

**PRODUCTION OF ETHANOL FROM REFINERY WASTE GASES
Phase III. Engineering Development**

Annual Report
April 1, 1995 - May 15, 1996

by

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PREFACE

This report documents the technical progress made on Phase III, Engineering Development, of the DOE funded project "Production of Ethanol from Refinery Waste Gases" for the time period covering April 1, 1995 through May 15, 1996. Merrill Smith is the Program Manager for the DOE Office of Industrial Technologies. Porter Grace is the Technical Manager for the DOE Albuquerque Operations Office. Frank Childs, the Project Technical Monitor, is on the staff of Scientech, Inc. (Idaho Falls, Idaho). 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. D. Arora, Dr. R. Basu, Mr. J. R. Phillips and Dr. C. V. Wikstrom.

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This is the second annual progress report for the project. This report and the previous report (DOE/AL/98770-1) can be obtained as indicated by the notice inside the front cover.

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PRODUCTION OF ETHANOL FROM REFINERY WASTE GASES

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EXECUTIVE SUMMARY

Refineries discharge large volumes of H_2 , CO and CO_2 from cracking, coking and hydrotreating operations. This research and development program is seeking to develop, demonstrate, and commercialize 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 grow rapidly over the next decade. 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 research program is being conducted in three phases: Phase II - Technology Development; Phase III - Engineering Development; and Phase IV - Demonstration. Phase I, Exploratory Development, had been successfully completed in the BRI laboratories prior to project initiation. The research effort has yielded two strains (Isolate O-52 and Isolate C-01) which are to be used in the pilot studies to produce ethanol from CO, CO_2 and H_2 in petroleum waste gas. Results from single continuous stirred tank reactor (CSTR) laboratory tests have shown that 20-25 g/L of ethanol can be produced, with less than 5 g/L acetic acid as a by-product. Laboratory studies performed with two CSTRs in series have yielded ethanol concentrations of 30-35 g/L with 2-4 g/L acetic as the by-product. Water recycle from distillation back to the fermenter shows that filtration of the water before distillation is sufficient to eliminate the recycle of toxic materials back to the fermenter.

Product recovery in the process will use direct distillation to the azeotrope, followed by adsorption to produce neat ethanol. This technology is less energy intensive than other alternatives such as solvent extraction, azeotropic distillation or pervaporation. The updated economic projections are quite attractive. The economics are refinery stream dependent, and thus vary depending upon refinery location and operation.

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) (2×10^9 L/d) (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 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 (3×10^7 L/d) 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 (3×10^7 L/d))

Gas Stream	Present Use	Quantity lbmole/h (gmole/h)	Composition, mole %				
			H_2	CO_2	CO	H-C	H_2S
Cat Cracker off gas	fuel gas	3826 (1.7×10^6)	19.4	-	-	80.0	0.6
Delayed Coker off gas	fuel gas	2024 (9.2×10^5)	10.7	0.2	-	83.2	5.9
Hydrotreater and cat reformer	fuel gas	5120 (2.3×10^6)	93.8	-	-	5.5	0.7
Catalyst regenerator dry, N_2 free	vent	5120 (2.3×10^6)	-	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 cell separator that retains the cells in the bioreactor to maximize the reaction rate. The aqueous permeate is sent to distillation to produce 95 percent ethanol. Finally adsorption is used to dry the ethanol to anhydrous ethanol. The use of distillation/adsorption is preferred over solvent extraction/distillation/azeotropic distillation for ethanol recovery.

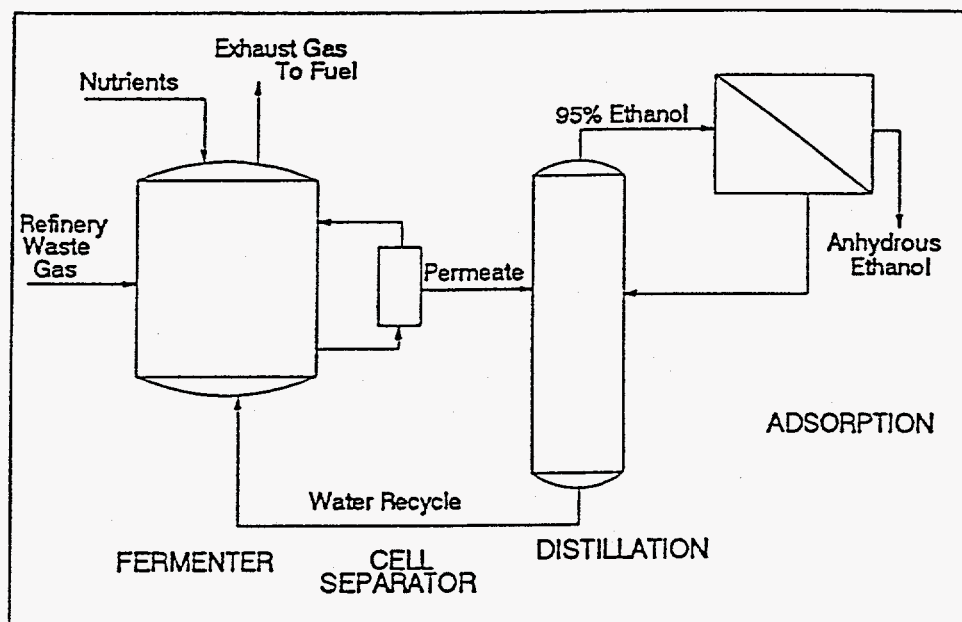


Figure 1. Biological Process for Ethanol Production from Refinery Waste Gas

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 catalyst is not poisoned by the gas components and does not have to be regenerated. Biological processes are compatible with the environment and no toxic or hazardous wastes are generated. The primary disadvantage of biological processes is generally the slow reaction rates. However, retention times of minutes have been achieved for the biocatalytic reaction, which makes this process very attractive economically.

The U.S. currently produces about one billion gallons (3.8×10^9 L) 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 (3×10^7 L/d) 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 (1.1×10^{10} L) 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 four year, three phase program is to develop a commercial process for producing ethanol from refinery waste gases. The exploratory development (Phase I) of the project had already been completed at contract initiation. In Phase II (Technology Development), experiments were conducted to screen and optimize cultures for ethanol production from refinery waste gases and to define reaction kinetics and retention times in stirred-tank reactors. Optimal parameters for ethanol extraction/ distillation were determined. 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 were developed for scale-up and commercialization of this process. An integrated bench scale unit was constructed and operated for an extended period to demonstrate the viability of the cultures and the unit operations in the process. This unit coupled continuous operation of the reactor with product recovery and recycle. Distillation was selected over solvent extraction for product recovery. Methods to enhance gas-liquid mass transfer and reduce reactor volume, such as high pressure operation and non-aqueous fermentation, were examined. Intrinsic reaction kinetics and mass transfer coefficients were determined for reactor scale-up. The design and economic projections for a commercial scale facility were modified as needed to reflect the data from Phase III. Phase IV (Demonstration) is to include the design, construction and operation of a pilot demonstration facility with refinery waste gases. Laboratory work in support of the design will also be performed. A prolonged period of continuous operation of this facility will provide data for scale-up of 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 III and Phase IV development programs performed during Year 2 of the program. These results include information from bioreactor studies, product recovery studies, advanced bioreactor studies, modeling and scale-up work and an updated process evaluation. In addition, the process design and commercialization plan is updated to reflect the results from this work.

RESULTS AND DISCUSSION

TASK III.1. CULTURE DEVELOPMENT

Culture Comparison

Several cultures have been developed for the conversion of CO, CO₂ and H₂ to ethanol by Equations (1) and (2), including:

- *Clostridium ljungdahlii*, strain PETC
- BRI Isolate O-52
- BRI Isolate C-01
- *Clostridium ljungdahlii*, strain ERI2
- several minor strains

Based upon the results from the Phase II and Phase II development studies, BRI Isolates O-52 and C-01 were selected for use in advanced studies. These strains behave quite similarly, showing a high tolerance to both CO and ethanol. Both biological systems use CO, CO₂ and H₂, and produce similar concentrations of ethanol with low by-product acetic acid concentrations.

Table 2 shows a comparison of BRI strains O-52 and C-01 in their ability to produce ethanol from CO, CO₂ and H₂. As is noted, both strains ferment CO, CO₂ and H₂, with CO as the preferred substrate. Designation of CO as the preferred substrate means that higher cell yields are obtained on CO, and that higher CO conversions are obtained on gas mixtures containing both CO and H₂. When faced with a fermentation process upset, the H₂ conversion falls prior to a drop in CO conversion. The products of the fermentation of CO, CO₂ and H₂ are ethanol and acetic acid. Both strains give very similar product concentrations with nearly identical fermentation conditions of medium composition and concentration, pH, gas and liquid flow rates, agitation rates and gas composition.

The maximum tested CO concentration used successfully in producing ethanol was 65 percent by both strains. Similarly, the maximum H₂ concentration was 50 percent, and the maximum H₂/CO ratio was 1:1. BRI has not been successful in fermenting H₂/CO₂ alone (no CO present), in producing ethanol.

The maximum achievable ethanol concentration in a single CSTR was about 25 g/L for both strains, and typical concentrations in the CSTR are 23 g/L ethanol and 3.5 g/L acetic acid. Strain C-01 is a bit more tolerant of CO as a substrate, allowing slightly higher dissolved CO concentrations in the liquid phase. Typical specific gas uptake rates for Isolate O-52 are 21 mmol CO/gcell•hr and 15 mmol H₂/gcell•hr. The typical specific uptake rates for Isolate C-01 are 25 mmol CO/gcell•hr and 10 mmol H₂/gcell•hr. Typical yields of ethanol from the H₂, CO, CO₂ substrates are 90 percent of theoretical. The specific productivities are 0.21 g ethanol/gcell•hr for Isolate O-52, and 0.23 g ethanol/gcell•hr for Isolate C-01. The isolates are thus nearly interchangeable in their ability to use CO, CO₂ and H₂ to produce ethanol.

Table 2. Characteristics of Ethanol-Producing Strains

	Isolate O-52	Isolate C-01
1. Gas Phase Substrates	CO, CO ₂ , H ₂	CO, CO ₂ , H ₂
2. Preferred Substrate	CO	CO
3. Operating pH Range	4.5-5.5	4.5-5.5
4. Liquid Products of Gas Phase Fermentation	acetic acid, ethanol	acetic acid, ethanol
5. Maximum Tested CO Concentration in Gas Phase (vol %)	65	65
6. Maximum Tested H ₂ Concentration in Gas Phase (vol %)	50	50
7. Maximum H ₂ /CO Ratio Used Successfully to Date	1:1	1:1
8. Maximum Achievable Ethanol Concentration in CSTR, g/L	25	25
9. Typical Product Concentrations Achieved in CSTR a. Ethanol, g/L b. Acetic Acid, g/L	23 3.5	23 3.5
10. CO Tolerance	high	very high
11. Typical Specific Gas Uptake Rate in CSTR, mmol/gcell•hr a. CO b. H ₂	21 15	25 10
12. Yield of Ethanol from Substrates, % of Theoretical	90	90
13. Specific Productivity, g ethanol/gcell•hr	0.21	0.23

H₂S/COS Tolerance

The tolerance of the strains to H₂S and COS was shown in the first annual report. Both strains are capable of growing and producing ethanol in the presence of typical (1-2 percent) levels of H₂S and COS. Sulfur is incorporated into cell mass, accounting for about 1 percent of the weight of the cell. Na₂S, an aqueous phase form of H₂S, is also used to help ensure anaerobic conditions inside the reactor.

TASK III.2. BIOREACTOR STUDIES/TASK IV.1. PROTOTYPE DESIGN

Several reactor designs have been evaluated for pilot plant demonstration including the single CSTR, CSTRs in series and trickle bed reactors. These systems may be operated with or without cell recycle to increase the concentration of cells (biocatalyst) inside the reactor. Of these alternatives, the CSTR arrangements appear to be preferred over the trickle bed systems. The following paragraphs present experimental results from various CSTR systems.

In addition, several process alternatives are being studied in the laboratory in order to prepare an optimum design package. The concepts of medium optimization, CO_2/H_2 utilization and water recycle are also discussed below.

CSTR With Cell Recycle

Cell recycle may be used to increase the cell concentration inside the reactor and thereby increase reactor productivity. The cells are simply separated from the reactor effluent in a suitable system and returned to the reactor. Cell separation is also necessary to remove cells and cell parts prior to distillation in order to prevent inhibition of the culture upon water recycle.

Steady state results from studies performed in a CSTR with cell recycle using hollow fiber filtration with Isolate O-52 are shown in Table 3. As is noted in the table, gas retention times (GRT) of 5-10 min may be used in converting more than 80 percent of the CO and 50-60 percent of the H_2 fed. Resulting product concentrations of 18-23 g/L ethanol and 4-5 g/L acetic acid were obtained. Thus, ethanol can be the dominant product in converting CO , CO_2 and H_2 in waste gas.

Cell purge is a necessity in operating with cell recycle. Table 4 shows the effects of cell purge rate on CSTR performance. Without cell purge, a gas retention time of 16.6 min and a liquid retention time of 31 hr were possible, yielding an ethanol concentration of about 21 g/L. The volumetric ethanol productivity was 0.68 g ethanol/L•hr. With 27 percent cell purge, the gas retention time can be reduced to 7 min and the liquid retention time can be reduced to 17 hr, with comparable ethanol concentrations. Under these conditions, the volumetric ethanol productivity increases to 1.3 g/L•hr. If the purge is slightly increased further to 35 percent, the gas retention time may be reduced to 5.8 min and the liquid retention time may be reduced to 12 hr, yielding an ethanol volumetric productivity of 1.6 g/L•hr. Thus, operation with cell recycle and a cell purge of 30-35 percent yields high productivities and small reactor systems.

Table 3. Results from Single CSTR with Cell Recycle.
Organism: O-52

XRT (hr)	LRT (hr)	GRT (min)	ETOH (g/L)	HAC (g/L)	CELLS (g/L)	Y _{VE} (mol EtOH/L·d)	Conversions	
							% CO	% H ₂
46.4	23.2	12.5	20.4	4.4	3.8	0.46	96.3	81.2
43.2	17.3	9.7	21.1	3.5	4.9	0.64	86.7	49.9
43.2	17.3	9.2	20.5	5.1	4.6	0.62	89.4	64.5
43.2	17.3	7.5	22.2	3.7	5.0	0.67	81.8	42.1
49.4	17.3	9.2	21.1	4.4	4.6	0.64	85.3	52.1
46.0	16.1	8.4	20.8	5.1	4.5	0.67	85.2	61.4
54.3	16.3	6.8	23.4	5.7	4.7	0.75	84.7	57.7
54.3	16.3	7.2	19.0	4.4	4.0	0.61	83.1	55.2
54.3	16.3	7.4	21.9	5.5	5.0	0.70	86.6	66.7
55.6	16.7	6.4	23.5	4.9	5.6	0.73	83.3	53.1
41.6	14.5	6.2	20.1	5.0	5.7	0.73	82.5	55.0
41.6	14.5	6.0	21.5	3.0	6.0	0.78	82.5	50.0
34.2	12.0	6.0	19.5	4.5	5.7	0.83	84.0	56.0
34.2	12.0	5.7	18.0	4.5	5.7	0.80	81.0	45.0

Table 4. The Effect of Cell Purge on Performance in the CSTR with Cell Recycle.
Isolate O-52

Cell Purge, %	0	27	35
GRT, min	16.60	7.11	5.85
LRT, hr	31	17	12
EtOH, g/L	20.8	22.3	19.4
HAc, g/L	3.5	3.9	3.3
Cell Conc., g/L	2.0	6.0	4.6
Productivity, g EtOH/L/h	0.68	1.34	1.61
Sp. Gas Uptake rate, mMol/g cell/h			
CO	33.3	23.7	35.7
H ₂	27.0	20.0	23.3
% of Theoretical Yield	77.9	74.7	84.7

Two CSTRs in Series

A system of two CSTRs connected in series was also studied as an alternative to the single CSTR system. In this system, effluent from the first reactor was used as feed to the second reactor. Gas flowed countercurrently to the liquid, and some fresh gas was also fed to both reactors. The concept of utilizing two reactors in series is to increase product concentration by utilizing one reactor primarily for growth, and one reactor primarily for ethanol production near the conditions where the product ethanol is inhibitory.

Steady state performance data from the series operation are shown in Table 5. In utilizing two CSTRs in series, ethanol concentrations exceeding 30 g/L are possible, again with only 4 g/L acetic acid. At an overall gas retention time of 9 min, the CO conversion in this study was 87 percent and the H₂ conversion was 62 percent, while yielding 24.5 g/L ethanol and 4 g/L acetic acid. This system is indeed promising in yielding higher ethanol concentrations, although productivities from the system are a bit lower than with the single CSTR with cell recycle.

Table 5. Results from Two Stage CSTR Reactor System.
Organism: O-52

XRT (hr)	LRT (hr)	GRT (min)	ETOH (g/L)	HAC (g/L)	CELLS (g/L)	Y _{VE} (mol EtOH/L•d)	Conversion	
							% CO	% H ₂
173.0	43.0	14.0	33.0	4.0	6.5	0.40	90	60
47.5	47.5	17.0	27.0	4.0	2.8	0.30	90	61
62.0	29.2	12.0	28.5	4.0	4.6	0.50	89	65
84.0	20.5	9.0	24.5	4.0	5.3	0.64	87	62
43.0	43.0	19.5	27.0	1.9	3.0	0.33	95	55
92.0	42.5	15.0	29.0	3.0	5.0	0.34	75	25
90.0	31.0	12.0	27.0	4.0	6.0	0.43	91	69

CO₂/H₂ Utilization

Refinery waste gases, depending upon their sources, may be rich in H₂ and deficient in CO. Examples of these types of gases are cat cracker offgas which contains about 20 percent H₂ in hydrocarbons, delayed coker offgas which contains 10 percent H₂ and hydrotreater and cat reformer gas which contains 90-95 percent H₂. Each of these gases does not contain CO. The studies to date performed with Isolates O-52 and C-01 have been restricted to gases containing high concentrations of CO (at least 15 percent). Studies were initiated in Year 2 of the cooperative agreement to utilize gases without CO present to serve as feed gas for ethanol production. Efforts to gradually reduce the CO content have not been successful, and these efforts will continue in Year 3.

Water Recycle

The recycle of water back to the fermenter after distillation is essential to minimize effluent production and to maximize the yield of ethanol from the process. Water is generated as the bottoms product during distillation. This water contains nutrients not used up during fermentation or destroyed during distillation such as trace metals and other minerals. The recycle of these nutrients minimizes the quantity of effluent which must be treated as well as the quantity of nutrients which must be subsequently added to the fermenter.

Water recycle experiments are thus a very important part of the ethanol production scheme. A number of water recycle experiments were performed in investigating various techniques for preparing the water prior to recycle. Water preparation includes filtration to remove cells and cell parts prior to distillation, and treatment of the water after distillation to remove any toxic materials which may have been formed during distillation.

Figures 2-5 show results from the initial water recycle experiments. In these experiments, the permeate from hollow fiber filtration was sent to distillation. After removing ethanol, the water was filtered through a 0.2 μm filter to remove any potentially toxic by-products. The fraction of water recycled compared to the total water (as medium) fed to the reactor in these experiments ranged from 10-75 percent.

Ten percent recycle was started at $t = 265$ hr on the plots. The percentage recycle water was increased to 50 percent at $t = 460$ hr. During the water recycle studies with 10 and 50 percent recycle, the CO and H_2 conversions held steady and the product concentrations held at 10-13 g/L ethanol and 3-4 g/L acetic acid. With 75 percent water recycle, however, the H_2 conversion fell and acetic acid began to accumulate in the reactor.

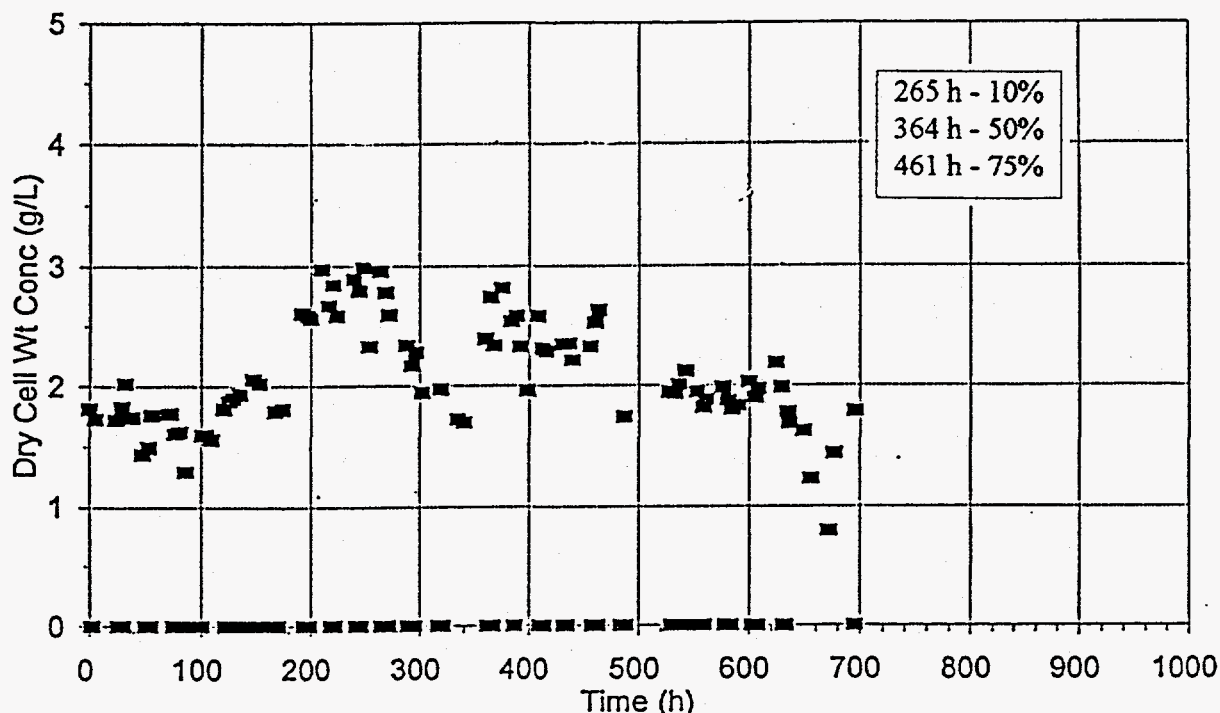


Figure 2. Cell Concentration in the Initial Water Recycle Experiments with Isolate O-52 in the CSTR

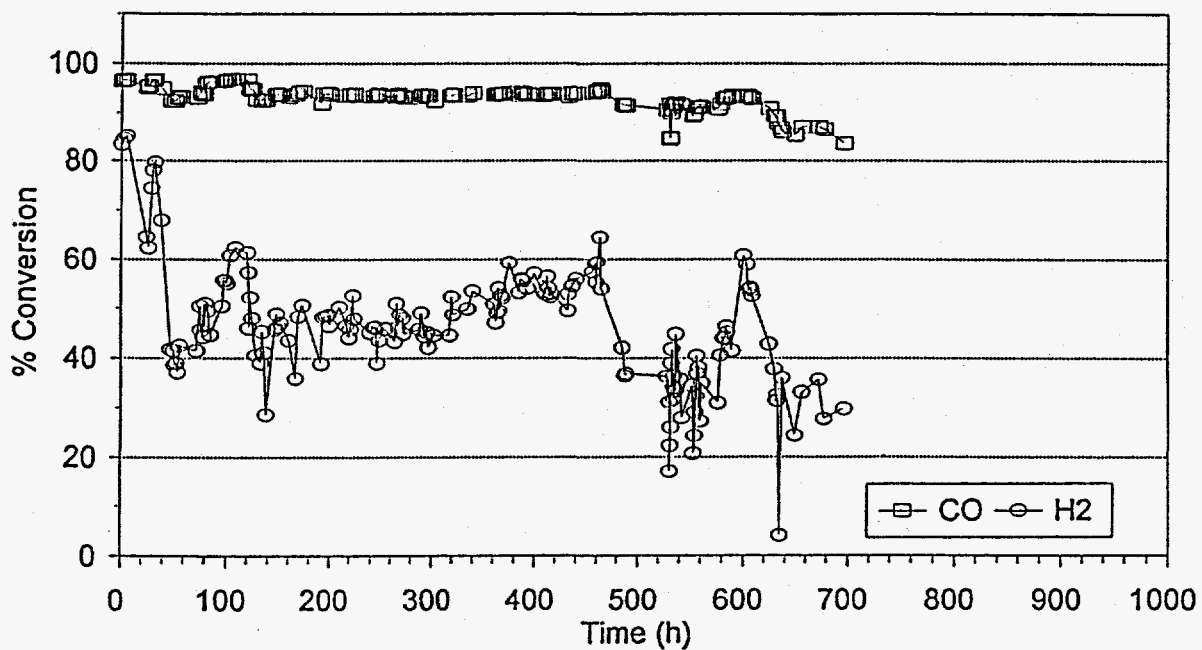


Figure 3. Gas Conversions in the Initial Water Recycle Experiments with Isolate O-52 in the CSTR

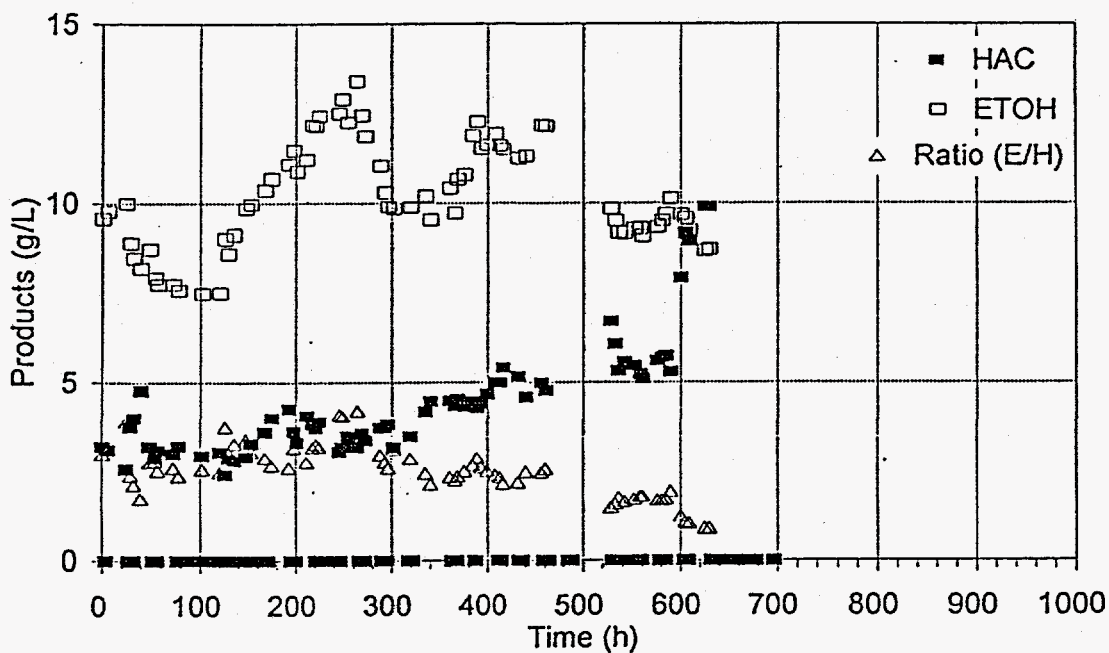


Figure 4. Product Concentrations in the Initial Water Recycle Experiments with Isolate O-52 in the CSTR

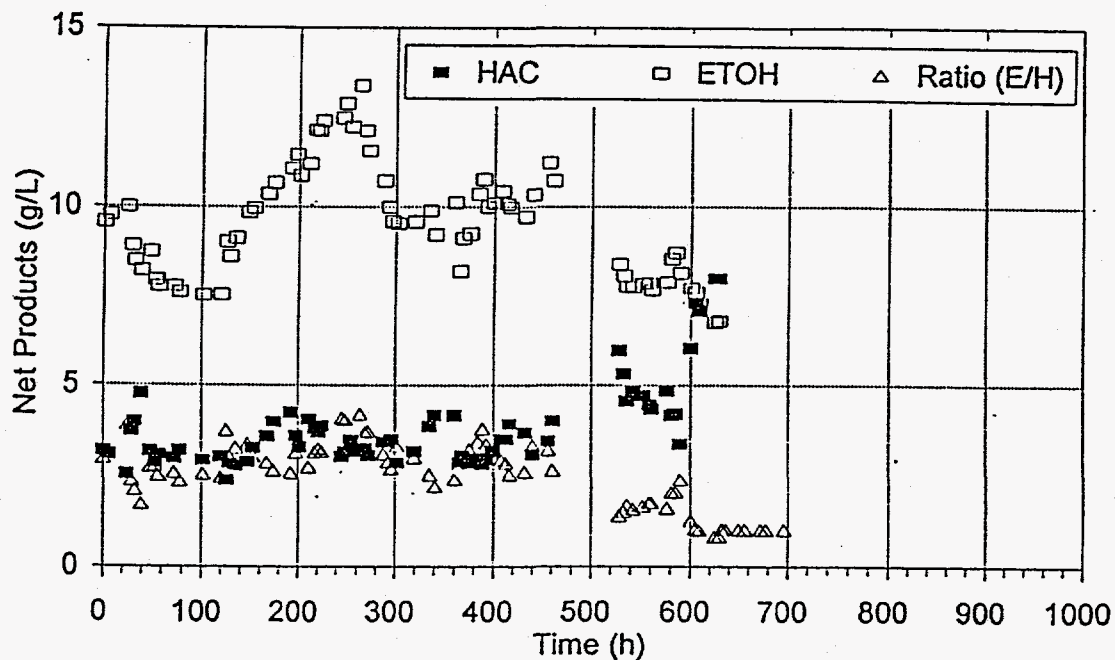


Figure 5. Net Product Concentrations in the Initial Water Recycle Experiments with Isolate O-52 in the CSTR

Water recycle was resumed after adjusting the medium composition slightly. The method for treating the water was the same as in the previous experiment. Figures 6-9 show results from this recycle study, now employing recycled water fractions of 25-100 percent. In this study, 100 percent water recycle was employed for nearly 500 hours, or about 20 retention times. The H_2 and CO conversions were 65 and 90 percent, respectively. The products ethanol and acetic acid were 25 g/L and 6.5 g/L, respectively.

In a third set of water recycle experiments, the hollow fiber filter was replaced by a gravity settling apparatus. This modification was made in an attempt to find an inexpensive method for removing cells prior to distillation as an alternative to hollow fiber filtration. Results from these experiments are shown in Figures 6-9 at $t = 1420$. With this change, the H_2 conversion fell and acetic acid accumulated in the reactor.

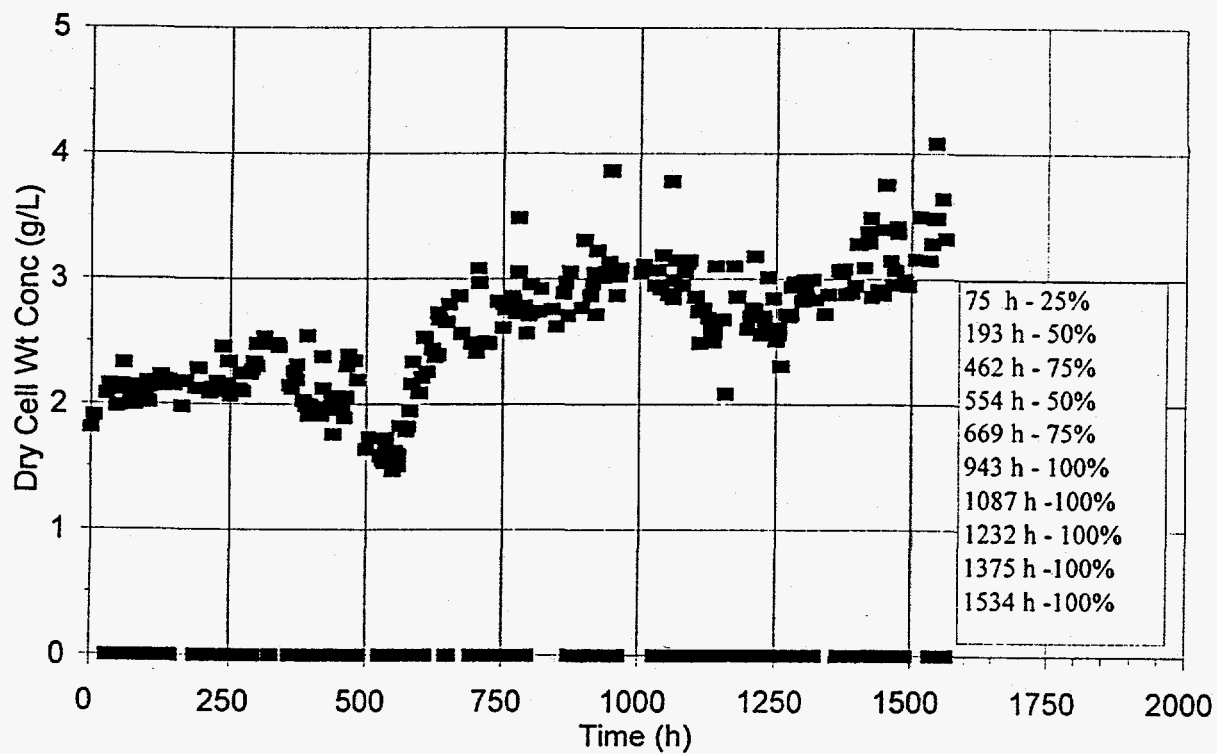


Figure 6. Cell Concentration in the Second Water Recycle Studies Performed with Isolate O-52 in the CSTR

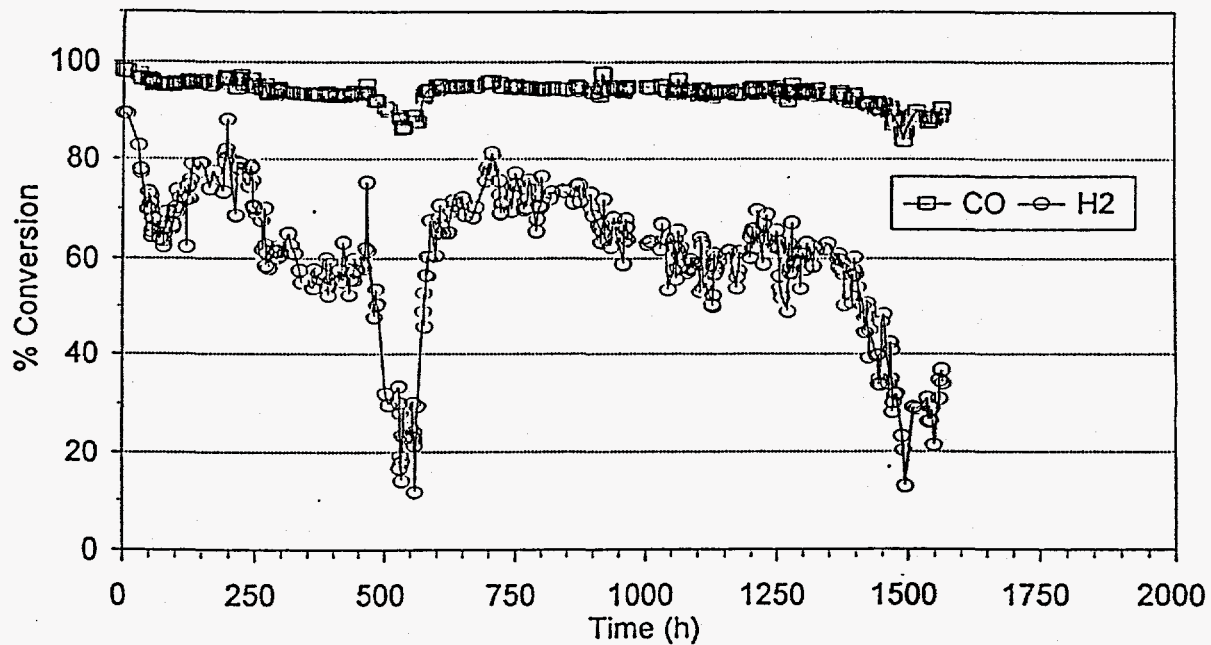


Figure 7. Gas Conversions in the Second Water Recycle Studies Performed with Isolate O-52 in the CSTR

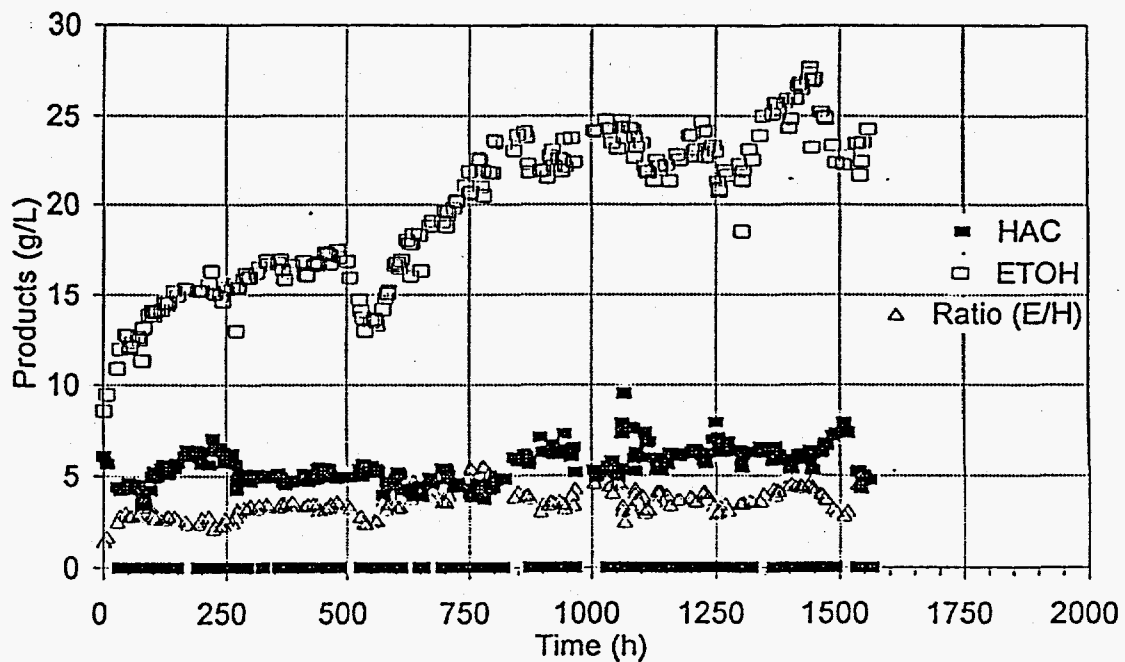


Figure 8. Product Concentrations in the Second Water Recycle Studies Performed with Isolate O-52 in the CSTR

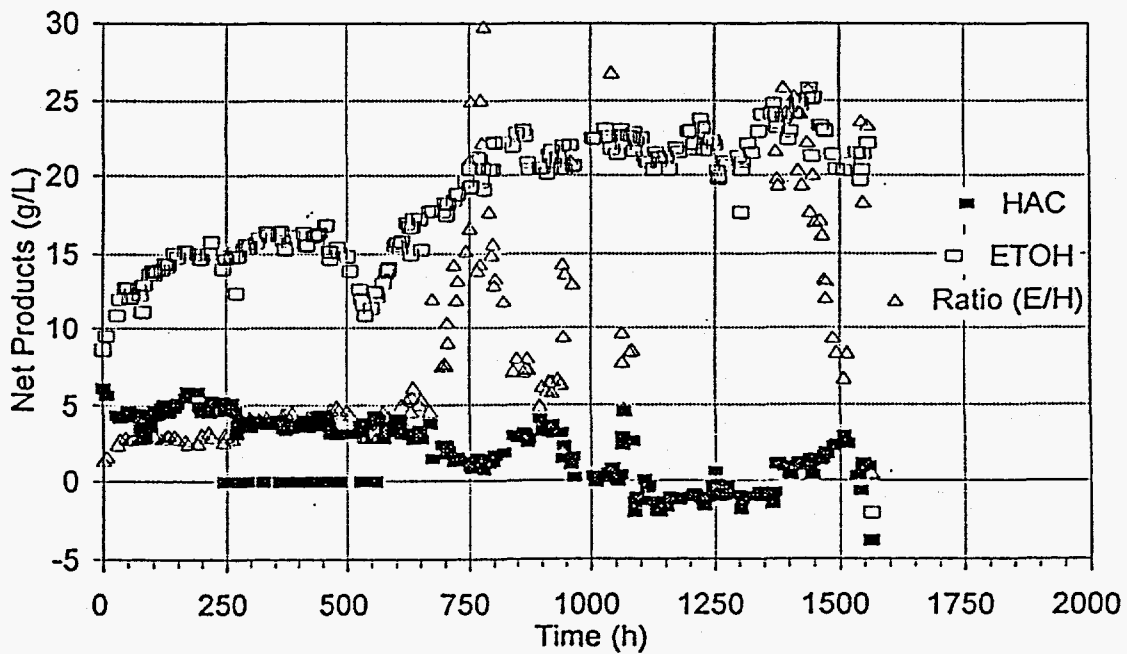


Figure 9. Net Product Concentrations in the Second Water Recycle Studies Performed with Isolate O-52 in the CSTR

A higher concentration of ethanol in the recycle water was tested in the next set of water recycle experiments. As is noted in Figures 10-13, the culture was first allowed to reach a good steady state. At $t = 2068$ hr, the recycle water containing 13 g/L ethanol and 5.2 g/L acetic acid was recycled to the reactor. The reactor was unable to sustain the projected 29 g/L ethanol concentration, and the H_2 conversion fell.

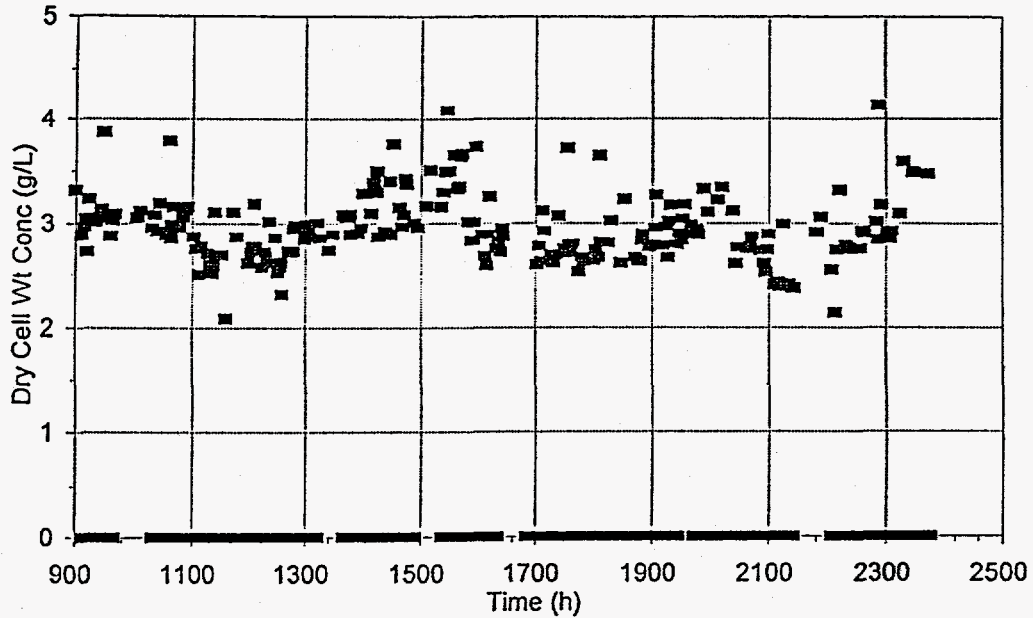


Figure 10. Cell Concentration in the Water Recycle Studies Employing a High Ethanol Concentration in the Recycle Water

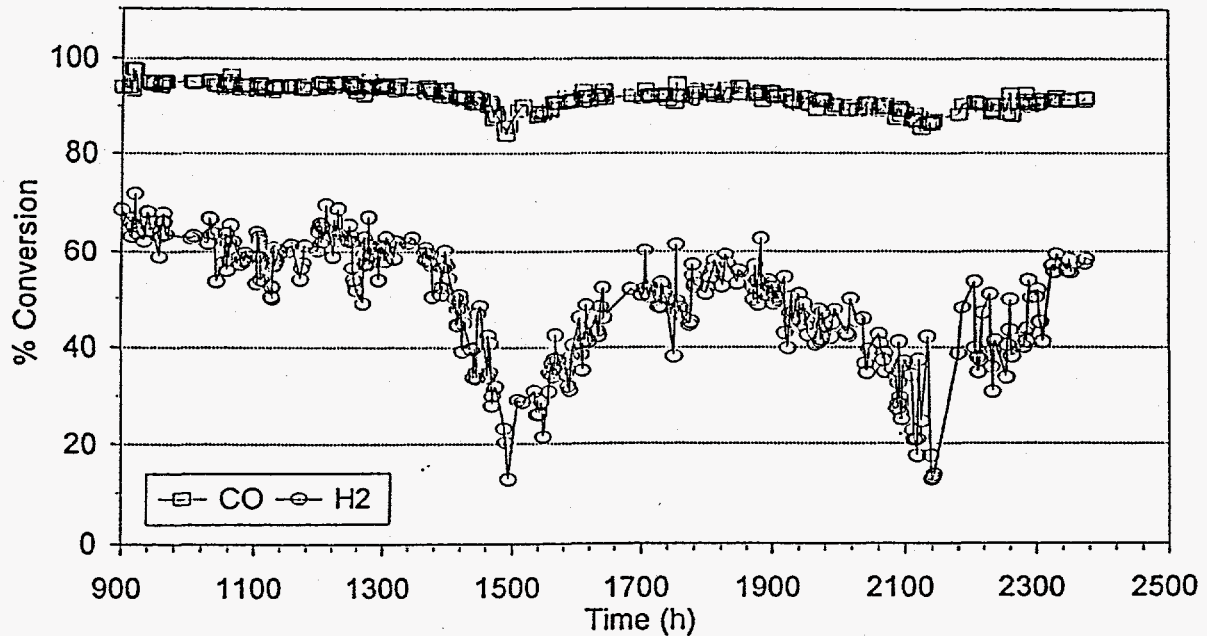


Figure 11. Gas Conversion in the Water Recycle Studies Employing a High Ethanol Concentration in the Recycle Water

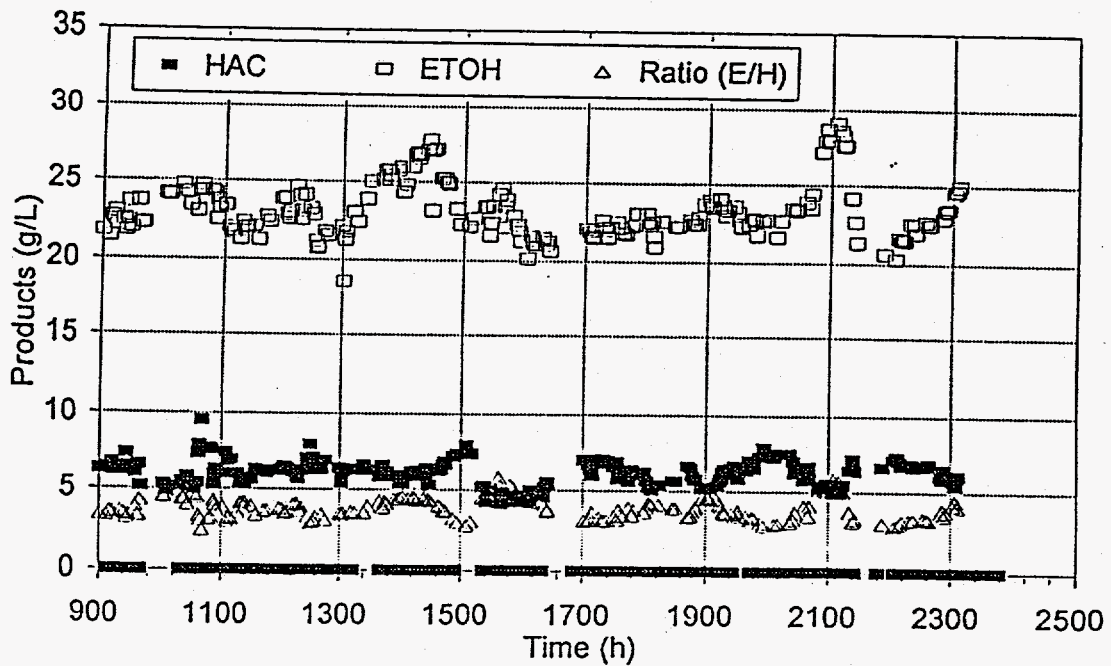


Figure 12. Product Concentrations in the Water Recycle Studies Employing a High Ethanol Concentration in the Recycle Water

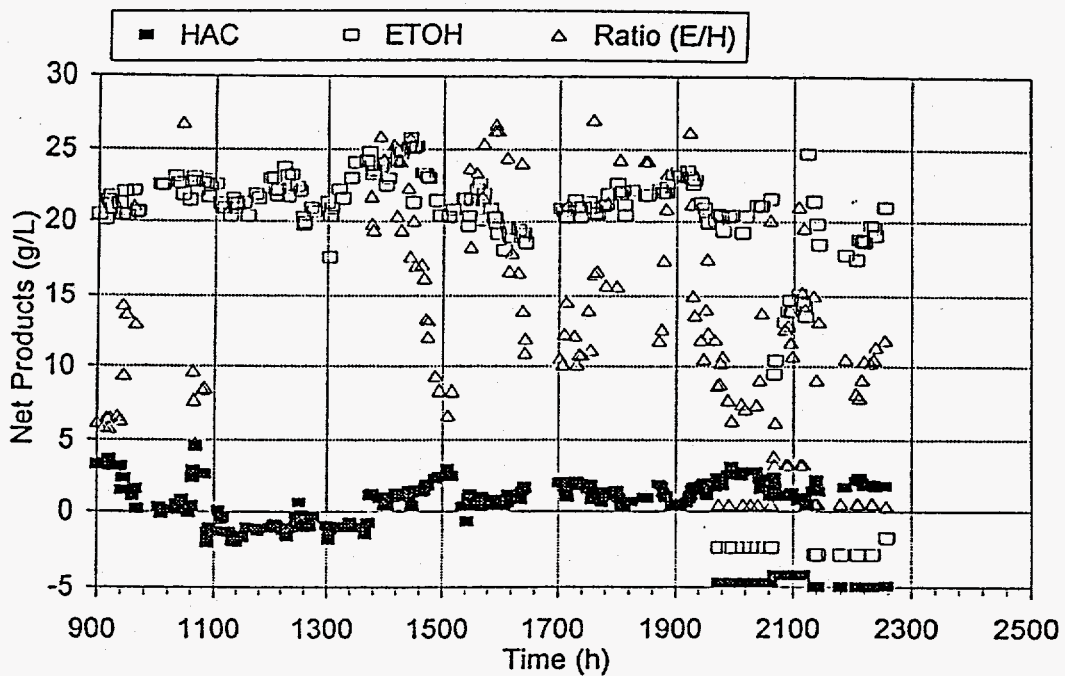


Figure 13. Net Product Concentrations in the Water Recycle Studies Employing a High Ethanol Concentration in the Recycle Water

The last set of water recycle experiments conducted in Year 2 involved different procedures for treating the culture effluent in preparing medium water. The following medium water treatments were used in the experiments:

- No filtration before or after distillation, heating to remove cells
- Hollow fiber filtration, followed by distillation, followed by filtration again
- Hollow fiber filtration, followed by distillation, and then NO filtration
- No filtration before or after distillation, delayed medium adjustment

Results from these experiments are shown in Figures 14-17. The experiment performed without filtration ($t = 311-415$ hr) was not successful. Cellular material in the medium water may have been harmful to the culture. Filtration before and after distillation ($t = 815-925$) seems to have worked. However, the higher ethanol concentration (25 g/L) may have resulted in lower gas conversions. In the third experiment, the filtration step after distillation was eliminated. It was shown that the first filtration step was necessary while the second filtration step could be eliminated. The last experiment was a repetition of the first experiment with the exception that the medium was adjusted late in the experiment. Like the first experiment, this experiment without filtration was also unsuccessful.

The conclusion from these water recycle studies is that 100 percent water recycle is possible if the permeate is filtered to remove cellular debris prior to recycle. Ethanol concentrations of 20-25 g/L are possible.

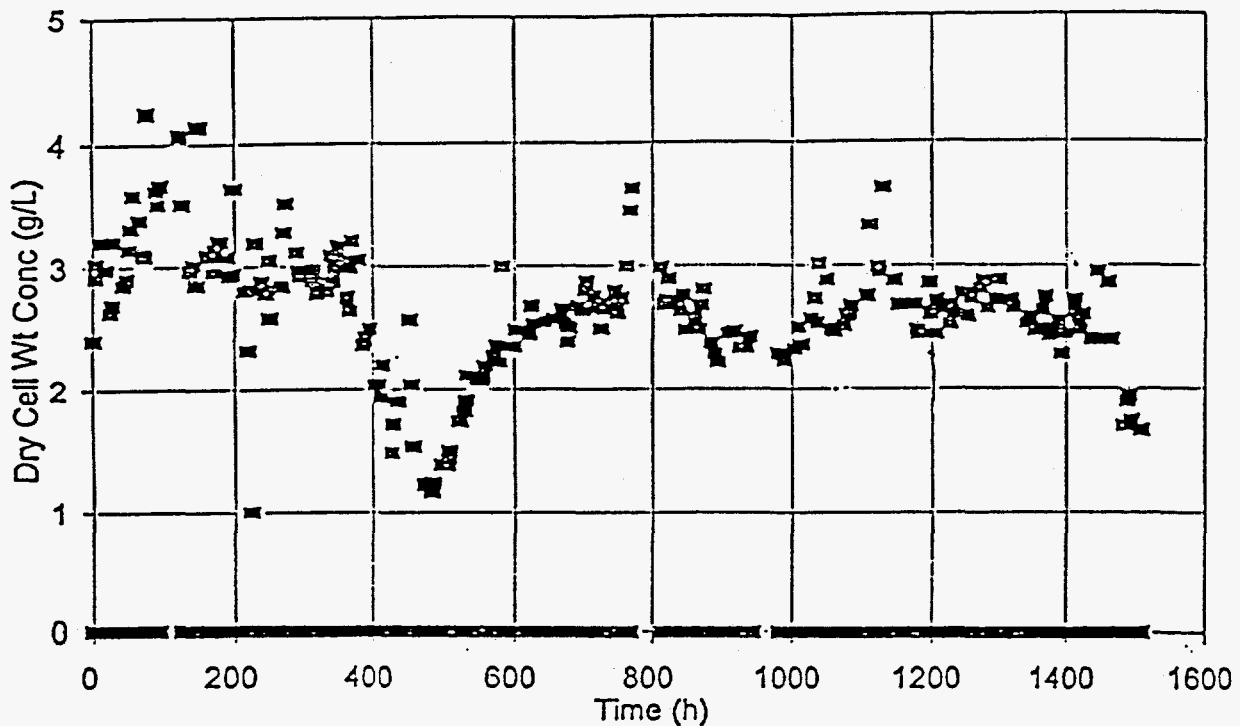


Figure 14. Cell Concentration in the Final Set of Water Recycle Experiments Using a Variety of Treatment Options

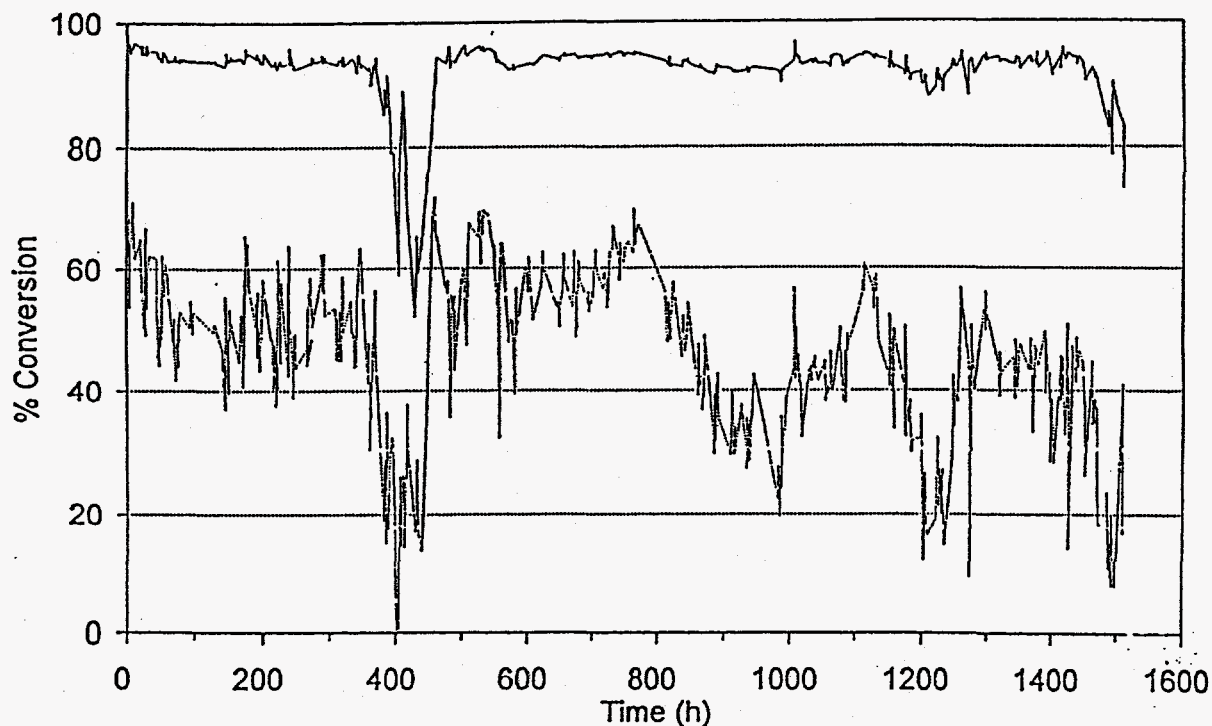


Figure 15. Gas Conversion in the Final Set of Water Recycle Experiments Using a Variety of Treatment Options

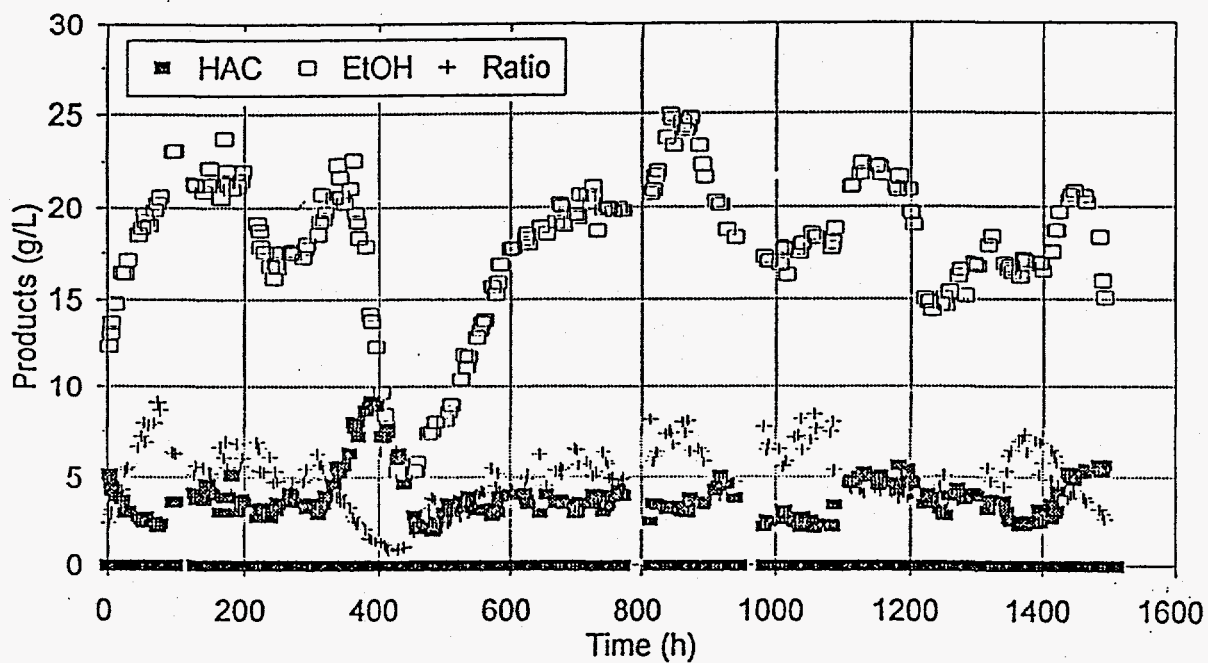


Figure 16. Product Concentrations in the Final Set of Water Recycle Experiments Using a Variety of Treatment Options

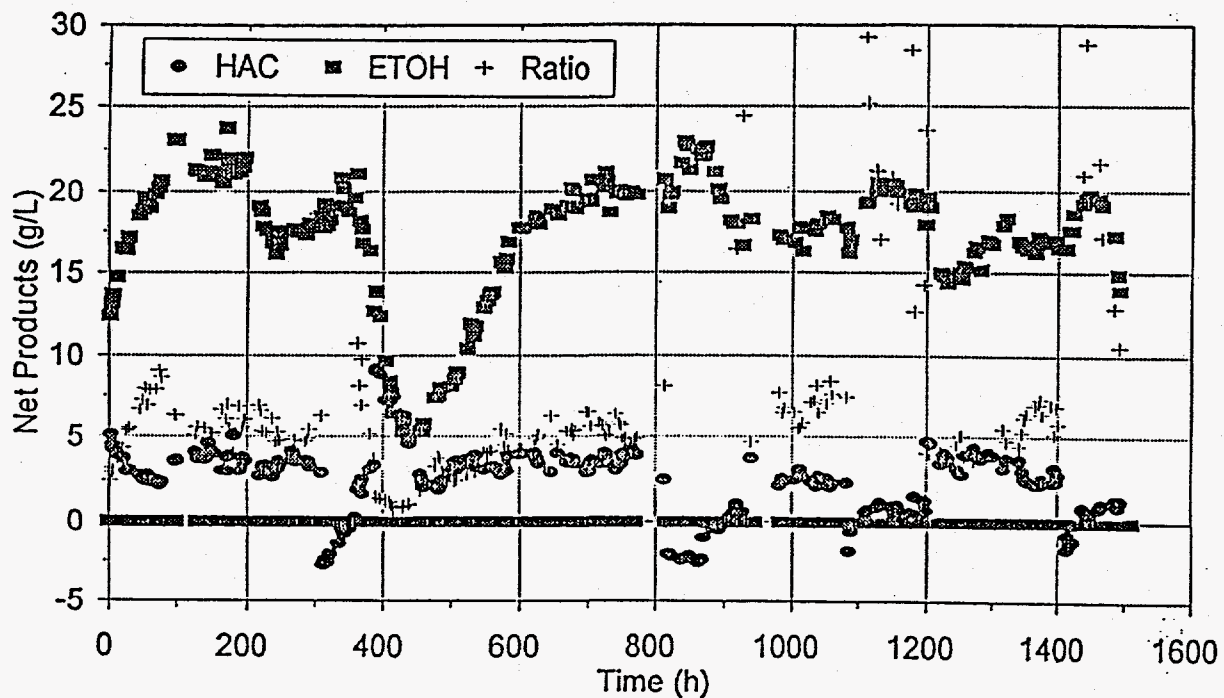


Figure 17. Net Product Concentrations in the Final Set of Water Recycle Experiments Using a Variety of Treatment Options

TASK III.3. PRODUCT RECOVERY

In Phase III, a wide variety of ethanol recovery techniques were evaluated for the process, including:

- solvent extraction followed by distillation, followed by azeotropic distillation, pervaporation or adsorption
- distillation alone followed by azeotropic distillation, pervaporation or adsorption
- a series of pervaporation steps
- reverse osmosis in place of solvent extraction or distillation

A host of solvents have been evaluated for the extraction of ethanol. In general, low ethanol distribution coefficients (0.3 - 0.5) were obtained which limits the desirability of solvent extraction. An economic evaluation of the recovery techniques shows that simple distillation followed by pervaporation or adsorption would be the most economical recovery technique. Adsorption was chosen over pervaporation due to cost considerations and its widespread use in the chemical process industry.

Another issue in product recovery is the recovery of the by-product acetic acid. Early design projections used a solvent extraction process followed by distillation for acetic acid recovery. However, Phase III activities have shown that acetic acid recovery is no longer needed.

Figure 18 shows typical operating data from the laboratory ethanol distillation process. Again, the purpose of this recovery process was not to produce ethanol, but to generate the bottoms water for recycle back to the fermenter. Typically 800 mL of permeate was loaded into the unit. A typical feed concentration was 19 g/L ethanol and 4.6 g/L acetic acid at pH 5. Approximately 35 mL of overhead product containing 400 g/L ethanol was collected over a temperature range of 78-95°C. This material was logged to meet permit requirements, and stored for later shipment to a molecular sieve adsorption vendor for testing. The bottom typically contained 765 mL of aqueous solution containing no ethanol and 4.7 g/L acetic acid at pH 5. The bottoms were used for water recycle.

Figure 18. Typical Laboratory Batch Permeate Distillation

Purpose:	Provide water for recycle back to the fermenter
Volume loaded:	800 mL
Feed Concentration:	19 g/L ethanol 4.6 g/L acetic acid pH 5
Overhead stream:	approximately 35 mL collected temperature range: 78-95°C all ethanol overhead (400 g/L, average)
Bottoms stream:	765 mL no ethanol 4.7 g/L acetic acid pH 5

TASK III. 4. ADVANCED BIOREACTOR STUDIES

High Pressure

High pressure studies have been previously reported. In summarizing these earlier results, it was shown that increased pressure proportionally decreased the required gas retention time for the process. Thus, operation at a pressure of 75 psig (6 atm, absolute) decreases the size of the reaction vessel by a factor of six over operation at atmospheric pressure. This operation is highly desirable if the gas stream is available at the increased pressure without compression. The selection of an operating pressure is thus an optimization between compression costs and reactor costs.

Solvent Compatibility with Fermentation

BRI has selected direct distillation over solvent extraction for ethanol recovery. In addition, acetic acid recovery is no longer required. Thus, solvent toxicity is not a problem in the system. Efforts to enhance gas phase solubility by the addition of solvents has not proved to be beneficial.

Kinetic Parameters

Finally, intrinsic kinetic parameters for the biological system have been obtained. The culture follows a standard Monod model with dissolved CO tension as the substrate, and a substrate inhibition term. The specific uptake rate, q , may be described by the equation:

$$q = \frac{0.8608 P_L^*}{0.7478 + P_L^* + \frac{(P_L^*)^2}{0.0303}}, \text{ mol/g} \quad (3)$$

where P_L^* is the liquid phase CO tension. The Monod constant K_p was 0.7478 atm, the maximum specific uptake rate was 0.8608 mol/g hr atm and the substrate inhibition constant, W , was 0.0303 atm.

TASK III. 5. MODELING AND SCALE-UP

Modeling and scale-up data have also been presented previously. Intrinsic kinetic and mass transfer relationships have been developed for the reactor design, and product recovery scale-up information has also been developed.

TASK III. 6. PROCESS EVALUATION

The economics for converting refinery waste gas to ethanol are quite attractive. However, they are also highly dependent upon the gas stream targeted by the refinery. Economic projections have been prepared which are company dependent and are considered proprietary through agreements between BRI and the refiners.

TASK III. 7. ECONOMIC UPDATE AND COMMERCIALIZATION PLAN

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 2010, 65 percent of the refining capacity will utilize this process for treatment of waste gas streams. By 2010, an energy savings of 0.45 Quad, equivalent to 300,000 barrels (4.5×10^7 L) of oil per day, will result from production of ethanol from a waste source rather than from grain. Waste reduction will total 19 million tons (1.7×10^{10} kg) of CO, H₂ and CO₂ per year.

Commercialization Plan

The commercialization plan involved identifying and selecting a refiner to participate in the pilot demonstration and then to build the first commercial facility at their location. Following this initial full scale demonstration, the technology would then be licensed to other refiners.

Refining partners were solicited by reviewing those with significant ethanol usage, as well as available refinery waste gases. A summary presentation was prepared to send to these companies. Following an expression of interest and execution of appropriate confidentiality agreement, meetings were held and data exchanged. The quantities and compositions of waste gases were then used to project ethanol capital requirements and economics.

At the end of this reporting period, four refiners had expressed interest in the technology and economic projections were underway. The projections were generally positive, even without ethanol tax credits.

PROJECT MANAGEMENT AND REPORTING

Project Management

The BRI management team for this project is as follows:

<u>BRI Employee</u>	<u>Function</u>
J.L. Gaddy, President (PhD - ChE)	Project Manager
E.C. Clausen, VP Research (PhD - ChE)	Principal Investigator
L.D. Gaines, VP Development (PhD - ChE)	Pilot Design
C. Wikstrom, Director Engr. Res. (PhD - ChE)	Project Director
C.W. Ko, Director Special Projects. (PhD - ChE)	Technology Assistance/Pilot Design
R. Basu, Director Engineering (PhD - ChE)	Laboratory Management
G. Sperl, Director Microbiology (PhD - Micro)	Microbiology Direction
G. Chen, Research Associate (PhD - Micro)	Microbiology Research
J.R. Phillips, Research Assoc. (MS - ChE)	Laboratory Research
D. Arora, Research Associate (PhD - ChE)	Laboratory Research
S. Adams, VP Operations (MS - IE)	Business Official
M. Williams, VP Finance (CPA)	Cost Accounting
Research Technicians	

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 and Phase III programs were completed on 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. Periodic meetings were held with DOE representatives to establish objectives and procedures, and to review progress.

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.

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. Annual progress reports have also been submitted.

CONCLUSIONS

Refineries discharge large volumes of H_2 , CO and CO_2 from cracking, coking and hydrotreating operations. This research and development program is seeking to develop, demonstrate, and commercialize 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 grow rapidly over the next decade. 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 research program is being conducted in three phases: Phase II - Technology Development; Phase III - Engineering Development; and Phase IV - Demonstration. Phase I, Exploratory Development, had been successfully completed in the BRI laboratories prior to project initiation. The research effort has yielded two strains (Isolate O-52 and Isolate C-01) which are to be used in the pilot studies to produce ethanol from CO, CO_2 and H_2 in petroleum waste gas. Results from single continuous stirred tank reactor (CSTR) laboratory tests have shown that 20-25 g/L of ethanol can be produced, with less than 5 g/L acetic acid as a by-product. Laboratory studies performed with two CSTRs in series have yielded ethanol concentrations of 30-35 g/L with 2-4 g/L acetic as the by-product. Water recycle from distillation back to the fermenter shows that filtration of the water before distillation is sufficient to eliminate the recycle of toxic materials back to the fermenter.

Product recovery in the process will use direct distillation to the azeotrope, followed by adsorption to produce neat ethanol. This technology is less energy intensive than other alternatives such as solvent extraction, azeotropic distillation or pervaporation. The updated economic projections are quite attractive. The economics are refinery stream dependent, and thus vary depending upon refinery location and operation.

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