Journal of Sustainable Technology and Applied Science (JSTAS)
Vol. 6 No. 1, May 2025, pp. 1- 7
ISSN: 2722-2403 (online)

CHEMICAL DELIGNIFICATION OF MALANG ARABICA COFFEE HUSK WASTE FOR ALTERNATIVE ENERGY

Dwi Ana A.[1*], Harimbi S.[2], Anitarakhmi H.[3], Rini K.D.[4], Sriliani S.[5]
[1-4]Chemical Engineering, National Institute of Technology Malang, Indonesia
[5]Civil Engineering, National Institute of Technology Malang, Indonesia

*Corresponding Email: anggoro_dwiana@yahoo.com

ABSTRACT: Malang Regency is an area with the potential to be Indonesia's largest coffee producer. The coffee processing will produce ± 65% of coffee beans and ± 35% of coffee husk waste, so in the Malang Regency area, with coffee productivity of 9,245 tons, it will produce coffee husk waste of ± 3,235 tons. The by-product of coffee processing in the form of coffee husk is a waste that has not been used optimally. Generally only used for fodder and compost. Looking at the presence of coffee husk waste and the composition of coffee husk, it has a lignin content of 29%, hemicellulose of 24%, and the highest cellulose of 33%. The adequate cellulose content of the material for the manufacture of bioethanol is more than 30%; from the composition of Arabica coffee husk, the cellulose content is more than 30%. So, it has the potential to be used as an alternative fuel, one of which is to produce bioethanol products. This research aimed to reduce lignin content and increase cellulose content from coffee husk waste by chemical treatment using NaOH chemical. The stages of the study were coffee husk powder with a size of 80 mesh weighing 5 grams, which was put into a glass beaker. Then, NaOH solution with a concentration of (5.0%, 5.5%, 6.0%, 6.5%, and 7.0% (v/v) with a volume of 50 ml. The sample was put in an autoclave at 121 °C for (15, 30, 45, and 60 minutes. The best time was 30 minutes with a NaOH concentration of 7%, with the highest cellulose content obtained at 55%.

Keywords: Delignification, Malang Arabica Coffee, Coffee husk waste, Lignocellulose.

1. Introduction

East Java Province contributes relatively highly to the national coffee production of 27,852 tons; the highest coffee productivity is in Malang Regency at 9,245 tons. Coffee processing, either on a small scale or industrial scale, will undoubtedly produce a by-product of coffee processing, a coffee husk. From this processing, it will produce ± 65% coffee beans and ± 35% coffee husk waste so that in the Malang Regency area, it produces ± 3,235 tons of coffee husk waste [1].

Meanwhile, the availability of waste generated from separating coffee husks from coffee beans (pulping process) in the form of biomass is very abundant, and only a few per cent is used for animal feed and compost. Coffee cherries consist of endosperm or seed keeping, part of the coffee bean used for processing into ground coffee. The epicarp, also known as the fruit skin, is the outermost part of the coffee fruit. The mesocarp is also called the flesh of the fruit husk, which tastes sweet and contains high enough water; the endocarp or horn skin is the most demanding coffee skin composed of cellulose and hemicellulose; the spermoderm called the epidermis is the thinnest, skin and sticks to the coffee skin [2]. The highest lignin content of the coffee skin sample was 31.58%, hemicellulose was 15.29%, and cellulose was 29.51% [3].

Figure 1 Coffee Husk

Delignification aims to reduce the lignin content in lignocellulosic materials. Delignification will open up the lignocellulosic structure to make the cellulose more accessible. The delignification process will dissolve the lignin content in the material so as to facilitate the process of separating lignin from fiber [4].

Delignification of bamboo powder (Gigantochloaapus) using H_2SO_4 and NaOH with variable changes in the concentration of H_2SO_4

Journal of Sustainable Technology and Applied Science (JSTAS)
Vol. 6 No. 1, May 2025, pp. 1- 7
ISSN: 2722-2403 (online)

(0.5%; 1%; 1.5%; 2%; 2.5%) and NaOH concentration (2%; 4%; 6%). ; 8%; 10%) which was heated at 121°C for 30 minutes, the optimum decomposition of lignin was 5.37% in the H_2SO_4 significator with a concentration of 2.5%. For the NaOH designator, the optimum decomposition of lignin was 9.53%, which occurred at a concentration of 6% [5].

Delignification of lignocellulosic waste in the form of sengon sawdust and oil palm leaf midrib using a delignificator $H_2SO_4$1% and fungal isolate MD-14 resulted in an optimum delignification of 35.1% for sengon sawdust and 29.3% for oil palm leaf midrib on chemical treatment variables, it is H_2SO_4 with a concentration of 1% [6].

This research was conducted to determine the effect of treatment and time during the delignification process to break down lignocellulosic compounds in Arabica coffee husks from the Malang area in the form of lignin, hemicellulose, and cellulose compounds so that they are easily converted in the hydrolysis process as a source of raw materials for making bioethanol. The delignification process was done using a physical method (size reduction) and a chemical method by adding a NaOH delignificator at varying times [7].

2. Lignoselulosa

The main components in lignocellulosic materials are cellulose, hemicellulose, and lignin: all three form a complex chemical bond, the basic material of plant cell walls [8]. Lignocellulose needs pretreatment before being converted into bioethanol. The pretreatment includes physical pretreatment (size reduction and heating), chemical pretreatment (acid and alkali) and biological treatment. Lignin is an amorphous heteropolymer bonded by different bonds. The primary function of lignin is to strengthen plant structures to resist microbial attack and oxidative stress. Lignin is difficult to degrade in plant tissue because it has a complex and heterogeneous structure that binds to cellulose and hemicellulose [9]. Cellulose is the main component of plant cell walls and is rarely found in a pure state, but it binds to lignin and hemicellulose to form lignocellulose.

3. Types of Delignifier

The type of delignification used in this research was Base Delignification with different concentrations and appropriate temperatures[10]. More precisely, using a delignifier in the form of NaOH. This type of delignification was used to prevent cellulose from being degraded in the delignification process. The use of NaOH (strong base) as a delignificator in this research was because NaOH can damage the lignin structure in the crystalline and amorphous parts. NaOH can extract hemicellulose by breaking down the amorphous structure of hemicellulose [11]. NaOH can also decompose lignin at temperatures less than 180^0C. Thus, NaOH can destroy lignin and extract cellulose and hemicellulose [12].

4. Base delignification process

In the delignification process with a base, the example was NaOH. Delignification using NaOH Sodium hydroxide (NaOH) or sodium hydroxide was a kind of caustic metallic base derived from the basic oxide of Sodium Oxide containing water. Sodium hydroxide has been studied intensively for several years and showed a disturbance to the lignin structure of biomass [13]. Most compounds used for alkaline treatment (alkaline delignification) were NaOH and $Ca(OH)_2$. OH- ions from NaOH broke bonds from the basic structure of lignin, while Na+ ions would bind to lignin to form sodium phenolate. This phenolic salt was soluble. Dissolved lignin was marked with a black colour in a black liquor solution. Based on this, the NaOH solution could separate lignin from cellulose.

Delignification of lignocellulosic material using NaOH was investigated on empty oil palm fruit bunches using 1% NaOH, 1.5%, 2 %, 2.5%, and 3% at 121°C. The highest glucose level was achieved by 3% delignification [14]. Delignification of rice straw has also been carried out under the optimum conditions of 10% NaOH concentration and a temperature of 100°C [15]. The delignification process of 20 grams of pineapple leaf fibre was also carried out with various concentrations of NaOH 0.1, 0.2, and 0.3 N at 100°C for 1 hour [16].

5. Experimental

The research was carried out at the Chemical Analysis Laboratory of ITN Malang. The variables used in this research were as follows: the control variable was the type of coffee husk: arabica; the weight of the coffee skin sample was 5 grams; the kind of delignifier used wasNaOH; the size of the material was 80 mesh powder, the temperature during the delignification process was 121^0C, the volume delignifier 50 mL. In comparison, the independent variables included the concentration of NaOH (delignificator): 5.0%, 5.5%, 6.0%, 6.5%, and 7.0% (v/v) and delignification time of 15, 30, 45, and 60 minutes.

Journal of Sustainable Technology and Applied Science (JSTAS)
Vol. 6 No. 1, May 2025, pp. 1- 7
ISSN: 2722-2403 (online)

The materials and equipment used:

The tools used were the following: Autoclave, Beakerglass, Blender, Sample bottle, Glass funnel, Desiccator, Erlenmeyer, Watch glass, Stove, Volumetric flask, Digital Balance, Oven, Volume pipette, Strainer, Gloves, Spatula, Stopwatch, Thermometer. The materials used were Aquadest, label paper, filter paper, coffee skin, sodium hydroxide, plastic warp, and tissue.

Research Procedure

The research procedure carried out included three stages: material preparation, delignification, and analysis. The following are the stages of each process.

Material Preparation:

The coffee husks were roughly crushed and then analysed for the levels of cellulose, hemicellulose, and lignin before physical treatment (Chesson method), then washed using distilled water, then dried in an oven at 105^0C for 24 hours to remove the moisture content in the coffee husks. The coffee husk is dried, blended into powder, and filtered to obtain a size of 80 mesh (the sample taken is a powder that passes through an 80 mesh sieve and is retained in a 100 mesh sieve).

The coffee husk powder was stored in a desiccator, and a preliminary analysis of cellulose, hemicellulose, and lignin was carried out using the Chesson method [17], using the following formula :

Selulosa Content : $\frac{C-D}{A}\ x\ 100\%$

Hemiselulosa Content : $\frac{B-C}{A} x\ 100\%$

Lignin Content : $\frac{D}{A} x\ 100\%$

Note:

[A] = Weight of dry sample; [B] = Weight of residue from the sample material (A) after adding 150 ml of distilled water refluxed at 100°C for 1 hour, filtered, washed with 300 ml of distilled water and dried in an oven at 105°C for 1 hour until the weight is constant; [C] = Weight of residue (B) after adding 150 ml of 1 N H_2SO_4, then refluxed at 100°C for 1 hour, the result is filtered, washed with 300 ml of distilled water until neutral and dried in an oven at 105°C for 1 hour until the weight is constant; [D] = Weight of residue (C) after adding 10 ml of 72% (v/v) H_2SO_4 and soaked at room temperature for 4 hours, then adding 150 mL of 1 N H_2SO_4, refluxed at 100°C for 1,5 hours. The results were filtered and washed with 400 ml of distilled water and dried in an oven at 105°C for 1 hour until the weight was constant.

Process Delignification

80 mesh coffee skin powder weighed 5 grams and was put into a glass beaker. Add a solution of NaOH with a concentration according to the variable with a volume of 50 ml (Comparison of coffee husk powder with the type of delignificator solution is 1:10), then put the sample in an autoclave at a temperature of 121^0C for a predetermined time variable then analyse the lignin, cellulose and hemicellulose by the Chesson method.

6. Results and Discussions

Comparison of % Content of Lignin, Hemicellulose and Cellulose before and after Physical Treatment (Size reduction to 80 mesh).

The following graph compares the percentages of Lignin, Hemicellulose and Cellulose content of coffee husks before and after treatment, reducing the size to 80 mesh.

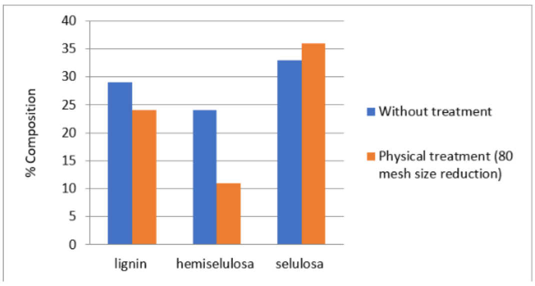

Figure 2 Comparison Graph of Lignin, Hemicellulose and Cellulose Contents before and after Physical Treatment (Size reduction to 80 mesh).

Figure 2 shows that with the physical treatment of the coffee skin, the lignin content decreased from 29% to 24%. The results of this research were based on what Hermiati [8] has done, which is that the levels of lignin contained in coffee husks can be influenced by the particle size of the material. By reducing the size to 80 mesh, the lignin content decreased from 24.625% to 23.36%. This process is also one of the delignification methods, namely physically. The purpose of reducing the size is not only to increase the material's porosity or facilitate the lignocellulose degradation process but also to dismantle the complex structure and degrade the lignin structure so that the lignin content will decrease [8]. The following is a picture of the breakdown of lignin through the delignification process.

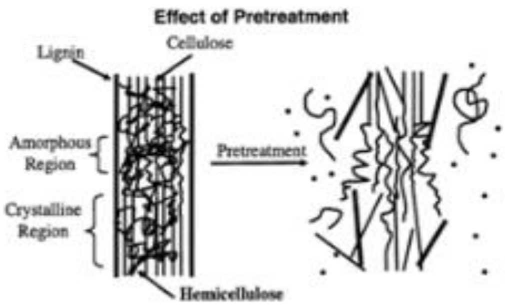

Figure 3 The breakdown of lignin elements

With the size reduction process, the hemicellulose content was originally 24%, but it decreased to 11% after the process. For the cellulose results, the more lignin is degraded, the higher the cellulose results, where the original 33% increased to 36%.

The conclusion is that the graph is used as a control to compare the results of lignin, hemicellulose, and cellulose produced by the physical delignification process. The results obtained are based on the theory, namely that there is a decrease in lignin and hemicellulose levels and an increase in cellulose levels. Because the primary function of lignin is to strengthen the plant structure in resisting microbial attacks and oxidation stress, lignin is difficult to degrade in plant tissue because it has a complex and heterogeneous structure that binds to cellulose and hemicellulose [9]. So, with the reduction in size of the coffee skin, lignin and hemicellulose can be degraded into simpler compounds by breaking down their polymer chains [2]. In addition, reducing the sample size will break the long polymer chains into shorter polymer chains, making it easier to separate lignin from cellulose bonds [19].

Effect of delignification time and NaOH concentration on lignin content

This discussion will focus on lignocellulosic yields from the coffee skin delignification process carried out in various types of time and with different variables. These results were obtained based on the analysis of Cesson Datta. The percentage of Lignin content data can be seen in Figure 4.

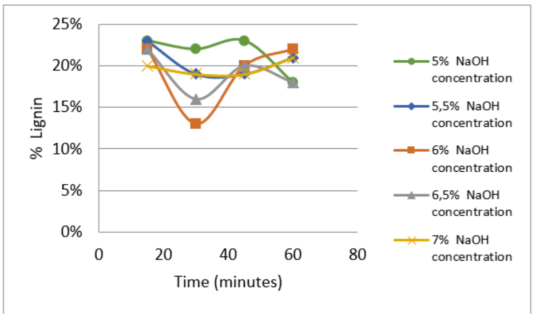

Figure 4 Effect of delignification time and NaOH concentration on % lignin

In Figure 4, it can be explained that the lignin removal process, the increasing concentration of NaOH and the length of delignification time significantly affect the percentage of lignin content. From the graph, it is explained that with the addition of 5% to 7% NaOH, the lignin content decreased at 30 minutes. After a soaking time of 30 minutes, the lignin content will increase. The delignification process is not optimal because the time is too long, making the delignification process less effective.

It should be noted that if the lignin content increases, the lignin degradation process is not optimal. In contrast, the lignin degradation process is optimal if the lignin decreases in value. NaOH solution is used at various concentrations because it can damage the lignin structure, releasing cellulose in the tissue and crystalline and amorphous parts and separating some hemicellulose and lignin. However, the concentration of NaOH solution that is too high will cause some of the cellulose to be hydrolysed so that the cellulose content will decrease. For all NaOH concentration variables, the best concentration is 6% NaOH with a time of 30 minutes, which is the best time for the lignin degradation process. The results obtained in this delignification process have an average value below 24%, which is by the theory, namely that the lignin results decrease from the initial material (without physical treatment) 29% and below the lignin results obtained from physical therapy 24%. The results are by research conducted by (Eka Ruriani, 2013), where the lignin content will be reduced by using a chemical process (better degradation process) than a physical process (particle reduction to 80 mesh). And the time used is also by the existing journal, which is 30 minutes. In the graph, there is a tendency for an increase in lignin levels after a decrease; this is because the cell walls experience condensation and sedimentation and affect the molecular weight.

Effect of delignification time and NaOH concentration on hemicellulose content in coffee husk.

Figure 5 compares the delignification time and the concentration of NaOH in the hemicellulose content of coffee husks.

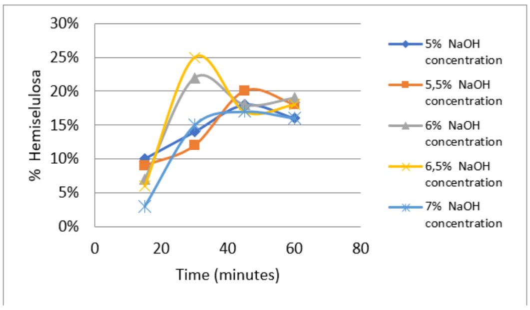

Figure 5 Effect of delignification time and NaOH concentration on % Hemicellulose

Figure 5 shows that the soaking time and NaOH concentration greatly influence the percentage of hemicellulose content. The graph shows that the rate of hemicellulose will increase, with the highest content being 25%, and then decrease to 3 %, along with the longer soaking time with the NaOH solution.

According to theory, after the complex structure of lignin is degraded, there is an increase in cellulose and a decrease in lignin and hemicellulose. However, this study found a difference: the cellulose content decreased, and lignin and hemicellulose increased after the maximum condition. Figure 5 explains the best NaOH concentration used to produce the lowest hemicellulose content, namely at a NaOH concentration variable of 7% with a soaking time of 15 minutes.

The results of this study are based on the theory that the higher the degree of delignification, the higher the degradation of polysaccharides in the form of cellulose and hemicellulose produced. The hemicellulose content that increased drastically after the pretreatment process was due to the influence of the addition of NaOH solution, causing the solubility of carbohydrates to be slower than oxidation or reactions with other compounds, so the carbohydrate content in the media decreased. When the solubility of carbohydrates slows down, an oxidation reaction occurs to form more complex compounds and finally accumulates until the hemicellulose content increases [20].

Effect of delignification time and NaOH concentration on cellulose content in coffee husk.

Figure 6 shows a comparison between the delignification time and the concentration of NaOH on the cellulose content of the coffee husk.

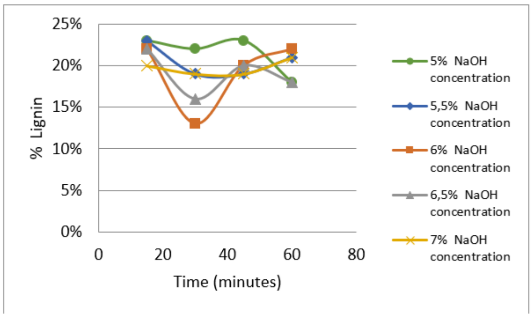

Figure 6 Effect of delignification time and NaOH concentration on the percentage of Cellulose content

Figure 6 shows that the soaking time and NaOH concentration greatly influence the percentage of cellulose content. The graph shows that the average cellulose percentage increases with the highest content being 55% and then decreases with the lowest content of 43%, along with the longer soaking time with the NaOH solution. Figure 6 explains the best NaOH concentration used to produce the highest cellulose content at a NaOH concentration variable of 7%, with a soaking time with the NaOH solution of 30 minutes.

Delignification will open the lignocellulose structure so that cellulose becomes more accessible. The delignification process will dissolve the lignin content in the material, making it easier to separate lignin from the fibre. So when the lignin has dissolved, or the lignin layer that protects the cellulose has decreased, the cellulose will be readily obtained to the maximum [3]. Several things cause a decrease in cellulose. First, according to [20], the reduction in total dissolved carbohydrates is caused by administering a high dose of NaOH, which causes the dissolved carbohydrates to oxidise and form complex bonds. The increasing hemicellulose content can prove the formation of this complex bond. Second, it is possible that there was an error during the lignocellulose testing process using the Chesson method.

For NaOH solution with a concentration of 7%, the cellulose content increased along with the increasing delignification process time; the optimum time was 30 minutes. After 30 minutes, the % of cellulose decreased. This is by research [14], where the optimum time for the delignification process on coffee skin was 30 minutes, using NaOH solution with a concentration of 1%, 1.5%, 2%, 2.5% and 3% at a temperature of 121°C. The highest glucose or cellulose content was achieved with a delignification process using a NaOH concentration of 3% (the highest concentration).

7. Conclusions

From this research, it can be concluded:

1. reducing the size of coffee waste powder to 80 mesh can reduce lignin levels by 5%.
2. The optimum time for the delignification process of coffee husk waste was 30 minutes with a concentration of 7% NaOH, and the combination of these two variables increased the cellulose content by 22%.

Reference

[1] Data from the Central Bureau of Statistics of East Java, 2007

[2] Ruriani E., Nafi A., Titi C.S., (2013), Characterization and pre-treatment of coffee husk by dry method of coffee processing for bioethanol processing, *Research* PEKERTI *Grant,* Jember University, pp 2-10.

[3] Raudah, Ernawati, (2012), Utilization of Arabica Coffee Skin from the pulping process to manufacture Bioethanol, Journal of Reaction Science and Technology, Vol. 10.

[4] Faisol A., Yoga, P.W., Reza, T.W., (2016), Effect of Base on Lignin Decrease and HCl Concentration on Hydrolysis of Coconut Coir to produce bioethanol, Journal of Chemical Engineering Vol. 2, No. 2, Sriwijaya University, Palembang.

[5] Permatasari H.R., Fakhili G., Bety L., (2014), Effet of Concentration of H_2SO_4 and NaOH on Delignification of Bambo Powder *(Gigantochloa Apus)*, Chemistry Education Study Program FKIP , Sriwijaya University, Palembang.

[6] Agustini L., Lisna Efiyanti, (2012), Effect of Delignification Treatment on Cellulose Hydrolysis and Ethanol Production from Lignocellulosic Waste, Forest product research journal, Vol. 33 No. 1.

[7] Rosmiati M., Aditiawati P., Zakaria A., (2018), Arabica Coffee Farming Development Strategy (Case of Coffee Farmers in Sutenjaya Village, Lembang District, West Bandung Regency, West Java Province), Journal of Sociotechnology, Vol. 16, N0. 3., School of Life Sciences and Technology, Bandung Institute of Technology.

[8] Hermiati E, Mangunwidjaja D, Sunarti T.C. Suparno O, Prasetya B., (2010), Utilization of Lignocellulosic Biomass Sugarcane Bagasse for Bioethanol Production, UPT BPP Biomaterial-LIPI, Bogor Agricultural Institute and Biotechnology Research Center, LIPI Bandung.

[9] Trisanti A, (2010), Cellulase Potential in Degrading Lignocellulosic Agricultural Waste for Organic Fertilizer, Cellulose Journal, *Vol. 45 No. 2*, Biotechnology Research Center, LIPI Cibinong, pp : 70-77.

[10] Fuadi, AM, K. Harismah, A. Setiawan, (2015), Enzymatic Hydrolysis of Waste Paper with Variation of Preheating, Univerity research Colloquium, Surakarta.

[11] Maysarah, Siti, Netti Herlina, (2015), Production of Lignin resorcinol Formaldehyde adhesive from sodium Lignosulfonate of Oil Palm Empty Fruit Bunches, Journal of Chemical Engineering, North Sumatra University, Medan.

[12] Harry Rizka P, Fakhli G, Bety L, (2014), Effect of Concentration of H_2SO_4 and NaOH on Delignification of Bamboo Powder *(Gigantochloa Apus)*, Chemical Education Research Journal, Vol. 1, No. 2, Sriwijaya University, Palembang

[13] Zhao J, Zhang H, (2008), *The Inhibition of Sacharomyces cereviseae Cells by Acetic Acid Quantified by Electrochemistry and Fluorescence, Journal Bioelectrochemistry, Vol. 72, Issue 2*.

[14] Kristina E.R., Sari, Novia, (2012), Alkaline Pretreatment and Simultaneous Saccharification-Fermentation Process for Ethanol Production from Oil Palm Empty Fruit Bunches, Journal of Chemical Engineering, Vol. 3 No. 18 : 34-43.

[15] Fitriani S., Bahri, Nurhaeni, (2013), Corn Cob Bioethanol Production (Zea mays) from the Delignification Process, Online Journal of Natural Science. 2(3) : 66-74.

[16] Jayanudin, (2010), Effect of Concentration and Bleaching Time of Pineapple Leaf Fiber Using Hydrogrn Peroxide, Chemical Engineering And Process Seminar 2010 ISSN : 1411-4216, Chemical Engineering Department, Faculty of Engineering, Diponegoro University, Semarang, pp : A20-1-A20-6.

[17] Ayu Lidya Panjaitan, Azhari, Rizka Mulyawan, Nasrul ZA, Zulnazri (2023), The Effect Of Cooking Solution Concentration (Naoh) On The Delignifying Process In The Production Of Pulp From Corn Cob Waste (Zea Mays), Chemical Engineering Journal Storage Vol. 3 No. 6, pp: 810-819.

[18] Edahwati L., Dyah S.P. Nana D.S., (2014), Lignin Reduction in Coffee Fruit Skin by Organosolve Method, Eksergi Journal, Vol. XI, No. 2, National Development "Veteran" East Java University, pp 7-10.

[19] Heradewi. 2007. Isolation of Lignin from Black Liquor of Organosolv Cooking Process of Empty Oil Palm Fruit Bunches (TKKS), Bogor Agricultural Institute, Bogor.

[20] Moh. Risal Siregar, Yusuf Hendrawan, Wahyunanto Agung Nugroho, (2014), The Effect Of NaOH Concentration And Microwave Heating Time On Pretreatment Process Toward Lignocellulose Content Of Chlorella vulgaris, Journal of Agricultural Technology, Vol. 15 No. 2,pp 129-138