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Response surface optimization of Entandrophragma cylindricum (Sapelli) pulping/delignification using a hybrid organosolv ethanol/soda process

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Abstract

The pulping potential of high lignin-containing tropical hardwoods is not well-reported in the literature. The forestry exploitation of these woods generates high amounts of residue each year of first and second transformations of the woods. This work studied the pulping of Sapelli (*Entandrophragma cylindricum*) wood species using a hybrid caustic soda solution/ethanol process using the Response Surface Methodology with Central Composite Design. The water/ethanol ratio was fixed at 40/60 (v/v) following preliminary experiments. The three pulping parameters namely temperature, time and alkali charge were chosen as independent variables. The pulp response characteristics were yield, kappa number and cellulose content, as well as the interactions between these pulping parameters. The results of the study and the quadratic equations models equations obtained provided the basis for selecting the optimal conditions of pulping according to the desired pulp characteristics. The generated mathematical relationship showed that the optimal pulping conditions were time 120 min, temperature 180°C and alkali charge 29.95%. The experimental yield, 45.01%, kappa number, 9.6 and cellulose content, 0.4028 g/g of initial wood obtained by applying the optimal conditions were close to the theoretical values generated by the experimental designs. The amount of cellulose in the pulp was also close to the amount of cellulose in the raw wood, showing that the hybrid pulping method caused only a slight degradation of cellulose. The cellulose in optimal pulp was type I cellulose as shown by X-ray diffraction. The optimal pulp was also characterized by Fourier Transformed Infrared spectroscopy and thermogravimetric analyses. Experimental designs can be used to optimize the caustic soda/ethanol pulping of wood to produce only slightly degraded cellulose as an intermediate for various industrial applications.

Introduction

Pulping processes are applied to extract cellulose from lignocellulosic materials for application in various sectors such as paper, textiles, food additives or coatings (Lindner et al. 2018; Eichhorn et al. 2022). Conventional methods established in the field include mechanical and chemical pulping in aqueous alkali (soda and Kraft) or aqueous acidic (sulfite) media. These processes differ from each other in yield, pulp quality, mechanical properties and cellulose degradation rate. In the mechanical pulping process, pulp is produced using a revolving grinding stone to crush wood into chips. The pulp produced is low-cost and high-yield (around 95%), but would not be easily bleachable, and resulting materials such as paper are photo-yellowing due to the formation of chromophores through the reaction of residual lignin with light or oxygen (Harmsen et al. 2010). The high lignin content of these pulps limits their use for other applications. The Kraft process uses a mixture of sodium hydroxide and sodium sulfide as pulping chemicals, and gives yields between 9.2 and 50.6% for hardwood species (Ardina et al. 2018; Mazar et al. 2021). It is nowadays the most used chemical pulping method in the world for pulp production and the pulp can easily be bleached. However, the main disadvantage of this process is the bad odour due to the release of sulfur oxides which, in addition, are harmful to the environment. Moreover, the Kraft process is selective of wood species, limiting its use to, for example, species with high ash content, especially silica¯rich species (Jardim et al. 2022). The sulfite process is another major sulfur-based process using sulfite or bisulfite salts as cooking chemicals. The process produces pulps with lower yields than the Kraft mainly attributed to increased damage of cellulose. The pulping liquor is also corrosive of steel digesters because of its acidity, and the pulp produced is slack (Luo et al. 2017). The soda process, which uses sodium hydroxide solution as a cooking solvent, was among the earliest chemical pulping processes, but was abandoned for the Kraft process. The soda is a low-cost process and reduces environmental impact because of the availability of sodium hydroxide and no sulfur-based chemicals involved, but it results in a sticky pulp and considerably alters carbohydrates which reduces the quality of cellulose (Potucek et al. 2014; Shuank et al. 2020) Several improvements of soda pulping have been considered in literature including the addition of anthraquinone (Martinez et al. 1997), EDTA (Mohamad and Junaidah 2022), sodium carbonate (Marin et al. 2017) and butanol (Akpakpan et al. 2012) applied to reduce the degradation of cellulose. However, these additives are expensive or not always available. The effect of adding ethanol as a cheap organosolv pulping solvent in the soda pulping process was studied in this work.

Organosolv pulping methods involving organic solvents are explored over the world for many decades as alternative to the conventional methods (Young 1985; Delmas and Avignon 1997; Muurinen 2000). Alcohols (ethanol, methanol, glycerol), ketones (acetone), carboxylic acids (formic acid and acetic acid) are commonly used as solvents for organoslov pulping because of their low cost, low boiling point and easy recovery. Organosolv pulping has exhibited good pulping yields with some agricultural lignocellulosic residues such as wheat straw (Jimenez et al. 1999), *Ceiba pentandra* (Assonfack et al. 2023), Jute (Sahin 2012), Corn stover (Kim and Lee 2005), Sugarcane bagasse (Vajellos et al. 2011) and rice straw (Akhouri and Dhanraj 2017) have provided sulfur-free lignin by-products which can be valorized in other applications such as adhesives, foams, and adsorbents (Khazraie et al. 2017). The reactions can be auto-catalyzed under certain experimental conditions, such as at higher temperatures, but usually require the addition of mineral or organic acids as catalysts. The addition of acid catalysts increases the degradation of lignin, turning it to a less useful co-product (Sannigrahi and Ragauskas 2013). Acetic and formic acids are good lignin solvents; however, their use has been somewhat limited due to their corrosive nature. Acetylation of cellulose has inhibited for example binding of cellulose enzymes to cellulose via hydrogen bonds (Vazquez et al. 2000). Performic and peracetic acids have been used in the Milox process, however there are major concerns linked to its stability and associated safety issues (Zhao et al. 2009). Primary alcohols (e.g. ethanol and butanol) as well as high-boiling polyols (e.g. ethylene glycol, glycerol) have been considered for pulping of lignocelluloses (Sun and Chen 2008). Ethanol pulping, although it removes a good amount of lignin, usually requires the addition of mineral acids which makes the process polluting and corrosive. In order to improve the cellulose pulp quality, reduce manufacturing costs and respect environmental standards, research is ongoing in this field. In addition, the scientific data about the organosolv pulping ability of tropical woods, especially Cameroonian woods, are scarce in the literature.

Most of equatorial countries, e.g. Cameroon, have a very rich forest plant variety. The natural forest covers now around 17.5-billion-hectares of national territory in Cameroon with approximately 300 wood species enumerated (Fonweban and Houiller 1997). Around twenty species are currently commercialized and their exploitation generates high amounts of residue (branches, upper part of trunk) each year that can be valorized through the production of cellulose pulp. The high lignin content of wood (up to 25% wt), the high density and ash content of tropical hardwoods may have been an obstacle to the development of pulp from these wood species compared to temperate species (up to 28% of lignin) (Hannrup et al. 2004). Preliminary laboratory work using Kraft and formic acid-acetic acid-water organosolv pulping showed that Sapelli (*Entandrophragma cylindricum*) was most prone to delignification among the wood species investigated (Ndikontar et al. 2015; Assonfack et al. 2023).

A hybrid pulping process combining soda and ethanol was applied to Sapelli sawdust. The influence of the parameters such as temperature, time, soda solution/ethanol ratio, active alkali and their impact on the pulping characteristics pulp yield, kappa number and cellulose content were studied. The Methodology of Experimental Design was applied to determine the optimal conditions (Tinarkwo et al. 2018; Arackal and Parameshwari 2019). The optimal pulp obtained was characterized by Fourier Transformed Infrared-Attenuated Total Reflectance (ATR-FTIR), X-ray diffraction (XRD), thermal analyses (TG/DTG) and the resulting pulp was compared to Kraft pulp prepared from the same wood.

Material and Methods

Materials

Sapelli (*Entandrophragma cylindricum*) wood was collected in the commune of Dimako in the East region of Cameroon (GPS coordinates of 4° 22’ 49.44” N and 13° 34’ 21.4176” E with an elevation of 647.738 m). Wood timber was air-dried in the laboratory, cut into small chips and dried in an oven at 50°C for 24 days. The wood was ground using a Retsch-DR 100 grinder. The sawdust obtained was sieved on an AFNOR standard sieves (NFB 52-001-1) with pores sizes 200 and 315 µm. Ethanol (96%) was a commercial product. All other chemicals were analytical grade and used without further purification.

Determination of chemical composition of the wood

Standard methods were used for the determination of the chemical composition of the wood. Ash content was assessed by TAPPI T-211, ethanol-benzene extraction was replaced by acetone extraction (ASTM G494-11). Acetone extraction was followed by hot water extraction (TAPPI T 207 cm-99) for the determination of extractive content, cellulose content was determined by using TAPPI T-203 OS-61 and lignin (Klason) content by TAPPI T-222 om-02.

Pulping experiments

Pulping experiments were carried out in a 0.8-L custom-made high-pressure steel reactor. The heating source was an oil bath. The soda solution was prepared by dissolving caustic soda (NaOH, 99% wt) in distilled water at concentrations between 0.625 and 2.188 M which corresponded to an alkali charge between 10 and 35%. Ethanol (96%) was used. In a typical experiment, 5 g (oven-dried basis) of wood sawdust was weighed and placed in the reactor. Soda solution and ethanol were mixed in mass ratios between 100/00 and 00/100 and added to the wood powder inside the reactor. The liquid-to-solid ratio was 10:1. The reactor was carefully closed and an impregnation time of 15 min was left before placing the reactor in the oil bath pre-set to the cooking temperature (160–180°C). The reactor was removed from the oil bath after the pre-set cooking time and cold down in cold water. The mixture of pulp and cooking solvent containing dissolved components was filtered and the solid residue was washed with distilled water, dried in an oven for a whole night at 75°C and weighed for pulp yield. The cellulose pulp was kept in plastic bags for further characterization.

The experiments were all carried in triplicate and the experimental results reported are the mean ± standard deviation of values.

Characterization of pulp

The cellulose pulps were characterized by yield, kappa number and cellulose content. The yield was determined by gravimetric method based on the initial of mass of wood used for pulping reaction. The Kappa number which determines the chemical requirement of the pulp for bleaching and is a function of residual lignin, was determined according to ISO 302:2004. The cellulose content was determined using the similar procedure for raw wood (TAPPI T-203 OS-61).

Experimental design, optimization and mathematical modeling

A central composite factorial design (CCF) was used to study the interactions between the factors (independent variables) and to identify the optimum pulping factors. Those factors were pulping time (X_1: 60–120 minutes), pulping temperature (X_2: 150–190°C) and active alkali (X_3: 10–35%). The variables were normalized using Equ. 1. The impact of the experimental factors on the variable response was studied using a quadratic model as shown by the Equ. 2. Analyses of variance (ANOVA) were used to determine the statistical significance (p value under or equal to 0.05) of the response to estimate the fit of the polynomial prediction equation for the studied responses, using the Student's t-test. The experimental design, data processing and the establishment of optimum conditions were performed by MINITAB 20 software.

$$X_i = \frac{2(X - X_m)}{X_{\max} - X_{\min}} \times 100 \qquad (1)$$

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \qquad (2)$$

where Y is the response variable, β_0 the value of the adjusted response at the center point of the design, β_i, β_{ii} and β_{ij} are the quadratic linear and cross-product regression coefficients separately, X_m the mean of the extreme values of the factor X, X_{max} and X_{min} are the maximum and the minimum value respectively.

The second-order polynomial equation was adjusted to the experimental data of each of the responses as given: Y_1 the pulp yield, Y_2 the kappa number, and Y_3 the cellulose content. The response surfaces were generated for the connection of

any of two factors while holding the third factor as consistent (at the central value).

Optimal pulp

The optimal pulp was characterized by Fourier Transformed Infrared (FTIR) spectroscopy, thermogravimetric analyses (TGA) and X-Ray diffractometry (XRD).

ATR-FTIR was conducted using a Brüker Alpha-P spectrometer equipped with a diamond crystal and driven by Opus/Mentor software. The spectra were recorded on 1 mg of the optimal and standard Kraft pulps by carrying out 32 scans over the spectral range from 4000 to 450 cm^{-1} with a 4 cm^{-1} resolution.

TG analyses were carried out in a nitrogen atmosphere using a TGA/SDTA 851 Mettler Toledo apparatus with a rate of 10°C/min, from 34.109 to 745.913°C.

XRD was carried out using an XPERT-PRO diffractometer equipped with a Cu-K_α anode tube (λ = 0.154 nm), 40 kV voltage generator, a 40-mA current tube at a scanning speed of 2°C/min. The crystallinity index, *CrI* was determined using the Segal's method (Segal et al. 1959) (Equ. 3).

$$\%CrI = (1 - \frac{I_{am}}{I_{200}}) \times 100 \quad (3)$$

where I_{am} is the minimum intensity of diffraction of the amorphous material and I_{200} is the maximum intensity of diffraction of the lattice peak.

Results and Discussion

Chemical composition of the wood

The moisture content and chemical composition of sapelli wood used in this study are shown in Table 1.

Table 1
Moisture and chemical composition of sapelli wood

Mean value	Constituent (%)				
	Moisture	Ash	Extractives	Lignin	Cellulose
	10.26 ± 0.17	0.26 ± 0.03	08.21 ± 0.21	29.52 ± 0.09	41.17 ± 0.32

The moisture content of the wood 10.26 ± 0.17% showed that the wood was quite dry when used (Hill et al. 2021). The equilibrium moisture content of air-dried wood is generally between 8 and 12% (Nepveu 1994; Natterer et al. 2000). The 29.52 ± 0.09% lignin and 41.17 ± 0.32% cellulose contents are in the range for tropical hardwoods, i.e. 25–35% for the lignin and 40–45% for the cellulose (Monica et al. 2009; Onuegbu and Olaide 2018). The chemical composition agrees with previous work carried out with the same species [30]. It can be mentioned that the lignin content of the wood was relatively low compared to the lignin content of other common commercial tropical woods in Cameroon which are between 31 and 36% as reported by Ndikontar et al. (2015). The ash content of the wood is quite low suggesting the wood can be efficiently used in sensitive pulping process such as Kraft pulping. Ash content, especially silica content, is known to a hindrance to the recovery of Kraft cooking chemicals for recycling (Zhaoyang et al. 2016).

Preliminary studies on the pulping conditions

The ratio of soda solution/ethanol in the cooking liquor was gradually decreased from 10:00 to 00:10 to determine the range that can provide pulp with convenient yield between 40% and 60%. Yields lower this this range result in increased degradation and loss of cellulose, while above the range, delignification would not be sufficient for efficient bleaching and recovery of cellulose. The liquid/solid ratio was fixed at 10:1, temperature at 170°C and reaction time at 90 min. A decrease of the ratio does not only increase the ethanol content of the cooking liquor, but also decreases the alkali content in the reaction medium. The pulp yields obtained from the different experimental conditions are shown in Fig. 1.

The results show pulp yields between 8.68% and 85.27%. As expected, cooking with high soda solution, such as pure soda solution (10:00 sample) led to low yields which can be attributed to high alkali content (22.5%) compared to the 20% in the soda process. The addition of ethanol has a considerable impact on the yield. Ethanol (96%) alone dissolved wood components to an extent of 17–18% higher than the extractive contents, revealing that the main components of wood were also affected. It has been shown in literature with *Populus euroamericana* and some hardwoods (*Populus alba*, *Carpinus orientalis*, *Salix alba* and *Robin opseudo* acacia) that ethanol led to a yield around 45% in the range of the temperature from 90 to 180°C (Agkul and Kirci 2009). The low lignin content of these wood samples can explain higher dissolution rates with ethanol compared to this study. The pulps obtained with high ethanol content (01/09 and 00/10 ratios) were not bleachable. Ethanol alone is not sufficient for pulping of sapelli wood in the experimental conditions investigated.

The pulp yields were very low for low white liquor with ethanol content revealing a high deterioration of wood components under these conditions. The result agrees with literature (Monica et al. 2009) where it is stated that soda pulping considerably deteriorates carbohydrates. Ogunsile (2010), pulping *Cyperus articulatus* wood using soda process and different reaction parameters (time, temperature, liquor to solid ratio, and alkali charge), reported a highest pulp yield of 30.3% at lower time and temperature than the time and temperature ranges applied in this work. Soda pulping alone causes much degradation of cellulose. The addition of ethanol can reduce this degradation depending on relative amounts and the experimental conditions. The results in Fig. 1 showed a complex combination of the effects of caustic soda solution and ethanol on wood.

It is difficult at this level of knowledge to correlate the effect only to their ratio because of the concomitant change of the several other parameters such active alkali/solid wood ratio, water and ethanol contents with the ratio. The cooking solutions 05/05, 04/06 and 03/07 provided acceptable yields between 40% and 56% with the best performance obtained with 04/06 (55.84%). This result agrees with the result of Lee et al. (2022) who found for a yield of around 50.2% for a hardwood pulping with such solvent mixtures (with the ethanol amount less than 60%).

Experimental design, optimization and mathematical modeling

The influences of temperature, time and alkali content on the pulp yield, kappa number and cellulose content were studied by experimental design; ethanol/caustic soda solution ratio was kept at 60/40 for all the experiments.

The experimental results of all the pulping trials of the wood in various mixtures of ethanol and sodium hydroxide solution are reported on Table 2.

Table 2
Experimental values of responses and dependent variables

1	60	150	10	-1	-1	-1	55.16	46.67	0.3342
2	120	190	10	+ 1	-1	-1	49.11	36.67	0.2716
3	60	150	10	-1	+ 1	-1	46.59	23.33	0.4037
4	120	190	10	+ 1	+ 1	-1	53.21	20.33	0.3982
5	60	150	35	-1	-1	+ 1	51.47	30.67	0.2841
6	120	190	35	+ 1	-1	+ 1	41.63	20.67	0.4078
7	60	150	35	-1	+ 1	+ 1	41.44	11.33	0.3894
8	120	190	35	+ 1	+ 1	+ 1	48.93	10.33	0.3832
9	141	170	22.5	+ 1.682	0	0	46.44	16.67	0.4078
10	40	170	22.5	-1.682	0	0	52.27	26.67	0.4036
11	90	203.64	22.5	0	+ 1.682	0	63.07	10.00	0.4103
12	90	136.36	22.5	0	-1.682	0	54.31	33.33	0.4057
13	90	170	43.525	0	0	+ 1.682	30.04	11.67	0.4049
14	90	170	1.475	0	0	-1.682	81.45	36.67	0.3981
15	90	170	22.5	0	0	0	48.50	15.00	0.3658
16	90	170	22.5	0	0	0	60.43	17.66	0.3935
17	90	170	22.5	0	0	0	54.25	16.33	0.3985
18	90	170	22.5	0	0	0	44.66	15.67	0.4021
19	90	170	22.5	0	0	0	49.43	18.33	0.4026
20	90	170	22.5	0	0	0	47.76	17.00	0.4062

Influence on pulp yields (Y_1)

The surface responses are shown in Fig. 2.

On the 2**a** surface, the pulp yield is greatly affected by both time and temperature, the pulp yield decreases when time and temperature decrease. The result is in line with the result of Neiva et al. (2014) who stated that hardwood pulping results are highly dependent on the maximum time and temperature. On the 2**b** and **2c** surfaces, the alkali charge highly affected the pulp yield either when related to time or temperature (Ogunsile and Quintana 2010). At high alkali contents, the yield is low. These results are in accordance with many studies which found that increasing the content of sodium hydroxide in the white liquor eases the pulping process (Hassan et al. 2018; Amibo 2021; Lee et al. 2022; Vedoya et al. 2022). High temperature and time also tend to reduce the pulp yield. Pulping of a hardwood species showed drastic decreases of pulp yield with increase of sodium hydroxide concentration of the cooking liquor (Lee et al. 2022). The lowest pulp yield was reported on pulping of oil palm empty fruit bunches via soda-anthraquinone process, when temperature, time and active alkali were all at their maximum (Hassan et al. 2018). Shatalov et al. (2002) stated that a cooking liquor with high alkaline content reduces the surface tension, improving the mass transfer of active chemicals and degradation products.

As can be seen in Fig. 3, the most influential factor on pulp yield is the active alkali content. However, this factor cannot be studied alone because of its interference with both time and temperature (**BC = 0.516** and **AC = 0.394**). The highest interaction was between cooking time and temperature (**AB = 1.000**).

The second order polynomial equation with the corresponding value of R^2 and R^2 (adjust) for the pulp yield response (Y_1) is as follow (Equ. 3):

$Y_1 = -75 - 0.35\,A + 1.85\,B + 0.40\,C + 0.00531\,AB - 0.00318\,AC - 0.0079\,BC - 0.00284\,A^2 + -0.00668\,B^2 + 0.0135\,C^2$ with $R^2 = 0.6067$ and R^2 (adj) = 0.5262 **(4)**

Table 3
Influence of input cooking variables (A- time, B- temperature, C- active alkali) affecting the pulp yield

Source	Model	A	B	C-	AB	AC	BC	A^2	B^2	C^2	Lof[b]
SS[a]	28443.3	378.1	7.9	19809.0	1880.9	326.3	651.9	2513.6	1334.7	1540.7	15751.3
DF	9	1	1	1	1	1	1	1	1	1	5
F-value	1.71	0.16	0.47	8.28	1013	0.14	0.35	1.03	0.70	0.69	5.85
P-value[c]	0.207	0.697	0.507	0.016	0.339	0.712	0.565	0.333	0.422	0.426	0.037
SS[a]: Sum of Squares, LoF[b]: lack of Fit, Prob[c]> F											

The F-value of 1.71 suggests the model is significant. There is only 0.01% of chance that such an F-value could be due to noise. P-values lower than 0.050 show that the model terms are significant. Hence C is a significant model term. The F-value lack of fit of 5.85 implies it is not significant relative to the pure error. The coefficient of variation (CV) refers to the degree of precision with which experiments are similar. The value of CV of 4.10 shows the high reliability and reproducibility of the design. The value of R^2 was 0.6067, and the value of adjusted R^2 = 0.5262. The value of R^2 higher than 0.5 indicated a good reliability regarding the relationship between the observed experimental data and the designed predictions; hence the model was good.

Influence on kappa number (Y_2)

The surface responses are shown in Fig. 4.

On the 4**a** surface, the kappa number is more affected by cooking temperature than time. Kappa number decreases more with temperature than with time. This result agrees with the study by Ogunsile (2010) who found that for pulping a hardwood (*Cyperus articulatus*), the kappa number is low when the time and temperature are high; with temperature being the more consistent of the two reaction parameters. On 4**b** surface, the active alkali has a higher effect on the kappa number than time, similar for the 4**c** surface in which active alkali has a high effect on the kappa number than temperature. The Pareto chart (Fig. 5) confirms that the most influential factor on the kappa number is the active alkali (**C = 11.4**). This is in line with the study by Vedoya et al. (2022) who reported that alkali content has a better influence on the kappa number than cooking time and temperature.

However, the influence of active alkali is only slightly higher than the influence of cooking temperature (**B = 10.7**), meaning that the effect of the temperature is also to be considered. It is reported that an increase in temperature considerably alters lignin, consequently decreasing the kappa number of the pulp (Akgul and Tozluoglu 2010; Hassan et al. 2018). The most

important interaction on this response is also between time and temperature (**AB = 2.20**) as in the case of pulp yield, showing that temperature cannot be studied separately from time.

The second order polynomial equation with the corresponding value of R^2 and R^2 (adjust) for the response kappa number (Y_2) is as follow (Equ. 4):

$Y_2 = 358.3 - 1.166\ A - 2.552\ B - 2.446\ C + 0.00324\ AB + 0.00106\ AC + 0.00489\ BC + 0.002721\ A^2 + 0.00513\ B^2 + 0.02123\ C^2$, with $R^2 = 0.9727$ and R^2 (adj) = 0.9480 **(5)**

Table 4
Significance of input cooking variables (A: time, B: temperature, C: active alkali) influencing the kappa number

Source	Model	A	B	C-	AB	AC	BC	A^2	B^2	C^2	Lof[b]
SS[a]	707.2	48.0	274.9	256.0	11.7	0.4	4.2	27.5	19.3	65.2	16.7
DF	9	1	1	1	1	1	1	1	1	1	5
F-value	39.52	24.28	113.33	131.13	5.42	0.23	2.14	18.37	7.77	33.14	5.30
P-value[c]	0.001	0.001	0.000	0.000	0.042	0.643	0.174	0.002	0.019	0.000	0.045
SS[a]: Sum of Squares, LoF[b]: lack of Fit, Prob[c]> F											

The model F-value of 39.52 revealed the model is significant. There is only 0.01% of chance that such an F-value could happen due to noise. P-value lower than 0.050 show that the model terms are significant. Hence A, B, C, AB, A^2, B^2, C^2 are significant model terms. The lack of fit F-value of 5.30 implies it is not significant relative to the pure error. The CV of 0.837 shows the high reliability and reproducibility of the design. The R^2 was 0.9727, the adjusted R^2 was 0.9480. The value of R^2 is fairly close to 1, indicating a good reliability regarding the strong relationship between the observed experimental data and the designed predictions.

Influence on cellulose content (Y_3)

The surface responses are shown in Fig. 6 and the Pareto chart on Fig. 7.

It is important to remember that the cellulose content of the sapelli wood was 41.17%, i.e. 1 g of the wood contains 0.4117 g cellulose. On the 6a surface, the highest value of the cellulose content (0.432 g/g) was obtained when both the time and temperature were high, this could mean that cellulose is not seriously damaged by high temperatures and long reaction times. Regarding time and temperature, the moderate cellulose content (about 0.4000 g/g) is obtained with low time and high temperature and vice versa. This result is in line with the work of Abdel-Aal (2013). On the 6**b** surface, moderate amounts of cellulose are obtained with average times and active alkali. The same observation can be made on the surface 6**c**. The degradation of cellulose depends more on the solubilization of the other components of the wood than its own degradation, it probably happens at high cooking times values (Sanjay and Dhanraj 2017).

The most influential factor on the cellulose content is the cooking time (**A = 0.8**), but the factor cannot be studied separately from the active alkali since both has the highest interaction (**AC = 1.22**).

The second order polynomial equation with the corresponding value of R^2 and R^2 adjust for the response cellulose content (Y_3) is as follow (Equ. 5):

$Y_3 = -0.02 + 0.00397\ A + 0.00007\ B + 0.0098\ C - 0.000021\ AB + 0.000072\ AC - 0.000073\ BC - 0.000008\ A^2 + 0.000010\ B^2 - 0.000074\ C^2$ with $R^2 = 0.7012$ and R^2 (adj) = 0.7004 **(6)**

Table 5
Significance of input variables (A- time, B-temperature, C-active alkali) influencing the cellulose content

Source	Model	A	B	C-	AB	AC	BC	A^2	B^2	C^2	Lof[b]
SS[a]	0.8124	0.116	0.053	0.063	0.061	0.253	0.128	0.032	0.004	0.102	1.700
DF	9	1	1	1	1	1	1	1	1	1	5
F-value	0.48	0.64	0.35	0.15	0.33	1.48	0.67	0.22	0.04	0.51	8.85
P-value[c]	0.300	0.043	0.019	0.0232	0.0224	0.0936	0.0472	0.0121	0.0014	0.0378	0.6286
SS[a]: Sum of Squares, LoF[b]: lack of Fit, Prob[c]> F											

The model F-value of 0.48 showed the model is significant. There is only 0.01% of chance that such an F-value could happen due to noise. Value of P less than 0.050 show that the model terms are significant. Hence A, B, C, AB, BC, A^2, B^2, C^2 are significant model terms. The lack of fit F-value of 5.30 implies it is not significant relative to the pure error. The coefficient of variation (CV) refers to the degree of precision with which experiments are similar. The value of CV is 0.0228 shows the high reliability and reproducibility of the design. The value of R^2 is 0.7012, the value of adjusted R^2 = 0.7004. The value of R^2 is greater than 0.5 indicating a good reliability regarding the relationship between the observed experimental data and the designed predictions, hence the model is good.

Optimization of the process and comparison with the Kraft pulp

Optimal conditions for a pulping process were selected according to the pulp characteristics targeted to produce a pulp with the highest cellulose content, lowest kappa number and a pulp yield value between 45 and 50%. The optimal cooking parameters provided by the simulation were time 120 minutes, temperature 180°C and the active alkali 29.95%. A Kraft pulp was also prepared for comparison using the following cooking parameters: time 90 minutes, temperature 170°C and an active alkali of 20% (sulfidity 25%). The predicted and experimental results are shown in Table 6.

Table 6
Predicted, experimental and Kraft responses

Value	Studied response		
	Pulp yield, Y_1 (%)	Kappa number	Cellulose content (g/g)
Predicted	45.01	9.6	0.4028
Experimental	46.37	7.6	0.4085
Kraft pulp	39.81	10.0	0.3578

The optimal pulp properties were slightly different form the predicted optimal values. The optimal pulp exhibited better properties compared to the Kraft pulp, i.e., high cellulose content corresponding to lower cellulose degradation, lower kappa number indicating low residual lignin content and low demand of chemicals for bleaching. Despite the high alkaline content applied for the optimal pulping, there was little degradation of cellulose. The percentage of cellulose recovered was around 99.2%. However, higher degradation of cellulose was obtained with low alkaline charge in the absence of ethanol as observed with pure soda pulp in the preliminary experiments (sample soda/ethanol 100/00, alkaline charge 22.5%, pulp

yield 15.53%) and Kraft pulp (active alkaline content 20%, cellulose recovered 86.9%). It is obvious that the presence of ethanol reduces the degradation of cellulose during the soda/ethanol pulping. These results are in agreement with literature reports that soda-ethanol pulping improve the delignification and reduce the carbohydrate degradation (Akpakpan et al. 2012; Vedoya et al. 2022; Lee et al. 2022).

Pulp characterization

ATR-FTIR spectra

Figure 8 shows the ATR-FTIR spectrum of optimal pulp obtained by the hybrid soda/ethanol process, and the Kraft pulps.

The spectra of both samples exhibited almost the same vibration bands characteristic of unbleached pulp. In addition to cellulose, the unbleached pulp contains residual lignin and hemicelluloses which make its ATR-FTIR spectrum close to the spectrum of raw wood. The band at 3367 cm^{-1} was assigned to the stretching vibration of the hydroxyl bond (O-H) in cellulose (Djomi et al. 2018) while the band at 2916 cm^{-1} was assigned to the symmetric stretching vibrations of C-H in methylene and methyl groups (Kommula et al. 2016; Couret et al. 2017). The bands at 1592 cm^{-1} (aromatic ring vibrations) present on both spectra, 1733 cm^{-1} (C = O stretching in hemicellulose) were assigned to the presence of residual lignin and hemicelluloses and 1364 cm^{-1} (C-H deformation in cellulose and hemicelluloses) appears even strengthened (Yang et al. 2018). The band at 1615 cm^{-1} was attributed to the vibrations of water molecules absorbed inside the pulp (Rosa et al. 2010, Salim et al. 2021), the band at 893 cm^{-1} was attributed to amorphous region of cellulose while the band at 1423 cm^{-1} was assigned to the crystalline cellulose (Rivai et al. 2018). The band at 1033 cm^{-1} was assigned to the C-O stretching at C6 of the cellulose, the band at 1056 cm^{-1} was assigned to C-O stretching provided by cellulose, hemicelluloses and lignin. The bands at 1100 cm^{-1}, 650 cm^{-1} and 615 cm^{-1} on the spectrum of Kraft pulp were absent or appeared with a lower intensity in the spectrum of the optimal pulp; these peaks are attributable to the S = O vibrations of sulfonates groups in Kraft pulp. The soda/ethanol was free of sulfonation.

X-ray diffraction pattern

The X-ray diffraction pattern of optimal pulp is shown in Fig. 9.

The diffraction has a global feature of cellulosic Type alpha with pics at 2θ 17.05° and 22.73° characteristic of the planes (110) and (200) respectively. On the 2θ value of 17.05° the widened peak shows the amorphous part of the cellulose whereas on the 2θ value of 22.73° the sharp peak shows the crystalline part of the cellulose obtained (Rivai et al. 2018).

It was found to be 68.7%, is slightly higher than to crystallinity of 66% of Kraft fibers reported in literature (Yang et al. 2018). Cellulose is optimal is slightly less altered than cellulose in the Kraft pulp. Type I cellulose can exhibit crystallinity up to 91% with a mean around 78% as shown by cotton fibers (Teixeira et al. 2010).

TG/DTG spectra

The thermal stability of the optimal pulp was studied by TGA/DTG as shown on Fig. 10.

The thermal degradation of the optimal pulp took place in one domain confirmed by the DTG curve. A thermal accident occurring between 32.65 and 78.23°C, with a mass change of 2.22%, can be attributed to the departure of the water absorbed. The second accident occurred between 254.99 and 347.44°C, with a mass change of 65.28% can be attributed to degradation of the cellulose. The thermal degradation of cellulose occurred around 296–350°C and is characterized by one main peak compared to the spectrum of raw lignocelluloses (Feng et al. 2018; Gindl-Altmetter et al. 2020; Sartika et al. 2020; Assonfack et al. 2023). This result shows that our pulp is mainly made up of cellulose.

Conclusion

A hybrid caustic soda solution/ethanol process was applied for pulping of a tropical hardwood, sapelli or sprague (*Entandrophragma cylindricum*). A central composite Methodology of Experimental Design has been used to study the influence of cooking parameters (temperature, time and alkali charge) on the pulp properties (yield, kappa number and cellulose content). The caustic soda solution/ethanol ratio was fixed at 40/60% based on preliminary experiments. The optimal cooking conditions were found to be 119.8 minutes, 180.3°C and active alkali 29.95% which could lead to a theoretical pulp with yield 45.01%, kappa number 9.6 and cellulose content 0.4028 g/g initial dry wood. A pulping experiment at the optimal parameters led to slightly different results: pulp yield 46.37%, kappa number 7.6 and cellulose content 0.4085 g/g initial wood related to the complex interactions between the investigated reactions or cooking parameters. The closeness between these results means the model can be accepted for optimization of the pulping process. Pulping of a hardwood species such as sapelli can be successfully achieved by applying a caustic soda solution/ethanol mixture with high alkali load 29.5% to produce high cellulose-containing pulps. These pulps can be easily bleached, as suggested by their kappa number to cellulose, for many applications.

Declarations

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Ethical approval

Not applicable

Competing interest

The authors have no conflict of interest to declare.

Author contributions

All the authors contributed to the conception, realization and design.

Material preparation, pulping experiments and the theoretical part were performed by Hubert Justin Nnanga Guissele.

Data collection and analyses with the aim of pulp characterization were performed by Hubert Justin Nnanga Guissele, Emmanuel Njungap and Derek Tantoh Ndinteh.

Advice on the conception of this work was supplied by Jean-Bosco Saha Tchinda and Arnaud Maxime Cheumani Yona.

This work was made step by step under the supervision of Arnaud Maxime Cheumani Yona and Maurice Kor Ndikontar.

The first draft of the manuscript was written by Hubert Justin Nnanga Guissele and all the authors commented on all the subsequent versions of the manuscript.

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Data availability

All the data that support the findings of this study are available from the corresponding author on reasonable request.

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Figures

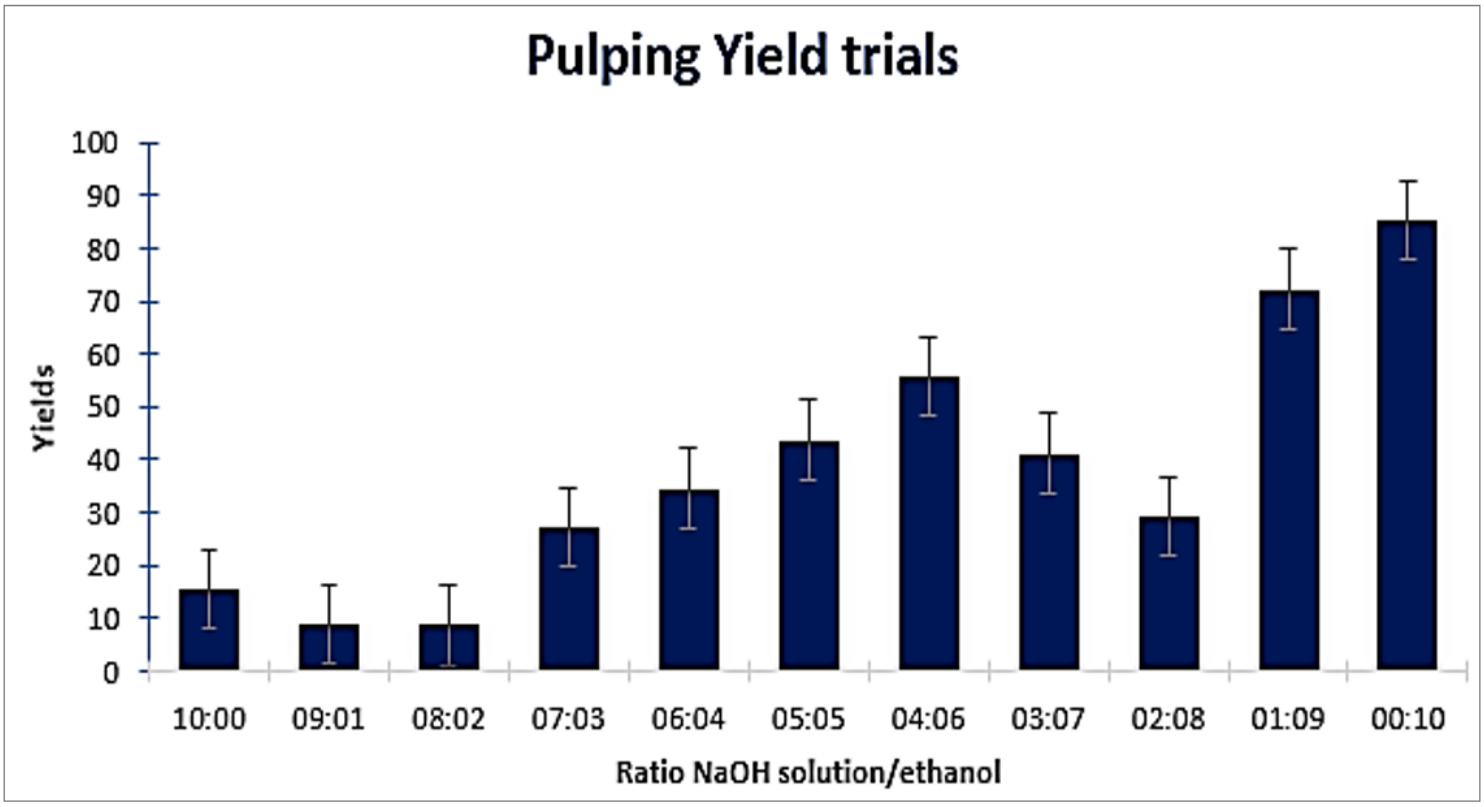


Figure 1

Effect of sodium hydroxide solution in the white liquor (sodium hydroxide solution 0.125 M/ethanol) on the pulp yield, temperature 170 C and time 90 min

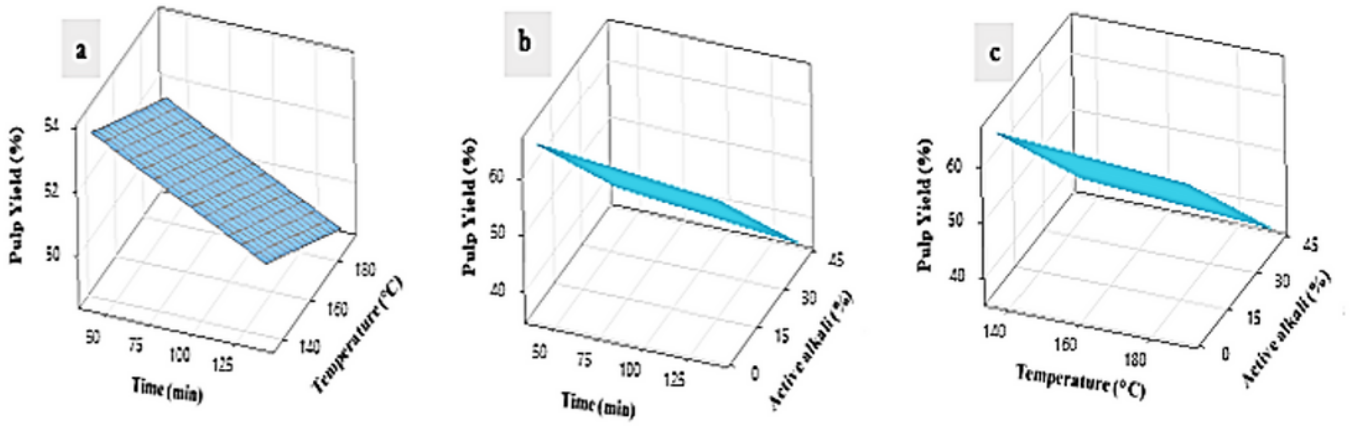


Figure 2

Responses surfaces of pulp yield as a function of (**2a**) time and temperature, (**2b**) time and active alkali and (**2c**) temperature and active alkali

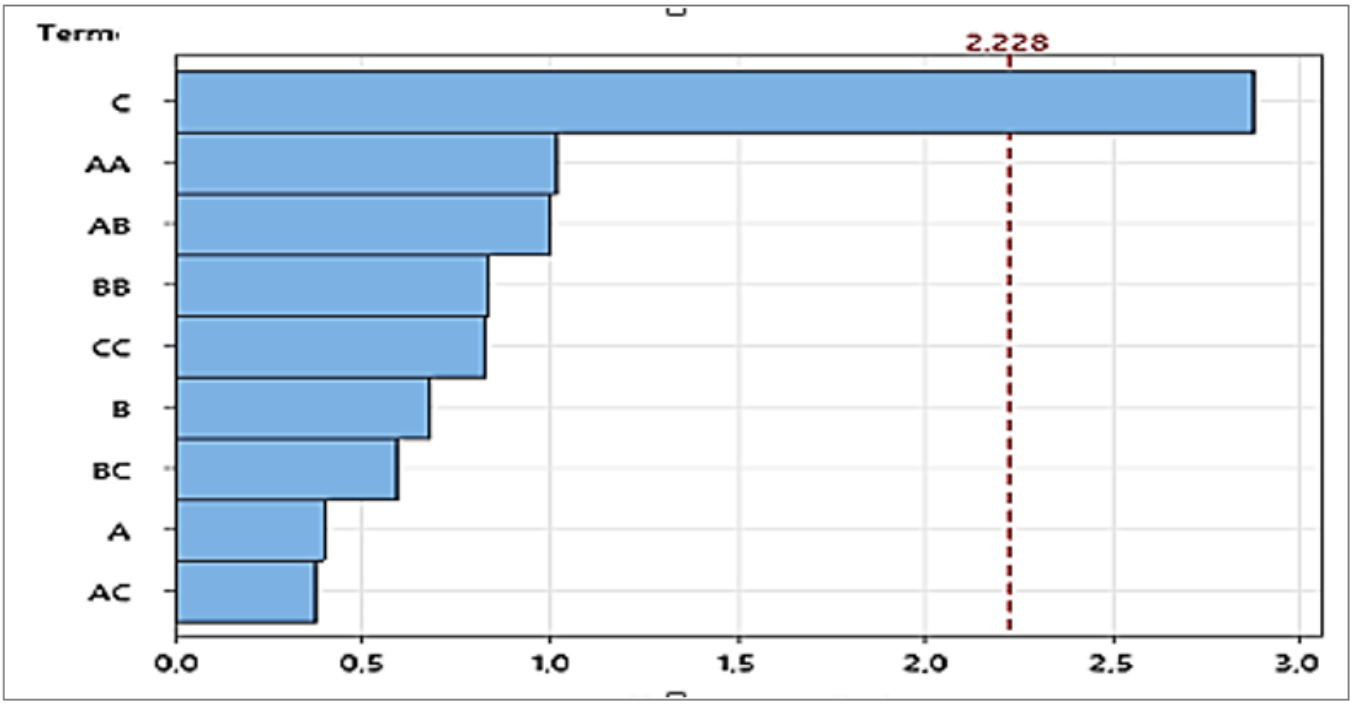


Figure 3

Pareto charts standardized effects of pulp yield

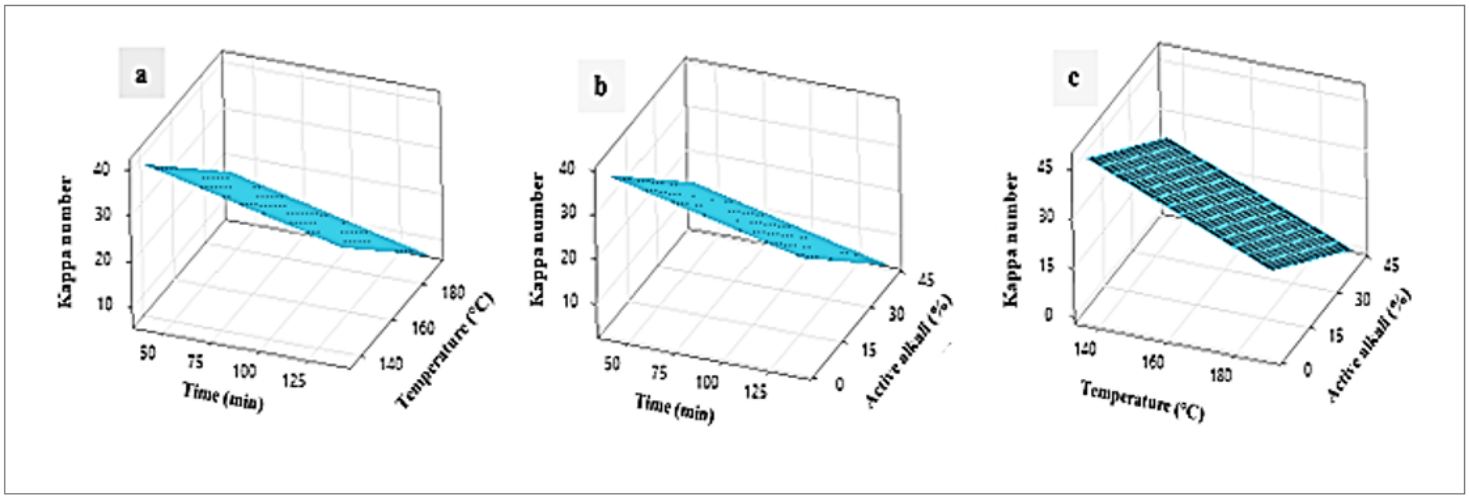


Figure 4

Responses surfaces of kappa number as a function of time and temperature (**a**), of time and active alkali (**b**) and of temperature and active alkali (**c**)

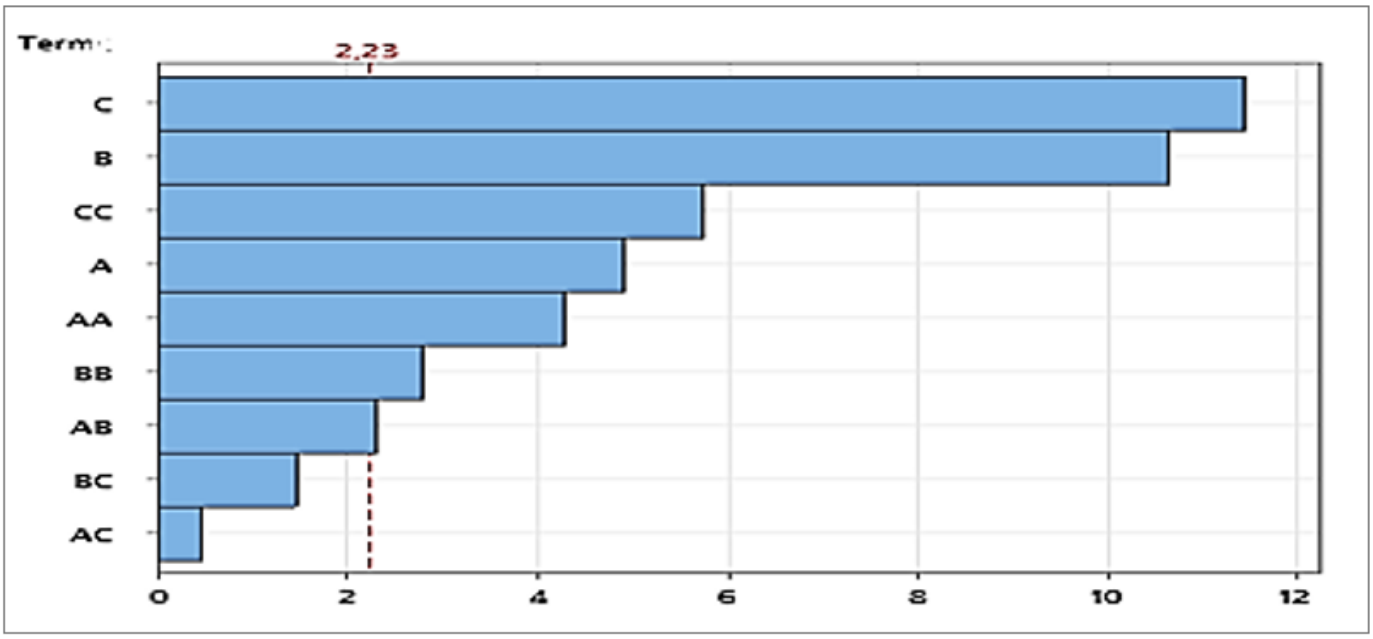


Figure 5

Pareto charts standardized effects of kappa number

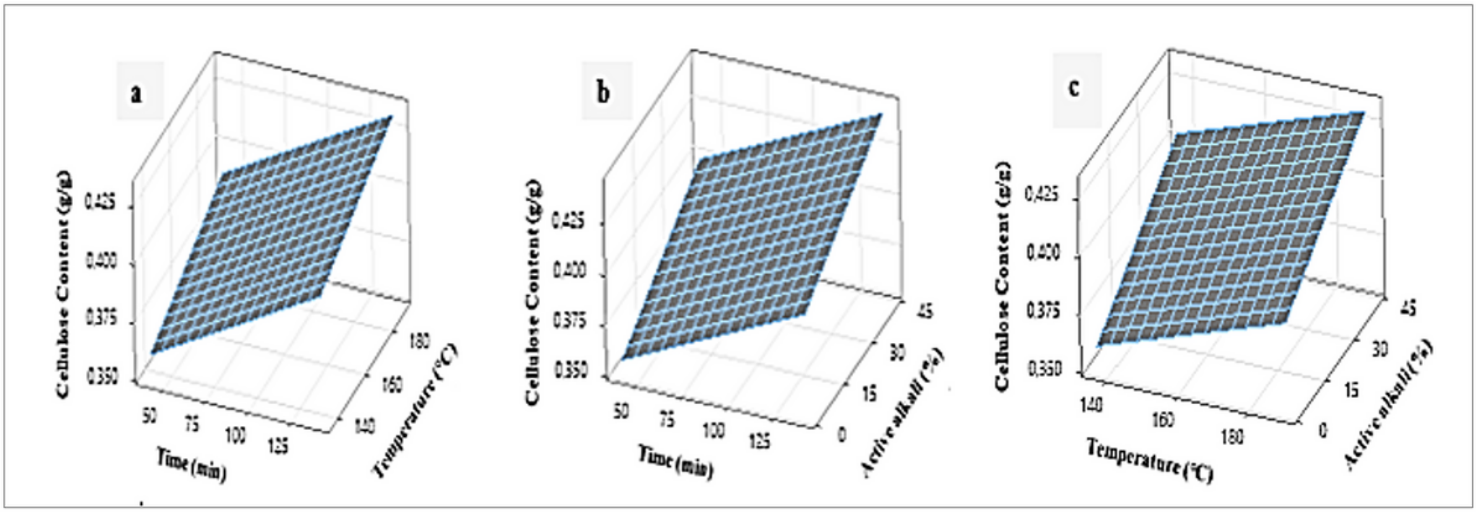


Figure 6

Responses surfaces of cellulose content as a function of (**a**) time and temperature, (**b**) time and active alkali and (**c**) temperature and active alkali

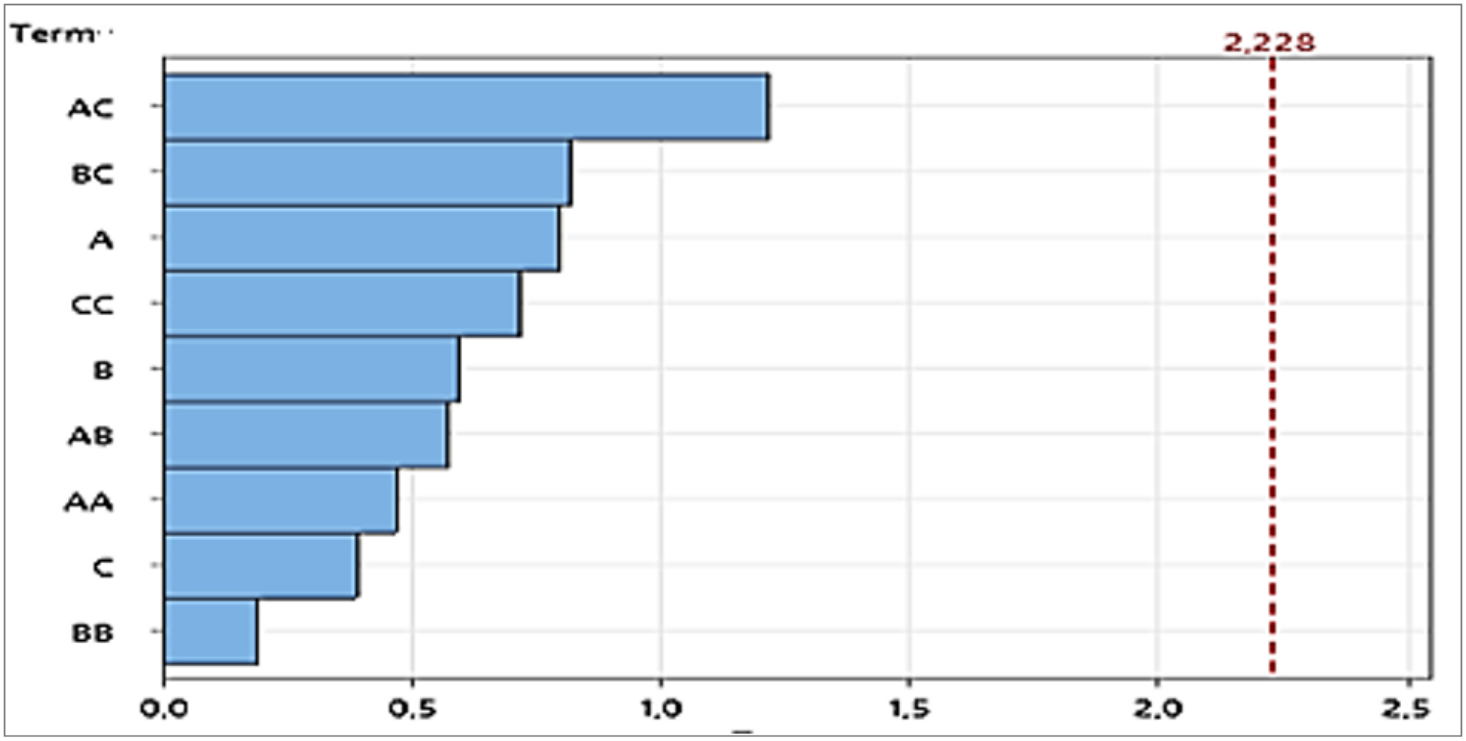


Figure 7

Pareto charts standardized effects of cellulose content

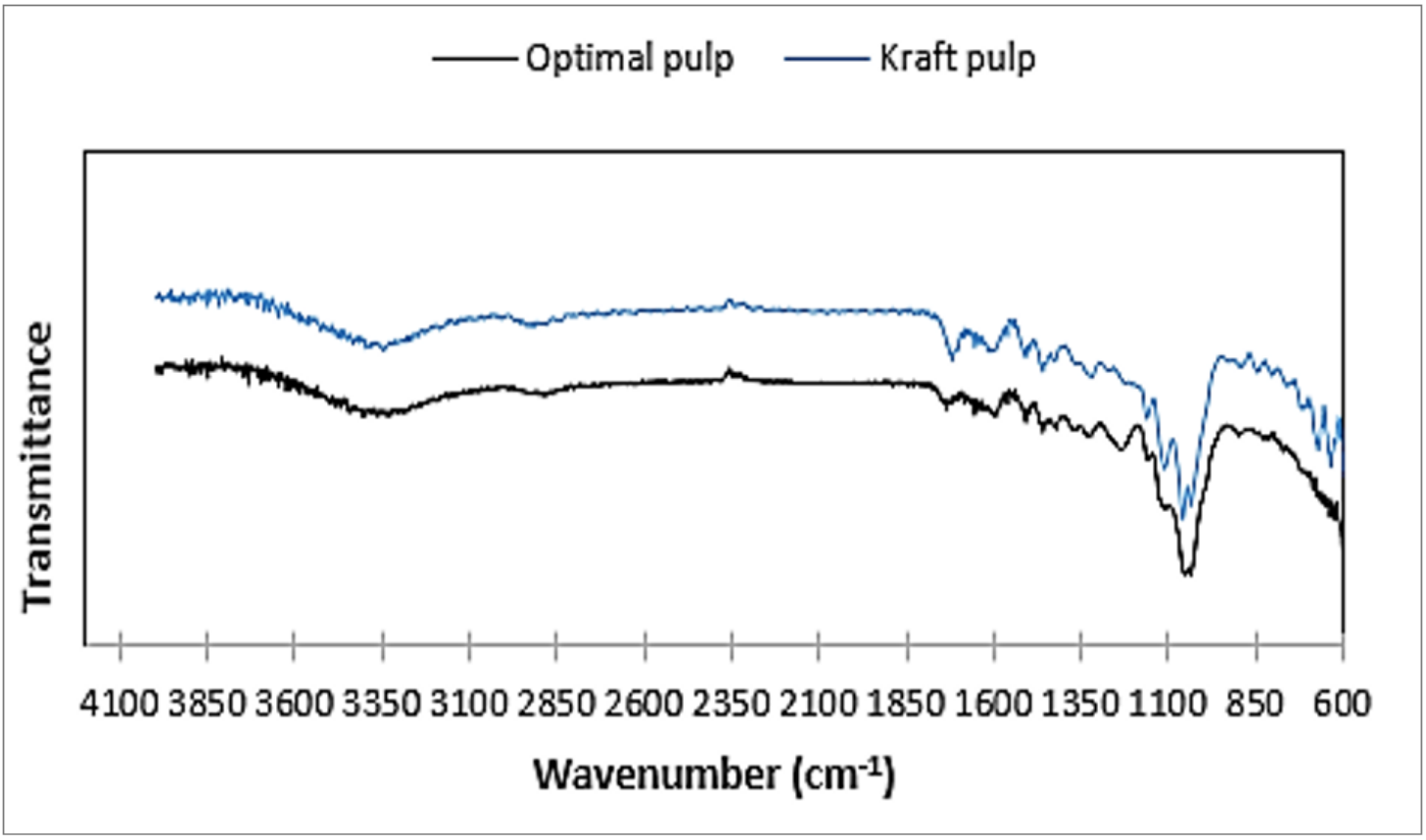


Figure 8

Comparison of the ATR-FTIR spectra of the unbleached optimal pulp and the kraft pulp

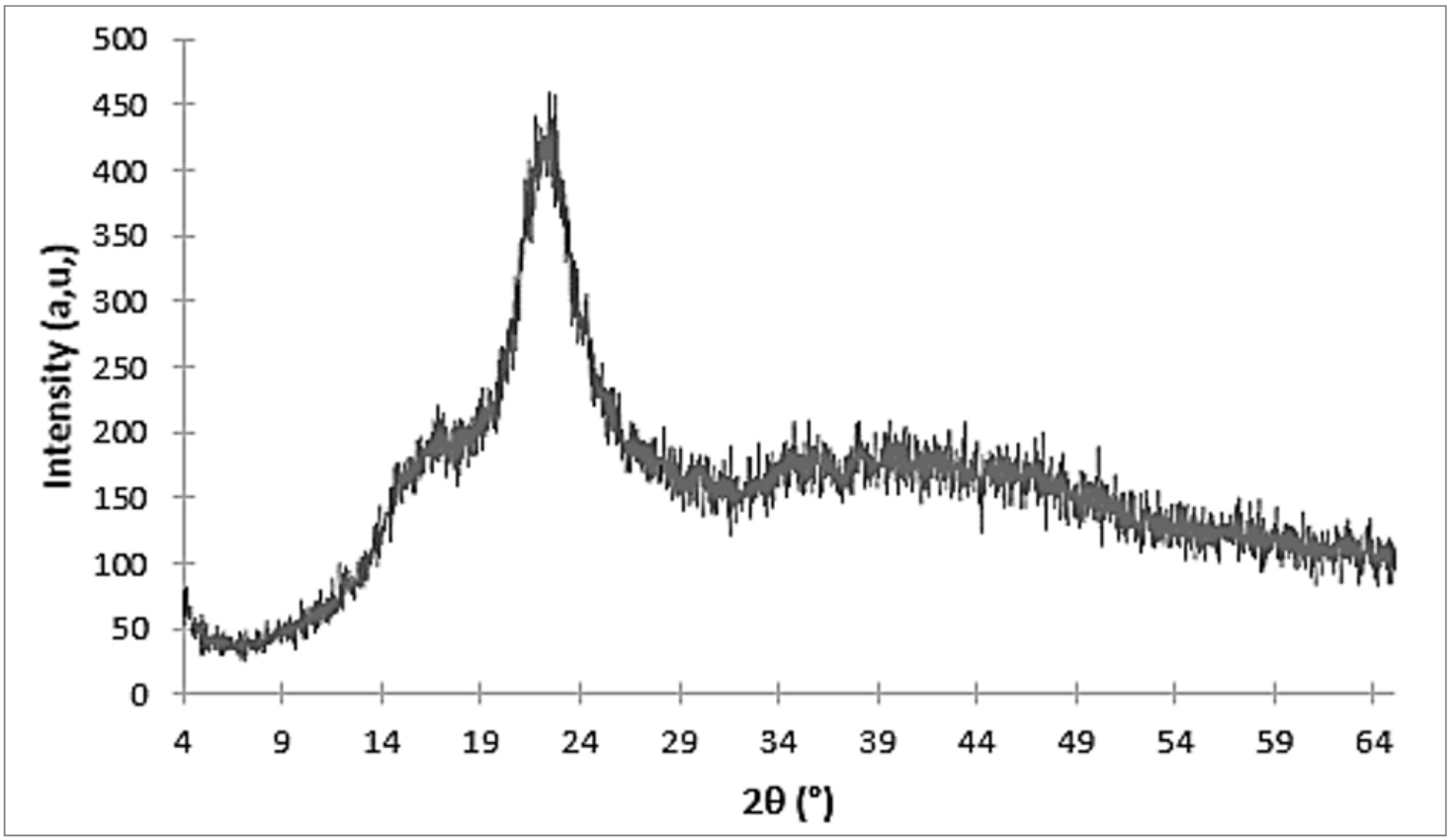


Figure 9

X-ray diffraction pattern of the optimal pulp

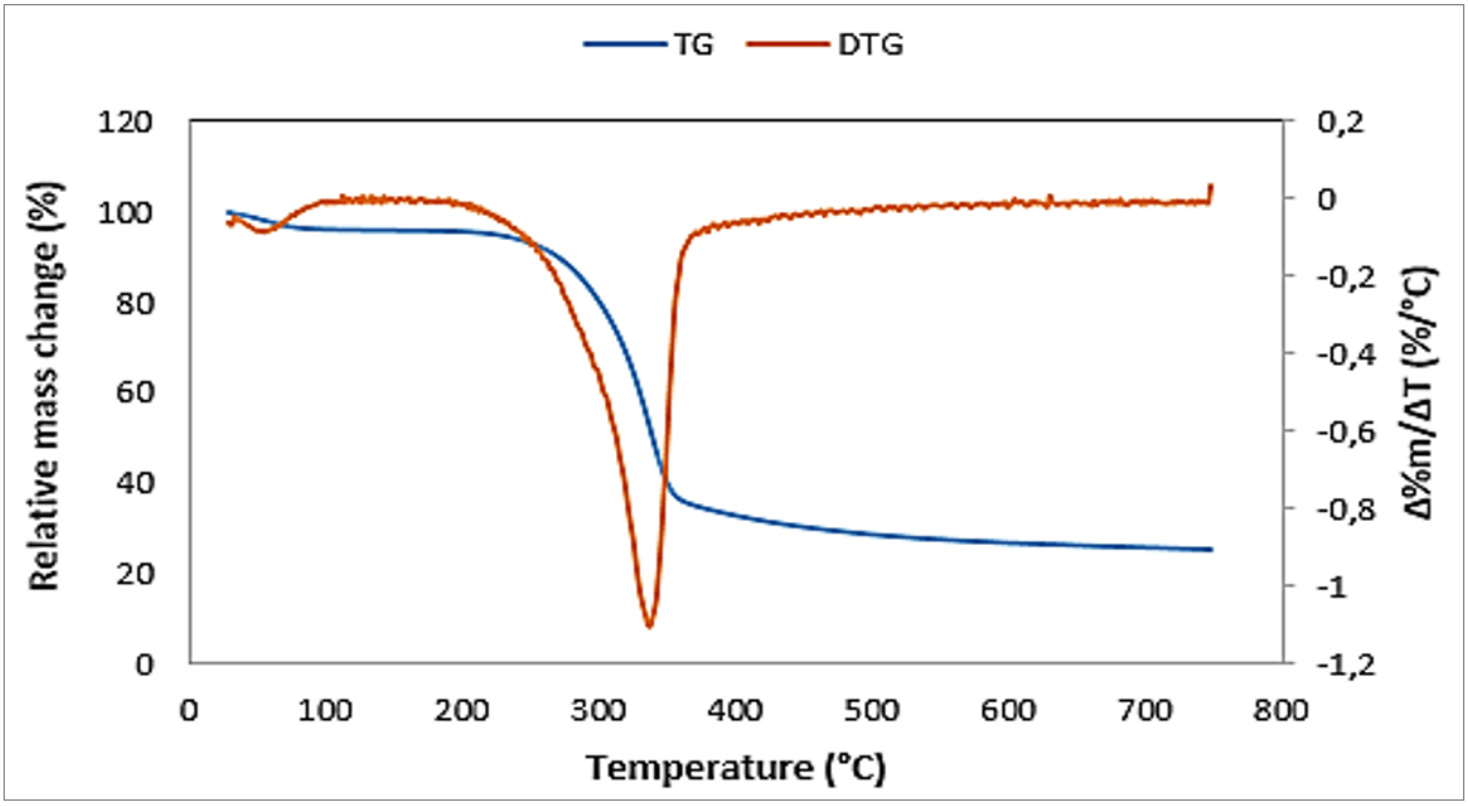


Figure 10

TG and DTG curves of the optimal pulp