Preparation and characterization of cellulose by delignification of Eteng (Ceiba pentandra) wood in formic acid-acetic acid-water solvent mixtures

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Abstract

Cellulose is a natural polymer obtained from plants with applications in various industrial sectors such as pulp and paper, textiles, coatings, fiber composites, and nanomaterials. This work studied the extraction of cellulose from a tropical agricultural plant residue (*Ceiba pentandra*) using formic acid (FA)-acetic acid (AA)-water (Wa) mixtures as a function of temperature, time, and composition the cooking solvent mixture. Three different volume ratios FA: AA: Wa of 50:30:20, 40:40:20 and 20:30:50 were investigated. Reaction temperature was varied between 80° and 107°C and the duration between 40 and 200 min. The efficacy of the cooking reaction was determined by the fiber percent yield and kappa number of the cooking residue. Cooking residues with relatively higher yields (50–70%) were obtained compared to the conventional Kraft method. The residues with yields between 50–60% were bleachable as revealed by their Kappa numbers of around 10–12. Some residues were bleached and the products were characterized by Fourier Transform Infrared (FTIR) spectroscopy, thermogravimetric analyses (TG-DTG) and X-ray diffraction (XRD). The results showed that the bleached products had properties close to those of commercial cellulose exhibiting almost similar FTIR spectra and TG-DTG curves. The activation energy of the cellulose was between 93–141 kJ mol^{-1} showing that, for the case of high activation energy (141 kJ mol^{-1}), cellulose of high quality was obtained. Formic acid, acetic acid and water mixtures can be used as relatively a soft route (at mild temperatures, atmospheric pressure) to produce cellulose from the tropical lignocellulosic residues of *Ceiba pentandra*.

Introduction

Lignocellulosic biomass is a natural resource which can be converted in a large scale into various industrial products. Lignocellulosic materials are made up of cellulose, hemicelluloses, lignin and extractives. Cellulose, which generally represents 30–55% of lignocellulosic material dry mass, is the most abundant natural polymer on earth [1]. Cellulose has found many applications in various industrial sectors including pulp and paper, textiles, paint, plastic, water treatment and composite materials, adhesives, and coatings [2–4]. A step-wise process comprising a preliminary delignification, followed by bleaching and purification, is required to obtain cellulose from the lignocellulosic materials. Generally, alkaline processes such as soda and NaOH-Na_2S or acidic bisulfite are used in the delignification step [5, 6]. Some drawbacks, e.g. corrosion of the equipment, cost of the investment and energy consumption due to high temperatures and pressures, and environmental awareness related to the toxicity of released gases and wastewater, are raising the need for improvements or alternative delignification processes [7]. Several routes using aqueous organic solvents such as acetone, ethanol, methanol, and formic acid are being developed around the world [8]. These alternatives aim also to minimize energy consumption and reduce carbon dioxide (CO_2) emissions during pulping.

The delignification of lignocellulosic materials using mixtures of low boiling carboxylic acids (formic and acetic acids) and water has received much attention recently. It is reported that this technology can allow work at relatively low temperatures under atmospheric pressure, recycling the solvents, and recovery of

lignin and hemicelluloses for various applications. Hemicelluloses obtained by this method have been used for biofuel production and animal feed, while lignin extracted by formic acid/acetic acid/water mixtures has shown promising applications in phenoplast and aminoplast resins, adhesives, and polyurethane products [9–11]. However, the application of this technology is subject to some drawbacks related to the quality of the pulp (cooking residues) and bleaching requirements, and selectivity towards the raw lignocellulosic materials [12]. The ability of a lignocellulosic material to undergo delignification under some specific conditions varies with the nature and chemical composition of the material; softwoods are, for example, are easier delignified than hardwoods because of their relatively lower lignin content and higher impregnability by delignification reagents [13]. Agricultural residues, which usually have lower lignin contents, are more susceptible to delignification than wood species. For instance, the treatment of wheat straw using formic acid/water (90:10 mass ratio), at a temperature of 100°C for 1 h was reported to remove 85% of lignin with a pulp yield of 44.4% [14]. The yield of delignification under the experimental conditions (HCOOH/Water ratio of 80:20; 90°C; 90 min) was 46 % for a softwood (Eucalyptus globulus) and 39 % for a hardwood (chestnut) [15, 16]. It has been reported that a formic acid-acetic acid-water mixture has both hydrophilic and hydrophobic behaviors which improve the dissolution of lignin and some polar and non-polar extractives and cause hydrolysis of hemicelluloses without degrading the linear cellulosic polymer [17]. The influence of the combination of formic acid, acetic acid and water and their relative contents in the delignification process and nature of the cellulosic fibers is not well understood.

In this work, eteng wood (*Ceiba pentandra*), an agricultural residue, was investigated as a raw material for the production of cellulosic fibers. The wood species was selected for its high cellulosic and low lignin contents which make this resource a potential candidate. Different solvent compositions of formic acid (FA)-acetic acid (AA)-water (Wa) were applied to eteng wood particles of sizes between 315 and 200 µm. The cooking process was characterized by its delignification yield and Kappa number. The cellulosic fibers obtained in the best conditions were bleached and characterized by Fourier Transform Infrared spectroscopy, X-ray diffraction, and thermal analysis (ATG-DTG). The delignification was studied as a function of temperature (80°C, 90°C and 107°C) and reaction time (40–200 min).

Materials And Methods

Materials

Eteng (also known as the cheese tree) (*Ceiba pentandra*) wood was collected in the district of Mbalmayo in the Centre region of Cameroon. The wood residues were air-dried in the laboratory, cut into small pieces and dried in a vacuum oven at 40°C for 24 hours. The wood was then ground using a Retsch-DR 100 grinder. The powder obtained was sieved using AFNOR standard sieves (NFB 52-001-1) with pore sizes of 200 and 315 µm. All chemicals used were reagent-grade and without further purification.

Delignification reaction

The cooking liquors were freshly prepared before each experiment by mixing formic acid (FA), acetic acid (AA) and distilled water (Wa). Three volume ratios FA: AA: Wa were investigated: $Cell_3$ (50:30:20), $Cell_2$ (40:40:20) and $Cell_1$ (20:30:50).

The delignification treatment was carried out according to the method proposed by Sarwar with a slight modification [18]. In a typical experiment, wood powder and the solvent mixture were put, at a solid-to-liquid ratio of 1:15 (m/v), in a 250-mL conical flask and left to soak for 1 h at room temperature (25 ± 5°C). The mixture was then placed in an oil bath stabilized at the reaction temperature and refluxed while stirring for a defined reaction time. A pre-heating time of 15 min was considered at the beginning of each cooking for the mixture to reach the temperature of the reaction. After the defined reaction time, the suspension was cooled in cold water and filtered on a glass crucible n° 4 to remove the solubilized components. The solid residue was successively washed with hot water, 1% NaOH solution, and cold distilled water to neutral pH. The yield of the treatment was calculated using Eq. 1:

$$R = \frac{M_i - M_s}{M_i} \times 100$$

1

where M_i is the dry mass of the sawdust and M_s the dry mass obtained after extraction. Delignification reactions in FA/AA/Wa mixtures were compared with Kraft and Alcell delignification of the same wood species. The Kraft delignification was carried out in a closed reactor at 170°C for 180 min. The alkaline charge was 25.6%, sulfidity was 30% and the solid-to-liquid ratio was 1:8. The Alcell delignification was also carried out in closed reactor at 150°C for 180 min in a mixture of ethanol and water in the ratio 60:40 with the addition of 15% sodium hydroxide based on the mass of wood sawdust. The solid-to-liquid ratio was then 1:10.

Bleaching and purification of cellulose-rich residues

A peroxide-soda treatment and purification with sodium chlorite were applied according to the protocol described by Fitriana with modifications [19]. The solid residue obtained after the treatment with FA/AA/Wa mixtures was introduced into a 100-mL ground-glass neck flask, and a hydrogen peroxide-NaOH-water solution, prepared by mixing (H_2O_2, 2%):(NaOH, 1%) in a ratio 5:1 (v: v), was added. The mix was placed in a thermostatic bath at 80°C for 1.5 h. The experiment was repeated four to six times until the paste became white. The white solid was washed with hot water and then cold water to a neutral pH. Purification was performed by extraction with a sodium chlorite solution ($NaClO_2$, 5%) at 70°C for 1 h, repeated four (4) times. The purified white residue was washed with hot water and then cold water and dried. The photographs of the raw eteng wood and solid residues at different stages of the process are shown in Fig. 1.

Chemical composition of Eteng wood

The chemical composition, i.e. the extractive, ash, cellulose, lignin and hemicellulose contents of eteng wood, was determined according to the protocols widely described in literature [20, 21]. All analyses were performed in triplicate for each sample and the average result was reported.

Kappa number of delignified Eteng wood

The Kappa numbers of the unbleached pulps were determined according to the TAPPI standard T236 cm-85. A mass of 30 mg (oven dry) of the unbleached pulp of each treatment was introduced into a 50-mL conical flask. The pulp was disintegrated in 10 mL of distilled water and put in a thermostatic bath at 30°C for 10 min. 1 mL of a sulphuric acid solution (4 N) and 1 mL of a potassium permanganate solution (0.1 M) were added. After 10 min of stirring, the reaction is stopped by adding 200 µL of potassium iodide KI (0.1 M). The iodine remaining in solution was titrated with a sodium thiosulphate (0.1 N) solution. The Kappa index K was determined by the Eq. 2:

$$K = \frac{(b-a)N}{0.1W}$$

2

where a is the volume of sodium thiosulphate consumed to the equivalent point, b the volume of sodium thiosulphate consumed for the blank (without solid residue), N the normality of sodium thiosulphate, and W mass of the solid residue for the experiment.

Characterization

Fourier Transform Infrared-Attenuated Total Reflectance (FTIR- ATR) spectra were recorded using a Bruker Alpha-P spectrometer equipped with a diamond crystal and driven by Opus/Mentor software. Each spectrum was recorded by carrying out 32 scans over the spectral range from 500 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

Thermogravimetric analyses were carried out in a nitrogen atmosphere using a TGA/SDTA 851 Mettler Toledo apparatus at a heating rate of 10°C/min. This analysis was used to evaluate the purity of the cellulose and to determine the activation energy (E_a). The activation energy was calculated using the mathematical model of Broido (Eq. 3). The activation energy value provides information on the suitability of pulp as a reinforcing filler in certain composites [22]. It was evaluated in the temperature range of 320 to 350°C.

$$\ln\left[\ln\left(\frac{1}{y}\right)\right] = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}+K\right)$$

3

where R is the universal gas constant (8.31 J mol^{-1} K^{-1}) and y the normalized weight (W_t/W_o).

The normalized form of the mass decrease data from the decomposition, noted βwas calculated as follows (Eq. 4):

$$\beta = \frac{W_0 - W_t}{W_0 - W_f}$$

4

where W_o is the initial mass of the sample, W_t the mass at the temperature T and W_f the residual mass after combustion

The analyses were carried out using an XPERT-PRO diffractometer, equipped with a Cu kα anode tube (λ = 0.154 nm), a 40 kV voltage generator, a 40-mA current tube at a scanning speed of 2°C/min. The crystallinity was obtained according to Segal's method in Eq. 5.

$$CI = \frac{I_M - \mathrm{I}_m}{I_M} \times 100$$

5

Where CI is the crystallinity index, I_M the maximum diffraction intensity at 2θ = 22 to 23° and I_m the background scattering intensity observed around 2θ = 18°.

Results And Discussion

Chemical and physical compositions of eteng wood powder

The chemical composition and some physical properties of eteng wood are shown in Table 1.

Table 1
Chemical composition, equilibrium moisture content and density of eteng wood

Chemical Composition				**Physical Properties**		
Cellulose (%)	Hemicellulose (%)	Total Lignin (%)	Extractives (%)	Ash (%)	Moisture (%)	Density (g cm^{-3})
48.1 ± 0.7	19.1 ± 0.4	19.5 ± 0.2	6.5 ± 0,5	2.60 ± 0.1	8.2 ± 0.2	0.33 ± 0.01

The density in Table 1 shows that eteng wood is relatively light. This density is closer to the density range of softwoods than that of hardwoods. The equilibrium moisture content of the wood is in line with the result of Soares who found that moisture content of low-density wood species was around 8% [23]. The cellulose content of eteng wood is relatively high while the lignin content is low. The percentage of cellulose in other agricultural residues such as corn stalk (*Dracaena fragrans* Massangeana) and wheat

straw (*Triticum*) is around 37 % while the lignin content is estimated between 7 and 19% [24, 25]. In tropical hardwood species, the lignin content is generally between 25 and 40% which means more lignin to depolymerize for cellulosic fiber recovery [26]. As a result, delignification of tropical woods becomes very difficult, making eteng a credible source for cellulose preparation in the tropics. These results place eteng wood among the potential candidates for cellulose production.

Influence of temperature, reaction time and solvent concentration on delignification yield

The delignification reactions were followed by the determination of percent yield, i.e. the percentages of the raw material dissolved and extracted in the cooking process. The results are shown in Fig. 2 as a function of temperature, of reaction time, and of cooking solvent composition.

The results of FA/AA/Wa treatments in Table 2 show higher pulp yields than Kraft and Alcell treatments. The pulp obtained for 20:30:50 ratio was unbleachable, proof that the delignification was not successful under this condition. The bleaching capacity of the pulp obtained with the 50:30:20 ratio was 10.5 for a yield of 62.8%. The Kappa number for the Kraft pulp was in the same range, 10.9 with a yield of 53.7%. Although the pulp yield of Alcell pulp was relatively lower compared to FA/AA/Wa pulps, its Kappa number was high. These results show that the treatment of eteng wood in FA/AA/Wa solvent system can produce cellulosic pulps with good yields and acceptable Kappa numbers for bleaching

Table 2
Comparison of pulp yields of eteng wood by FA/AA/Wa treatment, Kraft and Alcell processes (reaction time 180 min)

Process	Proportion	Temperature (°C)	Pulp yield (%)	Kappa number
FA:AA:Wa	50:30:20	107	62.8	10.5
	40:40:20	107	69.8	12.1
	20:30:50	107	70.18	-
Kraft	-	170	53.7	10.9
Alcell	-	150	57.7	15.2

FTIR analyses of bleached cellulose from eteng wood

Figure 4 shows the FTIR spectra of cellulose obtained from delignification in FA/AA/Wa and bleached with alkaline hydrogen peroxide and sodium chlorite solutions. The assignments of the vibration bands were carried out based on literature and reported in Table 3.

Table 3
Assignment of the main FTIR vibration bands spectra eteng celluloses

Wavenumber cm^{-1}	Band assignment	References
3269	O-H stretching	[28]
2912	C-H stretching in methylene and methyl groups	[29]
1740	C = O stretching in lignin and hemicellulose	[30]
1652	H-O-H adsorbed bending	[31]
1507	Aromatic nucleus vibration	[32]
1343	Stretching and deforming vibrations of the C-H group of cellulose	[33]
1035	C-O stretching	[34]
888	Stretching of C-H glysidic β-1,4 bond of cellulose	[35]

Raw eteng wood showed a spectrum similar to the spectra of other lignocellulosic materials reported in literature [36]. Most vibrations bands are the sum of contributions of functional groups present in carbohydrates and lignin. The band at 3269 cm^{-1} is assigned to O-H stretching and the bands at 2912 cm^{-1} and 2851 cm^{-1} due to symmetric and asymmetric stretching vibrations of C-H in methylene and methyl groups, and the band at 1053 cm^{-1} is assigned to C–O stretching provided by the three main components of cellulose, hemicelluloses and lignin [35]. However, the vibration bands of carbonyl (C = O) group centered at 1740 cm^{-1} and the double bands at 1600 cm^{-1} and 1507 cm^{-1}, attributed to vibrations of aromatic rings, are proof of the presence of hemicelluloses and lignin in the material. The decrease of the intensity of these bands, especially observable with the bands at 1740 cm^{-1} and 1500 cm^{-1}, show the removal of lignin and hemicelluloses. The band at 1507 cm^{-1} was still observed in $Cell_0$, $Cell_1$ and $Cell_2$, showing the presence of residual lignin in these samples even after bleaching and purification. However, this band was not observed in $Cell_3$ and the spectrum of commercial cellulose, suggesting the complete absence of lignin in these two samples. All the spectra exhibited a vibration band around 1652 cm^{-1} associated to the bending deformation of adsorbed water due to the hydrophilic nature of cellulose and lignocellulosic materials.

Thermal Analyses

The TG-DTG thermograms of the prepared celluloses are presented in the Fig. 5.

The degradation of the raw eteng wood occurred in two main steps corresponding to a DTG shoulder at 296°C and a peak at 345°C. The small shoulder was associated to the degradation of hemicelluloses which is the least thermally stable component of wood. The second peak corresponds to the degradation of cellulose and lignin. The DTG curves (Fig. 5(b)) of $Cell_3$, $Cell_2$, $Cell_1$ and $Cell_0$ exhibited only one peak

confirming at least the absence or relatively low amount of hemicelluloses in the samples. DTG analyses of cellulose in literature revealed one peak [37]. Degradation begins at 300°C and above. Literature reports that β-cellulose degradation occurs at 330°C and α-cellulose occurs at 351.3°C [38].

The activation energy obtained by the Broido method in Fig. 6 using the Arrhenius equation at temperatures ranging from 320 to 340°C are presented in Table 4. This the activation energy (E_a) was obtained from the slope of each line presented in the Fig. 8. This energy (E_a) justifies the suitability of the reinforcement in composite materials at high temperature [39]. The energy values of raw and treated wood particles depend on the optimization of the treatment parameters. The energy of raw particles and treated $cell_0$, $cell_1$, $cell_2$, $cell_3$ were 73.8 kJ K^{-1} mol^{-1} and 93.0 kJ K^{-1} mol^{-1}, 93.5 kJ K^{-1} mol^{-1}, 130.03 kJ K^{-1} mol^{-1} and 141.12 kJ $K^{-1}mol^{-1}$ respectively. The activation energy depends on the nature and purity of extracted cellulose. $Cell_3$ exhibited the highest value of E_a compared to $Cell_0$, $Cell_1$ and $Cell_2$. The increase of E_a values implies an increase of the thermal stability of the samples. Hemicelluloses degrade generally at low temperatures and their presence in the sample can facilitate the degradation of cellulose lowering the activation energy. E_a values of 118 kJ/mol K were reported for a Kraft pulp from hardwoods [40]. The high values of E_a obtained for $Cell_2$ and $Cell_3$ suggest that these celluloses are of higher quality.

Table 4
Activation energy for cellulose degradation

Test	Linear equation	$E_{a\ (kJ\ K^{-1}mol^{-1})}$	R^2	rate convection β
Raw	Y= -8871.9 x + 13.987	73.8	0.996	0.974
Cell0	Y= -11204x + 18.035	93.2	0.997	0.967
Cell1	Y= -11249 x + 18.408	93.5	0.998	0.966
Cell2	Y= -15640 x + 25.447	130.03	0.999	0.957
Cell3	Y= -16981 x + 27.385	141.12	0.998	0.955

X-ray diffraction analysis (XRD)

The X-ray diffraction patterns of raw eteng wood, reference cellulose (Ref) and cellulose ($Cell_3$) are shown in Fig. 7. The cellulose obtained by Alcell ($Cell_0$) was added for comparison.

The structural parameters of the cellulose microcrystals deduced from Fig. 7 are shown in Table 5.

Table 5
recapitulated structural parameters of raw sample and resulting celluloses

Sample	Intensity	Angle 2θ (°)	Theoretical Intensity	h. k. l	Crystallinity (%)
Raw	204.21	22.2	100	2.0.0	53.9
	122.86	16.7	60	1.1.0	
Ref	320.57	22.7	100	2.0.0	65.1
	144.7	18.3	47	1.1.0	
$Cell_0$	309.99	22.4	100	2.0.0	69.3
	144.15	15.8	47	1.1.0	
$Cell_3$	388.84	22.6	100	2.0.0	72.95
	165.15	16.5	42	1.1.0	

The peaks at 2θ between 15° and 17° and 2θ between 22° and 23° are attributed to the planes (110) and (200) of the crystalline area of the samples [37, 41]. The similarity of the XRD spectra demonstrates that the extraction process does not modify the structure of the cellulose. The increase of the crystallinity of the cellulose samples compared to that of the raw wood can be explained by the extraction of amorphous polymers (lignin and hemicelluloses) [42]. The same order of crystallinity is generally presented in the literature for cellulose, and even high values up to 90% for cotton [37]. The crystallinity of $cell_3$ obtained by this FA/AA/Wa process is slightly higher than the crystallinity of reference commercial cellulose and Alcell cellulose ($Cell_0$). This shows that the process can be efficiently used to production of cellulose.

Conclusion

The extraction of cellulose from a tropical wood material (Eteng) using formic acid-acetic acid-water solvent mixtures was studied under mild conditions (temperature between 80°C and 107°C, atmospheric pressure, and reaction times between 40 and 200 min). Formic acid: acetic acid: water volume ratios of the solvent mixtures investigated were 50:30:20, 40:40:20, and 20:30:50. These solvent mixtures produced bleachable residues under some conditions with relatively good yields between 50 and 60%. The solvent mixture with high formic acid content appeared to be most suitable for producing cellulose. The increase of temperature to 107°C and longer reaction times appeared to increase the delignification rate and the Kappa number of the cooking residues. FTIR spectra, TG-DTG and XRD diffractograms of cellulose obtained were comparable to those of reference commercial cellulose, Kraft and Alcell celluloses from eteng obtained by this route. The best cellulose sample obtained in 50:30:20 formic acid-acetic acid-water mixture exhibited high activation energy (E_a = 141.12 kJ mol^{-1} K^{-1}) and high

crystallinity rate (72.95%) compared to Kraft and Alcell celluloses. The results suggest that high quality cellulose can be obtained from tropical species using this route for pulp and nanocellulose-based composite materials.

Declarations

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The authors declare that they have no conflict of interest.

AUTHOR CONTRIBUTIONS

All authors contributed to the study’s conception and design.

Material preparation and synthesis were performed by Herman Lekane Assonfack and Josiane Bertille Nga.

Data collection and analysis were performed by Herman Lekane Assonfack, Derek Ndinteh and Jordan Tonga Lembe.

The first draft of the manuscript was written by Herman Lekane Assonfack and all authors commented on previous versions of the manuscript.

All authors read and approved the final manuscript.

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Figures

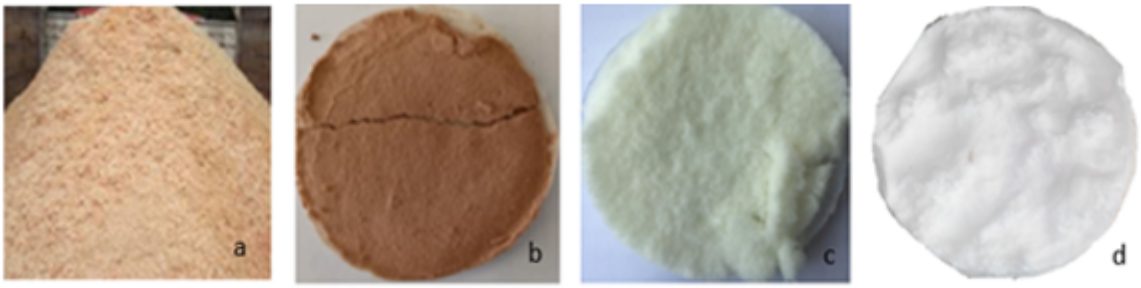

Figure 1

Physical appearance of solid residues at different stages of the delignification process (CelL3) (a) raw material (b) after delignification (c) bleaching with H2O2: NaOH and (d) purified with NaClO2 solution

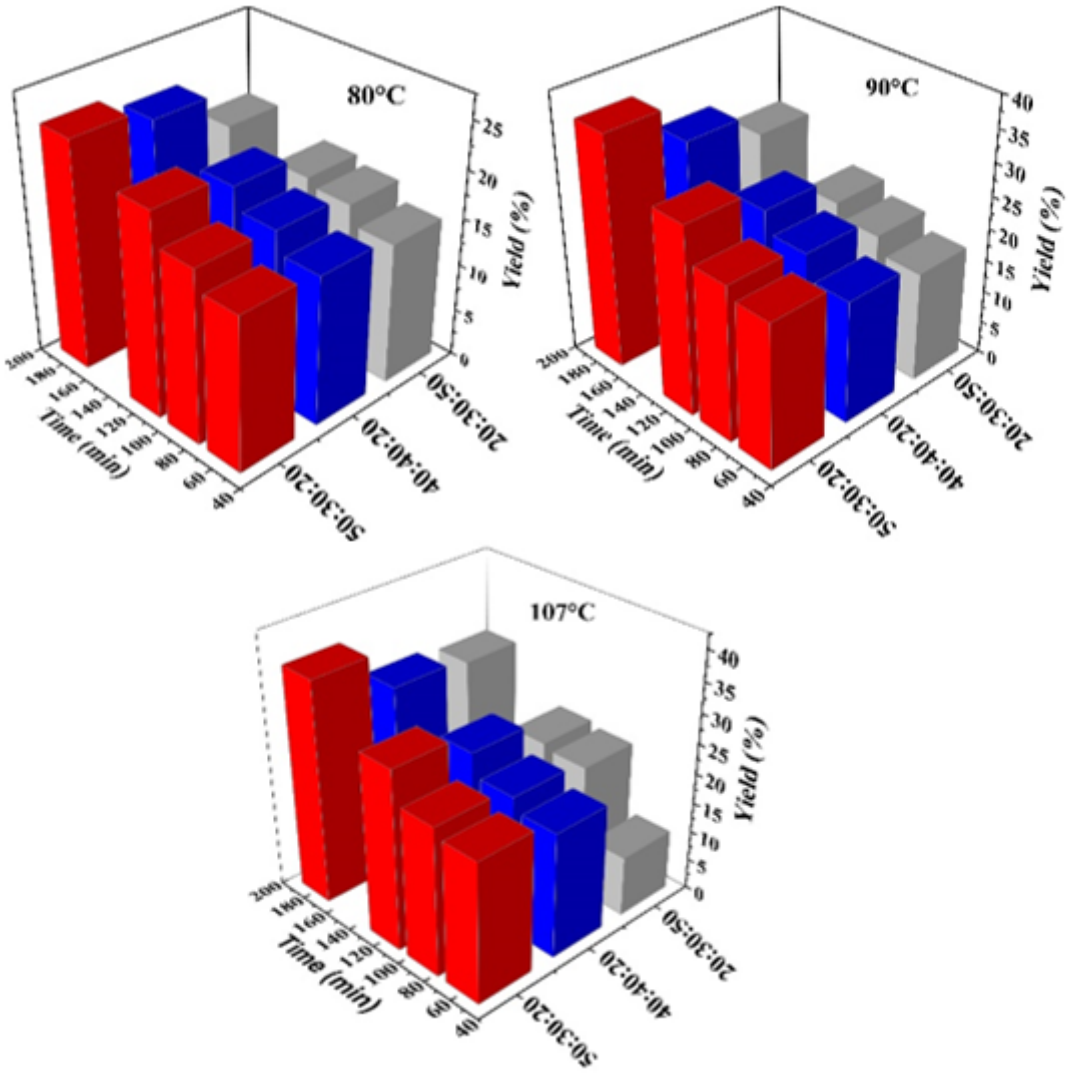

Figure 2

Delignification yield as a function of reaction time and solvent composition et different reaction temperatures

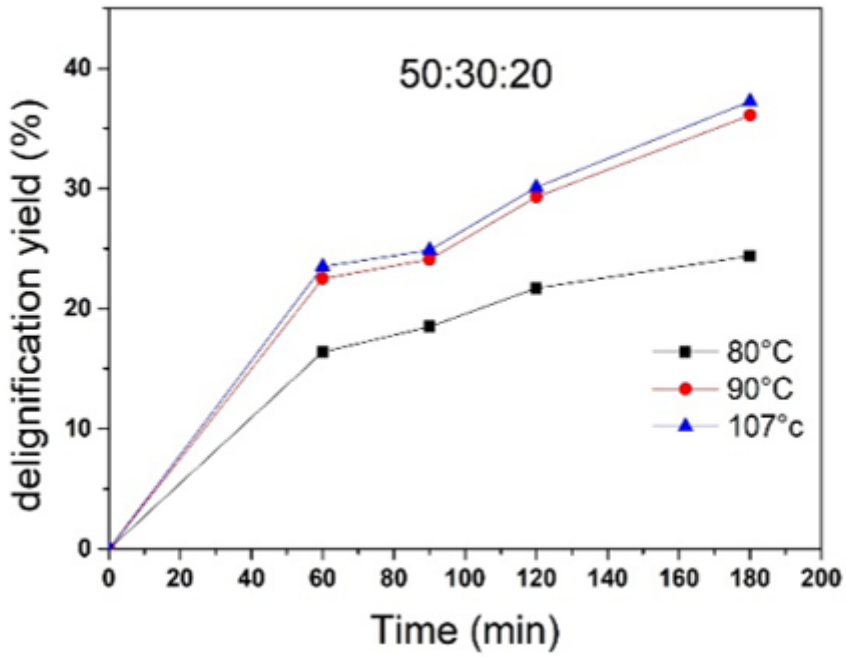

Figure 3

Influence of reaction temperature on delignification yield for the FA:AA:Wa solvent mixture 50:30:20

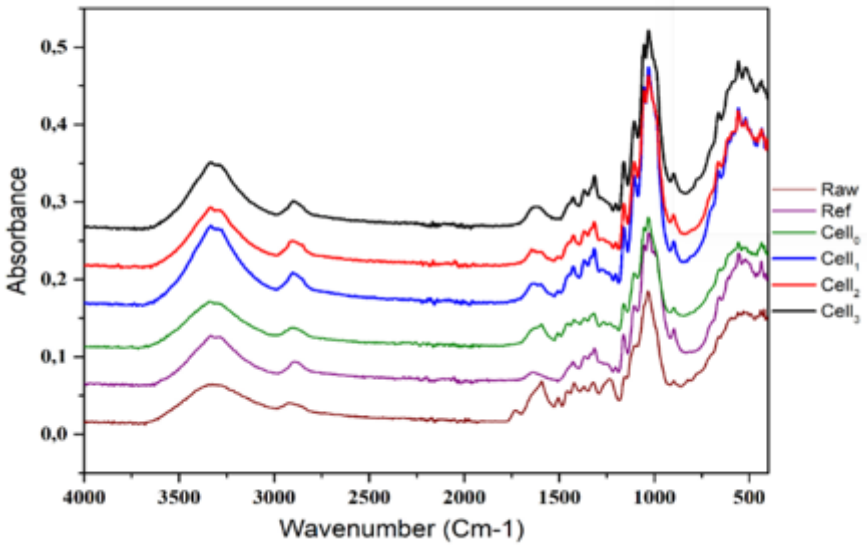

Figure 4

FTIR spectra of bleached eteng wood cellulose obtained in different FA:AA:Wa solvent mixtures (Cell1) 20:30:50, (Cell2) 40:40:20, (Cell3) 50:30:20 at 107°C and 180 min. Cell0is Alcell cellulose from Eteng wood obtained 150°C and 180 min. (Raw) is the raw Eteng wood and (Ref) a commercial cellulose were added for comparison.

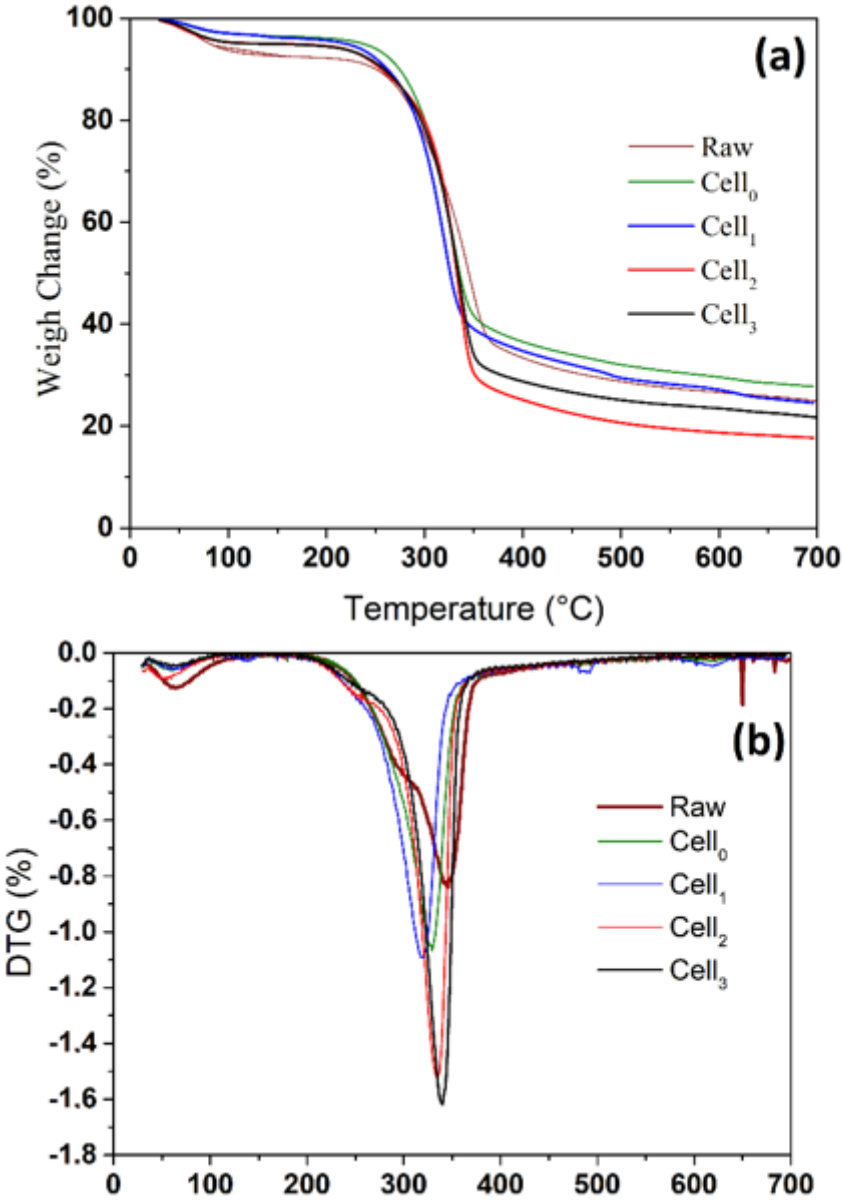

Figure 5

The TGA (a); DTG (b) curves of raw eteng wood and celluloses obtained

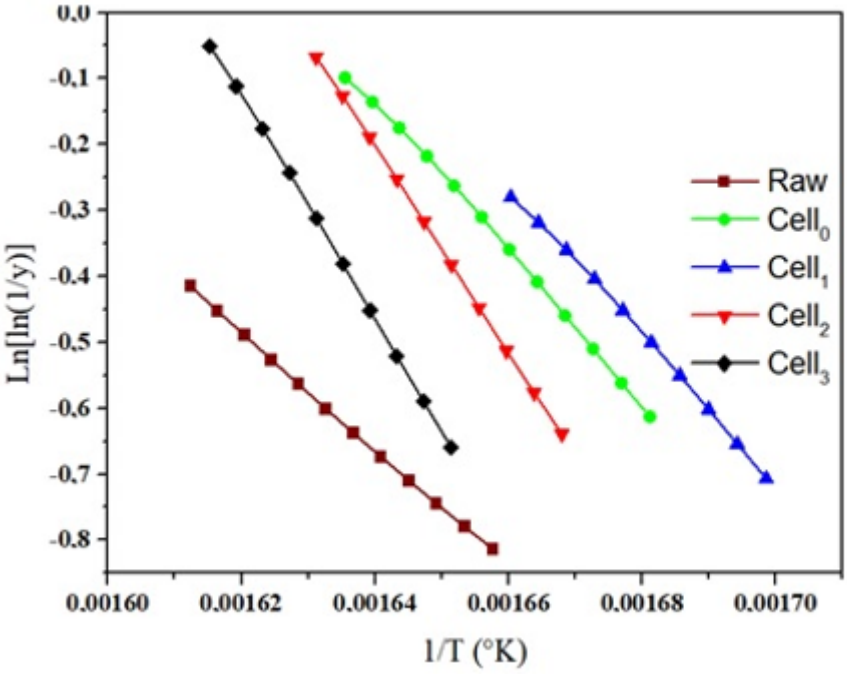

Figure 6

Broido diagram of resulting celluloses

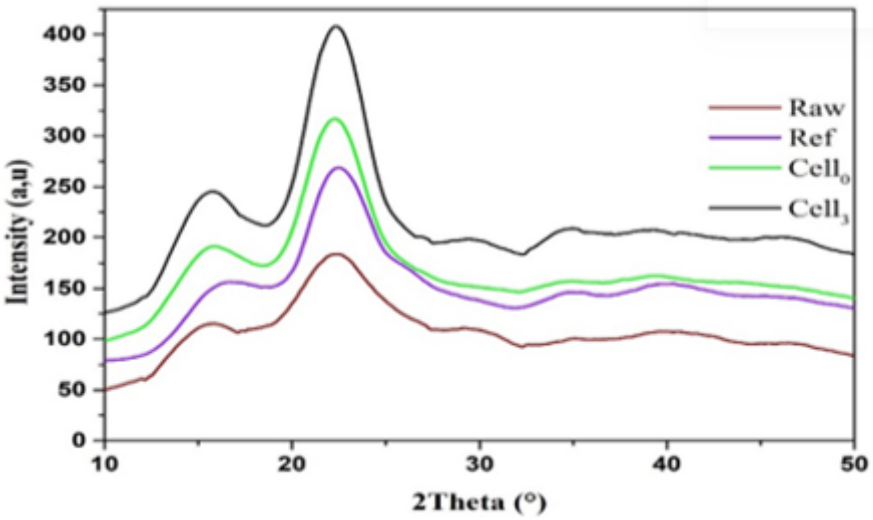

Figure 7

X-ray diagrams of raw wood and treated residues (Cell3and Cell0)