Thermal Stability Evaluation of Refined Bleached Deodorized Palm Oil (RBDPO) from Different Refining Parameters for Standard Crude Palm Oil

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***Abstract*—Palm oil is naturally free from trans-fat with equally saturation and unsaturation fatty acids. The absence of large amount of highly unsaturated fatty acids indicates that palm oil have good stability at high temperature. Therefore, the main goal of this work was to investigate the thermal stability of standard quality palm oil when refined by 4 different altered refining processes as compared to premium quality palm oil. Standard crude palm oil was treated with different refining parameters and followed by a 5-day thermal stability monitoring at 90^{o}C. Initial and treated samples were analyzed for its FFA (free fatty acid) %, PV (peroxide value), AnV (anisidine value), TOTOX (total oxidation), UV, colour, tocopherol and total polar compound at initial, 1st day, 3rd day and 5th day. The results showed that refining process with 2-stage bleaching conditions exhibited positive correlation or similar properties to premium quality palm oil, except for color darkening effect (r=0.997). Further study need to be carried out to fine tune the refining duration towards achieving desired color stability.**

***Index Terms*—CPO, refining, bleaching**

I. Introduction

The crude palm oil (CPO) is obtained by pressing the mesocarp of oil palm fruits (*Elais guineensis*). Palm oil contains about 44% of saturated palmitic acid, 40% of monounsaturated oleic acid, 10% of diunsaturated linoleic acid, and the rest being 5% stearic acid and small proportions of lauric, myristic, palmitoleic, linolenic, and arachidic acids [1]. CPO also contains small proportions of minor components. The minor constituents of palm oil play an important role in determining the quality of the oil. These include the naturally occurring carotenoids, tocopherols and tocotrienols, sterols, phosphatides, glycolipids as well as impurities such as Free Fatty Acid (FFA), dirt, moisture and metallic contaminants. Some of these impurities contribute undesirable effects to the oil, particularly in colour, flavour, odour, stability, and foaming [2]. These impurities need to be removed through purification, or most commonly known as refining steps in order to produce desirables good quality refined oil.

Generally, refining of vegetable oil are segregated into two ways; physical and chemical refining. More than 95% of palm oil refineries in Malaysia are opted for physical refining [3]. The difference between both refining routes are how the FFA is removed. In chemical refining, FFA is removed by introducing caustic soda that reacts with FFA and converts them into soap stock which is removed for further refining processing. Alternatively, physical refining excludes the need for soap stock management. In physical refining, there are degumming, bleaching, and deodorization stages. Degumming is to remove most of the unwanted gums or phosphatides that will interfere the stability of the oil in the later stage. This can be achieved by treating the CPO with phosphoric or citric acid in order to convert them into a form that is easily be removed during bleaching. During bleaching stage, trace metallic contaminants such as iron and copper, pigments, phosphatides, and oxidation products are removed by adsorptive effect of the bleaching earth. Adsorbent that are commonly used in vegetable oil industry are acid-activated bleaching earth, natural bleaching earth, activated carbon, and silica. The degummed and bleached oil obtained is then subjected to deodorization for deacidification. In deodorization process, FFA is stripped off as palm fatty acid distillate (PFAD) with the aids of steam as the stripping agent at temperature around 260^{o}C. FFA, pigments, volatile compounds as well as other impurities that may contribute to off-flavours and off-color are removed during deodorization stage [2], [4]. Refined palm oil, or more precise, named as degummed, bleached, and deodorized palm oil (RBDPO) obtained after the refining process.

The characteristics of palm oil such as equally saturation and unsaturation fatty acids, stable against oxidation permit the use of palm oil in many food applications, especially in frying activities. Premium quality palm oil, that is produced from selected and segregated palm fruits with special handling and stringent quality requirements exhibits superior frying ability and oil stability. Premium quality palm oil showed longer shelf life and slower quality deterioration [5]. The premium quality CPO is refined until FFA and Peroxide Value (PV) of less than 0.05% and 1 meq O_2/kg, respectively. In contrast, according to Palm Oil Refiners Association of Malaysia (PORAM) specification, the requirement of standard RBDPO obtained from standard

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CPO are as showed in Table I. Due to the high quality performed by the premium quality palm oil, it is traded at a higher price than standard palm oil [6]. Therefore, the objective of the present study is to obtain premium quality palm oil from standard CPO using different refining parameters.

TABLE I. PORAM SPECIFICATION OF STANDARD RBDPO

	Specification
FFA (As Palmitic)	0.1% max.
Moisture & Impurities	0.1% max.
Iodine Value (Wijs)	50-55
Melting Point °C (AOCS Cc 3-25)	33-39
Colour (5 1/4" Lovibond cell)	3 Red max.

II. MATERIALS AND METHODS

A. Materials

CPO was provided by Sime Darby Jomalina Sdn. Bhd. located at Telok Panglima Garang, Selangor, Malaysia. All chemicals used were either of analytical or chromatographic grades purchased from Merck (Darmstadt, Germany) or Fischer Scientific (Loughborough, UK).

B. Methods

1) Experimental design

CPO were kept for 5 days at 90°C and undergo scheduled refining processed for day 1, day 3 and day 5. The control was premium oil and standard oil with refining process. There were 4 altered refining processes in this study towards the samples. Treatment 1 was submitted to one additional bleaching process on top of the normal process, Treatment 2 had one additional bleaching and one additional deodorization process, Treatment 3 was subjected to an additional deodorization process and finally Treatment 4 was subjected to double deodorization process (Table II). Samples were then analyse for FFA, PV, AnV, UV, colour test and tocopherol content.

2) Free fatty acid

Free fatty acid (FFA) composition was determined based on the AOCS Official Method Ca5a-40 [7]. The oil (1.0g) is dissolved in an isopropanol solution which was titrated with sodium hydroxide (NaOH). The FFA content was calculated as palmitic acid percentage.

3) Peroxide value

Determination of peroxide value (PV) was based on the AOCS Official Method Cd 8b-90 [8]. Sample is dissolved in acetic acid/*iso*-octane solution and is treated with potassium iodide solution. The liberated iodine is titrated with a standard volumetric sodium thiosulphate solution. The PV is expressed in meq O_2/kg

4) Anisidine value

Anisidine value (AnV) was determined based on AOCS Official Method Cd 18-90 [9]. Sample is dissolved in 2,2,4-trimethylpentane (*iso*-octane) and add in to glacial acetic acid and anisidine reagent. The absorbance is measured at 350nm. AnV is expressed in 1g/100mL of solution.

5) Ultraviolet absorption at 233nm and 269nm

This analysis is to provide an indication of the purity and deterioration of palm oil products. It was determined based on MPOB Test Method [10]. Sample is dissolved into 2,2,4-trimethylpentane (*iso*-octane) and read absorbance at 233nm and 269nm.

6) Colour (red) analysis

The color of oil was measured using Lovibond Tintometer in Red and Yellow.

7) Antioxidant (Tocopherol) analysis

Tocopherols were determined in normal phase HPLC using hexane/iso-propyl alcohol (99.5:0.5 %v/v) as mobile phase. HPLC details: column – GENESIS SILICA 120A 4 µm, 4.6 x 250 mm (Jones Chromatography), G 1321A FLD detector (Agilent). Measurement conditions: absorbance 290 nm, column temperature 30 ℃, flow 1.4 ml/min, analysis time 22 min, injection volume 20 µl.

III. RESULTS AND DISCUSSION

A. Free Fatty Acid (FFA)

FFA percentage in crude palm oil is an indicator of palm oil quality. FFA is removed from CPO during refining process during deodorization stage [3]. In this experiment, Treatment 1 showed similarities of 0.02% FFA with premium oil right after treatment. Treatment 2 showed 0.09%. Treatment 2, 3 and 4 showed 0.09%, 0.05% and 0.04% respectively. After day 1, premium oil

A% increased to 0.13%, followed by further increment on day 3 at 0.47% and 0.68% at day 5. Treatment 1 showed the most similar FFA% pattern with premium oil which, on day 1, was 0.17%, 0.44% on day 3 and 0.58% on day5. Whereas, treatment 2 was 0.57% on day 1, 1.47% day 3 and 2.23% on day 5. Treatment 3 0.29% on day 1, 0.82% on Day 3 and 1.29% on day 5 whilst treatment 4 showed 0.48% FFA on day 1, 0.69% on day 3 and 0.98% on day 5.

TABLE II. EXPERIMENTAL DESIGN

Refining parameter	Premium oil	CPO FFA 3%	Treatment1	Treatment2	Treatment3	Treatment4
Degumming	H3PO4 0.06%	H3PO4 0.06%	H3PO4 0.06%	H3PO4 0.06%	H3PO4 0.06%	H3PO4 0.06%
	85 ℃, 20mins	85 ℃, 20mins	85 ℃, 20mins	85 ℃, 20mins	85 ℃, 20mins	85 ℃, 20mins
Bleaching	1.2% BE	1.2% BE	0.7% BE	0.7% BE	1.2% BE	1.2% BE
	95 ℃, 30mins	95 ℃, 30mins	95 ℃, 30mins	95 ℃, 30mins	95 ℃, 30mins	95 ℃, 30mins
Deodorization	260 ℃, 90mins	260 ℃, 90mins	X	260 ℃, 60mins	260 ℃, 60mins	260 ℃, 60mins
Bleaching	X	X	0.5% BE	0.5% BE	X	X
			95 ℃, 30mins	95 ℃, 30mins		
Deodorization	X	X	260 ℃, 90mins	260 ℃, 30mins	220 ℃, 30mins	240 ℃, 30mins

TABLE III. ANALYSIS RESULT

Analysis parameter	Day	Premium oil	CPO FFA 3%	Treatment1	Treatment2	Treatment3	Treatment4
FFA (%)	0	0.02	0.01	0.02	0.09	0.05	0.04
	5	0.68	1.17	0.58	2.23	1.29	0.98
PV (meq O_2/kg)	0	0.00	0.00	0.00	0.00	0.00	0.00
	5	15.08	10.12	14.46	6.38	10.14	13.57
AnV (g/100mL)	0	0.34	0.44	0.82	1.36	1.02	1.02
	5	2.90	5.26	4.53	4.40	5.42	4.37
TOTOX (2PV+AV)	0	0.34	0.44	0.82	1.36	1.02	1.02
	5	33.06	25.50	33.45	17.17	25.71	31.51
UV (233+269)	0	1.64	1.83	1.94	2.03	1.82	1.98
	5	3.22	2.40	3.27	2.82	3.30	3.46
Colour (red)	0	1.10	1.80	1.90	1.90	1.90	1.90
	5	2.10	2.90	3.30	3.50	3.60	3.60
Tocopherol (ppm)	0	466.50	457.00	460.00	513.58	520.83	477.00
	5	185.50	177.83	142.83	215.67	263.00	207.67

B. Peroxide Value Result

Detection of peroxide value (PV) gives the initial evidence of rancidity in saturated fats and oils [11]. In this experiment, PV result revealed that Treatment 2 has the least rancidity based on PV result on day 1 until day 5. At day 1 the PV value was 2.44 meq O_2/kg, 5.24 meq O_2/kg on day 2 and 6.38 meq O_2/kg on day 5. Whereby Treatment 1 had 3.73 meq O_2/kg on day 1, 9.66 meq O_2/kg on day 3 and 14.46 meq O_2/kg on day 5. Treatment 3 had 5.03 meq O_2/kg on day 1, 7.17 meq O_2/kg on day 3 and 10.14 meq O_2/kg on day 5. Whilst Treatment 4 had 5.45 meq O_2/kg on day 1, 8.03 meq O_2/kg on day 3 and 13.57 meq O_2/kg PV on day 5.

C. p-Anisidine Value Result

p-Anisidine (AnV) detect secondary oxidation products such as aldehydes (principally 2 – alkenals) in palm oil and palm oil products [12]. AnV result showed almost similar value for all types of treatments after day 5. Treatment 1 was 4.53g/100mL, Treatment 2 was 4.40g/100mL, Treatment 3 was 5.42g/100mL and Treatment 4 was 4.37g/100mL

D. Ultraviolet Absorbance at 233nm and 269nm

Ultraviolet (UV) wavelength absorbance provides an indication of the purity and deterioration of palm oil and palm oil products. The autoxidation product of oils and fats display characteristic spectra in the ultraviolet region: linoleic hydroperoxide and conjugated dienes which may result from decomposition show an absorption band at about 232nm; secondary products of autoxidation and, particularly, ethylenic diketones, show and absorption band at about 268nm [10]. In this experiment, we fixed the detection wavelength into 233nm and 269nm. The UV absorbance at 233nm and 269nm were calculated as combined. For treatment 1, on day 1, the UV absorption was 2.18, day 3 was 2.86 and day 5 was 3.27. Whilst for treatment 2, 2.16 day 1, 2.38 day 3 and 2.82 on day 5. Treatment 3 showed 2.24 reading on day 1, 2.61 on day 3 and 3.30 on day 5. Whereby treatment 5 was 2.43 on day 1, 2.75 on day 3 and 3.46 on day 5.

E. Colour (Red) Analysis Result

Color (red) analysis showed as follows. Treatment 1 and 2 was similar on day 1 and day 3 respectively 2.50 and 2.80 whilst on day 5 treatment 1 was 3.30 and treatment 2 was 3.50. Whereby treatment 3 and 4 was similar at day 1 for 2.80, slight differ at day3 for 3.20 and 3.10 and again similar at day 5 for 3.60.

F. Tocopherol Analysis Result

Tocopherol and tocotrienol are antioxidant in palm oil. It will deteriorate overtime in palm oil by heat, water and time. In this analysis, the tocopherol value showed deterioration at the most with Treatment 1 at 86% by day 5, 61% at day 1 and 74% at day 3. Treatment 2 exhibit 57% deterioration at day 1, 66% at day 3 and 79% at day 5. While Treatment 3 showed 57%, 61% and 75% respectively on day 1, day 3 and day 5. Treatment 4, showed deterioration of tocopherol of 61%, 56% and 80% on day 1, day 3 and day 5.

IV. CONCLUSION

The results (Table III) showed that Treatment 1 with double bleaching process resembled the most (r=0.997) to the premium oil stability based on Day 0 (initial) and Day 5 in term of its FFA, PV, AnV, UV (233+269nm), and TPC except for darker colour. Therefore, the double bleaching process has strong potential in producing premium oil. Further studies need to be carried out to fine tune the double bleaching process to obtain lower colour.

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