1	<u>Original Research Article</u>
2	Influence of storage conditions on fuel functionality of palm
3	oil methyl ester
4	
5	ABSTRACT
6	The stability of biodiesel generally depends on the nature of fatty acid composition of the
7	parent oil. Unsaturated compounds are significantly more reactive to oxidation than saturated
8	compounds. The palm olein vegetable oil, derived from crude palm oil, contains higher unsaturated
9	compounds in comparison to other forms of palm oils. An experiment was intended to investigate the
10	impact of storage degradation of palm oil methyl ester in terms of fuel chemical properties, engine
11	performance and exhaust emission. The degradation study was carried out by keeping methyl ester of
12	palm oil, derived from raw palm olein oil through base catalytic trans-esterification, in two different

environment conditions (one in a transparent closed-lid container exposed to light and another in a 13 14 container exposed to air and light) at three different temperature (5°C, 25 °C and 38 °C) over 10months. 15 It was observed that degradation of biodiesels through oxidative reaction led to a series of changes in its properties, with severely increase in peroxide value, acid value and decrease in heating value at higher 16 temperature storage irrespective of storage conditions. The fuel sample with highest degradation rate, 17 18 after 10 months of storage, was considered for the evaluation of engine performance and emission by 19 making blends with petroleum diesel at different proportion. And the comparisons were made with fresh 20 biodiesel blends and diesel fuel. The engine performance of the biodiesels (fresh and oxidized) and their blends was similar to that of diesel fuel with non-significant difference in thermal efficiency, but higher fuel 21 22 consumption. The emission quality (CO and smoke density) of oxidized biodiesel was significantly better than that of fresh biodiesel and diesel fuel. But, the NO<sub>x</sub> emission was comparatively higher than diesel 23 24 fuel for both the biodiesel. The effect of fuel oxidation on the NOx emissions was also found to be 3% to 4% higher. 25

26 Keywords

27 Methyl ester of palm oil; Oxidation; Peroxide value; Temperature; bsfc; Emissions

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# 29 INTRODUCTION

Biodiesel is an oxygenated, sulfur-free, biodegradable, non-toxic, and environmentally friendly alternative <u>for</u> diesel fuel. Biodiesel is defined as the alkyl monoesters of fatty acids from renewable resources, such as vegetable oils, animal fats, and waste cooking oils. Biodiesel has positive performance attributes such as increased cetane, high fuel lubricity, and high oxygen content. However, biodiesel still has many disadvantages related to their long term storage and thermal stability. Biodiesel is a mixture of fatty acid mono alkyl esters with relatively high concentrations of long –chain mono and poly-

unsaturated compounds are present. Unsaturated compounds are significantly more reactive to oxidation 36 37 than saturated compounds; increasing the degree of un-saturation further increases reactivity [1,2]. The 38 unsaturated and polyunsaturated fatty acids in biodiesel are significantly more reactive to oxidation than saturated compounds, this is because the unsaturated fatty acids contains the most reactive site which 39 40 are particularly susceptible to the free radical attack particularly oxygen [3,4]. The stability of biodiesel generally depends on the nature of fatty acid composition of the parent oil as well as certain 41 42 functional groups present in biodiesel molecule. All biodiesels have significant amount of esters of oleic, 43 linoleic or linolenic acids and the trend of increasing stability is linolenic<linoleic<oleic etc [5,6]. In the 44 past, several studies reported the effects of biodiesel degradation at different storage time and conditions 45 on the changes in chemical properties of biodiesel [7,8]. It was found that storage time and conditions led 46 to changes in oxidative stability, iodine, acid and peroxide values as well as the flash point and cetane index. The storage stability of biodiesel was first studied by du Plessis et al. in 1985, they found that 47 48 exposure to heat and air greatly accelerated degradation of biodiesel, but when stored at 20 °C in closed 49 containers or stored after the addition of an antioxidant, the biodiesel remained stable [9]. Further 50 research on the stability of biodiesel for 180 days of storage showed that exposure to metals also increased the rate of degradation, and that exposure to higher temperatures in pro-oxidizing conditions 51 52 accelerated loss of stability [10]. Studies show that ambient temperature is one of the important factors 53 that affect the degradation of biodiesel that contain organic components. Accordingly, the increasing of degradation rate might best be viewed as high humidity conditions and high ambient temperature [11,12]. 54 55 The oxidation of biodiesel is also affected by several other factors such as light, the presence of air and metals, that accelerate oxidation[13]. 56

57 However, these studies did not systematically cover the effects of biodiesel degradations on 58 engine performance and exhaust emission. The auto oxidation reaction produces hydro-peroxides which 59 can polymerize with other radicals to produce high molecular weight insoluble sediments and gums. In 50 some cases, the oxidized fatty acid chains may break apart producing shorter chain acids and aldehydes. 51 The most likely impact of the sediment and gum formation will be fuel filter plugging and varnish deposits 52 on fuel system components and these phenomena have been observed [14–16]. The acid formation may 53 cause fuel system corrosion.

64 There are few studies on engine performance and exhaust emissions on degraded biodiesel and still have no analysis on the correlation between the changes in chemical and engine properties. 65 66 Thompson et al, studied the degradation of rapeseed biodiesel and found that the degradation led to 67 changes of brake power by less than 2% and reduction of black smoke by 3.2% [17]. Monyem and 68 Gerpen, reported that the exhaust emissions of oxidized soybean biodiesel contained less CO and hydrocarbon by 15% and 16%, respectively, with no significant changes in nitric oxide and black smoke 69 70 emissions [18] . However, a study by Pattamaprom et al, on Storage degradation of palm-derived 71 biodiesels found that biodiesel detrition led to higher emission of NOx [19].

The Palm, as a primary source of energy crop in the tropical region, has potential to meet the demand for an alternate source of biofuel in the growing need for clean fuel. The palm olein vegetable oil, derived from crude palm oil, can be chosen for its high yielding capacity and it contains higher degree of unsaturation in comparison to other forms of palm oils, for studying oxidation effect. It has also been studied that the methyl ester of palm oil has partial for replacement of diesel fuel [20]. To substantiated the studies done on palm oil biodiesel and to ascertain its long term storage stability, it was intended to experiment on the fuel Palm oil methyl ester, derived from palm olein oil, for its long term storage stability at different environmental condition and its influence on engine performance and emission.

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# 81 2. MATERIALS AND METHODS

# 82 2.1 Raw Material

The biodiesele produced from palm olein used in this study iewas purchased from market. The percentage content of different fatty acids in palm oil is shown in Table 1 and the characteristics of Palm oil is shown in Table 2 .The FFA (Free Fatty Acid) content of palm oil was found to be 0.811% (1.63mg KOH/g of oil), therefore this oil can be used directly for base catalyzed trans-esterification reaction [21]. The maximum percentage of FFA content allowed is 1%. Here, the abbreviations POME will be used for Palm oil methyl ester. The commercial petroleum-based diesel fuel used as a reference fuel was purchased from a gas station.

# 90 **Table 1** Composition of palm olein used as a reactant

Fatty acid	Percentage by weight	Reference (CODEX STAN
	Of Methyl Ester	210-1999)
Palmitic Acid (C16:0)	33.73	32-45
Stearic Acid (C18:0)	4.0	4.0- 4.8
Oleic Acid (C18:1)	42.5	40.7-43.4
Linoleic Acid (C18:2)	10.1	5-11
Myristic Acid (C14:0)	1.5	0.6-1.6
Others	8.17	-

91

92 **Table 2** Characteristics of palm olein oil

Characteristics	Value	Reference (CODEX STAN 210-
		1999)
lodine No. (g/100g)	55	50-56
Acid value (mgKOH/g)	1.63	6.00
Peroxide Value (meq/Kg)	8.5	10.00
Kinematic Viscosity (40 <sup>°</sup> C)(mm <sup>2</sup> /s)	35	-
Specific gravity (30°C/30°C)	0.889	0.890-0.912

# 94 2.2 Preparation of Biodiesel and Storage

The base catalytic transesterification method having KOH concentration of 0.1% was used to derive Palm oil methyl ester from raw pam olein. The fresh Palm oil methyl ester was collected in transparent glass bottles to make two different sample types, one having lidded tightly and another having lid open and both the samples were exposed to light. These biodiesels were stored in three different temperature (i.e. low (6<sup>o</sup>C), <u>m</u>Medium (25<sup>o</sup>C) & <u>h</u>High (38<sup>o</sup>C)) conditions for the period of 10 months, during which the chemical properties were analyzed with the interval of 2months.

#### 101 2.3 Analysis of chemical properties

To evaluate the effect of oxidation on fuel characteristics, the biodiesels were characterized for Peroxide Value (PV), Acid Value (AV), kinematic viscosity and heating value. The peroxide values were determined by titrating 5g of oil sample with 0.01N sodium thiosulfate solution following ISO 3960 and EN 14111 standard. The acid value was also approximated by titrating 5g of oil sample with 0.1N KOH according to ASTM D 664. Viscosities of biodiesels were tested using Redwood viscometer at 40°C according to according to ASTM D 445. The heating values were recorded as the high heating value (HHV) by the Toshniwal Microprocessor Bomb Calorimeter according to ASTM D 2015.

#### 109 2.4 Fuel Sampling for Engine Test

To evaluate the effect of oxidation on engine performance and emission, different blends of POME (Palm oil methyl ester) and Diesel were prepared in the ratio of 10:90, 20:80, 30:70 and 100:0 respectively, for two different types of Biodiesel (i.e. Fresh and Oxidized POME). The oxidized samples were taken from the POME stored at 35<sup>o</sup>C exposed to air and light after 10 months of storage period.

## 114 2.5 Test Engine

A Hindustan Motors make variable speed, four stroke, four cylinder, direct injection (DI) compression ignition (CI) engine was selected for- the- study. The major specifications of- the engine- are shown in Table 3. The engine <u>wasis</u>- attached with hydraulic dynamometer for subjecting the engine to various loads. The engine was operated at different load levels at a constant speed of 2000±50 rpm.

#### 119 Table 3 Engine specifications

Make	Hindustan Motor
Max. Brake Power (hp/kW)	50/37.3 at 4200rpm
Max. Torque (N-m)	106 at 2000rpm
Number of Cylinders	4
Bore X Stroke (mm)	84x 90
Displacement Volume (cc)	498.76

Compression Ratio	21:1
Strokes	4

# 121 2.6 Emission Test

122	An INDUS model PEA205 of gas analyzer was used for monitoring CO, $\text{CO}_2$ and $\text{NO}_x$ in automotive
123	exhaust. CO and $CO_2$ are measured by NDIR technology and NO by electrochemical sensors. An INDUS
124	model OMS 1o1 smoke meter was used to measure smoke density in diesel exhaust

125 Table 4 Specifications of Exhaust gas analyzers

Principle of	Species	Measured unit	Range	Resolution	Accuracy
measurement					
NDIR	CO	%	0-15%	0.001%	±0.06%
NDIR	CO <sub>2</sub>	%	0-20%	0.01%	±0.05%
Electrochemical	NO <sub>x</sub>	ppm	0-5000ppm	1ppm	±1%
Attenuation of	Smoke	k	0-∞	0.01m <sup>-1</sup>	±0.1 m⁻¹
light beam	density				

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# 127 2.7. Statistical Analysis

Experimental data were analyzed using statistical package "SPSS 23" at 5 % level of significance by multivariate analysis of general linear model. A Simple two-way analysis of variance (ANOVA) was done for dependent variables, and p-values were used to analyze the effect of independent variables. The experimental design of different variables is shown in the Table 5.

#### 132

133 **Table 5:** Design of experiment of oxidation effect on fuel characteristics

SI. no	Variables	Level
	Independent	
1	Storage conditions (Closed and Open container)	2
2	Time period in months (M0, M2, M4, M6, M8 & M10)	6
3	Temperature in °C	3
	(Low-6° C, Medium- 25° C and High – 38° C)	
	No of replication	3
	Dependent	Unit
4	Peroxide Value (PV)	meq/kg
5	Acid Value (AC)	mg KOH/g

	6 Kinematic Viscosity (KV)	mm²/s	
	7 Heating Value (HV)		MJ/kg
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135	3. RESULTS AND DISCUSSION	ı	
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137	Add information in text form a	bout the Table 6.	
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139	Table 6: Characteristics of Palm oil	methyl ester	
	Observatoriation	Mahara	Man
	Characteristics	values	Methods
	Density @ 15°C, Kg/m <sup>3</sup>	881	ASTM D 4052
	KinematicViscosity@ 40 °C,	4.4	ASTM D 445
	mm²/s		
	Peroxide Value, meq/kg	8.15	ISO 3960
	Acid Value, mg KOH/g	0.21	ASTM D 664
	Heating Value, MJ/kg	40.1	ASTM D 2015
	Flash point, °C	173	ASTM D 93
	Carbon residue, % wt	0.46	ASTM D 4530
	Pour point, °C	15	ASTM D 2500
	Copper Strip Corrosion	1a	ASTM D130
		*	

# 141 3.1 Chemical Properties

## 142 3.1.1 Effect of storage on Peroxide Value (PV)

The peroxide value is a measure of the amount of oxygen chemically bound to an oil or fat as hydro-143 peroxide. Hydro-peroxides are unstable and can easily form secondary oxidation products which can 144 145 further undergo degradation [22]. Therefore, the changes in peroxide value can be used to indicate the 146 initial oxidation of oil. The changes in peroxide values of the two different POME samples stored at 147 different temperatures are shown in Fig. 1 and Fig. 2. It can be read from the figures that the Peroxide 148 values of both the samples were increased over time for each temperature condition. The percentage 149 increase in peroxide values were observed to be 3-4% and 8-9% per month for storage temperature of 150 5°C and 25°C respectively, over the storage period of 10 months. But, in cash of higher temperature (38°C) the sharper increase in values were observed i.e. about 45-50% per month. From the statistical 151 152 analysis, the P-values, presented in the Table 7, show the high significance of storage conditions, storage

**Comment [M1]:** In Table 7, \* represents "5% level of significance". What the level of significance for the other values?

**Comment [M2]:** Bring Table 7 closer to this paragraph.

153 time and temperature on PV in terms of the main and interaction effect. This results indicated that high

temperature and the presence of oxygen played a significant role in biodiesel degradation, probably due

to the higher oxidation rate leads to form hydro-peroxide compounds (ROOH) at higher temperature [13].





157 Fig. 1 Estimated marginal means of peroxide value stored at different temperature in a closed container





159 **Fig. 2** Estimated marginal means of peroxide value stored at different temperature- in an open container

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# 3.1.2 Effect of storage on Acid Value (AV)

163 The acid value is a measure of the amount of acidic substances in fuel. During storage, the hydro-164 peroxide produced from the oxidative degradation can undergo the complex secondary reactions 165 including a split into more reactive aldehydes, which further oxidize into acids, leading to an increase in 166 acid value [7]. Fig. 3 and Fig. 4 show the trend of increasing Acid Vyalue commensurate with the 167 Peroxide value. The rate of changes for Aacid Vvalue in low and medium temperature storage were 5-168 10% and 20-30% respectively, which seemed to be slower compared to high temperature i.e, about 200-169 250%. The AV at higher temperature condition for closed and open POME samples were 5.24 mg KOH/g 170 and 6.13 mg KOH/g respectively, which were way more amount than the standard requirement of 0.5 mg 171 KOH/g. The significance of the effect of different fixed parameters like, storage condition, time period and temperature on AV is clearly seen from the P-values presented in the Table 7. The reason for the 172 173 increase in Aacid Vyalue is the hydrolysis of methyl ester by the reaction of moisture in the ambient air 174 with methyl ester [13]. Moreover, the samples wereare stored in transparent glass container and exposed 175 to light. Light or sunlight gives higher rate of increasing in acid value [23].





176

177 Fig. 3 Estimated marginal means of acid value stored at different temperature in a closed container



--⊕--Low(5°C) – - - Medium(25°) – - High(38°C)

Fig. 4 Estimated marginal means of acid value stored at different temperature in an open container

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## 183 3.1.3 Effect of storage on Kinematic viscosity (KV)

Viscosity affects the fuel injection into the engine combustion chamber. The higher is the viscosity of a 184 185 fuel, the greater theits tendency to cause engine and injection problems. The oxidation of biodiesel leads 186 to the formation of high molecular weight polymer compounds that increase biodiesel viscosity. Fig. 5 and Fig. 6 indicate the change in viscosity of POME at different temperature conditions over time. It was 187 found that biodiesel stored at a lower temperature (up to 25 °C) experienced the lower increase in 188 kinematic viscosity (5 to 5.5 mm²/s) compare to the sample stored at 38 °C, which had the highest 189 190 increase in kinematic viscosity (from 7 to 8 mm<sup>2</sup>/s). It is inferred from results that, during storage period 191 due to oxidation the concentration of high molecular weight long-chain saturated fatty acids increases, particularly in the samples subjected to high temperatures [8]. The main effects of different fixed 192 variables on KV is found to be highly significant, where as the overall interaction effect is non-significant 193 as indicated by the P-values in the Table 7. 194

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Fig 5 Estimated marginal means of kinematic viscosity stored at different temperature in a closed
 container



--⊕--Low(5°C) – - - Medium(25°C) — - High(38°C)

#### 200

Fig 6 Estimated marginal means of kinematic viscosity stored at different temperature in an open
 container

#### 203 3.1.4 Effect of storage on Heating Value (HV)

204 Heating Vyalue is thea-important property of fuel which decides the heat release capacity of the fuel. The Heating Vvalue is higher for fuel with longer chain and higher degree of saturation [24]. As it was 205 observed that the HV of POME was 40.1 MJ/Kg, which is excellent for consideration of fuel in engine with 206 207 reference to diesel. This is because the major component of palm oil shown in Table 1 comprises molecules with mostly 18 carbon (long chain) atoms. But, with longer storage time its value deteriorated 208 209 gradually as shown in the Fig. 7 and Fig. 8. The deterioration rates of HV were between 0.13 and 0.18 MJ/month at lower to medium temperature. But, at higher temperature values were between 0.22 and 0.3 210 MJ/month. Over time degradation of POME is due to the breakdown of long chain compounds into shorter 211 212 peroxide compounds. This change led to a reduction in the percentage of carbon and hydrogen in the fuel 213 molecules and thus lowering the heating values. The heating value of Palm oil methyl ester is also 214 significantly affected by different fixed factors individually but the combine effects of different factors are 215 found to be non-significant, like kinematic viscosity, as clearly seen from the P-values presented in the 216 Table 7.







220 Fig 8 Estimated marginal means of heating value stored at different temperature in an open container



Variables	Main Effect (P- value)			In	teraction Effe	ect (P- value)	
_	S	М	Т	S*M	M*T	S*T	S*M*T
Peroxide	<.0001*	<.0001*	<.0001*	< 0001*	< 0001*	< 0001*	< 0001*
value				1.0001	1.0001	1.0001	1.0001
Acid value	<.0001*	<.0001*	<.0001*	<.0001*	<.0001*	<.0001*	<.0001*

Kinematic	<.0001*	<.0001*	<.0001*	.018*	<.0001*	.117	.583
viscosity							
Heating	.002*	<.0001*	<.0001*	650	463	427	990
value				.000	.+00	121	.000

222 Note: S – Storage condition, M- months, T- temperature (° C)

\* Significant at 5% level of significance.

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# 225 3.2 Engine Performance

The engine performance, of the selected blends of fresh and 10 months old oxidized sample of methyl ester of palm oil mixed with diesel in the ratio of 100:00, 10:90, 20:80, & 30:70 proportions, was evaluated in terms of brake specific fuel consumption (bsfc) and brake thermal efficiency (bte) by comparing with petroleum diesel. All tests were performed at constant speed (rpm) of 2000±50 and varying load. Data at full (100%) load were taken for statistical analysis to evaluate the

231 significance of degradation effect of different fuel blends on engine performance.

# 232 3.2.1 Brake Specific Fuel Consumption (bsfc)

Fig. 9 represents the relationship between the brake specific fuel consumption of engine at different fuel 233 234 blends of fresh and oxidized methyl ester of palm oil at the full load condition. All points shown in this 235 figure were the average of three data points and the error bars show the spread between the maximum 236 and the minimum of the three data points. The bsfc of diesel was found to be 177 g/kW-h at full load 237 (100% load). The bsfc of fresh methyl ester of palm oil was found to be 11.02% higher than that of diesel. 238 But, the oxidized methyl ester of palm oil was 17.5% and 4.5% higher than, respectively, that of diesel 239 and fresh methyl ester at full load and this change wasie verified by the ANOVA test, to compare the variation between fresh and oxidized biodiesel, where p=0.02 qualified the existing of statistically 240 241 significant difference in fuel consumption. The amount of fuel consumption iswas increased as the percentage volume in methyl ester palm oil increased in the blends of both the-fuel types. To produce 242 243 same energy at a particular load, the fuel consumptions of different blends wereare increased. As it iswas 244 observed from the fuel properties that the calorific values of methyl ester of palm oil were less than 245 that of diesel and also its values were reduced after oxidation. The hHeating vValue of oxidized 246 biodiesel was about 7% less than that of fresh biodiesel. With much lower calorific values of oxidized 247 methyl ester of palm oil consumed, more fuel is necessary to obtainmaintain same energy. At each of the 248 load conditions, the torque and the rpm were kept constant, so the brake power was also constant.

Comment [M3]: Divide into two sentences.

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Fig. 9 Brake specific fuel consumption and brake thermal efficiency developed by engine at full load on 251 different fuel blend at rated speed.

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#### 3.2.2 Brake Thermal Efficiency (bte) 253

Fig. 9 shows the brake thermal efficiency of the engine at full load. The efficiency indicates the engine's 254 ability to convert chemical energy of fuel into mechanical power. From the data, it was calculated that 255 256 both types of POME (Fresh and Oxidized) Fresh and oxidized POME possessed slightly higher fuel 257 conversion efficiency than petroleum diesel by 3% and 4% respectively. This can be deduced from the 258 results that the presence of oxygen and additional lubricity helped in proper combustion of fuel and 259 reduction in heat losses leading to improved conversion efficiency. However, the variations of efficiencies 260 wereare almost at par with the diesel fuel and the ANOVA test showeds there is no significant difference between both the samples. Similar results were found by [25,26]. 261

#### 262 3.3 The effect of fuel oxidation on exhaust emissions

#### 263 3.3.1 Smoke Density and CO emission

264 Smoke density and CO emissions indicate the degree of incomplete combustion of fuel. The smoke 265 density is defined by the number of carbon particle in the collected sample. In this experiment, the average values of these emissions are shown in Fig. 10. The highest CO and smoke density of 266 267 emissions were found for the diesel fuel, while the oxidized POME fuel had the lowest. The o-Oxidized 268 biodiesel hads reduction in percentage CO emission with compare to diesel and fresh biodiesel by 48% 269 and 15%. Similarly, for smoke density the reductions are 13% and 3% in comparison to diesel and fresh 270 sample, respectively. The change in emission between samples was found to be highly significant, as 271 indicated by P<0.0001 for CO emission and P=0.02 for CO emission and for smoke density respectively. 272 This result wasie due to the molecular structure of biodiesel contains oxygen atoms leading to more 273 complete combustion compared to petroleum diesel. Moreover, the emissions tended to decrease with 274 storage time due to the higher oxygen contents in the degraded biodiesels. A study by Abdul Monyem 275 also found a reducing effect of CO and HC emission of oxidized biodiesel in comparison to the un-276 oxidized biodiesel [18].





278 Fig. 10 CO and Smoke Density produced by engine at full load on different fuel blend at rated speed.

## 279 3.3.2 Oxides of nitrogen (NO<sub>x)</sub> emission

280 Nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) are usually combined together as NOx. High NOx emission 281 usually occurs when excessive amount of oxygen is used in the combustion engine at high temperature [27]. Fig. 11 shows the NOx emission of engine at full load condition for different blends of fuel. The NOx 282 283 emissions for POME and OPOME were higher than the diesel fuel by (8-10)% and (10-12.6)%, 284 respectively. But, in case of the oxidized POME the rise in NOx emissions were between 4% and 5% from 285 fresh POME, which wasis statistically significant as P=0.02. Higher NOx emission by biodiesel can be 286 attributed to the excess of oxygen content in fuel molecules that leads to higher combustion temperature. 287 Moreover, NOx emissions from all fuels were highly loading dependent. Increased load at a fixed engine 288 speed naturally requires more fuel that inevitably results in longer combustion duration and increased 289 flame temperatures, which relates directly to increase in NOx production [28]. The values of NOx 290 emission wereare not statistically significant at lower loads (up to 60% of full load). The values were which 291 are not shown in the Efig. 11, but, theyit was gradually increased afterwards. As the biodiesels degraded, 292 the NOx emissions of biodiesels were increased, this can be explained by the higher degree of oxidation

and higher content of oxygenated products in biodiesel.



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#### 297 CONCLUSION

The objective of this study was to access the impact of palm oil methyl ester degradation on its chemical properties, engine performance and <u>NOx</u> emission. Based on the experimental results, the following conclusions can be drawn.

Fig. 11 NO<sub>x</sub> produced by engine at full load on different fuel blend at rated speed.

- The peroxide and acid value of palm oil methyl ester samples, stored at temperature less than
   25°C, are found to be compatible with ASTM standard for duration up to 6\_months, irrespective of
   their storage conditions. But, in case of storage at higher temperature (38°C), its suitability
   deteriorates severely after 2 months, mostly in the case of storage condition exposed to air.
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  2. Similarly, in the case of kinematic viscosity and heating value, the storage suitability of palm oil
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   3. The changes in chemical properties directly affected the engine performance and <u>NOx</u> emission.
   The engine performance of the oxidized and un-oxidized biodiesel and their blends was nearly
   similar to that of diesel fuel with slight increase <u>nearly</u> about 2-3% in thermal efficiency, but with
   higher fuel consumption by 17% and 11%, respectively, in comparison to diesel fuel.

Comment [M5]: Devide into two sentences.

- In terms of emission, the CO and smoke density of fuel decreased with increase in percentage
   load and biodiesel content in the blend. Oxidation hade also seen to be improved the emission
   guality of biodiesel. The oxidized biodiesel reduced the CO emission.
- The NOx emission from all fuel blends arewere highly loading dependent. Percentage of biodiesel content in the blend has-also playeds a significant role in NOx emission. The obtained NOx emissions, up-to 60% of full load and 10% of methyl ester of palm oil, arewere obtained to be statistically non-significant. The un-oxidized and oxidized biodiesels produced NOx emissions that were respectively, 10% and 12% higher than the diesel fuel. The effect of fuel oxidation on the NOx emissions was also found to be 3% to 4% higher.

# 322 **REFERENCE**

- 323 [1] E. Natarajan, Stability Studies of Biodiesel, Int. J. Energy Sci. (2012) 4.
- E.C. Zuleta, L. Baena, L.A. Rios, J.A. Calderón, The oxidative stability of biodiesel and its impact on
   the deterioration of metallic and polymeric materials: a review, J. Braz. Chem. Soc. 23 (2012) 2159–
   2175. doi:10.1590/S0103-50532012001200004.
- [3] G. Knothe, R.O. Dunn, Dependence of oil stability index of fatty compounds on their structure and
   concentration and presence of metals, J. Am. Oil Chem. Soc. 80 (2003) 1021–1026.
   doi:10.1007/s11746-003-0814-x.
- [4] A. Sarin, R. Arora, N.P. Singh, M. Sharma, R.K. Malhotra, Influence of metal contaminants on oxidation stability of Jatropha biodiesel, Energy. 34 (2009) 1271–1275.
   doi:10.1016/j.energy.2009.05.018.
- [5] H.L. Fang, R.L. McCormick, Spectroscopic Study of Biodiesel Degradation Pathways, SAE
   International, Warrendale, PA, 2006. doi:10.4271/2006-01-3300.
- S. Jain, M.P. Sharma, Stability of biodiesel and its blends: A review, Renew. Sustain. Energy Rev.
   14 (2010) 667–678. doi:10.1016/j.rser.2009.10.011.
- [7] D.Y.C. Leung, B.C.P. Koo, Y. Guo, Degradation of biodiesel under different storage conditions, Bioresour. Technol. 97 (2006) 250–256. doi:10.1016/j.biortech.2005.02.006.
- [8] C.-Y. Lin, C.-C. Chiu, Effects of Oxidation during Long-term Storage on the Fuel Properties of Palm
   Oil-based Biodiesel, Energy Fuels. 23 (2009) 3285–3289. doi:10.1021/ef900105t.
- [9] L.M. Du Plessis, J.B.M. De Villiers, W.H. Van Der Walt, Stability studies on methyl and ethyl fatty
   acid esters of sunflowerseed oil, J. Am. Oil Chem. Soc. 62 (1985) 748–752.
   doi:10.1007/BF03028746.
- [10] P. Bondioli, A. Gasparoli, A. Lanzani, E. Fedeli, S. Veronese, M. Sala, Storage stability of biodiesel,
   J. Am. Oil Chem. Soc. 72 (1995) 699–702. doi:10.1007/BF02635658.
- [11] X. Shi, X. Pang, Y. Mu, H. He, S. Shuai, J. Wang, H. Chen, R. Li, Emission reduction potential of using ethanol–biodiesel–diesel fuel blend on a heavy-duty diesel engine, Atmos. Environ. 40 (2006)
   2567–2574. doi:10.1016/j.atmosenv.2005.12.026.
- [12] H. Zakaria, A. Khalid, M.F. Sies, N. Mustaffa, B. Manshoor, Effect of Storage Temperature and
   Storage Duration on Biodiesel Properties and Characteristics, Appl. Mech. Mater. 465–466 (2013)
   316–321. doi:10.4028/www.scientific.net/AMM.465-466.316.
- [13] M. Mittelbach, S. Gangl, Long storage stability of biodiesel made from rapeseed and used frying oil,
   J. Am. Oil Chem. Soc. 78 (2001) 573–577. doi:10.1007/s11746-001-0306-z.
- [14] S.J. Clark, L. Wagner, M.D. Schrock, P.G. Piennaar, Methyl and ethyl soybean esters as renewable
   fuels for diesel engines, J. Am. Oil Chem. Soc. 61 (1984) 1632–1638. doi:10.1007/BF02541648.
   [15] Sample Analysis From Biodiesel Test, (n.d.) 180.
- [16] M. Ziejewski, H. Goettler, G.L. Pratt, Comparative Analysis of the Long-Term Performance of a
   Diesel Engine on Vegetable Oil Based Alternate Fuels, SAE International, Warrendale, PA, 1986.
   doi:10.4271/860301.
- [17] J. C. Thompson, C. L. Peterson, D. L. Reece, S. M. Beck, TWO-YEAR STORAGE STUDY WITH
   METHYL AND ETHYL ESTERS OF RAPESEED, Trans. ASAE. 41 (1998) 931–939.
   doi:10.13031/2013.17250.

#### Comment [M6]: Confused sentence.

- A. Monyem, J.H.V. Gerpen, The e ect of biodiesel oxidation on engine performance and emissions, 363 [18] 364 Biomass Bioenergy. (2001) 9.
- 365 [19] C. Pattamaprom, W. Pakdee, S. Ngamjaroen, Storage degradation of palm-derived biodiesels: Its 366 effects on chemical properties and engine performance, Renew. Energy. 37 (2012) 412-418. 367 doi:10.1016/j.renene.2011.05.032.
- Deepanraj, Úse of Palm oil Biodiesel Blends as a Fuel for Compression Ignition Engine, Am. J. [20] 368 369 Appl. Sci. 8 (2011) 1154-1158. doi:10.3844/ajassp.2011.1154.1158.
- U. Schuchardt, R. Sercheli, R.M. Vargas, Transesterification of vegetable oils: a review, J. Braz. [21] 370 Chem. Soc. 9 (1998) 199-210. doi:10.1590/S0103-50531998000300002. 371
- G. Knothe, Structure indices in FA chemistry. How relevant is the iodine value?, J. Am. Oil Chem. 372 [22] Soc. 79 (2002) 847-854. doi:10.1007/s11746-002-0569-4. 373
- [23] A. Bouaid, M. Martinez, J. Aracil, Long storage stability of biodiesel from vegetable and used frying 374 375 oils, Fuel. 86 (2007) 2596-2602. doi:10.1016/j.fuel.2007.02.014.
- A. Demirbag, Fuel properties and calculation of higher heating values of vegetable oils, (n.d.) 4. 376 [24]
- 377 [25] L. G. Schumacher, S. C. Borgelt, W. G. Hires, Fueling a Diesel Engine with Methyl-ester Soybean Oil, Appl. Eng. Agric. 11 (1995) 37-40. doi:10.13031/2013.25714. 378
- 379 [26] D.Y.Z. Chang, J.H. Van Gerpen, Fuel Properties and Engine Performance for Biodiesel Prepared from Modified Feedstocks, in: 1997. doi:10.4271/971684. 380
- M.S. Graboski, R.L. McCormick, COMBUSTION OF FAT AND VEGETABLE OIL DERIVED FUELS 381 [27] IN DIESEL ENGINES, (n.d.) 40. 382
- [28] M.E. Tat, P.S. Wang, J.H. Van Gerpen, T.E. Clemente, Exhaust Emissions from an Engine Fueled 383 384 with Biodiesel from High-Oleic Soybeans, J. Am. Oil Chem. Soc. 84 (2007) 865-869. doi:10.1007/s11746-007-1109-6. 385 386
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# 406 ACRONYMS

Nomenclature	
ASTM American society for testing and	KOH potassium hydroxide
materials	mg KOH/g milligram potassium hydroxide per
EU European standard	gram
POME Palm oil methyl ester	kW kilowatt
POME (0) neat diesel	hp horsepower
POME (10) % Palm biodiesel in diesel	N-m Newton meter
POME (20) % Palm biodiesel in diesel	cc cubic centimeter
POME (30) % Palm biodiesel in diesel	MJ/kg mega-joule per kilogram
POME (100) % Palm biodiesel in diesel	mm millimeter
POME O Oxidized Palm oil methyl ester	N m Newton meter
O POME (0) neat diesel	NO nitric oxide
O POME (10) % Oxidized palm biodiesel in	NO2 nitrogen dioxide
diesel	NOx nitrogen oxides
O POME (20) % Oxidized palm biodiesel in	O2 oxygen
diesel	ppm parts per million
O POME (30) % Oxidized palm biodiesel in	rpm revolutions per minute
diesel	w/v% weight in volume percent
O POME (100) % Oxidized palm biodiesel in	k unit of opacity meter (m <sup>-1</sup> )
diesel	kg/m3 kilogram per cubic meter
bsfc brake specific fuel consumption	FFA Free fatty acid
bte brake thermal efficiency	g/100g gram per hundred gram
CH3OH methanol	meq O <sub>2</sub> /kg milli-equivalent of oxygen per
CI compression ignition	kilogram
CO carbon monoxide	PV Peroxide value
CO2 carbon dioxide	AV Acid value
mm <sup>2</sup> /s millimetre square per second	KV kinematic viscosity
°C degree Celsius	HV Heating value
DI direct injection	HHV High heating value
g gram	
g/kW h gram per kilowatt hour	
HC hydrocarbon	

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