Screening the Quality of Coconut Oil Heated on Several Temperatures by Liquid Chromatograph Mass Spectrometry

I P M Nasution¹, K Fahmy¹, Andasuryani¹, D Syukri¹, K Nakano², T Immaizumi²

¹ Andalas University, Faculty Agricultural Engineering, Padang-Indonesia  
² Gifu University, United Graduate School of Agricultural Sciences, Gifu-Japan

Corresponding author: khandrafahmy@ae.unand.ac.id

Abstract. The objective of this study was to screen the quality marker of stored coconut oil on several temperatures. The method used in this research is a degree date method with sample observations carried out regularly. Coconut oils were stored at 30°C, 40°C and 50°C. The quality of coconut oil after storage were determined with viscosity was measured by Capillary Viscometer SIBATA S0-6818 and carbonyl compounds analysis were analyzed using Liquid Chromatograph Mass Spectrometry (LC/MS). The results showed, viscosity decreased with increasing of temperature. The significant decreased in viscosity occurs at 50°C, which is 23.6138 mm²/s. Principle component analysis and discriminant analysis (PCA-DA) on compound carbonyl analysis showed the presence that formed at each temperature. A decreased in viscosity and the presence compounds are marker decline in the quality of coconut oil.

Keywords: Carbonil Compounds, Coconut Oil, Liquid Chromatograph Mass Spectrometry, Temperatures, Viscosity

1. Introduction

Coconut (Cocos nucifera, L.) is one of the largest plantation commodities in Indonesia with a production of 18.30 million tons per year [1]. The main processed from coconut is crude coconut oil (CCO). Coconut oil is produced by crushing copra with low moisture content (6–8%) and which contains about 60–65% of oil by expellers [2, 3]. It is an edible oil that has been consumed in Indonesia and other countries for thousands of years.

CCO is commonly used in baking industries, foodstuffs, pharmaceuticals industries, cosmetics industries and biodiesel. It is known Indonesia is the second largest country after the Philippines which exports CCO to various countries such as Germany with a contribution of 35.31% [4].

The oil has natural sweet taste of coconut and contains high compositions of medium chain fatty acids (MCFAs) as well as saturated fatty acids (90%). The major fatty acids are lauric (12:0) and myristic (14:0) at about 48% and 18% respectively, while no other fatty acid is present at more than about 8%. Coconut oil also contains active compositions namely tocopherol, fitosterol, and polyphenols. In addition to triacylglycerols and free fatty acid, crude coconut oil contains about 0.5% of unsaponifiable matter. This material consists mainly of sterols, tocols, squalene, colour compounds, carbohydrates and odour compounds (such as lactones) [5, 6, 7].

In Indonesia CCO is produced by small industries. After being obtained from small industries, CCO is transported to the location of the processing plant and to the port using tanker trucks via land
transportation modes, then it will be export to destinations via sea transportation modes. During the transportation and storage process, coconut oil may change a decrease in quality.

There are three causes of damage that can occur during the storage and transportation of vegetable oils, the occurrence of oxidation reactions, hydrolysis reactions, and contamination [8]. In addition, chemical and physicochemical properties of coconut oil may change due to the external environmental conditions, such as temperature. It is one of the major factors influencing the decline in the quality of CCO [9]. During transportation, CCO is expected to remain liquid to avoid repeated heating, but normally, the tanker trucks don’t have heating systems or temperature controls. This causes a change in the quality of CCO, one of which will decrease is viscosity. Viscosity is one of the most important physical properties of oil. The viscosity of all of vegetable oils decreased as the temperature increased. The foodstuffs such as oil often experience temperature treatment during processing, storage, and transportation. It is very influential on viscosity [10].

Besides the temperature factor, the length of time used for transportation can cause a decrease in the quality of CCO. The coconut oil will be stored for a long time to the processing plant and destination country. The coconut oil stored at room temperature for 12 months showed a significant increase in the value of peroxide value, caused by oxidative damage [11]. This might make changes to the constituent components of fatty acids and the active composition in coconut oil. Effect of uncontrolled temperature and the length of time required during transportation, can also allow the formation of new carbonyl compounds that cause a decrease in the quality of CCO. The decrease in viscosity and the formation of other compounds in coconut oil is expected to be a marker as an indicator of determining the quality of CCO during distribution.

2. Methods
This research was conducted at the Food Distribution Engineering Laboratory, Gifu University -Japan. The main ingredients used in this research are coconut oil from Indonesia. It was purchased from a local industry in Padang Pariaman, West Sumatera, Indonesia.

For preparing the sample, 50 ml of CCO is added in an Erlenmeyer and stored in an incubator at various temperature of 30°C, 40°C and 50°C. The method used in this research is a degree date method with sample observations carried out regularly. At temperature 30°C, the coconut oil stored for 96 hours with a sampling interval every 12 hours. For temperature 40°C, it was stored for 72 hours with a sampling interval every 9 hours and 50°C for 57 hours with a sampling interval every 7 hours. Illustration of the degree date method can be seen in Table 1.

| Degree (°C) | Date (t) | °C x t |
|------------|----------|--------|
| 30         | 96       | 2880   |
| 40         | 72       | 2880   |
| 50         | 57.6     | 2880   |

The parameters are determined in this study include the viscosity of coconut oil and the analysis of coconut oil carbonyl compounds using LCMS.

1. Viscosity
Viscosity of coconut oil samples was carried out using ASTM D445-14 using SIBATA capillary viscometer S0-6818.

2. Analysis of Carbonyl Compounds
The carbonyl compounds in coconut oil was analyzed using the derivative method with dansyl hydrazine and analyzed with LC / MS Shimadzu UFLC-AB SLIEX 4500 Qtrap according to Syukri, et al., 2018.

3. Results and Discussion
3.1 Viscosity
Viscosity is one of the parameters to determine the quality of a product. During the process of transportation and storage of a product will experience a heating process that can affect the value of its
viscosity [12]. The temperature greatly influences viscosity, in general viscosity decreases with increasing temperature [10]. The relationship of temperature with the viscosity of CCO samples can be seen in Figure 1.

![Figure 1. CCO Viscosity Chart](image)

Figure 1 shows the effect of temperature on the viscosities of CCO. It can be seen that viscosity decreases nonlinearly with increasing temperature. It could be due to the energy obtained to overcome the resistance to flow, which may be due to the attractive forces among the oil molecules. This is an indication that temperature has a significant effect on the viscosity of coconut oil. The significant reduction occurred at 50°C, with a viscosity of 23.6138 mm²/s. The decreased in viscosity that occurs showed that there is an indication of damage or deterioration in the quality of CCO during the heating process.

The decrease in viscosity due to an increase in temperature is caused by the movement of molecules in oil and a decrease in cohesive pressure between molecules which causes a decrease in viscosity [13, 14]. In addition, according to the longer the number of fatty acids that make up fatty acids, the greater the amount of viscosity and double bonds in fatty acid compounds, the greater the amount of viscosity [15].

2. Analysis of Carbonyl Compounds Using LC/MS

LC / MS is a liquid chromatography technique with a mass spectrometer detector. The working principle of a mass spectrometer is to shoot the material being analyzed with electrons and quantitatively record the results as a spectrum of positive ion fragments. The fragments are grouped according to their mass [16]. Mass spectroscopy that produces mass provides information about the molecule, structure, identity, number, and purity of the sample so as to improve the quality of the results obtained in quantitative and qualitative analysis [17].

LC-MS analysis is widely used in the field of bioanalysis because it has the ability to separate and detect molecules with a wide range and can be used for quantitative and structural analysis with sensitivity values reaching pg / mL [18]. The results of the analysis of Crude Palm Oil using LC / MS are then presented in the form of a PCA diagram which can be seen in Figure 2.
Based on the results of the PCA shows that the model is able to successfully separate the three different classes/groups that can be made to show there has been a decrease in the quality of the CCO that has been heated. The results of the PCA analysis above explained that there were 63.9% of the total variations with a D1 score of 33.8% and D2 of 30.1%.

Figure 2 above it can be seen that 3 classes/groups of samples were formed clearly. The score graph shows that CCO is heated at 30°C and 40°C closer to the center compared to 50°C. This shows that there has been a significant change in the CCO which is heated at 50°C so that it is located separate and far from other groups. In the next groups, it appears that the temperature of 30°C and 40°C were in the same group, this shows that heating is carried out at CCO at 30°C and 40°C resulting in almost the same compound profile. The similarity of this compound can also be known based on the loading plot which can be seen in Figure 3.

New variable or score generated by PCA is a linear combination of the original measurement variables [19]. Skor dinilai bersama dengan satu set vektor yang disebut loading. The response score along with a set of vectors is called loading. Each point on the loading of the PCA plot is a component and a component that contributes significantly to differences between groups is the component that is furthest from the main group.

From the results of the loading plot, it can be seen that when CCO is heated at 50°C, it is thought to cause the formation of new compounds with m/z value of 321. While CCO which is heated at temperatures of 30°C and 40°C is also thought to form new compounds that have similarities with m/z values of 499 and 500. The formation of these compounds can be used as a sign that there has been a
decrease in the quality of CCO due to heating at several temperatures.

4. Conclusion
Based on the research that has been done, it can be concluded that the decrease in viscosity that occurs due to the heating process can be used as a sign that CCO damage has occurred. The significant reduction occurred at 50°C with a value of 23.6138 mm²/s. In addition to decreasing viscosity, other markers that can be used to mark a reduction in the quality of CCO can be seen from the analysis of the carbonyl composition using LC/MS. Analysis of the carbonyl composition showed the formation of CCO which led to the emergence of new compounds formed with m/z values 321, 499 and 500. Further research is needed to elucidate the appropriate compositions to be validated for use as an indicator of determining the quality of CCO during distribution.

Acknowledgements
The author Indah Pertiwi Mardani Nasution has a scholarship “UGSAS-GU 6-month Sandwich Program” Gifu University supported by JASSO. This work was financial supported by a grant from Postharvest Engineering Laboratory Gifu University, Japan.

References
[1] Food and Agriculture Organization of the United Nations Statistic (FAOSTAT) 2014 Production (Crops) Coconuts Commodity Statistic http://www.fao.org/faostat/en/#data/QC (Accessed, 25 October 2019)
[2] Rahman H 2000 The chemistry of coconut oil
[3] Canapi E C, Augustin Y T V, Moro E A, Pedrosa Jr E, and Bendano M L J 2005 Coconut oil, in Edible Oil and Fat Products: Edible Oils, Bailey’s Industrial Oil and Fat Products, F. Shaihdi Ed. 123–147 JohnWiley and Sons USA: Hoboken NJ
[4] United Nation Commodity Trade [UN comtrade]. 2016 Available at: CommodityStatistic.http://comtrade.un.org/db. (accessed on,19 October 2019).
[5] Carandang E V 2008 Health benefits of Virgin Coconut Oil Indian Coconut Journal 31(2): 8-12
[6] Marina A M, Che Man Y B and Nazimah S A H 2009 Chemical properties of virgin coconut oil Journal of the American Oil Chemists’ Society 86 301-307
[7] Young E V K 1983 Palm kernel and Coconut Oils: Analytical Characteristics, process technology and uses JAOCs 60 374-379
[8] [CAC] CODEX Alimentarius Commission 2005 Recommended International Code of Practice for the Storage and Transport of Edible Fats and Oils in Bulk CAC/RCP 36–1987 (Rev.1-1999, Rev.2-2001, Rev.3-2005)
[9] Araújo J M A 2004 Química de alimentos: Teoria e prática Viçosa: UFV 416
[10] Rao M A 1999 Rheology of Fluid and Semifluid Foods: Principles and Applications Gaithersburg: Aspen Publication
[11] Moigradea D, Poiana M A, and Gogoasa I 2012 Quality characteristics and oxidative stability of coconut oil during storage Journal of Agroimetry Processes and Technologies 18(4) 272-276
[12] Permatasi R 2011 Kajian Pengaruh Suhu Terhadap Densitas Dan Sifat Reologi Minyak Sawit Kasar (Crude Palm Oil) Bogor: Institut Pertanian Bogor
[13] Munson B R, Young D F, and Okiishi T H 2001 Fundamentals of Fluid Mechanics 4th Ed New York: John Wiley and Sons
[14] Santos J C O, Santos I M G, and Souza A G 2005 Effect of heating and cooling on rheological parameters of edible vegetable oils J. Food Eng 64 401-405
[15] Knothe G., Garpen J V, and Krahl J 2005 The Biodiesel Handbook Illinoi: Champaign AOCs Press
[16] Fessenden R J and Fessenden J S 1992 *Kimia Organik* Jilid 2 Edisi ketiga Jakarta: Erlangga

[17] Lee M S and Kerns E H 1999 LC/MS application in drug development *Mass Spectrometry Reviews* **18** 187-279

[18] Theodoridis G, Helen G G, and Wilson I D 2008 LC-MS-based methodology for global metabolite profiling in metabonomics/metabolomics *Trends in Anal Chem* **27** 251-260

[19] Miller J C and Miller J N 2000 *Statistic and Chemometrics for Analytical Chemistry* 4th Ed Harlow: Pearson Education