REDUCTION OF FREE FATTY ACID (FFA) FROM CRUDE PALM OIL BY USING HIGH AMPLITUDE SONIC WAVE

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***Abstract*— The amount of free fatty acid (FFA) in crude palm oil (CPO) is a parameter to determine a good quality in palm oil production. FFA is present as a consequence of cell damage in vegetable tissue during each process from harvesting until it can be processed into oil. Producing a high-quality CPO with lower than 5% of FFA required high cost, longer time treatment and at high temperature. Using the treatment from the ultrasonic can increase the quality of palm oil from the cavitation of the bubbles produced which creates the compression and decompression of energy. Comparison of various method of a magnetic stirrer, aerator and ultrasonic by using different parameters of solvent, temperature and time are studies. The results of using ultrasonic with the ratio of oil to solvent at 1:1.8 for ethanol and hexane solvent at the temperature of 45ºC in 60 minutes give a significant result to reduce the FFA in low percentage. The removal of FFA and yield extraction from this study are 43.74% and 45.61%. The study concludes that the ultrasonic method can be applied as an alternative method for pre-treatment of CPO which reduces FFA below 5%.**

***Keywords*— Crude Palm Oil (CPO), deacidification, free fatty acid (FFA), liquid-liquid extraction, ultrasonic.**

I. INTRODUCTION

Vegetable oils are widely used and produced every year to meet consumer demand. Crude palm oil (*Elaeis guineensis*) produces a lot in the Asian countries which including Indonesia and Malaysia. It is the biggest palm oil production that contributes to 85% of the world palm oil production [1]. Malaysia itself contributing to 32% of global production and export in 2017 thus becoming an important agricultural crop and economic growth. However, there is an abundant of vegetable oil produce which gives a low-grade quality of oil including the crude palm oil which can be converted to biodiesel. In the CPO standard, one of the quality parameters need to consider is the amount of free fatty acids (FFA) [2].

Palm oil containing glycerol and fatty acids known as triacylglycerides and at lower levels, other constituents such as free fatty acids, partial acylglycerides, sterols, tocopherols, hydrocarbons, pigments are present [3]. Basically, FFA are produced by hydrolysis of oils and fats. The fatty acid chains present in the palm oil triglycerides are varied in the chain length and structure due to the number of carbons present[4]. The fatty acid composition of crude palm oil is mainly palmitic (44 %), stearic (4 %), oleic (40.6 %) and linoleic (9.8%) [5]. The high level of FFAs in CPO indicates its lower ability due to the enzymic and microbial lipase reactions of palm fruit, as well as the storage of CPO under bad conditions such as high temperature and high moisture which can affect the quality of oil [3], [6]. Moreover, FFA is unstable compared to neutral oil because it tends to oxidize and cause rancidity [7]. Therefore, it needs to be removed until it meets the Palm Oil Refiners Association of Malaysia (PORAM) standard specifications for the FFA content (as palmitic acid) that is 5% maximum in CPO [8].

In general, the deacidification process to remove free fatty acids during the process refining are chemical and physical refining methods. Physical refining is more preferable due to a simple process and high efficiency in removing FFA rather than chemical refining because it can cause high losses of neutral oil from the saponification process[9]. Studies show that liquid-liquid extraction can be an alternative to reduce FFA in the refining process by using an appropriate solvent as a carrier such as ethanol [9]. Ultrasonic is one of the approaches to improve the liquid-liquid extraction which is being reported in recent studies [10], [11]. The significance of using ultrasonic is because the acoustic cavitation of bubbles breaks down the cell wall and produce wave to create agitation effect. The benefit of using ultrasonic is due to shorter time treatment and required low energy.

The aim of the present work was to determine the FFA content in crude palm oil (CPO) and deacidification of palm oil (DPO) and to identify the optimal combination parameters of solvents, oil to solvent mass ratio, temperature, and time for best processing condition when using ultrasonic equipment.

II. METHODOLOGY

A. Crude Palm Oil

In this study, the crude palm oil (CPO) was obtained from Sime Darby Plantation, Carey Island, Selangor Darul Ehsan, Malaysia. These oils were stored in room temperature until further use.

B. Preparation of Crude Palm Oil

The preparation of CPO was started by pouring the semi-solid CPO into a 250mL beaker and heated on a hot plate until the temperature at 40ºC for 5 minutes. It is to ensure that the CPO is melted completely before it can be used for further experiments.

C. Analysis of free fatty acid (FFA content)

The test to determine the FFA content in the palm oil was using the titration method that is referred from the American Society for Testing and Materials (ASTM D5555). These methods were applied to the palm oil sample before and after the extraction by using ethanol 95% purity solvent, phenolphthalein indicator solution 1% and it was titrated with sodium hydroxide, NaOH solution until it the changes of colour appears.

For the CPO sample, it required 7g of the sample, 75 mL of ethanol solvent and 0.25M of NaOH, whereas, for the deacidification palm oil (DPO) sample, it required 30g of the sample, 50 mL of ethanol solvent and 0.1M of NaOH [12]. The

percentage of FFA content in CPO and DPO was calculated using equation (1):

$$FFA\ content\ (\%) = \frac{V \times N \times 25.6}{m} \quad (1)$$

Where, V and N are the volume and concentration of sodium hydroxide solution, respectively, and m is the mass of the sample before and after extraction. The percentage of FFA in CPO was calculated as palmitic acid and interpreted as the weight of NaOH.

D. Method treatment of CPO

The preparation of the CPO sample before treatment was design according to the experiment conducted from the previous research [9], [13]. The mass ratio of oil to solvent used for the experiment was equal to 1:1.8 and water content is 7.4% of oil [13]. The temperature used is 45°C. In this study, ethanol and hexane were used as a solvent.

The experiment was started by determining the effectiveness of removing FFA using different methods by a magnetic stirrer, aerator and ultrasonic. The chosen method was continued to study the operating condition, such as solvent used, temperature and time were investigated. Three different solvents used were ethanol, methanol, and glycerol. The good removal of FFA solvent was selected to undergo the next condition which to determine the right temperature and time. The condition of the temperature was studied at 27°C, 35°C, 45°C, and 55°C, whereas the time was studied at 15, 30, 45, and 60 minutes. After each treatment, the deacidification palm oil (DPO) sample will be separated and dried before it can be weighted and analyzed.

E. FFA removal

FFA removal was calculated using equation (2):

$$FFA\ removal\ (\%) = \frac{FFA\ (CPO) - FFA\ (DPO)}{FFA\ (CPO)} \times 100 \quad (2)$$

Where, FFA (CPO) and FFA (DPO) were the results obtained from the analysis of FFA content.

F. Yield produced

The yield produced from the extracted oil after treatment was calculated by using equation (3):

$$Yield\ (\%) = \frac{W_e}{W_t} \times 100 \quad (3)$$

Where, W_e= weight of the sample after treatment and W_t= weight of the sample before treatment.

III. RESULTS AND DISCUSSION

A. Effect of different methods treatment of oil from CPO

Various types of method were used for their efficiency in reducing FFA to a lower percentage below than 5%. The solvents, temperature and time were kept constant. Figure 1 shows that the ultrasonic was the best method to reduce the FFA in CPO which was 41.9% FFA removal and it is also been supported in the previous studies [10], [11], [14].

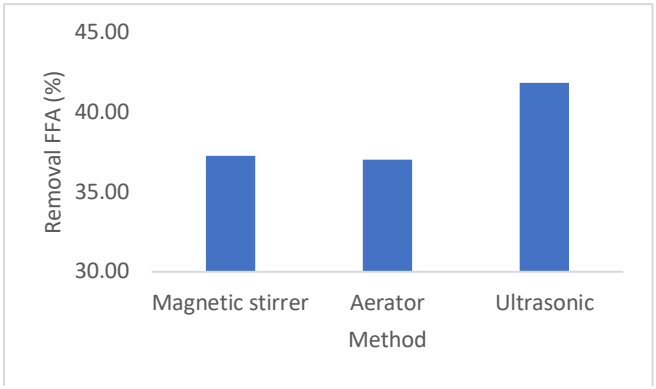

Figure 1: Effect of different methods treatment of oil from CPO

Based on the result obtained as shown in Table 1, the method treatment used was to create the kinetic energy due to the physical contact of oil, solvent, and water. The cavitation bubbles and mechanical agitation created from these methods will disrupt the cell walls and helps the solvent to penetrate in the oil particle and allowing the intracellular product to release. Ultrasonic produces cavitational bubbles which will be exploded with relatively greater force, thus increased cell tissue disruption during treatment.

Table 1: Overall result obtained from different methods of treatment of oil.

Method	FFA of CPO (%)	FFA of DPO (%)	Removal FFA (%)	Yield Extraction (%)
Magnetic stirrer	5.12	3.21	37.30	43.50
Aerator	4.94	3.11	37.04	37.00
Ultrasonic	4.94	2.87	41.90	43.30

B. Effect of solvent

The effect of the differences was due to the different solubilities of solutes in the immiscible solvents phase [13]. The removal of FFA using different types of solvent in Figure 2 shows that the ethanol is more preferable on the selectivity in reducing FFA content that was 41.09%. The studies by Gutte et al., (2015) also support that ethanol is the best solvent since it is low cost and easy to produce from biological material. It is because ethanol has high electronegativity of oxygen which allowing the hydrogen bonding to take place which attracts polar and ionic molecules.

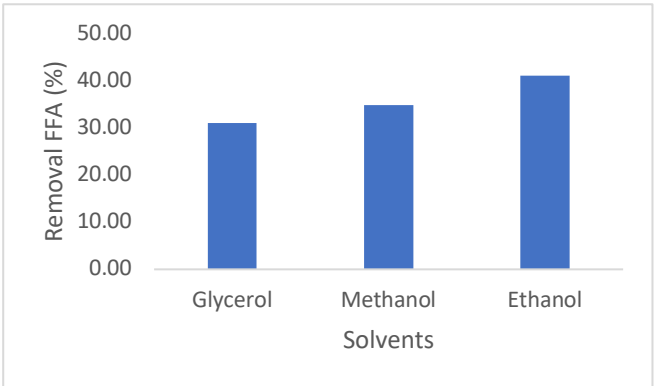

Figure 2: Effect of different solvent used

From these process a high yield of product was produced as shown in Table 2. In this study, the removal of FFA in glycerol was the lowest due to the difficulty in splitting the region to produce the cavitation bubbles by ultrasonic equipment. However, previous research studied that with the use of optimum mass ratio can help to overcome the problem [15].

Table 2: Overall result obtained from the effect of different solvent used.

Method	Solvent	FFA of CPO (%)	FFA of DPO (%)	Removal FFA (%)	Yield Extraction (%)
Ultrasonic	Glycerol	4.94	3.41	30.97	35.40
	Methanol	5.12	3.34	34.77	37.91
	Ethanol	4.94	2.91	41.09	41.70

C. *Effect of temperature*

The DPO samples at various temperature of 27ºC, 35ºC, 45ºC, and 55ºC were studied by using ethanol as solvent for 15 minutes. The results showed the removal of FFA is gradually increasing with the increase in the temperature until it reached 45ºC and before it reached 55ºC as shown in Figure 3. The increasing temperature allowed the mobility of biopolymers in the cell walls due to the reducing of oil kinematic viscosity. In which there is a resemblance of pressure and temperature. The correlation between vapor pressure and temperature creates more cavitation bubbles. The same studies on ultrasonic showed that at low temperature tends to dissolve more air in the liquid which then the air creates active nuclei for acoustic cavitation [14]. However, due to the high temperature of 55ºC the bubbles tend to burst with less intensity because of the smaller pressure difference between inside and outside of bubbles [10].

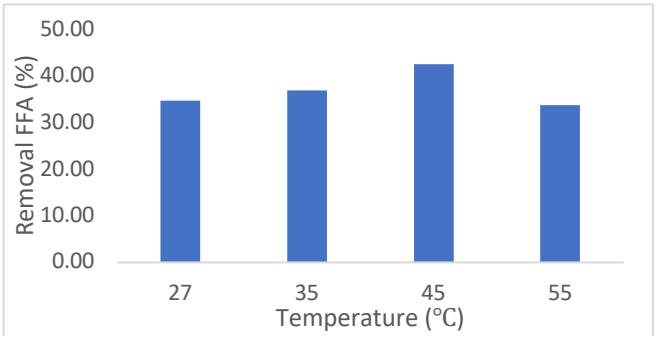

Figure 3: Effect of different temperatures used.

Based on yield extraction as shown in Table 3, at high temperature it produces more product rather than in low temperature. Therefore, the results show that at temperature 45°C is more preferable to proceed for the continuing experiment because it had the highest percentage removal despite the fact that the yield extraction is at the average among the other results obtained.

Table 3: Overall result obtained from the effect of different temperature.

Method	Temp (°C)	FFA of CPO (%)	FFA of DPO (%)	Removal FFA (%)	Yield Extraction (%)
Ultrasonic	27	5.03	3.28	34.79	42.46
	35	5.03	3.17	36.98	43.14
	45	5.03	2.89	42.54	42.96
	55	5.03	3.33	33.80	43.53

D. *Effect of time*

The time treatment was an important parameter in producing high grade of quality oil. During this process, the ethanol at temperature of 45°C were kept constant to determine the most efficient time treatment required. Based on the result from Figure 4, at 60 minutes, the removal of FFA and yield produced were the highest which are 43.74% and 45.61% respectively. It shows that in the previous study, by using ultrasonic more than 40 minutes is more effective[10]. Similar studies by other researchers also suggest increasing the time to 150 minutes for sonication time to complete [11].

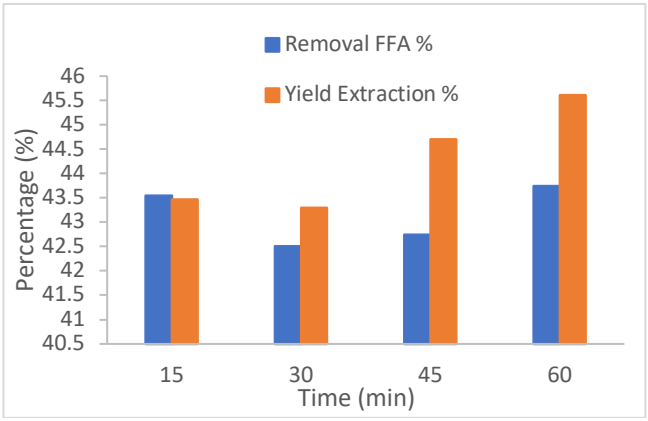

Figure 4: Different percentage on FFA removal and yield extraction based on time.

The result may be due to a longer time of ultrasonic that can create energy to disrupt the cell wall, which created longer time contact areas of the solvents, oil, and water. The high yield extraction may be due to the ultrasonic waves in the solvent penetration stage which affect the mass transfer rate [10]. Table 4 shows the overall result obtained from the effect of time treatment.

Table 4: Overall result obtained from the effect of different time treatment.

Method	Time (min)	FFA of CPO (%)	FFA of DPO (%)	Removal FFA (%)	Yield Extraction (%)
Ultrasonic	15	5.12	2.89	43.55	43.46
	30	4.94	2.84	42.51	43.29
	45	5.03	2.88	42.74	44.70
	60	5.03	2.83	43.74	45.61

IV. Conclusion

Treating of CPO using the ultrasonic method in a laboratory scale showed that the highest recovery combination of each experiment after been concluded was by using ethanol and hexane as a solvent using oil to solvent ratio of 1:1.8. The most effective temperature needs to be maintained at 45°C and the treatment should be done in 60 minutes which the FFA removal and yield produced were 43.74% and 45.61% respectively. Moreover, using ultrasonic successfully reduced the FFA content in the pretreatment of CPO to an acceptable value according to the industrial standard. This study enlightens the usage of ultrasonic technology to reduce FFA in CPO.

Acknowledgment

Thank you to Mr. Sharizan Najib, Mr. Mohibah Musa, Universiti Teknologi MARA and Sime Darby Plantation for supporting this research.

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