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Potential development of an optical sensor to determine the quality of heated palm cooking oil

Wan Shafiq Salleh[1], Nurulain Shaipuzaman[1], Muhd Sharfi Najib[1], Mohd Rashidi Salim[2], Hadi Manap[1]
[1]Faculty of Electrical and Electronic Engineering Technology, Universiti Malaysia Pahang (UMP), Pahang, Malaysia
[2]School of Electrical Engineering, Faculty of Engineering, Universiti Teknologi Malaysia (UTM), Johor, Malaysia

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ABSTRACT

Palm oil is an edible vegetable oil yielded from the mesocarp of the palm oil's fruit. It is commonly used as cooking oil as compared to other cooking oil such as olive or coconut oil because it is inexpensive and has high oxidative stability when used for frying. However, after frequent frying, the oil undergoes some physical and chemical reactions which affect the quality. This leads to the formation of compound that is dangerous to human body which is called free fatty acid (FFA). Therefore, a measurement device needs to be developed to determine the quality of heated cooking oil. In this paper, a spectroscopy study using an open-path method which focus on the palm cooking oil is proposed to examine the reaction of palm oil upon prolonged heating process. Open-path method is a technique where the incident beam will travel through the sample (palm oil) before it is detected by a spectrometer. The result shows that the FFA samples have the optimum absorbance peak at the UV wavelength 339.15 nm and each prolonged heated oil show different absorbance value. Hence, there is a potential to develop an optical sensor to determine the quality of the heated cooking oil.

Corresponding Author:

Hadi Manap
Faculty of Electrical and Electronic Engineering Technology, Universiti Malaysia Pahang (UMP)
Pekan 26600, Pahang, Malaysia
Email: hadi@ump.edu.my

1. INTRODUCTION

Palm oil is widely produced and consumed in South East Asia and Equatorial Africa. As of now, oil palm agriculture covered almost 44,900 square kilometer of land in Malaysia, which is producing 1.773×10^{10} kg of palm oil and 2.13×10^{3} kg of and palm kernel oil. As one of the main producers and exporters of palm oil in the world, Malaysia produce 11% of the world's oils & fats and export 27% of them [1]. There are two kinds of oil that can be yielded from oil palm. The first one is known as crude palm oil. Crude palm oil is produced from the flesh of the fruit (mesocarp), and the second part is palm kernel oil which is squeezed from the seed or kernel [2].

Due to palm oil characteristic that is not easily oxidized and resistance to heat at prolonged higher temperatures; it makes palm oil is the best substance in frying oil blends. In fact, palm oil has been consumed as a replacement for hydrogenated seed oils such as soybean oil, and canola oil. The quality of palm oil or crude palm oil is determined by the oil contents such as fatty acids, phospatides, odoriferious matter, water and impurities. All this content can be removed through several methods such as refining process. The fatty acids of palm oil is mainly consist of Palmitic C16, Myristic C14, Oleic C18:1, Stearic C18, and Linoleic C18:2 [3]. Details of the content percentage is also reported in [4] and can be referred in Figure 1. The quantity of free fatty acids (FFA) or known as acid value (AV) will determine the oil quality. The palm oil with high content of free fatty acid will be denoted as a poor quality and not healthy to consume [5].

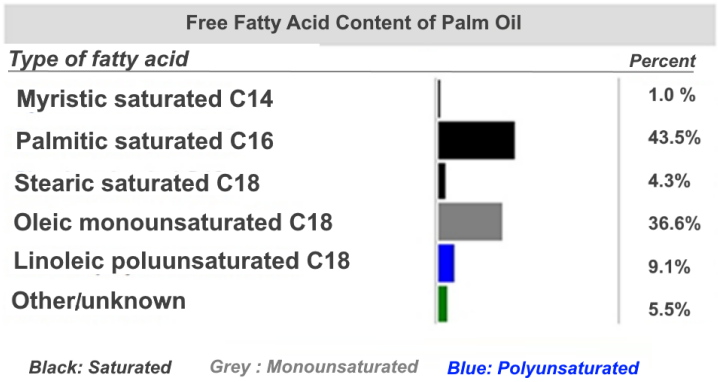

Figure 1. Fatty acid content of palm oil [4]

Malaysia Palm Oil Board (MPOB) has set a quality standards specification whereby the maximum amount of free fatty acids for crude palm oil (CPO) is 5% and should be less than 0.1% in refined bleached deodorized oil (RBDO) [6]. According to the report [7], crude palm oil will produce high level of free fatty acid because of its less ability of the oil enzymic and microbial lipase reactions. The quality of the oil also can be deteriorated if they are stored in high moisture and high temperature place [7].

Basically, free fatty acids in palm oil is produced through the hydrolysis process during the manufacturing of palm oil [8], [9]. Furthermore, it also can be produced naturally in CPO due to the action of enzyme in the palm fruits, which is produced by microbial lipases and by the reaction of oil with eater during storage [10]. There are a few methods to determine the concentration of free fatty acid reported previously. The methods to determine the free fatty acid in palm oil are the same with the method used in other edible oils. However, most of the methods applied is time consuming and requires many operation manually. In this paper, an optical open path method is used to determine the free fatty acid absorption spectrum. By having the absorption frequency, the concentration of the free fatty acid can be determined.

Supposedly, oil becomes a source of flavours and nutrition to fried food because oil/fat is absorbed during frying process. However, the oxidation of oil during frying process will degrade the quality of oil where it leads to the changes of nutrition value, taste and safety of fried food [11]. In addition, Plessis et al discussed the performance of palm oil under continuous heating and frying condition [12]. Therefore, the present study is to investigate the reaction of palm oil during the heating process by using an open-path spectroscopy method. A miniature UV-Vis spectrometer is used as a detector because it has been proved that this optical instrument and method consume less time in term of data acquisition and data processing [13].

2. RESEARCH METHOD

Palm cooking oil products from local brand was used in this experiment. This palm cooking oil was bought from local supermarket and from the same brand. The manufactured date was also checked to ensure it comes from the same batch. This is to avoid other factors to influence the result of the experiment such as different color and concentration from different brand.

2.1. Theory

In the optical spectroscopy studies, the interaction between the light with the absorbing material can be described using Beer's Lambert Law formula. A solution of chemical species absorbs the light at a different particular wavelength. The photons of the light beam encounter the number of the absorbing species. For a low concentration solution, the light beam encounters small number of the absorbing species. The absorbance is low and a large amount of light can pass through the solution. It means that the transmission percentage, %T is high. If the light beam passes through a highly concentrated solution, the number of the absorbing species is higher which means more light is absorbed by the solution. Thus, the absorbance is high and only a small amount of light can transmit. On the other hand, the transmission percentage is low. This describes that the proportional relationship between the concentration and absorbance. The transmittance is counted based on the ratio of incident light intensity, Io and transmitted light intensity, I_T which travels through the sample. The transmitted light can be measured based on the following (1). On the other hand, absorbance is inversely related to transmittance. It is defined as the logarithmic value of the ratio of incident to transmitted intensity through a sample and the formula is given (2).

$$Transmittance, T = IT / Io \quad (1)$$

$$Absorbance, A = Log10\ (Io/ IT) \quad (2)$$

2.2. Sample preparation

Six samples were prepared which each of them contains 500 ml of palm cooking oil. All the six palm oil samples were heated using usual cooking heating method. A butane gas stove is used in the heating process and the flame is set at the same level. This is a precaution step to ensure all the samples will be heated at the same rate. The first sample of palm oil was poured in a frying pan and heated for 1 hour. The frying pan is used rather than a beaker because of the imitation of real heating during cooking. This process is repeated for the rest of the samples with different duration time. The heated time for all the samples is shown in Table 1. The heating process is carried out by continuous heating. This is to ensure a uniformly heating process for all the samples. Once the oil samples are completely heated based on the time set, the oil temperature is allowed to cool down to room temperature before it is placed in a plastic container. Before the cooking oil is poured into the container, all the containers are checked to ensure that they are clean and no other particles like dust or water inside the container.

Table 1. Heated time for palm oil samples

Oil sample	Heated time (hour)
1st	1
2nd	2
3rd	3
4th	4
5th	5
6th	6

2.3. Experimental setup

There are many types of optical sensor mentioned by Eid [14] and the main configuration of the optical sensor setup consists of three parts: optical source, modulator, and the optical detector. In this experiment, UV light source, optical cables, cuvette, cuvette holder, UV-Vis spectrometer, computer and SpectraSuite software are used for the setup to acquire the absorbance spectra for the heated palm cooking oil. The pictorial diagram of the experimental setup is shown in Figure 2. Light Source equipment used in this experiment is from model DH-2000-BAL which is supplied by the leading brand, Ocean Optics. It is known that a balanced deuterium halogen source can produce a smooth and balanced spectrum over the entire wavelength range from 215 to 2,500 nm [15], [16].

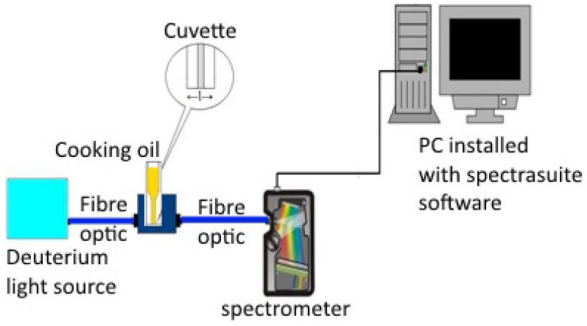

Figure 2. Experimental setup of the optical sensing system

However, deuterium light source is selected as the light source for detection of free fatty acid in the UV wavelength range. Deuterium light can cover the ultraviolet wavelength range from 200 nm to 400 nm. According to the writers from the book "Methods in food analysis", it is mentioned that absorption of fatty acids happen at various wavelengths in UV range depends on the length of conjugation and configuration of the double-bond system [17]. Therefore, this experiment will focus on this wavelength band. A miniature UV-Vis Maya spectrometer from Ocean Optic is used as a detector since it can detect the absorbance in the UV wavelength region. Figure 3 shows deuterium light source device and UV-Vis Spectrometer used in this

experiment. Since the oil samples are in liquid form, a cuvette is used to place the sample. Each oil sample was filled in different cuvette. Then the cuvette is placed at the cuvette holder one at a time. The cuvette holder is used to hold the cuvette at the same perpendicular angle while doing an experiment. Light beam intensity that propagate through the sample can varies if the angle is changed. Thus, it can reduce the accuracy of the data collection if the angle is keep changing.

Figure 3. UV-Vis Maya spectrometer (left) and Deuterium light source (right)

2.4. Procedure

Firstly, an initial intensity, Io of the light beam is captured. Empty plastic cuvette is placed inside cuvette holder and the initial intensity being measured. The cuvette is used to place the sample before the light beam is transmitted through it. The cuvette is placed in a holder as shown in Figure 4 in order it can stand still and perpendicular to the light beam. Next step is to measure the intensity of the heated oils samples. Once the heated oil is placed in the cuvette, the transmitted intensity, I_T is captured. SpectraSuite software was used in this experimental setup and it was developed by Ocean Optics Inc. SpectraSuite is a spectroscopy software program which can be used to capture and analyze spectral data from light sources with the use of a spectrometer. In this optical sensing system setup, it is used to display the absorption spectra of 6 samples of palm cooking oil in the UV wavelength region. Before the experiment is carried out, the calibration process for the spectrometer is performed in order to ensure the spectrometer can perform the correct reading. According to spectrometer's manufacturer, the value for R^2 attained during the calibration process must be close to one, or else the spectrometer might display incorrect reading [18]. The initial test is required to determine either palm cooking oil molecule absorbs the UV light at particular absorption curve. Then the spectra of each oil samples are collected and absorbance analysis on each of them are carried out. In this experiment, the intensity data are taken starting from 200.55 nm since there is no UV light absorption occurs lower than 200.55 nm due to detector limitation.

Figure 4. Cuvette holder

3. RESULTS AND DISCUSSION

According to Mustaffa *et al.* [19], each palm fruit will produce different color of oil based on its maturity. However, in this experiment, the cooking palm oil from the same batch is used for all samples. After the palm oil samples are heated, they undergo several physical reactions for example the colour changes as compared to the unheated palm cooking oil which is light yellowish colour. The longer the palm oil been

heated, the colour become darker as shown in Figure 5. There are six samples of cooking oil labelled from A to F where sample A is lighter color as compared to sample B and so on due to less heating duration. This finding is aligned with the experiment that has been carried out by Tarmizi *et al.* [20]. According to their paper, the presence of trace phenolic compounds caused the changes of oil colour. The same observation is also reported by Pantzaris [21]. In addition, the presence of unsaturated carbonyl compounds provides the ability of the sample to absorb light and contributes to absorbance magnitude [20], [22].

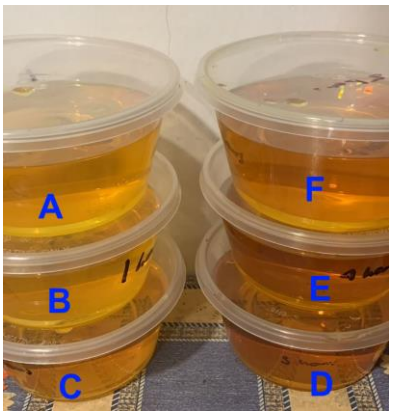

Figure 5. Color scheme of heated cooking oil at different duration

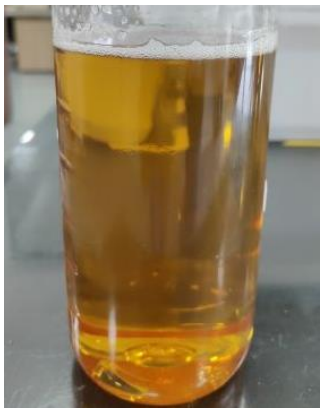

Figure 6. Foam exist at the surface after several time heating

In further observation, other effects of oil heating process are the formation of foam at the oil surface as shown in Figure 6, oil viscosity increased and the change of oil odour. This observation is aligned with the report done by Fang *et al.* [23]. According to the report [23], reheating process not only cause the physical reaction but it also can cause the chemical reaction which can change the chemical structure of triacylglycerol molecule.

In previous study done by Azeman *et al.* [24], the absorbance of palm oil was observed at 364 nm. In addition, research done by El-Rahman [25] mention that the absorption percentage for palm oil were increased by decreasing the wavelength (in the lower wavelength band). Therefore, El-Rahman concluded that to use ultraviolet (UV) light band instead of visible or near infrared region. El-Rahman have selected the wavelength region from 200 nm to 400 nm to measure absorption percentage and identify the quality of palm oil [25]. Therefore, the absorbance of the palm cooking oil in this experiement is focused in this UV wavelength region. The initial and transmitted intensity of the heated palm cooking oil at various duration is explained in previous section. The initial and transmitted intensity data were collected and inserted in the (2) before an absorbance graph is plotted as shown in Figure 7.

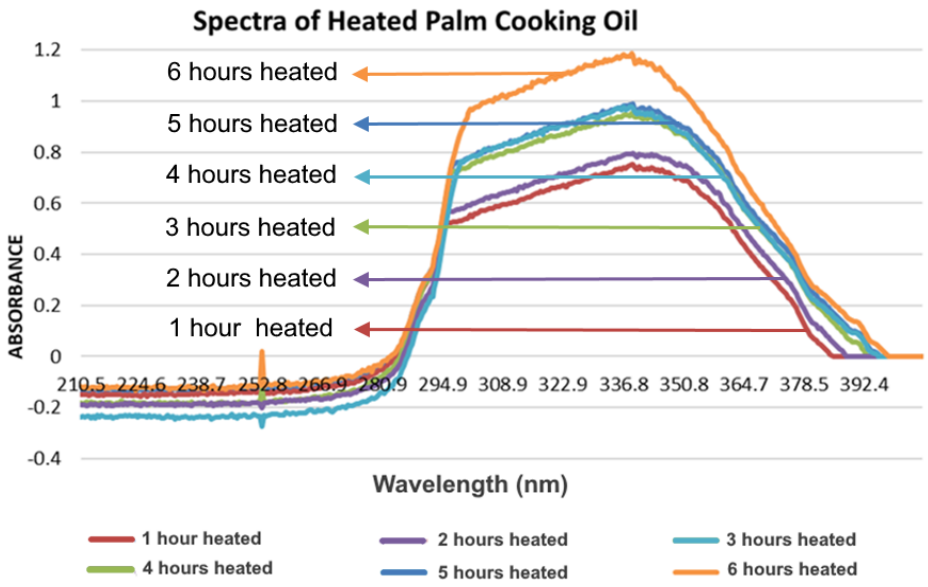

Figure 7. Palm cooking oil absorbance peak at 339.15 nm

As it can been seen from the Figure 7, the absorbance take place from approximately 294 nm to 392 nm. However, the highest peak happens at 339.15 nm for all samples. This indicates that the absorbance curve of palm oil compound absorbs most UV light at 339.15 nm. High absorbance value indicated high sample concentration; thus, it shows that the free fatty acid value is also high. This is aligned with the experiment carried out by Azeman *et al*. [24]. According to Beer's Lambert Law, the absorbance is directly proportional to the concentration. Thus, as carbonyl double bonds, C = O stretch increased, the absorbance also increased indicating higher free fatty acid content in the oil sample [26].

Based on Figure 7, it shows that the absorbance values for palm cooking oil that being heated from 1 hour up to 6 hours are different. When the oil heated continuously, the oil colour becomes darker and viscosity increased. The concentration of free fatty acid value also increased when the oil continuously heated [20], [25], [27]. Thus, more UV light is absorbed when the sample heated at longer hours. By increased the heating time of the palm oil, it's not only increased the oxidize fatty acid but also increased the viscosity, reflective index, peroxide value (PV), polymer and acid value (AV). Meanwhile, the iodine value (IV) decreased when heating the palm oil [25].

During the heating operation, oxidation and thermal reaction will occur whereby it can develop polymer compounds in the oil. Furthermore, molecular weight compounds (carbon-to-carbon and/or oxygen-to-carbon bridges) between fatty acids become higher due to this polymerisation [20], [23]. In addition, Karimah [28] did mention in her research paper that the excess polymer compounds can produce a bitter taste to the fried foods and also generate foam.

4. CONCLUSION

In this paper, the objective to determine the amount of free fatty acid on repeatedly heated palm cooking oil by using a spectroscopy open path method was achieved. From the absorbance curve line graph, it shows that all the free fatty acid samples have the absorbance peak at the same wavelength which is 339.15 nm. The result also shows that the light absorbance is high when the sample was heated at longer hours. This indicates that the concentration of free fatty acid is high; thus, the quality of the palm cooking oil is degraded. It is recommended to avoid long hours or repeated heated cooking oil to reduce the consumption of free fatty acid which is dangerous to human health. In addition, the heating operation also causes the physical reaction in palm oil such as the viscosity, odour and colour which could result the cooking taste.

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BIOGRAPHIES OF AUTHORS

Wan Shafiq Salleh was born in Tanah Merah, Kelantan in 1998. He finished his degree in Bachelor of Science in Physics in UPM in 2021. During his degree, he has participated in a research competition and won a silver medal. He also participated in Expository Quantum Lecture Series in 2020. Currently, he is a Master degree student. His research topic is based on the optical fiber and the development of optical fiber sensors in College of Engineering UMP. He can be contacted at email: wanshafiqsalleh@gmail.com.

Nurulain Shaipuzaman was born in Kota Bharu, Kelantan in 1993. She finished her first degree in Electrical and Electronics Engineering Technology at UMP in 2016. She was sponsored by UMP and received Masters Research Scheme (MRS) to continue her Masters degree in optical sensing and graduated in 2018. Currently, she is a Ph.D. candidate at Faculty of Electrical & Electronics Engineering Technology, UMP and received a scholarship (Drs). Her research topic is about the design and development of an optical sensor to measure the visibility of air in open space. During her Masters and Ph.D. studies, she has published more than 10 journal articles and conference proceedings. She also has participated in a few research competitions and won silver and bronze medals. She can be contacted at email: ainnadhirah93@gmail.com.

Muhd Sharfi Najib is currently as an Associate Professor at Universiti Malaysia Pahang (UMP), Malaysia with more than 12 years experience as an academic lecturer at Faculty of Electrical & Electronics Engineering Technology, UMP. He completed his Ph.D. journey in Engineering from Universiti Teknologi MARA, Malaysia. He is able to work in a strategic management specifically in academic financing management role and having capability in handling academic and research assets, facilities, as well as materials. He did hold various important post and resposibilities in the faculty management and academician works including as a Head of Technical in FTKEE, Head of Research Group, fellow of Bioaromatic Centre of Excellence, project leader for the research grants (exploratory research, commercialised research) and member for several engineering education research. His research expertise are in Instruments, Smart Sensors (E-nose), Artficial Intelligence, Case-based Reasoning applied in several applications such as environment, food quality, waste-management, biotechnology and automotive. He can be contacted at email: sharfi@ump.edu.my.

Mohd Rashidi Salim was born in Johor Bahru, Johor. Currently, he is a Senior Lecturer at School of Electrical Engineering and researcher in the field of optical sensors in the Lightwave Communication Research Group (LCRG), School of Electrical Engineering, Faculty of Engineering, Universiti Teknologi Malaysia (UTM). He obtained his Bachelor of Engineering (Electrical-Mechatronics) and was appointed as a tutor in December 2008. He started his Master study in July 2009 and was awarded Masters of Engineering (Electrical-Electronics and Telecommunication) from UTM in June 2011. Subsequently, he pursued his Ph.D. in Electrical Engineering at UTM from September 2011 until September 2015. He was awarded his Ph.D. degree in April 2016 at UTM. He is a member of the Institution of Engineers Malaysia (IEM) and the Institute of Electrical and Electronics Engineers (IEEE). His research interests are in spectroscopic sensors, optical fibre sensors and electromagnetics. He can be contacted at email: mrshidi@utm.my.

Hadi Manap was appointed as an academic staff in UMP since July 2002. He received his Ph.D. from University of Limerick, Ireland in 2011 and currently attached to Faculty of Electrical & Electronic Engineering Technology, UMP. His primary research area is about optical sensor development for various industries such as automotive, medical instruments and environmental monitoring. As a researcher in optical sensing, Hadi Manap studies on the absorption cross section of many gases in a few wavelength regions. Throughout his research, Hadi Manap has won many research competition awards by local and international body. He won a silver medal in Malaysian Technology Expo, MTE 2013, PWTC, Malaysia. He also won Double Gold award by Invention New Product Exposition, INPEX, Pittsburgh, USA in 2013. A Bronze medal was also awarded by Int. Engineering invention & Innovation Exhibition (i-ENVEX) in 2015. He can be contacted at email: hadi@ump.edu.my.