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Amir Kapic
Iowa State University

Samuel T. Jones
Iowa State University

Theodore J. Heindel
Iowa State University, theindel@iastate.edu

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Abstract
A myoglobin assay for measuring concentrations of dissolved carbon monoxide (CO) from an artificial synthesis gas blend (20% CO, 18% CO2, 52% N2, and 10% H2) was utilized to determine volumetric CO–water mass-transfer rates in a 0.211-m-diameter stirred-tank reactor (STR). The data are well correlated using the power density and superficial gas velocity, but this correlation is valid only for this STR size. A gas–liquid scale-up model developed for dissolved oxygen mass-transfer rates using air was used to develop a CO–liquid scale-up model for syngas fermentation. The model is applicable in the STR hydrodynamic range associated with after-large-cavity (ALC) formation and assumed to hold for other STR sizes.

Disciplines
Complex Fluids | Mechanical Engineering | Thermodynamics

Comments
Carbon Monoxide Mass Transfer in a Syngas Mixture

Amir Kapic, Samuel T. Jones, and Theodore J. Heindel*

Department of Mechanical Engineering, 2025 Black Engineering Building, Iowa State University, Ames, Iowa 50011

A myoglobin assay for measuring concentrations of dissolved carbon monoxide (CO) from an artificial synthesis gas blend (20% CO, 18% CO2, 52% N2, and 10% H2) was utilized to determine volumetric CO–water mass-transfer rates in a 0.211-m-diameter stirred-tank reactor (STR). The data are well correlated using the power density and superficial gas velocity, but this correlation is valid only for this STR size. A gas–liquid scale-up model developed for dissolved oxygen mass-transfer rates using air was used to develop a CO–liquid scale-up model for syngas fermentation. The model is applicable in the STR hydrodynamic range associated with after-large-cavity (ALC) formation and assumed to hold for other STR sizes.

Introduction

Fermentation is a potential pathway for converting synthesis gas (syngas) into organic compounds such as bioplastics, ethanol, butanol, acetic acid, butyric acid, and methane.1 Lynd2 has suggested that syngas fermentation offers cost and efficiency advantages in the production of biobased products from a wide variety of biomass feedstocks. In replacing petroleum-based products with biobased products, the syngas approach employs waste gases from refinery operations into usable products, such as plastics, chemicals, and fuels.1 Some microorganisms, such as Rhodospirillum rubrum, need for a solid substrate,4 making them well suited for converting syngas into various fuels and chemicals.

In the fermentation industry, two fermentation types are typically distinguished, namely, aerobic fermentation and anaerobic fermentation, as discussed in detail by Bellgardt.3 Aerobic fermentations require an oxygen supply that is normally acquired from the surrounding environmental air. Anaerobic fermentations are conducted in an oxygen-free environment and might utilize, for example, carbon monoxide (CO) as the sole carbon source from a gas mixture. For both fermentation types, a general premise is that microorganisms take one component and biologically convert it into another component. Therefore, dissolved gas (e.g., CO and O2) mass-transfer rates are very important in determining reactor performance.

Stirred-tank reactors (STRs) operating with continuous feed and overflow can be used for carrying out biochemical processes such as anaerobic fermentation for the conversion of waste gases from refinery operations into usable products, such as plastics, chemicals, and fuels.1 Some microorganisms, such as Rhodospirillum rubrum, can directly utilize CO and have no need for a solid substrate,4 making them well suited for converting syngas into various fuels and chemicals.

The transfer of CO from syngas to the microorganisms in a fermentation process occurs in a number of steps: (i) transfer of CO from a syngas bubble into the fermentation liquid medium, (ii) transfer of the dissolved CO from the fermentation liquid medium to the microorganisms, and (iii) uptake of the dissolved CO by the microorganisms. A significant bottleneck in the syngas fermentation process appears to be syngas–liquid mass-transfer limitations,1,5 which are a result of the low solubilities of the major syngas components (CO and H2) in the aqueous fermentation broth when it contains a high cell concentration. If the cell concentration is too low, the system yield will be low, and the conversion process will be kinetically limited.6

This work investigates CO mass transfer from an artificial syngas blend of 20% CO, 18% CO2, 52% N2, and 10% H2, which represents the composition from an actual syngas mixture.7 To focus only on the CO–liquid mass-transfer process, tap water is used as a model fluid (i.e., in the absence of microorganisms) in a benchtop STR. A scale-up model developed from O2 mass-transfer studies,8 and based on expected STR hydrodynamic flow regimes, is shown to work well at correlating the dissolved CO–liquid mass-transfer rates from this study.

Experimental Methods

Experimental Facility. Experiments were carried out in a 14-L BioFlo 110 fermentor (New Brunswick Scientific Co., Edison, NJ) filled with water to a height (H) equal to the vessel diameter (T = 0.211 m); this corresponds to a working volume of V1 = 7 L. A six-bladed Rushton impeller of diameter D = 0.075 m (D/T = 0.35) was used at a constant clearance ratio of one-quarter of the static liquid height above the base of the tank (i.e., c = 1/4H). Four symmetrically located baffles suppress vortex formation. The impeller blade and baffle dimensions, as well as all other vessel geometric characteristics in the system, correspond to the well-known standard vessel configuration.9 Figure 1 shows a schematic of the experimental facility used in this study. The tank was filled with a single charge of tap water and maintained at a constant temperature of 30 °C using a heat blanket and a recirculating water bath. With a single charge of fluid and a continuous gas supply, the STR was operated in semibatch mode. An artificial syngas mixture of 20% CO, 18% CO2, 52% N2, and 10% H2 was supplied through a multi-gas component rotameter having four inlets and one exit and a needle valve for precise control of the flow rate (Cole-
This gas mixture represents the composition from an actual gasified biomass. Artificial syngas was then fed to the reactor through Tygon FEP-lined tubing to minimize gas diffusion through the tube walls and through a ring sparger located at a distance of \( r/3 \) below the impeller. The ring sparger was the standard sparger that accompanies the BioFlo 110 fermentor: a 6.3-mm stainless steel tube with a 78-mm-diameter ring at its base and five 0.8-mm-diameter holes symmetrically located on the top side of the ring. The tank was also equipped with a pH electrode (New Brunswick Scientific Co., Edison, NJ). More detailed information of the equipment and the STR geometry is given by Kapic.10

The \( k_L a \) values for dissolved CO from syngas were determined by introducing a step change in CO concentration and then measuring the dissolved CO concentration as a function of time. The specified syngas flow rate of interest was adjusted prior to the start of the experiment. Liquid samples were collected at the sample port (Figure 2) while a continuous gas-liquid mixture was recirculated from the tank bottom and back into the reactor. A Masterflex L/S peristaltic pump system was used in the Tygon LFL recirculation line that was capable of a maximum liquid pumping rate of 2.2 L/min. When the pump was operated at its maximum flow rate, less than 0.5 s was required for the liquid to travel from the tank bottom to the sample port. Even though liquid was withdrawn from the STR, the same liquid was returned immediately, so that the liquid in the STR and recirculation pump formed a closed system. Therefore, with a continuous gas flow through it, the STR operated in a semibatch mode.

While the recirculation pump was recirculating a small liquid stream throughout the STR, the syngas valve mounted in the exiting stream of the multi-gas rotameter was opened, and a digital stopwatch was simultaneously started. A single 10-\( \mu \)L liquid sample was withdrawn every 5 or 10 s from the sample port (Figure 2) using gastight syringes from Hamilton. To allow for manual sampling at 5- or 10-s intervals, multiple syringes were loaded into the sampling port prior to each test, as shown in Figure 2. A single syringe sample was then removed at the designated sample time. Each syringe was labeled appropriately to eliminate confusion between sample times. After approximately 4–5 min of syngas sparging through the STR, two CO-saturated liquid samples were taken to determine the steady-state dissolved CO saturation from syngas. Usually, steady state was reached in less than 2 min, as tested from multiple sample runs.

The impeller was driven by a variable-speed dc motor (Magmotor Corporation, model C32-E-450X), which was connected to the primary control unit (PCU) of the BioFlo 110 fermentor for dissolved carbon monoxide measurements or to an Electro (model PS-5R) ac/dc converter for power measurements. Power measurements, recorded at a frequency of 2 Hz, were repeatable with a maximum standard deviation of ±1.25% within the mean and were typically reproducible to within ±0.5%. The maximum uncertainty in gassed power measurements at the full flow meter scale was estimated to be ±0.83%, with the worst-case percent uncertainties in measured gassed and ungassed power numbers of ±1.6% and ±1.4%, respectively. Complete details of the power measurements and their results are provided by Kapic.10

**Syngas–Liquid Mass-Transfer Measurements.** Dissolved CO concentrations were determined using a myoglobin-protein assay as described by Kundu et al.11 The same method was used by Riggs and Heindel12 to determine pure CO concentrations in water. A Cary-50 Bio spectrophotometer from Varian (Mulgrave, Victoria, Australia) was used to assess the dissolved CO concentration in the liquid samples. The spectrophotometer was set up to measure light absorption in the wavelength range of 400–700 nm, as the peak absorbance for CO-bound myoglobin occurs at 423 nm. The myoglobin used in the dissolved CO concentration measurements, purchased from Sigma-Aldrich, was derived from horse heart as lyophilized powder and was at least 90% pure. Samples were prepared and scanned in 1.5-mL-nominal-volume semimicro disposable polystyrene cuvettes. These cuvettes, having a 1-cm path length, are usable in the spectral range of 340–800 nm. Measuring the dissolved CO concentration with the myoglobin technique has been shown to be repeatable.10,12 The associated uncertainty in
the dissolved CO concentrations was estimated to be typically about ±10%. A more detailed explanation of preparing and collecting liquid samples and measuring the dissolved CO concentration can be found elsewhere.10,12

Assuming that the liquid phase is well mixed, that CO mass transfer from the gas phase to the liquid phase is liquid-phase-controlled, and that the CO concentration in the liquid at the syngas—liquid interface is in equilibrium with the CO concentration in the syngas, the volumetric mass-transfer coefficient \((k_La)\) can be determined from

\[
\frac{dC}{dt} = k_La(C_i - C)
\]

\[\tag{1}
\]

where \(C\) is the dissolved CO concentration in the liquid at time \(t\) and \(C_i\) is the CO concentration at the syngas—liquid interface assumed to be in equilibrium with the bubble. The solution of eq 1 yields

\[
\ln \left( \frac{C_i - C}{C_i - C_o} \right) = (-k_La)t
\]

\[\tag{2}
\]

where \(C_o\) is the initial dissolved concentration. Equation 2 was used with a nonlinear least-squares regression technique in JMP 5.1 statistical software (SAS Institute, Inc.) and the experimental data to determine values for \(C_i\), \(C_o\), and \(k_La\), where \(k_La\) is the parameter of interest. Figure 3 shows an example of the \(k_La\) determination for CO in water at an impeller speed \((N)\) of 700 rpm and a gas flow rate \((Q_g)\) of 12 L/min from an artificial syngas mixture of 20% CO, 18% CO\(_2\), 52% N\(_2\), and 10% H\(_2\).

The \(k_La\) value for a given condition was typically determined by fitting eq 2 to three data sets, as shown in Figure 3. Note that the three data sets used to determine \(k_La\) were very repeatable. Also note that \(C_o\) was nonzero from the nonlinear least-squares regression, but was extremely small. This satisfies the experimental initial condition of a negligible initial dissolved CO concentration.

Experimental Results

Dissolved CO Mass-Transfer Rates. Benchtop gas—liquid mass-transfer studies should be completed under operating conditions that are physically realistic for operation of an industrial-scale STR. Kapic and Heindel\(^8\) have shown that, for a proper STR scale-up, it is desirable that similar hydrodynamic regimes be achieved between different reactor sizes. They suggested that STR scale-up should be performed when the reactor operates in the “after-large-cavity” (ALC) region, described by Smith and Warmoeskerken,\(^13\) because the ALC region is associated with minimum power consumption as shown on a typical power curve.\(^8\) Additionally, the STR must be operated between the complete dispersion and recirculation limits discussed by Nienow et al.\(^14,15\) for the most economical reactor performance. Kapic and Heindel\(^8\) used an STR identical to that used in this study, with gas flow rates of 5 ≤ \(Q_g\) ≤ 15 L/min and impeller speeds of 400 ≤ \(N\) ≤ 800 rpm, to maintain STR operation in the ALC region. When the gas flow rates fell in the range of 1 ≤ \(Q_g\) ≤ 5 L/min, before-large-cavity (BLC) conditions were observed, and data in this region were not correlated with data in the ALC region. Therefore, the operating conditions corresponding to the ALC region (5 ≤ \(Q_g\) ≤ 15 L/min, 400 ≤ \(N\) ≤ 800 rpm), as determined by Kapic and Heindel\(^8\) for this STR, were used for the dissolved CO mass-transfer measurements in this study.

The \(k_{L,a}\) values for dissolved CO from the artificial syngas mixture at constant impeller speed \((N)\) and at constant syngas flow rate \((Q_g)\) are shown in Figures 4 and 5, respectively. Figure 4 shows that the \(k_{L,a}\) trends are similar to those observed for air and pure O\(_2\) for similar operating conditions.\(^10\) The error bars represent the standard error from the mean \(k_{L,a}\) values typically obtained from three runs. Furthermore, at constant syngas flow rate in Figure 5, the \(k_{L,a}\) values for dissolved CO increase in an approximately linearly fashion, which agrees with observations for air and pure O\(_2\).\(^10\) The higher \(k_{L,a}\) values at higher impeller speeds and gas flow rates in Figure 5 are most likely caused by a pH change due to the formation of carbonic acid (H\(_2\)CO\(_3\)), involving a simultaneous chemical reaction and CO\(_2\) mass transfer. The initial pH value for all experiments in pure tap water was ~9.2, and by the time all liquid samples had been withdrawn, the pH had dropped to ~5.7. If CO\(_2\) is excluded from the artificial syngas mixture, the pH remains constant throughout the experiment.\(^10\) Thus, it can be assumed that the
change in liquid acidity had an instantaneous effect on the CO solubility, resulting in greater sensitivity of the CO mass-transfer rates to increases in impeller speed and gas flow rate as shown in Figure 5. The higher impeller speeds can also cause liquid recirculation in the STR. This will increase the mass-transfer rate as a result of the increased gas residence time in the tank.

The $k_L a$ values reported in Figures 4 and 5 range from 0.02 to 0.08 s$^{-1}$ (from 72 to 288 h$^{-1}$). These values are generally higher than those reported by others$^{6,16-18}$ because the current study focuses on syngas–water mass-transfer measurements in the absence of microorganisms, whereas Cowger at al.$^{16}$ Klassen et al.$^{17}$ and Vega et al.$^{6,11}$ measured the transport of CO from the gas phase into the liquid phase, followed by microorganism uptake. Hence, the current study does not include the additional resistances to mass transfer. Those authors also used continuous stirred-tank reactors that were much smaller than the STR used in this study (i.e., liquid volumes of 1250 and 350 mL compared to 7 L in this study), so the hydrodynamic conditions might not be similar. Kapic and Heindel$^8$ concluded that, when comparing values from different sized tanks, STR hydrodynamics should be similar. Furthermore, the above authors measured mass-transfer rates under steady-state conditions, whereas the current study uses a transient method. The CO mass-transfer rates in this study are also higher than those reported by Riggs and Heindel$^{12}$ because the current study ensured that the STR was operating in the ALC region, whereas Riggs and Heindel were operating in the BLC region. This emphasizes that similar STR hydrodynamics are required for the comparison of mass-transfer rates.

Although all of the data in this study were acquired in the ALC region, most of the literature correlations disregard the STR hydrodynamics in $k_L a$ correlation development and use a mass-transfer correlation as a function of power density ($P_g/V_L$) and superficial gas velocity ($U_g$), following the general form

$$k_L a = C \left(\frac{P_g}{V_L}\right)^\alpha U_g^\beta$$

Figure 6 shows the $k_L a$ values for dissolved CO from the artificial syngas mixture in the ALC region measured in tap water at 30 °C and correlated in the form of eq 3

$$k_L a = 2.63 \times 10^{-2} \left(\frac{P_g}{V_L}\right)^{0.607} U_g^{0.609}$$

Equation 4 correlates dissolved CO mass-transfer rates from 25 data points, and as shown in Figure 6, the correlation fits the data to within ±20%. The exponents in eq 4 are also comparable to expected results in the literature.$^{19}$ Various researchers have shown that a correlation in the form of eq 3 was unsuccessful when used in an STR scale-up analysis, and the exponential constants appear to be a complicated function of reactor size and/or other variables.$^{20,21}$ For example, a correlation for O$_2$–liquid mass transfer based on the energy input criteria of the form in eq 3 was shown to be flow-regime-dependent and restricted to a single STR size.$^8$

Geometric similarity is usually satisfied in an STR scale-up analysis, and therefore, if eq 3 is used for an STR scale-up model, it should account for the hydrodynamic similarity between different reactor sizes. It is likely that the power density ($P_g/V_L$) term alone is not enough to achieve gas–liquid hydrodynamic similarity in the STR flow patterns, and additional terms for scale-up are needed to account for required flow pattern similarity.

**CO Mass-Transfer Scale-Up in an STR.** Scale-up in mixing applications, such as the volumetric gas–liquid mass-transfer coefficient ($k_L a$) in an STR, is based on a similarity principle. To transfer benchtop data to an industrial-scale reactor, according to the similarity principle, it is reasonable to assume that the following scaling criteria are applicable: (i) geometric similarity, (ii) kinematic similarity, and (iii) dynamic similarity. Geometric similarity requires constant ratios between length dimensions in the two vessels. Kinematic similarity requires that the ratios of the velocities between corresponding points in geometrically similar vessels are equal. Dynamic similarity occurs between two vessels if they are geometrically and kinematically similar and the ratios of forces between the corresponding points in the two vessels are the same.

It is often not possible to achieve “complete similarity”, and a dimensional analysis cannot be used to solve every problem.$^{22}$
Kinematic and dynamic similarities can be combined into a single hydrodynamic similarity. Geometric similarity is usually satisfied in practice, as the benchtop and industrial-size STRs are generally of similar geometries. Hence, one might think that an STR scale-up is possible if a complete hydrodynamic similarity between the two geometrically similar vessels is satisfied; this implies a similarity in flow patterns. Studies on flow patterns in STRs have been reported. For example, Smith\(^2\) stated the following: “Gas flow pattern is important. It controls the degree of recirculation and back mixing of the gas phase, which in turn determines the mean concentration driving force for mass transfer.” Similar flow patterns imply similar ratios of mass-transfer driving forces between the benchtop and industrial-scale STRs. A scale-up model developed from literature data on \(O_2\)–liquid mass transfer in a wide range of STR sizes (0.211 m \(\leq T \leq 2.7\) m) has been shown to be applicable when the STR is operated in the ALC region.\(^8\) and Kapic and Heindel\(^8\) have shown that the dispersion parameter \((N/ND)\) is reliable in achieving hydrodynamic similarity in different STR sizes. This can be explained by rearranging eq 6 to read\(^15\)

\[
\left( \frac{N}{ND} \right) = 4 \left( \frac{Q}{T} \right)^{0.25} \frac{D^2}{Q_g} \tag{8}
\]

For a single reactor size, \(N/ND\) is directly proportional to the square root of \(Q_g\), or the amount of gas at complete dispersion. Similarly, the \(N/ND\) ratio is then proportional to the ratio of the amount of gas at impeller speed \(N\) relative to the amount of gas at impeller speed \(ND\). Hence, the dispersion parameter \(N/ND\) accounts for the gas–liquid hydrodynamics of the various bulk flow regimes such as those discussed by Nienow et al.\(^14,15\) and Smith and Warmoeskerken\(^13\) (i.e., flooding, loading, complete dispersion, recirculation, and the ALC–BLC transition).

Conclusions

Volumetric mass-transfer rates for carbon monoxide from an artificial syngas mixture were obtained in a 0.211-m-diameter STR operated in the after-large-cavity region. A myoglobin assay was used to determine the dissolved CO concentrations as a function of time. The resulting CO–liquid volumetric mass-transfer rates were correlated based on the power density (eq 4). This correlation, however, is only valid for the given STR size. A scale-up correlation based on hydrodynamic similarity principles as proposed by Kapic and Heindel\(^8\) was used to develop a scale-up correlation for CO–liquid mass transfer (eq 7).

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$C_i =$ equilibrium dissolved gas concentration (mol m$^{-3}$)
$C_t =$ experimental constant
$c =$ impeller clearance above the base (m)
$D =$ impeller diameter (m)
$Fl_g =$ gas flow number, $Fl_g = Q_g / ND^3$
$Fr =$ Froude number, $Fr = N^2/Dg$
$g =$ gravitational constant (m s$^{-2}$)
$H =$ liquid height in vessel (m)
$k_{dl} =$ liquid-side volumetric mass-transfer coefficient (s$^{-1}$)
$N =$ impeller rotational speed (rev s$^{-1}$, unless otherwise noted)
$P_g =$ gassed power input from impeller to liquid (W)
$Q_g =$ volumetric gas flow rate (m$^3$ s$^{-1}$, unless otherwise noted)
$T =$ vessel inside diameter (m)
$t =$ time (s)
$U_g =$ sparged superficial gas velocity (m s$^{-1}$)
$V_i =$ liquid volume in vessel (m$^3$)

**Subscript**

CD =$ complete dispersion

**Abbreviations**

ALC =$ after-large-cavity
BLA =$ before-large-cavity
STR =$ stirred-tank reactor

**Greek Symbols**

$\alpha, \beta =$ exponents

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**Literature Cited**


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