Waste Technology (WasTech)
Journal homepage: http://ejournal.undip.ac.id/index.php/wastech
An International Journal

Effect of Water Content on Free Fatty Acid Value Reduction in Nyamplung Crude Oil (*Calophyllum Inophyllum L.*) Extracted by N-Hexane Solvent and Using Factorial Design Experiment

Farah Salsabillah Maulidinoor[1], R.TD. Wisnu Broto[1*]

[1]Industrial Chemical Engineering Technology, Department of Industrial Technology, Vocational School, Diponegoro University, Jl. Prof Soedarto, S.H., Tembalang, Semarang, 50275, Indonesia
Email: vieshnoe@gmail.com

Abstract – *This study aims to determine the effect of water content on free fatty acid levels in nyamplung (Calophyllum inophyllum L.) seed oil. Nyamplung fruit seeds have a relatively high oil content ranging from 40%-73%, which can be used as a biodiesel raw material. Nyamplung seed oil has a high FFA content that ranges from 15%-30%. The process of extracting nyamplung seed oil is done by the soxhletation method because it is considered the most efficient and uses nhexane solvent, which has non-polar properties and can increase oil yield (more than 50%). This study will use the factorial design level 2 method to determine the most influential process variables to produce optimum operating conditions in making nyamplung seed oil with the lowest FFA content. The variables used in this study are moisture content (8% and 12%), particle size (15 mesh and 25 mesh), and the ratio of materials and solvents (1:1 and 1:3). The analysis results showed that water content had the most significant influence on free fatty acid content with a value of 0.25 and the lowest free fat content of 13.30%.*

Keywords – *Optimization, raw material*
Doi: http://dx.doi.org/10.14710/wastech.11.2.97-101
[How to cite this article: Maulidinoor, F.S., Broto, R.TD.W. (2023). Effect of Water Content on Free Fatty Acid Value Reduction in Nyamplung Crude Oil (*Calophyllum Inophyllum L.*) Extracted by N-Hexane Solvent and Using Factorial Design Experiment. Waste Technology, 11(2), 97-101 doi: http://dx.doi.org/10.14710/wastech.11.2.97-101]

1. Introduction

Nyamplung (*Calophyllum inophyllum L.*) is a plant that belongs to the *family Gutiferae* and the genus *Callophylu.* It is distributed in almost all tropical and sub-tropical countries, including Indonesia. The oil content in nyamplung seeds is strongly influenced by the age of nyamplung seeds when harvested, how to care for or cultivate plants, and the area where they grow (Rejeki, 2015). Nyamplung fruit seeds have considerable potential to be used as raw material in making biodiesel because they have a high oil content of around 40-73% (Emilda, 2019).

Nyamplung fruit seeds also have several advantages as a biodiesel raw material because they have a high yield reaching up to 74%. (Ilham Adi *et al.,* 2021). Nyamplung oil is classified as an oil with a relatively high content of unsaturated fatty acids. It has a main content of oleic acid 37.57%, linoleic acid 26.33% and stearic acid 19.96%, and has myristic acid, palmitic acid, linolenic acid, arachidic acid, and erucic acid (Balitbang Kehutanan, 2008).

However, the oil produced from nyamplung seeds has a very high Free Fatty Acid (FFA) content of 15-30%. This is one of the shortcomings of nyamplung seed oil because the higher the FFA content of an oil, the lower the biodiesel yield that will be obtained, and the biodiesel production process will be more complicated. This can cause a process of oil hydrolysis, where triglycerides will be able to react with water, glycerol, and FFA content (Adenuga et al., 2021). This research has the novelty of reducing free fatty acid levels by looking at the effect of water content on free fatty acid levels by making pretreatment effective in the raw material preparation process. In the research of Ika Amalia et al. (2017), the study was conducted using a mixture of N-Hexane-Etanol solvents as the main parameter in the extraction of nyamplung seed oil, while the oven temperature in drying was not the main parameter. This research aims to (1) Know the effect of water content on free fatty acids contained in nyamplung seed oil. (2) Knowing the extraction variables in the form of moisture content of nyamplung seeds, solute and solvent ratio, and seed particle size to crude nyamplung seed oil. (3) To determine the optimum operating conditions to obtain the best crude oil of nyamplung (*Calophyllum inophyllum L.*) seeds.

2. Materials and Methods

The materials used were nyamplung seeds from Central Java, N-Hexane, distilled water, NaOH, Ethanol, and Wijs solution. The tools used in this research are a set of soxhletation tools, a set of distillation tools, a grinder, Erlenmeyer, oven, analytical balance, filter paper, burette, measuring cup, measuring flask, glass stirrer, watch glass, magnetic stirrer, hot plate, pH meter, sieve, and porcelain cup.

a. Raw Material Preparation

The pretreatment stage is carried out by preparing nyamplung seeds by cleaning and washing. After that, the oven process is carried out at a temperature of 105 ° C until in accordance with the variable moisture content of 10% and 12%. Then the grinding and sizing process is carried out according to the variables, namely 15 mesh and 25 mesh.

b. Papaya Seed Oil Extraction

The 15 mesh nyamplung seed powder was put into filter paper and then wrapped tightly and put into Soxhlet using a technical N-Hexane solution with a material and solvent ratio of 1:3, and the extraction process was carried out up to 4 times circulation at a temperature of 60°C.

Table 2.1 Extraction Variables

No.	Variables	Lower Limit (-)	Upper Limit (+)
1.	Water content	8%	12%
2.	Material size	15 mesh	25 mesh
3.	Ratio of ingredient and solvent	1:1	1:3

Figure 2.1 Soxhletation equipment circuit

c. Distillation

After the extraction process, proceed with distillation which aims to separate the solvent in nyamplung seed oil. Distillation is done by preparing a simple distillation device and using a temperature of 60°C for 50 minutes. The distillation process is stopped until there is no dripping extract, then weigh the oil obtained.

Figure 2.2 Distillation equipment circuit

d. Free Fatty Acid Analysis

Analysis of free fatty acid content in nyamplung seed oil extract was carried out by using 0.1 N NaOH solution and standardization. After that, weigh the sample as much as 5 grams into erlenmeyer and add 50 mL ethanol PA. Then drop 3-5 drops of phenolphthalein (PP) indicator solution and titrate with 0.1 N NaOH standard solution until the sample turns pink. Then record the volume of NaOH used and the free fatty acid content in the sample is calculated using the following equation:

$$FFA = \frac{56{,}1\ x\ V\ x\ N}{W}$$

V = Volume of titration result (mL)
N= Normality of titration solution
W= Sample weight (g)

e. Water Content

According to (SNI 01-2891-1992) how to calculate the water content is done by entering 10 grams of oil put into the oven 104-106o C for 30 minutes. The oil is removed from the oven and desired in a desiccator until it reaches room temperature, after which it is weighed. The procedure is repeated until the weight is stable. Moisture content can be calculated by the formula below:

$$Kadar\ Air(\%) = \frac{(W + W_0) - W_1}{M_0}$$

3. Result and Discussion

This study uses factorial design method 23 with different extraction conditions. It uses three changing variables, namely: Moisture content factor (I), material size factor (L), and material and solvent ratio (J), with two levels that produce oil weight from nyamplung seed extraction with different amounts as the response. To optimize this research, it is necessary to know the most influential method in this research by using the quicker method, namely the calculation of the main effect and interaction on the levels of Free Fatty Acid (FFA) produced. The results of the calculation of influential variables can be seen in Table 3.1, Table 3.2, and Figure 3.1.

Table 3.1. Results of Main Effect and Interaction Calculation on FFA

Effect	Total
I_{23}, LJ	0.12
I_{123}1, ILJ	0.12
I_2, L	0.13
I_3, J	0.17
I_{13}, IJ	0.19
I_{12}, IL	0.22
I_1, I	0.25

Table 3.1 shows the results that the most influential variable in the oil extraction process from nyamplung seeds is the moisture content variable when viewed from the quicker method calculation, which produces the largest number of effects.

Table 1.2 Determination of Influential Variables

Effect	Total (%)
0.12	7.14
0.12	21.43
0.13	35.71
0.17	50.0
0.19	64.29
0.22	78.57
0.25	92.86

Table 3.2 shows that the moisture content variable has the most significant influence, with a value of 0.25.

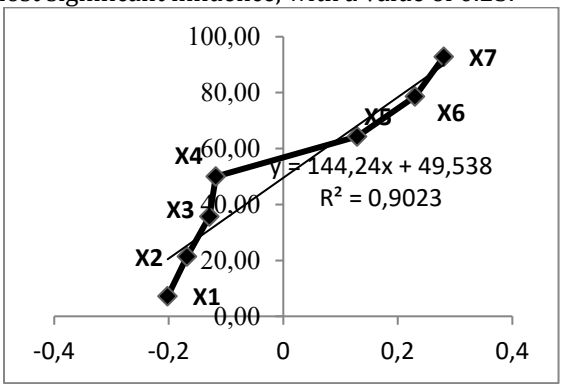

Figure 1.1 Normal Probability Plot (P vs Effect)

Figure 3.1 is a normal probability plot graph between the P value and the effect obtained by regression (R2). The chart shows that water content is the variable that has the most influence on reducing free fatty acid (FFA) levels. Then, process optimization will be carried out from the analysis results obtained to get the best results with the lowest FFA levels.

- **Optimization of Nyamplung Seed Oil**

Based on the analysis of variance in the research that has been done, it can be seen that the most influential process variable in the nyamplung seed oil extraction research process is water content, so in this optimization process, the variable L (material size) and variable J (material:solvent ratio) become fixed variables and variable I (water content) becomes a variable change. The optimization results that have been carried out in the study can be seen in Table 3.3.

Table 3.3 FFA content of Nyamplung Seed Oil in the Optimization Process

% Water Content	Material (Mesh)	Solvent Mass	FFA (%)
8	25	60:180 (1:3)	13.4
9	25	60:180 (1:3)	13.6
10	25	60:180 (1:3)	13.8
11	25	60:180 (1:3)	13.9
12	25	60:180 (1:3)	14.8

The table above shows that in the variable water content of 8% to 12%, there tends to be an increase in the FFA content produced, which is directly proportional to the water content. Still, there is a decrease in FFA content in the 11% water content variable and an increase again in the 12% water content variable. The depiction of the optimization graph of nyamplung seed oil extraction can be seen in Figure 3.2.

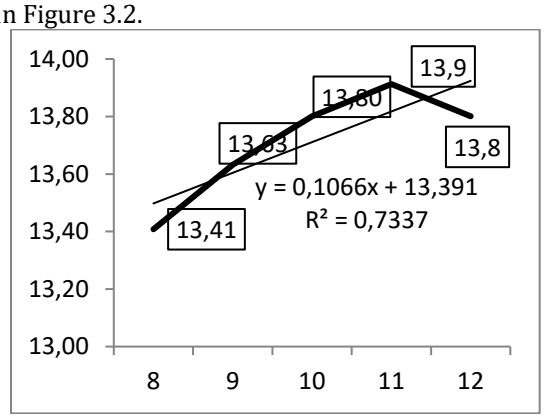

Figure 3.2 FFA Optimization Chart of Nyamplung Seed Oil

Based on the Free Fatty Acid (FFA) levels produced, as contained in the table and figure above, it can be seen that the best optimization was obtained with a variable moisture content of 8%, a variable material size of 25 mesh, and a ratio of raw materials to solvent of 1:3. Water content is very influential on the FFA content produced because the higher the water content, the FFA value produced will also be directly proportional.

- **Free Fatty Acid Content Analysis**

Table 3.4 FFA Optimization Results of Nyamplung Seed Oil

	Research Optimization	Previous Research	FFA (%)
Analysis	13.41	Sri Seno, *et.al., (2020)*	31.15
		Ika Amalia *et.al., (2017)*	14.89

	Adenuga., *et.al., (2021)*	10.86
	Wisnu *et.al., (2009)*	19.8
	Widiastuti *et.al., (2019)*	33.79

From the results of the research that has been done, when compared with previous research, it can be directly proportional to the results of the study, where the lower the moisture content of the material, the free fatty acid content produced will decrease as well. The lowest FFA content was found in previous research (Adenuga et al., 2021), which amounted to 10.86%. The research conducted by (Adenuga et al., 2021) shows that the moisture content of raw materials affects the decrease in free fatty acid levels produced in nyamplung seed oil. Whereas in the research conducted by (Pambayun, 2023), the optimization of free fatty acids in nyamplung seed oil was found to be 13.30%. This can be caused by differences in the type of solvent used in this research, using N-hexane, while the study conducted by Pambayun used petroleum ether solvent. Based on the above, when referring to previous research, it is found that the average FFA value ranges from 10.86% - 33.79%. So it can be concluded that the optimization results are following the literature because its have a value of 13.41%.

- **Yield Analysis**

Table 3.5 Optimization Results of Yield Level of Nyamplung Seed Oil

	Research Optimization	Previous Research	Yield
Analysis	59.83%	Sri Seno, *et.al., (2020*	54.9%
		Ika Amalia *et.al., (2017*	58.2%
		Adenuga., *et.al., (2021)*	61.6%
		Wisnu *et.al., (2009)*	46.9%
		Widiastuti *et.al., (2019)*	65%

Analysis of the yield content test in the study obtained results of 59.83%. In comparison, the yield in previous studies had values ranging from 46.95% - 65%. Previous research conducted by Widiastuti et al. (2019) using nyamplung seeds extracted using n-hexane solvent with a time of 5 hours and an operating temperature of 70^{o}C obtained a yield of 65%. Compared with the yield of research optimization results, there is a difference that is not too significant, which is only ± 5%. The difference can be caused by differences in solvents used, time, and operating temperature during extraction. The yield analysis results obtained cannot be concluded whether it meets the requirements because there are no quality standard requirements regarding the yield of nyamplung seed oil.

- **Iodine Number Analysis**

According to Sri Seno et al. (2020), the iodine number reflects the level of unsaturation of fatty acids that make up the oil or fat. The amount of iodine that can be bound by oil or fat indicates the number of double bonds in the oil or fat. The optimization results on iodine number analysis was 71.25 g iod/100 g oil and classified as non-drying oil (<100 g iod/100 g oil). The analysis results of the obtained iodine content cannot be concluded whether it meets the requirements because there are no quality standard requirements for nyamplung seed oil. However, when compared based on previous research with iodine number values ranging from 60.75 - 160.31 g iod/100 grams where the optimized oil and literature are included in non-drying oil.

Table3.6 Optimization Results of Iodine Numbers of Nyamplung Seed Oil

	Research Optimization	Previous Research	Iod
Analysis	71.2	Sri Seno, *et.al., (2020*	160.3
		Ika Amalia *et.al., (2017*	60.7
		Adenuga., *et.al., (2021)*	81.6
		Wisnu *et.al., (2009)*	93.8
		Widiastuti *et.al., (2019)*	98.7

4. Conclusion

The extraction process of nyamplung seed oil using N-hexane solvent shows that the amount of water content of nyamplung seeds affects the Free Fatty Acid (FFA) content of nyamplung seed oil produced. In this study, the results of process optimization were obtained with a moisture content of 8% with a material size of 25 mesh, and a material weight ratio with a solvent of 1: 3, resulting in an FFA content of 13.30%. In this study, the factorial design method was used with three variables, and by using the quicker method to calculate the main effects and variable interaction effects with a total of 8 experiments and obtained process variables that were influential in the oil of nyamplung seeds extraction

optimization process was the variable moisture content of raw materials (I) with an effect value of 0.25.

References

Adenuga, A. A., Oyekunle, J. A. O., & Idowu, O. O. (2021). Pathway to reduce free fatty acid formation in Calophyllum inophyllum kernel oil: A renewable feedstock for biodiesel production. Journal of Cleaner Production, 316(July), 128222. https://doi.org/10.1016/j.jclepro.2021.128222

Amalia Kartika, I., Dwi Kurnia Sari, D., Febriani Pahan, A., Suparno, O., & Ariono, D. (2017). Ekstraksi Minyak Dan Resin Nyamplung Dengan Campuran Pelarut Heksan-Etanol. Jurnal Teknologi Industri Pertanian, 27(2), 161–171. https://doi.org/10.24961/j.tek.ind.pert.2017.27.2.161

Balitbang Kehutanan. (2008). Nyamplung Sumber Energi Biofuel yang Potensial (Badan Pene). Departemen Kehutanan.

Emilda, E. (2019). Tumbuhan Nyamplung (Chalohyllum inophyllum Linn) dan Bioaktifitasnya. Simbiosa, 8(2), 136. https://doi.org/10.33373/sim-bio.v8i2.2000

Handayani, S. S., Gunawan, E. R., Suhendra, D., Murniati, M., & Aditha, I. M. (2020). Karakterisasi Sifat Fisiko Kimia Minyak Nyamplung Sebagai Bahan Baku Sabun Padat Transparan. Jurnal Pijar Mipa, 15(4), 411–415. https://doi.org/10.29303/jpm.v15i4.1328

Ilham Adi Pratama, Ika Kurniaty, Ummul hHbibah Hasyim, G. F. (2021). REVIEW: PEMANFAATAN BIJI NYAMPLUNG (Calophyllym Inophyllum) SEBAGAI BAHAN BAKU BIODIESEL BERDASARKAN PROSES PRODUKSI DAN PENAMBAHAN KATALIS. Journal of Chemical Information and Modeling, 10(01).

Rejeki, S. (2015). Ekstraksi Dan Penetapan Nilai SPF Minyak Nyamplung Dengan Metode Sektrofotometri (Extraction And SPF Value Determination Of Tamanu Oil By Spectrofotometri Methode). Indonesian Journal On Medical Science, 2(1), 7–10.

Syafei, S. W. dan M. (2009). PENGARUH JUMLAH TRAY DAN PERBANDINGAN SOLVENT TERHADAP YIELD EKSTRAK MINYAK NYAMPLUNG. Jurnal Teknik Kimia, 024.

Widiastuti, H., Pratiwi, M., Neonufa, G. F.,Soerawidjaja, T. H., & Prakoso, T. (2019). Comparative Study of Nyamplung (Callophylum inophyllum) Kernel Oil Obtained from Mechanical and Chemical Extraction for Biofuel Production. Jurnal Rekayasa Proses, 13(2), 81. https://doi.org/10.22146/jrekpros.42816

Pambayun, F., and Broto, R.T.D.W. (2023). The Effect of Moisture Content on Reducing the Free Fatty Acid Content of Nyamplung Seed Oil (Callophylum Inophyllum) Using Factorial Design Method. Journal of Vocational Studies on Applied Research, 5(1), 31-35. doi: http://dx.doi.org/10.14710/jvsar.v5i1.17619