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1 **Production, characterization, engine performance and emission characteristics of**

2 *Croton megalocarpus* **and** *Ceiba pentandra* **complementary blends in a single-cylinder**

3 **diesel engine**

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12

13 **Abstract**

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14 Compounding energy demand and environmental issues necessitate suitable alternative or 15 partial replacement of fossil fuels. Among the possible sources, biodiesel from non-edible 16 vegetable oil source is more economically feasible and possesses characteristics close to 17 petroleum diesel. Two potential non-edible biodiesel feedstocks "*Croton megalocarpus*" and 18 "*Ceiba pentandra*" were used for biodiesel production through esterification and 19 transesterification process in laboratory scale. Biodiesel characterization, engine performance 20 and emission characteristics were investigated in an unmodified direct injection, naturally 21 aspirated, single-cylinder diesel engine. 20% (v/v) of each *C. megalocarpus* (CM), *C.* 22 *pentandra* (CP) and their combined blends (CMB20, CPB20, CMB15CPB05, 23 CMB10CPB10, and CMB05CPB15) were tested under varying engine speed ranging from 24 1000 rpm to 2400 rpm at full load condition. CMB20 and CPB20 reduced the brake power 25 (BP) by 2.63% and 3.70%, brake thermal efficiency (BTE) by 5.97% and 3.72%, carbon

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35 **Keywords:** Performance, Emission, Croton oil, Ceiba oil, Esterification, Transesterification.

36 **Nomenclature and Abbreviations**

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68 **1. Introduction**

69 The consumption of fossil fuel is increasing day by day due to the increase in energy demand 70 worldwide, which results in diminishing fossil fuel reserve. The quick consumption and 71 rising costs of petroleum fuel other than their harmful emission are the primary concerns to 72 look for alternative renewable sources. Thus, research on alternative and renewable energy 73 source is always a burning issue for future energy demand fulfillment. Biofuel is one of the 74 potential alternative resources. The term biofuel refers to liquid or gaseous fuels that are 75 predominantly produced from biomass. A variety of fuels can be produced from biomass 76 resources including liquid fuels, such as bioethanol, methanol, biodiesel, Fischer–Tropsch 77 diesel, and gaseous fuels, such as hydrogen and methane $¹$. Biodiesel is the most convenient</sup> 78 alternative source that could play a very important role to meet the energy demand, especially 79 in automobile and power generation sector. Generally, it is synthesized from edible oils due 80 to abundance and low free fatty acid content. Biodiesel contains alkyl ester which could be 81 derived by transesterification of triglycerides or esterification of free fatty acids with lower 82 weight alcohol. On the other hand, the consideration is essentially engaged towards biodiesel 83 from non-edible feedstocks as dependency on edible source pose threat to food supply. In 84 addition, production of biodiesel from non-edible feedstocks decreases the expense of biodiesel as these are fundamentally less expensive 2, 3 85 . *Croton megalocarpus* and *Ceiba* 86 *pentandra* are two of the potential non-edible feedstocks which have recently drawn attention 87 of the researchers⁴⁻⁷.

88 Silitonga et al.⁴ produced biodiesel from *Ceiba pentandra* feedstock through combined acid 89 esterification and base transesterification process. For acid esterification, 1% (v/v) of H_2SO_4

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90 acid catalyst, 60°C reaction temperature and 2 h reaction time was used. During base 91 transesterification, 1% (w/w) of NaOH catalyst, 50° C temperature and 2 h time was used was 92 used. In both cases they have used 8:1 methanol to oil molar ratio and 1200 rpm stirring 93 speed. They also characterized different properties of different blends of up to 50% with 94 diesel. Ong et al. 8 and Silitonga et al. 9 investigated engine performance and emission with 95 up to 50% *C. pentandra* biodiesel blending with diesel in every 10% composition interval. 96 They found that 10% blend provides better results in terms of torque, power, and fuel 97 consumption than other blend ratios. Vedharaj et al. 10 obtained 4% superior thermal 98 efficiency than conventional diesel for 25% CPB-diesel blend. Bokhari et al. ¹¹ introduced 99 the microwave-assisted technique to optimize the conversion of *C. pentandra* oil using 100 response surface methodology (RSM). They recorded optimized condition of 1:9.85 oil to 101 methanol molar ratio, 2.15 wt. % KOH catalyst loading, 57.09°C reaction temperature and 102 3.29 minute reaction time for 98.9% yield.

103 Kafuku et al. 12 investigated the production optimization and the effects of different 104 parameters of transesterification reaction during converting the methyl ester from *C.* 105 *megalocarpus*. They varied the catalyst from 0.5 wt.% to 1.5wt.% with 0.25 wt.% interval, 106 reaction time from 30 minutes to 90 minutes with 15 minute interval, methanol to oil ratio 107 from 10% (w/w) to 50% (w/w) with 10 wt. % interval, reaction temperature 30 °C to 60 °C 108 with 10°C interval, and stirring speed 20 rpm to 800 rpm with 200 rpm interval. They found 109 that 1 wt.% catalytic loading, 30 wt.% methanol loading and 60 minutes reaction time gives 110 an optimum yield of 90%. Aliyu et al. 13 investigated the performance and emission 111 characteristics of *C. megalocarpus* based biodiesel on 4 stroke 3-cylinder unmodified diesel 112 engine. They found lower BTE and higher exhaust temperature for biodiesel blends compare 113 to diesel.

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114 Earlier studies have addressed the suitability of the biodiesel and its blends derived from 115 these feedstocks in diesel engines. However, combined blend of multiple feedstocks are being 116 tested nowadays to improve the biodiesel economics while simultaneously enhancing fuel 117 performance ¹⁴. Habibullah et al. ¹⁵ studied the effect of 20% (v/v) palm, coconut, palm-118 coconut (PB5CB15, PB10CB10 and PB15CB5) biodiesel and 30% (v/v) ¹⁶ palm, coconut and 119 palm-coconut (PB15CB15) biodiesel separately on an unmodified direct injection diesel 120 engine. Among 20% blends, palm-coconut combined blends reduced 0.54% to 1.85% NO_x 121 emission with slightly improved BP. Compared to 30% palm and coconut blends, PB15CB15 122 provided improved BTE and emissions except NO_X . Arbab et al. ¹⁷ optimized the palm-123 coconut blending ratio by evaluating the combustion, performance and emission by palm-124 coconut blend (up to 20%) in a turbocharged and non-turbocharged unmodified diesel engine. 125 They observed that combined palm-coconut blend provides superior performance and 126 emission over individual palm biodiesel-diesel blend.

127 This experimental study examines the potential of using a combined blend of *Ceiba* 128 *pentandra* and *Croton megalocarpus* biodiesel as a partial replacement for diesel fuel in a 129 single-cylinder diesel engine. These biodiesels were blended based on the difference of 130 cetane index between these two as the higher the cetane index, the better the combustion 131 properties. ASTM D7467 suggests the blending of biodiesel with diesel from 6% to 20% 132 (B6–B20). Biodiesel blends of up to 20% with diesel (B20) can be easily used in the existing 133 diesel engines without the need for engine modification 18 . This study has particular relevance 134 to South East Asian region where the potential exists for availability of both of these 135 feedstocks and the establishment of economically viable application of biodiesels from these 136 oils.

137 **2. Materials and methodology**

138 The crude of *C. pentandra* oil and *C. megalocarpus* oil were purchased from local markets. 139 Highly pure analytical grade chemicals were chosen e.g. 96% pure H₂SO₄ (sulfuric acid), 140 99.8% pure CH3OH (methanol), 85% pure KOH (potassium hydroxide) and 99% pure 141 Na2SO4 (sodium sulfate) etc. The biodiesel production was carried out through a double 142 jacketed batch glass reactor in laboratory scale with 2100 ml capacity.

143 **2.1. Esterification process**

144 As the crude *C. megalocarpus* and *C. pentandra* oil both contains the high acid value (more 145 than 4 mgKOH/g), first pretreatment or esterification process was required to lower the FFA 146 content of vegetable oil before going through the transesterification step. Acid catalyzed 147 esterification of vegetable oil is recommended before transesterification if the acid value 148 equal or more than 4 mgKOH/g $^{19, 20}$. The basic esterification reaction of a triglycerides is 149 representing in the **Figure 1** where R represents small alkyl group and $R¹$ fatty acid chains.

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151
$$
R^{\perp} \stackrel{\text{O}}{C} \longrightarrow O + H + H - O + R \xrightarrow{\text{Acid Catalyst}} R^{\perp} \stackrel{\text{O}}{C} \longrightarrow O - R + H_2O
$$

152 **Figure 1: Basic esterification reaction**

153 In this process 1000 ml crude oil from both type was taken and preheat the oil at two different 154 batch glass reactor at 60° C to conduct the experiment. Methanol (CH₃OH) to oil molar ratio 155 12:1 (50% v/v oil) was maintained for *C. megalocarpus* and 18:1 (75% v/v oil) for *C.* 156 *pentandra*. After preheating and adding methanol, 1% (v/v oil) of sulfuric acid (H₂SO₄) was 157 added and maintain 60°C reaction temperature for 3 h with 900 rpm stirring speed. After 158 finishing the reaction, the reactants and products were poured into a separation funnel for 4h 159 to separate excess $CH₃OH$, $H₂SO₄$ and other impurities that were presented in upper layer of 160 the separation funnel. Esterified lower layer products were collected and removed the

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161 dissolved methanol and water with the help of rotary evaporator (IKA, RV-10). 60°C water 162 bath temperature and 339 mbar vacuum pressure for methanol removal and then 70°C 163 temperature and 72 mbar vacuum pressure for water removal from the esterified product. 164 This process was continued till confirming the absence of dissolved methanol and water into 165 the esterified vegetable oil. By lowering the acid value less than 4 mgKOH/g through this 166 process the esterified product becomes ready for transesterification.

167 **2.2. Transesterification process**

168 In this process the esterified *C. megalocarpus* and *C. pentandra* preheated at 60°C in 169 different batch glass reaction and 6:1 (25% v/v oil) methanol to oil molar ratio added. 1% 170 (w/w oil) of potassium hydroxide (KOH) was mixed as catalyst with methanol before adding 171 with the esterified oil. Then 60°C reaction temperature was maintained for 2h under 900 172 stirring speed. After finishing the reaction, the reactants and products were poured into a 173 separation funnel for 12h to separate glycerol from biodiesels. This time upper layer holds 174 desire products or biodiesel (methyl ester) and lower layer contains impurities and glycerol. 175 An ordinary outline of the transesterification reaction for fatty acid methyl ester (FAME) is 176 showed in **Figure 2.** Where R^1 , R^2 , R^3 represents fatty acid chains ²¹.

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182 **2.3. Post treatment**

183 After draining the lower layer out from separation funnel, upper layer or biodiesel layer were 184 washed with 60°C warm distilled water. The washing process was including sprays warm 185 water in upper surface of the biodiesel, surface on separation funnel, shaking and stirred 186 gently. The washing process was performed several times to properly remove the impurities 187 from the produced methyl ester. Then the produced biodiesel was undergoing to the 188 mechanical and chemical drying process. For mechanical drying, a rotary evaporator was 189 used to evaporate methanol and water content from the biodiesel same condition like 190 esterification process was applied for this removal process. For chemical drying, sodium 191 sulfate anhydrous (Na₂SO₄) powder was used. Finally, the qualitative filter paper was used 192 for separating the anhydrous from the biodiesel. The filtered and clean methyl ester is the 193 desired biodiesel. It was observed that 96.5% yield and 97% yield was observed for *C.* 194 *megalocarpus* and *C. pentandra* respectively.

195 Conventional biodiesel production technology associated with higher cost compared to per 196 unit petroleum diesel production. About 60-75% biodiesel production cost is dependent on the sources 22 . Thus non-edible and second generation biodiesel sources have more popularity 198 in the context of production cost and food security. Compared to Palm-Jatropha biodiesel 199 production from low quality feedstocks (high free fatty acid and water content present) like 200 Ceiba associated with higher processing cost at pretreatment and purification stage. By 201 optimizing the production process and reaction condition, the production costing could be 202 minimized about 1%-5% compared to other well-known biodiesel production like Palm or 203 Jatropha. Ceiba takes production cost around \$0.36/L whereas Jatropha takes \$0.36/L and 204 Calophyllum $$0.35/L$ for a 5kton capacity plant⁶.

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205 **3. Physicochemical property analysis** 206 The physicochemical property of crude *C. megalocarpus* and *C. pentandra* oil were presented 207 in Table 1. It was found that the acid value for both feedstocks are higher than 4 mgKOH/g.

- 208 *C. pentandra* have the higher acid value (17.3 mg KOH/g) than *C. megalocarpus* but lower
- 209 density (912.3 kg/m³) and viscosity (33.5 mm²/s) at 40°C. Also the fatty acid composition of
- 210 the crude *C. megalocarpus* and the *C. pentandra* oil is represented on the **Table 1.**
- 211

213

214 **Table 1: Physicochemical property of crude** *Croton megalocarpus* **and** *Ceiba pentandra* 215 **oil**

216

Property	Unit	*CCMO	^a CCMO	$*CCPO$	${}^{\rm b}$ CCPO
Density	Kg/m^3	938.5	916.8	912.3	905.2
Kinematic viscosity $@40^{\circ}$ C	mm^2/s	44.5	49.4	33.5	34.45
Acid value	$mg \text{ KOH/g}$	4.9	4.8	17.3	16.8
FFA	$\frac{0}{0}$	2.46	2.45	8.69	8.44
Flash point	$^{\circ}C$	$\qquad \qquad \blacksquare$	$\qquad \qquad$	$\qquad \qquad \blacksquare$	170.5
a Ref. ^{7,12}					
$h \rightarrow a$					

b Ref. **⁴**

Measured value

217

218 Fatty acid composition of the biodiesel sample was measured with the help of a GC (gas 219 chromatographer). Agilent 7890 series, USA GC machine was used to measure the weight 220 percentage of each FAME. **Table 2** shows the GC operation condition for measuring the 221 FAME composition.

222

223 **Table 2: GC operating condition**

²¹²

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225 It was observed that CPB contains the 28.1% saturated, 23.4% mono-unsaturated, and 48.6 % 226 poly-unsaturated methyl ester. Among them methayl oleate (C18:1) contains 22.6% and 227 methyl lioleate (C18:2) contains 40.7%. On the other hand, CMB contains 11.7% saturated, 228 13.2% mono-unsaturated and 75.1% poly-unsaturated methyl ester. Among them majority 229 portion (about 71.2%) was possessed by methyl linoleate (C18:2). It was observed that about 230 16.3% higher unsaturated FAME contains in CMB than CPB. The details FAEM contents are 231 presented in **Table 3**.

232 **Table 3: Fatty acid composition of** *Croton megalocarpus* **and** *Ceiba pentandra* **biodiesel**

234

235 Cetane Number (CN) were calculated from the percentage of fatty acid content, Iodine Value

236 (IV), Saponification Number (SN) and using the equation $1-3^{23}$.

237

SN

$$
=\sum \left(\frac{560\times A_i}{MW_i}\right) \tag{1}
$$

IV

$$
=\sum \left(\frac{254\times D\times A_i}{MW_i}\right) \tag{2}
$$

$$
CN = \left(46.3 + \left(\frac{5458}{SN}\right) - (0.225 \times IV)\right)
$$
\n(3)

238 The physicochemical property of the produced biodiesel and different diesel-biodiesel blends 239 (CMB20, CMB15CPB05, CMB10CPB10, CMB05CPB15, CPB20) were determined 240 experimentally. The equipment's which were used for measuring the physicochemical 241 property characterization are represented in the **Table 4**.

242 **Table 4: List of equipment used for measuring the physicochemical properties**

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245 The comparison of measured result with diesel and biodiesel ASTM standard were 246 represented in **Table 5.** All the properties were measured for three times and the average 247 value was considered for getting more accurate result. Croton and Ceiba are of the 248 Euphorbiaceae and Malvaceae family respectively due to which there are some 249 physicochemical non-linearities between these two biodiesels. These non-linearities occurs 250 mainly due to the type of their oil extraction sources (i.e. seeds). The seeds of these two shrub 251 and tree are different in nature. Thus, they contain different type and percentage of saturated 252 and unsaturated FAC in its crude oil. Thus, when these biodiesels are blended with diesel in 253 different proportions, the physicochemical properties of the final blends changes according to 254 the saturation level to each biodiesel. The degree of saturation of FAC of the final blends 255 changes with the bleeding ratio. Thus, the cetane index of any blend increases when 256 saturation percentage increases, whereas heating value increases when saturation percentage 257 decreases of the final blends. Other properties also change in this manner.

- 260
- 261
- 262
- 263

278 **Table 5: Physicochemical properties of** *C. megalocarpus* **and** *C. pentandra* **biodiesel and their blends**

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^a Calculated from FAC, ^b Density @15°C, ^c Calculated from ASTM 4737 method, ^d Cetane Number, * Experimental result

280

283 The experiment was performed in the heat engine laboratory of the Mechanical Engineering 284 department of University of Malaya. To carry out the experiment a single-cylinder, four stroke, 285 naturally aspirated, direct injection engine was used. A pump-line-nozzle injection system was 286 integrated in the engine to inject fuel into the combustion chamber. An eddy current 287 dynamometer was coupled with the engine for setting the load condition to the engine. Besides a 288 laptop pc with Dynomax 2000 software and electronic interface was used to extract the engine 289 performance data. A digital fuel flow meter was connected with the fuel flow line to measure the 290 fuel consumption. BOSCH gas analyzer was used to measure the smoke opacity. AVL DiCom 291 4000 was connected to the engine exhaust line to measure the CO , CO_2 , NO_x , and unburned HC 292 emissions. All experiment was performed in full load condition and variable speed, speed 293 variation form 1000 rpm to 2400 rpm. For a specific fuel, engine test was performed for three 294 times in each condition and the average was considered as the result value of a specific 295 condition. The engine test bed layout was presented in **Figure 3.** More details technical data of 296 the engine and dynamometer were shown on the **Table 6**.

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301 **Table 6: Engine and Dynamometer technical specification**

302 **4.1. Accuracy and uncertainty analysis**

303 Instrumental accuracy and measuring uncertainty are kind of error during measuring data.

304 Accuracy is the resolution of a measuring instrument which were provided by the manufacturer

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305 for a specific instrument. It indicates that how precisely the instrument can measure the value. 306 Uncertainties in any experiments appear depending on the experimental conditions, instrument 307 calibrations, observation, data input, test assembly etc. 24 . Therefore, uncertainty analysis is a 308 significant technique to validate the accuracy of the experimental results. A sample calculation 309 for uncertainty and error analysis of brake power (BP) for diesel was presented in the Appendix 310 "A" and "B", respectively. In this study percentage relative uncertainty was determined by the 311 linearized approximation method of uncertainty. However, uncertainty calculation was 312 performed based on the three test result of each parameter as well as for each condition.

313 **Table 7** represents the other exhaust emission parameter measuring instruments with its accuracy 314 and experimental uncertainty level. After calculating the individual uncertainty of measuring 315 instrument, overall experimental uncertainty was computed by the equation (4).

Overall experimental uncertainty =
$$
\sqrt{\sum (Uncertainty of each parameter)^2}
$$
 (4)

316 Overall experimental uncertainty = Square root of [(uncertainty of BP)² + (uncertainty of 317 BSFC)² + (uncertainty of BTE)² + (uncertainty of NO_X)²+ (uncertainty of CO)² + (uncertainty of 318 HC)² + (uncertainty of Smoke)²] = Square root of $[(\pm 1.72)^2 + (\pm 1.02)^2 + (\pm 1.41)^2 + (\pm 1.67)^2 +$ 319 $(\pm 1.4)^2 + (\pm 1.92)^2 + (\pm 1.82)^2 = \pm 4.21\%$

320

321 It was observed that the overall experimental uncertainty was less than 5% (95% confidence 322 level), which was within the acceptable range.

323

325 **Table 7: Gas analyzer specification**

327

328 **5. Results and discussion**

329 **5.1. Performance analysis**

330 Engine performance and fuel consumption were strongly governed by the physical and chemical 331 properties of the fuel used. Engine performance parameters include BP, BSFC and BTE. This 332 section represents the impact of 20% different biodiesel blends (CMB20, CMB15CPB05, 333 CMB10CPB10, CMB05CPB15, and CPB20) of CMB and CPB in direct injection diesel engine 334 at full throttle (100% load) condition with different engine speeds. The engine speed was varied 335 for 1000 rpm to maximum 2400 rpm with an interval of 200 rpm.

336 **5.1.1. BP**

337 The engine performance mostly depends on fuel properties such as oxygen content, density, 338 viscosity, calorific value etc. and fuel injection system ¹⁵. Basically, these fuel property affects 339 spray formation during fuel injection as well as it affects the combustion 25 . **Figure 4** 340 demonstrates the effect on BP with the variation of speed at full load condition. It was clearly 341 observed that for both diesel and biodiesel-diesel blend BP increases with the increasing of the 342 engine speed up to rated speed 2200 rpm. At maximum speed (2400 rpm) power output

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343 decreased due to poor fuel atomization during combustion 26 and increase of piston cylinder 344 frictional loses associated with higher engine speed 27 . Maximum BP was observed at 2200 rpm. 345 The maximum BP were recorded 7.60, 7.45, 7.42, 7.54, 7.59 and 7.55 kW for diesel, CMB20, 346 CPB20 CMB15CPB05, CMB10CPB10 and CMB05CPB15, respectively. BP output level was 347 lower (about 1.09% to 3.7%) for biodiesel blends than petro diesel in all speeds. This can be 348 attributed to combined effect of higher specific density, lower calorific value, higher viscosity 349 and lower volatility (higher flash point compared to diesel) of biodiesels 28 . However, combined 350 effect of this properties creates high injection in premixed region, poor fuel spray formation, 351 incomplete combustion and high global fuel-air ratio equivalence ratio for lowering the BP of 352 biodiesel blends than petro diesel $19, 29$. This result, together with almost 12.07% lower calorific 353 value of biodiesels can be attributed to the lower BP output than diesel. Among all the 20% 354 biodiesel blends CMB10CPB10 showed the higher BP output at higher engine speed. This 355 outcome may be attributed to the combined effect of the density and viscosity that diminish the 356 inner spillage in the pump $30, 31$ and flash point that affects atomization or spray formation of fuel 357 during combustion. Another reason could be the combined effect of additional oxygen content 358 in biodiesels 17 and improvements of CN of combined blends. Accumulating lowest calorific 359 value among all the combined blends, CPB20 demonstrated somewhat least BP. Addition of 360 CPB with CMB improves the Cetane Index as well as the BP of the engine.

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362 **Figure 4. Brake power vs. engine speed for full load condition**

363 **5.1.2. BSFC**

364 BSFC is defined as fuel consumption per unit BP output for a specific fuel. Fuel properties e.g. 365 density, viscosity and calorific value have significant influences on engine BSFC. **Figure 5** 366 illustrates the BSFC in g/kWh with variation of engine speed. The figure shows that BSFC of 367 biodiesel blends is higher than that of petro diesel. This may be attributed to higher density and 368 viscosity of biodiesel compared to diesel 32 . The figure also demonstrates that initially the BSFC 369 for all fuels gradually decreased with increasing engine speed till 1800 rpm. This may be 370 attributed to increased fuel atomization ratio, subsequently, the air-fuel equivalence ratio, which 371 influences air and fuel mixing ¹⁵. The lowest BSFC for diesel, CMB20, CPB20, CMB15CPB05, 372 CMB10CPB10 and CMB05CPB15 were recorded 250.16, 278.23, 271.14, 264.05, 260.50 and 373 262.10 g/kWh, respectively at 1800 rpm. BSFC gradually increased with the engine speed after

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374 1800rpm. Maximum BSFC for diesel, CMB20, CPB20, CMB15CPB05, CMB10CPB10 and 375 CMB05CPB15 were recorded 355.62, 395.93, 386.00, 376.10, 370.53 and 372.41 g/kWh, 376 respectively at the maximum engine speed (2400 rpm). Volumetric efficiency decrease and 377 increased frictional loss at higher speed might be the reason for this increase. In addition, BSFC 378 increases with increasing engine speed and blend ratio of biodiesel 26 . Higher density and 379 viscosity of biodiesel blends leads to higher mass flow rate in mechanically controlled pump-380 line-nozzle system as fuel is injected volumetrically affecting the fuel atomization³³. Individual 381 blends of CMB and CPB possess higher density and viscosity respectively, rather than combined 382 blends which results in higher BSFC. With increasing amount of CPB in blend results in lower 383 density but increased viscosity, which in turn increased surface tension of the blend. This 384 resulted in a decrease in BSFC.

386 **Figure 5. BSFC vs. engine speed for full load condition**

387 **5.1.3. BTE**

388 BTE is defined as break power of heat engine as a function of the heat input by the fuel. **Figure** 389 **6** shows the BTE for all tested diesel and biodiesel-diesel blends. The graphs demonstrated that 390 BTE increased with engine speed up to 1800 rpm. This outcome is usually attributed for the 391 highest BSFC was attained due to the consolidated impact of poor fuel atomization time and 392 elevated piston-cylinder frictional force at this speed 34 . The height BTE value for diesel, 393 CMB20, CPB20, CMB15CPB05, CMB10CPB10 and CMB05CPB15 were recorded 31.42%, 394 29.14%, 30.03%, 30.74%, 31.19% and 31.04, respectively. After 1800 rpm, BTE eventually 395 decreased along with engine speed and achieved the lowest value at 2400 rpm for each of the 396 investigated fuels. This results attributed to the higher fuel consumption for the increased engine 397 speed. Compared to diesel maximum BTE of biodiesel-diesel blend were decreased by 0.50% to 398 5.97%. This changes due to the fuel variation were significant. BTE changed with the variety in 399 BSFC and calorific value of the biodiesel. Though individual CMB20 possess higher calorific 400 value that CPB20 as well as opposite for viscosity and CN, thus CMB20 showed lower BTE than 401 CPB20. On the other hand, combined blending provides better combination of density, viscosity 402 as well as CN rather than individual biodiesel (CMB20 and CPB20) blends. Addition of higher 403 percentage of CPB with CMB increases BTE and thus 10% combined blend of CMB and CPB 404 provides the higher BTE as well as the lower BSFC among the biodiesel-biodiesel blends. 405 Combustion phasing additionally impacts the energy conversion of heat energy to work. Quick 406 injection of biodiesel together with high CN results in the early start of combustion (SOC) 35 . 407 Early SOC, raises pumping function and endorses heat decrease in the cycle $31, 33$. This trend, 408 collectively along with low heating value and higher density, viscosity, negatively impacts 409 engine performance $36, 37$.

412 **5.2. Emission analysis**

413 Emission parameter such as NO_X , CO, HC and Smoke opacity were investigated throughout the 414 experiments.

415 **5.2.1. NO^X**

416 NO_x emission mainly includes nitric oxide (NO) and nitrogen dioxide (NO₂) emission to the 417 environment. NO is the prevalent oxide delivered inside the engine cylinder. During combustion, 418 atmospheric nitrogen (about 78.09% by volume) come into reaction and become the main source 419 for NO_X emission for the internal combustion engine, this is treated as the thermal NO_X . 420 Atmospheric tripled bonded nitrogen behaves as an inert gas but in high combustion temperature 421 it splits up and undergoes with a series of reaction with oxygen and creates NO_2 . This NO_X 422 formation mechanism is known as Zeldovich mechanism. NO_x forms in prompt (Fenimore) 423 mechanism because of the generation of hydrocarbon radicals via molecular unsaturation $38, 39$.

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424 **Figure 7** demonstrate the NO_x emission for variable speed for full load. NO_x was gradually 425 increasing with engine speed as the combustion temperature increase, with higher engine speed. 426 The highest NO_x emission were observed for diesel, CMB20, CPB20, CMB15CPB05, 427 CMB10CPB10 and CMB05CPB15 were recorded 12.18, 13.80, 13.90, 13.70, 14.05 and 13.99 428 g/kWh, respectively at 2400 rpm. NO_X formation through the biodiesel blend is quite high due to 429 12-13 % higher oxygen content in biodiesel, which provides high in-cylinder temperature for 430 both premixed and diffusion combustion condition rather than diesel 40 . Together with higher 431 CN, air surplus co-efficient, residence time and higher bulk modulus of elasticity can be ascribed 432 as the reason for NO_X formation^{41, 42}. Bulk modulus of elasticity causes the early nozzle opening 433 and advancement of the ignition, which increase global fuel-air equivalence 43 . Higher CN 434 provides shorter ignition delay and higher oxygen content in biodiesel results higher combustion 435 temperature. Because of the higher in-cylinder temperature during combustion CMB10CPB10 436 gives slightly higher and CMB15CPB05 provides relatively lower NO_X emission among the 437 tested biodiesel blends.

439 **Figure 7. NO**X **emission vs. engine speed for full load condition**

440 **5.2.2. CO**

441 The partial combustion is the real cause of higher CO content in exhaust emissions ,which 442 caused by insufficient oxygen supply 44 during combustion. All this happens because of engine 443 speed, air-fuel equivalence ratio, fuel pressure, fuel type and injection timing. Among them, 444 ignition mixture because of lower air-fuel equivalence ratio can be considered as the main cause 445 of CO emissions. **Figure 8** illustrates CO variation in different engine speeds at full load 446 condition. Initially CO emission increased with increasing the engine speed ranging from 447 1000rpm to 1400rpm. This can be attributed to the lower air-fuel equivalence ratio, lower 448 combustion temperature, poor atomization due to density, viscosity and flash point at low speed. 449 On the other hand, at higher speed (after 1800rpm) BSFC was found higher for biodiesel. With 450 increasing of engine speed, higher air-fuel equivalence ratio, higher cylinder temperature and 451 pressure was introduced during combustion, which ensures relatively better combustion and thus 452 reduced the CO emission $31, 45$. Overall biodiesel and biodiesel-diesel blends provides relatively 453 lower CO emission in every speeds. This can be ascribed as higher oxygen content and higher 454 CN of biodiesel, which shorting the ignition delay, thus provides better combustion and prevents less over-lean zones ⁴⁶ 455 . Maximum CO emission for diesel, CMB20, CPB20, CMB15CPB05, 456 CMB10CPB10 and CMB05CPB15 were recorded 474.04, 469.97, 472.00, 461.13 and 466.51 457 g/kWh, respectively at 1400 rpm. CO emission reduction for the biodiesel were obtained 1.09% 458 to 5.21% with compare to diesel.

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461 **5.2.3. HC**

462 The reasonable factors that creates the HC emission for petro diesel are fuel trapping in the 463 crevice volume of combustion 35 , low temperature bulk quenching of oxidation reaction, locally 464 over-lean or over-rich mixture, liquid wall filaments for excessive spray impingement and 465 incomplete fuel evaporation 47 . The **Figure 9** illustrates the HC emission; it shows alike CO 466 emission reduction. HC emission gradually decreases with increasing engine speed. It happens 467 because of presence of oxygenate compounds in biodiesel. Also. This can be attributed to high 468 in-cylinder temperature due to the high in cylinder pressure 48 . The maximum HC emission for 469 diesel, CMB20, CPB20, CMB15CPB05, CMB10CPB10 and CMB05CPB15 were recorded as 470 0.537, 0.530, 0.513, 0.524, 0.484 and 0.496 g/kWh, respectively at 1000 rpm. Compare with 471 petro diesel, biodiesel blends and combined biodiesel blends reduces HC emission ranging from 472 1.48% to 8.38%. The biodiesel blend CMB10CPB10 gives the lowest HC emission.

474 **Figure 9. HC emission vs. engine speed for full load condition**

475 **5.2.4. Smoke opacity**

476 Smoke emission refers to dark-black smoke or dry soot which is one of the principal source of particulate matter ¹⁹ 477 . Smoke emission can be measured by the term smoke opacity. **Figure 10** 478 illustrate the smoke opacity of diesel and biodiesel-diesel blend at variable engine speed. It 479 shows smoke opacity of all blends of biodiesel is lower than petro diesel for all the engine speed 480 due to oxygenated biodiesel fuel structure 49 . Inborn oxygen of biodiesel provides better 481 combustion, thus lowering the smoke emissions than diesel 4^1 . Smoke emission gradually 482 increases up to certain speed (in this case up to 1800rpm), then gradually decreases up to 483 maximum speed. The increases smoke opacity can be attributed to incomplete combustion of the 484 hydrocarbon fuel and partial reaction of the carbon content in the liquid fuel 28 due to lower 485 combustion temperature and poor atomization (due to density, viscosity and flash point) at low 486 speed ranging from 1000 rpm to 1800rpm. Maximum smoke opacity for diesel, CMB20, CPB20,

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487 CMB15CP05, CMB10CPB10, CMB05CPB15 were recorded 65.15%, 60.90%, 58.60%, 59.80%, 488 57.20% and 57.90%, respectively at 1800 rpm. After 1800rpm, air-fuel equivalence ratio 489 increases with engine speed and introduced higher combustion temperature which provides 490 better burning of HC during combustion, thus decreased smoke opacity. However, Tested 491 biodiesel blends provides on an average 12.35% to 20.71% smoke emission reduction than petro 492 diesel. Addition of CPB in CMB leads to an increase in viscosity and decrease in density, thus 493 provides better BSFC and fuel atomization. Among all tested biodiesels and combined biodiesel 494 blends, CMB10CPB10 provides slightly lower smoke opacity.

495

497 **Figure 10. Smoke opacity vs engine speed for full load condition**

498 **6. Conclusions**

499 In this study biodiesel was produced from *C. megalocarpus* and *C. pentandra* feedstock and their 500 physiochemical properties were examined. In addition, performance and emission characteristics

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516 **Acknowledgement**

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521 **References**

- 522 1. S. A. Shahir, H. H. Masjuki, M. A. Kalam, A. Imran, I. M. R. Fattah and A. Sanjid, 523 *Renewable and Sustainable Energy Reviews*, 2014, **32**, 379-395.
- 524 2. A. E. Atabani, T. M. I. Mahlia, H. H. Masjuki, I. A. Badruddin, H. W. Yussof, W. T. 525 Chong and K. T. Lee, *Energy*, 2013, **58**, 296-304.
- 526 3. M. Tabatabaei, K. Karimi, I. S. Horváth and K. Rajeev, *Biofuel Research Journal*, 2015, 527 **2**, 258-267.
- 528 4. A. S. Silitonga, H. C. Ong, T. M. I. Mahlia, H. H. Masjuki and W. T. Chong, *Fuel*, 2013, 529 **108**, 855-858.
- 530 5. T. M. Y. Khan, A. E. Atabani, I. A. Badruddin, R. F. Ankalgi, T. K. M. Khan and A. 531 Badarudin, *Industrial Crops and Products*, 2015, **65**, 367-373.
- 532 6. H. Ong, A. Silitonga, H. Masjuki, T. Mahlia, W. Chong and M. Boosroh, *Energy* 533 *conversion and management*, 2013, **73**, 245-255.
- 534 7. G. Kafuku, M. K. Lam, J. Kansedo, K. T. Lee and M. Mbarawa, *Bioresource technology*, 535 2010, **101**, 7000-7004.
- 536 8. H. C. Ong, H. H. Masjuki, T. M. I. Mahlia, A. S. Silitonga, W. T. Chong and T. Yusaf, 537 *Energy*, 2014, **69**, 427-445.
- 538 9. A. Silitonga, H. Masjuki, T. Mahlia, H. C. Ong and W. Chong, *Energy Conversion and* 539 *Management*, 2013, **76**, 828-836.
- 540 10. S. Vedharaj, R. Vallinayagam, W. M. Yang, S. K. Chou, K. J. E. Chua and P. S. Lee, 541 *Energy Conversion and Management*, 2013, **75**, 773-779.
- 542 11. A. Bokhari, L. F. Chuah, Y. Suzana, A. Junaid, M. R. Shamsuddin and M. K. Teng, 543 *Biofuel Research Journal*, 2015, **2**, 281-287.
- 544 12. G. Kafuku and M. Mbarawa, *Fuel*, 2010, **89**, 2556-2560.
- 545 13. B. Aliyu, D. Shitanda, S. Walker, B. Agnew, S. Masheiti and R. Atan, *Applied Thermal* 546 *Engineering*, 2011, **31**, 36-41.
- 547 14. B. R. Moser, *Renewable Energy*, 2016, **85**, 819-825.
- 548 15. M. Habibullah, I. Rizwanul Fattah, H. Masjuki and M. Kalam, *Energy & Fuels*, 2015, **29**, 549 734-743.
- 550 16. M. Habibullah, H. H. Masjuki, M. A. Kalam, I. M. Rizwanul Fattah, A. M. Ashraful and 551 H. M. Mobarak, *Energy Conversion and Management*, 2014, **87**, 250-257.
- 552 17. M. I. Arbab, M. Varman, H. H. Masjuki, M. A. Kalam, S. Imtenan, H. Sajjad and I. M. 553 Rizwanul Fattah, *Energy Conversion and Management*, 2015, **90**, 111-120.
- 554 18. M. Kalam, H. Masjuki, M. Jayed and A. Liaquat, *Energy*, 2011, **36**, 397-402.
- 555 19. I. M. Rizwanul Fattah, M. A. Kalam, H. H. Masjuki and M. A. Wakil, *RSC Advances*, 556 2014, **4**, 17787-17796.
- 557 20. I. M. Rizwanul Fattah, H. H. Masjuki, M. A. Kalam, M. A. Wakil, H. K. Rashedul and 558 M. J. Abedin, *Industrial Crops and Products*, 2014, **57**, 132-140.
- 559 21. G. Moradi, M. Mohadesi, M. Ghanbari, M. Moradi, S. Hosseini and Y. Davoodbeygi, 560 *Biofuel Research Journal*, 2015, **2**, 236-241.
- 561 22. A. Ruhul, M. Kalam, H. Masjuki, I. R. Fattah, S. Reham and M. Rashed, *RSC Advances*, 562 2015, **5**, 101023-101044.
- 563 23. K. Krisnangkura, *Journal of the American Oil Chemists Society*, 1986, **63**, 552-553.
- 564 24. M. A. Kalam and H. H. Masjuki, *Energy*, 2011, **36**, 3563-3571.
- 565 25. S. Murillo, J. Miguez, J. Porteiro, E. Granada and J. Moran, *Fuel*, 2007, **86**, 1765-1771.

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610 **Appendix**

611

612 **Appendix A: Uncertainty level calculation of BP, BSFC and BTE for diesel**

614

615 **Appendix B: Sample calculation of the error bar for Power of diesel**

616

617

618 **Appendix C: Sample of Calculated Cetane Index for diesel (ASTM D4737-10)**

Where, CCI= Calculated Cetane Index by Four Variable Equation, $D =$ Density at 15°C, g/mL, $DN = D - 0.85$, $B = [e^{(-3.5)(DN)}] - 1$, $T_{10} = 10$ % recovery temperature, °C, $T_{10N} = T_{10} - 215$, $T_{50} = 50$ % recovery temperature, $T_{90} = 90 \%$ recovery temperature, $^{\circ}C$, $T_{90N} = T_{90} - 310$.

Calculate Cetane Index for Pure Diesel **= 45.31**

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620

621