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Biological Production of Liquid and Gaseous Fuels from Synthesis Gas

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ABSTRACT

Liquid and gaseous fuels may be produced biologically from coal by the indirect conversion of coal synthesis gas. Methane has been produced from synthesis gas using acetate and CO_2/H_2 as intermediates, utilizing a number of CO-utilizing and methanogenic bacteria. Also, a bacterium that is capable of producing ethanol from synthesis gas through indirect liquefaction has been isolated fron natural inocula. This paper summarizes research to optimize the performance of some of these cultures. These conversions, involving H_2 and CO, which are only slightly soluble in the liquid media, may be mass transfer limited, and methods to enhance mass transport are examined. Experimental results and models for several reactor designs, including CSTR and packed columns, are presented and discussed.

Index Entries: Synthesis gas; ethanol; methane; mass transfer limited bioreactors.

NOMENCLATURE

a	Interfacial area/unit volume of liquid	cm^{-1}
G	Gas flow rate	mL/h
h	Column height	cm
H	Henry's law constant	atm-L/mmol
K_L	Overall gas–liquid mass transfer coefficient	cm/h
n	Molar flow in the gas phase	mmol/h
P	Partial pressure	atm

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Q	Substrate uptake rate	mmol/L h
R	Gas constant	atm-L/mol K
S	Column internal cross-sectional area	cm^2
T	Reaction temperature	K
V	Volume	L
Y	Gas phase concentration ratio to an inert gas	-
ϵ_L	Liquid porosity	-

Subindices or superindices:
CO : carbon monoxide
i : inlet
I : inert
L : liquid
T : total

INTRODUCTION

Synthesis gas, a mixture of CO, H_2, CO_2, and small amounts of CH_4 and sulfur gases, is an excellent substrate for the biological production of liquid and gaseous fuels using anaerobic bacteria. Biological processes, although generally slower than purely chemical reactions, have several advantages over catalytic processes, such as higher specificity, higher yields, lower energy costs, and possible higher resistance to poisoning. Furthermore, the irreversible character of biological reactions allows complete conversion and avoids thermodynamic equilibrium relationships.

The biological conversion of synthesis gas components to methane and liquid fuels involves contacting the gas and microorganisms in liquid culture. The gas must then absorb into the gas–liquid interface and diffuse through the culture medium to the cell surface to be consumed by the microbes. For sparingly soluble gases, such as CO, O_2, and the like in contact with suspended cells, it has been established that the primary resistance to transport lies in the liquid film (*1–3*). In the case where the overall reaction rate is transport controlled, the rate of transport, and thus the rate of reaction, is proportional to the partial pressure in the gas phase. Contacting schemes to maximize gas–liquid contact are thus very important.

The purpose of this paper is to present the results of laboratory experiments carried out in various contacting schemes for converting synthesis gas components to methane, acetate, and ethanol. As an example of gas phase substrate conversion in continuous contacting systems, CO is converted to acetate by *Peptostreptococcus productus* in a stirred-tank reactor, a packed-bubble column, and a trickle-bed reactor. Mathematical models predicting reactor performance under mass transfer limited conditions are used in correlating the experimental data. As a second example, two stirred-tank reactors are connected in series (one for culture growth and the other for ethanol production) in producing ethanol in favor of acetate from CO, CO_2, and H_2 by *Clostridium ljungdahlii*.

BIOLOGICAL SYNTHESIS GAS CONVERSION

Methane Production

The primary reactions in the biological conversion of synthesis gas to methane are the formation of methane precursors (acetate, CO_2/H_2) and biomethanation of the precursors. Table 1 shows the known biological routes to CH_4 from synthesis gas components and some of the biocatalysts capable of carrying out these reactions. All of these reactions are carried out anaerobically and usually require very low redox potentials in the liquid medium in which the microorganisms are suspended (*4*). As is seen in the table, the formation of CH_4 can be accomplished by direct conversion of either CO or CO_2 and H_2, or by the indirect formation of CH_4 intermediates (acetate or H_2 and CO_2). Of the one-step reactions, only Reaction I-3, the direct formation of CH_4 from H_2 and CO_2, has been well-studied and verified (*5*). This reaction is known to be carried out by most methanogens (*6*), although some methanogens, such as *Methanothrix* sp., are not capable of this conversion (*7*).

The one-step reactions, I-1 and I-2, that convert CO directly to CH_4 have been suggested in the literature (*8*). However, it is likely that the CO reduction to CH_4 in these experiments proceeded via the multiple-step reactions II-3 and I-3 (*8,14*).

With the exception of Reaction I-3, an indirect formation of CH_4 seems more viable than the direct routes. These multistep reactions may involve the formation of a liquid intermediate, acetate, or the utilization of CO to produce CO_2 and H_2 by the water gas shift reaction (II-3). In the latter case, the products, H_2 and CO_2, can be directly converted to CH_4 (Reaction I-3) or may enter the multiple-step process that produces acetate as an intermediate (Reaction II-2).

Two species of purple nonsulfur bacteria, *Rhodopseudomonas gelatinosa* (*11,12*) and *Rhodospirillum rubrum* (*13*) are known to perform the water gas shift reaction (II-3). *R. gelatinosa* can grow under strict anaerobic conditions in the dark with CO as the only carbon and energy source. *R. rubrum* requires tungsten light and the presence of a carbon source other than CO (sugars, acetate, amino acids, and so on) for growth and is presently used at the University of Arkansas laboratories. In comparing these two operational methods for industrial application, *R. rubrum* growth in the presence of light is preferred because of its ability to grow faster, thereby reaching higher cell concentrations that uptake CO more rapidly. Attempts to use *R. gelatinosa* in the dark did not result in an industrially viable process (*15*).

Another approach to indirect methane production is the formation of acetate as a CH_4 precursor. In anaerobic digestion processes, 80% of the CH_4 is produced from acetate by Reaction II-4. Acetate can be transformed by methanogens of the *Methanosarcinaceae* family, such as *Methanosarcina barkeri,* as well as *Methanothrix soehngenii* (*6*).

The two indirect routes mentioned above have been studied both in batch and in stirred-tank experiments employing various pure and mixed

Table 1
Biological Routes to Methane and Ethanol from Synthesis Gas Components

Equation	Reaction	$\Delta G°$, kcal/reac	Biocatalyst
I-1	$4CO + 2H_2O \rightarrow CH_4 + 3CO_2$	−50.3	*Methanobacterium thermoautotrophicum* (*8*)
I-2	$CO + 3H_2 \rightarrow CH_4 + H_2O$	−36.0	
I-3	$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$	−31.3	*Methanosarcina barkeri* *Methanobacterium formicicum*
II-1	$4CO + 2H_2O \rightarrow CH_3COOH + 2CO_2$	−32.2	*Peptostreptococcus productus, Clostridium ljungdahlii* (*9*), *Eubacterium limosum* (*10*)
II-4	$CH_3COOH \rightarrow CH_4 + CO_2$	−18.1	*Methanosarcina barkeri* *Methanothrix soehngenii* (*6,7*)
II-2	$4H_2 + 2CO_2 \rightarrow CH_3COOH + 2H_2O$	−13.1	*Peptostreptococcus productus, Clostridium ljungdahlii* (*9*), *Eubacterium limosum*
II-3	$CO + H_2O \rightarrow H_2 + CO_2$ To Reaction I-3	− 4.8	*Rhodopseudomonas gelatinosa*[a] (*11,12*) *Rhodospirillum rubrum* (*13*)
III-1	$6CO + 3H_2O \rightarrow CH_3CH_2OH + 4CO_2$	−51.7	*Clostridium ljungdahlii* (*9*)
III-2	$2CO_2 + 6H_2 \rightarrow CH_3CH_2OH + 3H_2O$	−23.2	*Clostridium ljungdahlii* (*9*)

[a] Also named *Rhodocyclus gelantinosus*.

cultures of the microorganisms listed above (*16*). Although the production of acetate from CO is readily accomplished by acetogenic bacteria, such as *P. productus,* the utilization of the acetate by methanogens is a rather slow process that is usually limited by the acetate inhibition of the bacteria. Methane formation through H_2 and CO_2, on the other hand, is not limited by intermediate product accumulation. The photosynthetic bacterium *R. rubrum* is first used to produce H_2 and CO_2 from CO and H_2O by Reaction II-3, followed by stoichiometric conversion of the CO_2 and H_2 to CH_4 by Reaction I-3, using *M. formicicum* and/or *M. barkeri.*

Ethanol Production

Although many anaerobic, facultatively anaerobic, and even some strictly aerobic microorganisms form various amounts of ethanol from glucose (*17*), no organism was known to form ethanol autotrophically from synthesis gas components. In 1987, a strict anaerobic mesophilic bacterium, which was capable of converting CO, H_2, and CO_2 to a mixture of acetate and ethanol (*18*), was isolated from animal waste. Identification and characterization studies have shown that the bacterium is a new clostridial species, named *Clostridium ljungdahlii,* Strain PETC, in honor of Dr. Lars G. Ljungdahl for his work on clostridia and acetogens (*19*). As with other class I clostridia, it is expected that ethanol and acetate are formed through acetyl-CoA as the central intermediate (*20*).

The overall stoichiometry for the formation of acetate and ethanol from CO and H_2/CO_2 are listed in Table 1. Under typical laboratory conditions, *C. ljungdahlii* produces acetate as the major product, with only small quantities of ethanol present in the product stream.

Studies at the University of Arkansas have recently focused on minimizing the amount of acetate produced by the organism while maximizing ethanol production. In addition to studying the physical parameters affecting product distribution, such as nutrient concentrations and pH, techniques for increasing the solvent-to-acid ratio that have been applied to other class I clostridial species have also been employed. The use of 30 ppm benzyl viologen as a reducing agent in a batch experiment, for example, brought about a 4.5-fold increase in the product ratio in comparison to a control experiment without the reducing agent. The same type of behavior has been noted in *Clostridium acetobutylicum* by other researchers (*21–23*).

MATERIALS AND METHODS

Peptostreptococcus productus, Strain U-1, was kindly supplied by Professor M. P. Bryant, University of Illinois, Department of Dairy Science. *Clostridium ljungdahlii,* Strain PETC, was isolated from animal waste at the University of Arkansas, Department of Chemical Engineering and characterized at the University of Oklahoma, Department of Botany and

Table 2
Liquid Media Composition for *P. productus* and *C. ljungdahlii*,/100mL

	P. productus	*C. ljungdahlii*
Pfennig's mineral solution	5.0 mL	5.0 mL
Pfennig's trace metal solution	0.1 mL	0.1 mL
B-vitamins solution	0.5 mL	0.5 mL
$NaHCO_3$	0.35 g	-
Resazurin	-	0.1 mL
Reducing agent		
$Na_2S \cdot 9H_2O$ (2.5% soln)	2.0 mL	-
Cysteine HCl (2.5% soln)	-	2.0 mL
Complex nutrient[a]		
Yeast extract	0.2 g	0.02 g
Cellobiose	-	0.02 g
pH	7.0	5.0

[a]Either yeast extract or cellobiose was used in studies with *C. ljungdahlii*.

Microbiology. The cultures were maintained by 37°C in Wheaton serum bottles containing liquid media of the compositions shown in Table 2. The gas phase contained synthesis gas or a 80% CO/20% CO_2 mixture.

Experimental Equipment

Several reactors were employed in the continuous studies. The continuous stirred-tank reactor (CSTR) experiments with *P. productus* were conducted anaerobically in a New Brunswick Bioflow C.30 (New Brunswick, NJ) chemostat. The reactor vessel was made of Pyrex™ glass, 750 mL nominal size, operated with a 350 mL working volume. The system was equipped with agitation, temperature and pH control, and gas and liquid inlet flow meters.

The experiments carried out in the packed-bubble column and the trickle-bed reactor employed a 5.1-cm-id, 63.5-cm-long Plexiglas™ cylinder. The empty reactor had a volume of 1091 cm^3 with a packing height of about 50 cm. Twenty mesh wood shavings were used in the packed-bubble column, with an initial void volume after packing of 860 cm^3. The trickle bed contained ceramic Intalox saddles, 1/4″ nominal size, with an initial column porosity of 0.59. Operation of the packed-bubble column was carried out countercurrently and the trickle bed was run cocurrently to avoid liquid flooding and foaming, with both fluids flowing from the top to the bottom.

In all of the experimental studies involving *P. productus*, a gas containing 63.43% CO, 20.61% CH_4 (inert), and 15.96% CO_2 flowed from the pressurized tank through a fine metering valve and rotameter into the reactors.

Experiments with *C. ljungdahlii* were carried out in two New Brunswick Bioflo C.30 chemostats connected in series. Basal medium as described in Table 2 was fed continuously to Reactor A (first stage) using a Masterflex™ pump, with gravity overflow of the effluent and cells to Reactor B (second stage). Temperature and pH controls were provided for each system. No additional liquid medium was fed to Reactor B; the agitation rate was maintained at 400 rpm in each vessel by a magnetic stirring device.

Each stage was supplied with synthesis gas (55.25% CO, 10.61% CO_2, 18.11% H_2, and 15.78% Ar [inert]) at identical flow rates. By using a flow breaker between the reactors, it was assured that Reactor B received only overflow liquid from Reactor A, along with a fresh gas supply.

Analytical Methods

The cell concentrations for the cultures were determined by measuring the optical density of samples withdrawn from the flasks at 580 nm in a Bausch and Lomb Spectronic 20 spectrophotometer.

A 3 mm × 1.8 m 60/80 mesh Carbosphere™ column and a HWD detector system were used to determine CO, CH_4, CO_2, and Ar in the gas phase by GC. In using this procedure, the oven temperature was maintained at 135°C, the detector and injector temperatures were both 175°C, and the carrier gas was helium at a flow rate of 40 mL/min. GC was also used in measuring the acetate concentration in the liquid phase. A 1.8-m column packed with Porapak™ Q, 100/120 mesh, was used in these tests. The oven temperature was maintained at 125°C, the detector and injector temperatures were both 220°C, and the carrier gas was helium at a flow rate of 40 mL/min.

RESULTS AND DISCUSSION

Conversion of CO to Acetate by *P. productus*

The choice of a suitable reactor for gas–liquid reaction or adsorption is very often a question of matching the reaction kinetics with the capabilities of the proposed reactor. In the case of biological systems, special care must be taken to ensure the viability of the biocatalyst at the operating conditions. The specific interfacial area, liquid holdup, and mass transfer coefficients are the most significant characteristics of a reactor, and special schemes have been devised to maximize mass transfer. Mechanically agitated reactors, bubble columns, packed columns, plate columns, spray columns, gas-lift reactors, and the like are examples of various kinds of contacting systems employed in these types of processes. Several of these reactors have been employed at the University of Arkansas with the strict anaerobic bacterium *P. productus* to convert CO to acetate. A brief review of the results obtained in these reactors, as well as the efforts

toward modeling reactor performance, are given below for *P. productus* as a model system. The mass-transfer-limited concepts shown for this organism are applicable to other gas-phase fermentation systems.

The Stirred-Tank Reactor

The traditional reactor used in fermentation processes is the CSTR. As it relates to gas-phase substrates, the CSTR utilizes continuous gas flow into a constant-volume liquid-phase reactor. A small liquid feed stream is utilized to supply nutrients to the microorganism in the reactor system and to remove products. The agitation rate in the system is relatively high in order to promote transfer of the sparingly soluble gas into the liquid culture medium.

Experiments were performed with *P. productus* in a CSTR at different gas flow rates under mass transfer limited conditions. In these experiments, the progress of the reaction was followed by use of an inert component, whose partial pressure did not change throughout the system. Assuming perfect mixing in both the gas and the liquid phases, the outlet ratio of CO to an inert (Y) may be related to the operating parameters according to Eq. (1):

$$1 / Y_{CO} = 1 / Y^{i}_{CO} + (V_L / Y^{i}_{CO}) (K_L a / H) (P_I / n_I) \quad (1)$$

The agreement of the experimental data gathered with the model equation, as well as the procedure to evaluate the volumetric mass transfer coefficient achieved under the operating conditions, is shown in Fig. 1. A model including Eq. (1), as well as material balances for the gases flowing into the reactor and equilibrium relationships for the gas-phase CO_2 with the bicarbonate and the pH level in the liquid, has been developed (*24*). The solutions of the model for various volumetric mass transfer coefficients are shown in Fig. 2. Experimental data at a mass transfer coefficient of 30 are also included in the figure. As observed in the model results, increases in the mass transfer coefficient lead to higher reactor productivities. Because of the perfect mixing in a CSTR, complete conversion is possible only when the gas flow rate is zero. The use of the model allows the extrapolation of performance of the CSTR system and will permit the preliminary economic evaluation of an industrial-scale process when coupled with suitable equations for scale-up of such properties as the mass transfer coefficient.

Mechanically agitated bubble contactors are very effective with viscous liquids or slurries and very low gas flow rates and large liquid volumes. They are also noted for the ease with which the intensity of agitation can be varied and the heat can be removed. Their principal disadvantages are the cost of high agitation rates and the fact that they do not allow for complete conversion of the inlet gas except at a zero gas flow rate.

Packed-Bubble Column

Bubble columns are commonly used in industrial processes, both as reactors and absorbers, whenever a large liquid retention time and/or a

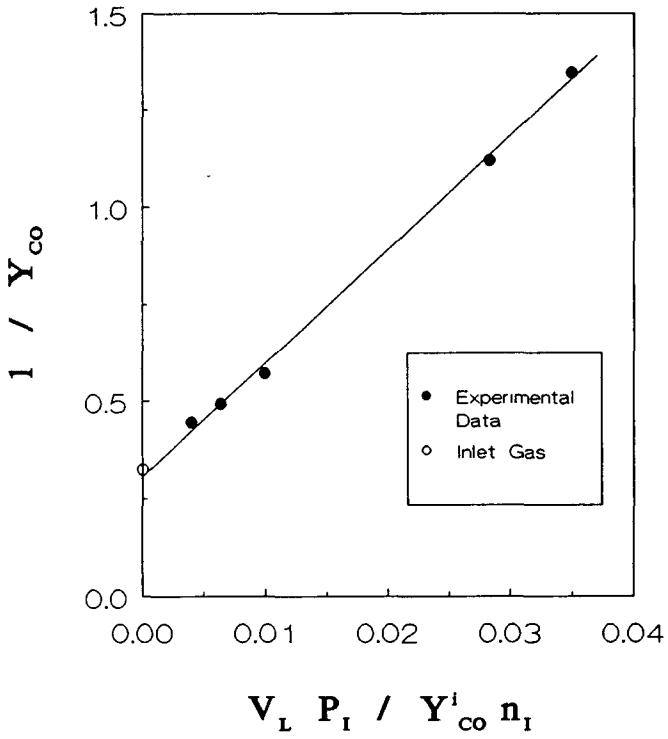

Fig. 1. Model verification and evaluation of the volumetric mass-transfer coefficient in a CSTR.

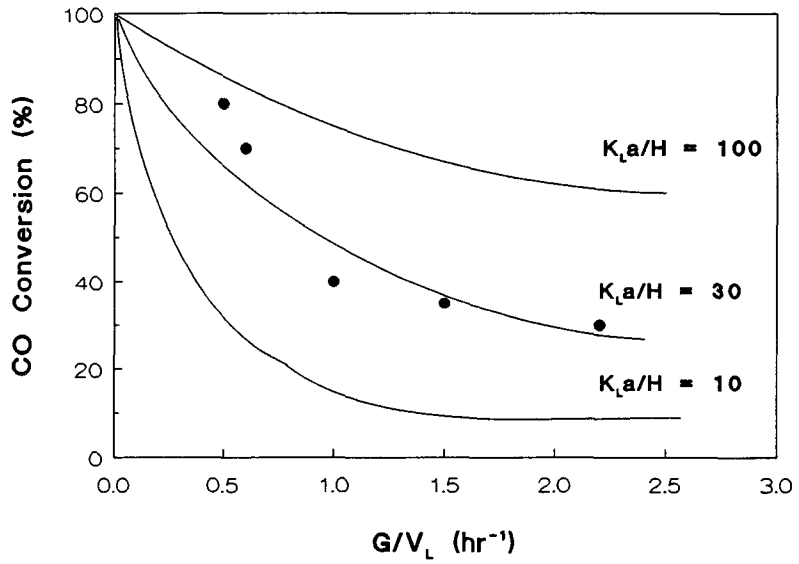

Fig. 2. Model results for carbon monoxide conversion as a function of the gas flow rate/unit of culture volume for various volumetric mass-transfer coefficients (K_La/H in mmol CO/atm-L-H).

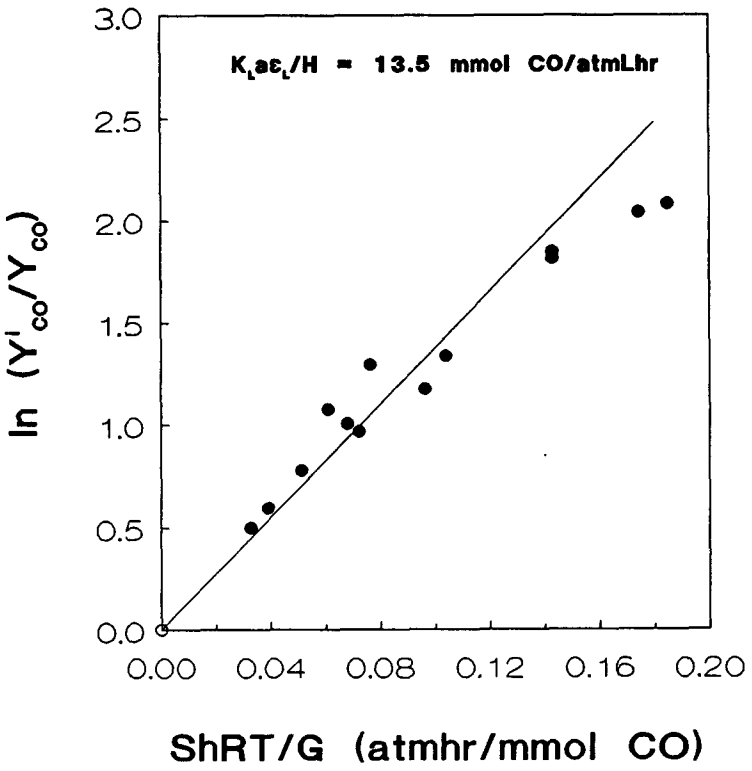

Fig. 3. Model verification and evaluation of the volumetric mass-transfer coefficient in the packed-bubble column.

large liquid holdup is needed. Some advantages of bubble columns are the elimination of mechanical agitation, minimum maintenance, relatively low costs, high interfacial area and high mass transfer coefficients (*25*). The principal disadvantages are a large extent of backmixing and coalescence. These two drawbacks can be minimized by employing packing inside the column.

Experiments have been conducted with *P. productus* in a packed-bubble column at various gas flow rates in a manner similar to that in the CSTR studies. For this system, assuming perfect plug flow in the gas phase ascending through the column and constant partial pressure of the inert gas in the system (as closely substantiated from experimental data), the outlet ratio of CO to the inert component can be related to other operating conditions (*26*) according to

$$\ln Y^{i}_{CO} / Y_{CO} = (K_L a / H)\, \epsilon_L\, (ShRT / G) \qquad (2)$$

A plot of ln (Y^{i}_{CO}/Y_{CO}) vs $ShRT/G$ yields a straight line with slope $K_La\epsilon_L/H$ (Fig. 3). Regression of the experimental data of this plot gives an operating value for $K_La\epsilon_L/H$ of about 13.5 mmol CO/atm-L-h. The numerical solution (Runge-Kutta) of the differential equations that describe the system were then applied to other operating conditions of contacting and are shown in

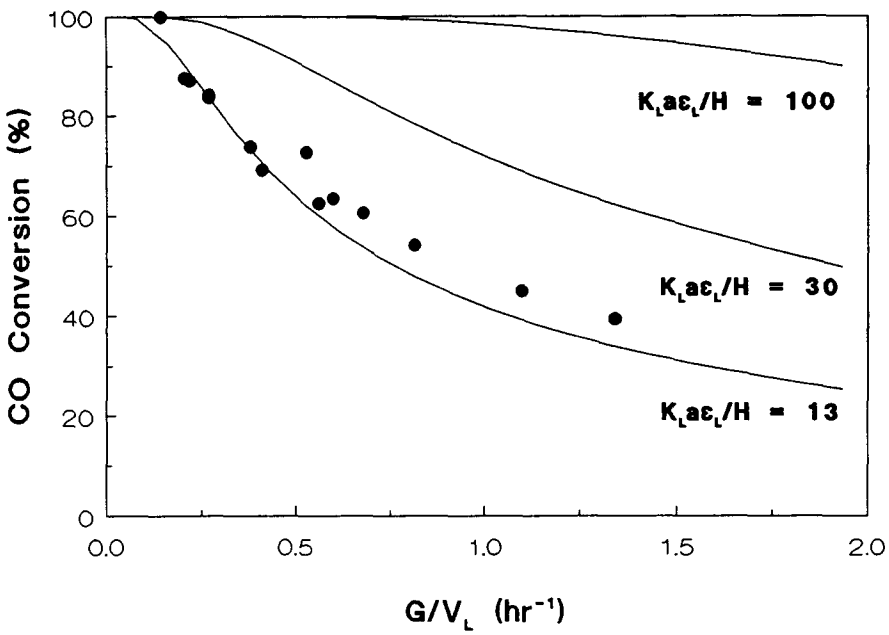

Fig. 4. Model results for carbon monoxide conversion as a function of the gas flow rate/unit of culture volume for various volumetric mass-transfer coefficients in a packed-bubble column (K_La/H in mmol CO/atm-L-h).

Fig. 4. Experimental data are given for $K_La\epsilon_L/H = 13.5$. The slight deviation of the experimental data with respect to the model predictions in Fig. 4 is caused by departure from the assumptions in the derivation of Eq. (2). A comparison of the data shown in Fig. 4 with the results obtained for the CSTR (Fig. 2) indicates the benefit of plug flow operation in the gas phase by allowing almost complete conversions at gas flow rates above zero.

The packed-bubble column achieves higher rates of specific CO conversion in comparison with the stirred-tank reactor without the need for more expensive mechanical agitation. More importantly, at the same mass transfer coefficients as in the CSTR, conversions are substantially higher. The major disadvantage of a bubble or packed-bubble column is the lack of flexibility in operating conditions, since the contacting capabilities are mainly fixed with the design of the column dimensions and packing.

Trickle-Bed Reactors

Trickle-bed reactors are used conventionally to obtain a low pressure drop or low liquid holdup when there is practically no heat to remove or supply, or when the liquid is corrosive. They are usually operated countercurrently, since a higher driving force can be achieved in that manner than with cocurrent operation. However, when an irreversible reaction occurs between the dissolved gases and the absorbent (as in biological systems), the mean concentration driving force is the same for both modes of operation. In this case, the capacity of cocurrent columns is not

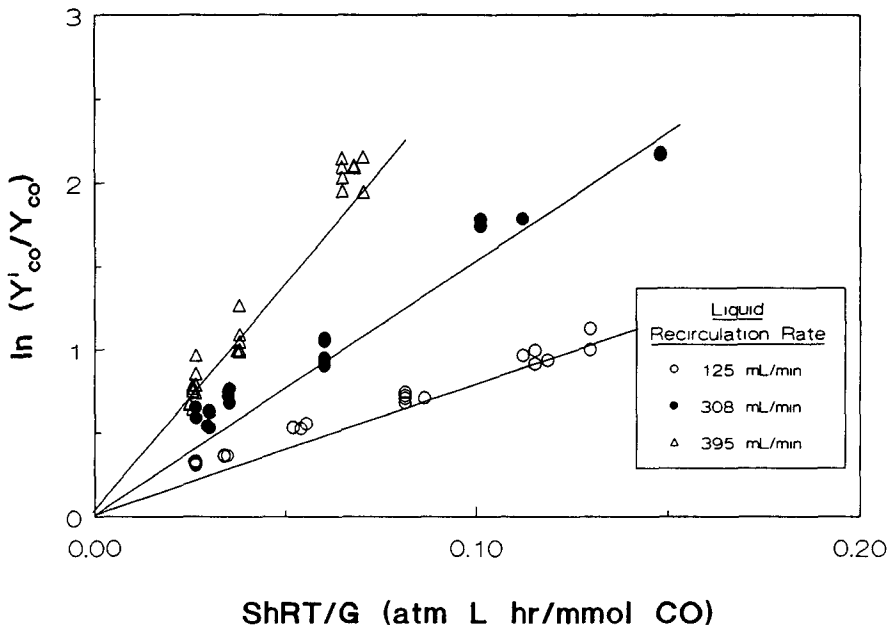

Fig. 5. Model verification and evaluation of the volumetric mass-transfer coefficient in the trickle-bed reactor.

limited by flooding, and at any given flow rates of gas and liquid, the pressure drop in a cocurrent column is less (*25*).

Experiments have been conducted with *P. productus* in a cocurrent column packed with ceramic Intalox saddles. In this experimental setup, the liquid and the gas are disengaged in a liquid/gas separator, and the culture is recirculated back to the top of the column. In this manner, a high concentration of cells can be maintained inside the reactor while using high liquid/gas operating conditions inside the column. For the results obtained in this column, the same general considerations used in the bubble column can be used, and a model based on Eq. (2) can be developed.

The arrangement of the experimental data gathered with *P. productus* in the trickle-bed column at three different recirculation rates according to Eq. (2) is shown in Fig. 5. The slope of the lines obtained by linear regression of the data corresponds to the value of the volumetric mass transfer coefficent ($K_L a \epsilon_L / H$) achieved at each operating condition. The experimental data for CO conversion in the trickle bed at three liquid recirculation rates, along with the model simulation, are then presented in Fig. 6 as a function of the gas flow rates employed/unit of initial void volume in the column. The initial void volumn has been chosen as the volume basis to allow direct comparison with the bubble-column results, where the culture volume is the initial void volume. As may be observed in Fig. 6, the mass transfer capability of the column is greatly enhanced by increasing the liquid recirculation rate. At the highest recirculation rate employed,

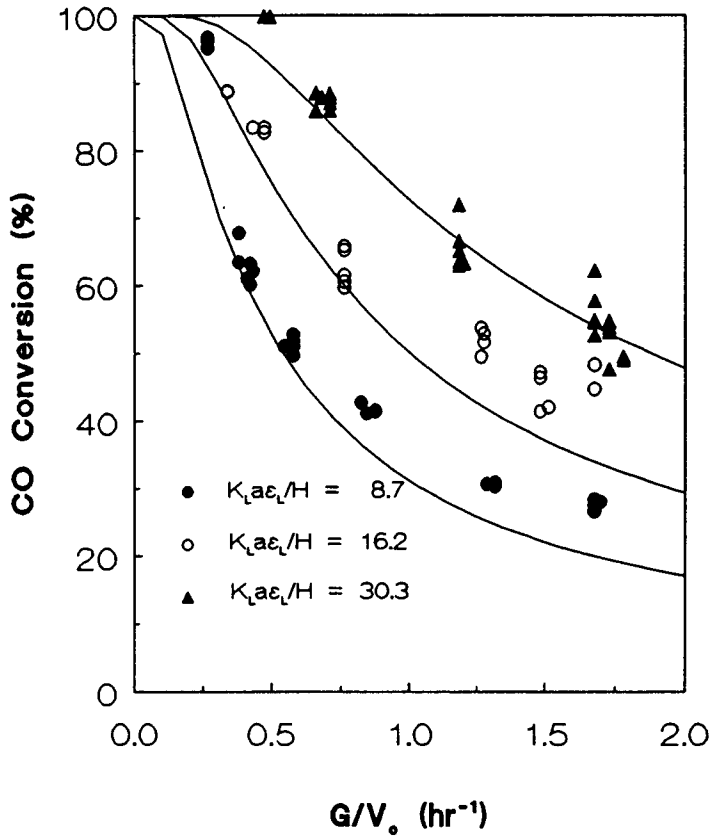

Fig. 6. Model results for carbon monoxide as a function of the gas flow rate/unit of initial column void volume for various volumetric mass-transfer coefficients in a cocurrent tricle-bed reactor.

a $K_{L}a\epsilon_L/H$ value around 30 mmol CO/atm-L-h was obtained, more than twice the value obtained during bubble column operation in the same reactor.

Conversion of CO, CO_2, and H_2 to Ethanol by *C. ljungdahlii*

As was mentioned previously, *C. ljungdahlii* produces significant levels of acetate as a byproduct of converting CO, CO_2, and H_2 to ethanol. The initial product ratio (moles ethanol/mole acetate) in batch culture was about 0.05, with an ethanol concentration of less than 1 g/L (*18*). Many techniques, such as nutrient limitation, pH shift, and the addition of reducing agents or alterate nutrient sources to the liquid medium, have been used in improving both the product ratio and ethanol concentration.

One technique that has proven to be particularly useful in enhancing ethanol production by *C. ljungdahlii* has been the use of two CSTRs in series. The first reactor in the series arrangement is used to promote cell

growth, and the second reactor is used for increased ethanol production. A pH shift between the reactors, from 4.5 to 4.0, is used to cause the onset of ethanol production while causing growth to cease. Media constituents to promote growth can thus be added to the first reactor, and constituents to promote ethanol production at the expence of acetate production can be added to the second reactor.

Figures 7 and 8 show the results of an experimental study employing the stirred-tank reactors. Yeast extract (0.02%) was added to the liquid medium of Reactor A (the first reactor of the two-stage system) during the first 8 d of operation, and cellobiose (0.02%) replaced the yeast extract during the last 10 d. Little difference was observed in cell concentration in Reactor A when using yeast extract instead of cellobiose, with both nutrients yielding approximately 200–250 mg/L cells (data not shown). As noted in Fig. 7, the ethanol concentration in Reactor A increased rapidly during the first 3 d of operation before stabilizing at a 1 g/L concentration. The use of cellobiose stimulated ethanol production only slightly, to about 1.3 g/L. Ethanol concentration in Reactor B increased to nearly 3 g/L and seemed to be stimulated somewhat by the use of cellobiose as the nutrient for cell growth in Reactor B. Substrate CO and H_2 conversions were essentially 100% in Reactor A, but fluctuated considerably in Reactor B (data not shown).

Figure 8 shows the molar product ratios (ethanol/acetate) for both reactors as a function of time of operation. As noted, the ratios increased with time in both reactors, reaching a value of about 1.0 in Reactor A and a value of about 1.5 in Reactor B. The addition of cellobiose seemed to improve the product ratio over yeast extract. In subtracting the product concentrations produced in Reactor A from those exiting Reactor B, it is seen that steady ratios of 4 moles ethanol/mole of acetate were obtained. A system has thus been developed that shows significant promise in improving both product ratio and ethanol concentration.

Specific productivities in a single CSTR were previously reported for *C. ljungdahlii* at 9 mmole ethanol/gcell-day (*9*). Presently, specific productivities in the range of 250–300 mmol ethanol/gcell-day have been attained by utilizing the two-stage CSTR system.

CONCLUSIONS

Synthesis gas may serve as an important raw material for the biological production of liquid and gaseous fuels by fermentation. This paper presents the results of CO conversion studies to form acetate and ethanol in continuous reactors, using the anaerobic bacteria *P. productus* and *C. ljungdahlii*. The conversion of CO to acetate by *P. productus* was carried out in continuous stirred-tank, packed-bubble column, and trickle-bed reactors. Models were used to estimate the mass transfer coefficients in

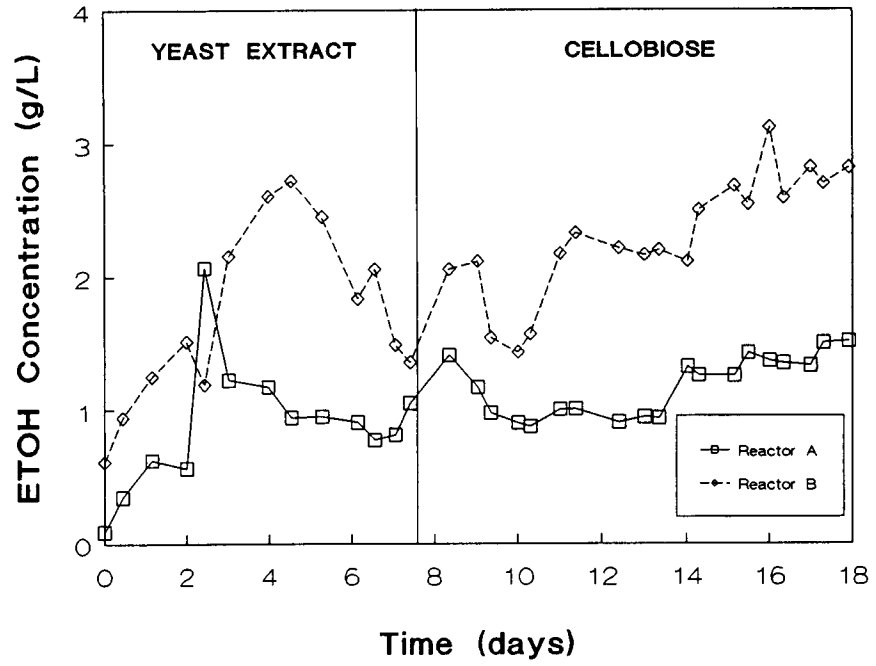

Fig. 7. Ethanol concentrations attained in a two-stage CSTR system with *C. ljungdahlii.*

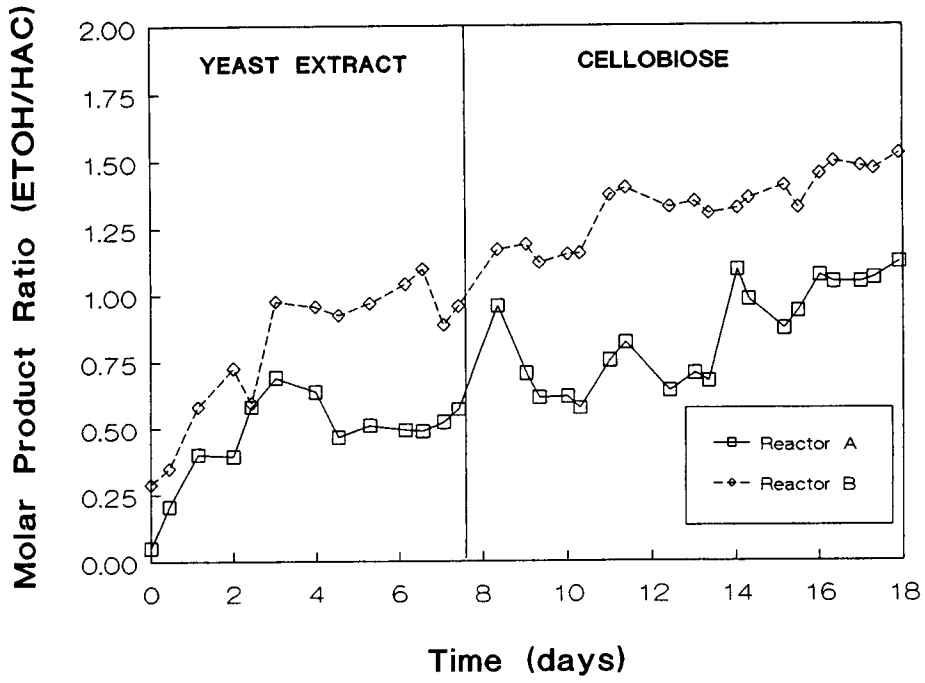

Fig. 8. Molar product ratios attained in a two-stage CSTR system with *C. ljungdahlii.*

these systems and to estimate substrate conversion as a function of the mass transfer coefficient and total system pressure.

C. ljungdahlii has been used to convert CO, CO_2, and H_2 to ethanol. Using a two-stage CSTR system, ethanol concentrations of nearly 3 g/L have been obtained, with a product ratio of 4 moles ethanol/mole of acetate in the second stage. Specific ethanol productivities of 250–300 mmole/gcell-day were obtained, which represents a 30-fold improvement over previously reported results.

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REFERENCES

1. Tsao, G. T. and Lee, Y. H. (1977), *Ann. Reports Ferm. Proc.* **1,** 115.
2. Blanch, H. W. (1979), *Ann. Reports Ferm. Proc.* **3,** 47.
3. Yoshida, F. (1982), *Ann. Reports Ferm. Proc.* **5,** 1.
4. Ljungdahl, L. G. and Wiegel, J. (1986), *Manual of Industrial Microbiology and Biotechnology,* Demain, A. L. and Solomon, N. A., eds., American Society for Microbiology, Washington, DC, pp. 84–96.
5. Escalamente-Semerena, J. C., Rinehart, K. L., Jr., and Wolfe, R. S. (1984), *Proceedings of the 4th International Symposium,* Crawford, R. L. and Hanson, R. S., eds., American Society for Microbiology, Washington, DC.
6. Jones, W. J., Nagle, D. P., Jr., and Whitman, W. B. (1978), *Microbiol. Rev.* **51,** 135.
7. Huser, B., Wuhrmann, K., and Zehnder, A. J. B. (1982), *Arch. Microbiol.* **132,** 1.
8. Daniels, L., Fuchs, G., Thauer, R. K., and Zeikus, J. G. (1977), *J. Bacteriol.* **132,** 118.
9. Vega, J. L., Prieto, S., Elmore, B. B., Clausen, E. C., and Gaddy, J. L. (1989), *Appl. Biochem. Biotech.,* in press.
10. Genther, B. R. S. and Bryant, M. P. (1983), *Appl. Environ. Microbiol.* **43,** 70.
11. Uffen, R. L. (1976), *Proc. Natl. Acad. Sci. USA* **73,** 3298.
12. Dashkevicz, M. P. and Uffen, R. L. (1979), *Int. J. Sys. Bacteriol.* **29,** 145.
13. Breed, R. S., Murray, E. G. D., and Smith, N. R. (1977), *Bergey's Manual of Determinative Bacteriology,* 8th ed., Williams and Wilkins, Baltimore, Maryland.
14. Kluyver, A. J. and Schnellen, C. G. (1947), *Arch. Biochem.* **14,** 57.
15. Tracy, C. A. and Ashare, E. (1983), *Fuel Gas Developments,* Wise, D. L., ed., CRC Press, Boca Raton, Florida, pp. 107–132.

16. Vega, J. L., Holmberg, V. L., Ko, C. W., Clausen, E. C., and Gaddy, J. L. (1988), "Advanced Studies of the Biological Conversion of Coal Synthesis Gas to Methane. Topical Report 1: Reactor Optimization," USDOE, Morgantown Energy Technology Center, Contract No. DE-AC21-86MC23281.
17. Wiegel, J. (1980), *Experientia* **36,** 1.
18. Barik, S., Prieto, S., Harrison, S. B., Clausen, E. C., and Gaddy, J. L. (1988), *Appl. Biochem. Biotech.* **18,** 363.
19. Clausen, E. C. and Gaddy, J. L. (1989), "Advanced Studies of Biological Indirect Liquefaction of Coal. Topical Report 1. Culture Identification," USDOE, Pittsburgh Energy Technology Center, Contract No. DE-AC22-88PC79813.
20. Rogers, P. (1986), *Adv. Appl. Microbiol.* **31,** 1.
21. Rao, G. and Mutharasan, R. (1988), *Biotech. Lett.* **10,** 313.
22. Rao, G., Ward, P. J., and Mutharasan, R. (1987), *Ann. Acad. Sci.* **506,** 77.
23. Kim, T. S. and Kim, B. H. (1988), *Biotech. Lett.* **10,** 123.
24. Vega, J. L., Antorrena, G. M., Clausen, E. C. and Gaddy, J. L. (1989), *Biotech. Bioengr.* **34,** 785.
25. Charpentier, J. C. (1981), *Adv. Chem. Engr.* **11,** 1.
26. Antorrena, G. M. (1987), University of Arkansas, Department of Chemical Engineering.