

## The Structural Analysis of the Lignocellulose, Champaca Timber (*Elmerrilliaovalis*) Modified by the Microwave

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The present work aims to analyze the structural change of a biomass from champaca timber (*Elmerrilliaovalis*) pretreated by the microwave. The treated substrates were analyzed employing XRD, FTIR, and SEM and compared with an original substrate (without pretreatment) and an acetylcellulose. The microwave was set its electrical power at 300 W; 40min., 300W; 10min., 1000W; 8min. Results showed that the pattern of XRD curves of the treated biomass significantly changed compared with that of native solid. The crystalline index (Crl) of an original substrate was of 0.60 and decreased to 0.36 for solid treated by the microwave 300W for 40min. When the microwave power increased to 1000W for 8min, the Crl value decreased to 0.12 that was relatively similar with an acetylcellulose. Meanwhile, the intensity of transmitted infrared wave increased for a microwave-treated substrate that was indicative many hydrogen bonds via hydroxyl groups were broken. SEM image showed that the surface morphology of microwave-treated substrate was completely transformed in which it was modified significantly and could increase the enzymatic hydrolysis of sugar production. While, structural surface of acetylcellulose was quite different if compared with the *Elmerrilliaovalis* substrates.

### 1. Introduction

The lignocellulose is one of the options considered as a resource for renewable material for wide range applications and a candidate of an alternative energy in coming years to substitute the fossil based fuel (Chatzidakoula et al., 2017). However, since connections of cellulose are  $\beta(1\rightarrow4)$ -glycosidic bonds, lignocelluloses were difficult to trim into simple monomers. It was known the beta (1 $\rightarrow$ 4)-glycosidic bond in cellulose is much stronger than that of  $\alpha(1\rightarrow4)$ -glycosidic chains of starch which are an amorphous structure. The rate of liberation of monomers from polysaccharides into simple monomers in hydrolysis process depends on the strengths of bonds and the crystallinity of biomass. Pretreatments are very critical in lignocellulosic processing becoming sugars and biofuels. Prior to conversion to fermentable sugars, lignocellulose should be pretreated, which was aimed to modify its structure in order to improve an enzymatic hydrolysis. Many methods have been applied to pretreat the lignocellulose as follows: ionic liquid, sub-critical, explosion, super-critical, acid and alkaline.

Acid and alkaline have been used for decades to pretreat biomass, such as rice straw, wood and organic waste (Chaudhary et al., 2012). The results showed that crystal changed into an amorphous structure and then enzymatic hydrolysis increased significantly. Alkaline (NaOH) could transform the biomass structure and could dissolve the lignin (Zhang et al., 2016). Authors reported that the synthesized ionic liquids had a capability to undermine a cellulose structure and to decrease the lignin content of lignocellulose but pretreatment temperature and time were relatively high and long.

Authors, Asghari and Yoshida (2010) studied that the lignocellulosic structure could be changed by applying sub- and supercritical techniques. As abruptly pressure decrease or explosion has the ability to damage the biomass structure and to break the glycosidic bonds (Rocha et al., 2012). On the other hand, sub- and supercritical liquids were performed on some biomass, in which those were conducted in extreme conditions. Authors Piasecka et al., (2014) proposed a physical method to treat micro-algal biomass producing

a valuable product. These methods showed the good results as follows: substrates changed into amorphous form, monomers liberated directly from polysaccharides and the reaction time was 1 hour.

Those described techniques, however, face some difficulties that must be addressed in order to they are affordable and feasible in the mass production. The chemical agents, which were used on pretreatment generated a negative effect on soil and water. Since physical methods (Sub- and supercritical fluids treatments), which were performed at high pressure and temperature are considered insecure and expensive. The safety and clean technologies for pretreatment should be developed and fulfill conditions and standards of environmentally-friendly procedures. The present work is to modify the biomass structure before hydrolyzing using microwave pretreatment. Procedures are as follows: biomass drying and milling, washing step and characterization. The structures of the treated solids were measured using XRD (X-ray diffraction), SEM (Scanning electron microscopic) and FTIR (Fourier transform infrared) and those were compared to native substrates and nano acetylcellulose.

## 2. Experimental

The biomass used was timber whose its Latino name is *Elmerrilliaovalis* that grows abundantly in tropical countries like Indonesia. The wood dust was obtained freely from a traditional home industry in Minahasa Regency North Sulawesi Province Indonesia. After drying for days, biomass was milled until their size of 80-120 mesh and then powders were pretreated using a microwave (*Sharp Model R-728(W)-IN 509411215 Japan*). The nano acetylcellulose was obtained from *Bolab GmbH, Bonn, Germany* through an N-55 project, Indonesia-Germany. The original biomass was put inside cabin and then electricity was turned on by choosing power and time at 300 W; 40min., 300W; 10min., and 1000W; 8min.

All treated- and original substrates and nano acetylcellulose were characterized to analyze the structural change before and after pretreatment that followed the methods as published previously by investigators (Park et al., 2010). The XRD and FTIR employed were *PAN analytical, Type: Xpert Pro* and *SHIMADZU, type : IR PRESTIGE 21*. Meanwhile, surface morphology was imaged by *SEM FEI, Type: Inspect S50* and all measurements were done at *Central Laboratory Universitas Negeri Malang (UM) East Java*. An XRD was begun angle ( $2\theta$ ) from  $10.01^\circ$  until  $89.9^\circ$  at  $25^\circ\text{C}$  and the electricity current and potential were set at 35mA, 40kV, respectively. Waves K-alpha ( $1.54\text{\AA}$ ) and K-Beta ( $1.39\text{\AA}$ ) were scanned the samples. While FTIR measurement used the frequencies at a range of 400 - 4000/cm and the SEM performed was set its conditions as follow: electrical voltage was of 15kV; image magnifications were set at 500 and 1000x; parameters WD, the spot were maintained at 10.8 and 5.5 mm.

The crystallinity index (CrI) and crystalline percentage used equations that adapted from previous work (Kalia and Kaith 2009) and were formulated as:  $CrI = \frac{I_{22}-I_{18}}{I_{22}}$  and  $\%Crystalline = \frac{I_{22}}{I_{22}+I_{18}}$ .

## 3. Results and Discussion

### 3.1 XRD Analysis

The characteristics of cellulosic crystal are unique and the XRD patterns showed that the clear angles were at  $14.20^\circ$ ,  $16.70^\circ$ ,  $22.41^\circ$  and  $34.75^\circ$ , whose apexes belonged to planes (101), ( $10\bar{1}$ ), (002) and (040) as shown in Fig. 1. The figure shows the XRD patterns of the champaca wood treated by microwave and compared to that of the original substrate and acetylcellulose. After pretreatment, the height of XRD peak changed that was caused by the alteration of cellulosic structure and the breaking of OH-bonds, which connected between fibers (Feng and Chen 2008). It was found that (002) plane was the most damaged of planes after microwave performed. As (101) plane changed slightly not as big as of (002) and (040) planes. While the amorphous part which was represented by valley and located at  $18.53^\circ$  was relatively constant. The alteration of the crystal structure before and after pretreatment can be also seen from Table 1. The intensities of X-Ray of treated solid declined significantly at around  $22.41^\circ$  and  $34.75^\circ$  that belonged to (002) and (040) planes as shown in the table.

There is another change of XRD pattern of the substrate treated by microwave compared to original solid and acetylcellulose as shown. The symmetry of curve of treated solid significantly shifted at  $0.5-1.0^\circ$ . The crystal structure was not only changed from high- to low crystallinity but also it carried out a spacious dilatation. It was an indication that the type of crystal altered from cellulose I into cellulose II (Prado and Spinacé 2015). The parameters  $I_{22}$  and  $I_{18}$  were a diffracted X-Ray intensity at  $2\theta=22.41^\circ$  and  $18.53^\circ$  and their calculations are shown in Table 1. The crystalline index of original solid was of 0.60 and declined significantly to 0.36 after microwave treatment. The similar trend was showed of crystalline percentage. The native solid was 71.46% and treated substrate decreased to 60.89% which were relatively similar to other works (Abdulkhani et al.,

2013). The data shows that the CrI value of acetylcellulose is the least recorded at 53.10% if compared to those of treated- and original substrates.

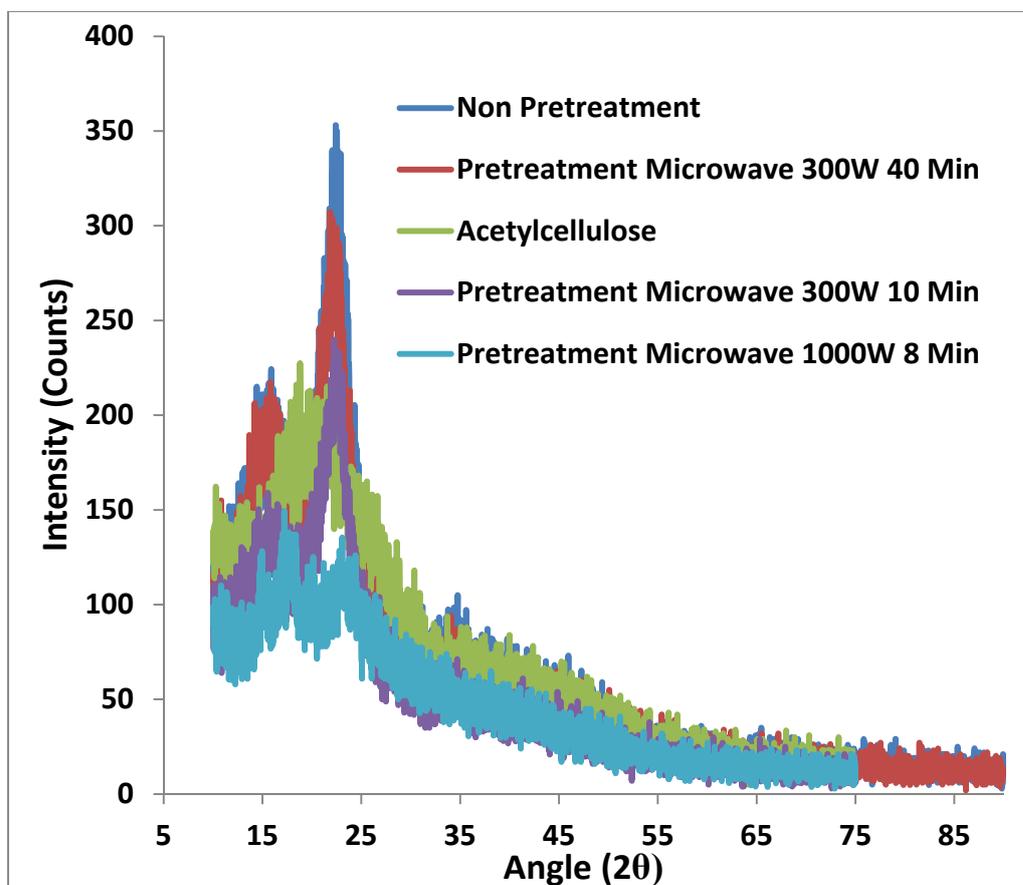


Figure 1. The XRD pattern of wood treated by microwave and compared to that of non-pretreatment.

Table 1. The crystalline index and crystalline percentage of the treated and original samples and compared with acetylcellulose

Sample	$I_{22}$	$I_{18}$	CrI	%Crystallinity
non pretreatment	353	141	0.60	71.46
Microwave pretreatment (300W; 40min.)	246	158	0.36	60.89
Microwave pretreatment (300W; 10min)	233	107	0.54	68.30
Microwave pretreatment (1000W; 8min)	114	100	0.12	53.27
Acetylcellulose	180	159	0.12	53.10

### 3.2 FTIR Analysis

The absorption of chemical bonds the infrared photons was investigated by studying the fingerprint of FTIR as shown in Fig. 2. The valley located between 750-1000/cm was absorbed by the glycosidic bonds transformed into a motion. The lowest transmittance ranged from 1029-1039/cm was absorbed by stretching vibrations of C-C, C-O, and C-C-O on cellulose, hemicellulose, and lignin. The photon energy with the wave number of 1232/cm was transferred to O-H bending motion of cellulose and hemicellulose. The wave number 1232/cm belonged to C-H bending motion on the crystalline cellulose. The C-O vibration of lignin whereby it absorbed infrared photon energy was located of 1327/cm. Meanwhile, the wave number 1369.46 was probably the bending motion of cellulose, hemicellulose, and lignin. The deformation of C-H in the plane (lignin) and OH in-plane oscillation of cellulose, hemicellulose, and lignin needed energy that was transferred by 1421.54 and

1440/cm. Vibration aromatic rings and C=O stretching of lignin was equivalent with wave number 1510 and 1595/cm. The C=O stretching that was unconjugated on lignin was of 1680/cm. The vibration of ketone or aldehyde (C=O) of hemicellulose was verified at 1732/cm, meanwhile, C-H and O-H oscillations of lignin were positioned at 2842 and 2935, and 3400/cm, that was comparable to other reports (Poletto et al., 2012; Zhao et al., 2017).

Like previously mentioned, the structural change of substrate could be also analyzed the infrared intensity transmitted before and after pretreatments as shown in Table 2 and Fig. 2. All wave numbers showed that transmittance intensities of treated substrate increased significantly if compared to that of nonpretreatment (de Souza et al., 2014). As an example, the treated substrate transmitted photon intensity at 94.49 counts at a frequency of 900.75/cm while nonpretreatment was 80.60 counts. When the 1701.21/cm beam was directed to sample, transmittance of nonpretreatment solid was recorded at 88.03 and inclined to 94.16 counts for treated solid. The prepared substrate passed through 3408.21/cm counted at 129.07 and the native solid was just 99.82 counts.

For being conducted without a solution, the microwave pretreatment could not dissolve lignin nor liquefied hemicellulose and cellulose. The intensity the transmitted infrared of treated solid increased significantly if referred to that of original powder. The most possibility was the decrease of bonds that could absorb infrared moving. The bonds that decreased significantly were hydrogen connections, which was a bridge between cellulose-cellulose, cellulose-hemicellulose, cellulose-lignin and lignin-lignin modelled following: Cellulose-OH-OH-cellulose-OH-OH-hemicellulose-OH-OH-lignin-OH-OH-lignin-OH-OH-cellulose-OH-OH-lignin (Nomanbhay, 2013).

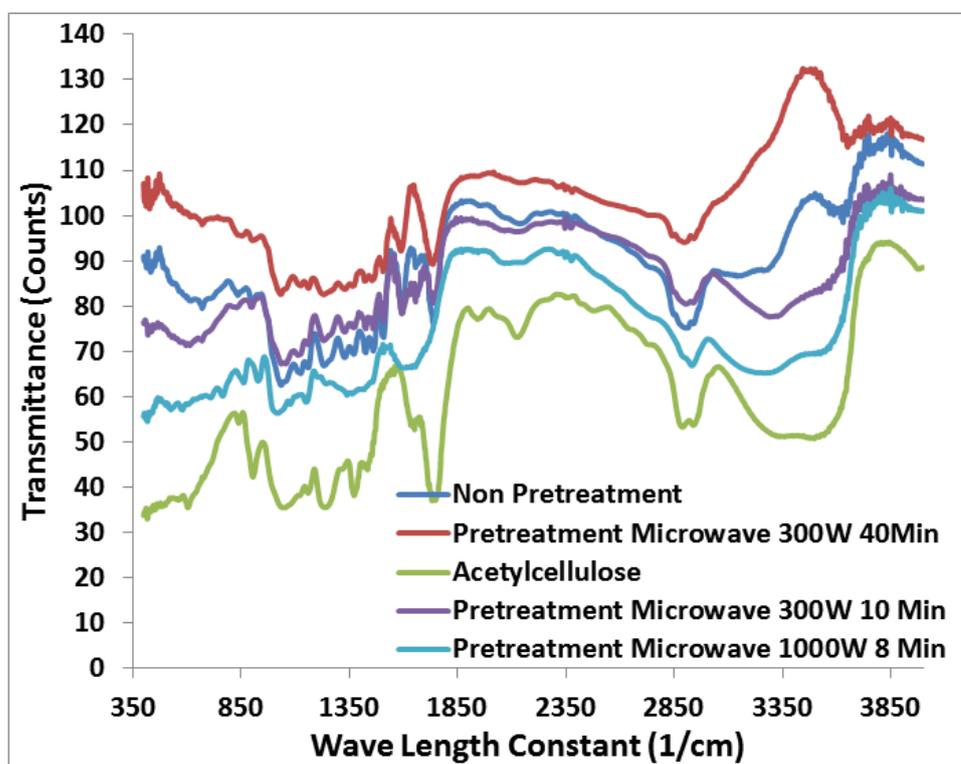


Figure 2. FTIR comparison of microwave treated- and original champaca timbers and chemical acetylcellulose

The FTIR spectra were extremely different between treated- and original timber as shown in the fingerprints. The peak of treated solid that was positioned at 3500/cm was appeared more clear and its summit increased from 105 to 132 counts. Two low peaks and valley located at around 3050, 3300, 3150/cm were diminished completely after pretreatment. The valley deep at 2150/cm was lowered significantly while the peak at 2000/cm was relatively not changed. Two peaks between 1700 and 1750/cm were disappeared and the line of treated solid was smoother than that of the native substrate. Unlike peaks located at bigger wave numbers, the peak of treated substrate that was close to 1500/cm was decreased. All peaks between 1000 and 1450/cm were smaller than those of original solid and peak located at 850/cm almost vanished after microwave applied on champaca timber. Even though it did not use liquid agents dissolving lignin, microwave pretreatment was

effective to modify the structure of lignocellulosic crystal. The change of peak heights and increase of intensity after pretreatment added the proof that crystalline alteration occurred on the substrate when the microwave was applied for pretreatment. The microwave could damage bonds between fibers inside biomass as explained before. The intensity height of a transmitted wave of the nano acetylcellulose, however, was lower than those of the rest of substrates. It was an indication that the structure of acetylcellulose was more amorphous than an original and the treated substrates whereby it was similar to that obtained in XRD analysis. The acetyl presence in a cellulose substance can change significantly the properties if compared to those of cellulose and lignocellulose.

### 3.3 SEM Analysis

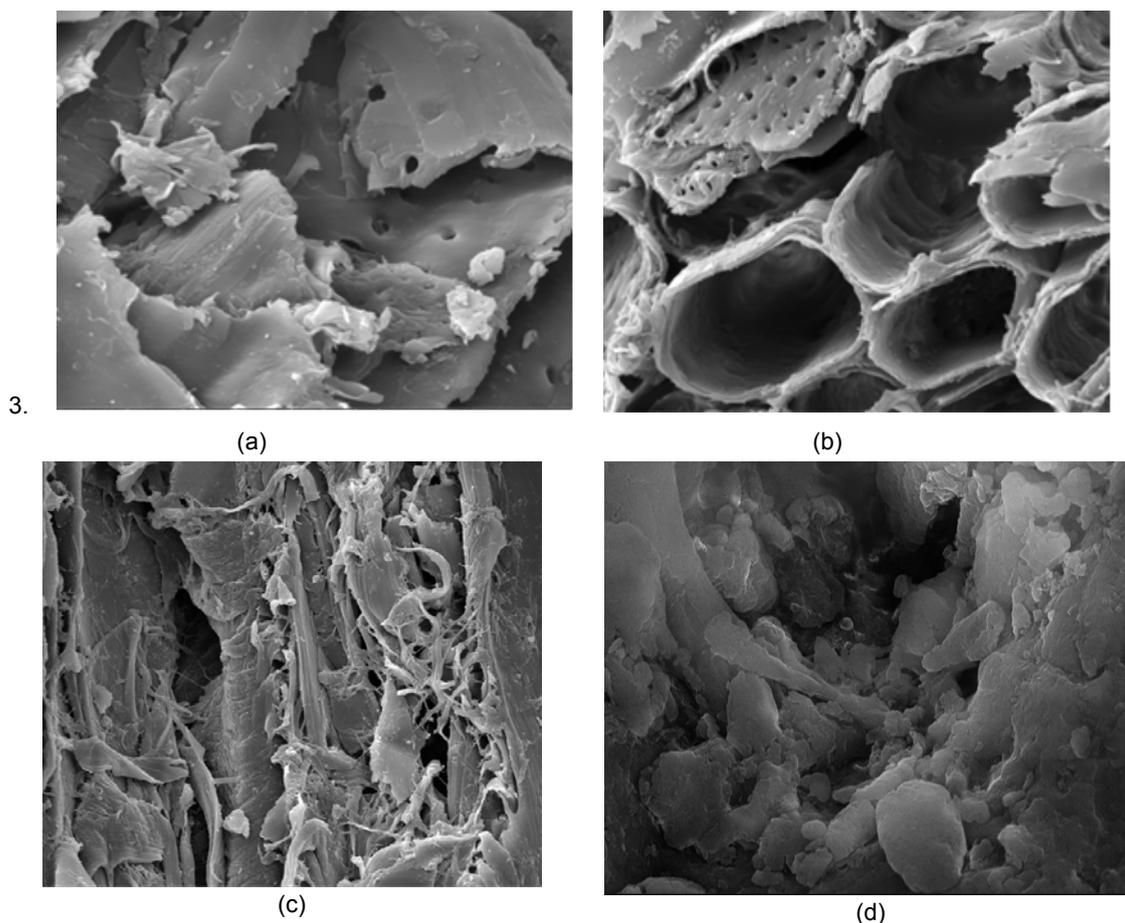


Figure 3. The SEM images of original substrate (a) and microwave treated timbers for 300W; 40min.(b), 300W; 10min. (c), and acetylcellulose (d).

Figure 3 is the surface images of an original substrate (a) and microwave treated solids (b,c) and chemical acetylcellulose (d) pictured by SEM and magnified by 5000 times. The first image in the left column seems clearly that the substrate surface that is not conducted pretreatment was not defective. The surface looked like irregular form that was caused by lignin and hemicellulose which were amorphous. Parts of cellulose, hemicellulose, and lignin were contributed toward surface morphology of samples. It was very clear that the surface of the native timber was smooth and almost not faulty. When microwave was performed for pretreatment, the surface morphology totally transformed as shown in b and c images. The effect of molecular vibration caused by an electromagnetics induction was tremendous damage. After pretreatment (300W for 40min), the tunnel likeness of treated substance appeared vivid and laid in the one direction, which verified previous report (Fiore et al., 2014).

As shown in a figure, many pits, however, were destroyed and exposed. It was indicative that the treated substance was changed its surface morphology and was more porous than that of nonpretreatment. From image magnified 5000x, the treated solid surface emerged spots that were not seen on the original solid as described previously. Meanwhile, the chemical acetylcellulose surface is quite different if compared with the

original- and treated lignocellulose. The significant difference of surface was caused by the presence acetyl groups bounded with cellulose. This surface properties were very interested in the stage for sugar, bioethanol, and bioplastics production.

#### 4. Conclusions

The microwave pretreatment on the lignocellulose was a clean technology for it did not employ the chemical substances and conducted for a short duration. The result showed that microwave pretreatment could transform the structures of substrate indicated by the change of CrI parameter, finger print and the surface morphology. The electromagnetic waves induced the substances in polysaccharides and then occurred a resonance and vibration in high frequency. Because of friction between substances and fibers, the heat was generated and temperature increased fast only in minutes. The CrI data shows that the substrate was treated by microwave conducted at 1000W for 8min which was relatively close to the acetylcellulose structure. The acetylcellulose surface was quite different with lignocellulose both original- and treated substrates.

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