

# Characterization of Waste Palm Cooking Oil for Biodiesel Production

Zahoor Ullah, Mohamad Azmi Bustam, and Zakaria Man

**Abstract**—Used cooking oils are of increasing interest as inexpensive feedstock for biodiesel production. In this work, we characterized the used cooking oil collected from the cafeteria in Universiti Teknologi PETRONAS. The spectroscopic analysis was performed for the used and unused cooking oil samples. Comparison of the data indicated that no significant spectroscopic and structural changes occurred for used and unused oil samples. The results indicate high degree of saturation and mono unsaturated fatty acids in the oil. The viscosity and acid value of the used oil was considerably higher than the unused oil. It can be concluded on the basis of our results that the difference in the behaviour and performance of oil is not only due to the main components (triglycerides) but also due to minor components (Vitamin E).

**Index Terms**—FTIR, <sup>1</sup>HNMR, TGA, triglycerides, unused and used palm oil.

## I. INTRODUCTION

Biodiesel, a liquid fuel consisting of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, can be used as a substitute for diesel fuel [1], [2]. Some of the advantages of using biodiesel fuel are its renewability, easy biodegradability, non-toxicity and safer handling due to its higher flash point compared to those of fossil fuels [3]. In addition, biodiesel fuel is also primarily free of sulfur and aromatics, producing more tolerable exhaust gas emissions than conventional fossil diesel [4]. Biodiesel produced from virgin vegetable oils costs much more than petro-diesel, this is a major drawback to the commercialization of biodiesel in the market. Therefore, it is necessary to find the ways to minimize the production cost of biodiesel. In this context, methods that can reduce the costs of raw materials as well as the energy consumption are of special concern. The use of waste cooking oils (WCO) is one of attractive options to reduce the raw material cost. However, many harmful compounds are produced during the frying of vegetable oils. Therefore EU banned the use of waste cooking oils in the composition of animal feed in 2002. Most of the toxic compounds in the waste cooking oil are oxidation products from fatty acids, especially from polyunsaturated fatty acids [5], [6].

FTIR and <sup>1</sup>HNMR are nondestructive techniques that are very useful in the study of edible oils and fats [7]. Today, the

application of Fourier transform infrared (FTIR) spectroscopy has increased in food studies, and particularly has become a powerful analytical tool in the study of edible oils and fats. There have been several studies concerning with the characterization, classification, and authentication of edible fats and oils using infrared spectroscopy [8].

The NMR technique can be useful in the characterization of food. However, to assess the role of NMR in food chemistry, we must know the specific problem it has to solve, how conclusive the evidence can be that derives from it and how it compares to other methods that can be brought to bear on the same problems. In literature many NMR studies have been reported on different type of food such as wine, olive oil, coffee, fruit juices, milk, meat, egg, starch granules, flour, etc) using different NMR techniques [9].

Thermogravimetric analysis (TGA) is an analytical technique for measuring changes in the mass of a material that occur in response to programmed temperature changes. The changes in the mass can be caused by a variety processes such as decomposition, degradation, sublimation, vaporization, adsorption, desorption, oxidation, and reduction [10]. If any weight loss processes determined during the TGA analysis reflect the physical and chemical changes in the structure. Thermogravimetric analysis has other desirable features as well [11].

The different vegetable oils are used for different food purpose. Another reason is that the oils or fats are likely exposed to varying degrees of use such as temperature and time. But to study the acid value and viscosity is especially useful, because these two properties have been shown to an increase steadily during degradation and is expected from the used cooking oils [12]. The aim of this work is to study the physicochemical indices of oil after frying.

## II. EXPERIMENTAL WORK

### A. Materials

Oil samples of Malaysian palm cooking oil of same type (used and unused) were collected, from the Universiti Teknologi PETRONAS cafeteria. The physio-chemical properties were determined as shown in Table I.

### B. FTIR Spectra Measurement

The infrared spectra were recorded with Perkin Elmer-FTIR, spectrum one 54841.

*Spectral acquisition:* A drop of oil each sample was deposited on the surface of the glass disc of the instrument and the standard was set earlier. All spectra were recorded from 4000 to 650 cm<sup>-1</sup>. The oil was removed with dry tissue and the surface of glass disc was washed with acetone, and

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finally it was dried and cleaned with tissue.

### C. <sup>1</sup>H-NMR Analysis

<sup>1</sup>H-NMR analyses was performed on Bruker Avance 500 MHz. Each oil sample, weighing 100  $\mu$ L, was dissolved in 600-700  $\mu$ L of deuterated chloroform CDCl<sub>3</sub>, (Sigma-Aldrich) and the resulting mixture was placed into a 5-mm diameter ultra-precision NMR sample tubes. The temperature of the probe was at room temperature. The chemical shifts are reported in ppm, using the solvent proton signal as standard. The acquisition parameters were: spectral width, 10330.578 Hz; relaxation delay, 1 sec; number of scans, 16; number of dummy scans, 2; pulse width, 90°, with a total acquisition time of 1.6 min. The calibration of the signals was determined by using the equipment software (Topspin 3.0).

TABLE I: PHYSICOCHEMICAL PROPERTIES OF USED AND UNUSED COOKING OIL

Properties	Unused Cooking Oil Values	Used Cooking oil Values
Acid value (mg KOH/gm)	0.3	4.03
Calorific value (J/gm)	-----	39658
Saponification value (mg KOH/gm)	194	177.97
Peroxide value (meq/kg)	< 10	10
Density (gm/cm <sup>3</sup> )	0.898	0.9013
Kinematic Viscosity (mm <sup>2</sup> /s)	39.994	44.956
Dynamic Viscosity (mpa.s)	35.920	40.519
Flash point (°C)	161-164	222-224
Moisture content (wt %)	0.101	0.140

TABLE II: FUNCTIONAL GROUPS AND MODES OF VIBRATION IN THE SPECTRUM OF EXTRA VIRGIN OLIVE OIL (EVOO) AND PALM OIL (PO)

Frequency (cm <sup>-1</sup> )	Functional group assignment
3005	cis double-bond stretching
2924 and 2852	Asymmetrical and symmetrical stretching vibration of methylene (CH <sub>2</sub> ) group
1743	Ester carbonyl functional group of the triglycerides
1465	Bending vibrations of the CH <sub>2</sub> and CH <sub>3</sub> aliphatic groups
1417	Rocking vibrations of CH bonds of cis-disubstituted olefins
1402	=C-H bending vibration
1377	Bending vibrations of CH <sub>2</sub> groups
1236 and 1160	C-O stretching
1117 and 1098	Stretching vibration of the C-O ester group
1030	C-O stretching
962	Bending vibration of CH functional groups of isolated transolefin
850	=CH <sub>2</sub> wagging
721	Overlapping of the methylene (-CH <sub>2</sub> ) rocking vibration and to the out of plane vibration of cis-disubstituted olefins

Source: A. Rohman and Y.B. Che Man, 2010.

### D. TGA Analysis

The used and unused palm oil decomposition experiments were performed by TGA. For all experiments, N<sub>2</sub> was used as an inert carrier gas; oils sample with the weight of about 2-5 mg placed in a balance pan, and was used in all experimental runs. Next, the sample was heated at heating rate of 10 °C /min, from 30 to 800 °C.

## III. RESULTS AND DISCUSSION

The physicochemical properties of oil as mentioned in Table I was determined by the already established methods to check their properties before and after frying. All the edible oils are constituted basically of fatty triglyceride esters with different substitution patterns, lengths and degree of saturation of the chains and of other minor components. The importance of FTIR spectroscopy in the identification of molecular structures originates from the much information content obtained and the possibility to assign certain absorption bands related to its functional groups. The FTIR spectra of used cooking oil and unused cooking oil shows similar spectra features, can be related to those of triglycerides because triglycerides are the principle component in them. The already reported analytical evaluation of the palm oil and EVOO spectra is given in Table II. All the values of used and unused palm cooking oil spectra is in the range of the reported Table II. Most of the peaks and shoulders of the spectrum are attributed to the specific functional groups. As in Fig. 1 shows the spectrum of used cooking oil has weak band at 3469.54 cm<sup>-1</sup> associated with the overtone of the glyceride ester carbonyl absorption. Band at 3006.20 cm<sup>-1</sup>, resulting from the stretching vibration of the *cis* olefinic CH double bond. The bands at 2920.30 cm<sup>-1</sup> and 2851.91 cm<sup>-1</sup>, assigned to (C-H) symmetrical and asymmetrical stretching of the saturated carbon-carbon bond. The C=O group of triglycerides resulting a stretching vibration at 1743.10 cm<sup>-1</sup>. A small band at 1656.69 cm<sup>-1</sup> resulting from *cis* C=C bond. The Bands at 1463.79 cm<sup>-1</sup> resulting from the bending vibrations of CH<sub>2</sub> and CH<sub>3</sub> aliphatic groups. The result which shows the bands at 1236.91, 1157.19, 1116.87 and 1096.86 cm<sup>-1</sup>, some of them could be assigned to the stretching vibrations of the (C-O) esters group. According to Paulina [13], the band near 723 cm<sup>-1</sup> is due to the overlapping of the (CH<sub>2</sub>)<sub>n</sub> rocking vibration and the out-of-plane vibration (CH wag) of *cis*-di-substituted olefins. Different oils show slight differences both in the position and absorbance of the bands because of their different triglyceride composition. The region from about 500-1500 cm<sup>-1</sup>, usually this region is very complicated series of absorptions due to variety of bending and stretching within the molecule. It is difficult to know about the individual bands and assign them reliably to a particular functional group or bond in a molecule, this part of the IR spectrum is called the fingerprint region. The importance of fingerprint region is that, in this part of the spectrum each type of different compound produces different pattern of troughs. The FTIR spectra of both used cooking oil and unused cooking oil have a great similarity showing almost unappreciable variations either in the frequency or in the absorbance of the bands.

<sup>1</sup>H-NMR spectra of used and unused palm cooking was investigated to analyze the difference before and after the use of oil. As shown in the Fig. 2. A good resolution was obtained from the <sup>1</sup>H-NMR spectra. The spectra for used and unused palm oil presented the characteristic signals, intensities and multiplicity are illustrated. The <sup>1</sup>H-NMR spectrum of any oil sample shows at least 9 or in some cases, even 10 signals of significant intensity. These signals are due to protons of the main components i.e. triglycerides. The

peaks of  $^1\text{H-NMR}$  spectrum in both the spectra, at  $\delta$  5.19 – 5.35 ppm showing the unsaturated fatty acids are those of the olefinic hydrogen and also include to glycerol proton. The hydrogen attached to methylene glycerol carbons shows a peaks at  $\delta$  3.99 – 4.29 ppm respectively, The bis-allylic carbons proton shows at  $\delta$  2.63 - 2.77 ppm, the chemical shift value at  $\delta$  2.15 - 2.31 due to  $\alpha$ -carbonyl methylene proton, and at  $\delta$  1.47-1.62 ppm resonance to  $\beta$ -carbonyl methylene proton. The allylic protons ( $-\text{C}=\text{C}-\text{CH}_2-\text{C}=\text{C}-$ ) give at  $\delta$  1.88 - 2.02 ppm, the saturated  $(\text{CH}_2)_n$  groups give the broad resonance at  $\delta$  1.14 - 1.26 ppm, and the signals at  $\delta$  0.75 – 0.88 ppm corresponds to the methyl protons.

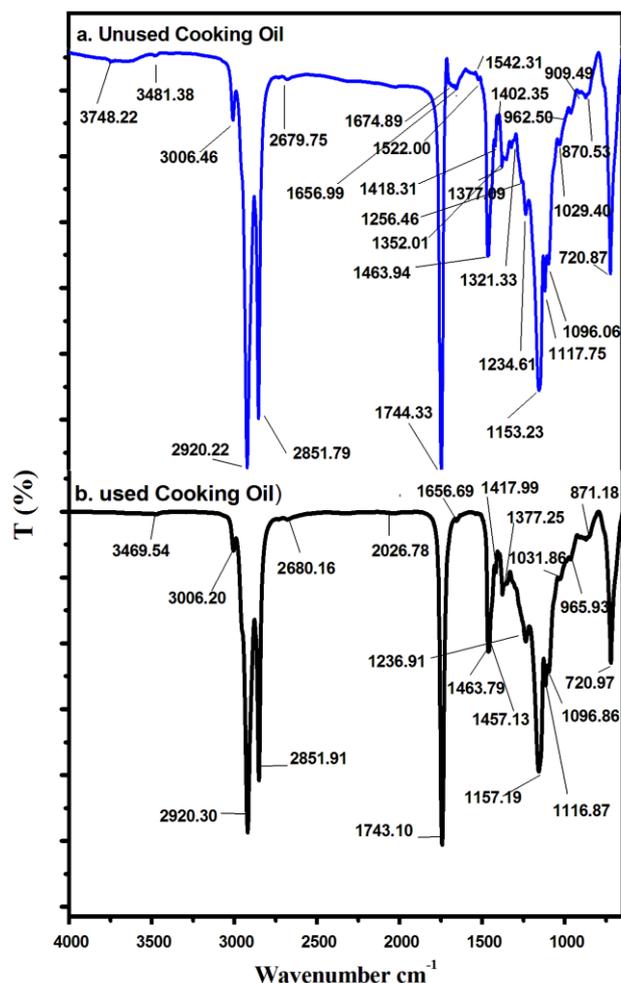


Fig. 1. FTIR spectra of (a). Unused and (b) Used cooking oil.

It is also noted that the line intensities (integrals) of the signals are proportional to the number of protons present in each functional group. Both the spectrum showed similar which shows slow rate of oxidation or thermal degradation. But when calibrate each of the signal then it shows that there is some slight changes in chemical shift values and also in intensity and multiplicity, it means that there is something oxidized or degrade. According to Mar á [14], differences related to the oxidative stability, reported of the three oils studied are evident, virgin olive oil being the most stable and hazelnut oil the least. Additionally, other factors, such as the presence of minor antioxidant components, play an important role in the oxidation rate of the oils. For example, hazelnut oil contains less linoleic and more oleic acyl groups than peanut oil, but its oxidation rate is higher, which makes it evident

that differences in the oxidative stability among different oils are due not only to the structure and composition of the main components but also to minor components. By comparison with this study palm oil is naturally rich in antioxidant components (vitamin E). According to Malaysian palm oil board and references [15]-[17], it is very stable edible oil because of its balanced fatty acid composition and high content of natural antioxidant, the vitamin E.

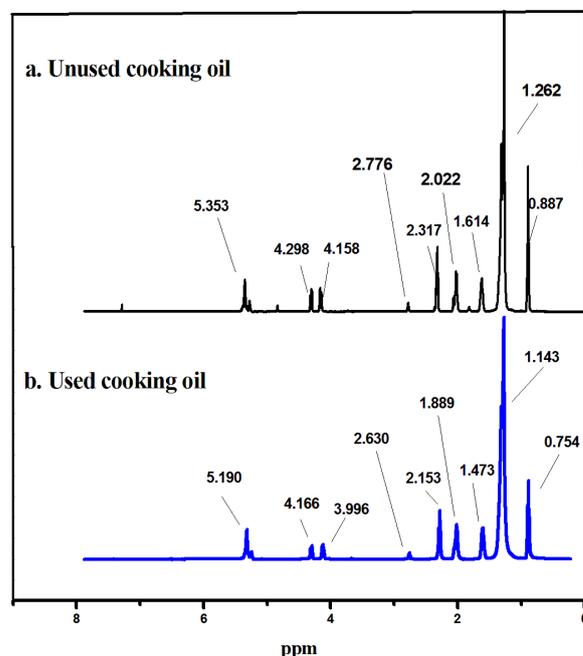


Fig. 2.  $^1\text{H-NMR}$  spectra of (a). Unused and (b). Used cooking oil.

Thermogravimetric analysis (TGA) results of both the used and unused cooking oil shows that it is thermally stable up to 240 °C. The TGA curve of both the oils sample are plotted in Fig. 3, showing their degradation range. The decomposition range of unused oil is between 240-350 °C, and used oil is 340-390 °C, respectively, at heating rate of 10 °C/min. The high the decomposition temperature means that there are some complex chemical compounds in the material [18]. The thermogravimetric profile of unused oil also shows that the oil is stable up to a temperature of 240 °C, above that, temperature started producing a loss in mass. The stability could be attributed to an expressive quantity of saturated fatty acids in the oil [15]-[17], as the palm oil contain equal ratio of saturated and mono saturated fatty acids. The presence of antioxidants also improves oil stability. Normally, oil with high concentrations of unsaturated fatty acids is more susceptible to thermal deterioration. It is also reported and explain earlier that several other vegetable oils that contain a high concentration of unsaturated fatty acids possess stability equivalent to other oils with lesser instauration showing that there are other factors which influence the thermal stability of vegetable oils. From reported literature, that the thermal decomposition of saturated fatty acids requires more energy than the unsaturated fatty acids. According to Zeomar [19], when acids are present in low concentrations, they are eliminated during the refining process due to their sensibility to heat. However, these fatty acids are responsible for certain physiological disorders in animals, especially for their co

carcinogenic activity. High temperatures catalyze the reactions of hydrolysis and oxidation of oils. The products of these reactions react among themselves and produce cyclic monomers, dimers, and polymers.

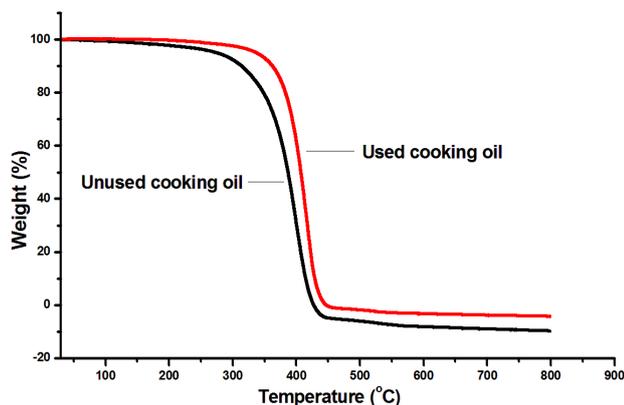


Fig. 3. TGA spectra of used and unused cooking oil.

#### IV. CONCLUSION

The samples studied to investigate the physico-chemical properties of especially palm used cooking, used cooking oil which is a very potential feedstock for biodiesel production in term of fatty acid composition and properties. These trends are due to the reaction such as hydrogenation and oxidation degradation occurring during cooking or frying. Comparison of the spectroscopic data of both the oil samples indicate that there are no significant spectroscopic and hence no structural changes occur after frying because the main signals in both oil spectra are similar. Different oils show slight differences both in the position and absorbance of the bands because of their different triglyceride composition. The profile of NMR and FTIR spectra of the both samples are more likely with triglycerols nature than free fatty acids. The TGA spectrum shows a clear change in both oils. By monitoring the frying process was carried out, by continuous observation of the physical changes like change in colour, odour, viscosity, etc with respect to original oil. Furthermore spectroscopic study like GC/MS is required for fatty acid determination.

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