PRODUCTION OF ETHANOL FROM REFINERY WASTE GASES

Phase II. Technology Development

Annual
~~Final~~ Report

By
D. Arora
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July, 1995

Work Performed Under Cooperative Agreement No. DE-FC04-94AL98770

For
U.S. Department of Energy
Office of Industrial Technologies
Washington, DC

By
Bioengineering Resources, Inc.
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PREFACE

This report documents the technical progress made on Phase II, Technology Development, of the DOE funded project "Production of Ethanol from Refinery Waste Gases" for the time period covering April 1, 1994 through March 31, 1995. Bruce Cranford and Merrill Smith are the Program Managers for the DOE Office of Industrial Technologies. Porter Grace is the Technical Manager for the DOE Albuquerque Operations Office. Charles Quinn and Frank Childs, the Project Technical Monitors, are on the staff of Sciencetech, Inc. Dr. J. L. Gaddy is the Project Manager on this project and Dr. E. C. Clausen is the Principal Investigator. They are co-authors on the report along with Dr. R. Basu, Dr. G. Chen, Mr. J. R. Phillips and Dr. C. V. Wikstrom.

Work supported by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial technologies, under DOE Albuquerque Operations Office Cooperative Agreement DE-FC04-94AL98770.

This is the first annual progress report for the project. This report can be obtained as indicated by the notice inside the front cover.

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PRODUCTION OF ETHANOL FROM REFINERY WASTE GASES

EXECUTIVE SUMMARY

Refineries discharge large volumes of H_2 , CO and CO_2 from cracking, coking and hydrotreating operations. This research program is seeking to develop a biological process for the conversion of these waste gases into ethanol, which can be blended with gasoline to reduce emissions. Ethanol demand is expected to triple to 3 billion gallons per year by 1997. A typical 200,000 BPD refinery could produce up to 38 million gallons of ethanol per year from the waste gases. The technology does not require purification of the gases and no modifications to existing refinery processes are required. The production of ethanol from all 194 U.S. refineries would save 450 billion BTU annually, would reduce crude oil imports by 110 million barrels per year and would reduce emissions by 19 million tons per year. By the year 2010, this technology could create 12,000 permanent new jobs and make the nation more competitive by saving \$2.8 billion annually in manufacturing costs. In addition, the construction of 78 new plants over the next 15 years would create employment to support capital expenditures of \$160 million per year.

The research program is being conducted in three phases: Phase II - Technology Development; Phase III - Engineering Development; and Phase IV - Demonstration. Phase I, Exploratory Development, has been successfully completed in the BRI laboratories. The Phase II research effort has yielded at least three cultures (*Clostridium ljungdahlii*, Isolate O-52 and Isolate C-01) which are able to produce commercially viable concentrations of ethanol from CO, CO_2 and H_2 in petroleum waste gas. Results from single continuous stirred tank reactor (CSTR) studies have shown that 15-20 g/L of ethanol can be produced, with less than 5 g/L acetic acid as a by-product. It is believed that the culture and reactor optimization studies of Phase III will yield even higher ethanol concentrations and hopefully minimal concentrations of acetic acid. Product recovery studies have shown that ethanol is best recovered in a multi-step process involving

- solvent extraction, followed by distillation to the azeotrope, followed by azeotropic distillation or pervaporation, or
- direct distillation to the azeotrope, followed by azeotropic distillation or pervaporation

Of these options, direct distillation followed by pervaporation appears to be less energy intensive. The economic projections for commercialization of this technology are quite attractive. These projections show that the ethanol facility for a typical refinery would require an investment of about \$30 million, which would be returned in less than two years.

PRODUCTION OF ETHANOL FROM REFINERY WASTE GASES

INTRODUCTION

The current crude oil refining capacity in the United States is 15.5 million barrels per day (BPD) (Thrash, 1991). There are 194 refineries in 35 states, producing over 2,000 products from fuels and lubricants to petrochemicals and waxes (Hyd. Proc., 1992a; Gary and Handwerk, 1975). However, refinery design and operation are controlled by a relatively few products, like gasoline, jet fuel and diesel fuel. Storage and waste disposal are expensive and all components of the crude must be sold or upgraded. In general, the lowest value for a product is its heating value or fuel oil equivalent.

The major refining steps include atmospheric distillation, vacuum distillation, catalytic cracking, hydrocracking, catalytic reforming, hydrotreating and thermal cracking (delayed coking). Each refinery has its own unique processing scheme dictated by the crude oil quality and product demand. The various processing steps are generally designed to produce a liquid product having specific properties for fuel blending. These steps also produce gases that consist of light hydrocarbons along with H_2 , CO and CO_2 . These gases are waste streams, and are flared or burned for fuel.

Table 1 lists various waste gas streams from a typical 200,000 BPD refinery. Catalytic cracking, which converts heavy oils into gasoline and lighter products, produces a by-product gas stream consisting primarily of light hydrocarbons, but with 20 percent hydrogen. The cracking reactions also produce coke which remains on the catalyst particle, thereby lowering its activity. The coke is removed by catalyst regeneration, which continuously burns the carbon to produce a waste gas stream of CO and CO_2 . Hydrocracking converts those oils that are refractory to catalytic cracking into gasoline fuelstocks at high pressure in the presence of hydrogen. Hydrotreating is used to stabilize petroleum products and to remove sulfur by reaction with hydrogen. These processes result in waste gas streams containing large amounts of hydrogen that cannot be recycled. Residual fuel oils are thermally cracked into lighter hydrocarbons and coke at extreme temperatures in a process termed delayed coking. This process generates a waste gas stream containing a significant fraction of H_2 .

Table 1. Refinery Waste Gas Streams (Basis: 200,000 BPD)

Gas Stream	Present Use	Quantity lb mol/h	Composition, mole %				
			H_2	CO_2	CO	H-C	H_2S
Cat Cracker off gas	fuel gas	3826	19.4	-	-	80.0	0.6
Delayed Coker off gas	fuel gas	2024	10.7	0.2	-	83.2	5.9
Hydrotreater and cat reformer	fuel gas	5120	93.8	-	-	5.5	0.7
Catalyst regenerator dry, N_2 free	vent	5120	-	56.3	43.6	-	-

This research program deals with the conversion of refinery waste gas streams into liquid fuel by a novel new technology. Bioengineering Resources, Inc. (BRI) has recently identified proprietary bacteria that convert H_2 , CO and CO_2 into ethanol by the equations:

A conceptual flow diagram has been developed for converting the waste gases into ethanol and is shown in Figure 1. The refinery gases are now flared or used for fuel, so that no changes in refinery operation would be necessary. The gases would be introduced into a bioreactor where the culture of bacteria is maintained. The CO , H_2 and CO_2 are converted into ethanol and the unreacted exhaust gases are returned for fuel use. The biocatalyst is automatically regenerated in the bioreactor by slow growth of the bacteria. An aqueous stream of ethanol is continuously removed through a hollow fiber membrane that retains the cells in the bioreactor to maximize the reaction rate. The aqueous permeate is contacted with an immiscible and insoluble organic solvent that extracts the ethanol. Solvents have been identified that have very low distribution coefficients for water, thereby minimizing the energy required for ethanol dehydration. Two distillation steps separate water and solvent from the ethanol product.

Figure 1. Biological Process for Ethanol Production

This biological process offers the advantages of high efficiency, and low capital and operating cost. The microorganisms use only a small fraction of the substrate for growth and energy, and high yields are obtained. Ambient temperatures and pressures are used and energy requirements are minimal. Only a single product is produced and separation technology is simplified. The biocatalyst (microorganisms) is not poisoned by the gas components, and is regenerated by growth of the culture. Biological processes are compatible with the environment and no toxic or hazardous wastes are generated. The primary disadvantage of biological processes is generally slow reaction rates. However, retention times of minutes have been achieved for this biocatalytic reaction, which makes this process very attractive economically.

The U.S. currently produces about one billion gallons of fuel ethanol annually from grain as a gasoline additive. The potential market is ten times this amount if all gasoline is blended with ten percent alcohol or 100 times greater with pure ethanol as fuel. Ethanol increases the octane rating and reduces emissions. The recent Clean Air Act has mandated the use of oxygenated fuels in many metropolitan areas and the demand for ethanol is expected to triple in the next five years (Hyd. Proc., 1992b).

The quantity of waste gases from a typical refinery of 200,000 BPD, given in Table 1, would produce 38 million gallons of ethanol per year, generating \$45 million at current prices. Nationwide, refineries could produce 3 billion gallons of ethanol annually from their waste gases. The refineries, of course, have a ready market for this product. The application of this technology will reduce emissions from refineries, improve our balance of payments by reducing fuel imports by up to \$3 billion annually, and save up to 0.3 Quad of energy. Clearly, this technology has significant environmental, economic, and political incentives for rapid commercial application.

The objective of this three year, three phase program is to develop a commercial process for producing ethanol from refinery waste gases. The exploratory development (Phase I) of this project has already been completed. In Phase II (Technology Development), experiments were conducted to screen and optimize cultures for ethanol production from refinery waste gases and define reaction kinetics and retention times in stirred-tank reactors. Optimal parameters for ethanol extraction/distillation were investigated. A preliminary process design and economic analysis was prepared for a commercial scale unit to define the economic potential and determine high cost areas for further research.

In Phase III (Engineering Development), data will be developed for scale-up and commercialization of this process. An integrated bench scale unit will be constructed and operated for an extended period to demonstrate the viability of the cultures and the unit operations in the process. This unit will couple continuous operation of the reactor with product recovery and recycle of the aqueous and solvent streams. Methods to enhance mass transfer and reduce reactor volume, such as high pressure operation and non-aqueous fermentation, will be examined. Intrinsic reaction kinetics and mass transfer coefficients will be determined for reactor scale-up. The design and economic projections for a commercial scale facility will be modified to reflect the data from Phase III. Phase IV (Demonstration) will involve the design, construction and operation of a pilot demonstration facility with refinery waste gases. A prolonged period of continuous operation of this facility will provide data for scale-up to a commercial unit. Successful completion of this development program will provide an optimal design that should be readily commercialized.

PURPOSE

The purpose of this report is to present results from the Phase II research and development program aimed at further developing the technology prior to engineering development and demonstration. Results from laboratory culture screening studies, stirred tank reactor studies and product recovery studies are presented and discussed. In addition, the process design and commercialization plan is updated to reflect the results from the Phase II studies.

PHASE II - TECHNOLOGY DEVELOPMENT

The following tasks (from the project Statement of Work) are designed to move the technology from the laboratory to the engineering and demonstration phases.

TASK 1. CULTURE DEVELOPMENT

BRI shall screen culture isolates to determine the best available bacterial cultures to produce ethanol from CO, CO₂ and H₂. Batch experiments shall be conducted to define yields, growth and production rates, and near optimal ranges for other parameters. The other parameters shall include CO tolerance, doubling time, and production kinetics. Those organisms providing the highest yields, and fastest growth and production rates shall be selected for optimization.

For the most promising cultures to produce ethanol, the fermentation parameters shall be manipulated to maximize the yields and production rates. Variables to be studied include nutrient levels, pressure, temperature, reaction pH, agitation levels, inoculum level, maximum substrate concentrations to avoid inhibition, and maximum product concentrations to avoid inhibition.

TASK 2. REACTOR STUDIES

BRI shall determine the yields, kinetic parameters, retention time, minimum agitation rate, recommended nutrients, and optimum pH for the best bacterial cultures in a continuously-stirred tank reactor (CSTR). Experiments shall include varying gas flow rates, gas compositions, and agitation rates to determine gas conversion rates and limits. The minimum retention time and reactor size for each organism shall be defined for the various industrial conditions expected.

TASK 3. PRODUCT RECOVERY

BRI shall conduct solvent screening experiments in both batch and continuous reactor modes to determine the effect of the solvents on performance. Data for each solvent shall be used to project the enhancement in ethanol yield and the capital and energy cost for product recovery for comparison with equilibrium data for distillation that is available in the literature. Calculations for equipment size and cost and energy requirements shall be predicted for a nominal size ethanol facility.

TASK 4. ECONOMIC UPDATE AND COMMERCIALIZATION PLAN

Economic Update - BRI shall perform an economic analysis of the complete system to update and expand on the projections in the proposal. This shall include predictions of capital, equipment and operating costs for a typical facility. The potential revenue from ethanol sales shall be determined. A profit and economic return calculation shall be made. The data shall be used to assess economic feasibility and to identify potential high cost areas for further research in Phase III.

The analysis shall include estimates of overall market penetration (to the year 2010), process performance, plant and national energy savings, plant and national emissions reductions, and economic viability. Data may be required in a format suitable for the DOE Threshold Analysis. The evaluation of long-term industry trends and the extent of market penetration shall be updated if needed. Differences from economic, energy, and environmental benefits previously predicted shall be noted. The Updates shall be revised if new data causes significant changes from those used earlier. DOE shall be notified promptly if test results indicate a significant change in performance projections.

Commercialization Plan - BRI shall prepare a general plan for scaling up and commercializing this technology. Assumptions shall be stated and specific roles and commitments from the project Industrial Participant(s) shall be documented.

RESULTS AND DISCUSSION

TASK 1. CULTURE DEVELOPMENT

Culture Isolation

Clostridium ljungdahlii was the first bacterium isolated which was capable of producing ethanol from CO, CO₂ and H₂ by Equations (1) and (2). In addition, BRI has isolated several other bacteria which are also capable of the conversion. The bacteria were isolated from a variety of natural sources including sewage sludge, mud and sediment, oil-contaminated soils, and hot springs. To obtain an enrichment capable of utilizing CO, CO₂ and H₂ to produce ethanol, the consortia were inoculated into serum bottles containing basal medium at pH 6.5 under anaerobic conditions at 30, 37 or 55°C. A mixture of CO, CO₂, H₂ and CH₄ at 1 atm served as the gas head space. The bottles were monitored for CO and H₂ utilization, as well as product formation, over a period of several weeks. Successful consortia found to produce ethanol from CO and H₂ were transferred to fresh medium, and the process repeated. Enrichments were obtained from this successive transfer procedure which were then used to obtain pure cultures in roll tube experiments.

Figures 2 and 3 illustrate this procedure with eight enrichments and their transfers, each isolated from natural sources. As is noted in Figure 2, the subcultures produced up to 0.5 g/L of ethanol in batch culture after 150 hr of incubation. Acetic acid was the dominant product, with 0-1.2 g/L produced. First transfer subcultures of these enrichments, shown in Figure 3, produced up to 0.22 g/L ethanol with acetic acid as the major product. Other cultures produced similar results. As is noted in Table 2, ethanol/acetate ratios from these early enrichments ranged from 0.04-1.3 on a gram ethanol/gram acetate basis.

Table 2. Fermentation Product Analysis from Fifteen Enrichments

Strain	Ethanol (g/L)	Acetate (g/L)
0-126	0.135	1.654
0-127	0.114	2.770
0-128	0.128	1.492
0-129	0.287	1.534
0-130	0.167	0.510
0-131	0.127	0.100
0-132	0.156	1.093
0-133	0.125	1.407
0-134	0.320	2.132
0-135	0.216	1.371
0-136	0.200	3.000
0-137	0.203	0.215
0-138	0.188	2.110
0-139	0.324	1.400
0-140	0.268	2.282

Incubated at 37°C for 8 days on CO, CO₂, H₂

Figure 2. Ethanol Production from CO, CO₂ and H₂ by Eight Selected Enrichments

Figure 3. Ethanol Production from CO, CO₂ and H₂ by Subcultures of the Eight Selected Enrichments

Batch Comparison Studies

Nearly 200 cultures capable of producing ethanol from CO, CO₂ and H₂ were isolated in the early screening studies. Acetic acid was always the dominant product. Batch culture experiments were performed with several of the more promising enrichments. The cultures were grown anaerobically in mineral medium at 37°C. Samples were analyzed for gas phase composition, liquid phase product concentrations and reaction pH. Several of the enrichments were capable of producing more than 2 g/L ethanol in batch culture. By comparison *C. ljungdahlii*, strain PETC, produced only small concentrations (< 1 g/L) of ethanol after several weeks in incubation. Product formation by two of these isolates is shown in Figures 4 and 5. Isolate ERI2 produced nearly 1.5 g/L ethanol in 11 days, with an equal concentration of acetic acid. Isolate ERI8 produced 2.5 g/L ethanol in 8 days, with only 1.0 g/L acetic acid formed as a by-product. Both isolates consumed both CO and H₂ rapidly, requiring re-gassing of the batch bottle reactors at least once per day.

Figure 4. Ethanol and Acetic Acid Production from CO, CO₂ and H₂ by Isolate ERI2 in Batch Culture

Figure 5. Ethanol and Acetic Acid Production from CO, CO₂ and H₂ by Enrichment ERI8 in Batch Culture

Culture Enhancement

Several techniques have been developed to maximize ethanol production by the isolates, including nutrient limitation at decreased pH, re-isolation for ethanol producers with a calcium agar technique and the induction of sporulation. The induction of sporulation refers to the tendency of spore-producing bacteria to produce solvents along with spores under stressed conditions. Results from experiments utilizing these techniques are discussed briefly below.

Elimination of Yeast Extract in the Medium. Previous studies with *Clostridium ljungdahlii* showed that the elimination of yeast extract from the liquid medium limited growth while, simultaneously, enhancing ethanol production. An enhanced ethanol-producing strain of ERI8 was first obtained by calcium-agar selection, a technique which selects ethanol-producing strains, but unfortunately does not guarantee that acetic acid will be eliminated from the medium.

Table 3. Ethanol and Acetic Acid Production from CO, CO₂ and H₂ by ERI8 Isolates (Values are highest concentration in g/L)

Strain	CA15	CA17	CA20	CA29	CA30	CA31	CA32	CA33	CA34	CA35	CA36	CA37
HAc	3.81	2.88	2.75	4.64	8.75	5.31	3.62	4.79	4.38	3.93	2.54	2.27
Ethanol	1.04	0.65	0.55	1.59	0.75	1.03	0.92	0.24	0.21	0.22	0.62	0.70

The strains were inoculated into mineral medium at pH 5.5. The gas space contained CO, CO₂ and H₂ at 1 atm pressure. Table 3 shows selected results from the ERI8 studies. Of particular interest are strains CA15 and CA29, which produced 1.0 and 1.5 g/L ethanol, respectively, in batch culture.

Induction of Sporulation. The use of a medium which induces sporulation often results in increased solvent formation in clostridial species, the genus to which Isolate ERI8 belongs. Isolate ERI8, a strain shown to produce both ethanol and acetate in batch culture, was incubated into such a medium. The gas space again was CO, CO₂ and H₂ at 1 atm.

Table 4 presents results from several of the sporulation experiments. As is noted, each of the cultures/conditions produced over 2 g/L ethanol in 8-10 days. Gas consumption by the ERI8 strains was rapid in most of the experiments and a significant number of spores were observed in the culture when observed under the microscope. It indeed appears that ethanol production is related to the induction of sporulation.

Table 4. Ethanol and Acetic Acid Production from CO, CO₂ and H₂ in Sporulation-Inducing Medium (Values are highest concentration in g/L)

Strain	CB1	CB7	CB8	CB9	CB10	CB11	CB12
HAc	3.62	3.54	4.56	3.85	3.85	3.97	4.22
Ethanol	2.43	2.34	2.35	2.52	2.51	2.22	2.32

Alternative Growth Substrates. The concept of supplying an additional growth substrate (carbon source for growth) in order to support culture growth with simultaneous gas utilization to produce only ethanol as the product was examined with isolate ERI2. Glucose was supplied as the additional growth source and the acetate kinase inhibitor, N-thylmaleimide, was used to stop acetic acid production. The study was performed in a 1000 mL CSTR with an agitation rate of 1000 rpm, and with a liquid dilution rate of 0.03 to 0.04 hr⁻¹ and gas flow rate of 30 mL/min. A rich medium containing yeast extract was used along with 2.5 g/L glucose. Figures 6 and 7 show gas conversion and product concentrations from this study. The gas flow rate was increased to 60 mL/min and the glucose concentration was increased to 4 g/L on the seventh day after the 2.5 g/L glucose was completely consumed. The liquid dilution rate was increased to 0.04 hr⁻¹ on day 14. On the 17-th day, yeast extract was removed from the medium. The culture still consumed around 80 and 20 percent of the CO and H₂, respectively. 0.5 mM N-thylmaleimide, an acetate kinase inhibitor, was added to the medium on the 27-th day. The addition did not affect either the gas consumption or the resulting concentrations. The N-thylmaleimide concentration was increased to 2 mM on the 29-th day. However, the culture failed to consume gas after this latter addition. Thus, experimentation with this concept was abandoned.

**Figure 6. Gas Conversion in the CSTR Using ERI2.
Alternate Carbon Source and Acetic Acid Suppression**

Figure 7. Product Concentration Measurements in the CSTR Using ERI2.
Alternative Carbon Source and Acetic Suppression

TASK 2. REACTOR STUDIES

Continuous reactor studies were performed with *Clostridium ljungdahlii* and Isolates ERI2, ERI8, O-52 and C-01. In addition, parameters thought to significantly affect continuous ethanol production such as agitation rate, gas flow rate, liquid flow rate and dissolved CO were studied in the CSTR.

Studies with *C. ljungdahlii*

Both reactors used in the study were fed a designed basal salts and vitamins medium. The gas composition was 65 percent CO, 20 percent H₂, 11 percent CO₂ and 4 percent CH₄. The first reactor was operated at a gas retention time of 14 min, a liquid dilution rate of 0.04 hr⁻¹, a temperature of 38.8°C and an agitation rate of 550 rpm. These conditions were held essentially constant throughout the course of the study. Figures 8-10 show gas conversion, cell concentration and product concentration profiles for 200 hr of operation at essentially constant conditions. As is noted in Figure 8, the CO and H₂ conversions ranged from 25-90 and 20-60 percent, respectively, in a cyclic fashion. The average CO conversion was about 70 percent and the average H₂ conversion was 30 percent. These fluctuations demonstrate the instability of operation with the culture at constant process conditions. The cell concentration as optical density was also cyclic, ranging from 1.3-2.5 (see Figure 9). The product concentrations were also a bit unstable, with a maximum ethanol concentration of 12 g/L (see Figure 10). The most encouraging results from the study were the rapid start-up (approximately 50 hr) and high ethanol concentrations obtained in a relatively short period of time.

As an alternative to operation at constant conditions, a second reactor was started with *C. ljungdahlii* using a constant CO conversion by manipulating the gas flow rate (retention time). The gas retention time in this study ranged from 10-35 min (decreasing retention time with operating time), the liquid dilution rate 0.071 hr^{-1} , the temperature was 38.8°C and the agitation rate was 880 rpm. The results from this 200 hr study are shown in Figures 11-13. As is noted in Figure 11, the CO conversion was essentially constant at 80 percent throughout the study. The corresponding H_2 conversion ranged from 5-80 percent, with an average of about 30 percent. The cell concentration steadily increased with decreasing retention time, with a maximum of about 2.5 (see Figure 12). The product concentrations were a bit more stable than in the first study, showing a maximum ethanol concentration of 9 g/L (see Figure 13). The control of this system at constant conversion was found to be more difficult than in the first system, but the overall system performance was more stable.

Figure 8. CSTR Stability Studies with *C. ljungdahlii*: Reactor 1 Gas Conversion Profiles

Figure 9. CSTR Stability Studies with *C. ljungdahlii*: Reactor 1
Cell Concentration Profiles

Figure 10. CSTR Stability Studies with *C. ljungdahlii*: Reactor 1
Product Concentration Profiles

Figure 11. CSTR Stability Studies with *C. ljungdahlii*: Reactor 2
Gas Conversion Profiles

Figure 12. CSTR Stability Studies with *C. ljungdahlii*: Reactor 2
Cell Concentration Profile

Figure 13. CSTR Stability Studies with *C. ljungdahlii*.
Product Concentration Studies (Reactor 2)

Studies with Isolate ERI2

Because of the promising ethanol production data from the batch culture studies, Isolate ERI2 was inoculated into a CSTR. The culture employed a mineral medium with 1 g/L trypticase. The reactor temperature was 38.5 - 39.0°C and the agitation rate was 700 rpm. A gas containing 65 percent CO, 20 percent H₂, 11 percent CO₂ and 4 percent CH₄ was introduced into the reactor at 5 mL/min and liquid medium was fed at a dilution rate of 0.06 hr⁻¹.

The performance of isolate ERI2 in the CSTR for a short period of time is shown in Figures 14 and 15. As is noted in Figure 14, the CO conversion reached 90 percent and the H₂ conversion reached 20-30 percent in 4 days. The corresponding product concentrations, shown in Figure 15, were 2 g/L ethanol and 4.3 g/L acetate.

Figure 14. CO and H₂ Consumption by Isolate ERI2 in the CSTR

Figure 15. Ethanol and Acetic Acid Production by Isolate ERI2 in the CSTR

Studies with Isolate ERI8

Isolate ERI8 was also inoculated into a CSTR. The culture again employed a mineral medium with 1 g/L trypticase. The reactor temperature was 38.5 - 39.0°C and the agitation rate was 700 rpm. A gas containing 65 percent CO, 20 percent H₂, 11 percent CO₂ and 4 percent CH₄ was introduced into the reactor at 5 mL/min and liquid medium was fed at a dilution rate of 0.06 hr⁻¹. The performance of ERI8 is shown in Figures 16 and 17. As is shown in Figure 16, the CO conversion reached 90 percent and the H₂ conversion reached 10 percent after 5 days of operation. The corresponding product concentrations, shown in Figure 17, were 0.5 g/L ethanol and 4.0 g/L acetate.

Figure 16. CO and H₂ Consumption by Isolate ERI8 in the CSTR

Figure 17. Ethanol and Acetic Acid Production from CO, CO₂ and H₂ by Isolate ERI8 in the CSTR

ERI8 was next inoculated into a basal mineral ("basal") medium in the CSTR with 1.0 g/L cysteine HCl minus trypticase and yeast extract at 38°C. The elimination of trypticase and yeast extract has, in the past, been effective in promoting ethanol formation in place of acetic acid. The agitation rate was held at 1000 rpm. The reactor was first operated batchwise with a gas flow rate of 5 mL/min (200 min gas retention time). After this initial batch stabilization period, the gas flow rate and liquid dilution rate were gradually increased to the eventual steady state values of 12 mL/min (83.3 min gas retention time) and 0.025h^{-1} , respectively.

The optical density at steady state was approximately 0.3. The CO conversion was roughly 60 percent and the H_2 conversion was 14 percent. Figure 18 shows product formation by the isolate as a function of time in the CSTR. As is shown, the acetate concentration held at approximately 4-4.5 g/L during the entire period of operation at the 83.3 min gas retention time and 0.025h^{-1} liquid dilution rate. The ethanol concentration, on the other hand, increased from about 1 g/L to 1.5 g/L during the same period.

Isolate ERI8 was again grown in a CSTR using basal medium without yeast extract and trypticase at 38°C. In this study, the concentrations of salts, trace metals, vitamins and cysteine-HCl were doubled in comparison to the previous work due to the success found with concentrated medium on *C. ljungdahlii*. The agitation rate was 800 rpm for this 1.0 liter reactor. The liquid dilution rate was 0.02 hr^{-1} during the first 275 hr of fermentation, and then was changed to 0.04 hr^{-1} . The gas flow rate was increased gradually with time as the conversion permitted. The maximum gas flow rate was 65 mL/min (15.4 min gas retention time), during the late stages of the fermentation.

Figure 19 shows gas consumption by ERI8 during the study. The CO conversion was generally 70-80 percent, with the H_2 conversion 20-30 percent. This behavior is quite similar to the gas conversion results obtained with *C. ljungdahlii*. The optical density, shown in Figure 20, was rather low (0.3) until a filtered vitamin B mixture was added at $t = 180\text{ hr}$. The resulting O.D. after vitamin addition was 1.5-1.8.

Ethanol and acetic acid production in the CSTR with time is shown in Figure 21. The ratio of ethanol to acetic acid was just under 1.0, a level found to be very stable in the studies with *C. ljungdahlii*. Both ethanol and acetic acid were boosted significantly with vitamin addition, reaching 7.2 and 8 g/L, respectively.

Finally, ERI8 was utilized in a CSTR with cell recycle at constant conditions for a period of 350 hr. The gas retention time was 14.3-15.4 min, the liquid dilution rate was 0.1 hr^{-1} , the hollow fiber filtration rate was 0.085 hr^{-1} , the temperature was 38°C, the pH was 4.5 and the agitation rate was 1000 rpm.

Figures 22-24 show gas conversion, cell concentration and product formation profiles for ERI8 in the CSTR with cell recycle. As is noted in Figure 22, the gas conversion by ERI8 in this study with constant conditions was similar to *C. ljungdahlii* operation in the initial study. The maximum CO conversion was 100 percent and the maximum H_2 conversion was 80 percent. Figure 23 shows the cell concentration profile for operation with cell recycle. As expected, the optical density increased as cells were separated and returned to the reactor. A maximum optical density of 3.7 was obtained. The product profiles showed increasing product formation for the first 200 hr, followed by a drop in the ethanol concentration (see Figure 24). The maximum ethanol concentration was 6 g/L, with a product ratio of 0.83 g ethanol/g acetic acid.

Figure 18. Ethanol Production from CO, CO₂ and H₂ with ERI8 (CSTR)

Figure 19. Gas Conversion by ERI8 in the CSTR

Figure 20. Optical Density Measurements for ERI8 in the CSTR

Figure 21. Ethanol and Acetic Acid Production by ERI8 in the CSTR

Figure 22. H₂ and CO Conversion with ERI8 in the CSTR with Cell Recycle

Figure 23. Cell Concentration vs Optical Density with ERI8 in the CSTR with Cell Recycle

Figure 24. Ethanol and Acetic Acid Production with ERI8 in the CSTR With Cell Recycle

Studies with Isolate O-52

Isolate O-52 was shown in previous batch studies to be capable of producing ethanol instead of acetic acid as a product from syngas conversion. This was accomplished by utilizing basal medium without yeast extract and trypticase. However, transfer of the culture to the CSTR brought about the renewed production of acetic acid in addition to ethanol. In fact, acetic acid was overwhelmingly produced in favor of ethanol in the CSTR.

Recently, Isolate O-52 has shown ethanol production in the CSTR with only small amounts of acetic acid as a by-product. The CSTR (without cell recycle) employed a 45.5-50 min gas retention time, a $0.024\text{-}0.031\text{ hr}^{-1}$ liquid dilution rate, a temperature of $36.5\text{-}39.0^{\circ}\text{C}$ and an agitation rate of 750-1000 rpm. The gas consisted of 65 percent CO , 20 percent H_2 , 11 percent CO_2 and 4 percent CH_4 . The operating conditions were variable because of fine tuning to yield the maximum ethanol concentration.

Figures 25-27 show gas conversion, cell concentration and product concentration profiles for Isolate O-52 in the CSTR. The CO conversion ranged from 20-60 percent, with higher conversions occurring during the maximum ethanol production (see Figure 25). The H_2 conversion remained at about 10 percent. The maximum cell concentration (as optical density) was 4.2, reached at a time of 1040 hr (see Figure 26). The optical density fell to a level of about 3.5, which corresponded to the time of maximum ethanol production and minimum acetic acid production (see Figure 27). The maximum ethanol concentration was about 5 g/L, with a corresponding acetic acid concentration of 0.5 g/L.

Figure 25. Gas Conversion in the CSTR Using Isolate O-52

Figure 26. Cell Concentration Profile in the CSTR Using Isolate O-52

Figure 27. Product Concentration Profile in the CSTR Using Isolate O-52

Additional experiments were performed in the CSTR with Isolate O-52. The gas retention time was approximately 26 min and the liquid retention time was 24 hr. Figures 28 and 29 show CO and H₂ conversions for the study, while Figures 30 and 31 show product concentrations. Following a period of product stabilization of 240 hr, the culture shifted from predominantly acetate production to ethanol production. The CO conversions were stable at 85-90 percent and the H₂ conversions were erratic with an average of 20-30 percent (see Figures 28 and 29). Low H₂ conversions are typical when obtaining relatively high ethanol concentrations in a single CSTR. The ethanol concentration maximized at 20 g/L soon after the switch from acetate to ethanol production, and then stabilized at 10.5-11.0 g/L over the next 250 hr. The corresponding acetate concentration was 2-3 g/L (see Figures 30 and 31). The dry cell weight concentration was stable throughout the study at 1.5-2.0 g/L.

Studies with Isolate C-01

CSTR studies were also performed with Isolate C-01, which had produced high ratios of ethanol to acetic acid in serum bottle studies. The gas contained 32 percent H₂, 34 percent CO, 5 percent CH₄, and 29 percent CO₂. The liquid retention time (LRT) was 32 hr and the gas retention time was 14.2 min. Results from this reactor are shown in Figures 32 and 32. The reactor has been operating at these conditions for nearly 500 hr. The CO conversion has been maintained at about 85 percent, and the H₂ conversion has been fairly steady at about 50 percent (see Figure 32). The product from the reactor contains 20-24 g/L ethanol and 3-4 g/L acetic acid (see Figure 33). The dry cell weight concentration is 1.8-2.4 g/L.

Figure 28. Gas Conversion by Isolate O-52

Figure 29. Gas Conversion by Isolate O-52

Figure 30. Product Concentrations and Ratios for Isolate O-52

Figure 31. Product Concentrations by Isolate O-52

Figure 32. Gas Conversions for Isolate C-01

Figure 33. Product Concentrations and Ratios for Isolate C-01

TASK 3. PRODUCT RECOVERY

Solvent Extraction

Data have been collected from the laboratory and the literature for the extraction of ethanol from aqueous solution. A summary of the collected data is presented in Figures 34-44. Figure 34 shows the distribution coefficients of all published and measured alcohol solvents as a function of their separation factors (alcohol distribution coefficient divided by the water distribution coefficient) on a log-log scale. The separation factor represents the amount of water that must be removed per unit volume of solvent; the higher the value, the less water extracted by the solvent. The distribution coefficient determines the amount of solvent required per unit amount of alcohol extracted. The ideal case would be large values for both the distribution coefficient and the separation factor. However, as is shown in Figure 34, an increase in the distribution coefficient results in a reduction of the separation factor, and vice versa. Thus, a log-log plot of the distribution coefficient as a function of the separation factor results in a linear function with a negative slope. As is shown in the figure, the performance with alcohols can be classified into two groups: the primary alcohols and the secondary or branched alcohols, including a few tertiary alcohols. The secondary and/or branched alcohols have higher distribution coefficients than the primary alcohols, for a constant separation factor. Thus, secondary and/or branched alcohols are a better choice for ethanol recovery than primary alcohols.

Figures 35-43 show the distribution coefficient as a function of the separation factor for aromatics, ketones, halocarbons, carboxylic acids, phosphates, amines, esters, ethers, and hydrocarbons, respectively. The average performance of primary and secondary and/or branched alcohols are also included on the figures as straight lines for comparison. As is shown in these figures, aromatics, ketones, amines, esters, ethers and hydrocarbons are all worse than primary alcohols. Phosphates perform close to primary alcohols. However, most phosphates also have separation factors around 10. Carboxylic acids and some of the halocarbons performed as well as secondary and/or branched alcohols. Chloroform and tetrachloroethane were acceptable halocarbons. However, chloroform and tetrachloroethane were ultimately rejected for safety reasons. The carboxylic acids usually required a long phase separation time. Thus, the best candidates for ethanol recovery are still the secondary and/or branched alcohols.

One potential method to enhance the performance of secondary and/or branched alcohols is the addition of a hydrocarbon as a co-solvent to increase the separation factor. Figure 44 shows such an example. Orfom SX-18 (C9-C11 isoalkanes, Philips Mining Co.) was added to 3-methyl pentanol and 2,6 methyl 4-heptanol. The separation factors for 3-methyl pentanol and 2,6 methyl 4-heptanol were increased from 12 to 25 and from 47 to 71, respectively. However, the resulting reductions in the distribution coefficient were significant. Thus, the best solvent candidates should be secondary and/or branched alcohols having distribution coefficients greater than 0.4 and separation factors greater than 40. One such candidate is 2,6 methyl 4-heptanol which has a measured distribution coefficient of 0.44 and a separation factor of 47.

Figure 34. Distribution Coefficients and Separation Factors for Alcohols

Figure 35. Distribution Coefficients and Separation Factors for Aromatics

Figure 36. Distribution Coefficients and Separation Factors for Ketones

Figure 37. Distribution Coefficients and Separation Factors for Halocarbons

Figure 38. Distribution Coefficients and Separation Factors for Carboxylic Acids

Figure 39. Distribution Coefficients and Separation Factors for Phosphates

Figure 40. Distribution Coefficients and Separation Factors for Amines

Figure 41. Distribution Coefficients and Separation Factors for Esters

Figure 42. Distribution Coefficients and Separation Factors for Ethers

Figure 43. Distribution Coefficients and Separation Factors for Hydrocarbons

Figure 44. Distribution Coefficients and Separation Factors for Mixed Solvents

Three Component Solvent Studies. Studies using a three component mixed solvent have been described in the patent of Tedder (Patent No. 4,510,242 April 9, 1985). Table 5 shows distribution coefficients and separation factors for the system consisting of Orfom SX-18 (Philips Mining Co.), dodecanol and tributyl phosphate (TBP). As is noted in the table, increasing the proportion of dodecanol increased the distribution coefficient slightly at the expense of the separation factor. This same phenomena was observed when increasing the TBP concentration. Table 6 shows results from a system utilizing another alcohol complex former, butyl sulfone, instead of tributyl phosphate. Butyl sulfone exists as a solid at room temperature. Thus, butyl sulfone was dissolved in the mixture SX-18 and dodecanol. As is shown in this table, the distribution coefficient was typically around 0.25, while the separation factor was under 25. These results are similar to the results obtained when using TBP. As no significant advantage was obtained from the use of the alcohol complex former, no further tests will be performed with these solvent systems.

Table 5. Distribution Coefficients and Separation Factors for the SX-18, Dodecanol, and TBP System

Solvent	Distribution Coefficient	Separation Factor
50% SX-18, 50% Dodecanol	0.189 0.197	24.34 26.86
40% SX-18, 40% Dodecanol, 20% TBP	0.216	22.72
30% SX-18, 50% Dodecanol, 20% TBP	0.271	20.87
20% SX-18, 60% Dodecanol, 20% TBP	0.301	20.97
20% SX-18, 40% Dodecanol, 40% TBP	0.376	19.07
15% SX-18, 45% Dodecanol, 40% TBP	0.370	17.43

**Table 6. Distribution Coefficients and Separation Factors
for the SX-18, Dodecanol and Butyl Sulfone System**

Solvent	Distribution Coefficient	Separation Factor
50% SX-18, 50% Dodecanol	0.189	24.34
50% SX-18, 50% Dodecanol, 125 g/L Butyl Sulfone	0.208	21.23
25% SX-18, 75% Dodecanol, 62.5 g/L Butyl Sulfone	0.263	16.58
37.5% SX-18, 62.5% Dodecanol, 125 g/L Butyl Sulfone	0.254	19.27
37.5% SX-18, 62.5% Dodecanol, 187.5 g/L Butyl Sulfone	0.261	20.07

Salt Addition to Enhance Extraction. The use of salt to enhance alcohol extraction was studied using the selected solvent, 2,6 dimethyl 4-heptanol and NaCl as the salt. In this study, various amounts of salt were added into the aqueous solution containing 20 g/L alcohol. Table 7 shows the results of these extractions. As is shown in the table, not only was the separation factor significantly increased by adding salt to trap water remaining in the aqueous phase, but the distribution coefficient was also increased because of a reduction in alcohol affinity. With saturated NaCl, the distribution coefficient was increased from 0.44 to 2.0, and the separation factor was increased from 47 to 309. However, this excellent result cannot be directly utilized in a process because of the problems in recycling a saturated salt solution. A study with the addition of salt or a salt solution to the extracted solvent will provide the necessary information for any improvements.

Table 7. The Effect of Salt on Alcohol Extraction by 2,6 Dimethyl 4-heptanol

Salt Concentration, g/L	Distribution Coefficient	Separation Factor
0	0.4425	46.58
50	0.4405	48.95
200	0.6126	63.16
400	1.71	215.5
Saturated	2.039	309

Other Solvents. Cyanex 923 was also evaluated as a potential solvent for ethanol extraction. Cyanex 923 is a mixture of tertiary octyl hexylphosphine oxides, manufactured by Cyanamid. The distribution coefficients and separation factors for Cyanex 923 are shown in Table 8, along with similar data for the solvent 2,6 dimethyl 4-heptanol, the best candidate for ethanol extraction to date. As is shown in Table 8, Cyanex 923 has a higher distribution coefficient for ethanol than 2,6 dimethyl 4-heptanol. However, the distribution coefficient fell with increasing alcohol concentration. Another disadvantage of Cyanex 923 is that, like all phosphate-type chemicals, it forms a water complex.

Thus, Cyanex 923 extracted a significant amount of water in addition to ethanol. In fact, the separation factor was only 6 when extracting 2 percent ethanol in water. 2,6 Dimethyl 4-heptanol, on the other hand, has stable ethanol distribution coefficients of around 0.29, but also very high separation factors above 30. Thus, the best solvent for ethanol extraction still appears to be 2,6 dimethyl 4-heptanol.

3,7 Dimethyl 3-octanol, a tertiary alcohol, was also studied. In this study, aqueous ethanol solutions containing 5-30 g/L ethanol were extracted with equal volumes of 3,7 dimethyl 3-octanol at 25°C. Table 9 shows the results of the extractions. As is noted, 3,7 dimethyl 3-octanol gave ethanol distribution coefficients of 0.33-0.36 and separation factors of 20-23. 2,6 Dimethyl 4-heptanol gave a distribution coefficient of 0.29 and a separation factor of 33 in extracting a 20 g/L ethanol solution. Since the separation factor is of utmost importance in extracting ethanol, 3,7 dimethyl 3-octanol is not a better solvent.

Table 8. Distribution Coefficients and Separation Factors for Cyanex 923 and 2,6 dimethyl 4-heptanol at Various Ethanol Concentrations

ETOH, Mass %	K_{ETOH}	$K_{\text{H}_2\text{O}}$	Separation Factor	% ETOH Solvent Free Basis
Cyanex 923				
0.505	1.167	0.074	15.84	4.3
1.035	0.879	0.072	12.21	6.72
1.507	0.536	0.073	7.33	6.32
1.954	0.457	0.078	5.89	7.03
2,6 dimethyl 4-heptanol				
0.511	0.294	0.008	36.8	12.1
1.017	0.295	0.009	32.87	20.1
1.491	0.297	0.009	32.22	26.82
1.977	0.285	0.009	31.71	31.66
2.862	0.296	0.01	29.91	40.16

Table 9. Separation Characteristics for 3,7 dimethyl 3-octanol

ETOH Conc. (g/L)	Aqueous Phase ETOH Conc. (g/L)	Solvent Phase ETOH Conc. (g/L)	Water Conc. in Solvent (g/L)	K_{ETOH}	$K_{\text{H}_2\text{O}}$	Separation Factor
5.0	3.83	1.36	15.28	0.355	0.015	23.2
10.0	7.79	2.63	14.87	0.338	0.015	22.6
15.0	11.6	3.88	14.66	0.334	0.015	22.7
20.0	15.43	5.18	16.11	0.336	0.016	20.7
30.0	22.9	7.84	16.73	0.342	0.017	20.3

One option to improve the extraction efficiency of 2,6 dimethyl 4-heptanol is to add a co-solvent to reduce water uptake. Potential co-solvents include the hydrocarbon ORFOM SX-18, a mixture of C9-C11 isoalkanes from Phillips Mining Chemicals. Table 10 shows the results of adding SX-18 to 2,6 dimethyl 4-heptanol in the extraction of 2 weight percent ethanol. As is shown in the table, the maximum separation factor was 46.3 when using a 60 percent by volume SX-18 along with 2,6 dimethyl 4-heptanol. If separation is based on the percentage ethanol in the solvent on a solvent free basis, a 40 volume percent SX-18 addition has the maximum extraction capability (41.1 percent). The increase in the separation factor and relative percentage of alcohol in the solvent were about 32 and 23 percent, respectively over 2,6 dimethyl 4-heptanol alone. This improvement will require further evaluation to determine the effects of SX-18 addition on distillation.

Table 10. Distribution Coefficients and Separation Factors of Mixtures of 2,6 dimethyl 4-heptanol, and SX-18 in Extracting 2 Percent Ethanol

SX-18, Vol. %	K_{ETOH}	$K_{\text{H}_2\text{O}}$	Separation Factors	% ETOH, Solvent Free Basis
0	0.288	0.009	32.8	33.5
20	0.224	0.006	37.3	36.7
40	0.173	0.004	43.3	41.1
60	0.139	0.003	46.3	39.7
80	0.059	0.003	19.8	27.3

Other Product Recovery Techniques

The potential product recovery methods for removing ethanol from aqueous solution are summarized in Table 11. Basically, these methods include distillation, extraction, gas stripping, and alcohol selective pervaporation to concentrate the ethanol at low concentration. Depending upon the initial process and the resulting ethanol concentration, some of these processes such as distillation and hot gas stripping can yield an ethanol product of sufficiently high concentration to allow recovery by azeotropic product separation. Alcohol selective pervaporation requires further distillation to bring the

ethanol concentration closer to the azeotropic concentration. If extraction is the initial operation, the solvent must either be removed by solvent distillation or the water removed by adsorption or pervaporation. In the first case, pure ethanol can be obtained after solvent distillation. The last step for each of the other processes requires azeotropic concentration to a high purity product by extractive distillation, adsorption, or pervaporation. The conventional method is using distillation to concentrate alcohol, followed by extractive distillation to overcome the problem with the azeotrope.

Table 11. Summary of Ethanol Recovery Processes

First Operation	Second Operation	Third Operation
Distillation	Extractive Distillation	
Distillation	Pervaporation, or Adsorption	
Extraction	Solvent Distillation	Extractive Distillation
Extraction	Extractive Distillation*	
Extraction	Solvent Distillation	Pervaporation
Extraction	Pervaporation (Remove H ₂ O)	Solvent Distillation
Extraction	Adsorption (Remove H ₂ O)	Solvent Distillation
Hot Gas Stripping to Azeotropic Conc.	Extractive Distillation, or pervaporation, or adsorption	
Pervaporation (Alcohol Selective Membrane)	Distillation	Pervaporation, or adsorption, or extractive distillation

* Extraction solvent may also function as solvent in extractive distillation; needs confirmation.

The potential of utilizing pervaporation has been studied in detail. There are two possible methods for utilizing pervaporization technology. The first method is direct recovery of alcohol from the dilute alcohol stream; the other method is to remove water from the alcohol extracted solvent. This second method has the advantage of avoiding azeotropic distillation which may require an energy consumption as high as 7,000 Btu/gallon alcohol.

The potential of direct recovery of alcohol from dilute solution by pervaporation was based on the case of Shabtai, *et al.* The article states that a pervaporation unit of 800 cm² was operated at 45°C under 30 MB or 22.5 mm Hg vacuum. The ethanol vs water selectivity was as high as 7 when the circulation rate through the pervaporation unit was 9 L/min. The average product flux was 150 mL/hr with the ethanol concentration between 17 to 20 weight percent when the feed contained 4 percent alcohol.

Based on the assumption that all of the above information still holds when the ethanol feed concentration is reduced from 4 to 2 percent, the through-membrane flux for one kg of ethanol product was 5.8058 kg of 17.63 percent alcohol solution. Assuming that air leakage from the pervaporation unit was 10 percent of the flux, a steam jet is needed to provide a vacuum of 22.5 mm Hg for the flow of 7.4 kg dry air equivalent at 70°C. The energy consumption in the steam jet was 44.5 kg of 100 psig motive steam. Since the enthalpies of 0 and 100 psig steam are 1167.4 and 1,190.1 Btu/lb,

respectively, the energy used in the steam jet is 2,220 Btu/kg of ethanol. By assuming the heat vaporization is not affected by pressure and temperature, the vaporization energy needed in the pervaporation unit is 10,471 Btu/kg ethanol if an ideal solution is applied. Based upon a circulation rate of 9 L/min, this heat of vaporization will reduce the temperature in the circulation stream by only 0.24°F. Thus, no additional energy is required in the system. However, there is circulation pump energy and energy for heating of the feed stream. The circulation energy is 1,730 Btu/kg ethanol with a friction loss of 7.35 psi, and the heating energy is 12,579 Btu/kg ethanol. Thus, the total energy used in the pervaporation system is 16,530 Btu/kg ethanol. The distillation energy for concentrating 17 percent alcohol to 95 percent requires 2,886 Btu/kg using 1.1 times the minimum reflux ratio. Thus, the total energy required to produce 1 gal of 95 percent ethanol will be 58,000 Btu. This number is more than double the value obtained when utilizing 3 ethyl 3-heptanol for extraction (21,600 Btu/gal). Thus, the use of pervaporation in directly recovering dilute alcohol is not a suitable method. The potential of using pervaporation for solvent dehydration will be evaluated based on literature information.

Another solvent dehydration method, adsorption, was also investigated. In the initial screening for adsorbents, 3 g of NaCl, silica gel, and alumina were used to treat 10 mL of extract solvent, 2,6 dimethyl 4-heptanol. The extracted solvent contained about 0.5 percent of alcohol and water. NaCl removed 5 percent of the extracted water and none of the alcohol. Silica gel removed 35 percent of water, but also removed 40 percent of the alcohol. Alumina removed 30 percent of the water and only 10 percent of the alcohol and was thus selected for further study.

The adsorption ability of alumina for water and alcohol was studied in a 1 inch diameter column. Alumina (10g) was packed inside the column to a bed height of approximately 1 inch. 2,6 Dimethyl 4-heptanol (40 mL) that had previously been used for extraction (containing 0.5 percent water and alcohol) was passed through the column. Both water and alcohol were completely removed in the initial few drops of the solvent collected. However, the last few drops of the solvent collected contained 84 percent alcohol and no water. These results indicate that alumina has a stronger adsorption ability for water than alcohol, and has the potential to dehydrate the extracted solvent.

In order to evaluate adsorption's economic potential and provide the basis for scale-up, a study of the breakthrough curve must be undertaken. The breakthrough curve study will be conducted in a small diameter fixed-height bed using the same particle size and superficial liquid velocity as in a large scale unit. The concentration of adsorbate in the liquid out of the column will be continuously measured. The breakthrough point occurs when the relative adsorbate concentration reaches 0.05 or 0.1. In this special case, a short breakthrough point for ethanol and long breakthrough point for water is desired.

A summary of the energy requirements for various ethanol recovery processes based on current information is shown in Table 12. Direct distillation or ethanol distillation after solvent extraction appear to be the best options to concentrate ethanol from 2 weight percent to azeotropic levels. The pervaporation process is unable to compete with traditional distillation methods because of high energy requirements. Solvent extraction followed by distillation will require about 5.5 percent more energy than direct distillation alone, however, the solvent system has the advantage of reusing unreacted nutrients while direct distillation may thermally degrade a portion of the unused nutrients. To produce pure ethanol from ethanol at a near azeotropic composition, pervaporation has the advantage of requiring only 70 percent of the azeotropic distillation energy. Thus, the best process for ethanol recovery appears to be either direct distillation or solvent extraction distillation to concentrate ethanol near the azeotrope, followed by pervaporation dehydration to produce pure ethanol.

Table 12. Summary of Energy Requirements for Ethanol Recovery

Process	Concentrated to near Azeotropic Composition	Dehydrated to Pure Ethanol
Pervaporation	>123,700 Btu/gallon	
Direct Distillation	29,600 Btu/gallon	
Solvent Ext. & Dist.	31,200 Btu/gallon	
Azeotropic Dist.		7,000 Btu/hr
Dehydrate Pervaporation		4,800 Btu/hr

Significance

Several techniques have been evaluated for recovering ethanol from the fermentation broth. Of these techniques, solvent extraction with 2,6 dimethyl 4-heptanol followed by distillation or direct distillation appear to be the best methods for concentrating 2 percent ethanol to near the azeotrope. Azeotropic distillation or pervaporation may then be used to produce neat ethanol.

TASK 4. ECONOMIC UPDATE AND COMMERCIALIZATION PLAN

Task 4.1 Economic Projections

This technology converts waste gases from refinery processes into a liquid fuel resulting in waste reduction and energy savings. It is projected that by the year 2010, 65 percent of the refining capacity will utilize this process for treatment of waste gas streams. The production of ethanol from all 194 U.S. refineries would save 450 billion BTU annually, would reduce crude oil imports by 110 million barrels per year and would reduce emissions by 19 million tons per year. By the year 2010, this technology could create 12,000 permanent new jobs and make the nation more competitive by saving \$2.8 billion annually in manufacturing costs. In addition, the construction of 78 new plants over the next 15 years would create employment to support capital expenditures of \$160 million per year.

Task 4.2 Commercialization Plan

A strategy for commercialization of this technology has been developed. This strategy involves the selection of an oil refiner and an engineering company as partners in the commercial development. The purpose of the refinery partner is to provide guidance during the laboratory and pilot phases on the availability and concentration of various refinery gas streams and to provide direction for the commercial design requirements for an ethanol production facility in a refinery environment. The refiner will also establish market requirements and projections for the ethanol product. The engineering contractor will provide guidance for the design and operation of the pilot facility and for the design and construction of commercial facilities. Economic projections will be made to define high cost areas that require more intensive research efforts.

Initially, quarterly meetings will be held with the industrial partners to review the laboratory data and economic projections to direct the development efforts. During the pilot design and operation periods, more frequent meetings will be held. The refinery partner will provide a cost share for equipment in the pilot plant and will also build the first commercial plant at one of their refinery locations. In exchange for these contributions, the refiner will receive an interest in the technology. The engineering contractor will also provide a cost share of \$300-500 K for engineering time to design the pilot unit, prepare economic projections and attend review meetings. The engineering company will receive the rights to design and construct all commercial facilities in exchange for their cost share.

The Phase III, Engineering Development, (laboratory and bench-scale) will develop design data for the Phase IV, Demonstration, prototype unit, which will in turn provide the data for scale-up of the first commercial facility to be built at one of the industrial partners refineries. The size of this facility will be defined later and will depend upon the quantity and composition of waste gases available at the chosen refinery, the scale-up required, and the product market. Once this project demonstration plant is operating, the technology will be licensed to refineries worldwide. There are 194 U.S. refineries. Ethanol prices are rising and the demand of oxygenated fuels is increasing. With the very favorable economic projections that show production costs much lower than from grain alcohol, the technology should be readily adapted by all refiners.

TASK 5. PROJECT MANAGEMENT AND REPORTING

Task 5.1 Project Management

The BRI management team for this project is as follows:

BRI Employee

J.L. Gaddy, President (PhD - ChE)
 E.C. Clausen, VP Research (PhD - ChE)
 C. Wikstrom, Director Engr. Res. (PhD - ChE)
 C.W. Ko, Director Tech. (PhD - ChE)
 G. Sperl, Director Microbiology (PhD - Micro)
 G. Chen, Manager Microbiology (PhD - Micro)
 R. Basu, Lab Manager (PhD - ChE)
 J. Lu, Research Assoc. (PhD - Chem)
 R. Phillips, Research Assoc. (MS - ChE)
 S. Adams, VP Operations (MS - IE)
 W. Haley, Adm. Director (MS - Phys)
 M. Williams, VP Finance (CPA)

Function

Project Manager
 Principal Investigator
 Project Director
 Technology Assistance
 Microbiology Direction
 Microbiology Research
 Laboratory Management
 Laboratory Research
 Laboratory Research
 Business Official
 Contract Administration
 Cost Accounting

Weekly technical meetings have been held to review the laboratory data, to plan further experiments and to redirect resources where necessary. Technical progress has been quite good and all milestones were achieved either on schedule or earlier. Periodic budget meetings were also held to insure that expenditures were within budget. The Phase II program was completed in schedule and below the projected budget requirements.

The technical status was reviewed frequently with DOE representatives to report on progress and receive overall program direction. A project initiation meeting was held with DOE representatives to establish objectives and procedures. The DOE-OIT Project Description was prepared and published.

Task 5.2 Technology Transfer

General presentations describing this process have been made at the Annual OIT DOE Review Meeting and elsewhere. Process patents have been filed covering this technology. Extensive presentation and publication of the detailed results of this study have been delayed until patents are issued and until industrial partners are selected.

Task 5.3 Reports

A detailed Management Plan was prepared during the first month of this project. Monthly technical reports describing the technical progress have been submitted as specified. Also, monthly cost and management reports have been prepared and submitted showing the milestone progress and cost management.

CONCLUSIONS

The Phase II research effort has yielded at least three cultures (*Clostridium ljungdahlii*, Isolate O-52 and Isolate C-01) which are able to produce commercially viable concentrations of ethanol from CO, CO₂ and H₂ in petroleum waste gas. Results from single continuous stirred tank reactor (CSTR) studies have shown that 15-20 g/L of ethanol can be produced, with less than 5 g/L acetic acid as a by-product. It is believed that the culture and reactor optimization studies of Phase III will yield even higher ethanol concentrations and hopefully minimal concentrations of acetic acid. Product recovery studies have shown that ethanol is best recovered in a multi-step process involving

- solvent extraction, followed by distillation to the azeotrope, followed by azeotropic distillation or pervaporation, or
- direct distillation to the azeotrope, followed by azeotropic distillation or pervaporation

Of these options, direct distillation followed by pervaporation appears to be less energy intensive. The updated economic projections are quite attractive. When processing 50 million SCFD of petroleum waste gas to ethanol and acetic acid in a plant operating at 6 atm, the plant generates a return on investment of 72.1 percent and a payout of 1.4 years.

REFERENCES

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Thrash, L., "Annual Refining Survey," Oil Gas J., (Mar 18, 1991).

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_____, "Oxygenated Fuel Demand to Increase Markedly," Hyd. Proc., (Dec, 1992b).

APPENDIX A

INDUSTRIAL WASTE PROGRAM REPORT

United States Department of Energy
Energy Efficiency and Renewable Energy
Office of Industrial Technologies
Office of Waste Reduction Technologies
Waste Material Management Division
Washington, DC 20585

IWP PROJECT DESCRIPTION FORMAT

SECTION 1: GENERAL

1.1 PRODUCTION OF ETHANOL FROM REFINERY WASTE GASES (Bioengineering Resources, Inc.) (AL)

1.2 Problem/Need:

Refineries discharge large volumes of H_2 , CO and CO_2 from cracking, coking and hydrotreating operations. A typical refinery of 200,000 BPD discharges 324,000 tons of waste H_2 and CO per year. This research program will develop a biological process for the conversion of these waste gases into ethanol, which can be blended with gasoline to reduce emissions. Currently, the U.S. produces 1.2 billion gallons of ethanol annually from grain and sharp growth of oxygenated fuels is expected. A typical 200,000 BPD refinery could produce 58 million gallons of ethanol per year from the waste gases. The technology does not require purification of the gases and no modifications to existing processes are required. The biological process is very efficient and retention times of a few minutes have been obtained for virtually complete conversion of H_2 and CO. Preliminary economics show that ethanol can be produced for \$.30 per gallon and would yield an annual rate of return in excess of 90 percent at current prices.

Currently, ethanol is produced by batch fermentation of grain, primarily corn, requiring large fermenters and high capital costs. Raw material costs are about \$.90 per gallon, with corn priced at \$2.20 per bushel; consequently, grain alcohol requires a tax credit to be economical. Substantial increases in the grain alcohol production to meet future oxygenated fuel requirements is expected to significantly raise corn prices. Production of ethanol from waste refinery gases will significantly reduce ethanol costs, allow expansion of these markets, reduce air pollution, create new jobs, reduce fuel imports and improve the nation's competitiveness. Production of ethanol from all 194 U.S. refineries would save 450 billion Btu annually, reduce crude oil imports by 110 million barrels per year and reduce emissions by 19 billion tons per year.

1.3 Goal:

The purpose of this three year program is to develop an optimal process for converting refinery waste gases into fuel-grade ethanol for blending with refinery fuel streams.

1.4 Research (Technology Description):

BRI has independently developed cultures for ethanol production from CO and H_2 and has demonstrated the feasibility of converting refinery waste gases into ethanol. The purpose of this three year-three phase program is to develop a commercial process for producing ethanol from refinery waste gases. The exploratory development (Phase I) of this project has already been completed. Phase II (Technology Development - 6 months) will conduct experiments to screen and optimize cultures for ethanol production and define reaction kinetics and retention times in stirred-tank reactors. Optimal parameters for ethanol extraction/distillation will be determined. A preliminary process design and economic analysis will be prepared for a commercial scale unit to define economic potential and determine high cost areas for further research.

Phase III (Engineering Development - 12 months) will develop data for scale-up and commercialization of this process. An integrated bench scale unit will be constructed and operated for an extended period to demonstrate the viability of the cultures and the unit operations in the process. This unit will couple continuous operation of the reactor with product recovery and recycle of the aqueous and solvent streams. Methods to enhance mass transfer and reduce reactor volume, such as high pressure operation and non-aqueous fermentation, will be examined. Intrinsic reaction kinetics and mass transfer coefficients will be determined for reactor scale-up. The design and economic projections for a commercial scale facility will be modified to reflect the data from Phase III. Phase III (Demonstration - 18 months) will involve the design, construction and operation of a pilot demonstration facility with refinery waste gases. A prolonged period of continuous operation (9 months) of this facility will provide data for scale-up of a commercial unit. Successful completion of this three year development program will provide an optimal design that should be readily commercialized.

1.5 Standard Industrial Classification (SIC) Codes:

petroleum refineries	2911
methanol production	2869
ammonia production	2869
coke ovens	2999

1.6 Need for Government Funds:

The biological conversion of waste gases into ethanol is a new and novel process that has not previously been demonstrated. Oil refineries have no experience with this type of process and most of their available research and development funds are used to solve environmental problems and maintain production schedules. Consequently, securing funding from industry alone for laboratory and prototype demonstration experiments would be impossible. Government funding is essential for the continuation of this project.

1.7 Points of Contact:

Dr. James L. Gaddy, Project Manager
Bioengineering Resources, Inc.
1650 Emmaus Road
Fayetteville, AR 72701
(501) 521-2745
(501) 521-2749

Mr. W. Porter Grace, Program Manager
Energy and Technologies Division
Albuquerque Operations Office
U.S. Department of Energy
P.O. Box 5400
Albuquerque, NM 87185-5400
(505) 845-5210
(505) 845-5960

1.9 Major Publications/Papers:

Publication and presentation of the results of this project will be delayed until patents are in place.

1.10 References:

None to date.

1.9 Date of Last Revision:

November, 1994.

SECTION 2: ENERGY AND WASTE BENEFITS

2.1 Current vs. Proposed Technology Calculation:

Current technology for producing fuel ethanol involves an initial hydrolysis of grain to produce sugars that are fermented in batch reactors to produce a dilute ethanol mixture in water which is purified by distillation. The yield of ethanol is about 2.5 gallons per bushel of corn. Fermentation times of 36 hours are required and capital requirements are high. Energy consumption includes production of grain, grinding and hydrolysis, and distillation.

The proposed process would contact waste CO and H₂ with a culture of anaerobic bacteria to produce ethanol which would be purified by, distillation and pervaporation. The ethanol yield is 1.15 gallons per mol of CO or H₂ converted in the waste gas stream. Fermentation times of minutes have been achieved and nominal capital and operating costs result.

2.2 Market Penetration:

The production of ethanol from the CO, H₂ and CO₂ emitted from a typical crude oil refinery will reduce emissions and save energy by reducing feedstock and processing energy requirements for liquid fuel production. The energy savings and waste reduction data compiled for the application of this technology are based upon a current U.S. refining capacity of 15.5 million BPD, with a nominal growth rate of three percent per year until 2010. The following table presents a summary of these compilations. A typical unit size is chosen as 200,000 BPD. The data assumes average capacities for cracking, coking, hydrotreating etc.

MARKET PENETRATION	
Estimated Quantity	Estimate
Total units in 1994 market	78
Annual growth of market between now and 2010.	3%
Total units in 2010 market	121
Market penetration in 2010 (%)	65%
Number of units in 2010 based on the above	78

2.3 Energy and Waste Calculations:

Energy Savings

Based upon a 50 million gallon per year ethanol facility, the total energy consumption by the current technology is 7.82×10^{12} Btu/yr. Seventy five percent of this energy is in the feedstock, which is not required in the processing of the refinery waste gases. The energy for ethanol purification is about the same for both processes. Therefore, a net saving of 5.76×10^{12} Btu/yr results from each plant. In 2010, with 65 percent of the market, the total energy saving is 0.45 Quad. This energy savings is equivalent to 300,000 barrels of oil per day.

ENERGY SAVINGS					
A	B	C	D = B - C	E	F = D x E
Description	Current Technology (10^{12} Btus/year/unit)	Proposed Technology (10^{12} Btus/year/unit)	Energy savings per unit, current less proposed (10^{12} Btus/year)	Number of proposed units operating in 2010	Energy Savings in Year 2010 (10^{12} Btus/yr)
Oil	5.8	0	5.8	78	452
Gas	2.0	2.0	0	78	0
Coal					
Electricity (@10,500 Btus/kWh)	0.02	0.04	-0.04	78	-2
Renewable (solar, wind, biomass)					
Other (explain)					
Total:	7.82	2.04	5.76	78	450

Waste Reduction

Hydrogen is a highly flammable gas. CO is flammable and also toxic in very low concentrations. Both are reducing gases that react readily in the atmosphere and place an additional pollution burden on the environment. In addition, CO₂ is accumulating in the environment and poses risks for global warming. A typical oil refinery discharges 324,000 tons per year of these gases. With 75 percent conversion of this gas into ethanol, a net savings of 243,000 tons per year per plant results from conversion of these gases into ethanol. In 2010, the total waste reduction is 19 million tons per year.

WASTE REDUCTION					
A	B	C	D = B - C	E	F = D x E
Description	Current Technology (Tons/year/unit)	Proposed Technology (Tons/year/unit)	Waste Reduction per unit, current less proposed (10 ⁶ tons/year)	Number of units operating in 2010 (See Table 1)	Waste Reduction in Year 2010 (10 ⁶ tons/year)
H ₂ , CO and CO ₂	324,000	81,000	0.243	78	19.0
Total:	324,000	81,000	0.243	78	19.0

SECTION 3: BUSINESS

3.1 Economic Attractiveness:

ECONOMIC PROJECTIONS/US COMPETITIVENESS

The capital and operating costs have been projected for a plant to process the waste gases from a 200,000 TPD refinery to produce 58 million gallons of ethanol. These costs are compared to a conventional ethanol from grain plant of the same size. The capital costs for the new technology total \$31 million and include equipment and installation for the bioreactor and ethanol purification, with a 25 percent contingency. The operating costs include utilities, chemicals, labor, maintenance, depreciation, and taxes and insurance, which total \$17.1 million annually or \$0.30 per gallon. At the current price of \$1.20 per gallon ethanol, the revenue would be \$69.6 million annually. After income taxes of 40 percent, a cash flow of \$34.4 million is generated, which gives an annual return of about 110 percent. Clearly, this technology offers substantial economic incentive for commercialization.

With these very favorable economics, this technology should be rapidly applied to all refineries. By 2010, this technology would create 12,000 new jobs and make the nation more competitive by saving \$2.8 billion annually in manufacturing cost. Furthermore, the balance of payments is improved by \$2.2 billion per year through reduction in crude oil imports of 110 million barrels annually. The development of this technology is a wise investment choice for the nation.

END-USER ECONOMIC ATTRACTIVENESS		
Item	Current Technology or Practice	Proposed Technology or Practice
1. Plant, Line or Process	58 X 10 ⁶ GPY ETOH	200,000 BPD Refinery
2. Acquisition Investment	*****	*****
- Capital Cost of Equipment Purchase	\$29 million	\$10.3 million
- Installation Cost	\$58 million	\$20.7 million
Total Acquisition Investment	\$87 million	\$31.0 million
3. Useful Life of Equipment (Years for Depreciation)	10	10
4. Residual value of Equipment	0	0
5. Unit of Output	gallons	gallons
6. Total Annual Output	58 million	58 million
7. Annualized costs:	*****	*****
- Maintenance	\$3.5 million	\$1.2 million
- Energy	\$5.8 million	\$5.8 million
- Labor/Overhead	\$2.0 million	\$2.0 million
- Depreciation	\$8.7 million	\$3.1 million
- Other (Raw Materials - Net)	\$34 million	\$5.0 million
Total Annualized Costs:	\$54 million	\$17.1 million
8. Annualized Cost per Unit of Output	\$0.93	\$0.30
9. Current - Proposed Annualized Cost Per Unit of Output	N/A	\$0.30
10. Selling Price of Unit	\$1.20	\$1.20
11. Payback	4.8 yrs	11 mos.
12. Internal Rate of Return	16.3 percent	90 percent
13. Return on Investment	21 percent	111 percent
14. Interest Rate Applied	10 percent	10 percent
15. Base (Current) Year of Dollars Used	1994	1994

DEVELOPER ECONOMIC ATTRACTIVENESS	
Item	Proposed Technology or Practice
1. Plant, Line, or Process	58 million gallons/yr
2. Investment	
- Research	\$893,000
- Development	\$3,452,000
- Production Line	\$31 million
Total Investment	\$34.5 million
3. Useful Life of Plant, Line, or Process with Proposed Technology (Years for Depreciation)	10 yrs
4. Unit of Output	gallons
5. Total Annual Output	58 million
6. Cost per Unit	
- Research and Development	\$0.001
- Production Line Investment	\$0.006
- Manufacturing	\$0.30
Total cost per unit	\$0.307
7. Selling Price of Unit	\$1.20
8. Payback	1 yr
9. Internal Rate of Return	85 percent
10. Return on Investment	100 percent
11. Interest Rate Applied	10 percent
12. Base (Current) Year of Dollars used	1994

3.2 Industrial Participation:

INDUSTRIAL PARTICIPATION			
Partner	Cost Sharing, FAR*	Cost Sharing, Non-FAR	Total
BRI		\$68,000	\$68,000
Refiner	\$2,303,000		\$2,303,000
Engineering Contractor	\$300,000		\$300,000
Total	\$2,603,000	\$68,000	\$2,671,000

3.3 Industrial Competitiveness:

The competing technology for fuel ethanol production today is by fermentation of grain, primarily corn. The raw material (corn) cost for this technology is about \$.90 per gallon; whereas the use of waste gases involves no cost of raw materials. The total cost of ethanol produced from refinery waste gases is about one-third of the raw material cost from corn. The return on investment for the new process is over five times that for grain based ethanol. Furthermore, the Clean Air Act will impose increasing regulations on the future discharge of waste CO, H₂ and CO₂.

Ethanol, produced from renewable resources, has a tax credit of \$0.054 per gallon of gasoline, or \$.54 per gallon of ethanol. This tax credit would probably apply to ethanol from refinery wastes. However, without the subsidy, this process would still earn an IRR of over 50 percent. Therefore, ethanol produced from waste gases will have a substantial economic advantage over current technology, as well as environmental incentives from waste reduction.

3.4 Employment Impacts:

With these very favorable economics, this technology should be rapidly applied to all refineries. By 2010, this technology would create 12,000 permanent new jobs and make the nation more competitive by saving \$2.8 billion annually in manufacturing cost. In addition, construction of 78 new plants would create employment to support capital expenditures of \$160 million per year until 2010.

3.5 Commercialization Plans:

Companies that process 200,000 BPD or more represent 75 percent of the U.S. capacity. However, the technology for waste gas conversion applies to all refineries that have facilities for cracking, hydrotreating, coking, etc. Virtually all refineries, regardless of size, carry out one or more of these operations that generate waste gases. The process is expected to be economically attractive even for small gas streams that would produce less than 2 million gallons of ethanol per year that could then be blended with refinery products. In addition, this technology for ethanol production can be applied to other processes with waste CO and H₂ streams, such as methanol, ammonia and coke ovens, of which there are a total of about 250 in the U.S. The process reduces emissions and waste, without modification of existing operations and should be readily adapted by industry. It should be noted that this project represents new technology, not previously available to industry for implementation.

It is planned that the technology for producing ethanol from refinery waste gases will be jointly owned by Bioengineering Resources and a refining partner. Following Phase IV, commercial plants will be built at the refining partners locations and the technology would be licensed to other refineries and petrochemical plants in the U.S. and around the world. It is expected that two plants will be built in 1998 and that the potential is for 350 plants (refineries and others) to be built by 2010. These facilities would create 50,000 new jobs (direct and indirect).

3.6 Foreign Trade:

The widespread application of this technology will increase U.S. competitiveness by reducing fuel and operating costs. Net savings in fuel costs would total \$2.8 billion per year by 2010. In addition, crude oil imports would be reduced by 110 million and the balance of payments would be improved by \$2.2 billion annually. Foreign refineries also have the same waste gas streams that can be used to produce ethanol. Liquid fuel is in short supply in most countries around the world. Therefore, the commercialization strategy includes license of the technology to foreign refineries, which would generate royalty and engineering fees to further enhance the U.S. economy.

SECTION 4: PROJECT MANAGEMENT

4.1 Research Plan:

The purpose of this three year-three phase program is to develop a commercial process for producing ethanol from refinery waste gases. The exploratory development (Phase I) of this project has already been completed. Phase II (Technology Development - 6 months) will conduct experiments to screen and optimize cultures for ethanol production and define reaction kinetics and retention times in stirred-tank reactors. Optimal parameters for ethanol extraction/distillation will be determined. A preliminary process design and economic analysis will be prepared for a commercial scale unit to define economic potential and determine high cost areas for further research.

Phase III (Engineering Development - 12 months) will develop data for scale-up and commercialization of this process. An integrated bench scale unit will be constructed and operated for an extended period to demonstrate the viability of the cultures and the unit operations in the process. This unit will couple continuous operation of the reactor with product recovery and recycle of the aqueous and solvent streams. Methods to enhance mass transfer and reduce reactor volume, such as high pressure operation and non-aqueous fermentation, will be examined. Intrinsic reaction kinetics and mass transfer coefficients will be determined for reactor scale-up. The design and economic projections for a commercial scale facility will be modified to reflect the data from Phase III. Phase III (Demonstration - 18 months) will involve the design, construction and operation of a pilot demonstration facility with refinery waste gases. A prolonged period of continuous operation (9 months) of this facility will provide data for scale-up of a commercial unit. Successful completion of this three year development program will provide an optimal design that should be readily commercialized.

4.2 Milestones

SCHEDULE OF PERFORMANCE

MILESTONES				
Milestone (Number)	OIT No.	Planned	Actual	Date of Estimate
Phase II				
Select optimal bacterial strain and define fermentation parameters		7/94	7/94	
Determine ethanol recovery system		7/94	7/94	
Phase III				
Optimize fermentation parameters		7/95		8/94
Optimize fermentation and product recovery system		7/95		
Phase IV				
Design and build pilot plant		1/96		
Operate pilot plant		1/97		
Project Completed		1/97		

4.3 Accomplishments:

FY94 - This project was initiated in mid-1994 and Phase II is nearing completion. Following are preliminary achievements:

1. A new bacterial isolate has been identified that has faster rates and yields than previous cultures.
2. Retention times in continuous culture of 30 minutes have been achieved for near complete conversion of CO and H₂.
3. Ethanol to acetic acid ratios have been increased to 8:1.
4. Solvents for ethanol and acetic acid recovery have been screened. Excellent solvents for acetic acid have been identified. A combination of distillation and pervaporization has been identified as the best system for ethanol purification.
5. Economic projections for this process indicate that ethanol can be produced for \$0.30 per gallon.

4.4 Budget:

BUDGET								
ROW		PROJECT NAME >						
	OIT #	FY	93	94	95	96	97	98
A		DOE		287.4	585.1	801.5		
B		CAPITAL EQUIPMENT						
C = A + B + PREV YRS		CUMULATIVE DOE			872.5	1,674.0		
D		INDUSTRY		225.0	1,590.0	858.4		
E = D + PREV YRS		CUMULATIVE INDUSTRY			1,815.0	2,673.4		
F = A + B + D		PROJECT		512.4	2,175.1	1,659.9		
G = C + E		CUMULATIVE PROJECT			2,687.5	4,347.4		
		DATE OF ESTIMATE		8/94				

(\$ in thousands)

4.5 Policy/Regulatory:

Current regulations permit existing refineries to discharge waste H_2 , CO and CO_2 , often without flaring. The Clean Air Act imposes strict regulations on new facilities and future regulations on existing refineries will be much more stringent. The application of this technology will enable refiners to meet regulations and generate an excellent return from these installations.

4.6 Impacts on the U.S.:

With these very favorable economics, this technology should be rapidly applied to all refineries. By 2010, application of this technology will enhance the nation's competitiveness by reducing fuel costs by \$2.8 billion annually and by creating a total of 12,000 new permanent jobs. Air emissions would be reduced by 19 million tons per year and the nation would save 0.45 Quads annually. The balance of payments would be improved by \$2.2 billion annually, not including engineering and royalty fees from worldwide license of this technology.