Development of electro-optics method for evaluation of quality degradation of some vegetable oils

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Abstract. In this research we present a development of electro-optics effect to evaluate vegetable oil quality degradation. Some vegetable cooking oil samples after heating were placed in an external electric field to obtain the electro-optical characteristics, by measuring the polarization change using green pointer laser (532 nm). The results showed that the change on natural polarization and electro-optics effect were proportional to the duration of heating. An important result showed that the percentage of reduction in the quality of olive oil is the greatest from palm oil, rice bran oil, and corn oil. This provides electro-optics as a very potential method in the cooking oil quality test system and provides a new perspective for further research improvement in other relevant fields.

1. Introduction

Olive oil is a famous vegetable oil and is currently widely used and consumed because of its quality. The question most often arises when people talk about oil quality, namely what parameters can measure it, how to measure it, and most likely how to look for the best and find out the quality reduction. Currently there are many variables used to determine the quality of cooking oil. Current standard parameters such as peroxide value, free fatty acid values etc. have been used and it seems that additional parameters have also been developed to support or complement the previous parameters. At present many researchers have worked in developing various instrument systems to evaluate the degree of degradation of oil quality, such as for authentication, forgery, degradation during and after the heating process, oxidative stability etc. [1-16]. Several instrumental methods or systems that have been selected as additional support for assessing oil quality levels have also been reviewed to obtain fast and accurate authentication and sample falsification [17]. But in certain regions standard parameters and methods with additional combinations of various instruments must still be evaluated and developed to get the best results and to meet market demand in the community [18].

Evaluation of oil quality degradation through thermal oxidation before, during and after heating the sample is a very complex and time-consuming system. To speed up the process of evaluating oil quality, samples are often used only after heating. Some examples of standard quality parameters according to the Indonesian National Standardization that are evaluated are peroxide numbers, acid numbers, free fatty acid percentages, and iodine numbers [19]. These standard parameters have been discussed and lead to a conclusion, that there are too many variables and are very complicated to test at once [20]. With many additional complex methods and instruments, it is also time-consuming and expensive, and therefore Firdausi et al have proposed parameters of polarization change as quality indicators and electro-optics as methods for determining oil quality [20]. It has been found also that an expired sample
not always is accompanied by higher free fatty acids or peroxide number than a good one [21]. But expired and heated cooking oils are always accompanied by increasing polarization change [20-26]. The initial assumption stated that polarization was directly related to free radicals [20], but more precisely is the relationship between changes in the composition of fatty acids in triglyceride molecules with changes in polarization [22, 24-27]. By using electro-optics the increase in changes in polarization is related to only the development of electric dipoles that leads to non-linear optics or called electro-optic polarization and gives a more significant figure in determining oil quality through polarization changes [22, 24-27]. In another application, we also studied the effects of ozone addition in virgin coconut oil, and we found that the tendency for increased polarization was proportional to the amount of asymmetric molecular production [28]. At the moment, any disturbance on sample oil principally changes the condition or oil quality shown by small polarization change and it can be enhanced and observed significantly by using electro-optics effect. It seems that the polarization change provides powerful parameter as indicator of oil quality.

In this paper we develop the electro-optics to evaluate oil quality degradation of various vegetable oils. The polarization change measured in this experiment is to prove the role of optical activity of cooking oil after heating, to demonstrate the enhancement of polarization change through electro-optics effect, and also to find out an alternative potential variable that can describe the relation between polarization change and oil quality.

2. Methods
The experimental procedure refers to our previous work [27]. Various vegetable oils, e.g. olive oil, palm oil, corn and rice bran were heated in an oven at around 100 °C with a heating duration of 2, 4, 6, and 8 hours for each sample. The electro-optical characteristics of the sample were obtained by measuring the change in polarization using a green laser pointer with $\lambda = 532$ nm when the sample was applied to external electric fields using high DC voltage in the range of 0-9 kV. The percentage change in polarization of each sample was determined by comparing each heated sample with unheated one. For validation we used the GCMS procedure to evaluate the composition of fatty acids of each sample before and after heating.

3. Results and Discussion
According to GCMS results all samples are in accordance with these standard samples, however it showed slight changes in the composition of fatty acids and it was considered insignificant to be displayed in this paper. And for some reason GCMS data from each sample is not shown in this report. As we found in some of our studies [20, 22, 24-27], in this experiment, all samples also produced a non-linear optical response or the so-called electro-optic as shown in the polynomial curve of polarization changes to potential differences. Fig 1 shows non-linear curves of polarization changes $\theta$ against potential difference $V$ for olive at various heating time, and fig 2 expresses linear relation of the polarization changes against heating time for olive at various potential differences. We obtain also similar behaviour for palm, corn, and rice bran oil. In various other methods, heating the sample means reducing the oil quality through several chemical processes such as oxidation etc [1-16, 19]. By measuring difference of polarization we demonstrate quantitatively that polarization change is much related to the change of oil quality through the heating process. As we have found in previous studies [23] usually for vegetable oils, good oil quality is indicated by polarization change less than 1°. The polarization change enhancement through electro-optics effect, which is indicated by the increase polarization against potential difference, shows that it provides a potential method for oil quality evaluation. The reducing oil quality leads to increasing polarization change as we have also already discussed. The graphs in fig 1 confirm the oil quality degradation due to heating process that is significantly related to polarization changes and also are in agreement to the previous studies.
Figure 1. The average polarization change is polynomial against potential difference for olive oil at various heating time. Other samples show similar curves, as well.

Figure 2. The average polarization change is linear as function of heating time of olive oil at various potential difference with the same gradient. Other samples have identical graphs as well.

The polarization changes is contributed by natural polarization and electro-optics effect and can be written as \( \theta = \theta_0 + \theta_d \), where \( \theta_0 \) represents as natural polarization part measured at \( V = 0 \), and \( \theta_d \) describes electro-optics part measured from \( V = 1 \) to \( 9 \) kV. The term of natural polarization \( \theta_0 \) comes originally from the optical active characteristics of cooking oil due to the distribution of fatty acids in asymmetric triglycerides. And on the other hand, the term of electro-optics polarization \( \theta_d \) comes from non-linear optics consideration due to development of electric dipoles of triglyceride molecules in strong external field. With the polynomial second order in term of \( \theta = \theta_0 + \theta_1 V + \theta_2 V^2 \), the electro-optics contribution can be written as \( \theta_d = \theta_1 V + \theta_2 V^2 \), where \( \theta_1 \) and \( \theta_2 \) can be regarded as linear and quadratic coefficient, respectively. The developed electric dipoles that lead to non linear polarization response to the entire polarization changes provides clearly the relative difference of polarization between good quality and bad quality oil as we have found in our recent studies [20, 22, 24-27]. The polynomial term found in the experiment is strongly dependent on the strength of applied electric field. By using parallel plates, the electric fields that induced oil sample is considered as \( E = V/D \), and \( D \) is the distance between plates. The distance is circa 1.5 cm and in the plates it is produced electric field in the order of \( 10^5 \) V/m. This seems adequately to produce non linear optics response or electro-optics effect on the sample. In our recent study [22], by using \( D \approx 2 \) cm, we found only linear response as \( \theta_d = \theta_1 V \), and the \( \theta_1 \) is called as electro-optics gradient and provides also to evaluate the degradation of oil quality related to the development of the fatty acids composition in palm oil.

In fig 2, the linear curve of polarization change vs. heating time has the same gradient for various potential differences, and it indicates that increasing number of asymmetric triglyceride molecules is proportional to the heating time. By giving potential difference it is a similar condition with giving different states for each sample after heating. In recent study we also obtained linear relation for olive oil however only for 0-4 hours of heating time interval [26]. In the interval 0-8 h of heating time we have considered that the number of asymmetric triglycerides increases linearly. Applying electric fields or potential difference in the interval from 0-9 kV seems to change the condition of sample in different levels, similar to excited states in atomic or molecular systems. The similar situation has been discussed according to our studies [25], and it leads to the important parameter instead of polarization change, i.e. average dissociation energy that describes molecular Van der Waals interaction between triglyceride molecules. The observation of oil quality reduction through polarization change enhanced by electro-optics effect gives not only easily significant polarization changes in various cooking oils but also provides a breakthrough of a new prespective to the definiton of oil quality and leads to a new single oil quality parameter, i.e. average dissociation energy.
In fig. 3 and 4 the average polarization change on natural and electro-optics polarization increases linearly with the duration of heating time and with a similar gradient for all samples.

Figure 3. The change of natural polarization as function of heating time of sample.

Figure 4. The change of electro-optics polarization as function of heating time of sample.

The natural polarization ($\theta_0$) behaviours show the quality condition of the samples before and after heating. In the same experimental condition, the lowest polarization indicates that olive has relatively the best quality from the others. The similar curves of corn and rice bran oil show that both of them have similarity in quality and molecular composition of asymmetric triglycerides. This situation is apparently confirmed also by the electro-optics polarization change in fig 4. However the value of electrooptics contribution is relative higher than natural polarization that shows additional electric dipoles during applying external potential difference.

It is now very interesting how the quality reduction of sample (in 2, 4, 6, 8 h of heating time) relatively compared to the sample before heating (0 h). Referring to the fact that the decreasing oil quality is related to the increasing polarization change, therefore the quality reduction is calculated through the different fraction of polarization change between sample after heated and before heated.

Figure 5. The quality reduction of olive oil as function of potential difference for various heating time relative to the sample without heating (0 h). Other samples show also similar graphs.

Figure 6. The quality reduction as function of potential difference for various oil at heating time 8 h. The reducing fraction of olive is the greatest from others.
It is surprising that the fraction of the increasing polarization is reduced against potential difference. The curve in fig 5 represents for heated olive oil in comparison to olive before heated. All other samples illustrate also similar pattern. The reducing fraction against potential different explains that some asymmetric molecules play a role ineffectively as development of electric dipoles during applying external electric fields. In fig 6 the increasing fraction of olive oil is the greatest. It means that the rate of quality reduction of olive is highest from others. That could be understood if more symmetric triglycerides turn in to asymmetric molecules. The potential difference applied to the sample in classically consideration can be regarded as additional development of electric dipole which in turn becomes non linear electric polarization response. An asymmetric molecule could be changed into symmetric molecule relative to the direction of linear polarized light and led to decreasing polarization fraction during applying potential difference. In modern consideration, according to the previous proposed theory [25], the reduction of polarization fraction against potential difference should be led to average maximum dissociation energy during applying electric field instead of average polarization changes. The use of linear polarized light is to obtain the change of polarization direction of light and describe indirectly to the potential energy of each sample that fulfilled by Lenard-Jones potential energy as indicator of the molecular Van der Waals interaction among the triglyceride molecules. In this limitation of experimental condition, we have only examined the sample by using GCMS to obtain fatty acids composition, and unfortunately we have not found adequate results to elaborate the relation of maximum average dissociation energy and fatty acids composition. Although our previous work shows correlation between polarization changes and fatty acids composition [24, 26-27], yet it is insufficient according to our consideration to obtain a final single parameter related to oil quality. The most favorable parameter that could be best examined as experimental validation would be triglyceride composition. This is very important especially to prove experimentally the linear correlation between polarization changes and heating time of sample, because we almost certain concluded that it is proportional to the number of asymmetric triglycerides according to fig 2. At last but not least, the interaction of polarized light with cooking oil molecules provides to a new viewpoint of the relation between oil quality, polarization changes, and maximum average dissociation energy. This new idea provides also to further studies of molecular interaction in other related fields.

4. Conclusions
The vegetable oil in the external electric fields shows non linear optics or so called electro-optics effect in agreement to the previous studies. The degradation of oil quality after heating process is also indicated by increasing polarization changes in both natural and electro-optics polarization which is again verifies our preceding results. The linear relation between polarization changes and the duration of heating indicates directly proportionality of the number of asymmetric molecules formed, as the best physical explanation. By applying external potential difference it increases polarization changes as if it increases sample to the different states, and we suggested that it is similar to the giving additional potential energy. By comparing the heated sample to the unheated sample we obtained the greatest increasing fraction of polarization change, which means that the biggest rate of oil quality reduction is in olive oil. The electro-optics effect on cooking oil gives significantly increasing of polarization and it provides a very potential system instrument for evaluation of various oil conditions. And another advantage shows that it offers a new perspective about oil quality through polarization changes.

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