BIOREACTOR DEVELOPMENT FOR BIOLOGICAL HYDROGEN PRODUCTION

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Abstract

This report summarizes the work on the development of bioreactors for the biological water gas shift reaction at the National Renewable Energy Laboratory. The motivation and long-term goals of the project are described, and the specific accomplishments of the past year are presented. In the section outlining the mathematical modeling efforts, a number of mathematical models that describe the mass-transfer properties of trickle-bed bioreactors for the biologically-mediated water-gas shift reaction are presented. The work performed to develop a computer-controlled Research/Demonstration Unit to provide a "real-world" synthesis gas source is also reviewed.

Introduction & Background

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 water is simultaneously reduced to hydrogen. The overall stoichiometry of this reversible reaction is:

$$CO + H_2O \xleftrightarrow{K} CO_2 + H_2 \qquad\qquad (1)$$

The current "state-of-the-art" water-gas shift technology is a two-stage, high temperature, high-pressure catalytic process. The reaction is equilibrium-limited at the temperatures required for it to operate sufficiently rapidly, preventing very high CO conversion efficiencies. Polishing steps using thermal catalysis can oxidize the residual CO, but such processes inevitably oxidize H_2 as well as CO.

One significant advantage to using photosynthetic bacteria to perform the water-gas shift reaction is the ability to operate at ambient temperature, where the reaction equilibrium is much

more favorable to hydrogen production. The advantages of low operating temperature, rapid reaction rate, and lack of equilibrium limitation make the biological shift reaction a promising alternative to conventional shift technologies.

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 most aerobic fermentations, where metabolic rates are commonly limited by the transfer rate of a gaseous substrate to the liquid media.

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. The approach we are taking for this project is to collect laboratory performance data using common bioreactor designs, and then use these data in a bioreactor model to estimate the size of a full-scale system. During the course of the laboratory work (and through review of the literature), new bioreactor design ideas are developed for further testing.

Project Activities

Work on this project is divided into two parts. The first part involves the laboratory investigations of bioreactor designs, while the second part involves work on a research/demonstration unit (RDU) that combines syngas production with microbial CO shift for syngas cleanup. As part of the laboratory investigations, we have developed a comprehensive mathematical model of the bioreactor system, which is the principal subject of this report. For the RDU project, we are working to ready the RDU for long-term unattended operation as a supply of "real-world" syngas to a bioreactor.

Laboratory Bioreactor Model Development

We are investigating a number of different biological reactor designs to determine the maximum gas-liquid mass transfer rates we can achieve in the laboratory. In order to fully understand and interpret the laboratory results, we have developed a number of mathematical models to describe the operation of these reactors. This section of the report describes the operation and modeling of a trickle-bed reactor (TBR). TBRs are proven to be very effective for gas-liquid reactions where the mass transfer rate is limited by the resistance in the liquid phase. This is the case for biological processes utilizing sparingly soluble gases like carbon monoxide or oxygen. Figure 1 shows schematic diagrams of a co-current and counter-current TBR.

The reactor is filled with a high porosity support material, commonly called reactor packing. The liquid flows downward around the packing due to gravity, creating a thin film of liquid on the packing surface, and maximizing the amount of gas-liquid interfacial area. The liquid flow is low enough so that it "trickles" down the packing, giving the reactor its name. The gas can either flow upward or downward through the reactor. The relative flow directions of the gas and liquid phase give rise to the nomenclature "co-current" and "counter-current".

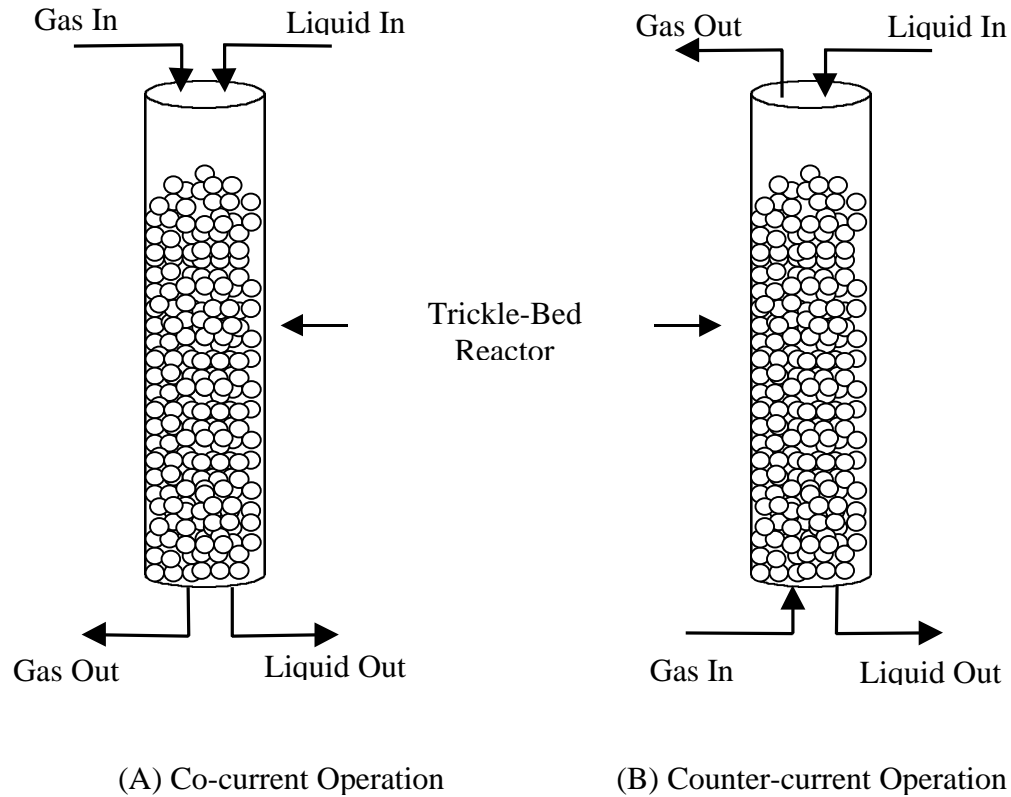(A) Co-current Operation   (B) Counter-current Operation

Figure 1. Schematic Diagram of Trickle Bed Reactors (TBRs) in (A) co-current and (B) counter-current operation. Liquid flow is downward in both cases.

The driving force for mass transfer between the gas and liquid phases is the concentration gradient across the interface. At equilibrium, Henry's Law describes the relationship between the gas and liquid phase concentrations:

$$yP = HC_L \qquad\qquad (2)$$

Any deviation from this equality causes an interphase mass transfer driving force. The rate of gas-liquid mass transfer depends on many factors, including the hydrodynamics of the system in question, the chemical composition of the gas being transferred, and the shape and porosity of the reactor packing. In the situation where the majority of the mass transfer resistance is in the liquid phase, the mass transfer rate is characterized by the liquid-side overall mass transfer coefficient $K_L a$. However, this parameter cannot be measured directly, so we have developed a number of reactor models to help interpret the experimental data.

Mathematical models are useful for a variety of reasons. They are most commonly used to predict the size (and therefore cost) of larger reactor assemblies based on laboratory data, and thereby point out areas where more research could result in significant cost savings in the scaled-up systems. However, reactor models can also be useful as a framework to understand

experimental data, and to help guide the design of future laboratory experiments. This second use is the subject of this section.

Model Descriptions

A number of similar models have been developed for this work. Consider the reactor geometry in Figure 1, with a gas stream flowing at flowrate G containing the gas to be transferred with mole fraction y_{in}. The liquid phase is flowing at flowrate L, with inlet concentration C_L^{in}. As the gas and liquid flow through the column, the concentration gradient across the gas-liquid interface provides the driving force for mass transfer.

Co-current TBR Model

The differential equations that describe the co-current TBR are:

$$\frac{dN}{dz} = -K_L a \cdot e_L \left[\frac{yP}{H} - C_L \right] \tag{3}$$

$$\frac{dC_L}{dz} = \frac{K_L a \cdot e_L}{L} \left[\frac{yP}{H} - C_L \right] \tag{4}$$

$$BC\#1: \quad @ \ z = 0 \quad y = y_{in} \tag{5}$$

$$BC\#2: \quad @ \ z = 0 \quad C_L = C_L^{in} \tag{6}$$

There is one equation for each phase, and two boundary conditions. Note that there is no reaction term included for the liquid phase differential equation (Eq. 4). That is, the liquid phase reaction rate is considered zero, and the gas concentration in the liquid phase will build up over time. In the opposite case, where the liquid phase reaction rate is significantly faster than the rate of gas-phase mass transfer, it is possible to simplify the model by assuming the liquid phase concentration C_L is essentially zero everywhere. In this case, Eq. 4 reduces to zero. These two cases (zero and infinite liquid phase reaction rates) bracket the range of possible liquid phase reaction rates.

These equations are easily solved numerically. For this work, a 4th Order Runga-Kutta technique was implemented in Microsoft Excel 97 Visual Basic for Applications (EXCEL/VBA).

Counter-current TBR Model

The model equations for the counter-current model are identical to the co-current model with one exception: the inlet boundary conditions of the gas phase are reversed:

$$BC\#1: \quad @ \ z = Z \quad y = y_{in}$$

$$BC\#2: \quad @ \ z = 0 \quad C_L = C_L^{in}$$

This adds slightly more complexity to the model, since the two boundary conditions are no longer co-located. Because of this, an iterative solution procedure is necessary. The outlet liquid phase concentration, $C_L(z=Z)$, is estimated, giving a new model with co-located boundary conditions. This new model is identical in formulation to the co-current model described above,

and is solved to give an estimate of the inlet liquid phase concentration $C_L(z=0)$. The model converges when this estimate is equal to the original boundary condition value.

In the case of infinitely fast liquid phase reaction rate, the model equations for the co-current and counter-current are identical, since the equation describing the liquid phase (Eq. 4) simplifies to zero. In reality, this means that if the reaction rate is limited by the rate of mass transfer, at a given value of K_La, operating the reactor in either co-current or counter-current mode will give identical results. It does not follow, however, that the two reactor modes are equivalent. That is, for the same gas and liquid flowrates (identical G and L), counter-current operation will always yield a higher value of K_La, since the relative velocity of the two phases is much higher than in co-current operation.

Model Results & Discussion

Figures 2 and 3 present some preliminary modeling results from the single-pass TBR models. The model parameter values for these simulations, unless otherwise stated, were as follows: $Z=100$ cm, $D=6$ cm, $L=3000$ cm^3 min^{-1}, $V_H=400$ cm^3, $G=2000$ cm^3 min^{-1}, $K_La=0.20$ s^{-1}, $y_{in}=0.2$, $C_L^{in}=0$.

Figure 2 shows the effect of the inlet CO concentration on the CO conversion at a fixed value of the mass transfer coefficient K_La. The conversion is almost 50% in the limit of very low CO mole fractions, and decreases to approximately 45% at CO mole fractions close to 0.5. This decrease is caused by an increase in the volume of the gas phase. The reaction stoichiometry states that the reaction of one mole of CO with water will form two moles of product, CO_2 and H_2. The model assumes that these gases are essentially insoluble in the liquid phase, and are transferred immediately to the gas phase. At CO mole fractions close to 0.5, this increase in gas volume becomes significant, and the residence time in the reactor drops slightly, causing the decrease in conversion. Effects of CO_2 dissolution in the liquid phase (gas volume changes, pH effects, etc.) will be examined in future work.

The co-current and counter-current TBR models with no liquid phase reaction show different behavior from the infinite reaction rate case. Since the liquid phase reaction rate is zero for these cases, CO transferred from the gas phase accumulates in the liquid phase. At high inlet CO mole fractions, enough CO gas is transferred to the liquid phase to appreciably decrease the total gas flowrate. As the gas flowrate drops, the residence time of the gas in the reactor increases, leading to higher conversions for high mole fractions. The equilibrium conversion for the counter-current model is slightly higher than for the co-current case for all inlet mole fraction values, since the exiting liquid phase is in equilibrium with the higher concentration inlet gas stream rather than the lower concentration exiting gas stream.

Figure 3 shows the effect of varying the overall mass transfer coefficient at a fixed value of the inlet CO mole fraction y_{in}. With infinitely fast liquid phase reaction kinetics, conversion increases steadily with the mass transfer coefficient, and will reach 100% at very high K_La values. For the case of no liquid phase reaction rate, the conversion is equilibrium-limited at high K_La values, with the conversion higher for the counter-current model than for the co-current model. Thus, the extent to which the chemical reaction is limited by equilibrium considerations depends on the relative values of the mass transfer rate and the liquid-phase reaction rate. It is
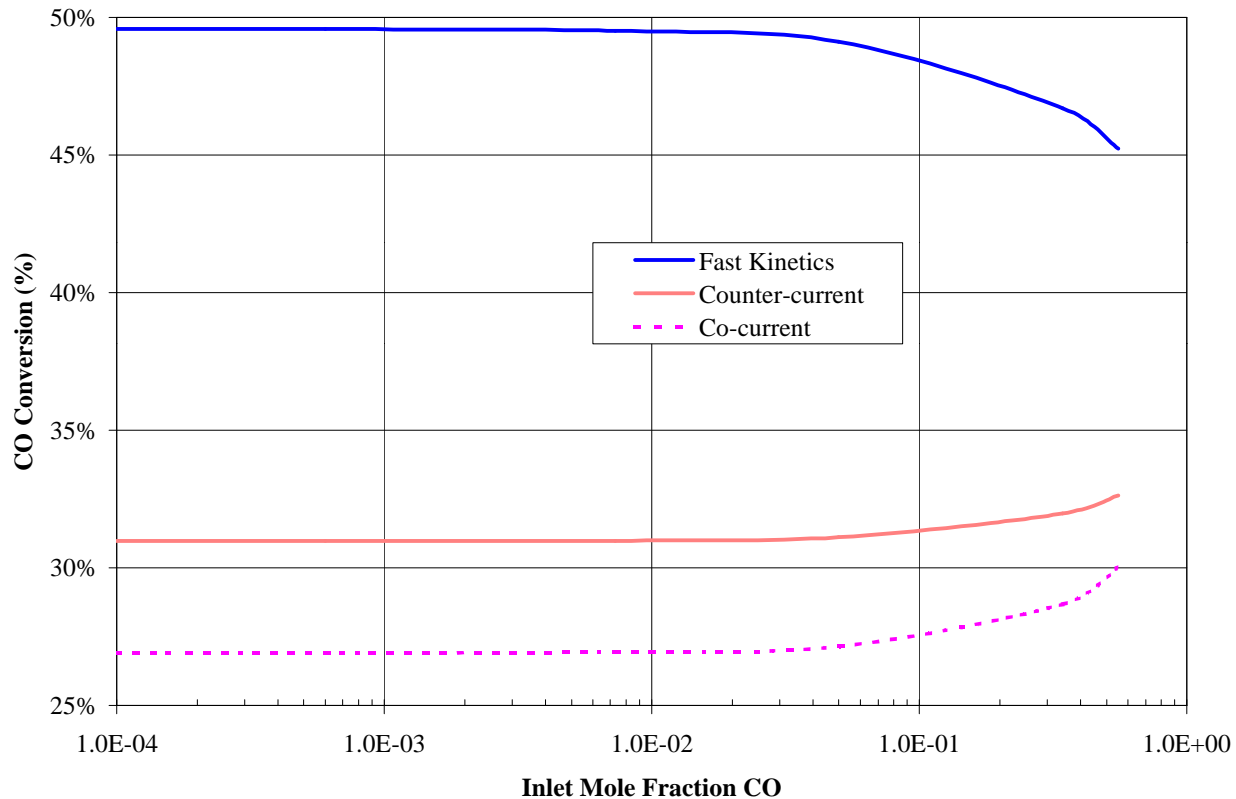
Figure 2. Effect of Inlet CO Mole Fraction (y_{in}) on CO conversion. Conversion is higher for the case with infinitely fast liquid phase kinetics, and the co-current and counter-current models are identical for this case. Conversion is lower for the case with no reaction in the liquid phase, and the co-current and counter-current models do not provide the same results.

entirely possible that the rate of the same reaction can be limited by mass transfer in one reactor assembly, and equilibrium-limited in another.

The models can be used to extract a mass transfer parameter from experimental data. Figure 4 shows experimental CO conversion by the photosynthetic bacterium *Rhodocyclus gelatinosus CBS-2* in a counter-current TBR at fixed gas and liquid flowrates, but varying inlet CO mole fraction. The CO conversion is approximately 20%, and independent of the three different inlet CO mole fractions examined. These conversion data were used, along with the counter-current TBR model, to extract a value of the mass transfer coefficient K_La=0.032 s^{-1}. This is in good agreement with literature data for similar reactor assemblies.

Modeling Conclusions & Future Work
The TBR models developed in this work demonstrate that in the limit of infinitely fast liquid phase reaction rate, the extent of CO conversion is not sensitive to the concentration of CO in the gas stream, except at very high concentrations (y_{in}~0.5) when the gas phase residence time is affected. The limited experimental data currently available support this conclusion.
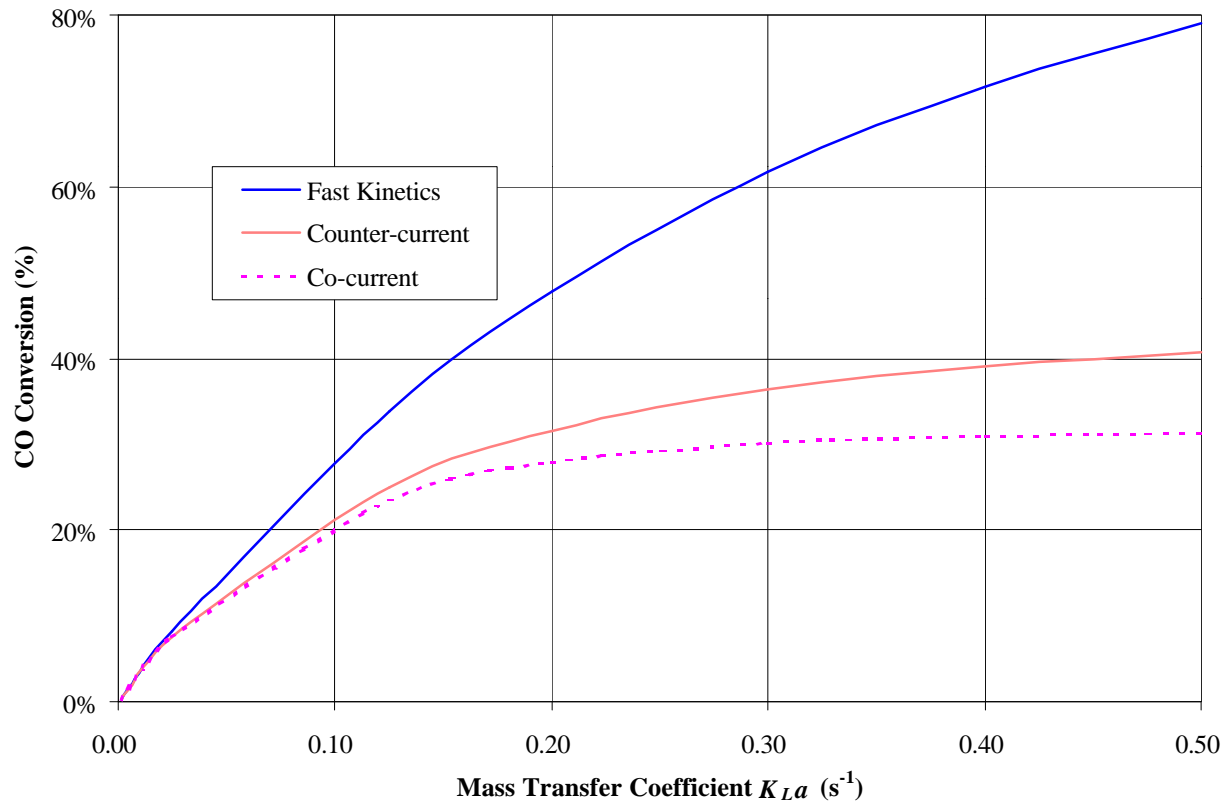
Figure 3. Effect of Mass Transfer Coefficient K_La on CO conversion. Conversion in the case of infinitely fast liquid phase kinetics increases steadily with K_La. Conversion is lower for the case of no liquid phase reaction, and reach equilibrium-limited values for both the co-current and counter-current models.

This result means that a reactor of a given size and overall throughput will convert the same fraction of carbon monoxide in the inlet feedstream, whether the stream contains 10% CO, 1% CO, or .01% CO. Another way of expressing this so-called "first-order behavior" is that the volumetric productivity of the reactor (the amount of CO converted per unit reactor volume per unit time) is directly proportional to the CO concentration.

The extent to which the reaction will be limited by equilibrium considerations depends very strongly on the relative rates of mass transfer and reaction. In particular, as new reactor designs with enhanced mass transfer rates are developed, it will be important to understand very clearly the maximum reaction rate required, since there is little reason to develop reactors that have mass transfer rates in excess of the maximum intrinsic reaction rate.

The TBR models allow the extraction of a mass transfer coefficient K_La from experimental conversion data, but not the *a priori* prediction of K_La. A number of correlations exist in the literature, but these have somewhat limited utility since the scatter in the data is quite significant.
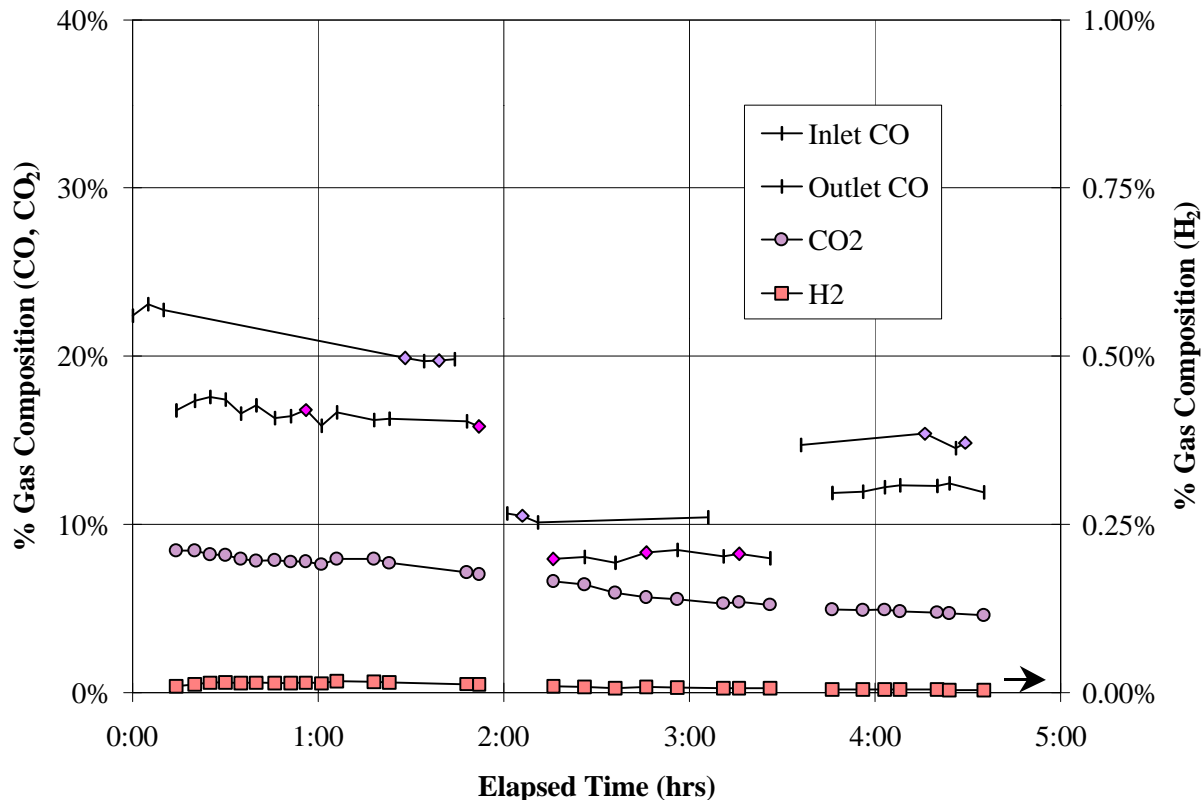
Figure 4. Representative CO conversion data from TBR assembly. *G*=1 SLPM, *L*=2 LPM. CO conversion was ~20% and independent of inlet CO concentration, but only very small amounts of H$_2$ were evolved.

A better technique for characterizing reactors is to perform experiments in the absence of chemical reaction. Measuring the rate of interphase mass transfer in the absence of reaction provides a conservative estimate of the mass transfer coefficient. A hypothetical experiment of this type would consist of operating the TBR reactor at a given set of reaction conditions with the liquid phase containing the required nutrients but without a microbial culture. These experiments, and the slightly more complex reactor modeling required to interpret the experimental data, are underway.

Research/Demonstration Unit (RDU)

Most work that has been reported in the literature on the use of photosynthetic bacteria to perform the water-gas shift reaction has involved experiments using synthetic CO/H$_2$ feedstreams. In a real-world application, the syngas will be supplied to the bioreactor either by reforming a gaseous or liquid hydrocarbon fuel, or by biomass gasification. The syngas produced by either of these processes will contain other species besides CO and H$_2$. For example, syngas produced by propane reforming will likely contain uncracked propane and other hydrocarbons, while syngas from biomass gasification is known to contain quantities of ash and tar. The ability

of the bacterial conditioning system to handle "real" syngas streams has not yet been demonstrated. We are developing a computer-controlled research/demonstration unit (RDU) to supply "real" syngas by reforming methane.

Current Year Results

During the last year, we made a number of modifications to the RDU, including modifying the LabView interface program, repairing the reactor, replacing the steam generator, and making improvements to the flow measurement and control system. We also modified the thermal reactor to hold a catalyst charge (the catalyst was kindly provided by Dr. Stefan Czernik of NREL). Figure 5 shows the effect of varying the steam/methane molar ratio on the performance of the RDU with a catalyst bed temperature of 850°C. At a steam/methane ratio of 1, the outlet CO concentration is 25%, which is in agreement with the theoretical stoichiometry. As the steam/methane ratio is increased, significant amounts of carbon dioxide are produced, again in agreement with theoretical stoichiometry.
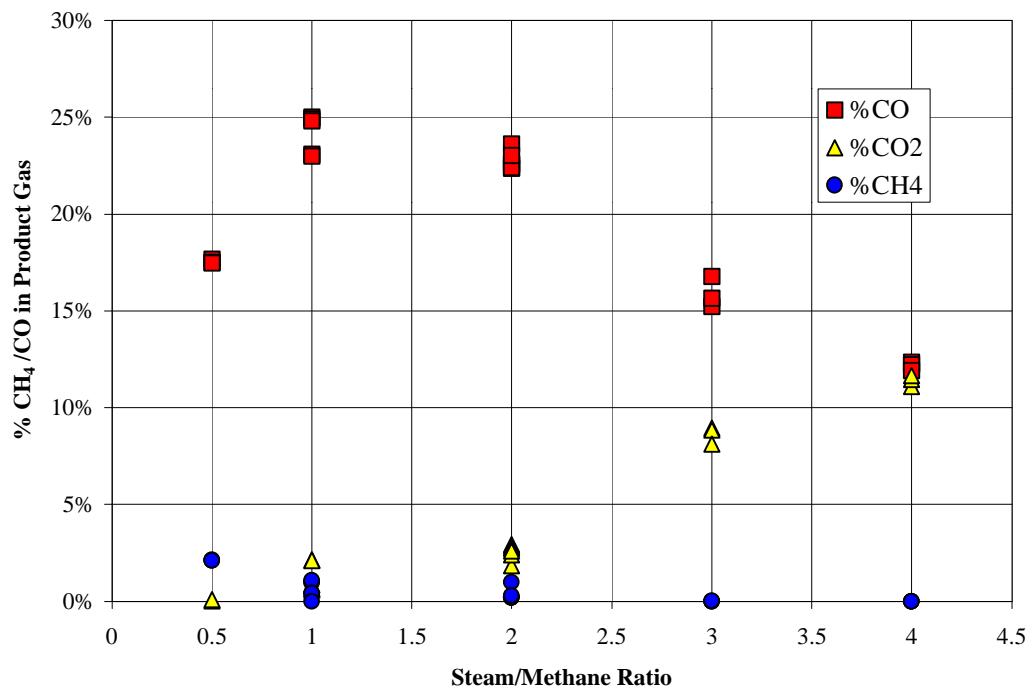

Figure 5. Effect of Steam/Methane Ratio on the Performance of the RDU.

RDU Conclusions & Future Work

As the data in Figure 5 suggest, the RDU is now ready for use as a source of syngas to test different bioreactor designs with a "real-world' feedstock. We will couple the RDU to a bioshift reactor to demonstrate the ability of the bacteria to perform the water-gas shift reaction on a syngas stream that may contain a number of different components besides hydrogen and carbon monoxide. Our longer-term goal is to modify the RDU to produce syngas from the pyrolysis of biomass, which should provide an even more realistic feedstream than methane reforming.

Nomenclature

Symbol	Description	Units
a_s	Reactor cross-sectional area	cm^2
C_L	Liquid-phase concentration	$mol\ cm^{-3}$
C_L^{in}	Initial liquid-phase concentration	$mol\ cm^{-3}$
G	Volumetric gas flowrate	$cm^3\ s$
H	Henry's Law coefficient	$cm^3\ mol^{-1}\ atm^{-1}$
$K_L a$	Overall mass transfer coefficient	s^{-1}
K	Chemical reaction equilibrium constant	--
L	Volumetric liquid flowrate	$cm^3\ s$
N	Molar flux of gas	$mol\ cm^{-2}\ s^{-1}$
P	ambient pressure	atm
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)	$cm\ s^{-1}$
V_L	liquid holdup volume	cm^3
V_R	total reactor volume	cm^3
V_{res}	reservoir volume	cm^3
V_T	total system volume	cm^3
y	gas-phase mole fraction of gas	--
y_{in}	inlet gas-phase mole fraction of gas	--
Z	reactor length	cm
z	axial dimension of reactor	cm
e_L	void fraction liquid phase (V_L/V_R)	---