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PROCESSING AND CHARACTERIZATION OF OIL PALM LOOSE FRUITS AS A RAW MATERIAL FOR BIODIESEL

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Abstract
The main product of oil palm plantations is oil palm fresh fruit bunches. However, there are loose oil palm fruits detached from the ripe fresh fruit bunch or found during the cutting process at harvest. Biodiesel can be obtained by processing crude palm oil (CPO) through a trans-esterification process; however, CPO is an important source of food, especially for cooking oil. Biodiesel production as a source of new renewable energy increases could threaten the food security programs. The oil palm loose fruits as industrial waste were investigated for renewable energy sources to overcome the conflict between the renewable energy program and food security. This research found that oil palm loose fruits consisted of about 55% of mesocarp (flesh of fruit) and around 45% of the seed. Increasing delays in the processing of oil palm loose fruits led to a decrease in the oil, and a processing delay of 12 days resulted in a significant reduction in extract yield. Increasing processing delay reduced the iodine value, and the study showed that oil palm loose fruits after 12 days have a high level of oil saturation and free fatty acid of CPO was 37%. Esterification followed by transesterification was conducted to synthesize biodiesel. The biodiesel was produced by transesterification, resulting in a yield of 14.5% and free fatty acid of 1.3%, while fatty acid methyl ester was achieved at 70.24%. Hence, we could convert oil palm loose fruits into biodiesel as a strategy to meet the renewable energy requirement produced from non-food crops.

***Keywords**: Biodiesel, crude palm oil characterization, oil palm loose fruits (LF), renewable energy*

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INTRODUCTION

The oil palm tree is originated from West Africa, which is an ancient tropical plant that has been known to contain a high oil and has a very large potential compared to other vegetable oils. Compared to the leading oilseed crops, one hectare of palm oil plantation could produce up to 10 times. Because of its high productivity, this plant has been cultivated in Asia and Central America, while the five largest palm oil-producing countries in the world are Indonesia, Malaysia, Thailand, Colombia, and Nigeria [1], [2]. Crude palm oil (CPO) or red palm is extracted from the mesocratic part of the palm fruit by a mechanic and physic process, then results in the liquid and solid fraction caused by triglycerides [3]. CPO is commonly used in the food industry (cooking oil and margarine), fuel sources (biodiesel), and commodities (cosmetic and cleaning products, textiles, and plastics [2], [4].

The core product of oil palm plantations is oil palm fresh fruit bunches (FFB), which weigh about 10-40 kg, and the fruitlet is around 6-20 g depending on their variety and oil palm age. However, oil palm loose fruits (LF) are usually used to indicate that the fresh fruit bunch (FFB) can be harvested. These LF mostly contain the highest oil content, naturally detached from the ripe FFB, and found on the ground scattered within a radius of 1.5-2.5 from the plant. Besides, the LF is also found during the cutting operation of the ripe FFB [5]. Hence, the LF can be distinguished. Table 1 presents the classification of oil palm loose fruit maturity level based on the number of loose fruits.

Table 1. The classification of oil palm loose fruit maturity level is based on the number of loose fruits [6].

No.	Number of oil palm LF	Remark
1	1 – 12.5% of the outer FFB fruits detached	Unripe
2	12.25 – 25% of the outer FFB fruits detached	Under ripe
3	25 – 50% of the outer FFB fruits detached	Ripe I
4	50 – 75% of the outer FFB fruits detached	Ripe II
5	75 – 100% of the outer FFB fruits detached	Overripe I
6	The inside FFB fruits detached, and some are rotting	Overripe II

Some time ago, farmers and plantations neglected the LF by leaving them on the ground because they perceived these fruits as small and not worth collecting. Today, they are considering collecting LF because of their high level of oil. Moreover, it has been reported that the LF from the outer of a FFB contributes up to 40% of palm oil compared to the middle and inner areas of the spikelet [7]. However, crude palm oil mills prefer to process FFB than LF, especially on fruits that have passed the processing period and have been damaged because they are overripe. The LF with longer storage time has high free fatty acid (FFA); hence, the oil palm mills are less preferred for processing because they produce a low quality of CPO with a high FFA content [8].

Biodiesel is a renewable energy. It is a vegetable oil-based fuel and runs in diesel engines. Biodiesel could be obtained by processing CPO with a trans-esterification process [9]–[11]. Meanwhile, CPO is an important source for food industries [12]. Research and development of renewable energy sourced from palm oil as a substitute for fossil energy increases; hence, it could threaten food security programs. Therefore, the use of non-food sources as biodiesel raw materials is a solution to overcome the conflict between the renewable energy program and food security. Some palm oil plants do not process the LF; they treat it as industrial waste and then utilize it for fertilizer or animal feed. This research explored the LF by characterizing the LF to know its potential so that it could be processed to increase the added value by utilizing it as an energy source. The characterization of LF was carried out by investigating the effect of the delay in processing time on the extract yield, density, free fatty acid level and acid values, moisture content, impurities level, and determining carotene. To the best of the author's knowledge, no study has been conducted to investigate biodiesel from LF. Therefore, in this research, we did not stop at the characterization of LF, but we also processed the crude palm oil of LF into biodiesel.

METHOD

Chemicals and equipment

The materials used in this experiment were FFB and LF type Dura and Tenera obtained from Penajam, North Penajam Paser Regency, East Kalimantan. CPO extracted from LF was given by CV. Karya Anak Negeri Gemilang Abadi Sawit, Kutai Kartanegara, East Kalimantan, Indonesia. Sulfuric acid (H_2SO_4, 95-97%), Ethanol, and Sodium hydroxide (pellets for analysis) were purchased from Supelco, Germany. Potassium hydroxide and methanol were purchased from Merck, Germany. Figure 1 shows the materials and tools used to obtain CPO.

The processing steps for CPO extraction from FFB and LF. Firstly, the FFB was steamed for 1 hour; then the palm fruit was separated from the kernel to get the mesocratic part (flesh of fruit), and then a chopper machine was employed to reduce the size of mesocratic before extracted by filter press to get CPO. The same process is carried out to obtain CPO from LF.

The equipment used for biodiesel synthesis includes a hotplate magnetic stirrer with speed control, digital scale, stopwatch, thermometer, Erlenmeyer, beaker glass, and rotary evaporator (Buchi, Switzerland).

Figure 1. a) Oil palm loose fruits (LF) and steam pans, b) Chopper machine, c) Mechanical press, d) Crude palm oil.

Characteristic of crude palm oil and biodiesel

In this study, the resulting CPO from FFB and LF were carried out in the form of extract yield of CPO, density, free fatty acid levels and acid values, moisture content, impurities level, and determining carotene. Extract yield was calculated based on the ratio of the final weight (weight of the resulting CPO) with the initial weight (weight of the mesocratic part). Determining density used the pycnometer in ISO standard (ISO 1183-1:2004) and ASTM standard (ASTM D85). Free fatty acid levels and acid values were determined by alkalimetric titration method using potassium hydroxide 0.1 N. Moisture content was determined by SNI standard (SNI 01-2901- 2006:5.2.1), impurities level by SNI 01-2901-2006:5.3 and carotene with UV-Vis spectroscopy.

Esterification and transesterification to biodiesel

There were two steps to produce biodiesel from crude palm oil: esterification and transesterification. Esterification was conducted before the transesterification process. In the esterification process, the ratio of oil and methanol was 1:10, with the weight of H_2SO_4 to oil being 2.5%, at an operating temperature of 60° C for 8 h. Then, followed by the esterification process, the ratio of oil and methanol was 1:9, with the weight of NaOH to oil being 1%, at an operating temperature 60° C for 2 h. In this research, the formed fatty acid methyl ester (FAME) was analyzed by GCMS-QP2010S Shimadzu.

RESULTS AND DISCUSSION

Figure 2 depicts the FFB and oil palm LF used in the research. Figure 2.c describes that white fungus grows on the surface of the LF, which has been delayed in processing for 12 days.

Figure 2. a) Fresh fruit bunch (FFB), b) Oil palm loose fruits (LF), and c) LF after 12 days.

Figure 3 shows the extract yield of FFB and LF at the different processing delays. The figure explains that the extract yield decreases with the processing delay. A delay in the processing of LF for 12 days results in a significant reduction in extract yield. Delays in processing cause the LF to shrivel because the water of fruits evaporates, and fungus present on the LF absorbs water for growing and living. Fungi consist of around 90% water and require water for all phases of life. Fungi secrete enzymes to degrade organic matter and need water to break down the substrate [13]. Hence, the moisture of the fruits decreases with the increasing processing delay of LF.

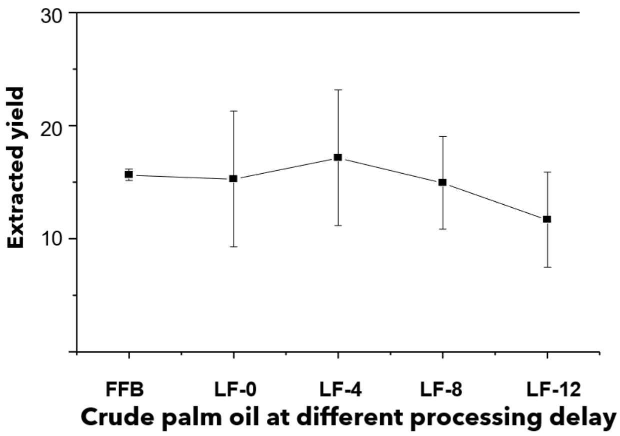

Figure 3. Extract yields from the oil palm fruits at different processing delays.

Figure 4 shows the densities and impurities levels in crude palm oil (CPO) from the FFB and LF at different processing delays. From the figure can be seen that there is no difference in density. Densities of CPO at room temperature of 27° C are around 0,9-1,01 g/ml. Impurities in CPO include phosphatides, gums, waxes, free fatty acid coloring pigment, etc. [13]. The figure shows that impurities in the CPO of FFB and LF during different processing delays are around 0,43-0,47%. The undesirable impurities could be removed by a refining process physically or chemically [14]. Nevertheless, the physical refining process is desirable due to its advantages, such as resulting in a higher oil yield, maintaining excessive oil loss, reducing the use of chemicals, and decreasing the environmental effect of palm oil processing. Generally, the physical refining process is degumming, bleaching, and deodorization [15], [16].

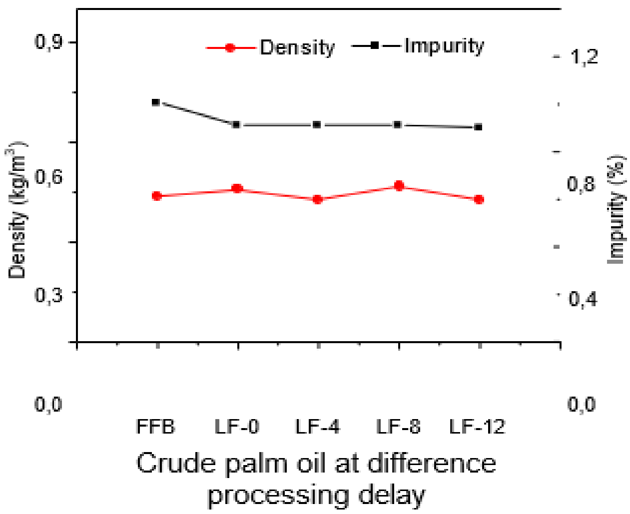

Figure 4. The densities and impurities level of CPO from the FFB) and oil palm LF at different processing delays.

Figure 5 explains the percentage of free fatty acid of the FFB and LF at different processing delays. The figure shows that free fatty acid increases along with the processing delay. Free fatty acid increases along with increasing processing delay due to the activity of lipase enzymes in the fruit. Chemical content in the mesocarp can still change as the respiration and physiological activities of harvested oil palm fruits. Moreover, this activity still undergoes after harvesting. In addition, delay processing creates contact between air and water, which triggers lipase enzymes in the fruit to accelerate the oil hydrolysis process, further producing high FFA [17].

Enhancing fatty acids in palm oil can be influenced by enzymatic hydrolysis. This process is significantly affected by the lipids present in the oil and the spontaneous autocatalytic hydrolysis that generally occurs in oil-producing plants. In particular, autocatalytic hydrolysis involves the breakdown of triglycerides into free fatty acids and glycerol, a reaction accelerated by water and heat.

Furthermore, free fatty acids in palm oil can also be formed due to microbial action or enzymatic activity, specifically by lipase enzymes found in the fruit. These enzymes catalyze the hydrolysis of fats into free fatty acids and glycerol. Various factors, including the type of microorganisms present, the temperature, and the moisture content of the environment, can influence the rate of this reaction.

The acidity of palm oil will increase rapidly under certain conditions. Damaged fruit, fruits left exposed in the open air, and those contaminated with mold are particularly susceptible to increased acid levels due to physical damage to the fruit, allowing more air and moisture to penetrate and promoting both microbial growth and enzymatic activity. Similarly, exposure to the open air can lead to oxidation and spoilage, further accelerating the formation of free fatty acids. Mold contamination can introduce additional enzymes and microorganisms contributing to hydrolysis.

These factors highlight the importance of properly handling and storing palm oil to maintain its quality. Controlling environmental conditions such as temperature and humidity, minimizing fruit damage, and preventing microbial contamination are crucial steps in reducing the rate of fatty acid formation and preserving the oil's quality and stability.

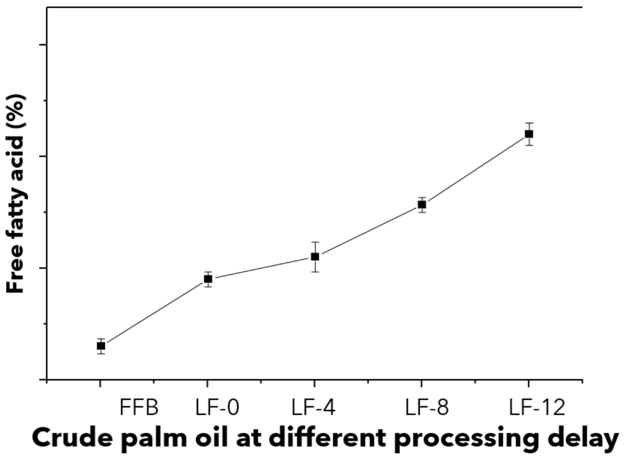

Figure 5. The percentage of FFA of the FFB and oil palm LF at different processing delays.

The graph depicts the increase in the percentage of FFA in crude palm oil at different processing delays. The x-axis represents various stages of processing delay, labeled as FFB, LF-0, LF-4, LF-8, and LF-12, while the y-axis shows the percentage of free fatty acids.

At the initial stage, FFB, the FFA percentage is the lowest. This indicates that freshly harvested palm fruits have minimal free fatty acids. The immediate processing stage, LF-0, shows a slight increase in the free fatty acid percentage compared to FFB. This demonstrates that even a short delay or minimal processing can start to increase the FFA levels.

After a short delay of 4 hours, LF-4, the free fatty acid percentage increases further. This suggests that short processing delays allow for more enzymatic activity and microbial action, leading to higher FFA formation. With an 8-hour delay, LF-8, the FFA percentage continues to rise significantly. This indicates that moderate delays exacerbate the breakdown of triglycerides into free fatty acids due to extended exposure to enzymes and possibly microbial contamination.

Finally, after a 12-hour delay, LF-12, the free fatty acid percentage is at its highest among the stages shown. This implies that prolonged delays in processing substantially increase the amount of free fatty acids, likely due to ongoing enzymatic hydrolysis and microbial action over time.

The graph shows a clear upward trend in the percentage of free fatty acids with increasing processing delay. This suggests that the longer the delay between harvesting and processing, the more free fatty acids are formed in the crude palm oil. Higher free fatty acid content can affect the quality of palm oil and its suitability for biodiesel production, as higher acidity can lead to more complicated refining processes and potentially lower yields.

To maintain lower levels of free fatty acids and ensure higher quality palm oil for biodiesel production, minimizing the delay between harvesting and processing is crucial. Prompt processing helps reduce the enzymatic and microbial actions that contribute to forming free fatty acids. This result highlights the importance of efficient logistics and processing techniques in the palm oil industry to preserve oil quality and optimize biodiesel production.

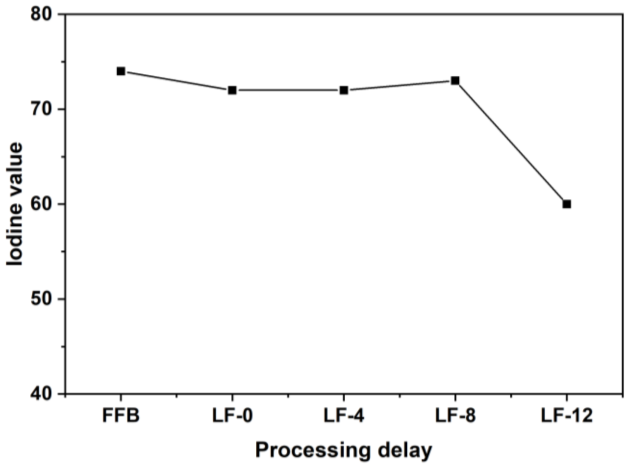

Figure 6. The iodine value of the FFB and oil palm LF at different processing delays.

Figure 6 shows the FFB and LF iodine values at different processing delays. The figure describes that increasing processing delay reduces the iodine value. Unsaturation of an oil could be determined by iodine number. Unsaturation indicates the presence of a double bond, the oxidative stability [18]. The lowest iodine value indicates that the oil has a high level of saturation. Figure 3.5 describes that LF after 12 days has a high oil saturation level.

The study found that the CPO of LF still contained oil that can be utilized to synthesize biodiesel. However, the FFA was high and increasing along with the processing delay.

CPO with high FFA (above 2% by weight of oil) forms soaps when it reacts with the base catalyst [19]–

[22]. Therefore, the CPO of LF with high FFA should be reduced before the trans-esterification process. Esterification to reduce FFA was conducted using H_2SO_4 (2.5% of oil) as an acid catalyst. 200 ml of CPO and 2.5% by weight of H_2SO_4 were prepared for esterification. The process was operated at 60 °C for 8 hours, then the product of esterification was separated from impurities by a decantation process for 24 hours. Subsequently, transesterification employed 1% NaOH as a base catalyst to convert triglycerides in the CPO into biodiesel. The product of esterification was mixed with 1% NaOH for the transesterification process. This process was managed at a temperature of 60 °C for 2 hours. In this study, the free fatty acid of CPO was 37%, the biodiesel was obtained after esterification followed by transesterification with a yield of 14.5% and free fatty acid of 1.3%. FAME in the biodiesel was determined using the GSMS report, as shown in Figure 7, and 70.24% was achieved.

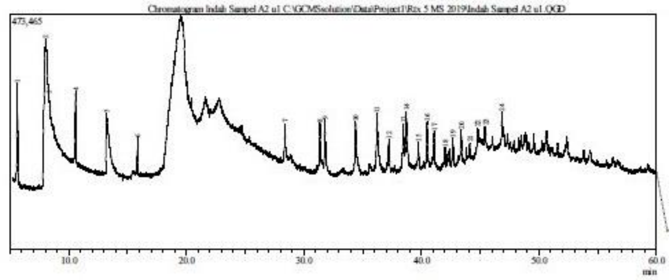

Figure 7. Chromatogram of biodiesel

The GC-MS chromatogram of the biodiesel sample illustrates the separation and identification of its constituent compounds over time. The x-axis represents retention time, indicating how long each compound takes to travel through the chromatography column. At the same time, the y-axis shows the detector response, corresponding to the quantity of each compound. The initial peaks within the first 10 minutes suggest the presence of lighter, more volatile substances, possibly residual methanol or impurities. The prominent peak around 20 minutes signifies a significant component, likely FAMEs, primarily in biodiesel. The subsequent peaks indicate a variety of FAMEs and other compounds, reflecting the complexity of the biodiesel mixture. This pattern of peaks provides insight into the biodiesel's composition, purity, and potential feedstock, essential for assessing its quality and suitability as a fuel.

CONCLUSION

In this research, we found that the extract yield decreased along with the processing delay and postponement of processing of oil palm loose fruits (LF) for 12 days, resulting in a significant decline in extract yield. Free fatty acid increased along with the enhancing processing delay because of lipase enzyme activity in the palm fruit. Increasing processing delay decreased the iodine value, and the LF after 12 days had the lowest iodine value, which means that it had a high level of oil saturation. Esterification employed 2.5% of H_2SO_2 as an acid catalyst followed by trans-esterification with 1% NaOH to produce biodiesel from crude palm oil of LF. It resulted in biodiesel containing 70.24% of FAME. Hence, we can conclude that oil palm loose fruits as oil palm industry waste could enhance their economic value by converting them into biodiesel. This could be one of strategy to meet the renewable energy requirement produced from non-food crops.

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