Bioreactor Development for Biological Hydrogen Production

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Introduction

The biologically mediated water-gas shift reaction may be a cost-effective technology for the conditioning of synthesis gas for storage or direct use within a hydrogen fuel cell. NREL researchers have isolated a number of photosynthetic bacteria that can perform the water-gas shift reaction, in which carbon monoxide is oxidized to carbon dioxide while simultaneously water is reduced to hydrogen. The overall reaction stoichiometry is of this reversible reaction is:

$$CO + H_2O \xleftrightarrow{K} CO_2 + H_2$$

Since the reaction is exothermic, the equilibrium constant decreases with increasing temperature. The currently accepted industrial process for this reaction uses a catalytic reactor operating at elevated temperatures where the equilibrium constant K is approximately 10. Since the photosynthetic bacteria operate at ambient temperatures, the equilibrium constant is approximately 10^4. Thus, there are significant advantages to operating at ambient temperature with respect to reaction equilibrium.

Whether the ambient temperature reaction kinetics are sufficiently rapid is not clear, however. The water-gas shift reaction occurs very rapidly within the photosynthetic bacterial cell during both light and dark periods. Preliminary data already collected at NREL suggest that this reaction is far more rapid than the rate at which CO can be supplied to the bacteria. This is consistent with many other gas/liquid biological reaction systems, including aerobic fermentations, which are commonly limited by the transfer rate of oxygen to the liquid phase.

One of the goals of this project is to accurately predict the economics of a full-scale water-gas shift reaction using photosynthetic bacteria. To increase the accuracy of economic estimates of the full-scale process, it is necessary to collect data from a laboratory-scale bioreactor whose mass transfer characteristics are well understood, and to incorporate these data into an appropriate bioreactor model. The model can then be used to predict the size of a full-scale system. Municipal wastewater treatment systems and biofilters for air pollution control are two examples of biological reactors that have been successfully modeled in this fashion.

The approach we are taking for this task is to assess the mass-transfer characteristics of current generation of NREL bioreactors, to collect performance data using these bioreactors, and then use these data both for a bioreactor model to estimate the size of a full-scale system, and to develop new bioreactor designs.

Past Results

A number of bioreactor designs have been built and tested at NREL. For example, a bioreactor using surface-immobilized bacteria treated a 10% CO/N_2 gas stream for over a year. Other bioreactors using both immobilized and suspended bacterial cultures have been tested as well. Figures 1 and 2 illustrate a bubble-column reactor and an immobilized bioreactor, respectively. Bubble column bioreactors have a suspended bacterial culture through which reactant gas travels, while immobilized bioreactors anchor the bacterial culture on a solid support. Each bioreactor type has certain advantages: a bubble-column bioreactor allows easy inoculation and harvesting of the culture, while an immobilized bioreactor generally exhibits lower pressure drop at a given gas flowrate. In the case of Figure 2, an inverted nylon carpet has been used to immobilize the bacteria.

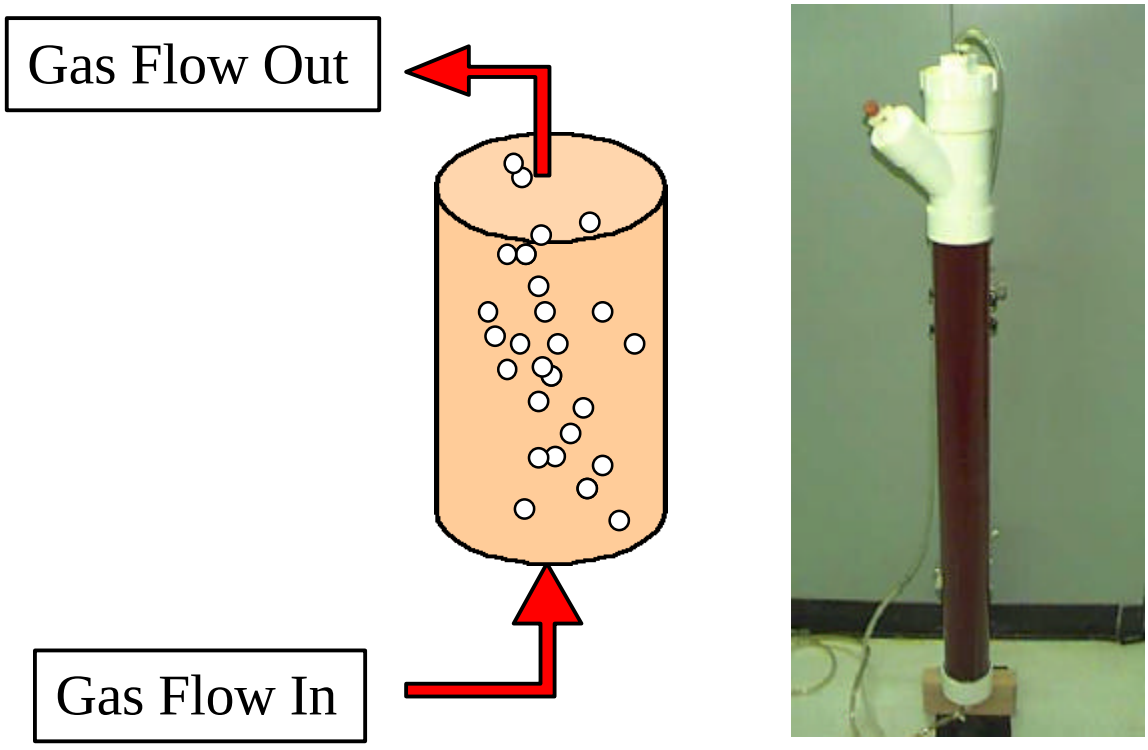

Figure 1. Schematic diagram and photograph of bubble-column bioreactor tested at NREL. The column is 7.6 cm in diameter and 90 cm in height. Reactor achieved 90% conversion of a 10% CO/N_2 feedstream flowing at 125 mL/min.

The bubble column reactor shown in Figure 1 is 7.6 cm in diameter and 90 cm height. It achieved 90% conversion of a 10% CO/N_2 gas stream flowing at 125 mL/min. By adding approximately 25 ppm TWEEN 80 surfactant to the media, the conversion increased to 99% at the same flowrate. The presence of the surfactant apparently stabilizes the bubble phase and prevents bubble coalescence, allowing a higher interfacial area for mass transfer in the reactor. The inverted carpet reactor in Figure 2 was able to achieve 94% conversion of a 10%/N_2 gas stream flowing at 8 mL/min after a bed length of only 22 cm.

Gas-Liquid Mass Transfer Modeling

One of the first significant biochemical engineering problems to be addressed was oxygen transfer to aerobic fermentations for penicillin production during World War II[1]. Since that time, there has been an enormous amount of research in the area of gas-liquid mass transfer in biochemical reactors.

In general, the solubilities of gases of biological interest in aqueous systems is quite low. This leads directly to significant mass transfer resistance by the liquid media. Under these conditions, the rate of mass transfer across the gas-liquid interface can be characterized by the volumetric liquid-side mass transfer coefficient K_La. For the case of extremely fast reaction rate, the rate-limiting step in the reaction is the transfer of the soluble gas to the liquid phase. In this case, the liquid phase concentration of the soluble gas is essentially zero. For the case of a column bioreactor, the appropriate model equations are:

$$u_G \frac{dc_G}{dz} = \frac{K_L a}{H} \cdot c_G$$

$$\frac{c_G(z)}{c_G^o} = \exp\left(-\frac{K_L a}{H \cdot u_G} z\right)$$

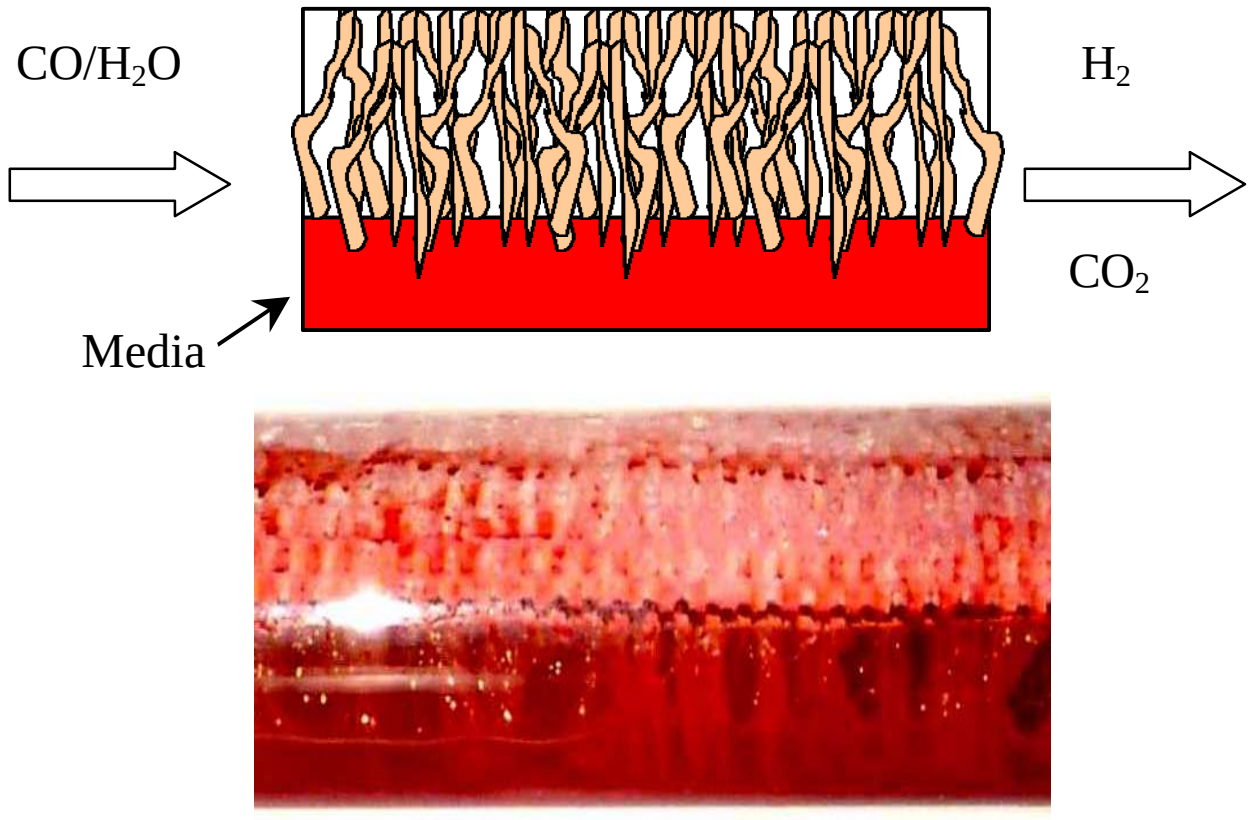

Figure 2. Schematic diagram and photograph of inverted carpet reactor tested at NREL. The nylon carpet fibers hold immobilized bacteria. Product gas CO_2 is absorbed by the liquid media, leaving only H_2 in the gas phase. Reactor achieved 94% conversion of a 10%CO/N_2 feedstream flowing at 8 mL/min in 22 cm of bed length.

Thus, the gas-liquid mass transfer is a first-order process, and the conversion of the gas in question is an exponential function of distance (and therefore residence time) in the reactor. Since the reaction is limited not by the intrinsic activity of the bacteria but by mass transfer rate, the performance of a given bioreactor can be predicted simply by calculating its' mass transfer coefficient, which is a function of reactor geometry, temperature, and liquid and gas flowrates. Thus, the mass transfer characteristics of a particular bioreactor can be determined *independently* of the biochemical reaction occurring in it.

Recently, researchers at the University of Arkansas investigated gas-liquid mass transfer issues for the biological water gas shift reaction. Using the equations to calculate mass transfer coefficients based on CO conversion in a number of different bioreactor configurations. Depending on the reactor configuration tested, the calculated values of the overall mass transfer coefficient were in the range 0.001-0.03 s^{-1}. Table 1 summarizes these results. In the original literature, the mass transfer coefficients were presented in a variety of units. These have been converted to consistent units in Table 1.

We have applied the mathematical model discussed above to the experimental data already collected at NREL. For the NREL bubble column reactor, we calculated values of the mass transfer coefficient K_La of 0.1-0.8 s^{-1}, while for the carpet reactor, we calculated a value of approximately 0.07 s^{-1}. These values are somewhat higher than the data in Table 1, but well within reported ranges for such reactors[2].

Reactor Type	K_La Value		Ref
	Reported	**Calc (s^{-1})**	
CSTR	K_La/H=29.3 mmol/atm/L/h	0.007	[3]
PBR	$K_La e_L/H$=13.3 mmol/atm/L/h; ε_L=.008-.012	0.005	[4]
TBR	$K_La e_L/H$ =450-640 hr^{-1}; ε_L=.008-.012	0.015	[5]
CSTR	28.1-101.1 hr^{-1}; at 300-450 rpm	0.01-0.03	[6]
PBR	2.1 hr^{-1}	0.001	ibid.
TBR	55.5 hr^{-1}	0.015	ibid.
CSTR	14-36 hr^{-1} at 300-700 rpm	0.004-0.01	[7]

Table 1. Literature Values of the overall mass transfer coefficient K_La reported by Klasson et al. The K_La units are presented both as originally reported and in consistent units (see text). CSTR: continuously stirred tank reactor, PBR: packed bubble column reactor, TBR: trickle bed reactor.

Status of Economic Evaluation/Systems Analysis

A preliminary economic evaluation was performed in 1996[8] which indicated that thermal gasification of biomass at $46/T coupled with the biological water-gas shift conditioning (but not including pressure swing adsorption, PSA) would result in a base case of $13/GJ H_2. The PSA step is normally required to remove CO_2, which is a product of the water gas shift reactor. However, since the CO_2 would be removed by the liquid media in the bioreactor, no separate removal process is required. No further economic analysis has been performed since 1996. The quantitative reactor performance data produced by this project will allow a more accurate estimation of the size (and therefore cost) of a full- scale system. In addition, bioreactors with enhanced mass transfer characteristics should reduce the size and therefore the cost of the full-scale systems.

Future Work

The ultimate goal of this task is the development of a cost-effective water-gas shift bioreactor design. To accomplish this goal, we will: characterize the mass transfer characteristics of the current generation of water-gas shift bioreactors at NREL, collect quantitative kinetic information that can be used to determine the size and cost of full-scale systems, and design and test new bioreactor designs with enhanced mass transfer capabilities. The major barriers to developing a bioreactor with enhanced mass transfer capabilities involve a trade-off between mass transfer and power requirements. Chemical reactors often use impellers or mixers to enhance mass transfer, which can significantly increase both the capital and operating costs of the reactors. We are seeking a bioreactor design that will provide very high mass-transfer rates with minimal power input.

Nomenclature

Symbol	Description	Units
a_s	reactor cross-sectional area	cm^2
c_G	gas-phase concentration	mol cm^{-3}
c^o_G	initial gas-phase concentration	mol cm^{-3}
c_L	liquid-phase concentration	mol cm^{-3}
c^o_L	initial liquid-phase concentration	mol cm^{-3}
H	Henry's Law coefficient	--
K_La	overall mass transfer coefficient	s^{-1}
K	chemical reaction equilibrium constant	--
L	reactor length	cm
Q_L	volumetric flowrate of liquid	$cm^3\ s^{-1}$
Q_G	volumetric flowrate of gas	$cm^3\ s^{-1}$
u_L	superficial liquid velocity (Q_L/a_s)	cm s^{-1}
u_G	superficial gas velocity (Q/a_s)	cm s^{-1}
z	axial dimension of reactor	cm

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