

## ETHANOL FROM BIOMASS BY GASIFICATION/FERMENTATION

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### ABSTRACT

Bacteria have recently been isolated from natural sources that produce ethanol from CO, H<sub>2</sub> and CO<sub>2</sub>. This paper describes a unique process for producing liquid fuel from biomass by gasification, followed by fermentation of the synthesis gas to ethanol. This process offers the advantage of very high yield (140 gal/ton), since the lignin and pentose fractions of the biomass can also be readily utilized. This presentation describes laboratory experiments with the culture and discusses bioreactor designs for this mass transfer limited fermentation.

### INTRODUCTION

The United States currently imports about 20 percent of its total energy requirements of about 70 quads annually. As petroleum reserves decline and prices rise, the U.S. must develop alternative energy resources.

The nation has about 1.5 billion tons of biomass residue and wastes that could be used as an energy source (Sitton *et al.*, 1979). These residues could furnish 10 quads, or about 15 percent of our energy requirements, if converted at a 50 percent efficiency. In addition, if energy crops were grown on idle arable rangeland and forestland (about 200 million acres), another 25 quads could be produced (Clausen *et al.*, 1977). Therefore, the U.S. could supply half of its energy needs from renewable biomass and wastes.

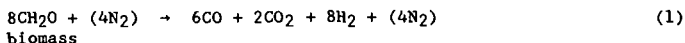
Lignocellulosic matter may be used as a solid fuel and burned directly to produce energy. However, efficiencies are low and handling problems are serious. Consequently, biomass must be converted into gaseous or liquid forms of energy to be utilized in conventional energy processes. The major components of cellulosic biomass are hemicellulose, cellulose and lignin. The compositions of the biomass resources vary; however, most materials contain 15-25 percent hemicellulose, 30-45 percent cellulose, and 5-20 percent lignin. The carbohydrates may be hydrolyzed to sugars and fermented to ethanol or they may be converted into methane by anaerobic digestion. These technologies are under development and may become economical in the future.

Biomass may also be gasified to yield a low Btu gas consisting of H<sub>2</sub>, CO, CO<sub>2</sub>, and N<sub>2</sub>. Technology for pyrolysis or gasification of biomass has been under intensive development during the last two decades (Stasson and Stiles, 1988). Large scale demonstration facilities have been tested (Fisher *et al.*, 1976) and small scale commercial facilities are now in operation. A major advantage of gasification of biomass is that all the carbohydrate and lignin are converted into energy forms, whereas the lignin is not converted by hydrolysis or digestion.

The problems with the application of biomass gasification have not been technical, but economic. The product from gasification is a heat source, which is very cheap today. Therefore, even nominal capital and operating costs for gasification cannot be justified with such low income. If the components of synthesis gas were converted into a higher value fuel product, biomass gasification could become a viable alternative energy technology.

#### BIOLOGICAL PRODUCTION OF ETHANOL FROM BIOMASS SYNTHESIS GAS

Synthesis gases, consisting of CO, H<sub>2</sub> and CO<sub>2</sub>, may be produced from biomass according to the approximate reaction (Alden *et al.*, 1991):



There are many gasifier designs that have been demonstrated and are commercially available. Gas composition is a function of the amount of air or oxygen necessary to generate the heat for pyrolysis of the biomass, as well as the type of gasifier and the moisture content of the biomass. Steam may also be added to adjust the hydrogen concentration. If oxygen is used, nitrogen is eliminated.

The components of synthesis gas may be converted into ethanol by certain anaerobic bacteria according to the equations (Klasson *et al.*, 1990a; 1990b; 1992; Barik *et al.*, 1988):



Equations (2) and (3) may be combined with Equation (1) to give



Since nearly all the biomass (including the lignin, but not the ash) can be converted into gas by Equation (1), yields of ethanol of about 50 percent of the total biomass are possible (135 gal per ton). This compares to yields of only about 30 percent for enzymatic or acid hydrolysis/fermentation processes.

Synthesis gas compositions from biomass are variable, depending upon the raw material, temperature and process used. Typical compositions show a CO:H<sub>2</sub> ratio of about one with CO and H<sub>2</sub> compositions of about 35 percent (Borgwardt *et al.*, 1991; Alden *et al.*, 1991). Yields of gas of about 90 percent are common. Gas composition can also be tailored for fuels production (Collaninno and Mansour, 1988).

Fuel ethanol production from grain is about one billion gallons per year and expected to increase steadily as oxygenated fuels usage is mandated in many metropolitan areas. Prices have been as high as \$1.85 per gallon, but have stabilized at about \$1.20 per gallon (wholesale gasoline price plus tax credit of \$0.54 per gallon) in recent years. The potential market for fuel ethanol is 10 billion gallons annually, at a 10 percent blend with gasoline. Higher percentages are, of course, possible and pure ethanol is marketed in Brazil. Therefore, the market for this product is quite large and the price is sufficient to support commercialization.

The biological process for producing ethanol from synthesis gas would be quite simple. The process would consist of an exchanger to cool the hot gases, a biological reactor, and a separator for ethanol purification. The cool gases would be passed through a liquid phase reactor where a culture of the desired microorganism is maintained. The microorganism would carry out the reaction to produce ethanol, converting only the CO, H<sub>2</sub>, or CO<sub>2</sub> present. The reactor would be operated at mild temperature (95°F) and atmospheric pressure. Higher pressure may be desirable to enhance gas mass transfer and can be used where the synthesis gas may be at elevated pressure. Ethanol would be removed in the aqueous phase from the reactor and recovered by extraction and distillation. Separation of ethanol from water is standard commercial technology.

The advantages of biological reactions, over chemical reactions, include operation at atmospheric conditions, which generally provides a more energy efficient process. Also, microorganisms give high yields (>95 percent), with only small amounts of raw materials used for growth and maintenance. Microorganisms are also quite specific in producing a single product, with only small quantities of by-products formed and requiring relatively simple recovery processes. Resistance to toxicity from substances that degrade other catalysts can often be developed in biological systems. Finally, the biocatalyst is continually regenerated in the biological process, which allows more dependable and consistent operation than catalytic processes.

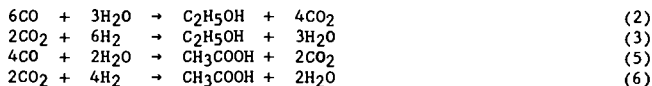
#### PURPOSE

The purpose of this paper is to present information on a unique bioprocess for the conversion of biomass to ethanol by gasification/fermentation. Following gasification of the biomass, CO, CO<sub>2</sub> and H<sub>2</sub> in synthesis gas are converted to ethanol using *C. ljungdahlii*. Data are presented for this fermentation, including results from both batch and continuous reactors. In addition, the effects of the sulfur gases H<sub>2</sub>S and COS on growth, substrate uptake and product formation are presented and discussed.

#### MICROBIOLOGY OF ETHANOL PRODUCTION

The bioconversion of the gases, CO<sub>2</sub>, CO, and H<sub>2</sub>, by anaerobic bacteria has been known for many years and recently demonstrated in our laboratories as having commercial potential (Clausen and Gaddy, 1985; Klasson *et al.*, 1990b; 1992). Several bacterial species are capable of converting these gases into acetate, which is an intermediate in many biological pathways. However, only one bacterium has been shown to produce ethanol from the components of synthesis gas.

In 1985, Barik *et al.* (1985) isolated a bacterium from animal waste that was capable of converting CO, CO<sub>2</sub> and H<sub>2</sub> to ethanol and acetate by the equations:



This strain was found to be a new bacterial species and named *Clostridium ljungdahlii* (Vega *et al.*, 1989a). Under normal conditions, the "wild strain"

produced approximately 20 moles of acetate per mole of ethanol (Barik *et al.*, 1988). However, by manipulating the culture and employing low pH and minimal nutrients, the culture has been found to be capable of producing only ethanol, with minimal amounts of acetate (Klasson *et al.*, 1992).

A kinetic analysis was performed on the data to determine kinetic parameters for growth and CO uptake. The following models were obtained with

$$P_{CO}^L \leq 1.1 \text{ atm:}$$

$$\mu = \mu_m = 0.04 \text{ h}^{-1} \quad (7)$$

and

$$q = q_m = 42.7 \text{ mmol CO/g cell}\cdot\text{h} \quad (8)$$

If the specific uptake rate of CO is converted to a carbon mass basis, a value of 0.22 g C/g cell·h is obtained for  $q_m$ , which is comparable to the rate of glucose uptake by *Saccharomyces cerevisiae* with a  $q_m$  of 0.27 g C/g cell·h (Vega, 1985). This rate indicates that *C. ljungdahliae* has reaction rates equivalent to other organisms that are used for commercial fermentations.

#### Culture Manipulation

As was shown in Equations (1,2,5,6) both ethanol and acetate are produced from the fermentation of CO, CO<sub>2</sub> and H<sub>2</sub> by *C. ljungdahliae*. Early results with the culture showed that acetate was the predominant product, with ethanol:acetate ratios of 0.1 or lower typically found in the "wild" strain. Many researchers have studied solvent/acid formation in clostridial cultures, reporting that factors including medium manipulation, decreased pH and the addition of reducing agents have brought about solvent formation in favor of acid production.

Research with *C. ljungdahliae* has shown that lowering of the pH to 4 - 4.5 coupled with a nutrient limited medium brings about a drastic shift in product formation in favor of ethanol (Phillips *et al.*, 1992). Figure 1 shows ethanol and acetate production from synthesis gas using *C. ljungdahliae* in the CSTR at reduced pH and with a specially designed nutrient limited medium. As is noted, ethanol concentrations exceeding 20 g/L with corresponding acetate concentrations of only 2 - 3 g/L are obtained. The cell concentration in these studies was approximately 1.5 g/L. Thus, an increase in ethanol concentration coupled with high product ratios were obtained by lower reaction pH in combination with employing a specially designed nutrient medium.

#### BIOREACTOR DESIGN

The choice of a suitable reactor for gas-liquid reaction or absorption 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 insure 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, etc. are examples of various kinds of contacting systems employed in these type of processes.

The rate of disappearance of CO from the gas phase can be related to the partial pressures in the gas and the liquid phase and the cell concentration,  $X$ , by the equation:

$$-\frac{1}{V_L} \frac{dN_{CO}^G}{dt} = \frac{K_L a}{H} \left( P_{CO}^G - P_{CO}^L \right) = \frac{X q_m P_{CO}^L}{K'_P + P_{CO}^L + \left( P_{CO}^L \right)^2 / w'} \quad (9)$$

Under mass transfer limiting conditions,  $P_{CO}^L$  approaches zero so that the rate of disappearance of CO is proportional to the gas phase CO concentration. As the cell concentration,  $X$ , reaches a value at which mass transfer is controlling, the concentration of carbon monoxide in the liquid becomes zero and the reaction rate is controlled by the rate of transport of the substrate into the liquid phase. Thus, both high cell concentrations and fast gas transport are necessary to minimize reactor size. High cell concentrations may be obtained in the reactor by employing a cell recycle system in which the cells are separated from the effluent and returned to the reactor. Fast mass transfer can occur by employing increased pressure or solvents to increase CO solubility.

#### The Use of Cell Recycle in the CSTR

A cell recycle apparatus was used in conjunction with a standard CSTR as a method to increase the cell concentration inside the reactor. This is particularly important since total product formation with *C. ljungdahlii* has been shown to be proportional to the cell concentration inside the reactor.

Figure 2 shows the product concentration profile for the CSTR with cell recycle. In this experiment, the cell concentration increased (with agitation rate and gas retention time increases) from approximately 800 mg/L to over 4000 mg/L. The maximum in the previous CSTR study without cell recycle was 1500 g/L. The CO conversion was consistently around the 90 percent level after 150 h of operation. The corresponding  $H_2$  conversion, on the other hand, averaged 70 percent up to a time of 500 h. At this time, the  $H_2$  conversion fell, probably due to an accumulation of CO in the liquid phase. The ethanol concentration ranged from 6 g/L at the beginning of the study to 48 g/L after 560 h of operation. The corresponding acetate concentrations at these times were 5 g/L and 3 g/L, respectively. The ratio of ethanol to acetate ranged from 1.2 g/g to 16 g/g. Thus, very high ethanol concentrations are possible and acetate production is nearly eliminated with high cell concentrations.

#### High Pressure Operation

As was mentioned previously, elevated pressure may be used to increase the rate of mass transfer of CO into the liquid phase. A high pressure system (both CSTR and trickle bed reactor) has been constructed in the University of Arkansas laboratories. The system has a maximum operating pressure of 5000 psig and can be used for both photosynthetic and non-photosynthetic bacterial systems. The system is presently being used to gradually acclimate *C. ljungdahlii* to increased pressure.

## CONCLUSIONS

The anaerobic bacterium *Clostridium ljungdahlii* has been shown to be effective in converting CO, CO<sub>2</sub> and H<sub>2</sub> to ethanol. Rates of carbon uptake by *C. ljungdahlii* comparable to the rate of carbon uptake by the yeast *Saccharomyces cerevisiae* have been obtained. A CSTR cell recycle system has been shown to be effective in permitting the cell concentrations necessary for high concentrations of ethanol. An ethanol concentration of 47 g/L with a corresponding acetate concentration of 3 g/L has been attained. *C. ljungdahlii* has been shown to be tolerant of H<sub>2</sub>S or COS in concentrations exceeding typical levels in synthesis gas.

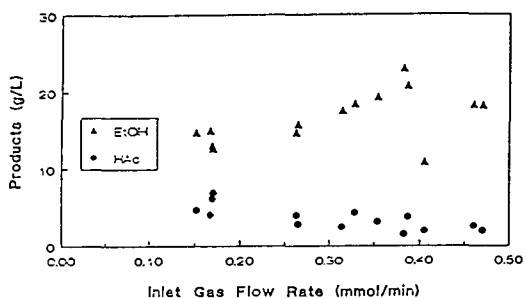


Figure 1. Product concentrations from growth of *C. ljungdahlii* in designed medium in the CSTR.

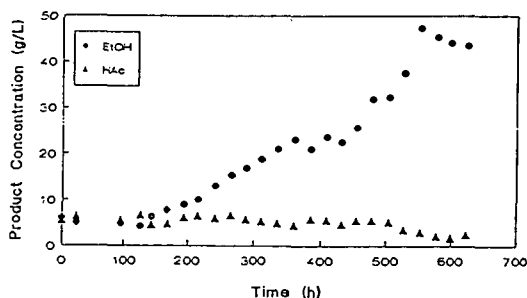


Figure 2. Product concentration measurements for *C. ljungdahlii* in the CSTR with cell recycle.

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