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Peroxide value and palm oil extraction yield from sterilised oil palm mesocarp

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Abstract

Conventional palm oil milling undergoes multiple processes including sterilisation and stripping process that introduce a significant amount of water, resulting in a large amount of wastewater. Sterilisation is the first step in milling, where it is the pre-treatment to deactivate enzymes that increase free fatty acid before oil extraction. Microwave heating softens the surface of the palm fruit mesocarp, making it much easier to extract by solvent extraction. To fill the gap of the previous study, which is to apply two processes of drying and extraction, Soxhlet extraction and microwave will be proposed as an alternative to extracting a higher yield of palm oil mesocarp, replacing the conventional method, which uses the screw pressing process. The power of microwave pretreatment was found to be the most significant factor contributing to poor oil quality. Hence, iodination titration will be used to study the peroxide value (PV) in the oil palm that was extracted. During the sterilisation process, the exposure time and weight of the fruit were constant at 6 minutes and 200 g, respectively. At 800 W of microwave power, without the presence of water, it demonstrated a higher yield, which is around 59.31 %. Peroxide values from sterilized oil palm mesocarp are less than 10 meq/kg; thus, using a microwave sterilisation process followed by the Soxhlet extraction method is an alternative technique to produce crude palm oil.

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1.0 Introduction

Conventional palm oil milling undergoes multiple processes including sterilisation and stripping processes that introduce a significant amount of water, resulting in a large amount of wastewater. It is crucial to heat the fruits as soon as possible after harvesting to prevent the degradation of palm oil into free fatty acids (FFA) (Zamanhuri et al., 2021). In palm oil milling, sterilisation and stripping process will be the first step for the initial detachment of individual fruits from its bunch (Cheng et al., 2011). Henderson & Osborne (1991) reported the first sterilisation of oil palm fruit in history as a traditional African activity. Due to the lipase activity during harvesting and storage of oil palm fruit bunches, palm oil is very prone to degradation and spoiling. Palm oil sterilisation is now an important procedure in palm oil milling to ensure that the quality of the oil is maintained. Sterilisation is a term which refers to a procedure that removes or destroys all types of microorganisms, including fungus, bacteria, viruses, enzymes, and so on. Sterilisation is also the pre-treatment process where an enzyme can be deactivated to generate free fatty acid content before oil extraction. This process will increase extraction yield and inactivate enzymes that affect the quality of crude palm oil (CPO) (Cheng et al., 2011). The typical method of pre-treatment, where fresh fruit bunches are sterilised inside an autoclave using steam, consumes a huge amount of energy and takes a much longer time. Pre-treatment of oil palm fruits is also an important step in the palm oil production plant, where the goal of this process is to soften the outer shell or mesocarp of the fruits. The steaming procedure, for example, takes roughly 70–90 minutes at 131 °C (Nadzim et al., 2020). This process is the first stage in the extraction of crude palm oil, by sterilising the palm oil fruit bunches in sterilisers under steam pressure of up to

40 psi at a temperature of 140 °C. Improper sterilisation technique impacts negatively on subsequent milling steps.

Aside from steaming, another conventional way for pre-treating oil palm fruit is to heat it in a hot air oven. Because of the long time and high heating temperature, this process also necessitates a significant level of energy consumption. Sterilisation of oil palm fruit is required to generate high-quality crude palm oil (CPO). However, while choosing a temperature and duration for the sterilisation procedure, one thing to keep in mind is the quality of palm oil that was produced. Meanwhile, peroxide value (PV) is an important indicator that influences CPO quality and stability (Kanjanapongkul, 2021). The PV is a great indicator of the start of rancidity, also known as lipid peroxidation or oxidative deterioration, is closely linked to the FFA level of the oil sample and the storage time (Shahbandeh, 2021). The current palm oil milling process does not use solvent extraction and instead relies on a combination of physical and mechanical methods. The traditional method leaves about 2% residual oil in the fruit fibre, which is wasted and adds to excessive oil loss, where the bunches are threshed in spinning threshers after sterilising to separate the individual fruits. The softened and mashed fruits are subsequently processed in digesters and the oil is extracted by screw pressing.

Microwave technology has recently been investigated as a possible substitute for this process in the production oil palm industry. Microwave heating of oil palm fruit is a method of producing and transferring heat in the fruit. Several factors are discussed in the process of microwave heating, which is where the process of heat generation and heat transfer in the oil palm fruit occurs. The palm fruits must be picked as soon as possible. Since the traditional sterilising process includes high temperatures, moist treatment, and mechanical screw pressing, the practice gives major contribution in creating an environmentally favourable condition to the chemical and enzymatic reaction of hydrolysis, including oxidation. Thus, many researchers and studies proposed the concept on the possibility of the utilisation of dry heating, which uses the microwave as a heating medium coupled with the solvent extraction process.

Fig. 1: Typical fresh oil palm fruit *(Tenera Species)*

Thus, the purpose of this research was to study and investigate the effect of microwave and solvent extraction for pretreatment processes with zero water or steam contribution to the yield and peroxide value (PV) of oil palm mesocarp. The effect of heating power on crude palm oil (CPO) quality were also examined.

2.0 Methodology

2.1 Material

Oil palm fruits were obtained from the mill near the research place. Oil palm fruits were cleaned to remove any dirt from the surface. All chemicals that were used were of analytical grade. Two samples of crude palm oil (CPO) were obtained from Sawit Raya Sdn. Bhd, and the CPO extracted from autoclave sterilisation analysis acted as a benchmark in this study. Fig. 1 shows a typical fresh oil palm fruit.

2.2 Methods

2.2.1 Palm oil fruitlets processing

The effects of heating power and water ratio on the sterilisation of oil palm fruits were investigated. The fruits were manually peeled off since this study was only focused on and aimed at the mesocarp part. Approximately 200 g of palm oil mesocarp was subjected to microwave pretreatment before being heated at the required temperature and time using an electrical oven.

2.2.2 Autoclave Sterilisation Process

An autoclave procedure was carried where this method was similar to the conventional steam heating method. Around 500g of palm oil fruit was subjected to the autoclave machine where the temperature was set at 121 °C for about 20 minutes. This machine was used to carry out processes in a palm oil mill as a heating equipment that required a lot of water. This machine also required elevated temperature and pressure in relation to ambient pressure and/or temperature, similar to steam heating process.

2.2.3 *Microwave sterilisation*

Two hundred grams (200 g) of the oil palm mesocarp was subjected to a microwave radiation as shown in Fig. 2(b). A modified domestic oven (Panasonic, NN-ST651M, Malaysia) with a frequency of 2450 MHz with maximum delivery power of 1000 W was used for the process. The time and weight of the sample were kept constant at 6 minutes and 200 g, respectively. Meanwhile, the power was varied accordingly at 400, 600, and 800 W to study the effect of the power during microwave pretreatment on the oil palm mesocarp. The sterilisation investigations were carried out with the absence of water and the presence of water (~ca. 100 mL). Next, the microwave power was fixed at 800 W while the water ratio was varied at 0 mL, 50 mL, and 100 mL. Fig. 2 (a) shows the setup of the microwave pretreatment process.

2.2.4 *Extraction of the yield from sterilised oil palm mesocarp microwave sterilisation*

Sterilised palm fruits were extracted using a Soxhlet extractor as shown in Fig. 3. Around 500 mL of n-hexane was placed at the bottom flask. The fruit to solvent ratio was 1:4. Once extraction was completed after 6 hours, the solvent was removed using a rotatory evaporator. A simple extraction procedure was set up as shown in Fig. 3(b). The oil yield was calculated using the Eq. (1):

$$\text{Oil yield (\%)}=\frac{\text{mass of leached oil}}{\text{mass of fresh palm fruits}}\times 100\% \quad (1)$$

2.2.5 *Peroxide value (PV): Iodometric titration*

The peroxide value (PV) is a chemical analysis that determines the concentration of peroxides in the oil, specifically hydroperoxides, which are formed during the initial stages of oxidation. The PV analysis was used to determine how much of the oil has been oxidised. The amount of free iodine generated during the reaction between the hydroperoxides, and the iodide ion was measured. A high value indicates that the oil under investigation has deteriorated significantly. PV analysis was carried out according to (Ainie, 2004).

(a) (b)

Fig. 2: **(**a) Microwave steriliser and (b) oil palm fruits in microwave chamber

(a) (b)

Fig. 3: Palm oil extraction procedure setup: (a) Soxhlet extractor; (b) rotatory evaporator

Acetic acid was measured around 9 0mL and poured into the reagent bottle. 60 mL of chloroform was also measured and poured into the same reagent bottle. The reagent bottle was labelled with acetic acid/ chloroform 3:2. The reagent bottle was then shaken. For 1% starch solution, 50 mL of distilled water was heated in the beaker until boiling. Then 0.5 g of starch soluble was added into the boiling water. The solution was stirred with a glass rod until the starch dissolved into water. Finally, the solution was filtered using filter paper. Saturated potassium iodide was prepared by mix with the distilled water in a test tube until the undissolved potassium iodide is left at the bottom. For 0.01 N Sodium Thiosulphate, the chemical is ready in the lab.

For titration process, 0.01 N Sodium Thiosulphate was taken into a burette and the initial reading was recorded. The sterilised oil was weighed around 5.0 ± 0.1 g into an Erlenmeyer. Next, one millilitre of potassium iodide was added and shaken for one minute. After one minute, 30 mL of distilled water was immediately added into the solution and the sample was shaken again for one minute until it mixed well. After that, 0.5 mL of starch indicator solution was added into the solution as an indicator. The solution was mixed and shaken until it turned black in colour.

The solution was titrated against standard 0.01 M Sodium Thiosulphate solution until the black colour disappeared. A blank determination was carried out concurrently. Fig. 4 shows the oil sample before and after the titration process. Peroxide value can be calculated using the Eq. (2) in milliequivalents of active oxygen per kilogram (meq/kg):

$$\text{Peroxide value (PV)} = \frac{1000\ (V\text{-}V_0)c}{m} \quad (2)$$

where: V is the volume of sodium thiosulphate for the sample determination, V_0 is the volume of sodium thiosulphate for the blank determination, c is the concentration of sodium thiosulphate and m is mass of test portion.

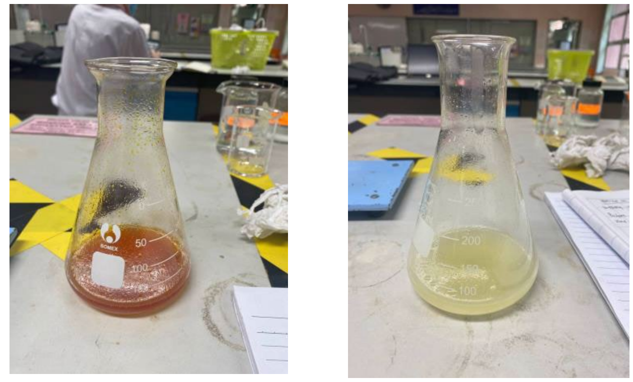
3.0 Results and Discussion

3.1 Effect of microwave power with zero and 100 mL of water

Fig. 5 shows the results of the oil yield using microwave sterilisation at different power levels (400 W, 600 W, and 800 W) and autoclave method. As shown in Fig. 5, the sample from the condition of 800 W with ratio of 1:0 and 1:0.5 produced the highest yield, which was around 59.31% and 55.68%, respectively when utilising the microwave sterilisation process. A ratio of 1:0.5 indicates a ratio of 200 g of fruits to 100 mL of water. To compare with the autoclave, which was the steam heating process, the yield value increased around 9%. However, the oil yield decreased as the power decreased to 600 W and 400 W in both conditions of water quantities i.e.,-water to 49.63% and 31.7% (0 mL of water) and 43.7% and 33.77% (100 mL of water), respectively. Microwave power rise in the oil palm mesocarp can cause physical damage such as burning and overheating.

During microwave heating of palm fruits, energy was generated by the electrical power of the microwave source and absorbed by the palm fruits. The required microwave power was proportional to the size and weight of the sample. In this case, the sample weight was constant across all experiment condition. Electromagnetic energy was created by an electron tube called a magnetron and absorbed by the mesocarp during microwave heating. Water molecules in the mesocarp vibrates, as a result of the microwave producing heat energy (Zamanhuri et al., 2021).

At 400 and 600 W of microwave power, this condition resulted in the formation of water vapours and a caramel-like scent, especially in the absence of water. When the exposure power was increased to 800 W during the experiment, the aroma turned into stronger scent. Higher microwave power, which was set at 800 W, also gave the fruits a crispy texture since there was significant increase in drying. The microwave power must be adequate to reach the boiling point of water where the presence of microwaves that are attracted to water, which might reduce the moisture content of the sample and cause breaking resulting in the release of the target molecule. As a result, the mesocarp's cell walls would easily break. One theory is that the necessary microwave



(a) (b)

Fig. 4: Titration procedure: (a) before titration and b) after titration

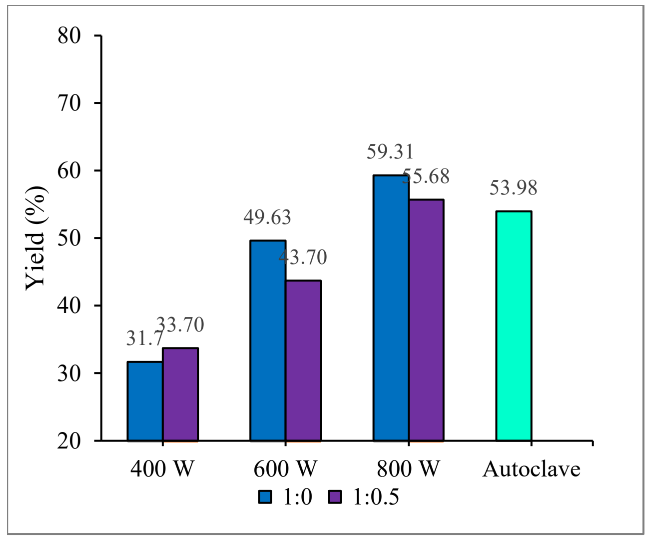
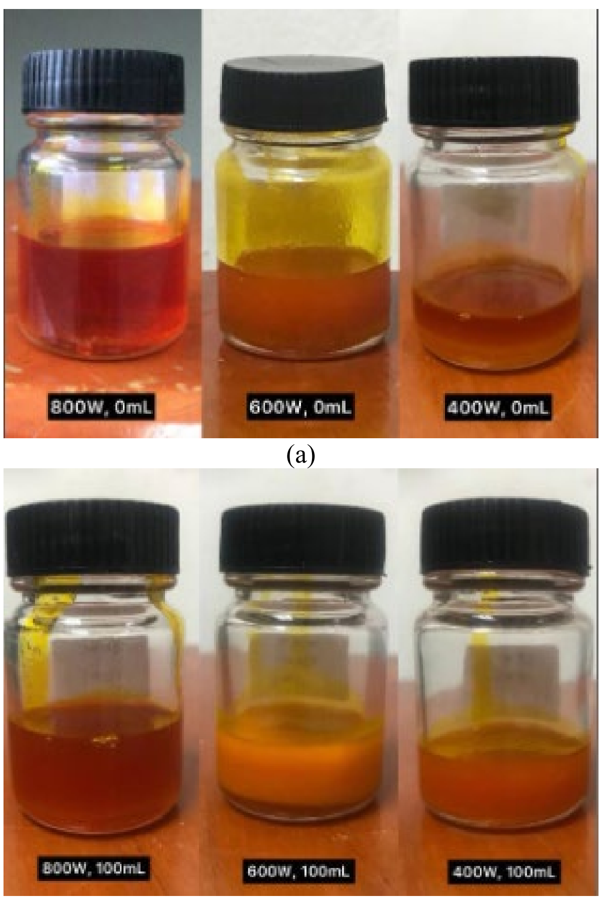


Fig. 5: Effect of microwave power to oil yield

power offers enough driving force to break down the plant cell matrix while not degrading the oil quality. Additionally, the colour of crude palm oil (CPO) that yielded at highest power (800 W) is still in an acceptable range.

Fig. 6 shows the colour of crude palm oil that were extracted using the microwave sterilisation process. All the oil that was extracted is still in the acceptable range of colour. According to Malaysian Palm Oil Council (MPOC), in crude form, palm oil is semi-solid at room temperature and bright orange-red in colour. The high concentration of carotenoids in the oil and the ratio of unsaturated to saturated fatty acids in the oil are responsible for these effects. As can be seen in Fig. 6(a) and (b), crude palm oil that has been produced after sterilisation and microwave irradiation shows an orange-red colour that can be visualised by the eyes. Fig. 6(a) with zero amounts of water and Fig. 6(b) with a visible 100-mL water amount form crude oil with an acceptable orange-red colour, not a burnt black colour. Since the highest yield can be achieved at 800 W, this condition was used in further observation. At a condition of 800 W and a ratio of 1:0, the colour was more like an orange-red due to the dry condition of the sterilisation process and increased extraction efficiency, although it was intended to be a dry and clean technique. This was similar to the findings by Cheng et al. (2011), where their aims were to couple microwave and solvent extraction methods to produce crude palm oil.



(b)

Fig. 6 Effect of sterilised oil palm mesocarp microwave power to the in terms of colour: (a) oil with 0 mL of water; (b) oil with 100 mL of water

Fig. 7 shows the effect of power on peroxide value (PV) in crude palm oil (CPO) that was extracted with zero and 100 mL of water during sterilisation process using microwave. In this study, only 400 W with zero presence of water resulted in less than the acceptable range which was 1.77 meq/kg of peroxide value. Additionally, for 800 W with both 0 mL and 100 mL of water present during the microwave sterilisation resulted in the highest PV, which were 3.90 meq/kg and 4.58 meq/kg, respectively. When the oil was exposed to air, it began to oxidise, and the rate of oxidation grew faster as the temperature rose. Evidently, because of the high temperature, the initial oxidation was considerable (Tang et al., 2017). The presence of water also showed a slight increase in peroxide value (about 14.85% error), which was similar to Chavarro et al. (2014).

In comparison to the PV that was present in industrial CPO and autoclave sterilisation, both oils contained high value of PV, which were 5.24 and 6.33 meq/kg, respectively. In the autoclave sterilisation process, the process condition was at 121 °C and 20 minutes. The performance of this process is similar to the

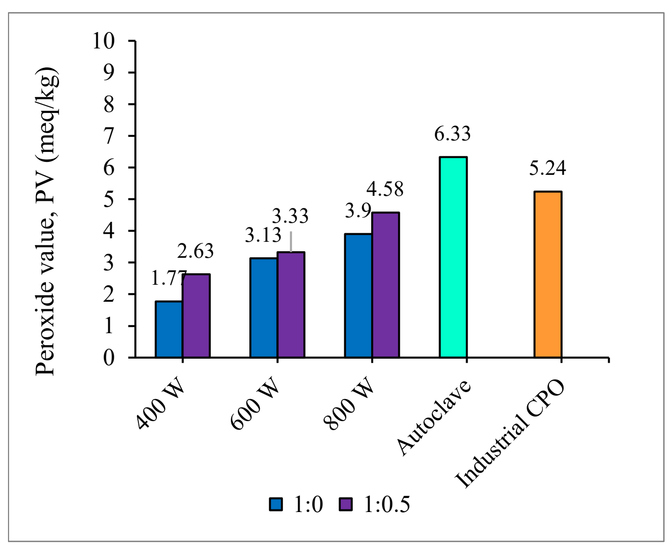


Fig. 7: Effect of power on peroxide value (PV)

conventional steam heating process where they require a lot of steam to operate. The study from Xern (2017) has found that an acceptable peroxide value that follows MS814:2007 must be less than 2 meq/kg when exposed to 600 W.

This is in agreement with the study by Ng et al. (2011), where they highlighted that CPO that was extracted in steam sterilisation process was high in PV, since the lipid peroxides was generated from a chain reaction mechanism involving free radicals as it intermediates between especially reactive hydrogen atoms from methylene (–CH2–) groups adjacent to double bonds.

The formation of an excessive amount of hydroperoxides in others set of samples could be owing to the oil being exposed to high power during the pretreatment process. Hence, the formation of hydroperoxide can occur under autoxidation.

Meanwhile, according to the standard that was proposed by Codex Alimentarius/FAO/WHO, an acceptable range of PV should be less than 10 meq/kg. According to Moigradean et. al. (2012), palm oil with a high PV content, which is less than 10 meq/kg, may still be odourless if secondary oxidation has not occurred. Products with low PV will arise from secondary oxidation. The hydroperoxides are degraded into carbonyls and other chemicals, mainly aldehydes, during secondary oxidation. These substances were important for the oil's rancidity and bad odour.

Therefore, peroxide value in CPO that was produced at 400 W with 0 mL of water was the lowest value, as the formation of an excessive amount of hydroperoxides did not occur when exposed to the lowest power.

3.2 Effect of water ratio during microwave sterilisation process

Observing from the effect of the microwave power towards yield and peroxide value, a set of experiment to study the effect of the water ratio during the sterilisation process has been done. Fig. 8 shows the result for CPO that was yielded during the extraction process. During the sterilisation process, the microwave power, weight of the sample, and exposing time were constant while the volume of water was manipulated to 0, 50, and 100 mL. The power was fixed at 800 W since at this maximum level power, the colour of the CPO that was extracted is still in the acceptable bright orange-red in colour.

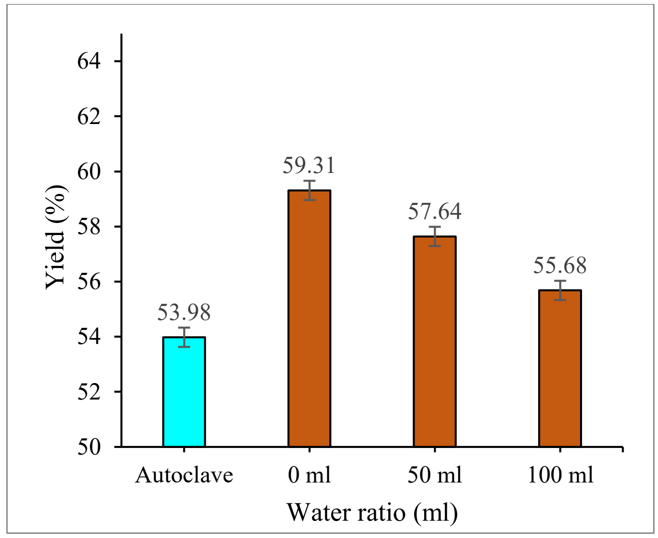


Fig. 8: Effect of water ratio to oil yield

The overall result depicted in Fig. 8 indicated that, palm fruit that was sterilised using microwave sterilisation process yielded more if no additional water was present during the process, which is 59.31%.

However, adding additional amounts of water during the sterilisation process (50 mL and 100 mL) resulted in a decrease in the yield. A combination process of microwave pretreatment followed by hexane extraction would provide high extraction efficiency of CPO, according to similar trend yields of CPO reported by Tan et al., (2016). This might be because the microwave created a rapid temperature increase inside the cellular structure within a few seconds, which may have caused the cell structure to rupture, allowing for the rapid release of oil. This observation was also discovered by (Law et al. (2018) where a similar work was done. It stated that the mesocarp shrunk due to moisture evaporating within the surface, which resulted to rapid release of oil. To compare with the autoclave, the yield value, which was 53.98%, was rapidly lower than with or without the presence of water if utilised by the microwave sterilisation process, followed by the solvent extraction procedure.

Fig. 9 summarises the oil quality analysis in terms of peroxide value (PV). The PV in the samples of oil increased as the water was presented during the microwave pretreatment process. When water was introduced during the sterilisation process, both industrial CPO and autoclave methods yielded a greater PV, 5.24 and 6.33, respectively. The process that introduced a lot of steam causes a higher rate of oxidation when the oil was in contact with oxygen in the air.

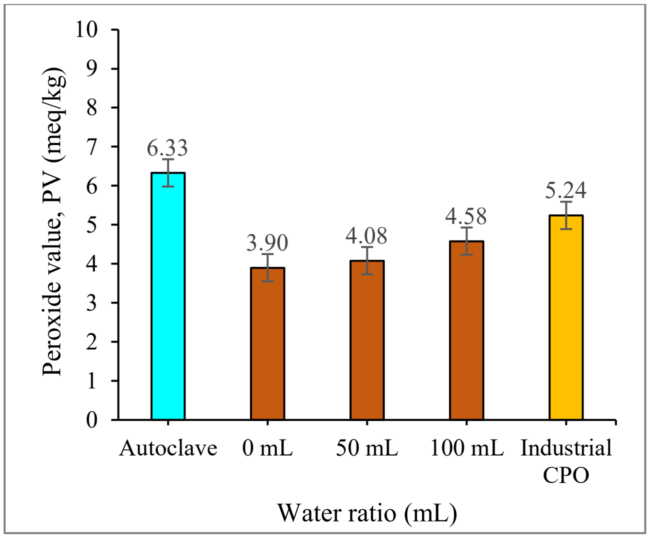


Fig. 9: Effect of water ratio to peroxide value

Additionally, the presence of water during the pretreatment process might have sped up the formation of hydroperoxides when the oil was exposed to oxygen in the air.

Similar observation was also noticed in the study by Abbas Ali et al. (2016) during the microwave heating of corn oil. These findings also suggest that at extreme heat, hydroperoxides decompose quickly into secondary oxidation products if no water is introduced during the process. These molecules are exceedingly unstable, and they breakdown into alcohols, aldehydes, ketones, acids, dimers, trimers, polymers, and cyclic compounds via fission, dehydration, and the generation of free radicals (Tan et al., 2001). Microwave exposure has also been found to have a substantial impact on the extracted oil. Excessive microwave exposure causes high PV, which can give effect to a second oxidation, if higher than 10 meq/kg.

4.0 Conclusion

The Soxhlet extraction procedure is highly efficient for the extraction of microwave sterilised palm oil mesocarp (at 800W power level with 0 mL of water), resulting in a higher yield of high-quality CPO (Crude Palm Oil) with a yield of 59.31%. The peroxide value (PV) contained in the CPO extracted using this method meets the standard proposed by Codex Alimentarius/FAO/WHO, which was 3.90 meq/kg. After post-treatment, a caramel-like aroma was released, which was then evaporated by the *in-situ* water in the oil palm mesocarp. In addition to sterilising the oil palm fruits, these innovative procedures also completely removed any remaining solvent from the cell walls, while the microwave energy significantly disrupted them. The combination of microwave sterilisation and the Soxhlet extraction procedure is a promising technology for CPO extraction, as it offers faster, more efficient, and environmentally friendly approaches.

Contribution statement

Siti Zulaikha Ruslan: Methodology, investigation, and writing original draft; **Norashikin Ahmad Zamanhuri**: Supervision & writing-review & editing.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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