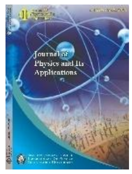
Journal of Physics and Its Applications

Journal homepage : https://ejournal2.undip.ac.id/index.php/jpa/index



Mapping various cooking oil using fluorescence polarization

K. Sofjan Firdausi[1], I. Afiefah[2], H. Sugito[3], and Much. Azam[4]

[1]*Department of Physics, Diponegoro University; firdausi@fisika.undip.ac.id*
[2] *Physics Undergraduate Study Program, Department of Physics, Diponegoro University; izzahafiefah@st.fisika.undip.ac.id*
[3] *Department of Physics, Diponegoro University;herinuha@gmail.com*
[4] *Department of Physics, Diponegoro University; azamfisika@gmail.com*

A R T I C L E I N F O

Article history:
Received : September 2018
Accepted : November 2018
Available online : November 2018

Keywords:
Mapping Cooking oils
Critical polarizer's angle
Fluorescence polarization
Change of polarization angle

A B S T R A C T

In this report we have succeeded to map various cooking oils using change of fluorescence polarization. The samples consisted of several vegetables oils and animal oils (chicken oil and lard), were used in the experiment, and some oils were measured in two different times. The change of polarization angle $\theta$was measured as the difference between linear polarized green pointer laser as incoming light and fluorescence light using a pair of polarizers. The direct measurement of fluorescence polarization gives a new unique result of critical polarizer's angle φ_c that can group vegetable cooking oils into group 1 (at φ_c = 10° for VCO, olive, and soybean), group 2 (at φ_c = 20°for palm, corn and rice bran), group 3 (at φ_c = 30° for sunflower and canola), and also animals cooking oils into group 4 (at φ_c = 20° for chicken oil), and group 5 (at φ_c = 40°for lard). Mostly cooking oils can be distinguished using modified maps. The samples that have similar fatty acids composition appear with similar result.The large difference φ_c and $\theta$of lard from vegetable oils provides an advantage to develop for testing halal oil due to lard contamination. The capability of this method has benefits, at least, as a complement and simple method in comparison to other expensive sophisticated instruments such as fluorescence spectroscopy or GCMS methods with their derivation's instruments.

1. Introduction

Fluorescence polarization of light is simply defined as a change of polarization angle of incoming light due to fluorescence scattering. The change of light polarization through fluorescence method in sample of cooking oils has been very interesting and considered as new finding in our works [1, 2], because we have used direct measurement of change of polarization angle between fluorescence light and the incoming light for determination of cooking oil quality and it has provided more significant results than standard methods. The direct measurement of change polarization angle is an unusual method for cooking oil quality testing due to very small polarization. However this problem can be overcome by repetition of measurement in several times to reduce error or uncertainties in parallax observation. The direct measurement of fluorescence polarization angle is simpler than other sophisticated standard methods. Usually, in case of fluorescence methods, the quality of cooking oils and their types are determined and measured using fluorescence spectroscopy methods with additional instruments [3-5] or additional assistant methods. Other method, as an example, for comprehensive investigation of halal food due to lard contamination, an expensive sophisticated GCMS and its derivative instrument are to be used [6].

In this paper we use direct measurement of polarization angle of light to observe various types of cooking oils. The difference of our method with fluorescence spectroscopy or GCMS method is very clear, that we use simply direct measurement of polarization angle. The new finding of our previous reports shows that the symmetry polarization between polarizer's angle φ from 0°-90° and from 90°-180° gives interesting results such as characteristics values of θ at φ = 0°, at φ = 90°, critical value of φ_c where the polarization θtends to zeroand also the average value of θ_{Avg} [1]. From our previous works[1, 2], the obtained data and its expression of the results are very possible to be developed for various types of oils, their quality and halal cases, and therefore it is still to be improved. The comprehensive physical explanation of the existence for critical value φ_c is still interesting to be discussed. In this report, the data of various cooking oils will be expressed through the change of fluorescence polarization θ against the polarization of the incoming light or polarizer's angleφ. From critical value φ_c, the cooking oils will be grouped and the best possible mapping various oil will be discussed.

2. Methods

The sample was various cooking oils presented in the table 1 below.

Table 1: [a]Various cooking oils examined in the research

Cooking oil	code	Date of measurement
VCO	*	
Olive	◊	
Soybean	□	
Corn	Δ	
Palm	×	
Chicken1	+1	24 October 2017
Chicken2	+2	
Chicken3	+3	
Lard1	o1	
Lard2	o2	
Lard3	o3	
Canola	–C	
Chicken1	+1*	
Chicken2	+2*	
Chicken3	+3*	19 September 2017
Lard1	o1*	
Lard2	o2*	
Lard3	o3*	
Olive	◊*	
Soybean	□*	
Corn	Δ*	
Palm	×*	Aug-Oct 2018
Rice bran	–R	
Sunflower	-S	
Chicken4	+4	
Lard4	o4	
Lard5	o5	

[a] the data acquisition for olive, soybean, corn, and palm was taken twice in 24 Oct 2017 and Aug-Oct 2018. Chicken oil 1, 2, 3 and lard 1, 2, 3 were taken twice in 24 Oct 2017 and 19 Sep 2017.

The basic data acquisition of the change of fluorescence polarization angle was referred to Firdausi et al [7]. To ensure the symmetry characteristics polarization angle, a measurement of scattering polarization of water molecules was used to calibrate the whole system of the instrument.

3. Results and Discussions

Fig. 1 shows profile θvs. φ of pure scattering polarization angle on water and we neglected absorption and Raman scattering due to verysmall size of water molecules relative to oil molecules.

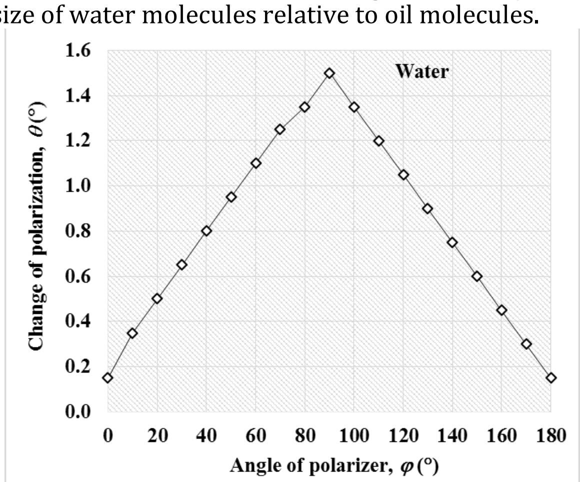


Fig. 1: Polarization angle θvs. φ of scattering on water

The symmetric value θas polarizer's angle φ goes from 0° to 90° and from 90° to 180° is considered sufficient that the system of instrument was well calibrated.

For the cooking oils, the profiles of fluorescence polarization angle θ vs. φ for all samples are symmetry at polarizer's anglefromφ = 0° to 180°, however each sample shows unique characteristics. Here, the profile of some examples (not all samples are shown) taken in Aug-Oct 2018 is shown in fig 2.

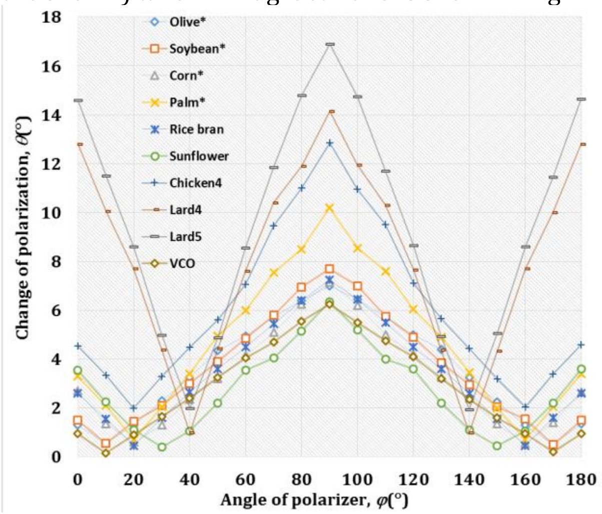


Fig. 2: Polarization angle θvs. φ for samples taken in Aug-Oct 2018

Since the data is symmetry from φ = 0° to 180°, we discuss only the unique values for each sample from φ = 0° to 90° only. The minimum value of fluorescence polarization angle $\theta_{min}$for each cooking oil results at different or unique polarizer's angle so called critical polarizer's angle φ_c. Comparing the minimum pure scattering angle of water at φ_c = 0° (fig.1) to fluorescence scattering angle of oil at$\varphi_c \geq$ 10°(fig.2), the possible physical explanation should be placed at characteristics molecules and different transition and emission of the different wavelength of fluorescence light from each most fatty acids composition for each oil. Since the molecules of cooking oil are in average much greater than water molecules, a complex combination of pure scattering and fluorescence scattering is taken place in oil and results in different φ_c and much high value θ in comparison to the pure scattering on water molecules. It is still an interesting task to answer questions, why φ_c for certain oil increases a different value in step 10°, 20°, 30° and 40° or why for lard is the greatest at 40°. Because the direct measurement is the change of polarization angle, the answers of the question should be based on the asymmetrical or symmetrical triglyceride molecules, the orientation of molecules, size of triglyceride molecules in oil, and characteristics of transition on energy levels in each sample. It should be comprehensively investigated through the role of the pattern of molecule orientation, transition level and the data of spectroscopy.

There are at least four characteristics values that can be noticed i.e. critical value φ_c,polarization angle θ_0 (at φ = 0°), peak polarization angle θ_P (at φ = 90), and minimum polarization angle θ_{min} in which $\varphi_c$takes place. In our previous reports, we have used average polarization angle θ_{Avg} vs. critical value $\varphi_c$and it has shown an interesting map of cooking oils, but the samples were only canola oil, chicken oil, and lard [1]. In this report, although some oils can be mapped and distinguished significantly, however some others show similar results with each other such as olive and soybean that have the same φ_c = 10°, and Corn, palm and chicken clearly have the same φ_c = 20°. Therefore to differentiate among them it should be modified using other unique values. More significant result shows that lard has greatest value φ_c = 40°. It is discriminated from other oils and it provides such as an example of a determination for lard contamination in the future. Table 2 shows the values φ_c, θ_{min},θ_0, and θ_P for all samples.

Table 2: The values φ_c, θ_{min}, θ_0, and θ_P for all samples

Sample	Code	φ_c (°)	θ_{min} (°)^b	θ_0 (°)	θ_P (°)
VCO	*	10	0.15	0.95	6.25
Olive	◊	10	0.30	1.05	6.90
Soybean	□	10	-0.90	1.80	7.35
Corn	∆	20	-0.40	2.55	6.95
Palm	×	20	-0.35	3.10	9.70
Chicken1	+1	20	-2.15	9.05	27.55
Chicken2	+2	20	-3.45	9.40	23.45
Chicken3	+3	20	-2.10	10.15	29.10
Lard1	o1	40	-2.10	15.85	18.15
Lard2	o2	40	-1.85	14.80	17.00
Lard3	o3	40	1.00	11.50	13.75
Canola	–C	30	-0.30	3.05	6.00
Chicken1	+1*	20	-1.25	9.70	26.15
Chicken2	+2*	20	-3.20	9.10	23.15
Chicken3	+3*	20	-1.65	10.10	27.05
Lard1	o1*	40	-1.80	15.60	17.95
Lard2	o2*	40	-1.60	14.20	16.00
Lard3	o3*	40	-0.80	11.60	13.55
Olive*	◊*	10	0.55	1.30	7.00
Soybean*	□*	10	-0.55	1.50	7.70
Corn*	∆*	20	-0.60	2.70	7.15
Palm*	×*	20	-0.70	3.30	10.20
Rice bran	–R	20	-0.45	2.60	7.25
Sunflower	–S	30	-0.40	3.55	6.35
Chicken4	+4	20	-2.00	4.55	12.85
Lard4	o4	40	1.00	12.8	14.15
Lard5	o5	40	-2.05	14.60	16.90

^{b}the minus "-" sign for θ_{min} indicates that the direction of polarization angle in the left at critical value φ_c

All uncertainties of values θ from measurement was obtained approximately 0.03° for all samples and it is considerably accurate. All samples are almost can be differentiated. The exception is at φ_c= 10°for VCO (θ_0 = 0.95°) vs. Olive (θ_0 = 1.05°), and at φ_c=20°for corn (θ_0 = 2.55°) vs. Rice bran (θ_0 = 2.60°), which is very small difference and will be seen overlapped each other in the map. This overlapping is considerably understandable because VCO and Olive are relatively very good oil quality. The similarity of VCO and Olive at φ_c and θ_0 is not situated at similarity of the composition, which is actually very different in composition. The composition in VCO shows medium chain of saturated fatty acid molecules that yields in to smallest homogeneous asymmetry and symmetry of triglyceride molecules from others and results to smallest θ_0. The olive oil shows usually highest monounsaturated fatty acids that yields in to highest symmetrical triglyceride molecules and results to small θ_0, as well. Meanwhile, the similarity between corn (saturated fat 25%, mono-saturated fat 38%, poly-unsaturated fat 37%) and rice bran (saturated fat 19%, mono-saturated fat 28%, poly-unsaturated fat 53%) is almost equal for three highest composition i.e. saturated, mono-unsaturated, and poly-unsaturated fatty acids that leads to the same proportional asymmetrical triglyceride molecules and results to the same relative intermediate change of polarization.

First, for mapping, we improve the previous results that only used θ_{Avg}vs. φ_c[1], and propose now to use θ_0 andθ_P instead of θ_{Avg}. From table 2 there are some significant figures that can be exploited, because the critical polarizer's angle is unique for certain cooking oils. The value θ_0 and $\theta_P$are also different among the sample. Definitely, θ_0 and $\theta_P$are relative smaller for vegetable oils (olive, soybean, corn, palm, and canola) than animal oils (chicken oil and lard). Therefore, to map each sample, we tried to choose two models of map which each consists of axis θ_0 vs. $\varphi_c$and axis θ_P vs. φ_c. Fig.3 and fig.4 show a model of map using axis θ_0 vs. $\varphi_c$and axis θ_P vs. φ_c, respectively.

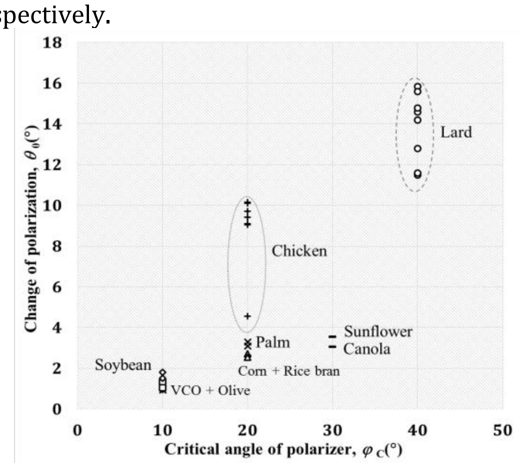


Fig. 3: Mapping sample using axisθ_0 vs. φ_c

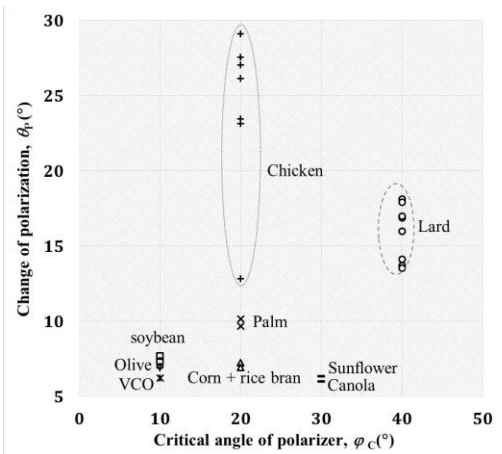


Fig. 4: Mapping sample using axisθ_P vs. φ_c

Relative to the range θ_0 from 0° to 16° (fig.3) and the range θ_P from 5° to 30° (fig.4), these values θ_0 and θ_P for pair of olive-olive*, soybean-soybean*, corn-

corn*, and palm-palm* show are not significantly difference, showing that there were no relative change of oil quality in two different time of measurement. Both of fig.3 and fig.4 are able to display several discriminant values among the cooking oils, although some different oils such as olive and soybean seem overlap each other due to the same φ_c = 10° and slightly different values of θ_0 and θ_P in the vertical axis. The critical value φ_c = 30° and the lowest value θ_P for canola and sunflower provide a most suitable place and a most unique map for this oil from others as seen in fig.4. Corn, palm, and chicken oil although have the same φ_c = 20° however can be distinguished each other due to significant different value θ_P. Particular consideration of chicken oil can be seen that it has very high value θ_0 and θ_P in comparison to vegetable oils. The most important information is provided by lard which shows very unique φ_c = 40°, θ_0 and θ_P. The highest φ_c for lard among the cooking oils has already differentiated significant characteristics. In addition, the high θ_0 and θ_P relative to the vegetable oils can be conducted to the halal examination or testing lard contamination. The lack of mapping in fig.3 and fig.4 is still the overlapping values of olive + soybean and corn + rice bran oil at the whole range θ_0 from 0° to 16° (fig.3) and the range θ_P from 5° to 30° (fig.4). To obtain the finest resolution,other modified mapping can be proposed using subtraction of value $\Delta\theta_- = \theta_P - \theta_0$ vs. φ_c and addition of value $\Delta\theta_+ = \theta_0 + \theta_P$ vs. φ_c as seen in fig.5 and fig.6.

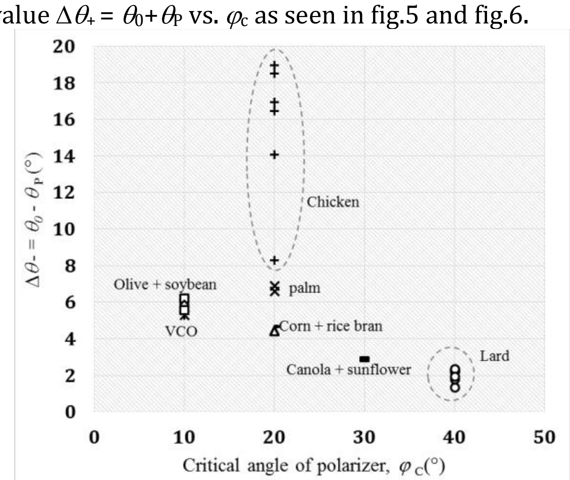


Fig. 5: Modified mapping sample using axis $\Delta\theta_-$ vs. φ_c

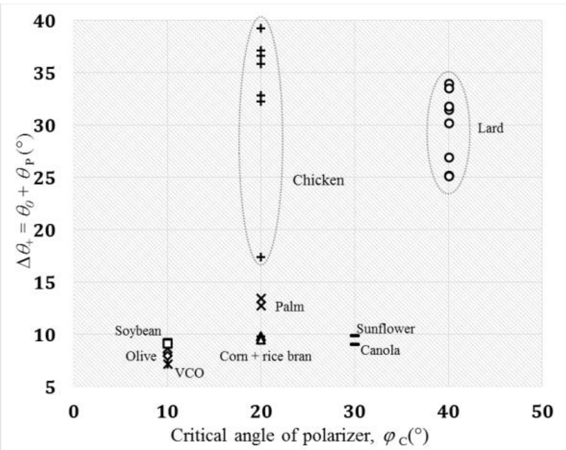


Fig. 6: Modified mapping sample using axis $\Delta\theta_+$ vs. φ_c

The modified map using subtraction of value $\Delta\theta_- = \theta_P - \theta_0$ vs. φ_c gives only smallest value $\Delta\theta_-$ of lard (fig.5) and still provides halal test of cooking oil in the next research. The lack remains by overlapping olive + soybean oil and corn + rice bran. And in other hand, the modified map using addition of value $\Delta\theta_+ = \theta_0 + \theta_P$ vs. φ_c (fig.6) just looks like mapping sample using θ_P vs. φ_c (fig.4) and still the discrimination between olive and soybean, and alsothe discrimination between corn and rice bran oil are to be increased. Therefore, for mapping various cooking oils should be restricted by range of vegetable only or by range of animal oils only. To differentiate chicken oil from lard, it is relatively simple because of the significantly different values φ_c, i.e. φ_c = 20° for chicken and φ_c = 40° for lard. It seems also that for mapping lard contamination, all models of the map in fig.3, fig.4, fig.5 and fig.6 give a good opportunity due to highest value φ_c = 40°. The model for mapping vegetable oils only seems operative if it is used narrow range of θ as shown in fig.7 using axis $\Delta\theta_+$ vs. φ_c.

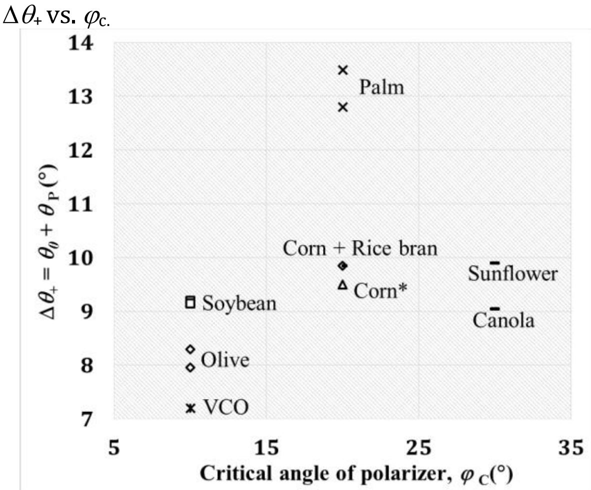


Fig. 7: Modifiedmapping sample using axis $\Delta\theta_+$ vs. φ_c for vegetable oils

The corn and rice bran could be overlapped as seen in fig.7 due to similar distribution of fatty acids. Palm oil has highest composition in saturated (>50%) and mono-unsaturated (>30%) fatty acids that could lead high value θ. Sunflower and canola have the same φ_c = 30° but their distribution of highest composition of fatty acids is different. Sunflower has two highest composition in mono- and poly-unsaturated fatty acids that can result asymmetry and symmetry of triglycerides in proportional number, while almost more 80% of mono-unsaturated fatty acids in canola could combine in to symmetrical triglycerides that results smaller θ than in sunflower. The model of map using axis $\Delta\theta_+$ vs. φ_c seems more advantage than using axis $\Delta\theta_-$ vs. φ_c since we have already known from table 2 that in average the value $\Delta\theta_+$ will group each type of cooking oil relatively more significant than the value $\Delta\theta_-$. It should be noticed that we cannot only use θ_{Avg} vs. φ_c [1], and in this method it should be modified using $\Delta\theta_+$ (or $\Delta\theta_-$) vs. φ_c for all samples and its derivation of $\Delta\theta_+$ vs. φ_c for vegetable oils.

Second, here we propose another possibility using $\theta_{\min}$ in which φ_c takes place. The value θ in the range $\theta_0 \leq \theta \leq \theta_{\min}$ is an absolute change of angle or positive angle. In the actual measurement, the change of polarization angle can be described in the left or right direction. At starting point of $\varphi = 0°$, relative to the axis of analyser, the change of polarization θ_0 always negative sign as indicated that the direction of polarization change in the leftand the value θapproaches zero at $\varphi = \varphi_c$. For $\varphi > \varphi_c$ the value $\theta$is positive and tends to maximum value at $\varphi = 90°$ for all samples. And we define then that polarization angle in left and in right direction with minus and positive sign of $\theta_{\min}$, respectively. The complement model of mapping cooking oils as shown in Fig. 8 uses axis $\theta_{\min}$ and φ_c for all samples.

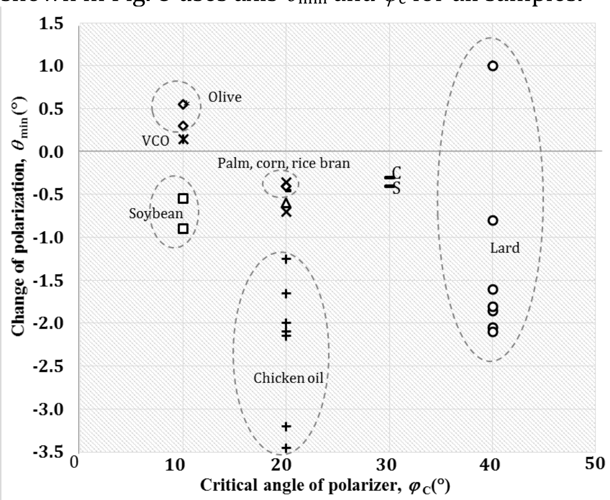


Fig. 8: Modified mapping sample using axis$\theta_{\min}$ vs. φ_c

Modified mapping using axis $\theta_{\min}$ and φ_c seems to be able to resolve olive and soybean oils significantly. The rice bran and corn look like to remain overlapped each other, and if we use restricted range -0.8 <$\theta_{\min}$< -0.2 the map becomes clear as shown in fig.9.

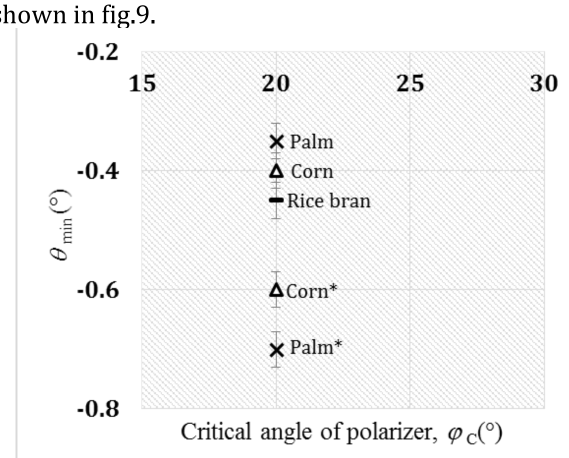


Fig. 9: Mapping using axis$\theta_{\min}$ vs. φ_c for rice bran and corn

Indeedwith narrow range -0.8 <$\theta_{\min}$< -0.2 it still shows that rice bran and corn are overlapped each other due to the value of rice $\theta_{\min}$ = -0.45°±0.03° and the value of corn $\theta_{\min}$ = -0.40°±0.03°. As we have mentioned above that this similarity is caused by the high similarity distribution of fatty acids composition. The discrepancy of value $\theta_{\min}$ between corn and corn*, and also between palm and palm*indicates that the modified combination of the model can also be used to evaluate relatively different oil quality among the cooking oils.

The overall models described before are better than the previous results [1, 2], by means we can combine the modified models such as: (1) a pair of mapping using axis θ_0 vs. φ_c and axis$\theta_{\min}$ vs. φ_c; (2) a pair of mapping using axis θ_P vs. φ_c and axis$\theta_{\min}$ vs. φ_c; (3) a pair of modified mapping using axis $\Delta\theta_-$ vs. φ_c and axis$\theta_{\min}$ vs. φ_c; or (4) a pair of modified mapping using axis $\Delta\theta_+$ vs. φ_c and axis$\theta_{\min}$ vs. φ_c.The later model in average shows much better than others. This map seems capable to group various vegetable oils or animal oils, to differentiate vegetable oils from animal oils, and to develop a testing lard contamination for halal case. The mapping cooking oils in overall can be also used to determine the degradation of cooking oil quality using modified map at very narrow range of polarization angle.

The change of fluorescence polarization angle in the measurement uses combination of pure scattering and fluorescence scattering, in which the pure scattering wavelength and fluorescence wavelength are overlapped. It is a very interesting research if we can use just pure scattering or just pure fluorescence that can be overcome by using filter of wavelength.In the transmission light, the transmission wavelength is the same with the incoming wavelengthandits direction [8], and so the change of polarization is observed in relative small angle and does not depend on the polarizer's angle.By applying electro-optics effect on sample in transmission case, it can increase the change of polarization and it has provided other interesting results [9].The physical variable of observation of fluorescence polarization that is perpendicular to the incoming light is the same with transmission polarization i.e. change of polarization angle, but provides more physical properties in fluorescence phenomena.The possibilities of combination transmission electro-optics and fluorescence electro-optics have been considering and developing. It is hopeful also to provide, at least, a complement results with other spectroscopy or GCMS methods. The mapping or grouping various cooking oils through the direct measurement of fluorescence polarization angle is simpler than other sophisticated expensive spectroscopy methods or GCMS methods with their derivation's instruments. This method provides also simply understanding of physical phenomenon especially for scattering light application in cooking oils.

5. Conclusions

The new result of critical polarizer's angle φ_c can group vegetable cooking oils as group 1 (at $\varphi_c = 10°$) for VCO, olive, and soybean, as group 2 (at $\varphi_c = 20°$) for palm, corn and rice bran, and as group 3 (at $\varphi_c = 30°$) for sunflower and canola. Due to the various different fatty acids composition, mostly vegetable cooking oils can be distinguished using a pair of combination of the best modified map in axis $\Delta\theta_+$ vs. φ_c and axis$\theta_{\min}$ vs. φ_c, The choice of axis$\theta_{\min}$ vs. φ_c provides not only physically explanation of polarization change in the left or in right direction, but also can increase the resolution using very narrow θ_{min} to differentiate between olive and soybean oil. However, it is an exception that the similarity of corn and rice bran with an overlapped value θcannot be resolved because ofidentical composition in fatty acids distribution. The mapping cooking oils in overall can be also used to determine the degradation of cooking oil quality using modified map at very narrow range of polarization angle. Generally, the various polarization angle θ and critical value φ_c can be caused by: (1) various fatty acids distribution in oil sample that can yield to a combination of small or (and)big size of triglyceride molecules and a combination of asymmetric or (and)symmetric triglyceride molecules; (2) orientation of the molecules that can effectively change of polarization of scattered fluorescence light; and (3) a complex process at transition of energy level of fluorescence polarization that the combination of pure scattering and fluorescence occurs.

The new finding of critical polarizer's angle φ_c can group also animals cooking oils as group 4 (at φ_c = 20°) for chicken oil and as group 5 (at φ_c = 40°) for lard. The chicken oil is distinguishable from vegetable oils due to very large valueθ.Lard with φ_c = 40° is automatically distinguished from chicken oil. The large difference φ_c and $\theta$of lard from vegetable oils provides an advantage to develop for testing halal oil due to lard contamination. The trace ofa test of lard contamination in minimum level detection is an important investigation to be conducted in future and developed widely for other halal food investigation. The capability of direct measurement of polarization angle for mapping various cooking oils has benefits, at least, as a complement and simple method in comparison to other expensive instruments such as IR or fluorescence spectroscopy or sophisticated GCMS methods with their derivation's instruments.

Acknowledgment
The research was supported by PTUPT and PDUPT scheme of Diponegoro University 2018.

References

1. M. Azam, I. Afiefah, R. W. Septianti, N. K. Putri, H. Sugito, and K. S. Firdausi, "Method of fluorescence polarization for a new alternative tool for investigation of cooking oil and lard," Journal of Physics: Conference Series (to be published).
2. K. S. Firdausi, N. Simbolon, and H. Sugito, "Polarisasi fluoresens untuk evaluasi mutu minyak goreng,"Jurnal Ilmiaheknosains, **3**, 34-39 (2017).
3. E.Sikorska, I.Khmelinskii, and M.Sikorski, *Analysis of Olive Oils by Fluorescence Spectroscopy: Methods and Applications*, In Tech Open 63-68 (2012).
4. Y. G. M. Kongbongan, H. Ghalila, M. B. Onana, Y. Majdi, Z. B. Lakhdar, H. Mezlini, and S. Sevetre-Ghalila, "Characterization of Vegetable Oils by Fluorescence Spectroscopy," Food and Nutrition Sciences **2**, 692-699 (2011).
5. M Saleem, Naveed Ahmad, H Ali, M Bilal, Saranjam Khan, RahatUllah, M Ahmed and S Mahmood, Investigating temperature effects on extra virgin olive oil using fluorescence spectroscopy, Laser PhysicsLetters, **27**, 125602, (2017).
6. C. T. Tan and S. Lock, "Are pork extracts present in my gummy bear? Gelatine speciation by LC-MS/MS," AB SCIEX (2014).
7. K. S. Firdausi, H.Sugito, and N. K. Putri," Simple direct observation of polarization changes of Rayleigh scattering on sugar solution at low concentration," Journal of Physics: Conference Series, **1025**, 012009 (2018).
8. K. S. Firdausi, H. Sugito, H. Rahmawati, A. B. Putranto,"The relationship between electro-optics gradient and fatty acids composition in a new investigation on palm oil quality," Advanced Science Letters,**23**, 6579-6581 (2017).
9. K. S. Firdausi, M. Azam, H. Sugito, R. W. Septianti, and I. Afiefah," Determination of relative dissociation energy from electro-optics as a new single-proposed parameter of vegetable oil quality,"Journal of Physics: Conference Series (to be published).