ISSN: …………..
ISSN: …………..

Contents List available at Zibeline International Publishing
I Tech Mag
Journal Homepage:
https://doi.org/....

ANALYSIS OF PORK ADULTERATION IN RECYCLED FRYING OILS USING RAMAN SPECTROSCOPY

HAIZATUL HADIRAH GHAZALI[1], NUR AZIRA TUKIRAN[2]*

[1]Department of Biotechnology, Kulliyyah of Science, International Islamic University Malaysia (IIUM), Jalan Sultan Ahmad Shah, Bandar Indera Mahkota, 25200 Kuantan, Pahang, Malaysia
[2]International Institute for Halal Research and Training (INHART), Level 3, KICT Building, International Islamic University Malaysia (IIUM), 53100 Jalan Gombak, Selangor, Malaysia

*Corresponding author email: aziratukiran@iium.edu.my

ARTICLE DETAILS

Article history:

Received .. September 20…
Accepted ….. December 20….
Available online January 20…

Keywords:

Frying oil, Palm oil, Raman spectroscopy, Principal Component Analysis (PCA), Pork adulteration, Spiked sample

ABSTRACT:

Unscrupulous food business operators may use recycled frying oil to save costs. Of particular concern is the recycled frying oil is usually taken from non-halal food premises which should not be used by halal food premises, and indeed may posing health treats to consumers. Hence, the objective of this paper is to analyse pork adulteration in recycled frying oils by using the combination of Raman spectroscopy and Principal Component Analysis (PCA). Samples of frying oils from homemade fried pork, fried chicken, fried fish and fried banana were analysed. Spiked samples were prepared by adding frying oil from homemade fried pork ranging from 10% to 50% (v/v) to frying oils from homemade fried chicken, fried fish and fried banana. The results found that Raman spectroscopy and PCA are able to differentiate adulterated frying oil and unadulterated frying oils. However, it could not distinguish the percentage of pork adulteration in the spiked samples. This method would beneficial to ensure food integrity in the frying oils.

1. INTRODUCTION

Palm oil is the most common vegetable oil used for cooking worldwide [1]. It has been used as a frying medium since it has a high smoke point of 230°C. However, it has a limit of useful life of 12 days continuous frying [2]. According to Park and Kim [3], the fats and oils in recycled frying oils would undergo thermal and oxidative decomposition which will increase viscosity of the oils, darken the colour, increase the foaming and decrease the smoking point. In addition, Mba et al. [2] reported that degradation of frying oils may affects the texture, taste and overall flavour perception of the food. Nevertheless, some unscrupulous food business operators used this recycled frying oil to save costs. The practice is considerable concern as recycled frying oil taken from non-halal food premises should not be used by halal food premises, and indeed may posing health treats to consumers [4-9]. Thus, there is an urgent need for reliable approach to identify the authenticity of recycled frying oils.

Current approaches for authenticity of recycled cooking oil include matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) [10], synchronous front-face fluorescence spectroscopy [11] and gas chromatography-mass spectrometry [12]. These approaches are efficient and have high sensitivity, yet they are also complex, relatively expensive, laborious, demand high skill personnel and require sophisticated instrument capability. Recently, the Raman spectroscopy has gained considerable interest as it is non-destructive, cheap and simple in nature. However, data about the assessment of recycled frying oil by using this method is limited [13-16]. Hence, the objective of this paper is to analyse pork adulteration in recycled frying oils by using the combination of Raman spectroscopy and Principal Component

Cite this article as: … ..(..)(2019), …..-.. I Tech Mag, (..) : …-

Analysis (PCA). Samples of frying oils from homemade fried pork, fried chicken, fried fish and fried banana were analysed. Spiked samples were prepared by adding frying oil from homemade fried pork ranging from 10% to 50% (v/v) to frying oils from homemade fried chicken, fried fish and fried banana.

2. MATERIAL AND METHODS

2.1. Materials

Palm frying oil (Delima Oil Products Sdn. Bhd.), pork and banana were purchased from local retail shop in Batu Caves, Selangor, Malaysia. While, chicken breasts and dory fish were purchased from local wet market in Gombak, Selangor, Malaysia. Electric stove with temperature indicator was used to fry the pork, chicken breast, dory fish and banana.

2.2. Sample preparation

Pork, chicken breast, dory fish and banana were cut into small pieces with the length of 1 cm x 1 cm dimension. 600 ml of palm frying oil was heated at 180 °C for 5 min. Subsequently, 100 g of pork, chicken breast, dory fish and banana were deep-fried separately in different heated palm frying oils at 180 °C for another 5 min. The used frying oils were filtered before transferring them into 4 clean containers and labelled as fried-pork oil (P), fried-chicken oil (C), fried-fish oil (F) and fried-banana oil (B). Two samples of non-heated palm oil (O) and heated palm oil (OH) at 180 °C for 10 minutes were also prepared as control samples. A set of experimental samples of P and OH was then prepared in five test tubes by adding different concentrations consisting of 10% (v/v), 20% (v/v), 30% (v/v), 50% (v/v) and 70% (v/v) of P in the OH samples. Another three sets of samples were prepared with the same proportions of P into each five test tubes of C, F and B samples respectively. A total of 31 samples mentioned above were then subjected to Raman spectroscopy analysis.

2.3. Raman spectroscopy

Renishaw InVia confocal Raman microscope was used for measurements. All measurements were collected with 10 s exposure time and 1 accumulation by using 50x magnification. The samples were scanned in extended range of 800 to 1800 cm^{-1} with 1 cm^{-1} spectral resolution for triplicates reading [17]. WiRE 4.0 software (Renishaw, UK) was used to focus the spot. The Raman spectra for each sample were recorded and analysed.

2.4. Principal Component Analysis (PCA)

PCA was used to analyse the collected data from each sample. The software used was The Unscrambler 9.7 (Camo, USA). All data from Raman spectra of the samples was selected by calculating the mean of the triplicate readings for each sample. There were 12 variables of the wave numbers chosen from Raman spectra to run the PCA; consisting of 845 cm^{-1}, 870 cm^{-1}, 890 cm^{-1}, 1065 cm^{-1}, 1083 cm^{-1}, 1122 cm^{-1}, 1303 cm^{-1}, 1440 cm^{-1} and 1745 cm^{-1}. The statistical analysis of the samples from the Raman spectra data were then collected and discussed by referring the score and loading plots of PCA.

3. RESULTS AND DISCUSSION

Raman spectra of all frying oil samples exhibited almost similar pattern, yet with different intensities at particular regions of wavenumbers (Figure 1). Three major peaks could be seen from the spectra such as 1303 cm^{-1}, 1440 cm^{-1} and 1656 cm^{-1}. The other nine minor peaks such as 845 cm^{-1}, 870 cm^{-1}, 890 cm^{-1}, 970 cm^{-1}, 1065 cm^{-1}, 1083 cm^{-1}, 1122 cm^{-1}, 1270 cm^{-1} and 1745 cm^{-1} could also observe through the Raman spectra. Velioglu et al. [18] had found seven significant Raman bands in palm oil and other vegetable oils such as soybean, sunflower, corn, mustard, canola and olive which consist of 869 cm^{-1}, 971 cm^{-1}, 1085 cm^{-1}, 1265 cm^{-1}, 1303 cm^{-1}, 1441 cm^{-1} and 1656 cm^{-1}. This shows that the resulted peaks of palm frying oil in this study might indicate the significant Raman spectra characteristics of vegetable oils. Similar pattern of Raman spectrum of palm oil which exhibited the similar significant peaks were also reported in other studies [17, 19-20]. There were also studies which reported some similar patterns of the Raman spectra of animal fats or oils such as desi ghee, pork lard, beef tallow, duck oil and chicken fat [21-22]. However, those Raman spectra had posed some differences in certain regions which might distinguish between vegetable oils and animal fats or oils although they posed some similar characteristic of Raman spectrum for edible oils.

Regions in Raman shifts or wavenumbers would have specific assignments that are related to the vibrational properties of chemical bonds in the samples. Raman shifts at 845 cm^{-1}, 870 cm^{-1} and 890 cm^{-1} is assigned to saturated fatty acids which correspond to C1-C2 stretching, CH3 rocking and C-O stretching [21, 23]. The region between ~1060 cm^{-1} to ~1180 cm^{-1} from the table reported by Czamara et al. [24] is assigned for C-C stretching which covers the peaks of 1065 cm^{-1}, 1083 cm^{-1} and 1122 cm^{-1}. Raman shifts assignment for 1270 cm^{-1} is =C deformation in unconjugated cis C=C [25]. At Raman peak of 1303 cm^{-1}, it was reported that the peak is assigned for the vibration of saturated CH2 in-plane twist [17]. The region from 1640 cm^{-1} to 1680 cm^{-1} reported to be the C=C stretching region to detect cis or trans isomers [26]. In addition to this region, the peak at 1656 cm^{-1} was also assigned to C=C stretching of unsaturated fatty acids and triglycerides [27]. The peaks at 970 cm^{-1} and 1440 cm^{-1} were assigned to the bending of C=C for trans RHC=CHR and the stretching of C-H for -CH2, respectively [28]. The last peak at 1745 cm^{-1} was attributed to the ester bond of carbonyl group (C=O) stretching [16].

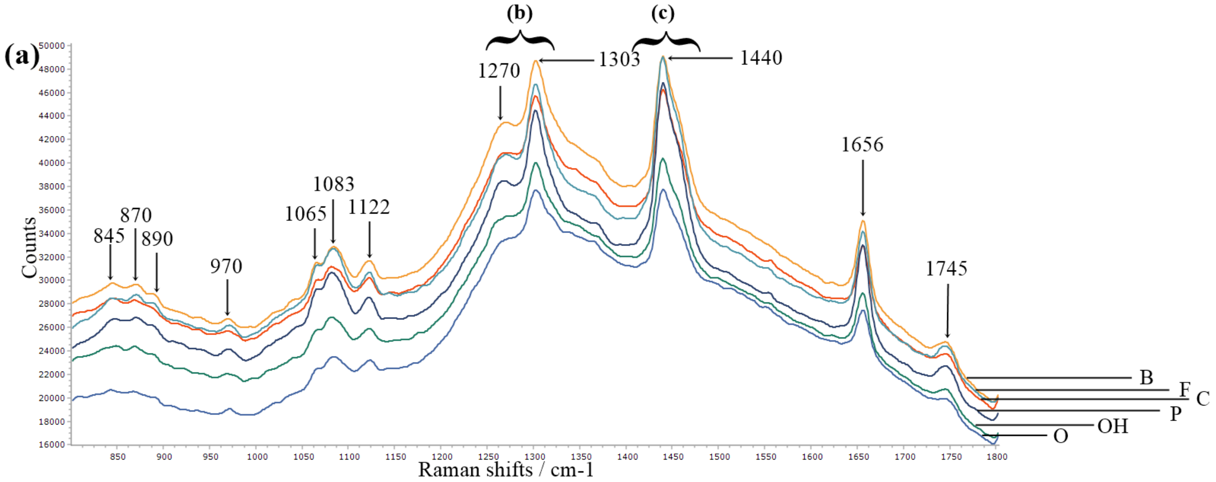

Figure 1. Raman spectra of recycled palm cooking oils. Arrows represent the labels of Raman peaks. O: non-heated palm cooking oil; OH: heated palm cooking oil; P: fried-pork oil; C: fried-chicken oil; F: fried-dory fish oil; B: fried-banana oil.

The spectral data of the samples were then analysed by using PCA. The PCA converts the set of data into a new set of PCs [29]. It also assesses the patterns in the data set and identifies the hidden similarities and differences [17]. Figure 2 shows the PCA of recycled frying oils. The graphs are comprised of two PCs such as PC1 and PC2.

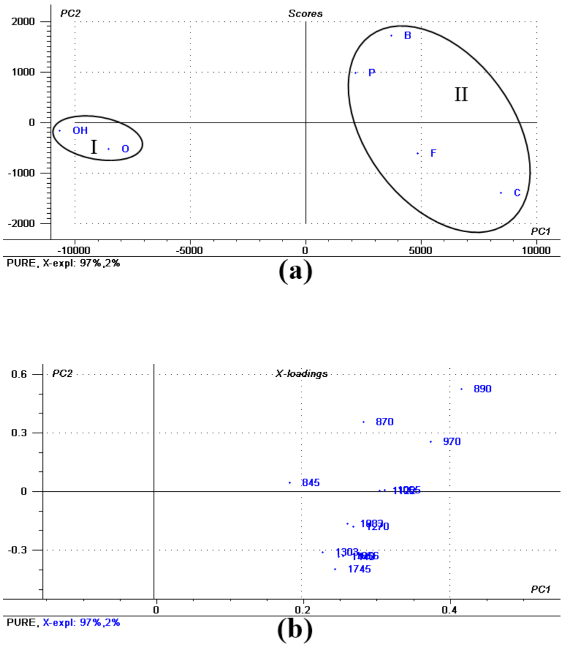

Figure 2. PCA of recycled frying oils. (a) Score plot and (b)loading plots

There are two groupings that can be classified by using PCA where, group I consists of non-adulterated palm frying oils (O and OH) while group II consists of adulterated palm frying oils (P, C, F and B). However, it could not distinguish the percentage of pork adulteration in the spiked samples.

4. CONCLUSIONS

Raman spectroscopy with combination of PCA was used to assess pork adulteration in recycled frying oils. The results found that Raman spectroscopy and PCA able to differentiate adulterated frying oil and unadulterated frying oils. However, it could not distinguish the percentage of pork adulteration in the spiked samples.

ACKNOWLEDGEMENTS

This work was supported by the IIUM Research Initiative Grant Scheme [RIGS16-068-0232] from the International Islamic University Malaysia (IIUM), Selangor, Malaysia.

REFERENCES

[1] Shahbandeh, M. 2019. Production volume of palm oil worldwide from 2012/13 to 2018/19 (in million metric tons), retrieved on 15 July 2019 at https:// www.statista.com/ statistics/613471/palm- oil-production- volume worldwide/

[2] Mba, O. I., Dumont, M. J., Ngadi, M. 2015. Palm oil: Processing, characterization and utilization in the food industry – A review. Food Bioscience, 10, 26–41.

[3] Park, J. M., & Kim, J. M. 2016. Monitoring of used frying oils and frying times for frying chicken nuggets using peroxide value and acid value. Korean Journal for Food Science of Animal Resources, 36, 612–616.

[4] Jaarin, K., Masbah, N., & Kamisah, Y. 2018. Heated oil and its effect on health. In Food quality: balancing health and disease (pp. 315–337). Handbook of Food Bioengineering.

[5] Tan, P. Y., Teng, K. T. 2019. Effects of oxidised oils on inflammation-related cancer risk. Journal of Oil Palm Research, 31, 1–13.

[6] Karimi, S., Wawire, M., Mathooko, F. M. 2017. Impact of frying practices and frying conditions on the quality and safety of frying oils used by street vendors and restaurants in Nairobi, Kenya. Journal of Food Composition and Analysis, 62, 239–244.

[7] Ganesan, K., Sukalingam, K., & Xu, B. 2017. Impact of consumption of repeatedly heated cooking oils on the incidence of various cancers- A critical review. Critical Reviews in Food Science and Nutrition, 59, 488–505.

[8] Vijaindren, A. 2016. Sunday Spotlight: Worry over consuming unhealthy, reused oil. New Straits Times, retrieved on 15 July 2019 at https:// www.nst.com .my/news/2016 /11/188244/ sunday- spotlight- worry-over -consuming-unhealthy-reused-oil

[9] Riggs, M. 2013. China's Frightening, Unpleasant Cooking-Oil Scandal. The Atlantic, retrieved on 15 July 2019 at https://www. theatlantic. com/china /archive/2013/10 /chinas- frightening-unpleasant-cooking-oi l-scandal/281000/

[10] Ng, T.T., So, P. K., Zheng, B., Yao, Z. P., 2015. Rapid screening of mixed edible oils and gutter oils by matrix-assisted laser desorption/ionization mass spectrometry. Analytica Chimica Acta, 884, 70-76.

[11] Tan, J., Li, R., Jiang, Z. T., Tang, S. H., Wang, Y., Shi, M., Xiao, Y. Q., Jia, B., Lu, T. X., Wang, H. 2017. Synchronous front-face fluorescence spectroscopy for authentication of the adulteration of edible vegetable oil with refined used frying oil. Food Chemistry, 274-280.

[12] Cao, G., Ding, C., Ruan, D., Chen, Z., Wu, H., Hong, Y., Cai, Z. 2019. Gas chromatography-mass spectrometry based profiling reveals six monoglycerides as markers of used cooking oil. Food Control, 96, 494 – 498.

[13] Hu, R., He, T., Zhang, Z., Yang, Y., Liu, M. 2019. Safety analysis of edible oil products via Raman spectroscopy. Talanta, 191, 324–332.

[14] Li, Y., Fang, T., Zhu, S., Huang, F., Chen, Z., Wang, Y. 2018. Detection of olive oil adulteration with waste cooking oil via Raman spectroscopy combined with iPLS and SiPLS. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 189, 37–43.

[15] Chen, Y., Luo, Q., Wang, J., Zheng, X. 2018. Rapid identification and characterization of recovered edible oil, based on raman and near-infrared spectroscopy. In 3rd International Conference on Modelling, Simulation and Applied Mathematics (MSAM 2018) (Vol. 160, pp. 321–324). Atlantic Press.

[16] Huang, F., Li, Y., Guo, H., Xu, J., Chen, Z., Zhang, J., Wang, Y. 2016. Identification of waste cooking oil and vegetable oil via Raman spectroscopy. Journal of Raman Spectroscopy, 47, 860–864.

[17] Vašková, H., Buckova, M. 2018. Multivariate study of raman spectral data of edible oils. WSEAS Transactions on Environment and Development, 14, 226–232.

[18] Velioglu, S. D., Ercioglu, E., Temiz, H. T., Velioglu, H. M., Topcu, A., Boyaci, I. H. 2016. Raman spectroscopic barcode use for differentiation of vegetable oils and determination of their major fatty acid composition. Journal of the American Oil Chemists Society, 93, 627–635.

[19] Ibrahim, N., Aziz, S. A., Hashim, N. 2017. Oil quality monitoring during deep fat frying using Raman spectroscopy. Acta Horticulturae, 1152, 307–312.

[20] Souza, G. K., Diório, A., Johann, G., Gomes, M. C. S., Pomini, A. M., Arroyo, P. A., Pereira, N. C. 2019. Assessment of the physicochemical properties and oxidative stability of kernel fruit oil from the acrocomia totai palm tree. Journal of the American Oil Chemists Society, 96, 51–61.

[21] Ali, H., Nawaz, H., Saleem, M., Nurjis, F., Ahmed, M. 2016. Qualitative analysis of desi ghee, edible oils, and spreads using Raman spectroscopy. Journal of Raman Spectroscopy, 47, 706–711.

[22] Lee, J. Y., Park, J. H., Mun, H., Shim, W. B., Lim, S.-H., Kim, M.-G. 2018. Quantitative analysis of lard in animal fat mixture using visible Raman spectroscopy. Food Chemistry, 254, 109–114.

[23] Ahmad, N., Saleem, M. 2019. Raman spectroscopy based characterization of desi ghee obtained from buffalo and cow milk. International Dairy Journal, 89, 119–128.

[24] Czamara, K., Majzner, K., Pacia, M. Z., Kochan, K., Kaczor, A., Baranska, M. 2015. Raman spectroscopy of lipids: a review. Journal of Raman Spectroscopy, 46, 4–20.

[25] Kwofie, F., Lavine, B. K., Ottaway, J., Booksh, K. 2019. Incorporating brand variability into classification of edible oils by Raman spectroscopy. Journal of Chemometrics, 1-14.

[26] Gong, W., Shi, R., Chen, M., Qin, J., Liu, X. 2019. Quantification and monitoring the heat-induced formation of trans fatty acids in edible oils by Raman Spectroscopy. Journal of Food Measurement and Characterization, 13, 2203–2210.

[27] Nokkaew, R., Punsuvon, V., Inagaki, T., Tsuchikawa, S. 2019. Determination of carotenoids and dobi content in crude palm oil by spectroscopy techniques: comparison of raman and FT-NIR spectroscopy. International Journal of GEOMATE, 55, 92 - 98.

[28] De Géa Neves, M., Poppi, R. J. 2017. Monitoring of adulteration and purity in coconut oil using raman spectroscopy and multivariate curve resolution. Food Analytical Methods, 11, 1897–1905.

[29] Karacaglar, N. N. Y., Bulat, T., Boyaci, I. H., Topcu, A. 2019. Raman spectroscopy coupled with chemometric methods for the discrimination of foreign fats and oils in cream and yogurt. Journal of Food and Drug Analysis, 27, 101–110.