

Biological Production of Liquid and Gaseous Fuels from Coal Synthesis Gas

by

G. M. Antorrena
J. L. Vega
E. C. Clausen
J. L. Gaddy

Abstract

Cultures of microorganisms have been isolated that convert CO, H₂ and CO₂ in coal synthesis gas into methane or ethanol. The reactions are severely mass transfer limited and bioreactor design will be a critical factor in the application of this technology. This paper presents results of culture isolation studies and development of continuous reactors for these cultures. The results of bubble columns and stirred tank reactors are presented and discussed. Methods for defining mass transfer coefficients and intrinsic kinetics are presented. Operation of these gaseous fermentations at high pressure has enabled complete conversion in reaction times of a few minutes.

INTRODUCTION

Coal synthesis gas represents an excellent raw material for the production of chemicals and fuels. A typical composition of coal-derived synthesis gas includes 25-35 percent hydrogen, 40-65 percent carbon monoxide, 1-20 percent carbon dioxide, 0-7 percent methane and other compounds in small quantities such as sulfur (as H₂S or COS), chlorine, etc. Many coal gasification processes exist or are currently under development that can produce synthesis gas economically.

Chemical catalytic processes are known to utilize syngas to produce a large variety of compounds such as methanol, formaldehyde, and acetic acid (Courty and Chaumette, 1978). Microorganisms may also be used to convert synthesis gas components into more desired products such as acetate, methane, and alcohols. 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 possibly 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 carbon monoxide, oxygen, etc. in contact with suspended cells it

has been well established that the main resistance to transport lies in the liquid film (Tsao and Lee, 1977; Blanch, 1979; Yoshida, 1982). The rate of transport from the gas phase into the culture medium is, therefore, faster for higher partial pressures in the gas phase. In the case where the overall reaction rate is transport controlled, that is, the dissolved gas concentration in the liquid phase is zero, 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. The batch reactor and two continuous reactors, the continuous stirred tank reactor (CSTR) and the bubble column, are employed. Also, the effects of increased pressure on improving mass transfer and microorganism performance are presented and discussed.

BIOLOGICAL SYNTHESIS GAS CONVERSION

Methane Production

The primary reactions in the biological conversion of synthesis gas to methane are the formation of methane precursors and biomethanation of the precursors. 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 (Ljungdahl and Wiegel, 1986). As is seen in the table, the formation of methane can be accomplished by direct conversion of CO, CO₂ and H₂ or by the indirect formation of methane intermediates (acetate or H₂ and CO₂). Of the one-step reactions, only reaction I.3, the direct formation of methane from H₂ and CO₂, has been well-studied and verified (Escalante-Semerena et al. 1984). This reaction is known to be carried out by most of the methanogens (Jones et al., 1987), although some methanogens such as Methanotrix sp. are not capable of this conversion (Huser et al. 1982).

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 Equation I.1 (Daniels et al. 1977). 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 Equation I.2 (Fisher et al. 1932; and Stephenson and Strickland, 1933). It is more likely, however, that the carbon monoxide reduction to methane in these experiments proceeded via the multiple-step reactions II.3 and I.3 (Daniels et al. 1977; and Kluyver and Schnellen, 1947).

With the exception of Equation I.3, an indirect formation of methane seems more viable than the direct routes previously discussed. These multi-step 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 (Equation II.3). In the latter case, the products hydrogen and carbon dioxide can be directly converted to methane (Equation I.3) or may enter the multiple step process that produces acetate as an intermediate

(Equation II.2). The organisms Rhodopseudomonas gelatinosa (Uffen, 1976; and Dushekvicz and Uffen, 1979), and Rhodospirillum rubrum (Breed et al. 1977) are known to perform the water gas shift reaction.

Another approach to indirect methane production is the formation of acetate as a methane precursor. In anaerobic digestion processes, 80 percent of the methane is produced from acetate by Equation II.4. The organisms Peptostreptococcus productus and Eubacterium woodii (Genther and Bryant, 1983) have been found to produce acetate by Equation 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 (Equation 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 as well as Methanothrix soehngeni (Jones et al. 1987). While Methanosarcina barkeri, for example, will utilize acetate only in the absence of other preferred substrates (such as H₂ and CO₂), Methanothrix sp. does not utilize normal methanogenic substrates and growth and methane formation is exclusively observed in the presence of acetate (Huser et al. 1982). Both microorganisms show comparable specific growth rates at low acetate concentrations (< 3mM). On the other hand, in view of the Monod saturation constants available for the two microorganisms, (K_S = 0.7 mmol/l for Methanothrix), it is expected that at low acetate concentrations Methanothrix is the more predominant of the two.

Ethanol Production

While many anaerobic, facultatively anaerobic and even some strictly aerobic microorganisms form various amounts of ethanol from glucose (Weigel, 1980), no organism was known to form ethanol autotrophically from synthesis gas components. In 1987, a strict anaerobic mesophilic bacterium was isolated from animal waste that was capable of converting CO, H₂, and CO₂ to a mixture of acetate and ethanol (Barik et al. 1987). Preliminary identification studies have indicated that the bacterium has a strong possibility of being a new clostridium species (Tanner, 1988). It is likely that in the same manner as with other clostridia growing on sugars, ethanol and acetate are formed from acetyl-CoA by this organism, with product distribution highly dependent on the regulation of electron flow (Rao, et al. 1987).

The overall stoichiometry for the formation of ethanol from carbon monoxide and hydrogen/carbon dioxide has been established by Vega et al. (1988):



Acetate formation from CO, CO₂ and H₂ by the organism is carried out using the same stoichiometric equations presented in Table 1.

BIOREACTOR DESIGN

Gas-Liquid Mass Transfer Concepts in Bioreactors

The transfer of gases in fermentation systems involves three phases: gas, culture medium and microbial cells suspended in the medium. In general, a combination of the following resistances can be expected (Bailey and Ollis, 1977):

- 1.- Diffusion from the bulk gas to the gas-liquid interface;
- 2.- Movement through the gas-liquid interface;
- 3.- Diffusion of the solute through the relatively unmixed liquid region (film) adjacent to the bubble into the well mixed bulk liquid;
- 4.- Transport of the solute through the bulk liquid to a second stagnant film surrounding the microbial species;
- 5.- Transport through the second unmixed liquid region associated with the microbes;
- 6.- Diffusive transport into the microbial floc, mycelia, or particle, if appropriate. (When the microbes take the form of individual cells, this resistance disappears); and,
- 7.- Consumption of the solute by biochemical reaction within the microorganism.

As is the case with the conventional chemical engineering analysis of absorption processes, interfacial resistance to mass transfer can be neglected. In systems where agitation is provided, transport through the bulk liquid is assumed to be instantaneous. Finally, when individual cells are suspended in a medium, the liquid film resistance around the cells is usually neglected with respect to other resistances because of the minute size and the enormous total surface of the cells (Finn, 1954). Thus for the transfer of sparingly soluble gases such as CO and H₂, the main resistance to transport lies in the liquid film. Reaction schemes should thus concentrate on minimizing the liquid film resistance of the gas transfer into the liquid phase. Other techniques for promoting gas-liquid mass transfer should also be considered, including the use of alternative liquid phases and the use of high pressure to promote higher solubility.

The conversion of carbon monoxide to acetate by reaction II.1 (see Table 1) using P. productus was chosen as a model system for bioreactor comparisons. The mass transfer limited concepts shown for this organism are applicable to other gas phase fermentation systems.

The Batch Reactor

Batch fermentation systems are typically used in determining fermentation kinetics by following the concentration of substrate in the liquid phase with time. For gas phase systems, however, the liquid phase concentration cannot be measured since sensors are not generally available for most systems. A method has been developed for determining mass transfer and intrinsic kinetic parameters in gas phase fermentation systems for sparingly soluble gases such as CO and H₂. In a typical experiment, batch reactors are started with different initial gas, partial pressures, and monitored with time for gas consumption, cell density and product formation.

Figure 1 presents the volumetric rate of disappearance of CO from the gas phase using P. productus as a function of its partial pressure. The data for each partial pressure shows a period of increase in the rate of uptake of carbon monoxide from the gas phase while the partial pressure of the gas decreased slowly. During this period and because the cell concentration is low, the reaction rate is mainly under kinetic control, since the concentration of substrate in the liquid culture is above zero. The actual shape of these curves in the figure bear no physical meaning and the continuous lines drawn correspond to a best visual fitting of the data. As the cell concentration reached a value at which mass transfer controlled, the concentration of carbon monoxide in the liquid became zero and the reaction rate was that of the rate of transport of the substrate into the liquid phase. This rate of transport is then proportional to the partial pressure of carbon monoxide in the liquid phase and the proportionality constant is K_{La}/H . Because the fermentation conditions for all experiments (medium composition, agitation, temperature, etc.) were very similar if not the same, all the data in Figure 1 followed a single straight line. The value of the slope on the straight line as obtained from least squares of all data in the mass transfer limited region was 5.91 mmol CO/L·hr·atm. Taking for H the value for water at 37°C ($H = 1.21 \text{ atm}\cdot\text{L}/\text{mmol CO}$), the calculated value for K_{La} was 7.15 hr⁻¹. Once the volumetric mass transfer coefficient is known, intrinsic kinetic parameters may be estimated using the data in the region where mass transfer does not control. Typically, Monod-type kinetics are used, utilizing calculated values of dissolved CO in the liquid phase.

The Stirred Tank Reactor

The traditional reactor used in fermentation processes is the continuous stirred tank reactor or CSTR. As it relates to gas phase substrates, the CSTR has continuous gas flow into a constant volume liquid phase reactor. A smaller liquid feed stream is utilized to supply nutrients to the microorganism in the reactor system. 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 have been conducted with P. productus in a CSTR at different gas flow rates in order to develop suitable equations for modeling and process scale-up. The model which includes material balances for carbon monoxide, methane, and carbon dioxide in the gas phase and for the carbon dioxide/bicarbonate equilibrium system in the liquid medium. The model assumes that the carbon dioxide in equilibrium with the gas phase carbon dioxide partial pressure and the bicarbonate and pH level in the liquid.

Figures 2 and 3 show the solution of the model for various volumetric mass transfer coefficients (Figure 2) and various total operating pressures (Figure 3). Experimental data at 1 atm and a mass transfer coefficient of 30 are also included in the figures. As observed in the model results, increases in the mass transfer coefficient or in total operating pressures lead to higher reactor productivities. However, due to the perfect mixing in a CSTR, complete conversion is only attained when the gas flow rate is zero. The use of the model allows the extrapolation of performance of the CSTR system and permits preliminary economic evaluation of coupled with suitable equations for scale-up of properties such as the mass transfer coefficient.

Bubble Columns

Bubble columns are commonly used in industrial processes both as reactors or absorbers whenever a large liquid retention time and/or a large liquid hold-up is needed. Some advantages of bubble columns are the lack of moving parts, minimum maintenance, relatively low costs, high interfacial area and a high mass transfer coefficient (Charpentier, 1981). The principal disadvantages are a large extent of backmixing and coalescence. These two drawbacks can be minimized by employing packing inside the column.

The performance of a bubble column for CO conversion to acetate by P. productus is shown in Figure 4. The bubble column is capable of achieving similar rates of CO conversion as the stirred tank reactor without agitation. In addition, the bubble column is capable of yielding complete conversion due to plug flow operation.

By combining a CO material balance along the column with the rate expression for CO transport into the liquid phase, the following expression for the partial pressure of CO leaving the reactor is obtained:

$$\ln P_{CO}^o = \ln P_{CO}^i - \frac{K_{La} \epsilon_L h}{H} \frac{RTS}{G} \quad (1)$$

where ϵ_L = fraction of liquid in the column;
h = height of the column;
S = cross-sectional area of the column;
R = ideal gas constant;
T = absolute temperature; and
G = gas flow rate

Verification of Equation (1) is shown in Figure 5 for the data of Figure 4. As is shown, a single straight line is obtained, indicating that the model satisfactorily predicts column performance. In addition, K_{La}/H can be obtained from the slope of the line in Figure 5, once the numerical values of the constants in Equation (1) are supplied. This mathematical model can also be used for process design and scale-up in a similar manner as the CSTR model.

Pressure Effects

As was shown in Figure 3, an increase in the operating pressure brought about a significant increase in the rate of CO uptake in a CSTR. Thus, operation at increased pressures can be highly beneficial in minimizing reactor volume requirements. However, CO has been shown to inhibit growth and CO uptake at dissolved CO tensions of 0.8-1.0 atm. Methods to avoid CO inhibition by maintaining low dissolved CO tensions at increased pressures must be developed. The key to maintaining low dissolved CO tensions at increased pressures is to develop high cell concentrations that are capable of uptaking the increased quantities of CO. Higher cell concentrations can be achieved by feeding alternate substrates such as glucose, or by gradually increasing the cell concentration in a stepwise fashion.

When P. productus inside a high pressure Parr reactor with an initial cell concentration of about 18 mg/L was directly pressurized to a total pressure of 5.7 atm (carbon monoxide partial pressure of 3.6 atm), no sign of carbon monoxide consumption was observed after 93 hours. On the other hand, when the pressure was raised stepwise with small increases in the carbon monoxide partial pressure at 10 hr time intervals, carbon monoxide consumption occurred at total pressures as high as 14.6 atm (carbon monoxide partial pressure of 9.3 atm). Figure 6 shows a carbon monoxide disappearance profile for P. productus grown on CO where a 14.6 atm total pressure (9.3 atm carbon monoxide partial pressure) was achieved in five smaller pressure increments. As is seen, carbon monoxide was consumed at fast rates even at these high pressures. Thus, low dissolved CO tensions were achieved by gradually increasing cell growth. A proportional decrease in reactor volume is then possible through increased pressure operation.

CONCLUSIONS

Anaerobic bacteria have been utilized in the biological conversion of sparingly soluble gas phase substrates such as CO and H₂ to the products methane, ethanol and acetate. Several reactor designs may be utilized in these conversions including batch reactors and continuous stirred tank and bubble column reactors. The batch reactor has been utilized to obtain mass transfer correlations for the mass transfer controlled regime, and intrinsic kinetic parameters have been obtained in the non-mass transfer limited regime.

The continuous stirred tank reactor has been utilized to develop suitable equations for modeling and process scale-up. The model includes material balance equations and carbon dioxide/bicarbonate chemical equilibrium. The effects of the mass transfer coefficient and total pressure on CO uptake and conversion were modeled.

The bubble column has also been utilized for CO utilization. Higher conversions and similar rates of CO conversion were obtained without the required agitation in the CSTR. The results were successfully modeled and the resultant mass transfer coefficient obtained.

The benefits of increased pressure on CO utilization were demonstrated in batch and continuous culture. A gradual stepwise procedure was utilized in increasing the cell concentration to achieve low dissolved CO tensions.

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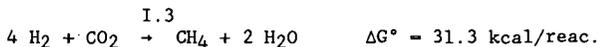
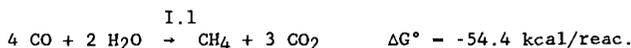
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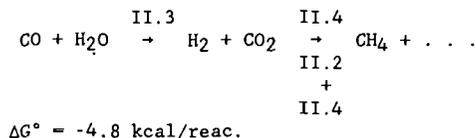
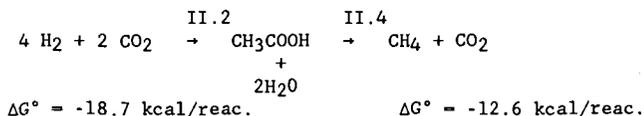
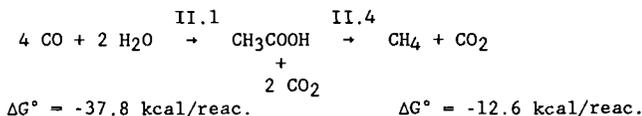
Table 1

Biological Routes to Methane From Synthesis Gas Components

I) ONE-STEP REACTIONS



II) MULTIPLE-STEP REACTIONS



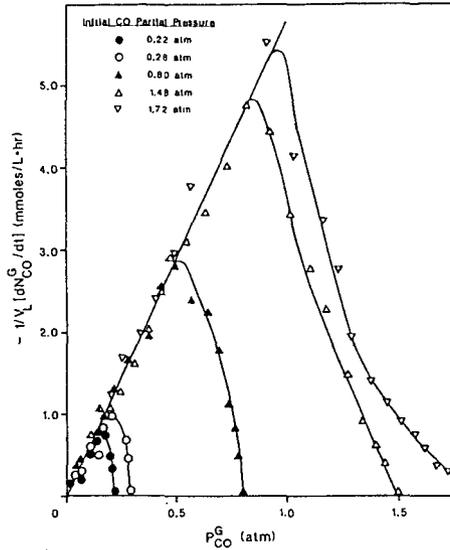


Figure 1. Determination of the volumetric mass transfer coefficient for *P. productus* in batch culture.

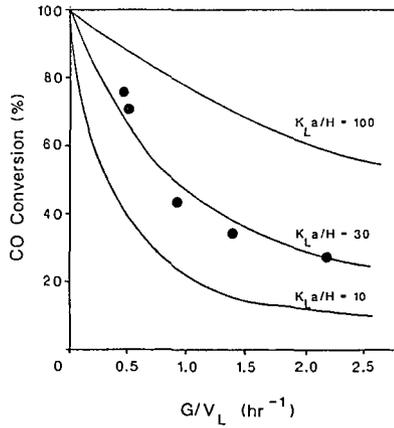


Figure 2. Model results for carbon monoxide conversion as a function of the gas flow rate per unit of culture volume for various volumetric mass transfer coefficients ($K_L a/H$ in mmol CO/atm L hr).

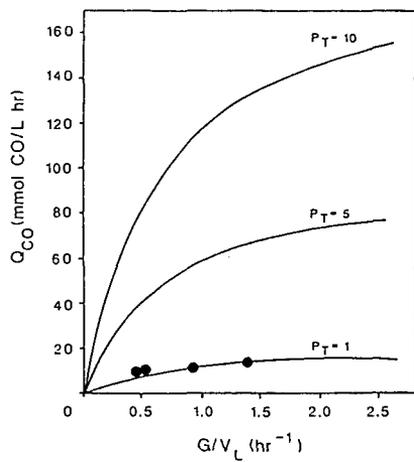


Figure 3. Model of results for carbon monoxide uptake as a function of the gas flow rate for various total operating pressures (P_T in atm).

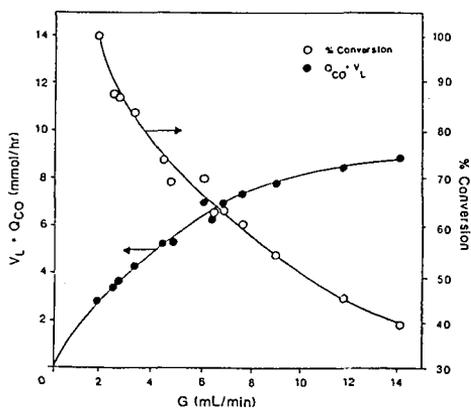


Figure 4. Carbon monoxide uptake rate and conversion level as a function of gas flow rate in the column for *P. productus*.

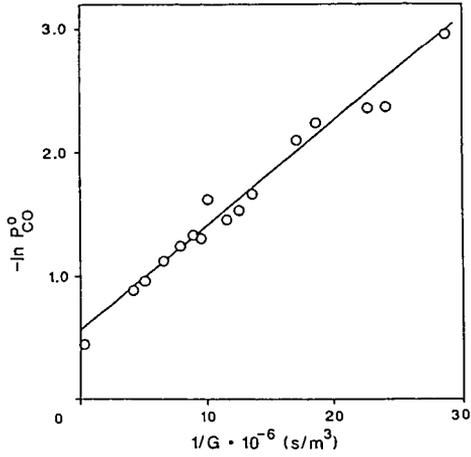


Figure 5. Testing the proposed bubble column model of Equation 1.

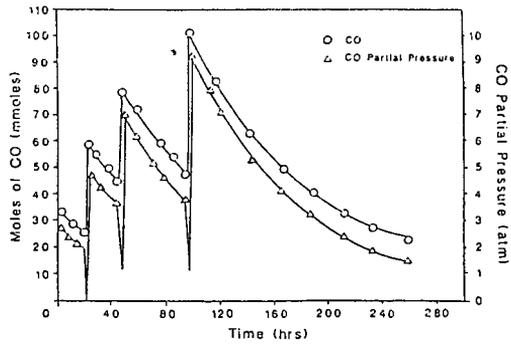


Figure 6. CO consumption and CO partial pressure as a function of time for *P. productus* start-up with CO alone.