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Survey of measurement techniques for gas–liquid mass transfer coefficient in bioreactors

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Abstract

In many fermentation processes, oxygen transfer is the rate limiting step. Correct measurement and subsequent estimation of the volumetric mass transfer coefficient is a crucial step in the design procedure of bioreactors. This article discusses some of the methods that are commonly used for the measurement of the mass transfer coefficient and their applicability for measurement in large scale bioreactors. It has been found that among the methods discussed here, the dynamic pressure method appears most useful for industrial scale bioreactors, with a small degree of approximations for gas–liquid mixing in the reactor and is suitable for large scale bioreactors with errors less than 10%, over the entire range of the operating conditions encountered in the fermentor operation. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Mass transfer; Measurement techniques; Dynamic pressure method; Bioreactors

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1. Introduction

Oxygen transfer in aerobic bioprocesses is essential and any shortage of oxygen drastically affects the process performance. Almost always, bioprocesses are carried out in aqueous media where the solubility of oxygen is very low owing to the presence of ionic salts and nutrients and the rate of oxygen utilization by the microorganisms is rather high. Hence, oxygen transfer is important and is frequently a rate limiting step for aqueous bioprocesses. Because of this, during the design procedure, correct estimation of the mass transfer coefficient is very important. Some of the measurement techniques, which are used for this purpose, are discussed and assessed in this paper. Chemical methods [1] are now generally not used for the determination of mass transfer coefficients in bioreactors because of the enhancement of $k_l\bar{a}$ values obtained due to chemical reaction and these are subjected to many uncertainties and may even physically alter the system's physicochemical properties. We present a survey of various methods employed in the industry and comment upon, their suitability under specific operating conditions.

2. Dynamic methods

2.1. Dynamic oxygen electrode method

This technique is widely used for the measurement of the volumetric mass transfer coefficient. The oxygen concentration of the inlet gas is changed stepwise and the dissolved time varying concentration of the oxygen in the liquid phase is measured with an oxygen electrode. The determination of $k_l\bar{a}$ needs information about complete system dynamics for greater accuracy. The method of moment can also be used successfully, with some degree of accuracy. The area between the transient concentration curve and its asymptote is evaluated for the dissolved concentration curve measured in the liquid after a step concentration change in the gas inlet. From the area calculated, the first moment of the system (μ_1) is obtained, as we know the electrode response to step disturbance. The following models (continuous gas phase and batch liquid phase) have been widely used in the literature [2] for calculating the value of mass transfer coefficient from the moments:

Liquid perfectly mixed and gas perfectly mixed (MM model)

$$\mu_1 = 1 + (1-\epsilon)\left(\frac{1}{m\epsilon} + \frac{1}{K}\right) \tag{1}$$

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Liquid perfectly mixed and gas in plug flow (MP model)

$$\mu_1 = \frac{(1-\epsilon)}{K} + \frac{[1+(1-\epsilon)/m\epsilon]\times[1-m\epsilon/(K\times[1-\exp(-K/m\epsilon)])]}{[1-\exp(-K/m\epsilon)]} \tag{2}$$

Liquid perfectly mixed and gas at its inlet composition (thus ignoring the oxygen depletion)

$$\mu_1 = \frac{(1-\epsilon)}{K} \tag{3}$$

Hanhart et al. [3] have shown that there is a significant spread in the residence time distribution of gas phase and this also depends on the impeller speed, gas load, impeller diameter and the agitator clearance from the bottom. Assuming the extreme conditions of gas phase mixing results in errors in the estimation of mass transfer coefficient. Nocentini et al. [4] have shown that significantly higher values are obtained if simple MM model is used and error in measurement is negative, i.e. the estimated values are higher if MP model or Eq. (3) are used (The errors are in the range 10–35% and increase as the real value of $k_l\bar{a}$ increases). Eq. (3) gives still lower values as compared to MP model. This can be also explained from the fact that the bubbles have compositions in between the feed composition and the concentration in equilibrium with the liquid phase due to the residual bubble population containing old gas concentration.

2.2. Start -Up method

The effect of nonideal mixing in the gas phase is largely suppressed in the start-up variant of the dynamic method. In this method aeration is started into deoxygenated liquid without gas hold-up so that no mixing of the new and original gas can take place. There are instances where this method is used for the measurements in the case of multiple impeller systems [4,5]. They concluded that reasonable estimates for $k_l\bar{a}$ can be obtained when a simple model of perfect mixing for the liquid and plug flow for the gas is assumed and the oxygen concentration in liquid is measured at the middle of the vessel height. The above assumption will essentially be valid over a fixed operating regime, i.e., when the speed is just below the critical speed required for complete dispersion. If complete dispersion regime is there, then the values of the mass transfer coefficient obtained using the above assumption will be significantly lower than the actual values. The errors are likely to be even higher if gas recirculation or recycle takes place.

Formation of gas hold-up in the experiment, i.e., unsteady state nature results into some sort of uncertainty. The dynamics of the hold-up formation needs to be considered, especially for the vessels with high aspect ratio and having liquids with higher viscosity. A relevant comment is made afterwards while discussing the suitability of the method. Linek et al. [6] have shown that the $k_l\bar{a}$ values obtained by assuming linear time dependence of gas hold-up and interfacial area development during the startup period are substantially lower than the steady state values. Hence this technique is not suitable for $K_l\bar{a}$ measurement when the startup period is comparable with the duration of the dynamic experiment. This can be attributed to the exponential variation of the hold-up with time. The steady state value of the gas phase hold-up will be reached after a certain time, typically in the range 1–4 h and during the unsteady state behavior, the contribution due to the small bubbles cannot be neglected, which are commonly observed in the liquids showing viscous and non-coalescing behavior.

Machon et al. [7] used another variation of the dynamic method where the batch is first degassed by vacuum and then aerated for some time. After aeration ceased and bubbles escaped the batch, the steady state concentration of dissolved oxygen is measured. This sequence is repeated for different and long periods of aeration.

The above mentioned techniques used so far [4,7,8] do not allow the measurement of $k_l\bar{a}$ in individual stages of the multiple impeller systems and suffers with the same drawback as discussed before, i.e., time required for the establishment of the steady state gas hold-up.

2.2.1. Drawbacks of dynamic methods

The dynamic methods are significantly affected by the following two effects :

1. Since air is used for the experimentation purposes, there can be simultaneous transport of nitrogen with oxygen which affects the value of $k_l\bar{a}$ for oxygen transfer (affecting the start-up variant to a larger extent).
2. The system is brought to one steady state from another by changing the oxygen concentration of gas, entering the system without interrupting the gas supply into the contactor and agitation of the charge. Values of the gas phase hold-up and $k_l\bar{a}$ are assumed to be steady during entire period of saturating the charge with oxygen. This assumption will not be valid due to the flushing of the original gas phase hold-up by the newly supplied gas (affecting the dynamic oxygen electrode method to a larger extent).

These two effects considerably lower the measured/observed values of the mass transfer coefficients and the difference is observed to a larger extent when they are applied for large scale bioreactors. Also the dynamic methods require extensive knowledge of the gas–liquid mixing patterns. Hence, the dynamic methods are not recommended for the measurement of the same in the large scale bioreactors.

3. Steady state sulfite method

The common version of the steady state sulfite method [9–13] cannot be used for the high aeration intensities as in the case of large scale bioreactors. When pure oxygen is absorbed in the sulfite solution, the high absorption rate due to chemical reaction causes the bubble to shrink considerably and this effect which results into a decrease in $\bar{a}$ must be taken into consideration while evaluating the mass transfer coefficient values. The shrinkage of the bubbles significantly affects the interfacial area and the variation of interfacial area is also a function of the physio-chemical properties of the fermentation broth. The correction used for this purpose by Linek and Mayrhoferova [14] is found to be unreliable at such high absorption rates. Various authors [15–17] have used air instead of pure oxygen, but on absorption of air, the high oxygen depletion in the bubbles leads to an error in $k_l\bar{a}$ in the range 20–40% which is beyond the acceptable limit of <10%. A new variant of this method was suggested by Linek et al. [15], which eliminates these negative effects by lowering the absorption rates.

The 0.5 M Na_2SO_3 solution is slowly fed into the 0.5 M Na_2SO_4 solution so that the oxygen concentration in the liquid (during continuous pure-oxygen absorption) is decreased to 90–95% of the equilibrium value. Thus, the oxygen absorption rate is lowered 10 to 20 times that in the usual version of the sulfite method with negligible oxygen concentration in the liquid. The back pressure of the dissolved oxygen can be measured with the help of probes. The $K_l\bar{a}$ values then can be calculated by following relationship:

$$K_l\bar{a} = \frac{1}{2}\frac{C_1 V_1}{V_l C_{l,o}(1-G')} \tag{4}$$

where V_1 and C_1 are the volumetric flow rate and the concentration of the input sulfite solution respectively, $C_{l,o}$ is the equilibrium oxygen concentration in the liquid and G' is the actual probe signal normalized by the probe signal in the liquid saturated with oxygen (i.e., the probe signal after closing the sulfite solution inlet).

Linek et al. [15] have shown that the $k_l\bar{a}$ values obtained from this variation of sulfite method and those obtained by the dynamic pressure method (widely used and recommended in the case of the bioreactors) are in agreement over the interval of $K_l\bar{a}$ values studied (up to $K_l\bar{a} = 0.8\,s^{-1}$).

The greatest disadvantage of the above method lies in the fact that the method yields correct values only when pure oxygen is used. Use of pure oxygen may not be favorable for experimentation purposes on a industrial scale due to the economic considerations. Also very high concentration of oxygen is not favorable for the microorganisms. Linek et al. [13] have shown that the values of the mass transfer coefficient obtained by any version of the steady state sulfite method are significantly lower (up to 50% less for $K_l\bar{a} > 0.1\,s^{-1}$) than the actual if air is used instead of pure oxygen.

The value of $K_l\bar{a}$ is dependent on the concentration of Na_2SO_4 which reduces the average size of the bubble. Imai et al. [9] have shown that below a critical concentration of 10 mol/m^3, the $K_l\bar{a}$ values are unaffected and hence the steady state sulfite method should be operated below this concentration. They have also shown that the concentration of Na_2SO_4 affects the energy dissipation patterns of the impellers as the exponent on RPM is found to be affected by the concentration of Na_2SO_4 and the exponent on V_g is unaffected.

4. Dynamic pressure method (DPM)

Linek et al. [15] have in detail described the DPM. This method employs a small change in total pressure to generate a concentration change in the dispersed gas. The oxygen concentration is changed simultaneously in all bubbles of the dispersion irrespective of the gas phase mixing. Only upward pressure changes should be used for the measurement since a downward pressure change may be accompanied by spontaneous nucleation of bubbles because of supersaturation and consequently, by increased $k_l\bar{a}$ values. Linek et al. [18] have shown that, for the coalescing system, the difference between the values obtained by the upward and downward pressure steps was negligible but was significant for the non-coalescing systems and the method gives correct $k_l\bar{a}$ values for coalescing, noncoalescing and viscous systems even if the simple MM model (liquid perfectly mixed and gas perfectly mixed) is used. As compared to the earlier technique $k_l\bar{a}$ values obtained by DPM are less sensitive to the mixing effects and DPM suits best for measurement in multi-impeller vessels where complex gas–liquid mixing pattern can be expected.

Moucha et al. [19] used DPM to measure $k_l\bar{a}$ in individual stages of the vessel stirred with four rushton turbines on a common shaft. The method employs a small pressure change of about 15 kPa in vessel to force a simultaneous change in oxygen concentration in all bubbles of dispersion regardless of the gas flow pattern. The pressure change is performed by temporary throttling and subsequent reopening of the gas outlet. Oxygen concentration in liquid in response to the pressure change is measured by oxygen probes in individual stages of the vessel and the rest of the calculation procedure for the mass transfer coefficient is similar to the conventional DPM [15]. Moucha et al. [19] also observed that only 30–40% of the supplied gas is engaged in impeller region of upper stages. Correlation was developed for the calculation of mass transfer coefficient based on the concept of Lu and Yao [20]. $K_l\bar{a}$ is calculated from the correlation for bottom stage (derived assuming to be a single impeller configuration) by substituting power dissipated and effective gas velocity (From the correlations for power consumption in individual stages, an effective gas velocity in calculated which gives same power consumption in bottom as well as upper stages at equal impeller frequency and gassing rate) in upper stages. The equation proposed is:

$$K_l\bar{a} = 8.27 \times 10^{-4}\, N^{2.01}(V_g)^{0.259} \tag{5}$$

The equation derived gives lower values than the actual as concept on which the equation is based takes into account

Table 1
Comparison of initial and double response methods

P/V ($\mathrm{W\,m^{-3}}$)	V_g ($\mathrm{m\,s^{-1}}$)	MTC by double response method ($\mathrm{s^{-1}}$)	MTC by initial response method ($\mathrm{s^{-1}}$)	Difference
5000	0.03	0.22016	0.3436	35.93
4500	0.026	0.1977	0.2922	32.33
4000	0.02	0.17457	0.24167	27.76
3500	0.015	0.1504	0.1918	21.57
3000	0.01	0.12468	0.14217	12.3

Table 2
Correlations given on the basis of different methods

Method	Correlation	Conditions	Reference
Dynamic method	$K_l\bar{a} = 0.0149(P/V)^{0.59}(V_g)^{0.55}$	Four six-bladed rushton turbines, $T = 0.23$ m, $D = T/3$, 0.1–0.7 vvm , Impeller Re >1000	[4]
Sulfite method	$K_l\bar{a} = 3.11\mathrm{e}{-4}(P/V)^{1.24}(V_g)^{0.4}$	Six-bladed disc turbine, $T = 0.29$ m, $D = T/3$, Clearance from bottom = 0.10 m, $N = 4.17$–$14.17\ \mathrm{s^{-1}}$, $V_g = 0.00212$ and $0.00424\ \mathrm{m\,s^{-1}}$	[13]
Dynamic pressure method	$K_l\bar{a} = 6.46\mathrm{e}{-3}\ (P/V)^{0.675}(V_g)^{0.494}$	Four rushton turbines with $T = 0.19$ m, $H/D = 4$, $D = T/3$, $V_g = 0.00212$–$0.00848\ \mathrm{m\,s^{-1}}$, 5.5–18.83 $\mathrm{s^{-1}}$ where $P/V = (P/V)_{\mathrm{agitator}} + V_g\rho_l g$	[27]
Peroxide method	$K_l\bar{a} = 0.046(P/V)^{0.47}(V_g)^{0.67}$	Six-bladed disc turbine, $T = 0.60$ m, $D = T/3$, $P/V = 0$–$5000\ \mathrm{W\,m^{-3}}$, Speed = 8.33–15 $\mathrm{s^{-1}}$	[22]
Initial response	$K_l\bar{a} = 2.57\mathrm{e}{-3}(P/V)^{0.76}(V_g)^{0.45}$	Six-bladed disc turbine, $D = T/2$, $T = 0.31$–0.61 m, operating variables V_g and N not mentioned	[23]
Double response	$K_l\bar{a} = 2.044\mathrm{e}{-3}(P/V)^{0.64}(V_g)^{0.22}$	Six-bladed disc turbine, $D = T/2$, $T = 0.31$–1.83 m, operating variables V_g and N not mentioned	[23]

only that part of gas which enters into upper impeller regions affecting the dissipated power. The rest of the gas which bypasses the impeller region is not considered although it does contribute to gas–liquid mass transfer in upper stages similar to a bubble column effect, i.e., to overall as well as individual $K_l\bar{a}$ values.

Results obtained in noncoalescing batch of sulfate solution differ in value even by hundreds of percents from those, measured by other standard methods when evaluated using MM model. Results on a pilot plant scale fermentor(Capacity = 1 $\mathrm{m^3}$) have also shown that the conventional dynamic method and start-up method yields values that differ by 60–100% [18].

Linek et al. [15,18] have shown that the $k_l\bar{a}$ values obtained from the pressure method by absorption of pure oxygen and air are identical. This observation is also confirmed by Moucha et al. [19]. Thus, in dynamic pressure method, air can be used for the absorption of oxygen which also nullifies the effect of the non-ideal mixing in the dispersion and many other disadvantages offered by dynamic methods. This is a great advantage of this method that suggests that it may well be used for the measurement of the mass transfer coefficient in large-scale fermentors. Linek et al. [21] have shown that the extent of error caused by neglecting simultaneous nitrogen transport is within the acceptable limit (<10%) for commonly observed values of $K_l\bar{a}$ ($\leq 0.2\ \mathrm{s}^{-1}$).

5. Peroxide method

Hickman et al. [22] used hydrogen peroxide for the in situ production of oxygen.

Hydrogen peroxide in the solution is broken down by enzyme catalase according to the equation:

$$2\mathrm{H_2O_2} \rightarrow 2\mathrm{H_2O} + \mathrm{O_2}$$

This oxygen then transfers to gas phase and the only byproduct is water which helps in achievement of steady state by continuous addition of hydrogen peroxide. Gassing (gas used is not mentioned) is provided to carry the released oxygen and the concentrations of oxygen in the gas phase at the inlet and outlet are measured for the calculation purposes. The reaction is first order with respect to catalase and hydrogen peroxide and hence,

$$r_1 = K_1[\mathrm{H_2O_2}][\mathrm{Catalase}] \tag{6}$$

At steady state

$$\frac{Q_\mathrm{i}[\mathrm{H_2O_2}]_\mathrm{i}}{V_1} = r_1 \tag{7}$$

and rate of production of oxygen = rate of transfer of oxygen

$$\mathrm{OTR} = \frac{r_1}{2} = K_1\bar{a}\Delta c \tag{8}$$

whereΔc is concentration of driving force.

For a fully backmixed gas phase $\Delta c = C_\mathrm{L} - HC_\mathrm{G}$where

$$C_\mathrm{G} = C_\mathrm{Go} = \frac{C_\mathrm{Gi}\,Q_\mathrm{Gi} + \mathrm{OTR} \times V}{Q_\mathrm{Go}} \tag{9}$$

and

$$Q_\mathrm{Go} = \frac{P_\mathrm{i}}{P_\mathrm{o}} \times \left(Q_\mathrm{Gi} + \frac{\mathrm{OTR} \times V \times RT}{P_\mathrm{l}}\right) \tag{10}$$

Thus, the reaction rate, catalase concentration (enzyme catalase is unaffected by the oxygen concentration existing in the reactor), H_2O_2 concentration in the reactor do not need to be known for calculation of $K_l\bar{a}$. Only incoming flow rate, concentration of H_2O_2 in the inlet stream, liquid volume, flow rate of the incoming carrier gas and dissolved oxygen at the steady state are required. This makes the calculation of $K_l\bar{a}$ more easy.

The main characteristics of the method can be given as:

- The method does not require complex models of gas phase mixing.
- It provides full range of $K_l\bar{a}$ values in a short period of time as steady states are rapidly achieved following a change in operating variables such as agitator speed or the gassing rate.
- The method can be used in low and medium viscosity systems and gives data comparable to conventional dynamic and steady state techniques.
- The method is insensitive to variables such as catalase concentration and hydrogen peroxide addition rate.

The method is applied to low and medium viscosity solutions and its applicability to the high viscosity solutions needs to be tested. Also the catalyst used, catalase is a protein and proteins are widely regarded as foam enhancing agents, which will alter the values of mass transfer coefficients. Due to reactivity of H_2O_2, catalase may lose activity and hence use of method is not permitted in many complex solutions such as fermentation broths.

6. Response methods

The response methods are discussed in detail by Davies et al. [23], Gibilaro et al. [24] and are classified as initial response where initial response of the dissolved gas concentration in the liquid is measured and double response method where both the liquid and outlet gas dynamic responses are measured for the sake of material balance. The initial response method also requires accurate estimation of the time of gas sparging in the solution as derivatives of the liquid response at time $t = 0$ has to be estimated. The computational procedure for these response methods have been well described by Davies et al. [23], Gibilaro et al. [24] and Chapman et al. [25]. The main advantage of the method is that the $K_l\bar{a}$ values obtained are independent of the gas phase mixing. Gibilaro et al. [24] have shown that there was good agreement between double and initial response method for smaller tank ($T = 0.305$ m) used in the experimentation and also the results from larger tank ($T = 0.61$ m) correlate well with the smaller tank. This suggests that assumption of perfect liquid mixing remains acceptable for the larger tank also. The double response method is reliable and consistent as compared to other methods and insensitive to the operating such as hold-up and geometric parameters. The initial response method was less reproducible than the double response method and had a greater dependency on the volumetric gas flow rate and hold up. Davies et al. [23] have presented the following equations from the experimental data obtained for the Initial and Double response methods.

Double response method:

$$K_l\bar{a} = 2.044\mathrm{e} - 3 \left(\frac{P_g}{V}\right)^{0.64} (V_g)^{0.22} \tag{11}$$

Initial response method:

$$K_l\bar{a} = 2.57\mathrm{e} - 3 \left(\frac{P_g}{V}\right)^{0.76} (V_g)^{0.45} \tag{12}$$

The initial response method depends more on the volumetric gas flow rate and the hold-up while dependence is lower on power consumption as compared to the double response method as evident from the exponents in the equation (Exponents of 0.64 and 0.76). The initial response method uses only the initial part of the response curve as compared to whole response in the double response and in the initial part the exponential increase in the hold-up gives a greater dependence of initial response method on hold-up and thus, higher exponent over V_g. Same explanation can be given for the dependence of $K_l\bar{a}$ on the power consumption. As there is steady increase in gas quantity in the vessel, the extent of enhancement caused in the interfacial area would be larger than when steady state is reached as in double response method. The discrepancy between the two methods is largely due to the assumption of perfectly backmixed liquid phase. The effect of poor liquid mixing on double response will be lower as the whole response is used in the analysis. The two methods agree for small scale but on a large scale at high values of V_g and P_g/V, there is a significant departure (Table 1). This again confirms the earlier arguments used to explain the variation in the prediction of Eqs. (11) and (12).

7. Comparison of various methods

In this article only the methods which involve air, oxygen or nitrogen as the transferring gas are discussed as these are helpful in the determination of mass transfer coefficient in the large scale bioreactors.

Table 2 gives the various correlations given by various authors based on the above mentioned measurement techniques.

From the equations given in Table 2, for commonly observed values of power consumption (500 to 5000 W m $^{-3}$) and the superficial velocity ($V_g = 0.001$ to 0.03 m s^{-1}) , mass transfer coefficient value is evaluated and these are given in the Tables 3–6. Also Figs. 1–5 represent the plots of the mass transfer coefficient calculated from different methods against Power consumption per unit volume at a constant value of V_g. The plot does not include Steady state sulfite method as the values predicted are about 150% higher as compared to other methods. The plots and various values of the mass transfer coefficients are based on the correla-

Table 3
$(P/V) = 5000\,\mathrm{W\,m^{-3}}$ and $V_g = 0.001\,\mathrm{m\,s^{-1}}$

Method	MTC (s^{-1})	Difference[a] (%)
Dynamic	0.050918	23.79
Steady state	0.7576	1033
DPM	0.066813	–
Peroxide	0.024611	63.16
Initial response	0.07437	11.31
Double response	0.1042	55.92

[a] The difference is evaluated as % variation from the DPM method as it is found to be most useful for the bioreactors.

Table 4
$(P/V) = 5000\,\mathrm{W\,m^{-3}}$ and $V_g = 0.017\,\mathrm{m\,s^{-1}}$

Method	MTC (s^{-1})	Difference[a] (%)
Dynamic	0.2418	10.68
Steady state	2.353	768.8
DPM	0.2708	–
Peroxide	0.16426	39.34
Initial response	0.26614	1.73
Double Response	0.194	28.25

[a] The difference is evaluated as % variation from the DPM method as it is found to be most useful for the bioreactors.

Table 5
$(P/V) = 900\,\mathrm{W\,m^{-3}}$ and $V_g = 0.02\,\mathrm{m\,s^{-1}}$

Method	MTC (s^{-1})	Difference[a] (%)
Dynamic	0.09617	4.273
Steady state	0.2994	224.7
DPM	0.09223	–
Peroxide	0.08181	11.3
Initial response	0.0778	15.66
Double response	0.0672	27.13

[a] The difference is evaluated as % variation from the DPM method as it is found to be most useful for the bioreactors.

Table 6
$(P/V) = 500\,\mathrm{W\,m^{-3}}$ and $V_g = 0.03\,\mathrm{m\,s^{-1}}$

Method	MTC (s^{-1})	Difference[a] (%)
Dynamic	0.08497	12.132
Steady state	0.1699	124.25
DPM	0.07581	–
Peroxide	0.08143	7.45
Initial response	0.05719	21.12
Double response	0.05043	33.44

[a] The difference is evaluated as % variation from the DPM method as it is found to be most useful for the bioreactors.

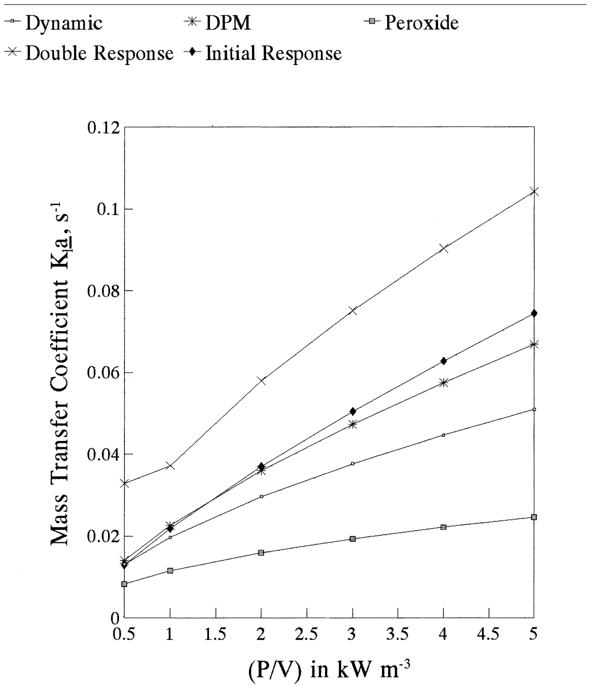

Fig. 1. Mass transfer coefficient value from different methods as a function of P/V in $\mathrm{kW\,m^{-3}}$ at $V_g = 0.001\,\mathrm{m\,s^{-1}}$.

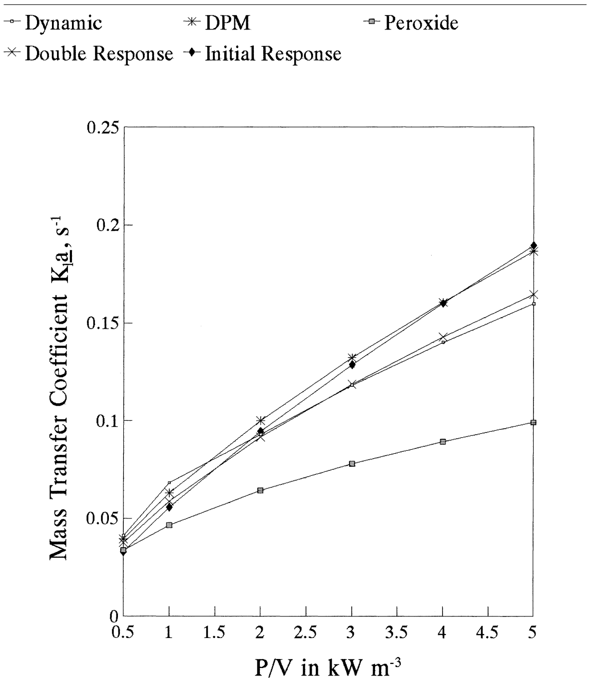

Fig. 2. Mass transfer coefficient value from different methods as a function of P/V in $\mathrm{kW\,m^{-3}}$ at $V_g = 0.008\,\mathrm{m\,s^{-1}}$.

tions developed by various authors who have used different methods for estimation of the mass transfer coefficient.

It can be seen from the graphs and the tables, that the different methods give values of $k_l\bar{a}$ which are far apart and errors defined as the variation from the values given by DPM are calculated assuming the DPM as the base.

Figs. 1–5, indicate at a glance, the range of applicability of the various correlations and hence the techniques used for the development of these correlations. Comparison of the figures indicate, that at very low values of gas superficial velocities and at low power consumption per unit volume, all the methods except the peroxide method and steady state sulfite method give reasonable(within ± 25%) estimates of $K_l\bar{a}$. At low to medium V_g values, the predictions of various methods differ by more than few hundred percents. At rela-

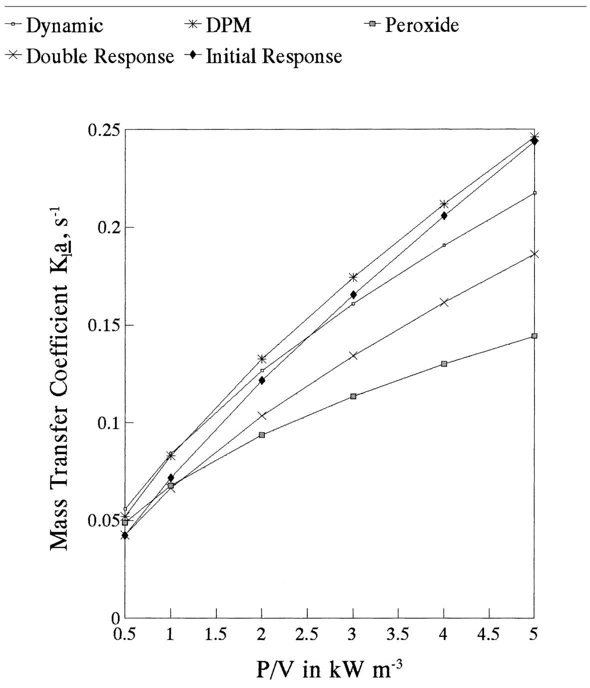

Fig. 3. Mass transfer coefficient value from different methods as a function of *P*/*V* in kW m^{-3} at $V_g = 0.014\,\mathrm{m\,s^{-1}}$.

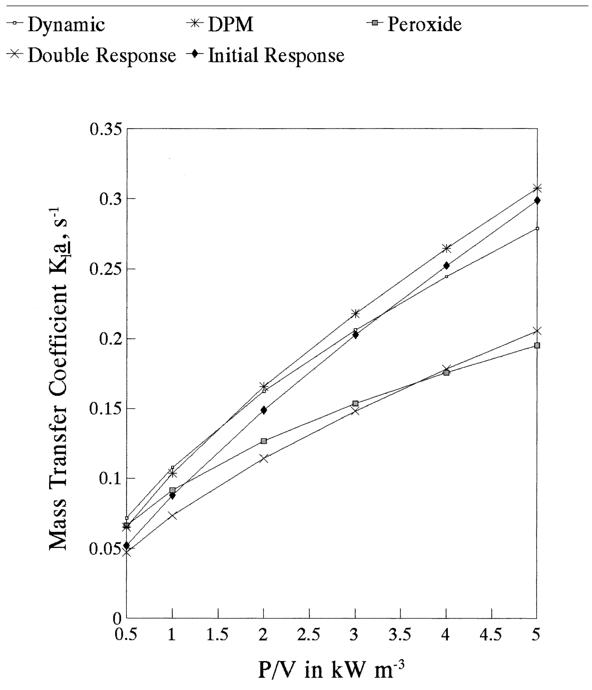

Fig. 4. Mass transfer coefficient value from different methods as a function of *P*/*V* in kW m^{-3} at $V_g = 0.022\,\mathrm{m\,s^{-1}}$.

tively higher superficial gas velocities, peroxide and double response methods underestimate $K_l\bar{a}$ whereas other methods predict $K_l\bar{a}$ which are somewhat higher but equal. The steady state sulfite method, not plotted in the figures, is not useful over the entire range (Tables 3–6 clearly illustrate this fact).

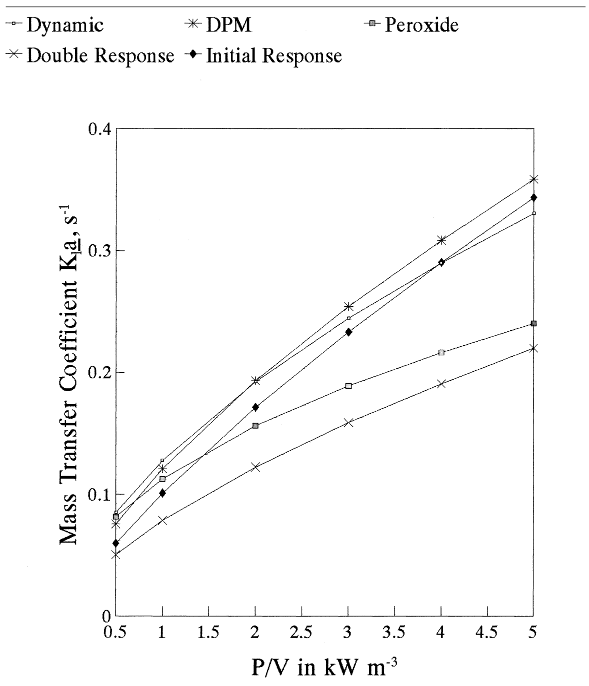

Fig. 5. Mass transfer coefficient value from different methods as a function of *P*/*V* in kW m^{-3} at $V_g = 0.03\,\mathrm{m\,s^{-1}}$.

8. Conclusion

The errors associated with the dynamic methods range from 15 to 100% as compared to DPM depending on the value of the mass transfer coefficient and other hydrodynamic conditions existing in the reactor such as gas phase mixing. Also dynamic method require extensive knowledge of the gas–liquid mixing patterns which may not be the case always in complex systems observed in bioreactors. Any simplification regarding this would necessarily result in the errors of measurement. The various other drawbacks are already discussed in detail.

The DPM eliminates most of the errors associated with the dynamic methods and also use of air instead of oxygen does not affect the accuracy of the method. It can also be used for measurement in individual stages of a multiple impeller systems which are nowadays becoming increasingly important [26] with acceptable degree of accuracy.

The steady state sulfite method is not recommended as it gives inaccurate values as compared to other methods for industrial scale and also use of pure oxygen for accurate estimation of mass transfer coefficient is highly uneconomical when other methods are available with a sufficient degree of accuracy.

The applicability of the peroxide method to large scale fermentors and high viscosity systems requires some comments. Also the foam enhancement due to catalase and reduction of activity of catalase due to higher reactivity of H_2O_2, would give errors in the measurement. No exact quantification in this area is available still and hence could form an area for research.

The response methods are also found to be satisfactory for the measurement in the stirred vessels but their applicability to the bioreactors where one encounters medium to high viscosity of the broth and non-coalescing fermentation media has to be tested. Also the assumption of perfectly mixed liquid phase may not be valid for large scale vessels as is evident from the discrepancies observed for the initial and double response methods.

Thus, with the quantification of $K_l\bar{a}$ values based on the various correlations given in literature for various methods, it appears that, depending on the range of the variables i.e. (P/V) and V_g, appropriate method needs to be chosen, whereas the dynamic pressure method is the most useful method with a small degree of approximations for gas–liquid mixing in the reactor and is suitable for large scale bioreactors with errors less than 10%, over the entire range of the operating conditions encountered in the fermentor operation.

9. Notations

$\bar{a}$	Interfacial area (m^{-1})
Δc	Concentration driving force ($kg\,m^{-3}$)
C_G	Oxygen concentration in gas phase ($kg\,m^{-3}$)
C_{Gi}	Oxygen concentration in gas phase at inlet ($kg\,m^{-3}$)
C_{Go}	Oxygen concentration in gas phase at outlet ($kg\,m^{-3}$)
C_L	Oxygen concentration in liquid phase ($kg\,m^{-3}$)
D	Diameter of the impeller (m)
H	Henry's constant
K	Dimensionless mass transfer coefficient
$K_l\bar{a}$	Mass transfer coefficient (S^{-1})
N	Impeller speed (rpm)
P	Power consumption (W)
P_i	Inlet pressure (Pa)
P_o	Outlet pressure (Pa)
Q_{Gi}	Gas flow rate at inlet ($m^3\,s^{-1}$)
Q_{Go}	Gas flow rate at outlet ($m^3\,s^{-1}$)
Q_i	Hydrogen peroxide flowrate ($m^3\,s^{-1}$)
Q_l	Volumetric gas flow rate at the inlet ($m^3\,s^{-1}$)
R	Gas constant
r_1	Rate of the reaction
T	Diameter of the Vessel (m)
V, V_l	Liquid volume (l)
V_g	Gas superficial velocity ($m^3\,s^{-1}$)
$[H_2O_2]_i$	Concentration of Hydrogen peroxide in inlet ($mol\,l^{-1}$)

9.1. Greek Notations

μ_1	First moment of the oxygen response to the pulse disturbance
ϵ_g	Steady state value of gas hold up in dispersion
ϵ	Dimensionless gas hold-up

9.2. Acronyms

OTR	Oxygen transfer rate
DPM	Dynamic Pressure Method
MM	Liquid perfectly mixed and gas perfectly mixed model
MP	Liquid perfectly mixed and gas in plug flow model
MTC	Mass transfer coefficient

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