Available Online at http://www.journalajst.com

ISSN: 0976-3376

ASIAN JOURNAL OF SCIENCE AND TECHNOLOGY

Asian Journal of Science and Technology
Vol. 6, Issue 05, pp. 1441-1446, May, 2015

RESEARCH ARTICLE

EFFECT OF ULTRASOUND ON THE QUALITY OF CRUDE PALM OIL-IN-WATER

[1]Suraya Suhaimi Khalis, [*,1,2,3]Zurina Zainal Abidin and [1,2]Robiah Yunus

[1]Institute of Advanced Technology, Selangor, Malaysia
[2]Department of Chemical and Environmental Engineering, Faculty of Engineering
[3]Aerospace Material Research Centre, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

ARTICLE INFO

Article History:
Received 03rd February, 2015
Received in revised form
14th March, 2015
Accepted 20th April, 2015
Published online 31st May, 2015

Key words:
Ultrasound,
Crude Palm Oil,
Bleachability Index,
Emulsion,
Free Fatty Acid.

ABSTRACT

The need to attain a good oil extraction rate and hence reduce oil loss is very important in palm oil industry. Some of the oil loss is encountered at the digestion process and ultrasound has been proposed as an alternative method to assist better oil recovery at this step of milling process. Hence, this work investigates the effect of ultrasound on crude palm oil (CPO) quality when mixed with various amount of water. A combined level of ultrasound amplitude (0 - 90 %), treatment time (5 - 30 min) and heat treatment (30 – 100 °C) were selected. Two sets of different initial qualities of CPO were studied. The initial free fatty acids (FFA) were 3.1 % and 4.5 % with deterioration of bleachability index (DOBI) value of 2.8 and 2.7 respectively. It was found that FFA quality did not show any significant changes on the treatment conditions, however, a slight deterioration of DOBI value was observed when the oil-in-water content decreased. It was also found that addition of water (as hot water or live steam) in the milling process has caused undesirable emulsification due to mechanical agitation. Applying ultrasound to oil/water mixtures promote formation of emulsion due to acoustic cavitation and high interfacial shear forces.

INTRODUCTION

One of the major concerns in the palm oil industry is the oil losses which is not recovered where it gives a significant impact on the oil extraction rate (OER) and hence, the overall revenue to the industry. This also leads to the total accumulated national income on taxations. According to the Malaysian Palm Oil Board (MPOB a, b, c) Official Portal (MPOB Statistics, 2013) the national average of OER and total CPO production for the year 2013 marked at 20.25 % and 19,216,459 MT respectively. Throughout the states in Malaysia, the OER varies from as low as 18.25 % for December 2013 in Terengganu, and, as high as 21.59 % for September 2013 in Sabah. Considering the price range from RM2,221 in January 2013 to RM2,574.5 in December 2013 per tonne of CPO, the substantial oil losses throughout the milling process operations urge many parties to fine-tune the process operating procedures. The oil bearing in a perfectly ripe fresh fruit bunch is between 25 to 30 % with respect to palm's age, clones, soil quality, as well as weather conditions and fertilizer application program. Comparing the OER achieved throughout Malaysia, there is a considerate amount of oil loss at least 30 % of the total oil content in a ripe bunch.

Corresponding author: Zurina Zainal Abidin
Department of Chemical and Environmental Engineering, Faculty of Engineering

In awareness of this substantial loss, continuous improvement is carried out to raise the OER. Besides that, more researches and breakthroughs were achieved to make use of the palm oil wastes (effluent waste water, kernel shells, empty fruit bunches, pressed fibre and even sludge). Unfortunately, despite all the efforts, the OER figure still remains around 18 to 21 % (MPOB a). The basic operations in processing palm fruit into palm oil include; fruit sterilisation, fruit loosening, fruit digestion, oil extraction and oil clarification (Owolarafe and Faborode, 2008).

The process may also be divided into 3 steps which include; preparative step (fresh fruit bunch (ffb) reception, sterilisation and thresher), extraction step (digestion and pressing) and purification step (clarification) as outlined (Ariffin 1991; 2006). The extraction step begins when sterilized oil palm fruit is macerated in a cylindrical digester vessel complete with stirring arms fitted at the central rotating shaft. The whole digestion process takes approximately 25 minutes. Hot water, or live steam, is injected at the bottom of the vessel to maintain its mash temperature within 90 to 95 °C. The high temperature helps to reduce the viscosity of the oil, soften the fruits exocarp and ease separation of the mesocarp fiber from its nut hulls by rupturing the fruits. With the hot water addition, the oil globule is easily liberated and flushed, or washed off, from the cell fiber wall. The continuous, and rather vigorous, live steam injection into the bottom of the digester is a contributing factor that promotes emulsification of oil and water. In this situation, the formation of emulsion is due to mechanical agitation. More is formed with a prolonged period of contact which allows surfactant molecules of polar (water) and non-polar (oil) to bind at the interface of the two phases. This formation of emulsion increases viscosity of the liquid resulting poor oil separation during clarification hence, low OER. Therefore, emulsion of oil and water in palm oil milling process is undesirable. The emulsion is rather unstable but its strength depends on the generation of di- and mono-glycerides, that act as emulsifier, from the milling process or from lipase activity (Ariffin, 2006).

Nonetheless, by increasing the temperature, both viscosity and interfacial tension of emulsion decrease. This deterioration of emulsion allows oil and water to separate again. This is why the crude oil collected after screw-pressing is further diluted with hot water in a dilution crude oil tank. This is to allow pure oil to separate from other foreign materials in a large clarifying tank by a slow centrifugal stir (3 – 5 rpm) for duration of 4 to 6 hours enabling gravitational settlement of more viscous water and heavy particles, or sludge, at the bottom, and least viscous oil at the top layer. Ultrasound application is popular in food industry, specifically on lignocellulosic material which has significantly improved the production rate and liquid fraction yield (Mason *et al*., 1996; Povey and Mason, 1998; Garcia *et al*., 2011; Sayyar *et al*., 2011; Abidin *et al*., 2013). The treatment of ultrasound on vegetal materials exerts a mechanical energy that affects its cellular wall hence improves the extractability of its components into the solvent media (Ebringerová and Hromádková, 2002; Liu *et al*., 2007; Chua *et al*., 2009). It was also found that no significant modifications were suffered on the physicochemical properties of the lignin (Garcia *et al*., 2011).

The ultrasound treatment can be applied at the digester where oil ruptures occur with water acts as the solvent media. Ultrasound treatment on light liquid paraffin oil-in-water is believed to produce more stable emulsion when compared to mechanical stirring due to the thermodynamically stabilized small size droplets (Ramisetty and Shyamsunder, 2011). In aqueous media, cavitation bubbles that collapse induces local shock waves, while cavitation bubbles that oscillate causes hydrodynamic shearing stress. This leads to lipid degradation which could occur due to hydrolysis or oxidation. However, in a study on sunflower seed (Chemat *et al*., 2004a; 2004b) and jatropha seeds (Sayyar *et al*., 2013) reported that ultrasound treatment did not alter any of the chemical parameters including FFA but confirmed that lipid oxidation had occurred due to the decrease amount of linoleic acid and a slight increase of conjugated dienes value.

The goal here is to investigate the effect of ultrasound on the quality of CPO when mixed with water at various ultrasound treatment conditions. The purpose is to evaluate the potential of using ultrasound treatment on fruit mash in palm fruit digester vessel. The milling conditions within the digester taken into considerations include digestion duration of approximately 25 minutes, fruit mash temperature between 90 to 95 ^{o}C and addition of hot water with varied amount based on fruit mash temperature. A combined level of ultrasound-assisted extraction (UAE) with amplitude (0 - 90 %), treatment time (5 - 30 min) and heat treatment (30 – 100 ^{o}C) were selected. The effects by varying the amount of oil as well as the amount of water were also observed. The two key contractual quality parameters (Malaysian Standard M.S. 814:2007 and SIRIM 2008) of palm oil which are free fatty acid (FFA) and deterioration of bleachability index (DOBI) were determined. These two quality parameters show the results of chemical reactions due to hydrolysis and oxidation that are also taking place during milling process.

MATERIALS AND METHODS

Materials

Two fresh productions crude palm oil (CPO) (labelled as CPO 1 and CPO 2 throughout the experiments) were obtained from production line after the removal of dirt and excessive water at a local mill in Negeri Sembilan, Malaysia. The initial FFA and DOBI qualities for the CPO samples were determined before they undergo any treatment. CPO1 and CPO2 has 3.15% and 4.57% FFA values respectively and also 2.83 and 2.67 DOBI values. The samples were selected based on their FFA qualities to represent different grades of CPO quality parameters. The CPO standard quality specifications are outlined by (Kuntom and MPOB, 2005) where the FFA specification is 5 % max (as palmitic). The FFA quality for CPO 1 is on an average standard range and rather achievable and desirable quality for CPO production during good season. Whereas, the FFA quality for CPO 2 is a lower quality standard of CPO production normally produced during bad, rainy season. The CPO samples were stored at freezing temperature (~18 ^{o}C) until further analysis. All solvents and chemicals for experimental works were supplied by Merck (Darmstadt, Germany) and Fisher Scientific Co. (Pittsburgh, PA, USA).

Main Experiments

In each preparation, CPO was pre-heated gradually to 60 ^{o}C to ensure homogeneity of both oil and fat in the sample. Distilled water at room temperature was used to add to the oil. The sample mixtures were stirred at minimum speed throughout treatment with ultrasound. After treatment with ultrasound, each sample product was allowed to settle for a minimum of 24 hrs in glass vacuum desiccators. The oil phase on top layer was then pipette out and weighed into a glass petri dish. Then, it was dried in air-dry oven for 3 hrs, that is, until the moisture reached below 0.1%. This was to ensure that the sample portions for analyses were free from moisture as the presence of moisture shall contribute to overall sample weight affecting the calculation of FFA content and DOBI value. These two parameters were determined accordingly. Analyses were performed at least in triplicates, and the mean values were reported.

Effect of Oil and Water Contents

To study the effect of oil content, 50 g of distilled water were added to each CPO bottles weighed at 60 g, 70 g, 80 g, 90 g and 100 g respectively. Whereas, to study the effect of water content, 100 g of homogenized CPO were weighed in each bottle and amount of distilled water used to add to each bottle containing the CPO were 0 g, 10 g, 20 g, 30 g and 40 g respectively. The temperature of each sample mixture was maintained at 60 ^{o}C during treatment. The ultrasound treatment time was fixed at 15 min with amplitude 20 %.

Effect of Ultrasound Treatment Conditions

An ultrasound device (300 V/T, Biologics, Inc., Virginia, USA) assembled with a piezoelectric transducer connected to the frequency generator of 20 kHz was used in this study. The device delivers 0 to 300 watts of ultrasonic power to the titanium tip (horn) and maximum amplitude of 175 µm. In the experiment, the titanium tip (diameter 1”) was immersed in a 250 ml Schott bottle with its horn positioned at 1 cm above the bottom of the bottle. The acoustic power selected throughout the experiment was 30%. To study the effect of ultrasound amplitude, each of the sample mixture was prepared with 100 g of homogenized CPO and 30 g of distilled water. The treatment time was fixed at 15 min with product temperature maintained at 60 ^{o}C. The selected ultrasound amplitudes were 0 %, 10 %, 30 %, 60 % and 90 %. To study the effect of ultrasound treatment time, each of the sample mixture was prepared with 100 g of homogenized CPO and 30 g of distilled water. The ultrasound amplitude was fixed at 20 % and the product temperature was maintained at 60 ^{o}C. The treatment times selected were 0 min, 10 min, 20 min, 25 min and 30 min.

Effect of Ultrasound on Heat Treatment

To study the effect of temperature, each sample mixture was prepared with 100 g of homogenized CPO and 30 g of distilled water. The selected temperatures were 30 ^{o}C, 50 ^{o}C, 70 ^{o}C, 90 ^{o}C and 100 ^{o}C. Each time, the temperature of sample product was raised until the desired temperature was achieved. The desired temperature was then maintained throughout the treatment for 15 min with ultrasound amplitude 20 %.

Analytical Methods

Determination of Free Fatty Acids (FFA)

The sample products before treatment with ultrasound and after treatment with ultrasound were weighed between 3 to 5 g into a 250 ml Erlenmeyer flask. Methods applied to determine the acidity was MPOB Test Method (Kuntom and MPOB, 2005). The solvent used was 50 ml neutralised and warmed 2-propanol and the solution was titrated with standardized 0.1 N potassium hydroxide solution using 1% phenolphthalein as indicator.

Determination of Deterioration of Bleachability Index (DOBI)

The sample products were pre-heated in a water bath at 60 ^{o}C and manually stirred to ensure homogeneity before weighed. Using a glass dropper, the product was weighed accurately to 0.1 ± 0.01 g in a 25 ml volumetric flask. Methods applied to determine the DOBI value was MPOB Test Method (Kuntom and MPOB, 2005). A spectroscopic grade n-hexane was used to dissolve the oil and filled up to the 25-ml mark. The absorbance of the solution was measured using a UV/VIS Spectrophotometer at wavelengths 446 nm and 269 nm.

RESULTS AND DISCUSSION

Effect of Oil and Water Contents

During the treatment, formations of colloid were observed at bottom of bottle as in Fig. 1. Mild generations of off-flavors were also detected. Fig 1 shows the products of ultrasound-treated CPO-in-water with 5 % of water mixed in bottle labelled B95 and, 10 % of water mixed in bottle labelled B90. The amount of emulsions formed in B90 was seen to be more than double of that in B95.

Fig. 1. Formation of emulsions observed at bottom of bottles labelled as B90 and B95 after ultrasound treatment

According to Chemat *et al*., 2004a; 2004b six major compounds were identified on the treatment of ultrasound on sunflower oil. Those were limonene (smell of fresh, light and sweet citrusy), (E)-But-2-enal (smell of pungent, glue, green, grassy), hexanal (smell of pungent, green, grassy), (Z)-Hept-2-enal (smell of fishy, sweet), (2E, 4E)-Deca-2,4-dienal (smell of deep-fried) and 2-methylfuran (smell of glue). These volatiles were believed to be the results of linoleic acid and sterols degradation.

It was observed that the FFA content in the oil phase did not show any significant changes for both sets of CPO qualities (CPO 1 and CPO 2) when varying the amount of oil (Fig. 2) or varying the amount of water (Fig. 3). However, Fig 4 shows a slight increase of DOBI value when increasing the oil content. Vice versa, a slight decrease of DOBI value was noted when the water content is increased as can be seen in Fig. 5. This phenomenon showed that increasing the water content (or decreasing the oil content) had increased the oil and water interactions to form the emulsion. The treatment of ultrasound produces acoustic cavitation which forms an implosion of micro-bubbles as sound wave that propagates through the liquid. Polar phase (oil) and non-polar phase (water) dispersed themselves either way to form the emulsion and promoted lipid oxidation (Chemat *et al*., 2004a; 2004b; Sayyar *et al*., 2011). This had resulted in the decrease of DOBI value due to the linoleic acid and sterols degradation as mentioned previously (Chemat *et al*., 2004a; 2004b).

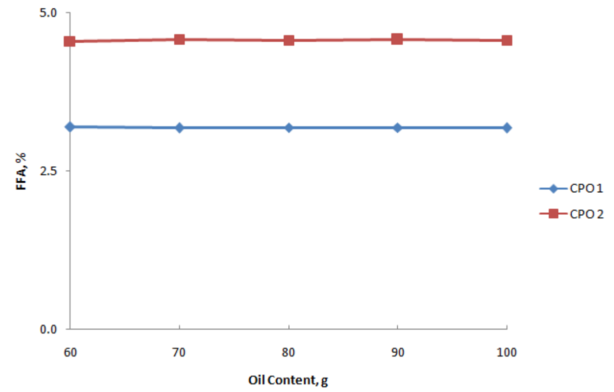

Fig. 2. Effect of FFA on Amount of Oil Content

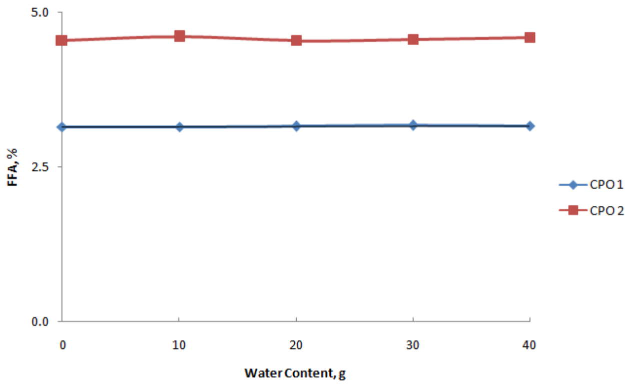

Fig. 3. Effect of FFA on Amount of Water Content

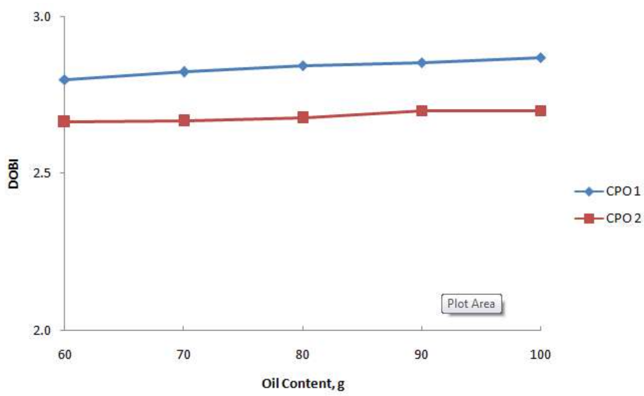

Fig. 4. Effect of DOBI on Amount of Oil Content

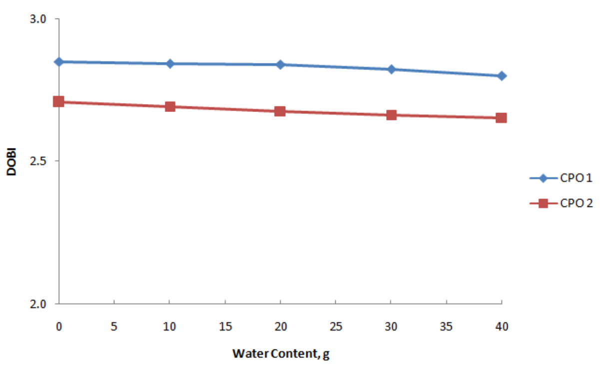

Fig. 5. Effect of DOBI on Amount of Water Content

Effect of Ultrasound Treatment Conditions

Similar observations on the formation of colloids and off-flavors applied to all the treated samples. The FFA contents for both treatment conditions on varying the ultrasound amplitude (Fig. 6) and treatment time (Fig. 7) showed insignificant effect on FFA quality.

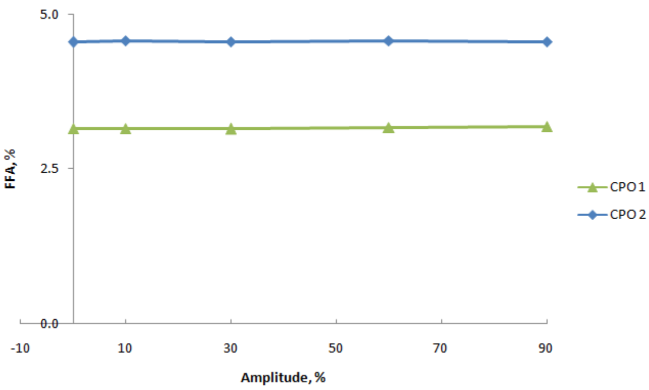

Fig. 6. Effect of FFA on Ultrasound Amplitude

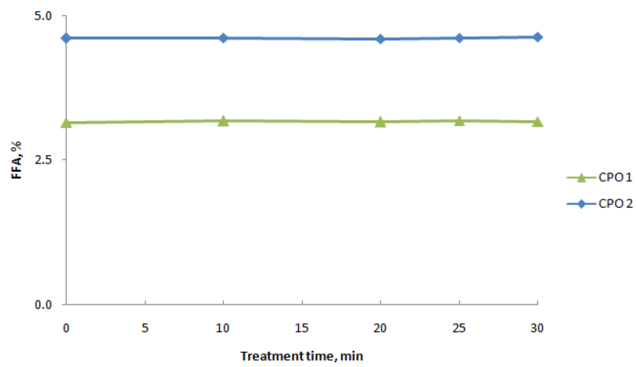

Fig. 7. Effect of FFA on Ultrasound Treatment Time

Figure 8 and 9 accordingly showed that the two treatment conditions also did not alter the DOBI values. This phenomenon is seen probably due to the same amount of emulsions formed throughout the treatment since the oil and water amount were fixed.

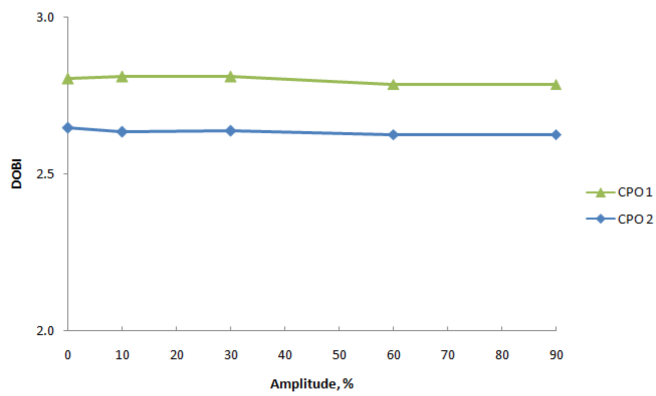

Fig. 8.Effect of DOBI on Ultrasound Amplitude

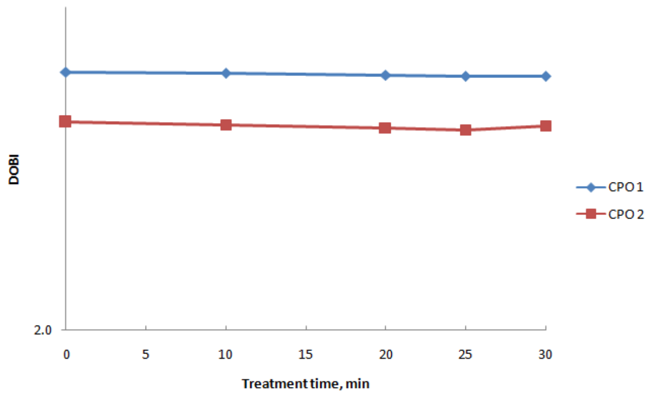

Fig. 9. Effect of DOBI on Ultrasound Treatment Time

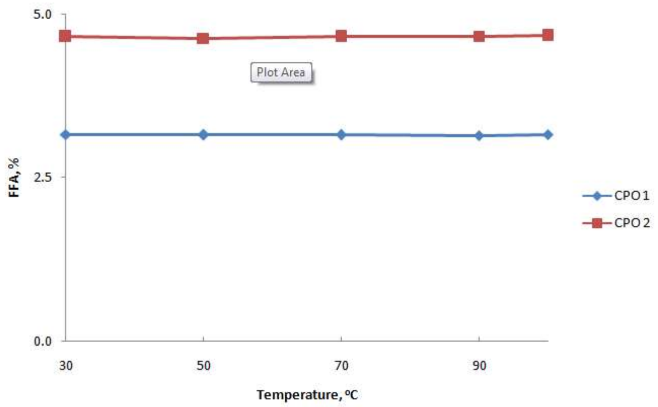

Fig. 10. Effect of FFA on Ultrasound Heat Treatment

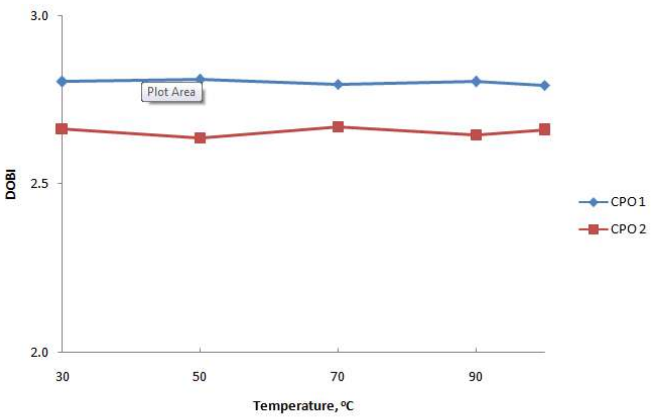

Fig. 11. Effect of DOBI on Heat Treatment

Effect of Ultrasound on Heat Treatment

The formation of colloid was observed at temperatures 30 ^{o}C, 50 ^{o}C and 70 ^{o}C after treatment with ultrasound. Similarly, generations of off-flavors were noted at these temperatures. However, only slight formation of lines of bubbles was seen during treatment with temperatures at 90 ^{o}C and 100 ^{o}C which subsided within seconds after treatment was completed. No generation of off-flavors were noted at these temperatures. The FFA contents and DOBI values as shown in Figure 10 and 11 respectively for all the treatment temperatures did not show any significant changes on the CPO quality parameters. With the same treatment conditions, the temperature variations did not alter the CPO qualities on FFA and DOBI. In a study of a combined heat and ultrasound effect on fruit and vegetable juices (Kuldiloke, 2002), it was found that this so–called thermosonication treatment had improved the induction of protein unfolding and the inactivation of enzyme. The cavitation effect from ultrasound wave propagation created the local hot spot, which led to enzyme inactivation hence, it had enhanced the effectiveness of heat treatment. Heat treatment practised on palm oil digester vessel and clarifying tank was intended to reduce the viscosity of CPO. The combined treatment with ultrasound had reduced the formation of emulsion hence, also reduced the viscosity of the CPO.

Conclusion

The indication that FFA quality did not significantly affected by ultrasound wave propagation shall lead to potential application of ultrasound on palm fruit mash be it before, within or after the digester. This finding is supported with effects on DOBI values where the quality slightly deteriorates with increasing amount of water content at treatment temperature 60 ^{o}C. The quality was not affected with treatment temperature above 70 ^{o}C. This shall not be of concern since the actual digestion condition on heating temperature is maintained at 90 to 95 ^{o}C. With above findings, it is expected that ultrasound treatment on fruit mash in the digester vessel with current conditions may improve the liberation of oil globules from cell fiber wall hence, increase the oil yield without affecting the oil quality. In addition, the use of hot water injected at bottom of digester may be excluded or minimised. As a result, emulsification issue can be eliminated or minimised. On the other hand, the hot water temperature can be lowered and maintained at a minimum of 70 ^{o}C. But these hypotheses are yet to be determined on the fruit fibre mash and the extracted oil yield. Nonetheless, further determinations on CPO quality such as glycerides content, peroxide value, iodine value, carotene and others need to be determined to strengthen the findings. This shall also include the oil stability, viscosity and the emulsion characteristics under microscopic view.

Acknowledgment

The authors wish to thank the palm oil millers in Labu, Negeri Sembilan and Trolak, Perak, for providing the fresh productions of CPO for this specific work and many more to come. This work was supported by Long Term Research Grant Scheme from the Ministry of Education, Malaysia.

Nomenclatures

CPO	Crude palm oil
DOBI	Deterioration of bleachability index
FFA	Free fatty acids
MPOB	Malaysian Palm Oil Board
MT	Metric Tonne
OER	Oil extraction rate
UAE	Ultrasound-assisted extraction

REFERENCES

Abidin, Z.Z., Awang Biak, D.R., Mohamed, H. and Harun, M.Y. 2013. Solid–Liquid Extraction in Biorefinery, in: S. Ramaswamy, H.-J. Huang and B. V. Ramarao (Eds.), Separation and Purification Technologies in Biorefineries. John Wiley and Sons, Chichester, pp. 351-371. doi: 10.1002/9781118493441.ch13

Ariffin, A.A. 1991. Chemical changes during sterilization process affecting strippability and oil quality, Proceedings of Workshop on Quality in the Palm Oil Industry, 16 – 17 May, PORIM.

Ariffin, A.A. 2006. The effect of specific quality parameters of crude palm oil (CPO) on the recovery and quality of the intended final palm oil products, MPOB National Seminar on Palm Oil Milling, Refining Technology, Quality and Environment.

Chemat, F., Grondin, I., Sing, A.S.C. and Smadja, J. 2004b. Deterioration of edible oils during food processing by ultrasound. Ultrason. Sonochem. 11: 13-15.

Chemat, F., Grondin, I., Costes, P., Moutoussamy, L. and Sing, A.S.C., Smadja, J. 2004a. High power ultrasound effects on lipid oxidation of refined sunflower oil. Ultrason. Sonochem. 11: 281-285.

Chua, S.C., Tan, C.P., Mirhosseini, H., Lai, O.M. and Long, K. 2009. Optimisation of ultrasound extraction condition of phospholipids from palm-pressed fiber. *J. Food Eng.,* 92: 403-409.

Ebringerová, A. and Romádková, Z. 2002. Effect of ultrasound on the extractibility of corn bran hemicelluloses. Ultrason. Sonochem. 9: 225–229.

García, A., Alriols, A.G., Llano-Ponte, R. and Labidi, J. 2011. Ultrasound-assisted fractionation of the lignocellulosic material. Bioresource Technol. 102: 6326-6330.

Kuldiloke, J. 2002. Effect of ultrasound, temperature and pressure treatments on enzyme activity and quality indicators of fruit and vegetable juices. Thesis. Technischen Universität Berlin.

Kuntom, A. and (MPOB) 2005. MPOB test methods: A compendium of test on palm oil products, palm kernel products, fatty acids, food related products and others. Kuala Lumpur: Malaysian Palm Oil Board.

Liu, C., Sun, R., Qin, M., Zhang, A., Ren, J., Xu, F., Ye, J. and Wu, S. 2007.Chemical modification of ultrasound-pretreated sugarcane bagasse with maleic anhydride. Ind. Crop. Prod. 26: 212–219.

Malaysian Palm Oil Board (MPOBa) Official Portal, Economics & Industry Development Division, statistics for Oil Extraction Rate (http://bepi.mpob.gov.my/index.php/statistics/oil-extraction-rate/122-oil-extraction-rate-2013/632-oil-extraction-rate-of-crude-palm-oil-2013.html

Malaysian Palm Oil Board (MPOBb) Official Portal, Economics & Industry Development Division, statistics for tonnage production http://bepi.mpob.gov.my/index.php/statistics/production/118-production-2013/603-production-of-crude-oil-palm-2013.html

Mason, T.J. 1998. Power Ultrasound in Food Processing – The Way forward, in: M.J.W. Povey, Mason, T.J., (Eds.) Ultrasound in Food Processing, Springer, Berlin, pp. 119.

Mason, T.J., Paniwnyk, L. and Lorimer, J.P. 1996. The uses of ultrasound in food technology. Ultrason. Sonochem. 3:253-260.

Owolarafe, O.K. and Faborode, M.O. 2008. Micro-structural characterisation of palm fruit at sterilisation and digestion in relation to oil expression. *J. Food Eng*., 85:598-605.

Ramisetty, K.A. and Shyamsunder, R. 2011. Effect of ultrasonication on stability of oil in water emulsions*. Int. J. Drug Deliv*., 3:133-142.

Sayyar, S., Abidin, Z.Z. and Yunus, R. 2013. Optimisation of solid liquid extraction of jatropha oil using petroleum ether. *Asia-Pacific J. Chem. Eng.,* 8:331–338.

Sayyar, S., Abidin, Z.Z., Yunus, R. and Muhammad, A. 2011. Solid Liquid Extraction of Jatropha Seeds by Microwave Pretreatment and Ultrasound Assisted Methods. *J. Appl. Sci*., 11 (13):2444-2447.

****