

Study on the utilization of palm fruit waste as a pulp raw material organosolv method with hydrothermal pretreatment

R Apriani¹, N N Manik¹, E H Mahardhika¹ and M J Inayatullah¹

¹ Study Program of Pulp and Paper Processing Technology, Institute of Technology and Science Bandung, Indonesia.

E-mail: rachmawatiapriani46@gmail.com

Abstract. Palm fronds contain high cellulose, so it can be used as an alternative raw material for making pulp. The purpose of this study is to look at the potential of palm fronds as raw material for making pulp. The process of making pulp used in this study is the organosolv process, which is releasing palm frond fibers with a solution of acetic acid with hydrothermal pretreatment. This study observed the effect of cooking time and cooking solution volume on percent yield. The range of variables used in this study was cooking time of 125,150 and 175 minutes with concentrations of acetic acid cooking solution of 10 percent and 15 percent. The results of pulp quality were analyzed by comparing the results of the cold soda process to obtain physical properties. The best pulp was obtained at 30 minutes cooking time and 175 °C with a tensile value of 0.63 kN / m, tear 228.49 mN and brightness 13.18.

1. Introduction

The development of the pulp and paper industry in Indonesia is currently very rapid. This is indicated by the increase in pulp production capacity from around 6.5 million tons per year to around 11 million tons per year. The increase makes paper base material namely wood pulp decreases due to the imbalance between planting and logging. The alternative that can be done is to look for alternative raw materials in addition to paper raw materials. In order for pulp production to be produced in the international market, efforts must be made to find alternative technologies that are safer for the environment.

Actually the raw materials that can be processed to produce pulp are of several types, including wood, straw, bamboo, bagasse, and others. However, the researchers tried to utilize the palm fronds which had only been used as fuel.

Palm fronds are one example of waste originating from oil palm plantations, as a by-product. As a lignocellulosic material, consisting of cellulose, palm fronds actually have potential as a raw material for pulp. Previous studies have shown that palm fronds can be made into pulp that has the same quality as pulp from other non-wood materials. However, the use of conventional processes in making pulp is relatively not eco-friendly.

Pulp making with organic solvents (organosolv pulping) is one of the alternative process in pulp making. The principle of the organosolv process is to sort out the main components of biomass (cellulose, hemicellulose, and lignin) without damaging to these component [1]. and also, the



organosolv process also has several advantages, such as the process is relatively easy, eco-friendly and requires less energy than conventional pulp manufacturing processes. Some organic solvents used as cooking solutions in the manufacture of pulp are alcohols, organic acids, amines, ketones, esters and phenols

Based on the description above, it is necessary to conduct research on pulping with alternative raw materials, and technologies that are safer for the environment, in this case the researchers use palm fronds from plantations that are no longer used, thus becoming waste. The main purpose of pulping is to release fibers that can be processed chemically, mechanically or by a combination of the two treatments. While in the research of making pulp from bagasse carried out chemically by organosolv process.

In this method, wood chips are cooked with the right chemicals in an aqueous solution by increasing the temperature and pressure. The goal is to degrade and dissolve lignin and leave most of the cellulose and hemicellulose in the form of whole fibers. There are three methods of chemical pulping, namely the kraft process (alkaline) process, sulfite (acid) process, and organosolv process.

1.1 Sulfate Process (Kraft)

Pressurized alkaline cooking systems at high temperatures were known in the 1850s. According to the method proposed [2], sodium hydroxide solution was used as cooking leachate and the resulting leachate was concentrated by evaporation and burned.

Use of sodium sulfate instead of sodium carbonate [3]. Similar ideas are followed [4] presented the pulping process which was easily carried out technically in Danzig. These inventions initiate the process (Kraft). But the breakthrough of the Kraft process first occurred in the 1930s after the introduction of many multilevel bleaching systems.

At present the process of sulfate is not only the main alkaline pulping process for wood, but also the most important pulp process. The sulfate process involves cooking the chip with a solution of NaOH and Na₂S. The reaction with alkali causes the breakdown of lignin to be a smaller group where sodium salt can dissolve in cooking liquid. In the process of sulfate it produces strong paper but the bleached pulp is dark brown. This process was discovered more than 100 years ago as a modification of the soda process.

1.2. Sulfite Process

In this process, a mixture of sulfite acid (H₂SO₃) and bisulfite ion (HSO₃) is used to dissolve lignin. Sulfites are united with lignin to form salts of lignosulfonic acids which can dissolve in cooking solutions and the chemical structure of lignin is still intact. The basic chemicals for bisulfite can be calcium, magnesium, sodium or ammonium ions. Sulfite pulp can be carried out in a large pH range. Sulfite acid shows the process of pulp with excess free sulfuric acid (pH 1-2), where bisulfite cooks in a slightly acidic state. Colored sulfite pulp is brighter than kraft pulp and bleach easier but paper sheets are weaker than kraft paper.

1.3. Organosolv Process

The organosolv process is the process of removing fiber using organic chemicals such as methanol, ethanol, acetone, acetic acid, and others. This process has been proven to have a good impact on the environment and is very efficient in utilizing forest resources. By using the organosolv process, it is expected that the environmental problems faced by the pulp and paper industry will be overcome. This is because the organosolv process provides several advantages, including the yield of high-yield pulp, does not use sulfur so it is safer for the environment, can produce by-products in the form of high purity lignin and hemicellulose.

Research on the use of organic chemicals as cooking ingredients in the pulping process has actually been done for a long time. There are various types of organosolv processes, but the ones that have developed rapidly at this time are the all cell process (cellulose alcohol), which is the process of

making pulp using chemicals that cook alcohol and the process of acosolv using the chemicals of acetic acid cooking.

The organosolv process has been studied [5]. The research used ethanol, methanol, and acetic acid as solvents. The process of making pulp using acetic acid is called the acetosolv process. According to [6] that in 1980 the method of making organosolv had begun to be developed in the direction of application. The organosolv process is not only effective for blends and lignin but also the characteristics of the pulp produced are comparable to the kraft process.

[7] that an important feature of organosolv is pulp bleaching is easier and can be done using non-chlorine compositions and recycling of cookers is relatively easy through the evaporation method.

Acetic acid in the form of colorless liquid. The term most often used in industry is vinegar. Acetic acid can form crystals at freezing point 16.7 °C. Acetic acid is corrosive to many metals such as iron, magnesium and zinc, forming hydrogen gas and acetate salts (called metal acetate). Acetic acid is an organic acid chemical compound known as an acidic flavor and aroma in food. Acetic acid is also used in the production of polymers such as polyethylene terephthalate, cellulose acetate, and polyvinyl acetate, as well as various kinds of fibers and fabrics. The solution of acetic acid in water is a weak acid, meaning that it only decomposes partially into H⁺ and CH₃COO⁻ ions. The influential factors in pulping are as follows:

a. Solvent Concentration

The higher the concentration of the solution, the more lignin is dissolved.

b. Comparison of Raw Materials for Cooking Cookers

The comparison of cooking liquid to the raw material must be sufficient so that lignin decomposes and can dissolve completely in cooking liquid.

c. Temperature and Cooking Time

Temperature and cooking time are two related variables. Temperature and cooking time affect the yield of pulp produced and the solubility of lignin. Processing pulp with high temperatures will require a short cooking time. However, at high temperatures with long cooking times it will cause cellulose decomposition so that the yield and a pulp produced are low [3].

d. Fiber

Fiber affects the resistance of the paper to be made.

2. Methodology

The tools used in this implementation consisted of reactor, electric heaters, erlenmeyer, filter paper, pH meter, oven, scales, hand sheet maker, freeness tester, and press. The materials used in this study consisted of palm fronds, aquadest, 95 percent acetic acid, and materials for analysis.

Work procedure of this research are following, the first preparation of oil palm fronds. The size of the palm frond chips in this process is cut by 2-3 mm, 3-5 cm long. Chip making is done manually. The chip is dried with the help of sunlight until the water content is reduced.

The second hydrothermal process (pre-treatment). The dried palm fronds are weighed as much as 200 g. Then add distilled water. Temperature variations of 125, 150 and 175 °C with variations of time 30 and 60 minutes. After the pre-treatment is complete, the chip is separated by filtering and weighing.

The third cooking process. Palm fronds and cooking fluids are inserted into the reactor according to the experimental variable. Then the reactor is closed and heated to temperature according to the experimental variable. After that the reactor is turned off, all moisture is released from the reactor slowly from the discharge valve. Then the pulp is removed from the reactor. Then solids separated by cooking liquid through a funnel equipped with filter paper. After that the solution is washed again with acetic acid, and the filtrate is accommodated with another container. Then solids are rinsed with water until the filtrate looks clear, and used laundry water can be immediately discarded. After that the washed solid is then dried. And finally the dried solid is weighed.

3. Results and discussion

Table 1. Data on pulp acquisition of temperature and solution volume at pretreatment

Number	Aquadest mass (grams)	Temperature (T) (°C)	Time (t) (minute)	Overshoot (°C)	Pressure (bar)	Total mass after impregnation (grams)
1	1750	125	30	143	4	1972
2	1750	150	30	164	7	1973
3	1750	175	30	181	11	1972

Note : A temperature of 30 minutes does not affect the results of impregnation.

Variation of cooking solution (15 percent acetic acid), Impregnation: T = 175 °C, t = 60 minutes. Samples in the form of oil palm midrib as much as 802 grams (wet weight after the pretreatment process with a solution of organosolv cooking ie 19 grams of acetic acid with a temperature set of 125 °C with a waiting time of 30 minutes, aquadest: 1946 gr / 2000 ml and overshoot time: 137 °C. After the pulping process, a total mass sample of 2075 grams was obtained with a mass of water of 1306 grams, solid mass = 769 grams. Then proceed with making handsheets at the itsb pulp and paper laboratory through the beating process, csf 450 determination and handsheet making. Then followed by sample testing at the Pulp and Paper Center in the form of tensile strength, tear strength and brightness testing. The bleaching process of pulp with hydrogen peroxide was carried out with a sample of 15 percent NaOH) to TC (total consistency) 0.8 percent. In the sample there is a stock that is still hard so it will be difficult to do the fiber decomposition process. The concentration of NaOH cooking solution varied by 10 percent and 15 percent. Pulping process by using cooking solution in the form of NaOH as much as 15 percent of dry weight carried out in the pulp lab and paper at the Bandung Institute of Technology and Science.

The steps taken in making handsheets are to determine the moisture (water content) of the sample that has gone through the impregnation and cooking process which aims to determine the dry weight of the sample so that it becomes a reference to determine the concentration of cooking solution to be used. After the cooking process, the sample through the pH measurement process then proceed to the washing stage to make the pH reach normal pH 7 followed by the H₂O₂ bleaching process to whiten the pulp. After bleaching, the beating process is carried out to break down the fibers. Pulp samples were carried out testing of kappa numbers, lignin levels, cellulose levels etc. at the center for pulp and paper (bbpk). The consistency of the fiber decomposition process used is 0.3 percent, 0.67 percent and 0.8 percent which indicates how much fiber is in the water. This will affect the final result of the beating process. The consistency of each sample should be the same. In the manufacture of pulp handsheets, it is calculated freeness and 450-500 csf which aims to find out how much fiber is fibrillated (decomposed).

Table 2. Test results of paper with organosolv cooking and cold soda

Number	Parameter	Unit	Test Result			Method
			Acetic Acid 15 percent (T =150 °C, t=30 min)	NaOH 15%	NaOH 15 percent (Pulp 80 percent +LBKP 20 percent)	
1	Tensile Strength	kN/m	0,99	0,385	1,321	SNI ISO 1924-2-2010
2	Tearing Strength	mN	137,3	175,73	307,54	SNI 0436-2009
3	Brightness	%	13,3	11,47	14,35	SNI ISO 2470-2010

Note : Room temperature 23 ± 1°C; RH 50 ± 2 percent

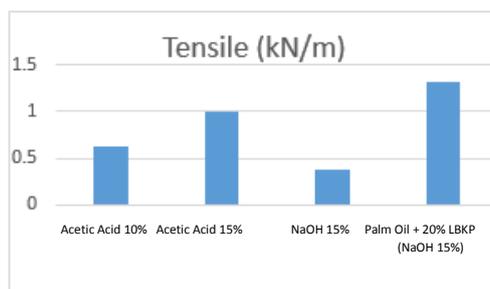


Figure 1. Relationship of type and concentration of cooking solution with tensile strength

From the results obtained tensile strength in oil palm midrib pulp with a dose of 15% higher compared to pulp palm oil palm midrib at a dose of 10 percent. This can indicate the level of cellulose (alpha, gamma, betha) in the pulp with a dose of 15 persen higher while the level of lignin is lower than the dose of 10 percent so that the pulp tensile strength is higher because the bond between fibers produced fibrils -fibril fiber can be formed and the carboxylic acid group (COOH) is easier to release OH⁻ which is caused by COOH interaction with more and less water which is blocked by lignin so that the fiber swells and when refining it can be easier and many parts of the fiber fibrillation therefore the tensile resistance of the paper is higher and can increase.

The brightness value is higher at a dose of 15 percent, this is caused by the remaining lignin (residual lignin) in the fiber less than the 10 percent dose so that the pulp will be brighter and white, so that it can be concluded optimal cooking at a dose of 15percent. It is better to test the kappa number (to measure the residual lignin) to strengthen the analysis because like the above explanation, besides the lignin residual being the factor that most influences brightness, it is 15 percent higher but the difference in value is not too far from the quality of water used making different handsheets and testing or other external factors.

4. Conclusion

Paper with palm fronds has better tensile strength with higher concentrations of acetic acid. When compared with NaOH cooking solution of 15 percent is not good, then the addition of 20 percent lbpk can increase tensile due to the fiber content of wood.

In this case it can be seen from the graph, the higher the concentration of acetic acid the tearing value gets smaller. Then it's optimum at 10 percent. If compared with 15 percent NaOH it is still not good, so adding lbpk can increase the Tearing value.

Tensile strength is one of the main parameters to see the use of cooking chemicals to the strength of the fiber itself. the higher the concentration of acetic acid, the better the attraction. If compared to NaOH cooking solution of 15 percent is not good, then the addition of lbpk 20 percent can increase tensile due to the fiber content of wood.

Tear resistance is the force needed to tear the paper in a standard condition, the higher the tearing value, the greater the tear resistance of the paper. The higher the concentration of acetic acid the smaller the tearing value. Then it's optimum at 10 percent. If compared with 15 percent NaOH it is still not good, so adding lbpk can increase the Tearing value.

Brightness increases because there is an indication that lignin is reduced in the cooking process, it can be seen the higher the concentration of the cooking solution the higher the brightness value. While the addition of lbpk will also affect brightness.

5. References

- [1] Zulfansyah*, Muhammad Iwan Fermi, Said ZulAmraini, HariRionaldo, Meilany Sri Utami. 2010 Pembuatan Pulp Pelepah Sawit dengan Pelarut Asam Formiat Research in Chemical

- Engineering Department of Riau University.
- [2] C. Watt and H. Burgess (1850). Wood Chemistry: Fundamentals and Applications Second Edition. Academic Press, Inc. Harcourt Brace Jovanovich, Publishers. Finland
 - [3] A.K. Eaton patents (1870). Wood Chemistry: Fundamentals and Applications Second Edition. Academic Press, Inc. Harcourt Brace Jovanovich, Publishers. Finland
 - [4] C.F. Dahl (1885). Modern Pulp And Paper Making. Reinhold Publishing Corporation, New York.
 - [5] Kleinert et al (1930). Pulping with Organic Solvents other than Alcohols Rodríguez, A. and Jiménez, L. Departamento de Ingeniería Química, Universidad de Córdoba, Campus de Rabanales, C-3, 14071 Córdoba, Spain
 - [6] Ararki et al., (1989). Biofunctionalization of Polymers and their Applications. Springer. Austria.
 - [7] Kleinert (1974). High Yield Catalysed Organosolv Pulping of Nonwood Fiber Sources.
 - [8] Casey, James P (1960). Pulp and Paper. Chemistry and Chemical Technology, Volume 2. Interscience Publishers,
 - [9] Rydholm. 1965. Microbes: Health and Environment. I.K. International Publishing House Pvt. Ltd. New Delhi.