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Methane Production from Synthesis Gas Using a Mixed Culture of *R. rubrum*, *M. barkeri*, and *M. formicicum*

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ABSTRACT

The components of synthesis gas, CO, H_2, and CO_2, may be converted into CH_4 biologically through either acetate or H_2/CO_2 as intermediates. Of these two routes, conversion through H_2/CO_2 is preferred. This paper presents results of mixed-culture studies employing the photosynthetic bacterium *R. rubrum* for converting CO to CO_2 and H_2 by the water gas shift reaction and two methanogens, *M. formicicum* and *M. barkeri*, for converting CO_2 and H_2 into CH_4. Results are presented for triculture operation in two types of reactors, the packed bubble column and the trickle-bed reactor.

Index Entries: Synthesis gas; methane; mixed culture; packed bubble column; trickle-bed reactor.

INTRODUCTION

Synthesis gas, a mixture of primarily CO, H_2, and CO_2, is a major building block in the production of fuels and chemicals. The gas is derived from nongaseous raw materials such as coal, shale oil, tar sands, heavy residue, and biomass. The composition of synthesis gas is dependent upon the raw materials used and the gasification process. Coal-derived gas is rich in CO and H_2, with lower concentrations of CO_2 and traces of CH_4, H_2S, and COS (*1*).

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The conventional method of producing gaseous fuel from the synthesis gas first employs the catalytic shift reaction. In this reaction, CO and H_2O are converted into H_2 and CO_2. Following the removal of sulfur contaminants, such as H_2S, COS, and excess CO_2, the H_2 and CO_2 are catalytically methanated to CH_4 and H_2O. After drying, the product gas contains 95–98% CH_4.

Most methanation processes require temperatures of 300–700°C and operating pressures of 3–20 atm (*2*). The catalysts used for the methanation step include nickel- and potassium-based catalysts, as well as mixtures of iron/chromium oxides and zinc/copper oxides (*3,4*). Poisons for these catalysts include chlorine and sulfur (*5,6*). In addition, chemical catalytic processes are known to produce by-products such as methanol, formaldehyde, and acetic acid (*7*).

The biological conversion of low-Btu synthesis gas to CH_4 represents an alternative to the technology described above and may be carried out at low operating temperatures and pressures. Biocatalytic processes also have higher specificities and yields, and the microorganisms have proved to be essentially unaffected by the above-mentioned sulfur gases (*8,9*).

The triculture system presented in this paper carries out the same reactions as in the chemical catalytic reactions above, namely water gas shift conversion and methanation. These two reactions may be written as

$$CO + H_2O \rightarrow H_2 + CO_2 \quad (1)$$

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \quad (2)$$

The organisms *Rhodopseudomonas gelatinosa* and *Rhodospirillum rubrum* are able to carry out the reaction described in Eq. (1) (*10*). Both of these photoorganotrophs grow either anaerobically in the presence of light or aerobically in the dark (*11*). However, Brown (*10*) indicated that *R. rubrum* had a higher tolerance of CO and grew faster than *R. gelatinosa*. Consequently, *R. rubrum* was used in all fermentations in this triculture study. Preliminary experiments at the University of Arkansas have indicated that Eq. (1) is carried out by *R. rubrum* both in the presence of light and in the dark. However, light is required for growth.

Most methanogens are able to convert CO_2 and H_2 to CH_4 by Eq. (2) (*11*). The conversion of H_2 to CH_4 by *M. formicicum* and *M. barkeri* has been shown by Kluyver and Schnellen (*12*). The reason for using both cultures rather than one was the fact that *M. formicicum* expresses a high rate of H_2 uptake, but is inhibited by the presence of CO. *M. barkeri*, on the other hand, shows a higher tolerance to CO, but has a lower H_2 conversion rate (*13*).

As noted in Eqs. (1) and (2), the reactions that produce CH_4 from synthesis gas components involve the consumption of gaseous substrates and, in return, a gaseous product is produced. It is important to realize that, in a system such as this, the conversion rate is likely to depend upon

mass-transfer properties, rather than microbial reaction kinetics. In general, a fermentation system may be said to work under mass-transfer limitations when the microbial uptake rate exceeds the rate of mass transport of the substrate to the cells. In examining the resistances that have to be overcome, the rate-limiting step in a mass-transfer limited fermentation is the transport (by diffusion) of the solute through the relatively unmixed liquid region (film) adjacent to the gas–liquid interface into the well-mixed liquid (*14*).

Purpose

The purpose of this study was to carry out the conversion of H_2, CO, and CO_2 present in synthesis gas to CH_4 in a single reactor. Two types of reactors were chosen: a packed bubble column and a trickle-bed reactor. Both reactor types were inoculated with the same biocatalyst system, and conversion data were collected in order to compare the performance of the two reactors.

MASS-TRANSFER CONSIDERATIONS

The transport of a sparingly water-soluble substrate from the gas phase to the liquid phase may be described by the equation

$$\text{moles transported} = k_l a / H (P^G - P^L) \quad (3)$$

where P^G is the partial pressure of the substrate in the gas phase. In the same manner, P^L refers to the partial pressure of the substrate in equilibrium with the concentration of the substrate in the bulk liquid phase, $k_l a$ is the overall mass-transfer coefficient and H is the Henry's law constant. In the liquid phase, the substrate is consumed at a maximum rate by the cells according to the equation

$$\text{moles consumed} = q X \quad (4)$$

where q is the specific uptake rate and X is the cell concentration. For a system not operating under mass-transfer limitation, the limiting step for substrate consumption is the microbial kinetics described by Eq. (4). On the other hand, under mass-transfer limitation, the uptake rate is generated by the mass-transfer limitation of the reactor and Eq. (3). It is important to realize that in both cases the moles of substrate transported from the gas phase to the liquid (Eq. [3]) must be equal to the consumption rate by the cells (Eq. [4]) at steady state.

In the column reactors used in this study, the outlet concentration of, for example, CO may be related to the gas flow rate and column parameters through the following equation (*15*):

$$\ln (P^o_{CO}/P^o_{TOT}) = \ln (P^i_{CO}/P^i_{TOT}) - [k_l a / H] \epsilon_L [\text{hSRT} / G] \quad (5)$$

where P^i_{CO}/P^i_{TOT} and P^o_{CO}/P^o_{TOT} correspond to the mole fractions of CO in the inlet and outlet gases, respectively. If the total pressure in the reactor is approximately constant ($P^i_{TOT}=P^o_{TOT}$), Eq. (5) may be reduced to Eq. (6):

$$\ln (P^i_{CO}/P^o_{CO}) = [k_1a / H]\, \epsilon_L\, [\text{hSRT} / G] \quad (6)$$

Thus, by varying the gas flow rate, G, and measuring the partial pressure of carbon monoxide in the outlet gas, P^o_{CO}, the mass transfer properties of the column reactors may be estimated.

MATERIALS AND METHODS

Rhodospirillum rubrum, ATCC 25903, and *Methanobacterium formicicum*, ATCC 33274, were obtained from the American Type Culture Collection, Peoria, IL. *Methanosarcina barkeri* was kindly supplied by M. P. Bryant, Department of Dairy Science, University of Illinois, Urbana, IL.

The medium used in all experiments contained the following components per 100 mL of medium: 5 mL Pfennig's mineral solution (*16*), 0.1 mL Pfennig's metal solution (*16*) with the addition of 10 mg Na_2SeO_3 (*17*), 0.5 mL B vitamins solution (17), 0.1 g yeast extract (Difco), 0.58 g $NaCH_3COO{\cdot}3H_2O$ and 0.45 g $NaHCO_3$. Typically, 7 L of medium were prepared in a 13.5-L Pyrex™ carboy (New Brunswick Scientific, New Brunswick, NJ) and autoclaved at 2 atm for 45 min. Cooling was acccomplished by bubbling a sterile mixture of He and CO_2 (75%/25%) through the medium. The cooled medium was reduced with 10 mL of Na_2S (2.5%).

Equipment

Bubble Column Experiment

Experiments performed in the packed-bed bubble column were conducted using a triculture of *R. rubrum, M. formicicum,* and *M. barkeri.* Since *R. rubrum* requires light for growth, an annular design was used in the construction of the column. It consisted of three annular segments: the light supply section, the packed bed section, and the cooling jacket section. A cross-sectional schematic diagram is shown in Fig. 1. The packed-bed section had an inner diameter of 51 mm and an outer diameter of 102 mm, yielding an active cross-sectional area of 6128 mm^2. Glass Raschig rings (6mm x 6mm) were used as the inert packing material, with a total height of the packed section of 440 mm. The reactor was run in a counter-flow pattern, with the liquid medium entering from the top of the column and the gas sparged from below the packed section. A schematic diagram of the reactor set-up is shown in Fig. 2. Specific operating conditions are listed in Table 1.

Trickle-Bed Reactor Experiments

The second type of reactor used in this study was a packed-bed tower reactor or trickle-bed reactor. The column height was 515 mm, with an in-

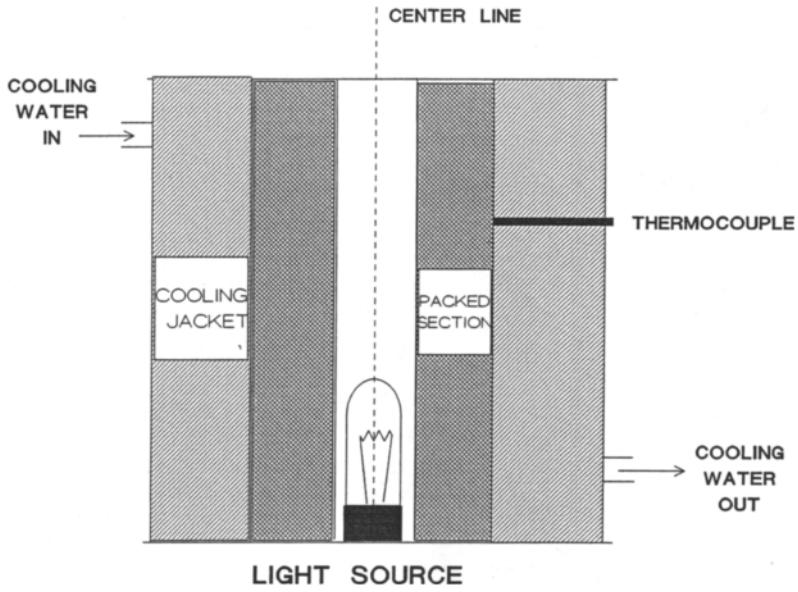

Fig. 1. Schematic diagram of the cross-section of the packed bubble column.

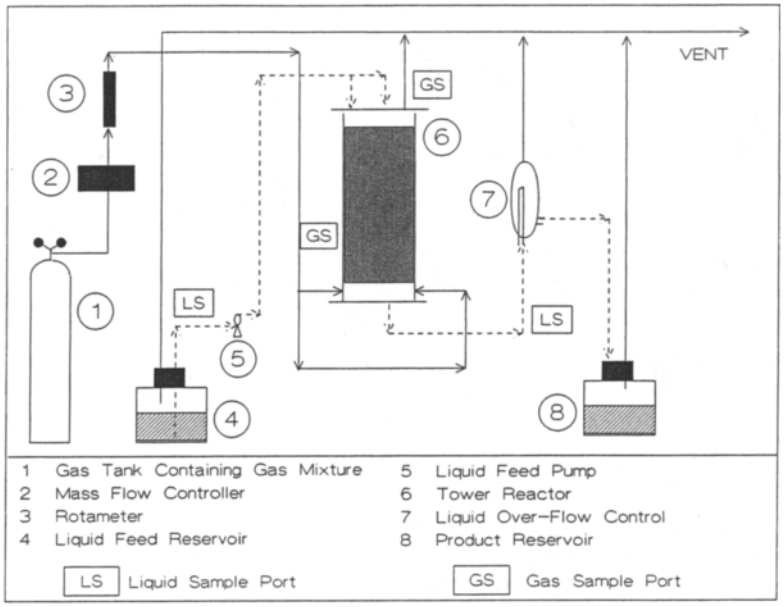

Fig. 2. Equipment set-up for the annular packed bubble column.

Table 1
Operating Conditions for the Column Reactors

	Packed bubble column	Trickle-bed reactor
Liquid flow rate (mL/min)	0.28	0.28
Liquid recycle rate (mL/min)	-	125
Temperature (°C)	34	37
pH	6.8–7.2	6.8–7.2
Gas inlet composition		
Ar	15.0	14.8
CO_2	9.6	9.9
CO	55.0	55.6
H_2	20.4	19.7

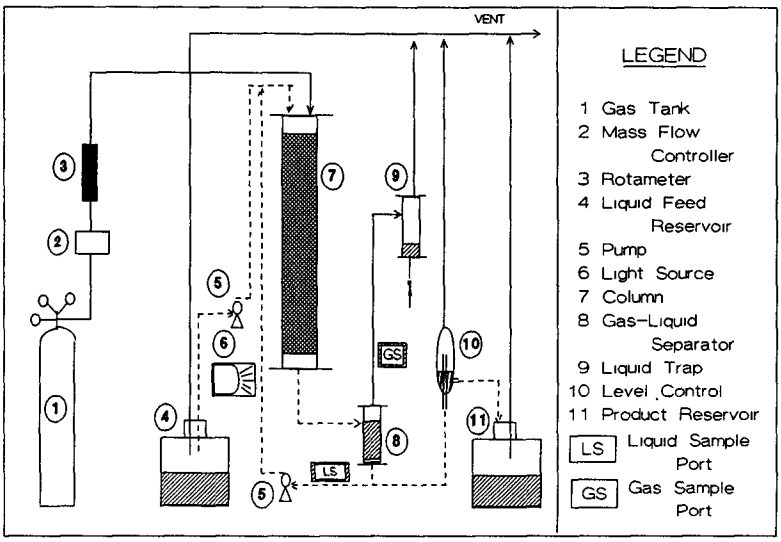

Fig. 3. Equipment set-up for the trickle-bed reactor.

ner diameter of 51 mm. After packing with 6.35-mm Intalox saddles, the void volume in the packed section was 623 mL, which corresponds to an initial porosity of 0.592. The total volume in the packed section was 1052 mL. The reactor and equipment set-up are shown in Fig. 3. The reactor installation was assembled to operate in a cocurrent mode, which has been found to present fewer problems with cell clogging, foaming, and channelling. The liquid make-up stream was combined with the recirculated liquid and entered at the top of the reactor. Gas and liquid flowed downward through the packing and exited in a combined stream at the bottom of the reactor. The separation of the two streams occurred in a

separator outside the reactor. A constant temperature was maintained by locating the equipment in a constant-temperature environment. External cooling surrounded the light source to assure constant temperature.

Analytical Methods

Gas Analysis

A Perkin-Elmer (Norwalk, CT) gas chromatograph, Model Sigma 300, and Perkin-Elmer integrator, Model LCI-100, were used for the analysis of the gas-stream compositions. The column used was a 1.8 m x 3 mm stainless steel column packed with Carbosphere, 60/80 mesh (Alltech, Deerfield, NJ). Helium was used as the carrier gas at a flow rate of 40 mL/min. The oven temperature was held constant at 135°C and the injector and HWD detector temperature was 175°C.

Other Measurements

Gas flow rates through the columns were measured by a precalibrated rotameter mounted before the gas inlets of the columns. The liquid flow rates and liquid recycle rates were determined during the experimentation by timing medium broth displacement in a pipet. The temperatures inside the columns were monitored by the use of thermocouples mounted through the walls of the columns.

RESULTS AND DISCUSSIONS

The overall performance of the bubble column and the trickle-bed reactor were good in converting the components of synthesis gas to CH_4 through the H_2/CO_2 intermediates. After an initial start-up period of approximately 10–14 d, both reactors stabilized at a constant conversion rate. Consistent data were obtained during the entire fermentation. The only operating problem encountered after long-term operation was clogging of the gas distributors at the bottom of the packed bubble column.

With the triculture used in these experiments, both reactor types showed CH_4 production from CO, H_2, and CO_2 at all experimental conditions used. In Fig. 4, CH_4 production is plotted as a function of the estimated H_2 consumption for both reactors. The estimated H_2 consumption was found by adding the consumption rates of H_2 and CO from the gas phase, since the rate of uptake of CO by *R. rubrum* equals the rate of H_2 production as described in Eq. (1). As seen in Fig. 4, a single straight line may be used to estimate the CH_4 yield on H_2 for both reactors. Using this single straight line, the CH_4 yield on H_2 was found to be 0.214, which is 83% of the theoretical yield of 0.25 shown in Eq. (2). In considering bubble column and trickle-bed reactor performance separately, the product yields were 0.34 and 0.20, respectively. As noted, the yield obtained in the bubble column was 36% higher than the theoretical yield. Higher-than-theoreti-

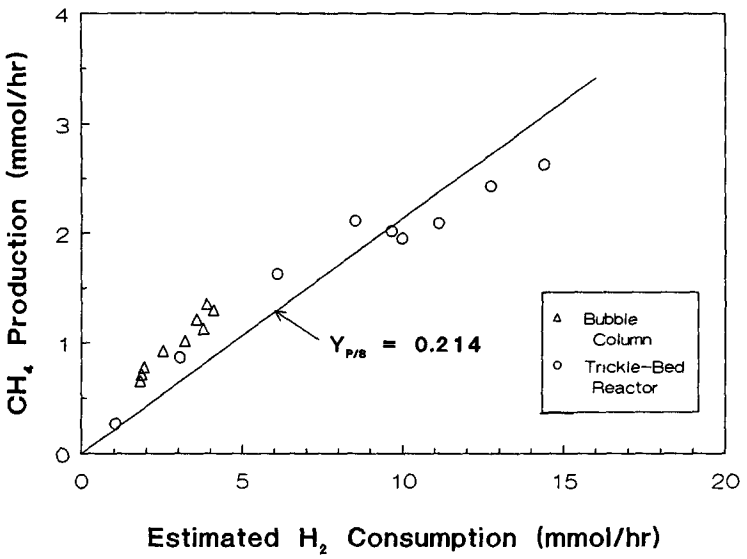

Fig. 4. Methane production as a function of the estimated hydrogen consumption in the packed bubble column and trickle-bed reactor.

cal CH_4 yields on H_2 have been found in other mixed-culture studies with methanogens under similar conditions (*18*).

CO conversion in the two reactors is plotted as a function of the average gas flow rate in Fig. 5. As is seen, a conversion of 100% was obtained in the trickle-bed reactor for gas flow rates below 300 mL/hr. The outlet gas composition was typically 28–32% CH_4 in those cases, the rest being Ar (inert) and CO_2. The packed bubble column, on the other hand, did not reach a CO conversion higher than 79%, found at a gas flow rate of 80 mL/hr. At this conversion, the CH_4 content in the outlet gas stream was 18%. Higher conversions were found in the trickle-bed reactor, probably because of better mass-transfer properties and longer gas residence time as a result of a lower value of ϵ_L than encountered in the bubble column (*see* Table 2).

The CH_4 productivity based on total reactor volume is plotted as a function of gas flow rate for the two reactors in Fig. 6. The total reactor volume for the trickle-bed reactor was 736 mL, including the volume of the separator and the liquid recycle-loop, and the total volume of the bubble column was 3260 mL. The trickle-bed reactor showed significantly higher productivities than the packed bubble column. Productivities of 3.4 mmol CH_4/L·h were typically obtained at flow rates above 300 mL/h in the trickle-bed reactor. The productivities in the packed bubble column reached only 0.4 mmol CH_4/L·h at gas flow rates of 800–1000 mL/h. Again, it is seen that the trickle-bed reactor appears to be the better system when it comes to the conversion of CO and the productivity of CH_4.

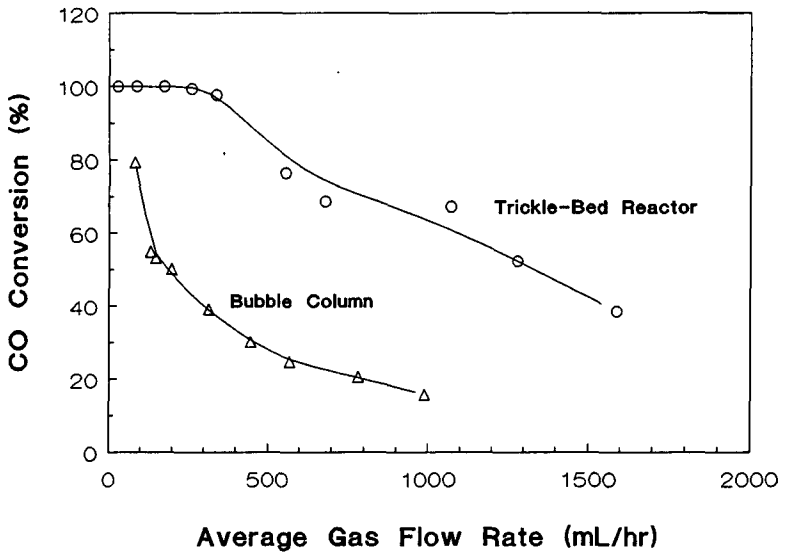

Fig. 5. CO conversion as a function of average gas flow rate for the packed bubble column and trickle-bed reactor.

Table 2
Reactor Characteristics for the Two Columns

Property	Packed bubble column	Trickle-bed reactor
Active height, h (cm)	44.0	48.0
Cross-sectional area, S (cm^2)	61.3	20.4
Liquid porosity, ϵ_L (cm^3/cm^3)	0.621	0.07
Temperature, T (°K)	307	310
Henry's law constant, H		1210 atm·L/mol CO
Ideal gas law constant, R		0.0821 atm·L/mol °K

The apparent mass-transfer coefficients for the two reactors were derived by plotting the natural logarithm of the ratio of the partial pressures of CO in the inlet and outlet gas streams as a function of $1/G$ (*see* Fig. 7). If the relationship in Eq. (6) holds, the mass-transfer coefficient, k_1a, may be calculated from the slope of the straight line using the characteristics of the two columns found in Table 2. The slopes of the lines in Fig. 7 were found to be 122 mL/h for the bubble column and 1122 for the trickle-bed recctor. Thus, the mass-transfer coefficients, k_1a, may be calculated as 3.5 h^{-1} for the bubble column and 780 h^{-1} for the trickle-bed reactor. Comparable values for mass-transfer coefficients for packed bubble columns in the literature range from 20 to 430 h^{-1} (*19*). For packed absorption columns operating in cocurrent mode (trickle-bed reactors),

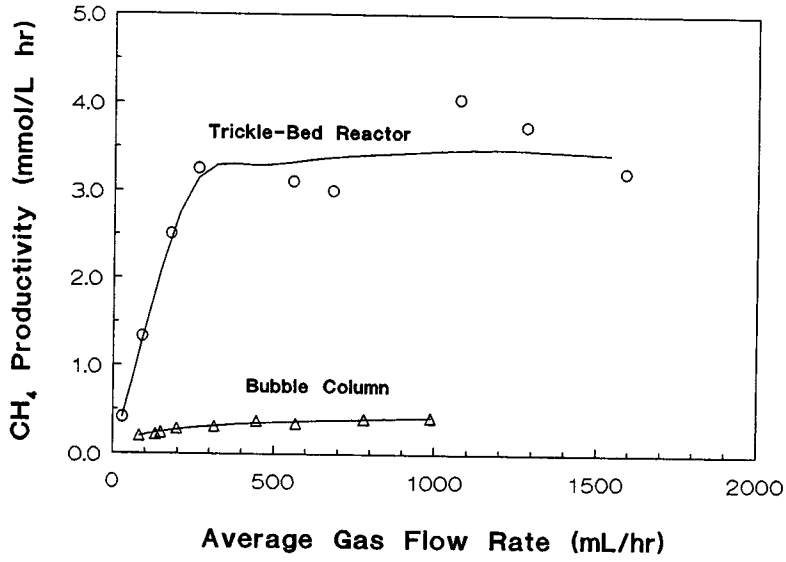

Fig. 6. CH_4 productivity as a function of gas flow rate for the packed bubble column and trickle-bed reactor.

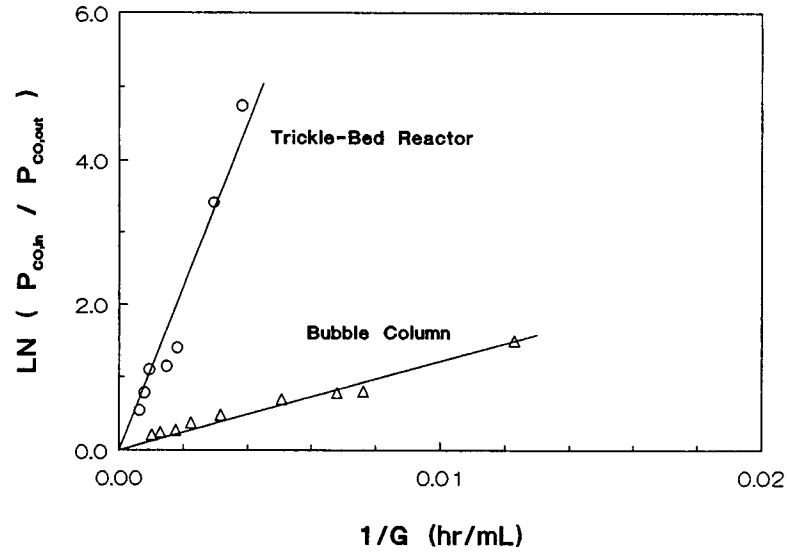

Fig. 7. Determination of mass-transfer properties in the packed bubble column and trickle-bed reactor.

k_1a values ranging from 1.5 to 3670 h^{-1} were shown (*19*). The obtained k_1a value of 3.5 h^{-1} for the bubble column is considerably lower than values found in the literature. One explanation for this low value could be that the gas-to-liquid flow-rate ratio in the present experimental work was considerably lower than listed values typically used for the same reactor type (*19*). Another reason could be the poor gas distribution at the low gas flow rates and the annular design used for the bubble column. Whatever the reason, the absorption column was shown to provide a much higher mass-transfer coefficient than the bubble column.

CONCLUSIONS

CO, CO_2, and H_2 in synthesis gas has been successfully converted to CH_4 in packed bubble column and trickle-bed reactors using a triculture of *R. rubrum, M. barkeri,* and *M. formicicum.* Methane yields from H_2 were estimated at 0.214, which is 83% of the theoretical yield of 0.25. Carbon monoxide conversions of 100% were obtained in the trickle-bed reactor, whereas the maximum CO conversion in the bubble column was 79%. Maximum CH_4 productivities of 0.4 mmol/L·h were obtained in the bubble column and productivities of 3.4 mmol/L·h were obtained in the trickle-bed reactor. Mass-transfer coefficients of 3.5 h^{-1} and 780 h^{-1}, respectively, were estimated for the bubble column and trickle-bed reactor.

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