Production of biofuel from AD digestate waste and their combustion characteristics in a low-speed diesel engine

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PII: S0960-1481(23)01799-8

DOI: https://doi.org/10.1016/j.renene.2023.119884

Reference: RENE 119884

To appear in: Renewable Energy

Received Date: 11 March 2023

Revised Date: 29 September 2023

Accepted Date: 21 December 2023

Please cite this article as: Hossain AK, Sharma V, Serrano C, Krishnasamy A, Ganesh D, Production of biofuel from AD digestate waste and their combustion characteristics in a low-speed diesel engine, *Renewable Energy* (2024), doi: https://doi.org/10.1016/j.renene.2023.119884.

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# **Credit Author Statement**

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1	Production of biofuel from AD digestate waste and their
2	combustion characteristics in a low-speed diesel engine

3	
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# Abstract

Anaerobic digestion biogas plants generate large amounts of digestate that cannot always be valorised as fertilizer. This study proposes an alternative use through pyrolysis of the digestate for the production of liquid fuels for compression ignition engines. The digestate pyrolysis oil (DPO) and two types of biodiesel were produced and mixed with different alcohols. A total of five blends of DPO, biodiesel and alcohol were prepared and characterized, showing that their acidity and viscosity were higher than for pure diesel, and their heating value was lower. Blends containing 60% biodiesel, 20% DPO, and 20% butanol were then tested in an engine, showing that the maximum in-cylinder pressure and heat release rate were 4.6% and 3% lower, respectively, compared to diesel, and the engine thermal efficiency at full load was 6-8% lower. 

The nitric oxide and smoke emissions were 7% and 40% lower, respectively, but the carbon dioxide emissions were 7-10% higher than with diesel. The blends showed retarded start of combustion by 1.5° crank angle, which delays the ignition by about 6.4%. This study concludes that blends can be used as a fuel for agriculture and marine diesel engines, although their viscosity should be reduced by improving the pyrolysis conditions.

- 31 *Keywords*: Biodiesel; Combustion; Digestate; Emission; Engine; Pyrolysis;
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# 33 Abbreviations

AD	Anaerobic digestion
BT	Butanol
BD	Burn duration
DPO	Digestate pyrolysis oil
DEE	Diethyl ether
HHV	Higher heating value
HC	Hydrocarbons
HRR max	Maximum heat released rate
FLP	Fuel line pressure
CHRR	Cumulative heat release rate
ID	Ignition delay
LFB	Lamb fat biodiesel
Me	Methanol
NO	Nitric oxide
РТ	Pentanol
Pmax	Maximum cylinder pressure
SoC	Start of combustion
WCOB	Waste cooking oil biodiesel
DPO20+PT20+WCOB60	20% DPO + 20% Pentanol + 60% WCOB
DPO10+DEE20+WCOB70	10% DPO + 20% Diethyl ether + 70% WCOB
DPO20+BT20+WCOB60	20% DPO+ 20% 1-butanol + 60% WCOB
DPO20+BT20+LFB60	20% DPO+ 20% 1-butanol + 60% LFB
DPO20+Me20+WCOB60	20% DPO+ 20% Methanol + 60% WCOB

# 34 1. Introduction

- 35 Worldwide, about 1.3 billion tonnes per year of food waste is generated by industries,
- households, and associated supply chains [1], and 20% of human-related methane emissions
- comes from the waste sector [2].

In general, the disposal of biodegradable waste from industry, forestry, farming and agriculture 38 has always been through landfilling, releasing methane that contributes to the rise in 39 40 greenhouse gas emissions (GHG). To mitigate that, landfilling is banned in many European countries, and today we are already able to convert a high variety of biodegradable waste into 41 different chemicals and products [3]. Anaerobic digestion of the more moist bio-waste and 42 43 thermal treatment of the drier fractions are common waste-treatment solutions. Liquid biofuels 44 are already widely used and provided some 3% of transport energy globally in 2017 [4]. While electric vehicles are gradually replacing light-duty vehicles, long-distance and heavy-duty 45 46 transport are harder to electrify, and biofuels are expected to be primarily used in aviation, shipping and trucks after 2030 [3]. About half of the technologies that will decarbonise our 47 energy system are not yet fully developed [5]. While ethanol, biodiesel, hydrogenated 48 vegetable oils and biomethane are well established biofuels, pathways for pyrolysis oils, 49 methanol, butanol, dimethyl ether (DME) and other ethers are still under development. 50

Every year, several million tonnes of digestate are produced worldwide as a co-product of the anaerobic digestion [6]. Although it is excellent as organic fertilizer and for soil improvement and amendment, the environmental risk that intense digestate land application pose [7] [8] has led to restrictive regulations in many countries. To maximize its utilization and minimize its adverse effects, the thermo-chemical valorization has been widely explored, mainly via pyrolysis of the digestate to produce pyrolysis oils, biochar and pyrolys gases [10], [11], [12], [13], [14], [15], [16].

58 Pyrolysis oils are renewable biofuels that typically exhibit a high viscosity, high acidity, low 59 energy density, and a complex chemical composition that includes various hydrocarbons and 60 oxygen-containing compounds [17, 18]. While they offer the potential to mitigate waste 61 disposal issues, they need necessitate blending in order to enhance their stability, energy 62 content, and combustion efficiency in engines.

For example, the engine performance of blends of diesel with pyrolysis oil derived from waste
cooking oil was investigated by Gad et al., revealing a 29% drop in the engine thermal
efficiency when compared to pure diesel [19]. Similar results were found for blends of diesel
with 30% tyre pyrolysis liquid and 20% Karanja biodiesel [20].

This blending approach with diesel facilitates the integration renewable fuel sources into 67 68 existing infrastructure, but high decarbonisation targets can be achieved only with neat biofuel applications. To explore more sustainable fuel blends, Hossain et al. [21] combined waste 69 cooking oil and digestate pyrolysis oil (up to 30%) with butanol (20%). The introduction of 70 butanol into the mixture led to the formation of stable blends, and resulted in a viscosity 71 reduction of over 90%. Moreover, while the blends exhibited a decrease in the engine brake 72 thermal efficiency of up to 7% compared to diesel, they demonstrated a significant reduction 73 in smoke and CO emissions [21]. As part of the study, they also assessed the miscibility and 74 stability of digestate pyrolysis oil with various fuels, over a 30-day period at room temperature. 75 76 While the pyrolysis oil could form stable mixtures with waste cooking oil and soybean oil, it was incompatible with biodiesel or fossil diesel, unless a cosolvent was added. 77

Building on these findings, the current study evaluates the characteristics of blends comprising
digestate pyrolysis oil, biodiesel, and various cosolvents. Although the cosolvents were not
obtained from renewable sources here, they could be produced through fermentation of
lignocellulosic materials, thus making the blends 100% renewable [4].

This study aims to (i) convert digestate into liquid biofuel through pyrolysis, (ii) produce biodiesel from two different waste streams, (iii) formulate and characterize various blends, and (iv) evaluate their engine performance against conventional fuels.

85

### 87 2. Materials and methods

## 88 2.1. Production of digestate pyrolysis oil

Digestate from the anaerobic digestion of maize stover and green rye was obtained from a
company called MeMon BV (Dorset Group, The Netherlands). The digestate pellets have a
composition of 11.5% moisture, 47.8% of volatile matter, 9.1% fixed carbon and 31.6% ash,
and a HHV of 13.3 MJ/kg (all based on a 11.5% moisture content).

As part of this work, the pyrolysis oil was produced in a pyrolysis pilot plant, using a feeding 93 94 rate of 5 kg/h of digestate pellets. The plant, shown in figure 1, consists of a pyrolysis reactor and an oil condensing train [21]. The pyrolysis reactor (Pyroformer<sup>®</sup>) is a horizontal cylindrical 95 reactor made of carbon steel (1800 mm long, 200 mm diameter) with two screw conveyors 96 97 inside for the movement and recirculation of the solid material within. Each run starts by purging the reactor with nitrogen to eliminate any oxygen, and setting the electrical heating 98 jackets of the reactor at 500°C. Once steady state is reached, the vapours produced in the reactor 99 100 have a temperature of 390°C. Condensation of these vapours takes place in a shell and tube heat exchanger, an electrostatic precipitator for aerosols removal (20 kV) and a dry ice 101 condenser. The pyrolysis liquid is collected in three glass containers connected to each of these 102 three units. Once mixed and poured into separating funnels, the liquid separates into an organic 103 104 phase (pyrolysis oil) and an aqueous phase (with 50% of light organics). The non-condensable 105 vapours are filtered, measured, and flared off. The biochar is collected in a sealed carbon steel pot for further analysis. Overall, the products yields on weight basis were: 20% pyrolysis oil, 106 20% aqueous phase, 50% biochar and 10% of gas. The ash content of biochar was 60%, and 107 108 its higher heating value 10 MJ/kg. The water content shows that 50% of this liquid is aqueous phase and 50% is organic phase (pyrolysis oil). 109

111



# 116 **2.2. Production of biodiesel**

Waste cooking oil (WCO) and waste animal fat (Lamb Fat – LF) were chosen as viable 117 feedstock for biodiesel production. The free fatty acids content (FFA) was about 2.1 mgKOH/g 118 for waste cooking oil and 1.6 mgKOH/g for lamb fat. These values are obtained after titration 119 and using Equations 1 and 2 [22]. The FFA content shows that biodiesels can be produced 120 121 from these feedstock without esterification. Extraction of LF and LF biodiesel production is shown in Fig. 2. WCO and LF was transformed into biodiesel via transesterification process, 122 using potassium hydroxide (KOH) as catalyst. Two different types of biodiesel were thus 123 produced using animal fat and vegetable oil, respectively, with a methanol to oil molar ratio of 124 4:1 and 1 wt.% KOH [23]. Using a 5L glass reactor and a stirring hot plate (65°C and 600 rpm 125 at 90 minutes), several batches were produced to obtain biodiesel from lamb fat (LFB) and 126 biodiesel from waste cooking oil (WCOB). In total about sixteen litres of WCOB and LFB 127

were produced. Each batch was transferred into a decantation funnel and allowed to settle
overnight to separate the glycerol (bottom layer) from the biodiesel (top layer). The biodiesel
was separated, washed, analysed, and stored for subsequent blending.

131 Acid value (mgKOH/g) = 
$$\frac{Vx0.1NxMw}{m}$$
 (1)

132 FFA % = 
$$\frac{Acid value}{2}$$
 (2)



133

134

Figure 2. Lamb fat biodiesel production

# 135 **2.3. Preparation of blends**

Using 60-70% of biodiesel and 10-20 % of digestate pyrolysis oil (DPO), the five blends shown in Table 1 were prepared for characterization and stability analysis. Since biodiesel and the pyrolysis oil are immiscible, 20% of solvent was used for each blend, which also reduced its viscosity. By using pentanol, 1-butanol, methanol, or diethyl ether as cosolvents; homogeneously stable blends were achieved in all cases (Fig. 3). Initially, these cosolvents were selected due to their high energy content and low viscosity values. Four different types of cosolvents were used to assess the miscibility performance with DPO and biodiesel. The

proportion of the cosolvents were kept in the range of between 10-20% in all blends. For miscibility analysis, the quantity of each blend prepared was 100 ml. The blends samples were stored at room temperature for 30 days. No phase separation was observed, and mixture was found to be homogeneous after 30 days.

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_	-	,

Table 1.	Blend	samples	and	composition

Blend	Acronym	Composition	Homogeneous mixture (Yes/No)
Sample 1	DPO20+PT20+WCOB60	20% DPO + 20% Pentanol + 60% WCOB	Yes
Sample 2	DPO10+DEE20+WCOB70	10% DPO + $20%$ Diethyl ether + $70%$ WCOB	Yes
Sample 3	DPO20+BT20+WCOB60	20% DPO+ 20% 1-butanol + 60% WCOB	Yes
Sample 4	DPO20+BT20+LFB60	20% DPO+ 20% 1-butanol + 60% LFB	Yes
~			
Sample 5	DPO20+Me20+WCOB60	20% DPO+ 20% Methanol + 60% WCOB	Yes

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149

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Figure 3. Blend samples 1, 2, 3, 4, and 5

# 151 **2.4. Materials characterization**

The acid value, density, viscosity, flash point and higher heating value of biodiesel, pyrolysis oil, alcohols and their blends were analysed and compared with those for fossil diesel, biodiesel (EN14214) and marine diesel oil standards (ISO 8217). Fossil diesel was purchased form a local filling station, and properties of fossil diesel were measured in the lab. The results are shown in Table 2. The ester content profile of biodiesel samples and DPO blends was also

obtained using a GC-MS (Table 3). The calculation of the saturated fatty acids (SFA %), 157 monounsaturated fatty acids (MUSFA %) and polyunsaturated fatty acids (PUSFA %) were 158 159 derived from Eq. 3, 4 and 5 [24]. Canon Fenski u-tube viscometers (with measurement uncertainty of 0.16–0.22 %) and a thermostatic water bath (0.1° C) were used to measure the 160 kinematic viscosity of the samples. Density was measured using an ASTM-D7544 hydrometer 161 and the higher heating value (HHV) was measured using a Parr 6100 bomb calorimeter (0.1% 162 163 accuracy). The flashpoint was determined using an ASTM121 D1655-compliant Setaflash Series 3 plus closed cup flash point tester (model 33000-0, accuracy 0.5%). The acid number 164 165 was determined using a Mettler Toledo G20 compact titrator following ASTM-664-04. It was found out that none of the blends meet the biodiesel standard, but they are mostly within the 166 limit of the marine fuel one, meaning they are suitable for marine applications but not as road 167 transportation fuels. Fuel samples 3 and 4 shows slightly lower viscosity values than other 168 blends, hence these two blends were chosen for an experimental investigation to determine 169 engine performance, combustion, and emissions characteristics. 170

171 SFA % = 
$$\sum C - C$$
 single bond FAs (3)

172 MUSFA % = 
$$\sum$$
 More then one (-C - C -)bouble bond FA s (4)

173 PUSFA % = 
$$\sum$$
 More then one (-C = C -)bouble bond FA s (5)

- 174
- 175

# Table 2. Properties of the different fuels and materials

Properties	Acid Value	Density	Higher	Viscosity	Flash Point	Latent heat of
	(mgKOH/g)	) (kg/m³)	Heating Value (MJ/kg)	(mm <sup>2</sup> /s) at 40°C	(° <b>C</b> )	vaporization (kJ/kg) [25]
DPO (Hossain et	al.,					-
2016)	8.4	1077.14	26.77	473	120	
WCOB	0.5	882	38.821	4.16	165	-
LFB	0.23	887	39.62	3.23	135	-
Fossil Diesel	0.02	835	45.3	3.01	65	375
Methanol	-	792	22.79	0.397	12	1162.64

1-butanol	-	809.6	35.45	0.259	35	585.40
1-Pantanol	-	814.9	36.5	0.402	33	308.05
Sample 1	2.987	857	38.983	42.35	140	-
Sample 2	3.062	856	37.775	40.86	155	-
Sample 3	4.343	866	37.446	35.86	160	-
Sample 4	4.712	882	37.701	33.35	145	-
Sample 5	2.876	976	38.792	40.28	148	-
Biodiesel EN14214	0.5	860-900	>37.5	3.5-5	>120	-
Marine diesel oil ISO -						-
8217	2.0-5	975-1010	-	<700/50°C	>60	

# Table 3. Ester content profile of WCOB, LFB and their blends (wt.%)

Formula	Fatty acid methyl ester	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	WCOB	LFB
$C_9H_{16}O_4$	Dimethyl pimelate	-	-	-	0.3	-	-	-
$C_{15}H_{30}O_2$	Myristic acid (C15:0)	-	0.1	-	1.7	-	-	2
$C_{13}H_{26}O_2$	Undecanoic acid (C13:0)	-	-	-		-	-	0.2
$C_{16}H_{32}O_2$	Pentadecanoic acid (C16:0)	-	-	-	-	-	-	0.4
$C_{15}H_{30}O_2$	Tetradecanoic acid	-	-		-	-	-	0.3
$C_{17}H_{34}O_2$	(C16:0;OH) Palmitic acid (C17:0)	14	14.7	14.1	20.5	14	12.5	24.5
$C_{17}H_{32}O_2$	Hexadecenoic acid			-	-	-	1.7	0.9
$C_{18}H_{34}O_2$	(C17:0;OH) Heptadecenoic acid (C17:1)	-		-	-	-	-	0.4
$C_{18}H_{36}O_2$	Methyl isoheptadecanoate	-	-	-	1.1	-	-	1.4
$C_{18}H_{36}O_2$	(C18:0) (C18:0;OH)		-	-	0.7	-	-	0.9
$C_{19}H_{38}O_2$	Stearic acid (C19:0)	3.9	4.3	3.7	27.3	3.8	3.6	27.7
$C_{19}H_{36}O_2$	Methyl petroselinate (C19:1)	1.7	-	-	-	-	-	-
$C_{19}H_{36}O_2$	Elaidic acid (C19:1)	_	-	1.6	5.6	-	-	-
$C_{19}H_{36}O_2$	Oleic acid (C19:1)	-	-	-	0.3	-	-	-
$C_{19}H_{36}O_2$	(C19:1)	32.6	-	-	-	-	-	-
$C_{19}H_{36}O_2$	(C19:1 cis)	-	25.5	31.7	37.5	33.2	33.6	32.7
$C_{19}H_{36}O_2$	(C19:1trans)	-	-	-	-	-	-	6.4
$C_{19}H_{34}O_2$	(C19:2cis,trans)	-	54.1	-	-	49	-	-
$C_{19}H_{34}O_2$	Linolelaidic acid, (C19:2trans)	-	-	-	1.2	-	48.2	1.2
$C_{19}H_{34}O_2$	(C19:2)	47.8	-	47.9	-	-	-	-
$C_{19}H_{34}O_2$	Methyl linolate (C19:2cis)	-	-	-	0.7	-	-	0.9
$C_{19}H_{32}O_2$	Linolenic acid C19:3	-	0.5	-	-	-	-	-
$C_{20}H_{40}O_2$	Palmitic acid, butyl ester	-	-	-	1.1	-	-	-
$C_{21}H_{42}O_2$	(C20:0) Nonadecanoic acid C21:0	-	0.2	-	-	-	-	-
$C_{21}H_{40}O_2$	(C21:1)	-	0.1	-	1.2	-	-	-
$C_{21}H_{38}O_2$	(C21:2)	-	-	1	-	-	-	-
$C_{22}H_{44}O_2$	(C22:0)	-	-	-	0.8	-	-	-
$C_{23}H_{46}O_2$	(C23:0)	-	0.3	-	-	-	-	-
$C_{25}H_{50}O_2$	Methyl lignocerate C25:0	-	0.1	-	-	-	-	-
Saturated fatty	y acids (SFA) (%)	17.9	19.7	17.8	52.4	17.8	17.8	58.3
Monounsatura	ated fatty acids (MUSFA) (%)	34.3	25.6	33.3	44.6	33.2	33.6	39.5
Poly-Unsatura	ated fatty acids (PUSFA) (%)	47.8	54.6	47.9	1.9	49	48.2	2.1

## 179 **2.5. Engine test rig**

The engine was a 3-cylinder, naturally aspirated, Lister-Petter Alpha series, water-cooled, 180 181 indirect injection diesel engine (Fig. 4). The test engine's parameters are stated in Table 4. The speed was kept constant at 1500 rpm to better emulate agricultural engines, which often run at 182 a constant speed and variable torque. A Froude Hofmann AG80HS eddy current dynamometer 183 184 was used to load the engine. Six engine loads were chosen for this study: 20 percent (1.9 kW), 40 percent (3.8 kW), 60 percent (5.7 kW), 70 percent (6.65 kW), 80 percent (7.6 kW), and 100 185 percent (9.75 kW). A Kistler cylinder pressure sensor (6.2 mm, installed near the fuel injector) 186 and KiBox data acquisition system were used for the combustion analysis. Engine exhaust gas 187 emissions were analysed with a Bosch BEA 850 gas analyser, specification shown in Table 4. 188



190 Figure 4. Experimental engine test rig and measurements devices191 Table 4. Engine performance analysis instruments

Test engine specification				
Parameter				
Engine model & manufacture	LPWS Bio3 & Lister Petter, UK			
Number of cylinders	3			
Bore/stroke	86x88 mm			
Cylinder volume	1.395 litres			
Rated speed	1500 rpm			
Engine power	9.9 kW			
Fuel injection timing	20 deg. bTDC			

Compression ratio	22						
Bosch BEA 850 emission gas analyser							
Parameter	Measuring range	Resolution					
Carbon monoxide (CO)	0-100 % vol.	0.001 %vol.					
Carbon dioxide (CO <sub>2</sub> )	0-18 %vol.	0.01 %vol.					
Hydrocarbon (HC)	0-9999 ppm vol.	1.0 ppm vol.					
Oxygen (O <sub>2</sub> )	0-22 %vol.	0.01% vol.					
Nitric oxide (NO)	0-5000 ppm vol.	1.0 ppm vol.					
Smoke (opacity)	0-100 %	1 %					

192

# 193 **3. Results and discussions**

## **3.1. Properties of the blends**

The properties of the different fuels and materials used in the study are shown in Tables 2 and 195 Table 3. In general, the heating value of DPO is lower than the WCOB, LFB and fossil diesel 196 197 due to higher oxygen content in DPO. Higher the fuel bound oxygen lower the heating value. On the other hand, the viscosity of DPO is much higher than neat biodiesels and fossil diesel 198 viscosity values. This is due to polar nature of the DPO fuel molecules which produce strong 199 200 interparticle force. This force tighten the molecules very closely resulting higher viscosity. The GC-MS analysis shows that DPO have long hydrocarbon chain (Table 3). Long carbon chain 201 is another reason for higher viscosity of DPO. The density is an important property, since high 202 density fuels require higher injection pressures and lead to increased ignition delays [26]. The 203 density of neat DPO is quite high, 22% higher than fossil diesel, due to dipol-dipol attraction 204 205 of the molecules and longer hydrocarbon chain. The density was decreased when biodiesel and 206 cosolvent was added to DPO. Some of the blends comply with the density requirements for biodiesel (samples 3 and 4), and one of them (sample 5) complies with that for marine diesel 207 208 (Table 2).

DPO, biodiesel and the solvents are all oxygenated, and therefore the heating value of their blends is lower than that for fossil diesel (Table 2). They all comply though with the minimum heating value required in the biodiesel standard (EN 14214). Higher acid value promotes

corrosion in the fuel line and can damage the fuel injector. Apart from acidity, the parameter 212 that is more negatively affected is the viscosity of the fuel. During engine combustion, high 213 214 viscosities lead to poor atomization and longer ignition delay [23]. Since the viscosity of DPO is 100 times higher than that for biodiesel, DPO and its blends can only be used as marine 215 diesel oil, for which standard ISO 8217 sets a maximum of 700 mm<sup>2</sup>/s. The higher the flash 216 point of a fuel, the safer it is to store, handle and transport. DPO has a flash point comparable 217 218 to that of biodiesel, only slightly lower, but still 45% higher than the flash point of diesel fuel. This makes the flash point of the DPO blends about 55% higher than diesel fuel, and thus safe 219 220 to store and transport. The ester content profile of the blends and the individual biodiesels are provided in Table 3. The chemical properties of the fuel such as saturated fatty acids (SFA) 221 and unsaturated fatty acids (USFA) affects the ignition quality of the fuels. Table 3 shows that 222 LFB contains of higher amount of SFA, about 58.3%. When LFB was mixed with DPO, the 223 SFA level of the blend (sample 4) was improved. This would help to improve the ignition 224 quality of the fuel blends. 225

226

227 **3.2.** Combustion behaviour in the engine

Considering their fuel properties, samples 3 (DPO20+BT20+WCOB60) and sample 4 228 (DPO20+BT20+LFB60) closely align with the marine diesel fuel standard. Consequently, 229 these two blends were chosen for the subsequent engine tests. The research encompassed an 230 examination of combustion characteristics, performance metrics, and emissions at 1500 rpm 231 across varying engine loads for five distinct fuels: conventional diesel, WCOB, LFB, 232 233 DPO20+BT20+WCOB60, and DPO20+BT20+LFB60. The results of the engine combustion characteristics were meticulously recorded and are presented graphically in Figure 5 and 6, 234 illustrating in-cylinder pressure, heat release rate, fuel line pressure, ignition commencement 235

and termination, ignition delay, combustion duration, Pmax, HHRmax, and the cumulative heatrelease rate.

## 238 **3.2.1.** In-cylinder pressure

Figure 5 shows the in-cylinder pressure at three different engine loads: (a) 20%, (b) 60%, (c) 239 240 and 100%. The DPO blends present a lower in-cylinder pressure than diesel, WCOB and LFB. The maximum in-cylinder pressure (Figure 6b) for DPO blends DPO20+BT20+WCOB60 and 241 DPO20+BT20+LFB60 were reduced by 1.7% and 0.5% at 20% load, 0.5% at 60% load, and 242 243 3% and 4.6% at 100% load, respectively. The higher viscosity of the DPO blends reduces the rate of fuel atomization, evaporation, and fuel/air mixing rate [21]. Therefore, the start of 244 combustion and ignition delay increase, reducing the in-cylinder pressure of DPO blends 245 (Figure 5). Moreover, a higher latent heat of vaporization of 1-butanol (585.40 kJ/kg) results 246 in higher heat absorption during combustion and reduces the cylinder pressure and temperature 247 [25]. The start of combustion of the DPO blends was retarded compared to diesel, WCOB and 248 LFB (Fig. 6a). The start of combustion at 20% load of DPO20+BT20+WCOB60 and 249 DPO20+BT20+LFB60 was retarded by 1.2° and 0.5° CA, respectively, and 1.5° and 1° CA at 250 251 100% load, compared to diesel. It is due to the higher viscosity of DPO blends which results in poor atomization and air/fuel mixing [21]. Another reason for the late SoC was because of 252 the cooling effect of 1-butanols laten heat of vaporisation. The lower cetane number and higher 253 heat of vaporization of 1-butanol increase the auto-ignition temperature [27]. 254

## 255 **3.2.2. Ignition delay**

As shown in Fig. 6a, the ignition delay (ID) period for the blends were longer than those for diesel fuel and biodiesel. Compared to diesel fuel, the ID for DPO20+BT20+WCOB60 and DPO20+BT20+LFB60 were longer by 5% and 2.3% at 20% load, 4.6% and 0.6% at 60% load, and 6.4% and 4.4% at 100% load. The longer ID period of the DPO blend samples is due to

the higher viscosity and butanol cooling effect. The higher viscosity affects the fuel spray characteristics such as fuel droplet sizes, atomization, vaporization and fuel/air mixing rate [28]. This fuel spray characterstic phenonea strongly affected by the visocity of the fuel which results longer ID. Moreover, higher latent heat of vaporization of butanol consume heat from the compressed air and take time to reach to the ignition stage. This reduced the cylinder temperature (due to the cooling effect) resulting longer ID periods [25].

266 Compared with biodiesel, blend DPO20+BT20+WCOB60 shows longer IDperiods by 2.5% and 3% at 20% load, 6.7% and 6.8% at 60% load, and 5% at 100% load than WCOB and LFB, 267 respectively. Neat WCOB and LFB have lower viscosity and higher ignition quality and hence 268 shows better combustion efficiency. On the other hand, blend DPO20+BT20+LFB60 shows 269 lower ID by 0.9% at 20% load than WCOB due to higher cetane number and lower viscosity 270 of LFB [23]. Moreover, the ID for DPO20+BT20+LFB60 was increased by 1-3% at 60% and 271 100% load than WCOB (Fig. 6a). The ID of DPO20+BT20+LFB60 blend was found to be 1-272 273 3% lower than LFB at all engine loads (Fig. 6a). The higher ignition quality and lower viscosity of LFB improved combustion efficiency, which increases in-cylinder temperature and reduces 274 the ID periods. It has also been observed that DPO20+BT20+LFB60 resulted in 1.66% shorter 275 ID than DPO20+BT20+WCOB60. It is due to a higher SFA% of LFB (Table 3) than WCOB, 276 which results in better ignition quality [23]. The delay can also be observed from the fuel line 277 pressure (FLP) profile (Fig. 6b) due to high viscosity. It was observed that blend 278 DPO20+BT20+WCOB60 shows higher FLP about 4-16% then diesel fuel (Fig. 6b) due to 279 higher viscosity. The conventional fuel pump governor could apply more force to inject fuel 280 281 into the cylinder [21, 29].

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## 284 **3.2.3.** Combustion duration

The end of combustion (EoC) and burn duration (BD) are shown in Fig. 6a. Both blends show shorter EoC and BD as compared to diesel. Blend DPO20+BT20+WCOB60 shows 1-2.5°CA shorter EoC at 20% and 60% load but increased by 1.2°CA at 100% load as compared to diesel fuel. Whereas, blend DPO20+BT20+LFB60, shows 0.2-1.9°CA shorter BD than diesel fuel when the engine was operated at low (20%) and full (100%) load condition (Fig. 6a). Oxygenated fuels improves the combustion efficiency. Neat DPO, butanol and biodiesels all are oxygenated fuels and hence DPO blends gave shorter BD.

## 292 **3.2.4.** Heat release rate

The heat release rate increases with increased engine load (Fig.s 5 and 6b) due to the higher 293 amount of fuel injected per stroke [30]. Compared to diesel, DPO blends show a slightly higher 294 295 heat release rate (Fig. 5a-c). The HRRmax for DPO20+BT20+WCOB60 and DPO20+BT20+LFB60 at low load (20%) was 28.49 J and 26.91 J, respectively, which are 11% 296 297 and 4%, higher than diesel fuel, 7% and 0.3% higher than WCOB and LFB (Fig.s 5a and 6b). 298 At 60% load, HRRmax for DPO20+BT20+WCOB60 fuel was found to be 1.3% and 5% higher than diesel and WCOB, respectively. Whereas DPO20+BT20+LFB60 shows 3% and 2.6% 299 lower HRRmax when compared to diesel fuel and LFB, respectively (Fig.s 5b and 6b). The 300 higher HRR for DPO20+BT20+WCOB60 at low and medium load could be due to late start of 301 combustion, longer ID period and leaner fuel mixture. The longer ID allows more fuel to burn 302 in premixed combustion phase, and as a result of that increases the HRR [27]. Moreover, 303 304 DPO20+BT20+LFB60 shows lower HRR at 60% load (Fig. 5b & 6b). This is probably due to the higher cetane number and lower viscosity of LFB as compared to WCOB. A comparative 305 study of WCOB and chicken fat biodiesel (CFB) was carried out by Sharma et al.,[23]. They 306 reported that, compared to vegetable derived biodiesel, animal fat-based biodiesel gave lower 307

HRR; due to the higher percentage of short chain saturated fatty acids and higher cetane

number. LFB also shows shorter ignition delay period due to higher cetane number [23].

At 100% load, **HRRmax** for DPO blends DPO20+BT20+WCOB60 and 310 DPO20+BT20+LFB60 were found lower by 6% and 3% than diesel fuel (Fig. 5c & 6b). The 311 low HRRmax at full load is mainly due to the rich fuel/air mixture and cooling effect of 1-312 313 butanol through latent heat of vaporisation. Even though ID was longer at full load due to higher viscosity, the BD was smaller to complete the combustion. Moreover, higher heat of 314 vaporization of 1-butanol absorbed heat during the combustion and reduced the cylinder 315 temperature, which resulted lower heat released rate[25]. 316

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318 **3.2.5.** Cumulative heat release rate

Figure 5 (d-f) compares the cumulative heat release rate at engine loads for the blends, diesel, 319 and biodiesel samples, providing more detail about the overall energy released during 320 combustion. The CHRR for the blends was lower than for diesel fuel at low and medium engine 321 load, not much changes was observed at full load. At 20% and 60% loads (Fig. 6d), the in-322 cylinder temperature was lower, which reduced the fuel combustion efficiecny rate due to 323 higher latent heat of vaporisation of butanol, which slows down the combustion efficiency [31]. 324 Moreover, higher viscosity of the blends affects fuel spray characteristics which affects 325 combustion efficiency. 326

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Figure 6. Combustion behaviour of diesel, biodiesel and DPO blends at different engine loads
- (a) SoC, EoC, ID and BD (b) Pmax, HHRmax and FLP.

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## 343 **3.3. Engine performane**

Figure 7 shows the variations in brake thermal efficiency (BTE) and brake specific fuel consumption (BSFC) with respect to brake power.

346 **3.3.1. Brake thermal efficiency** 

347 At low load, in-cylinder temperature was lower, which reduced the fuel combustion rate due

to lean air/fuel mixture [27]. Therefore, the BTE was observed lower at low load. As the engine

load increases, fuel consumption also increases to attain a constant speed of 1500 rpm (Fig. 7).

This increases the combustion efficiency and raises the in-cylinder temperature due to the rich 350 fuel/air mixture [31]. It was observed that the BTE of biodiesel and DPO blends were lower 351 compared to diesel fuel. Lower heating values of neat biodiesels and DPO caused this. of the 352 later. Blends DPO20+BT20+WCOB60 and DPO20+BT20+LFB60 show lower BTE as 353 compared to WCOB and LFB, by 8% and 6% respectively. This can be explained because of 354 the higher viscosity, lower heating value and addition of the 1-butanol [32, 33]. As higher 355 356 viscosity affects the fuel spray characteristics, fuel combustion efficiency was reduced due to incomplete combustion of the fuels. Another factor of lower BTE for DPO blends is the higher 357 358 latent heat of vaporization of 1-butanol [32, 33].



359

Figure 7. DPO blends engine performance

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# **361 3.3.2. Brake specific fuel consumption**

The brake specific fuel consumption (BSFC) for biodiesel and the blends was higher than that for diesel fuel (Fig. 7), due to the lower heating value and higher viscosity of the biodiesel and the blends. Results show that the BSFC of blends DPO20+BT20+WCOB60 and DPO20+BT20+LFB60 are 23% and 20%, higher than for diesel fuel at full load, respectively. At 100% load, DPO20+BT20+WCOB60 shows 7% higher BSFC than neat WCOB, and for DPO20+BT20+LFB60 it is 0.5% higher than neat LFB. It is a well-known fact that biodiesel

- 368 has higher BSFC due to lower calorific value, but the addition of 1-butanol increases the auto-
- ignition temperature, which further increases the fuel consumption [27].



# 370 **3.4. Engine emission characteristics**



Figure 8. Engine emission (a-e) characteristics at different engine loads

## 372 **3.4.1.** Carbon monoxide

The formation of carbon monoxide (CO) is a sign of incomplete combustion, which decreases 373 with the increase of the engine load [19]. This is due to increase in the in-cylinder temperature, 374 375 resulting in the rapid oxidation of CO to CO<sub>2</sub> [23]. This rate is higher with oxygenated fuel such as biofuel and biodiesels. DPO blends show higher CO emissions than biodiesel and diesel 376 377 fuel (Fig. 8a). The CO emissions for blends DPO20+BT20+WCOB60 and 378 DPO20+BT20+LFB60 were increased by around 86% and 25% with respect to diesel fuel at 379 100% load. At the same time, it was 40% and 44% higher with respect to neat WCOB and LFB (Fig. 8a) at 100% load, respectively. Higher CO emission of DPO blends are due to higher 380 381 viscosity, leading to poor atomization, resulting in incomplete combustion. The cooling effect of butanol's latent heat of vaporisation reduced in-cylinder temperature, which reduced the 382 oxidation rate of CO to CO<sub>2</sub> [31]. Furthermore, DPO blends consists of longer hydrocarbon 383 chain (Table 3), these longer chains also responsible for higher carbon emission; higher the 384 carbon, higher is the carbon emissions. 385

## 386 **3.4.2.** Carbon dioxide

The formation of CO<sub>2</sub> emissions gradually increases with increased engine load due to increased fuel consumption [34]. Compared to diesel fuel, DPO20+BT20+WCOB60 and DPO20+BT20+LFB60 show 7% and 4% higher CO<sub>2</sub> at 20% load and 10% and 7% at 100% load (Fig. 8b). The formation of higher CO<sub>2</sub> with the DPO blends is due to their higher oxygen content. This fuel bound oxygen increased the CO<sub>2</sub> gases during diffusion combustion by increasing CO to CO<sub>2</sub> formation [27]. The longer hydrocarbon chain present in DPO fuel also responsible for higher CO<sub>2</sub> emissions.

## 394 **3.4.3.** Oxygen and smoke emission

Figure 8c shows how oxygen decreases with higher engine loads. It is because of the rich fuel/air mixture. The DPO blends show approximately 10% less oxygen at full load. It

decreased due to increases the quantity of the fuel/strokes. Smoke formation increases with 397 increased engine load, as shown in Fig. 8d. Smoke emissions for all the biodiesels and DPO 398 399 blends were lower than the diesel fuel at 100% load (refer to Fig. 8d). Due to incomplete combustion, DPO20+BT20+WCOB60 and DPO20+BT20+LFB60 blends show 2% and 60% 400 higher smoke than diesel at 20% load. The cylinder temperature is lower under low load than 401 at full load, higher viscosity of blends reduces fuel evaporation rate, lowering combustion 402 403 efficiency [35]. The presence of butanol in the blend reduces in-cylinder temeprature due to cooling effect through latent heat of vaporisation of butanol, which resulted in incomplete 404 405 combustion and increases the smoke emission. Furthermore, because of the high in-cylinder temperature at full load, this effect is reduced [31]. As the engine load is increased, the cylinder 406 temperatures are increased. Therefore, at full load, DPO blends DPO20+BT20+WCOB60 and 407 DPO20+BT20+LFB60 show 1% and 40% lower smoke than diesel (refer to Fig. 8d). The fuel 408 bound oxygen present in the blends and high in-cylinder temperatures at high loads played an 409 important role on producing reduced levels of smoke emissions. 410

411 **3.4.4.** Nitric oxide

Figure 8e shows the formation of NO emissions for all tested fuels. The NO gas emission 412 increases due to formation of thermal-NOx caused by higher in-cylinder temperatures. 413 Compared to diesel fuel, blends DPO20+BT20+WCOB60 and DPO20+BT20+LFB60 show 414 415 0.6% and 2% higher NO emissions at low load. Fuel bound oxygen of the DPO blends caused this behaviour.At 100% load, DPO20+BT20+WCOB60 and DPO20+BT20+LFB60 blends 416 show 2% and 7% lower NO emissions than diesel (Fig. 5f). The formation of reduced NO with 417 DPO blends is due to the addition of 1-butanol wherein more heat was absorbed due to higher 418 heat of vaporization, which reduces the flame temperature during combustion [35]. Presence 419 420 of butanol in the blend helped in reducing the NO gas emission at full load condition [31].

422 4. Challenges and Limitations

The adoption of any sustainable biofuels is greatly influenced by the producing cost. Non edible oil has higher acid values than edible oils. Hence, a two stage process known as esterification is required to produce biodiesels from non edible oils. Table 5 shows estimated cost parameters for biodiesls and DPO blends. At laboratory scale, estimated cost of producing LFB at laboratory is £6.53/litre. In contrast, estimated cost of a blend sample produced at laboratory scale is £6.02 per litre. Even though this cost is high, large scale production of biodiesel and pyrolysis oil would lower the overall cost of both biodiesel and DPO blends.

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Table 5. Economic analysis of LFB and DPO blend sample

Material	Price/quantity	Required quantity	Price in GBP					
Lamb fat biodiesel (LFB) production cost:								
Waste lamb fat	£0.35/kg	1100g	£0.38					
Methanol	£5/ litre	245ml	£1.25					
Potassium hydroxide (KOH)	£75/kg	9.5g	£0.72					
Distilled water	£0.7/litre	3-5 litre	£3.5					
Power (unit)	£0.34p/kWh	2-3	£0.68					
Unit cost of LFB			£6.53/litre					
Price of DPO blend sample:								
Unit cost DPO/ pyrolysis oil	5.5/litre	200ml	£1.1					
Butanol	£5/ litre	200ml	£1.00					
LFB	6.53/litre	600ml	£3.918					
Total cost of blend sample (20%DPO + 20% butanol + 60LFB) £6.02/litre								

<sup>432</sup> 

Current study shows that digestate oil can be blended successfully with biodiesels and used in
low speed diesel engines. However, there are still challenges associated with the storage and
use of the DPO blends. One of the big challenges is to meet the fuel standards, although the
blends are not far from standards, further research is needed to meet the standard so that the

engine manufacturers allow to use the blends in the engines. Another challenge is the long-437 term stability of the pyrolysis oils, as pyrolysis oils composition changes with time. In some 438 439 cases, digestate oils may contain high water content, dewatering the pyrolysis oil could be expensive as high-water content fuels would corrode and erode the engine components. Proper 440 training is needed to prepare the blends and utilise them in the engines. Some pyrolysis oils 441 442 may contain trace metals, so careful analysis of oils and engine emission is important. Engine 443 maintenance frequency may increase due to the solids content present in the blends. The DPO blends could be suitable for using in marine engines for shipping application. These oils can 444 445 also be used in stationary engines for power generation, and to power construction and agricultural machineries. These oils may also be suitable for using in small trucks for 446 transportation of goods in rural areas. 447

448

## 449 5. Conclusions and recommnedations

The present study aims to see how blends of digestate pyrolysis oil, biodiesel and alcohol 450 perform in a multi-cylinder indirect injection CI engine. In the present investigation, an 451 452 analysis was made to assess the combustion, performance and emissions characteristics of pyrolysis oil produced from anaerobic digestion. Digestate pyrolysis oil and biodiesel were 453 produced and blended with WCOB and LFB using different cosolvents to reduce the blend 454 viscosity and improve miscibility. A total of five samples were prepared and characterized by 455 456 using DPO, waste cooking oil biodiesel (WCOB), lamb fat biodiesel (LFB) and alcohols.. Out of these, blends DPO20+BT20+WCOB60 and DPO20+BT20+LFB60 were chosen for the 457 engine tests due to better stability and fuel properties. The important findings and novelty of 458 the study are summarised below: 459

(i) The fuel physical and chemical properties of neat fuel and blends directly influenced
the engine performance, combustion efficiency and emissions. Fuel properties such as
viscosity and heating value directly effects the fuel spray characteristics, and
combustion efficiency. The chemical properties such as molecular structure, short and
long charbon chain, higher % of long carbon chain increases the viscosity; whereas
saturation and unsaturation level effect the heating and ignition quality of the fuels.
Hence, it is important to match the fuel properties with the fuel standards.

- (ii) Two stable blends were obtained by mixing 20% DPO and 20% 1-butanol with 60%
  WCOB and LFB, respectively. The DPO blends show a reduction in acid value, density,
  viscosity, and heating value about 60%, 18%, 90% and 18% compared to pure DPO,
  but they are all still higher than those for diesel fuels.
- 471 (iii) The start of combustion for DPO blends were observed to be retarded by 1-1.5° CA
  472 and ignition delay was increased by 6% compared to diesel fuel at full engine load.
- (iv) The maximum in-cylinder pressure for blends DPO20+BT20+WCOB60 and
  DPO20+BT20+LFB60 were observed to be 3% and 4.6% lower with diesel fuel at full
  engine load, respectively, whereas DPO20+BT20+LFB60 shows 3% lower HRRmax
  than diesel at full load. This could be due to the addition of butanol which reduced the
  overall in-cylinder combustion temperature. Due to higher latent heat of vaporization,
  butanol consume heat from the fuel combustion to reach the combustible stage.
- (v) DPO blends emit 7% more CO<sub>2</sub> than diesel fuel at full load. This increase in CO<sub>2</sub>
  emissions is due to the addition of oxygenated butanol, and its cooling effect due its
  higher latent heat of vaporization. The NOx emissions for DPO blends was 7% lower
  than with diesel fuel at full load, again due to the butanol.

In summary, this study affirms that DPO blends hold promise as a viable alternative fuel forboth power generation, agricultural and construction machineries, and marine engine

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485 applications. Future research avenues include exploring the utilization of higher proportions of

486 DPO blends in engines and conducting a durability study to assess the long-term performance

- 487 of engines using these blends.
- 488

## 489 Acknowledgements

The study was made possible through the support of the UKIERI project, identified by Grant
Number DST-UKIERI 18-19-04, titled "Waste to Energy - Low Temperature Combustion of
Sustainable Green Fuels".

493

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## **Declaration of interests**

☑ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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