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Biological Conversion of Coal Gas to Methane

Scientific Note

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ABSTRACT

Biological conversion of low-Btu coal synthesis gas to higher Btu methane was demonstrated using both pure co-cultures and/or adapted-mixed anaerobic bacteria. *Peptostreptococcus productus* metabolized coal gas to mainly acetate and CO_2. The co-cultures containing methanogens converted these products to methane. In mixed culture studies, CH_4 and small amounts of acetate were produced. Reactor studies using stirred-tank and immobilized cell reactors exhibited excellent potential to convert CO, CO_2 and H_2 to methane at higher gas flow rates. Gas retention times ranging from 0.7 to 2 hours and high agitation were required for 90 percent CO conversion in these systems. This paper also illustrates the potential of biological methanation and demonstrates the need for good mass transfer in converting gas phase substrates.

Index Entries: Coal synthesis gas; *Peptostreptococcus productus*; carbon monoxide; methane; anaerobic.

INTRODUCTION

A synthesis gas containing principally hydrogen and carbon monoxide is produced during the catalytic hydrogasification of coal. To upgrade the low-Btu gas, a catalytic shift conversion reaction is traditionally employed to convert carbon monoxide and water to carbon dioxide and hy-

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drogen. Following purification to remove excess carbon dioxide and hydrogen sulfide, the hydrogen and carbon dioxide are catalytically reacted to methane and water. The water is then removed to give a gas that is 95–98% methane, with an energy content of 980–1035 Btu/scf.

Microorganisms may also be used to convert coal to methane by their action on syngas. Microbial processes offer certain advantages over chemical conversions. Microorganisms exist and carry out conversions at ambient temperatures and pressures, which should result in substantial energy and equipment savings. Also, yields from microbial conversions are quite high, since the microorganism utilizes only a small fraction of the substrate for energy and growth. Under proper conditions, microbial conversions are quite specific, generally converting a substrate into a single product, with perhaps a few byproducts. These advantages are offset by slower reaction rates and special reactor considerations, such as sterility, nutrient provision, and so on.

The purpose of this paper is to present an overview of the possible biological routes to produce methane from coal synthesis gas substrates. The paper focuses on the feasibility of the reactions from an industrial approach and topics such as operation at increased pressure, conversion levels under various conditions, and mass transfer difficulties are addressed. Experimental results comparing mixed culture performance and various pure culture microorganisms are presented and discussed.

MICROBIOLOGY OF BIOLOGICAL CONVERSION

The primary reactions in the biological conversion of synthesis gas to methane are the formation of methane precursors and the biomethanation reactions. Table 1 shows the known biological routes to methane from synthesis gas components. 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 (*1*). As is seen in the table, the formation of methane can be accomplished by direct conversion of CO, CO_2, and H_2 or by the indirect formation of methane intermediates (acetate or H_2 and CO_2). Of the one-step reactions, only reaction I.3, the direct formation of methane from H_2 and CO_2, has been well-studied and verified (*2*). This reaction is known to be carried out by most of the methanogens, (*3*). Still, some methanogens such as *Methanothrix* sp. are not capable of this direct conversion (*4*).

The one-step reactions that convert carbon monoxide directly to methane have been suggested in the literature. *Methanobacterium thermoautotrophicum* has been reported to produce methane from carbon monoxide according to Eq. (I.1) (*5*). The growth of *M. thermoautotrophicum* on CO was reported to be very slow and was inhibited by high substrate concentrations. It has also been reported that other methanogenic bacteria may convert carbon monoxide and hydrogen directly to methane according to Eq. (I.2) (*6,7,8*). It is more likely, however, that the carbon

Table 1
Possible Routes to Methane from Coal Gas Components

(I) One-step reactions

$$4CO + 2H_2O \xrightarrow{I.1} CH_4 + 3CO_2 \qquad \Delta G^0 = -50.4 \text{ kcal/reac.}$$

$$CO + 3H_2 \xrightarrow{I.2} CH_4 + H_2O \qquad \Delta G^0 = -36.0 \text{ kcal/reac.}$$

$$4H_2 + CO_2 \xrightarrow{I.3} CH_4 + 2H_2O \qquad \Delta G^0 = -31.3 \text{ kcal/reac.}$$

(II) Multiple-step reactions

$$4CO + 2H_2O \xrightarrow{II.1} CH_3COOH + 2CO_2 \xrightarrow{II.4} CH_4 + CO_2$$
$$\Delta G^0 = -37.8 \text{ kcal/reac.} \qquad \Delta G^0 = -12.6 \text{ kcal/reac.}$$

$$4H_2 + 2CO_2 \xrightarrow{II.2} CH_3COOH + 2H_2O \xrightarrow{II.4} CH_4 + CO_2$$
$$\Delta G^0 = -18.7 \text{ kcal/reac.} \qquad \Delta G^0 = -12.6 \text{ kcal/reac.}$$

$$CO + H_2O \xrightarrow{II.3} H_2 + CO_2 \xrightarrow{II.3 \text{ or } II.2 + II.4} CH_4 + \ldots$$
$$\Delta G^0 = -4.8 \text{ kcal/reac.}$$

monoxide reduction to methane in these experiments proceeded via the multiple-step reactions II.3 and I.3 (*5,9*).

With the exception of Eq. (I.3), an indirect formation of methane seems more viable than the direct routes previously discussed. These multistep reactions may involve the formation of a liquid intermediate, acetate, or the utilization of carbon monoxide to produce carbon dioxide and hydrogen by the water gas shift reaction [Eq. (II.3)]. In the latter case, the products of hydrogen and carbon dioxide can be directly converted to methane [Eq. (I.3)] or may enter the multiple step process that produces acetate as an intermediate [Eq. (II.2)]. The organisms *Rhodopseudomonas gelatinosa* (*10,11*), and *Rhodospirillum rubrum* (*12*) are known to perform the water–gas shift reaction. Unfortunately, *R. gelatinosa* requires complete darkness and *R. rubrum* will not grow in the absence of light.

The most promising approach to indirect methane production is probably the formation of acetate as a methane precursor. In anaerobic digestion processes, 80% of the methane is produced from acetate by Eq. (II.4). The organisms *Peptostreptococcus productus* (*13*), *Acetobacterium woodii* (*14*), and *Eubacterium limosum* (*15*) have been found to produce acetate by Eq. (II.1). Among these bacteria, *P. productus* has shown the fastest growth rate and the highest tolerance to carbon monoxide. These microorganisms have also been found to carry out the conversion of hydrogen and carbon dioxide to acetate [Eq. (II.2)], although in *P. productus*, carbon monoxide appears to be a preferred substrate.

Acetate can be transformed by methanogens of the Methanosarcinaceae family such as *Methanosarcina barkeri* and *Methanothrix soehngenii* (3).

While *Methanosarcina barkeri*, for example, will utilize acetate only in the absence of other preferred substrates (such as H_2 and CO_2), *Methanothrix* sp. does not utilize normal methanogenic substrates and growth and methane formation is exclusively observed in the presence of acetate (*4,16*). Both microorganisms show comparable specific growth rates at low acetate concentrations (< 3 mM). On the other hand, in view of the Monod saturation constants available for the two microorganisms, (K_s = 0.7 μmol/L for *Methanothrix*), it is expected that at low acetate concentrations *Methanothrix* is the more predominant of the two.

MATERIALS AND METHODS

Sources of Organisms

Peptrostreptococcus productus, strain U-1, and *Acetobacterium woodii* were kindly supplied by Professor M. P. Bryant, University of Illinois, Urbana, IL 61801. *Rhodopseudomonas gelatinosa* and *Rhosospirillum rubrum* (Strains I and II) were obtained from the American Type Culture Collection, Rockville, MD 20852.

Media and Conditions of Cultivation

The anaerobic techniques for the preparation and use of media were essentially those of Hungate (*17*), as modified by Bryant (*18*) and Balch and Wolfe (*19*). A basal salts medium supplemented with yeast extract and vitamins was used to grow the bacterial cultures (*20*).

Sodium sulfide (2.5%) was used to reduce the media prior to use. The medium was always inoculated (5–10% inoculum) with a log-phase culture. The CO or synthesis gas mixture was added using either a sterile syringe fitted with a one-way valve or a gas manifold in connection with a vacum pump.

Control tubes without CO or synthesis gas were run simultaneously with each experiment. The cultures of *P. productus* were incubated (flat) in the dark at 37°C, and *A. woodii* was incubated at 30°C. All incubations of *R. rubrum* (Strains I and II) were performed under tungsten light at 30°C. *R. gelatinosa* was grown in an incubator at 30°C.

Synthesis Gas Composition

Two synthesis gas compositions as shown in Table 2 were used in the experimental studies. These compositions were chosen as typical compositions from coal gasification processes. As noted, the synthesis gas contained small amounts of carbon dioxide and methane, as well as carbon monoxide and hydrogen as the major components.

Table 2
Laboratory Synthetic Coal Gas Composition

	Mole Percent	
	Gas I	Gas II
Carbon Monoxide	45	65
Hydrogen	30	22
Carbon Dioxide	15	11
Methane	10	2

Reaction Vessels

Two types of reaction vessels were utilized, the stirred-tank reactor and a plug flow fixed film or immobilized cell reactor. The stirred-tank reactor consisted of a New Brunswick Model C30 chemostat modified for continuous gas flow and anaerobic operation. The fixed-film reactors were packed column reactors utilizing either Raschig rings or wood chips as the inert support.

Analytical Procedures

Several analytical procedures were used on a routine basis to monitor the progress of the experiments. Gas composition was measured on a daily basis. On a periodic basis, the liquid culture was analyzed for bacterial growth, pH, ammonia, ATP, and volatile fatty acids. These experimental methods will be described briefly in the following sections.

Bacterial Growth

Bacterial growth was determined by optical density (OD) measurement using a Bausch and Lomb Spectronic-20 spectrophotometer. Growth of *P. productus, A. woodii,* and mixed cultures were measured at 580 nm whereas the optical densities of *R. gelatinosa* and *R. rubrum* (Strains I and II) were taken at 600 nm.

Liquid Analysis

An Orion Research Ionalyzer (Model 407A) was used for measuring ammonia in the bacterial culture. Cellular ATP was measured by luminescence techniques using a Pico-Lite Luminometer Analyzer (Packard Instruments Company). The fermentation products were determined as free acids using a Perkin-Elmer Sigma 3B gas chromatograph. The samples were injected into a 2′ × ⅛″ Teflon column packed with Poropak QS and the amount of the acids were calculated using an area percent—concentration standard curve for the individual acids.

Gas Analysis

Gas compositions were determined by gas-solid chromatography using a Perkin-Elmer Sigma 300 gas chromatograph equipped with a hot

wire detector. A 6′ × ⅛″ stainless steel column packed with 60–80 mesh Carbosphere was used for this purpose.

RESULTS

As illustrated in Table 1, several combinations of reactions may be used to produce methane from the components of synthesis gas. In a series process, methane precursors are first produced in pure culture from CO, CO_2, and H_2. Because these gas phase reactants are, for the most part, only slightly soluble in the liquid phase, mass transfer is an important consideration. Methane is then produced from the precursors in a second reaction vessel. In a one-step process, methane is produced directly from CO, CO_2, and H_2 by a single culture, a co-culture, or an acclimated mixed culture isolated from natural sources. This reaction scheme is much the same as methane precursor formation in the series process.

Pure Culture Studies

A schematic of a process to produce methane from synthesis gas components using a series of pure cultures is shown in Fig. 1. Synthesis gas is first fed to a reactor where the conversion of CO to acetate takes place according to Eq. (II.1). This reaction alternative is superior to other possibilities, as will be described later. The CO_2, H_2, and methane present in the synthesis gas is then converted in a second reactor either to methane by Eq. (I.3), or to acetate utilizing Eq. (II.2). Both of these reactions are under study, so that the preferred process is uncertain at this time. The production of acetate from CO_2 and H_2 will probably not occur in the presence of CO, so that a second reactor is required. Finally, the acetate is converted to methane by Eq. (II.4).

In analyzing the process scheme of Fig. 1, two types of reactions are observed. The utilization of CO, CO_2, and H_2 to produce acetate or methane are reactions in which mass transfer is quite important, since the reactants must first be transferred into the liquid phase prior to reaction. Methane production from acetate is a liquid phase reactant so that reactor design is controlled by kinetic analysis.

Reactions Significantly Affected by Mass Transfer

The conversion of CO, CO_2, and H_2 to acetate or methane can be viewed as a series of elementary steps by which the substrate is transported to the cells, where the reaction takes place. The gas phase substrate must pass through a series of transport resistances, the magnitudes depending upon the characteristics of the system employed (*21*).

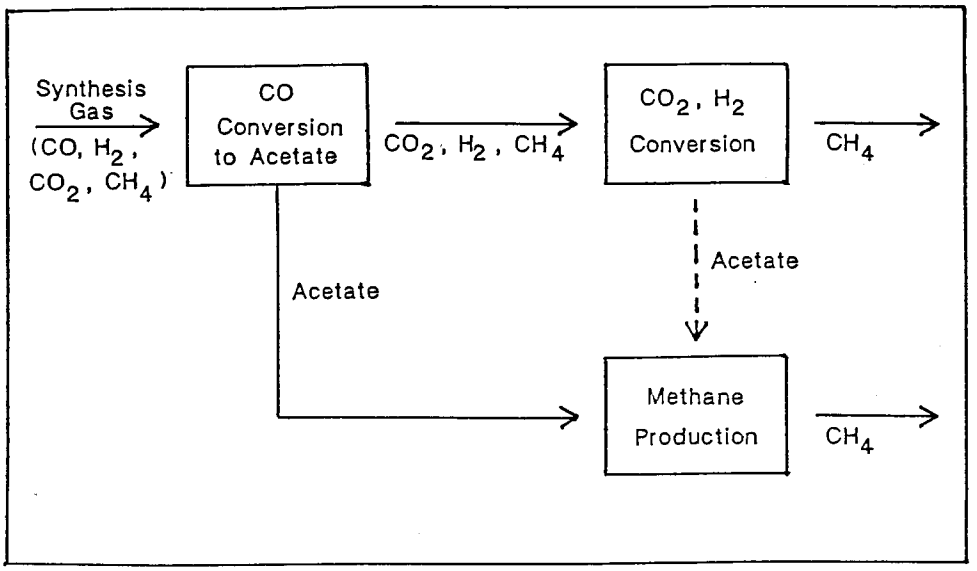

Fig. 1. Series production of methane from synthesis gas.

For slightly soluble gases, all of the resistance essentially lies in the liquid-side film. Thus, special attention must be given to maximizing mass transfer in producting acetate or methane from CO, H_2, and CO_2.

Pure cultures of CO converting bacteria were screened for their ability to convert CO to methane intermediates. CO converters were chosen since the natural sources, such as sewage sludge, are deficient in these bacteria, thus requiring long acclimation times. Methane bacteria are well defined and were not included in these screening studies. Conversion to both acetate and CO_2 and H_2 were considered since pure culture methane bacteria are able to use both products as substrates. The results of this screening study are shown in Table 3. On the basis of prolonged screening and optimization studies, two anaerobic bacteria were selected as having significant promise. *Rhodospirillum rubrum,* Strain II, utilizes CO to produce CO_2 and H_2. *Peptostreptococcus productus* utilizes CO to produce acetate. Both of these organisms have been found to be capable of utilizing up to 90% CO in producing methane intermediates. Neither H_2S nor COS, in concentrations up to 2%, affect the rate of production, although bacterial growth is inhibited by higher concentrations of COS. These organisms are available for use in combination with methane bacteria in series reactors and as a coculture in a single reactor.

To demonstrate the feasibility of gas phase conversion, CSTR and fixed film reactors were used in the conversion of CO to acetate. The anaerobic bacteria *Peptostreptococcus productus* was fed synthesis gas at various gas retention times in a chemostat with continuous gas flow. The liquid was exchanged as needed on a periodic basis. A summary of the results of these experiments is shown in Table 4. As noted, a 90% conver-

Table 3
Survey of Shift Conversion Organisms

Organism	Maximum Optical Density[1]	Conditions of Growth	Doubling Time	Time Required to Utilize CO (days)	Max % CO Tolerance	Major Products
P. productus	0.83(50)[2]	37°C, dark	4–6 hours	4(50)[2]	90	Acetate + CO_2
R. gelatinosa	0.16(20)	20°C, dark	30 hours	12(20)	30	H_2 + CO_2
R. rubrum (I)	0.46(50)	30°C, tungsten light	35 hours	11(50)	60	H_2 + CO_2
R. rubrum (II)	1.0 (50)	30°C, tungsten light	24 hours	10(50)	60	H_2 + CO_2
A. woodii	0.50(25)	37°C, dark	28 hours	7(25)	Tested up to 40	Acetate + CO_2

[1]Initial O. D. substrated
[2]Growth with %CO and %CO utilization

Table 4
Conversion of Coal Gas by *P. productus* in a Bioflo Reactor

Agitation (rpm)	Gas Retention Time (hrs)*	CO Conversion (%)
250	1.56	13.7
	0.73	12.4
300	1.56	32.3
	0.73	23.3
400	1.56	69.8
	0.73	54.7
500	1.56	87.1
	0.73	60.2
600	1.56	88.0
	0.73	80.6
700	1.56	88.0
	0.73	80.6
800	1.56	90.2
	0.73	86.9
850	1.56	91.7
	0.73	87.3

*A minimum of 3–4 gas retention times were required to reach optimum conversion

Note: feed gas composition was 65% CO, 22% H_2, 11% CO_2

sion of CO can be obtained at a gas retention time of 0.73 h. High agitation rates of 800–850 rpm are required to provide adequate transfer of the CO into the liquid phases.

Peptostreptococcus productus was also employed in a fixed-film reactor in an effort to reduce the operating costs for agitation. This reactor is characterized by the attachment of bacteria to an inert support in order to yield a very high cell density. This type of reactor has been shown to yield productivities as high as 20 times the values of batch and stirred-tank vessels when producing ethanol by fermentation. Also, because of the high cell densities, reactor size is significantly reduced for a given retention time and conversion. Since a plug-flow column reactor is employed, no agitation is required. Preliminary results (not shown) indicate that a 50-min retention time can be utilized to give high conversions of CO to acetate. The performance of the reactor is a function of cell mass and performance continues to improve with increasing cell density.

Reactions Not Limited by Mass Transfer

The conversion of acetate to methane is a reaction not limited by mass transfer because the substrate is present in the liquid phase. Reaction vessels for liquid phase substrates are thus much smaller than gas-phase substrate reactors since provisions for mass transfer are unnec-

essary. Traditional fermentation vessels, such as stirred-tank and immobilized cell reactors, may thus be used for acetate conversion.

Immobilized cell reactors are particularly effective for liquid phase reactions. In these systems, the high cell density allows for throughputs which far exceed washout in a CSTR. Reactor volume can thus be minimized for a given conversion.

A fixed-film or immobilized cell reactor has been utilized for acetate conversion to methane. In the reactor, a mixed methane bacterial culture attached to an inert support was fed acetate at pH 5. No buffering of the feed was required to maintain the pH at 7.0 in the reactor.

Table 5 presents the data for the conversion of acetate to methane in an ICR using *Methanothrix* sp. A retention time of either 12 or 6 h gives total acetate conversion with a stoichiometric methane concentration of 50%. The retention time probably can be reduced as the cell mass builds up in this reactor. However, the size of this second-stage reactor is not large since it converts only the small liquid stream from the gas phase reactor. A 6-h retention time translates into a reactor of about one-thirtieth the size of the gas phase reactor. Therefore, the retention time in this reactor is less critical, and 6 h is acceptable.

Mixed Culture Studies

As an alternative to multistep pure culture processes, synthesis gas may be converted to methane in a single reactor utilizing a consortium of bacteria in a mixed culture from natural sources, or by using a coculture of pure culture bacteria. Because a single mixed culture is utilized, reactors used for these studies must necessarily be concerned with the transfer of CO, H_2, and CO_2 into the liquid phase prior to reactions. Thus, a process scheme for mixed culture conversion copies the first half of the flow diagram shown in Fig. 1. Synthesis gas is merely fed to the reactor where both the conversion to intermediates and methane occurs.

Acclimated Mixed Culture Studies

Studies have been conducted to determine the feasibility of developing an acclimated mixed culture to produce methane from synthesis gas. A sewage sludge inoculum was utilized.

Table 5
Conversion of Acetate to Methane by *Methanothrix* in a Fixed-Film Reactor

Retention Time (Hours)	Acetate Conversion (Percent)	Methane Concentration in the Gas Phase (Mole Percent)
12	100	50
6	100	50

Development of the culture was achieved by acclimation to synthesis gas first in batch and then with continuous gas flow. Culture acclimation was a slow procedure requiring approximately 3 mo of gradual gas introduction into the sludge culture. Since CO is toxic to many organisms, the liquid culture was buffered to pH 7.3 to prevent pH increase during the death of non-contributing organisms in the system. As the culture began to produce methane, the flow rate of synthesis gas was increased, and a viable cell mass began to emerge. As the culture continued to acclimate, data collection began.

The results of biomethanation studies carried out with the acclimated mixed culture at a 1.94-h gas retention time (based upon liquid volume) and variable agitation rates are shown in Table 6. Continuous gas flow was utilized in a batch liquid culture with periodic media exchange as required. These data were collected after approximately one year of continuous operation and acclimation of the mixed culture. These results indicate that a 90% conversion of CO and H_2 can occur at a 2-h retention time and an agitation rate of 500 rpm. It should be noted that a 2-h retention time is quite good for a biological reactor; ethanol fermentation, for example, requires 30–40 h in a batch culture. Nevertheless, a 2-h retention time translates into very large reactors for synthesis gas conversion. Though these reactors are simple and inexpensive, future efforts should concentrate on improving reaction rates to reduce retention time.

Early experiments with the acclimated mixed culture required an 8-h gas retention time for complete conversion. It is felt that the major reason for the improvement in the culture with time was the enrichment of the culture. Organisms necessary for CO and H_2 conversion became more dominant in the mixed culture, and thus the population of the essential CO and H_2 utilizing organisms increased. Therefore, with time the mixed culture evolved toward a consortia of organisms capable of converting CO and H_2 to methane. No efforts have been made at this time to identify the organisms present in this culture.

As with other mass transfer limited reactions, the conversions are improved with agitation rate, requiring 600 rpm for nearly complete conversion. At low agitation rates, the biological reactions are mass transfer limited. Solubilities of the reacting gases are very low and transport of

Table 6
Mixed Culture Single Stage Conversion of CO and H_2

Agitation (rpm)	Gas Retention Time (hrs)	O.D. at 580 rm	Conversion (%)	
			CO	H_2
200	1.94	2.25	0	36.6
300	1.94	2.35	40.48	62.28
400	1.94	2.30	85.16	85.78
500	1.94	2.55	89.80	90.52
600	1.94	2.15	96.28	93.03

the reactants from the gas into the liquid phase and to the solid phase is quite slow. Therefore, high agitation rates are necessary to enhance the conversion. The product gas composition under these conditions provides a closed mass balance, with a concentration of almost 40% methane and 60% CO_2.

Co-Culture Operation

An obvious economically beneficial alternative to series operation is to utilize two bacteria together in a co-culture to produce methane. In this manner, a CO-utilizing bacteria can produce a methane precursor, and a methane bacteria can utilize the precursor to produce methane in the same reactor. Co-culturing, if successful, can eliminate a reaction vessel, while maintaining reaction conditions near optimal for each individual bacteria.

A successful co-culture was employed using *P. productus* with an enrichment of *Methanothrix* sp. The results of continuous conversion studies as shown in Table 7. The conversion of CO parallels the performance of *P. productus,* which was nearly identical to the pure culture *P. productus* results of Table 4. Methane formation was 88% of the stoichiometric maximum.

The co-culturing process was not always successful. When *Peptostreptococcus productus* and *Methanosarcina* sp. were co-cultured in continuous reactors, the *Methanosarcina* sp. did not grow, but instead washed out of the reactor in a short period of time. *P. productus* was unaffected and continued to produce acetate. *Methanosarcina* sp. is sensitive to the presence of CO, and did not grow even at low CO concentrations. Similar attempts at co-culturing *P. productus* with *Methanobacterium* sp. and *Methanospirillum* sp. were also unsuccessful.

CONCLUSIONS

Methane may be produced from CO, CO_2, and H_2 in synthesis gas by the action of anaerobic bacteria. Two types of reactions should be con-

Table 7
Coal Gas Conversion by *P. productus* in Co-Culture with *Methanothrix* sp. in a CSTR

Agitation (rpm)	Retention Time (hours)	Conversion (%)	
		CO	H_2
250	1.45	21.36	21.82
300	1.45	38.74	54.60
400	1.45	72.94	72.19
500	1.45	79.40	82.47
600	1.45	91.10	85.10

sidered: those that involve mass transfer difficulties, and those that are not limited by mass transfer. Methane may be produced from synthesis gas by utilizing a serves of pure culture organisms, in which acetate or CO_2 and H_2 series as the methane precursor. Alternatively, a mixed population may be employed, either as a co-culture of organisms or as an acclimated mixed culture isolated from natural sources.

Reaction studies in a stirred-tank reactor with continuous gas flow and periodic liquid media exchange showed that the strict anaerobe *Peptostreptococcus productus* requires a 0.73-h gas retention time and 850 rpm for a 90% conversion of CO to acetate. This high agitation rate is indicative of the mass transfer difficulties associated with gas phase substrate conversion. A smaller liquid phase immobilized cell or fixed-film reactor was then utilized to convert the acetate to methane using an enriched culture of *Methanothrix* sp.

As an alternative to using a series of pure cultures, a co-culture of *P. productus* and *Methanothrix* sp. was used to convert CO, CO_2, and H_2 to methane. A 1.45-h gas retention time at 600 rpm was required for 90% conversion of CO and H_2. Finally, an acclimated mixed culture isolated from sewage sludge was used for synthesis gas conversion. A 1.94-h gas retention time at 600 rpm was required for nearly complete conversion of CO and H_2.

These results illustrate the potential of biological synthesis gas methanation, and show the need for a good understanding of gas–liquid mass transfer as it relates to gas phase substrate conversion. Future work will concentrate on determining mass transfer and kinetic relationships for the various systems, and optimizing process conditions for design and scaleup.

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