1   **Optimization of a chemical scrubbing process based on a Fe-EDTA-**

2   **carbonate based solvent for the simultaneous removal of CO$_2$ and H$_2$S**

3   **from biogas**

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14 **ABSTRACT**

15 The potential of a novel Fe/EDTA/carbonate-based scrubbing process for the

16 simultaneous removal of H$_2$S and CO$_2$ from biogas was studied by evaluating the

17 influence of Fe/EDTA molarity (M), carbonate concentration (IC), biogas (B), air (A) and

18 liquid (L) flow rates on biogas upgrading performance using a Taguchi L$_{16}$(4^5)

19 experimental design. The ANOVA demonstrated that molarity of the Fe/EDTA solution

20 was a significant factor influencing H$_2$S concentration (0.035% at 0.00M to 0.000% at

21 0.05M). IC impacted on the concentrations of CO$_2$ (13.1 and 4.5% at 4000 and 10000mg

22 IC L^{-1}, respectively), N$_2$ and CH$_4$ (85.9 and 94.5% at 4000 and 10000mgIC L^{-1},

23 respectively). The biogas flow rate affected the concentrations of CO$_2$ (2.5 to 13.8% at

24 10 and 40mL min^{-1}, respectively), O$_2$, N$_2$ and CH$_4$ (95.9 to 85.4% at 10 and 40mL min^{-1},

25 respectively). Likewise, the recycling liquid flow rate affected CO$_2$ (8.3 and 5.9% at 5

26 and 30mL min^{-1}, respectively), O$_2$, N$_2$ and CH$_4$ (90.5 and 93.3% at 5 and 40mL min^{-1},

27   respectively) concentrations. Finally, the air flow rate impacted on CO_2 (10.8 and 6.7%

28   at 800 and 1000mL min^{-1}, respectively), H_2S, N_2 and CH_4 (87.9 and 92.2% at 800 and

29   1000mL min^{-1}, respectively) concentrations. Process optimization provided the optimal

30   conditions for each control factor. Continuous biogas upgrading operation at M_2-IC_1-B_2-

31   A_4-L_4 (0.05M, 10000mgIC L^{-1}, 10mL min^{-1}, 1000mL min^{-1} and 30mL min^{-1},

32   respectively) provided CH_4, CO_2, O_2, N_2 and H_2S concentration in the upgrading biogas

33   of 97.4, 1.4, 0.29, 0.97 and 0%, respectively, which complied with biomethane

34   regulations.

35

36   **Keywords:** Absorption-stripping process; Biogas upgrading; Biomethane; Chemical

37   scrubbing; Taguchi's design.

38

39   **1. Introduction**

40   Biogas from anaerobic waste treatment represents a renewable energy vector that can be

41   used as a fuel to power vehicles or to generate electricity and heat for domestic and

42   industrial applications, which can partially mitigate Europe's dependence on imported

43   fossil fuels [1,2]. In this context, the number of biogas plants in Europe has increased

44   from 6227 in 2009 to 17783 by the end of 2017, while biomethane production capacity

45   has also increased from 752 GWh in 2011 to 19352 GWh by the end of 2017 [3]. An

46   upgrading of biogas into biomethane is required prior use as a vehicle fuel or for the

47   injection into natural gas grids due to the high concentration of impurities present in raw

48   biogas: CO_2 (15-60%), CO (<0.6%), H_2S (0.005-2%), N_2 (0-2%), O_2 (0-1%), NH_3

49   (<1%), siloxanes (0-0.2%) and volatile organic compounds (<0.6%) [4]. Hence, most

50   international biomethane standards require a composition of $CH_4 \geq$ 90-95%, $CO_2 \leq$ 2-

51   4%, $O_2 \leq$ 1% and negligible amounts of H_2S [2,5,6].

52

Multiple technologies are nowadays commercially available or under validation phase to remove CO_2 and H_2S from biogas in order to fullfil with biomethane standards. Biological technologies are being succesfully scaled-up since the past decade and exhibit lower environmental impacts and lower operating costs. However, biotechnologies require either a cost-effective H_2 production from renewable energy surplus (in the case of hydrogenotrophic upgrading) or large areas and favourable environmental conditions (in the case of photosynthetic biogas upgrading) [2,7]. On the other hand, membrane separation, chemical/water/organic scrubbing, cryogenic separation or pressure swing adsorption can remove CO_2 from biogas, while *in-situ* chemical precipitation or adsorption onto activated carbon or metal ions provide an effective H_2S removal [2,7]. These physicochemical methods present high operating costs (2-5 ct€ kWh^{-1}) and environmental impacts as a result of their high energy demand, entail process operation at high temperatures and pressures, and can not support a simultaneous H_2S and CO_2 removal [8]. Therefore, there is an urgent need to develop cost-effective technologies operating under ambient conditions capable of supporting an integral biogas upgrading (H_2S and CO_2 removal in a single step process), which will increase the environmental and economic sustainability of biogas upgrading and boost biomethane industry.
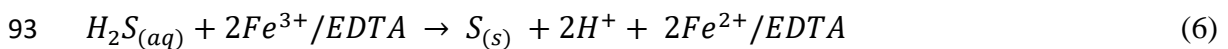
In this context, the use of an absorption-stripping process based on an aqueous solution of Fe-EDTA-carbonate represents an innovative physicochemical technology capable of simultaneously removing H_2S and CO_2 from biogas [9]. Highly carbonated aqueous solutions at high pH mediate a rapid and effective CO_2 capture at ambient pressure and allow an air-aided CO_2 desorption. The absorption and dissociation of CO_2 is described by equations (1) to (4):

3

77 $$CO_{2_g} \rightarrow CO_{2_L} \tag{1}$$

78 $$CO_{2_L} + H_2O \rightarrow H_2CO_3 \tag{2}$$

79 $$H_2CO_3 + H_2O \rightarrow HCO_3^- + H^+ \tag{3}$$

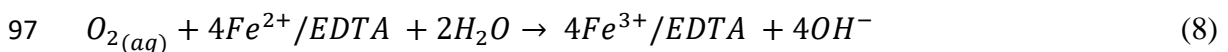80 $$HCO_3^- \rightarrow CO_3^{2-} + H^+ \tag{4}$$

81 The mass transfer of CO_2 from the biogas to the aqueous chemical solution can be

82 described as a function of a volumetric mass transfer coefficient (k_La), multiplied by the

83 concentration gradient in the liquid phase ($\frac{CO_{2_g}}{H} - CO_{2_L}$), where H is the dimensionless

84 Henry`s law constant. At this point it should be stressed that the high pH of the scrubbing

85 solution maintains the value of CO_{2L} very low, and therefore, the gas-liquid concentration

86 gradient as a maximum value. In addition, the high ionic strength of the scrubbing

87 solution prevents the coalescence of biogas bubbles, which enhances k_La.

88

89 On the other hand, Fe^{3+}-EDTA solutions support a cost effective H_2S oxidation to

90 elemental sulphur. According with Wubs and Beenackers [10], the absorption and

91 oxidation of H_2S with Fe-EDTA is described by equations (5) and (6):

92 $$H_2S_{(g)} \leftrightarrow H_2S_{(aq)} \tag{5}$$

93 $$H_2S_{(aq)} + 2Fe^{3+}/EDTA \rightarrow S_{(s)} + 2H^+ + 2Fe^{2+}/EDTA \tag{6}$$

94 The Fe^{2+}/EDTA resulting from H_2S oxidation to S can be regenerated into its active ferric

95 form (Fe^{3+}/EDTA) by oxidation with the air used for CO_2 stripping (equations 7 and 8).

96 $$O_{2_{(g)}} \leftrightarrow O_{2_{(aq)}} \tag{7}$$

97 $$O_{2_{(aq)}} + 4Fe^{2+}/EDTA + 2H_2O \rightarrow 4Fe^{3+}/EDTA + 4OH^- \tag{8}$$

98 Several studies have investigated the potential of Fe^{3+}/EDTA to remove H_2S from biogas.

99 In this sense, Horikawa et al., [11] studied the purification of biogas and reported a 90%

100 removal of H_2S from biogas using a 0.2 M Fe/EDTA aqueous solution in a system

4

101   composed of an absorption and a regeneration column with a total volume of 0.82 L.

102   Similarly, Schiavon Maia et al., [12] observed a 91% removal of H_2S in a similar

103   absorption-regeneration system using a 0.2 M Fe/EDTA solution, at biogas and liquid

104   flow rates of 340 mL min^{-1}. Finally, Frare et al., [13] investigated the absorption

105   efficiency of H_2S in a similar absorption-regeneration system using a 0.4 M Fe/EDTA

106   solution at a biogas flow rate of 265 mL min^{-1} and at different liquid flow rates (22, 48,

107   61, 70, 80, 122, 162, 207, 250 mL min^{-1}). Despite the promising results obtained in terms

108   of H_2S removal, the use of Fe/EDTA solutions has been exclusively studied for H_2S and

109   NOx removal [14]. In this context, the performance of novel Fe/EDTA solutions enriched

110   with carbonates must be tested in order to support a simultaneous removal of CO_2 and

111   H_2S from biogas at ambient pressure and temperature, which is expected to decrease both

112   the investment and operating costs (the latter by one order of magnitude compared to

113   conventional physical/chemical biogas upgrading technologies).

114

115   This study investigated, for the first time, the use of a chemical scrubbing process based

116   on a Fe/EDTA/carbonate solution for the simultaneous removal of CO_2 and H_2S from

117   biogas in a single step process composed of a biogas absorption column interconnected

118   to an air-aided regeneration column. A Taguchi $L_{16}(4^5)$ experimental design was used in

119   order to evaluate the influence of Fe/EDTA molarity, carbonate concentration, and

120   biogas, air and liquid flow rates on biogas upgrading and to elucidate the optimal values

121   of the parameters.

122

123   **2. Materials and methods**

124   **2.1 Biogas and Fe/EDTA solution**

5

125 The synthetic gas mixture used as a model biogas was composed of CH_4 (70%), CO_2

126 (29.5%) and H_2S (0.5%) (Abello Linde; Spain). The Fe/EDTA/carbonate solution was

127 prepared using iron (III) monosodium ethylenediaminetetraacetic (Alfa Aesar, Germany),

128 sodium carbonate and sodium bicarbonate (Cofarcas, Spain).

129

130 **2.2 Experimental set-up**

131 The experimental lab scale set-up was located at the Institute of Sustainable Processes of

132 Valladolid University (Spain). The lab scale set-up consisted of a biogas absorption

133 column with a working volume of 1.8 L (internal diameter = 4 cm; height = 150 cm) and

134 a regeneration column with a working volume of 2.0 L (internal diameter = 4 cm; height

135 = 198 cm). Both columns were interconnected by a recirculation pump using a degassing

136 chamber of 0.45 L (internal diameter = 8 cm; height = 9 cm). Biogas was injected in the

137 absorption column under counter-current flow operation using a metallic diffuser of 2 μm

138 pore size installed at the bottom of the column. Similarly, air was injected in the

139 regeneration column under counter-current flow operation using a metallic diffuser of 2

140 μm pore size installed at the bottom of the column (Fig. 1). The air and biogas flow rates

141 were controlled via rotameter and mass flow controller, respectively (Aalborg, USA).

142 **< Figure 1>**

143

144 **2.3 Optimization of operational conditions by Taguchi's parameter design**

145 Five operational parameters (control factors) were selected in order to optimize the

146 simultaneous removal of CO_2 and H_2S from biogas, while preventing a negative O_2 and

147 N_2 stripping from the scrubbing solution to biomethane: Fe/EDTA molarity (M),

148 inorganic carbon concentration (IC), biogas flow rate (B), air flow rate (A) and

149 recirculating liquid flow rate (L). M is an important factor determining the absorption of

6

150   H_2S, while IC mediates the absorption of CO_2 from biogas. B, L and A were selected in

151   order to study the influence of the recycling liquid/biogas ratio in the absorption column

152   on biomethane quality and the efficiency of CO_2 desorption in the regeneration column.

153   Four different levels were established for each control factor based on literature (Table

154   1). The selection of such a high number of factor levels aimed at elucidating the behavior

155   of the parameters within the tested range by identifying quadratic and sinusoidal effects

156   [15]. The main objective of this work was the minimization of the concentration of CO_2,

157   H_2S, O_2 and N_2 and the maximization of the concentration of CH_4 in the upgraded biogas.

158   **< Table 1>**

159   The optimization of these five factors at the four different levels was carried out using a

160   Taguchi's orthogonal array $L_{16}(4^5)$ design [16]. The selected orthogonal array was a

161   highly fractional factorial design that reduced the number of experiments from $4^5=1024$

162   (required by a full factorial design) to 16, while still obtaining statistically meaningful

163   results. The experimental design matrix resulted in a set of 16 experiments whose factor

164   level combinations are depicted in Table 2. The order of execution of the 16 experiments

165   was randomized and each test accounted for triplicate measurements of the upgraded

166   biogas under steady state in order to be able to estimate the residual error of the analysis

167   of variance (ANOVA). Each experiment lasted eight hours and a new solution was

168   prepared for each replica. The pH value in each was set at 9.25 in order to allow an

169   effective CO_2 and H_2S capture from biogas at ambient pressure, while allowing a cost-

170   effective air-aided CO_2 desorption. The investigation of the influence of pH on CO_2 and

171   H_2S removal was not necessary since its beneficial effect has been previously proved in

172   many publications [17,18]. Mean results of the 16 experiments are shown in Table 2 and

173   the results for each triplicate measurement are included in Table S1.

174   **< Table 2>**

175 At this point it should be highlighted that the $L_{16}(4^5)$ design has 15 degrees of freedom,

176 (*d.f.*), which were all consumed by the use of five four-level control factors ($5 \times (4-1) = 15$

177 *d.f.*). No degrees of freedom were left to evaluate the interactions between control factors

178 and therefore, interactions were integrated with the main effects according with the

179 triangular interactions table of the design [19]. The L_{16} array was initially designed for

180 two-level experiments. However, sets of mutually interactive columns of the $L_{16}(2^{15})$

181 array were merged to accommodate five four-level factors in order to use it for four-level

182 experiments. The merging of mutually interactive columns minimized the above

183 mentioned interactions [20].

184

185 The influence of the control factors on the performance of biogas upgrading was

186 evaluated using ANOVA. The interactions between the most influential control factors,

187 although integrated with the main effects, were graphically represented to evaluate their

188 contribution. A Duncan´s multiple range test was carried out in order to identify

189 significant differences amongst factor levels and therefore to select those levels providing

190 the optimum response during biogas upgrading [21].

191

192 All statistical calculations (ANOVA, Duncan's test and predictive models) were

193 performed using Excel (Microsoft, USA).

194

195 **2.4 Analytical procedures**

196 The concentrations of CH_4, CO_2, H_2S, O_2 and N_2 in the biogas and biomethane were

197 determined using a gas chromatograph coupled with a thermal conductivity detector

198 (Varian CP-3800 GC-TCD, Palo Alto, USA) and equipped with a CP-Molsieve 5A (15

199 m $\times$ 0.53 mm $\times$ 15 µm) and a CP-PoraBOND Q (25 m $\times$ 0.53 mm $\times$ 15 µm) columns.

The injector and detector temperatures were maintained at 150 and 175 °C, respectively.

Helium was used as the carrier gas at 13.7 mL min^{-1}. The pH was determined with an

Eutech Cyberscan pH 510 (Eutech Instruments, The Netherlands). IC concentration was

analyzed using a Shimadzu TOC-VCSH analyzer (Japan).

3. Results and discussion

3.1 Influence of the control factors on biogas upgrading

The ANOVA of the experimental results (Table 3) demonstrated that the molarity of the

Fe/EDTA solution was a significant factor influencing the concentration of all five biogas

components according to the significance level used in all statistical calculations

($p<0.05$). The concentration of inorganic carbon in the solution directly impacted on the

concentrations of CO_2, N_2 and CH_4, while the concentrations of CO_2, O_2, N_2 and CH_4

were affected by the biogas and recycling liquid flow rates. Finally, the air flow rate in

the stripping column also influenced the CO_2, H_2S, N_2 and CH_4 content.

<center>**<Table 3>**</center>

The effect of each factor level on the mean values of the concentration of the target

components in the upgraded biogas is shown in Fig. 2. The CO_2 concentration values

obtained at the four different levels of M (0, 0.01, 0.03, 0.05) were 4.3, 6.9, 5.6 and 16.1%,

respectively. At this point, it is important to stress that this increase in CO_2 concentration

recorded at the highest molarity was not likely influenced by the increase in the molarity

of the Fe/EDTA solution but related to the interactions of the different levels of each

control factor assessed in the test at 0.05 M of Fe/EDTA. A decrease in CO_2 concentration

was observed at increasing inorganic carbon concentration, from 13.1% at 4000 mg IC L^{-1} to 4.5% at 10000 mg IC L^{-1}. The pH values recorded in each experiment in the

absorption column are collected in Table S2. A higher inorganic carbon concentration in

<center>9</center>

225 the absorption solution entailed a higher pH and buffer capacity, which provided an

226 enhanced transfer of CO_2. The increase in biogas flow rate brought about an increase in

227 CO_2 concentration of the upgraded biogas, from 2.5% at 10 mL min^{-1} to 13.8% at 40 mL

228 min^{-1}, as a result of the corresponding reduction in the biogas residence time in the

229 absorption column. Air flow rates of 200, 500 and 1000 mL min^{-1} in the desorption

230 column supported CO_2 concentrations of 7.5, 8.0 and 6.7%, respectively, while a higher

231 CO_2 concentration value of 10.8% was recorded at 800 mL min^{-1}. Finally, CO_2

232 concentrations of 8.3 and 7.9% were achieved at recycling liquid flow rates of 5 and 20

233 mL min^{-1}, respectively; while a higher CO_2 concentration of 10.9% was recorded at 10

234 mL min^{-1}. A liquid flow rate of 30 mL min^{-1} provided a CO_2 concentration of 5.9% (Fig.

235 2a).

236 **\<Figure 2\>**

237 A decrease in H_2S concentration was observed as the Fe/EDTA molarity increased, from

238 0.035% at 0.00 M to 0.000% at a concentration of 0.05 M. These results can be explained

239 by the capacity of the Fe/EDTA solution to partially oxidize the H_2S present in biogas.

240 No clear correlation between the H_2S concentration and the air flow rate in the upgraded

241 biogas was observed, with values of 0.021, 0.014, 0.024 and 0.011% at air flow rates of

242 200, 500, 800 and 1000 mL min^{-1}, respectively (Fig. 2b). The IC concentration, biogas

243 and liquid flow rates did not exert a significant effect on the elimination of H_2S according

244 to the statistical analysis at $p > 0.05$ (Table 3). The increase in biogas flow rate induced a

245 slight decrease in H_2S levels, which suggests the interference of other factors since a

246 decrease in biogas residence time in the absorption column should entail a reduction in

247 H_2S removal efficiencies.

248

249 O_2 concentrations of 0.25, 0.14, 0.25 and 0.18% were recorded at Fe/EDTA molarities of

250 0.00, 0.01, 0.03 and 0.05 M, respectively. A decrease in O_2 concentration was observed

251 at increasing biogas flow rates, from 0.34% at 10 mL min^{-1} to 0.16% at 40 mL min^{-1}, as

252 a result of the enhanced dilution of the stripped oxygen. Finally, the decrease in O_2

253 concentration at increasing liquid flow rates, from 0.24% at a flow rate of 5 mL min^{-1} to

254 0.15% at a flow rate of 30 mL min^{-1}, suggests the interference of other factors, since a

255 higher recycling liquid flow rate should entail a higher O_2 stripping (Fig. 2c). The IC

256 concentration and air flow rate did not exert a significant effect on O_2 content (ANOVA

257 test at p>0.05, Table 3).

258

259 Although all the parameters significantly influenced the elimination of N_2 (p < 0.05,

260 Table 3), no clear correlations between N_2 concentration in the upgraded biogas and the

261 experimental parameters were observed. The N_2 concentrations recorded at a Fe/EDTA

262 molarity of 0.00, 0.01, 0.03 and 0.05 M were 1.00, 0.87, 0.58 and 0.80%, respectively.

263 N_2 concentrations of 0.84, 0.62, 0.96 and 0.83% were recorded at IC concentrations of

264 4000, 6000, 8000 and 10000 mg L^{-1}, respectively. Similarly, N_2 concentrations of 1.28,

265 0.54, 0.77 and 0.65% were achieved at biogas flow rates of 10, 20, 30 and 40 mL min^{-1},

266 respectively, and of 0.84, 0.61, 1.00 and 0.79% at air flow rates of 200, 500, 800 and 1000

267 mL min^{-1}, respectively. Finally, recycling liquid flow rates of 5, 10, 20 and 30 mL min^{-1}

268 supported N_2 concentrations of 0.95, 0.72, 0.91 and 0.67%, respectively (Fig 2d).

269

270 CH_4 concentrations in the upgraded biogas at Fe/EDTA molarities of 0.00, 0.01, 0.03 and

271 0.05 M were 94.4, 92.0, 93.5 and 82.9%, respectively. It is important to stress that the

272 decrease in CH_4 concentration recorded at 0.05 M of Fe/EDTA was due to the high CO_2

273 concentration in the upgraded biogas likely caused by the interactions of the different

11

274   levels of each control factor assessed in the tests at 0.05 M of Fe/EDTA. An increase in

275   CH_4 concentration was observed at increasing IC concentrations, from 85.9% at 4000 mg

276   IC L^{-1} to 94.5% at 10000 mg IC L^{-1}. The increase in biogas flow rate mediated a decrease

277   in the CH_4 concentration of the upgraded biogas, from 95.9% at 10 mL min^{-1} to 85.4% at

278   40 mL min^{-1}. On the other hand, air flow rates of 200, 500 and 1000 mL min^{-1} in the

279   stripping column supported CH_4 concentrations of 91.5, 91.2 and 92.2%, respectively,

280   while a lower CH_4 concentration of 87.9% was observed at 800 mL min^{-1} when the

281   medium contained the lowest IC concentration. Finally, recycling liquid flow rates of 5,

282   10, 20 and 30 mL min^{-1} corresponded to CH_4 concentrations of 90.5, 88.1, 91.0 and

283   93.3%, respectively (Fig. 2e).

284

285   In the particular case of CO_2, N_2 and CH_4 concentrations, the five control factors tested

286   were decisive in order to fulfill any biomethane standard. The Fe/EDTA molarity and air

287   flow rate were significant to minimize H_2S concentration, while the most relevant factors

288   determining the O_2 concentration in the upgraded biogas were the liquid and biogas flow

289   rates and the Fe/EDTA molarity.

290

291   **3.2 Process optimization**

292   A Duncan's multiple range test was performed in order to verify the optimal level for

293   each control factor and to obtain the operational conditions optimizing the upgrading of

294   biogas. The test was applied to the factors with a significant effect on the concentration

295   of the different gases measured in the upgraded biogas. According to the test results, the

296   combination of levels of each control factor that minimized the concentration of CO_2,

297   H_2S, O_2 and N_2 in the upgraded biogas and maximized the concentration of CH_4 was

12

298   M_4-IC_1-B_2-A_4-L_4, which corresponds to 0.03 M Fe/EDTA, 10000 mg IC L^{-1}, 10 mL min^{-}

299   ^{1} of biogas flow rate, 1000 mL min^{-1} of air flow rate and 30 mL min^{-1} of liquid flow rate.

300

301   A visual analysis of the interaction between Fe/EDTA molarity and the inorganic carbon

302   concentration was also performed by jointly representing the mean responses obtained

303   for CO_2 and H_2S at the tested levels of Fe/EDTA molarity and IC (Fig. 3). According to

304   this analysis, a change in Fe/EDTA molarity from 0.03 M to 0.05 entailed an increase in

305   CO_2 concentration above 15% for IC levels ranging from 4000 to 8000 mg L^{-1}, but the

306   impact is negligible if the maximum 10000 mg L^{-1} IC level is used, at which CO_2

307   concentration is around 5% independently of the Fe/EDTA concentration. On the other

308   hand, a change in Fe/EDTA molarity from 0.03 to 0.05 M corresponded to changes in

309   H_2S concentrations from 0.023, 0.006, 0.016 and 0.014% (at IC concentrations of 4000,

310   6000, 8000 and 10000 mg L^{-1}, respectively) to 0.000% regardless of the IC concentration

311   level (Fig. 3b). Therefore, the optimum combination resulting from the Duncan's multiple

312   range test (M_4-IC_1-B_2-A_4-L_4) can be changed to the optimum combination resulting

313   from the analysis of interactions, M_2-IC_1-B_2-A_4-L_4: 0.05 M Fe/EDTA - 10000 mg L^{-1}

314   IC- 10 mL min^{-1} biogas - 1000 mL min^{-1} air - 30 mL min^{-1} liquid.

315   **\<Figure 3\>**

316   The model equations for each design response, calculated with Excel using multiple linear

317   regression (MLR) [22], can be represented by equations (9) to (13). The confidence

318   intervals of the coefficients were calculated as the product of the standard deviation of

319   the coefficient and the student-t statistic for 0.05 significance level and n - k degrees of

320   freedom, were *n* is the number of experiments (16) and *k* the number of model coefficients

321   (6).

322     $CO_2\ (\%) = 8.25 + 2.57M - 2.09IC + 2.75B + 0.13A - 0.86L$ (9)

323 $R^2 = 81.0\%$

324 $H_2S\ (\%) = 0.0175 - 0.0079M - 0.0006IC - 0.0026B - 0.0014A + 0.0009L$ (10)

325 $R^2 = 77.8\%$

326 $O_2\ (\%) = 0.205 - 0.003M - 0.007IC - 0.043B + 0.015A - 0.024L$ (11)

327 $R^2 = 53.6\%$

328 $N_2\ (\%) = 0.811 - 0.060M + 0.023IC - 0.123B + 0.023A - 0.043L$ (12)

329 $R^2 = 32.3\%$

330 $CH_4\ (\%) = 90.72 - 2.50M + 2.08IC - 2.58B - 0.17A - 0.93L$ (13)

331 $R^2 = 79.1\%$

332 where R^2 is the coefficient of determination. Low R^2 values may result from uncontrolled

333 influencing factors (noise factors) or unconsidered quadratic interactions or effects. The

334 biomethane composition predicted by the model under the operational conditions

335 optimized according to the analysis of the effect of interactions (M_2-IC_1-B_2-A_4-L_4) was:

336 $CO_2 = 2.6\%$, $H_2S = 0.004\%$, $O_2 = 0.25\%$, $N_2 = 0.92\%$ and $CH_4 = 96.3\%$. These values

337 comply with the requirements of most international biomethane standards ($CH_4 \geq 90$-

338 95%, $CO_2 \leq 2$-4%, $O_2 \leq 1\%$ and negligible amounts of H_2S) [2,5,6].

339

340 Models with interactions and quadratic terms can be described by equations S1 to S5,

341 which have been included in the supplementary material document, seem to fit better to

342 the experimental data derived from the design of experiments (improving the coefficient

343 of determination). However, the prediction of the concentration of CO_2, H_2S and CH_4

344 (7.0%, 0.000% and 92.1%, respectively) derived from these models for the experiment

345 performed under the selected optimal conditions did not match the results obtained

346 experimentally. The prediction from the models that only included the main effects was

347   much closer to the experimental results, which ultimately supported the use of linear

348   regression instead of quadratic interactions.

349

350   **3.3 Continuous biogas upgrading operation**

351   The optimal combinations of factor levels identified in the Duncan's multiple range test

352   and in the analysis of the effect of interaction $M \times IC$ were not tested in any of the 16

353   experiments of the Taguchi´s $L_{16}(4^5)$ orthogonal array. Thus, both combinations were

354   subsequently tested under continuous operation in order to confirm the expected results

355   and to evaluate the stability of the process over time. The optimum Duncan test

356   combination M_4-IC_1-B_2-A_4-L_4 (0.03 M - 10000 mg L^{-1} - 10 mL min^{-1} - 1000 mL min^{-1} -

357   30 mL min^{-1}) was tested from days 0 to 9, and the optimum combination derived from

358   the analysis of the effect of interaction $M \times IC$ (M_2-IC_1-B_2-A_4-L_4: 0.05 M - 10000 mg

359   L^{-1} - 10 mL min^{-1} - 1000 mL min^{-1} - 30 mL min^{-1}) was tested from days 9 to 19.

360

361   The CO_2 concentration in the biomethane using the optimum Duncan's test combination

362   (stage I) was $1.5 \pm 0.3\%$, corresponding to CO_2 removal efficiencies (REs) of 95.1%.

363   Biogas upgrading under the optimum combination from the analysis of the effect of

364   interactions (stage II) entailed a CO_2 concentration of $1.4 \pm 0.2\%$, which corresponded to

365   CO_2-REs of 95.5% (Fig. 4a). These CO_2-REs were higher than those previously reported

366   by Horikawa et al., [11], who recorded CO_2-REs ranging from 4.0% to 16.0% using an

367   aqueous solution of 0.2 M Fe/EDTA in a system composed of an absorption and a

368   regeneration column with a total volume of 0.82 L, and operated with a biogas flow rate

369   of 1000 mL min^{-1} and a liquid flow rate of 83 mL min^{-1}. CO_2 absorption at industrial

370   scale can be increased by operating at a high pH value in the scrubbing solution and by

371   increasing the liquid to biogas ratio without compromising O_2 and N_2 levels in

biomethane. The former would increase the gas-liquid concentration gradient in the biogas absorption column, while the latter would increase both the overall mass transfer coefficient between the liquid and the biogas and the total absorption capacity of the column.

H_2S concentration during stage I was $0.013 \pm 0.004\%$, corresponding to H_2S-REs of 96.8%, while the increase in Fe/EDTA concentration from 0.03 to 0.05 M applied in stage II resulted in a complete removal of H_2S from biogas (Fig. 4b). These results confirmed that the analysis of the effect of interactions provided the best combination of operational parameters due to its capacity to completely remove H_2S from biogas. These results were superior than those previously reported by Horikawa et al., [11], who recorded H_2S-REs of 90.0% in a similar experimental set-up operated at 0.2 M Fe/EDTA, a biogas flow rate of 1000 mL min^{-1} and a liquid flow rate of 83 mL min^{-1}. Likewise, Schiavon Maia et al., [12] reported H_2S-REs of 91.4% in a similar system configuration operated at 0.2 M Fe/EDTA, with biogas and liquid flow rates of 340 mL min^{-1}.

The O_2 concentration in the upgraded biogas remained roughly constant in both stages, the recorded values being $0.37 \pm 0.11\%$ and $0.29 \pm 0.03\%$ for stages I and II, respectively (Fig. 4c). On the other hand, the N_2 concentration recorded during stage I was $1.17 \pm 0.24\%$ and $0.97 \pm 0.08\%$ during stage II (Fig. 4d).

Finally, CH_4 concentrations in the upgraded biogas of $97.0 \pm 0.3\%$ in stage I and $97.4 \pm 0.2\%$ in stage II were achieved (Fig. 4e). These high CH_4 concentration values together with the high CO_2-REs and H_2S-REs confirmed that this innovative technology represents a superior option for the upgrading of biogas compared with conventional

16

397   biological or physicochemical technologies. These results confirmed that the use of this

398   single step technology at ambient temperature and pressure, and without continuous

399   chemical addition, was feasible since the biomethane obtained during stage I and II

400   complied with the European Biomethane Standard EN 16723 for injection into natural

401   gas grids or use as a vehicle fuel ($CH_4 \geq$ 90-95%, $CO_2 \leq$ 2-4% and $O_2 \leq$ 1%) [2,5,6]. A

402   siloxane and water removal would be however required to fulfill the above mentioned

403   biomethane Standard. The results also confirmed the values predicted by the model

404   equations resulting from the experimental design and support the use of fractional

405   factorial experimental designs in optimization of multifactor processes.

406   **\<Figure 4\>**

407   Despite a new chemical solution was prepared for each replica when assessing the

408   upgrading capacity of each series of operational conditions, the Fe/EDTA/carbonate

409   solution herein proposed can be used during long operational periods. Thus, the absorbed

410   CO_2 decreases the pH of the scrubbing solution, which is further restored as a result of

411   the air-aided CO_2 stripping. Similarly, H_2S is oxidized using Fe^{3+} following equation 6,

412   and the resulting Fe^{2+} is regenerated in the stripping column according to equation 8.

413

414   The main limitation encountered during the continuous operation of this technology was

415   foam formation in the regeneration column due to the high air flow rate used (1000 mL

416   min^{-1}). To overcome this problem, 10.0 mL of antifoam 204 (Sigma-Aldrich, USA) were

417   added on day 6 and 2.0 mL were added on days 7, 8 and 13. For the design of the

418   absorption and stripping columns at industrial scale it is important to consider the fact

419   that the air flow required in the regeneration column is significantly higher than the biogas

420   flow pumped into the absorption column. This results in the need of larger regeneration

421   columns compared to the absorption column. The sulphur produced from H_2S oxidation

422   throughout the continuous operation was easily recoverable from the bottom of both

423   columns at the end of the process.

424

425   **3.4 Energy study**

426   An energy analysis was conducted in order to obtain the power consumption of this

427   technology for the upgrading of 300 Nm^3 h^{-1} of biogas. Power consumption for biogas

428   sparging in the absorption column and air sparging in the regeneration column were

429   calculated according to Eq. (14), and the power required for liquid recirculation between

430   both columns was calculated according to Eq. (15).

431    $$E_{gas} = \frac{Q_{gas} \times \Delta P}{0.7} \tag{14}$$

432    $$E_{liq} = \frac{Q_{liq} \times \rho \times g \times H}{0.7} \tag{15}$$

433   where Q_{gas} is the flowrate of biogas or air (m^3 s^{-1}), ΔP is the pressure drop (kPa), Q_{liq} is

434   the flowrate of liquid between both columns (m^3 s^{-1}), H is water column height (m), ρ is

435   the water density (kg m^{-3}), g is the Earth gravity constant (m s^{-2}).

436

437   The electricity demand of the system accounted for 0.02 kW-h $(Nm^3)^{-1}$ of biogas treated.

438   This low value of the Fe/EDTA/carbonate-based scrubbing process compare positively

439   with the 0.2 – 0.3 kW-h $(Nm^3)^{-1}$ of biogas treated of conventional processes such as water

440   or organic solvent scrubbing, pressure swing adsorption and membrane separation.

441

442   **4. Conclusions**

443   This study demonstrated the effectiveness and stability of Fe/EDTA/carbonate-based

444   scrubbing for the simultaneous removal of H_2S and CO_2 from biogas. This innovative

445   process was able to operate at ambient pressure and temperature, and without external

446   chemical addition, which supported an energy demand 10 times lower than their

18

physical/chemical counterparts. The experimental Taguchi´s design revealed the significant influence of Fe/EDTA molarity, inorganic carbon concentration, biogas flow rate, air flow rate and recirculating liquid flow rate on biomethane quality. An effective optimization via a Duncan's multiple range test and an analysis of the effect of interactions provided the optimal conditions for each control factor in order to maximize the CH_4 content and minimize CO_2, O_2, N_2 and H_2S content in biomethane. Continuous biogas upgrading in this innovative absorption-stripping system at 0.05 Fe/EDTA, 10000 mg IC L^{-1}, 10 mL biogas min^{-1}, 1000 mL air min^{-1} and 30 mL liquid min^{-1} supported concentrations of $CH_4 > 97\%$, $CO_2 < 2\%$ and $O_2 < 1\%$, which complied with most international biomethane regulations.

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542

543 **FIGURE CAPTIONS**

544 **Figure 1**. Schematic diagram of the experimental plant used for the integral upgrading of

545 biogas.

546 **Figure 2.** Influence of the control factors on the mean response of (a) CO_2 (■), (b) H_2S

547 (●), (c) O_2 (▲), (d) N_2 (□) and (e) CH_4 (○) concentration in the upgraded biogas.

548 **Figure 3.** Effect of interactions between Fe/EDTA molarity and inorganic carbon

549 concentration ((■) 4000, (○) 6000, (▲) 8000 and (◇) 10000 mg L^{-1}) on the

550 concentrations of (a) CO_2 and (b) H_2S in the upgraded biogas.

551 **Figure 4.** Time course of the concentration of (a) CO_2 (■), (b) H_2S (●), (c) O_2 (▲), (d)

552 N_2 (□) and (e) CH_4 (○) in the upgraded biogas.

553

554   **Figure 1.** Schematic diagram of the experimental plant used for the integral upgrading

555   of biogas.

556

557

558 **Figure 2.** Influence of the control factors on the mean response of (a) CO_2 ($\blacksquare$), (b) H_2S

559 ($\bullet$), (c) O_2 ($\blacktriangle$), (d) N_2 ($\square$) and (e) CH_4 ($\circ$) concentration in the upgraded biogas.

560

561

Figure 3. Effect of interactions between Fe/EDTA molarity and inorganic carbon

concentration (($\blacksquare$) 4000, ($\circ$) 6000, ($\blacktriangle$) 8000 and ($\diamond$) 10000 mg L^{-1}) on the

concentrations of (a) CO_2 and (b) H_2S in the upgraded biogas.

567   **Figure 4.** Time course of the concentration of (a) CO_2 (■), (b) H_2S (●), (c) O_2 (▲), (d)

568   N_2 (□) and (e) CH_4 (○) in the upgraded biogas.

569

570

Table 1. Factors and levels for the optimization of biogas upgrading

Factor	Acronym	Levels			
		1	2	3	4
Fe/EDTA Molarity (M)	M	0.00	0.05	0.01	0.03
Inorganic Carbon Concentration (mg L^{-1})	IC	10000	4000	6000	8000
Biogas Flow rate (mL min^{-1})	B	20	10	30	40
Air Flow rate (mL min^{-1})	A	800	200	500	1000
Recycling Liquid Flow rate (mL min^{-1})	L	10	5	20	30

Table 2. Taguchi's $L_{16}(4^5)$ orthogonal array and mean results

	Control factors and levels					Mean results of biomethane concentration				
Trial	M	IC	B	A	L	CO_2 (%)	H_2S (%)	O_2 (%)	N_2 (%)	CH_4 (%)
1	1	1	1	1	1	4.5	0.035	0.27	0.85	94.4
2	1	2	2	2	2	2.7	0.046	0.37	1.65	95.3
3	1	3	3	3	3	5.6	0.034	0.21	0.66	93.5
4	1	4	4	4	4	4.3	0.025	0.14	0.83	94.7
5	2	1	2	3	4	4.0	0.000	0.21	0.93	94.8
6	2	2	1	4	3	17.8	0.000	0.16	0.64	81.4
7	2	3	4	1	2	24.9	0.000	0.25	0.78	74.0
8	2	4	3	2	1	17.9	0.000	0.11	0.84	81.2
9	3	1	3	4	2	3.2	0.011	0.12	0.96	95.7
10	3	2	4	3	1	19.7	0.007	0.08	0.45	79.8
11	3	3	1	2	4	3.1	0.025	0.10	0.30	96.5
12	3	4	2	1	3	1.7	0.038	0.25	1.78	96.2
13	4	1	4	2	3	6.3	0.014	0.16	0.56	93.0
14	4	2	3	1	4	12.2	0.023	0.14	0.61	87.0
15	4	3	2	4	1	1.6	0.006	0.51	0.74	97.2
16	4	4	1	3	2	2.5	0.016	0.20	0.39	96.9

577

Table 3. ANOVA for the regular analysis

Factor	p Value				
	CO_2	H_2S	O_2	N_2	CH_4
M	$5.51 \times 10^{-35*}$	$2.50 \times 10^{-7*}$	$8.52 \times 10^{-3*}$	$4.26 \times 10^{-3*}$	$2.21 \times 10^{-36*}$
IC	$1.01 \times 10^{-29*}$	7.04×10^{-1}	7.77×10^{-2}	$2.92 \times 10^{-2*}$	$3.55 \times 10^{-31*}$
B	$2.62 \times 10^{-33*}$	1.39×10^{-1}	$1.41 \times 10^{-5*}$	$5.24 \times 10^{-7*}$	$6.21 \times 10^{-34*}$
A	$3.72 \times 10^{-20*}$	$2.58 \times 10^{-2*}$	2.63×10^{-1}	$9.43 \times 10^{-3*}$	$1.75 \times 10^{-22*}$
L	$6.75 \times 10^{-22*}$	2.48×10^{-1}	$4.36 \times 10^{-2*}$	$3.48 \times 10^{-2*}$	$1.02 \times 10^{-23*}$

578   *A significance level $p < 0.05$ was used to identify significant factors

579

Figure 1. Schematic diagram of the experimental plant used for the integral upgrading of biogas.

Figure 2. Influence of the control factors on the mean response of (a) CO_2 (■), (b) H_2S (●), (c) O_2 (▲), (d) N_2 (□) and (e) CH_4 (○) concentration in the upgraded biogas.

Figure 3. Effect of interactions between Fe/EDTA molarity and inorganic carbon concentration (($\blacksquare$) 4000, ($\circ$) 6000, ($\blacktriangle$) 8000 and ($\diamond$) 10000 mg L^{-1}) on the concentrations of (a) CO_2 and (b) H_2S in the upgraded biogas.

Figure 4. Time course of the concentration of (a) CO_2 (■), (b) H_2S (●), (c) O_2 (▲), (d) N_2 (□) and (e) CH_4 (○) in the upgraded biogas.

Table 1. Factors and levels for the optimization of biogas upgrading

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Air Flow rate (mL min^{-1})	A	800	200	500	1000
Recycling Liquid Flow rate (mL min^{-1})	L	10	5	20	30

Table 2. Taguchi's $L_{16}(4^5)$ orthogonal array and mean results

| Trial | Control factors and levels | | | | | Mean results of biomethane concentration | | | | |
	M	IC	B	A	L	CO_2 (%)	H_2S (%)	O_2 (%)	N_2 (%)	CH_4 (%)
1	1	1	1	1	1	4.5	0.035	0.27	0.85	94.4
2	1	2	2	2	2	2.7	0.046	0.37	1.65	95.3
3	1	3	3	3	3	5.6	0.034	0.21	0.66	93.5
4	1	4	4	4	4	4.3	0.025	0.14	0.83	94.7
5	2	1	2	3	4	4.0	0.000	0.21	0.93	94.8
6	2	2	1	4	3	17.8	0.000	0.16	0.64	81.4
7	2	3	4	1	2	24.9	0.000	0.25	0.78	74.0
8	2	4	3	2	1	17.9	0.000	0.11	0.84	81.2
9	3	1	3	4	2	3.2	0.011	0.12	0.96	95.7
10	3	2	4	3	1	19.7	0.007	0.08	0.45	79.8
11	3	3	1	2	4	3.1	0.025	0.10	0.30	96.5
12	3	4	2	1	3	1.7	0.038	0.25	1.78	96.2
13	4	1	4	2	3	6.3	0.014	0.16	0.56	93.0
14	4	2	3	1	4	12.2	0.023	0.14	0.61	87.0
15	4	3	2	4	1	1.6	0.006	0.51	0.74	97.2
16	4	4	1	3	2	2.5	0.016	0.20	0.39	96.9

Table 3. ANOVA for the regular analysis

Factor	p Value				
	CO_2	H_2S	O_2	N_2	CH_4
M	$5.51 \times 10^{-35*}$	$2.50 \times 10^{-7*}$	$8.52 \times 10^{-3*}$	$4.26 \times 10^{-3*}$	$2.21 \times 10^{-36*}$
IC	$1.01 \times 10^{-29*}$	7.04×10^{-1}	7.77×10^{-2}	$2.92 \times 10^{-2*}$	$3.55 \times 10^{-31*}$
B	$2.62 \times 10^{-33*}$	1.39×10^{-1}	$1.41 \times 10^{-5*}$	$5.24 \times 10^{-7*}$	$6.21 \times 10^{-34*}$
A	$3.72 \times 10^{-20*}$	$2.58 \times 10^{-2*}$	2.63×10^{-1}	$9.43 \times 10^{-3*}$	$1.75 \times 10^{-22*}$
L	$6.75 \times 10^{-22*}$	2.48×10^{-1}	$4.36 \times 10^{-2*}$	$3.48 \times 10^{-2*}$	$1.02 \times 10^{-23*}$

*A significance level $p < 0.05$ was used to identify significant factors

Optimization of a chemical scrubbing process based on a Fe-EDTA-carbonate based solvent for the simultaneous removal of CO_2 and H_2S from biogas

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Table S1. Biomethane composition for the orthogonal array

a)

Trial	Control factors and levels					Biomethane composition in steady state replicate 1				
	M	IC	B	A	L	CO_2 (%)	H_2S (%)	O_2 (%)	N_2 (%)	CH_4 (%)
1	1	1	1	1	1	4.2	0.025	0.24	0.84	94.7
2	1	2	2	2	2	2.7	0.063	0.28	1.72	95.3
3	1	3	3	3	3	5.1	0.033	0.22	0.73	93.9
4	1	4	4	4	4	3.8	0.017	0.22	0.69	95.3
5	2	1	2	3	4	3.8	0.000	0.31	1.27	94.6
6	2	2	1	4	3	18.4	0.000	0.16	0.60	80.8
7	2	3	4	1	2	25.3	0.000	0.21	0.65	73.8
8	2	4	3	2	1	17.8	0.000	0.07	1.29	80.9
9	3	1	3	4	2	3.0	0.011	0.15	0.77	96.1
10	3	2	4	3	1	18.7	0.021	0.18	0.84	80.3
11	3	3	1	2	4	2.8	0.031	0.07	0.42	96.7
12	3	4	2	1	3	1.9	0.039	0.46	1.97	95.6
13	4	1	4	2	3	6.2	0.041	0.16	0.55	93.0
14	4	2	3	1	4	11.4	0.028	0.16	0.67	87.8
15	4	3	2	4	1	1.6	0.006	0.32	1.11	97.0
16	4	4	1	3	2	2.6	0.000	0.10	0.25	97.1

17

18

19 **b)**

Trial	Control factors and levels					Biomethane composition in steady state replicate 2				
	M	IC	B	A	L	CO$_2$ (%)	H$_2$S (%)	O$_2$ (%)	N$_2$ (%)	CH$_4$ (%)
1	1	1	1	1	1	4.3	0.039	0.28	0.90	94.5
2	1	2	2	2	2	2.4	0.031	0.48	1.72	95.3
3	1	3	3	3	3	5.9	0.037	0.19	0.63	93.3
4	1	4	4	4	4	5.0	0.035	0.10	0.40	94.5
5	2	1	2	3	4	3.6	0.000	0.25	1.12	95.0
6	2	2	1	4	3	17.6	0.000	0.16	0.62	81.6
7	2	3	4	1	2	25.0	0.000	0.16	0.47	74.3
8	2	4	3	2	1	18.4	0.000	0.16	0.56	80.9
9	3	1	3	4	2	3.3	0.006	0.10	1.06	95.6
10	3	2	4	3	1	20.1	0.000	0.01	0.13	79.8
11	3	3	1	2	4	3.6	0.022	0.12	0.33	96.0
12	3	4	2	1	3	1.4	0.044	0.16	1.68	96.7
13	4	1	4	2	3	6.4	0.000	0.15	0.55	92.9
14	4	2	3	1	4	12.8	0.026	0.11	0.55	86.5
15	4	3	2	4	1	1.5	0.006	0.61	0.56	97.3
16	4	4	1	3	2	2.3	0.000	0.21	0.49	97.0

20

21 **c)**

Trial	Control factors and levels					Biomethane composition in steady state replicate 3				
	M	IC	B	A	L	CO$_2$ (%)	H$_2$S (%)	O$_2$ (%)	N$_2$ (%)	CH$_4$ (%)
1	1	1	1	1	1	4.9	0.042	0.29	0.80	93.9
2	1	2	2	2	2	2.9	0.042	0.36	1.52	95.2
3	1	3	3	3	3	6.0	0.032	0.20	0.63	93.2
4	1	4	4	4	4	4.3	0.024	0.11	1.41	94.2
5	2	1	2	3	4	4.6	0.000	0.08	0.40	95.0
6	2	2	1	4	3	17.3	0.000	0.018	0.69	81.9
7	2	3	4	1	2	24.5	0.000	0.36	1.21	74.0
8	2	4	3	2	1	17.4	0.000	0.11	0.67	81.8
9	3	1	3	4	2	3.3	0.017	0.12	1.06	95.5
10	3	2	4	3	1	20.3	0.000	0.06	0.37	79.3
11	3	3	1	2	4	2.9	0.022	0.10	0.13	96.8
12	3	4	2	1	3	1.9	0.031	0.14	1.70	96.3
13	4	1	4	2	3	6.3	0.000	0.16	0.59	92.9
14	4	2	3	1	4	12.3	0.016	0.14	0.61	86.9
15	4	3	2	4	1	1.6	0.006	0.60	0.57	97.2
16	4	4	1	3	2	2.6	0.049	0.29	0.44	96.6

22

25 **Table S2.** Mean steady state pH for each experiment in the absorption column

	Control factors and levels						
Trial	**M**	**IC**	**B**	**A**	**L**	**Initial pH**	**Final pH**
1	1	1	1	1	1	9.25	8.80
2	1	2	2	2	2	9.24	8.75
3	1	3	3	3	3	9.24	8.96
4	1	4	4	4	4	9.24	8.73
5	2	1	2	3	4	9.23	8.80
6	2	2	1	4	3	9.26	7.60
7	2	3	4	1	2	9.22	7.91
8	2	4	3	2	1	9.22	8.01
9	3	1	3	4	2	9.25	8.90
10	3	2	4	3	1	9.23	8.04
11	3	3	1	2	4	9.23	8.79
12	3	4	2	1	3	9.25	9.00
13	4	1	4	2	3	9.22	8.67
14	4	2	3	1	4	9.22	8.21
15	4	3	2	4	1	9.22	8.87
16	4	4	1	3	2	9.22	8.91

26

27 **Models with interactions and quadratic effects**

28 The model equations for each design response using quadratic effects can be represented

29 by equations (S1) to (S5).

30

31 CO_2 (%) $= 4.621 + 1.752M - 1.938IC + 2.680B - 0.536L - 0.309M \times C +$

32 $0.645M \times B - 1.765B \times IC + 0.981M \times M + 1.141A \times A - 0.555L \times L$ (S1)

33 $R^2 = 98.7\%$

34

35 H_2S (%) $= 0.0265 - 0.0072M - 0.0027B - 0.0012A + 0.0030L - 0.0002M \times$

36 $IC + 0.0022M \times B + 0.0030IC \times B - 0.0042A \times A + 0.0002L \times L$ (S2)

37 $R^2 = 96.5\%$

38

39 $O_2 \, (\%) = 0.220 - 0.003IC - 0.037B + 0.055A - 0.014L + 0.028M \times IC +$

40 $0.013M \times B + 0.013IC \times B - 0.006IC \times IC$ (S3)

41 $R^2 = 71.5\%$

42

43 $N_2 \, (\%) = 0.600 - 0.089M + 0.039IC - 0.119B + 0.002L + 0.021IC \times IC +$

44 $0.069M \times M + 0.017M \times IC + 0.065M \times B + 0.006IC \times B$ (S4)

45 $R^2 = 52.2\%$

46

47 $CH_4 \, (\%) = 94.34 - 1.66M + 1.91IC - 2.52B + 0.54L + 0.29MIC - 0.70M \times B +$

48 $1.70IC \times B - 1.06M \times M - 1.08A \times A + 0.57L \times L$ (S5)

49 $R^2 = 98.2\%$

50