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COMPARATIVE STUDY OF PROPERTIES AND FATTY ACID COMPOSITION OF NEAT AND WASTE PALM OILS

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ABSTRACT

The properties, fatty acid composition and degree of saturation of palm oil are believed to be altered when subjected to repeated high temperature during frying. This work compares the properties and fatty acid composition of neat palm oil and waste palm oil samples. Neat palm oil (NPO), waste palm oil used to fry fish and chips (WPO_{FC}) and another waste palm oil used to fry sausage and chips (WPO_{SC}) were collected at the point of disposal and subjected to property determination and pyrolysis gas chromatography-mass spectrometer (PYGCMS) analysis. Repeated high temperature frying was found to trigger the change of congealing temperature, density, viscosity @ 40 ^oC of NPO from -10.25 ^oC, 919.48 kg/m^3 and 27.96 mm^2/s respectively to 12.3 ^oC, 904.3 kg/m^3 and 44.25 mm^2/s for WPO_{FC} and 14.7 ^oC, 913.4 kg/m^3 and 38.41 mm^2/s for WPO_{SC} respectively. Also, the 76 % polyunsaturated fatty acid in NPO became 77 % and 80 % saturated fatty acid for WPO_{FC} and WPO_{SC} respectively. The results of the WPO samples validate the suitability of waste palm oil as a feedstock for biodiesel production and other industrial purposes but unsafe for human consumption.

Keywords: FAME, fatty acid, feedstock, PYGCMS, waste palm oil

1. INTRODUCTION

The continued necessity for biodiesel to replace petroleum-based diesel fuel (PBDF) has renewed interest in the search for cheap and readily available feedstock for biodiesel production. Despite some shortcomings, including the high cost of feedstock, low energy conversion, degradation during transportation and storage, biofuel offers obvious advantages in the world's quest to meet its energy needs [1, 2]. Biodiesel, also known as fatty acid methyl ester (FAME), is an important member of the biofuel family. FAMEs are fatty acid (FA) esters that are produced from the transesterification of feedstocks, mainly vegetable oils (edible or inedible), animal fats using methanol in the presence/absence of a catalyst.

Despite its renewability, low sulfur content, safer handling, higher cetane number, etc, commercial production and application of FAME has been hampered by the high cost of feedstock, food vs fuel debate and the long time required to cultivate inedible vegetable feedstocks e.g it takes 3 - 4 years for palm tree to bear fruit [3], 2 - 3 years for moringa tree to bear fruit [4]. Compared to the use of PBDF, application and combustion of FAME in compression ignition (CI) engines is more environmentally friendly as it generates less carbon monoxide (CO), between 75 % and 90 % reduction in unburnt hydrocarbon (UHC) and polycyclic aromatic hydrocarbons (PAHs) [5].

One of the strategies to make the commercial production of FAME attainable and affordable is the adoption of waste cooking oil (WCO) as feedstock. Also, saturated straight chain WCO are preferred as feedstock for FAME production because of its paraffinic properties which improves ease of conversion, FAME stability, and performance as compression ignition engine fuel unlike the unsaturated and branched structure of most vegetable oils [6, 7]. These properties of unsaturated vegetable oils precipitate combustion difficulties and inefficiency in CI engines.

The global production and consumption of palm oil have continued to increase as shown in figure 1 [8]. According to a report by the Institute of Medicine [9], palm oil constitutes 33 % of global vegetable oil production. Though palm oil has industrial and social

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applications, waste palm oil is extensively used for frying in homes and restaurants. During frying, the oil is heated repeatedly to between 170 ^{O}C and 220 ^{O}C in the presence of oxygen, and sometimes moisture, which causes the palm oil to be exposed to physical, thermal and chemical degradations. This degradation affects the properties, fatty acid composition and the degree of saturation of the oil thereby lowering the quality of the oil. Repeated exposure of palm oil to high temperatures for a long period of time has been found to render the oil harmful for human consumption. Inappropriate disposal of the used palm oil has created environmental problems, block the sewer pipes, corrode metals and concrete structures [10-13].

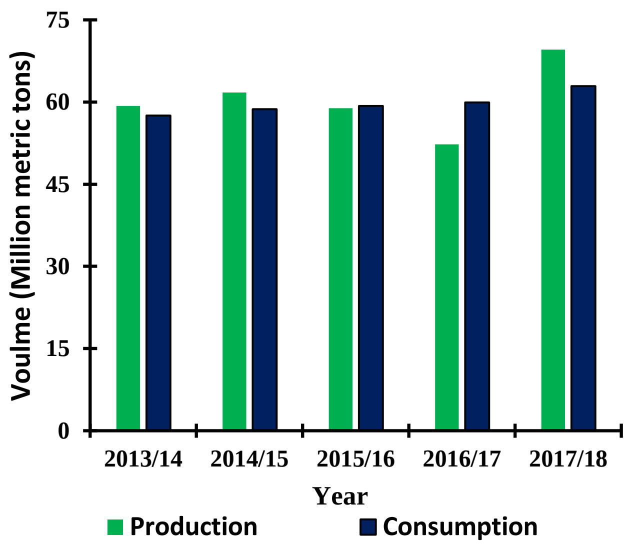

Fig. 1. Global palm oil production and consumption (million metric tons)

Researches on the utilization of waste palm oil (WPO) as affordable and readily available feedstock for biodiesel production has been conducted in recent years with encouraging outcomes [14-16]. The relevant question to ask, however, is whether the various food items the palm oil is used to fry affects its properties, FA compositions and degree of saturation. Also slated for determination is the variations in the properties and FA compositions of neat palm oil (NPO) compared with WPO and the suitability of such WPO for possible biodiesel production. This present effort, therefore, aims to investigate the effects of usage of NPO on the properties and FA compositions of samples of WPO used to fry two varieties of food items and compare same with that from NPO with a view to establishing their propriety of WPO as FAME feedstock. This current effort is limited to determining the properties and FA compositions of NPO and comparing the same with that of two samples of WPO used to fry varying food items.

2. MATERIALS AND METHODS

2.1 Material collection and treatment

Three palm oil samples were collected from a local take away restaurant in Central Durban, KwaZulu-Natal province, South Africa. The palm oil samples were a NPO sample, used palm oil sample used to fry fish and chips (WPO_{FC}) and another used oil sample used to fry sausage and chips (WPO_{SC}). The WPO samples were collected at the point of disposal, though the frequency and temperature of usage could not be ascertained. Details of the samples are as shown in Table I

The two WPO samples were heated to 100 ^{O}C for 10 minutes to allow for the evaporation for any moisture that might have been trapped in the samples and later filtered to remove any food debris and other foreign bodies in the oil.

Table I. Details of the oil samples

Sample notation	Sample name	Food items fried with oil	Duration of usage (Days)
NPO	Neat palm oil	-	-
WPO_{FC}	Waste palm oil	Fish and chips	14
WPO_{SC}	Waste palm oil	Sausage and chips	14

2.2 Properties determination and PYGCMS analysis

The NPO, $WPO_{FC,}$ and WPO_{SC} were subjected to property determination and characterization through pyrolysis gas chromatography-mass spectrometer (PYGCMS) analysis. Table II shows the list and method adopted for the property determination and characterization of the samples. The FA composition of the samples was determined using a Shimadzu Gas Chromatograph Mass Spectrometer using an ultra-alloy-5 capillary column and GCMS-QP2010 Plus software. Helium was used as the carrier gas while 2 µL of the sample was injected at column oven temperature and injection temperature of 40 °C and 240 °C respectively using split injection mode spanning a total time of 92.33 minutes.

Table II: Method/instrument of the analysis

Property	Unit	Method/Instrument
Density @ 20°C	Kg/m^3	ASTM D 1298
Viscosity @ 40°C	mm^2/s	ASTM D445
Acid value	mg/g	AOCS Ca 4a-40
Iodine value	Cg/g	AOCS Cd 1B-87
pH	-	pH meter
Congealing temperature	°C	Digital thermometer
FA composition	-	PYGCMS

3. RESULT AND DISCUSSION

3.1 Effect of usage on properties

The result of property determination of NPO, WPO_{FC} and WPO_{SC} samples are shown in Table III. The density of NPO is higher than that of the two WPO samples. This can be attributed to the effect of repeated heating and contamination which has made the waste palm oil samples become less dense. The pH of NPO is higher than that of waste oil samples with WPO_{FC} as the most acidic of the three samples. This is due to the influence of the contamination of fish oil in the sample during usage [16]. This result is also confirmed by the acid value of the waste oil samples where the WPO_{FC} presented a lower acid value than WPO_{SC}. In terms of viscosity, usage makes the oil to be more viscous while WPO_{FC} is found to be more viscous than WPO_{SC}.

Table III: Properties of neat and waste oil samples

Properties	NPO	WPO_{FC}	WPO_{SC}
pH	6.34	5.73	6.19
Congealing temperature (°C)	-10.25	12.3	14.7
Density @ 20 °C (kg/m^3)	919.48	904.3	913.4
Viscosity @ 40 °C (mm^2/s)	27.96	44.25	38.41
Iodine value (cg/g)	-	81.7	54.2
Acid value	-	0.66	1.13

Considering the fingerprint of both the WPO_{FC} and WPO_{SC}, particularly the density and viscosity, it can be seen that a lower density and higher viscosity trigger a lower saturated fatty acid (SFA) and a higher monounsaturated fatty acid (MUFA) as shown in figure 2. This is unlike the case of NPO where a higher density and a lower viscosity resulted in a predominantly polyunsaturated fatty acid (PUFA). The pH of the neat and waste palm oil samples showed that NPO presented the highest pH followed by WPO_{SC} and WPO_{FC} in that order. The NPO is predicted to have higher acid value when compared with the WPO_{FC} and WPO_{SC} samples. The pH trend also followed the acid value trend of WPO_{FC} and WPO_{SC} and will enhance the transesterification process.

The viscosity of NPO of this research, as shown in table III, is 27.96 mm^2/s which falls within the 25.6 mm^2/s reported by Maneerung et al. [17] and 31.78 mm^2/s reported by Zein et al. [18]. Also while the density of both WPO_{FC} and WPO_{SC} are found to be higher than the 902 kg/m^3 reported by Maneerung et al. [17], most of the waste palm oil samples presented low acid value. These fingerprints affect the FA compositions and the degree of saturation, and invariably their tendency to be converted to FAME.

3.2 Effect of usage on FA composition

The FA composition of the NPO, WPO_{FC}, and WPO_{SC} as determined by the PYGCMS is shown in Table IV. NPO is found to make up of mainly linoleic acid, while WPO_{FC} and WPO_{SC} consist of majorly of palmitic acid (45.5 %). The WPO_{FC} contains 46.21 % in oleic, palmitic and stearic acids while WPO_{SC} showed 71.64 % FA composition and in only three acids. The NPO, on the other hand, showed a total of about 60 % FA in about seven different acids. These results differ from those reported by Kadapure et al. [14]. This may be due to the difference in the types and species of palm oil used as well as the method of determining the FA composition. It should be noted that Kadapure et al. [14] got their palm oil sample and carried out their research in Belgium and analyzed by gas chromatographic method as against the PYGCMS used for this research. Also, the food items the palm oil was used to fry and the duration of usage were not disclosed. There was no guarantee that waste palm oil was obtained from the same source as the neat oil.

Table IV: Fatty acid composition of oil samples

Fatty Acid		Palm Oil Samples		
Common name	Acronym	NPO	WPO_{FC}	WPO_{SC}
Oleic acid	C18:1		10.72	14.39
Palmitic acid	C16:0		25.73	40.21
Linoleic acid	C18:2	45.5	-	-
Erucid acid	C22:1	6.83	-	-
Caprylic acid	C8:0	0.56	-	-
Capric acid	C10:0	2.43	-	-
Lauric acid	C12:0	0.86	-	-
Stearic acid	C18:0	2.67	9.76	-
Enanthic acid	C7:0	0.82	-	-
Myristic acid	C14:0	-	-	17.04
Total		**59.67**	**46.21**	**71.64**

Also, it was discovered that the total FA composition of the NPO was higher than that of WPO_{FC} but lower than that of WPO_{SC}. Maneerung et al. [17] attributed this outcome to the fact that high temperature cooking or frying brake down some triglyceride molecules and trigger the formation of free fatty acids. The FA composition of NPO was however lower than that of WPO_{SC}. This same pattern of the result was reported by Kadapure et al. [14] who reported a slight increase in the FA of WCO compared to the FA of NPO. This can be due to the effect of thermal degradation and contamination by food item during frying.

As shown in figure 2, the effects of frying beef and chips led to a slight increase in SFA from 77 % in WPO_{FC} to 80 % in WPO_{SC}. The variety of food items marginally affect the degree of saturation of the waste oil unlike the effect of thermal degradation which appeared to be well pronounced. Frying converts polyunsaturated fatty acid in NPO to saturated fatty acid in WPO as a result of the high temperature involved in frying. The SFA composition of the NPO was considerably increased by thermal degradation from 12 % in NPO to 77 % and 80 % in the WPO_{FC} and WPO_{SC} respectively. The MUFA changed from 12 % for NPO to 23 % and 20 % for WPO_{FC} and WPO_{SC} respectively.

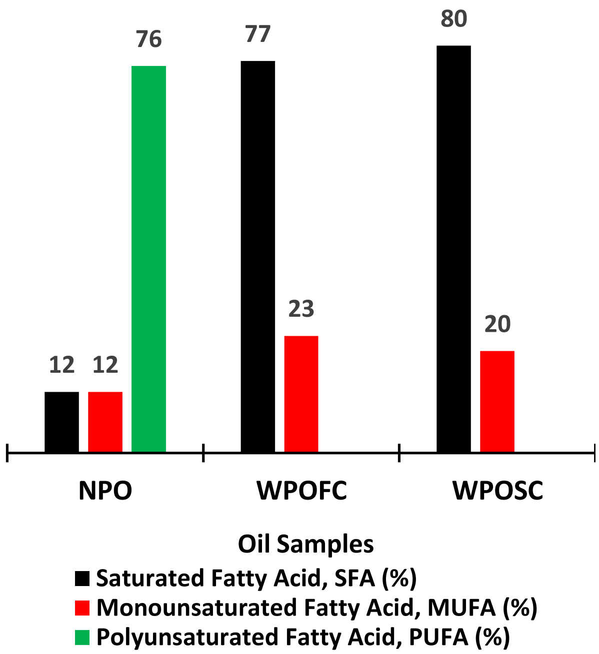

Fig. 2. SFA, MU FA and PUFA compositions of oil samples

The NPO used in this research consists of 76 % polyunsaturated fatty acid compared with the two waste palm oil samples the major portions of which consists of saturated fatty acids and no polyunsaturated fatty acid. This trend is due to the effect of usage on the saturation of NPO. However, the high percentage of PUFA in NPO differed greatly from the result of similar research by Kadapure et al. [14] and Maneerung et al. [17] as shown in figure 3. No explanation was found for the differences in the FA compositions other than the different geographical sources and species of the palm oil samples.

Maneerung et al. [17] reported slight changes in the FA compositions of neat oil and waste cooking oil. This might be due to very low degradation temperature the oil was subjected to since the degradation temperature, the frying cycle and the food items fried were not disclosed. The neat palm oil, however, witnessed appreciable changes in the FA from the neat palm oil to used pal oil as reported by Kadapure et al. [14]. The SFA, MUFA, and PUFA changed from 47%, 43% and 10% to 92%, 6% and 2% in the waste palm oil respectively. Thermal pyrolysis and usage have increased the degree of saturation considerably. The FA composition for the WPO_{FC} and WPO_{SC} are similar and the same trend to the outcome of FA analysis of waste palm oil by Kadapure et al. [14].

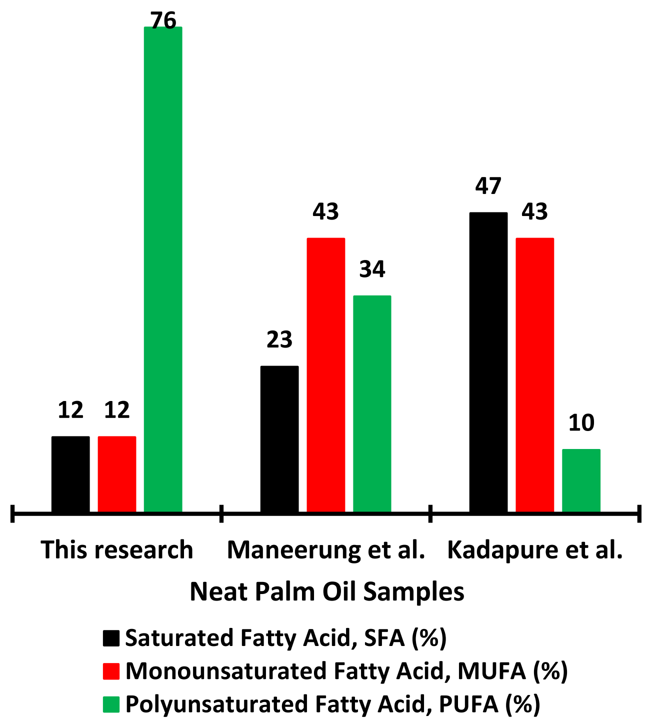

Fig. 3. SFA, MUFA and PUFA compositions of neat oil samples

Figure 4 compared the FA composition of WPO_{FC} and WPO_{SC} to that obtained from six other researchers mined from literature. Maneerung et al. [17], Zein et al. [18] and Nuyeng et al. [19] reported almost the same value for MUFA while Maneerung et al [17] and Nayak et al [20] have close values of PUFA though lower than that presented by Rahamanlar et al. [21]. From the eight samples of waste palm oil shown in figure 4, it can be deduced that there is no consensus on the degree of saturation and type of chain. Degradation temperature, usage, duration and degree of usage, type food items that were fried, among others will dictate the FA composition and degree of saturation of the waste palm oil.

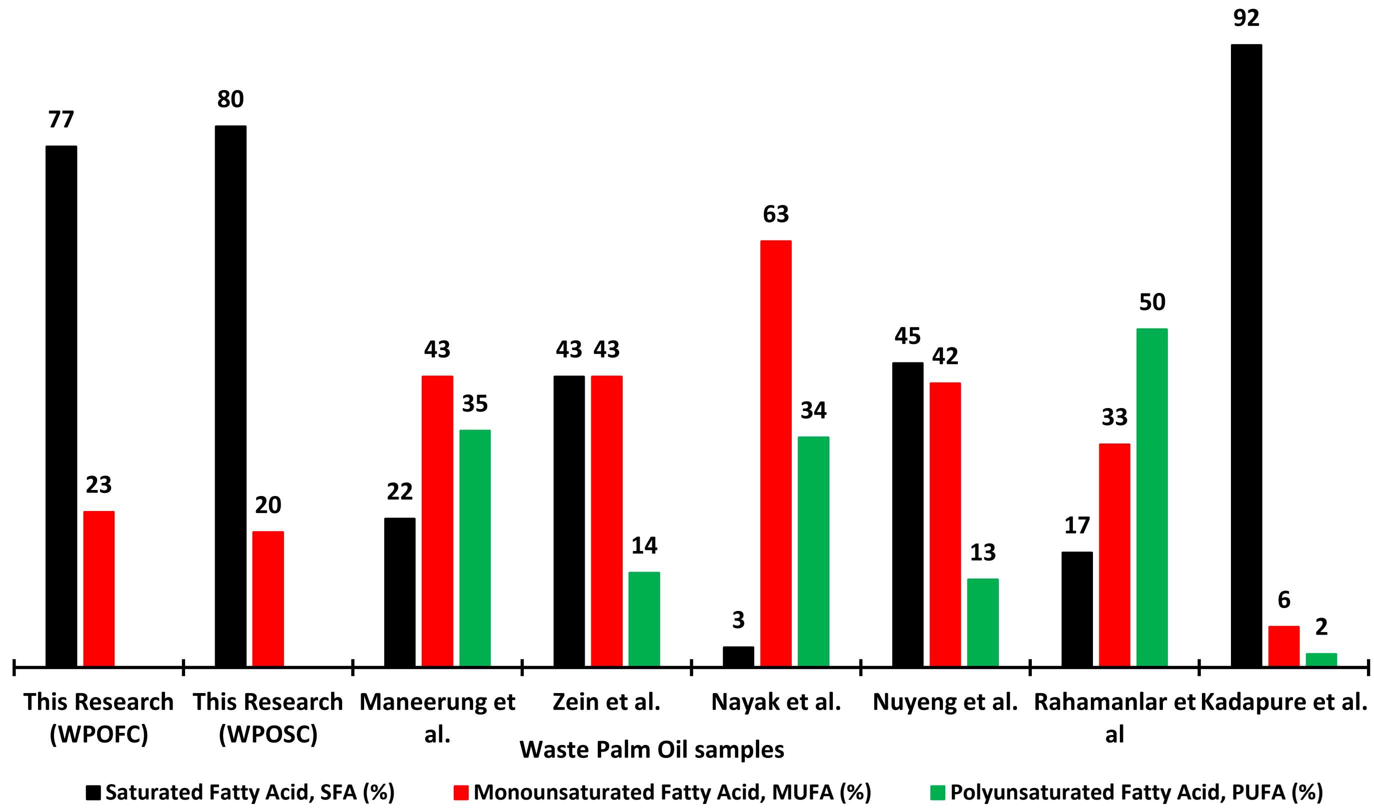

Fig. 4. SFA, MUFA and PUFA compositions of Waste Palm Oil samples

4.0 Conclusion

The effects of usage and food items on the properties and FA composition of palm oil have been investigated and reported, namely;

- The pH and density of WPO samples were found to be lower than that of NPO while the congealing temperature and viscosity of NPO were found to be lower than that of the WPO sample.
- The pH, congealing temperature, density and acid value of WPO_{FC} were found to be lower than that of WPO_{SC} but presented higher iodine and viscosity values.
- The low acid value of the WPO samples signifies their suitability for FAME production by transesterification.
- The degree of usage, the type of food palm oil was used to fry and the source of the neat palm oil has been found to affect its FA composition and degree of saturation. The FA composition affects the properties which in turn affect the transesterification outcomes.
- Neat palm oils were also found to consist of predominantly PUFA as against WPO which consists mainly of SFA.
- The composition of saturated fatty acid and unsaturated fatty acid were found to be affected by the degree of usage, the degradation temperature, species of palm oil and the food items the oil was used to fry.
- The degree of saturation of WPO_{FC} and WPO_{SC} is less than that of neat palm oil, in most cases, and agree with some of the results reported in the literature.

Conclusively, in selecting WCO as feedstock for transesterification, attention should be paid to the three factors namely the degree of usage, the type of food palm oil was used to fry and the neat palm oil source.

Going forward, considerable research opportunities still exist on the effect of frying temperature and time, the cycle of frying, palm oil species, etc. towards establishing the optimal conditions to get the best feedstock for FAME production from palm oil. This will no doubt lead to the conversion of waste palm oil to biodiesel.

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