012	0	0	0
Total	1	1	1	1	1	1	1	1	1	1	1

were subjected to batch distillation processes for determining the effective solvents recovery degree. In such cases, a first distillation step carried out at 100 °C allowed the separation of 86 wt% water from the ethylene glycol–water filtrate. In the second distillation process, designed to separate ethylene glycol and by-products, a stream containing 82 wt% ethylene glycol, furfural, acetic acid and 14 wt% water was isolated. A residual stream, composed by lignin, sugars and remaining ethylene glycol (18 wt%), was also obtained.

In the proposed recovering Scheme 6271 kg/h of black liquors were treated in order to precipitate lignin. By means of this scheme, 116 kg/h of lignin, which accounted 48 wt% of total raw material content and 69 wt% of black liquors content, were obtained. Low MW lignin was also obtained at the end of the recovering process within the by-products stream, resulting in 22 wt% the total lignin content originally present in raw material and 31 wt% in black liquors. Also 81 kg/h of sugars were isolated within by-products stream, accounting 35 wt% that contained in the original EFB fibres.

4. Conclusions

The scheme proposed, based on the organosolv pulping of an agricultural residue provided cellulose, hemicelluloses and lignin, all of them valuable products, while improving ecological drawbacks related to traditional pulping processes. Water consumption was considerably diminished, as 88 wt% of water recycling allowed the reduction of 80 wt% on fresh water input, avoiding the post-treatment of huge quantities of wastewater. Solvent recovery, 91 wt% of ethylene glycol exiting the reactor, involved an input reduction of 70 wt%. Moreover, the subsequent applications of obtained products from renewable resources could contribute to make organosolv processes economically feasible increasing the efficiency of the process.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2008.08.008.

References

[1] J.H.J. Clark, Green chemistry for the second generation, biorefinery—sustainable chemical manufacturing based on biomass, Chem. Technol. Biotechnol. 82 (2007) 603–609.

[2] D. Koufos, T. Retsina, Practical energy and water management through pinch analysis for the pulp and paper industry, Water Sci. Technol. 43 (2) (2001) 327–332.

[3] A.L. Ahmad, S.S. Wong, T.T. Teng, A. Zuhairi, Optimization of coagulation–flocculation process for pulp and paper mill effluent by response surface methodological analysis, J. Hazard. Mater. 145 (2007) 162–168.

[4] D. Berryman, F. Houde, C. DeBlois, M. O'Shea, Nonylphenolic compounds in drinking and surface waters downstream of treated textile and pulp and paper effluents: a survey and preliminary assessment of their potential effects on public health and aquatic life, Chemosphere 56 (2004) 247–255.

[5] S. Asiz, K. Sarkanen, Organosolv pulping: a review, Tappi J. 72 (3) (1989) 169–175.

[6] H.L. Hergert, Developments in organosolv pulping. An overview, in: R.A. Young, M. Akhtar (Eds.), Environmental Friendly Technologies for the Pulp and Paper Industry, John Wiley and Sons Inc., New York, 1998, p. 551.

[7] E. Muurinen, Doctoral thesis, University of Oulu, Finland (2000).

[8] L. Paszner, Catalysed alcohol organosolv pulping, in: R.A. Young, M. Akhtar (Eds.), Environmental Friendly Technologies for the Pulp and Paper Industry, John Wiley and Sons Inc., New York, 1998, p. 69.

[9] L. Jiménez, E. Navarro, I. Pérez, F. Maestre, Availability, storage, and characterization of agricultural wastes for the manufacture of paper pulps, Investigación y Técnica del Papel 34 (131) (1997) 130–152.

[10] J.E. Atchison, World wide capacities for non-wood plant fiber pulping—increasing faster than wood pulping capacities, in: Proceedings of the TAPPI Pulping Conference, New Orleans, LA, USA, 1988, pp. 25–45 (Book 1).

[11] A.M. Hurter, Utilization of annual plants and agricultural residues for the production of pulp and paper, in: Proceedings of the TAPPI Pulping Conference, New Orleans, LA, USA, 1988, pp. 139–160 (Book 1).

[12] M. Thykesson, L.-A. Sjöberg, P. Ahlgren, Pulping of grass and straw, Nordic Pulp Paper Res. J. 12 (2) (1997) 128.

[13] I. Akamatsu, M.B. Husin, H. Kamishima, A.H. Hassan, Industrial utilization of oil palm (*Elaeis guneensis*) by-products. 1. Kraft-anthraquinone pulping of oil palm empty fruit bunches, Cell. Chem. Technol. 21 (1) (1987) 67–75.

[14] S.H.A. Rahman, J.P. Choudhury, A.L. Ahmad, A.H. Kamaruddin, Optimization studies on acid hydrolysis of oil palm empty fruit bunch fiber for production of xylose, Biores. Technol. 98 (2007) 554–559.

[15] Z. Husain, Z.A. Zainal, M.Z. Abdulla, Analysis of biomass-residue-based cogeneration system in palm oil mills, Biomass Bioenergy 24 (2003) 117–124.

[16] S. Yusoff, Renewable energy from palm oil e innovation on effective utilization of waste, J. Cleaner Prod. 14 (2006) 87–93.

[17] H.P.S.A. Khalil, H. Ismail, M.N. Ahmad, A. Ariffrin, K. Hassan, The effect of various anhydride modifications on mechanical properties and water absorption of oil palm empty fruit bunches reinforced polyester composites, Polym. Int. 50 (2001) 396.

[18] H.D. Rozman, K.R. Ahmadhilmi, A. Abubakar, Polyurethane, (PU)-oil palm empty fruit bunch (EFB) composites: the effect of EFBG reinforcement in mat form and isocyanate treatment on the mechanical properties, Polymer Testing 23 (2004) 559–565.

[19] R. Tanaka, W.D. Wan Rosli, K. Magara, T. Ikeda, S. Hosoya, Chlorine-free bleaching of kraft pulp from oil palm empty fruit bunches, JARQ 38 (4) (2004) 275–279.

[20] W.D. Wan Rosli, K.N. Law, J.L. Valade, Chemical pulping of oil palm fruit bunches, Cell. Chem. Technol. 32 (1998) 133–143.

[21] K.N. Law, X. Jiang, Comparative papermaking properties of oil-palm empty fruit bunch, Tappi J. 84 (1) (2001) 95.

[22] P. H'ng, Potassium based pulping of oil palm empty fruit bunches, in: M.P. Koh, et al. (Eds.), Proceedings of the 4th National Seminar on Utilisation of Oil Palm Tree Residues-Progress towards Commercialisation, Oil Palm Fibre Utilisation Committee, Kuala Lumpur, Malaysia, 1997, p. 211.

[23] R.C. Sun, J. Tomkinson, Fractional separation and phsyco-chemical analysis of lignins from the black liquor of oil palm trunk fibre pulping, Sep. Purif. Technol. 24 (2001) 529–539.

[24] Y. Suleman, M.N.M. Yusoff, in: M.P. Koh, et al. (Eds.), Proceedings of the 4th National Seminar on Utilisation of Oil Palm Tree Residues-Progress towards Commercialisation, Oil Palm Fibre Utilisation Committee, Kuala Lumpur, Malaysia, 1997, p. 13.

[25] A. Rodríguez, L. Serrano, A. Moral, A. Pérez, L. Jiménez, Use of high-boiling point organic solvents for pulping oil palm empty fruit bunches, Biores. Technol. 99 (2008) 1743–1749.

[26] J.H. Lora, W.G.J. Glasser, Recent industrial applications of lignin—a sustainable alternative to nonrenewable materials, Polym. Environ. 10 (2002) 39–48.

[27] A. Tejado, C. Peña, J. Labidi, J.M. Echeverria, I. I. Mondragon, Physico-chemical characterization of lignins from different sources for use in phenol–formaldehyde resin synthesis, Biores. Technol. 98 (2007) 1655–1663.

[28] M.N. Belgacem, A. Blayo, A. Gandini, Organosolv lignin as a filler in inks, varnishes and paints, Ind. Crops Prod. 18 (2003) 145–153.

[29] S. Kubo, J.F. Kadla, Poly(ethylene oxide)/organosolv lignin blends: relationship between thermal properties, chemical structure, and blend behavior, Macromolecules 37 (2004) 6904–6911.

[30] J.F. Kadla, S. Kubo, R.A. Venditti, R.D. Gilbert, A.L. Compere, W. Griffith, Lignin-based carbon fibers for composite fiber applications, Carbon 40 (15) (2002) 2913–2920.

[31] D. Feldman, D. Banu, Contribution to the study of rigid PVC polyblends with different lignins, J. Appl. Polymer Sci. 66 (9) (1997) 1731–1744.

[32] R.A. Northey, Low-cost uses of lignin, in: Proceedings of the Materials and Chemicals from Biomass. Symposium Series, vol. 476, American Chemical Society, 1992, pp. 146–175.

[33] D.K. Johnson, J. Bozell, J.E. Holladay, J.F. White, Use of lignin in the biorefinery, in: Proceedings of the International Lignin Institute 7th Forum, Barcelona, 2005, pp. 31–34.

[34] X.F. Sun, F. Xu, R.C. Sun, Z.C. Geng, P. Fowler, M.S. Baird, Characteristics of degraded hemicellulosic polymers obtained from steam exploded wheat straw, Carbohyd. Polymer 60 (2005) 15–26.

[35] ASPEN PLUS. <http://www.aspentech.com>.

[36] L.E. Wise, M. Murphy, A.A. D'Adieco, Chlorite holocellulose, its fractionation and bearing on summative wood analysis and on studies on the hemicelluloses, Paper Trade J. 122 (2) (1946) 35–43.

[37] R. Rowell, The Chemistry of Solid Wood, Based on Short Course and Symposium Sponsored by the Division of Cellulose, Paper, and Textile Chemistry at the 185th

meeting of the American Chemical Society, Seattle, Washington, 20–25 March, 1983, pp. 70–72.

[38] M.N.M. Ibrahim, S.B. Chuah, W.D.W. Roski, Characterization of lignin precipitated from the soda black liquor of oil palm empty fruit bunch fibers by various mineral acids, J. Sci. Technol. Dev. 21 (1) (2004) 57–67.

[39] J.I. Botello, M.A. Gilarranz, F. Rodríguez, M. Oliet, Recovery of solvent and by-products from organosolv black liquor, Sep. Sci. Technol. 34 (12) (1999) 2431–2445.

[40] R.C. Sun, J.M. Fang, L. Mott, J. Bolton, Fractional Isolation and characterization of polysaccharides from oil palm trunk and empty fruit bunch fibres, Holzforschung 53 (1999) 253–260.

[41] W.G. Glasser, V. Dave, C.E. Frazier, Molecular weight distribution of (semi-) commercial lignin derivatives, J. Wood Chem. Technol. 13 (4) (1993) 545–559.

[42] M. González, L. Cantón, A. Rodríguez, J. Labidi, Effect of organosolv and soda pulping processes on the metals content of non-woody pulps, Biores. Technol. 99 (2008) 6621–6625.

[43] R.C. Sun, J. Tomkinson, J. Bolsteton, Effects of precipitation pH on the physico-chemical properties of the lignins isolated from the black liquor of oil palm empty fruit bunch fibre pulping, Polym. Degrad. Stab. 63 (1999) 195–200.

[44] R.C. Sun, J. Tomkinson, B. James, Fractional characterization of ash-AQ lignin by successive extraction with organic solvents from oil palm EFB fibre, Polym. Degrad. Stab. 68 (2000) 111–119.

[45] M. Kacurakova, M. Mathlouthi, FTIR and laser-Raman spectra of oligosaccharides in water: characterization of the glycosidic bond, Carbohydr. Res. 284 (1996) 145–157.

[46] D. Stewart, G.J. McDogall, A. Baty, Fourier-transform infrared microspectroscopy of anatomically different cells of flax (*Linum usitatissimum*) stems during development, J. Agric. Food Chem. 43 (1995) 1853–1858.

[47] S. Gupta, R.N. Madan, M.C. Bansal, Chemical composition of *Pnus caribaea* hemicellulose, Tappi J. 70 (1987) 113–114.

[48] N.E. El Mansouri, J. Salvadó, Structural characterization of technical lignins for the production of adhesives: application to lignosulfonate, kraft, soda-anthraquinone, organosolv and ethanol process lignins, Ind. Crops Prod. 24 (2006) 8–16.

[49] A.R. Gonqalves, P. Benar, Hidroxymethylation and oxidation of organosolv lignins and utilisation of the products, Biores. Technol. 79 (2001) 103–111.

[50] J.C. Domínguez, M. Oliet, M.V. Alonso, M.A. Gilarranz, F. Rodríguez, Thermal stability and pyrolysis kinetics of organosolv lignins obtained from *Eucalyptus globulus*, Ind. Crops Prod. 2 (7) (2008) 150–156.

[51] F. Xu, J.-X. Sun, R.C. Sun, P. Fowler, M.S. Baird, Comparative study of organosolv lignins from wheat straw, Ind. Crops Prod. 23 (2006) 180–193.

[52] E. Sjöström, Wood polysaccharides, in: Wood Chemistry, Fundamentals and Applications, Academic Press, New York, 1981, pp. 51–67.

[53] A. Pizzi, Advanced Wood Adhesives Technology, Marcel Dekker, New York, 1994, pp. 219–241.

[54] P. Benar, A.R. Gonqalves, D. Mandelli, U. Schuchardt, Eucalyptus organosolv lignins: study of the hydroxymethylation and use in resols, Biores. Technol. 68 (1999) 11–16.

[55] R.C. Sun, Q. Lu, X.F. Sun, Psycho-chemical and thermal characterization of lignins from *Caligonum monogoliacum* and *Tamarix* spp., Polym. Degrad. Stab. 72 (2001) 229–238.

[56] S. Caparrós, J. Ariza, F. López, J.A. Nacimiento, G. Garrote, L. Jiménez, Hydrothermal treatment and ethanol pulping of sunflower stalks, Biores. Technol. 99 (2008) 1368–1372.

[57] L. Jiménez, V. Angulo, E. Ramos, M.J. De la Torre, J.L. Ferrer, Comparison of various pulping processes for producing pulp from vine shoots, Ind. Crops Prod. 23 (2006) 122–130.

[58] L. Jiménez, I. Pérez, M.J. De la Torre, F. López, J. Ariza, Use of formaldehyde for making wheat straw cellulose pulp, Biores. Technol. 72 (2000) 283–288.

[59] P. Rezayati-Charani, J. Mohammadi-Rovshande, S.J. Hashemi, S. Kazemi-Najafi, Influence of dimethyl formamide pulping of bagasse on pulp properties, Biores. Technol. 97 (2006) 2435–2442.

[60] A. Rodríguez, A. Pérez, M. De la Torre, E. Ramos, L. Jiménez, Neural fuzzy model applied to ethylene-glycol pulping of non-wood raw materials, Biores. Technol. 99 (2008) 965–974.

[61] L. Jiménez, I. Pérez, F. López, J. Ariza, A. Rodríguez, Ethanol–acetone pulping of wheat straw. Influence of the cooking and the beating of the pulps on the properties of the resulting paper sheets, Biores. Technol. 83 (2002) 139–143.

[62] J.H. Lora, E.K. Pye, Solvent pulping opens door to viable chlorine-free, effluent-free options, Pulp Paper 69 (1995) 109–110.

[63] X. Yongjian, L. Kecheng, Z. Meiyun, Lignin precipitation on the pulp fibers in the ethanol-based organosolv pulping, Colloids Surf. A: Physicochem. Eng. Asp. 301 (2007) 255–263.

[64] P. Mutjé, M.A. Pélach, F. Vilaseca, J.C. García, L. Jiménez, A comparative study of the effect of refining on organosolv pulp from olive trimmings and kraft pulp from eucalyptus wood, Biores. Technol. 96 (2005) 1125–1129.

[65] W.D. Wanrosli, Z. Zainuddin, S. Roslan, Upgrading of recycled paper with oil palm fiber soda pulp, Ind. Crops Prod. 21 (2005) 325–329.