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BIOLOGICAL PRODUCTION OF ETHANOL FROM COAL

Task 5 Report: Economic Evaluation

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Prepared by

University of Arkansas
Department of Chemical Engineering
Fayetteville, Arkansas 72701

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1.0 INTRODUCTION

A significant research effort has occurred over the past 15 years concerning the conversion of coal to liquid fuels. Researchers at the University of Arkansas have concentrated on a biological approach to coal liquefaction, starting with coal-derived synthesis gas as the raw material. Synthesis gas, a mixture of CO, H₂, CO₂, CH₄ and sulfur gases, is first produced using traditional gasification techniques. The CO, CO₂ and H₂ are then converted to ethanol using a bacterial culture of *Clostridium ljungdahlii*.

C. ljungdahlii converts CO, CO₂ and H₂ to ethanol and acetate by the equations:

In these equations, ethanol is the desired product if the resultant product stream is to be used as a liquid fuel. However, under normal operating conditions, acetate is produced in favor of ethanol in conjunction with growth in a 20:1 molar ratio. Thus, research was conducted to determine the conditions necessary to maximize not only the ratio of ethanol to acetate, but also to maximize the concentration of ethanol resulting in the product stream.

Significant progress has been made toward reaching this goal. Several factors have been identified that cause the culture to produce ethanol in favor of acetate. These factors include manipulation of the nutrients composition and concentration and reduction of the medium pH. These

techniques have been demonstrated in batch and continuous culture, both individually and together as multiple parameter experiments. Manipulation of these parameters has led to the realization that acetate is produced in conjunction with growth and energy production, whereas ethanol is produced when growth is minimized and when energy is used instead of produced. The parameters that enhance ethanol production suppress growth and/or produce energy for ultimate use by the cell during ethanol production.

The purpose of this report is to present an economic evaluation of the bioprocess to produce ethanol from syngas using *C. ljungdahlii*. This evaluation is based upon the results of laboratory studies with the bacterium in continuous culture.

2.0 BACKGROUND ON CLOSTRIDIUM LJUNGDAHLII

In 1987, researchers at the University of Arkansas reported the isolation of a strictly anaerobic mesophilic bacterium from animal waste that was capable of converting CO, H₂ and CO₂ to a mixture of acetate and ethanol. This discovery was the result of extensive screening studies utilizing natural inocula, such as sewage sludge, animal waste, coal pile runoff and soils. The method of successive transfer was applied, while simultaneously blocking methanogenesis.

Early batch fermentation experiments with the newly isolated microorganism, tentatively identified as a member of the *Clostridium* genera, did not show a high degree of reproducibility. Although product ratios of 1 mole ethanol to 10 moles of acetate (1:10) were sometimes obtained, the standard product ratio in these early studies was 1:20. Ethanol concentrations were also quite low, although the concentration could be

increased in batch culture through multiple gas additions. Clearly, an experimental program was needed to increase the product ratio and concentration of ethanol while, at the same time, carrying out parallel studies on culture identification and process stoichiometry.

An experimental program was developed to identify and characterize the bacterium, evaluate overall culture stoichiometry, improve the ethanol/acetate ratio and optimize culture operating conditions. Highlights of this work include improving the product ratio from 1:20 (ethanol to acetate) to a product which is almost entirely ethanol, and improving the ethanol concentration to 47 g/L. These and other results are summarized in the paragraphs below.

2.1 Culture Isolation and Characterization

Bacterial isolation and characterization studies showed that the culture is a new clostridial species, named *Clostridium ljungdahlii*, Strain PETC, in honor of Dr. Lars G. Ljungdahl. *C. ljundahlui* is a gram-positive, motile, rod-shaped anaerobic bacterium which sporulates infrequently. The bacterium only produces ethanol at pH levels below 6.0. At higher pH levels, acetate is the only liquid phase product.

A list of substrates tested for growth as the sole carbon and energy source is shown in Table 2.1. In these studies, 1 g/L of yeast extract was added to the medium along with the substrate, and all fermentations were carried out at an initial pH of 6.0. As noted in Table 2.1, growth was obtained when H₂/CO₂, ethanol, pyruvate, xylose, arabinose and fructose were used as substrates. *C. ljungdahlii* grew weakly in the presence of fumarate, ribose, glucose and casamino acids.

Table 2.1

Growth of *C. ljungdahlii* on Substrates as the Sole
Carbon/Energy Source

H ₂ :CO ₂	+	ribose	w
CO	+	xylose	+
formate	-	arabinose	+
methanol	-	fructose	+
ethanol	+	glucose	w
pyruvate	+	galactose	-
lactate	-	mannose	-
glycerol	-	sorbitol	-
succinate	-	sucrose	-
fumarate	w	maltose	-
citrate	-	lactose	-
		starch	-
		casamino acids	w

+ positive growth

- no growth

w weak growth

C. ljungdahlii is distinguishable from related organisms by its substrate use, pH requirements, end-products of fermentation and physical characteristics. It can be distinguished from *Clostridium aceticum* by its pH optimum, and the utilization of glucose, formate, ribose and xylose as substrates. The bacterium can be distinguished from *Clostridium barkeri* by the end-products of fermentation, motility, and the utilization of glucose, lactate and xylose as substrates. *C. ljungdahlii* is distinguishable from *Clostridium formicoaceticum* by the utilization of glucose, lactate, ribose and H₂/CO₂ as substrates, and is distinguished from *Clostridium thermoaceticum* and *Clostridium thermoautotrophicum* by thermophilicity and the utilization of glucose as a substrate.

Figure 2.1. Electron micrograph of *Clostridium ljungdahlii*, strain PETC.

The bacterium can also be differentiated from other acetate forming species. It is distinguished from *Acetobacterium* sp. by spore formation and the utilization of formate, lactate and pentoses as substrates. It is distinguished from *Eubacterium limosum* by motility, spore formation, and the utilization of glucose, lactate, methanol, ethanol and arabinose as substrates.

Figure 2.1 shows an electron micrograph of *C. ljungdahlii*, Strain PETC. As is seen in the micrograph, the cells are petrichously flagellated. Also, there is good evidence for an internal membrane structure, which is visible both in fixed and unfixed preparations and in fixed and unfixed cells stained with uranyl acetate or phosphotungstic acid. The membranes are also seen in different culture preparations. These internal structures, which have not been observed in clostridial species before and which usually require thin sectioning to visualize in any eubacteria, may explain how the organism can metabolize in the presence of acetic acid at pH 4.

DNA composition studies have shown that *C. ljungdahlii* contains 22 mole percent guanine plus cytosine. This composition is at the lowest end of bacteria, with only one other clostridia having a composition this low. This result further substantiates the fact that *C. ljundahlii*, Strain PETC is a new clostridial species.

2.2 Evaluation of Reaction Stoichiometry

The stoichiometry for the formation of acetate from carbon monoxide, as well as hydrogen and carbon dioxide, has been well-established for many acetogenic bacteria. These reactions are:

$$\Delta G^\circ = -37.8 \text{ kcal/gmole CH}_3\text{COOH}$$

and

$$\Delta G^\circ = -18.6 \text{ kcal/gmole CH}_3\text{COOH}$$

Similar equations may be written for the formation of ethanol from CO, CO₂ and H₂:

$$\Delta G^\circ = -59.9 \text{ kcal/gmole C}_2\text{H}_5\text{OH}$$

and

$$\Delta G^\circ = -23.2 \text{ kcal/gmole C}_2\text{H}_5\text{OH}$$

Experiments were carried out in the University of Arkansas laboratories to verify the stoichiometries of Equations (1.1-1.4) for *C. ljungdahlii*. Both single substrate (CO or CO₂/H₂) studies and mixed substrate (CO, CO₂ and H₂) studies were conducted. The results of these studies indicated that stoichiometric quantities of acetate and ethanol were produced from CO, CO₂ and H₂ as indicated in Equations (1.1-1.4), thus verifying the stoichiometric relationships.

3.0 PROCESS DESCRIPTION AND ECONOMIC EVALUATION

3.1 Process Description

A process for the production of ethanol from syngas by fermentation with *C. ljungdahlii* would be quite simple. Syngas is fed continuously to a continuous stirred tank reactor along with a small liquid medium stream. Ethanol and unused gases (CO₂, CH₄, sulfur gases) exit the reactor in a single stream. The liquid stream flows to a cell recycle apparatus, where the cells are concentrated and returned to the reactor. The gas stream is vented to the atmosphere, although it may first be further treated biologically for sulfur gas removal, if desired.

The liquid permeate exiting the cell recycle apparatus flows to an extraction column where n-hexanol (or other suitable solvent) is used to remove ethanol from the permeate stream. Distillation is then used to separate solvent from ethanol/water, with another distillation unit used to separate ethanol from water to the azeotropic concentration. If desired, the azeotrope may be broken to produce 100 percent ethanol using azeotropic distillation. Water from distillation is recycled back to the reactor.

3.2 Process Assumptions

An economic evaluation has been developed to process 100 million standard ft³ of syngas per day. This quantity of gas produces 561 million pounds of ethanol per year. It is assumed for this analysis that the syngas contains 65 percent CO and 22 percent H₂.

For the purposes of this evaluation, it is assumed that *C. ljungdahlii* has a cell yield of 0.33 g cells/mole gas. It is further assumed that the culture is not inhibited until an ethanol concentration of 50 g/L is attained. The maximum specific growth rate, μ_m , is 0.04 mole gas/g cell·hr. Each of these assumptions has been demonstrated in previous reactor studies.

In this simulation, the operating pressure is 20 atm, the temperature is 37°C, the CO conversion is 90 percent and the cell recycle is 90 percent of the active cells.

3.3 Economic Evaluation

Table 3.2 presents a summary of the equipment necessary to produce ethanol from syngas in the process described above. Eleven 1250 m³ stirred tank reactors at 20 atm are required for the process. Centrifuges are utilized for cell recycle. The total costs for reaction, extraction and the two distillations are \$38.36 million.

Utility requirements are summarized in Table 3.2. As is noted, 8955 hp of electricity is required, 274 million Btu/hr of steam are required and 3 million gal/hr of cooling water are required.

The economic evaluation for the process is summarized in Table 3.3. Ethanol at \$1.20/gal yields just over \$100 million/yr. Chemicals in the form of medium chemicals, solvent (n-hexanol) and syngas total \$17.9 million - \$52.8 million depending upon the cost of the raw synthesis gas. Three synthesis gas costs (shown as 1, 2 and 3) are shown:

(1) \$0.50/MSCF

(2) \$1.00/MSCF

(3) \$1.50/MSCF

Thus, all cost analyses shown later in the table are indicated for the three scenarios.

Utilities total \$9.2 million, depreciation (at 10 percent of the fixed capital investment (FCI)) totals \$3.8 million and maintenance (5% of the FCI) total \$1.9 million. Labor is estimated at \$0.25 million/yr. The total operating cost is \$33.5 - \$68.5 million/yr depending upon the syngas cost.

The profit before taxes (38 percent) is \$67.5 - \$32.5 million/yr and the profit after taxes is \$41.8 - \$20.1 million/yr. The cash flow is \$45.7 - \$24.0 million/yr and the payout is 0.8 - 1.6 yr.

4.0 CONCLUSIONS

The technical and economic feasibility of producing ethanol from syngas using *C. ljungdahlii* has been demonstrated. A plant processing 100 million SCF of syngas per day and generating 561 million pound of ethanol per year has a payout of 1.6 yr using a syngas price of \$1.50/MSCF. If the raw syngas can be obtained for \$0.50/MSCF, the payout time reduces to 0.84 yr.

Table 3.2

Utilities

<u>Section</u>	<u>Electricity</u>	<u>Steam</u>	<u>Cooling Water</u>
Reactor	8800 hp		
Extraction	50 hp		
First Distillation	80 hp	189 $\bar{M}$ Btu/hr	2231 M gal/hr
Second Distillation	25 hp	85 $\bar{M}$ Btu/hr	782 M gal/hr
Total	8955 hp	274 $\bar{M}$ Btu/hr	3013 M gal/hr

Electricity cost: \$0.06/kwhr

Steam cost: \$2/ $\bar{M}$ Btu

Cooling water cost: \$0.05/M gal

Table 3.3

Economic Evaluation

A. Revenue

Ethanol @ \$1.20/gal	\$101.01 MM/yr
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B. Chemicals Cost

Medium \$20/hr	\$ 0.17 MM/yr
Solvent \$20/hr	\$ 0.17 MM/yr
Syngas	
(1) \$0.50/1000 SCF	\$ 17.50 MM/yr
(2) \$1.00/1000 SCF	\$ 35.00 MM/yr
(3) \$1.50/1000 SCF	\$ 52.50 MM/yr

Total Chemicals Cost	(1)	\$ 17.84 MM/yr
	(2)	\$ 35.34 MM/yr
	(3)	\$ 52.84 MM/yr

C. Utilities

Electricity	\$ 3.34 MM/yr
Steam	\$ 4.59 MM/yr
Cooling Water	\$ 1.27 MM/yr
Total Utilities	\$ 9.20 MM/yr

D. Depreciation (10% FCI)	\$ 3.84 MM/yr
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E. Maintenance (5% FCI)	\$ 1.92 MM/yr
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F. Labor	\$ 0.50 MM/yr
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G. Supervision (1/2 of Labor)	\$ 0.25 MM/yr
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H. Total Operating Costs	(1)	\$ 33.54 MM/yr
	(2)	\$ 51.04 MM/yr
	(3)	\$ 68.54 MM/yr

I. Profit Before Taxes	(1)	\$ 67.47 MM/yr
	(2)	\$ 49.97 MM/yr
	(3)	\$ 32.47 MM/yr

J. Taxes (38%)	(1)	\$ 25.64 MM/yr
	(2)	\$ 18.99 MM/yr
	(3)	\$ 12.34 MM/yr

Table 3.3 (continued)

K. Profit After Taxes	(1)	\$ 41.83 MM/yr
	(2)	\$ 30.98 MM/yr
	(3)	\$ 20.13 MM/yr
L. Cash Flow	(1)	\$ 45.67 MM/yr
	(2)	\$ 34.82 MM/yr
	(3)	\$ 23.97 MM/yr
M. Payout	(1)	0.84 Yr
	(2)	1.10 Yr
	(3)	1.60 Yr

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