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Palm pressed fibre oil: A new opportunity for premium hardstock?

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Abstract: Palm pressed fiber (PPF) is a by-product from oil extraction of oil palm fruits. It has unique characteristics resulting from the combination of palm mesocarp fiber, kernel shell and crushed kernel. The present study on different extraction methods for PPF indicated that conventional hexane cold extraction would be the more preferable method compared to soxhlet and reflux method due to the yield recovered (4.35%) and diacylglycerol (19.93% ± 0.07) obtained. Acylglycerol composition using cold extraction gave high Diaclyglycerol and Triacylglycerol (67.04% ± 0.05) with reasonable amount of Monoaclyglycerol / Free Fatty Acid (13.02% ± 0.02). Lauric acid which was not present in crude palm oil were found to be significant in PPF (5.89 to 9.09%), thus making this oil suitable for application in the food industry in products such as shortening and margarine.

Keywords: Palm pressed fiber, monoaclyglycerol, diaclyglycerol, triacylglycerol, lauric acid

Introduction

Palm pressed fibre (PPF) is a by-product from oil extraction of oil palm fruits. It is a form of recovered fibre from pressed palm fruit. In the bio-based economy, the availability of biomass as feedstock for energy and products depend partly on residues from the agro-food chain. Elbersen, 2004 reported that the concept to increasing the sustainability of the palm oil value chain is to produce certifiable sustainable biomass. It is shown that combined utilisation of both the appreciated edible oil and biomass residues will result in a more sustainable value chain. This means that it should be environmentally sound, economically viable and socially acceptable.

Recovered fiber from pressed palm fruits which is normally burned as fuel to provide energy for the palm oil mills, has now been found to be a rich source of carotenoids, vitamin E (tocopherol and tocotrienols), and sterols. Residual oil (5–6% on dry basis) extracted from palm press fibers contains significant quantities of carotenoids (4000–6000 ppm), vitamin E (2400–3500 ppm), and sterols (4500–8500 ppm), (Choo *et al*., 1996). Separation of coenzyme Q10 in CPO and palm fibre oil was carried out using supercritical fluid chromatography with ultra violet detection. Calibration with authentic standard shows that there is 10-80 ppm of coenzyme Q10 in CPO while its concentration in palm fibre oil is 1000-1500 ppm (Ng *et al*., 2006).

Palm pressed fiber is a combination of palm mesocarp fiber, kernel shell, crushed kernel and debris. Hence, the oil recovered from this fiber has combined characteristics of all these products. This study illustrated that PPF oil inherited high triglycerides, palmitic and oleic content from the mesocarp while obtaining high DAG and lauric acid from palm kernel. Lau *et al*. (2006) reported that 1.14% of DAG was detected in fresh fiber using hot hexane extraction. Vegetable oils mainly constitute of 90-98% of triacylglycerol, 2-6% diaclyglycerides, 2-5% monoacylglycerol/ free fatty acids and minor composition of phytonutrients. Diacylglycerol (DAG) is a glyceride consisting of two fatty acid chains covalently bonded to a glycerol molecule through ester linkages. DAG, particularly the 1,3-isoform, has been identified as having beneficial nutritional effects such as the ability to reduce serum triacylglycerol (TAG) concentration, body weight and visceral fat. Today, DAG is marketed as functional cooking oil in Japan and the US. The commercial DAG oil contains approximately 80% DAG, consisting sn1,3-DAG and sn1,2(2,3)-DAG, and about 20% TAG. (Razam *et al*, 2009)

Lauric acid or dodecanoic acid ($CH_3(CH_2)_{10}COOH$), is a medium-length long-chain fatty acid similarly found in human milk. It offers advantages in food processing as it acts as a kind of preservative, staving off oxidation and spoilage. Lauric acid is known for its antimicrobial properties that are able to fight viruses, bacteria, yeasts and various pathogenic protozoa. Most recently lauric acid has been examined as part of the drug therapy for treating HIV infections by reducing the patient's viral load. It is also highly used in the oleochemical industry due to its properties as an emulsifier.

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Up to now, very little is known about the oil composition of palm pressed fiber and the application of its novel oil. Physical and chemical oil quality checks illustrated that PPF oil contains 15-20% of diacylglycerol (DAG) and 47-70% of triacylglycerol (TAG). Concurrent with the global vision of 'waste to wealth' recycling of PPF would utilize green technology while generating more revenue for the organization. As the raw material consists of several palm mill by-products with different properties, it would be wise to study the composition of oil using various extraction methods. By naming diacylglycerol and lauric acid as key components, selection of the extraction method could be made to produce a high quality intermediate product for premium hardstock.

The main objective of this study was to compare composition diacylglycerol and lauric acid extracted using various hexane extraction techniques to identify the most high quality PPF oil for premium hardstock production. Herein, we reported the oil yield extracted from PPF and composition of acylglycerols and fatty acids in PPF oil. The mean of diacylglycerol and lauric acid content obtained from ANOVA test assisted in selection of extraction method. The acquired results also indicated the difference of extraction methods through Post Hoc test.

Materials and Methods

Raw material

Fresh palm pressed fibre collected from Tennamaram Oil Mill, Batang Berjuntai, Selangor were air- dried for 3 days under ambient room conditions. The dried fibre was then ground (0.4 – 0.6 mm mesh) and sealed, and stored in room temperature before extraction.

Reagent and standards

All chemicals used were of analytical – reagent grade; HPLC- grade acetone, acetonitrile, (Fisher, Malaysia), and GR-grade Hexane, Methanol (Merck, Malaysia). Sodium methoxide was purchased from Sigma- Aldrich, Malaysia.

Reference material

Crude palm oil (CPO) and refined bleached deodorised palm olein (RBDPOo) were used as the reference control obtained from Tennamaram Oil Mill, Batang Berjuntai, Selangor Darul Ehsan and Kempas Edible Oil Refinery, Malaysia, respectively.

Comparison of extraction methods

Three respective sets of PPF (200 g) were subjected to cold extraction, soxhlet and reflux in 1 L hexane for eight hours. Solvent of filtrate was then removed via vacuum rotary evaporator.

High performance liquid chromatographic

The high performance liquid chromatographic (HPLC) system consisted of a pump (Waters 2695 Separation Module), a refractive index detector (RI, Waters 2414), photodiode array (PDA,Waters 2996) and reverse phase column. The columns used in this study were LiChroCART® 250-4, LiChrospher®100 RP-18 endcapped (5 µm) with guard column LiChroCART® 2504-4, LiChrospher®100 RP-18e (5 µm) (Merck, Malaysia).

Diacylglycerol determination via Acylglycerol test

200 mg of samples were dissolved in 1 mL acetone and filtered with 0.45 um syringe filter before subjected to HPLC-RI analysis. The HPLC methodology used was modified from Halimah *et al*. (1997). Mixture of eluents (acetone/ acetonitrile: 70/30) were used as mobile phase, with reverse phase column as stationary phase. The complete run took 40 minutes with flow rate of 1 mL/min. CPO and RBDPOo were used as the reference material. The composition of acylglycerols was calculated using the following formula:

$$\text{Individual Class Acylglycerol Content},\% = \frac{\text{Total Peak Area of Individual Class Acylclycerol}}{\text{Total Peak Area of Acylglycerol}} \times 100$$

Gas chromatography mass spectrometry (GC-MS)

One microliter aliquot of samples were injected at a 1:100 split ratio into a gas chromatography mass spectrometry system consisting of an Agilent 6890N Gas Chromatograph (GC) coupled with an Agilent 5973i Mass Detector and 6890 series auto sampler. Chromatography was performed using a 30 cm x 0.25 mm id x 0.25 µm film thickness HP-5MS column (Agilent, Malaysia). Mass spectra were recorded at 2.48 scans s^{-1} with a mass scanning range of 50 to 650 m/z. Metabolite identifications were determined using GC-MS spectral database matching against the current National Institute of Standards and Technology library (NIST05).

Lauric acid determination via Fatty acid composition test (FAC)

Esterification of crude PPF oil was done with the modifications of (Malaysian Palm Oil Board's (MPOB) test methodology (Ainie *et al*., 2005). Derivatised methyl esters were injected at 280°C, interface 280°C. Separations were achieved using the following temperature program: 3 minutes of isothermal heating at 80°C, followed by a 5°C min^{-1} oven ramp to 315°C, and a final isothermal heating at

315°C, 14 minutes for polar samples and 12 minutes for lipophilic samples. Identification of compounds was determined using GC-MS spectral database benchmarked against the current National Institute of Standards and Technology library (NIST05).

Statistical analysis

Quantitative data from the HPLC and GCMS analysis were compared using analysis of variance (ANOVA) by comparing the homogenous using p-value.

Result and Discussion

Comparison of extraction methods

Solvent extraction was used to recover oil trapped in the PPF after being double pressed in the oil mill. Non-polar solvent, namely hexane, has been utilized in various vegetable oil extractions such as rapeseed and soybean. The extraction process will be enhanced by using finer or powdered raw material due to the larger surface area. Hence, fibre collected from palm oil mill was ground to a fine mesh before subjected to extraction.

Solvent extraction covers cold extraction, reflux and soxhlet. The cold extraction could be defined as extraction without involving heat, where the raw material is soaked in the solvent with or without stirring or shaking. Both reflux and soxhlet methods involve heating with different theoretical concept and hence produced different amount and quality of extracts.

The physical condition, extraction time and sample to solvent ratio were standardized to compare the efficiency of three different extraction methods. Three sets of samples were subjected to different extraction methods; conventional hexane extraction in room temperature, soxhlet with condensed hexane and reflux with boiled hexane. Generally, increase of extraction temperature is proportionate to the increase of oil yield. Oil recovered via soxhlet extraction gave the lowest yield where only 3.78% were extracted (Table 1). Cold extraction gave 4.35% of PPF oil, being 0.57% higher than soxhlet extraction. This might be due to the exposure of raw material surface area against contact with solvent. Reflux extraction with heat gave the highest oil yield (4.94%) with darker brown colour compared to the other methods.

Table 1. Oil recovered from palm pressed fiber via various extraction methods

	Cold extraction	Soxhlet	Reflux
Physical	Powdered	Powdered	Powdered
Extraction time	8 hours	8 hours	8 hours
Sample: Solvent	1:5	1:5	1:5
Oil yield, %	4.35	3.78	4.94

Diacylglycerol determination via acylglycerol test

Triplicate injection to HPLC gave good reproducibility where overall standard deviation was less than 0.34 (Table 2). CPO (Figure 1) and RBDPOo were used as reference material and both possess low MAG, DAG with high TAG. PPF oil extracted via conventional cold extraction, soxhlet and reflux using hexane (Figure 2) indicated that at least 24% lower TAG compared to CPO and RBDPOo but with higher content of MAG and DAG. MAG from cold extraction and soxhlet were almost similar due to the solvent used for conventional extraction being cold while the solvent used in soxhlet was a condensate. TAG in reflux was found to be lower with high MAG/FFA compared to both soxhlet and cold extraction methods. It is believed that the TAG had degraded and formed MAG and FFA during heating process due to similar content of DAG in soxhlet. Rapid increase of MAG and FFA will then increase the tendency for oil deterioration.

Table 2. Acylglycerol composition in palm pressed fiber, crude palm oil and RBDPOo via various extraction methods

Acylglycerides	CPO	RBDPOo	PPF		
			Cold extraction	Soxhlet	Reflux
Monoacylglycerol, %	2.10 ±0.12	0.98 ±0.33	13.02 ±0.02	13.16 ±0.22	37.55 ±0.04
Diacylglycerol, %	4.53 ±0.15	6.06 ±0.07	19.93 ± 0.07	16.81 ±0.20	15.45 ± 0.34
Triacylglycerol, %	93.38 ±0.04	92.96 ±0.27	67.04 ±0.05	70.02 ±0.16	47.00 ±0.12

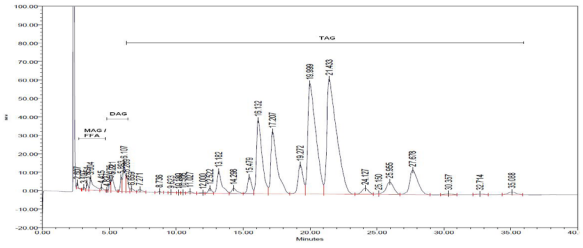

Figure 1. HPLC-RI chromatogram of reference control, crude palm oil (CPO)

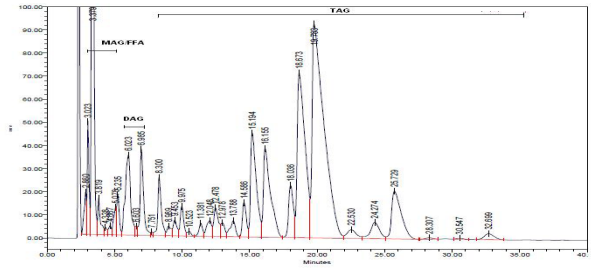

Figure 2. HPLC-RI chromatogram of palm pressed fiber oil (PPFo) extracted via cold extraction

One way ANOVA test was conducted to evaluate the extraction method of cold extraction, soxhlet and reflux on diacylglycerol content. Diacylglycerol test of homogeneity of variance gave the p-value, 0.233 which was > 0.05 and thus indicated the homogeneity and equality of variances assumption is met. The mean of diacylglycerol indicated that cold extraction (19.93%) gave the highest diacylglycerol

content compared to reflux (15.4767%) and soxhlet (16.8133%) methods. The ANOVA test revealed that the diacylglycerol content differed significantly between methods of extraction $F(2,6) = 193.84$ with $p<0.01$. The Tukey Post Hoc test on diacylglycerol indicated that all three extraction method falls into individual subsets and differ significantly with other extraction methods ($p<0.05$).

Lauric acid determination via fatty acid composition test (FAC)

Three technical replicates of samples underwent esterification before subjected to GCMS analysis. Consistency of CPO and RBDPOo indicated the highest fatty acid presence in palm oil was palmictic acid followed by oleic acid while lauric acid was not present in the mesocarp oil (Table 3). As PPF consisted of mesocarp fiber, kernel shell and crushed kernel, significant amount of lauric and linoleic acid were detected. Amount of lauric acid detected in PPF was higher as compared to myristic and stearic acid.

One way ANOVA test was conducted on lauric acid content against the extraction method of cold extraction, soxhlet and reflux. The lauric acid test of homogeneity of variance gave the p-value, 0.53. The p-values lauric acid (0.530) was >0.05 and thus indicated the homogeneity and equality of variances assumption is met. The mean lauric acid revealed reflux method (9.0933%) recorded the highest lauric acid as compared to cold extraction (5.8933%) and soxhlet (7.1233) methods. Lauric acid content differed significantly between methods of extraction $F(2,6)=407.13$, $p<0.01$. Similar to diacylglycerol test on the extraction methods, the Tukey Post Hoc test on lauric acid indicated that all three extraction method falls into individual subsets and differ significantly with other extraction methods ($p<0.05$).

Table 3. Fatty acid composition in palm pressed fiber, crude palm oil and RBDPOo via various extraction methods

Free Fatty Acids	CPO, %	RBDPOo, %	PPF,%		
			Cold extraction	Soxhlet	Reflux
C12:0	-	-	5.89 ±0.17	7.12 ±0.13	9.09 ±0.09
C14:0	0.55 ± 0.05	0.60 ±0.11	2.62 ±0.12	2.91 ±0.15	3.43 ±0.05
C16:0	46.93 ±0.02	46.30 ±0.04	39.34 ±0.09	40.70 ±0.06	37.01 ±0.08
C18:2	6.29 ±0.02	6.70 ±0.03	10.00 ±0.04	9.48 ±0.09	8.00 ±0.11
C18:1	42.94 ±0.10	42.79 ±0.07	37.74 ±0.08	36.51 ±0.14	39.01 ±0.05
C18:0	3.14 ±0.08	3.37 ±0.13	3.58 ±0.10	3.27 ±0.09	3.45 ±0.02

Conclusion

Single extraction of Palm Pressed Fiber using cold, soxhlet and reflux extraction showed that reflux and cold extraction gave higher recovered oil yield compared to soxhlet extraction. Cold extraction would be the most preferred method for acylglycerides extraction as the method provides higher DAG and TAG with reasonable amount of MAG. ANOVA test suggested the cold extraction gave the highest amount of diacylglycerol while reflux method yielded more lauric acid. Tukey Post Hoc test on diacylglycerol and lauric acid also indicated that all three extraction methods differed significantly. The author suggested that cold extraction would be a preferable method for premium hardstock's raw material production due to the high diacylglcerol content with reasonable amount of lauric acid. Besides, this extraction method also gave significant amount of oil yield with minimal effort. Somehow, further studies on the effect of differing physical condition and composition of fiber, kernel shell and crushed kernel in PPF on fatty acid composition should be carried out.

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