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SCIENTIFIC PAPER

UDC

EXPERIMENTAL INVESTIGATION OF O₂ AND CO₂ MASS TRANSFER IN BIOREACTORS

Highlights

- Dual analysis of O₂ and CO₂ mass transfer kinetics
- Validated regression model predicts k_{La} from agitation and airflow
- Novel CO₂ method using carbonate hardness and pH kit
- U-shaped tubular sparger gives faster initial CO₂ transfer; ring sparger reaches higher final CO₂ concentration
- Practical, low-cost tools for optimizing bioreactor gas exchange

Abstract

Gas-liquid mass transfer of oxygen (O₂) and carbon dioxide (CO₂) was studied experimentally in a stirred bioreactor. Oxygen k_{La} was measured by the dynamic method using nine combinations of agitation speed and gas flow rate, with two runs performed for each condition. Multiple linear regression explained 93.8% of the variation in k_{La} ($R^2 = 0.938$), and the model was statistically significant ($F = 114.0$, $p < 0.001$). Over the range studied, gas flow rate had a greater effect on oxygen k_{La} than agitation speed. For the CO₂ experiments, dissolved CO₂ concentration was estimated from carbonate hardness (KH) and pH measurements using a simple and low-cost procedure. The U-shaped tubular and ring spargers were then compared under the same operating conditions. The U-shaped tubular sparger gave a slightly higher k_{La} (0.625 min^{-1}) than the ring sparger (0.59 min^{-1}) and showed a faster initial CO₂ transfer. However, the ring sparger reached a higher final dissolved CO₂ concentration, about 1300 mg/L compared with 1050-1080 mg/L for the U-shaped sparger. These results suggest that sparger performance should be considered in terms of both transfer rate and the final dissolved-gas concentration when selecting operating conditions for bioprocess applications.

Keywords: gas-liquid mass transfer, CO₂ solubility, carbonate hardness test, volumetric mass transfer coefficient.

INTRODUCTION

Gas-liquid mass transfer plays an important role in many bioprocess and environmental applications. At the same time, increasing population and industrial activity continue to increase global energy demand [1]. Although oil, coal, and natural gas still supply a considerable part of this demand, concerns remain about their environmental effects and long-term availability [2,3]. These concerns have encouraged the development of cleaner energy routes, including processes based on renewable and biological resources [4]. Among these alternatives, syngas fermentation has received attention because waste-derived

and non-food biomass can be converted into useful fuels and chemicals [3-6]. Syngas produced from biomass or waste gasification mainly contains CO, CO₂, and H₂. These gaseous components can serve as carbon and energy sources for acetogenic microorganisms [3]. CO is particularly relevant in this process because of its relatively high energy content [7].

Industrial off-gases, biomass, coal, and municipal wastes are among the possible feedstocks for syngas-based conversion. Fermentation also provides an alternative route to catalytic ethanol production. One of its main limitations, however, is the low transfer of gaseous substrates into the liquid phase [3-6]. For example, CO has a water solubility of about 1.1 mM/bar at 295 K, which can limit its availability in bubbling continuous stirred-tank reactors [8]. For this reason, different reactor designs, gas-distribution systems, mixing conditions, and additives such as nanoparticles have been investigated to improve gas transfer [6].

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Gas flow rate and agitation speed are commonly adjusted in bubbling reactors because both can influence gas-liquid transfer [5]. Their combined effect is often evaluated through the volumetric mass transfer coefficient, $k_L a$. Here, k_L represents the liquid-side mass transfer coefficient, and a represents the available gas-liquid interfacial area per unit volume. Therefore, $k_L a$ reflects both transport through the liquid film and the extent of gas-liquid contact, making it useful for evaluating poorly soluble gases such as CO [9,10].

Gas-liquid mass transfer is driven by a concentration difference between the two phases. Diffusion contributes to this process through molecular movement from regions of higher concentration toward regions of lower concentration [11]. In practice, the transfer rate depends on the concentration driving force, the available interfacial area, and the mass transfer coefficient [11].

The mass transfer coefficient expresses how readily a species crosses the phase boundary under the prevailing conditions. It is affected by properties such as solubility and diffusivity, but also by the hydrodynamics of the system. Depending on which phase controls the resistance, liquid-side and gas-side coefficients, commonly written as k_L and k_G , may be used. For stirred gas-liquid bioreactors, the volumetric form, $k_L a$, is especially useful because it also reflects the interfacial area generated inside the vessel [9].

Gas-liquid transport is often interpreted using the two-film theory. In this description, thin films adjacent to the gas-liquid interface provide resistance to transfer before the solute reaches the bulk phases. Contributions may arise from both the liquid and gas sides, represented by k_L and k_G , respectively. Mixing changes this resistance by renewing the interface and increasing turbulence, which is why hydrodynamic conditions strongly influence measured $k_L a$ values [12]. For this reason, $k_L a$ is widely used when comparing the mass-transfer performance of bioreactor configurations [13].

A number of physical, chemical, and biological procedures are available for measuring $k_L a$ [14,15]. In laboratory-scale gas-liquid studies, the dynamic or gassing-out method is among the most widely used. Its reliability depends on how well the gas flow, mixing, and transient response are controlled. These requirements become more difficult to satisfy as reactor scale increases, where non-uniform gas distribution and unsteady behaviour may affect the result. Linek *et al.* [15] also emphasized the importance of carefully defined experimental conditions. Thus, the selected $k_L a$ method should always be considered together with its practical limitations.

Dissolved oxygen can be followed directly with an O₂ probe, whereas CO₂ measurement is less straightforward. Once CO₂ enters water, it is distributed among dissolved CO₂, carbonic acid (H₂CO₃), bicarbonate (HCO₃⁻), and carbonate (CO₃²⁻), and the relative fractions change with pH [16]. A practical CO₂ estimate therefore needs to account for this carbonate equilibrium rather than only one species. Measurements based on alkalinity or carbonate

hardness together with pH provide one possible route, because these quantities are related to bicarbonate, carbonate, and dissolved CO₂ levels [17].

The present study first examines oxygen $k_L a$ in a stirred bioreactor over a range of agitation speeds and gas flow rates and uses the resulting data to establish an empirical correlation for the system. A second part of the work focuses on CO₂. Here, a commercially available titration kit, combined with pH measurement, is used as a low-cost way to estimate dissolved CO₂ and to compare two sparger geometries. The study therefore addresses both operating-condition effects on oxygen transfer and a practical approach for following CO₂ transfer in the same bioreactor.

MATERIALS AND METHODS

Determination of experimental system

Experiments were carried out in a cylindrical bioreactor with an internal diameter of 190 mm and a height of 700 mm. Mechanical mixing was provided by a four-blade turbine-type impeller with a diameter of 4 cm. Gas was introduced through two perforated sparger configurations with comparable total gas-distribution lengths. The U-shaped tubular sparger had an overall tube length of approximately 12 cm and contained 12 gas-discharge holes, each 0.5 mm in diameter, distributed at approximately 1 cm intervals along the tube. The ring sparger had a diameter of 4 cm, corresponding to a circumference of approximately 12.6 cm, and also contained 12 uniformly distributed gas-discharge holes. Both spargers were installed at the bottom of the reactor. Dissolved oxygen and pH were monitored with Hamilton probes. A data acquisition system (DAQ) together with a MATLAB-Simulink interface was used for monitoring and flow control. Two rotameters (0-1 m³/h) were used to set the gas flow rates. Nitrogen was supplied through the ring sparger at 0.23 m³/h during oxygen removal, while compressed air was used for the oxygen-transfer experiments. Compressor pressure, initially 4-5 bar, was reduced to 1-2 bar before the gas entered the reactor. The P&ID, Simulink model, and photographs of the experimental system are shown in Figure 1.

Each experiment was carried out with 15 L of tap water under room conditions. The ambient temperature was approximately 23 °C, and the liquid height in the vessel was maintained between 160 and 200 mm.

For the CO₂ experiments, collected samples were kept in sealed glass containers at room temperature until analysis.

The P&ID in Figure 1(a) summarizes the connection between the gas-handling equipment, reactor, sensors, and control system. In the Simulink interface shown in Figure 1(b), the required gas flow rate was entered through the "oxflow" block in m³/h, and the mixer set point was entered through the "mixrpm" block. The dissolved-oxygen (DO) signal from the Hamilton probe was displayed continuously, allowing the DO profile to be recorded during each run.

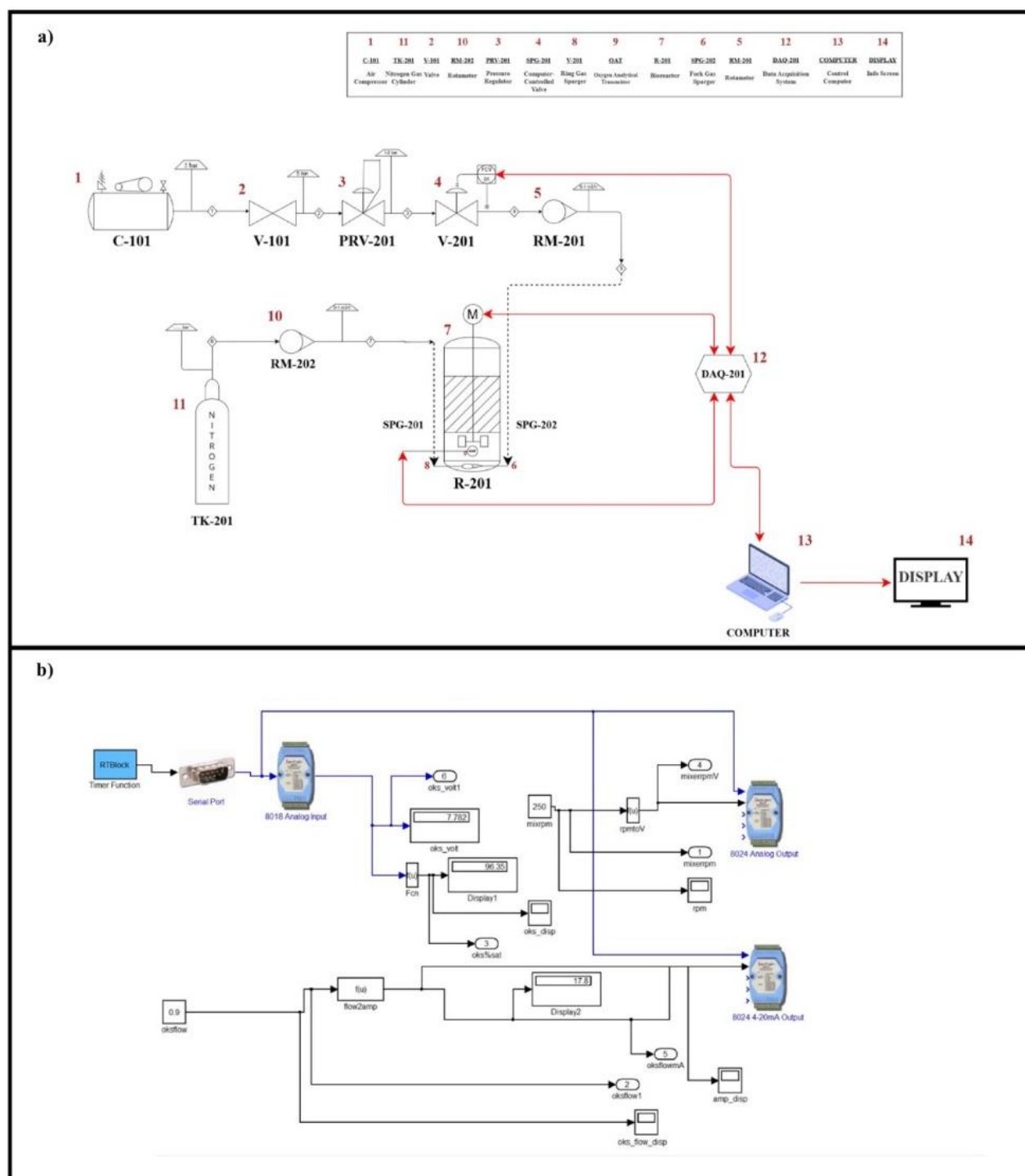


Figure 1. Process and Instrumentation Diagram (P&ID) and Simulink model of the experimental system: (a) overall arrangement of the experimental setup; (b) Simulink interface used for monitoring and control.

Calculation of the volumetric mass transfer coefficient ($k_L a$) of oxygen

The oxygen transfer rate (OTR) acts as the limiting factor when calculating the volumetric mass transfer coefficient of the oxygen-water system. The mass balance of dissolved oxygen in a well-mixed liquid phase can be written as follows [18]:

$$\frac{dC_{O_2}}{dt} = k_L a (C_{O_2}^* - C_{O_2}) - r_{O_2} = OTR - OUR \quad (1)$$

where C_{O_2} is the dissolved oxygen concentration in the liquid phase, $C_{O_2}^*$ is the saturation dissolved oxygen

concentration, k_L is the liquid-side mass transfer coefficient, a is the gas-liquid interfacial area per unit liquid volume, r_{O2} is the oxygen consumption rate, t is time, OTR is the oxygen transfer rate, and OUR is the oxygen uptake rate.

When the oxygen uptake rate, $OUR = 0$, the oxygen mass balance in the liquid phase can be simplified to:

$$\frac{dC_{O_2}}{dt} = k_L a (C_{O_2}^* - C_{O_2}) = OTR \quad (2)$$

where C_{O_2} , $C_{O_2}^*$, k_L , a , t , and OTR are as defined above; OUR is zero under the present oxygen-transfer experiments.

The oxygen mass transfer rate can be described as proportional to the concentration gradient. For aerobic fermentation, the maximum value of the concentration gradient is limited due to the low solubility of oxygen. Therefore, the maximum mass transfer rate from the gas to the liquid in the bioreactor can be estimated in this way:

$C_{O_2}^*$ is the saturation concentration in the liquid phase.

$$\int_{C_{O_2,1}}^{C_{O_2,2}} \frac{1}{(C_{O_2}^* - C_{O_2})} dC = k_L a \int_0^t dt \quad (3)$$

where $C_{O_2,0}$ and $C_{O_2,t}$ are the dissolved oxygen concentrations at $t = 0$ and at time t , respectively; the remaining symbols are as defined above.

$$\ln \left(\frac{C_{O_2}^* - C_{O_2,t}}{C_{O_2}^* - C_{O_2,0}} \right) = k_L a \cdot t \quad (4)$$

where $C_{O_2,0}$ and $C_{O_2,t}$ are the initial and time-dependent dissolved oxygen concentrations, respectively, t is time, and $k_L a$ is the volumetric mass transfer coefficient.

The experimental $k_L a$ value was obtained from the slope of the linearized concentration-deficit expression plotted against time.

Experimental design and procedure for oxygen $k_L a$ determination

Oxygen-transfer experiments were performed at agitation speeds of 50, 150, and 250 rpm and gas flow rates of 0.3, 0.6, and 0.9 m³/h. The full factorial combination of these settings produced nine operating conditions. Each condition was run in duplicate, giving 18 experiments in total, and $k_L a$ was calculated using the dynamic procedure described above.

Before each run, dissolved oxygen was lowered by feeding nitrogen at 0.23 m³/h while the impeller was operated at 150 rpm. Once deoxygenation was completed, the nitrogen stream was stopped, and compressed air was supplied at the gas flow rate assigned to that experiment. The DO response was recorded continuously with time. The oxygen $k_L a$ value, expressed in min⁻¹, was obtained from the slope of the logarithmic oxygen-deficit plot [10,14,19].

Nitrogen was introduced through the ring sparger until the DO reading fell below 40%. The nitrogen line was then closed, and aeration with compressed air was started. Air supply continued until the DO signal approached its maximum, or steady-state, value. Recorded data were exported from the control system and processed in Microsoft Excel.

The same sequence was followed for all combinations of gas flow rate (0.3, 0.6, and 0.9 m³/h) and agitation speed (50, 150, and 250 rpm). Thus, nine operating conditions were examined, with two independent runs at each condition.

The DO (%) profiles recorded during the experiments are presented as a function of time in Figure 2(a). Figure 2(b) presents the $k_L a$ values obtained from the duplicate runs together with the corresponding standard deviations.

Correlation for $k_L a$ of oxygen gas

Many researchers have proposed empirical $k_L a$ correlations valid for different systems and experimental conditions. These correlations are usually defined

depending on variables such as agitation speed (N), gas flow rate (Q), power input (P/V), reactor volume (V), and physical parameters (viscosity, surface tension, etc.). It also varies from system to system (i.e., air-water).

In stirred tank reactors, mechanical stirring speed, gas flow rate, and system viscosity are among the prominent parameters.

The correlations proposed for bubble column reactors are based on the assumption that only gas flow is effective in the system, but a more complex model that takes into account many physical parameters such as viscosity, surface tension, density, etc., has also been proposed.

Correlations with airlift reactors usually include reactor geometry (riser/downcomer area ratio) and gas flow rate. These correlations are valuable for engineers to predict system behavior during both design and scale-up. Correlations are usually developed under a specific system or set of conditions and are not directly generalizable. Therefore, it is recommended to assess system similarity before using them in practice [10,17,19-30].

To characterize the mass transfer in the gas-liquid phase, experimental studies were carried out under different gas flow rates (Q , m³/h) and agitation speeds (N , rpm) conditions. The mass transfer coefficient $k_L a$ was determined for each condition, and the data obtained were subjected to regression analysis. Based on the experimental correlation form commonly used in the literature, the following equation was proposed:

$$k_L a = a \cdot Q^b \cdot N^c \quad (5)$$

where $k_L a$ is the volumetric mass transfer coefficient, Q is the gas flow rate (m³/h), N is the agitation speed (rpm), a is the empirical coefficient in Eq. (5), and b and c are dimensionless empirical exponents.

To linearize this relation, a natural logarithm transformation was applied, and the following form was obtained:

$$\ln(k_L a) = \ln(a) + b \ln(Q) + c \ln(N) \quad (6)$$

where $\ln$ denotes the natural logarithm and the remaining symbols are as defined for Eq. (5).

Regression analysis was conducted with the multiple linear regression method in Microsoft Excel software. $\ln(Q)$ and $\ln(N)$ were used as independent variables, and $\ln(k_L a)$ was taken as the dependent variable. A total of 18 different experimental conditions were measured. The accuracy of the model was evaluated using statistical criteria such as R^2 , F -test, and p -value.

Approach for determination of CO₂ $k_L a$ via carbonate hardness (KH) test

In order to improve the mass transfer from gas phase to liquid phase in bioreactors, water was initially used as the liquid phase and oxygen as the gas phase. In this way, necessary optimizations were achieved. In light of the experience gained, water as the liquid phase and CO₂ as the gas phase were used in the second experimental group.

The effect of sparger configuration on gas-liquid mass transfer was investigated experimentally by comparing the performance of U-shaped tubular and ring spargers. In addition, since there is no electronic device to determine

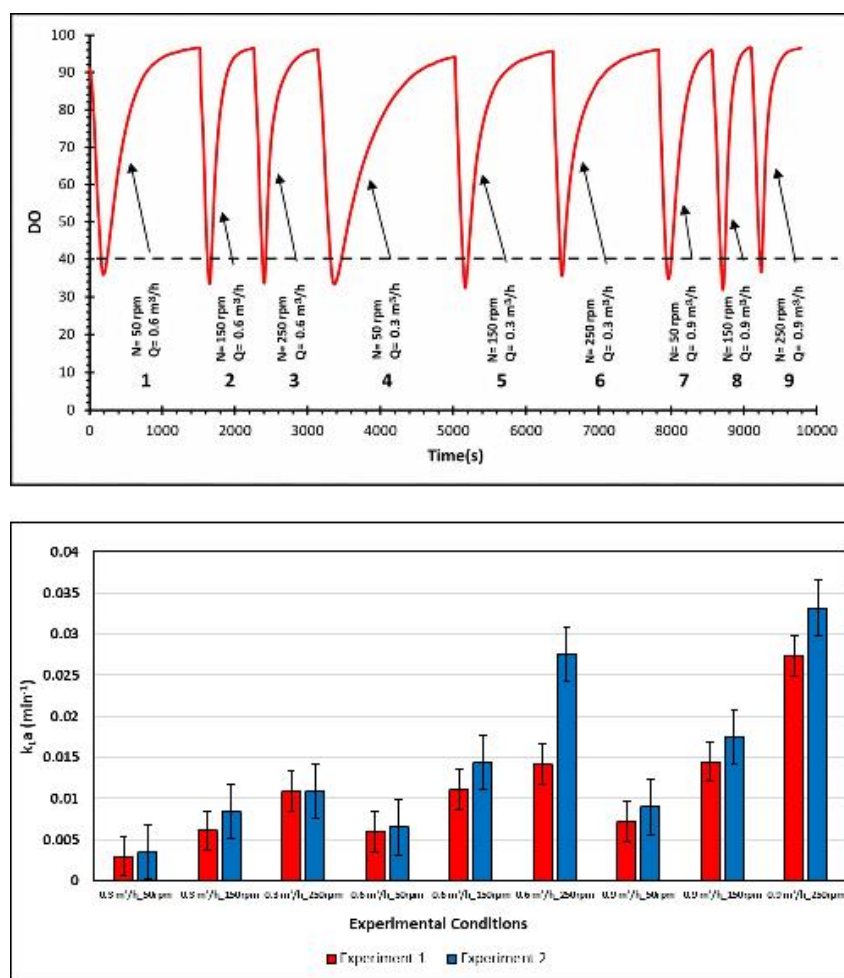


Figure 2. (a) Dissolved oxygen (DO) profiles recorded during the experimental runs. (b) Oxygen $k_L a$ values from duplicate measurements; error bars show the standard deviation ($n = 2$).

the amount of CO_{2(g)} dissolved in the liquid phase, a new test method was also investigated. Within the scope of this research, the concentration of CO₂ dissolved in the liquid phase was determined with the help of the carbonate water hardness Test (JBL Pro AQUATEST brand KH Water Analysis test kit was used), which is frequently used in aquarium chemistry based on aquariums, and the data obtained were used to calculate the Carbon dioxide transfer coefficient from the gas phase to the liquid phase. The test is based on the titration technique, one of the most well-known analytical chemical analysis methods.

The KH test (acid binding test) is a test that measures the alkalinity of water. This test determines the buffering capacity of water against acidic substances. That is, it shows how resistant the water is to acidic substances. The KH test is commonly used to determine the concentrations of bicarbonate (HCO₃⁻), carbonate (CO₃²⁻), and hydroxide (OH⁻) ions. The KH test measures the buffering capacity of water with acid added to the water. Acetic acid (CH₃COOH) or sulfuric acid (H₂SO₄) is usually used in this test. The KH test measures the alkalinity level of water and indicates its capacity to resist acids. The test is performed by adding acid, and the pH change is monitored. The result determines how much water can buffer against acidic substances. This is an important factor in maintaining the pH balance of water. Based on this, relationships between

pH-KH-CO₂ can be established based on various tables in the literature [16,17,20].

Dissolved CO₂ analysis with kit

The measuring cup was shaken several times with the liquid samples, and the cup was washed with distilled water after each measurement. With the help of a syringe, 5 mL of the sample was taken into the measuring vessel, and the liquid in the kit was added dropwise into the measuring vessel. Titration was continued until the sample color changed from blue to yellow/orange. Each drop consumed corresponds to 1 °dH, 1.78 °fH, 0.36 mmol/L acid-binding capacity, and 21.8 mg/L hydrogen carbonate. After determining the KH degree, the samples were subjected to pH analysis. Data were noted, and the amount of dissolved CO₂ was determined using the optimized pH-KH-CO₂ relationship described below. The volumetric mass transfer coefficient for CO₂ was also calculated using Eq. (4) and linear regression analysis. The difference in performance between the U-shaped tubular and the ring spargers was observed.

Mathematical modelling of pH-KH-CO₂ relationship

The concentration of dissolved CO₂ in water can be easily obtained in ppm (mg/L) with the carbonate water hardness test, a widely used method. When the literature

data are examined, it is possible to create charts that vary for various conditions. Examples of these conditions are aquariums with plants and fish, aquariums with plants, structures and fish, or empty aquariums. The presence of other chemicals also changes the results of this test. In the literature, for systems containing only water and CO₂, the concentration is calculated using Eq. (7) below. Our bioreactor system has the same characteristics as this system, and there is no problem in using this equation. However, it is not possible to fully represent our bioreactor with this equation because the charts used in the literature and daily life are basically based on this equation, but the coefficients of the equation are optimized due to factors such as ambient temperature or structural characteristics of the aquarium. For this reason, in order to better represent our system and to reduce possible errors, the data from the charts used in the literature and daily life were examined in MATLAB, and the equation was optimized. In this process, an error function was defined, and the coefficients with the lowest error were determined by iteration method, and the equation was updated.

$$CO_2(ppm) = 3 \cdot KH \cdot 10^{(7.6-pH)} \quad (7)$$

where CO₂ is the dissolved carbon dioxide concentration (mg/L), KH is carbonate hardness (°dH), and pH is the measured pH value.

Initially, our equation has the following form.

$$CO_2 = a \cdot KH \cdot 10^{(b-pH)} \quad (8)$$

where CO₂ is the dissolved carbon dioxide concentration (mg/L), KH is carbonate hardness (°dH), pH is the measured pH value, and a and b are empirical coefficients.

To find the optimal form of the a and b coefficients in the equation, the pH-KH-CO₂ 2D Interpolation tables given in the literature were re-prepared as a vector list. In this way, in a sense, the interpolation process will be done with higher accuracy, and a correlation with fast results will be obtained. In order to minimize the difference between the CO₂ values in the data tables and our model, the original equation in the literature, $a = 3$ and $b = 7.6$, were taken as initial values.

Since our model is in a non-linear form, it is linearized by taking logarithms.

$$\log CO_2 = \log a + \log KH + (b - pH) \quad (9)$$

where log denotes the base-10 logarithm, and CO₂, KH, pH, a, and b are as defined for Eq. (8).

After this process, the equation was made solvable by linear regression. After logarithmization, the coefficients a and b were optimized by the least-squares method. Before starting the optimization, the error function was defined and coded in MATLAB.

$$Error = \sum_{i=1}^N (CO_{2,real,i} - CO_{2,model,i})^2 \quad (10)$$

where error is the least-squares objective function, N is the number of data points, i is the data-point index, $CO_{2,real,i}$ is the reference/tabulated CO₂ concentration, and $CO_{2,model,i}$ is the concentration predicted by the model.

The "lsqcurvefit" function was used in the MATLAB program to find the most appropriate a and b values. At the end of these procedures, the coefficients producing the smallest errors were $a = 0.879$ and $b = 7.53$. At the end of

these procedures, the current equation to calculate the CO₂ concentration is Eq. (11) below.

$$CO_2(ppm) = 0.879 \cdot KH \cdot 10^{(7.53-pH)} \quad (11)$$

where CO₂ is the dissolved carbon dioxide concentration (mg/L), KH is carbonate hardness (°dH), pH is the measured pH value, and 0.879 and 7.53 are the optimized model coefficients.

Design and execution of CO₂ mass transfer experiments

The above-mentioned bioreactor was used in the experiment with fresh tap water at room temperature.

In the first experimental system, CO₂ gas was fed into the system with a volumetric flow rate of 1.5 L/min with the help of a ring gas sparger. The initial CO₂ concentration of the liquid phase is zero. At $t = 0$, before CO₂ was fed into the system, at 150 rpm agitation speed, a sufficient sample of the liquid phase in the bioreactor was taken into a beaker for examination. Then CO₂ was fed to the experimental system. Samples were collected and analyzed every 30 s over a period of 6 min. For pH measurement, a Hamilton-brand pH probe was immersed in the bioreactor, enabling real-time monitoring of the pH value. The experimental system was operated until the CO₂ concentration reached steady-state conditions, corresponding approximately to a pH range of 4-5. The most appropriate curve passing through these points in the x - y plane was determined.

In the second experiment, the experiment was repeated under the same operating conditions using the U-shaped tubular sparger. The agitation speed was 150 rpm, and the volumetric flow rate of CO₂ gas was 1.5 L/min. The liquid in the bioreactor was completely replaced, and the experiment was started after making sure that there was no CO₂ gas in the system. Samples were collected every 30 seconds over a period of 6 minutes. For each gas sparger, three experiments were conducted under identical operating conditions, resulting in a total of six experiments. The k_La for each sparger was obtained by fitting Eq. (9) directly to the pooled individual data points from all three replicates, rather than to an averaged concentration profile; the mean $\pm$ standard deviation values reported in Table 3 are provided solely for concise presentation of the raw dataset and were not used as the basis for the regression.

RESULTS AND DISCUSSION

Effect of gas flow rate and stirring speed on mass transfer coefficient of oxygen

To observe the effect of agitation speed and air flow rate on the k_La of oxygen, the results of 18 measurements made at 50, 150, 250 rpm agitation speeds and 0.3, 0.6, 0.9 m³/h air flow rates are shown in Table 1 with standard deviation values. It is observed that both changes in agitation speed and mixing speeds effect on k_La value of oxygen. At all air flow rates, the k_La value of oxygen reached higher values at high agitation speeds. In the experiments, the optimum mean k_La value of oxygen was 0.0303 min⁻¹ at 0.9 m³/h air flow rate and 250 rpm agitation speed.

Table 1. Effect of air flow rate and agitation speed on oxygen k_La .

Gas flow rate (m ³ /h)	50 rpm	150 rpm	250 rpm
0.3	0.003 ± 0.0004	0.007 ± 0.0	0.0109 ± 0.0
0.6	0.006 ± 0.0004	0.013 ± 0.0	0.0209 ± 0.0
0.9	0.008 ± 0.0013	0.016 ± 0.0	0.0303 ± 0.0

Correlation and statistical analysis for determination of volumetric mass transfer coefficient (k_La) for oxygen

Multiple linear regression analysis was applied to examine the relationship between the k_La and the variables. In the model, k_La was used as the dependent variable and Q (air flow rate) and N (agitation speed) were used as independent variables. The reliability of the regression model was evaluated by regression statistics and ANOVA analysis results. ANOVA analysis results and regression statistics are given in Table 2.

In the model, a strong relationship was observed between the independent variables and k_La , with a multiple correlation coefficient (R) of 0.969 and a coefficient of determination (R^2) of 0.938. This result shows that the model explains approximately 93.8% of the variation in k_La . With an adjusted R^2 value of 0.930, the validity of the model was maintained despite the relatively small sample size ($n = 18$).

According to the ANOVA analysis, the regression model is statistically significant ($F = 114.0$, $p = 8.50 \times 10^{-10}$).

This shows that the combined effect of the Q and N variables on k_La is highly significant, and the model can be used reliably. The expression obtained from the regression equation for k_La oxygen is as follows:

$$k_La = (0.000475) \cdot Q^{0.833} \cdot N^{0.748} \quad (12)$$

where k_La is the oxygen volumetric mass transfer coefficient (min⁻¹), Q is the air flow rate (m³/h), and N is the agitation speed (rpm).

The fitted exponents indicate a stronger dependence on gas flow rate than on agitation speed over the conditions examined. This trend is also consistent with the experimental data. Increasing gas flow introduces more bubbles into the liquid and can raise gas holdup and interfacial area, whereas faster agitation mainly changes turbulence and bubble breakup. In the present operating window, the additional effect produced by agitation was smaller than the effect associated with gas flow rate.

ESTIMATION OF THE MASS TRANSFER COEFFICIENT OF CO₂ IN GAS-LIQUID PHASE BY A KH BASED APPROACH AND COMPARISON OF THE EFFICIENCY OF DIFFERENT GAS SPARGERS

The KH-pH method described above was applied to the CO₂ experiments to compare the U-shaped tubular and ring spargers under the same operating conditions. The measured pH and KH values and the corresponding calculated CO₂ concentrations are listed in Table 3.

Table 2. ANOVA and regression statistics for the dependence of oxygen k_La on air flow rate and agitation speed.

ANOVA	df	SS	MS	F	Significance F	Regression Statistics		
Regression	2	7.104	3.552	114.0	8.500E-10	Multiple R	0.969	
						R^2	0.938	
Residual	15	0.467	0.031			Adjusted R^2	0.930	
						Standard Error	0.177	
Total	17	7.571				Observations	18	
	Coefficients	Standard Error	t Stat	p-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-7.652	0.306	-24.978	1.233E-13	-8.305	-6.998	-8.305	-6.998
-1.2039	0.832	0.092	9.079	1.754E-07	0.637	1.028	0.637	1.028
3.9120	0.748	0.062	12.063	4.0247E-09	0.615	0.880	0.615	0.879

Table 3. Time-dependent pH, KH, and dissolved CO₂ concentration for the U-shaped tubular and ring spargers.

U-SHAPED TUBULAR SPARGER				RING SPARGER		
t (min)	pH	KH	CO ₂ (mg/L)	pH	KH	CO ₂ (mg/L)
0	6.94 ± 0.0	4.0 ± 0.0	13.57 ± 0.4	6.97 ± 0.01	4.0 ± 0.0	12.57 ± 0.2
0.5	6.50 ± 0.1	3.0 ± 0.0	28.66 ± 7.6	6.68 ± 0.03	3.0 ± 0.0	18.55 ± 1.3
1	5.93 ± 0.0	3.0 ± 0.0	106.44 ± 14.8	6.11 ± 0.05	3.0 ± 0.0	69.69 ± 8.6
1.5	5.59 ± 0.0	3.0 ± 0.0	231.45 ± 3.1	5.60 ± 0.04	3.0 ± 0.0	224.91 ± 17.5
2	5.4 ± 0.0	3.0 ± 0.0	359.04 ± 24.9	5.26 ± 0.12	3.0 ± 0.0	503.18 ± 127.7
2.5	5.28 ± 0.0	3.0 ± 0.0	473.72 ± 40.3	5.15 ± 0.08	3.0 ± 0.0	640.66 ± 119.7
3	5.18 ± 0.0	3.0 ± 0.0	588.52 ± 67.9	5.06 ± 0.07	3.0 ± 0.0	779.73 ± 127.5
3.5	5.11 ± 0.0	3.0 ± 0.0	699.70 ± 82.9	5.01 ± 0.06	3.0 ± 0.0	891.79 ± 113.7
4	5.05 ± 0.1	3.0 ± 0.0	804.13 ± 110.3	4.94 ± 0.05	3.0 ± 0.0	1014.01 ± 104.3
4.5	5.00 ± 0.1	3.0 ± 0.0	905.13 ± 110.5	4.90 ± 0.04	3.0 ± 0.0	1119.45 ± 101.2
5	4.94 ± 0.0	3.0 ± 0.0	1020.95 ± 92.3	4.85 ± 0.04	3.0 ± 0.0	1256.05 ± 113.6
5.5	4.93 ± 0.0	3.0 ± 0.0	1044.73 ± 94.5	4.84 ± 0.04	3.0 ± 0.0	1295.80 ± 126.3
6	4.92 ± 0.0	3.0 ± 0.0	1069.07 ± 96.7	4.84 ± 0.04	3.0 ± 0.0	1295.80 ± 126.3

For both spargers, calculated CO₂ concentration increased with aeration time and began to level off after about 5 min. The same general response was observed in the three replicate runs, although the absolute concentration differed between experiments.

During the earlier part of the experiment, the U-shaped tubular sparger showed the faster increase in dissolved CO₂. At longer times, however, the ring sparger reached the higher concentration, approximately 1300 mg/L compared with about 1050–1080 mg/L for the U-shaped sparger. The difference between the initial transfer rate and the final concentration indicates that sparger geometry affected the hydrodynamics of gas dispersion as well as the approach to the final dissolved-CO₂ level. Although the two spargers had similar total gas-distribution lengths and the same number of gas outlets, their geometries and spatial distribution of the outlets were different, which may have affected bubble formation, gas dispersion, and consequently the observed mass-transfer behavior.

The CO₂ k_La values were calculated from the concentration-time data by linear regression. Individual measurements from all three runs for each sparger (3 × 13 time points) were used in the regression rather than a pre-

averaged concentration profile. At 150 rpm and a CO₂ flow rate of 1.5 L/min, the fitted k_La values were 0.6253 min⁻¹ for the U-shaped tubular sparger ($R^2 = 0.834$) and 0.59 min⁻¹ for the ring sparger ($R^2 = 0.819$), as shown in Figure 3.

The larger k_La obtained with the U-shaped sparger is consistent with its steeper early concentration rise. The R^2 values of the linear fits were moderate, particularly because the logarithmic concentration-deficit term becomes increasingly sensitive as $C(t)$ approaches the saturation value at the later sampling times. By contrast, the ring sparger produced the higher final dissolved-CO₂ concentration. These two observations describe different aspects of the transfer process and should therefore not be interpreted as contradictory.

Taken together, the results show that sparger performance cannot be judged from a single quantity alone. The U-shaped tubular sparger gave the higher fitted transfer coefficient under the tested conditions, whereas the ring sparger produced the higher final CO₂ concentration. Selection of a sparger should therefore consider both the required transfer rate and the dissolved-gas level needed for the intended process.

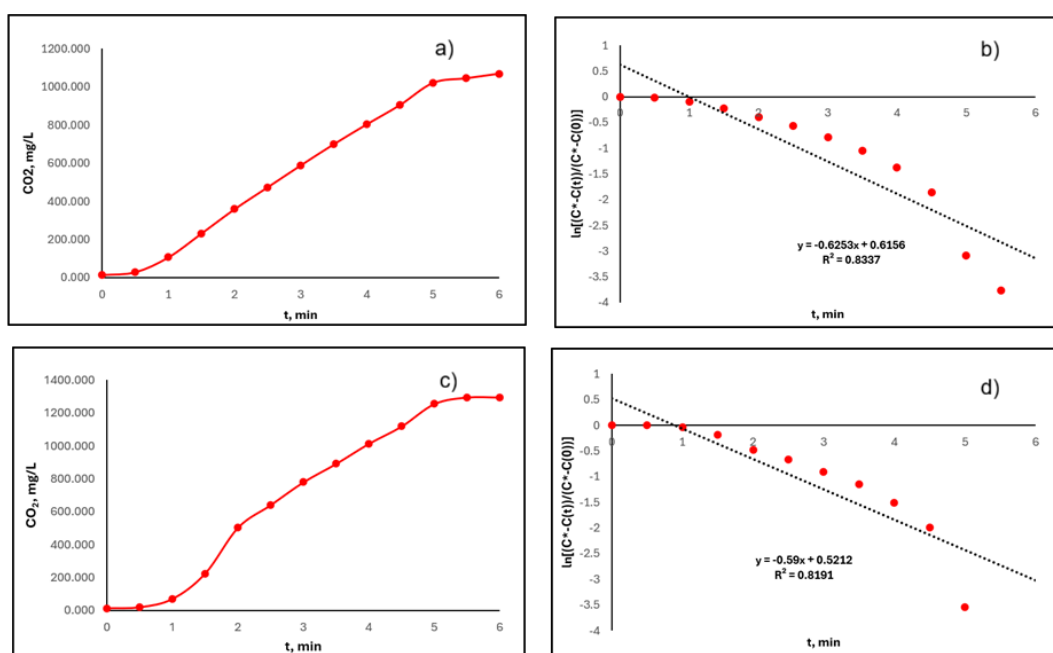


Figure 3. CO₂ mass-transfer results obtained with the U-shaped tubular and ring spargers: (a, b) CO₂ concentration profile and linearized fit used to determine k_La for the U-shaped tubular sparger. (c, d) CO₂ concentration profile and linearized fit used to determine k_La for the ring sparger.

CONCLUSION

This study investigated oxygen and CO₂ mass transfer in a stirred bioreactor using complementary experimental approaches. For oxygen transfer, both gas flow rate and agitation speed affected k_La , with gas flow rate showing the stronger influence within the investigated range. The resulting correlation can therefore be used to describe the mass-transfer behavior of the studied system and support the selection of suitable operating conditions.

For CO₂ transfer, the performances of the U-shaped tubular sparger and ring sparger were compared under the same operating conditions. The U-shaped tubular sparger showed a slightly higher k_La , indicating faster initial CO₂ transfer, whereas the ring sparger reached a higher final dissolved CO₂ concentration. These findings show that sparger performance should be evaluated by considering both transfer kinetics and final dissolved-gas accumulation.

The KH-pH-based method also provided a simple and economical way to follow dissolved CO₂ concentration when a dedicated CO₂ sensor is not available. Overall, the

study provides a practical approach for evaluating gas-liquid mass transfer and comparing sparger configurations in bioreactor systems. Further studies are recommended to validate the KH-pH method against an independent CO₂ measurement technique and to examine its applicability under broader operating conditions.

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NAUČNI RAD

EKSPERIMENTALNO ISTRAŽIVANJE PRENOSA MASE O₂ I CO₂ U BIOREAKTORIMA

Eksperimentalno je ispitan prenos mase kiseonika i CO₂ između gasne i tečne faze u bioreaktoru sa mešalicom. Zapreminski koeficijent prenosa mase kiseonika (k_{La}) određivan je dinamičkom metodom, pri devet kombinacija brzine mešanja i protoka gasa, uz izvođenje dva ponavljanja za svaki eksperimentalni uslov. Višestrukom linearnom regresijom objašnjeno je 93,8% varijabilnosti vrednosti k_{La} ($R^2 = 0,938$), pri čemu je dobijeni model bio statistički značajan ($F = 114,0$; $p < 0,001$). U ispitivanom opsegu radnih uslova, protok gasa imao je veći uticaj na vrednost k_{La} za kiseonik nego brzina mešanja. U eksperimentima sa CO₂, koncentracija rastvorenog ugljen-dioksida procenjivana je na osnovu merenja karbonatne tvrdoće (KH) i pH vrednosti, primenom jednostavnog i ekonomičnog postupka. Zatim su, pri istim radnim uslovima, upoređene karakteristike dva tipa distributera gasa: cevastog distributera u obliku slova U i prstenastog distributera. Cevasti distributer u obliku slova U ostvario je nešto veću vrednost k_{La} ($0,625 \text{ min}^{-1}$) u poređenju sa prstenastim distributerom ($0,59 \text{ min}^{-1}$), kao i brži početni prenos CO₂. Međutim, primenom prstenastog distributera postignuta je veća konačna koncentracija rastvorenog CO₂, od približno 1300 mg/L, u poređenju sa 1050-1080 mg/L kod distributera u obliku slova U. Dobijeni rezultati ukazuju na to da prilikom izbora radnih uslova za primenu u bioprocesima efikasnost distributera gasa treba procenjivati uzimajući u obzir kako brzinu prenosa mase, tako i konačnu koncentraciju rastvorenog gasa.

Ključne reči: prenos mase između gasne i tečne faze, rastvorljivost CO₂, test karbonatne tvrdoće, zapreminski koeficijent prenosa mase.