PULPING OF EMPTY FRUIT BUNCHES (EFB) FROM THE PALM OIL INDUSTRY BY FORMIC ACID

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Empty fruit bunches (EFB) from palm oil were characterized. The holocellulose (66.97%), α-cellulose (47.91%), and lignin (24.45%) are similar to wood materials, and various non-wood materials, but the fiber length is shorter (0.53 mm). The influence of operational variables in the EFB pulping [formic acid (75-95%), hydrochloric acid (0.05-0.15%), and time (30-150 min)], on the yield, kappa number, viscosity, and brightness of the pulps was studied. By using a factorial design, equations that reproduced the experimental results for the dependent variables, errors less than 10% were obtained. These equations could be used to find suitable conditions, so that operating with not too high values of operating variables (with minor costs of capital and of operation), pulps could be obtained with acceptable properties. In this way, a cellulosic pulp with a 42.3% yield, 22.7% brightness, and a 512 mL/g viscosity was obtained under the following conditions: 92.5% of formic acid, 0.075% of hydrochloric acid, and a time of 60 min. A pulp (31.1 kappa number and 606 mL/g viscosity) was bleached by EPabOPoP sequence, achieving a brightness of 69.4%, a loss of viscosity and yield of 34.8% and 13.1%, respectively. The residual liquor from the pulping with formic acid 95%, 0.05% hydrochloric acid and 30 min, provides a liquor with 18.2% residual lignin, 4.1% glucose, 9.8% xylose, and 1.2% arabinose, all on dry weight of original material.

Keywords: Empty fruit bunches; Biorefinery; Formic acid; Pulp; Lignin; Sugars

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INTRODUCTION

Bio-renewable resources have been important in all cultures as a source of products and energy during the evolution of humanity. Subsequently, the discovery of huge deposits of petroleum and the development of engineering and industry led the petrochemical industry to become dominant in the production of energy and chemicals. After the first oil crisis the risk of dependence on fossil fuels, the need for revision of these energy models and the interest in the search for traditional sources based on renewable resources were revealed.

This, coupled with increasingly important social and legal pressures to implement transformation processes more environmentally acceptable, has made the vision of plant biomass as a raw material become more interesting. Among the many forms of plant biomass available, lignocellulosic wastes from certain processing industries can play an important role in combustion and the subsequent production of energy or in chemical

processing for the isolation of its fibers, which can be used for making paper, cellulose derivatives, and other chemicals; this fractionation of the raw materials contributes to the development of a industrial concept known as the biorefinery (Rodríguez *et al.*, 2010).

An interesting biomass is Empty Fruit Bunches (EFB), which consists of certain lignocellulosic material residue from the palm oil industry (Wan Rosli and Law, 2011). The first published work concerning applications of EFB was that of Muthurajah and Peh (1977), who used the kraft process with a concentration of active alkali 16%, for 3 hours at 160°C, obtaining a pulp with a yield of 56% and a kappa number of 16.9. The chemical properties of EFB fibers are similar to those of hardwood, except for the pentosan content, which is higher. Subsequently, the kraft process has also been studied by other authors (Akamatsu et al. 1987a; Khoo and Lee 1991; Ibrahim 2002).

Ibrahim (2002) compared the composition of EFB pulp obtained by the kraft, kraft-anthraquinone, soda, and soda-anthraquinone processes; the pulp obtained with the soda process had the highest content of lignin, holocellulose and α-cellulose and a higher viscosity. The soda process has also been studied by Law and Jiang (2001), producing fibers with more wall thickness, greater rigidity, higher solubilities in hot water and 1%-soda, as well as a higher ash content. These pulps were bleached with hydrogen peroxide more easily than those of aspen; their paper sheets had a lower tensile index, but a greater stretch and tear index than those of aspen. Moreover, Daud *et al*. (1998) pulped the EFB with soda, sodium carbonate, and sodium sulfite processes; it was found that the soda process provided the best pulp.

Wanrosli et al. (2004) studied, using a central composite experimental design, the influence of operating conditions (temperature, time, and alkali concentration) on the properties of EFB pulps (yield, kappa number, tensile and tear index). They obtained pulp yields in the range 30 to 45%. It was considered that the values of 160°C, 60 to 120 minutes, and 20 to 30% of alkali are sufficient for the proper pulping.

The semi-chemical pulp for board by soda-anthraquinone process (Roliadi and Pasaribu 2004) has also been studied. The study of thermomechanical pulp has also been made by several researchers (Akamatsu et al. 1987b; Kamishima et al. 1988; Khoo and Lee 1991; Daud et al. 2005; Ghazali et al. 2006).

Organosolv processes have also been studied. Pulping was done with ethanol (Suleman and Yusoff 1997; Aziz et al. 2002) and with a modified IDE process (ethanol containing soda) (Quader and Lonnberg 2005).

Finally, biopulping has been investigated using a white fungus K14 (Goenadi et al. 1998).

The kraft process for obtaining cellulose pulp remains, due to its favourable characteristics, predominant in the global paper industry. It is well known that this method has certain implicit environmental problems arising from the use of inorganic sulphur agents in cooking and chlorinated derivatives in bleaching. Although there have been significant improvements in the overall process (extended delignification, use of oxygen bleaching agents, etc.) researching alternative methods of delignification has continued intensively. Among these alternatives, the organosolv processes, where delignification is carried out with the aid of an organic solvent, are among the most investigated. Organosolv processes can be understood from a conceptual point of view as being different from sulphate or sulphite cooking. Thus, they can be designed as

fractionation treatments rather than simple delignification (Dapia et al. 2002), so it is possible to try to extract the main polymeric components of plant tissues in the least degraded form. The possibility to work under milder conditions, in some cases, is a factor that facilitates the fractionation. Low investment costs for a new plant, less pollution problems, easy solvent recovery, low prices of some organic agents used, and the possibility of cooking at atmospheric pressure and low temperatures, among others, are often cited as additional advantages (Rodríguez et al. 2010). All this has produced the investigation of these process in recent years, both with traditional substrates and new plant vegetables

The use of short-chain organic acids (mainly formic and acetic) has emerged as an attractive and feasible alternative for the delignification of lignocellulosic materials (Shahriarinour et al. 2011). After the pioneering work of Pauly in 1917 and the studies of Freudenberg et al. and Wright and Hibbert in the decade of the 1930s (Ligero et al. 2008, 2010), formic acid has attracted the attention of researchers. Formic acid has been proved to be a good delignification agent with a wide variety of starting materials. Thus, it has been used for pulping different woody species such as eucalyptus (Baeza et al. 1991a; Erismann et al. 1994, Ligero et al. 2008), pine (Baeza et al. 1991b), and beech (Dapía et al. 2002). It has also shown its effectiveness in treating a wide variety of non-woody materials such as wheat straw (Jiménez et al. 1998), rice straw (Lam et al. 2001), *Miscanthus* (Caridad et al. 2004, Ligero et al. 2010), and corn cobs (Zhan et al. 2010), among other new plant vegetables.

Formic acid delignification uses the properties of this compound to act simultaneously as an organic solvent and as an acid. In fact, a significant amount of materials can be dissolved at relatively low processing temperatures (Baeza et al. 1991a; Ligero et al. 2010; Zhan et al. 2010), even working without mineral acid added as catalyst (Jiménez et al. 1998). Formic acid acts through a chemical reaction by partial depolymerisation of lignin and hemicelluloses, producing oligomers that are soluble in the liquid mixture. Cellulose and liquor are separated by filtration, and the dissolved lignin can be recovered easily by the modification of the ionic strength of the liquor (water dilution). Furthermore, the distillation of the liquor enables the recovery of formic acid, leaving a fraction rich in sugars that can be fermented for alcohols.

When the formic acid concentration is high (e.g., > 80% by weight) the organosolv liquors have a great delignification power (Baeza et al. 1991a; Jahan et al. 2007; Jiménez et al. 1998; Ligero et al. 2008; Zhan et al. 2010). But, increasing formic acid proportion above 80% damages the cellulose (especially when hydrochloric acid is used as catalyst), which is reflected in lower viscosity values. Thus, it is necessary to reach a compromise between the values of the formic acid concentration, hydrochloric acid, and treatment time, so controlling these variables is of primary importance.

This paper reports the characterization of EFB (holocellulose, α-cellulose, lignin, hot-water solubles, 1%-NaOH solubles, ethanol-benzene extractives, ash, and fibers length distribution). On the other hand, the influence of operational variables in the formic acid pulping of EFB (*viz.* formic acid concentration, hydrochloric acid concentration, and processing time) on the dependent variables of pulps obtained (yield, kappa number, viscosity, and brightness) was studied, in order to find mathematical models that can simulate the pulping process and find the optimal operating conditions, while achieving

some acceptable values for the properties of the resulting pulp. A pulp was also bleached by the sequence EPabOPoP (alkali Extraction-Peracetic in basic medium-Oxygen-hydrogen Peroxide with oxygen-hydrogen Peroxide). Finally, the residual liquor was characterized by determining the lignin and fermentable sugar contents.

EXPERIMENTAL

Raw Material

In this work, EFB have been obtained from African palm (*Elaeis guineensis*) provided by Straw Pulping Engineering S.L of Zaragoza (Spain) company.

Raw Material Characterization

Following drying at room temperature, the raw material was cold ground in a Retsch SM 2000 mill to avoid alterations in its components. The ground product was sieved, and the 0.25–0.40 mm fraction (sieves No. 60 and 40 in the Tyler series) was saved for analysis

Chemical properties of EFB were determined in accordance with the respective TAPPI standards for the different components, namely: T-9m-54 for holocellulose, T-222 for lignin, T-203 0S-61 for α-cellulose, T-257 for hot-water solubles, T 212 for 1%-NaOH solubles, T-204 for ethanol-benzene extractives, and T-211 for ash.

Fibre length was determined biometrically, under a Visopan projection micro-scope with 10X objective for 100x magnification, after microcooking the raw material with 10% soda at 80ºC for 1 h and subsequent staining the fibers with 1% safranin. 100 fibers were measured.

Pulping

Mixtures of shredded EFB, water, and formic acid (proportions ranging from 75 to 95% by weight of liquor) were heated to the boiling point (approximately 108°C) in glass Pyrex flasks. Hydrochloric acid was added (0.05-0.15% by weight of liquor) when boiling started (zero time), and mixtures were maintained at total reflux with stirring for different times (30-150 min) at atmospheric pressure. After the reaction, the pulps were separated by filtration and the solids washed with concentrated formic acid solutions (80%w) in order to avoid the deposition of the dissolved lignin on the pulp. Four washings were performed using 2.5, 2.5, 5, and 5 volumes of formic solution with respect to the initial dry weight EFB. Finally the pulps were treated with water until neutrality and let to dry at room temperature (Ligero et al. 2010).

Pulps Characterization

For all experiments the main parameters defining delignification and pulping were measured as follows: pulp yield after oven drying of a pulp aliquot to constant weight, kappa number as per TAPPI T236, and intrinsic viscosity as per TAPPI T230. To measure the ISO brightness, paper sheets from pulps were formed according to TAPPI method T272, and diffuse blue reflectance measured as per TAPPI T525 in a Photovolt 577 reflectometer.

Experimental Design

A second order factorial design of experiment was used (Montgomery 1991), which consisted of a central experiment (in the centre of a cube) and several additional points (additional experiments lying at the cube vertices and side centers). Experimental data were fitted to the following second-order polynomial,

$$Y_e = a_0 + a_1X_F + a_2X_H + a_3X_T + a_{11}X_F^2 + a_{12}X_FX_H + a_{13}X_FX_T + a_{22}X_H^2$$

$$+ a_{23}X_HX_T + a_{33}X_T^2 \quad (1)$$

where Y_e denotes the response variables [*viz.*, yield (YI), kappa number (KN), viscosity (VI), or brightness (BR)]; X_F, X_H, and X_T are the normalized values of the operational variables (formic acid concentration –F-, hydrochloric acid concentration –H- and processing time –T-, respectively); and a_0 to a_{33} are constants.

The values of the operational variables were normalized to values from -1 to +1 by using the following expression,

$$X_n = 2\,(X - \bar{X}) / (X_{max} - X_{min}) \quad (2)$$

where X_n is the normalized value of F, H, or T; X is the actual experimental value of the variable concerned; $\bar{X}$ is the mean of X_{max} and X_{min}; and X_{max} and X_{min} are the maximum and minimum value, respectively, of such a variable.

The normalized values for the independent variables in the 15 experiments conducted are given in Table 1.

Table 1. Values of Operational Variables and Experimental Values of the Properties of Pulps Obtained by Formic Acid Pulping of EFB

Experiment	Normalized values of operational variables (X_F, X_H, X_T)	Yield, %	kappa number	Viscosity, mL/g	Brightness, %
1	-1,-1,-1	46.4	45.1	455	17.7
2	+1,-1,-1	43.6	31.1	606	22.3
3	-1,+1,-1	44.6	35.3	458	18.0
4	+1,+1,-1	43.1	33.9	468	22.2
5	-1,-1,+1	39.7	23.6	389	28.8
6	+1,-1,+1	40.5	31.7	479	22.1
7	-1,+1,+1	39.1	23.4	354	26.5
8	+1,+1,+1	38..5	26.3	425	25.6
9	-1,0,0	40.0	30.4	402	23.4
10	+1,0,0	41.5	35.3	462	19.7
11	0,-1,0	41.3	24.2	465	27.1
12	0,+1,0	39.3	18.7	420	29.3
13	0,0,-1	44.1	32.7	498	20.0
14	0,0,+1	37.3	26.2	387	25.2
15	0,0,0	39.9	27.9	431	25.0
16	-0.5,-0.5,-0.5	43.4	29.9	461	21.9
17	+0.5,+0.5,+0.5	36.8	26.0	430	26.4

Characterization of Residual Liquor

After the fractionation/pulping process, the lignin was precipitated by treating one volume of black liquor with seven volumes of water and then stirring (Ligero *et al*. 2010). The precipitated solids were washed repeatedly with water until neutrality in order to remove the maximum amount of carbohydrates possible.

The quantitative determination of monosaccharides was performed using liquid chromatography. The samples were diluted with water to a suitable concentration of sugars, neutralised with barium carbonate, and filtered through a 0.45 mm membranes. A Waters 1500 Series HPLC equipped with a Biorad Aminex HPX-87P column thermo-stated to 85°C enabled the determination of individual monosaccharides (refractive index detector at 30°C) and furfural (UV/VIS wavelength detector at 254 nm). HPLC-grade water was used as mobile phase at a flow of 0.6 mL/min .

RESULTS AND DISCUSSION

Analysis of EFB

Table 2 shows the results of the chemical analysis of EFB, various agricultural residues (olive prunings, wheat straw, sorghum stalks, rice straw, sugarcane bagasse, vine shoots, and cotton stalks, (Jiménez *et al.* 1990, 1993, 2006)), alternative raw materials (Jiménez *et al.* 2005, 2006), and hardwoods and softwoods (Alonso 1976). A comparison of the data for EFB (Table 1) with those for the other raw materials (Table 2) revealed the following:

(*a*) The content in hot water solubles of EFB is similar to that of bagasse and cotton stalks, but lower than those of the other alternative raw materials –except paulownia and *Prosopis julyflora*–, pine, and eucalyptus wood.

(*b*) The content in 1% NaOH solubles of EFB is higher than those of olive prunings, bagasse, cotton stalks, the alternative raw materials, and pine and eucalyptus wood, but similar to those of the other agricultural residues studied.

(*c*) The content in ethanol-benzene extractives of EFB is similar to those of rice straw, bagasse, cotton stalks, and pine and eucalyptus wood, but lower than those of the other agricultural residues and the alternative raw materials.

(*d*) The ash content of EFB is higher than those of olive prunings, bagasse, and cotton stalks, similar to those of the other agricultural residues, and much higher than those of pine and eucalyptus wood.

(*e*) The holocellulose content of EFB is higher than those of olive prunings and sorghum stalks, similar to those of vine shoots, and lower than those of the other agricultural residues (wheat straw, sunflower stalks and cotton stalks). It is also higher than those of *Phragmites* and *Prosopis*, lower than those of the other raw materials, and between those of pine and eucalyptus wood.

(*f*) The lignin content of EFB is higher than those of the agricultural residues, alternative raw materials and eucalyptus wood, but lower than that of pine wood.

Table 2. Chemical Properties of Various Agricultural Residues, Alternative Raw Materials, and Hardwoods and Softwoods

Analysis(%)	Hot water solubles	1% soda solubles	Ethanol Benzene extractives	Ash	Holocellulose	α-cellulose	Hemicellulose	Lignin
EFB	4.03	20.22	1.17	3.2	66.97	47.91		24.45
Leucaena diversifolia (Jiménez et al. 2006)	3.24	17.38	4.44		77.88	40.10		19.09
Leucaena colinsi (Jiménez et al. 2006)	4.30	20.02	4.64		80.79	43.77		17.04
Leucaena leucocephala (Honduras) (Jiménez et al 2006)	5.01	20.26	6.01		74.11	41.21		19.39
Leucaena leucocephala (India) (Jiménez et al. 2006)	3.98	18.44	4.64		75.92	44.43		21.43
Tagasaste(Australia) (Jiménez et al. 2006)	2.96	15.55	2.17		82.16	47.65		15.71
Tagasaste (Nueva Zelanda) (Jiménez et al. 2006)	2.99	16.15	3.43		75.36	43.59		14.84
Tagasaste(La Palma) (Jiménez et al. 2006)	2.41	16.62	3.30		76.47	44.99		14.10
Retama monosperma (Jiménez et al. 2005)	3.84	16.93	5.03		71.76	42.75		21.50
Phragmites (Jiménez et al. 2005)	5.38	34.77	6.36		64.16	39.76		23.66
Arundo donax (Jiménez et al. 2005)	4.73	26.80	7.30		70.20	40.46		22.34
Prosopis julyflora (Jiménez et al. 2005)	6.49	22.56	5.30		62.77	36.55		20.60
Prosopis alba (Jiménez et al. 2005)	4.67	20.86	4.65		63.56	41.55		19.27
Paulownia fortunei (Jiménez et al. 2005)	9.6	31.5	5.50		70.7	37.40		22.4
Olive prunings (Jiménez et al. 1990)	8.16	30.04	10.36	1.36	61.47	35.67	25.8	19.71
Wheat straw (Jiménez et al. 1990)	12.27	43.58	4.01	6.49	76.2	39.72	36.48	17.28
Sunflower stalks (Jiménez et al. 1990)	22.72	47.81	4.07	7.9	71.76	42.1	29.66	13.44
Sorghum stalks (Jiménez et al. 1993)	21.7	45.58	7.99	4.85	65.93	41.5	24.43	15.64
Rice straw (Jiménez et al. 2005b)	16.57	46.94	1.4	15.39	70.6			25.23
Sugarcane bagasse (Jiménez et al. 2005)	4.4	33.92	1.73	2.1	80.2			19.8
Vine shoots (Jiménez et al. 2006)	16.09	39.21	4.87	3.49	67.14	41.14	26	20.27
Cotton stalks (Jiménez et al. 2006)	3.33	20.34	1.42	2.17	72.86	58.48	14.38	21.45
Pinus Pinaster	1.99	7.98	2.57	0.54	69.59	55.92	13.67	26.22
Pine varieties (11 varieties)	2.04	10.33	1.29	0.33	67.60			28.83
Eucalyptus globulus	2.84	12.42	1.15	0.57	80.17	52.79	27.68	19.96
Eucalyptus varieties (20 varieties)	4.19	14.69	2.09	0.57	77.21			25.54

EFB Fibers Length

Figure 1 shows a photograph of the EFB fibers. The maximum, average, and minimum values of fiber lengths were 1.48, 0.53, and 0.27 mm, respectively, and the maximum, medium, and minimum thicknesses or widths were 26, 14, and 8 µm. Figure 2 shows the length distribution curve, showing that more abundant are the fibers having a size of 0.50 to 0.70 mm are more abundant. The average length of the EFB fibers (0.53 mm) is lower than that of other raw materials: wheat straw (1.14 mm), sorghum stalks (1.32 mm), olive pruning (1.03 mm), sunflower stalks (1.30 mm), vine shoots (0.79 mm), cotton stalks (1.03 mm), *Eucalyptus globulus* (1.05 mm), and *Pinus pinaster* (2.50 mm).

Figure 1. Microphotography of EFB fibers

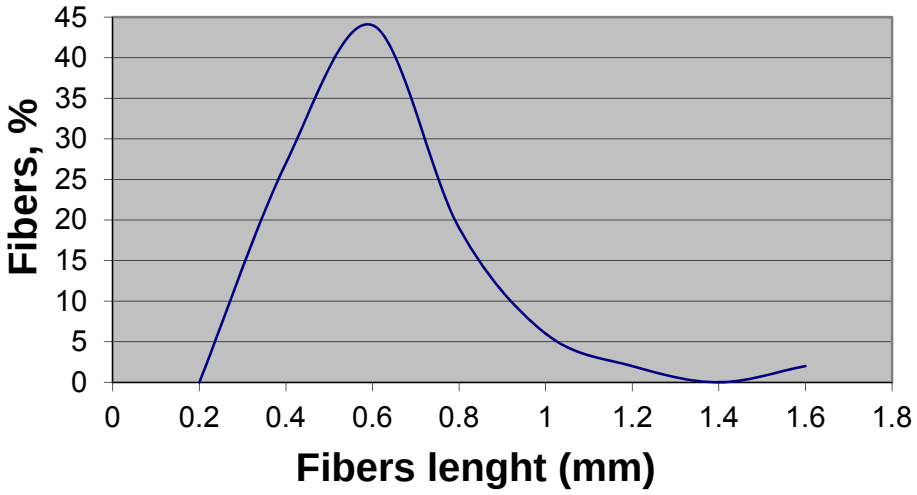

Figure 2. Distribution curve of the length of the fibers of the EFB

Pulping Models

Preliminary experiments of trial and error was carried out, based on the results of other researchers on different raw materials, in order to define the ranges of operating variables. In this way the following ranges were chosen: formic acid concentration from 75 to 95%, hydrochloric acid concentration, which usually acts as a catalyst, from 0.05 to 0.15%, and processing time from 30 to 150 min. Constant conditions were maintained with respect to operating temperature (108 ºC) and the liquid/solid ratio (10:1).

Table 1 shows experimental values of the pulp properties, which differed by less than 5-10% from their means as obtained in triplicate measures. The experimental results were fitted to a polynomial model by multiple regression using the software BMDP.© The terms showing a Snedecor F-value greater than 2.5 and a Student t value greater than 1.5 were deemed statistically significant. Table 3 gives the coefficients of the different terms in the equations, as well as the highest p and lowest Student t values for the terms.

Table 3. Polynomial Models for the Properties of Pulp Obtained by Formic Acid Pulping of EFB. (Values of the constants in the polynomial equations)

Dependent variable	Values of the constants in the polynomial equations									Values of p and t-Student	
	a_0	a_1	a_2	a_3	a_{11}	a_{12}	a_{13}	a_{22}	a_{33}	p<	>t
Yield	40.0	-	-0.7	-2.7	1.0	-	0.6	-	0.9	0.09	1.9
Kappa	26.7	-	-1.8	-4.7	6.4	-	3.3	-5.0	3.0	0.13	1.6
Viscosity	436	38	-27	-45	-	-20	-	16	-	0.14	1.6
Brightness	24.8	-	-	2.8	-3.2	-	-2.1	3.4	-2.2	0.04	2.4

The predictions of the previous equations reproduced the experimental results for the dependent variables with errors less than 3% for yield, 10% for kappa number, 6% for viscosity, and 10% for brightness of pulps (Table 4).

Table 4. Values of the Dependent Variables as Estimated with the Polynomial Models and Deviations from their Experimental Counterparts (in brackets)

Experiment	Yield, %	kappa number	Viscosity, mL/g	Brightness, %
1	45.9 (1.08)	40.9 (9.31)	466 (2.42)	17.9 (1.13)
2	44.7 (2.52)	34.3 (10.29)	582 (3.96)	22.1 (0.90)
3	44.5 (0.22)	37.3 (5.67)	452 (1.31)	17.9 (0.56)
4	43.3 (0.46)	30.7 (9.44)	488 (4.27)	22.1 (0.45)
5	39.3 (1.01)	24.9 (5.51)	376 (3.34)	27.7 (3.82)
6	40.5 (0.00)	31.5 (0.63)	492 (2.71)	23.5 (6.33)
7	37.9 (3.07)	21.3 (8.97)	362 (2.26)	27.7 (4.53)
8	39.1 (1.56)	27.9 (6.08)	398 (6.35)	23.5 (8.20)
9	41.0 (2.50)	33.1 (8.88)	398 (1.00)	21.6 (7.69)
10	41.0 (1.20)	33.1 (6.23)	474 (2.60)	21.6 (9.64)
11	40.7 (1.45)	23.5 (2.89)	479 (3.01)	28.2 (4.06)
12	39.3 (0.00)	19.9 (6.42)	425 (1.19)	28.2 (3.75)
13	43.6 (1.13)	34.4 (5.20)	481 (3.41)	19.8 (1.00)
14	38.2 (2.41)	25.0 (4.58)	391 (1.03)	25.4 (0.79)
15	40.0 (0.25)	26.7 (4.30)	436 (1.16)	24.8 (0.80)
16	42.3 (2.53)	31.9 (6.69)	452 (1.95)	22.4 (2.28)
17	38.9 (5.71)	25.4 (2.31)	418 (2.79)	25.2 (4.55)

The proposed models were validated by conducting two pulping experiments (entries 16 and 17 in Table 1). The errors made in predicting pulp properties by using the polynomial models were quite small (Table 4). This testified to the accuracy of such models.

The values of the operational variables providing the best pulp properties (yield, kappa number, viscosity and brightness) were identified by using multiple non-linear programming as implemented in the method of More and Toraldo (1989). Table 5 shows the optimum values of the dependent variables and those of the operational variables required to obtain them.

Table 5. Optimal Properties in Pulp Obtained by Formic Acid Pulping of EFB

Dependent variable	Optimum (maximum or minimum*) value of the dependent variable	Values of the operational variables required to obtain the optimum values of the dependent variables		
		X_F	X_H	X_T
Yield, %	45.9	-1	-1	-1
kappa number	17.8*	-0.23	+1	+0.90
Viscosity, mL/g	582	+1	-1	-1
Brightness, %	29.3	-0.25	+1	+0.75

The polynomial equations allowed the identification of the more influencing operational variables on the pulp properties. The maximum variations in the dependent variables with changes in the operational variables over the studied range were obtained by altering one independent variable at a time while keeping all others constant. The results are shown in Table 6 together with the maximum percent differences in the dependent variables from their optimum values over the studied variation ranges.

Table 6. Maximum Changes in the Dependent Variables with Changes in One Operational Variable with Others Held Constant (the percent differences from the changes are given in brackets)

Equation	Variation with the operational variable		
	Formic acid	Hydrochloric acid	Processing time
Yield, %	1.6 (3.48%)	1.4 (3.05%)	6.6 (14.37%)
kappa number	9.7 (54.49%)	6.9 (38.76%)	10.9 (61.24%)
Viscosity, mL/g	116 (19.93%)	94 (16.15%)	90 (15.46%)
Brightness, %	5.0 (17.06%)	3.4 (11.60%)	6.8 (23.21%)

Figures 3 to 10 also show the changes of the dependent variables to vary the operating variables. The maximum yield (45.9%) corresponded to low values of operating variables. The processing time influences pulp yield more significantly than the concentration of formic acid (Fig. 3), while the latter variable has a greater effect than the concentration of hydrochloric acid (Fig. 4).

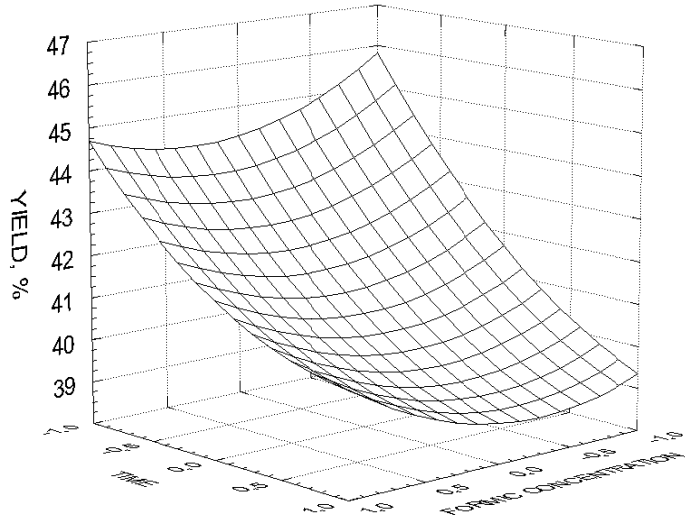

Figure 3. Variation of pulp yield with processing time and formic acid concentration, at low hydrochloric acid concentration (X_C = -1)

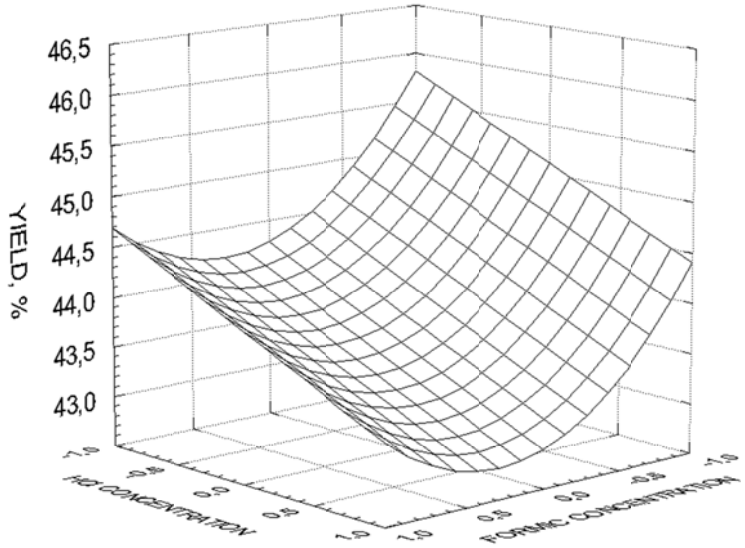

Figure 4. Variation of pulp yield with formic acid concentration and hydrochloric acid concentration, at short processing time (X_T = -1)

The kappa number decreased more sharply with time than with the formic acid concentration (Fig. 5), indicating that the hydrochloric acid concentration was the least influential variable (Fig. 6). The minimum kappa number was obtained when the hydrochloric acid concentration was high, the formic acid concentration near the middle, and close to the maximum time considered.

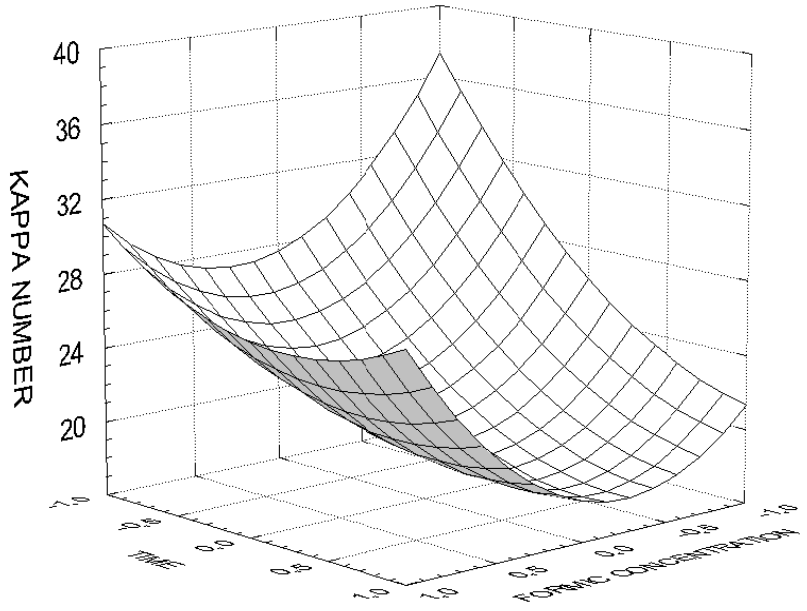

Figure 5. Variation of pulp kappa number with processing time and formic acid concentration, at high hydrochloric acid concentration (X_C = +1)

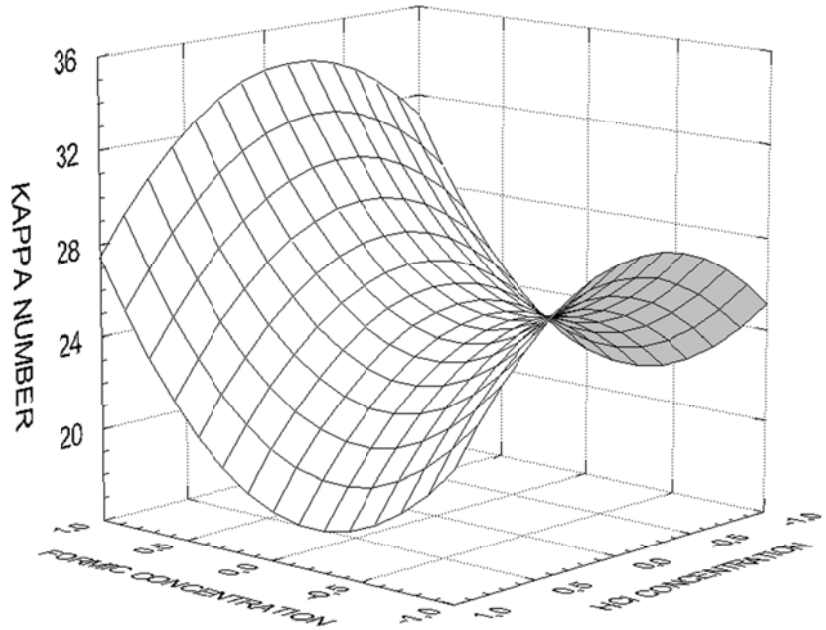

Figure 6. Variation of pulp kappa number with formic acid concentration and hydrochloric acid concentration at long processing time (X_T = 0.90)

The viscosity was maximum (582 mL/g) when operating with low levels of hydrochloric acid concentration and processing time and a high concentration of formic acid. The formic acid concentration had more influence on the viscosity than the hydrochloric acid concentration (Fig. 7), while time influenced the viscosity a little less than the concentration of hydrochloric acid (Fig. 8).

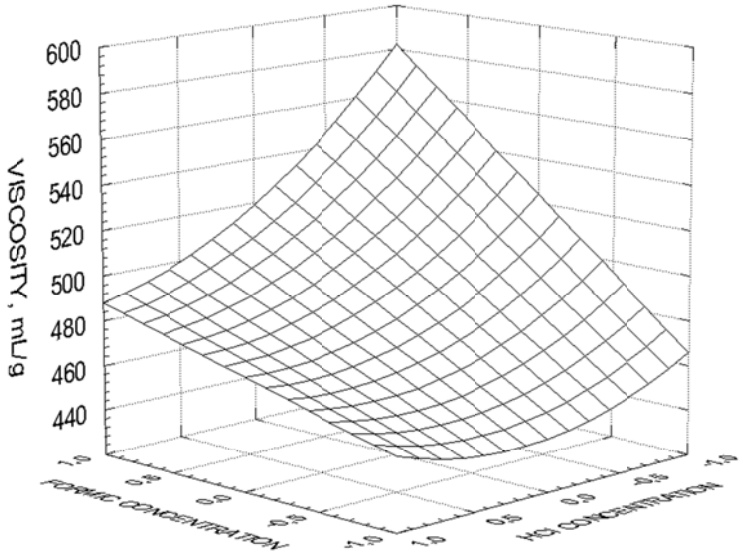

Figure 7. Variation of viscosity with formic acid concentration and hydrochloric acid concentration at short processing time (X_T = -1)

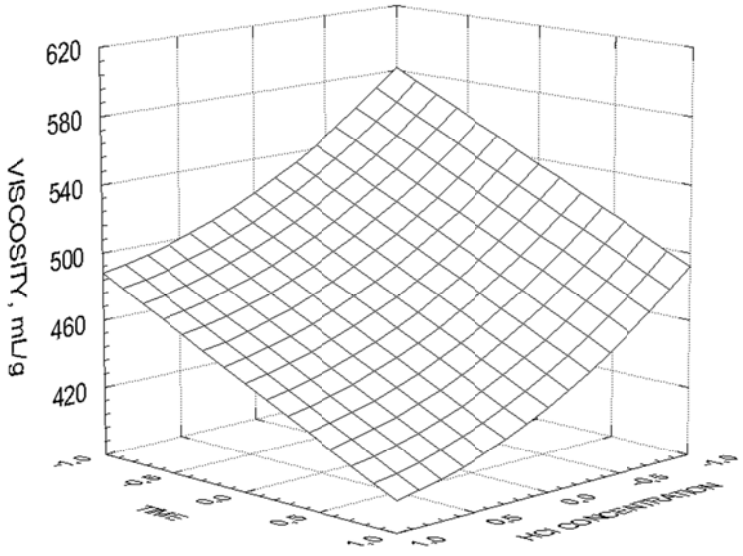

Figure 8. Variation of viscosity with hydrochloric acid concentration and processing time, at high formic acid concentration (X_F = +1)

The processing time had more influence on the brightness than the concentration of formic acid (Fig. 9), and again the concentration of hydrochloric acid was the least influencing variable (Fig. 10). The maximum brightness was achieved for an average-high time, a high concentration of hydrochloric acid and formic acid concentration close to the average used.

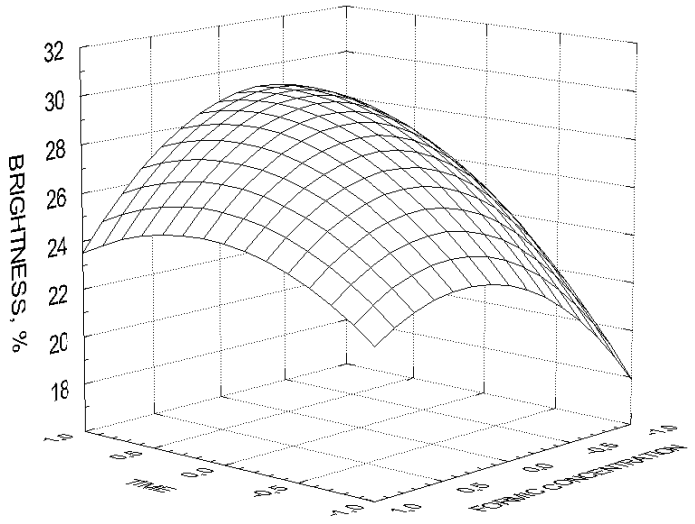

Figure 9. Variation of brightness with processing time and formic acid concentration, at high hydrochloric acid concentration (X_C = +1)

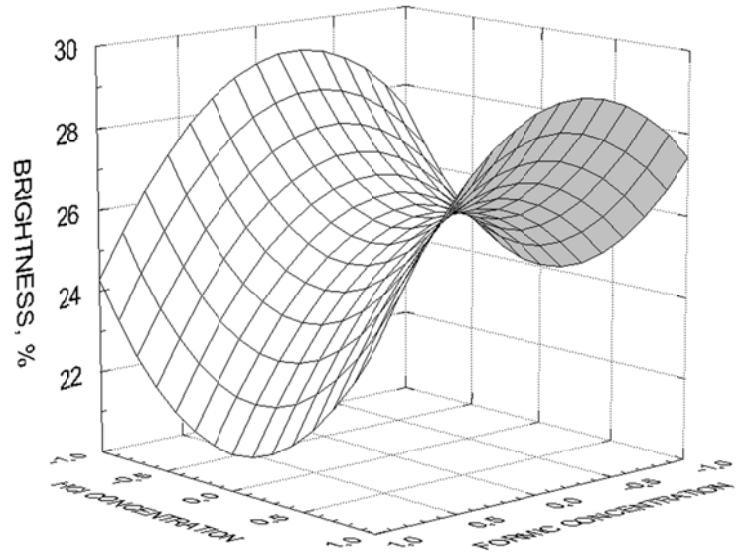

Figure 10. Variation of brightness with formic acid concentration and hydrochloric acid concentration, at medium-long processing time (X_T = +0.75)

Optimum Operating Conditions

Considering the "Yield/kappa" ratio (which is desirable to have at a high value), adjusting the experimental data to a polynomial model gives the equation:

$$\text{“Yield/kkappa”} = 1.53 + 0.07\ X_H + 0.12\ X_T - 0.31\ X_F^2 - 0.12\ X_F\ X_T + 0.34\ X_H^2 - 0.18\ X_T^2 \quad (p < 0.14;\ \text{t-Student} > 1.6) \qquad (3)$$

The values of the operational variables providing the maximum "Yield/kappa" were identified by using multiple non-linear programming as implemented in the method of More and Toraldo (1989). The maximum value of 1.94 is found when the formic acid concentration is medium (85%), hydrochloric acid concentration is high (0.15%), and the processing time is 90 minutes. Figure 11 shows the change of the "Yield/kappa" ratio with formic acid concentration and processing time, for a high concentration of hydrochloric acid.

Considering the "Viscosity/kappa" ratio (which is also desirable to be high), adjusting the experimental data to Eq. [1] gives the equation:

$$\text{“Viscosity/kappa”} = 16.58 + 0.98\ X_F - 3.71\ X_F^2 - 1.32\ X_F\ X_T + 3.97\ X_H^2 - 1.87\ X_T^2 \quad (p < 0.17;\ \text{t-Student} > 1.5) \qquad (4)$$

Operating in a similar way as equation (3), equation (4) gives the maximum value of the "Viscosity/kappa" ratio of 20.62, for operating conditions close to those found in the case of the "Yield/kappa" ratio. Figure 12 shows the changes in the "Viscosity/kappa" ratio by varying the formic acid concentration and the processing time, for a high hydrochloric acid concentration.

Chemicals, energy, and immobilized capital can be saved in industrial facilities by using lower formic acid and hydrochloric acid concentrations and shorter processing times, than considered in the previous paragraph. The data of Tables 3 and 4 can be used to select values of the operational variables providing near-optimal pulp properties while saving chemicals, energy, and immobilized capital by using lower values of operational variables. One combination leading to near-optimal properties with reduced costs with properties is using a processing time of 60 min, a formic acid concentration of 92.5%, and a hydrochloric acid concentration of 0.075%. Operating under these conditions the following values for the dependent variables were obtained: yield 42.25%, brightness 22.7%, and viscosity 512 mL/g; these values deviate by 7.8%, 22.5% and 12.0%, respectively of the maximum values of yield, brightness and viscosity, respectively. It is found that when operating under these conditions the values "Yield/kappa" ratio and "Viscosity/kappa" ratio of 17.60 and 1.68 are achieved, respectively; these values are far from the top surfaces presented in Figs. 11 and 12.

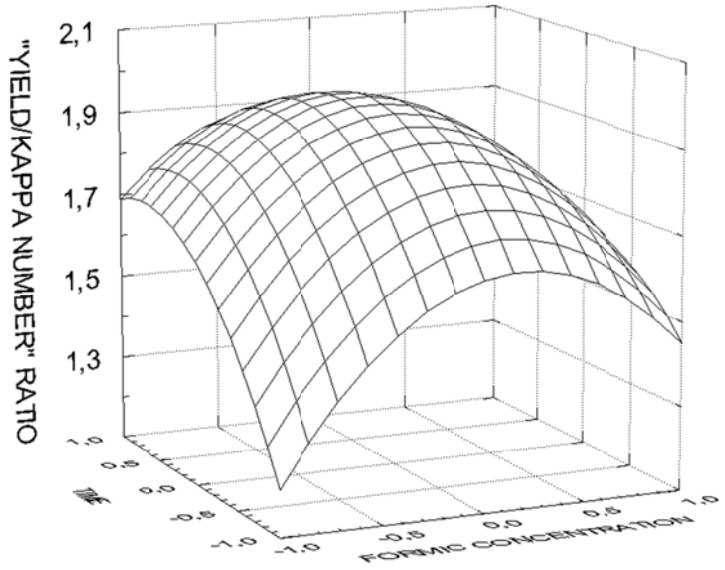

Figure 11. Variation of "Yield/kappa" with formic acid concentration and processing time, at high hydrochloric acid concentration

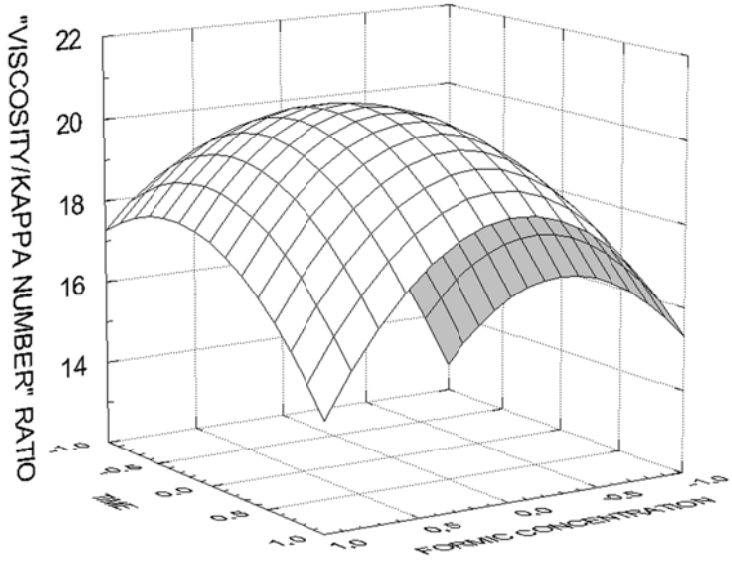

Figure 12. Variation of "Viscosity/kappa" with formic acid concentration and processing time, at high hydrochloric acid concentration

Bleaching

In order to obtain a bleached pulp with minimal degradation it is suitable to select an unbleached pulp with higher viscosity (Experiment 2). Applying the sequence EPabOPoP (alkali Extraction-Peracetic in basic medium-Oxygen-hydrogen Peroxide with oxygen-hydrogen Peroxide) gave the experimental results shown in Table 7. As can be seen, the pulp yield is decreasing with subsequent bleaching stages used near the end of

the value of 35.9%, representing a 17.7% loss in the performance of the original pulp. The viscosity of the pulps decreased significantly, especially in the Pab and O stages, reaching the final stage with a loss of viscosity in the complete sequence of 34.8%. Finally the brightness rose to 69.4%.

Table 7. Bleaching of Pulp from EFB

Properties	Original Pulp	Stage E	Stage Pab	Stage O	Stage Po	Stage P
Yield, %	43.6	41.6	40.7	37.3	36.5	35.9
Kappa number	31.1	16.2	13.0	10.1	7.8	5.6
Viscosity, mL/g	606	616	443	422	408	395
Brightness, %	22.3	37.0	42.0	50.6	50.2	69.4

Characterization of Residual Liquor

The residual liquor from Experiment 2 is considered (which gives rise to a pulp with high viscosity). Proceeding as specified in section Characterization of residual liquor (in Experimental), the lignin 18.2% of original dry raw material may be separated. The liquid fraction obtained after the removal of lignin contained 4.1% glucose, 9.8% xylose, and 1.2 % arabinose, based on the original dry raw materials.

Separated lignin may have several applications or it may be converted into fuel gas through gasification and pyrolysis operations (Sánchez *et al*. 2010). On the other hand, one can ferment sugars derived from the pulping and use them for the production of alcohols (Garrote *et al*. 2007a,b; Rodríguez *et al*. 2010)

CONCLUSIONS

1. A comparison of the chemical properties of EFB and various agricultural residues (olive prunings, wheat straw, sunflower stalks, sorghum stalks, rice straw, sugarcane bagasse, vine shoots, and cotton stalks), alternative raw materials (leucaena, tagasaste, bridal broom, *Phragmites*, giant reed, *Prosopis* and paulownia), and hardwood (eucalyptus) and softwood (pine) revealed that EFB is an alternative source of cellulose for producing cellulosic pulp.
2. Organosolv delignification of EFB could be effectively achieved with the formic acid-hydrochloric acid-water system, at atmospheric pressure.
3. Using polynomial equations, the properties of pulps (yield, kappa number, viscosity and brightness) have been estimated, with errors less than 10%, as a function of operating variables (formic acid and hydrochloric acid concentrations and processing time).
4. The search for a compromise between pulp properties and chemical and energy led to the following operating conditions: concentrations of formic acid and hydrochloric acid of 92.5% and 0.075%, respectively, and processing time of 60

min). Operating under these conditions provided a pulp with acceptable values of their properties (42.3% yield, 22.7 % brightness, and viscosity of 512 mL/g).

5. A pulp (31.1 kappa number and 606 mL/g viscosity) was bleached by EPabOPoP sequence, achieving a brightness of 69.4%, a loss of viscosity and yield of 34.8% and 13.1% respectively.
6. The residual liquor was separated 18.2% of lignin, 4.1% of glusose, 9.8% of xylose, and 1.2% of arabinose, all on dry weight of original raw material

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