The addition of pineapple flesh and pineapple peels extracts to increase the quality of used cooking oil

R Kusumawardani¹, N Hasanah¹ and Sukemi¹,²

¹Chemical Education Department, Faculty of Teacher Training and Education, Mulawarman University, Samarinda, Indonesia
²SMA N 2, Samarinda, Indonesia

*Corresponding author: ratna.kusuma@fkip.unmul.ac.id

Abstract. In Indonesia, reuse of cooking oil is high and common. Heating process and reuse of the cooking oil causes a change in its chemical constituents and decrease its qualities. This research aimed to investigate the addition of pineapple flesh extract (PFE) and pineapple peel extract (PPE) on the increment of the quality of oxidized (used) cooking oil. The cooking oil has been used three times. Treatment was done by mixing the used cooking oil with the extract (2:1) at 50°C. Peroxide value, FFA and iodine number of treated and untreated used cooking oils were measured by using titration method. The result showed that the treatment could increase the quality of the used cooking oils. PPE was better than PFE to increase the quality of the used cooking oil.

1. Introduction

The use of cooking oil in Indonesia is increasing and Indonesia is known as a leading global supplier of cooking oil [1-2]. It is proven by the increment of cooking oil brand produced by cooking oil industries. An increment on the number of cooking oil production is caused by the increment of society demand on the cooking oil. It is used in food processing, especially in cooking. Cooking oil is widely used for frying foods because it has a high smoke point. Moreover, cooking oil tasty taste), create a crisp texture and increase nutrition value of foods [1-3].

Heating process and reuse of the cooking oil causes a change in its chemical constituents. During heating process and contact with oxygen, the cooking oil is oxidized and produces some aldehydes, ketones, and aromatic compound that create rancid odors [3]. It also increases the number of free fatty acid (FFA) and produce trans-fatty acid which cause some diseases such as coronary heart disease and diabetes [3].

In Indonesia, reuse of cooking oil is high and common. Commonly the societies use the cooking oil 2 – 4 times [3]. Indonesian calls the used cooking oil as minyak jelantah. As mentioned above, reuse the cooking oil can change its chemical constituents and decrease its quality. Indonesian government establishes a standard quality of cooking oil. The cooking oil can be consumed maximum value 0.3% (w/w) of FFA, 0.01 mg O₂/g of peroxide, and 0.6 mg KOH/g of acid value (AV) [3-4].

To maintain the quality of cooking oil, antioxidant such as butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT), can be added to inhibit the oxidation of cooking oils. The use of BHA and BHT may contribute to carcinogenicity or tumorigenicity. There are some natural antioxidants that
can replace the function of BHA and BHT such as vitamin E and Carotenoid and other phenolic compounds that can be found from plants; herb, vegetable and fruits[5-7].

One of the fruits that can be used as antioxidant is pineapple. Each 100 g of pineapple consist 24.0 mg of vitamin C and 39 μg of vitamin A [8-9]. It has been known that pineapple contain some phenolic compounds e.g. ferulic acid, myricetine, quercetin and tyramin [10]. According to the reason above, this research was conducted to investigate the addition of pineapple and pineapple juice on the increment of the quality of oxidized cooking oil.

2. Materials and Methods

2.1. Sample and chemicals

Pineapple fruits were purchased from traditional market in Samarinda city, East Kalimantan, Indonesia. The pineapple fruits were cleaned from dirt and separated between its flesh and peels. Both of the flesh and peels were blended by using commercial blender. Then, the juices were squeezed and filtered. The filtrate was called as pineapple flesh extract (PFE) and pineapple peels extract (PPE) were kept at cleaned and sealed glass container.

The used cooking oil was obtained from food vendor at Jalan Perjuangan I, Samarinda, East Kalimantan, Indonesia. It has been used three times. All chemicals; acetic acid glacial, ethanol, hydrochloric acid, starch, phenolphthalein, chloroform, sulphuric acid, iodine, bromide, potassium iodide, potassium iodate, potassium hydroxide, sodium thiosulfate, were purchased from Merck.

2.2. Treatment procedure of used cooking oil

100 mL of used cooking oil was loaded into a 250mL beaker glass and followed by the addition of 50 mL PFE. The mixture was mixed using a stirring rod, heated at 50°C for 5 min using a water bath. After reaching room temperature, the mixture was filtered using Whatman filter paper. The procedure above was done also by substitute PFE with PPE. All the experiment was repeated twice.

2.3. Analysis of peroxide value (PV)

PV was determined by following the procedure of Andarwulan et al with some modifications [11]. Weighed sample (untreated and treated used cooking oils) was loaded into 100 mL Erlenmeyer flask. 30mL of acetate glacial – chloroform (3:2 v/v) was added into the flask followed by 0.5mL saturated potassium iodide. The Erlenmeyer flask was covered by using stopper and shaken strongly for 2 min. Then, 2 drops of starch solution was added and blackish-blue colour appeared. The mixture was titrated with 0.01 N sodium thiosulphate. The titration was stopped when the blackish-blue colour gone. Titration was also performed for blanks (distilled water). The PV was calculated by using formula:

\[ PV = \frac{(V_s - V_b) \times N \times 1000}{W} \]  

where: \( V_s \) is Na\(_2\)S\(_2\)O\(_3\) volume used in titration of sample (ml), \( V_b \) is Na\(_2\)S\(_2\)O\(_3\) volume used in titration of blank (ml), \( N \) is Na\(_2\)S\(_2\)O\(_3\) normality (N), and \( W \) is weight of sample (g).

2.4. Analysis of free fatty acid (FFA)

FFA was performed using a method of Andarwulan et al with minor modifications [11]. Weighed sample (untreated and treated sample) was loaded into weighed 100 mL Erlenmeyer flask. 25 mL of 95% ethanol (v/v) was added into the flask and the mixture was heated at 50-75°C for 5 min using a water bath and stirred. 3 drops of phenolphthalein solution was added and titrated with 0.1 N sodium hydroxide. The titration was stopped when pink colour appeared.

\[ FFA = \frac{(V \times N \times 25.6)}{W} \]  

where: V is volume of NaOH used in the sample until the pink color persisted (mL), N is the normality of NaOH, W is weight of the sample (g).

2.5. Analysis of iodine value (IV)
Iodine value (IV) was performed using a method of Daniali et al with minor modifications [12]. Weighed g sample (untreated and treated sample) was loaded into 100 mL Erlenmeyer flask with stopped cock followed by the addition of 10 mL of chloroform and 25 mL of iodine bromide. The mixture was rotated and left at the dark condition for 30 min after the addition of 10 mL 15% potassium iodide (w/v) and 100 mL of boiled water. The mixture was titrated with 0.1 N sodium thiosulfate until pale yellow colour appeared. Two drops of starch solution were added and the titration was continued until the blackish-blue colour gone. The IV of sample was calculated by following formula:

\[
IV = \frac{(V_b - V_s) \times N \times 12.69}{W}
\]

where: \(V_s\) is volume of sodium thiosulfate used in titration of blank (ml), \(V_b\) is the volume of sodium thiosulfate solution used in titration of sample, N is the concentration of sodium thiosulfate (N) and W is weight of sample/blank (g).

3. Result and Discussion
The used cooking oil in this research was the cooking oil that has been used 3 times. Physically, the oil was more viscous and darker than unused cooking oil and produced rancid odor. Its viscosity was thicker than that of unused cooking oil. The viscosity of treated used cooking oils with PFE and PPE were almost same as the viscosity of unused cooking oil. Its colour was also nearly the unused cooking oil (pale yellow) and their rancid odor was gone. There was pineapple odor on the treated used cooking oils, whereas the pineapple odor of treated used cooking oil with the PFE was stronger than that of treated used cooking oil with the PPE. The PV, FFA and IV of treated and untreated used cooking oil are shown in table 1.

**Table 1. The quality of untreated and treated used cooking oils**

| Samples                  | Odor           | Colour | PV   | FFA   | IV      |
|--------------------------|----------------|--------|------|-------|---------|
| Untreated used cooking   | Rancid         | Brown  | 2.40 | 0.19  | 24.66 ± 0.03 |
| oil                      |                |        | ±0.20| ±0.01 |         |
| Treated used cooking oil | Pineapple aroma| Yellow | 1.60 | 0.14  | 27.12 ± 0.58 |
| PPE                      |                |        | ±0.40| ±0.01 |         |
| Treated used cooking oil | Pineapple aroma| Yellow | 1.13 | 0.13  | 25.99 ± 0.47 |
| PPE                      |                |        | ±0.12| ±0.01 |         |

Lipid oxidation is one of the chemical reactions occurred in heat processing of cooking oil and produces peroxides [12]. According to Republic of Indonesia Standard, the maximum value of PV of cooking oil is 2 Meq/kg [3]. Tabel 1 shows that untreated used cooking oil was exceed the allowed PV and the PV of both of PFE and PPE treated used cooking oils were lower than that of maximum PV allowed. It means that the PPE and PFE could decrease the PV of used cooking oil. FFA indicates the hydrolysis reaction occurs. 0.3 % is the maximum amount of FFA in cooking oil that allowed by Republic of Indonesia Standard. Table 1 shows that the PFE and PPE could decrease the FFA of the used cooking oil and the amounts were lower than the maximum amount of FFA allowed. IV was used to determine the unsaturated fatty acid amounts. The IV is decrease during the heat and the saturation rate is increased [12]. The IV values of untreated and treated used cooking oils were low. It indicates that during the heat process, the unsaturated bonds were broken. The highest saturated fatty acid causes the cooking oil resistant to oxidation reactions.
4. Conclusion
The use of PFE and PPE to increase the quality of used cooking oil has been discussed. It can be concluded that the PFE and PPE could increase the quality of used cooking oil and the PPE was better than PFE to increase the quality of used cooking oil.

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References
[1] Wildan F 2002, Penentuan bilangan peroksida dalam minyak nabati dengan cara titrasi, Temu Teknis Fungsional Non Peneliti, p 63
[2] Andarwulan N, Gitapratiwi D, Laillou A, Fitriani D, Hariyadi P, Moench-Pfanner R, and Martianto D 2014, utility of vegetable oil prior to fortification is an important criteria to achieve a health impact, Nutrients, 6 p 5051
[3] Ilmi IMB, Khomsan A, and Marliyati SA 2015, Kualitas minyak goreng dan produk gorengan selama penggorengan di rumah tangga Indonesia, Jurnal Aplikasi Teknologi Pangan, 4 p 61
[4] Surosso AS 2013, Kualitas Minyak Goreng Habis Pakai Ditinjau dari Bilangan Peroksida, Bilangan Asam dan Kadar Air, Jurnal Kefarmasian Indonesia, 3 p 77
[5] Taghvaei M and Jafari SM 2015, Application and stability of natural antioxidants in edible oils in order to substitute synthetic additives, J. Food Sci. Technol., 52 p 1272
[6] Kahl R and Kappus H 1993, Toxicology of the synthetic antioxidants BHA and BHT in comparison with the natural antioxidant vitamin E, Z Lebensm Unters Forsch., 196 p 328
[7] Saito M, Sakagami H, and Fujisawa S. 2003, Cytotoxicity and apoptosis induction by butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT), Anticancer Res., 23 p 4693
[8] Rashad MM, Mahmoud AE, Ali MM, Nooman MU, and Al-Kashef AS 2015, Antioxidant and anticancer agents produced from pineapple waste by solid state fermentation, International Journal of Toxicological and Pharmacological Research, 7 p 287
[9] Santoso HB 1998 Manisan Nanas (Jakarta: Kanisius) p 13
[10] Yapo ES, Kouakou HT, Kouakou LK, Kouadio JY, Kouamé P, and Mérillon JM 2011, Phenolic profiles of pineapple fruits (Ananas comosus L. Merrill) influence of the origin of suckers, Australian Journal of Basic and Applied Sciences, 5 p 1372
[11] Andarwulan N, Gitapratiwi D, Laillou A, Fitriani D, Hariyadi P, Moench-Pfanner R and Martianto D 2015, Quality of vegetable oil prior to fortification is an important criteria to achieve a health impact, Nutrients, 6 p 5051
[12] Danialii G, Jinap S, Hajeb P, Sanny M, Tan CP 2016, Acrylamide formation in vegetable oils and animal fats during heat treatment, Food Chemistry, 212 p 244