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Multi-attribute decision-making approach for *Aegle marmelos* pyrolysis process using TOPSIS and Grey Relational Analysis: Assessment of engine emissions through novel Infrared thermography

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## **Graphical Abstract**



1 Multi-attribute decision-making approach for Aegle marmelos pyrolysis process using

2 TOPSIS and Grey Relational Analysis: Assessment of engine emissions through novel

- 3 Infrared thermography
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#### 13 Abstract

This research focuses on the selection of the optimum process parameters for Aegel marmelos 14 (AM) pyrolysis experiment based on multi-objective decision-making techniques. This 15 investigation presents the optimization report for obtaining maximum pyrolysis oil from AM 16 de-oiled seed cake through thermochemical conversion (pyrolysis) process. The pyrolysis 17 18 process has been conducted according to L<sub>27</sub> orthogonal array with chosen input control factors such as pyrolysis temperature (°C), heating rate (°C/min) and biomass particle size 19 (mm). The output response parameters measured are the bio-oil yield, bio-char yield and 20 biogas yield. The multi-objective decision-making approach namely Technique for order 21 preference by similarity to ideal solution (TOPSIS) and Grey relational analysis (GRA) 22 techniques are employed to determine the optimum pyrolysis process parameters to maximize 23 the yield of AM bio-oil. The optimized values of pyrolysis temperature (PT), heating rate 24 (HR) and feedstock particle size (PS) are 600°C, 10°C/min and 0.6 mm. At peak engine 25 loading condition, 20% AM bio-oil + 80% diesel fuel blend (AM20) emit lower carbon 26 dioxide (CO<sub>2</sub>=8.68%) and oxides of nitrogen (NOx=1401 ppm) emissions as compared with 27 diesel (D) CO<sub>2</sub> (10.33%) and NO<sub>x</sub> (1511 ppm) emissions. The association between exhaust 28 gas temperature and NOx emission was inferred using a novel approach of thermal imager by 29 30 sensing the infrared rays from the hot surface of the exhaust port. Infrared thermal images are

- 31 captured during the engine operations fuelled with bio-oil at the optimum pyrolysis
- 32 conditions concluded by TOPSIS and GRA results (PT=600°C, HR=10°C/min and PS=0.6
- 33 mm). According to the thermal imaging result, AM20 blend produces the lower amount of
- 34 NOx emissions compared with neat diesel and it is suggested that AM bio-oil can be used as

- engine fuel instead in order to preserve the eco-system stability and biodiversity.
- 36 Keywords: Aegle marmelos; Pyrolysis; TOPSIS; GRA; NOx emission; Thermal Imager.

#### 37 Nomenclature

AM	Aegle marmelos
AM 20	20% <i>Aegle marmelos</i> bio-oil + 80% diesel
ASTM	American Society for Testing and Materials
bTDC	Before the top dead centre
CC	Closeness coefficient
CI	Compression ignition
CO	Carbon monoxide (%)
$CO_2$	Carbon dioxide (%)
CR	Compression ratio
D	Neat diesel
Dp	Biomass particle diameter (mm)
$D(Tij)_{(x*v)}$	TOPSIS design matrix
GRA	Grey relational analysis
GRC	Grey relational coefficient
GRG	Grey relational grade
HC	Hydrocarbons (ppm)
HR	Heating rate (°C)
i	Trial number
IR	Infrared
$J_1$	Set of beneficial attribute
$J_2$	Set of non-beneficial attribute
k	Comparability sequence
MCC	Mean closeness coefficient
MGRG	Mean grey relational grade
$\max g_i(k)$	Maximum value of $g_i(k)$ for k <sup>th</sup> response
$\min g_i(k)$	Minimum value of $g_i(k)$ for k <sup>th</sup> response
NOx	Oxides of nitrogen (ppm)
nij	The normalized value of the design matrix
PCA	Principal component analysis
PS	Biomass particle size (mm)
PT	Pyrolysis temperature (°C)
RCC	Relative closeness coefficient
RSM	Response surface methodology
$S_i^+$	Positive separation measures
$S_i^-$	Negative separation measures
Т	Temperature
TGA	Thermogravimetric analysis

TOPSIS	The technique for order preference by similarity to an ideal solution
Tij	The measure of the j <sup>th</sup> attribute to the i <sup>th</sup> alternative
Х	Alternatives/Test trials
$x_i(k)$	The normalised value of output
у	Attributes/Output response
ξ <sub>ij</sub>	Weighted normalized matrix
ξ <sup>+</sup>	Positive ideal solution
ξ-	Negative ideal solution
$\Delta_{oi}(k)$	Deviation sequence
$\Delta_{min}$	Minimum deviation sequence
$\Delta_{max}$	Maximum deviation sequence
φ	Distinctive coefficient
$\varphi_i(k)$	Grey relational coefficient
$\vartheta_i$	Grey relational grade

#### 39 **1. Introduction**

38

Fossil fuels play a vital role in the transportation sector but emit harmful gases like 40 carbon mono oxide, oxides of nitrogen, hydrocarbons and sulphur content gases etc. which in 41 turn augments the global temperature. The Shortage of fossil fuel resources and its related 42 43 environmental problems grasped great attention towards bio-fuel research (Bordoloi et al., 2016). Biofuel usage decreases the global warming rate by adopting the closed carbon cycle 44 45 thereby reducing greenhouse emissions (D'Alessandro et al., 2016; Mi et al., 2016). Foremost benefits of biofuels are eco-friendliness, renewability and bio-degradability (Knothe et al., 46 2006). Biochemical and thermochemical conversion technologies are commonly used to 47 convert the biomass into solid (bio-char), liquid (bio-oil) and gas (biogas) products. As 48 compared to biochemical routes, thermochemical conversion possesses more advantages in 49 terms of time consumption and decomposing C<sub>5</sub> sugars (Bordoloi et al., 2016). Pyrolysis is 50 one of the most capable techniques among the available biomass conversion methods (Halim 51 and Swithenbank, 2016). In the pyrolysis process, biomass is heated in the absence of oxygen 52 atmosphere to derive useful products like bio-oil, biochar and biogas (Abas et al., 2018). The 53 notable advantages of pyrolysis products are that they are eco-friendly, reusable and valorised 54 into fuels and chemicals (Halim and Swithenbank, 2016). 55

From wide literature reviews, it can be inferred that significant works have been done in AM cold pressed oil. Very few researchers carry out their research in the study of AM vegetable oil properties and diesel engine performance and emission characteristics fuelled with AM seed oil blends (Katagi et al., 2011). AM tree falls under the Rutaceae family (Paramasivam et al., 2018) and it is generally seen in south Indian Shiva temples

3

(Baranitharan et al., 2019). AM seedswere collected from its matured fruits. The thermal
properties of AM seed cake were characterized with the help of thermo gravimetric analysis.

Anupam et al. (2016) optimized the process parameters of Leucaenal eucocephala 63 64 bark using RSM (Response surface methodology) method and determined the optimal pyrolysis temperature and time (Anupam et al., 2016). Optimization of the lignin pyrolysis of 65 66 wood was done using the PCA (Principal component analysis) method (shen How and Lam, 2018). Mohammed et al. (2016) optimized the napier grass pyrolysis oil using RSM in terms 67 68 of pyrolysis temperature, heating rate and nitrogen gas flow rate (Mohammed et al., 2017b). Mohammed et al. (2017a) optimized the pyrolysis temperature, heating rate and nitrogen flow 69 70 rate of Bambara groundnut using RSM tool and obtained the optimized parameters of 600°C, 50°C/min and 11 L/min respectively. The author also employed  $L_{27}$  orthogonal array to 71 design the experiments and analysed the effect of each parameter on bio-oil yield through 72 Taguchi method. Considering the pyrolysis process, the quality of experiments was based on 73 the yield of bio-oil. So, any numbers of quality characteristics can be considered for the 74 selection of best pyrolysis parameters (Mohammed et al., 2017a). Taguchi methodology is 75 restricted to optimizing single objective problems (Sahu et al., 2016). In the present research 76 scenario, it is inevitable to solve multi-criteria problems in complex engineering systems. In 77 this view, numerous techniques are offered like Technique for order preference by similarity 78 to ideal solution (TOPSIS) and Grey relational analysis (GRA). GRA tool works under the 79 grey system theory and suitable for solving multi-objective problems with the complex 80 relationship between several factors and variables (Kuo et al., 2008). The GRA technique tool 81 82 decreases the difficulty and increases the overall efficiency of the problems (Liu and Cheng, 2016). TOPSIS method is simple and efficient (Guo and Zhao, 2015) with a multi-objective 83 decision-making technique used to solve the multiple systems (Hussein et al., 2016). 84

Generally, bio-oil is rich in oxygenated compounds due to which it can be directly 85 used as an engine fuel along with baseline diesel fuel without any engine modifications 86 (Baranitharan et al., 2018; Sakthivel et al., 2018). Using fossil fuels as a fuel in internal 87 88 combustion engine operation emits harmful gases (Halim and Swithenbank, 2016). As compared to baseline diesel emission, pyrolysis bio-oil emits less pollutant (López et al., 89 90 2008). Compression ignition (CI) engine emit a higher amount of NOx emission value to the 91 atmosphere. The thermal imaging method is exhibited to be a novel technique for heat (Merino-Pérez et al., 2015). The equilibrium 92 distribution measurement investigations

4

concentration is of nitric oxidesis very high at high combustion chamber temperatures, which
is also encounted near the stoichiometric combustion. Zeldovich mechanism is a simple
reaction mechanism which defines the formation of thermal NOx which is given as Eqns. (1)
and (2),

97 
$$N_2 + O \stackrel{\leftarrow}{\rightarrow} N + NO$$
 (1)

(2)

98  $N + O_2 \leftarrow O + NO$ 

Hence, by evaluating the zeldovich mechanism, it is obvious that NOx emission value 99 greatly depends on the combustion chamber temperature. Hence, among the exhaust 100 emission, NOx can be investigated through green technology aided thermal images with 101 better understanding. Shameer and Ramesh (2017a,b) studied the relationship between  $NO_X$ 102 emission level and in-cylinder temperature via FLUKE thermal imager and concluded that 103 combustion temperature is a key parameter to the oxides of nitrogen emission measurement 104 (Shameer and Ramesh, 2017a, b). The Author used thermography to measure the radiation 105 emitted by an object at different points from a hot source in the infrared spectrum and 106 converted it into source temperature (Garcia-Gonzalez et al., 2016; Ramesh et al., 2019). The 107 novel approach of using FLUKE-Thermal imager for analysing the relationship between 108 exhaust gas temperature and engine test NOx emission characteristics has been executed in 109 this research. Table 1 presents a comparison of previous biofuel studies using TOPSIS and 110 GRA optimization techniques. 111

112 Table 1 Comparison of previous bio-fuel studies using TOPSIS and GRA techniques

Tools	Investigation	Parameters	Materials	Conclusion	Reference
TOPSIS	Optimization	Lignin cellulose,	Rice straw,	High volatile matter	(Madhu et
	of feed stock	Hemicellulose,	Sunflower shell,	content (79.2 wt%)	al., 2018)
	material to	Volatile matter,	Hardwood, Wheat	Hardwood biomass	
	obtain a	Fixed carbon,	straw, Palm shell	selected as the	
	maximum bio-	Moisture content,		bestfeedstock	
	oil yield	Ash content		material for	
				pyrolysis.	
TOPSIS	Optimization	Charge inlet	65% Diesel + 25%	Charge inlet	(Muniappan
	of CI engine	temperature,	Bael-oil + 10%	temperature=320K,	and

	parameters to	Exhaust gas	Diethyl ether blend	Exhaust gas	Rajalingam,
	obtain better	recirculation		recirculation=30%	2018)
	performance			gives better engine	
	and emission			characteristics.	
	characteristics				
GRA	Optimize the	Bed temperature,	Sea wood particles	Bed temperature has	(Wang et al.,
	influence	Fluidization		a great influence on	2013)
	factor of sea	velocity, Materials		the bed combustion	
	wood particle	height			
	combustion			()	
GRA	Optimization	Solid	Anaerobic digested	Solid	(Senthilkuma
	of bio-gas	concentration,	food waste	concentration=7.5%,	r et al., 2016)
	production	Temperature of		Temperature of food	
	process	food waste, Co-		waste= 50°C, Co-	
	parameters	digestion of poultry		digestion of poultry	
		waste		waste= 30%,	
				selected as an	
				optimal condition	
GRA	Performance	Blend,	Chicken-waste bio-	Blend 10 fuel, CR18,	(Hussain et
	optimization of	Compression ratio	diesel	Injection pressure	al., 2014)
	CI engine	(CR), Injection		220 bar, 19° bTDC	
	fuelled with	timing, Injection		(Before top dead	
	Chicken-waste	pressure		centre) engine	
	bio-diesel		parameters		
				combination were	
				delivered better	
		)		engine performance.	

113

Numerous literature studies reveal that huge research works have been focused on optimizing single objective problem in the pyrolysis process. Very few works were carried out in the multi-objective optimization of pyrolysis experiments. To the best of author's knowledge, no significant works have been carried out in the utilization of TOPSIS and GRA tools for optimizing the AM pyrolysis process. In order to fill this gap, the present research

focuses to apply TOPSIS technique for optimizing the process parameters of the AM pyrolysis process. The primary objective of this work is to examine the effect of each process parameters like pyrolysis temperature, heating rate and particle size on product yield. The next step mainly focuses to convert all process parameters into a single objective with the help of TOPSIS and GRA techniques.

#### 124 **2. Materials and Methods**

#### 125 2.1 Aegel marmelos biomass and pyrolytic oil

The fresh AM seed kernels were crushed by using a mechanical screw press to extract raw oil. During the extraction process, the remaining non-edible waste seed cake was collected and used as the feedstock for pyrolysis in this present research work.



Fig.1a AM seed cake



Fig.1b AM seed cake sieved particles

129

Figures 1a and 1b shows AM de-oiled seed cake and sieved powdered particles. The 130 moisture content of collected AM de-oiled seed cake was removed through drying in 131 sunlight. The proximate and ultimate analyses of biomass werecarried out as per (American 132 Society for Testing and Materials) ASTM D3172-07a and ASTM D5291-96 (Bordoloi et al., 133 2016). Physical and chemical properties of bio-oil such as calorific value (Bomb calorimeter), 134 kinematic viscosity (Redwood viscometer), flash point and fire point (Pensky Martin closed 135 136 cup apparatus), cetane number (Ignition quality tester), acid number (Potentiometric titration) and density (Density meter) of bio-oil were determined as per ASTM standards. 137

138

#### 139 **2.2 Taguchi experimental design approach**

Geneichi Taguchi developed a tool for designing the best quality system (Chen et al., 2014). In this method, the experimental design and quality loss function are related by Taguchi tool to suggest an effective design of experiment method through a systematic

approach for optimizing the system parameters with fewer trials. In this present research, three input factors (3) with three levels (3) full factorial design has been implemented  $(3^3=3x3x3=27 \text{ trial})$ . The L<sub>27</sub> orthogonal array is used to study the entire process parameters combined with the lesser experimental trials and it is a cost-effective and time-saving technique for optimizing the process parameters. Minitab 17 is used in this study to perform optimal calculations by employing design L<sub>27</sub> for 3 levels design and 3 control factors which afford 27 experimental trials.

- In the present investigation, three pyrolysis parameters such as pyrolysis temperature (°C), heating rate (°C/min) and particle size (mm) were selected according to the literature review and expert advice. All the input control factors along with their corresponding levels
- are given in Table 2.

Input parameters	Unit	Level 1 Level 2	Level 3
Pyrolysis temperature (PT)	°C	500 550	600
Heating rate (HR)	°C/min	10 20	30
Feed stock particle size (PS)	mm	0.6 1.6	2.4

**Table 2** Control factors and their levels

#### 155

## 156 **2.3 Technique for Order Preference by Similarity to Ideal Solution method**

TOPSIS technique was presented by Hwang and Yoon (Anupam et al., 2014). 157 TOPSIS technique is a multi-objective decision-making approach that assists to evaluate the 158 better optimum results among the large size of the alternative solution. TOPSIS is established 159 by the idea that the selected alternatives should have a minimum distance from the positive 160 ideal consequences and maximum from the negative ideal outcomes for solving a multi-161 attribute decision-making problem. The positive ideal consequences are a collection of all 162 greatest values, whereas the farthest ideal results are obtained by poorest values achievable of 163 criteria. It is an effective and simple multi-attribute decision-making approach used in several 164 applications like solar farms site selection, computer networks and process parameters 165 selection in machining/manufacturing industries. According to TOPSIS technique, all the 166 experimental response is segregated into beneficial or non-beneficial characteristics. Further 167 beneficial characteristics are higher the better, and the non-beneficial characteristics are lower 168

the better attributes. In the TOPSIS method the following steps are used to find out the multi-objective decision-making approach (Muniappan and Rajalingam, 2018).

171 Step I: TOPSIS decision-making formulation

172 Initially, the decision matrix should be created by using all the collected experimental 173 data. The decision matrix contains y attributes and x alternative solution. In the present 174 investigation, the output responses are attributes (y) and test trials are an alternative solution 175 (x). The TOPSIS design matrix  $D(T_{ij})_{x*y}$  is shown below

176 
$$D(T_{ij})_{(x^*y)} = \begin{bmatrix} T_{11} & T_{12} & T_{13} & \cdots & \cdots & T_{lj} \\ T_{21} & T_{22} & T_{23} & \cdots & \cdots & T_{2j} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ T_{i1} & T_{i2} & T_{i3} & \cdots & \cdots & T_{ij} \end{bmatrix}$$

177 Where  $T_{ij}$  is the measure of the j<sup>th</sup> attribute to the i<sup>th</sup> alternative. i=1,2,3,...,x and 178 j=1,2,3,...,y.

(3)

179 Step II: Normalization of TOPSIS design matrix

180 The normalization of TOSIS design matrix  $(n_{ij})$  was carried out using Eqn. (4)

181 
$$n_{ij} = \frac{T_{ij}}{\sqrt{\sum_{i=1}^{x} T_{ij}^2}}$$
 (4)

where  $n_{ij}$  is normalized value of design matrix for i=1,2,3,...,x; j=1,2,3,...,y.

183 Step III: Determination of weighted normalized matrix

The weights of each attribute are allocated and the sum of the weights of all attributes should be equal to 1. The weighted normalized matrix  $(\xi_{ij})$  is calculated through the following equation

187 
$$\xi_{ij} = w_j n_{ij}$$
 (5)  
188 Where  $\sum_{j=1}^{y} w_j = 1$ 

189 Step IV: Identification of positive ideal solution and negative ideal solution

The positive ideal solution (ξ<sup>+</sup>) and negative ideal solution (ξ<sup>-</sup>) are achieved through
the following equations

192 
$$\xi^{+}=(\xi_{1}^{+},\xi_{2}^{+},...,\xi_{y}^{+}) = \{(\max \xi_{ij}/j \in J_{1}), (\min \xi_{ij}/j \in J_{2}, i=1,2,3,...,y)$$
 (6)

193 
$$\xi^{-} = (\xi_{1}^{-}, \xi_{2}^{-}, \dots, \xi_{y}^{-}) = \{(\min \xi_{ij} / j \in J_{1}), (\max \xi_{ij} / j \in J_{2}, i=1,2,3,\dots,y)$$
 (7)

194 Where  $J_1 \rightarrow Set$  of beneficial attribute and  $J_2 \rightarrow Set$  of non-beneficial attribute

195 Step V: Calculation of separation measures

196 The positive separation measures  $(S_i^+)$  and negative separation measures  $(S_i^-)$  of 197 each alternative is achieved by following equations

198 
$$S_i^+ = \sqrt{\sum_{j=1}^{y} (\xi_{ij} - \xi^+)^2}$$
 (8)  
199  $S_i^- = \sqrt{\sum_{j=1}^{y} (\xi_{ij} - \xi^-)^2}$  (9)

## 200 Step VI: Assessment of relative closeness coefficient

The estimation of relative closeness coefficient of each alternative is estimated through the following equation

203 RCC=
$$\frac{S_i^-}{S_i^+ + S_i^-}$$
 (10)

204 Where i=1,2,3,....x.

205 Step VII: Ranking of alternatives

According to the performance value of relative closeness, the coefficient of each alternative is arranged and ranked in the descending order. The most suitable one (highest value) is ranked in position one and the least value is ranked in the last position.

209 2.4 Grey Relational Analysis method

The GRA technique is established by Deng in 1982. GRA methodology is employed to analyze the uncertainties in the system and the correlation between the systems etc. It is a mathematical oriented theory derived from the concept of the grey set. It is one of the best methods to solve uncertainty problems with incomplete information and discrete data (Rajeswari and Amirthagadeswaran, 2017). Owing to its simplicity and ability to evaluate the response within the required time, the GRA tool is mostly used in various engineering applications. GRA is a multi-response optimization method that converts the single-objective

problem into a single response optimization problem. In GRA technique all the output 217 responses are normalized between 0 and 1 for easy interpretation and data analysis purpose. 218 These normalized output response values are used to calculate Grey relational coefficient 219 (GRC) of every output data. The various quality characteristics of the optimization problem 220 are normalized from 0 to 1 to generate GRC. The GRC was assessed according to the 221 normalized experimental data. The GRC shows the correlation between the desired/ideal and 222 actual normalized experimental results (Rajeswari and Amirthagadeswaran, 2017). Next to it, 223 overall Grey relational grade (GRG) was obtained through averaging the GRC values respect 224 of each experimental trial. The overall performance of an experimental trial based on GRG 225 values. The higher the value of GRG attributes to the optimum solution of the experimental 226 trial. The following steps were adopted in GRA 227

228 Step 1: All the experimental output responses are normalized by the following equation,

## 229 Based on the required conditions, normalization for higher-the-better

230 
$$x_i(k) = \frac{g_i(k) - \min g_i(k)}{\max g_i(k) - \min g_i(k)}$$
 (11)

231 Normalization for lower-the-better

232 
$$x_i(k) = \frac{\max g_i(k) - g_i(k)}{\max g_i(k) - \min g_i(k)}$$
 (12)

Where  $x_i(k)$  is normalised value for attained experimental output response; min  $g_i(k)$  is the minimum value of  $g_i(k)$  for k<sup>th</sup> response; max  $g_i(k)$  is maximum value of  $g_i(k)$  for k<sup>th</sup> response; 'i' is the experimental number and 'k' is the comparability sequence.

Step 2: GRC shows the relationship between the desired and actual normalized experimentalresult. The GRC is computed as follows

238 
$$\varphi_i(k) = \frac{\Delta_{min} + \varphi \Delta_{max}}{\Delta_{oi}(k) + \varphi \Delta_{max}}$$
(13)

Where  $\Delta_{oi}(k)$  is deviation sequence, *i.e.*  $\Delta_{oi}(k) = |g_i(k) - x_i(k)|, \varphi$  is distinctive coefficient and this value lies between 0 and 1 (Normally taken as  $\varphi = 0.5$ ) (Rajeswari and Amirthagadeswaran 2017).  $\varphi_i(k)$  is a grey relational coefficient.  $\Delta_{min}$  (minimum deviation sequence) is the smallest value of  $\Delta_{oi}(k)$  and  $\Delta_{max}$  (maximum deviation sequence) the largest value of  $\Delta_{oi}(k)$ . Step 3: The average value of GRC is taken as a grey relational grade. The GRG computed asfollows

246 
$$\vartheta_i = \frac{1}{n} \sum_{i=1}^n \varphi_i(k) \tag{14}$$

247 Where  $\vartheta_i$  GRG of i<sup>th</sup> trial and n is a number of trials.  $\varphi_i(k)$  is a grey relational coefficient.

#### 248 2.5 Thermogravimetric analysis

Thermogravimetric analysis (TGA) provides the thermal activation range of biomass 249 (Park and Yoon 2012). The primary objective of TGA analysis is to find the degradation 250 temperature of the given sample (Bordoloi et al., 2016). The decomposition of lignin causes 251 sudden weight loss in the sample which can be interpreted by the steep curve in the TGA 252 graph. The temperature at which the maximum decomposition obtained is called as ultimate 253 decomposition temperature. The feedstock decomposition takes place in four different 254 regions, first decomposition (T<150°C) region is accredited to weight loss through removal 255 of moisture content present in the biomass. The second region (200°C<T<400°C) is attributed 256 to the removal of volatile matter present in the sample. The third one also called as active 257 258 pyrolysis region (400°C<T<600°C) formed by the decomposition of organic compounds like cellulose, hemicellulose and lignin. Figure 2 shows the TGA curve of AM biomass sample. 259 260 In this active pyrolysis region, cellulose, hemicellulose and lignin were decomposed in the temperature ranges of 500°C to 600°C. The chemical bonds present in the biomass are broken 261 262 due to an elevated temperature due to which the larger molecules were converted into smaller molecular organic vapours during pyrolysis. For the AM biomass material on set, end set and 263 the ultimate temperature are obtained from the TGA graph as 500°C, 550°C and 600°C 264 respectively. 265

Figure 3 shows the onset, end set temperatures, where the sudden rate of decomposition starts and end with respect to supply temperature. For AM biomass sample on set, end set and ultimate decomposition temperatures are found to be 500°C (set), 550°C (ultimate) and 600°C (end) respectively. Based on the result of TGA, the maximum temperature of the pyrolytic reactor was limited to 600°C because above which there is no decomposition observed in AM biomass sample. In the end of the decomposition region (T>600°C), no mass loss occurs.



TG curve

275

273

274

276

Fig.3 Set Temperatures in Thermo Gravimetric analysis curve

277

#### 278 2.6 Pyrolysis experimental method

Figure 4 depicts the schematic diagram of a pyrolysis experimental setup. The 279 pyrolysis reactor made up of stainless steel 310 materials, in order to withstand temperature 280 upto 1000°C with inner diameter 20 mm equipped with top feeding facilities. The reactor 281 heating rate can be varied from the range of 5°C/min to 50°C/min. The fixed bed type reactor 282 is well insulated and coupled with K-type thermocouple to measure the pyrolysis 283 temperature. The reactor contains a two kilogram feed capacity with 240 V and 9.5 A 284 285 electrical heater for heating purpose and the reactor temperature was controlled through the proportional integral derivative controller. 286



287

288

## Fig.4 Schematic diagram of pyrolysisreactor

The collected AM de-oiled seed cake was crushed and sieved into different sizesby sieves shaker of 0.6 mm, 1.6 mm and 2.4 mm. Mean size of feedstock particles is classified based on particle diameter. The performance of pyrolysis experiments mainly depends upon the pyrolysis temperature, heating rate and feed stock particle size ((Halim and Swithenbank, 2016).

The yield of pyrolysis products mainly depends on the biomass properties and 294 processing conditions (Palash et al., 2013). Pyrolysis reactor was initially cleaned properly 295 and ensured that there is no trace of char generated by previous runs. 2 kg of sieved AM 296 biomass is filled into the pyrolysis reactor and sealed with a gasket, to ensure that the 297 pyrolysis reaction is carried out in absence of oxygen. The pyrolysis reactor temperature was 298 controlled by the proportional integral derivative controller and once the thermochemical 299 conversion process was initiated, gases were evolved and passed through the water tube 300 condenser. The condensed pyrolytic oil was collected, whereas left out non-condensed gas 301 was also collected in the gas bladder for gas chromatography analysis. In the end, bio-char 302 was collected after cooling of pyrolysis reactor in atmospheric air. Every pyrolysis process 303 304 was repeated at least three times to achieve reliability in the test results. Then, the mean value of the result was taken for further analysis.  $L_{27}$  (3<sup>3</sup>) orthogonal array was used in this study 305 and Table 3 shows the pyrolysis experimentalvalues of the input parameters with 306 307 corresponding output responses.

308

**Table 3**  $L_{27}$  orthogonal array with output response

	Pyroly	sis process par	ameters	Output response			
Trial	РТ	HR	PS	Bio-oil	Bio-char	Bio-gas	
No.	(°C)	(°C/min)	(mm)	(wt%)	(wt%)	(wt%)	
1	550	10	0.6	32.92	23.44	43.64	
2	550	10	1.6	36.23	23.79	39.98	
3	550	10	2.4	34.50	32.15	33.35	
4	550	20	0.6	35.30	34.00	30.70	
5	550	20	1.6	37.93	29.91	32.16	
6	550	20	2.4	36.00	35.50	28.50	
7	550	30	0.6	35.50	44.10	20.40	
8	550	30	1.6	37.27	33.48	29.25	
9	550	30	2.4	38.75	30.85	30.40	
10	600	10	0.6	42.75	30.30	26.95	
11	600	10	1.6	41.39	25.58	33.03	
12	600	10	2.4	40.91	37.14	21.95	
13	600	20	0.6	40.51	34.73	24.76	
14	600	20	1.6	40.25	29.85	29.90	
15	600	20	2.4	39.89	39.10	21.01	
16	600	30	0.6	38.50	42.12	19.38	
17	600	30	1.6	37.21	34.30	28.49	
18	600	30	2.4	36.40	33.04	30.56	
19	650	10	0.6	19.45	25.55	55.00	
20	650	10	1.6	26.24	21.78	51.98	
21	650	10	2.4	27.00	45.50	27.50	
22	650	20	0.6	16.78	22.54	60.68	
23	650	20	1.6	16.15	24.25	59.60	
24	650	20	2.4	26.40	42.75	30.85	
25	650	30	0.6	21.12	37.25	41.63	
26	650	30	1.6	19.13	21.35	59.52	
27	650	30	2.4	25.75	44.25	30.00	

310

## 311 2.7 Compression Ignitionengine test method

A single cylinder Kirloskar Co. Ltd made research engine has been used for the 312 current experimental investigation and technical specification of the engine is given in Table 313 4. The CI engine coupled with AVL MDS (Modular diagnostic system) 250 gas analyser 314 (AVL Co. Ltd, Austria) is used to analyse the emission during the engine operations. Figures 315 5a and 5b show the CI engine and AVL MDS 250 gas analyser. The test engine rig is 316 incorporated with eddy current dynamometer for the purpose of providing the load to the 317 engine during the engine operation. Based on Indian bio-fuel policy, up to 20% of biofuel can 318 be blend with fossil fuel (Sakthivel et al., 2018). So the present work is carried out with 80% 319

- diesel+20% AM pyrolysis oil blend (AM20) as the engine fuel and emission characteristics
- 321 were analysed. The emission results were compared with standard neat diesel for further
- analysis. The engine was operated at different loads such as 3 kg (25%), 6 kg (50%), 9 kg
- 323 (75%) and 12 kg (100%) under the steady-state conditions at 1500 rev/min and 17.5:1
- 324 standard compression ratio. The Fluke-thermal images were captured for above engine speed,
- 325 CR and full engine load conditions.

326

327

328



Fig. 5a Compression ignition engine
 Fig.5b AVL 250 modular diagnostic system
 Initially, the engine was started with diesel, and it was warmed up to 15 min at
 no load condition. After the engine stabilization, the experiments were conducted with
 blended fuels in triplicate to ensure reliability.

## 329 Table 4 Compression ignition test engine description

Description	
Manufacturer name	Kirloskar Co. Ltd
Number of cylinders	1
Number of strokes	4
Cylinder diameter	87.5 mm
Stroke length	110 mm
Connecting rod length	234 mm
Orifice diameter	20 mm
Dynamometer arm length	185
Power	3.5 kw
Speed	1500 rev/min
CR range	12:1 to 18:1

Injection point variation  $0^{\circ}$  to  $25^{\circ}$  bTDC

330

#### 331 **2.8 Fluke-Thermal imager**

In this investigation, FLUKE-Thermal imager Ti400 was used to analyse exhaust gas 332 heat during engine operation. The thermal imaging works on the principal that the Infrared 333 (IR) energy emitted by the hot surface is converted into thermograph which implies the 334 temperature profile of the target object (Ramesh et al., 2019). Focusing the thermal imager to 335 the hot surface, senses the infrared energy from the hot exhaust gas during the engine 336 operation and provides the heat distribution of the tailpipe (Sakthivel et al., 2018). The 337 338 thermal imager was focused on the hot surface of the exhaust gas using a spotlight at the desired spot. The thermal imager displays the hot surface temperature distributed on the 339 exhaust port surface and the thermal images were captured manually at the required loading 340 condition and stored in an external pen drive for further analysis. 341

#### 342 **3. Result and discussion**

#### 343 **3.1 Elemental analysis of biomass**

344 **Table 5** Proximate and ultimate analysis of AM bio-mass

Proximate analysis*	Weight %
Fixed carbon	21.11
Volatile matter	73.69
Ash	2.19
Moisture content	3.01
Ultimate analysis*	Weight %
Carbon	46.96
Oxygen	42.87
Nitrogen	2.56
Sulphur	0.05
Hydrogen	7.56
Calorific value (MJ/kg)	20.59
*Dry basis	

345

Table 5 illustrates the proximate and ultimate analysis results of AM biomass material. The proximate and ultimate analysis is used to analyse the feed stock quality. The high volatile matter content of AM de-oiled seed cake was the main reason for its selection as the feed stock in this study. In typical biomass, presence of high volatile matter results in better bio-oil yield since the volatile contents are decomposed into short-chain organic vapours during pyrolysis.

The minimum percentage of fixed carbon shows the potential of the biomass material for better thermal conversion. A lesser amount of moisture content in feed stock material reveals that AM de-oiled cake can be used as a solid fuel for industrial applications. The ash content in the feed is solely based on the soil quality and plantation conditions. The ultimate analysis of the biomass shows that the de-oiled cake mainly contains carbon, hydrogen, oxygen, nitrogen and sulphur content and calorific value of biomass assure that AM seed cake can be effectively used as a feedstock material in pyrolysis experimentation.

359

#### 360 **3.2 Physical and chemical properties of bio-oil**

				_		
Characteristics	Unit	ASTM	@500°C	@550°C	@600°C	Diesel
Appearance	-	-	Dark brown	Dark brown	Dark brown	Yellow
Calorific value	MJ/kg	D240	40.53	41.12	41.35	45
Viscosity	cSt@40°C	D445	7.8	7.1	6.8	2.4
Density	g/cc @30°C	D4052	1.401	1.102	1.055	0.845
Flash point	°C	D93	82	79	76	65
Fire point	°C	D93	98	93	89	74
Water content	wt%	D1744	20.7	23.5	26.4	-
Cetane number	-	D613	39	42	44	51

361 **Table 6** Physical and chemical properties of AM bio-oil

362

Table 6 illustrates the physical and chemical properties of AM bio-oil obtained as per 363 ASTM standards. The physical and chemical properties of bio-oil depict that the viscosity of 364 the bio-oil is higher than diesel which may affect the spray pattern and injection capabilities 365 of the engine system (Singh and Shadangi, 2011). In this regard, it becomes essential to 366 upgrade the bio-oil through emulsification by blending with commercial diesel fuel with the 367 help of surfactants (Span 80 and Tween 80). However, compared to diesel, the calorific value 368 of bio-oil is low, where it can be compensated when blended with diesel. The physical and 369 370 chemical properties of the upgraded AM bio-oil show the possibility of using it as a commercial fuel in diesel engines (Singh and Shadangi, 2011). 371

The bio-oil contains an assorted range of compounds like methyl, ester, ether, alkanes, acids, ketones which ensure that bio-oil can be effectively used as a substitute for fossil fuels. However, it can also be used as a fuel in the furnace, agricultural generators, and boilers without up gradation (Sakthivel et al., 2018) and anti-microbial agent in pharmaceutical industries (Abas et al., 2018). The third product of the pyrolysis process is biochar, which can

be used as raw material for activated charcoal production. It is confirmed that the biochar can 377 also be used as solid fuel due to its low moisture content and high calorific value (Liew et al., 378 2018), cosmetic industries, waste water treatment plant, organic fertilizer (Nam et al., 2018), 379 chemical manufacturing industries (Mohammed et al., 2017b), natural mosquito destroyer 380 and separator for heavy metals (Lam et al., 2017). The presence of flammable components 381 like CH<sub>4</sub> (Methane), H<sub>2</sub> (Hydrogen) and C<sub>2</sub>H<sub>6</sub> (Ethane) in evolved biogas suggests that it can 382 be used to power the pyrolysis reactor (Meier et al., 2013) and CI engines in dual fuel mode 383 operation as gaseous fuel (Baranitharan et al., 2018). 384

385

#### **386 3.3 Technique for Order Preference by Similarity to Ideal Solution analysis**

In the TOPSIS technique, primarily the experimental results are altered into a decision 387 matrix containing experimental trials (alternatives) in rows and experimental output results 388 (attributes) in columns. Initially, the decision matrix is normalized by Eq.(4). Subsequently, 389 relative weights are to be allocated to each attribute. In this regard the entire output responses 390 like bio-oil yield, bio-char yield and biogas yield were given equivalent significance; hence 391 relative weighted of 1/3 is allotted to each output result. Using Eq.(5) weighted normalized 392 values are calculated and tabulated. Using Eqs. (6) and (7) positive ideal solutions and 393 394 negative ideal solutions are evaluated from the normalized matrix. Among the entire output responses, the positive ideal solution has maximum values, which are  $\xi_{PT}^+=0.0816127$ ,  $\xi_{HR}^+$ 395 =0.087446,  $\xi_{PS}^+$ =0.105495 and negative the ideal solution has minimum value of weighted 396 normalized values, that are  $\xi_{PT}$ =0.0308315,  $\xi_{HR}$ =0.041032,  $\xi_{PS}$ =0.033693. The separation 397 measures of positive ideal solutions and negative ideal solutions are computed by Eqs.(8) and 398 (9). Subsequently using these separation measures values, closeness coefficient of every 399 alternative is reckoned by using Eq.(10). Table 7 represents the normalized values, weighted 400 normalized values, separation measures values and closeness coefficient values of entire 401 alternatives. 402

403 **Table 7** Technique for order preference by similarity to the ideal solution analysis result

Trial	Normalization			Weighted normalization			Separation		CC
No.	Bio-oil	Biochar	Biogas	Bio-oil	Biochar	Biogas	S-	$S^+$	
1	0.1885	0.1351	0.2276	0.062	0.0450	0.0759	0.046	0.326	0.8756543
2	0.2075	0.1372	0.2085	0.069	0.0457	0.0695	0.038	0.339	0.8988317
3	0.1976	0.1854	0.1739	0.065	0.0618	0.0580	0.035	0.333	0.9035738
4	0.2022	0.1960	0.1601	0.067	0.0653	0.0534	0.034	0.340	0.9082067
5	0.2172	0.1725	0.1677	0.072	0.0575	0.0559	0.029	0.347	0.9226872

6	0.2062	0.2047	0.1486	0.068	0.0682	0.0495	0.034	0.345	0.9104124
7	0.2033	0.2543	0.1064	0.067	0.0848	0.0355	0.045	0.362	0.8876706
8	0.2135	0.1930	0.1526	0.071	0.0643	0.0509	0.030	0.348	0.9188598
9	0.2219	0.1779	0.1586	0.074	0.0593	0.0529	0.027	0.352	0.9274789
10*	0.2448	0.1747	0.1406	0.081	0.0582	0.0469	0.021	0.369	0.9446041
11	0.2370	0.1475	0.1723	0.079	0.0492	0.0574	0.025	0.360	0.9346365
 12	0.2343	0.2141	0.1145	0.078	0.0714	0.0382	0.030	0.371	0.9231686
13	0.2320	0.2002	0.1291	0.077	0.0667	0.0430	0.027	0.365	0.9294983
14	0.2305	0.1721	0.1559	0.076	0.0574	0.0520	0.025	0.358	0.9347756
15	0.2285	0.2254	0.1096	0.076	0.0751	0.0365	0.034	0.370	0.9144003
16	0.2205	0.2429	0.1011	0.073	0.0810	0.0337	0.040	0.370	0.9010401
17	0.2131	0.1978	0.1486	0.071	0.0659	0.0495	0.031	0.349	0.9177003
18	0.2085	0.1905	0.1594	0.069	0.0635	0.0531	0.032	0.343	0.9146600
 19	0.1114	0.1473	0.2869	0.037	0.0491	0.0956	0.076	0.276	0.7827157
20	0.1503	0.1256	0.2711	0.050	0.0419	0.0904	0.064	0.305	0.8250637
21	0.1546	0.2623	0.1434	0.051	0.0874	0.0478	0.057	0.327	0.8515141
22	0.0961	0.1300	0.3165	0.032	0.0433	0.1055	0.087	0.287	0.7668190
23	0.0925	0.1398	0.3109	0.030	0.0466	0.1036	0.086	0.278	0.7627217
 24	0.1512	0.2465	0.1609	0.050	0.0822	0.0536	0.055	0.315	0.8505408
 25	0.1210	0.2148	0.2171	0.040	0.0716	0.0724	0.064	0.270	0.8077158
 26	0.1096	0.1231	0.3104	0.036	0.0410	0.1035	0.083	0.293	0.7795702
27	0.1475	0.2551	0.1565	0.049	0.0850	0.0522	0.057	0.316	0.8458546

404 \*Optimal condition

The alternative solution having the highest closeness coefficient (CC) value is 405 selected as an optimum solution. In this investigation, experimental trial 10 has a maximum 406 closeness coefficient value of 0.944604123. Among the entire experiments, the alternative 407 trial 10 is the optimal solution and the next level of optimum solutions are experimental trial 408 14 and 11 respectively. The mean closeness coefficient (MCC) of every parameter at all level 409 is computed and tabulated in Table 8. Effect of pyrolysis process parameter on MCC is 410 depicted in Fig.6. By means of the chart, optimal process parameter for AM pyrolysis bio-oil 411 yield is recognized as PT2HT1PS1, which are pyrolysis temperature of 600°C, a heating rate 412 of 10°C/min and feedstock particle size is 0.6 mm. 413

414 **Table 8** Mean closeness coefficient

	PT	HR	PS		
Level I	0.905930644	0.901293098*	0.884598051*		
Level II	0.914881119*	0.887801476	0.880754685		
Level III	0.879273190	0.827242903	0.878635601		

415 PT- Pyrolysis temperature; HR- Heating rate; PS- Particle size

416 \*Optimal solution



417

418

Fig.6 Effect of pyrolysis control factors on Mean closeness coefficient

## 419

The main objective of the investigation is to obtain the maximum bio-oil yield from 420 the AM de-oiled seed cake pyrolysis process. The output responses of the pyrolysis 421 experiment were normalized for larger the better using Eq.(11) and smaller the better using 422 Eq.(12). Table 9 illustrate the normalized value of output responses, GRC and GRG using 423 Eqs. (11), (12), (13) and (14). For calculating the grey relational coefficient, the distinctive 424 coefficient ( $\varphi$ )value is taken as 0.5 (Rajeswari and Amirthagadeswaran, 2017). In the grey 425 relational analysis, the experimental trial having GRG near to one is selected as the optimum 426 solution. The experimental trial number 10 have a chief grey relational grade of 0.753589 427 among 27 experiments, this spectacles that trial 10 affords better bio-oil yield. The pyrolysis 428 temperature of 600°C, heating rate of 10°C/min and AM particle size of 0.6 mm provides the 429 desired result among the selected input condition. 430

A Mean Grey relational grade (MGRG) table should be calculated by including all the 431 parameters and their levels, in order to find out the optimal process parameters that give 432 maximum bio-oil, bio-char and bio-gas yields. Table 10 depicts the mean grey relational 433 grade of all parameters at each level. Considering each parameter, the level having the 434 highest MGRG is selected as the optimal solution. From the MGRG table, the optimum 435 process parameters are found to be pyrolysis temperature of 600°C, a heating rate of 436 10°C/min and AM particle size of 0.6 mm. Figure 7 represents the effect of pyrolysis process 437 parameters on GRG. The result reveals that intermediate pyrolysis temperature with the 438 lowest heating rate at small size AM particles results in maximum AM pyrolysis bio-oil 439 yield. 440

441 **Table 9** Grey relational analysis result

**3.4 Grey Relational Analysis** 

Trail	No	ormalized val	lues	GRC		GRG	
No.	Bio-oil	Bio-char	Biogas	Bio-oil	Bio-char	Biogas	
1	0.9304226	0.8262655	0.91970789	0.731585	0.876573	0.288816	0.632324
2	0.9559346	0.8301478	0.89837256	0.830005	0.856985	0.365560	0.684183
3	0.9429058	0.9090293	0.85420836	0.779742	0.458990	0.524422	0.587718
4	0.9490100	0.9236842	0.83404209	0.803291	0.385050	0.596961	0.595101
5	0.9681451	0.8901123	0.84535847	0.877110	0.554435	0.556256	0.662600
6	0.9542388	0.9349926	0.81593069	0.823463	0.327993	0.662109	0.604522
7	0.9505145	0.9918138	0.73448893	0.809095	0.041303	0.955060	0.601819
8	0.9634708	0.9196471	0.82225750	0.859078	0.405418	0.639351	0.634616
9	0.9738405	0.8982177	0.83165024	0.899082	0.513540	0.605565	0.672729
10	1	0.8935057	0.80231016	1	0.761109	0.532869	0.753589*
11	0.9913910	0.8491501	0.85185999	0.966788	0.537314	0.711103	0.749472
12	0.9882849	0.9468221	0.75232599	0.954805	0.268308	0.890899	0.704671
13	0.9856684	0.9292486	0.78166680	0.944712	0.356974	0.785359	0.695682
14	0.9839539	0.8895864	0.82761087	0.938097	0.557089	0.620095	0.705094
15	0.9815615	0.9602930	0.74166534	0.928868	0.200341	0.929246	0.686152
16	0.9721170	0.9797812	0.72199551	0.892433	0.102014	1	0.664816
17	0.9630418	0.9259853	0.81584522	0.857423	0.373440	0.662417	0.631093
18	0.9571812	0.9161819	0.83292881	0.834814	0.422902	0.600966	0.619561
19	0.7902944	0.8488427	0.97605963	0.190998	0.762660	0.086115	0.346591
20	0.8700303	0.8070257	0.96230431	0.498603	0.973647	0.135594	0.535948
21	0.8776332	1	0.80723090	0.527934	0	0.693403	0.407112
22	0.7509748	0.8160100	1	0.039311	0.928317	0	0.322545
23	0.7407847	0.8351642	0.99562362	0	0.831675	0.015742	0.282472
24	0.8716491	0.9836700	0.83522926	0.504848	0.082392	0.592691	0.393310
25	0.8122292	0.9475968	0.90822288	0.275618	0.264399	0.330128	0.290049
26	0.7858769	0.8018026	0.99529647	0.173956	1	0.016919	0.396958
27	0.8650107	0.9927032	0.82842412	0.479239	0.036816	0.617169	0.377741

442 \*Optimal solution

443 **Table 10** Mean grey relational grade

	РТ	HR	PS		
Level 1	0.630624	0.62740*	0.578551*		
Level 2	0.660319*	0.59057	0.571566		
Level 3	0.564388	0.564388	0.564388		

444 PT- Pyrolysis temperature; HR- Heating rate; PS- Particle size

445 \*Optimal condition





447

Fig.7 Effect of pyrolysis process parameter on Grey Relational Grade

# 3.5 Comparison of Technique for order preference by similarity to ideal solution and Grey relational analysis output responses

The optimum output responses obtained from TOPSIS and GRA techniques are compared. It can be observed that both the optimization tools give a similar combination of pyrolysis process parameters PT2HR1PS1as optimum solution. The output result confirms that TOPSIS tool executes efficiently like GRA tool and can be employed for multi-objective problem optimization.

455

## 456 **3.6 Compression Ignition engine emission characteristics**

Diesel engines are the foremost important engineering invention in the commercial engineering sectors (Ferguson and Kirkpatrick, 2015). At the same time, diesel engines emit the harmful gases into the atmosphere. Bio-fuel emits a lower amount of pollutants as compared to fossil fuels, owing to its rich oxygen content (Emberger et al., 2015). With the help of AVL gas analyser, exhaust gases like CO (Carbon monoxide), HC (Hydro carbons), NOx and CO<sub>2</sub> emissions are analysed during engine operation. Figures 8a-d represents the CO, HC, CO<sub>2</sub> and NOx emissions compared with neat diesel fuel.

Incomplete combustion and insufficient air-fuel mixing ratio generate CO emission at 464 engine exhaust (Atmanlı et al., 2014). Figure 8a represents the comparison between CO 465 emission of AM bio-oil and diesel fuel. According to the figure, AM bio-oil blends emit a 466 higher amount of CO as compared with diesel. The high viscosity and density (1.401, 1.102) 467 and 1.055 g/cc @30°C) of the AM fuel blends compared with neat diesel (0.845 g/cc @30°C) 468 leads to the poor atomization and incomplete combustion during combustion (Hellier et al., 469 2015). At the full load condition, diesel emits 0.17% volume of CO and AM20 blend emits 470 0.44% volume of CO emission. 471

Figure 8b illustrates the comparison between the effects of neat diesel and AM blend 472 on HC emission with respect to load. The inadequate combustion of fuel molecules emits the 473 HC (Wamankar et al., 2015). In general, the fuel having a high viscosity leads to poor 474 atomization during the fuel injection, which in turn causes the HC emission. The viscosity 475 difference between AM fuel blends (7.8, 7.1 and 6.8 cSt@40°C) with neat diesel (2.4 476 cSt@40°C) augments the higher amount of HC emission as compared to neat diesel since the 477 kinematic viscosity of bio-oil does not meet the diesel fuel ASTM standards (Shameer and 478 Ramesh, 2017a). At full load, condition dieselemits 58 ppm of HC and AM20 blend emits 99 479 ppm of HC. AM20 blend emits the higher value of HC compare to baseline fuel, due to high 480 viscosity and poor injection spray characteristics (Muniappan and Rajalingam, 2018). 481



At high temperatures around 1500°C, nitrogen and oxygen in combustion chamber react to form the respective oxides via a sequence of chemical reactions called as Zeldovich mechanism (Paramasivam et al., 2018; Sakthivel et al., 2018). Based on the Zeldovich mechanism, maximum thermal NOx emission is caused by higher temperature in the combustion chamber during the engine operation (Baranitharan et al., 2018)). Figure 8c spectacles the NOx emissions of diesel and AM20 fuel blend with respect to load. At peak

load condition D emits 1511 ppm of NOx and AM20 blend emits 1401 ppm of NOx. It can be due to the fact that, increasing load obviously increases the combustion chamber temperature and also the quenching effect of water content present in the pyrolysis oil reduces the flame temperature, thereby emitting less magnitude of NOx (Corsini et al., 2015).

Figure 8d represents the CO<sub>2</sub> emission of both AM fuel blends and neat diesel. The 492 complete combustion of fuel in the combustion chamber is straight away indicated by CO<sub>2</sub> 493 emission (Sakthivel et al., 2018). Muniappan and Rajalingam (2018) optimized the 494 495 performance and emission behaviours of a diesel engine fuelled with bael oil (25%) + diesel (65%) + Di-ethyl ether (10%) fuel blend using TOPSIS and found that brake thermal 496 497 efficiency increased 28.6%, CO reduced 0.025% and HC reduced 12.5 ppm. At low load condition, the CO<sub>2</sub> emission for diesel and AM fuel blends is lower. This reduction is caused 498 499 by the lower combustion temperature and the inefficient burning of fuel (Muniappan and Rajalingam, 2018). But, CO<sub>2</sub> emission consequently increased with increase in load for both 500 diesel and fuel blend ratio, due to increasing combustion temperature. Throughout the engine 501 operation, the CO<sub>2</sub> emission level was noted to increase with respect to load. As compare to 502 AM fuel blends, diesel emits a higher amount of CO<sub>2</sub> at all load condition. It is depicted that, 503 fuel blends were involved in better combustion as compared to diesel (Shameer and Ramesh, 504 2017a). At full load, condition diesel emits 10.33% of CO<sub>2</sub> and AM20 blend emits 8.68% of 505  $CO_2$ . 506

#### 507 **3.7 Fluke-Thermal images validation**

Figure 9a illustrates the location of the thermal image for the measurement of exhaust 508 gas temperature (heat). Figures9b-9d shows the exhaust gas temperature of AM bio-oil 509 derived from various pyrolysis temperatures are 600°C, 550°C and 500°C respectively. In 510 Fig.9e, the exhaust gas temperature of diesel fuel has been portraved. Once the combustion 511 process takes place in the in-cylinder chamber, the combustion chamber temperature raises. 512 The heat inside the combustion chamber flows via the cylinder and exhaust port. The 513 distributed heat on the exhaust port was sensed by using thermal imager. The IR thermal 514 images depict that the combustion chamber heat is distributed via cylinder head and exhaust 515 port emission (Shameer and Ramesh, 2017a). In engine operation, when combustion chamber 516 temperature increases at peak load condition, apparently engine components heat also highly 517 increases (Shameer and Ramesh, 2017b). During the engine operation, a higher value of 518

combustion chamber temperature leads to a higher amount of NOx emission (Hellier et al.,2015).

521 The location of the temperatures is mainly focused to exhaust port of the test engine 522 setup. In thermal images, boring tool temperature selected, according to the representation 523 "MAX", "MIN", and average values. "MAX" and "MIN" indicates the maximum and 524 minimum temperatures of the boring tool surface during machining operation and center 525 value is indicated the average tool (actual temperature) temperature value.



Fig.9a Location of measurement



Fig.9b Exhaust gas temperature of AM pyrolysis oil obtained from 600 °C



**Fig.9C** Exhaust gas temperature of AM pyrolysis oil obtained from 600 °C



**Fig.9d** Exhaust gas temperature of AM pyrolysis oil obtained from 600 °C

Fig.9e Exhaust gas temperature of diesel

A Non-contacting measuring technique gives accurate values than contact measuring 526 methods. The NOx emission value is greatly temperature dependent. The quenching effect of 527 moisture present in the pyrolysis oil (Moisture content= 20.7% @500°C, 23.5% @550°C and 528 26.4% @600°C) reduces the flame temperature (Corsini et al., 2015) thereby decreases the 529 amount of NOx as compared to diesel. According to the thermal images result, the low 530 exhaust gas temperature was recorded for AM bio-oil obtained at PT =600°C, HR=10°C/min, 531 532 PS=0.6 mm. It conforms that AM pyrolysis oil emits lower emission of NOx compare to plain diesel during engine operation. From the thermal imaging, it can be seen that 533 534 augmented gas temperature of diesel operation resulted in augmentation of NOx, whereas the reduction in NOx was validated through reduced gas temperature as exhaust during AM bio-535 oil operation (Garcia-Gonzalez et al., 2016). 536

#### 537 **3.8 Practical implications and Future work**

Stability of bio-oil is one of the inevitable characteristics, which influences the 538 commercialization of the fuel market. In general, bio-oil possesses poor stability 539 characteristics due to the presence of reactive organic compounds. This, in turn, affects the 540 541 physical and chemical properties of bio-oil during the prolonged storage period. Thermal and oxidative degradation affect the decomposition of compounds present in the bio-oil and 542 catalyses polymerization reaction which increases the viscosity, water content, gumming 543 activity and solid content. In this regard, it is mandatory to investigate bio-oil storage 544 stability. Since biochar contains an acceptable amount of carbons, it can be used as a 545 composites reinforcement face, nanotubes manufacturing and can also be used in the material 546 manufacturing industry as a catalyst instead of carbons. 547

#### 548 4. Conclusion

The requirements for fuel energy and reduced exhaust emissions of CI engines can be 549 accomplished by biofuel research. The aim of the present research work is to attain the 550 maximum bio-oil yield, in order to fulfil the energy requirements. The present AM pyrolysis 551 work considers pyrolysis temperature, heating rate and particle size as the input criteria to 552 obtain optimum pyrolysis condition for maximizing the bio-oil yield. At optimized pyrolysis 553 conditions, the maximum AM bio-oil, bio-char and biogas yields were 42,75, 30.30 and 554 26.95 (wt%) respectively. At peak load conditions AM20 bio-fuel blend emits lower NOx of 555 15.97% and lesser CO<sub>2</sub> of 7.28% as compared with D fuel and emission characteristics are 556 validated through a novel approach using FLUKE-thermal imager. Infrared thermography 557 images were confirmed the same NOx emission results for both D and AM20 fuel. According 558 to the emission results, as compared to D fuel, AM20 fuel blend emits lesser amounts of 559 harmful emissions at the exhaust. This depicts that AM20 is suitable for engine fuel in terms 560 of emission reduction. This investigation shows that similar results were obtained for both 561 TOPSIS and GRA techniques and they can be used as effective tools to optimize the multi-562 objective problem in AM pyrolysis experimental process and attain the maximum bio-oil 563 yield through optimized process parameters (PT=600°C, HR=10°C/min and PS=0.6 mm). 564

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## HIGHLIGHTS

- Pyrolysis oil was derived from the AM seed cake
- AM pyrolysis process parameters are optimized through TOPSIS and GRA
- Both TOPSIS and GRA techniques showed similar results
- Bio-oil was used as an alternative fuel in CI engine
- NOx emission behaviour is validated through Thermal images