

Full Length Research Paper

Some chemical properties of oil palm decanter meal

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The aims of this study were to investigate the rancidity and chemical properties of oil palm decanter meal (OPDM) after been kept over an extended period of time. Samples were collected daily and analyzed for some rancidity properties, including peroxide value (PV) and thiobarbituric acid (TBA), and for chemical composition, including proximate analysis, fiber, mineral and fatty acid (FA) content. The correlation coefficient between time of storage and the rancidity (PV and TBA) of OPDM were positive with R^2 of 0.9792 and 0.9678, respectively. During ten days of observation, the compositions of long-chain FA, including stearic, oleic, linoleic and linolenic except for palmitic were significantly ($P < 0.05$) different. The compositions of short-chain FA, including acetic, propionic, isobutyric, butyric, isovaleric and valeric, were also significantly ($P < 0.05$) different. Furthermore, PV and TBA were significantly ($P < 0.05$) different during the extended time of 10-days storage. The correlation coefficient between PV and long-chain FA (palmitic, stearic, oleic, linoleic, and linolenic) were 0.61, 0.16, -0.82, -0.3 and -0.84, respectively, and the correlation composition between TBA and the composition of long-chain FA (palmitic, stearic, oleic, linoleic and linolenic) were 0.40, 0.34, -0.91, -0.02 and 0.62, respectively. It could be summarized that physically and chemically, the fresh OPDM might be used as an alternative feed, especially for ruminant.

Key word: Oil palm decanter meal, fatty acid, oxidation, rancidity, peroxide, thiobarbituric.

INTRODUCTION

Oil palm decanter meal (OPDM) is a pasty-type by-product derived from mechanical extraction of crude palm oil (Afdal et al., 2011). It is slightly different from palm oil mill effluent or palm oil sludge as it is processed by a specific processing machine. The OPDM is produced after passing through a process of decanting, centrifuging and then drying within the machine system (Southworth, 1985). Utomo and Widjaja (2004) clarified that OPDM was produced by the separation of liquid from palm oil sludge so it looks like a solid by-product, like tofu. The typical characteristic color of OPDM is soft blackish brown. OPDM consists of 81.65, 12.63, 7.12, 25.79, 0.03 and 0.003%, respectively, of dry matter (DM), crude protein (CP), ether extract (EE), crude fiber, calcium and phosphorous, and 154.52 Kcal/kg energy (Southworth,

1985). The fatty acids (FA) components of OPDM are usually palmitic, oleic, linoleic, stearic and miristic acids (Macfarlane et al., 1975). OPDM is also rich in beta-carotene content and is a source of natural vitamin A with 900 IU g^{-1} . This is slightly higher than the content of natural vitamin A of fish oil (600 IU g^{-1}) (Macfarlane et al., 1975). It is a valuable and potential by-product that can be utilized as an alternative source of feed for animals (Southworth, 1985).

However, OPDM usually turns rancid when kept in the open air for a few days. Normally, oxygen and other environmental factors lead to its oxidation, and this may influence the chemical composition which subsequently affects the organoleptic, chemical and physical properties. The OPDM containing polyunsaturated FA was found to be easily oxidized and quick to develop rancid-off flavor (Hamilton, 1994). Rancidity could be one of the limiting factors when it is used as feed. In fact, there is less study concerning the rancidity and chemical

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properties of OPDM.

The aims of these studies were to describe some properties of OPDM namely, the chemical composition, rancidity (PV and TBA) and the involvement of the deterioration of FA such as palmitic, stearic, oleic, linoleic and linolenic after been kept at 10-extended days.

MATERIALS AND METHODS

Sample preparation and procedure

Fresh OPDM sample was collected from the palm oil plant in Kemaman Trenggano Malaysia and transported to the laboratory of Animal Nutrition, Universiti Putra Malaysia. The samples were placed in a big bucket and kept standing at a room temperature prior to the data collection. One kilogram of a composite sample was collected from the bucket at 05.00 pm everyday for 10 consecutive days. Collected samples were arranged inside the different plastic bags and subsequently transferred into a fridge at -20°C prior to the analysis.

Property evaluation

Fresh sample was evaluated for physical properties, including appearance, color, smell and tenderness. Samples from the fridge were analyzed for the rancidity (PV and TBA), the compositions of FA, nutrients, including DM, ash, CP, EE, neutral detergent fiber (NDF), acid detergent fiber (ADF), and some minerals. The pH was measured as soon as the fresh OPDM was collected from the factory using a pH meter (Scan 1 water proof, Eutech Instrument Pte Ltd Singapore).

Chemical analysis

Proximate analysis, including DM, ash, CP and EE was done according to the procedure of AOAC (1990). Analysis of fiber content, including NDF and ADF, was done following the procedure of VanSoest (1963). Mineral analysis for Cr, Fe, Mn, Ni and Cu were carried out using atomic absorption spectrometry (AAS).

Rancidity analysis

Peroxide value

Peroxide value was determined according to the procedure of Vanhanen and Savage (2006) with few modifications. Approximately 5 g of OPDM sample were placed into a beaker glass and 30 ml of mixture of acetic acids and chloroform (ratio of 3:2) were added, shaken by hand and kept standing on a table for 1 h. The mixture was filtered using filter paper (Whatman 125 mm Ø Cat No 1001 125, Whatman International Ltd Maidstone, England) into an Erlenmeyer flask and treated with 1.5 ml of saturated potassium iodide. The solution was kept on the table for a while and shaken by hand, after which 30 ml distilled water and one or two drops of an indicator (starch solutions) were added. The solution was subsequently titrated with sodium thiosulphate (0.1 N Na₂S₂O₃) until the purple color disappeared. The blank sample was also done under the same condition as PV determination itself. PV was calculated according to the formula:

$$PV = (A \times N \times 1000)/S$$

Where, PV (meq kg⁻¹) is peroxide value, A is ml amount of sodium

thiosulphate titrated, N is normality of sodium thiosulphate and S the sample weight.

Thiobarbituric acid

TBA number was determined according to the procedure of Tatlargis et al., (1960). 10 g of OPDM sample were mixed for 2 min with 50 ml distilled water using a blender. The mixture was then poured into a distillation flask and washed with 47.5 ml of distilled water. It was afterward treated with 2.5 ml of 4 N hydrochloric-acid together with an anti foam agent and marble. The flask was heated for about 10 min and 50 ml of distillate was collected. 5 ml of this distillate was pipeted into a 15-ml-glass stopper tube and 5 ml of 0.2883% (w/v) TBA solution in 90% glacial acetic acid was added. The tubes were capped, shaken and then heated to the boiling point in a water bath for 35 min. A blank tube preparation was made in the same way using 5 ml of distilled water and 5 ml of the reagent. Both sample and blank were cooled in tapped water for 10 min, and the absorbance (D) was recorded against the blank at 538 nm using 1.5 ml cuvette. The TBA number was calculated in mg of malondialdehyde kg⁻¹ of samples, which was equal to 7.8 times using the formula:

$$TBA = D \times 7.8$$

Where, TBA is thiobarbituric number and D is absorbance.

Fatty acids analysis

Extraction of lipids

The total fatty acids were extracted from OPDM sample based on the method of Folch et al. (1957) modified by Rajion et al. (1985), using chloroform/methanol (2:1 v/v) containing butylated hydroxy toluene to prevent oxidation during sample preparation. The 1 g samples were homogenized in 40 ml chloroform/methanol (2:1 v/v) using an Ultra-Turrax T5 FU homogenizer (IKA Analysentechnik GmbH, Heidolph, Viertrieb, Germany) in a 50-ml stoppered ground-glass extraction tube. After filtration of the mixture, 10 ml of normal saline solution was added to ease phase separation. After complete separation, the lower phase was collected in a round-bottom flask and rotary evaporated (Laborota 4000-efficient; Heidolph, Germany) at 70°C. An internal standard, heneicosanoic acid (C21:0) (Sigma Chemical, St. Louis, MO, USA), was added to each sample before transmethylation to determine the individual fatty acid concentration within the sample. Transmethylation of the extracted fatty acids to their fatty acid methyl esters (FAME) was carried out using KOH in methanol and 14% methanolic boron trifluoride (BF₃) (Sigma Chemical) according to methods by AOAC (2000). Finally, the petroleum ether containing the FAME was transferred to a 4 ml screw-capped vial (Kimble Glass Inc., USA), flushed with nitrogen, closed tightly and stored at 4°C until analysis by gas-liquid chromatography (GC).

GC analysis

The methyl esters were quantified by GC (Agilent 7890N) using a 30 m x 0.25 mm ID (0.20 µm film thickness) Supelco SP-2330 capillary column (Supelco, Inc., Bellefonte, PA, USA). 1 µl of the sample was injected by an auto sampler into the chromatograph, equipped with a split/splitless injector and a flame ionization detector (FID). High purity nitrogen (Malaysian Oxygen Bhd., Malaysia) was used as a carrier gas at a flow rate of 40 ml/min. High purity hydrogen (Malaysian Oxygen Bhd., Malaysia) and compressed air (Malaysian Oxygen Bhd., Malaysia) were used for the flame ionization detector in the gas-liquid chromatograph. The

Table 1. Physical properties, rancidity and chemical composition of fresh OPDM.

Parameter	Value
Physical appearance	
Appearance	Like tofu
Colour	Blackish Brown
Smell	good arouse appetite
Tenderness	Soft
pH	4.62 - 4.95
Rancidity	
PV (meq/kg)	1.86 - 1.98
TBA (mg/kg)	0.60 - 2.89
Chemical analysis (%)	
Dry matter	26.11 - 27.19
Ash	5.70 - 6.21
Crude Protein	11.58 - 11.87
Ether extract	2.10 - 3.51
NDF	73.33 - 76.84
ADF	40.47 - 48.48
Minerals (ppm)	
Cr	0.18 - 0.29
Fe	12.60 - 13.59
Mn	0.41 - 0.45
Ni	0.94 - 0.97
Cu	4.28 - 8.80
Fatty acids (%)	
Palmitic	40.09 - 41.28
Stearic	5.28 - 5.97
Oleic	40.84 - 41.45
Linoleic	10.85 - 11.23
Linolenic	0.95 - 1.66

injector temperature was programmed at 250°C and the detector temperature was 300°C. The column temperature program initiated runs at 100°C, for 2 min, warmed to 170°C at 10°C/min, held for 2 min, warmed to 200°C at 7.5°C/min, and then held for 20 min to facilitate optimal separation. The peaks of samples were identified, and concentrations were calculated based on the retention time and peak area of known standards (Sigma Chemical). The fatty acid concentrations were expressed as a percentage of total identified fatty acids.

Experimental design and statistical analysis

The completely randomized design with four treatments of sampling time (on day 0, 3, 5, 7 and 10) and three replications were applied to these experiments. ANOVA followed by Duncan test were applied to analyze the mean of FA, PV and TBA during these studies. Analysis of correlation was done for time of sampling, rancidity and FA content using Microsoft SAS 9 (SAS, 2008).

RESULTS

The properties of fresh OPDM are presented in Table 1. It included the physical appearance, rancidity, FA, chemical and mineral content, and was investigated 24 h after sample collection. The contents of palmitic and oleic were dominant; more than 40% of OPDM lipid. The CP content was moderate, and the contents of NDF and ADF were relatively high. The contents of Fe and Cu were also quite high and ranged from 12.60 to 13.59 ppm and from 4.28 to 8.80 ppm, respectively.

Figures 1 and 2 show the daily value of PV and TBA of OPDM during the 10 days of observation. The correlation between sampling time and rancidity (PV and TBA) was positive with the correlation coefficient (R^2) of 0.9792 and 0.9678 for PV and TBA, respectively.

The variation of FA composition and rancidity of OPDM during the 10 days after sample collection can be seen in Table 2. Most of the composition of long-chain FA significantly ($P < 0.05$) decreased except palmitic and all the compositions of short-chain FA significantly ($P < 0.05$) increased. In terms of rancidity, PV and TBA were significantly ($P < 0.05$) increased.

The correlation coefficient between rancidity (PV and TBA) and the composition of each long-chain FA as well as palmitic, stearic, oleic, linoleic and linolenic is shown in Table 3. The correlation coefficient between rancidity (PV and TBA) and the concentration of unsaturated FA namely oleic, linoleic and linolenic acid was negative. On the other hand, the correlation coefficient between rancidity (PV and TBA) and the concentration of saturated FA (palmitic and stearic) was positive.

DISCUSSION

The appearance of fresh OPDM physically was dark brownish pasty, like dark brownish tofu with the sour taste as its pH ranged from 4.62 to 4.95. Fresh OPDM was not categorized as rancid since PV and TBA numbers were very low; about 1.98 meq kg⁻¹ and 2.89 mg kg⁻¹ for PV and TBA, respectively. These numbers were still below the level of rancidity as reported by Nawar (1996), in which soybean oil and other linolenic containing oil frequently began to turn rancid at the PV of about 5 meq/kg.

The compositions of palmitic and oleic within OPDM were dominant and ranged from 40.09 to 41.28% and from 40.84 to 41.45%, respectively. There were some other FA, including stearic, linoleic and linolenic existing within OPDM. The FA component in this study was slightly different from the result found by Macfarlane et al. (1975) which analyzed the mesocarp palm oil in Nigeria, and found that it ranged from 22.5 to 35.5% and from 50.2 to 55.4%, for palmitic and oleic acids, respectively whilst, the palmitic and oleic composition of OPDM were somewhat comparable to those in Colombia's palm oil,

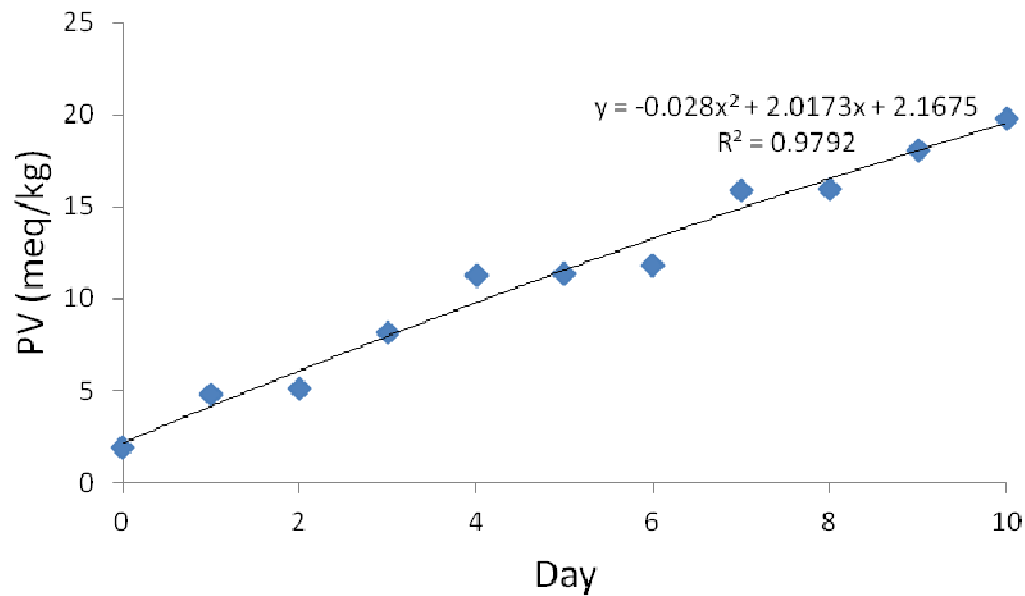


Figure 1. Peroxide value of OPDM during the 10 days observation.

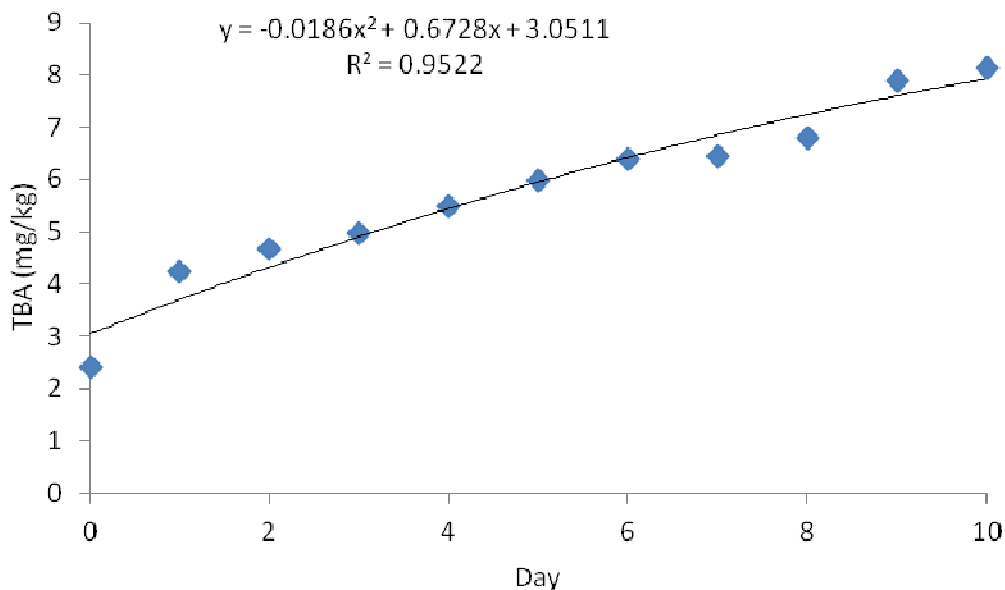


Figure 2. TBA value of OPDM during the 10 days observation.

which ranged from 22.9 to 48.6% and 34.6 to 54.8%, respectively (Macfarlane et al., 1975). All these might be due to the different breed and different geographical location. Oleic, linoleic and linolenic acids might possibly cause the rancidity of OPDM as it is an unsaturated FA. Nawar (1996) explained that hydrogen abstraction at a carbon chain on oleic, linoleic and linolenic resulted in formation of free allylic radical, causing rancidity.

The composition of CP was medium and ranged from 11.58 to 11.87%, while EE content was low and ranged

from 2.10 to 3.51%. The fiber composition was somewhat high with the content of NDF, ranging from 73.33 to 76.84% and ADF, ranging from 40.47 to 48.48%. Low content of EE might be linked to lipid that was previously extracted in the factory. The composition of NDF and ADF is nearly similar to those of grass or roughage. This could possibly be because OPDM was extracted from mesocarp, consisting of high fiber. As a result of these, OPDM could be recommended for ruminant feed as it was high in NDF and ADF and moderate in CP content in

Table 2. The composition of fatty acids, PV and TBA of OPDM over 10 days (%).

Parameter	Day					
	0	3	5	7	10	P
Long chain FA						
Palmitic	40.87±0.39	41.68±1.02	42.70±0.99	43.31±0.31	44.36±1.32	0.1539
Stearic	5.59±0.20 ^a	3.95±0.10 ^b	3.92±0.33 ^b	3.70±0.23 ^b	3.59±0.03 ^b	0.0021
Oleic	41.12±0.18 ^a	38.91±1.13 ^b	37.29±0.48 ^{bc}	36.91±0.53 ^c	36.56±0.06 ^c	0.0018
Linoleic	14.28±0.23 ^a	13.55±0.42 ^a	13.35±0.16 ^a	13.00±0.96 ^a	11.04±0.11 ^b	0.0092
Linolenic	2.90±0.20 ^a	2.65±0.06 ^a	2.50±0.57 ^a	1.38±0.22 ^b	1.30±0.12 ^b	0.0072
Short chain FA						
Acetic	34.56±0.46 ^d	38.37±1.35 ^{cd}	45.14±2.19 ^{bc}	48.40±5.27 ^{ab}	55.79±2.22 ^a	0.0026
Propionic	11.80±0.20 ^b	12.59±0.09 ^b	15.09±1.11 ^a	15.99±0.28 ^a	16.62±0.85 ^a	0.0012
Isobutyric	1.52±0.18 ^b	2.55±0.07 ^b	5.00±0.75 ^a	5.28±0.88 ^a	5.47±0.66 ^a	0.0024
Butyric	10.68±1.16 ^c	15.55±0.31 ^{bc}	19.15±2.33 ^b	23.11±2.44 ^b	27.55±0.77 ^a	<0.0001
Isovaleric	0.54±0.05 ^b	0.59±0.01 ^b	0.69±0.02 ^a	0.75±0.02 ^a	0.75±0.01 ^a	0.0005
Valeric	1.06±0.13 ^c	1.21±0.06 ^{bc}	1.27±0.01 ^{abc}	1.40±0.04 ^{ab}	1.49±0.03 ^a	0.0091
Rancidity						
PV (meq/kg)	1.92±0.04 ^c	8.16±1.73 ^b	11.84±0.54 ^b	17.05±1.32 ^a	18.12±0.04 ^a	0.0011
TBA (mg/kg)	2.40±0.40 ^b	4.99±0.14 ^a	5.99±0.47 ^a	6.43±2.30 ^a	8.13±0.21 ^a	0.0025

Different superscript within the same row is significantly different ($P < 0.05$).

Table 3. The correlation coefficient between TBA, PV and the composition of some FA within OPDM.

Parameter	Palmitic	Stearic	Oleic	Linoleic	Linolenic
PV	0.61	0.16	-0.82	-0.3	-0.84
TBA	0.4	0.34	-0.91	-0.02	-0.62

which ruminant could tolerate (McDonald et al., 1988; Utomo et al., 2004). It might be possibly prepared as a single feed or as a mixed diet for animal feeding.

The content of Fe and Cu was quite high and ranged from 12.60 to 13.59 ppm and from 4.28 to 8.80 ppm for Fe and Cu, respectively. The content of Fe might be a potential component to affect the rancidity of OPDM. Nawar (1996) reported that one of the factors influencing the rate of lipid oxidation in foods was Fe, a catalyst in lipid metabolism. Therefore, the Fe content of OPDM has to be considered in preserving OPDM and in preparing it in a diet of animal. Overall, the nutrient composition of OPDM is not so far different from those of the conventional feed.

Figures 1 and 2 show PV and TBA during 10-day extended time of storage. The correlation coefficient (R^2) between the extended time of storage and the rancidity was 0.9792 and 0.9678 for PV and TBA, respectively. This might probably be due to the enhancement of oxidative rancidity that forms hydroperoxide and increases attack of oxygen at allylic position of unsaturated FA (Nawar, 1996) during the period. The formation of hydroperoxide was probably as a result of the deterioration of

FA such as oleic, linoleic and linolenic acids, which are the main unsaturated FA, existing within OPDM. More specifically, the development of the hydroperoxide might have originated from the deterioration of the double bond of oleic acid since the oleic acid was the most concentrated unsaturated FA among the other three FAs within OPDM. In addition, the concentration of oleic acids significantly ($P < 0.05$) declined over 10 days of sampling (Table 2). The increase in the concentration of hydroperoxide was followed by a decrease in the concentration of unsaturated lipid over time of oxidation (Nawar, 1996).

OPDM easily becomes rancid because of its previous exposure to high temperature at the factory which obstructs the aldehyde, alkanal, hydrocarbon and other chemicals. Peroxide value is sensitive to temperature, which plays a role in the formation of carbonyl and hydroxy compound (Kamal-Eldin et al., 2003). There appears to be a strong correlation between time and PV ($R^2 = 0.9792$). This might possibly be the primary reason of oxidation with the formation and liberation of peroxide (H_2O_2) from unsaturated FA like oleic, linoleic and linolenic acids.

Moreover, rancidity is normally facilitated by a mineral

as a catalyst. High content of Fe and Cu in OPDM (Table 1) might possibly oxidize unsaturated FAs and then speed up the rancidity. This might also be related to the composition of unsaturated FA namely oleic, a dominant FA in OPDM. In this circumstance, mineral Fe and Cu might also possibly play a role as a catalyst to oxidize unsaturated FA, oleic, linoleic and linolenic (Nawar, 1996).

This might be interpreted as a lower rate of hydrolytic rancidity than oxidative rancidity as TBA regularly represents hydrolytic rancidity. TBA figures out the amount of aldehyde formations that previously comes from the attack of peroxide (Hamilton, 1994). Rancidity is normally initiated with the oxidative rancidity followed by hydrolytic rancidity. Therefore, the correlation between PV and TBA is usually positive. Hoyland and Taylor (1991) reviewed that malondialdehyde, a product of lipid oxidation, is the major TBA reactive substance and the chemical reaction is still uncertain (Labuza, 1971). The other oxidation products involved in TBA activity includes α,β -unsaturated aldehyde and several other unrecognized non-volatile precursor of these substances (Kamal-Eldin et al., 2003).

During 10 days of observation, it appears that the increase of rancidity was tagged along with the changes of FA composition. The increase rate of TBA and PV would be predicted faster after 10 days hence it is a challenge, which must be solved. It is necessary to incorporate any treatment into OPDM that would reduce the rancidity. Rancidity is usually caused by an oxidation process that is influenced by air, heat and light. It is a biochemical reaction that leads to an attack on the double bond within unsaturated FA, followed by the formation of free radical. This might be prevented by using a synthetic antioxidant like BHT, BHA and TBHQ which are forbidden in some developed countries or a natural antioxidant from a plant tree. Using a natural antioxidant might be a very good alternative approach to overcome the rancidity in OPDM as it is safe and natural.

Moreover, the correlation between long-chain FA (oleic, linoleic and linolenic) and both PV and TBA was both negative (Table 3). It could be highlighted that the rancidity was due to the deterioration of these unsaturated FA. The oxidation process usually occurs at a double-bond unsaturated spot of the glyceride molecules (Ladikos and Lougovois, 1990).

The composition of palmitic acid is also another dominant component of FA within OPDM. There was no significant difference ($P>0.05$) in the composition of the palmitic acid in over 10 days of sample collection. The increase of rancidity might not be linked to the degradation of palmitic acid since it is a saturated FA molecule which is relatively stable and is not susceptible to oxidation (Hamilton, 1994).

Overall, the unsaturated FA component of OPDM such as oleic, linoleic and linolenic would lead to formation of rancidity when it is kept in an open air condition. The

number of PV and TBA would increase within 10 days when fresh OPDM is kept standing in an open air without any treatment. The results show an initial rise in the composition of palmitic, linoleic and linolenic for the first few days before a subsequent decline. This might be due to the formation of FA by a microorganism in the initial step of the storage which was then followed by oxidation. Fulco (1977) explained that FA synthesis (FAS) could be done by a microorganism like bacteria and also by algae, fungi, protozoa and other higher plant and animals. The FAS might be in anaerobic and aerobic condition. Alberts and Greenspan (1984) reported that the action of bacterial FA synthetase enzyme might form FA from Acetil-CoA and 7 malonyl-CoA. Kaneda and Smith (1980) reported that there are bacteria producing the FA synthetase like *Bacterium subtilis*, *Corynebacterium cyclohexanicum*, *Micrococcus luteus*, *Pseudomonas maltophilia* (Bryan), *Escherichia coli* B and *P. fluorescens*. Furthermore, the decrease in the composition at the end might be due to the fact that FA has started to be oxidized. The decrease in the composition of stearic and oleic acids could be linked to the only oxidation that occurred in this circumstance without any synthesis of these FAs.

Table 3 represents the correlation coefficient between the rancidity (PV and TBA) and long-chain FA compositions for 10 days. The correlation coefficient between rancidity (PV and TBA) and the concentration of oleic, linoleic and linolenic acid was negative. This portrays that the increase of both PV and TBA might be attributed mostly to the degradation of oleic, linoleic and linolenic acids. The main source of rancidity in this study may possibly be indicated by the oxidation from unsaturated oleic and linolenic acids. This is marked by a strong negative correlation between the rancidity (PV and TBA) and the composition of oleic and linolenic acids, and a very low negative correlation between rancidity (PV and TBA) and the composition of linoleic acid.

Conclusion

Physically and chemically, the fresh OPDM might possibly be used as an alternative feed, especially for ruminant. Conversely, it becomes rancid after few days. The rancidity might be caused by oleic acid and other unsaturated FA component within the OPDM. The rancidity might also possibly be linked to high content of Fe and Cu oxidizing FA. The use of antioxidant is an alternative way to preserve OPDM and to overcome rancidity in order for it to be used as animal feed.

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