

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.

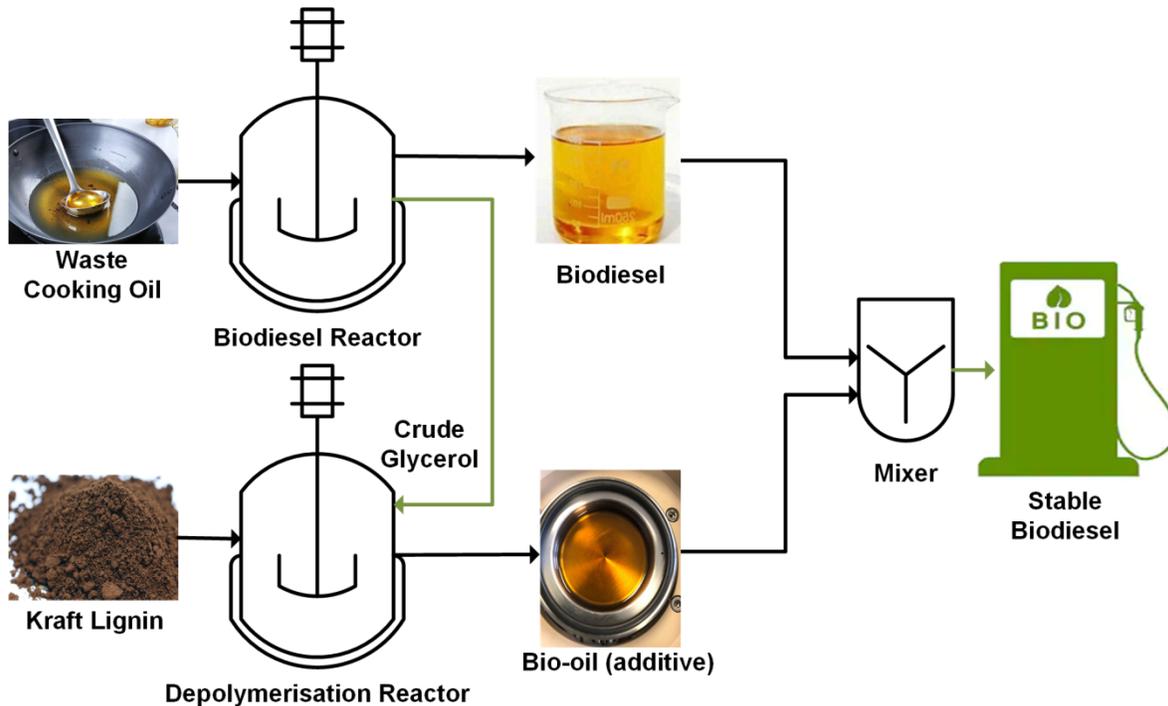
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41 **Keywords:**

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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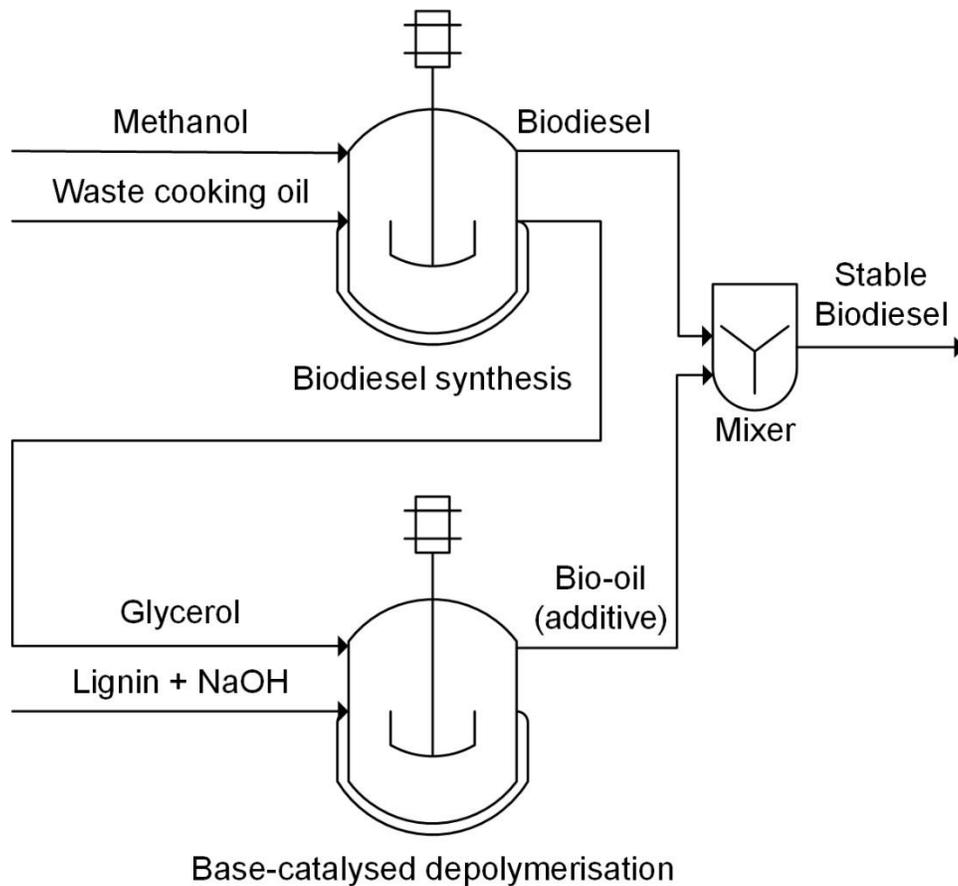


Fig. 1. A schematic of the proposed integrated biorefinery approach.

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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 CO₂ 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 CO₂ 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

198

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).

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

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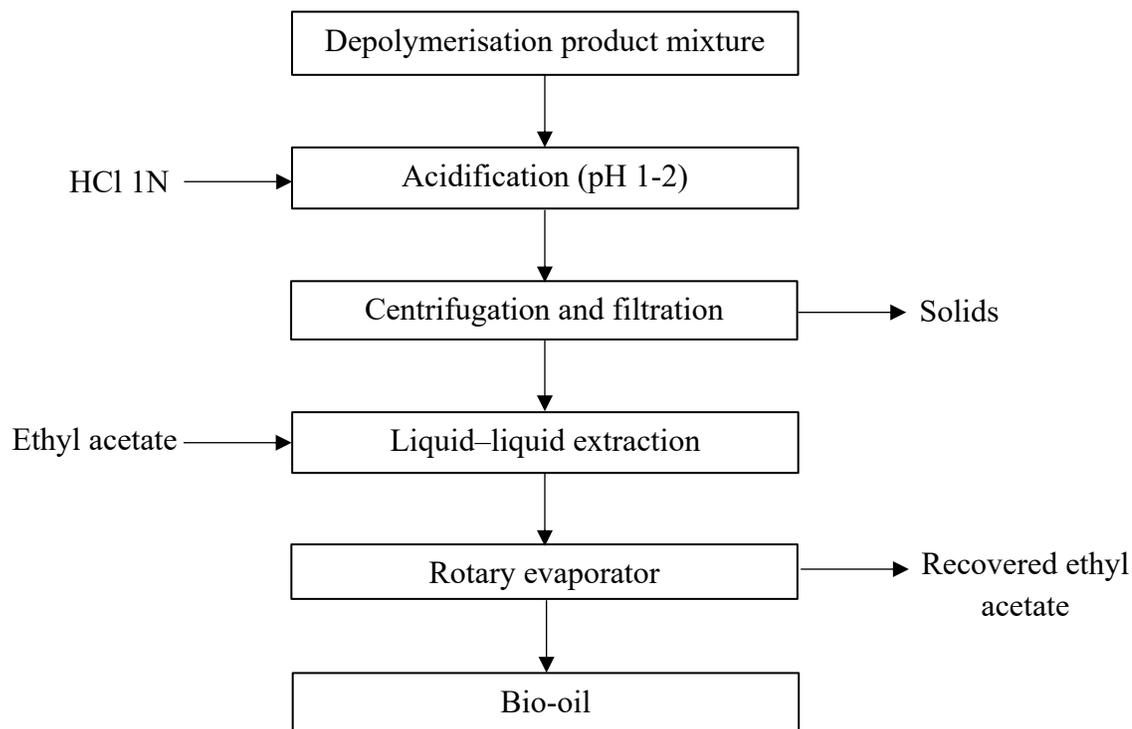


Fig. 2. Workup protocol after lignin depolymerisation to obtain the bio-oil fractions.

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 |

280

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 ε . 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**

305

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

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

315

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

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 ^a |
|-----------------------|----------------|------------|-------------|-----------------|-----------------|---------------------------|
| 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 ^a S, significant; NS, not significant

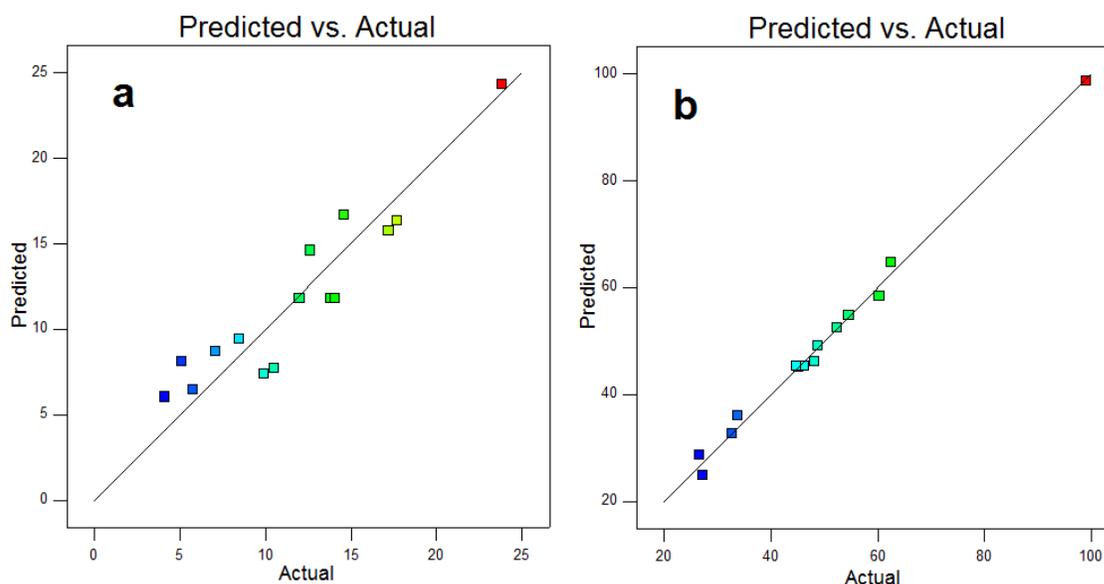
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348 **Table 4.** ANOVA for the PetroOxy IP using the quadratic model

| | Sum of squares | Difference | Mean square | <i>F</i> -value | <i>p</i> -value | Significance ^a |
|-----------------------|----------------|------------|-------------|-----------------|-----------------|---------------------------|
| 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> ² | 75.95 | 1 | 75.95 | 13.52 | 0.0143 | S |
| <i>B</i> ² | 142.37 | 1 | 142.37 | 25.35 | 0.0040 | S |
| <i>C</i> ² | 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 ^a S, significant; NS, not significant

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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
$$7.515 C^2 \quad (6)$$

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

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370 **3.3.1. Effect of reaction temperature**

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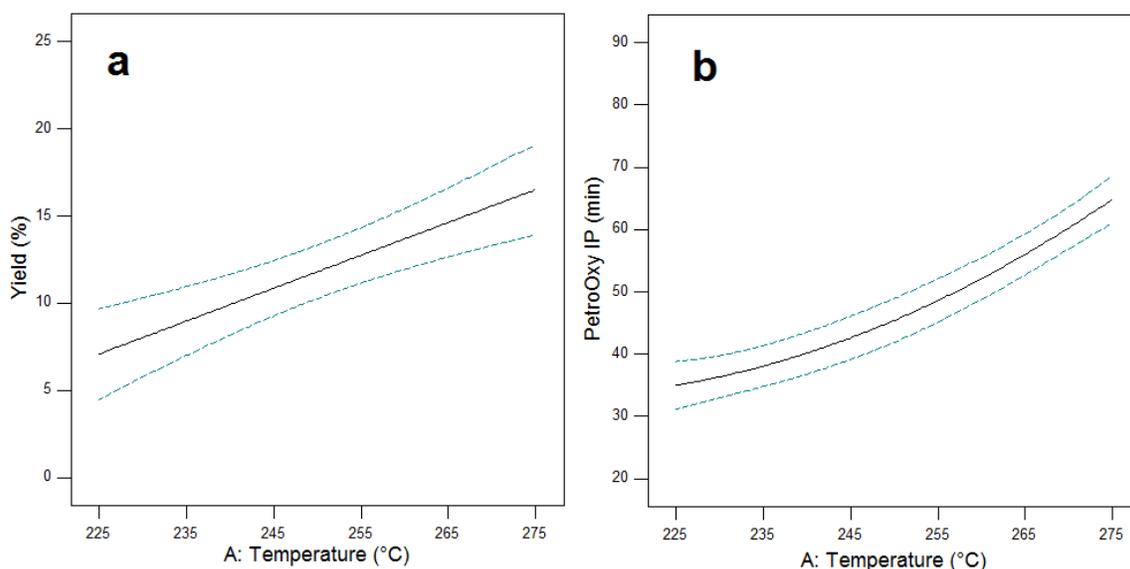
372 Temperature is an important factor that drives the fragmentation of lignin into low-
 373 molecular-weight products. In order to analyse the individual effect of temperature, other
 374 process variables were fixed at the optimal conditions (glycerol amount of 17.03 wt% and
 375 residence time of 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

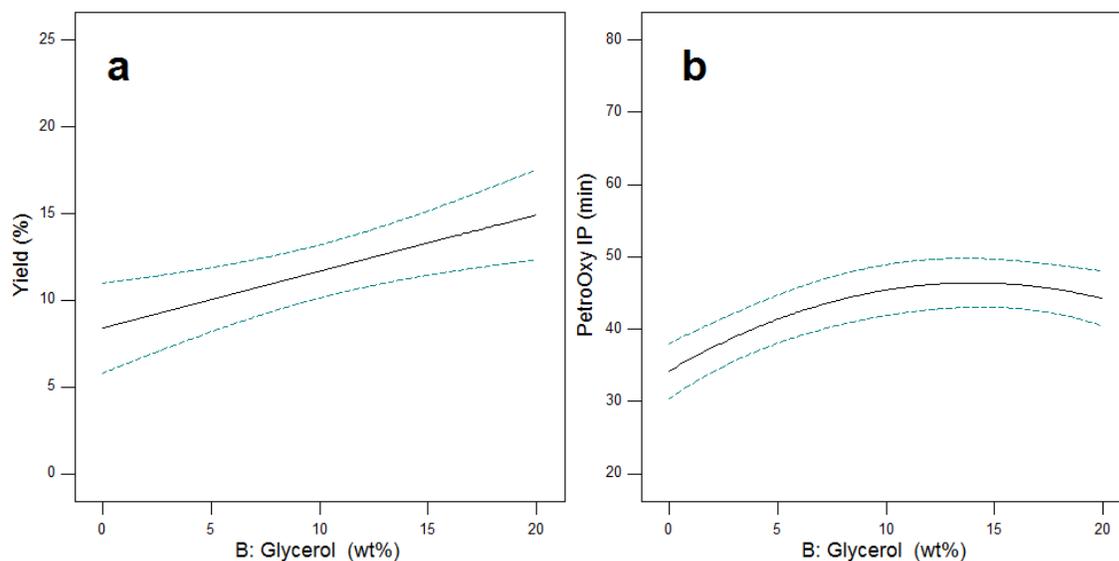


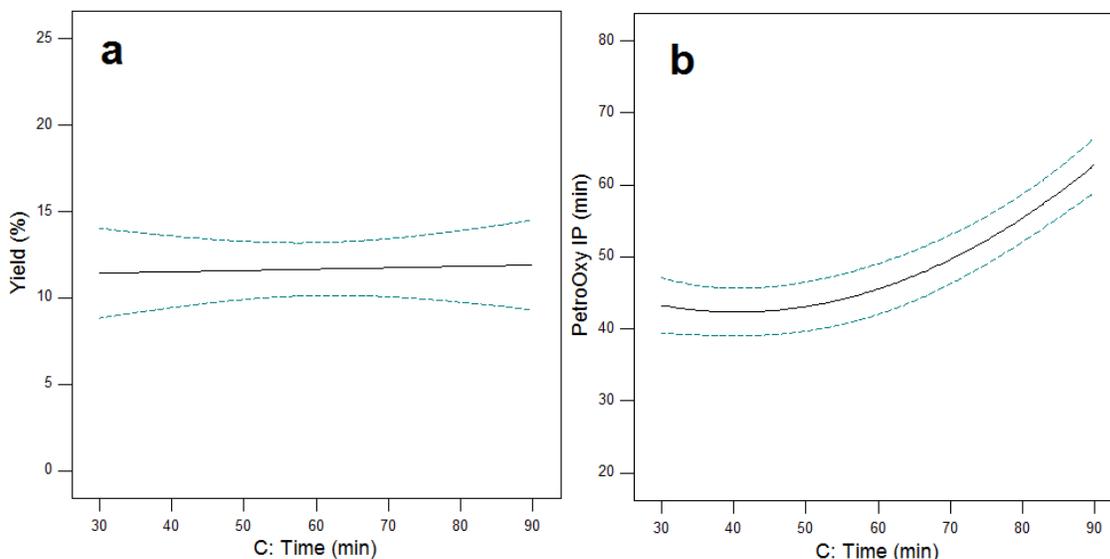
Fig. 5. The individual effect of the glycerol on (a) bio-oil yield (b) PetroOxy IP.

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.

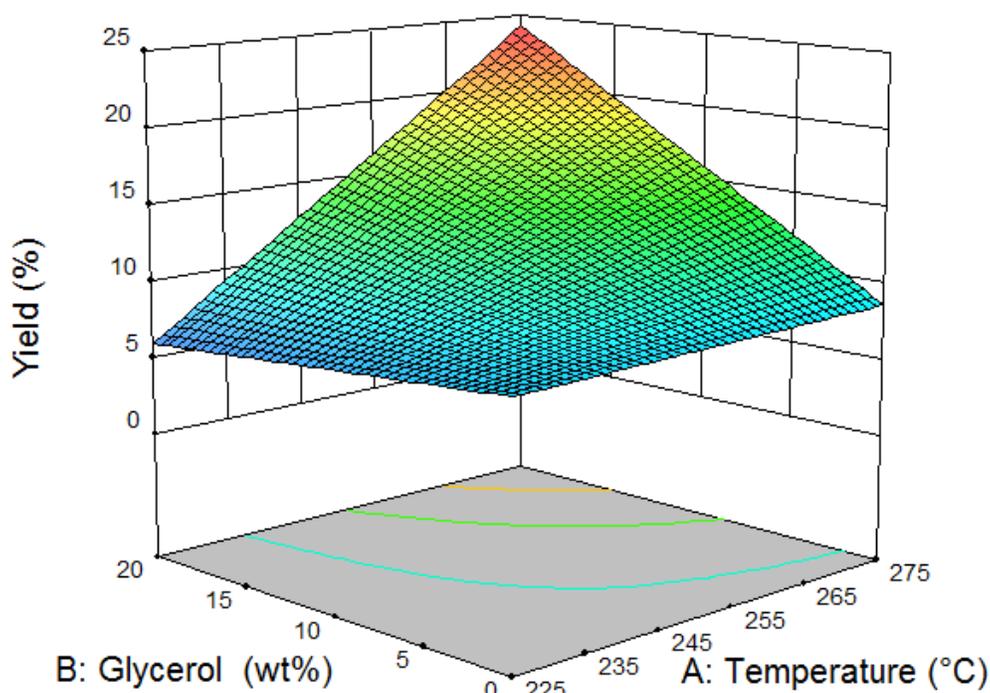
475
476 The highly significant interactive effect between reaction temperature and glycerol addition
477 is shown in Fig. 7, where the increasing effect of glycerol is highly dependent on the
478 temperature. For instance, the effect of glycerol at 225 °C would be negligible compared to
479 the increasing 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

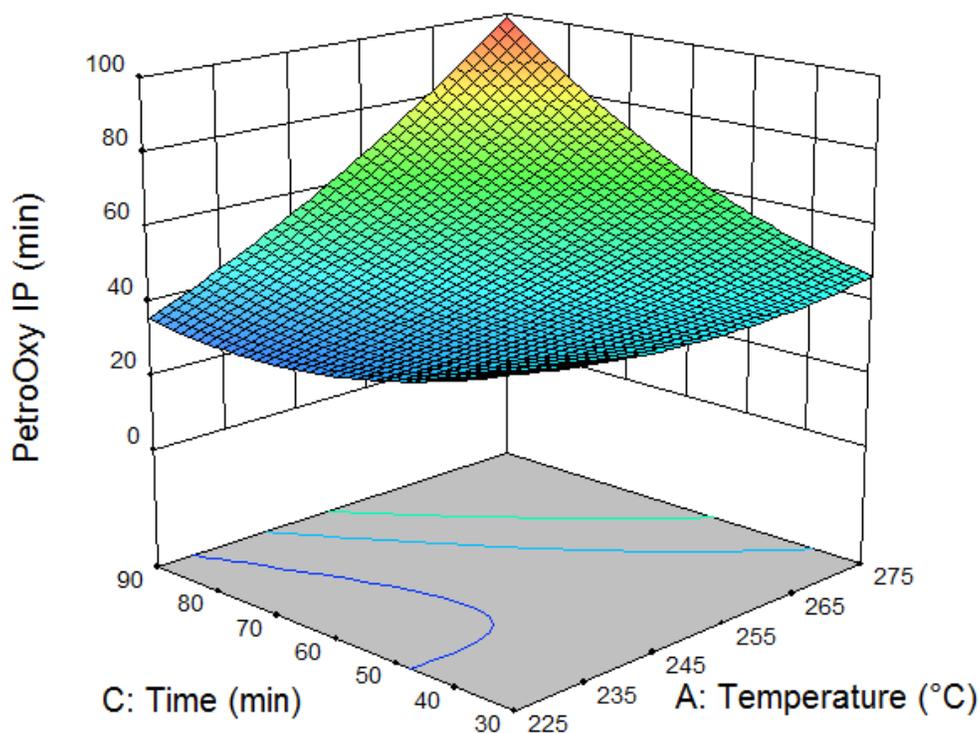


495

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

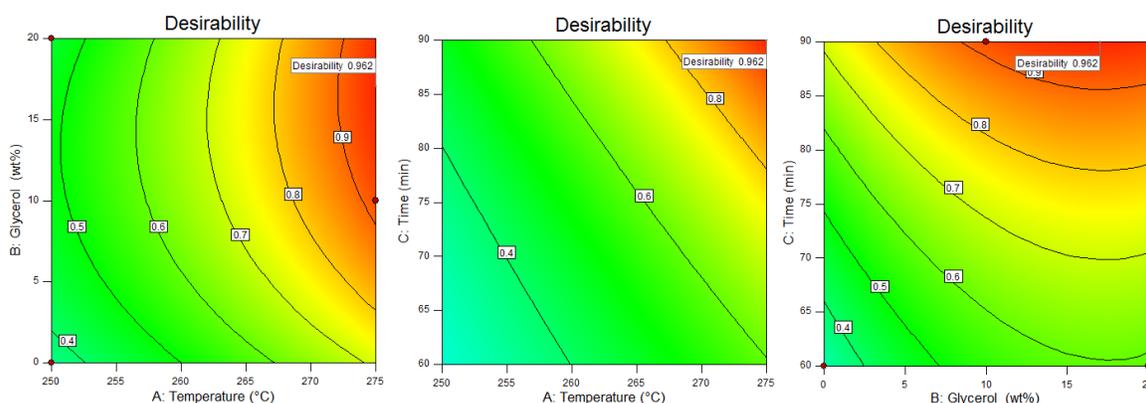
518 results at the predicted optimal conditions with a relative error between 1.4–1.6% for both
 519 responses.

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 ₁ | Maximise | 3 | 4.1 | 23.8 |
| PetroOxy IP (min) | Y ₂ | 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).

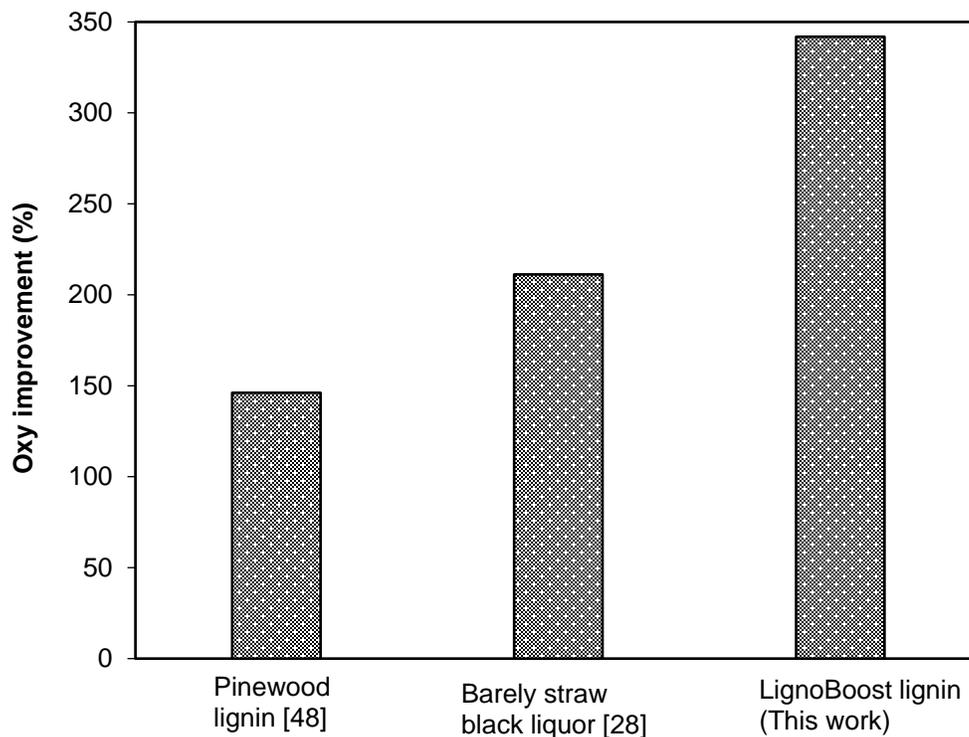
532

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

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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