Physicochemical characterization of recovered palm oil from palm oil mill effluent by progressive freezing

AMRAN Nurul Aini[1,2,a *], MOHAMED ANUAR Muhammad Athir[3,b] and RUSLAN Muhammad Syafiq[4,c]

[1]Chemical Engineering Department, Universiti Teknologi PETRONAS, 32610, Seri Iskandar, Perak, Malaysia

[2]HICoE-Centre for Biofuels and Biochemical Research (CBBR), Institute of Self-Sustainable Building (ISB), Universiti Teknologi PETRONAS, 32610, Seri Iskandar, Perak, Malaysia

[3]Renewable Energy & Green Technology, TNB Research Sdn. Bhd., 43000, Kajang, Selangor, Malaysia

[4]School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA, Shah Alam 40450, Malaysia

[a]nurul.amran@utp.edu.my, [b]athir.anuar@tnb.com.my, [c]syafiqhazwan@uitm.edu.my

Keywords: Progressive Freezing, Recovered Palm Oil, Palm Oil Mill Effluent, Free Fatty Acid, DOBI

Abstract. Oil extraction rate (OER) is essential in measuring palm oil mills' performance and competence. One of the attempts to achieving high OER is exploring the possibility of recovering residual oil from palm oil mill effluent (POME). A recent technique called progressive freezing (PF) has been proposed to reclaim the residual oil from POME, forming a block of solid oil in the system. This article focuses on evaluating the quality of the recovered oil through its physicochemical characterization (free fatty acid (FFA), deterioration of bleachability (DOBI), moisture content and dirt analysis) before deciding on the subsequent usage or suitable treatment if needed. The results show that the residual oil contained 25 to 27% free fatty acid (FFA), 1.01 to 2.02% moisture content, 0.049 to 0.055 dirt and had deterioration of bleachability (DOBI) between 2.3 to 2.7. The recovered oil had been proposed to be suitable for recycle or utilization as a value-added product such as biodiesel production.

Introduction

Palm oil has progressively become vital in agriculture, accounting for 32% and 54% of global palm oil production for Malaysia and Indonesia [1], respectively. Due to the production of flexible, practical, and valuable palm oil products, this industry has become Malaysia's major income earner [2]. Palm oil is a resourceful vegetable oil used as a resource for food and non-food industries [3]. The worldwide demand for palm oil has progressively expanded since the price is lower than the other oils. This expansion of palm oil as a food ingredient has assisted in realizing sustainable food production and healthy food intake since it accelerated food guarantee, health, and profit for millions worldwide [4]. Technically, palm oil is extracted from the fruit's outer layer (mesocarp). For a ripe bunch, it is ordinarily orange-yellow. CPO is mainly utilized for food preparation purposes and is commonly used in South-East Asia (SEA), where restaurants use it due to the cheap price [5].

In 2010, worldwide palm oil utilization recorded around 71.1% of palm oil usage distribution came from food products such as margarine, salad, and cooking oil. The remaining palm oil is used for industry (24.2%) and energy usage (4.7%). Palm oil has not only been used to produce soap, cosmetic products and candles but also to produce electricity, heating and fuel. Additionally, a number of research papers uncovered that palm oil/kernel oil decides the advancement of biodiesel and oleochemical since they became significant feedstocks [6 – 8].

As palm oil production is projected to rise at the present pace, the increment of by-products is also expected. Indeed, it is proven by previous research that abundant biomass wastes have been generated by palm oil mills [9, 10] as shown in Table 1.

Table 1: Approximate by-products produced by palm oil mills (MPOB)

By-products	Million Tons	Moisture Content	Heat Value (kcal/kg)
EFB	9.6	65	3700
Shredded Fibre	5.8	42	4420
Palm Kernel Shell	3.7	7	3700
POME	21.0	95	-

Among the listed by-products above, the most plentiful is POME. POME is mainly produced through the separation of oil from the CPO solution. The main composition of POME is water (95-96%), followed by 4 - 5% total solid, 2 - 4 % suspended solid and 0.6 - 0.7 % oil [11]. The palm oil industry is concerned about the oil losses through POME since it contributes to reducing OER. Although the oil loss from POME is fewer than 1.0%, the annual oil loss was found to be significantly high and worth recovering.

In addition, POME can cause water pollution, leading to reduced dissolved oxygen in the water, which threatens marine life. Besides, the POME is acidic with an incredibly unpleasant odour. Thus, it is difficult for the palm oil industry to meet strict environmental regulations before releasing the POME to the water body. Accounting for approximately 452 palm oil mills in Malaysia, a substantial POME discharge could dangerously affect the environment [12]. Table 2 displays that POME holds almost 4000 to 6000 mg/L of oil and grease, which surpasses the permissible discharge limits which make direct disposal illegal. Moreover, POME's treatment's degradation processes could be restrained by the triacylglycerols and degradative presence inside POME [13]. Thus, removing and recovering residual oil is vital before specific treatment and disposal.

Table 2: Composition of POME

Parameter	POME (mg/L)	Range (mg/L)
Oil / grease	4000	4000-6000
Total Solid	40000	11500 – 79000
Suspended solid	18000	5000 – 54000
Total volatile solid	34000	9000 – 72000
Biochemical Oxygen Chemical Demand (BOD)	25000	10250 – 43750
Chemical Oxygen Demand (COD)	51000	15000 – 100000
Total nitrogen	750	180 – 1400

Recovering the residual oil from POME could suggest a great alternative in searching for appropriate POME treatment strategies. A reported study had proven that over 70% of COD was considerably reduced, and 78% of the oil was efficiently recovered from a POME originating from one mill in Thailand, which intensified the residual oil recovery rate [14]. Various separation methods can be applied to remove oil from palm oil mill effluent (POME). However, this report focuses on a recent innovative oil recovery process, progressive freezing (PF), which has never been investigated in Malaysia.

PF is a method used to concentrate a solution by solidifying one liquid element into a pure solid and sequentially separating the solid from the concentrated liquid. The most significant benefit of PF is that it can retain the thermally sensitive materials in the concentrate due to the involvement of low process temperatures and low energy conditions compared to evaporation [15]. The introduction of the PF method for residual oil recovery from POME may remove a high quantity of oil from the waste due to the separation driven by the difference in freezing or melting points of the oil and water. Therefore, this particular article aims to examine the physicochemical characteristics of residual oil (FFA content, DOBI, moisture content and dirt), which can define the final quality of the oil.

Materials and Methods

Materials. A Palm oil−water mixture model consisting of 6000 mg of CPO per litre of water was prepared as the primary raw material. The palm oil was first collected from the bulk storage tank (BST) of FELCRA Nasaruddin Belia Berhad, Bota Kanan, Perak. The sample was stored at a low temperature to avoid decomposition, oxidation, and free fatty acid content changes. Next, a 50% volume ratio (v/v) of ethylene glycol and water was mixed and utilized as the PF coolant. The coolant's composition was employed to facilitate the supercooling of the solution and to avoid the slushy form (viscous) of the ethylene glycol−water solution.

Experimental Procedure. The PF procedure was conducted through a lab-scale setup shown in Fig. 1. The refrigerated waterbath containing the coolant was operated to achieve the required cooling temperature between 4 to 12 ºC. As it reached the desired reading, the storage tank was filled with 2.5 L of the POME sample. The sample was then circulated inside the tubed crystallizer using a peristaltic pump for the specified circulation flowrate (2600 to 3400 mL/min) and freezing time (20 to 60 minutes). After the designated freezing time, the circulation was stopped, the remaining unfrozen liquid in the crystallizer was flushed out, and an adequate amount was collected for characterization purposes. Similarly, sample of the solidified oil was also collected and melted melted before being sent for FFA, DOBI, moisture content and dirt analysis.

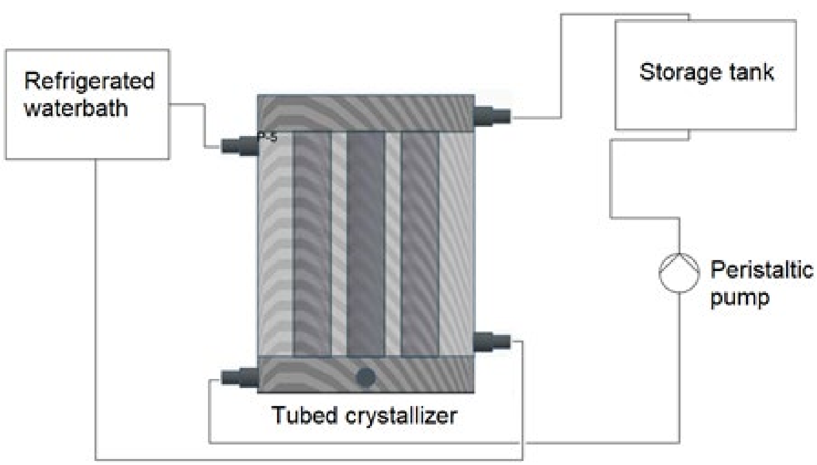

Fig. 1: Experimental setup for the PF process

The sodium hydroxide titration method was used to determine the FFA content, while DOBI was analyzed using a UV-VIS spectrophotometer. The absorbance of 446 nm signifies the carotene (pro-Vitamin A), while 269 nm reveals the secondary oxidation [16]. Table 3 shows the grades of crude palm oil based on the DOBI values. On the other hand, the moisture and dirt analysis were conducted through the standard heating and homogenization processes. Table 4 shows the quality guideline for CPO specifications released by palm oil refiners associations of Malaysia (PORAM).

Table 3: Crude palm oil grade at difference DOBI

DOBI	Grade
<1.68	Sludge palm oil or its equivalent
1.78-2.30	Poor
2.36-2.92	Fair
2.99-3.24	Good
>3.24	Excellent

Table 4: The quality limit for CPO specifications

Parameters	Quality Guideline
FFA	5.00% max
DOBI	2.3 min
Moisture Content	0.2% max
Dirt	0.02% max

Results and Discussion

Formation of Solid Palm Oil. After the PF process, the solid oil had been successfully formed on the tube crystallizer's wall, as shown in Fig.2. The amount of solid oil produced varied depending on the operating conditions.

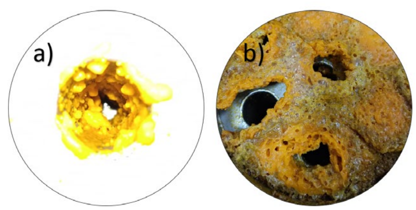

Fig. 2: Formation of solid oil on the crystallizer

Physicochemical Characteristics of Recovered Oil. Table 5 shows the physicochemical characteristics of the recovered oil by the PF process.

Table 5: Physicochemical sharacteristics of the recovered oil

Run	FFA (%)	DOBI	Moisture Content (%)	Dirt
1	27.24	2.5616	1.01	0.055
2	25.77	2.7059	1.74	0.062
3	26.51	2.3545	2.02	0.049
Previous study	27.67 ± 0.10%	1.94-2.43	2.20 ± 0.07%	-

Free Fatty Acid. As can be observed in Table 4.10, the minimum FFA value of 25.77 was obtained from the second run. The obtained values show that the quality of the residual oil was not meeting the specification limit of 5.00% maximum. A high value of FFA indicates a decline in oil quality owing to the hydrolysis of triglycerides in the residual oil [17]. FFA accumulation in the recovered oil can be due to the high moisture content or too long waiting time for the palm fruits to be processed [18]. Besides, nearly identical results had been obtained by previous researchers; for instance, a high amount of FFA was detected from the residual oil recovered by the soxhlet method (27.67 ± 0.10%) and novel polypropylene nanofiber (25%) [11,19]. Yet, this situation can be manipulated by processing the palm fruit or utilizing the recovered oil as value-added products. Residual oil with a high FFA content can produce biodiesel, which involves a simple production step. Additionally, the recovered oil can also be used to produce low-grade soap or fuel boilers.

DOBI. The extent of deterioration of palm oil can be determined by the DOBI analysis, which requires UV-VIS spectrophotometric analysis of absorbance ratio at A446 nm/A269 nm [20]. The absorbance of 446 nm corresponds to the carotene content and the absorbance of 269 nm corresponds to the secondary oxidation product. The minimum value for DOBI to indicate a reasonably good oil should be around 2.3 as it has been introduced in ISO, relevant to examine the fitness for refining a CPO. As can be seen in Table 5, all three runs fall within the fair grade range, and the lowest DOBI value was 2.3545. This value suggests an increase in secondary oxidation of the product content which could be caused by several considerations in the processing of oil palm fruit, such as the fruit ripeness, processing time and condition, supply process, storage, and contamination [20]. A quite similar result has been reported in the previous report at which the DOBI value of the residual oil obtained was yet in an satisfactory range of 1.94 to 2.43. Additionally, no substantial changes in the macronutrients and residual oil quality were reported, concluding that it can be utilized as a raw material for industrial purposes while enhancing the OER for the palm oil industry [21]. Nevertheless, the recovered oil for this study comprised a high FFA value; therefore, value-added products are preferable to recycling.

Moisture Content and Dirt. For CPO, the specification limits for moisture content and dirt are 0.2% and 0.02%, respectively. As shown in Table 5, the moisture and dirt content for all three runs exceeded these values; the lowest value obtained is 1.01%. The phenomenon might be due to the large quantities of non-toxic organic in the POME, supported by the obnoxious odour of the waste [11]. Ahmad et al. [22] had stated that just about 50% of water spent in the palm oil separation process was released as steam, while the remaining half resulted in POME. Consequently, the high water content in the residual oil will speed up the hydrolysis reaction, making the oil unsuitable for raw materials. Agreeing to earlier research, the water had been removed to reduce up to 2.20 ± 0.07% so that the utilization in the biodiesel production can be realized [19]. The removal was also crucial to avoid the reversible reaction of esterification; hence, the residual oil was pretreated by heat prior use [23].

On the other hand, dirt analysis test involves using hexane and a vacuum pump to wash the residual oil. Referring to Table 5, all three runs exceed the standard dirt limits for CPO production, where the nearest to the standard was 0.049. Nevertheless, the residual oil can be purified in the oil room to reduce the dirt percentage before further reuse or recycle [24]. So, it can be assumed that the residual oil that surpasses the specifications can be recycled or reused as value-added products, thus improving the oil extraction rate in the palm oil industry.

Conclusion

Through this study, PF process has successfully recovered the residual oil from POME by producing a single solid oil on the crystallizer's wall. The physicochemical representation had also been conducted to validate the quality of the recovered oil. The recovered residual oil shows free fatty acid (FFA) content from 25 to 27%, deterioration of bleachability (DOBI) from 2.3 to 2.7, moisture content from 1.01 to 2.02% and dirt content from 0.049 to 0.055. It can be concluded that the recovered oil can be either recycled or utilized as a value-added product such as biodiesel production.

Acknowledgement

The authors would like to acknowledge the funding supports from Ministry of Higher Education (MOHE) Malaysia through HICOE Grant (cost centre: 015MA0-052/015MA0-104/015MA0-136) to CBBR.

References

[1] H. Purnomo et al., Reconciling oil palm economic development and environmental conservation in Indonesia: A value chain dynamic approach, For. Policy Econ. 111 (2020). 102089. https://doi.org/10.1016/j.forpol.2020.102089

[2] I. Mukherjee, B. K. Sovacool, Palm oil-based biofuels and sustainability in southeast Asia: A review of Indonesia, Malaysia, and Thailand, Renew. Sust. Energ. Rev. 37 (2014) 1-12. https://doi.org/10.1016/j.rser.2014.05.001

[3] S. Kadandale, R. Marten, and R. Smith, The palm oil industry and non-communicable diseases, Bull. World Health Organ. 97 (2019) 118-128. https://doi.org/10.2471/BLT.18.220434

[4] W. Willett et al., Food in the Anthropocene: the EAT-Lancet Commission on healthy diets from sustainable food systems, The Lancet, 393 (2019) 447-492. https://doi.org/10.1016/S0140-6736(18)31788-4

[5] T. Silalertruksa et al., Environmental sustainability of oil palm cultivation in different regions of Thailand: Greenhouse gases and water use impact, J Clean. Prod. 167 (2017) 1009-1019. https://doi.org/10.1016/j.jclepro.2016.11.069

[6] P. Maneechakr and S. Karnjanakom, A combination of 2k factorial with Box-Behnken designs for FAME production via methanolysis of waste cooking palm oil over low-cost catalyst, J. Environ. Chem. Eng. 7 (2019) 103389. https://doi.org/10.1016/j.jece.2019.103389

[7] P. Alagi et al., Carbon Dioxide-Based Polyols as Sustainable Feedstock of Thermoplastic Polyurethane for Corrosion-Resistant Metal Coating, ACS Sustainable Chem. Eng. 5, (2017) 3871-3881. https://doi.org/10.1021/acssuschemeng.6b03046

[8] A. I. Matinja, N. A. Mohd Zain, M. S. Suhaimi, A. J. Alhassan, Optimization of biodiesel production from palm oil mill effluent using lipase immobilized in PVA-alginate-sulfate beads, Renew. Energy 135 (2019 1178-1185. https://doi.org/10.1016/j.renene.2018.12.079

[9] H.-M. Yoo, S.-W. Park, Y.-C. Seo, K.-H. Kim, Applicability assessment of empty fruit bunches from palm oil mills for use as bio-solid refuse fuels, J. Environ. Manage. 234 (2019) 1-7. https://doi.org/10.1016/j.jenvman.2018.11.035

[10] M. S. Umar, P. Jennings, T. Urmee, Sustainable electricity generation from oil palm biomass wastes in Malaysia: An industry survey, Energy 67 (2014) 496-505. https://doi.org/10.1016/j.energy.2014.01.067

[11] C. Hing Chung et al., Recovery of residual oil from palm oil mill effluent using polypropylene nanofiber: a field trial," MIJST 3 (2017) 276-294. https://doi.org/10.20319/mijst.2017.32.276294

[12] A. P. Ghulam Kadir, Oil palm economic performance in malaysia and R&D progress in 2019, JOPR, 2020. https://doi.org/10.21894/jopr.2020.0032

[13] A. Ahmad, Effect of Ozonation on Biodegradation and Methanogenesis of Palm Oil Mill Effluent Treatment for the Production of Biogas, Ozone: Sci. Eng. 41 (2019) 427-436. https://doi.org/10.1080/01919512.2019.1565987

[14] F. B. Ahmad, Z. Zhang, W. O. S. Doherty, and I. M. O'Hara, The prospect of microbial oil production and applications from oil palm biomass, Biochem. Eng. J. 143 (2019) 9-23. https://doi.org/10.1016/j.bej.2018.12.003

[15] M. J. Iskandar, A. Baharum, F. H. Anuar, and R. Othaman, Palm oil industry in South East Asia and the effluent treatment technology-A review, Environ. Technol. Innov. 9 (2018) 169-185. https://doi.org/10.1016/j.eti.2017.11.003

[16] M. Tapanwong, Effect of combination microwave and oven drying on the chemical properties of different ripeness crude palm oil, GEOMATE 18 (2020). https://doi.org/10.21660/2020.67.5567

[17] U. E. Shehu, T. Q. Chow, H. S. Hafid, M. N. Mokhtar, A. S. Baharuddin, N. M. Nawi, Kinetics of thermal hydrolysis of crude palm oil with mass and heat transfer in a closed system, Food Bioprod. Process. 118 (2019) 187-197. https://doi.org/10.1016/j.fbp.2019.09.009

[18] I. A. Kadir, L. S. Jurid, and S. I. Zubairi, Physico-chemical properties of recycled refined, bleached and deodorized (RBDPO) palm olein: which cycle should the olein considered spoilage, J. Teknol. 79 (2017). https://doi.org/10.11113/jt.v79.9829

[19] S. Suwanno et al., The production of biodiesel using residual oil from palm oil mill effluent and crude lipase from oil palm fruit as an alternative substrate and catalyst, Fuel. 195 (2017) 82-87. https://doi.org/10.1016/j.fuel.2017.01.049

[20] B. S. Baharin, R. A. Latip, Y. B. Che Man, R. A. Rahman, The effect of carotene extraction system on crude palm oil quality, carotene composition, and carotene stability during storage, J. Amer. Oil. Chem. Soc. 78 (2001) 851-855. https://doi.org/10.1007/s11746-001-0354-4

[21] N. S. H. Md Yunos et al., The Physicochemical Characteristics of Residual Oil and Fibers from Oil Palm Empty Fruit Bunches, BioResources. 10 (2014) 14-29. https://doi.org/10.15376/biores.10.1.14-29

[22] A. L. Ahmad, S. Sumathi, B. H. Hameed, Coagulation of residue oil and suspended solid in palm oil mill effluent by chitosan, alum and PAC, Chem. Eng. J. 118 (2006) 99-105. https://doi.org/10.1016/j.cej.2006.02.001

[23] S. R. Putri Primandari, Z. Yaakob, M. Mohammad, A. B. Mohamad, Characteristics of Residual Oil Extracted from Palm Oil Mill Effluent (POME), World Appl. Sci. J. 27 (2013) 1482-1484.

[24] C. Melches, H. Plate, J. Schürhoff, R. Buchfink, The Steps from Batchwise to Continuous Crystallization for a Fine Chemical: A Case Study, Crystals. 10 (2020) 542. https://doi.org/10.3390/cryst10060542