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Research paper

Effect of usage on the fatty acid composition and properties of neat palm oil, waste palm oil, and waste palm oil methyl ester

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Abstract

The need to find an environmentally friendly, renewable, and biodegradable fuel to reduce the growing dependence on fossil fuels and its attendant performance and emission inadequacies has increased research in biodiesel. Due to its low cost, availability, and a veritable means of waste disposal, waste vegetable oil from restaurants, waste fats from slaughterhouses, grease from wastewater treatment plants has gained prominence as biodiesel feedstock. This present effort compares the properties and fatty acid (FA) composition of neat palm oil (NPO), waste palm oil (WPO), and waste palm oil methyl ester (WPOME). WPO used to fry fish and chips (WPO_{FC}), and waste palm oil used to fry sausage and chips (WPO_{SC}) were collected at the point of disposal. The WPO_{FC} and WPO_{SC} were converted to $WPOME_{FC}$ and $WPOME_{SC}$, respectively, by transesterification and subjected to property determination and gas chromatography-mass spectrometer analysis. The characterization showed that the ratio of saturated FA to unsaturated FA changed from 19.64 %:80.36 % for NPO, to 37.67 %:62.33 % for WPO_{FC}, 54.75 %:45.25 % for WPO_{SC}, 30.43 %:69.58 % for $WPOME_{FC}$ and 16.2 %:83.8 % for $WPOME_{SC}$. These outcomes can be attributed to the effect of repeated heating and cooling during frying, contamination from moisture, food fried, and the transesterification reaction.

Keywords: *Characterization; FAME; Fatty Acid; Feedstock; Waste Palm Oil.*

1. Introduction

The increase in population, urbanization, and industrialization has an ongoing effect on energy demand putting enormous pressures on finite energy sources [1], [2]. Compression ignition (CI) engines have both on-road and off-road applications. The use of petroleum-based diesel fuel (PBDF) to power CI engines has attendant cost, performance, and environmental challenges. Unmodified CI engines fuelled with PBDF have been found to present lower engine power, lower thermal efficiency, lower combustion efficiency, and lower brake specific fuel consumption when compared with CI engines powered by biodiesel or its blends. In addition, compared with CI engines fuelled with biodiesel, PBDF triggers higher emissions of carbon monoxide, smoke opacity, and unburnt hydrocarbon in an unmodified engine under varying loads and engine speeds [3-5]. Despite some shortcomings, including the high cost of feedstock, low energy conversion, and degradation during transportation and storage, biofuel offers obvious advantages in the world's quest to meet its energy needs [6], [7]. Biodiesel, also commonly referred to as fatty acid methyl ester (FAME), is an important member of the biofuel family.
According to the European Biofuels Technology platform [8], FAMEs are fatty acid (FA) esters that are generated from the transesterification of feedstock, mainly vegetable oils (edible or inedible), and animal fats, using methanol in the presence or absence of a catalyst. Despite its renewability, low sulfur content, safer handling, higher cetane number, etc., large-scale production and application of FAME has been hampered by the high cost of feedstock, the food vs fuel debate, and the long time required to cultivate inedible vegetable feedstocks e.g. 3 to 4 years for a palm tree to bear fruit [9], and 2 to 3 years for a moringa tree to bear fruit [10]. Economically, it costs about US$0.35 to produce a litre of PBDF from fossil fuel compared to about US$0.5 to produce a litre of FAME, with raw materials accounting for most of the cost [11]. The feedstock is believed to account for between 70 % and 95 % of the cost of FAME production [12], [13]. One of the strategies to make the commercial production of FAME attainable and affordable is the adoption of waste cooking oil (WCO) as a feedstock. The initial hurdles in collection logistics and infrastructure pointed out by Janauna and Ellis [14] and Atadashi et al. [15] are being overcome by partnering with operators of fast food outlets, takeaways, and restaurants. The use of WCO as a feedstock will prevent its disposal to drainage and rivers thereby endangering aquatic habitats. A further advantage is that households and restaurant operators can make extra income by selling their used vegetable oils, including waste palm oil (WPO), to biodiesel producers.
Palm oil, one of the most widely used vegetable oils, is produced from palm fruit and the extracted red liquid has a range of industrial and domestic applications. The global production and consumption of palm oil have continued to increase as shown in Fig. 1 [16]. According to Barrientos [17], Malaysia is the largest global producer and exporter of palm oil, exporting 16 469 thousand metric tonnes in 2017,

contributing about 8 % gross national income per capita and creating thousands of jobs [18, 19]. In most Africa countries, smallholders account for between 70 % and 90 % of oil palm growers. Growing oil palm is credited with contributing to deforestation with damaging effects on wildlife and forests. Domestic palm oil consumption production has continued to marginally increase in most African countries in the last five years (Fig. 2) [17].

Many chemical reactions take place in palm oil during frying resulting in the generation of many chemical compounds. During frying, the oil is heated repeatedly to between 170 °C and 220 °C in the presence of oxygen, and sometimes moisture, which causes the palm oil to be exposed to physical, thermal and chemical degradation. This degradation affects the properties, fatty acid composition and the degree of saturation of the oil thereby lowering the quality of the oil.

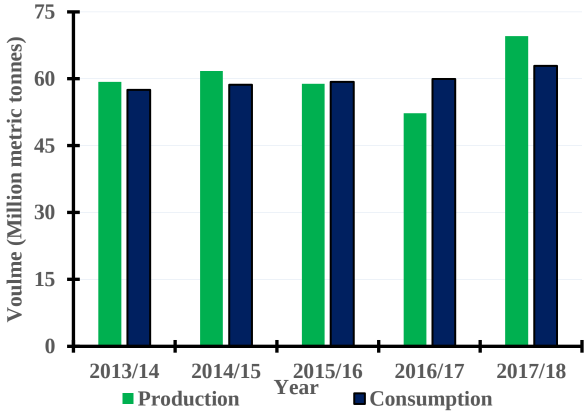

Fig. 1: Global Palm Oil Production and Consumption (Million Metric Tonnes).

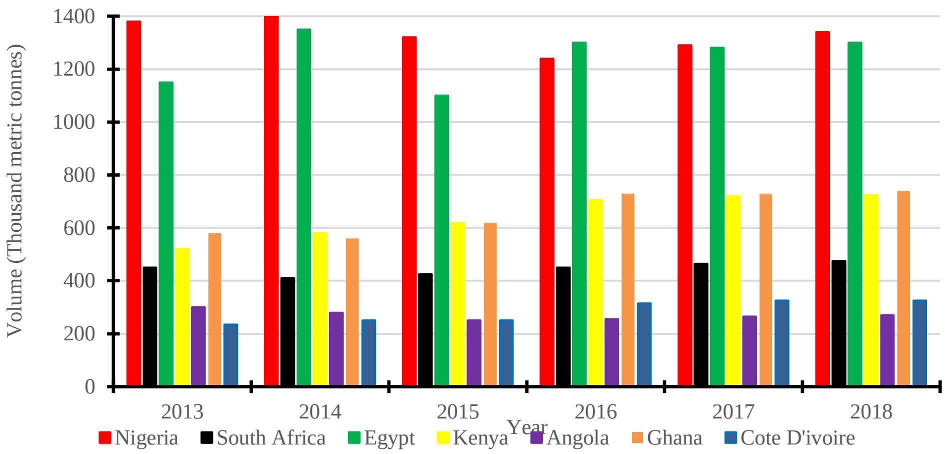

Fig. 2: Domestic Consumption of Palm Oil in Some African Countries (Thousand Metric Tonnes).

Repeated heating of palm oil at elevated temperatures for prolonged periods has been found to render the oil harmful for human consumption [20-23]. The process of transesterification is known to be a simple and low-cost conversion technique resulting in high conversion efficiency and better combustion in CI engines [24], [25].

Research on the utilization of WPO as an affordable and readily available feedstock for biodiesel production has been conducted in recent years with encouraging outcomes. Thushari et al. [26] employed esterification and transesterification to convert WPO into FAME and carried out investigations of the physicochemical properties and FA composition. Tran et al. [27] compared the chemical composition and physicochemical properties of both the WCO and the FAME derived from it and confirmed the viability of WPO for biodiesel production with 89.6 % yield. Similarly, Vargas et al. [28], Thushari and Babel [29], and Harahap et al. [30] confirmed that WPO is a readily available and cost-effective feedstock for biodiesel production with appreciable production and conversion efficiency. Ullah et al. [31] determined and compared the physiochemical properties of unused palm oil, used palm oil and waste palm cooking oil biodiesel. The waste palm cooking oil biodiesel was produced in a two-step process using an acidic ionic liquid as a catalyst and reported obvious differences in the values of the properties.

It has been established that WPO can be converted to FAME, but the question remains as to whether the food items fried in the oil affect its properties, FA composition and degree of saturation of the waste palm oil methyl ester (WPOME) derived therefrom. This present research effort, therefore, aimed to (i) investigate the food items fried in the palm oil affect its properties and FA composition; (ii) compare the properties, FA composition and degree of saturation of neat palm oil (NPO), WPO and WPOME samples; (iii) evaluate and compare the properties and FA composition of FAME produced from WPO used to fry two different types of food. The motivation for this research was to carry out a comparative study of the properties and FA compositions of NPO, WPO, and WPOME with a view to ascertaining the effect of food items on the feedstock and FAME. This current effort is limited to determining and comparing the properties and FA compositions of NPO, WPO, and WPOME with a view to determining their suitability as FAME feedstock.

2. Materials and methods

2.1. Material collection and treatment

Three palm oil samples were collected from a local takeaway restaurant in Central Durban, KwaZulu-Natal province, Republic of South Africa. The palm oil samples were an NPO sample, a WPO sample used to fry fish and chips (WPO_{FC}) and a WPO sample used to fry sausage and chips (WPO_{SC}). Other details of the samples are as shown in Table 1. The samples are treated according to Sahar et al. [32].
Waste chicken eggshells were collected from restaurants at the Howard College cafeteria, University of KwaZulu Natal, Durban, Republic of South Africa. The waste chicken eggshells were converted to calcium oxide (CaO) powder through high-temperature calcination as described by Awogbemi et al. [33]. The calcined eggshell powder was warehoused in an airtight glass vial in a desiccator to prevent contamination and oxidation. Methanol (99.5 %; Merck, South Africa, analytical grade, univAR) was used as alcohol. Activated magnesium silicate, also known by the tradename Magnesol® (analytical grade, 60-100 mesh, the molar weight of 100.39 g/mol, Sigma-Aldrich, Germany), was used as an adsorbent. Magnesol® is hygroscopic once the package is opened, so care was taken to re-seal as tightly as possible and contact with eyes was avoided.

Table 1: Details of the Oil Samples

Sample	Sample name	Food fried	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. Transesterification of waste palm oil

The acid value of WPO_{FC} and WPO_{SC} were determined to ensure that a one stage transesterification process would convert the samples to $WPOME_{FC}$ and $WPOME_{SC}$ respectively. The clean WPO_{FC} and WPO_{SC}, methanol and calcined calcium oxide (CaO) derived from waste chicken eggshell powder were mixed in a flat bottom flask in the required quantity and heated to 60 ºC. A digital thermocouple was utilized to verify the temperature of the reacting mixture throughout the 90 mins duration of the experiment. Methanol to oil ratio of 6:1, the catalyst particle size of 75 µm and 1 %w/w catalyst:oil ratio was the parametric process conditions for the transesterification reaction. Mixing was maintained by a magnetic stirrer at 1200 rpm to ensure homogeneous mixing of the reacting solution throughout the process. The resulting mixture was thereafter filtered in a vacuum filtration set up to recover the catalyst. The filtered mixture was transmitted to a separating funnel and permitted to settle for 12 hours and the glycerol coagulated at the bottom of the separating funnel. The glycerol was drained out from the bottom of the separating funnel followed by the draining of the crude biodiesel. Magnesol at 1 %w/w Magnesol:WPOME was added to the crude biodiesel and maintained at 60 °C for 30 min and mixed at 600 rpm by a magnetic stirrer. The resulting solution was filtered using vacuum filtration, heated to 110 °C to remove excess moisture and methanol trapped in the biodiesel, then further polished by using a 0.45 µm PTFE membrane syringe filter. The purified $WPOME_{FC}$ and $WPOME_{SC}$ were transferred into glass containers for further analysis and characterization.

2.3. Properties and FA determination of samples

The NPO, $WPO_{FC,}$ WPO_{SC}, and WPOME were subjected to property determination. Table 2 shows the list and method adopted for the property determination and characterization of the samples.
The concentration of FAME composition of the waste oil samples was determined by pyrolysis Gas Chromatograph Mass Spectrometer (PyGCMS) using a Shimadzu Gas Chromatograph Mass Spectrometer using an ultra-alloy-5 capillary column and GCMS-QP2010 Plus software. The choice of PyGCMS for the WPO_{FC} and WPO_{SC} samples as against the normal GCMS was to prevent clogging of the column of the GCMS machine due to the low volatility nature of the samples. Table 3 shows the PyGCMS configuration used for the analysis of neat and WPO samples. The concentration of FAMEs was determined using a Shimadzu gas chromatography-mass spectrometer (GCMS) with an ultra-alloy-5 capillary column and GCMS-QP2010 Plus software. Table 4 shows the GCMS configuration used for the analysis of WPOME samples.

Table 2: Method/Instrument of Analysis

Property	Unit	Method/Instrument	Ref.
Density @ 20 °C	Kg/m^3	ASTM D 1298	[34]
Kinematic viscosity @ 40 °C	mm^2/s	ASTM D445	[34]
Acid value	mgKOH/g	AOCS Ca 4a-40	[35]
Iodine value	Cg/g	AOCS Cd 1B-87	[35]
pH	-	pH meter	[36]
Congealing temperature	°C	Thermometer	[37]
FA composition (NPO, $WPO_{FC,}$ and WPO_{SC})	-	PYGCMS	[38]
FA composition (WPOME)	-	GCMS	[38]

Table 3: Pygcms Configuration

Injector		
Inlet temperature	240 °C	
Carrier gas	Helium	
Sample size	2 µL	
Injection mode	Split	
Split ratio	30	
Column temperature	40 °C	
Detector		
Type	PyGCMS	
Interface temperature	250 °C	
Detector gain	1.22 kV + 0.00 kV	
Oven temperature program		
Rate	Temperature (°C)	Holding time (min)
-	40	5
5.00	125	0
3.00	285	0
5.00	320	10

Column	
Type	Ultra alloy -5(MS/HT)
Specification	30 m, 0.25 mm ID, 0.25 µm
Flow rate	3.0 mL/min
Total flow	34 mL/min
Colum flow	1.00 mL/min

Table 4: GCMS Configuration

Injector		
Inlet temperature	250 °C	
Carrier gas	Helium	
Sample size	2 µL	
Injection mode	splitless	
Column temperature	50 °C	
Detector		
Type	GCMS	
Interface temperature	280 °C	
Detector gain	1.08 kV + 0.00 kV	
Oven temperature program		
Rate	Temperature (°C)	Holding time (min)
-	50	1
15.00	180	1
7.00	230	1
5.00	350	5
Column		
Type	Ultra alloy -5(MS/HT)	
Specification	30 m, 0.25 mm ID, 0.25 µm	
Flow rate	3.0 mL/min	
Total flow	4.9 mL/min	
Column flow	0.95 mL/min	

3. Result and discussion

3.1. Effect of usage on properties

The result of property determination of NPO, WPO_{FC}, WPO_{SC}, $WPOME_{FC}$, and $WPOME_{SC}$ samples are shown in Table 5. The density of NPO is higher than that of the WPO_{FC}, and WPO_{SC} samples. This can be attributed to the effect of repeated pyrolysis leading to the production of a lighter hydrocarbon fraction resulting in a lower density. The pH of NPO was higher than that of waste oil samples with WPO_{FC} being the most acidic of the three samples. This might be due to the effect of the fish oil that has adulterated the oil during frying [39]. This result was also confirmed by the acid value of the waste oil samples where the WPO_{FC} presented an acid value of 0.66 mgKOH/g compared to the acid value of 1.13 mg/KOH/g of WPO_{SC}. The lower acid value of WPO_{FC} compared to WPO_{SC} can be attributed to the effect of the fish and sausage respectively on the palm oil during frying. In terms of kinematic viscosity, usage makes oil more viscous; WPO_{FC} was found to be more viscous than WPO_{SC} as a result of the effect of the fish oil on the NPO. The kinematic viscosity at 40 °C of the WPO samples was higher than that of NPO. This is in agreement with earlier results reported by Chuah et al. [40].
Transesterification altered the density and kinematic viscosity of the samples. As shown in Table 5, the density and kinematic viscosity of the WPO samples were higher than those of the FAME derived from the WPO samples. This was due to the effect of the production processes involved in the conversion of the waste palm oil into methyl esters. The transesterification reaction caused the $WPOME_{FC}$ and $WPOME_{SC}$ to be less dense and less viscous than WPO_{FC} and WPO_{SC}. Kinematic viscosity of WPO samples are higher than that of NPO due to the formation

Table 5: Properties of Neat and Waste Oil Samples

Properties	NPO	WPO_{FC}	WPO_{SC}	$WPOME_{FC}$	$WPOME_{SC}$	ASTM D6751	EN 14214
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	860	870	-	860 - 900
Kinematic Viscosity @ 40 °C (mm^2/s)	27.96	44.25	38.41	4.5	3.8	1.9 – 6	3.5 - 5
Iodine value (cg/g)	-	81.7	54.2	72.5	52.3	-	120 max
Acid value (mg KOH/g)	-	0.66	1.13	0.28	0.42	0.05 max	0.5 max

of dimeric and polymeric acids and glycerides during usage, and normally higher than the viscosity of FAME while lowering the density [41], [42]. These trends agree with similar work by Uddin et al. [43], and Thushari et al. [26]. The iodine values of the WPOME samples were lower than those of the WPO samples. A higher iodine value was recorded for the WPO_{FC} sample compared to the WPO_{SC} sample, and for the $WPOME_{FC}$ sample compared to the $WPOME_{SC}$ sample. The difference in the lower iodine values of WPO samples can be traced to the effect of food fried, heating time, and probably the storage condition before analysis. The lower iodine value of WPOME samples compared with WPO samples can be adduced to the effect of heating during the transesterification process [44], [45]. High degree of unsaturation of WPO results in polymerization of FAME as a result of the formation of epoxide due to the addition of oxygen in double bonds [32]. This agrees with the outcome of previous research by Chuah et al. [46].
Considering the fingerprint of both 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 Fig. 4. 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 samples showed that NPO presented with the highest pH followed by WPO_{SC} and WPO_{FC}. The NPO had a 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 enhanced the transesterification process.

The viscosity of NPO in this research as shown in Table 5 was 27.96 mm^2/s which falls in the range of the 25.6 mm^2/s reported by Maneerung et al. [47] and 31.78 mm^2/s reported by Zein et al. [48] though the density of both WPO_{FC} and WPO_{SC} were found to be higher than the 902 kg/m^3 reported by Maneerung et al. [47]. These properties affect the FA compositions and the degree of saturation, and therefore their tendency to be converted to FAME.

3.2. Effect of usage on FA composition

The result of FA composition of the NPO, WPO_{FC}, and WPO_{SC} as determined by the PyGCMS and that of $WPOME_{FC}$ and $WPOME_{SC}$ as determined by GCMS are shown in Table 6. NPO was found to contain linoleic acid, and brassidic acid, WPO_{FC} consisted of mainly oleic and palmitic acids, while WPO_{SC} was made up of mainly palmitic and linoleic acids. However, $WPOME_{FC}$ and $WPOME_{SC}$ were made up of oleic and palmitic acids and linoleic and caproleic acid respectively. Unlike NPO, oleic and palmitic acids were present in the WPO samples, while the brassidic acid present in the NPO was absent in the WPO samples. This may be due to high-temperature degradation, oxidation as a result of moisture addition, and contamination occasioned by the food items. The effect of fish oil contamination triggered the presence of stearic acid only in WPO_{FC}. However, these results did not wholly agree with those reported by Kadapure et al. [49]. 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. [49] obtained their palm oil samples and carried out their research in Belgium and the samples were analyzed by means of a gas chromatographic method. Also, the food items fried in the palm oil and the duration of usage were not disclosed. There was no guarantee that WPO was obtained from the same source as the neat oil. Chuah et al. [40] reported the same FA composition for neat cooking oil and waste cooking oil which is not different from the outcome of this research as it relates to NPO and the WPO samples. Also the presence of some transition metals in the food items, for example, iron is present in meat, increased the rates of degradation and thermal degradation of the oil [50].

Oleic and palmitic acids were observed to be the most dominant FA in both WPO_{FC} and $WPOME_{FC}$ while the stearic and linoleic acids in WPO_{FC} were converted to brassidic acid, pelargonic acid, lauric acid, behenic acid, and caproleic acid in $WPOME_{FC}$ as a result of the transesterification process. Apart from the contamination of the oil by the food, moisture is also added to the oil during frying. Addition of salt, sauces, intermittent heating and cooling during repeated frying results into the deterioration of the oil and the change in its degree of saturation. The effect of hydrogenation which occurs during frying can also contribute to the conversion [51]. The process of conversion of WPO_{SC} to $WPOME_{SC}$ by transesterification introduced caproleic acid into FAME. Oleic, palmitic and caproleic acids are the common FA in both $WPOME_{FC}$ and $WPOME_{SC}$ which can be traced to the properties of the WPO sample, notwithstanding the type of food which they fried.

The NPO used in this research consisted of 52.55 % PUFA which was reduced to 37.35 % in WPO_{SC} and 3.76 % in WPO_{FC} as shown in Figure 3. The low percentage of SFA in NPO was increased in the WPO samples due to usage which confirmed the outcome of similar research by Kadapure et al. [49]. The effect of the food items the oil fried greatly influenced the degree of saturation of both the WPO_{FC} and WPO_{SC}. The 54.75 % SFA in WPO_{SC} was reduced to 37.67 % in WPO_{FC} while the 7.9 % MUFA and 37.37 % PUFA in WPO_{SC} became 58.57 % MUFA and 3.78 % PUFA in WPO_{FC}. The FA composition for the WPO_{FC} and WPO_{SC} were similar to the outcome of FA analysis of WPO by Kadapure et al. [49]. However, the high percentage of PUFA in NPO differed greatly from the result of similar research by Maneerung et al. [47]. No explanation was found for the differences in the FA compositions other than the different geographical sources and species of the palm oil samples.

The process of transesterification not only triggered the increase of the 58.57 % MUFA and 37.67 % SFA in WPO_{FC} to 69.58 % MUFA and 30.43 % SFA in $WPOME_{FC}$ but also caused the 3.76 % PUFA in WPO_{FC} to completely disappear. The percentage of PUFA in WPO_{SC} and $WPOME_{SC}$ remained almost the same while there was a drastic increment in MUFA from 7.9 % to 46.05 % as a result of the trans-esterification process. The influence of food items was noticeable in the FA composition and degree of saturation of both $WPOME_{FC}$ and $WPOME_{SC}$. Fig. 4 compares the FA composition of WPO_{FC} and WPO_{SC} in this research to the outcomes of similar research obtained from the literature. Maneerung et al. [47], Zein et al. [48] and Nguyen et al. [52] reported almost the same value for MUFA for waste oil samples. Maneerung et al. [47] and Nayak et al. [53] reported close values of PUFA though lower than that reported by Rahmanlar et al. [54]. From the eight samples of WPO shown in Fig. 4, it can be deduced that there is no consensus on the degree of saturation and type of chain in all the WPO samples. Degradation temperature, usage, duration and degree of usage, type food items that were fried, among other elements, dictates the FA composition and degree of saturation of the WPO samples.

Table 6: Fatty Acid Composition of NPO, WPO, and WPOME

Common name	Structure	NPO	WPO_{FC}	WPO_{SC}	$WPOME_{FC}$	$WPOME_{SC}$
Oleic acid	C18:1	-	58.57	7.9	63.96	20.35
Palmitic acid	C16:0	-	36.13	54.75	23.72	16.2
Capric acid	C10:0	5.92	-	-	-	-
Stearic acid	C18:0	13.72	1.54	-	-	-
Linoleic acid	C18:2	52.55	3.76	37.35	-	37.75
Brassidic acid	C22:1	27.81	-	-	-	-
Pelargonic acid	C9:0	-	-	-	1.1	-
Lauric acid	C12:0	-	-	-	3.47	-
Behenic acid	C22:0	-	-	-	2.14	-
Caproleic acid	C10:1	-	-	-	5.62	25.7

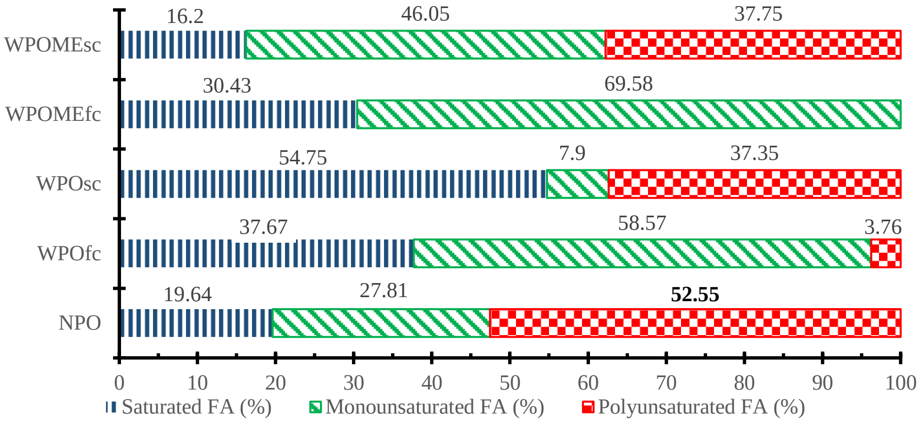

Fig. 3: Degree of Saturation of NPO, WPO_{FC}, WPO_{SC}, $WPOME_{FC}$ and $WPOME_{SC}$.

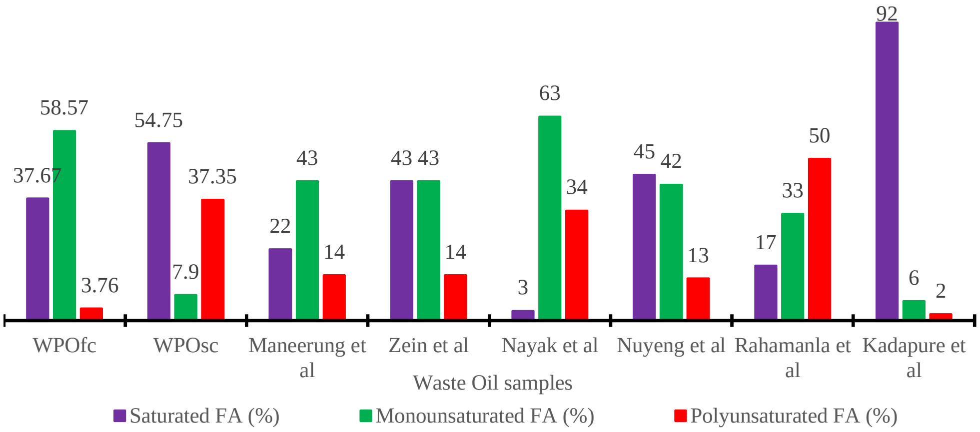

Fig. 4: SFA, MUFA and PUFA Compositions of WPO Samples.

4. Conclusion

The application of otherwise known waste raw materials such as used vegetable oil from restaurants, households and canteens and takeaway outlets, waste animal (beef, chicken, pig, etc) fats from slaughterhouses and abattoirs, rendered fats, and grease recovered from wastewater treatment plants have gained acceptance as biodiesel feedstock. Though they are low-grade feedstocks, appropriate selection of production and refining techniques ensure derivation of the benefits in their usage. They are cheaper than other forms of feedstock and help in solving problems waste oil and fats disposal challenges. The properties and the FA composition of NPO, WPO samples and WPOME were investigated with a view to determining the effects of usage and food items on the samples. The trajectory from NPO through WPO used to fry particular food items and the WPOME derived from the transesterification of the WPO samples were reported. The following inferences can be drawn:

- The pH and density of WPO samples were found to be lower than those 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 those of WPO_{SC} but WPO_{FC} had higher iodine and viscosity values.
- The degree of usage, the food fried, the effect of repeated heating and cooling, storage environment, the type of oil, the source of the NPO, and transesterification process have been found to affect the concentration of the FAME composition, and degree of saturation.
- NPO was found to consist of 52.55 % PUFA and 27.81 % MUFA.
- 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 fried.
- The degree of saturation of WPO_{FC} and WPO_{SC} was less than that of NPO, in most cases, and agrees with some of the results reported in the literature.
- The low acid value of the WPO samples signifies their suitability for FAME production by transesterification.
- The density of $WPOME_{FC}$ was found to be higher than that of $WPOME_{SC}$; on the other hand, the kinematic viscosity of $WPOME_{FC}$ was higher than that of $WPOME_{SC}$.
- The 52.55 % PUFA in NPO was converted to 3.76 % in WPO_{FC} and completely disappeared in $WPOME_{FC}$ while the MUFA was found to increase from 27.81 % in NPO to 58.57 % in WPO_{FC} and 69.58 % in $WPOME_{FC}$.
- The 19.64 % SFA in NPO increased to 54.75 % in WPO_{SC} but reduced to 16.2 % in $WPOME_{SC}$ while the MUFA which was 27.81 % in NPO reduced to 7.9 % in WPO_{SC} but increased to 46.05 % in $WPOME_{SC}$.

The significance of this investigation is that the type of food that NPO fries affects the FA composition, properties, and degree of saturation of palm oil and consequently influences the FA composition and properties of the resulting FAME. The FA composition and properties of FAME will, in turn, have considerable influence on the engine performance and emission characteristics of a CI engine fuelled by FAME as well as the stability of the FAME. In conclusion, when selecting WCO as a feedstock for transesterification, consideration should be paid to these three factors: the degree of usage, the type of food fried by the palm oil, and the NPO source.

Going forward, considerable research opportunities exist regarding the effect of frying temperature and time on NPO, the cycle of frying, palm oil species, etc. Such research will contribute towards establishing the optimal conditions to obtain feedstock for FAME production from palm oil.

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References

[1] P. Sadorsky, "Shifts in energy consumption driven by urbanization. In: Davidson," *The Oxford Handbook of Energy and Society,* p. 179, 2018. https://doi.org/10.1093/oxfordhb/9780190633851.013.17.
[2] Worldometers. "World Population by Year" . Available on http://www.worldometers.info/world-population/world-population-by-year/ [Online].
[3] F. Soto *et al.*, "A comparative study of performance and regulated emissions in a medium-duty diesel engine fueled with sugarcane diesel-farnesane and sugarcane biodiesel-LS9," *Energy,* vol. 176, pp. 392-409, 2019/06/01/ 2019. https://doi.org/10.1016/j.energy.2019.04.011.
[4] I. Örs, S. Sarıkoç, A. E. Atabani, S. Ünalan, and S. O. Akansu, "The effects on performance, combustion and emission characteristics of DICI engine fuelled with TiO2 nanoparticles addition in diesel/biodiesel/n-butanol blends," *Fuel,* vol. 234, pp. 177-188, 2018/12/15/ 2018. https://doi.org/10.1016/j.fuel.2018.07.024.
[5] L. A. Raman, B. Deepanraj, S. Rajakumar, and V. Sivasubramanian, "Experimental investigation on performance, combustion and emission analysis of a direct injection diesel engine fuelled with rapeseed oil biodiesel," *Fuel,* vol. 246, pp. 69-74, 2019/06/15/ 2019. https://doi.org/10.1016/j.fuel.2019.02.106.
[6] J. C. Kurnia, S. V. Jangam, S. Akhtar, A. P. Sasmito, and A. S. Mujumdar, "Advances in biofuel production from oil palm and palm oil processing wastes&58; A review," *Biofuel Research Journal,* vol. 3, no. 1, pp. 332-346, 2016. https://doi.org/10.18331/BRJ2016.3.1.3.
[7] M. Saifuddin, P. Goh, W. Ho, K. Moneruzzaman, and A. Fatima, "Biodiesel production from waste cooking palm oil and environmental impact analysis," *Bulgarian Journal of Agricultural Science,* vol. 20, no. 1, pp. 186-192, 2014.
[8] Biofuel Fact Sheet: Fatty Acid Methyl Esters (FAME) (2011) Available from: http://www.etipbioenergy.eu/images/fame-fact-sheet.pdf [Online].
[9] M. F. Awalludin, O. Sulaiman, R. Hashim, and W. N. A. W. Nadhari, "An overview of the oil palm industry in Malaysia and its waste utilization through thermochemical conversion, specifically via liquefaction," *Renewable and Sustainable Energy Reviews,* vol. 50, pp. 1469-1484, 2015/10/01/ 2015. https://doi.org/10.1016/j.rser.2015.05.085.
[10] A. K. Azad, M. Rasul, M. M. K. Khan, S. C. Sharma, and M. Hazrat, "Prospect of biofuels as an alternative transport fuel in Australia," *Renewable and Sustainable Energy Reviews,* vol. 43, pp. 331-351, 2015. https://doi.org/10.1016/j.rser.2014.11.047.
[11] A. E. Atabani, A. S. Silitonga, I. A. Badruddin, T. Mahlia, H. Masjuki, and S. Mekhilef, "A comprehensive review on biodiesel as an alternative energy resource and its characteristics," *Renewable and sustainable energy reviews,* vol. 16, no. 4, pp. 2070-2093, 2012. https://doi.org/10.1016/j.rser.2012.01.003.
[12] I. B. Banković-Ilić, I. J. Stojković, O. S. Stamenković, V. B. Veljkovic, and Y.-T. Hung, "Waste animal fats as feedstocks for biodiesel production," *Renewable and Sustainable Energy Reviews,* vol. 32, pp. 238-254, 2014/04/01/ 2014. https://doi.org/10.1016/j.rser.2014.01.038.
[13] H. H. Mardhiah, H. C. Ong, H. H. Masjuki, S. Lim, and H. V. Lee, "A review on latest developments and future prospects of heterogeneous catalyst in biodiesel production from non-edible oils," *Renewable and Sustainable Energy Reviews,* vol. 67, pp. 1225-1236, 2017/01/01/ 2017. https://doi.org/10.1016/j.rser.2016.09.036.
[14] J. Janaun and N. Ellis, "Perspectives on biodiesel as a sustainable fuel," *Renewable and Sustainable Energy Reviews,* vol. 14, no. 4, pp. 1312-1320, 2010. https://doi.org/10.1016/j.rser.2009.12.011.
[15] I. Atadashi, M. Aroua, A. A. Aziz, and N. Sulaiman, "Production of biodiesel using high free fatty acid feedstocks," *Renewable and sustainable energy reviews,* vol. 16, no. 5, pp. 3275-3285, 2012. https://doi.org/10.1016/j.rser.2012.02.063.
[16] Statista. Consumption of vegetable oils worldwide from 2013/14 to 2018/2019, by oil type (in million metric tons). Available from: https://www.statista.com/statistics/263937/vegetable-oils-global-consumption/ [Online].
[17] M. Barrientos. Palm oil. Available on https://www.indexmundi.com/about.html [Online].
[18] Roundtable on Sustainable Palm Oil (RSPO) - 2011 (2012) Malaysia sets record as world's largest producer of certified sustainable palm oil. 2011. Available from: https://rspo.org/news-and-events/news/malaysia-sets-record-as-worlds-largest-producer-of-certified-sustainable-palm-oil [Online].
[19] R. Abdullah, "World Palm Oil supply, demand, price and prospects: Focus on Malaysian and Indonesian Palm Oil industries," *Oil Palm Industry economic Journal,* vol. 11, no. 2, pp. 13 - 25, 2011.
[20] D. T. d. Almeida, F. M. Curvelo, M. M. Costa, T. V. J. F. S. Viana, and Technology, "Oxidative stability of crude palm oil after deep frying akara (Fried Bean Paste)," vol. 38, no. 1, pp. 142-147, 2018. https://doi.org/10.1590/1678-457x.02217.
[21] N. Idun-Acquah, G. Y. Obeng, E. J. S. Mensah, and Technology, "Repetitive Use of Vegetable Cooking Oil and Effects on Physico-Chemical Properties–Case of Frying with Redfish (Lutjanus fulgens)," vol. 6, no. 1, pp. 8-14, 2016.
[22] T. Mengistie, A. Alemu, and A. J. C. I. Mekonnen, "Comparison of physicochemical properties of edible vegetable oils commercially available in Bahir Dar, Ethiopia," vol. 4, no. 2, pp. 130-135, 2018.
[23] M. Wanjiya, M. Makangila, L. J. I. J. o. E. Mukosha, Energy, and Environment, "Used Cooking Oils as a Source Material for Biodiesel Production: Case Study for Kitwe Town, Zambia," vol. 3, no. 4, p. 32, 2018. https://doi.org/10.11648/j.ijeee.20180304.11.
[24] E. M. Shahid and Y. Jamal, "Production of biodiesel: a technical review," *Renewable and Sustainable Energy Reviews,* vol. 15, no. 9, pp. 4732-4745, 2011. https://doi.org/10.1016/j.rser.2011.07.079.
[25] M. Balat and H. Balat, "Progress in biodiesel processing," *Applied energy,* vol. 87, no. 6, pp. 1815-1835, 2010. https://doi.org/10.1016/j.apenergy.2010.01.012.
[26] I. Thushari, S. Babel, and C. Samart, "Biodiesel production in an autoclave reactor using waste palm oil and coconut coir husk derived catalyst," *Renewable Energy,* vol. 134, pp. 125-134, 2019/04/01/ 2019. https://doi.org/10.1016/j.renene.2018.11.030.
[27] T. T. V. Tran *et al.*, "Green biodiesel production from waste cooking oil using an environmentally benign acid catalyst," *Waste management,* vol. 52, pp. 367-374, 2016. https://doi.org/10.1016/j.wasman.2016.03.053.
[28] E. M. Vargas, M. C. Neves, L. A. Tarelho, and M. I. Nunes, "Solid catalysts obtained from wastes for FAME production using mixtures of refined palm oil and waste cooking oils," *Renewable Energy,* 2019. https://doi.org/10.1016/j.renene.2019.01.048.
[29] I. Thushari and S. Babel, "Preparation of solid acid catalysts from waste biomass and their application for microwave-assisted biodiesel production from waste palm oil," *Waste Management & Research,* vol. 36, no. 8, pp. 719-728, 2018. https://doi.org/10.1177/0734242X18789821.
[30] F. Harahap, S. Silveira, and D. Khatiwada, "Cost competitiveness of palm oil biodiesel production in Indonesia," *Energy,* vol. 170, pp. 62-72, 2019. https://doi.org/10.1016/j.energy.2018.12.115.
[31] Z. Ullah, M. A. Bustam, and Z. Man, "Biodiesel production from waste cooking oil by acidic ionic liquid as a catalyst," *Renewable Energy,* vol. 77, pp. 521-526, 2015/05/01/ 2015. https://doi.org/10.1016/j.renene.2014.12.040.
[32] Sahar *et al.*, "Biodiesel production from waste cooking oil: An efficient technique to convert waste into biodiesel," *Sustainable Cities and Society,* vol. 41, pp. 220-226, 2018/08/01/ 2018. https://doi.org/10.1016/j.scs.2018.05.037.

[33] O. Awogbemi, F. L. Inambao, and E. I. Onuh, "Development and Characterization of Chicken Eggshell waste as Potential Catalyst For Biodiesel Production," *International Journal of Mechanical Engineering and Technology,*, vol. 9, no. 12, pp. 1329 - 1346, 2018.

[34] *BS EN 14214:2012+A2:2019 (2019) Liquid petroleum products. Fatty acid methyl esters (FAME) for use in diesel engines and heating applications. Requirements and test methods. Available from: https://shop.bsigroup.com/ProductDetail/?pid=000000000030217517*.

[35] M. Bockisch, *Fats and oils handbook (Nahrungsfette und Öle)*. Amsterdam: Elsevier, 2015.

[36] Use of pH meter. Available from: webserver.mbi.ufl.edu/~rowland/protocols/phmeter.pdf [Online]. Congealing temperature. Available from: https://www.drugfuture.com/Pharmacopoeia/usp38/data/v38332/usp38nf33s2_c651.html [Online].

[37] *Shimadzu Corporation (2008) Equipment manual. Gas Chromatograph Mass Spectrometer GCMS-QP2010 Plus. Scimadzu Corporation, Japan,*. Scimadzu Corporation, Japan.

[38] P. Verma and M. P. Sharma, "Review of process parameters for biodiesel production from different feedstocks," *Renewable and Sustainable Energy Reviews,* vol. 62, pp. 1063-1071, 2016/09/01/ 2016. https://doi.org/10.1016/j.rser.2016.04.054.

[39] L. F. Chuah, J. J. Klemeš, S. Yusup, A. Bokhari, and M. M. Akbar, "Influence of fatty acids in waste cooking oil for cleaner biodiesel," *Clean Technologies and Environmental Policy,* vol. 19, no. 3, pp. 859-868, 2017. https://doi.org/10.1007/s10098-016-1274-0.

[40] M. Canakci and A. N. Özsezen, "Evaluating waste cooking oils as alternative diesel fuel," *Gazi University Journal of Science,* vol. 18, no. 1, pp. 81-91, 2005.

[41] T. H. Doğan, "The testing of the effects of cooking conditions on the quality of biodiesel produced from waste cooking oils," *Renewable Energy,* vol. 94, pp. 466-473, 2016/08/01/ 2016. https://doi.org/10.1016/j.renene.2016.03.088.

[42] M. N. Uddin, K. Techato, M. G. Rasul, N. M. S. Hassan, and M. Mofijur, "Waste coffee oil: A promising source for biodiesel production," *Energy Procedia,* vol. 160, pp. 677-682, 2019/02/01/ 2019. https://doi.org/10.1016/j.egypro.2019.02.221.

[43] J. Chebet, T. Kinyanjui, and P. K. Cheplogoi, "Impact of frying on iodine value of vegetable oils before and after deep frying in different types of food in Kenya," *Journal of Scientific and Innovative Research,* vol. 5, no. 5, pp. 193-196, 2016.

[44] E. A. Alhibshi, J. A. Ibraheim, and A. S. Hadad, "Effect of heat processing and storage on characteristic and stability of some edible oils," in *Proceedings 6th Int'l Conference on Agriculture, Environment and Biological Sciences. doi*, 2016, vol. 10.

[45] L. F. Chuah, S. Yusup, A. R. Abd Aziz, A. Bokhari, J. J. Klemeš, and M. Z. Abdullah, "Intensification of biodiesel synthesis from waste cooking oil (Palm Olein) in a Hydrodynamic Cavitation Reactor: Effect of operating parameters on methyl ester conversion," *Chemical Engineering and Processing: Process Intensification*, vol. 95, pp. 235-240, 2015/09/01/ 2015. https://doi.org/10.1016/j.cep.2015.06.018.

[46] T. Maneerung, S. Kawi, Y. Dai, and C.-H. Wang, "Sustainable biodiesel production via transesterification of waste cooking oil by using CaO catalysts prepared from chicken manure," *Energy Conversion and Management,* vol. 123, pp. 487-497, 2016/09/01/ 2016. https://doi.org/10.1016/j.enconman.2016.06.071.

[47] Y. M. Zein, A. K. Anal, D. Prasetyoko, and I. Qoniah, "Biodiesel Production from Waste Palm Oil Catalyzed by Hierarchical ZSM-5 Supported Calcium Oxide," *Indonesian Journal of Chemistry,* vol. 16, no. 1, pp. 98-104, 2016. https://doi.org/10.22146/ijc.21184.

[48] S. A. Kadapure *et al.*, "Studies on process optimization of biodiesel production from waste cooking and palm oil," vol. 11, no. 3, pp. 167-172, 2018. https://doi.org/10.1080/19397038.2017.1420107.

[49] W. E. Artz, P. C. Osidacz, and A. R. Coscione, "Iron accumulation in oil during the deep-fat frying of meat," *Journal of the American Oil Chemists' Society,* vol. 82, no. 4, p. 249, 2005. https://doi.org/10.1007/s11746-005-1063-8.

[50] E. Choe and D. Min, "Chemistry of deep-fat frying oils," *Journal of food science,* vol. 72, no. 5, pp. R77-R86, 2007. https://doi.org/10.1111/j.1750-3841.2007.00352.x.

[51] V. P. Nguyen, H. H. M. Nguyen, D. T. Nguyen, H. L. Nguyen, and T. M. Huynh, "Optimization of biodiesel production from waste cooking oil using static mixer technology in Vietnam," *Biofuels,* pp. 1-8, 2018. https://doi.org/10.1080/17597269.2018.1426165.

[52] S. K. Nayak, P. C. Mishra, and G. R. Behera, "Experimental investigation on dual-fuel engine utilizing waste cooking oil and producer gas," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects,* vol. 39, no. 4, pp. 369-376, 2017. https://doi.org/10.1080/15567036.2015.1122684.

[53] İ. Rahmanlar, S. Yücel, and D. Özçimen, "The Production of methyl esters from waste frying oil by microwave method," *Asia-Pacific Journal of Chemical Engineering,* vol. 7, no. 5, pp. 698-704, 2012. https://doi.org/10.1002/apj.620.