



## Physical and chemical characteristics of frying oil in Indonesia in a repeated frying model

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### ABSTRACT

Repeated use of frying oil is a common practice in Indonesia. Quality of oil easily changes during repeated frying. In this research, four types of oil obtained locally (palm, coconut, soybean, and corn oil) were used in a repeated frying model using tempeh as food model. The repetition was done until 15 batches at  $180 \pm 5^\circ\text{C}$  with 5 minutes frying time in each batch and 10 minutes intermittent time between each batch. Gas Chromatography analysis showed decrease in total fatty acid in all oils, particularly in those abundant in poly-unsaturated fatty acid, while there was no significant increase in trans fatty acids throughout the frying. There was a significant effect of oil type and frying repetition towards the deterioration level of frying oil. Soybean oil and corn oil have higher deterioration rate compared to palm oil and coconut oil, due to the difference in fatty acid composition. The deteriorations are also exhibited in the gradual increase of the free fatty acids (FFA), Totox values and the increase in the formation of secondary oxidation products (conjugated diene and triene).

**Keywords:** Frying oil, oil analysis, repeated frying model

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### INTRODUCTION

Frying is one of the most common types of food preparation in Indonesia, because it could create the distinct flavor and favorable golden color and crispy texture [1]. Frying oil as a medium for frying is often used repeatedly to overcome the cost of frying oil. This is a common practice for peddlers and several snack vendors in Indonesia. However, repeated use of frying oil tend to undergone several degradative chemical reactions, such as hydrolysis, oxidation and polymerization, resulting in numerous by-products such as free fatty acids, cyclic and dimers compounds and volatile compounds that are easier to be absorbed into fried foods and eventually end up in our body system[2][3]. Some of the new compounds formed during frying have been already proven as toxic materials [4][5]. The deterioration rate of the frying oil is highly affected by its fatty acids composition [6]. Therefore in this research, different fatty acid composition of frying oils is used as they might affect the quality of frying oil during repeated frying. Several types of frying oil are chosen to represent different fatty acid compositions. Corn oil and soybean oil were selected as a model of cooking oil with high percentage of polyunsaturated fatty acid, while palm oil was selected as a model for cooking oil with high percentage of saturated and monounsaturated fatty acid, and coconut oil was selected as a model for cooking oil with high percentage of saturated fatty acid [7].

As food is fried, the moisture inside of the food and the air of frying environment can initiate several reactions [3]. Hydrolysis reaction will eventually release free fatty acid, inducing a series of reaction, indicated by the formation

of rancid flavor. Tempeh, an original Indonesian food, was selected due to its high water content which might further induce the degradation of cooking oil during heating [8][9].

This research is aimed to study the changes in physical and chemical characteristics of oil during the repeated frying process. Chemical properties of frying oil will be examined through several parameters such as peroxide value, *p*-anisidine value, free fatty acid value, conjugated diene and triene, and their changes in fatty acid composition. Meanwhile physical analysis toward oil color was also examined to study the color change during repeated frying.

## EXPERIMENTAL SECTION

### Procedure of Repeated Frying

The repeated frying procedure was based on [10] with modification. Four types of cooking oils (coconut oil, corn oil, soybean oil and palm oil) and cooking oil from 1<sup>st</sup>, 5<sup>th</sup>, 10<sup>th</sup> and 15<sup>th</sup> cycle of frying were taken as samples for quality analysis. As a food model, one of the most common frying foods in Indonesia (tempeh) was used. Fresh tempeh was bought on the same day of frying and cut with the dimension of 3 cm x 8 cm x 5 mm. Electronic deep fat fryer (Restomart 2890) with a capacity of 4 L is used. Fresh oil was loaded into the fryer and heated to  $180 \pm 5$  °C before frying. Each batch of tempeh was fried for 5 min. A medium load 1:20 (kg/L) ratio of food to oil was applied. There were a total of 15 batches for frying with intermittent time between each batch was 10 minutes. There is no replenishment of fresh oil during the 15 batches; therefore the amount of tempeh added for each batch was determined first by measuring the amount of oil left after each frying batch

### Peroxide Value Analysis (IUPAC no. 2501) [11]

Peroxide value was determined using a redox titrimetric reaction. About 5 grams of oil samples were mixed with 30 ml solvent (acetic acid: chloroform =3:2). About 0.5 ml of saturated potassium iodide (KI) solution was also added and the mixture was shaken for 1 minute. After 1 minute, 30 ml of distilled water was added. The mixture was then titrated using 0.01N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution until the color changes to light yellow. About 0.5 ml of 1% starch indicator was added until the solution changed to blue color. Titration was continued while shaking the flask vigorously until blue color disappeared. Titration was also performed for blank solution. Peroxide value can be calculated by using the formula:

$$\text{Peroxide value} = \frac{(B - S) \times N \times 1000}{w}$$

Where:

Peroxide Value (PV) = mEq peroxide per kg of sample

B = volume of titrant (ml) for blank

S = volume of titrant (ml) for sample

N = Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> molarity (mEq/ml)

1000 = conversions of unit (g/kg)

W = sample weight (g)

### Acid Value Analysis (IUPAC no 2.201) [11]

Acid value represents the amount of KOH (mg) required to neutralize free acid in 1 g fat/oil. About 20 grams of oil samples was dissolved in 50 ml of solvent mixture (95% ethanol: diethyl ether = 1:1). About 0.2 ml of phenolphthalein solution and the mixture was titrated (with shaking) using 0.1 N potassium hydroxide solution in ethanol. The titration was carried out until pink color persisting for at least 10 seconds was formed. Acid value is then calculated based on formula:

$$\text{Acid value} = \text{ml KOH} \times \text{N KOH} \times 56.1 \text{ g/sample}$$

### Conjugated diene-triene analysis

1% solution of oil samples was made and diluted (or concentrated when necessary) with isooctane solvent to obtain an absorbance value between 0.1 and 0.8. The absorbance at 232 nm (for conjugated dienehydroperoxides) and 270 nm (for conjugated trienes) were measured with an UV spectrophotometer. Pure solvent was used as a blank.

***p*-anisidine value analysis (IUPAC no. 2.504) [11]**

*p*-anisidine value was determined using spectrophotometric method. About 0.5-0.7 gram of the oil samples were weighed into 25 ml volumetric flask and then diluted to volume with isooctane. The absorbance of the resulting solutions was measured at 350 nm using isooctane as the reagent blank. Each 5 ml of the solution and 5 ml of isooctane was mixed with 1 ml *p*-anisidine solution. The absorbance of both solutions at 350 nm was read with the isooctane as blank. The value can be calculated by using the formula:

$$p - AV = \frac{100QV}{m} [1.2(A_1 - A_2 - A_0)]$$

Where:

V = volume in which the test sample is dissolved, in milliliters (V=25 ml)

M = mass of the test portion, in grams

Q = sample content of the measured solution based on which the *p*-anisidine value is expressed, in grams per milliliter (Q 0.01 g/ml)

A<sub>0</sub> = absorbance of the unreacted test solution

A<sub>1</sub> = the absorbance of the reacted solution

A<sub>2</sub> = the absorbance of the blank

**Totox value [12]**

Totox value indicates the total oxidation of a sample using both the peroxide and *p*-anisidine values. Totox value can be calculated by using the formula: TV = (2 x PV) + AV.

**Color Measurement**

Chromameter (Konica Minolta) was used to measure oil color. About 20 ml of oil samples were placed in disposable Petri plate and the chromameter lamp was projected to the sample two times in three different spots. Before the color of oil samples was measured, calibration process was done by using chromametric calibration plate. From the measurement displayed (L\*, a\*, b\*), °Hue value and Yellowness Index (YI) were calculated.

°Hue value [13] can be calculated using the formula: °hue =  $\left(\tan^{-1} \frac{b^*}{a^*}\right) 360$ , while YI [14] can be calculated using formula: YI = 142.86 b\*/L\*

**Statistical Analysis**

The statistical analysis was performed using SPSS version 16.0. The factors that were used in this research were types of frying oil (palm oil, corn oil, soybean oil and coconut oil) and frying repetition. The results were analyzed using ANOVA and for the Post hoc test, Duncan test was used. All results were determined at p = 0.05.

**RESULTS AND DISCUSSION**

During repeated frying, triglycerides in the oil will undergo a series of chemical reactions, namely hydrolysis, oxidation, isomerization and polymerization, caused by exposure toward high temperature and the absorption of oxygen and water from food. The steam released during food frying will initiate the chemical reaction in oil degradation. Water, as a weak nucleophile, will attack the ester linkage in triacylglycerol producing combination compounds of di- and monoacylglycerols, glycerol, and free fatty acids [15], which is shown in the GC results (Table 1). There is a significant decrease in fatty acid composition of all the cooking oils, with the exception of coconut oil composition.

All cooking oils after repeated frying showed a decrease in the poly-unsaturated fatty acid content and a slight increase in the elaidic acid content, a *trans* monounsaturated fatty acids. *Trans* fatty acid is usually formed as a result of partial hydrogenation of vegetable oils [16]. This partial hydrogenation process produces a mixture of positional and geometrical isomers (*cis* and *trans*) [16]. In this research, the formation of *trans* fatty acids was recorded during an intense heat treatment which in accordance with previous study. Hydrolysis might also contribute to the isomerization of the double bonds in unsaturated fatty acids in frying oils which resulting in the

increase of *trans* fatty acids [17]. A small increase in *trans* fatty acid amount was found after four hours of heating, although these results suggest that in those period of frying, heat has little impact on *trans* fatty acid increment [16].

**Table 1 Fatty acid composition of cooking oil before and after 15<sup>th</sup> cycle of repeated frying**

Component	Palm (%w/w)		Corn (%w/w)		Soybean (%w/w)		Coconut (%w/w)	
	Before	After	Before	After	Before	After	Before	After
Total Fatty Acid	84.15	77.59	84.89	76.00	91.16	83.02	79.84	78.22
Saturated Fatty Acid								
- Short Chain	1.03	0.97	0.06	0.03	0.11	0.27	64.80	63.42
- Long Chain	35.51	33.00	11.54	10.05	13.15	16.13	9.04	9.00
Unsaturated Fatty Acid								
Monounsaturated	37.70	34.80	22.91	22.81	18.54	21.16	4.77	4.66
- Elaidic Acid, C18:1	0.06	0.07	0.03	0.04	0.03	0.04	0.05	0.07
Polyunsaturated	9.91	8.82	50.39	43.11	49.33	45.43	1.23	1.15
- Linoleic Acid, C18:2	9.69	8.63	49.58	42.25	44.27	40.94	1.23	1.13

The formation of free fatty acid compounds upon repeated frying, were also observed in the increasing acid value level (Table 2). During repeated frying model, a steady increase of acidity was observed for all type of oils, with final value between 0.8 to 1.2 mg KOH/g oil. Based on statistical analysis results, there was a significant effect of oil type and frying repetition toward the increase in acidity level of frying oil, but there was no interaction observed between the two factors ( $p < 0.05$ ). The initial acidity of palm and corn oil were significantly higher compared to soybean and coconut oil, which might be due to their high poly-unsaturated fatty acid content which makes them prone to lipid peroxidation during refining process [18]. Therefore the fresh palm and corn oil have already contained free fatty acids to certain extent.

Degree of oil rancidity was also observed in the change in peroxide value during repeated frying. Peroxide is the primary oil degradation product in which at later stage, peroxides will further broken down into various volatile and non-volatile compounds (aliphatic aldehydes, ketones, alcohols, acids and hydrocarbons) In general, the lower the peroxide value, the better the quality of the oil [7]. The results show a steady increase of peroxide value for all oils except corn oil. However, peroxide value cannot fully represent the condition of oxidized oil since it is very unstable at frying temperature [19]. Besides, peroxide value decreases as secondary oxidation products appear. Therefore, the degree of oil rancidity is usually also expressed using *p*-anisidine and Totox value.

**Table 2 Oxidation parameter of oils during repeated frying**

Oil Type	Acid value (mg KOH/g sample) during Frying Repetition					Reaction Rate
	0	1	5	10	15	
Palm	0.42 ± 0.36	0.52 ± 0.38	0.54 ± 0.11	1.17 ± 0.97	1.06 ± 0.10	0.049
Coconut	0.14 ± 0.13	0.34 ± 0.21	0.55 ± 0.07	0.69 ± 0.05	0.86 ± 0.14	0.043
Soybean	0.16 ± 0.13	0.26 ± 0.13	0.54 ± 0.04	0.78 ± 0.16	0.92 ± 0.14	0.051
Corn	0.38 ± 0.23	0.52 ± 0.14	0.77 ± 0.10	0.83 ± 0.03	0.97 ± 0.10	0.036
Oil Type	Peroxide Value (mEq) during Frying Repetition					Reaction Rate
	0	1	5	10	15	
Palm	0.80 ± 0.22	3.87 ± 0.71	7.69 ± 0.93	10.62 ± 0.53	10.73 ± 0.12	0.633
Coconut	1.24 ± 0.13	3.24 ± 0.23	8.37 ± 0.76	16.68 ± 0.41	20.06 ± 1.65	1.293
Soybean	2.18 ± 0.42	3.19 ± 0.21	5.45 ± 0.23	5.75 ± 0.82	6.87 ± 0.14	0.288
Corn	5.77 ± 0.51	3.22 ± 0.77	1.46 ± 0.21	1.53 ± 0.72	1.66 ± 0.34	-0.213
Oil Type	<i>p</i> -anisidine during Frying Repetition					Reaction Rate
	0	1	5	10	15	
Palm	24.99 ± 2.34	29.2 ± 3.23	26.13 ± 2.63	26.65 ± 3.23	27.22 ± 2.31	0.0168
Coconut	4.40 ± 0.23	7.54 ± 0.62	12.67 ± 1.31	24.22 ± 2.66	27.26 ± 2.64	1.575
Soybean	8.02 ± 0.53	14.21 ± 1.22	23.70 ± 3.78	32.94 ± 4.01	60.31 ± 5.13	3.173
Corn	10.33 ± 0.76	12.25 ± 0.23	10.45 ± 1.21	7.14 ± 1.52	47.76 ± 5.54	1.934
Oil Type	Totox Value during Frying Repetition					Reaction Rate
	0	1	5	10	15	
Palm	26.58 ± 3.54	34.40 ± 5.33	41.50 ± 5.11	47.90 ± 5.33	48.70 ± 5.28	1.267
Coconut	6.87 ± 1.12	14.02 ± 1.83	29.40 ± 3.15	57.57 ± 7.36	67.39 ± 5.63	2.163
Soybean	12.38 ± 2.17	20.59 ± 2.23	34.90 ± 3.22	44.44 ± 3.86	74.06 ± 5.69	3.746
Corn	21.80 ± 5.02	18.70 ± 2.23	13.36 ± 0.23	10.19 ± 4.44	52.07 ± 3.32	1.565

The Totox value indicates an oil's overall oxidation state, because Totox value is calculated using both peroxide value and *p*-anisidine value. The lower the Totox Value, the better the quality of frying oil [10]. *p*-anisidine value measures the formation of secondary oxidative products, thus the addition of both peroxide and *p*-anisidine values in Totox Value will give more accurate description related to the oxidative conditions of the cooking oil after repeated frying.

The increase in oxidation rate can also be observed in the change of OD specific absorptivity at 232 and 270 nm, which measures the contents of conjugated dienes (CDs) and conjugated trienes (CTs). After peroxides are formed, the non-conjugated double bonds present in unsaturated fatty acid will undergo rearrangement generating conjugated dienes (CD), which absorb at 232 nm. When polyunsaturated fatty acids containing three or more double bonds (e.g. linolenic acid) undergo oxidation, the conjugation will result in the formation of conjugated trienes (CT) which absorb at 268 nm [9]. Therefore the presence of peaks at both 232 nm and 268 nm will indicate that the oxidation reactions have advanced into the next stage. From Figure 1 and Figure 2, it can be observed that all samples exhibited a steady increase of absorbance in 232 nm and 268 nm, indicating an increase in the formation of both conjugated diene and triene during repeated frying. Corn and soybean oil showed a high absorptivity in the 268 nm region, showing a high formation of conjugated triene due to their high linoleic content. On the other hand, coconut oil, which has a fairly low polyunsaturated fatty acid, exhibited a very low formation of conjugated triene.

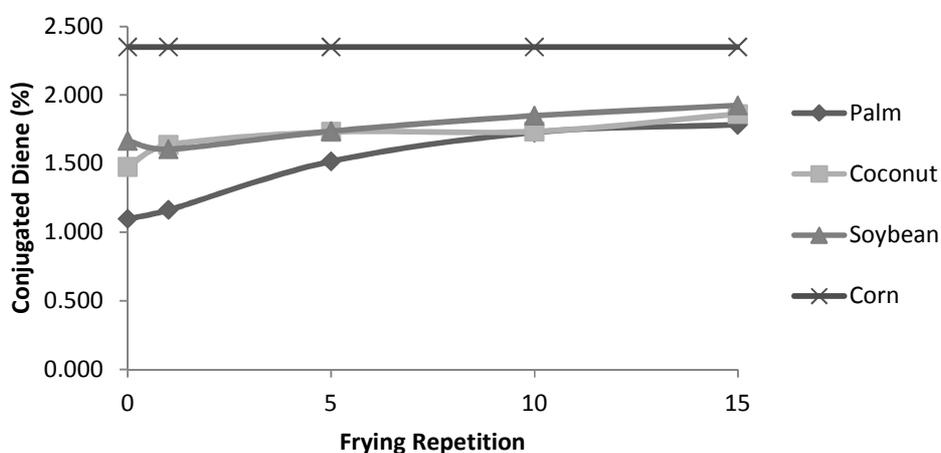


Figure 1 Correlation between frying repetition and conjugated diene content

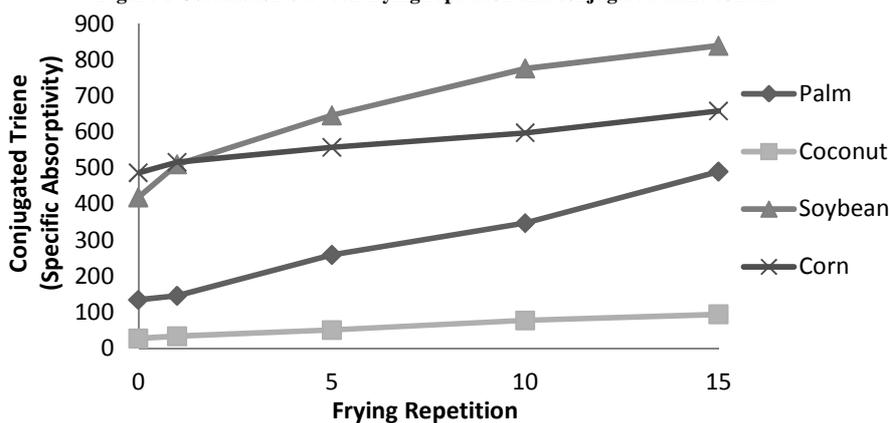


Figure 2 Correlation between frying repetition and conjugated triene content

Color change in frying oils after repeated frying was also observed. It is because color has been used as a subjective or objective parameter to determine the quality of used oil. When oils are repeatedly used for frying, they will change from a light yellow to a brown color. Color change could indicate that oxidation, polymerization or other chemical reaction have occurred as a result of frying [16]. In this research, yellowness index (YI) of palm oil steadily increased during repeated frying, meanwhile for other oils; statistically there was no significant increase of

YI (Figure 3). All samples from series of repeated frying had °Hue value in the range from 63.07 - 88.49 (all categorized as yellow color). Previous study stated that the color of used frying oils remained constant after 30<sup>th</sup> frying and then increased suddenly [16].

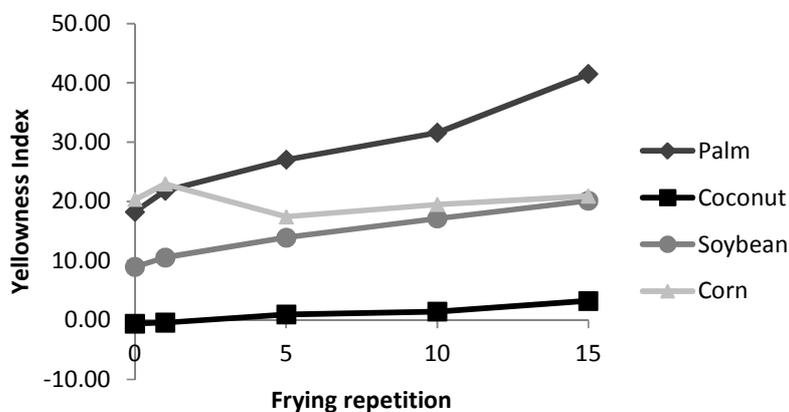


Figure 3 Change in yellowness index between frying repetition

### CONCLUSION

Repeated frying until 15 batches caused changes in fatty acid composition. Poly-unsaturated fatty acid (PUFA) (e.g. linoleic and linolenic) drastically decrease, meanwhile there is only a slight increase in *trans* fatty acid content. Oil composed mainly with unsaturated fatty acid (soybean and corn oil), have higher deterioration rate compared to palm oil (which is composed from a balance mixture of saturated and monounsaturated fatty acids) and coconut oil (which is mainly composed of short chain saturated fatty acid). The deteriorations are also exhibited in the gradual increase of the FFA, Totox values and the formation of secondary oxidation products (conjugated diene and triene). Color change in palm oil, expressed in Yellowness Index, steadily increased during repeated frying. However, the color change did not occur in other cooking oils.

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### REFERENCES

- [1] E Chloe; D Min, *Journal of Food Science*, **2007**,72(5), 77-86.
- [2] TNK Wai,*International Journal Medical University*,**2007**, 55-60.
- [3] K Warner. *Food Lipids*, Marcel Dekker, Inc, New York, **2002**, 205-221.
- [4] JL Sebedio; A Grandgirard. *Progress in Lipid Research*, **1989**, 28, 303-336.
- [5] S López-Varela; FJ Sánchez-Muniz; C Cuesta,*Food Chemistry and Toxicology*, **1995**, 33(3), 181-189.
- [6] SP Kochhar. *Frying: Improving Quality*, Woodhead Publishing Limited, Cambridge, **2001**, 87-114.
- [7] HD Belitz; W Grosch; P Schieberle. *Food Chemistry*, 4<sup>th</sup> Edition, Springer, New York, **2009**.
- [8] A Azman; M Sahrul; S Chan; A Noorhazliza; M Khairunnisak; MF Nur Azlina, *The Medical Journal of Malaysia*, **2012**, 67(1), 91-101.
- [9] C Wei An; CP Chih Wei; WC Cheng; CK Hsu, *Journal of Food and Drug Analysis*, **2013**, 21(1), 58-65.
- [10]E Kalogiani; T Karapantsios; R Miller,*Journal of Food Engineering*, **2011**, 169-179.
- [11]IUPAC. *Standard methods for the analysis of oil, fats and derivatives*, Pergamon Press Ltd, Oxford, **1979**.
- [12]WT Wai; B Saad; BP Lim,*Food Chemistry*, **2009**, 113(1), 285-290.
- [13] F Balestra; C Emiliano; P Giangaetano; R Santana,*Lebensmittel-Wissenschaft + Technologie*, **2011**, 44 (3), 700-705.
- [14]FJ Francis; FM Clydesdale. *Food Colorimetry: Theory and Applications*, Avi Publishing Company, Westport, **1975**.
- [15] W Sunisa; S Sunisa; U Worapong; J Saowaluck; W Saowakon, *International Food Research Journal*, **2011**, 18, 615-620.
- [16] W Tsuzuki; A Matsuoka; K Ushida,*Food Chemistry*, **2010**, 123, 976-982.

[17]S Hara; E Ogawa; Y Totani,*Journal of Oleo Science*, **2006**, 55 (4), 167-172.

[18]ER Sherwin,*Journal of the American Oil Chemists' Society*, **1978**, 55(11), 809 - 814.

[19]CW Fritsch,*Journal of the American Oil Chemists' Society*, **1981**, 58(3), 272-274.