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1	A Practical Method for Gas Changing Time Estimation Using a	
2	Simple Gas-Liquid Mass Transfer Model	
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24 valuable resources such as time and gases while providing greater comprehension of the

25 characteristics of the gas-liquid transfer of the studied system.

26 Keywords

27 Anaerobic fermentation; gas changing time; oxygen purging.

# 28 1. Introduction

Nowadays, the industry and research on bulk chemicals and third-generation biofuels based 29 on carbon gases are growing because of the rising sensibility and higher regulations about 30 decreasing greenhouse gas emissions. In particular, one of the more attractive carbon 31 32 feedstocks is CO<sub>2</sub> due to its large availability and contribution to climate change. Several different agents, such as chemical catalysts, enzymes, and microorganisms can convert it into 33 34 added-value compounds of industrial interest (Chauvy et al., 2019; Saravanan et al., 2021; Shi et al., 2015). According to the catalyst's nature, many CO<sub>2</sub> valorization processes occur 35 in a liquid phase (usually water). The constant development of these technologies led to the 36 establishment of different technologies to measure a specific gas (especially O2 and CO2) in 37 the liquid phase. 38

In the case of CO<sub>2</sub> valorization employing anaerobic bacteria, the lack of oxygen and supply of feedstock is required. Nevertheless, these needs are often performed in two steps before inoculation for technical, environmental, and economic reasons. The first step is sparging the liquid phase with nitrogen to purge oxygen, and then the second is providing the gaseous feedstock.

In the literature, many protocols used nowadays involve a preparation step before starting the 44 45 fermentation with anaerobic microorganisms, but these are described with huge variability between each other. To cite some examples, Maddipati and coworkers (2011) purged 3 L of 46 culture medium (7.5 L total volume reactor) from oxygen using 12 L/h of N<sub>2</sub> for 24 hours. 47 48 Then, syngas was piped in the fermenter at 9 L/h (for a not-reported period) before inoculation. Hoffmeister et al. (2016) purged 0.850 L of liquid culture medium (reactor of 2 49 L total volume), sparging N<sub>2</sub> for at least 12 h (in-flow gas rate was not reported). After this 50 step, feeding gas was provided at 30 L/h for 1 h. In Al Rowaihi and coworkers (2018) study, 51 a 1.6 L reactor was purged with 10 volumes of argon to remove any traces of oxygen from 52 the medium, followed by 10 purges with the feeding gas mixture. Other studies (Kantzow 53 and Weuster-Botz, 2016; Straub et al., 2014) describe a protocol in which 1 L of culture 54 medium, in a reactor of 2 L total volume, was sparged with the feeding gas mixture for at 55 least 12 h before inoculation of microorganism (in-flow gas rate was not reported). As 56 suggested from the abovementioned examples, this preliminary step for setting up an 57 58 anaerobic fermentation is time and resources consuming. Minimizing it would allow more sustainable processes concerning the environmental and economic point of view and 59 optimize human efforts and employment of instruments. Nevertheless, some technical 60 constraints often arise in experimental and pilot plants regarding monitoring the dissolved 61 oxygen concentration and gaseous substrates saturation. Indeed, reactors could be designed 62 without probes for dissolved gases to reduce capital costs. Moreover, the development of 63 protocols might require dissolving gases different from those detected by the provided 64 probes. 65

Gas solubilization in a liquid phase is explained by the gas-liquid mass transfer laws, which describe the concentration gradientof a certain gas between phases. In Figure 1 the difference in concentration through the interphase is shown. There are three major stages of transfer between the gas bulk and the liquid bulk: the first one being the transfer of the gas from the bulk to the gas-liquid interphase, then the interphase itself, and finally from the liquid interphase to the liquid bulk (Doran, 1995).

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Figure 1. Diagram of the gas-liquid interface, with their respective concentrations.  $C_{AG}$ , concentration of the compound A in the gas phase bulk;  $C_{AL}$ , concentration of A in the liquid phase bulk;  $C_{AG_i}$  and  $C_{AL_i}$ , concentration of A in the gas and liquid interphase, respectively.

80	The liquid-phase mass transfer dominates the overall phenomena when working with gases
81	with low solubility (like oxygen or hydrogen). The concentration at the liquid interphase can

be considered equal to the liquid concentration in equilibrium with the gas concentration in

83 the bulk.

$$N_A = k_L a \cdot (C_{AL}^* - C_{AL}) \tag{1}$$

where  $N_A$  is the rate of mass transfer of component A through the gas-liquid interphase,  $k_L a$ 85 is the combined mass-transfer coefficient,  $C_{AL}^*$  is the concentrations of A in the liquid phase 86 in equilibrium with  $C_{AG}$ , and  $C_{AL}$  is the actual concentration in the liquid phase. It can be 87 noticed that the driven force for the mass transfer is the difference between the equilibrium 88 89 and the current concentration. In some cases, these values can be directly measured. If it is not possible, they can be smoothly calculated. Nevertheless, the mass-transfer coefficient is 90 not easy to estimate due to the nature of the fluids and the experimental conditions. The 91 composition of the liquid and gas phases, the stirring conditions, the geometry of the fluids 92 93 container, and many other factors affect this coefficient. Most authors have proposed models with the following structure (Cooper et al., 1944; H Fukuda et al., 1968 (a); H. Fukuda et al., 94 1968 (b); Richards, 1961; Van'T Riet, 1979) 95

96

$$k_L a = K \cdot \left(\frac{P}{V}\right)^{\alpha} \cdot (v_s)^{\beta} \cdot N^{\gamma}$$
<sup>(2)</sup>

97 where K,  $\alpha$ ,  $\beta$  and  $\gamma$  are constants that depend on the operating conditions as well as the 98 geometry of the reactor, while P/V,  $v_s$  and N are the volumetric power, the superficial gas 99 velocity, and frequency of the rotation of the mixer, respectively. As can be presumed, using 100 Equation 2 outside the boundaries of confidence will give inaccurate values. Besides, these 101 equations were proposed for oxygen transfer, which obligates the researcher to use the 102 diffusivity correlation between the gases and estimate the  $k_L a$  of the scoped gas (Kery et al., 103 2019). Another option for calculating the  $k_L a$  is using dynamic methods (Munasinghe and Khanal, 2010), which take much time and resources and also require an online measure ofthe dissolved gas, which sometimes, as described before, is not available.

This work presents a feasible method to estimate the time needed to remove a gaseous component from a liquid medium by replacing it with another gas (gas changing time). It is estimated using a classical and simplified liquid-gas phase equilibrium model. In particular, this work aims to describe a method that can be easily applied in the laboratory. It considers actual operational conditions and requires a few analytical instruments (i.e. gas analyzer) and informatics tools (i.e. an informatics program able to manage spreadsheets).

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### 113 2. Materials and methods

#### 114 2.1 Liquid phase composition

The liquid phase used in gas changing experiments was a culture medium for anaerobic
bacteria. In 1 L of water, the medium contained K<sub>2</sub>HPO<sub>4</sub> 8.44 g; NaCl 2.9 g; yeast extract 2
g; KH<sub>2</sub>PO<sub>4</sub> 1.76 g; NH<sub>4</sub>Cl 1 g; cysteine hydrochloride 0.5 g; MgSO<sub>4</sub> 0.180 g; resazurin 1 mg.
Chemical reagents were purchased from Merck (DE).

#### 119 2.2 Bioreactors

The reactor used for N<sub>2</sub> to CO<sub>2</sub> gas change and *vice versa* was a custom-adapted bioreactor manufactured by the H.E.L group (UK). The system consisted of a 2 L oil-jacketed vessel, 5 piston pumps for liquid injection (culture broth, base, acid, trace elements, and anti-foam), 4 <u>Mass Flow Controller (MFC)</u> for high in-flow gas rates (H<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, CO) (Vögtlin Instruments, CH ) and 2 low in-flow gas rates MFCs (CO<sub>2</sub> and H<sub>2</sub>) (Bronkhorst High-Tech BV, NL). Sparging of the gas was applied from the bottom of the vessel (via a micrometric

sparger). Stirring of the medium was mechanically maintained by one level of Ruston blades 126 127 connected to an impeller driven by a motor and baffles. An oil bath connected to the jacket of the reactor allowed for sterilization (autoclaving of the vessel) and maintained the 128 129 operating temperature during experiments. The head plate of the reactor vessel was fitted with pH, redox, liquid level, pressure, and temperature probes. A Back Pressure Regulation 130 (BPR) valve allowed pressure control at defined setpoints. The vessel was filled with 1L of 131 sterile medium during the gas changing experiments. The in-flow gas rate applied was 4.5 132 L/h, the stirring 400 rpm, and the reactor temperature  $30^{\circ}$ C. 133

The gas from the reactor outlet was released in a chemical hood or collected in sample bags and analyzed by an off-line micro-GC. In experiments from N<sub>2</sub> to CO<sub>2</sub>, the liquid medium pumped in the reactor was previously sparged with 100% N<sub>2</sub> to remove oxygen. Gas out sampling started immediately after the activation of the MFC for CO<sub>2</sub>.

The reactor used for the gas change from air to N<sub>2</sub> and vice versa was a Biostat A reactor 138 (Sartorius Stedim Biotech, DE) consisting of a glass vessel of 1.5 L total volume, 4 peristaltic 139 140 pumps for liquid injection (culture broth, base, acid, and anti-foam), 2 MFCs (Air and N<sub>2</sub>). Stirring of the medium was mechanically provided by two levels of Rushton blades. The 141 reactor was sterilized by autoclaving. An electric heater placed around the outer side of the 142 143 glass vessel maintained a constant temperature during experiments. The head plate of the reactor vessel was fitted with pH, foam, and temperature probes. During the gas changing 144 experiments, the vessel was filled with 0.5 L of sterile medium. The in-flow rate applied was 145 146 6 L/h, the stirring was 100 rpm, and the temperature was 30°C. The gas out from the reactor was directly analyzed by a micro-GC. In the experiment from air to N<sub>2</sub>, the liquid medium 147 148 was pumped into the reactor without oxygen purging. Gas out sampling started when MFC for 100% N<sub>2</sub> was switched on. 149

### 150 2.3 Analytics and software

Gas composition for in-flowing and out-flowing gas was measured using an Agilent 490 Micro GC (Agilent, CA, USA) or a Micro GC Fusion (Inficon, CH). Agilent 490 Micro GC is equipped with the analytical columns Molsieve 5Å, using Argon as the carrier, and PoraPLOT U using Helium as the carrier. Micro GC Fusion is equipped with the analytical columns Molsieve 5Å and Rt-U-Bond, using Argon and Helium as carriers, respectively. Excel 2016 32-bit (Microsoft, USA) was used to analyze the experimental data to estimate the gas changing time.

158 2.4 Statistics

Two statistic indicators were calculated to evaluate how the predictive model and the real data correlated: the coefficient of determination  $(R^2)$  and the standard error of the estimate  $(\sigma_{est})$ , (Eq. (3) and (4) respectively). The statistical analysis was performed on the logarithmic results.

d the standard error of the estimate analysis was performed on the **Formatted:** Not Highlight **Formatted:** Not Highlight **Formatted:** Not Highlight

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	$P_{i}^{2} = 1 \sum_{i=1}^{n} (y_{i} - y_{i}')^{2}$ (2)		Formatted: Not Highlight
163	$R^{2} = 1 - \frac{\sum_{i=1}^{n} (v_{i} - \bar{v})^{2}}{\sum_{i=1}^{n} (v_{i} - \bar{v})^{2}} $ (3)	$\square$	Formatted: Not Highlight
			Formatted: Not Highlight
	$\sigma_{act} = \sqrt{\frac{\sum_{i=1}^{n} (y_i - y'_i)^2}{2}} $ (4)		Formatted: Not Highlight
164			Formatted: Not Highlight
-	N n (1)		Formatted: Not Highlight
		$\langle \neg \rangle$	Formatted: Not Highlight
165	where:		Formatted: Not Highlight
166	$y_{ik}$ is an actual experimental value.		Formatted: Not Highlight
			Formatted: Not Highlight
167	$y'_{i,i}$ is the predicted value.		Formatted: Not Highlight
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168	n: is the number of experimental data.		
			Formatted: Not Highlight
169	$\bar{y}$ ; is the mean value of the experimental data.		Formatted: Not Highlight

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### 171 3. Results

- 172 3.1 Model
- The model formulated was based on the following system (Figure 2). A certain gas (*i*) is bubbled at a rate of  $G_{in} \cdot y_{i,in}$  in a reactor with  $V_L$  volume of liquid and  $V_G$  volume of gas in the headspace. The temperature (*T*) and the pressure (*P*) is fixed. The gas outlet ( $G_{out}$ ) has a fraction of the *i* gas ( $y_{i,out}$ ). Inside the liquid phase, there is a certain concentration of dissolved gas ( $C_{i,L}$ ).



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Figure 2. The system considered in the model.

180

181 Where:

182 G: Molar Flow (mmol/min).

183 y: Molar fraction in the gas.

- 184 V: Volume (m<sup>3</sup>).
- 185 C: Concentration  $(mmol/m^3)$ .
- 186 T: Temperature (K).
- 187 P: Pressure (Pa).
- 188 Subscript:
- 189 L: in/of the liquid.
- 190 G: in/of the gas.
- 191 in: Inlet.
- 192 out: Outlet.
- 193 i: from compound i.
- 194 Three mass balances can be proposed for this system: the global balance of compound *i* (Eq.
- 195 5), the balance of compound i in the liquid phase (Eq. 6), and the balance of compound i in
- 196 the gas phase (Eq. 7) which assumes the gas as an ideal one.

$$\frac{dn_i}{dt} = G_{in} \cdot y_{i,in} - G_{out} \cdot y_{i,out}$$
<sup>(5)</sup>

$$\frac{dn_{i,L}}{dt} = k_L a \cdot V_L \cdot \left(C_{i,L}^* - C_{i,L}\right) \tag{6}$$

$$\frac{dn_{i,G}}{dt} = \frac{V_G}{R \cdot T} \cdot \frac{dp_i}{dt}$$
(7)

197 where  $n_i$  are the moles of the *i* compound,  $p_i$  is the partial pressure of *i* in the headspace, and

198  $C_{i,L}^*$  is the equilibrium concentration of *i* in the liquid.

199 The global accumulation of moles in the system will be equal to the sum of the accumulation

200 in both gas and liquid phases (Eq. 8).

201

$$\frac{dn_i}{dt} = \frac{dn_{i,L}}{dt} + \frac{dn_{i,G}}{dt}$$
(8)

202

203 This allows the generation of a new equation (Eq. 9) by replacing Eq (5), (6), and (7) in (8).

$$\frac{V_G}{R \cdot T} \cdot \frac{dp_i}{dt} = G_{in} \cdot y_{i,in} - G_{out} \cdot y_{i,out} - k_L a \cdot V_L \cdot \left(C_{i,L}^* - C_{i,L}\right)$$
(9)

204 On the other hand, from Eq (6), it is possible to obtain a relation between time and  $C_{i,L}$ 

205 (assuming  $C_{i,L}^*$  constant during short periods).

$$V_L \cdot \frac{dC_{i,L}}{k_L a \cdot V_L \cdot \left(C_{i,L}^* - C_{i,L}\right)} = dt \tag{10}$$

$$\int \frac{dC_{i,L}}{k_L a \cdot \left(C_{i,L}^* - C_{i,L}\right)} = \int dt \tag{11}$$

$$\frac{-1}{k_L a} \cdot \left( \ln \left( \mathcal{C}_{i,L}^* - \mathcal{C}_{i,L} \right) - \ln K \right) = t \tag{12}$$

$$\ln \frac{\left(C_{i,L}^* - C_{i,L}\right)}{K} = -t \cdot k_L a \tag{13}$$

$$\frac{\left(C_{i,L}^* - C_{i,L}\right)}{K} = e^{-t \cdot k_L a} \tag{14}$$

$$C_{i,L} = C_{i,L}^* - K \cdot e^{-t \cdot k_L a} \tag{15}$$

where *K* is the constant of integration. By replacing Eq. (15) into Eq. (9) the following expression is obtained

$$\frac{V_G}{R \cdot T} \cdot \frac{dp_i}{dt} = G_{in} \cdot y_{i,in} - G_{out} \cdot y_{i,out} - k_L a \cdot V_L$$

$$\cdot \left(C_{i,L}^* - C_{i,L}^* + K \cdot e^{-t \cdot k_L a}\right)$$
(16)

208 If no *i* compound is injected into the system  $(y_{i,in} = 0)$ , Eq. (16) could be expressed as

$$\frac{V_G}{R \cdot T} \cdot \frac{dp_i}{dt} + G_{out} \cdot y_{i,out} = -k_L a \cdot V_L \cdot K \cdot e^{-t \cdot k_L a}$$
(17)

Since the partial pressure of the *i* compound  $(p_i)$  in the headspace will be equal to the total pressure (P) times the molar fraction in the outlet stream, Eq. (17) becomes:

$$\frac{V_G}{R \cdot T} \cdot \frac{d(P \cdot y_{i,out})}{dt} + G_{out} \cdot y_{i,out} = -k_L a \cdot V_L \cdot K \cdot e^{-t \cdot k_L a}$$
(18)

### Assuming a constant pressure during the whole process, Eq. (18) can be rewritten as

$$\frac{V_G \cdot P}{R \cdot T} \cdot \frac{dy_{i,out}}{dt} + G_{out} \cdot y_{i,out} = -k_L a \cdot V_L \cdot K \cdot e^{-t \cdot k_L a}$$
(19)

#### 212 Besides, we can assume that:

$$\frac{V_G \cdot P}{R \cdot T} = n_G \tag{20}$$

$$n_G \cdot \frac{dy_{i,out}}{dt} + G_{out} \cdot y_{i,out} + k_L a \cdot V_L \cdot K \cdot e^{-t \cdot k_L a} = 0$$
(21)

- where  $n_G$  is the total amount of gas moles in the system. By solving the differential equation,
- 214 Eq. (22) is obtained:

$$y_{i,out} = K_1 \cdot e^{-t \cdot \frac{G_{out}}{n_G}} + \frac{k_L a \cdot V_L \cdot K \cdot e^{-t \cdot k_L a}}{k_L a \cdot n_G - G_{out}}$$
(22)

where  $K_1$  is a new constant that comes from the solution of the differential equation. In Eq. (22), it can be noticed that if  $G_{out} \ll k_L a \cdot n_G$  then

$$y_{i,out} \approx K_1 \cdot e^{-t \cdot \frac{G_{out}}{n_G}} + \frac{V_L \cdot K}{n_G} \cdot e^{-t \cdot k_L a}$$
(23)

- 217 Since the value of the first exponent will be greater than the second and if the constants have
- the same order of magnitude, the first term will dominate the value of  $y_{i,out}$ .

$$y_{i,out} \approx K_1 \cdot e^{-t \cdot \frac{G_{out}}{n_G}}$$
(24)

219 On the other side, if  $G_{out} \gg k_L a \cdot n_G$  then

$$y_{i,out} \approx K_1 \cdot e^{-t \cdot \frac{G_{out}}{n_G}} - \frac{k_L a \cdot V_L \cdot K}{G_{out}} \cdot e^{-t \cdot k_L a}$$
(25)

At the beginning of the gas change process, the value of  $\frac{k_L a \cdot V_L \cdot K}{G_{out}}$  in Eq. (25) makes the second term have a small influence on the value of  $y_{i,out}$ . As time passes, the rate of decrease is greater. Nevertheless, since  $y_{i,out}$  cannot take negative values, the value of the second term cannot be greater than the first one. Hence, for small values of time:

$$y_{i,out} \approx K_1 \cdot e^{-t \cdot \frac{G_{out}}{n_G}}$$
(26)

It can be noticed that the two variables that can be controlled by changing the stirring speed or the gas flow ( $k_L a$  and  $G_{out}$ ) can dominate the process. When the molar flow dominates the process ( $G_{out} \gg k_L a \cdot n_G$ ), the phenomenon occurs faster rather than when the volumetric gas transfer coefficient ( $G_{out} \ll k_L a \cdot n_G$ ) dominates the process. Besides, since  $k_L a$  depends on the volumetric power that is controlled by the stirring rate and the flow, the relation between  $G_{out}$  and  $k_L a$  can be described as a relation between *G* and the stirring velocity of the reactor. This could be researched in future work.

This simplified exponential model will describe the decay of the concentration of a purged gas and it can be applied to predict the gas exchange time of a determined system if the constant parameters are available. Using a semilogarithmic graph the slope will represent the value of  $\frac{G_{out}}{n_G}$  and the intercept the logarithm of  $K_1$ . The following section describes the protocol to obtain the gas change time.

### 236 3.2. Protocol

237 To estimate the gas changing time the following steps need to be executed:

238	1)	Take a sample of the outlet flow of gas from the reactor at the beginning of the gas	
239		changing process and measure its molar composition in percentage or fraction	
240		through a gas analyzer.	
241	2)	Repeat the same process regularly with an interval of time determined by the	
242		researcher. An interval of 5 minutes is recommended .	
243	3)	The sampling can stop after the fraction of the purged gas reaches half of its value at	
244		the beginning of the gas changing process.	
245	4)	On a spreadsheet, create a graph with the time values on the X-axis and the natural	
246		logarithm of the fraction or percentage of the purged gas on the Y-axis.	
247	5)	Obtain the linear regression of the data.	
248	6)	Obtain the equation of the linear regression line and the R-squared value.	
249	7)	The R-squared value needs to be higher than 0.99.	
250	8)	Graphically obtain the value of time that will fulfill the desired gas change. The linear	
251		regression intercept will be approximately $\ln(K_1)$ and the slope $-\frac{G_{out}}{n_G}$ of Eq. (22).	
252	3.3. M	lodel validation	

Figures 3-6 report the decrease of the gas purged from the reactor throughout the gas changing experiments. Figures 3 and 4 show data from N<sub>2</sub> to CO<sub>2</sub> and from CO<sub>2</sub> to N<sub>2</sub>, respectively. Similarly, Figures 5 and 6 describe experiments using air and N<sub>2</sub>. According to the analysis of the in-let gas, air sparged in the reactor had 20.9 % of O<sub>2</sub> and 79.05% of N<sub>2</sub>. The purge of air using pure nitrogen and *vice-versa* was evaluated by monitoring the variation of the oxygen molar fraction in the out-gas.





Figure 3: Purging of nitrogen using carbon dioxide. Triangles: experimental values; Dots:
natural logarithm of the experimental data; Dotted black line: exponential curve generated
by all the experimental data; Dashed black line: exponential curve obtained by using black
triangles; Dashed gray line: linear curve obtained by considering the black dots.



Figure 4: Purging of carbon dioxide using nitrogen. Triangles: experimental values; Dots:
natural logarithm of the experimental data; Dotted black line: exponential curve generated
by all the experimental data; Dashed black line: exponential curve obtained by using black
triangles; Dashed gray line: linear curve obtained by considering the black dots.



269

Figure 5: Purging of air using nitrogen. Triangles: experimental values; Dots: natural
logarithm of the experimental data; Dotted black line: exponential curve generated by all
the experimental data; Dashed black line: exponential curve obtained by using black
triangles; Dashed gray line: linear curve obtained by considering the black dots.







Experimental data were plotted and the model was applied. The correlation between data and 280 281 the model was evaluated. It can be seen that data from each experiment fit an exponential curve (dotted black lines in Figures 3-6). Following the protocol, the linear correlation 282 between the natural logarithm of the out-gas composition and the time was obtained for each 283 purged gas (black dots and dashed gray line in Figures 3-6). It can be seen that in experiments 284 involving carbon dioxide the predicting lines did not correlate accurately with the 285 experimental data, whereas in the experiments with air and nitrogen the predictive models fit 286 the experimental data with greater precision. Table 1 reports the statistics calculated for each 287 gas changing experiment. 288

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Experiment	N <sub>2</sub> to CO <sub>2</sub>	CO <sub>2</sub> to N <sub>2</sub>	Air to N <sub>2</sub>	N <sub>2</sub> to air
n	20	15	17	24
$\sum_{i=1}^{n} (y_i - y_i')^2$	8.57	7.98	0.17	7.82
$\sum_{i=1}^{n} (y_i - \bar{y})^2$	34.24	15.06	19.12	84.88
$R^2$	0.7496	0.47	0.9909	0.9079
$\sigma_{est}$	0.6547	0.6318	0.101	0.5707

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The value of the X-axis maked it possible to extract the time that fulfills the desired gas 292 293 change. For example, in the experimental condition applied, complete purging of oxygen using nitrogen required around 40 minutes (Figure 5). The maximum difference between the 294 modeled values and experimental data was 0.4%. For the experiments involving CO<sub>2</sub>, a 295 296 different reactor was used and other experimental conditions were applied. Therefore, a different gas changing time was needed. Figure 3 shows that the time required to completely 297 change the gas from nitrogen to carbon dioxide was around 200 minutes. The error between 298 the model and the experimental data was more variable. In fact, when the gas change was 299 completed, the error was 1.9 % of the gas composition. In the central part of the curve, at 300 around 70 minutes, the maximum error was of 9.9 %. 301

## 302 4. Discussion

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The protocol proposed describes an easily applicable method to estimate the gas changing time in the laboratory routine. It aims to consume little time and resources, considering actual operating conditions, and requires few analytic instruments and informatics tools.

In all the experiments, the error between the actual values and the values predicted by the model was less than 10% of the gas composition. The biggest difference recorded was in

experiments involving CO<sub>2</sub>. In experiments that did not involve carbon dioxide, the 308 309 maximum error was reduced to less than 0.8%. The bigger error found with CO<sub>2</sub> could be explained by the chemical equilibrium that carbon dioxide has in aqueous solutions, which 310 is not considered in the proposed model. In fact, carbon dioxide reacts with water and 311 produces carbonic acid. This reaction has slow kinetics (for more details see Stumm and 312 Morgan, 1995) and creates a stock of CO<sub>2</sub> in the liquid phase, which moves towards 313 equilibrium with the gas phase. It can explain why the predictive model showed a faster 314 decrease in the CO<sub>2</sub> fraction than the measured values (Figure 4). Another factor that could 315 316 have affected results with CO<sub>2</sub> was the variable pressure inside the reactor during the gas change. In the experiments that involved this gas, the pressure fluctuated between 1.51 bar 317 and 1.76 bar. In particular, the reactor pressure was set at 1.76 bar, with a constant in-flow 318 319 gas rate and opening of the valve for pressure regulation. After starting the sparging of the medium with  $CO_2$ , the pressure quickly decreased to 1.51 bar. It then returned to the initial 320 value (1.76 bar) when the gas change was completed. The assumption of a constant pressure 321 322 done during the deduction of the model might explain the discrepancy between the experimental data and the model. 323

324 According to the statistical analysis, the air to N<sub>2</sub> model best correlated to the experimental 325 data, followed by the  $N_2$  to air change. When the gas change was from nitrogen to carbon 326 dioxide, the coefficient of determination was higher than when it was from carbon dioxide to nitrogen. Considering the value of the standard error of the estimate, the accuracy of the gas 327 change from carbon dioxide to nitrogen is slightly more accurate than the reverse process 328 329 experiment. Nevertheless, in both cases, the statistical analysis suggested a worse accuracy 330 of the model in experiments involving  $CO_2$  than in experiments involving air, probably due to the effect of the chemical equilibrium of carbon dioxide in water. 331

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The model is for researchers looking for an affordable and practical method to improve their experiments' efficiency. The specific experimental conditions and the constraints related to the availability of analytical instruments can make the time between each measurement very variable. This work found out that, purging oxygen, the model could fit very well with the experimental data measuring only two samples, one at the beginning and another when the gas was half of its initial concentration (Figure 7).



Figure 7: Purging of air using nitrogen. Triangles: experimental values; Dots: natural
logarithm of the experimental data; Dashed black line: exponential curve obtained by using
only black triangles; Dashed gray line: linear curve obtained by considering the black dots.

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It is important to remember that the time required for gas change inside the reactor will vary with the conditions of stirring, temperature, pressure, gas in-flow rate, gas and media compositions. If the conditions do not change, the time predicted in one experiment can be 345 used in the following experiments. If one or more factors change, it is recommended to re-

evaluate the gas changing time using this protocol.

### 347 5. Conclusion

The proposed protocol allows researchers to predict the time required to completely exchange 348 the gas in a reactor containing liquid media, and it takes into account the actual experimental 349 condition applied in a specific run. Purging of an unwanted gas from the reactor often is 350 based on bibliographic data. These calculations, in many cases, are not accurate enough for 351 a specific situation because of the differences in both reactor and experimental settings 352 (reactor design, working volume of liquid and gas phases, in-flow rate of a specific gas, 353 354 stirring equipment and speed). The described protocol can be easily implemented in the laboratory. Hence, it seeks to be simple for sampling procedure, calculation, and 355 requirements in terms of human and time efforts, equipment, and software. 356

357 The model's correlation and accuracy were high when air was purged with nitrogen, which is often the first step in setting up an anaerobic fermentation. For cases involving CO<sub>2</sub>, the 358 359 correlation and the accuracy were lower. To improve the model, specific CO<sub>2</sub> modeling should include the chemical equilibrium of this gas in water. Moreover, a comparison 360 361 between the k<sub>L</sub>a-dominant process and the molar flow-dominant process should also be 362 performed for further model validation. Nevertheless, the proposed methodology for calculating the gas changing time will contribute to the efficient use of resources and time 363 during experiments involving other gases, mainly oxygen, which is a pivotal step for many 364 processes involving anaerobic reactions. 365

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