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Journal of Advanced Research in Fluid Mechanics and Thermal Sciences

Journal homepage: www.akademiabaru.com/arfmts.html
ISSN: 2289-7879

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ARTICLE INFO

Article history:
Received 5 September 2019
Received in revised form 22 October 2019
Accepted 23 October 2019
Available online 26 February 2020

Keywords:
Waste cooking oil; neutralization; acidity; insulating liquid; transformer

ABSTRACT

When an oil-immersed transformer fails because of a short circuit, fire can occur because of the relatively low flash point of the mineral insulating oil. One of the ways to overcome this problem is to replace mineral insulating oil with vegetable-based insulating oils of higher flash points. This study explores the potential of waste cooking oil as a transformer dielectric liquid. The waste cooking oil used in this study is a vegetable-based oil with a high flash point. However, its acidity is above the permissible limit, which hinders its use in transformers. Therefore, the waste cooking oil was neutralized with caustic soda (normality: 1.0, 2.0, 3.0, 4.0, and 5.0 N) at a temperature of 70°C and stirring speed of 400 rpm for 5 min. The physical, chemical, and electrical properties of the neutralized waste cooking oil samples were determined. The results showed that the waste cooking oil neutralized with caustic soda (normality: 2.0 N) had the lowest acidity (0.2825 mg KOH/g). The breakdown voltage and viscosity of this oil sample were 29 kV and 40.92 mm^2/s, respectively, which fulfilled the specifications of the IEEE C57.147 standard. In addition, this oil sample had a flash point of 260°C, which fulfilled the requirement of the IEC 62770 standard. Based on these results, it can be concluded that the neutralized waste cooking oil sample (normality: 2.0 N) has potential as a transformer dielectric liquid.

1. Introduction

In the early days of transformer insulating oil development, two types of oil were considered, namely: (1) petroleum-based mineral insulating (MI) oil and (2) vegetable-based natural ester insulating (NEI) oil. MI oils were the de facto standard at the time owing to the poor oxidation stability and unfavourable properties of NEI oils [1–3]. In addition, NEI oils were costly and incompatible for use in free-breathing transformers. By contrast, MI oils have higher oxidation stability and these oils are relatively inexpensive compared with NEI oils. MI oils are relatively inexpensive because they can be mass-produced owing to the availability of petroleum reserves worldwide, resulting in a boost of

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petroleum production. However, MI oils also have their own disadvantages. First, MI oils have relatively low flash points, which can lead to combustion when the oil-immersed transformer fails because of short circuits. In addition, MI oils are non-biodegradable, which can cause soil pollution in the event of spillage [1,3,4]. The International Energy Agency had forecasted a shortfall in conventional oil supply by 2010 [5]. In particular, the offshore conventional oil production in Malaysia reached its peak in 2004 and it is expected that the oil production will decline in the future at a rate of 4% annually [5]. This indicates that the 'Conventional Oil Era' days are numbered, which is estimated to be around 2050, according to Hubert's curve [6].

Owing to concerns of the following issues (fire hazards associated with the low flash points of MI oils, detrimental impact of MI oils on the environment, and gradual depletion of fossil fuel reserves over the years), much effort has been made to explore, develop, and improve NEI oils in order to replace MI oils. NEI oils are composed of triglycerides, where each triglyceride molecule consists of three fatty acids attached to the glycerol backbone. There are two types of fatty acids, namely: (i) saturated fatty acids (SFAs) and (ii) unsaturated fatty acids (UFAs). SFAs contain carbon chains without double bonds whereas UFAs contain carbon chains with one, two, or three double bonds. UFAs can be classified as mono-unsaturated (MUFAs), di-unsaturated, and tri-unsaturated fatty acids, depending on the number of double bonds. The latter two are also known as poly-unsaturated fatty acids (PUFAs). Table 1 shows the fatty acid compositions of various vegetable oils. It can be seen that the carbon chains vary from one oil to another, where the sunflower, coconut, and palm oils have 16–24, 8–18, and 12–20 carbon chains, respectively. This indicates that the carbon chains are dependent on the part of the plant from which the oil is extracted. In this case, the sunflower, coconut, and palm oils are extracted from the seeds, kernels, and husks of the respective plants.

Table 1
Fatty acid compositions of various vegetable oils

Fatty acid	Structure	Sunflower oil [7] (wt%)	Coconut oil [8] (wt%)	Palm oil [9] (wt%)
Caprylic	C8:0	—	6.21	—
Capric	C10:0	—	6.15	—
Lauric	C12:0	—	51.02	0.2
Myristic	C14:0	—	18.94	1.1
Palmitic	C16:0	5.7	8.62	44.0
Stearic	C18:0	4.0	1.94	4.5
Oleic	C18:1	35.2	5.84	39.2
Linoleic	C18:2	53.5	1.28	10.1
Linolenic	C18:3	0.1	—	0.4
Arachidic	C20:0	0.3	—	0.1
Eicosenoic	C20:1	0.2	—	—
Eicosadienoic	C20:2	0.1	—	—
Behenic	C22:0	0.7	—	—
Docosadienoic	C22:2	0.1	—	—
Lignoceric	C24:0	0.2	—	—
Total SFAs		10.9	92.88	49.9
Total MUFAs		35.4	5.84	39.2
Total PUFAs		53.8	1.28	10.5

The source of triglycerides for NEI oils is crude vegetable oil. The crude vegetable oil is extracted from the seeds, kernels, husks, or fruits of the plants, which can be edible or non-edible. The oil is extracted through different methods such as mechanical press, cold press, and hot extraction methods. The extracted crude vegetable oil is then refined, where the process involves degumming, neutralization, and bleaching [10]. Degumming is performed to reduce phospholipids. Neutralization is carried out to reduce the amount of free fatty acids in the oil because the high content of free fatty acids will accelerate the hydrolysis process, an aging mechanism of vegetable oil [11]. In addition, acids play a role in the deterioration of cellulosic materials as well as responsible for the corrosion of metal parts of a transformer [12]. Figure 1 shows neutralization reaction. The free fatty acids (RCOOH) of the crude vegetable oil react with caustic soda (NaOH), producing soap or sodium carboxylate (RCOONa) and water (H_2O). The neutralized oil is then bleached to decolorize the oil. Following this, the refined oil is deodorized to remove odour or directly reconditioned to ensure that the oil is suitable for transformer applications.

$$\underset{\text{free fatty acids}}{RCOOH} + NaOH \longrightarrow \underset{\text{sodium carboxylate}}{RCOONa} + H_20$$

Fig. 1. Neutralization reaction of the free fatty acids in the crude vegetable oil [13]

To date, vegetable oils have been studied for various applications [14–16]. Yet, there is a lack of studies concerning the use of waste cooking oil (WCO) as a transformer dielectric liquid z [17,18]. Interestingly, many studies have been carried out on the potential of WCO as biodiesels [19–21] and biolubricants [22–24]. Hence, this study is carried out to explore the potential of WCO neutralized with caustic soda as a transformer dielectric liquid.

2. Waste Cooking Oil

WCO is available in abundance owing to the increase in cooking oil production for food preparation and consumption. It is estimated that European countries generates up to 10 million tonnes of WCO annually [25]. Unlike petroleum-derived oils (which are expected to decrease owing to the increase in energy demands and gradual decrease in petroleum reserves), it can be expected that WCO will increase in parallel with human population growth. Hence, waste management becomes a major problem because significant amounts of WCO are discarded into drains, which will clog sewage systems and pollute water. Hence, recycling WCO is desirable in order to reduce sewage maintenance costs [26] and water pollution [27], as well as open up a new and profitable market by the development of useful products.

3. Methodology

3.1 Neutralization

Figure 2 shows the methodology adopted in this study. Prior to the neutralization process, 1 L of filtered WCO was heated at 110°C for 10 min to reduce its water content and then the WCO was cooled down to 70°C. Next, the WCO was neutralized with caustic soda (normality: 1.0, 2.0, 3.0, 4.0, and 5.0 N). Each sample was prepared by mixing caustic soda (each with a different normality) with WCO in a 2-L beaker. The samples were mixed thoroughly at a temperature of 70°C and stirring speed of 400 rpm for 5 min. Next, the samples were left to rest to separate the oil phase from the soap. After 24 h, it was observed that there were layers of liquid formed in each beaker, where the top layer was the neutralized WCO. The top layer of each sample was collected and then washed using hot water (> 90°C) to remove soap and the washing process was repeated several times. Next, the neutralized WCO samples were heated at 110°C for 10 min to reduce their water content and the samples were then cooled down to room temperature. The properties of each neutralized WCO sample were then measured.

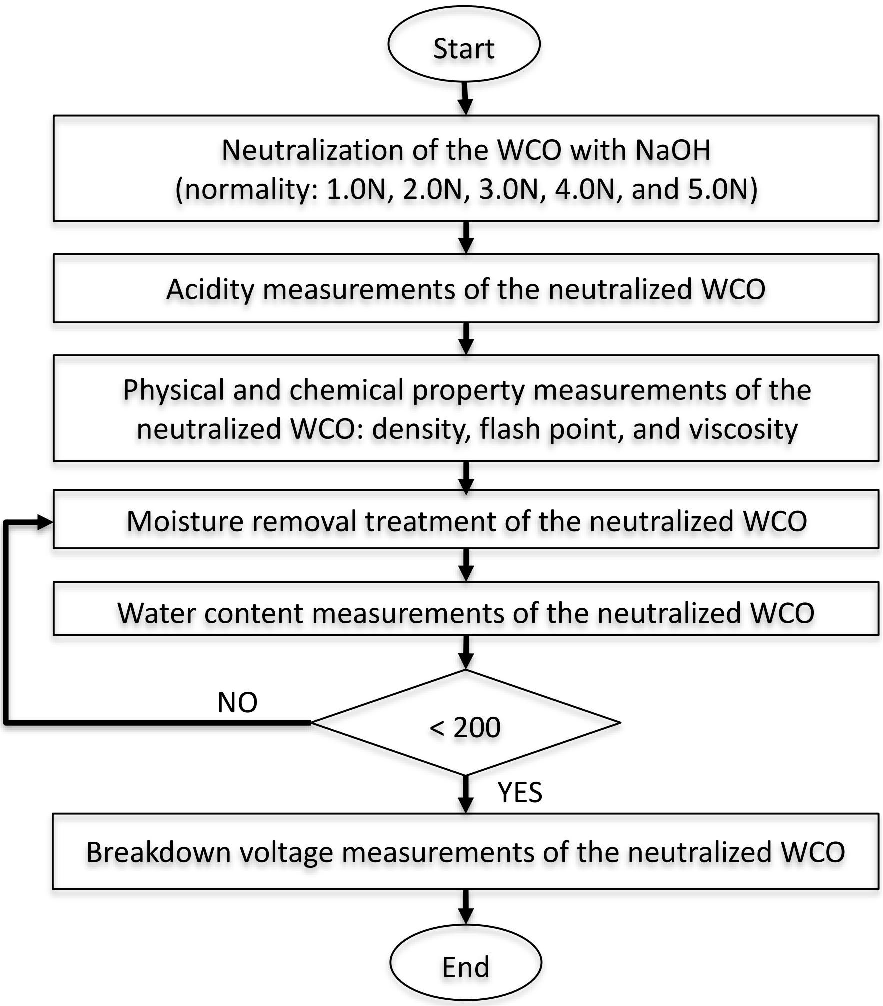

Fig. 2. Flow chart of the methodology adopted in this study

3.2 Physical, Chemical, and Electrical Property Measurements

The relative density, flash point, and viscosity of the WCO samples were measured in an ISO/IEC 17025-accredited laboratory according to the ISO 12185, ISO 2719, and ASTM D7042 standards, respectively. The acidity of the WCO samples was measured based on the amount of potassium hydroxide (KOH) in milligrams (mg) required to neutralize hydrogen ions (H^+) in 1 g of oil sample. The acidity was measured using a compact titrator (Model: 848 Titrino plus, Metrohm AG, Switzerland) according to the ASTM D974 standard.

The water content of the neutralized WCO samples was determined via oxidation of sulphur dioxide by iodine in methanolic hydroxide solution using Karl Fischer coulometer (Model: 899, Metrohm AG, Switzerland) according to the ASTM D1533 standard. The breakdown voltage of the neutralized WCO samples was measured using a portable dielectric strength oil tester (Model: OTS60PB, Megger Ltd., UK) according to the ASTM D1816 standard. Two semi-spherically capped *Verband der Elektrotechnik* (VDE) electrodes with a gap distance of 1.0 mm were used for the breakdown voltage tests. The voltage was increased gradually at a rate of 0.5 kV/s until breakdown occurred. The minimum volume of each oil sample was 350 mL.

3.3 Moisture Removal Treatment

The breakdown voltage is sensitive to the presence of impurities (i.e. moisture, particles, air, and gas bubbles) in the transformer insulating oil. For this reason, moisture removal treatment was carried out to ensure that the neutralized WCO samples were free from moisture, which would affect the ability of the oil samples to withstand electric stresses. The moisture removal treatment was performed by flowing nitrogen gas [28] through the neutralized WCO samples for 30 min.

4. Results and Discussion

The effects of neutralization on the physical appearance (colour) and acidity of the WCO samples are first presented and discussed in this section. The best neutralized WCO sample was then chosen based on the lowest acidity and its physical, chemical, and electrical properties were assessed according to the IEEE C57.147 and IEC 62770 standards, as described in this section.

4.1 Effect of Neutralization

Figure 3 shows the colour of the WCO and neutralized WCO samples. It can be observed that the WCO sample was dark brown whereas the neutralized WCO samples were clear yellowish, regardless of the normality of the caustic soda. The dark colour of the WCO sample is indeed expected because of the by-products present in the sample as a result of repeated frying and oxidation processes, which produce free fatty acids, among other by-products. Thus, the WCO becomes clearer by neutralizing the free fatty acids in the oil with caustic soda, as evidenced from the results.

Fig. 3. Colour of the WCO and neutralized WCO samples (normality of caustic soda: 1.0, 2.0, 3.0, 4.0, and 5.0 N)

Acidity indicates the total acidic components of an oil sample. The initial acidity of the WCO sample was found to be 5.4644 mg KOH/g. After the WCO was neutralized with caustic soda, its acidity reduced, depending on the normality of the caustic soda, as shown in Figure 4. It is apparent that the WCO neutralized with caustic soda (normality: 2.0 N, hereinafter $WCO_{2.0N}$) had the lowest acidity (0.2825 mg KOH/g). The difference in acidity between the WCO and $WCO_{2.0N}$ samples was 5.1819 mg KOH/g, which corresponds to a reduction in acidity of 94.83% relative to the acidity of the WCO sample. The acidity of the $WCO_{2.0N}$ sample (0.2825 mg KOH/g) was higher than the prescribed limit for “new natural ester fluids”, which should be less than or equal to 0.06 mg KOH/g according to the IEEE C57.147 standard. However, the acidity of the $WCO_{2.0N}$ sample was within the stipulated limits for “continued use of in-service natural ester fluids” in oil-immersed transformer, which should be less than or equal to 0.30 mg KOH/g. Thus, multi-filtration process [29]; an additional treatment in reducing the acidity of $WCO_{2.0N}$ sample; will be performed.

4.2 Physical and Chemical Properties

Density is a property that determines the suitability of insulating oil for use in cold climates because ice may form in oil-immersed transformers exposed to sub-zero temperatures. Flash point is related to fire safety and it is of great importance if the service transformer is located in a densely populated area. Viscosity is defined as the resistance of a fluid to flow, which will affect the ability of insulating oil to conduct heat, which is the primary heat removal mechanism in oil-immersed transformers. In this study, the $WCO_{2.0N}$ sample had the lowest acidity and therefore, the physical and chemical properties of this oil sample were measured. The density, flash point, and viscosity of the $WCO_{2.0N}$ sample were determined to be 0.913 g/cm^3, 260°C, and 40.84 mm^2/s, respectively. Both the density and viscosity fulfilled the specifications stipulated in the IEEE C57.147 and IEC 62770 standards. However, the flash point of $WCO_{2.0N}$ sample only fulfilled the specification of the IEC 62770 standard, where the flash point of the insulating oil should be at least 250°C.

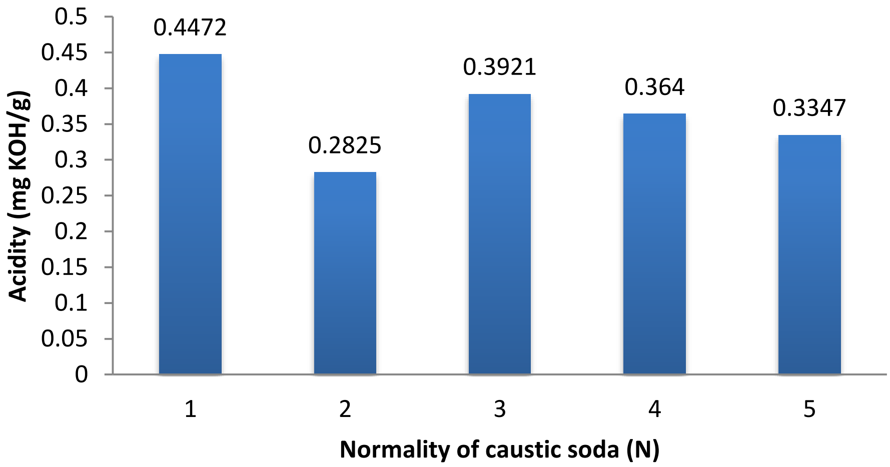

Fig. 4. Acidity of the neutralized WCO samples (normality of caustic soda: 1.0, 2.0, 3.0, 4.0, and 5.0 N)

4.3 Electrical Property

Breakdown voltage is defined as the applied AC voltage at which disruptive discharge begins. The breakdown voltage of the $WCO_{2.0N}$ sample after moisture removal treatment was found to be 29 kV, which was 45% higher than the minimum dielectric breakdown voltage required for new natural ester fluids (20 kV).

The physical, chemical, and electrical properties of the $WCO_{2.0N}$ sample measured in this study are summarized in Table 2.

Table 2
Comparison of the physical, chemical, and electrical properties of the $WCO_{2.0N}$ sample with those specified in the IEC 62770 and IEEE C57.147 standards

Property	Unit	IEC 62770	IEEE C57.147	$WCO_{2.0N}$
Density	g/cm^3	≤ 1	≤ 0.96	0.913
Flash point	°C	≥ 250	≥ 275	260
Viscosity	mm^2/s	≤ 50	≤ 50	40.92
Acidity	mg KOH/g	≤ 0.06	≤ 0.06	0.2825
Water content	mg/kg	≤ 200	≤ 200	136.6[a]
Breakdown voltage	kV	≥ 35[b]	≥ 20[c]	29[a,c]

[a] After moisture removal treatment, [b] IEC 60156 (2.5 mm gap), [c] ASTM D1816 (1 mm gap)

5. Conclusion

In this study, WCO was neutralized with caustic soda (normality: 1.0, 2.0, 3.0, 4.0, and 5.0 N). The neutralization process resulted in WCO with a clear, yellowish colour. In addition, the neutralization process reduced the acidity of the WCO, where the lowest acidity (0.2825 mg KOH/g) was achieved for the $WCO_{2.0N}$ sample (i.e. WCO neutralized with caustic soda having a normality of 2.0 N). The density, flash point, and viscosity of the $WCO_{2.0N}$ sample were determined to be 0.913 g/cm^3, 260°C, and 40.84 mm^2/s, respectively. Moisture removal treatment was carried out on the $WCO_{2.0N}$ sample and the results showed that the water content was 136.6 ppm while the breakdown voltage was 29 kV. In general, most of the properties of $WCO_{2.0N}$ sample investigated in this study fulfilled the specifications of the IEC 62770 and IEEE C57.147 standards, except for the acidity. The acidity of the $WCO_{2.0N}$ sample was within the recommended limit for “continued use of in-service natural ester fluids” in oil-immersed transformers specified in the IEEE C57.147 standard, where the acidity should be less than or equal to 0.30 mg KOH/g. Based on the results, it can be concluded that the $WCO_{2.0N}$ sample has potential to be used as a transformer dielectric liquid.

Acknowledgement
The authors gratefully acknowledge the financial support provided by the Universiti Teknikal Malaysia Melaka (UTeM) under the grant: Short Term Grant (PJP/2019/FKE(5A)/S01670) and Centre for Robotics and Industrial Automation (CeRIA). The authors specially thank Mr Muhammad Nazori Deraman from Fakulti of Electrical Engineering, UTeM, for his assistance on the preparation of materials and measurements conducted in this study.

References

[1] Liao, Ruijin, Jian Hao, George Chen, Zhiqin Ma, and Lijun Yang. "A comparative study of physicochemical, dielectric and thermal properties of pressboard insulation impregnated with natural ester and mineral oil." *IEEE Transactions on Dielectrics and Electrical Insulation* 18, no. 5 (2011): 1626-1637.
[2] Gnanasekaran, Dhorali, and Venkata Prasad Chavidi. "Vegetable Oil: An Eco-friendly Liquid Insulator." In *Vegetable Oil based Bio-lubricants and Transformer Fluids*, pp. 101-124. Springer, Singapore, 2018.
[3] Rafiq, M., Y. Z. Lv, Y. Zhou, K. B. Ma, W. Wang, C. R. Li, and Q. Wang. "Use of vegetable oils as transformer oils–a review." *Renewable and Sustainable Energy Reviews* 52 (2015): 308-324.
[4] Fernández, Inmaculada, Alfredo Ortiz, Fernando Delgado, Carlos Renedo, and Severiano Perez. "Comparative evaluation of alternative fluids for power transformers." *Electric Power Systems Research* 98 (2013): 58-69.
[5] Campbell, Colin J., and Alexander Wöstmann. *Campbell's atlas of oil and gas depletion*. New York: Springer, 2013.
[6] Gorelick, Steven M. *Oil panic and the global crisis: predictions and myths*. John Wiley & Sons, 2011.
[7] Dias, Joana M., Maria CM Alvim-Ferraz, and Manuel F. Almeida. "Comparison of the performance of different homogeneous alkali catalysts during transesterification of waste and virgin oils and evaluation of biodiesel

quality." *Fuel* 87, no. 17-18 (2008): 3572-3578.
[8] Chowdhury, Krishna, Laila Arjumand Banu, Selina Khan, and Abdul Latif. "Studies on the fatty acid composition of edible oil." *Bangladesh Journal of Scientific and Industrial Research* 42, no. 3 (2007): 311-316.
[9] Mancini, Annamaria, Esther Imperlini, Ersilia Nigro, Concetta Montagnese, Aurora Daniele, Stefania Orrù, and Pasqualina Buono. "Biological and nutritional properties of palm oil and palmitic acid: effects on health." *Molecules* 20, no. 9 (2015): 17339-17361.
[10] Ab Ghani, Sharin, Nor Asiah Muhamad, Zulkarnain Ahmad Noorden, Hidayat Zainuddin, Norazhar Abu Bakar, and Mohd Aizam Talib. "Methods for improving the workability of natural ester insulating oils in power transformer applications: A review." *Electric Power Systems Research* 163 (2018): 655-667.
[11] Tenbohlen, Stefan, and Maik Koch. "Aging performance and moisture solubility of vegetable oils for power transformers." *IEEE transactions on power delivery* 25, no. 2 (2010): 825-830.
[12] Carcedo, Juan, Inmaculada Fernández, Alfredo Ortiz, Fernando Delgado, Carlos J. Renedo, and Carmen Pesquera. "Aging assessment of dielectric vegetable oils." *IEEE Electrical Insulation Magazine* 31, no. 6 (2015): 13-21.
[13] Shaban, Seham A. "Biodiesel Production from Waste Cooking Oil." *Egyptian Journal of Chemistry* 55, no. 5 (2012): 437-452.
[14] Muhamad, N. A., and S. H. M. Razali. "Electrical and chemical properties of new insulating oil for transformer using pure coconut oil." *Journal of Advanced Research in Materials Science* 25, no. 1 (2016): 1-9.
[15] Kumar, B. Satheesh, G. Padmanabhan, and P. Vamsi Krishna. "Performance assessment of vegetable oil based cutting fluids with extreme pressure additive in machining." *Journal of Advanced Research in Materials Science* 19, no. 1 (2016): 1-13.
[16] Kumar, B. Satheesh, G. Padmanabhan, and P. Vamsi Krishna. "Multi response optimization for turning AISI 1040 steel with extreme pressure additive included vegetable oil based cutting fluids using grey relational analysis." *Journal of Advanced Research in Materials Science* 23, no. 1 (2016): 1-14.
[17] Chairul, Imran Sutan, Norazhar Abu Bakar, Md Nazri Othman, Sharin Ab Ghani, and Muhammad Nazori Deraman. "Development of waste cooking oil methyl ester as potential electrical insulating fluid for power transformer." *ARPN J. Eng. Appl. Sci.* 13, no. 20 (2018): 8154–8162.
[18] Raeisian, Leyla, Hamid Niazmand, Ehsan Ebrahimnia-Bajestan, and Peter Werle. "Feasibility study of waste vegetable oil as an alternative cooling medium in transformers." *Applied Thermal Engineering* 151 (2019): 308-317.
[19] Soufi, Masoud Dehghani, Barat Ghobadian, Gholamhassan Najafi, S. Mohammad Mousavi, and Joelle Aubin. "Optimization of methyl ester production from waste cooking oil in a batch tri-orifice oscillatory baffled reactor." *Fuel Processing Technology* 167 (2017): 641-647.
[20] Kathirvel, S., Apurba Layek, and S. Muthuraman. "Exploration of waste cooking oil methyl esters (WCOME) as fuel in compression ignition engines: a critical review." *Engineering Science and Technology, an International Journal* 19, no. 2 (2016): 1018-1026.
[21] Mohan, Balaji, Wenming Yang, Kun Lin Tay, and Wenbin Yu. "Experimental study of spray characteristics of biodiesel derived from waste cooking oil." *Energy conversion and management* 88 (2014): 622-632.
[22] Borugadda, Venu Babu, and Vaibhav V. Goud. "Physicochemical and rheological characterization of waste cooking oil epoxide and their blends." *Waste and biomass valorization* 7, no. 1 (2016): 23-30.
[23] Borugadda, Venu Babu, and Vaibhav V. Goud. "Improved thermo-oxidative stability of structurally modified waste cooking oil methyl esters for bio-lubricant application." *Journal of Cleaner Production* 112 (2016): 4515-4524.
[24] Chowdhury, Avisha, Debasish Sarkar, and Debarati Mitra. "Esterification of free fatty acids derived from waste cooking oil with octanol: Process optimization and kinetic modeling." *Chemical Engineering & Technology* 39, no. 4 (2016): 730-740.
[25] Yaakob, Zahira, Masita Mohammad, Mohammad Alherbawi, Zahangir Alam, and Kamaruzaman Sopian. "Overview of the production of biodiesel from waste cooking oil." *Renewable and sustainable energy reviews* 18 (2013): 184-193.
[26] Refaat, A. A., N. K. Attia, H. Aazid Sibak, S. T. El Sheltawy, and G. I. ElDiwani. "Production optimization and quality assessment of biodiesel from waste vegetable oil." *International Journal of Environmental Science & Technology* 5, no. 1 (2008): 75-82.
[27] Tomasevic, A. V., and S. S. Siler-Marinkovic. "Methanolysis of used frying oil." *Fuel Processing Technology* 81, no. 1 (2003): 1-6.
[28] Wada, Junichi, Genyo Ueta, Shigemitsu Okabe, and Tsuyoshi Amimoto. "Techniques to inhibit transformer insulating oil degradation-Effectiveness evaluation of the removal of degradation products using adsorbents." *IEEE Transactions on Dielectrics and Electrical Insulation* 20, no. 6 (2013): 2307-2316.
[29] Abderrazzaq, M. H., and F. Hijazi. "Impact of multi-filtration process on the properties of olive oil as a liquid dielectric." *IEEE Transactions on Dielectrics and Electrical Insulation* 19, no. 5 (2012): 1673-1680.