Degradation quality of reused palm cooking oil during storage: case study in fried shallot industry

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Abstract. Frying process in a fried shallot industry usually is carried out by deep fat frying. This method involves the use of much oil and repeatedly uses and storages. This practice will decrease the quality of oil and even the fried product. The objectives of this research were to measure the quality degradation rate of use cooking oil repeatedly during storage and to calculate the efficiency of zeolite to adsorb the impurities of the reused cooking oil. The Oil quality was based on the National Standard of Indonesia (SNI 7709:2012). The quality parameters observed in this research were water and evaporated material content, free fatty acid value, and peroxide number. Based on the results of this research, it was found that the oil still meets the quality standard until the 5th frying without storage. In this stage, the oil exposed the rate of degradation in water and evaporated material content, free fatty acid value, and peroxide number as 0.0046; 0.0878, and 0.303 respectively. The content of water, moisture and oxygen were the main cause of quality changes in cooking oil. The effort has been done to improve the quality of reused cooking oil by zeolite adsorption. Efficiency values obtained from this process by moisture and evaporated material content, free fatty acid value, and peroxide number was 8.20%; 52.38%; and 30.95% respectively.

1. Introduction
Shallot is one of the horticulture plants that is often used for recipe in fresh form, however, this product is easily rotten due to the high content of water. In order to extend the shelf life and increase the added value of shallots, then fresh shallot is processed into a fried one. Commonly, the shallot is fried in deep fat frying using much oil. This method is done by submerging all parts of the sliced fresh shallot in hot cooking oil. Deep fat frying requires large amounts of cooking oil, thus industry will use cooking oil repeatedly to reduce production costs. Meanwhile, the use of cooking oil repeatedly can decrease the quality of cooking oil and even fried products. According to research [1], repeated use of cooking oil can reduce the lightness and texture of potato chips and increase the consistency index of cooking oil and peroxide number. In addition, decreasing the quality of cooking oil can also occur during storage.

Generally, most consumers and producers detect the quality of cooking oil just by looking at the color of the oil. This method is very subjective and less accurate due to the formation of the color of the oil.
cooking oil do not solely by the heat process but also it is influenced by the type of fried food products and the type of oil used [2]. Therefore, it is necessary to characterize oil to know the quality of cooking oil objectively so that it can find the maximum frequency of the use and the storage time of cooking oil which still in accordance with the Indonesian National Standard (SNI) [3].

Efforts to improve the quality of used cooking oil have been widely studied and among them is the addition of adsorbents. Research conducted by [4] on the purification of used cooking oil with membranes requires expensive costs and short membrane life. Another study [5], bentonite and activated charcoal allow the loss of heavy metals such as Zn which are commonly used as activators in the manufacture of activated carbon. It has been conducted, a study to improve the quality of used cooking oil using active zeolite [6]. The method is quite simple, easy to obtain material because of its abundant availability, and low prices. In addition, the researcher [7] added that the zeolite has a high absorption capacity, large surface area, and has a lot of pores thus it is well used as an adsorbent. It is therefore, this research is done to calculate the efficiency of adsorption of used cooking oil by using activated zeolite. In many cases, later work was found to have been only independently researched between the quality of used cooking oil and the effort to purify this oil. In this study, the degradation of used cooking oil was measured in every frequency of frying and consequently, this study was purposed to know how to purify this oil. Thus it can be considered that this study was original and different from other research.

2. Materials and Methods

2.1. Materials
The materials used in this study were fresh and used cooking oil obtained from fried shallot home industry, glacial acetic acid, chloroform, potassium iodide (KI), sodium thiosulfate (Na₂S₂O₃) 0.01 N, 1% starch solution, neutral alcohol, phenolphthalein indicator, aluminum foil, Whatman filter paper No.42, zeolite, and potassium hydroxide (KOH) 0.1 N. The equipment used in this research were oven, aluminum cup, desiccator, furnace, magnetic stirrer, vacuum filter, analytical balance, erlenmeyer glass, measuring cup, drop pipette, and burette.

2.2. Methods

2.2.1. Fresh cooking oil characterization
The characterization of cooking oil was done to determine the initial quality of the cooking oil before use for frying. The quality parameters analyzed were water and evaporated material content, free fatty acid value, and peroxide number. The analysis was carried out in 2 replications with three analyses for each sample (triple) except for water and evaporated material content was done in 2 replications only. The data was obtained from the average of the two replications.

2.2.2. Kinetic of cooking oil quality change as repeating use
Shallot was fried in the ratio of shallot to the oil of 1:6 for 15 min. As much as 100 mL cooking oil was taken from the pan at each frying sequence of 1, 3, 5, 7, 9 and 11. The samples were then analyzed for water and evaporated material content, free fatty acid value and peroxide number. The analysis was carried out in two replication for each treatment with three (triple) measurements in each sample, except for the water and evaporated material content which only carried out in two replications with one analysis. The data was then plotted against the frequency of frying using the regression equation as the following equation.

\[ y = kx + a \]  (1)
Where \( y \) stands for quality parameter (moisture and evaporated material content, free fatty acid value, and peroxide number), \( k \) stands for value of slope or rate of decline in the quality of the cooking oil, \( x \) stands for frequency of the oil used for frying, and \( a \) stands for value of intercept (constant).

2.2.3. Kinetic of cooking oil quality change during storage

Samples at each frequency of frying were stored for one month at room temperature and it was analyzed for its quality every week. Quality parameters included the content of moisture and evaporated material, free fatty acid value, and peroxide number. The analysis was carried out in two replication with three analyses in each sample, except for water and evaporated material content was only carried out in two replication with one analysis. Set data from each test was then plotted against storage time. From the results of the graph, it will get a regression equation (equation 1) which shows the value of intercept and slope. The slope represents the decreasing quality of the cooking oil during storage (\( k \)) with \( x \) is the time of storage.

2.2.4. Zeolite efficiency for used cooking oil refinery

Used cooking oil for each sequence of frying was collected and stored for a month then analyzed for its quality, including moisture and evaporated material content, free fatty acid value and peroxide number, before being refined. The analysis was carried out in two replications with triple analysis in each sample of replication. The procedure for refining of the used cooking oil was done based on [8]. The adsorbent of 7% (w/w) has been physically activated by heating at 300 °C for 2 h in the furnace and then added to the filtered sample. Oil and adsorbent (zeolite) were stirred using a magnetic stirrer for 1 hour. After that, the oil was filtered by vacuum using Whatman filter paper No.42, until refined oil was obtained. Refined oil was then analyzed for water and evaporated material content, free fatty acid value and peroxide number. The experiment was done in two replication with triple analysis. The efficiency of the absorbing process was calculated by formula 2.

\[
\text{eff} = \left( \frac{\text{Maverage}_{AW_{i,j,k}} - \text{Maverage}_{AK_{i,j,k}}}{\text{Maverage}_{AW_{i,j,k}}} \right) \times 100\%
\]

Where \( \text{eff} \) is adsorption efficiency (%), \( \text{Maverage}_{AW_{i,j,k}} \) is the average value of the parameter before the adsorption process (where \( i \) = water and evaporated material content; \( j \) = free fatty acid value; and \( k \) = peroxide number) and \( \text{Maverage}_{AK_{i,j,k}} \) is the average value of the parameter after the adsorption process (where \( i \) = water and evaporated material content; \( j \) = free fatty acid value; and \( k \) = peroxide number).

3. Results and Discussion

3.1. Quality of fresh cooking oil

Fresh cooking oil was the oil which not yet used for frying. The cooking oil was commercial palm cooking oil bought from the retail. This quality parameter tested for the oil referred to SNI 7709:2012 [3] concerning the quality requirements for palm cooking oil. The results can be seen in Table 1.

| Table 1. The initial quality of fresh cooking oil |
|-----------------------------------------------|
| Quality parameters                           | Unit | Value | SNI 7709:2012 |
| Water content and evaporated material content | %    | 0.04  | 0.1          |
| Free fatty acid value                       | %    | 0.13  | 0.3          |
| Peroxide number                             | mEq O₂/kg | 0     | 10           |
Table 1 showed that the cooking oil was in accordance with the requirements set by SNI 7709: 2012. Water content was one parameter that determines the quality of oil which shows the amount of water containing in the oil. From the table above, it can be seen that the value of the water content and the evaporated matter of cooking oil was 0.04%. The result obtained in this research has differed from those [9], which reported that the water content of packaged cooking oil was 0.14%. This can be caused by storage during distribution or the different producing process of the oil. Oil can absorb moisture from the atmosphere which can contaminate and increase the water content on it.

Free fatty acid (FFA) is an acid that is released on the hydrolysis of fat. From Table 1, it can be seen that the free fatty acid content of cooking oil was 0.13%. Before it was processed into cooking oil, palm fruit bunches were sterilized, one of which proposed to kill palm fruit lipolytic enzymes thus the free fatty acid content in palm fruit was lower. The improper process will cause the formation of free fatty acids. In addition, high humidity and temperature conditions in storing and distributing of the cooking oil in packets could also accelerate hydrolysis to form the free fatty acids.

Peroxide is an indicator of oxidized fatty acids. The principle of determining peroxide number is to determine the amount of sodium thiosulfate solution that reacts with the released I₂ due to the reaction between peroxide compounds and saturated KI in an acidic atmosphere. From Table 1 the peroxide number obtained for cooking oil was 0 mEq O₂ / kg. This indicated that cooking oil has not been oxidized or has been oxidized but it was very little change. A researcher [10] added that the value of water content, free fatty acid value, and peroxide number of packaged cooking oil were influenced by the type and content of oil, the manufacturing process, and storage conditions.

3.2. Kinetic of quality change of cooking oil as repeating use
Cooking oil will experience a decrease in quality during the heating and frying process. The frequency of frying has a significant effect on the declining quality of the cooking oil (see Table 2). The results showed that there was a relationship between the frequency of frying with each quality parameter.

![Figure 1. Relationship between frequency of frying and moisture and evaporated material content (%) (■); free fatty acid value (%) (▲); peroxide number (mEq O₂/kg) (●)](image)

From Figure 1, it can be seen that the value of water and evaporated material content, free fatty acid value, and peroxide number were linearly related to the frequency of frying. The increasing frequency of oil used during frying, the higher the value of each test parameter, so that the graph obtained continues to rise. This showed that oil quality decreased and it can be determined the regression
coefficient \( k \) which shows the rate of decline in the quality of the cooking oil based on the frequency of frying (Table 2).

**Table 2. The rate of decrease in oil quality based on the frequency of frying**

| Parameter                          | Regression Equation | \( R^2 \) | \( k \)  |
|------------------------------------|---------------------|-----------|---------|
| Water and evaporated material      | \( 0.0101x+0.0351 \) | 0.9955    | 0.0101  |
| Free fatty acid value              | \( 0.0494x+0.0934 \) | 0.9318    | 0.0494  |
| Peroxide number                    | \( 0.1506x \)       | 0.8792    | 0.1506  |

From Table 2, each regression coefficient \( k \) was obtained for each frequency of frying correspond to quality parameters such as moisture and evaporated material content, free fatty acid value, and peroxide number respectively as 0.0101, 0.0494, and 0.1506. This showed that frying frequency will increase the average water and evaporated material content, free fatty acid value, and peroxide number. Based on this equation, the correlation \( R^2 \) between calculation data and experiment data was close to 1, which means that there was a strong linearity relationship between the frequency of oil use and the increasing content of water and evaporated material, free fatty acid content and peroxide number. Thus, from SNI requirements, it could be determined the maximum limit for the use of recurrent cooking oil as can be seen in Table 3.

**Table 3. The maximum number of the reuse of palm cooking oil**

| Parameter                          | Initial value | Value after several frying process | SNI 7709:2012 |
|------------------------------------|---------------|-----------------------------------|---------------|
| Water and evaporated material (%)  | 0.04          | 0.04 0.07 0.08 0.10 0.13 0.15 0.1 |               |
| Free fatty acid value (%)          | 0.13          | 0.17 0.23 0.30 0.36 0.51 0.73 0.3 |               |
| Peroxide number (mEq O₄/kg)        | 0             | 0.13 0.27 1.07 1.40 1.09 10        |               |

From Table 3, it can be seen that cooking oil after being used for several frying processes will increase the value of water and evaporated material content, free fatty acid value, and peroxide number. If one of the three quality parameters does not meet the cooking oil quality standards, it can be said that the cooking oil could not be used for frying anymore thus based on SNI 7709: 2012 [3], the maximum limit for using cooking oil was 5 times of frying. This finding in fact, was similar to [11] with the use of cooking oil should not exceed four times.

During the frying process, the water content in shallots will be evaporated and it is replaced by oil. The more water that is evaporated, the more water content in the oil will increase. This causes the water and evaporated material content continue to increase along with the increasing frequency of oil used. The high water and evaporated material content will accelerate the hydrolysis process so that the rate of formation of free fatty acids would be boosted. This is the reason for the increasing value of free fatty acids for the 11th frying oil. A researcher [12] added that the presence of water in oil is very undesirable because it can hydrolyze oil to produce free fatty acids which cause a rancid odor in oil.

Furthermore, Figure 1 showed that the peroxide number increase with increasing frying frequency. Peroxide number was obtained until the 11th of the frying process and it seems to continually increase, however, the value was still less than the quality standard (Table 3). The increase in peroxide number is caused by cooking oil was being exposed to oxygen for a long time so that an oxidation reaction occurred during repeated frying.
3.3. The Rate of decreasing quality of cooking oil during storage

3.3.1. Water and evaporated material content

The graph of the relationship between the shelf life (weeks) and water-evaporated material content (%) of the cooking oil can be seen in Figure 2. It was obtained that the value of water and evaporated material content in all frequency of frying during storage has increased. It is understandable that during storage, cooking oil will contact oxygen and produced water vapor. Corresponding to [13], the water content on the surface of the material during storage is influenced by the air humidity (RH) around it. However, when it was compared with SNI [3], the maximum use of cooking oil was found to be 5th frequency with storage in 4 weeks. From the graph in Figure 2 can be determined the regression coefficient (k) which shows the rate of decline in the quality of cooking oil during storage based on water and evaporated material content (Table 4).

![Figure 2. Relationship between time of storage and frequency of frying to water and evaporated material content](image)

Table 4 shows each regression coefficient at each frequency of frying. This showed that each addition of 1 week of storage would result in increasing the moisture and evaporated material content by each regression coefficient (k). Thus, based on the calculated correlation, the frequency of use of cooking oil could be determined as more than 3 times.

| Treatment         | Regression Equation | $R^2$ | k    |
|-------------------|---------------------|-------|------|
| First fried       | 0.0037x+0.0466      | 0.69  | 0.0037|
| Third fried       | 0.0037x+0.0668      | 0.78  | 0.0037|
| Fifth fried       | 0.0046x+0.0809      | 0.99  | 0.0046|
| Seventh fried     | 0.0055x+0.1048      | 0.99  | 0.0055|
| Ninth fried       | 0.0052x+0.1247      | 0.97  | 0.0052|
| Eleventh fried    | 0.0040x+0.1481      | 0.98  | 0.0040|
3.3.2. The free fatty acid content
The graph of the relationship between the shelf life (weeks) and free fatty acid value (%) can be seen in Figure 3. This figure shows that the value of free fatty acids in all frying frequency also increased during storage. This increasing indicated that the quality of the oil was declining. Accordingly, comparing the result and SNI 7709: 2012 [3], the value of free fatty acid at the fifth frequency of frying for 1 week of storage had already outside the quality requirements of cooking oil, which was equal to 0.34%. Further, it can be concluded that based on the value of free fatty acid, the frequency of the 5th frying and without storage was the maximum limit of the use of cooking oil for repeating frying. This was in line [11] which stated that the repetition of the use of cooking oil should be no more than four times and used on the same day with moderate heating. This graph has resulted in the regression coefficient (k) which showed the rate of decline in the quality of cooking oil during storage based on free fatty acid value (Table 5).

![Figure 3. Relationship between time of storage and frequency of frying to free fatty acid value](image)

**Table 5. The rate of decline in oil quality during storage based on free fatty acid value**

| Treatment       | Regression Equation | $R^2$ | k    |
|-----------------|---------------------|-------|------|
| First fried     | 0.0619x+0.1367       | 0.87  | 0.0619|
| Third fried     | 0.0810x+0.2005       | 0.92  | 0.0810|
| Fifth fried     | 0.0878x+0.2731       | 0.98  | 0.0878|
| Seventh fried   | 0.1023x+0.3330       | 0.97  | 0.1023|
| Ninth fried     | 0.1216x+0.4777       | 0.96  | 0.1216|
| Eleventh fried  | 0.1045x+0.7123       | 0.99  | 0.1045|

From Table 5, each regression coefficient was obtained at each treatment (frying frequency). These results showed that each addition of 1 week of storage will increase the level of free fatty acids of each regression coefficient (k) as can be seen in Table 5. The storage time effect was closely related to changes in the value of free fatty acids indicated by the correlation value $R^2$ which was in the range of 0.86 – 0.891.
3.3.3. Peroxide Number

Analysis of peroxide number can be used to determine the level of oil rancidity which is one indicator of oil off due to oxidation. Some of the factors that affect the oxidation include exposure to oxygen, light, and high temperatures [9]. In this research, the linear relationship between time of storage (week) of peroxide number (mEq O2 / kg) cooking oil can be seen in Figure 4.

Figure 4. Relationship between time of storage and frequency of frying to peroxide number

Figure 4 shows that the peroxide number obtained in all treatment of the frying frequency has increased during storage. This indicated that the longer the oil was stored, the lower the quality of the oil. However, the peroxide number obtained in this experiment was still in accordance with the standard. The highest peroxide number occurred at the frequency of the 11th frying with storage for 4 weeks, which was equal to 2.633 mEq O2 / kg. Hopefully, even though the number was lower than SNI requirement, it does not mean that the oil does not undergo oxidation, but the presence of peroxide compounds that do not participate in the degradation quality of the cooking oil. From the results of the graph above can be determined the regression coefficient (k) which shows the rate of declining quality of cooking oil during storage based on peroxide number (Table 6) and it looks strongly follow the linear pattern.

Table 6. The rate of decline in oil quality during storage based on peroxide number

| Treatment       | Regression Equation | R²   | k    |
|-----------------|---------------------|------|------|
| First fried     | 0.1634x             | 0.92 | 0.163|
| Third fried     | 0.210x+0.0601       | 0.94 | 0.210|
| Fifth fried     | 0.303x+0.2068       | 0.97 | 0.303|
| Seventh fried   | 0.220x+1.0398       | 0.99 | 0.220|
| Ninth fried     | 0.217x+1.4667       | 0.97 | 0.217|
| Eleventh fried  | 0.183x+1.8932       | 0.99 | 0.183|
3.4. Zeolite efficiency for used cooking oil refinery

The use of cooking oil repeatedly during storage has been shown to reduce oil quality indicated by increasing the value of the quality parameters obtained. Therefore a refinery or purify process is necessary to be done to maintain the quality of cooking oil. In this research, used cooking oil was purified using zeolite. The zeolite adsorbent will absorb the dye in the oil, colloidal suspension, and the results of oil degradation [14]. Zeolite is easily modified in surface area and acidity thus this material is widely used commercially for cooking oil purification [15]. The efficiency of zeolite adsorption on moisture and evaporated material content, free fatty acid value, and peroxide number of used cooking oil can be seen in Table 7.

Table 7. The value of efficiency of zeolite adsorption on moisture content and evaporating material, free fatty acid content, and peroxide number

| Quality parameters                           | Before adsorption | After adsorption | Efficiency (%) | SNI 7709:2012 |
|----------------------------------------------|-------------------|------------------|----------------|---------------|
| Water content and evaporate material (%)     | 0.11              | 0.12             | 8.20           | Maks. 0.1     |
| Free fatty acid level (ffa) (%)              | 0.90              | 0.43             | 52.38          | Maks. 0.3     |
| Peroxide number (mek O2 / kg)                | 2.80              | 1.90             | 30.95          | Maks. 10      |

It can be seen that the average value of the oil quality parameters after the adsorption process has decreased even though the value of water content and evaporating material and the level of free fatty acids do not meet the cooking oil quality requirements set by SNI 7709: 2012.

4. Conclusion

Repeated use of cooking oil during storage has a significant effect on quality degradation which was characterized by increasing water content and evaporating material, free fatty acid value, and peroxide number. The rate of decline in the quality of cooking oil continuously occurred during storage and followed a linear equation. The maximum frequency for repeated use of cooking oil based on the SNI requirement set was 5 times with the quality number of water and evaporated material content, free fatty acid value, and the peroxide number as 0.0046, 0.0878, and 0.303, respectively. In conclusion, the oil after being used for 5 time of frying should be neither stored or used anymore for food purpose due to off quality. The effort to maintain oil quality using zeolite could not result in the increasing quality of used cooking oil as its efficiency was only 8.20%; 52.38%; and 30.95% for the value of water and evaporated materials, free fatty acid, and peroxide number. Furthermore, the refine cooking oil did also not meet the cooking oil quality requirements set by SNI 7709: 2012.

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