Investigation of Anaerobic Digested Pyrolysis oil and Waste Derived Biodiesel Blends as Sustainable Fuel for Marine Engine Application

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Abstract

In anaerobic digestion (AD) plants around 40% of the feed waste is utilised for biogas generation while the remainder is used as a fertiliser that is rich in oil that could be further utilised through pyrolysis. Dry AD waste, subjected to intermediate pyrolysis, generated a digested pyrolysis oil (DPO) of high viscosity (473mm^2/s) and low energy content (26 MJ/kg). To improve its fuel characteristics, we blended DPO with either used cooking oils (high in unsaturated fatty acids) or lamb fat (high in saturated fatty acids) using solvents of differing polarity including alcohols varying in chain length and hence aqueous miscibility from C_1(methanol) to C_5 (pentanol) and diethylether (DEE, a non-polar solvent). Five blends were prepared, typically consisting of 10-20% DPO, 20% solvent (alcohol or DEE) and 60-70% cooking oil or lamb fat. Physical properties of DPO blends e.g., viscosity, density, heating value, total acid number and flash point were found to be lower than neat DPO but increased about 25-40% over a storage period of 8 months. The blends were more stable than neat biodiesel as assessed by FT-IR spectroscopy. The elemental analysis (C, H, N, S and O) showed that atomic ratio of DPO blends;

H:C, H:O, H:N and C:N were found to be lower than biodiesel and DPO fuels, respectively. Overall, the properties of DPO blends met the Marine Fuel Standard (Marine ISO 8217) and hence could be considered as a suitable replacement for bunker oil to protect marine environments following further testing and scale up studies.

Keywords: Characterisation, Ageing, Digested; Pyrolysis oil, Waste cooking biodiesel, Animal fat biodiesel

1. Introduction

According to International Maritime Organization's (IMO) regulations (IMO23), the organisation remains committed to decarbonising international shipping by at least 40% by 2030 [1]. The IMO23 greenhouse gas emissions (GHG) strategy states that technological innovations and global promotion of sustainable alternative fuels for shipping would be the integral to achieve its ambitions [2, 3]. As a matter of urgency, the IMO aims to phase out fossil fuels as soon as possible, while promoting the increase in the proportion of renewable energy produced from biomass such as agriculture, food and household wastes that currently create environmental issues [4]. Waste has an adverse environmental impact, causing pollution to air, water and soil which cause negative impact on our ecosystem [2] and affecting both humans that has been estimated to result in 4.1 million deaths per day [2]. Throughout the last three decades, several international accords have been signed to tackle the process of replacing fossil renewable sources on a global scale including the Paris Agreement [5]. Many nations have decided to establish their own domestic carbon and energy policy frameworks for 2030 and beyond, to make a transition to a low carbon economy [5]. As a result, initiatives have been taken to adopt alternatives resources that will allow fossil fuels to be gradually phased out of the power generation and transportation sectors [6].

The breakdown of organic bio-degradable wastes must be either aerobic or anaerobic [7]. Compost is created when organic matter is converted under aerobic conditions. Currently, there are 685 operational AD Plants in the United Kingdom (including sludge digesters at Wastewater Treatment Plants) according to ADBA. These AD plants generate AD waste [8] that can be used as a fertiliser. Excessive usage of dry AD waste as a fertiliser results in anthropogenic gases being produced which contributes to GHG emissions [9]. Furthermore, only around 40% of the feed waste is utilised for biogas generation in AD facilities, with the other 60% being digested waste [9]. This large volume of dry AD waste necessitates its use for a different waste management system or as an energy source [9, 10]. Pyrolysis is the most promising option for converting this dry AD waste into liquid oil [11]. In this regard, anaerobically digested rice straw was converted to pyrolysis oil by Liang et al. [11]. To produce digested pyrolysis oil (DPO), they used the rice straw for anaerobic digestion followed by pyrolysis [11]. The pyrolysis oil can easily blend with diesel and biodiesel for power generation. Recently, anaerobic digestates of algae have also shown improved pyrolysis oil characteristics suitable for fuel applications [10, 12].

The growth in food industries due to increased population has resulted in enormous waste in the form of used cooking oil and animal wastes [13]. Used cooking oil is a suitable choice for biodiesel production, because of the higher free fatty acid (FFA) content [14]. The most attractive source for biodiesel production is recycling the wastes into liquid biodiesel such as animal fat, used cooking oil and waste solid biomass [14]. To improve the biodiesel quality, many researchers have proposed different biodiesel blending methodologies such as pre-mixing and post-mixing based on saturation and unsaturation level of the feedstocks [15-17]. High levels of polyunsaturated fatty acids such as linoleic acid (18:2) and linolenic acid (α-18:3) are more prone to oxidation due to the presence of additional C=C bonds [18]. The breakdown products of the fatty acids such as ketones and aldehydes have corrosive characteristics and accelerate engine wear [18]. Since a higher unsaturation level of biodiesel is a problem for engine application, it can be eliminated by blending various biodiesels with different saturation levels. Acharya et al. [15], explained that blending of different biodiesels from Mahua and Jatropha can improve the oxidation stability due to an increase in the saturation level. Mejia et al. [17] investigated post-mixed palm and castor biodiesels that increased the saturation level of the blend oil, which eventually helped to reduce the viscosity of the biofuel. A similar investigation was done by Masera et al. [16], with the post-mixing of waste cooking oil and animal fat oil in different ratios. They found that increasing the level of saturation increased the cetane number as compared to individual biodiesel. Other advantages of animal fats for biodiesel production include less corrosive nature of the fuel, and the reduced disposal problem [16].

Most biodiesels have a poor storage stability, which is a big disadvantage to use it as fuel [19]. Biodiesel fuel qualities are known to be affected by oxidation, and prolonged oxidation alters the fuel properties beyond the maximum limit [19]. When a hydrogen atom is removed from the methyl carbon it generates a free radical, which subsequently reacts with ambient oxygen to form hydroperoxides, which are the principal oxidation products of biodiesel oxidation [20]. Bouaid et al. [21], stored biodiesel fuels with various saturated and unsaturated methyl ester compositions for 30 months and found that markers of oxidation increased while the unsaturation index fell indicating instability in the fuel. Long-term storage of biodiesel causes the creation of polymers formed from crosslinking of the oxidised fatty acids creating ‘sticky gums’ and sediments, which cause issues in the fuel supply system, particularly in the fuel injection pump. As a result, biodiesel's long-term storage stability is a major challenge that must be addressed before it can be used in automobile engines. In terms of the production of feedstock, the DETR (Department of Energy, Transport, and Regions) calculates that the UK produces about 100,000 tonnes of recoverable waste oil year [22]. Although it can be challenging to get an accurate determination because many businesses don't keep thorough records of their disposal [22]. The likes of British Petroleum (BP) and Crown Oil already use cooking oil and transesterify it into biodiesel. In many nations, the technology to create alcohols from agricultural waste is highly developed. The UK's bioethanol production grew by 24% to 326 million litres in 2020, which is 35% of the country's anticipated 927 million litre production capacity [23]. Therefore, the UK has the opportunity to apply cutting-edge blending techniques to employ the oil from AD pyrolysis.

Due the sustainability and renewable in nature, biodiesel/biofuels have great impact on marine diesel engine out emissions as compared to marine diesel fuel. A marine diesel engine running on *Parinari polyandra* biodiesel and diesel blends was the subject of an investigation by Ogunkunle et al., [24] Except for nitrogen oxides, they claimed that exhaust emissions were determined to be lower than those of diesel. Carbon dioxide and carbon monoxide both experienced significant percentage reductions of

81.7% and 65.7%, respectively. The B10 (10% biodiesel+90% diesel) blend was discovered to be the best one for enhancing engine performance, while B30 showed steady performance traits without any changes to the diesel engine. Yang et al.[25] used a variety of blend ratios of BD0 (from 0%, up to 100% at various engine loads and speeds to conduct a study that was identical to the one done with biodiesel and ultra-low sulphur diesel. According to their findings, the majority of the gaseous pollutants, particularly CO, dropped as the biodiesel blend ratio rose, while the number of particulates increased.

In this study, the digestate recovered from anaerobic digestion of food waste was subjected to intermediate pyrolysis and the derived bio-oil (pyrolysis oil, DPO) was blended with biodiesel derived from animal fats or waste cooking oil. The above literature survey shows that many research works have evaluated the use of different types of waste derived biodiesel and their blends. Recent research highlighted the potential of pyrolysis oils as renewable biofuels for non-road diesel engine applications. However, due to their low energy content, high acidity and viscosity, upgradation is required prior to use. Therefore, a long-term storage study of ternary blend of DPO oil, animal fat biodiesel, waste cooking oil biodiesel with oxygenated additives has been performed in this investigation. The objectives of the study were to: (a) prepare different homogeneous blends of DPO with waste cooking oil biodiesel (WCOB), lamb fat biodiesel with additives of varying polarity (determined by dielectric constant, (Ɛ) (methanol Ɛ=33.3butanol Ɛ=17.8, pentanol Ɛ=15.3, diethyl ether Ɛ=4.3) (b) thoroughly characterise DPO/biodiesel blends and evaluate the fuel properties after 8 months of storage period, and (c) compare the properties of the blends with diesel and marine fuel standards to demonstrate the applicability of the fuels.

2. Material and methods

The procedure for preparing the fuel blends is given in the flow diagram (Fig. 1). To decrease the viscosity of the DPO/biodiesel, alcohols of varying polarity or diethyl ether (DEE, a non- polar solvent) were used as co-solvents. It was observed that five of the blended samples (samples 1-5) were homogeneous (Table 1). On standing, phase separation was observed for sample 6. All samples were stored in tightly closed vessels in the dark for a period of 8 months at a temperature of15-20 °C. After 8 months, characterisation of all the blended sample was performed and their properties were compared with the fresh samples and Marine Fuel Standards (Marine ISO 8216 and Marine ISO 8217). for the use in marine diesel engine and boiler applications.

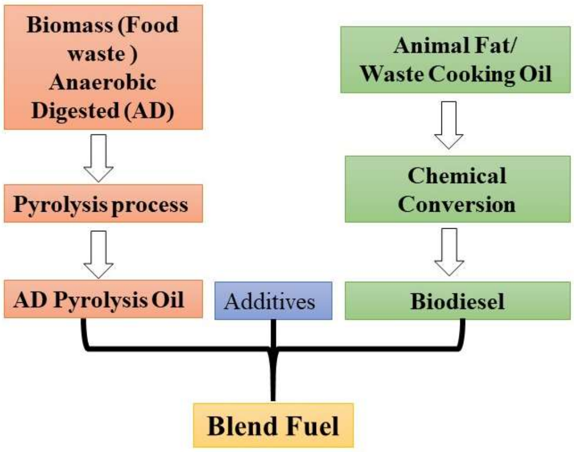


Fig.1. Flowchart depicting the procedure to prepare fuel blends.

Table 1. Blend compositions

Sl. No.	Acronym	Composition	Characterisation
Sample 1	DPO20+PT20+WCOB60	20%DPO+20% Pentanol +WCOB60%	Yes
Sample 2	DPO10+DEE20+WCOB70	10%DPO+20%Diethyl ether+WCOB70%	Yes
Sample 3	DPO20+BT20+WCOB20	20% DPO+ 20% 1-butanol + WCOB60%	Yes
Sample 4	DPO20+BT20+LFB60	20% DPO+ 20% 1-butanol + AFOB60%	Yes
Sample 5	DPO20+ME20+WCOB60	20% DPO+ 20% Methanol + WCOB60%	Yes
Sample 6	DPO20+DEE20+WCOB60	20%DPO+20%Diethyl ether+WCOB60%	No

2.1 Anaerobic digestion

In this research, AD waste material was obtained from the MeMon BV, a Dutch company where it was dried and pelletized for us. Prior to pelletization, the AD waste moisture content was decreased from 80% to 20%. Prior to pelletization, a centrifuge dewatered followed by the rotary oven was used to decrease the moisture % from 80% to 20%. Table 2 displays the characteristics of the digestate pellets

(6 mm in diameter and 20 mm in length). Later these pellets were used in Pyroformer to produce digested pyrolysis oil (DPO).

Table 2, AD waste pellets properties [9]

Proximate analysis	
Moisture content (wt.%)	11.5
Ash content (wt.%, dry basis)	35.7
Volatile matter (wt.%, dry basis)	54.1
Proximate analysis (wt.%, dry basis)	
Carbon	35.95
Hydrogen	3.91
Nitrogen	3.54
Chlorine	0.87
High heating value (MJ/kg)	15.02

2.2 Digested pyrolysis oil preparation

The work was performed on Aston University’s Pyroformer, an intermediate pyrolysis-based reactor shown in Fig.2). Increased gas yield and purity, low molecular weight bio-oil, and the capacity to process various challenging feedstocks with increased moisture content are all key advantages of the Pyroformer. The Pyroformer was pre-heated to reach the target temperature (500°C) in the Pyroformer reactor by 50°C increments every 30 minutes after general preparations of the feeding material and reactor. This gradual temperature increases guaranteed even temperature dispersion throughout the Pyroformer and to prevent any hot or cold areas. The pyrolysis was performed in a nitrogen flow of 20-25 ml/min to create an inert atmosphere and to carry the vapours releasing during the process from biomass. Using a screw motor, the biomass (digestate pellets) was fed from a hopper. Prior to heating up the reactor, the screw motor's rotational speed was calibrated to guarantee accurate feeding rate throughout the test. Feed was added via a hopper after the Pyroformer achieved the temperature of 500°C. The biochar was collected as the first product from the Pyroformer. The biochar to biomass ratio was 3:1. Hot pyrolysis vapours (condensable and non-condensable gases) then passed-through a counter-current shell and tube water-cooled heat exchanger to condense. The condensable gases were collected as bio-oil and the non-condensable gas was expelled from the other side. The yields of the products were measured and were as follows: 20% oil, 20% aqueous phase, 50% biochar, and 10% gas.

Bio-oil was collected in a glass bottle. The biochar had a 60% ash content and had an HHV of 10 MJ/kg [9, 26].

The biochar to biomass ratio was 3:1, and the feeding rate was roughly 5 kg/h. The speed of the inner and outer screws was 6 rpm and 4 rpm, respectively. The vapours heated to a temperature of roughly 390°C and then hot pyrolysis vapours were introduced into one side of a counter-current shell and tube water-cooled heat exchanger to condense, while non-condensable gas was expelled from the other side. The yields of the products were measured and were as follows: 20% oil, 20% aqueous phase, 50% biochar, and 10% gas. Bio-oil was collected in a glass bottle. The biochar had a 60% ash content and had an HHV of 10 MJ/kg [9, 26].

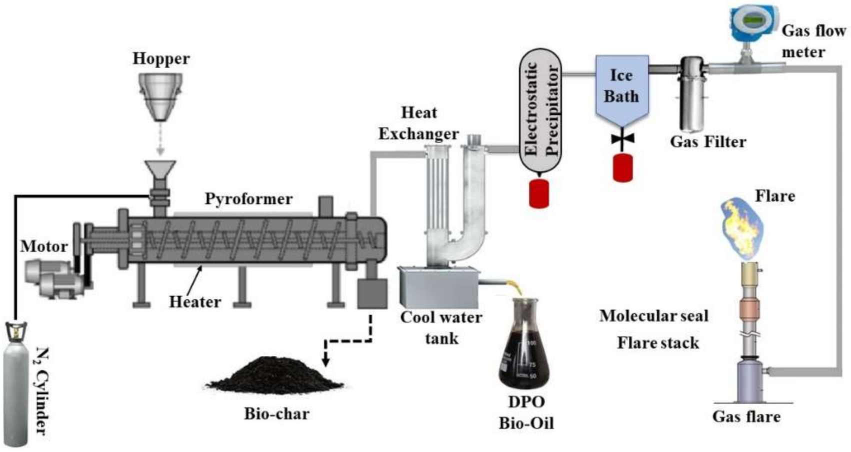


Fig.2. Schematic of the pyroformer pyrolysis reactor pilot plant

2.3 Lamb fat pre-treatment

In order to remove the contaminants, the waste lamb fat (WLFL) was rinsed with distilled water [27]. To increase the yield of WLF, large chunks were sliced into little pieces (5-10mm), and 1000 g of WLF was heated for one hour at 100 °C to melt the fat. As illustrated in Fig.3, the melted fat was filtered to eliminate insoluble impurities. The oil was then stored in an airtight bottle until it was used for biodiesel production.

2.4. Lamb fat biodiesel production

In a typical process, 4:1 methanol-to-oil molar ratio was used. 1% (wt./wt.) base-catalyst (KOH) was added to the pre-heated oil at 65 °C and stirred for 90 min at 600 rpm by a magnetic stirrer [28] as shown in Fig.4. After the completion of the reaction, the mixture was transferred to a separating flask and allowed to settle overnight for the separation of glycerol from the methyl ester. Raw biodiesel was separated carefully. In the post-treatment process, raw biodiesel was first washed with hot de-ionised water (80-85 °C) to remove the catalyst and soap, which formed during transesterification process. Washing with hot de-ionised water was repeated until 'clear' and clean water was collected at the bottom of the washed biodiesel (Fig.3). The washed biodiesel was then allowed to settle for 8 h prior to heating at 110 °C under nitrogen flushing for drying. (Fig.3). The same procedure was adopted to produce biodiesel from waste cooking oil.

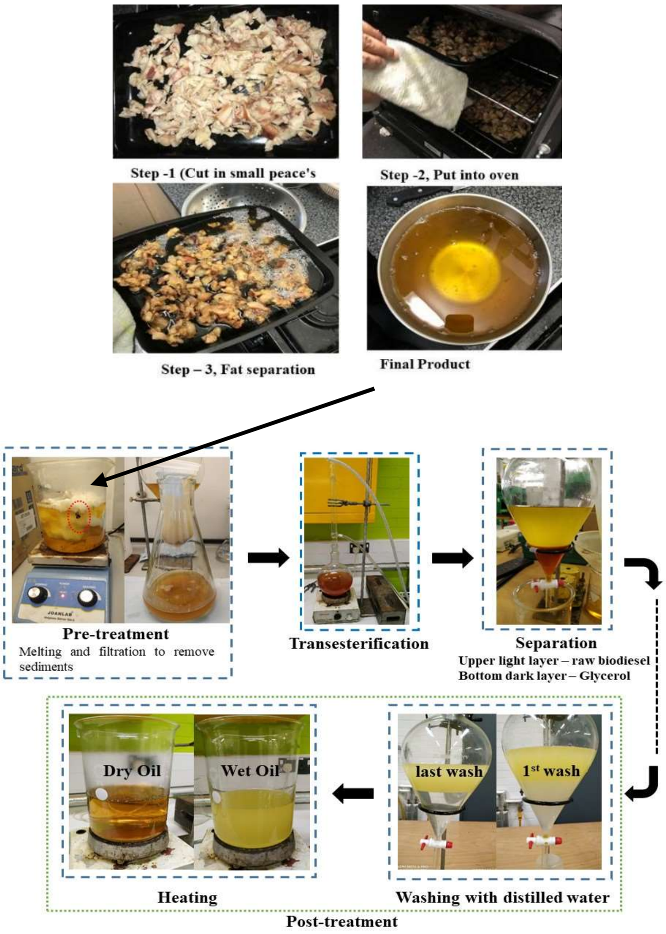


Fig.3. Biodiesel production from waste lamb fat

2.5 Post-mixing process

After the production of DPO bio-oil from AD waste and biodiesel from the WCO and LFB, a post-mix method was selected to prepare six different blends as given in Table 1. Due to the high viscosity of DPO, additives such as methanol (MeOH), diethyl ether (DEE), butanol (BT-OH) and pentanol (PT-OH) were used to reduce the viscosity. The mixing stability of the blends were examined physically by phase analysis. To ensure the consistency of the DPO blends, all six DPO blends were examined up to four days. Out of the six blends, sample 6 exhibited a phase separation. Diethylether is a non-polar solvent so readily mixes with the oil samples [28].

2.6 Fuel characterisation

The physical properties of the fuel samples were measured using “A Parr 6100 Bomb Calorimeter” with 0.1% precision and ASTM-D7544 hydrometer to measure the higher heating value (HHV) respectively. The kinematic viscosity of the samples was measured with Canon Fenski u-tube viscometers (with measurement uncertainty of 0.16-0.22%) and a thermostatic water bath (0.1° C). An ASTM121 D1655-compliant Setaflash Series 3 plus closed cup flash point tester (model 33000-0, accuracy 0.5%) was used to determine the flashpoint.

The total acid number (TAN) and free fatty acid (FFA) % of the fuel samples were measure through titration method (ASTM-664-04) and calculated from the Eq. 1 and 2 [29]. Fatty acids methyl ester compositions were identified from gas chromatography and mass spectrometer (GC-MS). GC-MS analysis was used to identify the different compounds of biodiesel and DPO blends (Table 4 and 5). From equations 3, 4, and 5 [30, 31], the percentages of saturated fatty acids (SFA%), monounsaturated fatty acids (MUSFA%), and polyunsaturated fatty acids (PUSFA%) were calculated and presented in Table 6. Ultimate analysis for the DPO blends and biodiesel were measured with CHNS analyzer. Elemental compositions (C, H, N, O and S) obtained shown in Table 6. None of the blends were found to fulfil the biodiesel criterion, however most were determined to be within the marine fuel standard's tolerance, making them viable for maritime purposes, but unsuitable as fuels for motor vehicles.

$$\text{TAN (mgKOH/g)} \qquad = \frac{(A-B)x0.1NxM}{m} \tag{1}$$

$$\text{FFA (\%)} \qquad = \frac{Acid\ value}{2} \tag{2}$$

$$\text{SFA \%} \qquad = \sum C - C\ single\ bond\ FAs \tag{3}$$

$$\text{MUFAs \%} \qquad = \sum More\ then\ one\ (-C - C -) bouble\ bond\ FA\ s \tag{4}$$

$$\text{PUFAs \%} \qquad = \sum More\ then\ one\ (-C = C -) bouble\ bond\ FA\ s \tag{5}$$

Note; A- titration volume, B-blank titration, N-normality of the titration solution, Mw-molecular weight of the catalyst and m-mass of the oil sample weight.

3. Results and discussion

3.1 Fuel blend physical properties

A range of parameters were determined for the various blends and are tabulated in Table 3. It is evident that kinematic viscosity, density, and flash point of the blends are reduced by using a range of additives namely, methanol, butanol, pentanol and DEE. It was observed that with an increase in the storage time, the acid value, viscosity, and density increased whereas the calorific value decreased. Similar trends were reported in [28]. All the properties of the blends match the specifications of marine diesel (ISO-8217) and for the EU biodiesel standard (EN1424) all parameters were in range except viscosity.

Table 3. Salient properties of the fuel samples and comparison with standards.

Properties	**TAN (mg KOH/g)**		**Density (kg/m3)**		**Calorific Value (MJ/kg)**		**Kinematic Viscosity (mm^2/s)**		**Flash Point (°C)**		**LHV (kJ/kg) [32]**
Time (months)	Zero	Eight	Zero	Eight	Zero	Eight	Zero	Eight	Zero	Eight	
DPO	8.4	11.6	1077.14	1087	26.77		473		120		-
WCOB	0.5	2.6	882	887	38.82	38.63	4.16	4.72	165	168	-
Animal Fat	0.23	1.3	887	890	39.62	39.05	3.23	3.45	135	137	-
Sample -1	2.9	4.8	857	884	38.98	38.57	42.35	45.32	140	152	-
Sample -2	3.1	4.8	856	897	37.78	37.53	40.86	43.95	155	162	-
Sample -3	4.3	7.7	866	894	37.45	36.84	35.86	37.28	160	168	-
Sample -4	4.7	7.5	882	889	37.70	37.47	33.35	36.87	145	151	-
Sample -5	2.9	6.7	976	985	38.79	38.55	40.28	43.32	148	157	-
Fossil Diesel	0.02	-	835	-	45.3	-	3.01	-	65	-	375
Methanol	-	-	792	-	22.79	-	0.397	-	12	-	1162.64

Butanol	-	-	810	-	35.45	-	0.259	-	35	-	584.40
1-Pantanol	-	-	811	-	36.5	-	0.402	-	33	-	308.05
EN14214 [3]	0.5		860-900		37.5 min.		3.5-5		>120		
Marine ISO 8217 [3]	2-5		975-1010				>70 @ 50°C		>60		

The data presented in Table 3 indicates that the DPO-blends could potentially have a marine application to replace heavy marine oil.

3.2 Chemical property analysis

Fatty acid methyl ester (FAME) profiles of the neat biodiesels are given in Tables 4. In lamb fat, the major fatty acid components are the saturated fatty acids, palmitic acid (hexadecenoic acid 16:0- 24.5%), stearic acid (18:0- 27.7%) and the monosaturated fatty acid, oleic acid (18:1-32.7%). Collectively, these account for 85% of the total composition.

Table 4, GC/MS composition of biodiesels

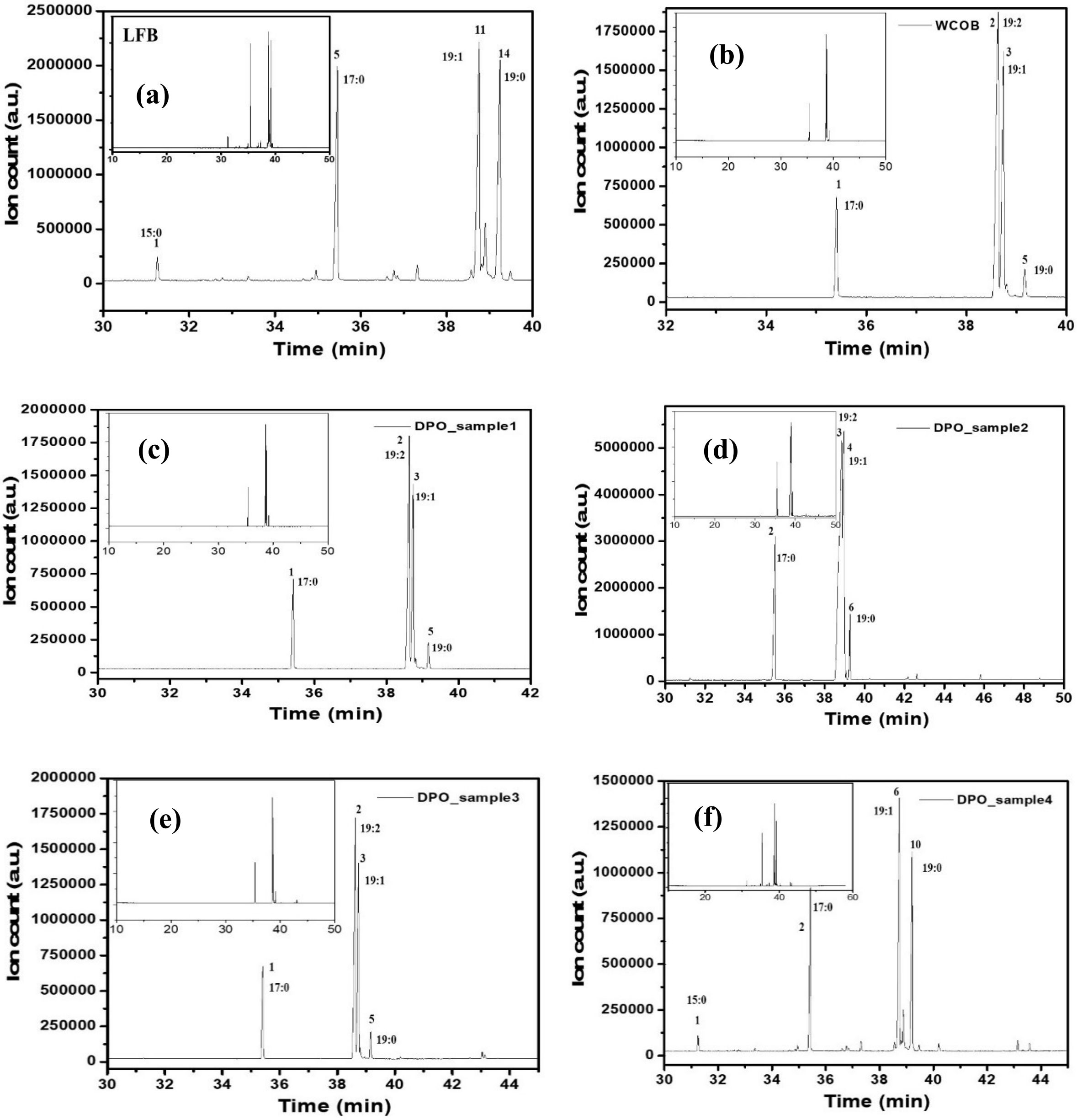
Peak No	RT (min)	Library/ID	Formula	Area %
		Lamb fat biodiesel		
1	31.3	Methyl tetradecanoate	C15H30O2	2.0
2	32.8	Undecanoic acid, 10-methyl-, methyl ester	C13H26O2	0.2
3	33.4	Pentadecanoic acid, methyl ester	C16H32O2	0.4
4	34.7	7-Hexadecenoic acid, methyl ester, (Z)-	C17H32O2	0.9
5	34.9	Hexadecanoic acid, methyl ester	C17H34O2	24.5
6	35.4	Tridecanoic acid, 12-methyl-, methyl ester	C15H30O2	0.3
7	36.6	Hexadecanoic acid, 14-methyl-, methyl ester	C18H36O2	0.9
8	36.8	cis-10-Heptadecenoic acid	C18H34O2	0.4
9	36.8	Hexadecanoic acid, 15-methyl-, methyl ester	C18H36O2	1.4
10	37.31	9,12-Octadecadienoic acid, methyl ester, (E,E)	C19H34O2	1.2
11	38.6	11-Octadecenoic acid, methyl ester	C19H36O2	32.7
12	38.8	trans-13-Octadecenoic acid, methyl ester	C19H36O2	6.1
13	38.9	13-Octadecenoic acid, methyl ester	C19H36O2	0.4
14	39.0	Methyl stearate	C19H38O2	27.7
15	39.22	Methyl 10-trans,12-cis-octadecadienoate	$C_{19}H_{34}O_2$	0.9
		Waste cooking oil biodiesel		
1	35.4	Hexadecanoic acid, methyl ester	C17H34O2	12.5
2	38.6	9,12-Octadecadienoic acid, methyl ester	C19H34O2	48.6
3	38.7	11-Octadecenoic acid, methyl ester	C19H36O2	33.6
4	38.8	7-Hexadecenoic acid, methyl ester, (Z)-	C17H32O2	1.7
5	39.2	Methyl stearate	C19H38O2	3.6

By contrast, in waste cooking oil the main fatty acid is the unsaturated fatty acid, linoleic acid (18:2$\Delta^{9,12}$) with significant levels of oleic acid (18:1Δ^{11}, 33.6%) and the saturate, palmitic acid (16:0-12.5%). Thus, lamb fat is highly saturated and waste cooking oil is highly unsaturated.

Table 4, GC/MS composition of blend samples

Peak No	**RT (min)**	**Library/ID**	**Formula**	**Area %**
		Blend sample 1		
1	35.4	Hexadecanoic acid, methyl ester	C17H34O2	14.0
2	38.6	9,12-Octadecadienoic acid, methyl ester	C19H32O2	47.8
3	38.7	11-Octadecenoic acid, methyl ester	C19H36O2	32.6
4	38.8	6-Octadecenoic acid, methyl ester	C19H36O2	1.7
5	39.2	Methyl stearate	C19H38O2	3.9
		Blend sample 2		
1	31.21	Methyl tetradecanoate	C15H30O2	0.1
2	35.5	Hexadecanoic acid, methyl ester	C17H34O2	14.7
3	38.9	Methyl 9-cis,11-trans-octadecadienoate	C19H34O2	54.1
4	38.9	11-Octadecenoic acid, methyl ester	C19H36O2	25.5
5	39.1	9,12,15-Octadecatrienoic acid, methyl ester,	C19H32O2	0.5
6	39.3	Methyl stearate	C19H38O2	4.3
7	42.2	cis-13-Eicosenoic acid, methyl ester	C21H40O2	0.1
8	42.6	Methyl 18-methylnonadecanoate	C21H42O2	0.3
9	45.8	Docosanoic acid, methyl ester	C23H46O2	0.3
10	48.8	Tetracosanoic acid, methyl ester	C25H50O2	0.1
		Blend sample 3		
1	35.4	Hexadecanoic acid, methyl ester	C17H34O2	14.1
2	38.6	9,12-Octadecadienoic acid, methyl ester	C19H34O2	47.9
3	38.7	cis-13-Octadecenoic acid, methyl ester	C19H36O2	31.7
4	38.8	11-Octadecenoic acid, methyl ester	C19H36O2	1.6
5	39.2	Methyl stearate	C19H38O2	3.7
6	43.0	n-Propyl 9,12-octadecadienoate	C21H38O2	1.0
		Blend sample 4		
1	31.2	Methyl tetradecanoate	C15H30O2	1.7
2	35.4	Hexadecanoic acid, methyl ester	C17H34O2	20.5
3	36.8	Hexadecanoic acid, 14-methyl-, methyl ester	C18H36O2	0.7
4	37.3	Heptadecanoic acid, methyl ester	C18H36O2	1.1
5	38.6	9,12-Octadecadienoic acid, methyl ester	C19H34O2	1.2
6	38.7	11-Octadecenoic acid, methyl ester	C19H36O2	37.5
7	38.9	9-Octadecenoic acid, methyl ester,	C19H36O2	5.6
8	38.9	9-Octadecenoic acid, methyl ester	C19H36O2	0.3
9	39.0	Heptanedioic acid, dimethyl ester	C9H16O4	0.3
10	39.2	Methyl stearate	C19H38O2	27.3
11	39.5	Methyl 10-trans,12-cis-octadecadienoate	C19H34O2	0.7
12	40.2	Hexadecanoic acid, butyl ester	C20H40O2	1.1
13	43.1	n-Propyl 9-octadecenoate	C21H40O2	1.2
14	43.6	Octadecanoic acid, butyl ester	C22H44O2	0.8
		Blend sample 6		
1	35.4	Hexadecanoic acid, methyl ester	C17H34O2	14.0
2	38.6	Methyl 9-cis,11-trans-octadecadienoate	C19H34O2	49.0
3	38.7	12-Octadecenoic acid, methyl ester	C19H36O2	33.2
4	39.1	Methyl stearate	C19H38O2	3.8

The GC-MS spectra of the biodiesel and DPO blends are shown in shown in Fig.4 (a-g). It should be noted that 17:0 is the methyl ester of endogenous 16:0, 19:0 is the methyl ester of 18:0, 19:1 is the methyl ester of 18:1 and 19:2 is the methyl ester of 18:2. DPO blend (sample 4) shows higher % of C16:0 and C18:0 due to the mixing with LFB. All the blends with WCOB show a similar acyl composition (high in 18:2) to the biodiesel.



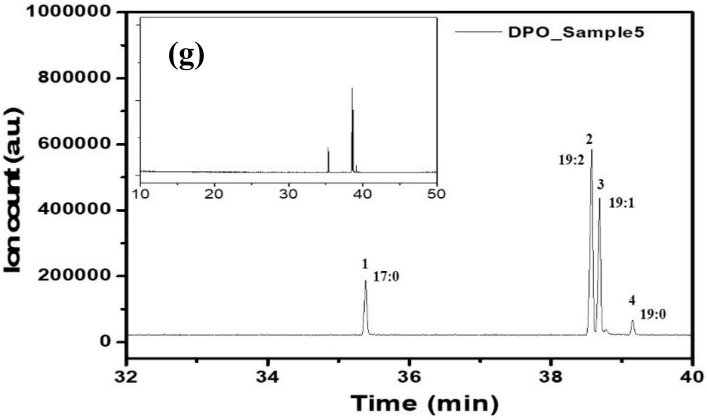


Fig.4. GC/MS total ion chromatograms of fuel blends

The level of the SFA, MUFAs and PUFAs were calculated from Eq. 3, 4 and 5 [30, 31] and shown in Table 6 and Fig.5. From Fig.5, it was confirmed that LFB contains 28% higher SFA% as compared to WCOB. The DPO blend sample 4 made from LFB and shows 5-9 % higher SFA % than other DPO blends with WCOB.

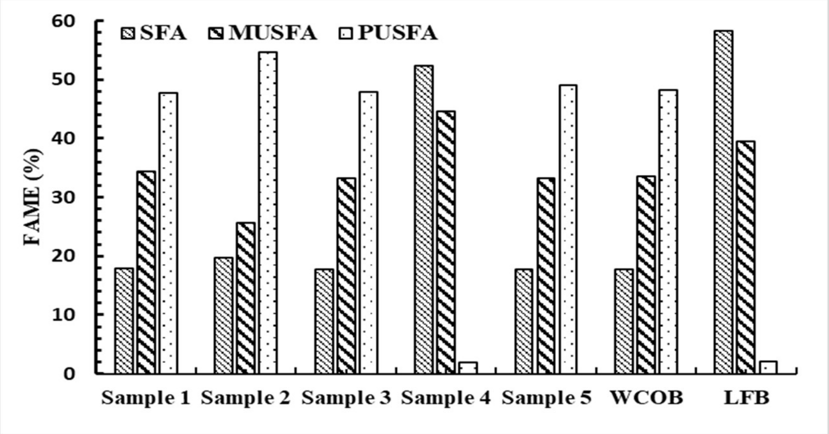


Fig.5. Fatty acid composition of blends showing the major fatty acid components

It was also observed that WCOB contained high % of PUFAs which is also reflected in the PUFA % of DPO blends made from WCOB (Fig.6(b)). Sharma et. al. [30], showed that the proportion of saturated to unsaturated fatty acids strongly influenced fuel properties[30]. An overall investigation of FAME shows that adding high SFA oil into blends is good from an engine performance point of view [30].

More recently, Anto et al., [33] investigated the biodiesel-biodiesel blends effect on fuel properties and engine performance reported that the dilution of high PUFAs by SFA improved fuel properties such as ignition quality. In addition, a higher SFA % increase the oxidation stability of the blend (Sharma et al [29]

3.3 Fourier Transformed Infrared (FT-IR)

FT-IR was used to understand lipid compositions presents in fuel. FT-IR spectroscopy is a great tool to observe the shift change of chemical composition in term of functional groups [34, 35]. The aliphatic loss process is represented by the band (2400 cm^{-1}) of FT-IR (Fig.7). The FT-IR spectrum of all DPO blends at zero months were showing similar spectrum with similar bands (Fig.6). From Fig.6, the changes in the functional groups were clearly observed. At zero-month, A broad band at 3550-3200 cm^{-1} was detected for O-H stretching, whereas it was absent after 8 months (Fig.6) for all the DPO blend samples. A band at 2830-2695 cm^{-1} was detected for both zero and eight months due to -C-H stretching. A weak alkyne functional group C=C stretching was observed due to 2260-2190cm^{-1} band for both the conditions (0 & 8 months) (Fig.6). The functional groups of C=C stretching (conjugated alkene) was detected at 1650-1600 cm^{-1} and 730-665 cm^{-1} for 8 months, but it's not present at zero month. A -C-O- stretching (aliphatic ether) was obtained due to the band 1150-1085 cm-1at zero month (Fig.6).

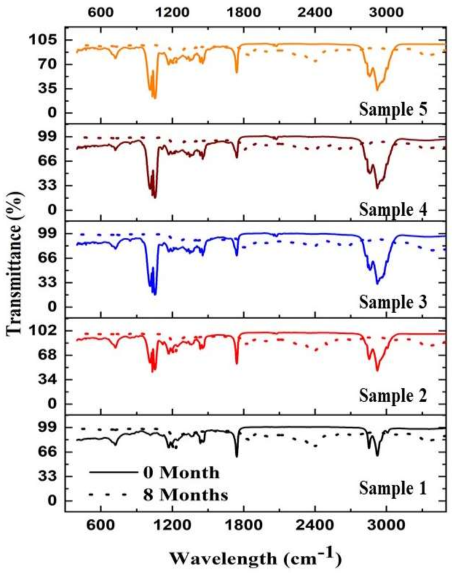


Fig.6, FT-IR spectrums of DPO blends

3.4 Elemental analysis

The elemental analysis and atomic ratio of elements (H:C & O:C ratio) are useful indications of the character of bio-oils [34, 35]. The data in Table 6 suggested that weight percentage of carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) have been changed by the composition ratios of the blend's compounds.

Table 6, Elemental and FAME analysis of the blends and single fuels

Ultimate analysis (%)	**Sample 1**	**sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**WCOB**	**LFB**	**DPO [9]**
C	70.52	73.23	70.86	72.62	69.5	77.65	76.38	68
H	7.98	8.92	7.84	8.23	7.6	10.35	11.23	8.3
N	0.06	0.062	0.06	0.04	0.04	0.06	0.06	6.5
S	0	0	0	0	0	0	0	0
O	12.7	11.21	12.59	11.78	12.87	8.59	10.15	14.4
Atomic ratio								
H:C	1.348	1.451	1.318	1.350	1.303	1.588	1.752	1.454
O:C	0.135	0.115	0.133	0.122	0.139	0.083	0.100	0.159
H:O	9.973	12.630	9.884	11.089	9.373	19.124	17.561	9.148
H:N	1848.014	1999.064	1815.593	2858.864	2640.020	2396.860	2600.651	17.743
C:N	1370.554	1377.312	1377.161	2117.050	2026.095	1509.125	1484.442	12.199
FAME (%)								
SFA (%)	17.9	19.7	17.8	52.4	17.8	17.8	58.3	-
MUSFA (%)	34.3	25.6	33.3	44.6	33.2	33.6	39.5	-
PUSFA (%)	47.8	54.6	47.9	1.9	49	48.2	2.1	-

The weight % of N was found low due to low N-containing functional groups present in biofuels and decreased due to thermal decomposition. All the blends show 73 ± 3% of C and 9 ± 2% H mass % due to addition of DEE and butanol. Whereas DPO blend 5 shows highest mass % of O due to methanol. Methanol shows a higher % of oxygen with respect to C and H [36]. The atomic H:C ratio of the DPO blends varied from 1.3 to 1.4 (Table 6 and Fig.7(a). The H:O ratio was observed within the range of 9-19 and DPO blend 2 and WCOB shows highest H:O ratios as compared to other DPO blends (Fig.7b). Moreover, H: N and C:N ratios was varied from1815-2858 and 1370-2117 respectively (Fig.7(c-d)).

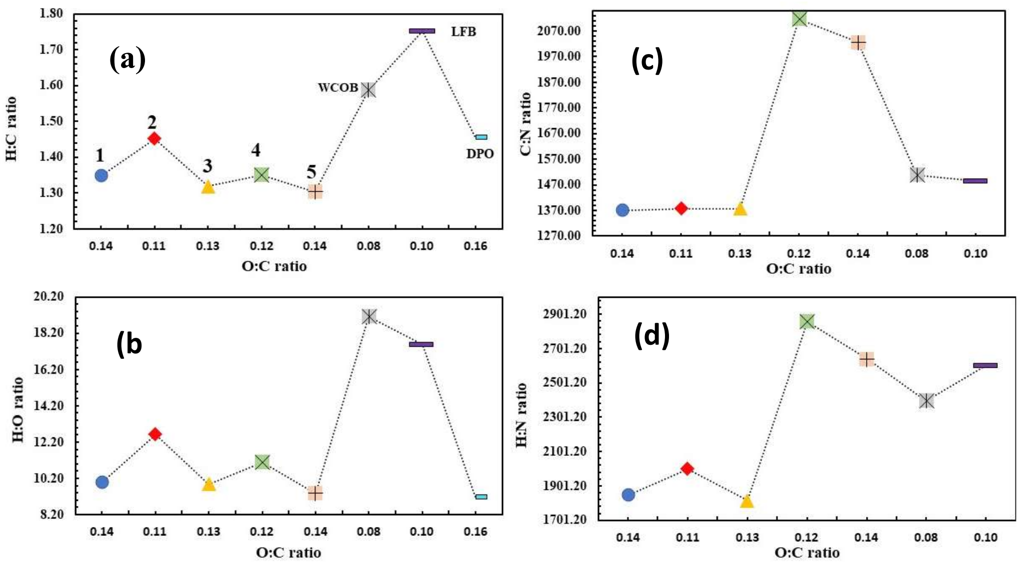


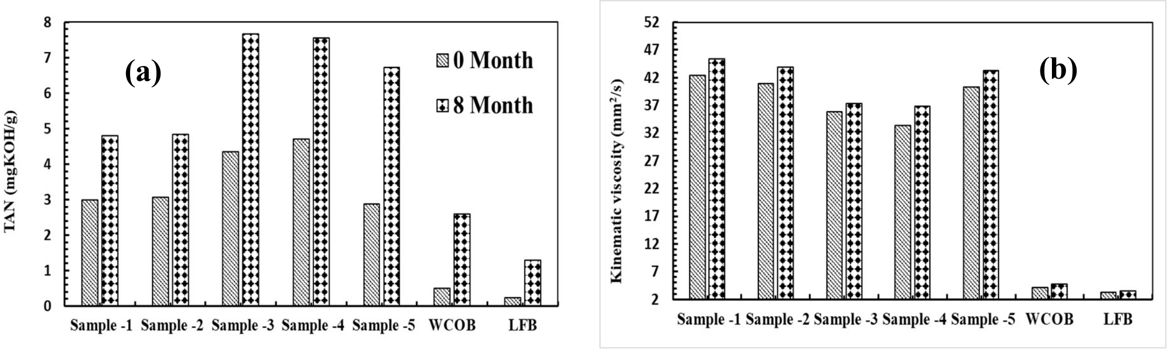
Fig.7, Van Krevelen diagram for atomic ratios of DPO blends

3.5 Total acid number

The total acid number (TAN) is a key quality control metric that is used to quantify the acidity of the fuel [36]. High TAN can cause damages to the fuel tank and engine components such as high fuel pressure line, fuel pump and fuel injector [30]. Typically, TAN should be lower than 0.5 mgKOH/g for automotive application and in the range of 2-5 mgKOH/g for marine engine application. By storing individual biodiesel and their blends for eight months, significant changes were observed in TAN and is shown in Table 3 and Fig.8(a). It was observed that TAN for LFB and WCOB increased by 82% and 80% from 0-8 months whereas, change in TAN for the DPO blends were found to be lower than the biodiesel which is in the range of 35-50% from 0-8 months. The high degradation rate of biodiesel could be due to high unsaturation (C=C) [37]. The effect of degradation with time can be observed from the Fig.6 (FTIR data). Additives play an important role to slow the degradation rate as alcohols and DEE have lower oxidation rate [38]. The degradation rate of neat biodiesel is faster than the blended sample due to high % of unsaturated fatty acids (UFA), number of carbon double bonds (C=C), and their positions trans or cis. These UFA double bonds react faster with atmospheric oxygen and increases the rate of degradation [18]. Sharma et al, [30, 36], investigated the molecular behaviour of plants oil on biodiesel degradation properties and other chemical properties reported that fuel consisting of a high percentage of UFA, degraded faster than those containing a high proportion of SFA. Although saturated aliphatic alcohols and DEE do not exhibit direct antioxidant activities themselves, they most likely act to suppress oxidation by diluting the oils and thereby dilute out the free radicals generated from the unsaturated fatty acids responsible for propagating further lipid oxidation. Anand et. al. [19], investigated the effects of Karanja and coconut biodiesel composition blends on its long-term storage stability. They reported that biodiesel with higher number of double bonds resulted in increases in TAN over storage time.

3.6 Kinematic viscosity

Higher viscosity creates resistance to fluid flow which deforms by either tensile stress or shear stress [30]. In general, high viscosity leads to poor atomization and vaporization of the fuel, and therefore, results in poor combustion and increased emissions from the engine [19, 30, 36]. From Table 3 and Fig.8(c), it observed that kinematic viscosity increases with time It was observed that viscosity for LFB and WCOB increased by 6% and 11% from 0-8 month (Fig.8(b), whereas the degradation rate of DPO blends were found lower (6-9%) than the biodiesel as shown in Fig.9(b). DPO blend samples 3 and 4 exhibit the lowest increment in viscosity about 3% and 5 % with 8 months of storage time.



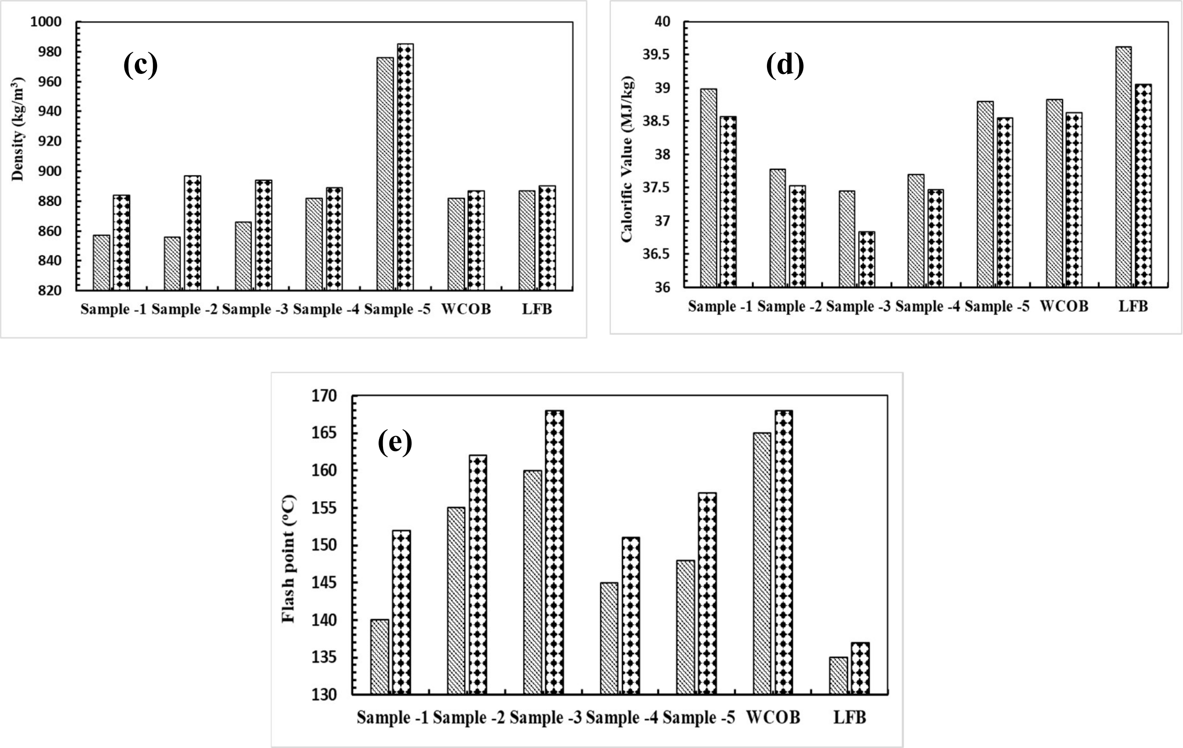


Fig.8, Physical properties of the fuel samples

3.7 Density

Fuel density directly influences the fuel performance because fuel injection pump injects fuel by volume and not by mass [30]. Therefore, air-fuel ratio and energy content of the fuel for better combustion are influenced by fuel density [19, 30, 36]. From Table 3 and Fig.8(c), it observed that density increases with time. Increases the moisture % with storage time could be the reason for high rate of density increment for blends [19, 36]. It was observed that density for LFB and WCOB increased slightly by 0.33% and 0.5% from 0-8 months (Table 3 and Fig.8(c)). However, the density of the DPO blend samples increased at a high rate than the biodiesel, which was in the range of 0.7-4 % Fig.8(c). The effect of degradation with time can be observed from the Fig.6 (FTIR data), This corelated with the increases of the density with time. Subhash et al.,[39] investigated the effect of reformulated biomixture with 10% butanol as additive on fuel properties. They prepared the mixture of raw oil by blending the edible and non-edible fuels and converted to bio-mix biodiesel and reported that by adding 10% butanol, oxidation stability, cetane number, saturated fatty acid methyl ester, cold flow properties were improved while flash point, viscosity, iodine number, density, free fatty acid and heating value decreased. This investigation concluded that the n-butanol additive to biodiesel fuel improve its quality [39].

3.8 Calorific value

The calorific value (CV) of the fuel refers to the heat of combustion. The availability of oxygen in biodiesel leads to reduced heating value than diesel fuel [19, 36]. From Table 3 and Fig.8(d), it is observed that CV decreases with time due to increases the moisture %. The observed reduction is attributed, at least partially, to the increase in moisture content of the biodiesel sample [19, 36]. The presence of moisture can also lead to reactions that tend to alter the molecular composition of the fuels by converting the carboxylic acids and esters to aldehydes and ketones. It was observed that CV for LFB and WCOB decreased by 1.4 % and 0.5 % from 0-8 months (Fig.8(d)). However, for the DPO blends, CV decreased at higher rate (0.7-1.6 %) as compared to that of the neat biodiesel (Fig.8(d)). The effect of degradation with time can be observed from the Fig.6 (FTIR data), This corelated with the decreases of the CV with time.

3.9 Flash point

Flash point (FP) is an important property of the fuel for safe transportation, handling, and storage [19, 36]. It was observed that FP for LFB and WCOB increased by 1.4 % and 1.7 % from 0-8 months as shown in Fig.9(e) and Table 3. Interestingly, the FP of the DPO blends increased at a higher rate than the individual oil, which is in the range of 5-7 % from 0-8 months (Fig.8(e)). The first step in the degradation of samples that have been stored is the abstraction of hydrogen from the unsaturated alkyl esters' double bond (C=C). This generates f free radicals, which in turn produced hydroperoxides when they reacted with ambient oxygen, increasing the water percentage over time. Increase in moisture content with storage time is reported to increase the rate of increase of FP for DPO blended fuel samples [19, 36]. Sharma et. al. [36], investigated the storage stability of the fish oil biodiesel diesel produced from different alcohols. They reported that higher double bonds (C=C) %, produced free radicals to react with oxygen and increased the degradation rate of biofuels [36].

4. Conclusions

Over the past ten years, both the volume of marine transport and the corresponding greenhouse gas emissions (GHG) have increased steadily. Between 2012 and 2020, ship carbon emissions increased by roughly 10%, and petroleum fuel is a major industrial user. So, a sustainable biofuel made from waste has the potential to lower transportation emissions of sulphur oxides (Sox), nitric oxide (NOx), and particulate matter (PM), leading to better air quality all around the world. Since biofuels do not contain sulphur, they could lower PM2.5 emissions [2]. The PM2.5 emissions would decrease childhood asthma by 3.6% while decreasing world fatalities from lung cancer and cardiovascular disease by 2.6% [2]. Biomass pyrolysis technology has been presented as a mature and sustainable technique to turn food and agricultural waste into biooil to enhance the percentage of biofuel or bio-oil. The availability of lamb fat for large scale transportation would be a limiting factor. However, in UK, generic tallow (animal fat) from slaughter- houses was 133K tonnes in 2016 and rose by 4.2% in 2021. Most fuel oil in the EU is used to power ships engaged in international navigation. In 2019 this market was estimated to be of the order 35,000kT.

The adoption of any sustainable biofuels is usually greatly influenced by production costs. Due to the increased acid value compared to edible oil, the generation of biodiesel from non-edible oil sources is higher [18]. Because leftover cooking oil is edible, even after being used twice for frying, its TAN value does not rise above 2.5. Transesterification, a single stage in manufacturing rather than esterification and transesterification, was necessary due to the lower TAN value. The cost of the two-step technique is higher overall since it requires more material. Transesterification, a one-step process, needed less time and material, which resulted in lower manufacturing costs. The cost of each individual element is shown in the table, and the estimated cost of producing biodiesel at laboratory size is £6.53/litre. In contrast, a single mix sample at laboratory size typically costs £6.02 per litre. Even though this cost is high, large manufacturing of the fuel might lower the overall cost of either DPO mixes or biofuels.

Table 7, Cost analysis of WCOB and blend sample

Sl. NO.	**Material**	**Price/quantity BGP**	**Required quantity**	**Price in GBP**
Waste cooking oil biodiesel (WCOB) production cost				
1	Waste cooking oil	£0.35/ litre	1100ml	£0.38
2	Methanol	£5/ litre	245ml	£1.25
3	Potassium hydroxide (KOH)	£75/kg	9.5g	£0.72
4	Distilled water	£0.7/ litre	3-5 litre	£3.5
5	Power (unit)	£0.34p/kWh	2-3	£0.68
Total price of WCOB at lab scale				**£6.53/litre**
Price of blend sample				
1	DPO/ pyrolysis oil	5.5/litre	200ml	£1.1
2	Methanol	£5/ litre	200ml	£1.00
3	WCOB	6.5/3litre	600ml	£3.918
Total price of one blend sample (20%DPO+20%methanol+60WCOB) at lab scale				**£6.02/litre**

In this study, long term storage stability of five DPO blend samples were studied for a period of eight months. These five DPO blends were prepared by blending of DPO, WCOB, LFB and additives (Table 1). The GC/MS analysis was done for the fresh oil samples to find the FAME% of the blend samples. LFB showed high SFA% nearly 58%. The properties of fresh individual biodiesels and DPO blends were characterised, and they agreed with the EU biodiesel standards except viscosity. High viscosity of the blend does not allow it to be used as a fuel for automotive transport. Whereas the properties of all the DPO blends were found to match the EU marine biodiesel standards, which means these DPO blends can be used for marine transportation. Adding alcohols as additives in DPO + biodiesel blends reduce the viscosity in addition to slowing down the degradation rate when stored for eight months. The FT-IR spectrum of DPO blends at 0 month and 8 month shows the changes in the functional groups. These are identified effects of aged on the fuel blends. The elemental analysis and atomic ratios show the improvement in C and H in DPO blends. These DPO blends can be considered for stationary diesel engines as well as marine diesel engines for power generation. Testing these blends in off-road diesel engines is a future scope of the study.

Acknowledgements

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