

# 1 **A renewable lignin-derived bio-oil for boosting the oxidation stability of** 2 **biodiesel**

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## 21 **Abstract**

22  
23 The valorisation of lignin is being increasingly recognised to improve the economics of pulp  
24 and paper making mills. In the present study, an integrated lignin–glycerol valorisation  
25 strategy is introduced with an overarching aim for enhancing the process value chains.  
26 LignoBoost kraft lignin was subjected to base-catalysed depolymerisation using glycerol as  
27 a co-solvent. The generated bio-oil was used as a renewable additive to biodiesel for  
28 enhancing the oxygen stability. The influence of three independent parameters including  
29 temperature, time and glycerol amount on lignin depolymerisation was investigated.  
30 Response surface methodology was applied to design the experiments and to optimise the  
31 process for maximising the yield and antioxidant impact of bio-oil. The results showed that  
32 glycerol has a positive qualitative and quantitative impact on the produced bio-oil, where an  
33 enhancement in the yield (up to 23.8%) and antioxidant activity (up to 99 min induction  
34 period) were achieved using the PetroOxy method (EN16091). The addition of 1 wt% bio-  
35 oil on biodiesel led to an improvement in the oxidation stability over a neat sample of up to  
36 ~340%, making it compliant with European standard (EN14214). The proposed process  
37 presents a biorefinery paradigm for the integrated utilisation of waste cooking oil, lignin and  
38 glycerol.

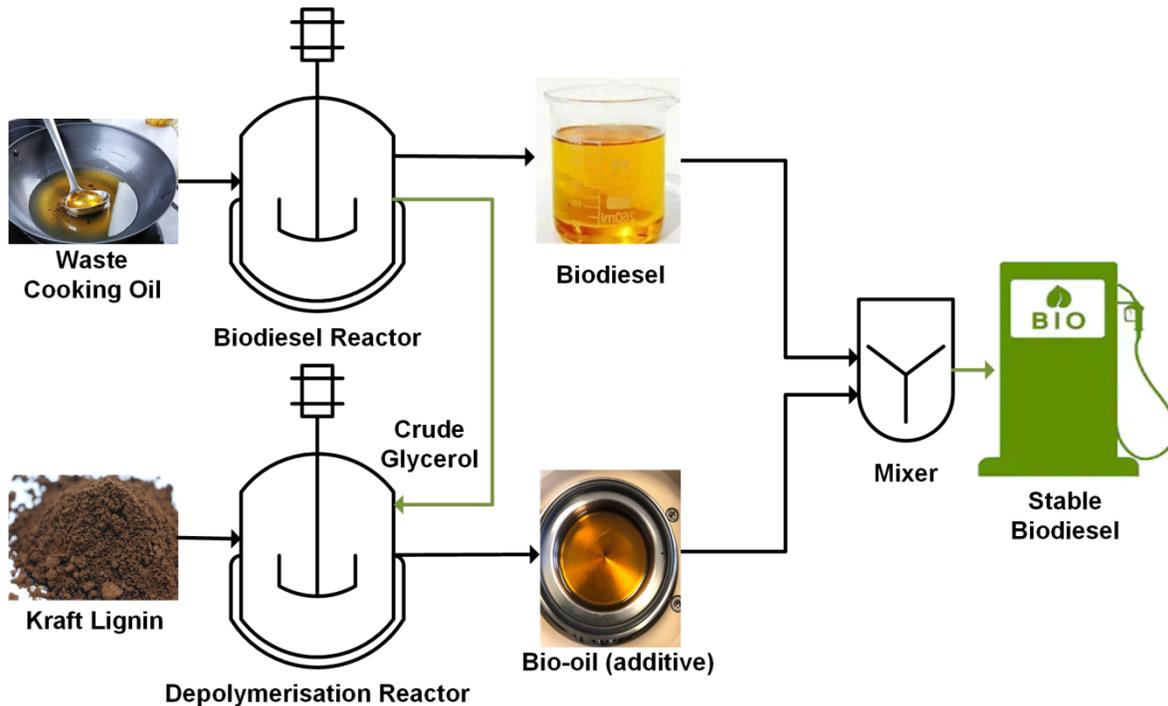
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41 **Keywords:**

42 Biodiesel; Lignin valorization; Renewable antioxidants; Supercritical methanolysis;  
43 Response surface methodology; Oxidation stability.

44 **Graphical abstract**

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**Highlights**

- 50 • Bio-additives from the base-catalysed depolymerisation of LignoBoost kraft lignin.
- 51 • Effect of reaction variables on bio-oil yield and biodiesel oxidation stability.
- 52 • Oxidation stability of biodiesel increased up to 340% by adding 1 wt% bio-additive.
- 53 • An integrated biorefinery concept for valorising lignin and glycerol waste streams.

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**Abbreviations:**

56 BBD, Box–Behnken design; FFA, free fatty acids; IP, induction period; RSM, response  
57 surface methodology; WCO, waste cooking oil.

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## 63 1. Introduction

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65 Biodiesel is identified as an alternative renewable fuel to petroleum diesel. It is composed of  
66 mono-alkyl esters of long-chain fatty acids derived from vegetable oil, algae and animal fats.  
67 It is conventionally produced via transesterification in the presence of a catalyst and an  
68 alcohol, such as methanol or ethanol, resulting in glycerol as the main side-product. Methanol  
69 is widely used as an alcohol due to its availability, low cost and the similar properties of  
70 methyl esters with petroleum diesel [1]. Second- and third-generation feedstocks, including  
71 non-edible vegetable oils and waste cooking oil, are considered as potential resources for  
72 biodiesel production as they do not compete with the resources of the food industry. Such  
73 feedstock are known to contain a high level of free fatty acids (FFA) of which are subjected  
74 to several pre-treatment steps prior to transesterification, including esterification and  
75 neutralisation. The presence of water during the conventional transesterification also results  
76 in saponification side reactions [2,3]. Recently, supercritical production of biodiesel has been  
77 reported as an efficient process for simultaneous transesterification and esterification of  
78 triglycerides and FFAs. The reaction occurs at elevated temperature and pressure to reach the  
79 supercritical condition of the used alcohol [4]. This technology offers several advantages,  
80 including simple product separation (only biodiesel and glycerol), elimination of wastewater  
81 (washing step), rapid reaction time and high yield of biodiesel. On the other hand, the high  
82 excess of alcohol and safety concerns in process operation are considered as the main  
83 drawbacks [1,5].

84

85 Our research group has comprehensively worked on the supercritical production of biodiesel  
86 from different waste cooking oil (WCO) feedstocks. The work has started with low acidity  
87 WCO collected from households, where the optimal yield of biodiesel achieved was 91%  
88 [6,7]. We have then considered high-acidity WCO collected from industries where we have  
89 observed an increase in biodiesel yield by up to 98% at relatively milder conditions [8] and  
90 an average of 99% conversion of the FFAs [9]. However, we have noticed that the produced  
91 biodiesel has relatively low oxidation stability, an aspect that initiated the present research.

92

93 One of the main concerns in commercialisation of biodiesel is the oxidation stability [10].  
94 Oxidation alters the physiochemical properties of biodiesel and leads to further complications  
95 by the formation of undesirable products in diesel engines. The products formed damage the  
96 engine by causing elastomer degradation, mechanical degradation, etc., and as a result,  
97 leading to failure of engine parts [11]. An antioxidant is a compound that delays the oxidation  
98 reactions of biodiesel. A naturally occurring antioxidant exists in biodiesel feedstock [12].  
99 Lima et al. [13] reported that *Buriti* oil showed high oxidative stability despite its high level  
100 of unsaturation ~80% due to the presence of natural antioxidant tocopherols. However,  
101 tocopherols have negligible effects compared to most of the commercial phenolic

102 antioxidants [14]. It has also been reported that tocopherols get destroyed during  
103 transesterification, caused by elevated temperatures, which could be the main reason for  
104 having low stability biodiesel from supercritical processes [15].

105

106 Lignin is the most abundant aromatic-based biopolymer on Earth, and its aromaticity makes  
107 it a platform macromolecule with high potential for the production of various valuable  
108 products [16]. The valorisation of lignin to higher-value applications is essential to improve  
109 the economics of biomass conversion [17–19]. Lignin in the pulp and paper industry is mostly  
110 considered as a waste side-product where it is conventionally used on-site and burnt in  
111 recovery boilers to generate energy. LignoBoost is a well-proven technology for commercial-  
112 scale lignin extraction from kraft black liquor [20]. This process enables the recovery of high-  
113 purity lignin with rather high solid content and low ash and carbohydrate contents. The  
114 recovered lignin has a diverse range of possible applications, from bulk uses, e.g. as a fuel  
115 for boilers and lime kilns, to value-added uses, e.g. carbon fibres. In view of the prevailing  
116 role of kraft technologies and that lignin is an abundant, inexpensive, renewable aromatic  
117 resource, new applications targeting the exploitation of kraft lignin from black liquor are  
118 anticipated [21].

119

120 Studies on base-catalysed (alkali) depolymerisation of lignin into phenolic compounds have  
121 been conducted in the literature and are still a mainstay of lignin conversion research [22–  
122 24]. The reactions are ordinarily carried out at elevated temperatures (240–330 °C) in the  
123 presence of a soluble base (mainly NaOH) as a catalyst and water as a solvent [25]. Sodium  
124 hydroxide is already used as an active cooking chemical in the pulping process. This aspect  
125 increases the potential of applying such homogeneous alkali catalytic system for lignin  
126 conversion from a process integration viewpoint and the implementation of this technology,  
127 for instance, in the pulp and paper industry or future biorefinery concepts.

128

129 The transition towards renewable antioxidants has gained interest due to non-toxicity  
130 compared to commercial phenolic antioxidants. Rial et al. [10] have evaluated the effect of  
131 renewable additive produced from cagaite leaves (*Eugenia dysenterica* DC.) on the oxidation  
132 stability of soybean biodiesel. The addition of 50 ppm of the extract has enhanced the  
133 induction period (IP) from 4.53 to 6.04 h (Rancimat method). They have also mentioned that  
134 the extract has higher efficiency than quercetin (commercial antioxidant) in retarding the  
135 oxidation of biodiesel. Similarly, Devi et al. [26] have evaluated the influence of leaf extract  
136 of *Thuja orientalis* L. as a renewable antioxidant. They have mentioned that 100 ppm of the  
137 *Thuja* extract has enhanced the IP from 4.55 h to 6.79 h (Rancimat method). Specifically, the  
138 application of lignin as a renewable antioxidant for biodiesel was introduced by Xin and Saka  
139 [27]. They reported that adding woody lignin together with vegetable oil and methanol prior  
140 to starting the reaction resulted in biodiesel with higher oxidation stability. They also stated

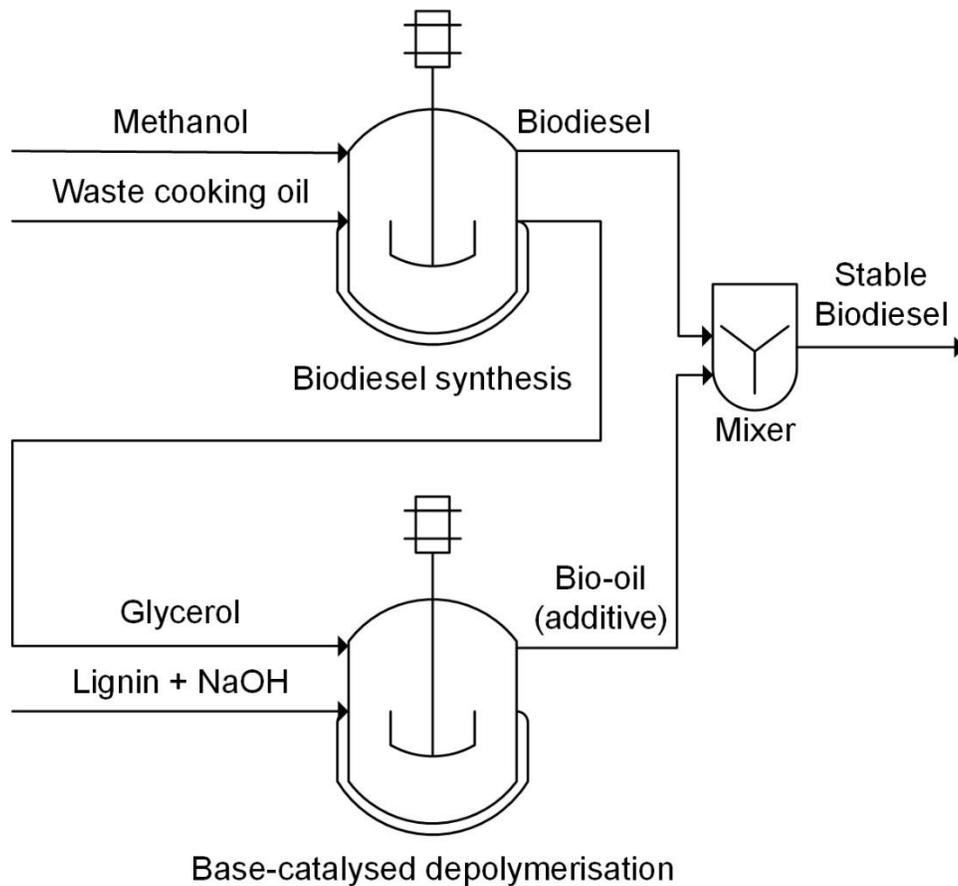
141 that lignin has a catalytic effect on biodiesel produced by the supercritical method. This was  
142 extended by the Thermochemical Processes Research Group in Spain, where they developed  
143 processes that enable producing renewable antioxidant additives from various lignin-derived  
144 bio-oils, reporting improvements between 135 and 250% in oxidation stability over neat  
145 biodiesel [28–30].

146

147 Glycerol is regarded as the main side-product during biodiesel production. The adaptation  
148 and increase in biodiesel production would eventually lead to an increase in waste crude-  
149 glycerol. Numerous studies have focused on the valorisation of glycerol to various value-  
150 added products [31,32]. For instance, Hulteberg and Leveau [33] investigated the process of  
151 converting glycerol to propane and recommended a commercial demo scale in the range of  
152 1,000–10,000 tonnes per annum. Moreover, the steam reforming of glycerol has attracted  
153 attention to generating hydrogen for applications in fuel cells [34]. Glycerol has also been  
154 identified as a green solvent for chemical industries [35,36].

155 This work demonstrates an integrated approach for the utilisation of glycerol as a co-solvent  
156 in lignin depolymerisation towards the production of renewable antioxidants that could  
157 enhance the oxidation stability of biodiesel (Fig. 1). The process integrates the biodiesel  
158 process side-product (glycerol) to enhance the production of high-quality bio-oil from lignin  
159 as a renewable antioxidant. The effects of reaction temperature, residence time and glycerol  
160 amount on the yield and antioxidant activity of bio-oil were investigated using the PetroOxy  
161 stability tester. Numerical and graphical optimisation of reactions variables were performed  
162 using response surface methodology (RSM) to identify conditions that can lead to a bio-oil  
163 fraction with the highest yield and antioxidant activity.

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**Fig. 1.** A schematic of the proposed integrated biorefinery approach.

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**2. Materials and methods**

**2.1. Materials**

WCO from various restaurants and industries located in Egypt were blended to form a realistic mixture. Methanol (MeOH, 99%), ethyl acetate (EtOAc), glycerol, sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Fisher Scientific UK Ltd (Loughborough, UK). Liquid CO<sub>2</sub> cylinder (99.9%) fitted with a dip tube was purchased from BOC Ltd., UK. Softwood kraft lignin was supplied as a dry powder from the LignoBoost demonstration plant (Bäckhammar, Sweden). This lignin material is described by its rather low carbohydrate and ash contents and a sulphur content usually below 3% [21] and has been characterised in more detail in our previous studies [37,38].

## 184 2.2. Experimental procedures

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### 186 2.2.1. Transesterification of biodiesel

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188 The detailed procedure for the transesterification of biodiesel using supercritical  
189 methanolysis has been described previously by our research group [8]. In brief, biodiesel was  
190 produced by mixing WCO with methanol at a methanol-to-oil ratio of 10:1 and deionised  
191 water at 6% molar. The reaction temperature was set to 245 °C at a pressure of 125 bar using  
192 CO<sub>2</sub> at a stirring rate of 320 rpm for about 20 min. After quenching the reactor, the product  
193 mixture was fed into a centrifuge to split glycerol and biodiesel. Biodiesel was loaded in a  
194 rotary evaporator to recover unreacted methanol. The physicochemical properties and the  
195 composition of the feedstock are reported in our previous work [9,39].

196

### 197 2.2.2 Base-catalysed depolymerisation of lignin

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199 The depolymerisation of lignin was performed in a 100 mL reactor (model 4590, Parr  
200 instrument company, USA) equipped with a thermocouple (type J), heating mantle, a  
201 controller (model 4848) and a mechanical stirrer. An aqueous solution of LignoBoost lignin  
202 (50 g/L) and 0.6 g of NaOH as a catalyst with glycerol as a co-solvent was mixed before  
203 being loaded to the reactor. The homogeneous mixture was loaded to the reactor where  
204 reaction time started once the desired temperature was reached. After achieving the specified  
205 reaction time, the reactor was then quenched with an ice bath. The product mixture exiting  
206 the reactor was acidified using 1N HCl to pH ≤ 2 prior to centrifugation (1500 rpm, 3 min  
207 per cycle). The filtered mixture was then extracted using a volume ratio of 3:1 of EtOAc,  
208 vigorously shaking and kept at room temperature for around 10–15 min in a decantation  
209 funnel. EtOAc was then separated after decantation of the aqueous phase using a rotary  
210 evaporator under vacuum conditions, indicating a recovery and reutilisation of the extraction  
211 solvent. The solvent-free portion of the organic phase (bio-oil) was used as an antioxidant  
212 additive for biodiesel. A schematic for the workup protocol is shown in Fig. 2. The yield of  
213 bio-oil was calculated on a weight basis, according to Eq. (1).

214

$$215 \text{Yield}_{\text{bio-oil}} (\%) = (\text{mass}_{\text{bio-oil}} / \text{mass}_{\text{initial-lignin}}) \times 100 \quad (1)$$

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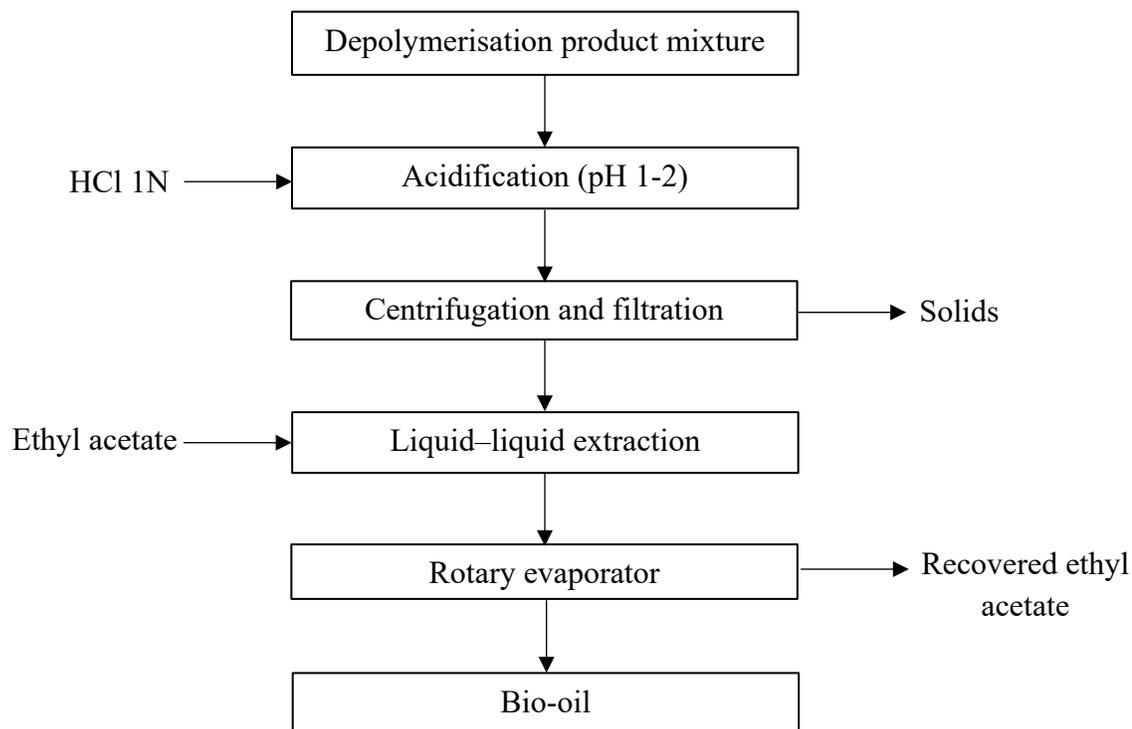
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**Fig. 2.** Workup protocol after lignin depolymerisation to obtain the bio-oil fractions.

### 2.2.3. Accelerated oxidation method

The relative resistance of the produced biodiesel to oxidation was analysed by a small-scale rapid oxidation tester known as PetroOxy. An accelerated oxidation test was used to analyse the oxidation stability of biodiesel. The test was carried out using the standard method of EN 16091 on a PetroOxy device (Anton Paar, Dahlewitz, Germany). The sample was prepared by adding 1 wt% of lignin-based bio-oil with biodiesel. The mixture was then fed to a centrifuge where the bio-oil-biodiesel soluble fraction was analysed for oxidation stability. The chamber cell was purged with oxygen twice before loading 5 mL of biodiesel/bio-oil mixture. The test cell was closed and automatically charged with oxygen up to 7 bar and heated to a standardised temperature of 140 °C. An initial pressure drop indicates that biodiesel has begun to oxidise after maximum pressure has been reached. The IP represents the elapsed time between the start of the test and the breakingpoint when the pressure drops by 10%, which indicates oxidation resistance.

### 260 2.3. Experimental design

261

262 RSM was applied to minimise the number of experiments and to investigate the relationship  
263 between the variables and responses via the Box–Behnken Design (BBD) method. The effect  
264 of three independent variables of lignin depolymerisation on the bio-oil yield and PetroOxy  
265 IP was investigated. The application of BBD in an experimental design specifies the position  
266 of design points and estimate the regression coefficients near the centre of the design space.  
267 This provides the probability of effective optimisation of the process variables. It also allows  
268 the development of a numerical model and study of the interactive effects of variables on the  
269 responses [40].

270

271 The independent variables were identified as temperature, glycerol content and time, which  
272 are labelled as A, B and C, respectively. Three levels of each variable were studied following  
273 the regulations of the BBD method. The selected three levels for each variable were coded  
274 as -1, 0 and +1, as shown in Table 1. The identified variables and levels resulted in the  
275 generation of 15 randomised experiments. To reduce the unexplained inconsistency in  
276 responses, the performed experimental runs were designed in a randomised manner and to  
277 meet the assumptions of the statistical methods in analysing the experimental data [41].

278

279 **Table 1.** Experimental design variables and their coded levels

Factor	Code	levels		
		-1	0	+1
Temperature (°C)	A	225	250	275
Glycerol (wt%)	B	0	10	20
Time (min)	C	30	60	90

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### 281 2.4. Statistical analysis

282

283 Design Expert 11 software (Stat-Ease Inc., Minneapolis, MN, USA) was used for the design  
284 of experiments, numerical optimisation, regression and graphical analysis. The regression  
285 models were developed to a general full quadratic equation, as presented in Eq. (2):

286

$$287 Y = b_o + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j>1}^n b_{ij} x_i x_j + \varepsilon \quad (2)$$

288

289 where  $Y$  is the expected response (bio-oil yield and oxidation stability),  $b_o$  represents the  
290 constant model coefficient,  $b_i$ ,  $b_{ii}$ ,  $b_{ij}$ , indicates coefficients for the intercept of linear,  
291 quadratic, interactive terms, respectively, while  $X_i$ ,  $X_j$  are independent variables ( $i \neq j$ ). The  
292 number of independent variables is shown in the parameter  $n$ , and the random error appears

293 in the term  $\varepsilon$ . The accuracy of the predicted models was examined using various statistical  
294 methods including adequacy precision, coefficient of correlation ( $R^2$ ), adjusted coefficient of  
295 determination ( $R^2_{adj}$ ) and the predicted coefficient of determination ( $R^2_{pred}$ ). The predicted  
296 models were evaluated and analysed using Analysis of Variance (ANOVA) to assess the  
297 significance of the selected parameters and the adequacy of the developed models. ANOVA  
298 works based on  $p$ -value test, where  $p$ -value less than 0.05 of a parameter indicates significant  
299 in the process. The lack of fit analysis was also employed to study the fitting accuracy of the  
300 predicted models to the experimental data.

301

### 302 **3. Results and discussion**

303

#### 304 **3.1. Regression model development**

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306 The software generated 15 randomised runs that were carried out experimentally to account  
307 for the PetroOxy IP, being in the range of 26–99 IP min, and bio-oil yield in the range of 4.1–  
308 23.8 % (Table 2). Numerous regression analyses were performed on the experimental results  
309 to match the experimental data with the mathematical models. Four mathematical regression  
310 models were used to fit the experimental data, including linear, two factors interactions (2FI),  
311 quadratic and cubic polynomials. The software suggested a 2FI and quadratic models for bio-  
312 oil yield and PetroOxy IP, respectively, as presented in Eqs. (3) and (4):

313

$$314 Y_1 = 11.79 + 4.71 A + 3.39 B + 0.22 C + 4.43 AB - 0.4 AC - 0.8 BC \quad (3)$$

315

$$316 Y_2 = 45.3967 + 14.9425 A + 4.9975 B + 9.8725 C + 1.1425 AB + 16.4175 AC - 3.2275 BC + \\ 317 4.53542 A^2 - 6.20958 B^2 + 7.51542 C^2 \quad (4)$$

318 where  $Y_1$  and  $Y_2$  represent the response variables the bio-oil yield and the PetroOxy IP of  
319 biodiesel, respectively, while  $A$ ,  $B$ , and  $C$  represent the independent variables, that is,  
320 temperature, glycerol and time, respectively.  $AB$ ,  $AC$  and  $BC$  represent the interaction  
321 between the independent variables.  $A^2$ ,  $B^2$  and  $C^2$  represent the excess of each independent  
322 variable. A positive sign of each variable coefficient has an indication of a synergistic effect  
323 on the response, while a negative sign indicates an antagonistic effect on the response.

324

325 **Table 2.** Experimental design matrix with the actual and predicted data

Run	Temperature (°C)	Glycerol (wt%)	Time (min)	Actual yield (%)	Predicted yield (%)	Actual PetroOxy (min)	Predicted PetroOxy (min)
1	275	20	60	23.8	24.31	62.5	64.8
2	250	10	60	14.1	11.79	44.8	45.4
3	225	0	60	5.1	8.11	27.2	24.9
4	225	20	60	4.1	6.04	32.7	32.6
5	275	10	30	14.6	16.67	48.2	46.1
6	250	20	90	12.6	14.60	60.3	58.4
7	250	10	60	12.0	11.79	46.2	45.4
8	275	0	60	7.1	8.69	52.4	52.5
9	225	10	30	5.8	6.45	48.7	49.1
10	250	0	30	9.9	7.37	26.7	28.6
11	275	10	90	17.7	16.32	99.0	98.7
12	250	20	30	17.2	15.75	45.3	45.1
13	250	10	60	13.8	11.79	45.2	45.4
14	250	0	90	8.5	9.42	54.6	54.8
15	225	10	90	10.5	7.70	33.9	36.0

326

327 **3.2. Statistical analysis**

328

329 The developed 2FI model for bio-oil yield reports a  $p$ -value of 0.0035 (Table 3), which  
330 implies that the model is highly significant. The PetroOxy IP, on the other hand, exhibited a  
331 high degree of significance with a  $p$ -value model of  $<0.0001$ , as presented in Table 4. The  
332 lack of fit analysis was observed as non-significance in both cases, i.e.  $p$ -values of 0.1394  
333 and 0.0593 for the 2FI and quadratic models, respectively. These results confirm the  
334 precision of the model in predicting the experimental results. Furthermore, the values of  $R^2$   
335 and  $R^2_{adj}$  were estimated to be 0.91 and 0.78, respectively, for the bio-oil yield response, and  
336 0.99 and 0.98 for the PetroOxy IP. In addition, the adequacy precision test, which defines the  
337 ratio between the predicted response and the relative error (signal-to-noise ratio), has been  
338 examined. The test resulted in values of 10.41, and 38.11 for bio-oil yield and PetroOxy IP,  
339 respectively, where a value higher than 4 is usually preferred [41]. A plot representing the  
340 predicted data against actual data is illustrated in Figs. 3a and b. The strong correlation  
341 between the actual and the predicted results are represented with minor deviations from the  
342 45° line.

343

344

345 **Table 3.** ANOVA for the bio-oil yield using the 2FI model

	Sum of squares	Difference	Mean square	<i>F</i> -value	<i>p</i> -value	Significance <sup>a</sup>
Model	351.39	6	58.57	8.87	0.0035	S
<i>A</i> -Temperature	177.66	1	177.66	26.89	0.0008	S
<i>B</i> -Glycerol	91.80	1	91.80	13.90	0.0058	S
<i>C</i> -Time	0.40	1	0.40	0.061	0.8107	NS
<i>AB</i>	78.32	1	78.32	11.86	0.0088	S
<i>AC</i>	0.64	1	0.64	0.097	0.7636	NS
<i>BC</i>	2.56	1	2.56	0.39	0.5509	NS
Residual	52.85	8	6.61		–	–
Lack of fit	50.27	6	8.38	6.49	0.1394	NS

346 <sup>a</sup> S, significant; NS, not significant

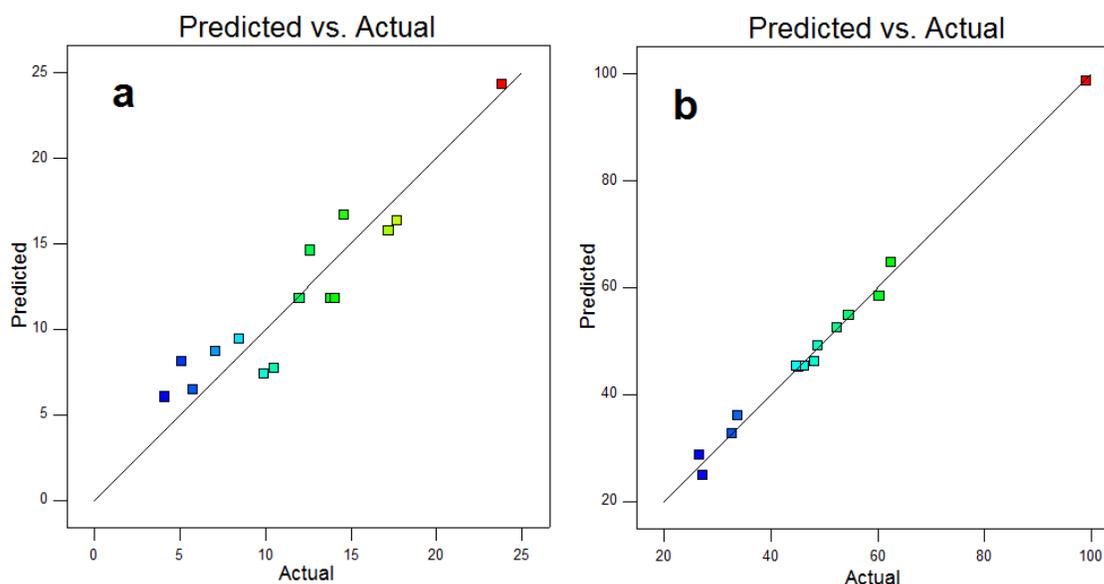
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348 **Table 4.** ANOVA for the PetroOxy IP using the quadratic model

	Sum of squares	Difference	Mean square	<i>F</i> -value	<i>p</i> -value	Significance <sup>a</sup>
Model	4344.12	9	482.68	85.94	<0.0001	S
<i>A</i> -Temperature	1786.23	1	1786.23	318.04	<0.0001	S
<i>B</i> -Glycerol	199.80	1	199.80	35.57	0.0019	S
<i>C</i> -Time	779.73	1	779.73	138.83	<0.0001	S
<i>AB</i>	5.22	1	5.22	0.9296	0.3792	NS
<i>AC</i>	1078.14	1	1078.14	191.96	<0.0001	S
<i>BC</i>	41.67	1	41.67	7.42	0.0416	S
<i>A</i> <sup>2</sup>	75.95	1	75.95	13.52	0.0143	S
<i>B</i> <sup>2</sup>	142.37	1	142.37	25.35	0.0040	S
<i>C</i> <sup>2</sup>	208.55	1	208.55	37.13	0.0017	S
Residual	191.65	8	23.96	–	–	–
Lack of fit	26.96	3	8.99	16.02	0.0593	NS

349 <sup>a</sup> S, significant; NS, not significant

350



351

352 **Fig. 3.** Predicted vs actual data for the response variables: (a) yield of bio-oil and (b)  
 353 PetroOxy IP.  
 354

355 It was observed from the ANOVA results, Tables 3 and 4, that some equation parameters are  
 356 non-significant, including C, AC and BC in Eq. (3) and AB in Eq. (4). However, the residence  
 357 time variable (C) was not excluded as it represents a core variable in this study. Accordingly,  
 358 the equations were simplified by excluding the non-significant variables. The simplified  
 359 equations are given in Eqs. (5) and (6).

360

361 
$$Y_1 = 11.786 + 4.712 A + 3.387 B + 0.225 C + 4.425 0.4 AC - 0.8 BC \quad (5)$$

362

363 
$$Y_2 = 45.397 + 14.943 A + 4.998 B + 9.873 C + 16.418 AC - 3.228 BC + 4.535 A^2 - 6.21 B^2 +$$
  
 364 
$$7.515 C^2 \quad (6)$$

365

366

367

368 **3.3. Effect of process variables and their interactions**

369

370 **3.3.1. Effect of reaction temperature**

371

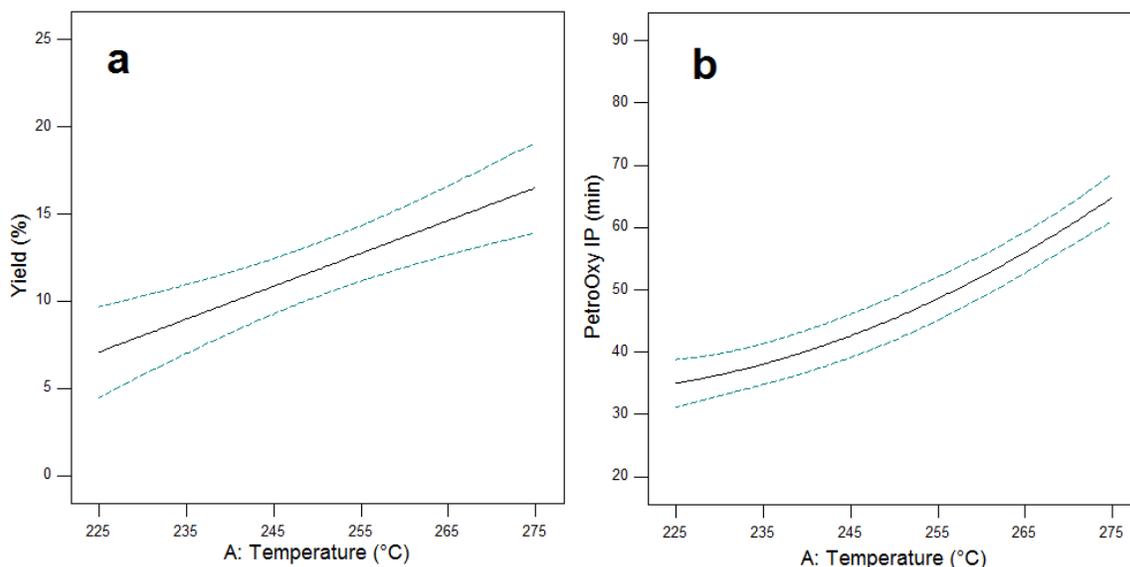
372 Temperature is an important factor that drives the fragmentation of lignin into low-  
 373 molecular-weight products. In order to analyse the individual effect of temperature, other  
 374 process variables were fixed at the optimal conditions (glycerol amount of 17.03 wt% and  
 375 residence time of 90 min). From the ANOVA results of Table 3, the reaction temperature  
 376 was found as significant positive parameter where it has a directly proportional relationship

377 with bio-oil yield as shown in Fig. 4a. The increasing effect of reaction temperature resulted  
378 in an equivalent increase in bio-oil yield up to 23.8% bio-oil yield (see Table 2). Although  
379 the maximum achieved bio-oil yield shown in Fig. 4a is 16.6%, higher values are reported in  
380 Table 2, which indicates the influence of other parameters together with temperature on bio-  
381 oil yield. The limited range of temperatures considered for this study was due to the  
382 restriction of glycerol inclusion in the reaction regime, as it has a boiling point of about 290  
383 °C. In addition, higher depolymerisation temperatures (>325 °C) may allow cracking and  
384 repolymerisation reactions which could lead to a decrease in bio-oil yield [42].

385

386 On the other hand, the reaction temperature was observed as a significant parameter on  
387 PetroOxy IP, as shown in Table 4. This means that the bio-oil produced at higher  
388 depolymerisation temperature has better antioxidant activity. The increase of temperature  
389 between 225 °C and 275 °C resulted in a 70% increase in PetroOxy IP (Fig. 4b). An increase  
390 in depolymerisation temperature suggests the increased production of low-molecular-weight  
391 phenolic compounds, including phenol derivatives, thus increasing the amount of hydrogen  
392 that can power up the antioxidant effect [43]. A similar observation has also been reported  
393 by Lavoie et al. [28] for black liquor obtained from semi-chemical pulping of straw. In their  
394 study, an increase of about 60% in the IP was attained upon increasing the reaction  
395 temperature from 250 °C to 300 °C during the catalytic depolymerisation of barley straw  
396 black liquor.

397



398

399 **Fig. 4.** The individual effect of the reaction temperature on (a) bio-oil yield (b) PetroOxy  
400 IP.

401

402

### 403 3.3.2. Effect of glycerol addition

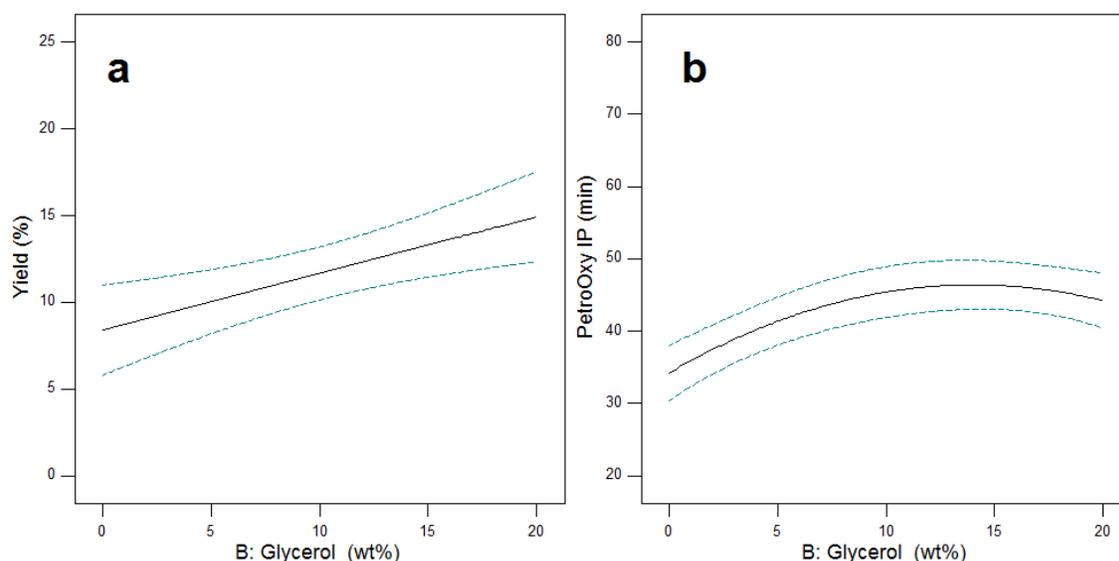
404

405 The addition of glycerol in depolymerisation reaction has significantly increased the yield of  
406 produced bio-oil. The effect of glycerol addition on the process responses was analysed at  
407 fixed conditions of temperature and residence time at 275 °C and 90 min, respectively. As  
408 shown in Fig. 5a, the bio-oil yield increased from 8.3% to 15% when glycerol was added up  
409 to 20 wt%. It was also observed as a significant parameter from ANOVA results shown in  
410 Table 3. Glycerol is a polyol, which contains three hydroxyl groups, and the increase in fibre  
411 liberation will promote the degradation of lignin. It has been used as an efficient co-solvent  
412 for hydrothermal liquefaction of rice straw where it has improved the yield and quality of  
413 produced bio-oil [44]. The addition of crude glycerol improves the bio-oil yield probably due  
414 to acids present, which could react with the lignin macromolecules to form a stable organic  
415 compound. A significant increase was also observed in the yield of bio-oil derived from waste  
416 materials upon adding glycerol as a co-substrate [45]. Higher values of bio-oil yield resulted  
417 at higher reaction temperatures, referring to the importance of studying the interactive effect  
418 of glycerol and temperature on bio-oil yield (Section 3.3.4).

419

420 Glycerol was found as a significant parameter affecting PetroOxy IP (Table 4). The increased  
421 glycerol amounts of up to 15 wt% during the depolymerisation of LignoBoost lignin resulted  
422 in an increase in the bio-oil antioxidant activity. As shown in Fig. 5b, the PetroOxy IP of  
423 biodiesel increased from 35 to 45 min. This indicates that glycerol addition has not only  
424 enhanced the bio-oil yield but also improved the quality of the produced bio-oil with higher  
425 antioxidant activity. To the best of the authors' knowledge, the effect of glycerol addition on  
426 antioxidant activity of lignin-derived bio-oil has not been reported previously. The results  
427 suggest possible enhancement of phenols production from lignin in the presence of up to 15  
428 wt% glycerol, which calls for further research on elucidating such chemical insights.

429



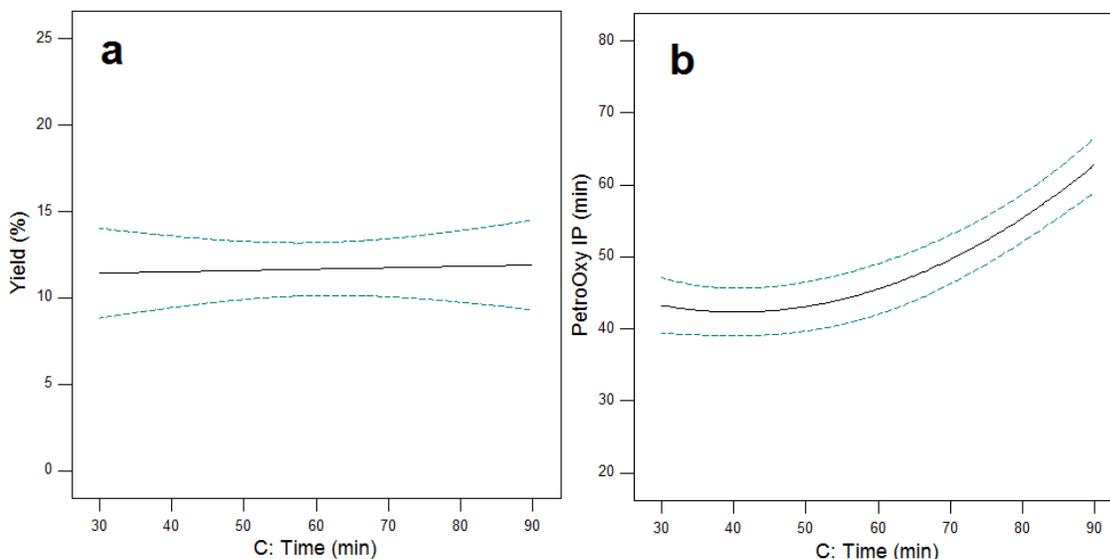
**Fig. 5.** The individual effect of the glycerol on (a) bio-oil yield (b) PetroOxy IP.

### 3.3.3. Effect of residence time

The single effect of residence time was studied at a constant temperature and glycerol addition of 275 °C and 17.03 wt%, respectively. The ANOVA results tabulated in Table 3 showed a non-significance of the residence time for the bio-oil yield. This means that the variation of reaction time between 30 to 90 min has no considerable effect on the bio-oil yield (Fig. 6a). This may be attributed to the pre-heating duration prior to reaching the reaction set temperature, as during this period (~20 min), the main reactions relevant to base-catalysed lignin depolymerisation could have likely occurred. Similar behaviour has also been described by Olarte et al. [46] in which there was no significant difference in the yields of the liquid products obtained between 15 and 60 min during depolymerisation of organosolv lignin with NaOH at temperatures between 165 and 350 °C. Short residence time favours bio-oil yield where lengthy residence time can influence the repolymerisation of lignin products dependent on temperature and secondary reactions that could lead to high char formation [42,47].

On the other hand, the residence time effect on PetroOxy IP was shown as a significant parameter in Table 4. An increase in time provides higher quality bio-oil with enhanced antioxidant activity with increased PetroOxy IP (Fig. 6b). The PetroOxy IP increased from 42 to 63 min when the reaction time increased from 30 to 90 min. Although the present study has observed no significant difference in bio-oil yield with increasing the reaction time, the produced bio-oil at longer reaction time has a higher antioxidant effect on biodiesel. This observation indicates that several decomposition reactions could occur to the produced fixed

456 amount of bio-oil through the reaction time, where the produced compounds are probably  
457 converted to phenols over time.  
458



459  
460 **Fig. 6.** Individual effect of reaction time on (a) bio-oil yield (b) PetroOxy IP.  
461

### 462 3.3.4 Interactive effects of process variables

463  
464 In the previous sub-sections, the individual effects of variables on bio-oil yield and PetroOxy  
465 IP were discussed. However, these effects were demonstrated, whilst keeping other variables  
466 at constant values. For instance, Fig. 5a showed that the range of bio-oil yield was lower than  
467 20% over the full range of glycerol, while higher values were observed experimentally. The  
468 reason behind this is the dependence of the effect of glycerol on bio-oil yield by the value of  
469 reaction temperature. Hence, it is crucial to study and analyse the interactive effects of  
470 variables, as each variable might have different effects on the response at different levels of  
471 other variables. Table 3 indicates that temperature and glycerol (AB) additions have a highly  
472 interactive effect on bio-oil yield with a  $p$ -value of 0.0035. In addition, the interaction of  
473 reaction temperature and time (AC) is highly significant on PetroOxy IP, as mentioned in  
474 Table 4.

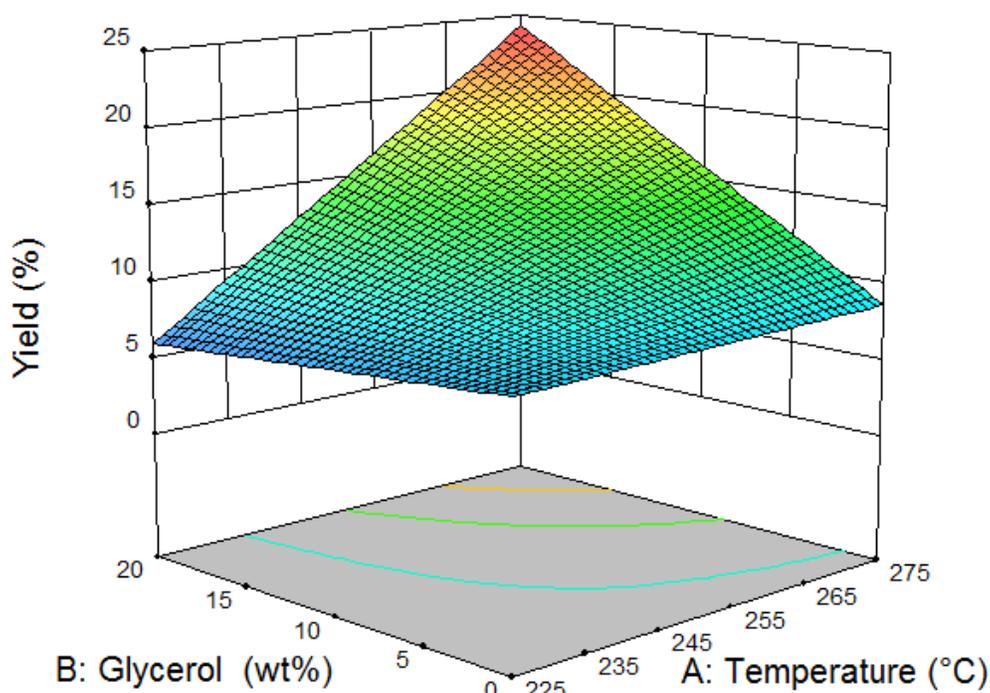
475  
476 The highly significant interactive effect between reaction temperature and glycerol addition  
477 is shown in Fig. 7, where the increasing effect of glycerol is highly dependent on the  
478 temperature. For instance, the effect of glycerol at 225 °C would be negligible compared to  
479 the increasing effect of glycerol at 275 °C. Accordingly, it is not accurate to highlight that  
480 glycerol addition has a significant effect on bio-oil without mentioning the range of the  
481 studied temperature. This may attribute that the activity of glycerol in enhancing the

482 depolymerisation of lignin is dependent on the reaction temperature. Accordingly, choosing  
483 the optimal glycerol addition should be considered together with the reaction temperature.

484

485 Similarly, the increasing effect of reaction time on PetroOxy IP is highly dependent on the  
486 value of temperature (Fig. 8). The increasing influence of reaction time on PetroOxy IP is  
487 not significant at 225 °C, while it is highly significant at 275 °C. The PetroOxy IP increased  
488 from 43 min to 99 min by increasing the reaction time from 30 to 90 min at 275 °C. Studying  
489 the individual effect of reaction time at a constant temperature would thus lead to a wrong  
490 indication of the true explanation, and this is why considering the interaction effect of  
491 variables is essential. This result has a critical indication for the high dependence of reaction  
492 temperature on the antioxidant activity of bio-oil. The extended reaction time enhances the  
493 conversion of bio-oil components into phenolic compounds only at elevated temperature.

494

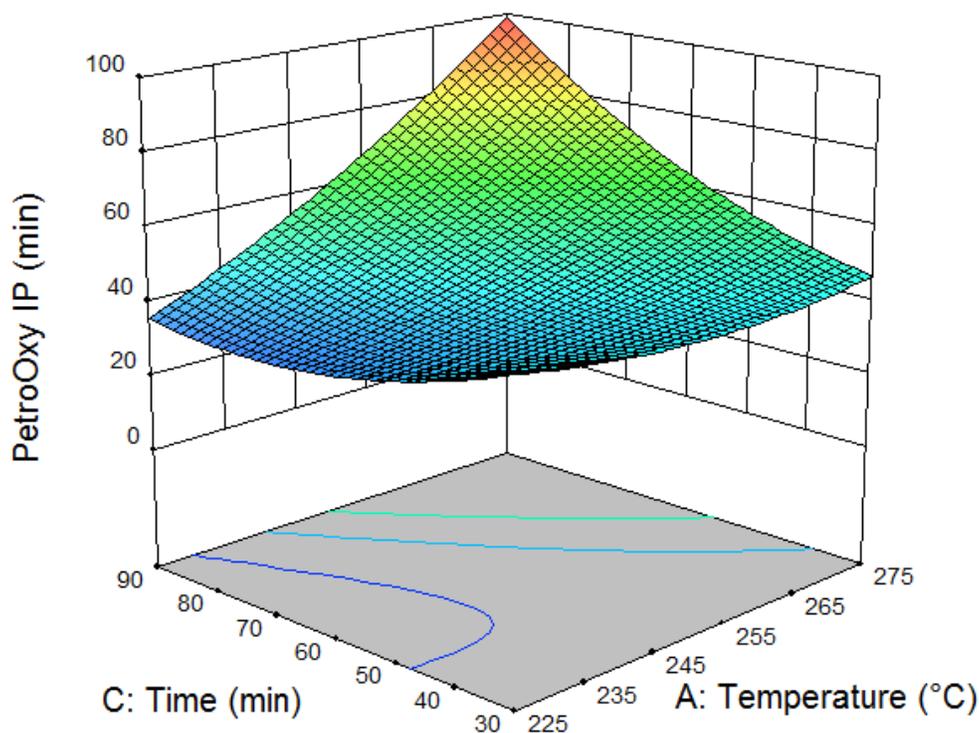


495

496

497 **Fig. 7.** Response surface plot for reaction temperature and glycerol amount vs bio-oil yield.

498



499

500 **Fig. 8.** Response surface plot for temperature and residence time vs PetroOxy IP.

501

### 502 **3.4. Process optimisation**

503 The application of RSM in experimental design enabled the development of a regression  
 504 model that was used to predict the optimal reaction conditions based on the specified targets.  
 505 The optimisation targets are set to maximise both process responses, i.e. the yield of bio-oil  
 506 and the PetroOxy IP, as shown in Table 5. However, the importance of maximising the  
 507 PetroOxy IP has set with the highest importance as this study is aiming to enhance the  
 508 oxidation stability of biodiesel. Furthermore, the reaction temperature and time were set to  
 509 be minimised to lower the process energy consumption (with lower importance). The  
 510 software generated some 49 solutions, where the solution with the highest desirability  
 511 percentage (96.2%) was selected as shown in Fig. 9. The developed optimal conditions have  
 512 achieved bio-oil yield of 21.25% and PetroOxy IP of 97.6 min at a reaction temperature of  
 513 275 °C, glycerol amount of 17.03 wt% within 90 min.

514

515 In an attempt to validate the developed optimal conditions, an experimental run was carried  
 516 out at the predicted conditions. The validation experiment has resulted in 20.9% and 96.2  
 517 min for bio-oil yield and PetroOxy IP, respectively. The experimental data show very similar

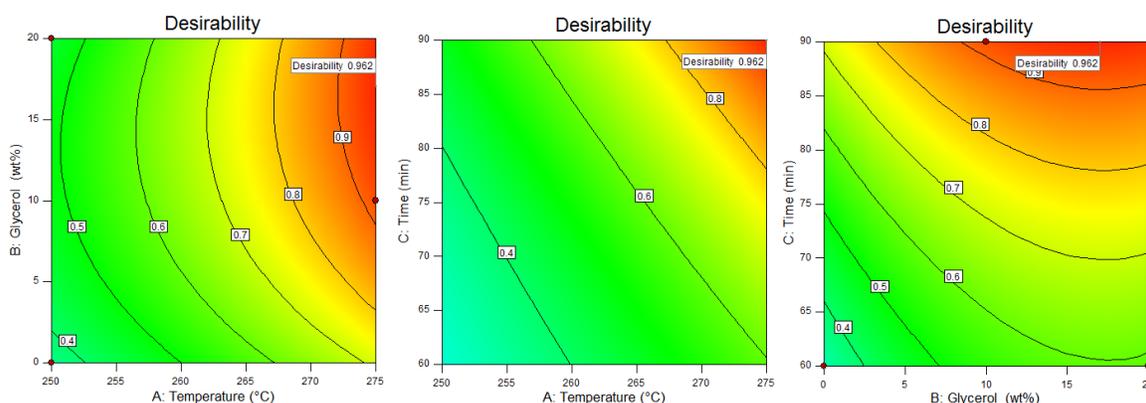
518 results at the predicted optimal conditions with a relative error between 1.4–1.6% for both  
 519 responses.

520

521 **Table 5.** Optimisation constraints to predict the optimisation targets for bio-oil

Factor	Code	Goal	Limits		
			Importance Scale 1–5	Lower	Upper
Temperature (°C)	A	Minimise	1	225	275
Glycerol (wt%)	B	In range	-	16	18
Time (min)	C	Minimise	1	30	90
Bio-oil yield (%)	Y <sub>1</sub>	Maximise	3	4.1	23.8
PetroOxy IP (min)	Y <sub>2</sub>	Maximise	5	28	99

522



523

524 **Fig. 9.** Contour plot for the interactive effect of process variables of the optimisation  
 525 desirability.

526

### 527 3.5 Oxidation stability of biodiesel

528

529 The PetroOxy IP of the neat biodiesel (without any additives) was estimated to be  $22.23 \pm$   
 530  $1.83$  min. The improvement of PetroOxy IP after doping biodiesel with bio-oil (oxy  
 531 improvement) was determined by Eq. (7).

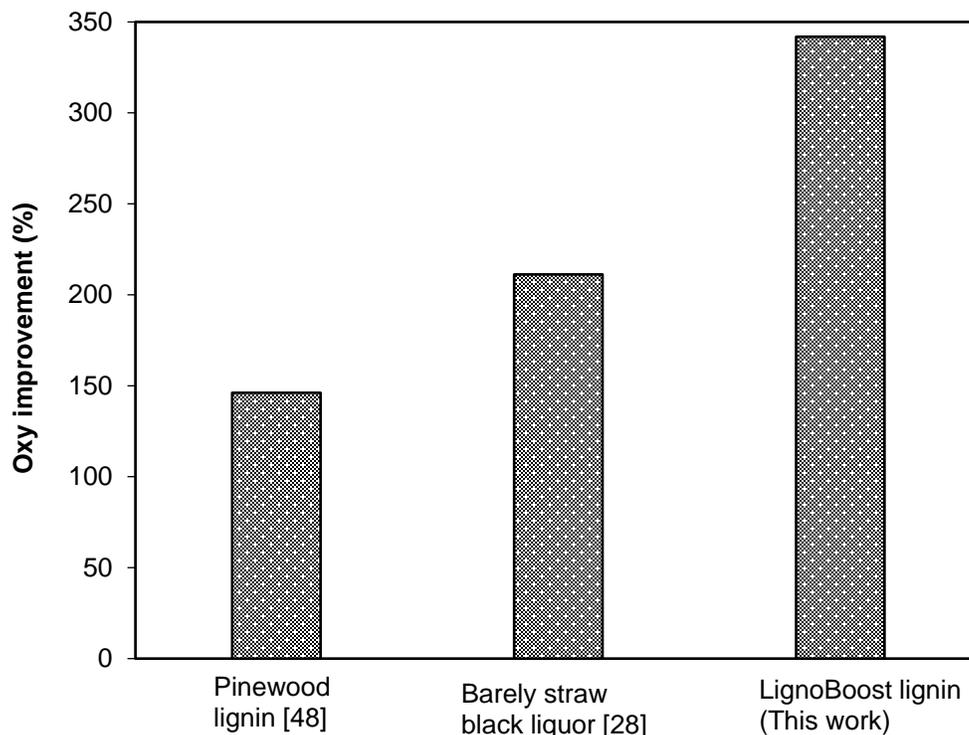
532

$$533 \text{ Oxy improvement} = ((\text{Oxy doped biodiesel} - \text{Oxy neat biodiesel}) / \text{Oxy neat biodiesel}) \times 100 \quad (7)$$

534

535 According to the designed optimum conditions, the PetroOxy IP reached 97.6 min by doping  
 536 biodiesel with 1 wt% of bio-oil. In comparison to the neat PetroOxy IP (22.23 min), the  
 537 addition of 1 wt% of bio-oil enhances the oxidation stability of biodiesel with up to ~340%.  
 538 The addition of 1 wt% of bio-oil synthesised from extracted fractions originating from  
 539 pinewood fast pyrolysis and from barely straw black liquor has previously enhanced the

540 oxidation stability of biodiesel with improvements of about 146% and 211%, respectively  
541 [28,48]. To the best of our knowledge, the present work reports a substantial improvement  
542 compared to relevant work in the literature (Fig. 10). It is worth mentioning that the doped  
543 biodiesel meets the EN 14214 biodiesel specification.



544 **Fig. 10.** Oxy improvement of biodiesel doped with various lignin-derived bio-oil additives.  
545  
546

#### 547 **4. Conclusions**

548  
549 A green approach for enhancing the oxidation stability of biodiesel using renewable additives  
550 extracted from kraft lignin has been developed. Glycerol, the side-product of biodiesel  
551 process, has been utilised as a co-solvent in lignin depolymerisation. A set of experiments  
552 based on BBD has been carried out to assess the influence of reaction temperature (225–275  
553 °C), glycerol content (0–20 wt%) and residence time (30–90 min). Two empirical models  
554 have been obtained, representing the process variables function in each process response.  
555 The results have shown that the introduction of glycerol as a co-solvent has not only enhanced  
556 the bio-oil yield but also improved the quality of the produced bio-oil. The addition of  
557 glycerol has resulted in bio-oil with higher antioxidant activity. Numerical and graphical  
558 optimisation have been carried out to determine the optimal conditions for the process, with

559 an overarching aim to maximise the antioxidant activity of the bio-oil. The developed optimal  
560 conditions have been validated experimentally resulting in bio-oil yield of 20.9% and  
561 PetroOxy IP of 96.2 min at a reaction temperature of 275 °C, glycerol amount of 17.03 wt%  
562 and residence time of 90 min. The experimental run at the developed optimal conditions has  
563 shown very similar results to the predicted data with a relative error between 1.4% and 1.6%  
564 for both responses. The addition of 1 wt% of the produced bio-oil at optimum conditions has  
565 significantly enhanced the oxidation stability of neat biodiesel by ~340%. Further research  
566 is however required to include detailed characterisation of the produced bio-oil in order to  
567 investigate its physico-chemical properties and to elucidate the compounds responsible for  
568 its antioxidant potential. This work introduces an integrated biorefinery approach that has the  
569 applicability of valorising kraft lignin and glycerol for the production of renewable  
570 antioxidants for enhancing the oxidation stability of biodiesel.

571

#### 572 **CRedit authorship contribution statement**

573

574 **Yusuf Umar:** Investigation, Methodology, Software application, Formal analysis,  
575 Validation, Data curation, Writing - original draft, Visualization. **Orlando Velasco:**  
576 Investigation, Validation. **Omar Y. Abdelaziz:** Conceptualization, Methodology, Writing -  
577 review & editing, Visualization, Project administration. **Omar Aboelazayem:**  
578 Conceptualization, Methodology, Software application, Formal analysis, Writing - review &  
579 editing, Project administration. **Mamdouh A. Gadalla:** Writing - review & editing,  
580 Supervision, Funding acquisition, Project administration. **Christian P. Hulteberg:**  
581 Resources, Writing - review & editing, Supervision, Funding acquisition, Project  
582 administration. **Basudeb Saha:** Resources, Writing - review & editing, Supervision, Funding  
583 acquisition, Project administration.

584

#### 585 **Declaration of competing interest**

586

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

589

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591

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597

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