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PRODUCTION OF ETHANOL FROM REFINERY WASTE GASES

Final Report, April 1994 – July 1997

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August, 1997

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

For
U.S. Department of Energy
Office of Industrial Technologies
Washington, DC 20585

By
Bioengineering Resources, Inc.
1650 Emmaus Road
Fayetteville, AR 72701

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PREFACE

This project consisted of Phase II, Technology Development, Phase III, Engineering Development and Phase IV, Demonstration, of the DOE funded project "Production of Ethanol from Refinery Waste Gases" for the time period covering April 1, 1994 through July 31, 1997. This report documents the technical progress made on Phases III and IV from May 16, 1996 through July 31, 1997. 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. Co-authors on the report along with Drs. Gaddy and Clausen are Dr. D. Arora, Dr. R. Basu, Mr. F. S. Breshears, Dr. L. D. Gaines, Mrs. K. S. Hays, 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 third and final report for the project. This report and the two previous reports DOE/AL/98770-1 (DE97006845) and DOE/AL/98770-2 (DE97009303) can be obtained as indicated by the notice inside the front cover.

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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 triple to 3 billion gallons per year as it replaces gasoline as the predominant liquid fuel. 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 was conducted in three phases: Phase II - Technology Development; Phase III - Engineering Development; and Phase IV - Demonstration. DOE budget constraints resulted in cancellation of Phase IV prior to construction and operation of the prototype demonstration. Phase I, Exploratory Development, had been successfully completed in the BRI laboratories prior to project initiation. The research effort has resulted in the development of two strains (Isolate O-52 and Isolate C-01) which produce ethanol from CO, CO_2 and H_2 in refinery waste gas. Fermentation of CO_2 and H_2 alone, without the presence of CO, does not work well. Also, low concentrations of CO invite methanogen contamination, which may be removed by bromoethanesulfonic acid (BESA) addition. Results from single continuous stirred tank reactor (CSTR) laboratory tests have shown that about 20 g/L of ethanol can be produced, with less than 5 g/L acetic acid produced as a by-product. Laboratory studies performed with two CSTRs in series have yielded ethanol concentrations of 25-30 g/L with 2-4 g/L acetic as the by-product. Hollow fiber filtration of the water before distillation is sufficient to eliminate the recycle of toxic materials back to the fermenter. As an alternative, flocculation may be used to aid in removing the cells, but the filtrate must be treated by carbon bed adsorption prior to distillation and water recycle. If cell recycle is employed, again carbon bed treatment is required prior to distillation and water recycle.

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.

A detailed process design has been prepared for the construction of a prototype unit to produce 2.63 lb/hr of ethanol from refinery waste gas containing 21.5 percent H_2, 20.0 percent CO, 9.5 percent CO_2, 4.0 percent CH_4 and 45.0 percent N_2 at 2.72 atm. The design includes plant layouts, piping diagrams, equipment sizing and cost estimates, P&IDs, a computer I/O list, and an instrument list. It is estimated that the total equipment cost will be about $250,000, and the total estimated cost of the facility, including engineering and construction costs will be $1.4 million.

Ernst and Young/Wright Killen was selected to identify industrial partners for this project. EY/WK prepared economic projections which were quite favorable. Several companies had been contacted and had expressed interest when the project was cancelled.

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) (2.8 X 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 (3.6 X 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 (3.6 X 10^7 L/d))

		Quantity	Composition, mole %				
Gas Stream	Present Use	lbmole/h (gmole/h)	H_2	CO_2	CO	H-C	H_2S
Cat Cracker off gas	fuel gas	3826 (1.7 X 10^6)	19.4	-	-	80.0	0.6
Delayed Coker off gas	fuel gas	2024 (9.2 X 10^5)	10.7	0.2	-	83.2	5.9
Hydrotreater and cat reformer	fuel gas	5120 (2.3 X 10^6)	93.8	-	-	5.5	0.7
Catalyst regenerator dry, N_2 free	vent	5120 (2.3 X 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:

$$6CO + 3H_2O \rightarrow CH_3CH_2OH + 4CO_2 \quad (1)$$

$$6H_2 + 2CO_2 \rightarrow CH_3CH_2OH + 3H_2O \quad (2)$$

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.

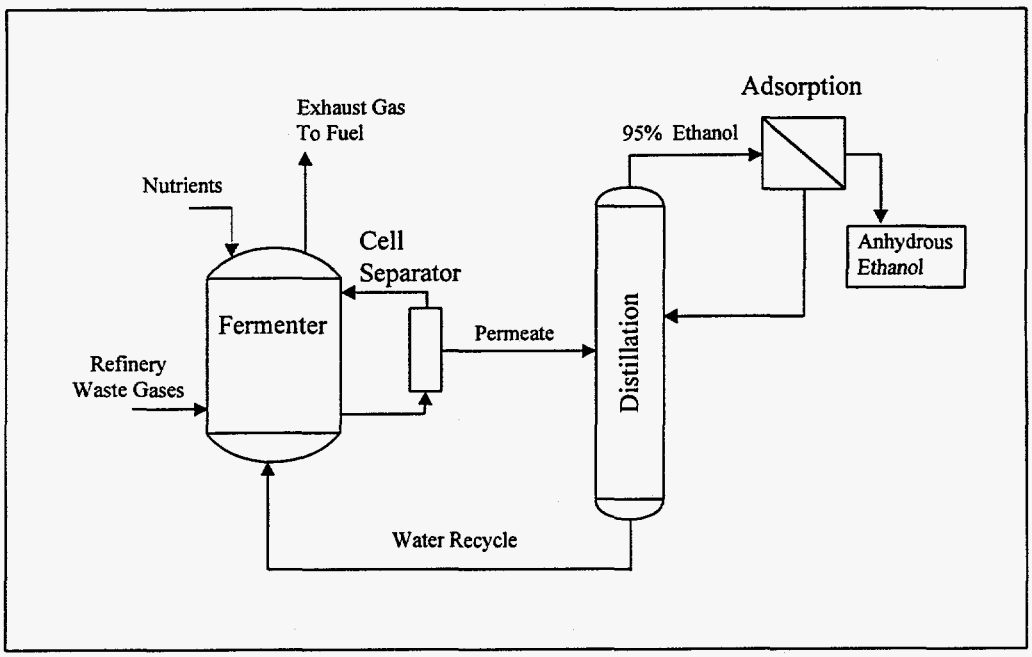

Figure 1. Biological Process for Ethanol Production from Refinery Waste Gas

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 (3.6×10^7 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 was 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. The Phase IV effort included a detailed design of a prototype unit for converting refinery waste gas to ethanol. Laboratory efforts were continued on important design areas, identified in the economic analysis, that will have a major impact on the economics of ethanol production from refinery waste gas. Construction and operation of the prototype unit, to have been conducted in conjunction with a refinery partner, were canceled by DOE in early 1997 because of funding limitations.

PURPOSE

The purpose of this report is to present results from the Phase III and Phase IV development programs performed during Year 3 of the program. The major focus of this work was the preparation of the prototype design which will demonstrate this technology in a 2.5 lb/hr ethanol production facility. Additional areas of focus included efforts in obtaining an industrial partner to help finance the prototype, and advanced engineering experiments concentrating on process optimization in various areas needing future development and optimization. The advanced engineering experiments were performed in the laboratory in the following areas:

- the treatment and use of recycle water from distillation back to fermentation
- alternative methods of removing cells from the fermentation broth
- the fermentation of streams containing CO_2/H_2 alone, with little to no CO present
- dealing with methanogen contaminants that are capable of fermenting CO_2 and H_2 to methane
- acetate tolerance by the culture

Results from the design, the industrial partner search and the laboratory R&D efforts are discussed in this report.

BRIEF REVIEW OF PREVIOUS R&D STUDIES

Previous studies performed at BRI showed that the isolates O-52 and C-01 were the best strains found to date for converting CO, CO_2 and H_2 to ethanol by Equations (1) and (2). Both strains in the "wild" state produce acetate/acetic acid as their major product. However, the researchers at BRI have been able to manipulate the cultures to produce ethanol as the predominant product. Both strains operate optimally at pH 4.5-5.5, and achieve maximum ethanol concentrations of about 25 g/L in the CSTR. The yield of ethanol from CO, CO_2 and H_2 is about 90 percent, and the specific productivity is 0.21-0.23 g ethanol/gcell•hr. The strains are tolerant of H_2S and carbonyl sulfide (COS) in their typical concentrations in waste gases.

Laboratory studies were performed with the strains in single CSTRs, single CSTRs with cell recycle to enhance productivity, two CSTRs connected in series, and two CSTRs in series with cell recycle. In a single CSTR with cell recycle, ethanol concentrations of about 20 g/L were obtained while yielding CO conversions of about 80-90 percent and H_2 conversions of 50-60 percent. Acetic acid/acetate was produced as a by-product at a concentration of 4-5 g/L. Results from a two-stage CSTR system showed slightly higher ethanol concentrations of 25-30 g/L. CO and H_2 conversions were essentially the same in both the single and dual reactor systems.

A number of water recycle studies were performed to define the necessary treatment, if any, of the water recycled from distillation back to the fermenter. If hollow fiber filtration is employed as a method of cell recycle back to the fermenter, the recycled water from distillation may be sent to fermentation with no further treatment.

Finally, several 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

An economic evaluation of the recovery techniques showed 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. An ethanol concentration of at least 20 g/L from fermentation is necessary for economical ethanol recovery by distillation/adsorption.

PROTOTYPE DESIGN

PROCESS AND MATERIAL BALANCE

The ethanol prototype plant was designed to produce 2.63 lb/hr of ethanol from refinery waste gas containing 21.5 percent H_2, 20.0 percent CO, 9.5 percent CO_2, 4.0 percent CH_4 and 45.0 percent N_2 at 2.72 atm pressure. A schematic of the process is shown in Figure 2. Refinery waste gas (1) is fed to a reactor where the conversion of CO, CO_2 and H_2 to ethanol takes place. The gas is fed at 40 psia (2.72 atm) and 25°C. The reactor is maintained at 37°C. Water in the reactor system is through water recycle from distillation (6), as well as make-up water in a concentrated nutrients stream (3). A CO conversion of 90 percent and a H_2 conversion of 68 percent are assumed. The yield of ethanol from CO, CO_2 and H_2 is 80 percent. It is further assumed that the product stream from the reactor contains 20 g/L ethanol and 4 g/L acetic acid/acetate. Spent gas (2) containing N_2, CH_4, CO_2 and unreacted CO and H_2 leaves the reactor at 37°C.

The effluent leaving the reactor (7) containing ethanol, acetic acid/acetate and cells is sent to a filter to separate the liquid phase products (11) from the recycled cells (4 and 5). In Figure 2, an option is shown for cell removal either by flocculation and settling or centrifugation which may be used in conjunction with or separately from hollow fiber filtration. Several options will thus exist in the prototype plant for cell recycle/cell removal:

- ultrafiltration alone
- ultrafiltration followed by flocculation and settling
- ultrafiltration followed by centrifugation
- flocculation and settling alone
- centrifugation alone

In Figure 2, the cell-rich stream from the hollow fiber filter (8) is sent to cell removal to separate the cells for disposal (9) from the liquid (10). The liquid from cell removal (10) and hollow fiber filtration (11) is then combined as feed (12) to the distillation column.

The distillation column separates the ethanol (15) from the recycle water containing acetic acid/acetate (13). A small purge (14) may be used as needed prior to sending the recycle water (6) to the fermenter. The overhead product (15) from distillation containing ethanol and water is sent to adsorption to produce the final dry ethanol product (16) and regeneration products (17).

Several design options are available for prototype operation, including operation without cell recycle at atmospheric pressure, operation with cell recycle at atmospheric pressure and operation with cell recycle at increased pressure (2.72 atm). In all cases, a reactor 2.0 ft (0.61 m) in diameter will be used, with a height to diameter ratio of 2.0.

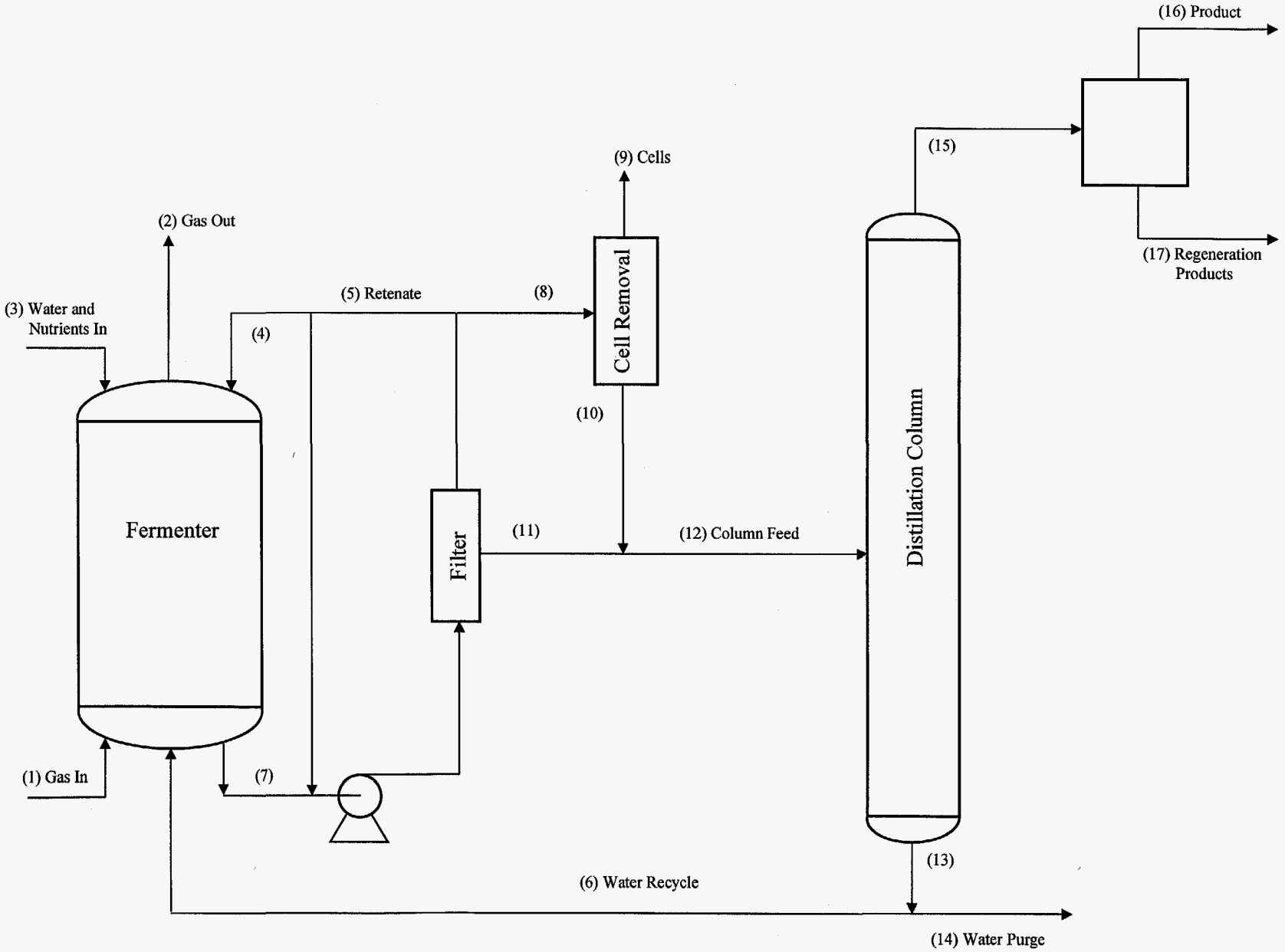

Figure 2. Prototype Schematic

SITE PLAN, EQUIPMENT LAYOUT, PIPING DIAGRAMS AND PROCESS AND INSTRUMENTATION DIAGRAMS

A site plan for the prototype unit is shown in Figure 3. Sufficient area is shown for gas delivery, employee parking and access to the process area. The process area is approximately 784 ft^2 (72.8 m^2) in size.

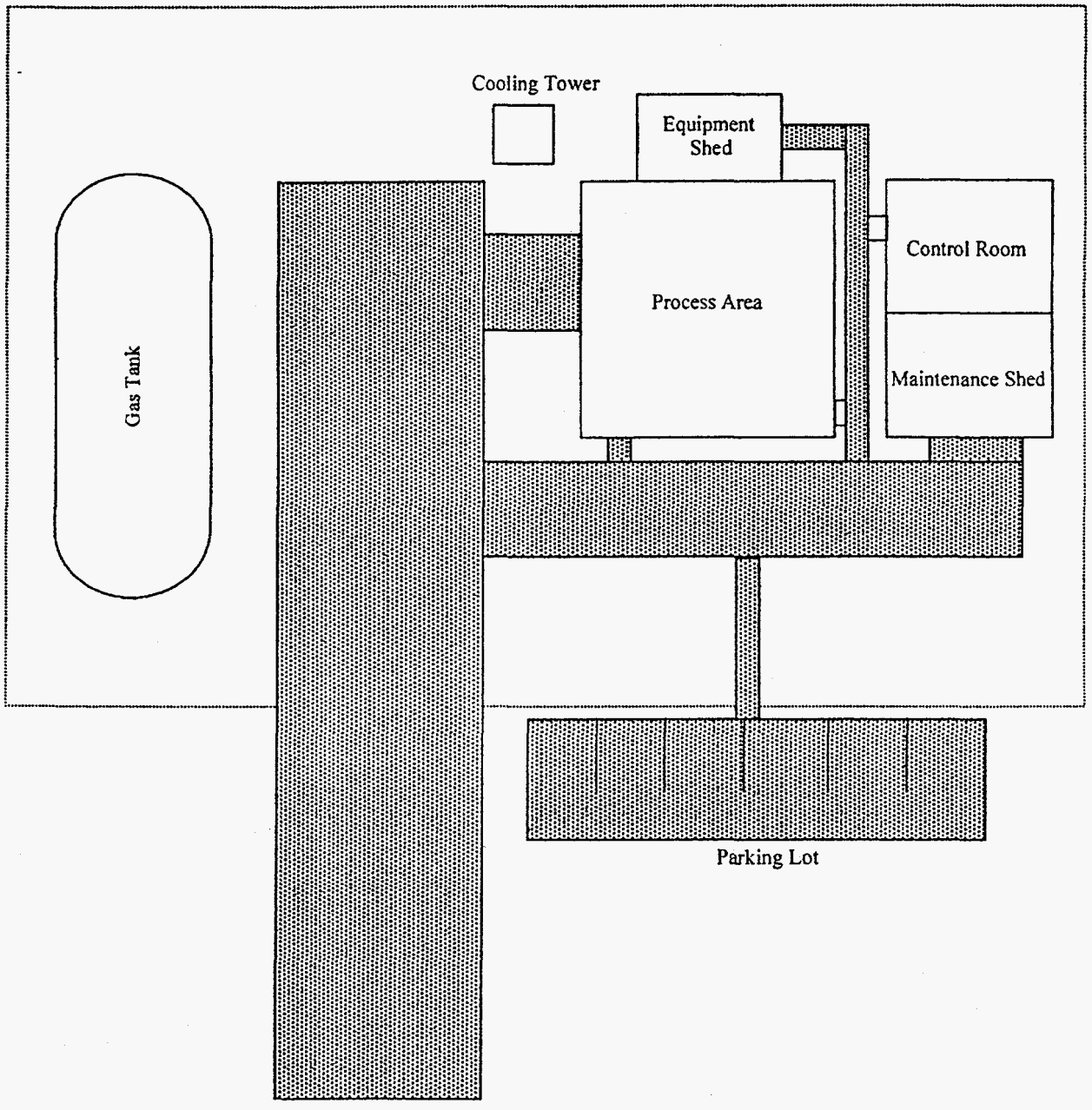

Figure 3. Ethanol Prototype Plant Site Plan

Figure 4 shows the equipment layout. Central to the layout is the reactor, T-101. Other major equipment items to be described later, are the hollow fiber units (HF-1, HF-2), the centrifuge (VF-201A, BC) and the distillation column (DC-401). Figure 5 shows the medium delivery piping, Figure 6 shows the culture and flocculant piping, Figure 7 shows the permeate piping, Figure 8 shows the product recovery piping, Figure 9 shows the feed gas and compressed air piping, Figure 10 shows the steam piping, and Figure 11 shows the utility water piping. Finally, Figure 12 shows the piping and instrumentation diagram including a legend for equipment, piping and instrumentation.

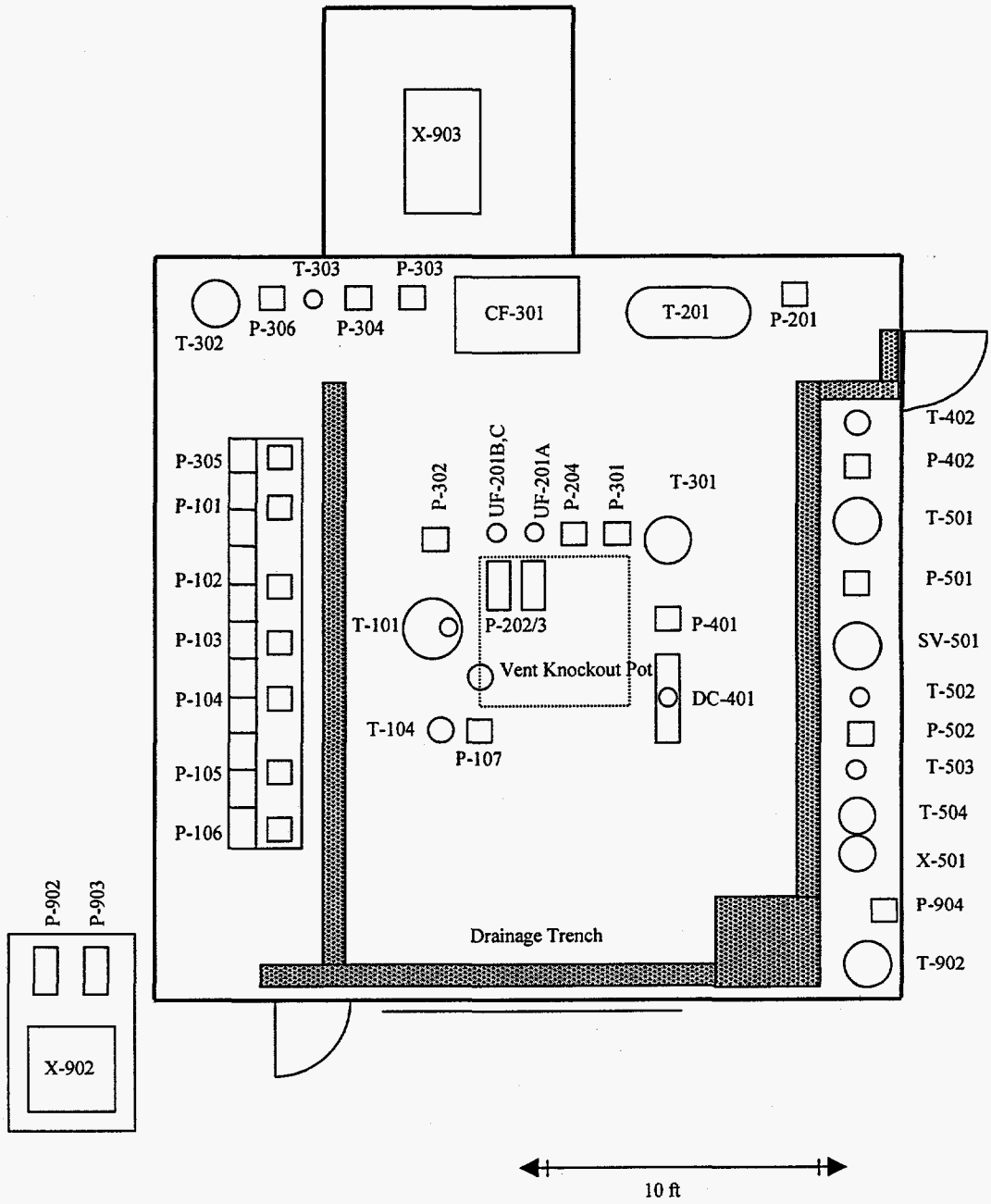

Figure 4. Ethanol Prototype Plant Equipment Layout

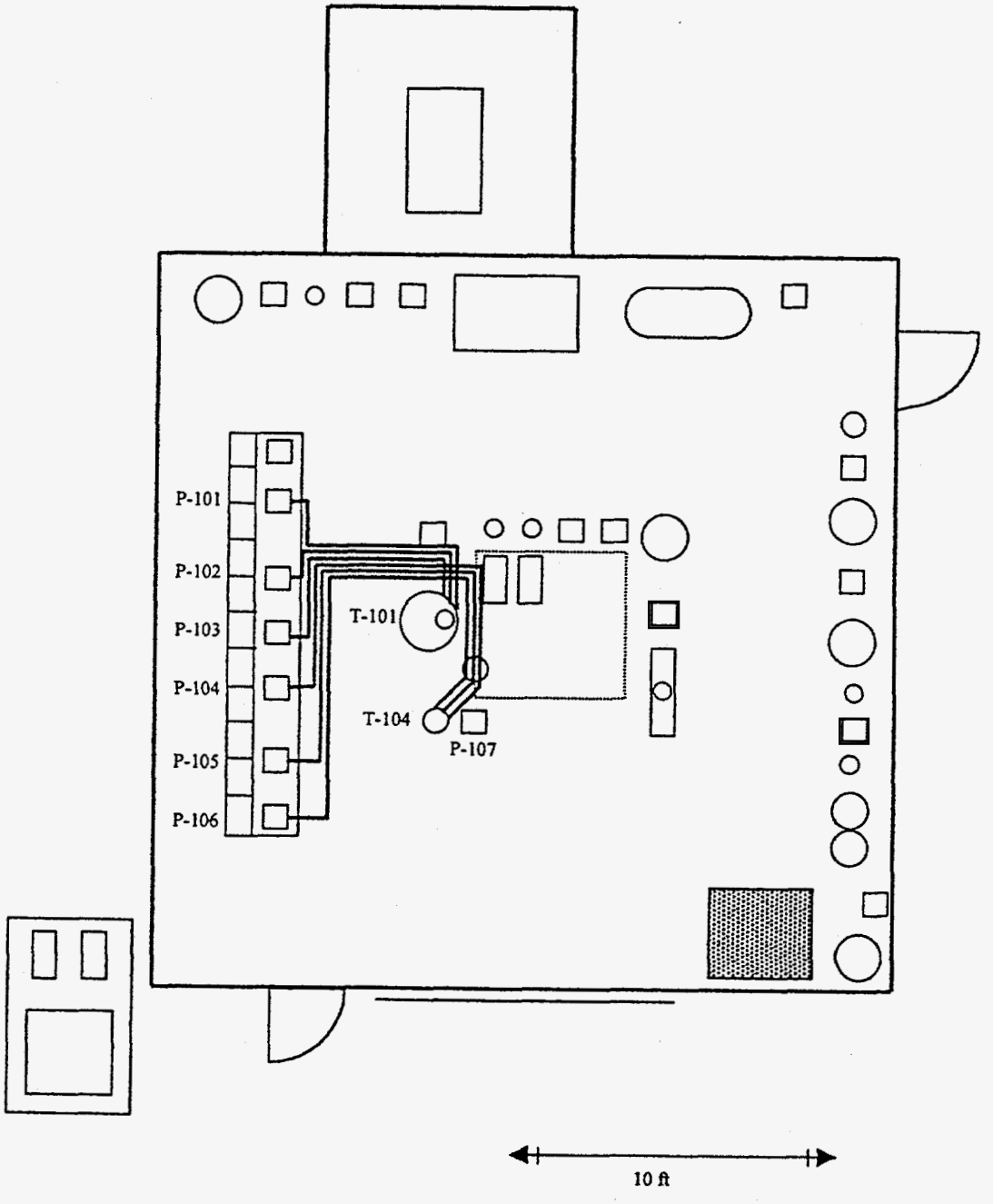

Figure 5. Ethanol Prototype Plant Medium Delivery Piping

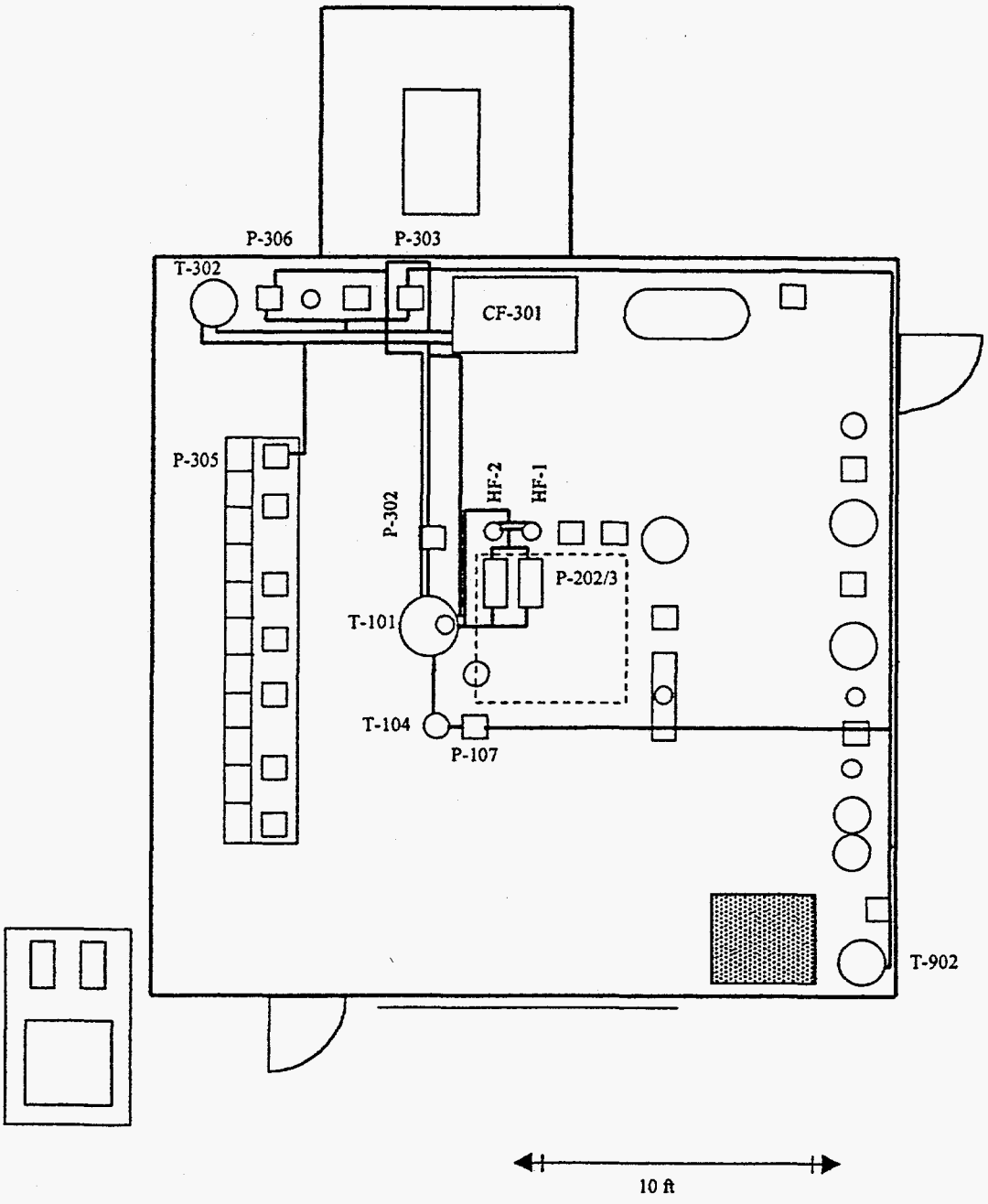

Figure 6. Ethanol Prototype Plant Culture and Flocculant Piping

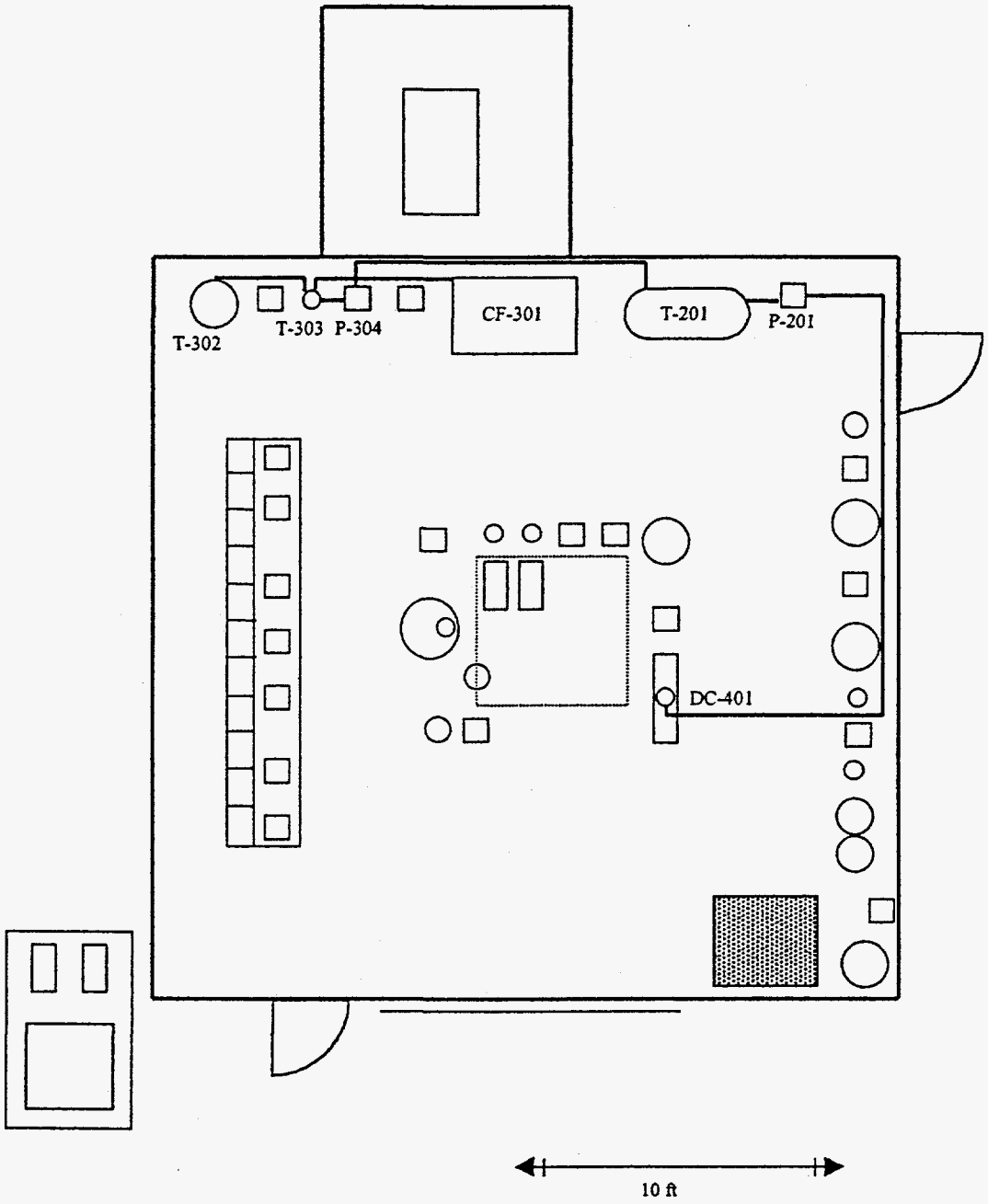

Figure 7. Ethanol Prototype Plant Permeate Piping

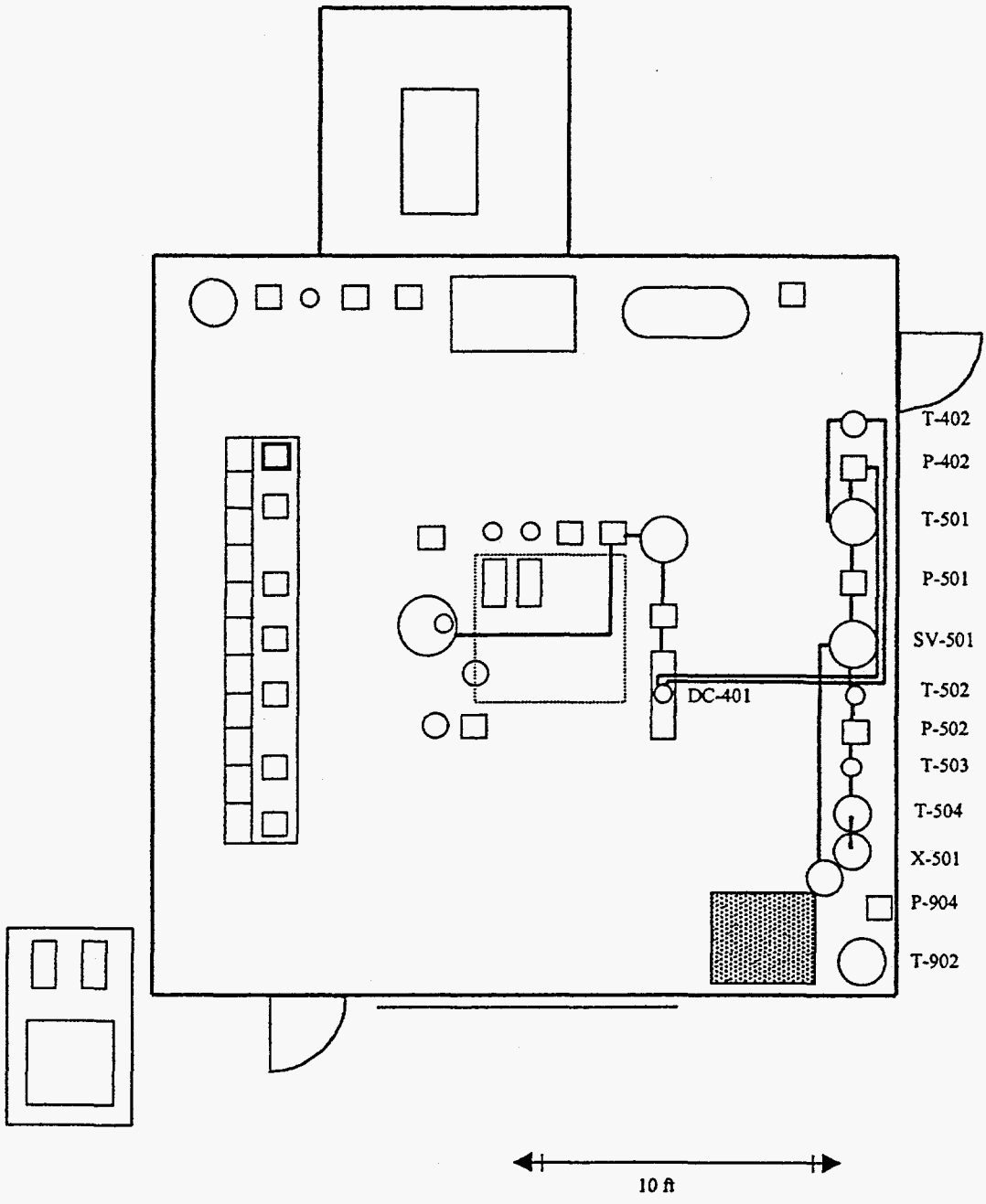

Figure 8. Ethanol Prototype Plant Product Recovery Piping

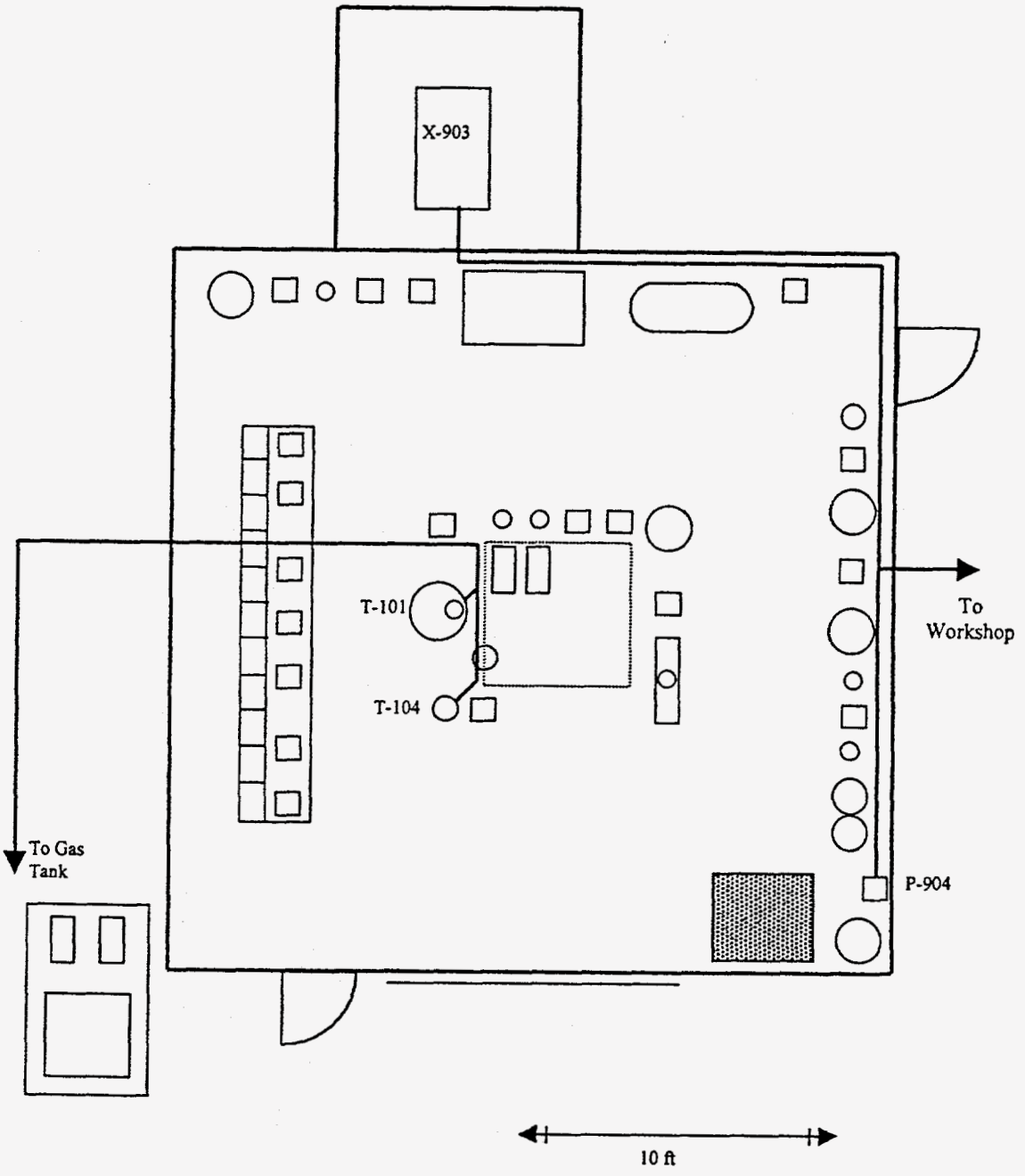

Figure 9. Ethanol Prototype Plant Feed Gas and Compressed Air Piping

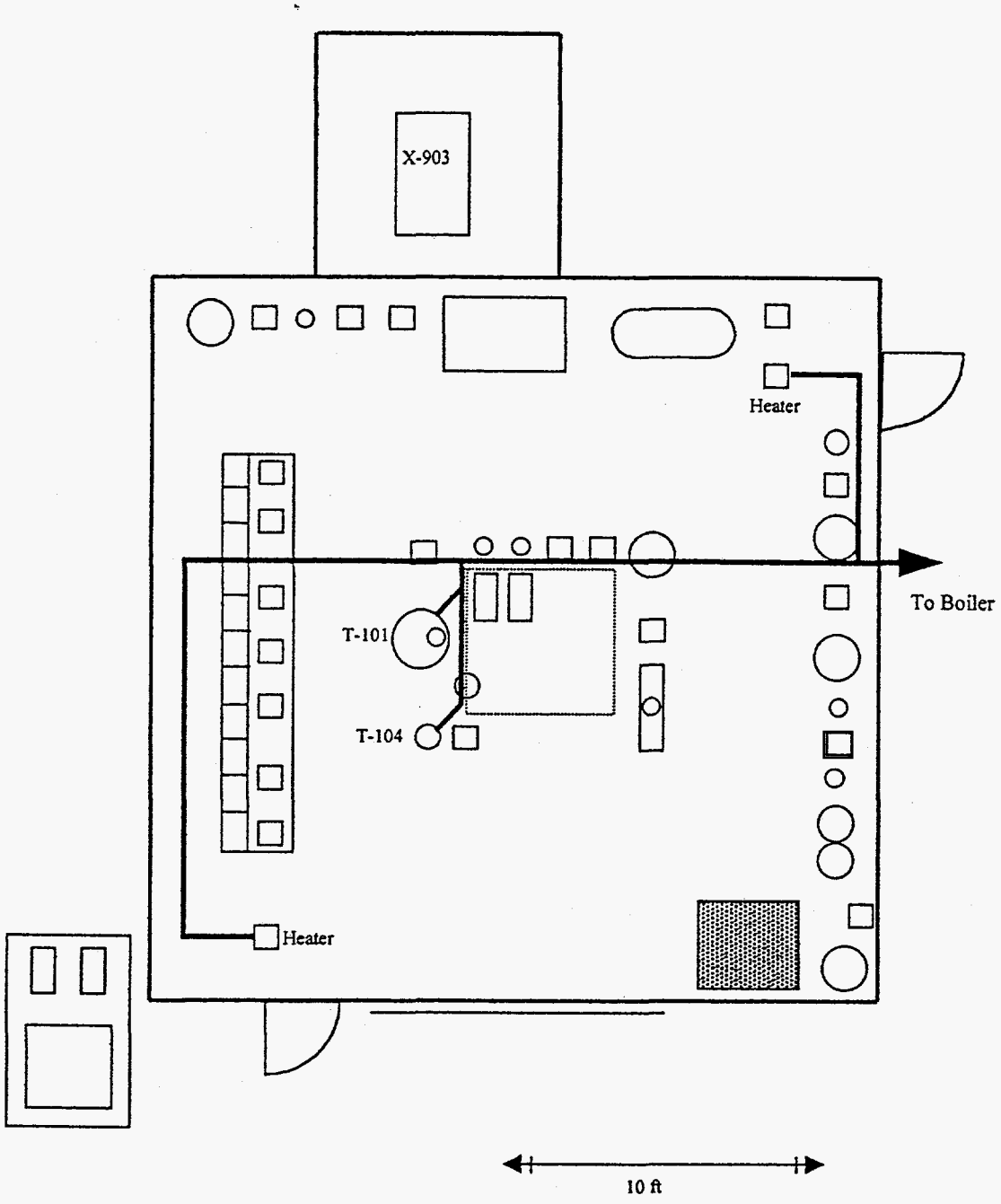

Figure 10. Ethanol Prototype Plant Steam Piping

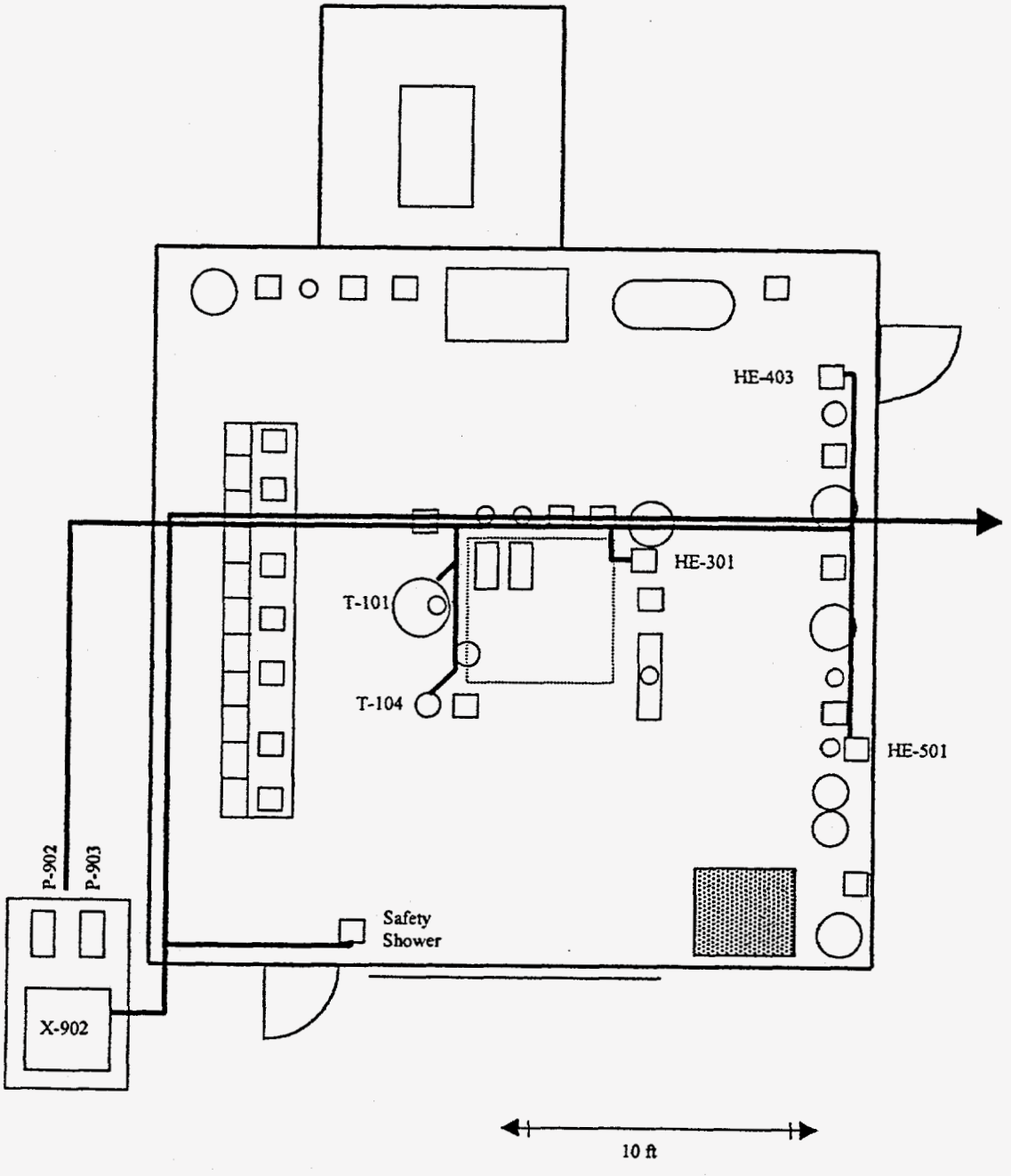

Figure 11. Ethanol Prototype Plant Utility Water Piping

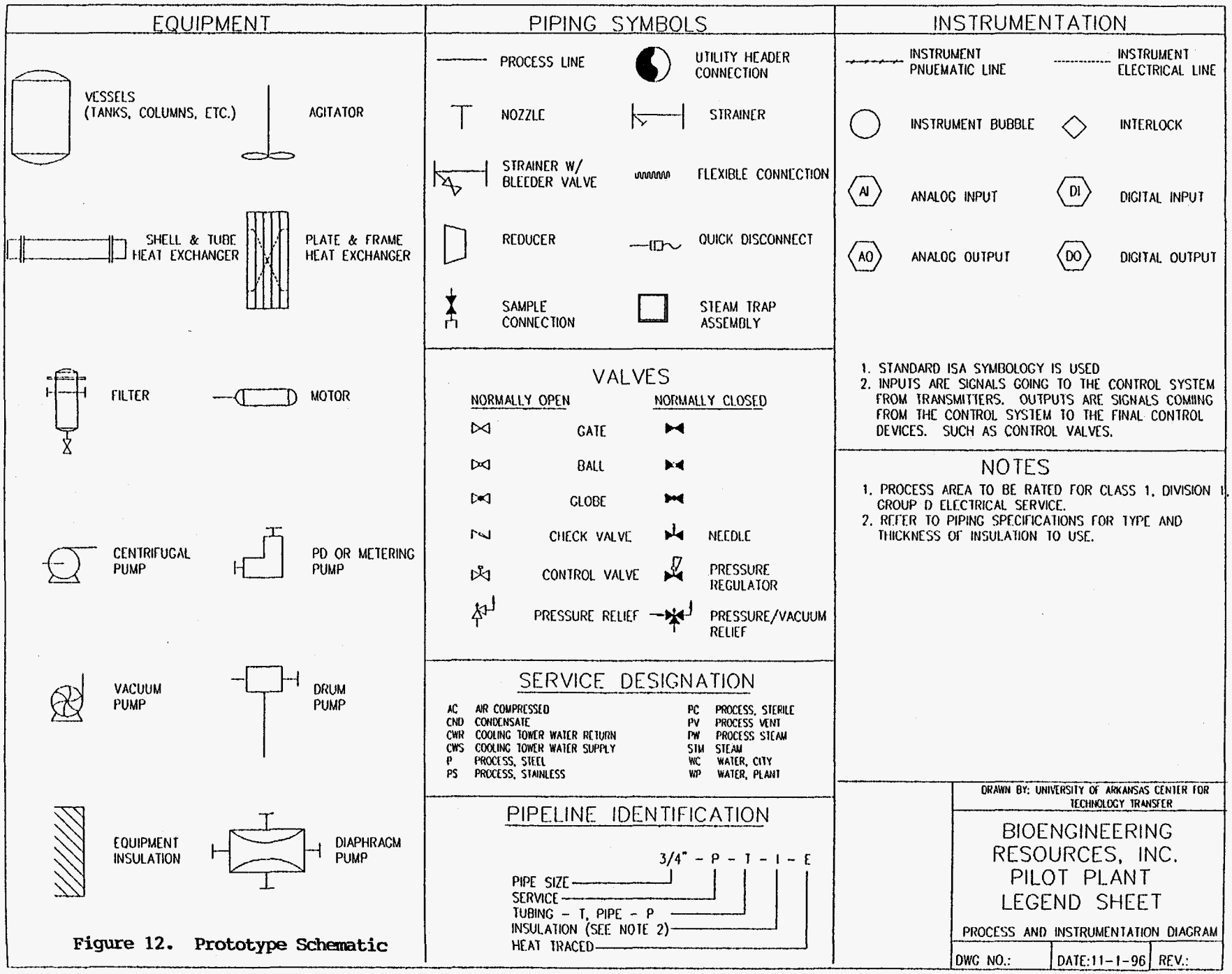

Figure 12. Prototype Schematic

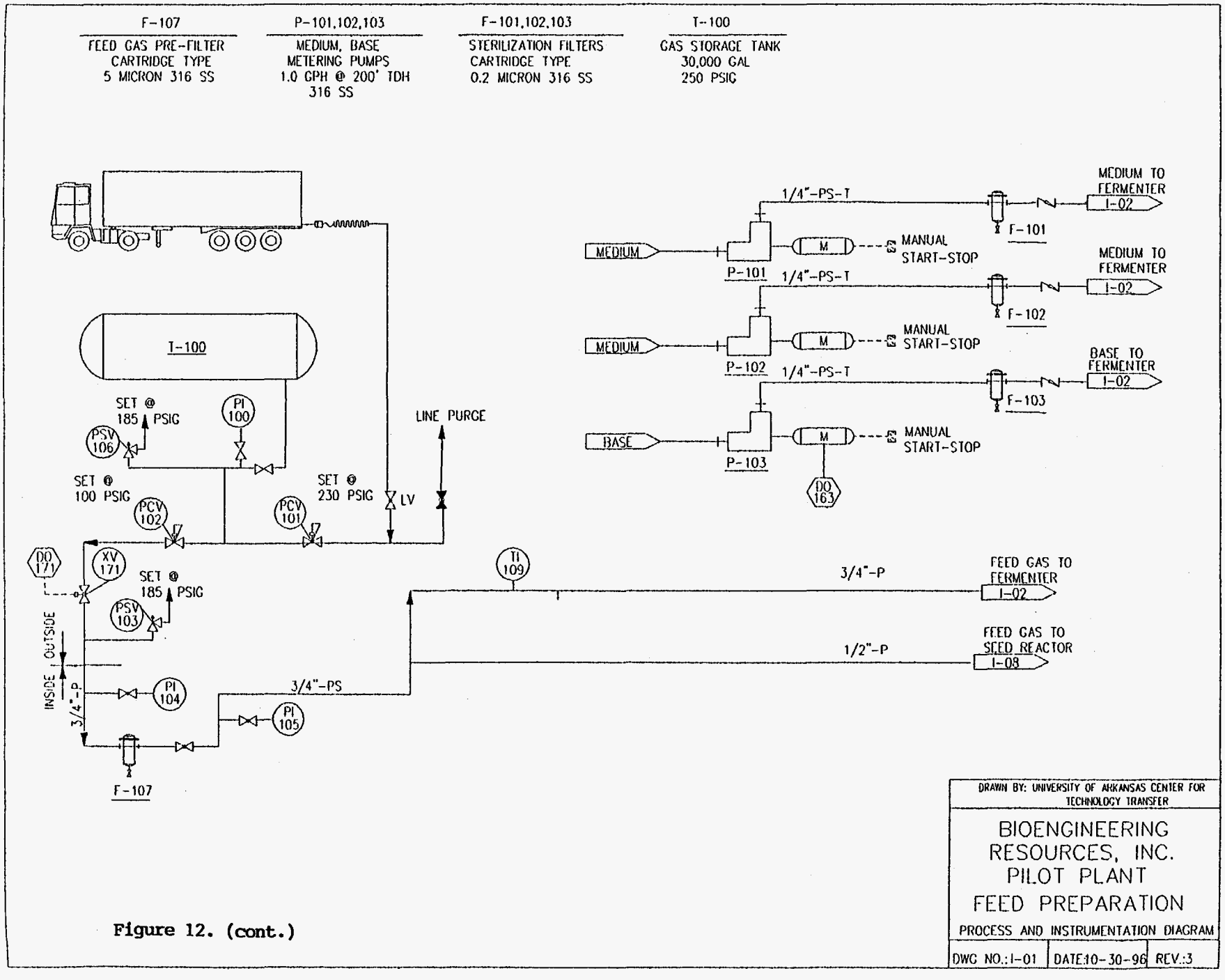

Figure 12. (cont.)

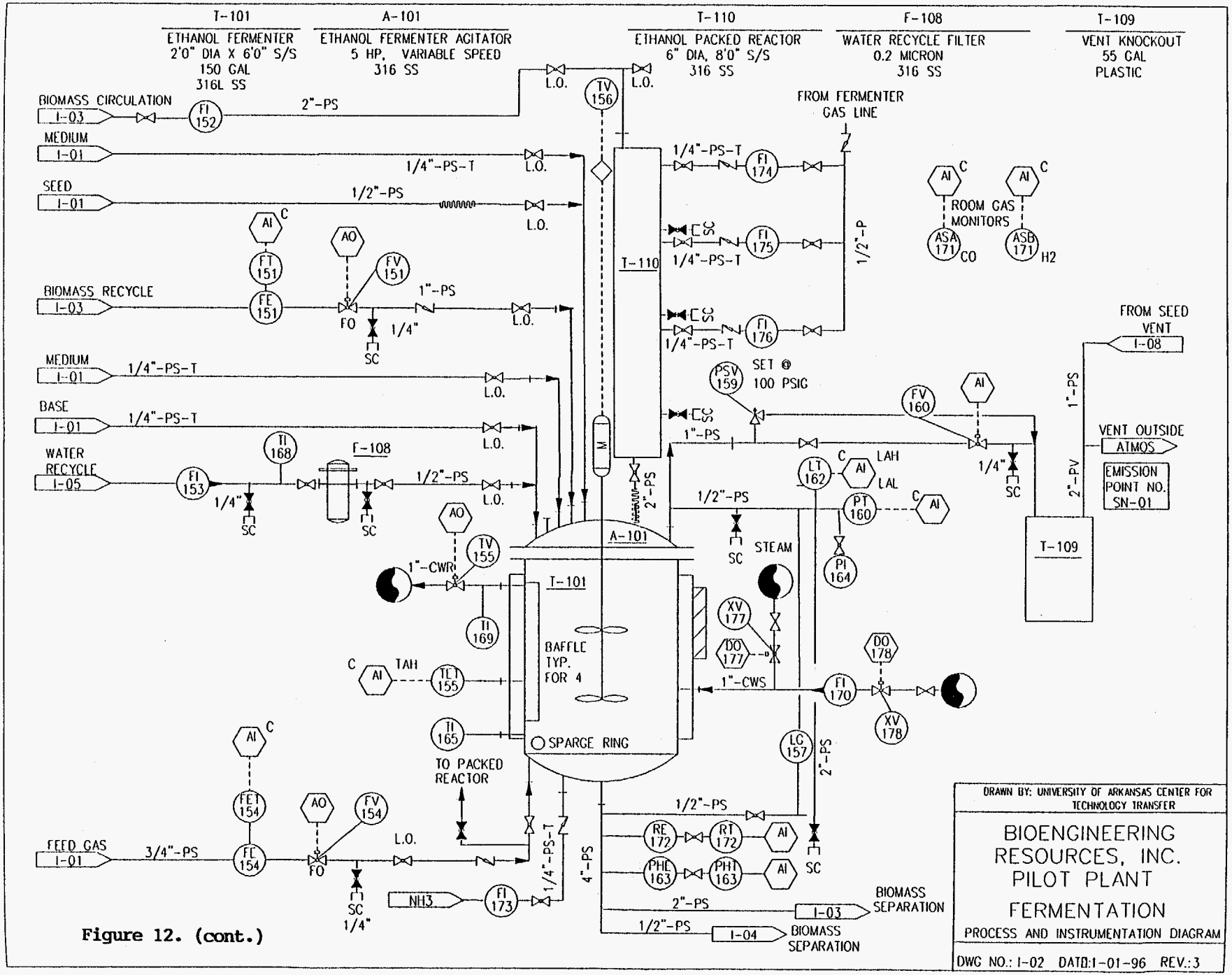

Figure 12. (cont.)

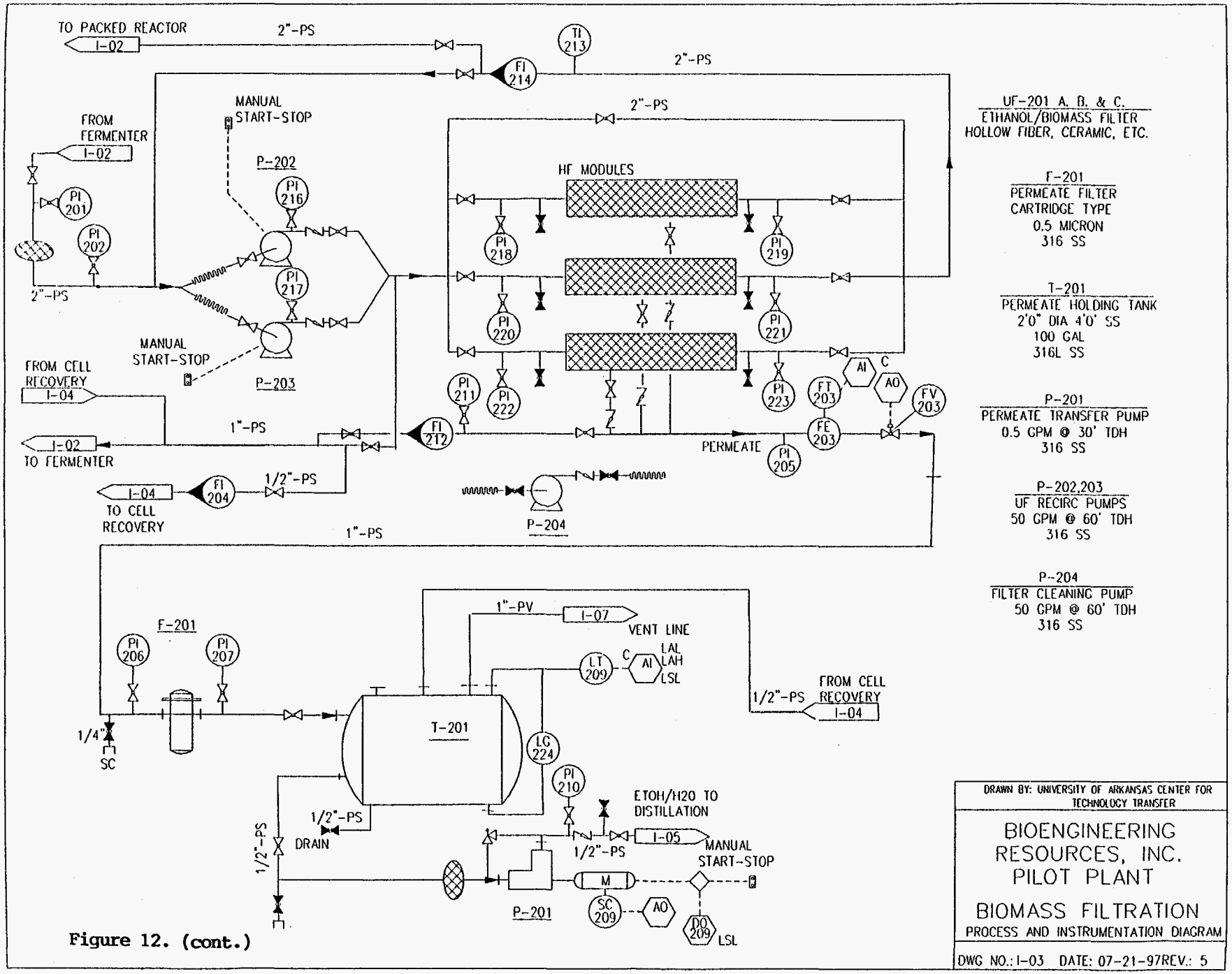

Figure 12. (cont.)

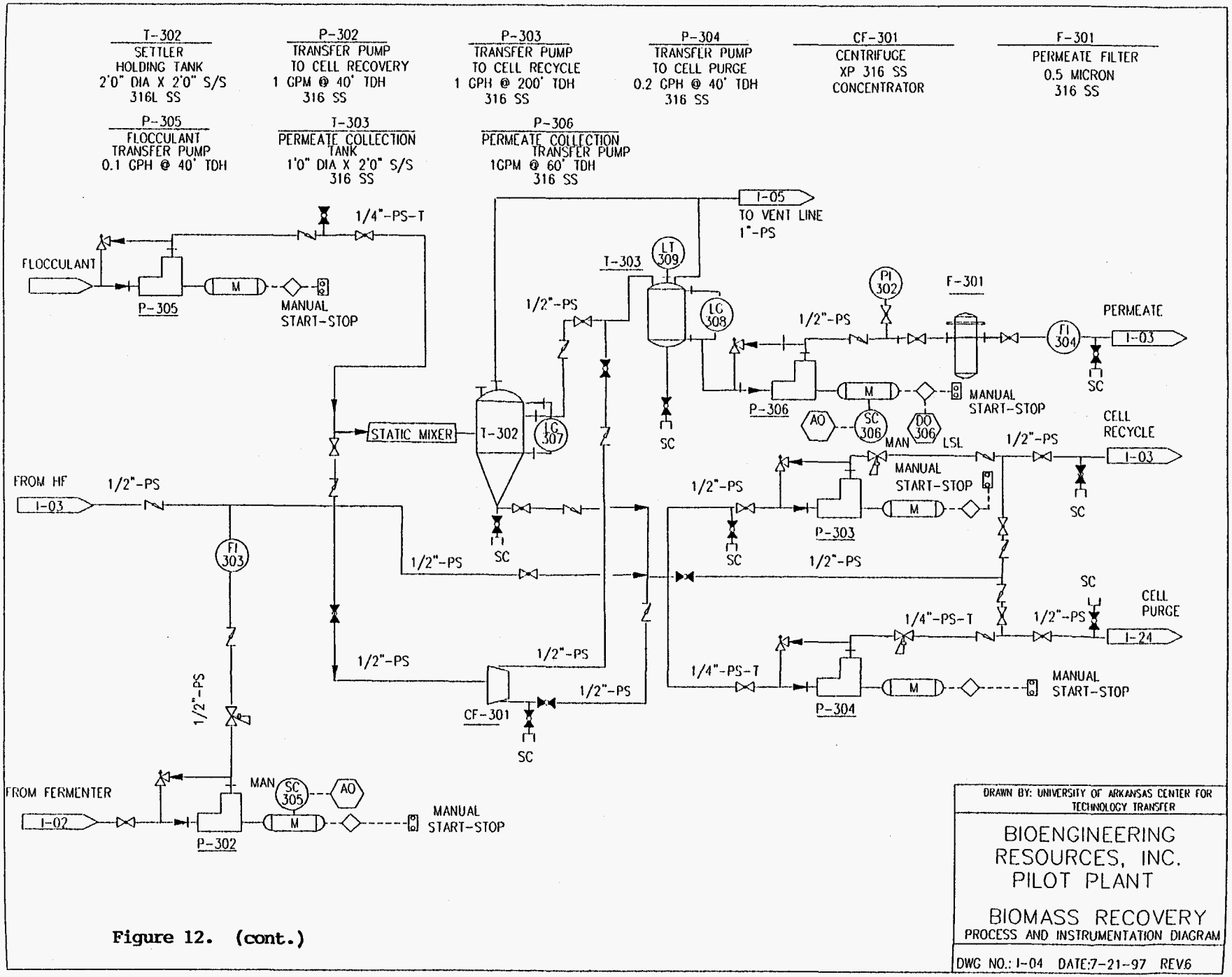

Figure 12. (cont.)

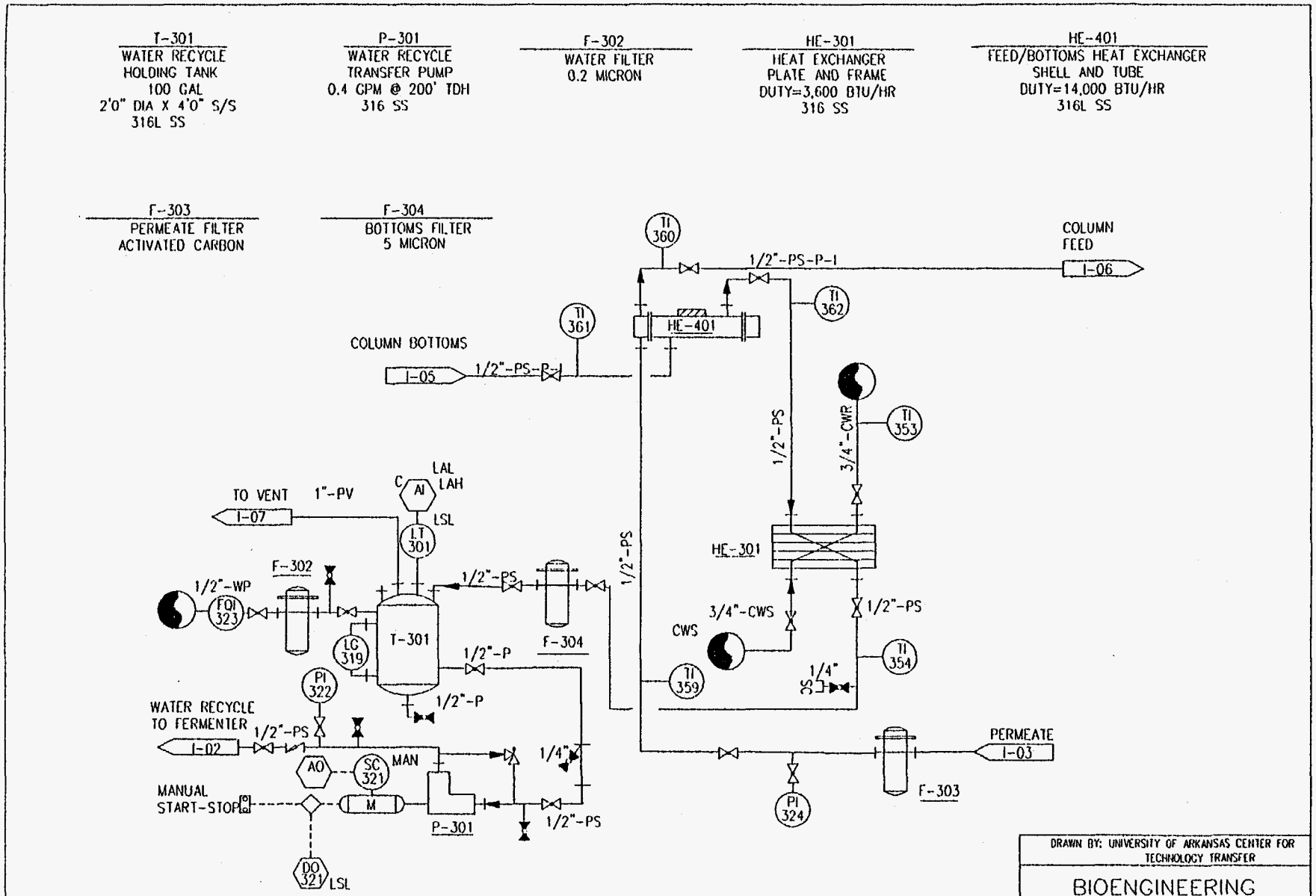

Figure 12. (cont.)

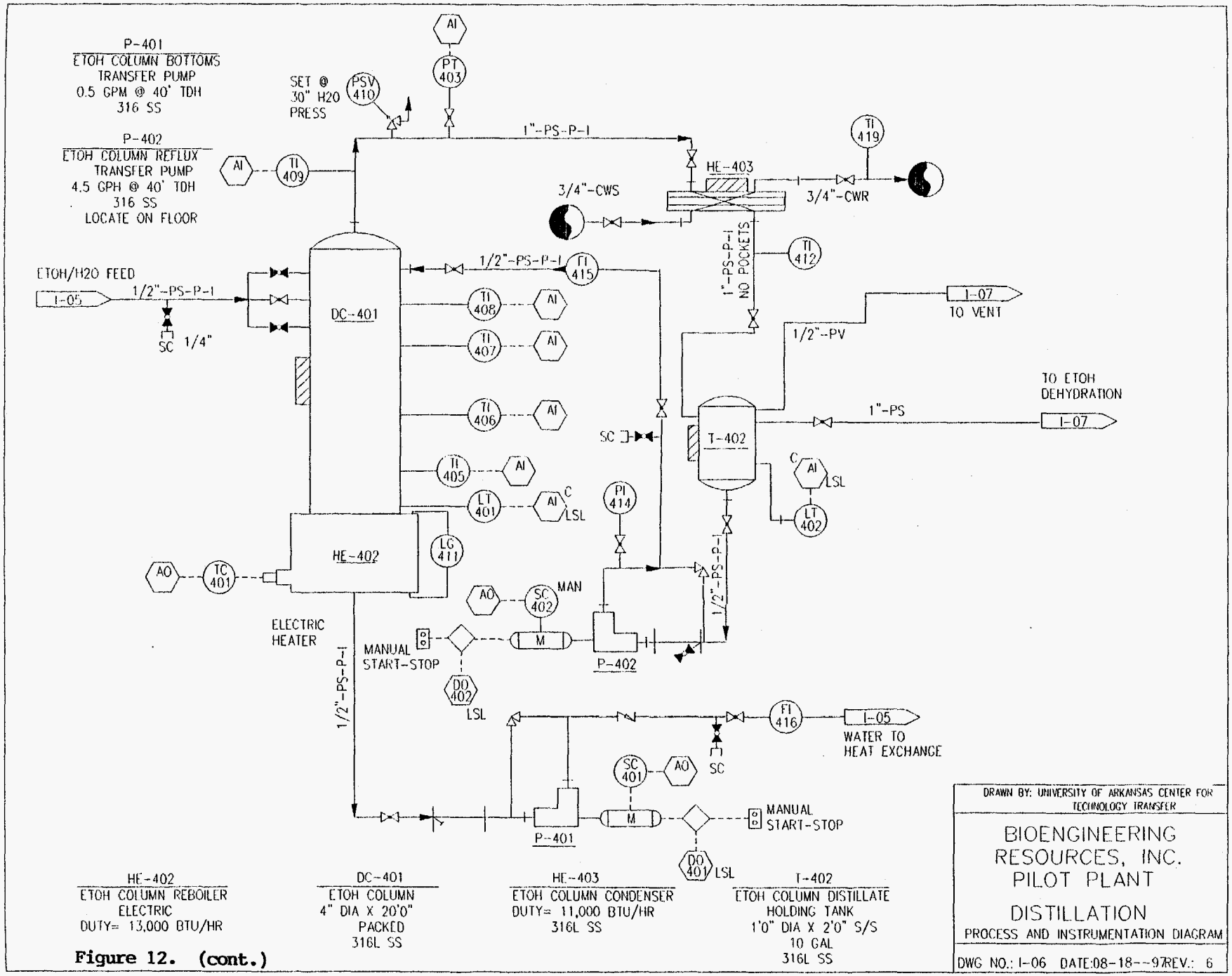

Figure 12. (cont.)

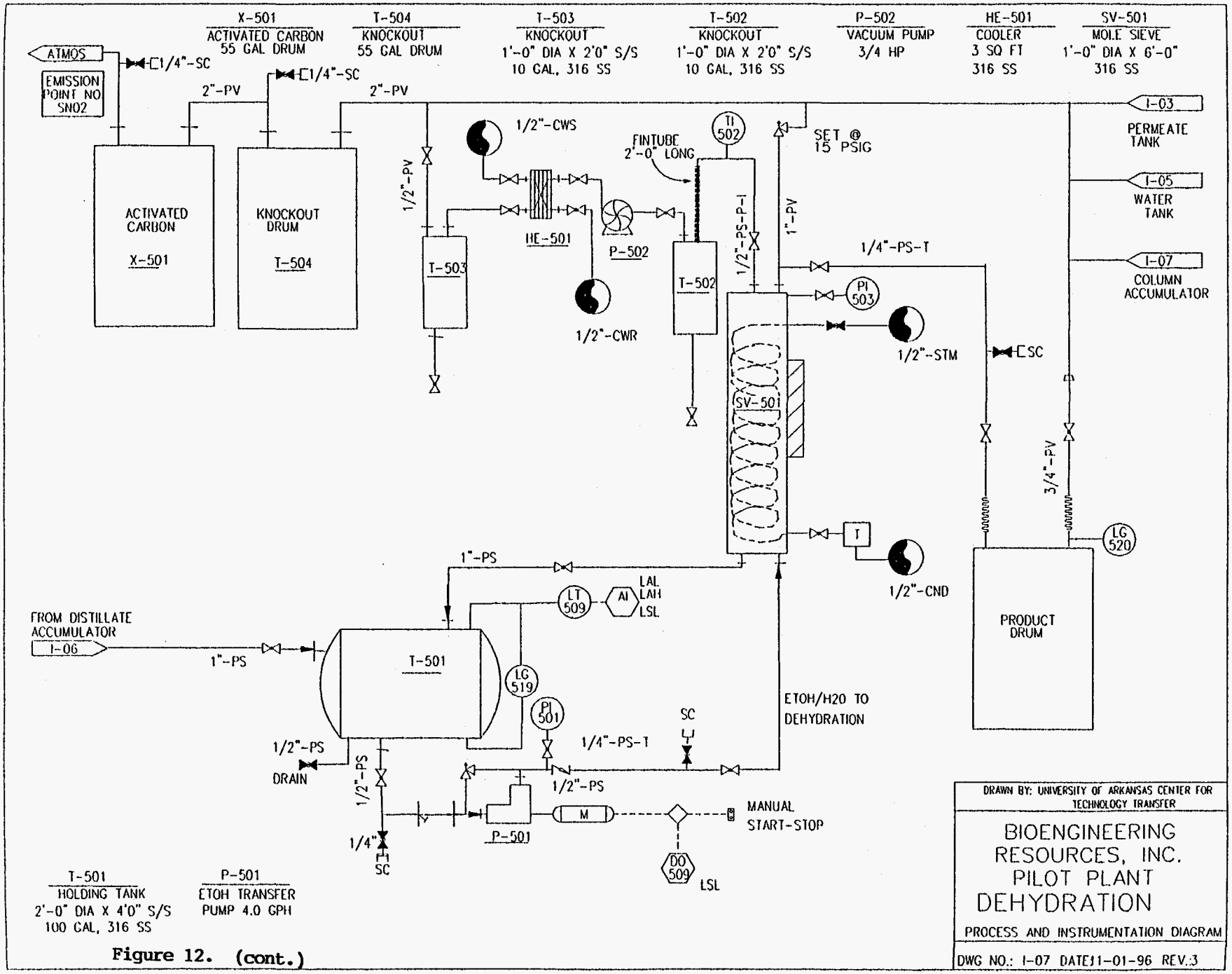

Figure 12. (cont.)

P-104,105,106	T-104	A-103	F-104,105,106	P-107
MEDIUM, BASE METERING PUMPS 1.0 GPH @ 200' TDH 316 SS	SEED INOCULUM TANK 40 GAL, 316 SS	SEED INOCULUM TANK AGITATOR 1 HP	STERILIZATION FILTERS 0.2 MICRON 316 SS	CULTURE PURGE PUMP 1 GPH 200' @ TDH 316 SS

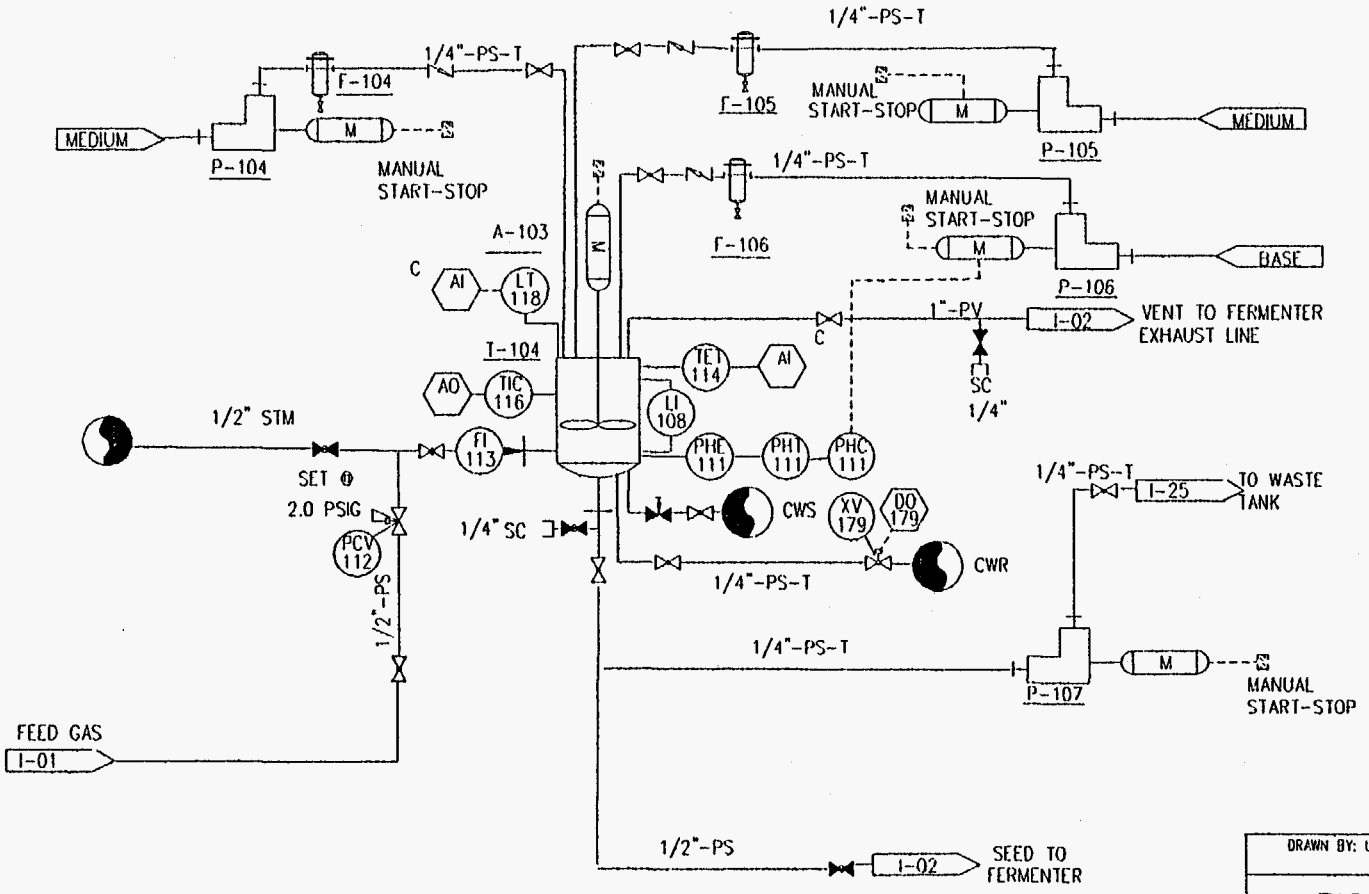

Figure 12. (cont.)

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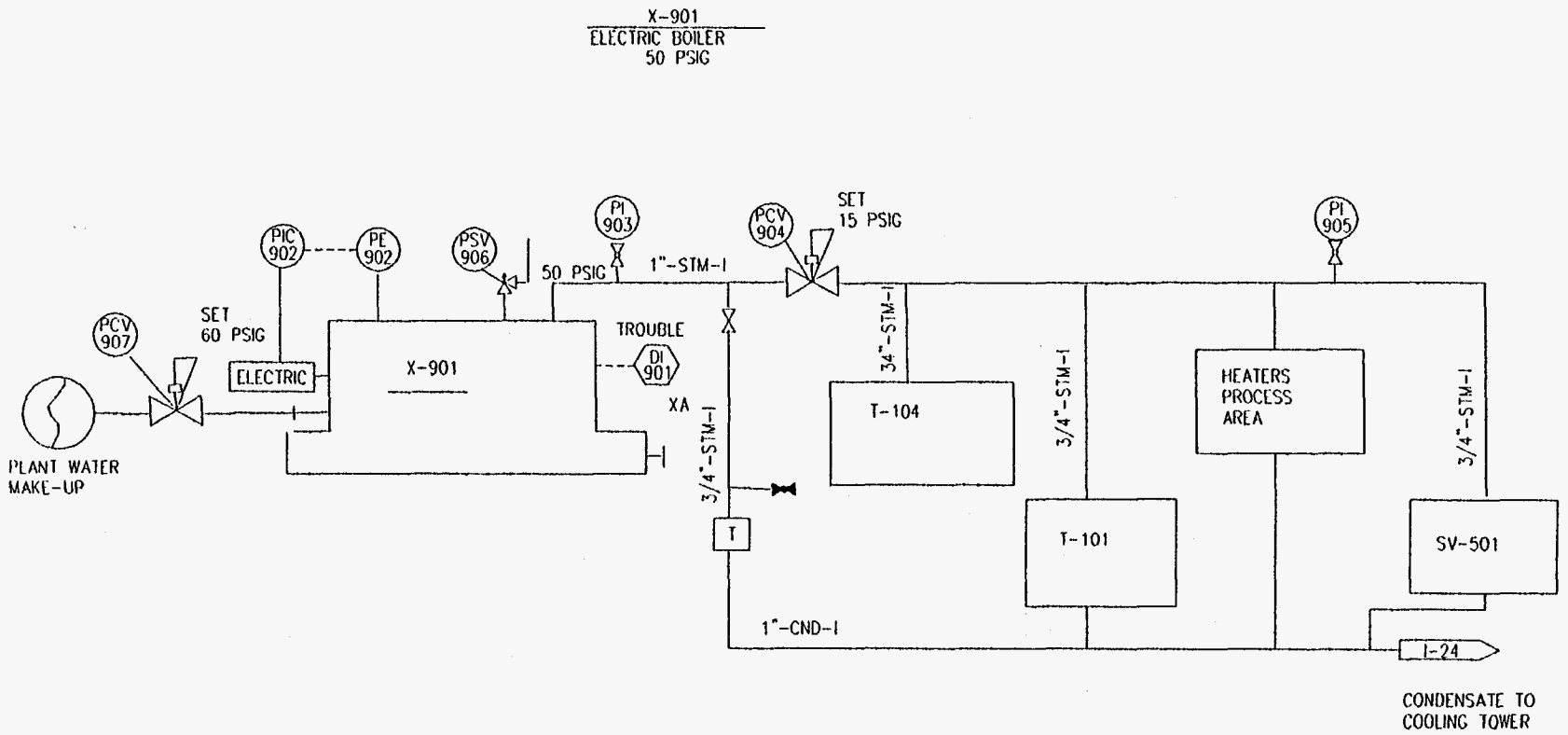
BIOENGINEERING RESOURCES, INC.
PILOT PLANT
SEED REACTOR
PROCESS AND INSTRUMENTATION DIAGRAM

DWG NO.: I-08	DATE: 11-01-96	REV.: 3



DRAWN BY: UNIVERSITY OF ARKANSAS CENTER FOR TECHNOLOGY TRANSFER

BIOENGINEERING RESOURCES, INC.
PILOT PLANT
STEAM/CONDENSATE SYSTEM
PROCESS AND INSTRUMENTATION DIAGRAM

DWG NO.: I-21 DATE: 10-30-96REV.:2

Figure 12. (cont.)

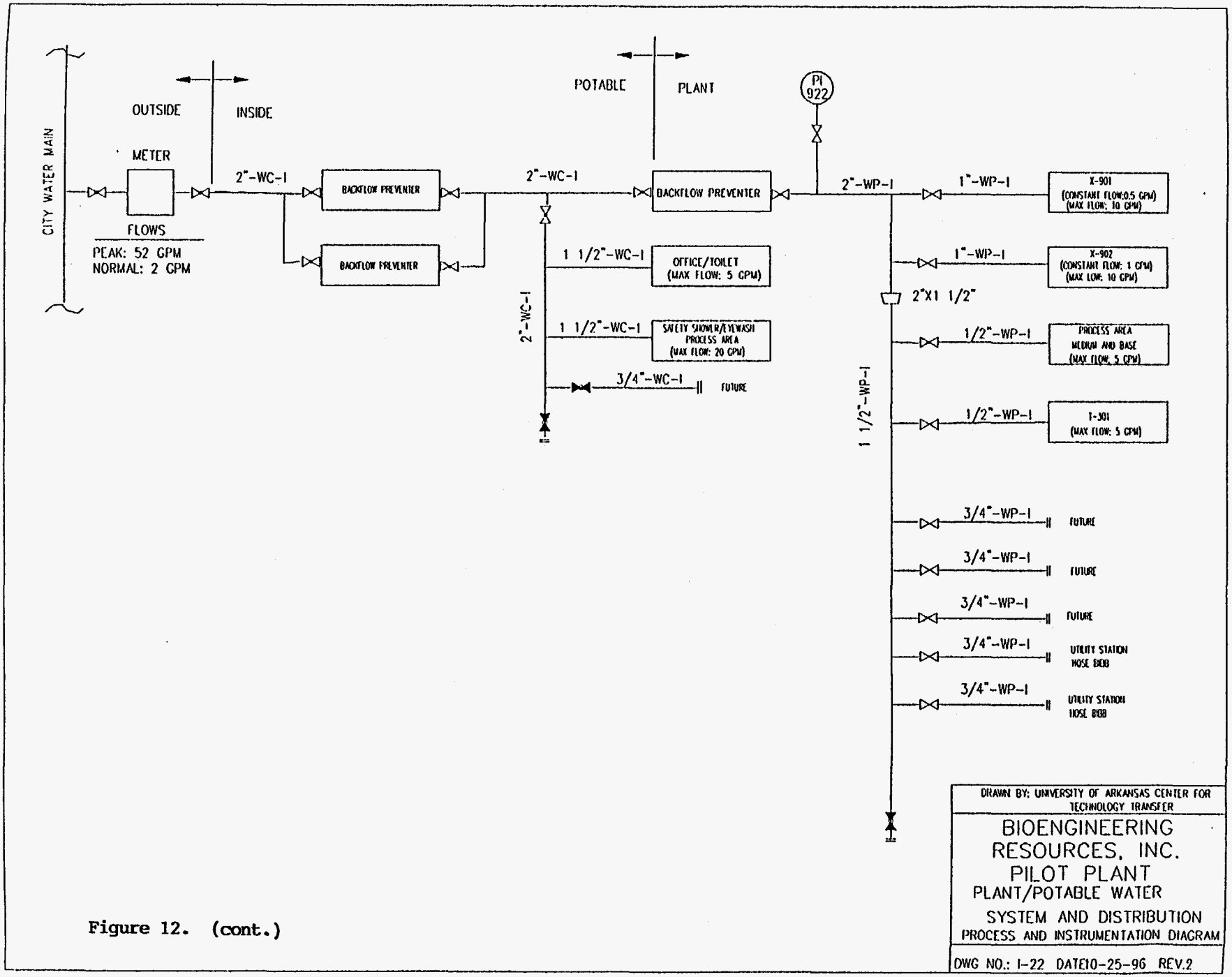


Figure 12. (cont.)

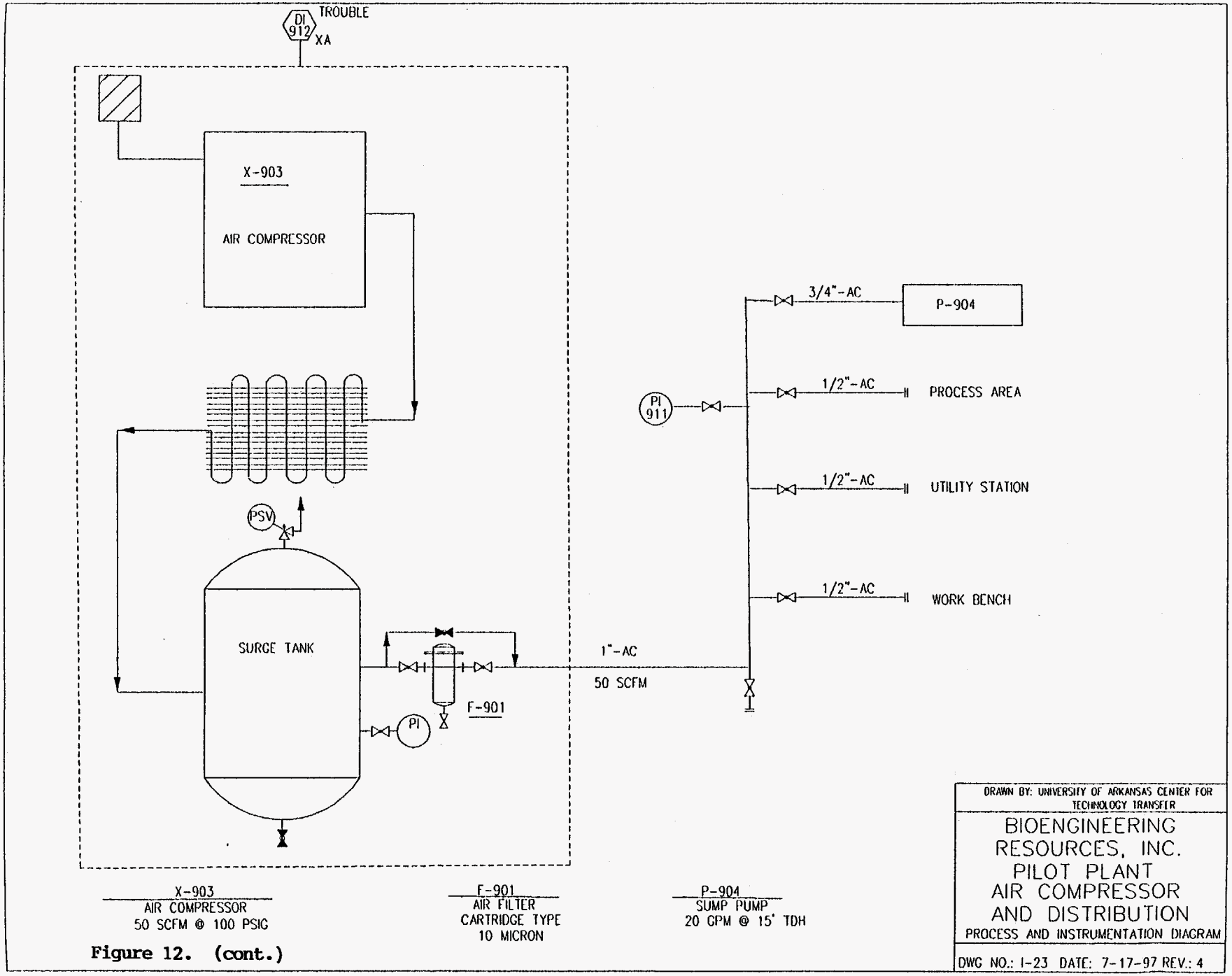
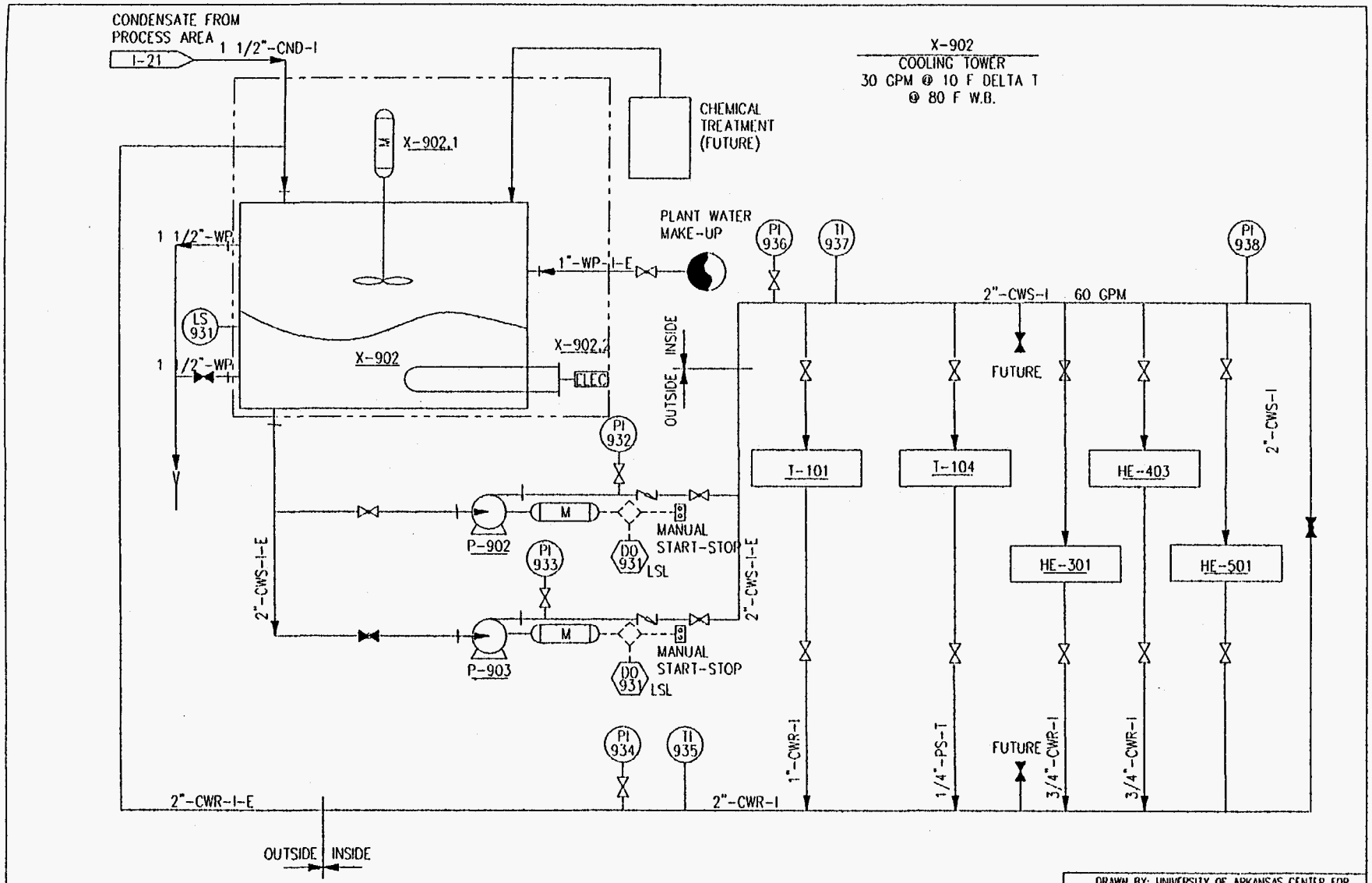


Figure 12. (cont.)



P-902
COOLING TOWER TRANSFER
PUMP NO. 1
30 GPM @ 115' TDH
D.I.

P-903
COOLING TOWER TRANSFER
PUMP NO. 2
30 GPM @ 115' TDH
D.I.

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BIOENGINEERING RESOURCES, INC.
PILOT PLANT
COOLING TOWER SYSTEM AND DISTRIBUTION
PROCESS AND INSTRUMENTATION DIAGRAM

DWG NO.: I-24 DATE: 11-1-96 REV.: 3

Figure 12. (cont.)

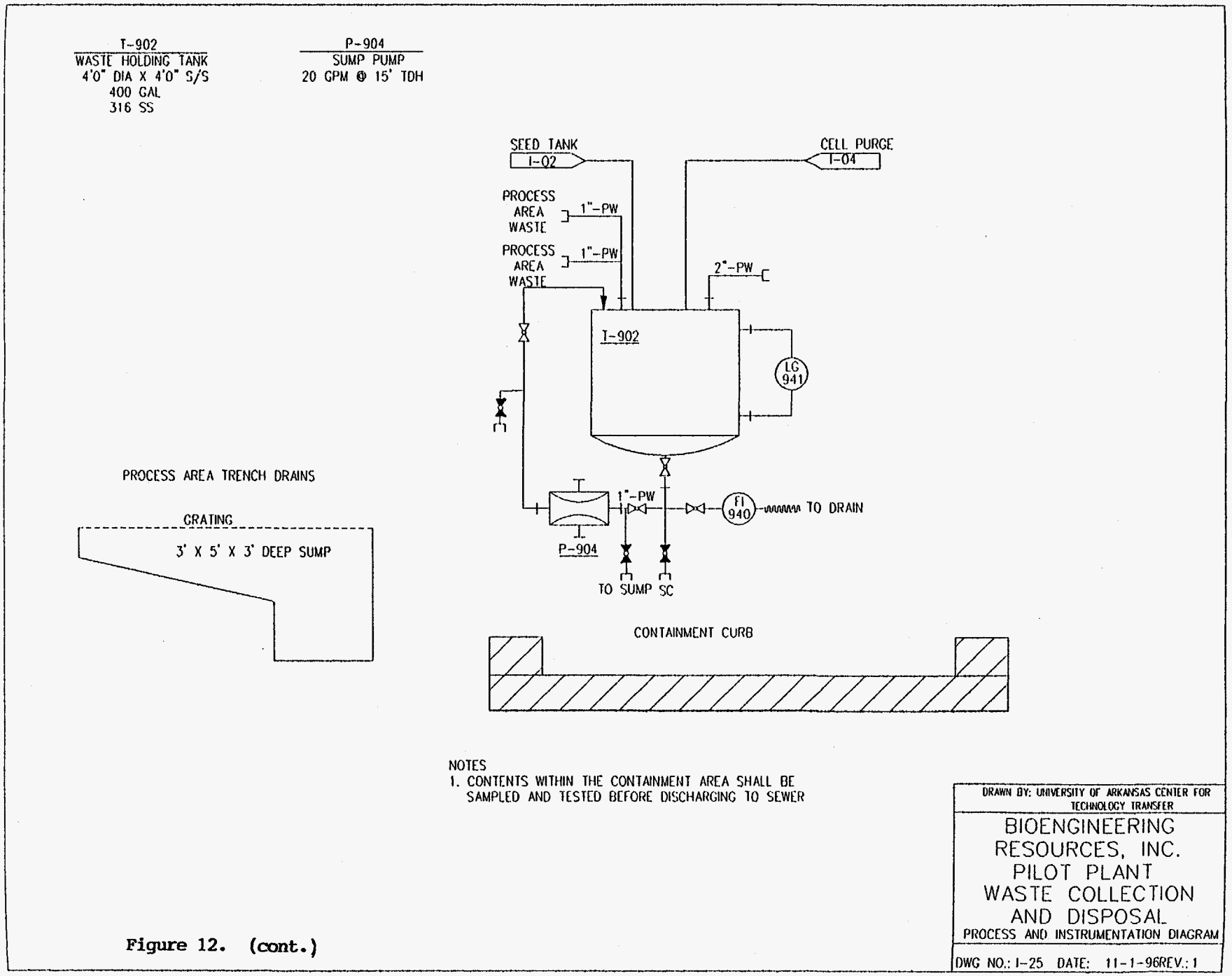


Figure 12. (cont.)

ESTIMATED EQUIPMENT COSTS

Table 2 presents a description of the various pieces of equipment for the prototype unit, as well as their estimated costs. The estimated equipment cost numbers are not based on quotes submitted for this equipment. Rather, these numbers are based on the cost of the equipment purchased for the BRI acetic acid pilot plant plus inflation. These numbers should be viewed as estimates only.

A summary of the equipment costs by section is shown in Table 3. The total estimated cost for the reactor section is $104,000 with the reactor and agitator accounting for 56 percent of this cost. The total estimated cost for the biomass separation section of the prototype is $67,000. The centrifuge is the largest cost item in this section, accounting for 37 percent of the estimated cost. The estimated cost of the product recovery section is $66,000 with the distillation column accounting for 42 percent of the estimated cost. Finally, the waste handling section requires about $6,500. The total estimated equipment cost is $244,000.

Equipment Number	Equipment Name	Equipment Description	Est. Cost
AGITATORS			
A-101	Ethanol Fermenter Agitator	316 SS	35,000
A-101.1	Motor	Variable Speed, 5Hp, 560 rpm	
A-103	Seed Inoculum Tank Agitator	316 SS	400
A-103.1	Motor	1 Hp, 1800 rpm	
COLUMNS			
DC-401	Ethanol Column	4"dia. x 20' 316 SS Design Pressure = 14 psig & full vacuum, Design Temperature = 220 deg F	28,000
DC-401.1	Column Packing	Top 10' Structured SS Packing, Bottom Packed	
SV-501	3A Molecular Sieve	1'-0"dia x 6'-0" 316L SS, 1/4" SS Heating Coil, Insulated	3,200
FILTERS			
F-101	Medium Sterilization Filter	Cartridge Type, 0.2 micron, 316 SS	150
F-102	Medium Sterilization Filter	Cartridge Type, 0.2 micron, 316 SS	150
F-103	Base Sterilization Filter	Cartridge Type, 0.2 micron, 316 SS	150
F-104	Medium Sterilization Filter	Cartridge Type, 0.2 micron, 316 SS	150
F-105	Medium Sterilization Filter	Cartridge Type, 0.2 micron, 316 SS	150

Table 2. Estimated Equipment Costs (1 of 7)

Equipment Number	Equipment Name	Equipment Description	Est. Cost
F-106	Base Sterilization Filter	Cartridge Type, 0.2 micron, 316 SS	150
F-107	Feed Gas Pre-filter	Cartridge Type, 5 micron, 316 SS	150
F-108	Water Recycel Filter	Cartridge Type, 0.2 micron, 316 SS	150
F-201	Permeate Filter	Cartridge Type, 0.5 micron, 316 SS	150
F-301	Cell Removal System Permeate Filter	Cartridge Type, 0.5 micron, 316 SS	150
F-302	Water Filter	Cartridge Type, 0.2 micron, Plastic	150
F-303	Permeate Filter	Activated Carbon Cartridges, Plastic	500
F-304	Bottoms Filter	Cartridge Type, 5 micron, 316 SS	150
F-901	Air Filter	Cartridge Type, 10 micron, Carb Stl	150
ULTRAFILTERS			
UF-201A	Biomass Ultrafilter	Ceramic	7,800
UF-201B	Biomass Ultrafilter	Spiral	2,800
UF-201C	Biomass Ultrafilter	Tubular	2,800
CENTRIFUGE			
CF-301	Centrifuge	Continuous discharge concentrator, 2.5 gpm, 316 SS	25,000

Table 2. Estimated Equipment Costs (2 of 7)

Equipment Number	Equipment Name	Equipment Description	Est. Cost
HEAT EXCHANGERS			
HE-301	Heat Exchanger	Plate & Frame, 3600 BTU/HR, 316 SS	1,200
HE-401	Feed/Bottoms Heat Exchanger	Shell & Tube, 14,000 BTU/HR, 316L SS	2,500
HE-402	Ethanol Column Reboiler	Electric Immersion Heater, 6KW, 13,000 BTU/HR, 316 SS	3,000
HE-403	Ethanol Column Condenser	11,000 BTU/HR, 316 SS	2,100
HE-501	Vapor Recovery Cooler	3 sq. ft., 316 SS	1,200
PUMPS			
P-101	Fermenter Medium Pump	Metering Pump, 1.0 gph, 200' TDH, 316 SS, 1/4 Hp, 1800 rpm	2,100
P-102	Fermenter Medium Pump	Metering Pump, 1.0 gph, 200' TDH, 316 SS, 1/4 Hp, 1800 rpm	2,100
P-103	Fermenter Base Pump	Metering Pump, 1.0 gph, 200' TDH, 316 SS, 1/4 Hp, 1800 rpm	2,100
P-104	Seed Medium Pump	Metering Pump, 1.0 gph, 200' TDH, 316 SS, 1/4 Hp, 1800 rpm	2,100
P-105	Seed Medium Pump	Metering Pump, 1.0 gph, 200' TDH, 316 SS, 1/4 Hp, 1800 rpm	2,100

Table 2. Estimated Equipment Costs (3 of 7)

Equipment Number	Equipment Name	Equipment Description	Est. Cost
P-106	Seed pH Pump	Metering Pump, 1.0 gph, 200' TDH, 316 SS, 1/4 Hp, 1800 rpm	2,100
P-107	Seed Culture Purge Pump	Metering Pump, 1.0 gph, 200' TDH, 316 SS, 1/4 Hp, 1800 rpm	2,100
P-201	Permieate Transfer Pump	Speed Control, 0.5 gpm, 30'TDH, 316 SS, 1/4 Hp, 1800 rpm	3,600
P-202,203	UF Recirculation Pump	Centrifugal, 50 gpm, 60' TDH, 316 SS 2 Hp, 3650 rpm	1,800
P-204	Filter Cleaning Pump	Speed Control, 50 gpm, 60' TDH, 316 SS, 2 Hp, 3650 rpm	1,800
P-301	Water Recycle Transfer Pump	Speed Control, 0.4 gpm, 200' TDH, 316 SS, 1 Hp, 1800 rpm	3,600
P-302	Transfer Pump to Cell Recovery	Speed Control, 1 gpm, 40' TDH, 316 SS, 1/2 Hp, 1800 rpm	2,100
P-303	Transfer Pump to Cell Recycle	Metering, 1 gpm, 200' TDH, 316 SS, 1/4 Hp, 1800	2,100
P-304	Transfer Pump to Cell Purge	Metering, 0.2 gph, 40' TDH, 316 SS 1/4 Hp, 1800 rpm	2,100
P-305	Flocculent Transfer Pump	Metering, 0.1 gph, 40' TDH, 316 SS 1/4 Hp, 1800 rpm	2,100
P-306	Permeate Collection Transfer	Metering, 1 gph, 60' TDH, 316 SS 1/2 Hp, 1800 rpm	2,100

Table 2. Estimated Equipment Costs (4 of 7)

Equipment Number	Equipment Name	Equipment Description	Est. Cost
P-401	Ethanol Column Bottoms Transfer Pump	Speed Control, 0.5 gpm, 40' TDH, 316 SS, 1/2 Hp, 1800 rpm	3,600
P-402	Ethanol Column Reflux Transfer Pump	Speed Control, 4.5 gph, 40' TDH, 316 SS, 1/4 Hp, 1800 rpm	3,600
P-501	Ethanol Transfer Pump	4.0 gph, 40' TDH, 316 SS, 1/4 Hp, 1800 rpm	2,100
P-502	Vaccuum Pump	3/4 Hp, 1800 rpm	2,000
P-902	Cooling Tower Transfer Pump No. 1	Centrifugal, DI, 30 gpm, 115' TDH 5 Hp, 3600 rpm	1,100
P-903	Cooling Tower Transfer Pump No. 2	Centrifugal, DI, 30 gpm, 115' TDH 5 Hp, 3600 rpm	1,100
P-904	Sump Pump	20 gpm, 15' TDH	1,200

Table 2. Estimated Equipment Costs (5 of 7)

Equipment Number	Equipment Name	Equipment Description	Est. Cost
TANKS			
T-100	Gas Storage Tank	30,000 gal, 9' dia x 66', 250 psig	20,000
T-101	Ethanol Fermenter	150 gal, 2' dia x 6', 316L SS, ASME, Elliptical Heads, Jacketed, Baffled, Sparge Ring, Des Press.=100 psig, vac. Design Temp.=325 deg F	24,000
T-102A,B	Fermenter Medium Tank	5 gal., Polyethylene	40
T-103	Fermenter Medium Tank	5 gal., Polyethylene	20
T-104	Seed Inoculum Tank	40 gal, 316 SS, Belt drive agitator	6,500
T-105A,B	Seed Medium Tank	5 gal., Polyethylene	40
T-106	Seed Medium Tank	5 gal., Polyethylene	20
T-107	Seed Base Tank	5 gal., Polyethylene	20
T-108	Main Base Tank	5 gal., Polyethylene	20
T-109	Vent Knockout	55 gal., Polyethylene	65
T-110	Ethanol Packed Reactor	6" dia x 8', 316 SS	2,400
T-201	Permeate Holding Tank	100 gal., 2' dia x 4', 316L SS, F&D Heads	3,100
T-301	Water Recycle Holding Tank	100 gal., 2' dia x 4', 316L SS, F&D Heads	3,100
T-302	Settler Holding Tank	2' dia x 2', 316L SS	3,600

Table 2. Estimated Equipment Costs (6 of 7)

Equipment Number	Equipment Name	Equipment Description	Est. Cost
T-303	Permeate Collection Tank	10 gal., 1' dia x 2', SS	1,300
T-402	Ethanol Column Distillate Holding Tank	10 gal., 1' dia x 2' SS, F&D Heads, 316L SS	1,300
T-501	Holding Tank	100 gal., 2' dia x 4', F&D Heads, 316L SS	3,100
T-502	Knockout Drum	10 gal., 1' dia x 2', F&D Heads, 316L SS	1,200
T-503	Knockout Drum	10 gal., 1' dia x 2', F&D Heads, 316L SS	1,200
T-504	Knockout Drum	55 gal., Plastic	65
T-902	Waste Holding Tank	400 gal., 4' dia x 4', 316 SS	4,600
UTILITIES & MISC.			
X-501	Activated Carbon Canister	55 gal. Drum	600
X-901	Electric Boiler	60 KW, 50 psig	5,500
X-902 X-902.1 X-902.2	Cooling Tower Motor Basin Heater	30 gpm, 10°F dT, @ 80°F wet bulb 1/3 Hp 1 KW	4,600
X-903 X-903.1	Air Compressor & Tank Motor	50 scfm, 100 psig 3 Hp	5,200
MCC-1	Motor Control Center		

Table 2. Estimated Equipment Costs (7 of 7)

Table 3. Ethanol Pilot Plant Equipment Cost Summary (1 of 4)

EQUIPMENT COST SUMMARY					
Equipment Number	Reactor Cost, ($)	Biomass Separation Cost, ($)	Product Recovery Cost, ($)	Waste Handling Cost, (4)	Total Cost, ($)
T-100	20,000				
A-103	400				
T-104	6,500				
T-105A, B	20 ea.				
T-106	20				
T-107	20				
F-101	150				
P-101,102	2,100 ea				
P-103,104, 105,106	2,100 ea				
P-107	2,100				
A-101	35,000				
T-101	24,000				
T-109	65				
T-110	2,400				
F-103,104, 105,106,107, 108	150 ea				
T-102A,B	20 ea				
T-103	20				
T-108	20				
F-102	150				
				Total Estimated Reactor Cost	$104,470

Table 3. Ethanol Pilot Plant Equipment Cost Summary (2 of 4)

EQUIPMENT COST SUMMARY					
Equipment Number	Reactor Cost, ($)	Biomass Separation Cost, ($)	Product Recovery Cost, ($)	Waste Handling Cost, (4)	Total Cost, ($)
UF-201A		7,800			
UF-201B		2,800			
UF-201C		2,800			
CF-201		25,000			
F-201		150			
T-201		3,100			
P-201		3,600			
P-201,203		1,800			
P-204		1,800			
T-302		3,600			
T-303		1,300			
F-301,302		150 ea.			
P-302,303, 304,305,306		2,100 ea.			
F-303		500			
F-304		150			
				Total Estimated Biomass Separation Cost	$67,000

Table 3. Ethanol Pilot Plant Equipment Cost Summary (3 of 4)

EQUIPMENT COST SUMMARY					
Equipment Number	Reactor Cost, ($)	Biomass Separation Cost, ($)	Product Recovery Cost, ($)	Waste Handling Cost, (4)	Total Cost, ($)
T-301			3,100		
P-301			3,600		
F-302,303			150 ea.		
HE-301			1,200		
HE-401			2,500		
DC-401			28,000		
SV-501			3,200		
HE-402			3,000		
HE-403			2,100		
HE-501			1,200		
P-401			3,600		
P-402			3,600		
P-502			2,000		
T-402			1,300		
P-501			2,100		
T-501			3,100		
T-502,503			1,200 ea.		
T-504			65		
				Total Estimated Product Recovery Cost	$66,365

Table 3. Ethanol Pilot Plant Equipment Cost Summary (4 of 4)

EQUIPMENT COST SUMMARY					
Equipment Number	Reactor Cost, ($)	Biomass Separation Cost, ($)	Product Recovery Cost, ($)	Waste Handling Cost, (4)	Total Cost, ($)
P-904				1,200	
T-902				4,600	
X-501				600	
F-901				150	
				Total Estimated Waste Handling Cost	$6,500
				TOTAL ESTIMATED EQUIPMENT COST	$244,340

COMPUTER I/O LIST AND INSTRUMENT LIST

The computer I/O list is shown in Table 4, and the instrument list is shown in Table 5. Instruments are shown as analog input, analog output, digital input or digital output.

Area	Tag	Loop	Service	Description	AI	AO	DI	DO
100	TET	114	Seed Inoculum Tank T-104 Temp	Thermocouple	1			
100	TIC	116	Seed Inoculum Tank T-104 Temp Cont	Heater Power		1		
100	LT	118	Seed Inoculum Tank T-104 Level	Capacitance Level Transmitter	1			
100	FET	151	Biomass Recycle to Ethanol Fermenter T-101	Turbinemeter with Integral Transmitter	1			
100	FV	151	Biomass Recycle to Ethanol Fermenter T-101	Control Valve		1		
100	FET	154	Feed Gas to Ethanol Fermenter T-101	Thermal Mass Meter	1			
100	FV	154	Feed Gas to Ethanol Fermenter T-101	Control Valve		1		
100	TET	155	Ethanol Fermenter T-101 Temp	Temp Element with Integral Transmitter	1			
100	TV	155	Ethanol Fermenter T-101 Temp	Control Valve		1		
100	PT	160	Ethanol Fermenter T-101 Press	Press Transmitter	1			
100	FV	160	Ethanol Fermenter T-101 Press	Control Valve		1		
100	LT	162	Water Recycle to Ethanol FermenterT-101	Level Transmitter	1			
100	PHB	163	Ethanol Fermenter Base Control	Configuration Program Switch				1
100	PHT	163	Ethanol Fermenter T-101 pH	pH Transmitter	1			
100	AS-A	171	CO Room Monitor	CO Monitor	1			
100	AS-B	171	H2 Room Monitor	H2 Monitor	1			
100	EV	171	Feed Gas From Truck	Solenoid Valve Software Switch				1
100	RT	172	Ethanol Fermenter T-101 Redox	Redox Transmitter	1			
100	EV	177	Steam Shutoff	Solenoid Valve Software Switch				1
100	EV	178	Water Shutoff	Solenoid Valve Software Switch				1
100	EV	179	Water Shutoff	Solenoid Valve Software Switch				1

Table 4. Ethanol Pilot Plant Computer I/O List (1 of 3)

Area	Tag	Loop	Service	Description	AI	AO	DI	DO
200	FET	203	Biomass Filter UF-201 Outlet Flow	Turbine Meter with Integral Transmitter	1			
200	FV	203	Biomass Filter UF-201 Outlet Flow	Control Valve		1		
200	LSL	209	Permeate Transfer Pump P-201 Cutoff	Configuration Program Switch				1
200	LT	209	Permeate Holding Tank T-201 Level	Capacitance Type Level Probe	1			
200	SC	209	Permeate Transfer Pump P-201 Speed Control	Speed Controller		1		
300	LT	301	Water Recycle Holding Tank T-301 Level	Capacitance Type Level Probe	1			
300	SC	305	Cell Recovery Transfer Pump P-302 Speed Control	Speed Control		1		
300	SC	306	Permeate Collection Transfer Pump P-306 Speed Control	Speed Control		1		
300	LSL	306	Permeate Collection Tank T-303 Level	Configuration Program Switch				1
300	LT	309	Permeate Collection Tank T-303 Level	Capacitance Type Level Probe	1			
300	LSL	321	Water Recycle Holding Tank T-301	Level Configuration Program Switch				1
300	SC	321	Water Recycle Transfer Pump P-301 Speed Control	Speed Control		1		
400	TC	401	Ethanol Column Bottoms Temp Control	Power Controller		1		
400	LT	401	Ethanol Column Bottoms Level	Capacitance Level Probe	1			
400	LSL	401	Ethanol Column Bottoms Transfer Pump P-401 Shutoff	Configuration Program Switch				1
400	SC	401	Ethanol Column Bottoms Transfer Pump P-401 Speed	Speed Control		1		
400	LSL	402	Ethanol Column Reflux Transfer Pump P-402 Shutoff	Configuration Program Switch				1
400	LT	402	Ethanol Column Distillate Holding Tank T-402 Level	Capacitance Level Transmitter	1			
400	SC	402	Ethanol Column Reflux Transfer Pump P-402 Speed	Speed Control		1		
400	PT	403	Ethanol Column Top Press	Press Transmitter	1			
400	TI	405	Ethanol Column Plate Temp	Thermocouple	1			
400	TI	406	Ethanol Column Plate Temp	Thermocouple	1			

Table 4. Ethanol Pilot Plant Computer I/O List (2 of 3)

Area	Tag	Loop	Service	Description	AI	AO	DI	DO
400	TI	407	Ethanol Column Plate Temp	Thermocouple	1			
400	TI	408	Ethanol Column Plate Temp	Thermocouple	1			
400	TI	409	Ethanol Column Overheads Temp	Thermocouple	1			
500	LT	509	Holding Tank T-501 Level	Capacitance Level Transmitter	1			
500	LSL	509	Ethanol Discharge Pump P-501 Shutoff	Configuration Program Switch				1
900	XA	901	Steam Boiler Trouble Alarm	FWE Control System Trouble Alarm			1	
900	XA	912	Compressed Air Trouble Alarm	FWE Control System Trouble Alarm			1	
900	LSL	931	Cooling Tower Basin Lower Level	Configuration Program Switch				1

Table 4. Ethanol Pilot Plant Computer I/O List (3 of 3)

Area	Tag	Loop	Service	Description	AI	AO	DI	DO
100	PI	100	Gas Storage Tank T-100 Pressure	Press Gauge				
100	PCV	101	Feed Gas Press Reducing - 1000/500 PSIG	Press Reducing Valve				
100	PCV	102	Feed Gas Press Reducing - 500/100 PSIG	Press Reducing Valve				
100	PSV	103	Feed Gas Press Relief	Press Relief Valve				
100	PI	104	Feed Gas Filter Inlet Press	Press Gauge				
100	PI	105	Feed Gas Filter Outlet Press	Press Gauge				
100	PSV	106	Gas Storage Tank T-100 Pressure Relief	Press Relief Valve				
100	LI	108	Seed Inoculum Tank T-104 Level	Sight Glass				
100	TI	109	Feed Gas Temp to Ethanol Fermenter	Temp Gauge				
100	PHE	111	Seed Inoculum Tank T-104 pH	pH Element				
100	PHT	111	Seed Inoculum Tank T-104 pH	pH Transmitter				
100	PHC	111	Seed Tank T-104 pH	pH Controller				
100	PCV	112	Feed Gas to seed Inoculum Tank T-104	Press Reducing Valve				
100	FI	113	Seed Inoculum Tank T-104 Gas Flow	Rotameter				
100	TET	114	Seed Inoculum Tank T-104 Temp	Thermocouple	1			
100	TIC	116	Seed Inoculum Tank T-104 Temp Cont	Heater Power		1		
100	LT	118	Seed Inoculum Tank T-104 Level	Capacitance Level Transmitter				
100	FET	151	Biomass Recycle to Ethanol Fermenter T-101	Turbinemeter with Integral Transmitter	1			
100	FV	151	Biomass Recycle to Ethanol Fermenter T-101	Control Valve		1		
100	FY	151	Biomass Recycle to Ethanol Fermenter T-101	Positioner				
100	FI	152	Biomass Circulation Flow to Packed Reactor	Rotameter				
100	FI	153	Water Recycle Flow to Ethanol Fermenter T-101	Rotameter				
100	FET	154	Feed Gas to Ethanol Fermenter T-101	Thermal Mass Meter	1			

Table 5. Ethanol Pilot Plant Instrument List (1 of 7)

Area	Tag	Loop	Service	Description	AI	AO	DI	DO
100	FV	154	Feed Gas to Ethanol FermenterT-101	Control Valve		1		
100	FY	154	Feed Gas to Ethanol Fermenter T-101	Positioner				
100	TET	155	Ethanol Fermenter T-101 Temp	Temp Element with Integral Transmitter	1			
100	TV	155	Ethanol Fermenter T-101 Temp	Control Valve		1		
100	TY	155	Ethanol Fermenter T-101 Temp	Positioner				
100	TV	156	Ethanol Fermenter Agitator Speed	RPM Control Device				
100	LG	157	Ethanol Fermenter Level	Sight Glass				
100	PSV	159	Ethanol Fermenter T-101 Press Relief	Press Relief Valve				
100	PT	160	Ethanol Fermenter T-101 Press	Press Transmitter	1			
100	FV	160	Ethanol Fermenter T-101 Press	Control Valve		1		
100	PY	160	Ethanol Fermenter T-101 Press	Positioner				
100	LT	162	Water Recycle to Ethanol FermenterT-101	Level Transmitter	1			
100	PHB	163	Ethanol Fermenter Base Control	Configuration Program Switch				1
100	PHE	163	Ethanol Fermenter T-101 pH	pH Element				
100	PHT	163	Ethanol Fermenter T-101 pH	pH Transmitter	1			
100	PI	164	Ethanol FermenterT-101 Press	Press Gauge				
100	TI	165	FermenterT-101 Temp	Temp Gauge				
100	TI	168	Water Recycle to Ethanol Fermenter T-101	Temp Gauge				
100	TI	169	Ethanol Fermenter T-101 Jacket Temp	Temp Gauge				
100	FI	170	Ethanol FermenterT-101 Cooling Water Flow	Rotameter				
100	AS-A	171	CO Room Monitor	CO Monitor	1			
100	AS-B	171	H2 Room Monitor	H2 Monitor	1			
100	XV	171	Feed Gas From Truck	Open/Close Valve				

Table 5. Ethanol Pilot Plant Instrument List (2 of 7)

Area	Tag	Loop	Service	Description	AI	AO	DI	DO
100	EV	171	Feed Gas From Truck	Solenoid Valve Software Switch				1
100	RT	172	Ethanol Fermenter T-101 Redox	Redox Transmitter	1			
100	RE	172	Ethanol Fermenter T-101 Redox	Redox Element				
100	FI	173	NH3 Flow	Rotameter				
100	FI	174	Ethanol Packed Column Feed	Rotameter				
100	FI	175	Ethanol Packed Column Feed	Rotameter				
100	FI	176	Ethanol Packed Column Feed	Rotameter				
100	XV	177	Steam Shutoff to Ethanol Fermenter T-101	Open/Close Valve				
100	EV	177	Steam Shutoff to Ethanol Fermenter T-101	Solenoid Valve Software Switch				1
100	XV	178	Water Shutoff to Ethanol Fermenter T-101	Open/Close Valve				
100	EV	178	Water Shutoff to Ethanol Fermenter T-101	Solenoid Valve Software Switch				1
100	XV	179	Water Shutoff to Seed Inoculum Tank T-104	Open/Close Valve				
100	EV	179	Water Shutoff to Seed Inoculum Tank T-104	Solenoid Valve Software Switch				1
100	PI	201	Biomass Ultrafilter UF-201 Strainer Inlet Press	Press Gauge				
100	PI	202	Biomass Ultrafilter UF-201 Strainer Outlet Press	Press Gauge				
200	FET	203	Biomass Filter UF-201 Outlet Flow	Turbine Meter with Integral Transmitter	1			
200	FV	203	Biomass Filter UF-201 Outlet Flow	Control Valve		1		
200	FY	203	Biomass Filter UF-201 Outlet Flow	Positioner				
200	FI	204	Cell Recovery	Rotameter				
200	PI	205	Permeate Pressure	Press gauge				
200	PI	206	Permeate Post Filter Inlet Press	Press gauge				
200	PI	207	Permeate Post Filter Outlet Press	Press Gauge				

Table 5. Ethanol Pilot Plant Instrument List (3 of 7)

Area	Tag	Loop	Service	Description	AI	AO	DI	DO
200	LSL	209	Permeate Transfer Pump P-201 Cutoff	Configuration Program Switch				1
200	LT	209	Permeate Holding Tank T-201 Level	Capacitance Type Level Probe	1			
200	SC	209	Permeate Transfer Pump P-201 Speed Control	Speed Controller		1		
200	PI	210	Permeate Transfer Pump P-201 Outlet Press	Press Gauge				
200	PI	211	Permeate Press (for filter testing)	Press Gauge				
200	FI	212	Permeate Flow (for filter testing)	Flowmeter				
200	TI	213	Biomass Recycle Stream Temp	Temp Gauge				
200	FI	214	Biomass Recycle Stream Flow	Rotameter				
200	PI	216	UF Recirculation Pump P-202 Discharge Pressure	Press Gauge				
200	PI	217	UF Recirculation Pump P-203 Discharge Pressure	Press Gauge				
200	PI	218	Filter Inlet Pressure	Press Gauge				
200	PI	219	Filter Outlet Pressure	Press Gauge				
200	PI	220	Filter Inlet Pressure	Press Gauge				
200	PI	221	Filter Outlet Pressure	Press Gauge				
200	PI	222	Filter Inlet Pressure	Press Gauge				
200	PI	223	Filter Outlet Pressure	Press Gauge				
200	LG	224	Permeate Tank Level	Sight Glass				
300	LT	301	Water Recycle Holding Tank T-301 Level	Capacitance Type Level Probe	1			
300	PI	302	Cell Removal System Permeate Press	Pressure Gauge				
300	FI	303	Biomass Stream Flow	Rotameter				
300	FI	304	Cell Removal System Permeate Flow	Rotameter				
300	SC	305	Cell Recovery Transfer Pump P-302 Speed Control	Speed Control		1		
300	SC	306	Permeate Collection Transfer Pump P-306 Speed Control	Speed Control		1		
300	LG	307	Settler Holding Tank T-302 Level	Level Gauge				

Table 5. Ethanol Pilot Plant Instrument List (4 of 7)

Area	Tag	Loop	Service	Description	AI	AO	DI	DO
300	LG	308	Permeate Collection Tank T-303 Level	Level Gauge				
300	LT	309	Permeate Collection Tank T-303 Level	Capacitance Type Level Probe	1			
300	LG	319	Water Recycle Holding Tank T-301 Level	Level Gauge				
300	LSL	321	Water Recycle Holding Tank T-301	Level Configuration Program Switch				1
300	SC	321	Water Recycle Transfer Pump P-301 Speed Control	Speed Control		1		
300	PI	322	Water Recycle Transfer Pump P-301 Discharge Press	Press Gauge				
300	FQI	323	Water Recycle Holding Tank T-301 Plant Water Flow	Flowmeter - Totalizer				
300	PI	324	Permeate Transfer Pump P-201 Discharge Press	Press Gauge				
300	TI	353	Plate and Frame Heat Exchanger HE-301 CW Temp Out	Temp Gauge				
300	TI	354	Plate and Frame Heat Exchanger HE-301 Temp Out	Temp Gauge				
300	TI	359	Feed/Bottoms Heat Exchanger Permeate Temp In	Temp Gauge				
300	TI	360	Feed/Bottoms Heat Exchanger Column Feed Temp Out	Temp Gauge				
300	TI	361	Feed/Bottoms Heat Exchanger Column Bottoms Temp In	Temp Gauge				
300	TI	362	Feed/Bottoms Heat Exchanger Temp Out	Temp Gauge				
400	TC	401	Ethanol Column Bottoms Temp Control	Power Controller		1		
400	LT	401	Ethanol Column Bottoms Level	Capacitance Level Probe	1			
400	LSL	401	Ethanol Column Bottoms Transfer Pump P-401 Shutoff	Configuration Program Switch				1
400	SC	401	Ethanol Column Bottoms Transfer Pump P-401 Speed	Speed Control		1		
400	LSL	402	Ethanol Column Reflux Transfer Pump P-402 Shutoff	Configuration Program Switch				1
400	LT	402	Ethanol Column Distillate Holding Tank T-402 Level	Capacitance Level Transmitter	1			
400	SC	402	Ethanol Column Reflux Transfer Pump P-402 Speed	Speed Control		1		
400	PT	403	Ethanol Column Top Press	Press Transmitter	1			
400	TI	405	Ethanol Column Plate Temp	Thermocouple	1			
400	TI	406	Ethanol Column Plate Temp	Thermocouple	1			

Table 5. Ethanol Pilot Plant Instrument List (5 of 7)

Area	Tag	Loop	Service	Description	AI	AO	DI	DO
400	TI	407	Ethanol Column Plate Temp	Thermocouple	1			
400	TI	408	Ethanol Column Plate Temp	Thermocouple	1			
400	TI	409	Ethanol Column Overheads Temp	Thermocouple	1			
400	PSV	410	Ethanol Column Press Relief	Press Relief Valve				
400	LG	411	Ethanol Column Reboiler Level	Sight Glass				
400	TI	412	Ethanol Column Condenser HE-403 Temp Out	Temp Gauge				
400	PI	414	Ethanol Column Reflux Transfer Pump P-402 Discharge Press	Press Gauge				
400	FI	415	Recycle Flow to Column	Rotameter				
400	FI	416	Ethanol Column Bottoms Flow to HE-401	Rotameter				
400	TI	419	Ethanol Column Condenser HE-403 Cooling Water Temp Out	Temp Gauge				
500	PI	501	Ethanol Discharge Pump P-501 Discharge Pressure	Pressure Gauge				
500	TI	502	Mole Sieve Outlet Temperature	Temp Gauge				
500	LT	509	Holding Tank T-501 Level	Capacitance Level Transmitter	1			
500	LSL	509	Ethanol Discharge Pump P-501 Shutoff	Configuration Program Switch				1
500	LG	519	Holding Tank T-501 Level	Sight Glass				
500	PI	503	Mole Sieve Pressure	Vacuum Gauge				
500	LG	520	Product Drum Level	Drum Level Gauge				
900	XA	901	Steam Boiler Trouble Alarm	FWE Control System Trouble Alarm			1	
900	PE	902	Boiler Press	Press Gauge				
900	PIC	902	Boiler Press	Press Controller				
900	PI	903	Steam Header Press	Press Gauge w/Siphon				
900	PCV	904	Steam Header Press Reduction	Press Reducing Valve				
900	PI	905	Steam Header Press	Press Gauge w/Siphon				

Table 5. Ethanol Pilot Plant Instrument List (6 of 7)

Area	Tag	Loop	Service	Description	AI	AO	DI	DO
900	PSV	906	Boiler Press Relief	Press Relief Valve				
900	PCV	907	Boiler Makeup Water	Press Reducing Valve				
900	PI	911	Compressed Air Header Press	Press Gauge				
900	XA	912	Compressed Air Trouble Alarm	FWE Control System Trouble Alarm			1	
900	PI	922	Process Water Header Press	Press Gauge				
900	LS	931	Cooling Tower Basin Lower Level	Level Switch				
900	LSL	931	Cooling Tower Basin Lower Level	Configuration Program Switch				1
900	PI	932	Cooling Tower Transfer Pump #1 Discharge Press	Press Gauge				
900	PI	933	Cooling Tower Transfer Pump #2 Discharge Press	Press Gauge				
900	PI	934	Cooling Tower Water Return Header Press	Press Gauge				
900	TI	935	Cooling Tower Water Return Header Temp	Temp Gauge				
900	PI	936	Cooling Tower Water Supply Header Press	Press Gauge				
900	TI	937	Cooling Tower Water Supply Header Temp	Temp Gauge				
900	PI	938	Cooling Tower Water Supply Header Press	Press Gauge				
900	FI	940	Waste Holding Tank T-902 Flow to Sewer	Flowmeter - Totalizer				
900	LG	941	Waste Holding Tank T-902 Level	Level Gauge				

Figure 5. Ethanol Pilot Plant Instrument List (7 of 7)

OVERALL COSTS

The estimated overall costs for the prototype unit are shown in Table 6. Included in the estimate are costs for site development, the process and auxiliary buildings, building services, process equipment, non-process equipment, process appurtenances, utilities, engineering costs, construction costs and miscellaneous costs including a contingency of $200,000. The total estimated overall cost is $1.4 million.

Table 6. Estimated Overall Cost for Ethanol Prototype Plant

Site Development	$ 65,000
Process & Auxiliary Building	135,000
Platforms, Supports, etc.	20,000
Building Services	
Sprinkler System	24,000
Process Equipment	
Total Reactor Cost	104,000
Total Biomass Separation Cost	67,000
Total Product Recovery Cost	66,000
Total Waste Handling Cost	6,500
Non-Process Equipment	
Safety Equipment	3,000
Shop Equipment	6,000
Laboratory Equipment	30,000
Office Furniture and Equipment	5,000
Process Appurtenances	
Piping/Insulation	120,000
Electrical	80,000
Instrumentation	36,000
Computer & Control System	36,000
Control Valves	15,000
Utilities	
Air Compressor	5,300
Boiler	5,500
Cooling Tower and Pumps	5,800
Engineering Costs	
Control System Programming	10,000
Manuals, Training	32,000
Equipment Drawings, Specifications & Project Administration	80,000
Procurement, Expediting and Inspection	10,000
Outside Architect and Engineering Fees	108,000
Construction Costs	
Construction Management, Permits, etc.	40,000
Equipment Installation	50,000
Miscellaneous	
Spare Parts, Supplies, etc.	13,000
Contingencies	200,000
TOTAL ESTIMATED OVERALL COST	**$1.4 million**

INDUSTRIAL PARTNER

The pilot demonstration was to be conducted in collaboration with an industrial partner (refinery or other) that would share costs, and provide gases and data for the construction and operation of the unit. In exchange, the partner would be granted ownership interest in the technology. Ernst & Young/Wright Killen (EY/WK) was selected to identify industrial partners to invest in the development of this technology. A copy of the brochure, with economic projections, prepared by EY/WK for distribution to possible partners follows.

The analysis by EY/WK included evaluation of the ethanol market conditions, which showed that about 1.4 billion gallons of ethanol was blended with motor fuel in 1995. Ethanol prices currently vary between $1.20 and $1.40 per gallon. This price includes a $.54 per gallon subsidy in taxes which might not be available to ethanol from waste gases, although this ethanol is from a renewable resource. Therefore, the EY/WK analysis included various ethanol price scenarios: equivalent MTBE spot price, $.82/gal; octane value, $.70/gal; no subsidy, $.67/gal; and full subsidy, $1.21/gal. Economic projections for a 30 million gallon per year facility showed returns of 18 to 75 percent for the $17 million capital investment over the price range. The cost for producing ethanol from refinery waste gases is $.50 per gallon compared to $.85-1.00 per gallon for corn based ethanol.

EY/WK made presentations and held discussions with several companies, all of whom were interested in pursuing the partnership. Due to federal budget constraints, DOE cancelled this project in early 1997 and all efforts to arrange a partnership ceased.

Bioengineering Resources, Inc.

Refinery Gas to Fuel Ethanol Project
Partner Search

Contents

- Mission
- The Opportunity
- The Company
- The Ethanol Technology
- The Ethanol Market
- Risk Elements for Technology Implementation
- Project Economics
- IRR Analysis
- The Deal
- BRI Qualifications

Mission

Objective

Develop a commercial process for producing fuel ethanol from refinery gas streams containing by-product CO or H_2. Effort is DOE funded and shall include an industry partner.

Role of Industry Partner

Partner is to provide a cost share amount of $2.0 million to $2.5 million for design, construction, and operation of a pilot plant facility. All demonstration data will be proprietary property of the partner and BRI, and the partner retains an ownership position in the technology for licensing or utilization.

The Opportunity

- Potential for new process creating a high value added product
- Capture new technology opportunity early
- Attractive upside for relatively small investment in co-funded pilot project
- Contributes to corporate objectives aimed at improving performance through the use of strategic new business initiatives

The Ethanol Technology

- Proprietary bacteria cultures that convert CO, H_2, and CO_2 into ethanol

$$6CO + 3H_2O \rightarrow CH_3CH_2OH + 4CO_2$$

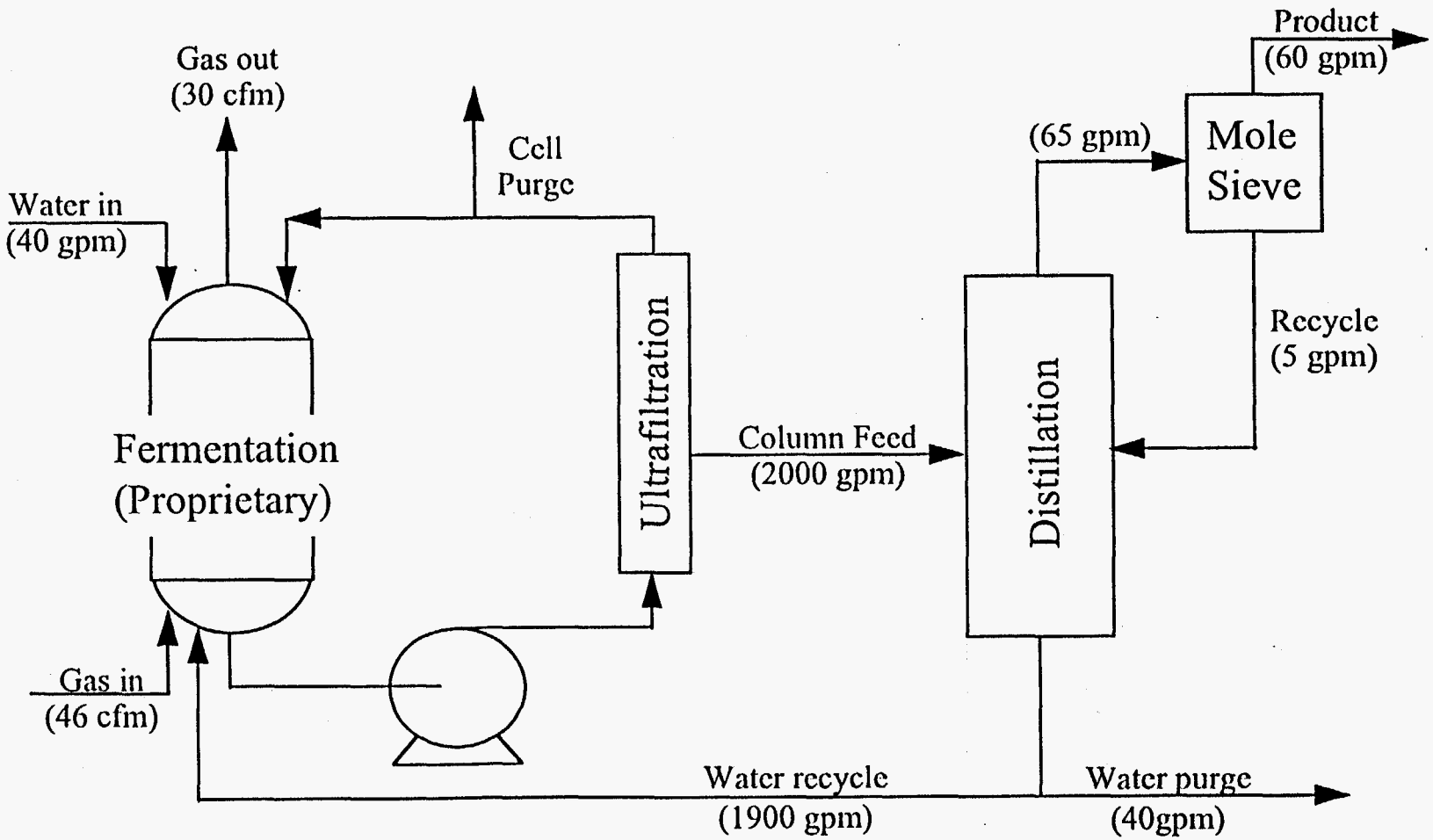
$$6H_2 + 2CO_2 \rightarrow CH_3CH_2OH + 3H_2O$$

- H_2S does not adversely affect the culture

- Retention times under three minutes have been achieved for near complete gas conversion

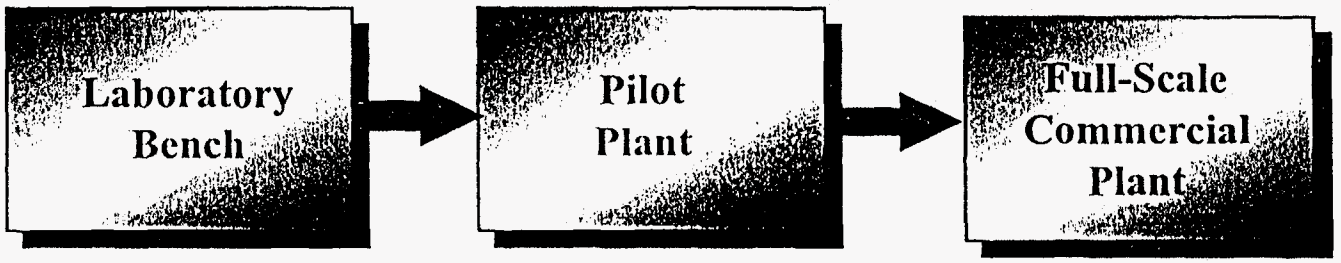
- Ethanol recovery is via traditional distillation/molecular sieve process

Ethanol Process Flow Schematic
(30.0 MM gallons ETOH/year)



Technology Commercialization

Steps In Scale-Up To Commercial Operations



Characteristics

Micro Volumes	Small Volumes	Full-Scale Volumes
Batch/Semi-Continuous	Semi-Continuous	Continuous
Short Runs	Longer Runs	Commercial Run Length

Scaling Factors - Based on Reactor Diameter

1/40	1/8	1/1

Scale-Up Status

Fuel Ethanol Plant Development Progress

- **Laboratory Bench Work** (1/40th Scale-Up) - successful completion

- Pilot Plant (1/8th Scale-Up) - currently seeking industry partner
  - Construction scheduled for six months
  - 18 months operation planned before commercial plant phase

- First Commercial Plant - goes to construction in 1999

The Ethanol Market

- Ethanol has favorable gasoline blending characteristics because of a road octane blending number of 112
- Ethanol contains 34.7 weight percent oxygen
- Ethanol blending is primary oxygenate source for gasoline in PADDs II and IV
- Feedstock for ETBE production

The Ethanol Market

- Total U.S. oxygenate demand in 1995 was 415,000 bpd
  - 220,000 bpd mandated
  - 80,000 bpd opt-in
  - 115,000 bpd discretionary

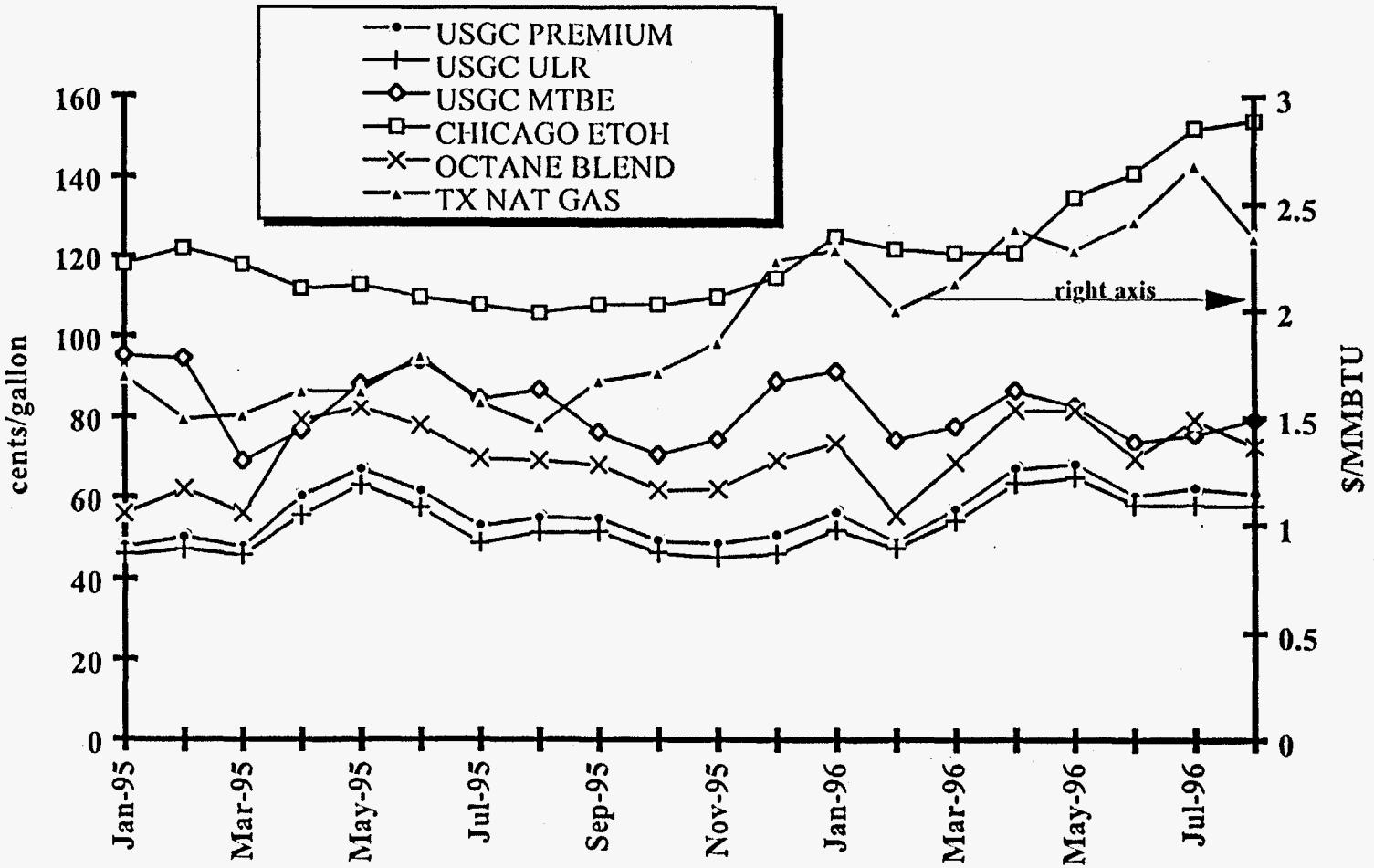
- Total U.S. oxygenate supply in 1995
  - 230,000 bpd MTBE
  - **90,000 bpd ETOH**
  - 15,000 bpd other (MTBE equivalent)

The Ethanol Market

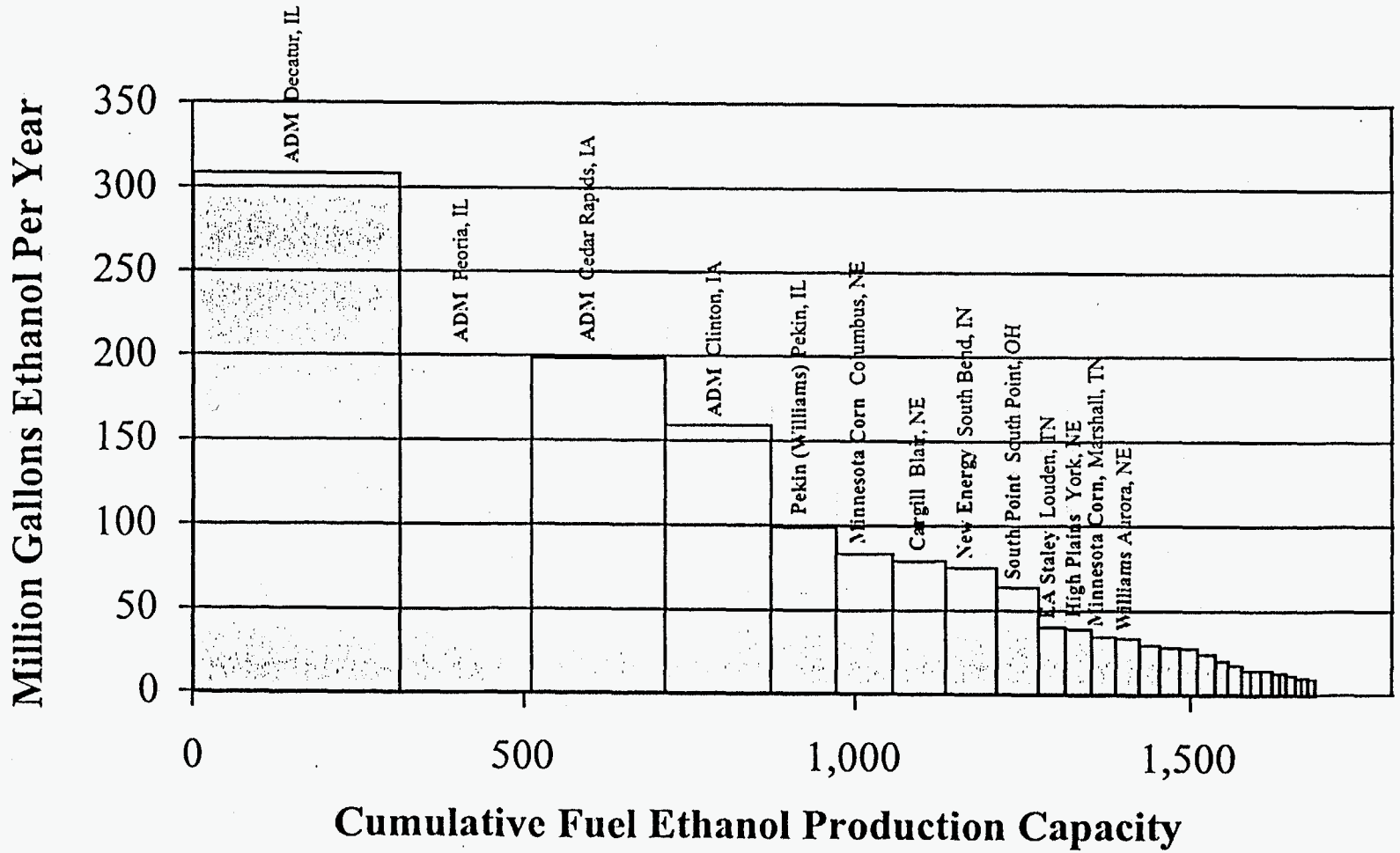
- Ethanol is a commodity whose price is set by the marginal costs of the highest cost producers and adjusted for federal and state subsidies

- Four product pricing scenarios to consider
  - DOE approves refinery waste gas as "renewable" and ETOH is sold at spot price (approx. $1.21/gal)
  - ETOH as compared with MTBE spot price (approx. $0.82/gal)
  - ETOH is sold for octane value only (approx. $0.70/gal)
  - DOE does not approve refinery waste gas as "renewable" or repeals subsidy and ETOH sells for spot less the subsidy of $0.54/gal (approx. $0.67/gal)

Ethanol Price Drivers



U.S. Fuel Ethanol Capacity (existing and under construction)



Risk Elements For Technology Implementation

Category Definitions: All Are Important, Key Areas Identified By E&Y/WK In Bold

- Technical risks
  - Technology employed
    - Scale-up to commercial operations
    - Schedule to achieve full operation after start-up
      - Throughput and yield
      - Product qualities
    - **Sensitivity to feedstock qualities and impurities**
  - Operating costs
- Construction risks
  - **Total capital cost**
  - Completion schedule

Risk Elements For Technology Implementation

Category Definitions (Continued)

- **Commercial risks - price and volume**
  - Input supplies
  - Ethanol market

- **Business risks**
  - New venture must establish all interface channels
    - Suppliers
    - Customers
    - Employees
    - Community
  - Limited existing support organizations
    - Technical
    - Commercial

Risk Management - Ethanol Project

Response

- Technical Risks
  - Laboratory scale indications are that reaction dynamic **improves** with scale
  - BRI has successfully completed operation and scale-up of similar acetic acid process
  - Operating costs should **decrease** relative to scale-up

- Construction Risks
  - Pilot plant engineering near completion
  - Design based upon successful acetic acid pilot plant
  - Capital costs are conservative

Risk Management - Ethanol Project

Response (Continued)

- **Commercial Risks**
  - Sensitivity analysis completed for feed and product price scenarios
  - **Worst case** yields 15 percent IRR

- **Business Risks**
  - Partner to be supplier and customer
  - **BRI requires assistance in commercialization effort**

Project Economics

Hypothetical Commercial Ethanol Plant
30.0 MM gallons ETOH/year
(median of existing U.S. facilities)

Capital Outlay	**BRI (Grassroots) ($MM)**	**Dry-Milling (Grassroots) ($MM)**	**Wet-Milling (Revamp) ($MM)**
Bioreactors	5.00		
Cell Separation	4.75		
ETOH Distillation	3.50		
Mole Sieve	3.75		
Total	**17.00**	**60.00**	**51.00**

Stand-Alone Plant Economics

Profitability Sensitivity (August 1996 price per gallon with $0.58 USGC ULR)	**A** **$1.54** (market w/sub)	**B** **$0.79** (MTBE price)	**C** **$0.73** (octane value)	**D** **$1.00** (market w/o sub)
Revenue	46.20	23.81	21.84	30.00
Expenses	(15.34)	(15.34)	(15.34)	(15.34)
EBITDA	30.86	8.46	6.50	14.66
Depreciation	(1.70)	(1.70)	(1.70)	(1.70)
EBIT	29.16	6.76	4.80	12.96
Taxes 40%	(11.66)	(2.71)	(1.92)	(5.18)
Net Income	**17.50**	**4.06**	**2.88**	**7.78**
ROI	**102.9%**	**23.9%**	**16.9%**	**45.7%**
Payout Year	0.97	4.19	5.90	2.19

Stand-Alone Plant Expenses

(August 1996 pricing basis)

Operating Costs	BRI Assumptions	BRI (Grassroots) ($/gal)	Dry-Milling (Grassroots) ($/gal)	Wet-Milling (Revamp) ($/gal)
Feedstock (see note)	2.34	0.34	0.86	0.57
Steam	2.34	0.06		
Electricity	0.045	0.02		
Energy		0.08	0.14	0.15
Supplies		0.02	0.06	0.07
Water, Misc.	0.05	0.01	0.02	0.02
Personnel	3 ops/shift	0.01	0.09	0.03
Maintenance	5.0%	0.03	0.08	0.07
Taxes and Ins.	2.0%	0.01	0.04	0.03
Total		**0.51**	**1.29**	**0.94**
Depreciation	10 yr s/l	0.06	0.20	0.17
Federal Producer Payment			(0.10)	
Total Cost		**0.57**	**1.39**	**1.11**

Note: $2.34/MMBTU natural gas; $4.40/bushel corn

Stand-Alone Plant Economics

Profitability Sensitivity (Average Price per gallon - 1995 through August 1996)	A $1.21 (market w/sub)	B $0.82 (MTBE price)	C $0.70 (octane value)	D $0.67 (market w/o sub)
Revenue	36.30	24.63	21.00	20.10
Expenses	(13.30)	(13.30)	(13.30)	(13.30)
EBITDA	23.00	11.33	7.70	6.80
Depreciation	(1.70)	(1.70)	(1.70)	(1.70)
EBIT	21.30	9.63	6.00	5.10
Taxes 40%	(8.52)	(3.85)	(2.40)	(2.04)
Net Income	**12.78**	**5.78**	**3.60**	**3.06**
ROI	**75.2%**	**34.0%**	**21.2%**	**18.0%**
Payout Year	1.33	2.94	4.72	5.55

Stand-Alone Plant Expenses

(1995 - 1996 average pricing basis)

Operating Costs	BRI Assumptions	BRI (Grassroots) ($/gal)	Dry-Milling (Grassroots) ($/gal)	Wet-Milling (Revamp) ($/gal)
Feedstock (see note)	1.94	0.28	0.47	0.31
Steam	1.94	0.05		
Electricity	0.045	0.02		
Energy		0.07	0.14	0.15
Supplies		0.02	0.06	0.07
Water, Misc.	0.05	0.01	0.02	0.02
Personnel	3 ops/shift	0.01	0.09	0.03
Maintenance	5.0%	0.03	0.08	0.07
Taxes and Ins.	2.0%	0.01	0.04	0.03
Total		**0.44**	**0.90**	**0.68**
Depreciation	10 yr s/l	0.06	0.20	0.17
Federal Producer Payment			(0.10)	
Total Cost		**0.50**	**1.00**	**0.85**

Note: $1.94/MMBTU natural gas; $2.40/bushel corn

Backcast Pro Forma
Stand-Alone Plant

	NI Case A	ROI Case A	NI Case B	ROI Case B	NI Case C	ROI Case C	NI Case D	ROI Case D
Jan-95	13.01	76.5%	8.91	52.4%	1.84	10.8%	3.29	19.3%
Feb-95	14.34	84.4%	9.41	55.3%	3.54	20.8%	4.62	27.2%
Mar-95	13.56	79.8%	4.74	27.9%	2.43	14.3%	3.84	22.6%
Apr-95	12.14	71.4%	5.75	33.8%	6.22	36.6%	2.42	14.2%
May-95	12.32	72.5%	7.86	46.2%	6.81	40.1%	2.60	15.3%
Jun-95	11.26	66.2%	8.42	49.5%	5.52	32.5%	1.54	9.1%
Jul-95	11.57	68.1%	7.37	43.4%	4.69	27.6%	1.85	10.9%
Aug-95	11.55	68.0%	8.12	47.8%	4.93	29.0%	1.83	10.8%
Sep-95	11.27	66.3%	5.55	32.7%	4.10	24.1%	1.55	9.1%
Oct-95	11.15	65.6%	4.43	26.1%	2.85	16.7%	1.43	8.4%
Nov-95	11.08	65.2%	4.66	27.4%	2.46	14.5%	1.36	8.0%
Dec-9510.81		63.6%	6.13	36.1%	2.59	15.2%	1.09	6.4%
Jan-96	12.46	73.3%	6.43	37.8%	3.20	18.8%	2.74	16.1%
Feb-96	12.78	75.2%	4.22	24.8%	0.84	5.0%	3.06	18.0%
Mar-96	12.20	71.8%	4.43	26.1%	2.82	16.6%	2.48	14.6%
Apr-96	11.43	67.2%	5.27	31.0%	4.42	26.0%	1.71	10.1%
May-96	14.26	83.9%	4.86	28.6%	4.68	27.5%	4.54	26.7%
Jun-96	14.91	87.7%	2.81	16.6%	2.08	12.3%	5.19	30.5%
Jul-96	16.09	94.7%	2.35	13.8%	3.03	17.8%	6.37	37.5%
Aug-96	17.50	102.9%	4.06	23.9%	2.88	16.9%	7.78	45.7%
Average	12.78	75.2%	5.79	34.1%	3.60	21.2%	3.06	18.0%

Case A - ETOH priced with subsidy
Case B - MTBE price
Case C - ETOH priced for octane value
Case D - ETOH priced without subsidy

IRR Analysis For Deal

Base Case Assumptions

- $2.5 million invested in 1997 for pilot plant
- $17.0 million invested in 1998 for 30 million gallons per year commercial ethanol plant
- 10-year project life (1999 to 2008) with zero salvage value
- $700,000 per year CAPEX (4 percent replacement cost)
- 10-year straightline depreciation and 40% tax rate
- No consideration given to licensing technology

Case	Annual CF	IRR
A	$13.75 MM	**65%**
B	$6.75 MM	**31%**
C	$4.5 MM	**18%**
D	$4 MM	**15%**

IRR Analysis For Deal

Assumptions Including Licensing

- Partner share of royalty (aftertax) equal to 1.8 percent of sales
- Technology license applied to 30 million gallon per year facility
- Base case assumptions continue to hold

Case	Annual CF	Royalty	Total Annual CF	IRR
A (License 10)	$13.75 MM	$6.5 MM	$20.25 MM	**80%**
B (License 10)	$6.75 MM	$4.25 MM	$11 MM	**46%**
C (License 10)	$4.5 MM	$3.75 MM	$8.25 MM	**34%**
D (License 10)	$4 MM	$3.5 MM	$7.5 MM	**30%**
A (License 20)	$13.75 MM	$13 MM	$26.75 MM	**94%**
B (License 20)	$6.75 MM	$8.5 MM	$15.25 MM	**57%**
C (License 20)	$4.5 MM	$7.5 MM	$12 MM	**45%**
D (License 20)	$4 MM	$7 MM	$11 MM	**42%**

The Deal

- Partner provides $2.0 million to $2.5 million in matching pilot plant funding
- Pilot plant to be located at BRI in Fayetteville, Arkansas
- Partner to provide representative feedstock via tube trailer or shall provide composition for purchase from local vendor
- Partner assistance in pilot plant R&D and commercialization effort desired
- Partner receives ownership position in technology for licensing or utilization

LABORATORY EFFORTS IN IMPORTANT DESIGN AREAS

Another important focus area of the Phase IV effort was the execution of various bench scale laboratory experiments aimed at optimizing either high cost areas or problem areas in the design. These experiments were concentrated in five areas:

- water recycle from distillation back to the fermenter, and the need for treatment of this water prior to fermentation
- alternative methods for removing cells from the system prior to distillation
- the use of CO_2/H_2 as a substrate
- eliminating methanogen contamination due to operating under unsterile conditions with a CO_2/H_2 feed
- tolerance of the culture to acetate recycled from distillation to the fermenter

Water recycle is an important part of the overall process scheme because it permits recycle of excess nutrients and minimizes water treatment as an effluent. Studies performed in Year 2 of the cooperative agreement showed that treatment of this recycled water was not required as long as a hollow fiber was used to remove cells prior to distillation. However, multiple recycles of the water were not considered, nor was water recycled when using alternative methods of removing cells from the product stream.

Hollow fiber filters were found to be a very expensive capital cost item in the commercial plant. Alternatives for cell recycle or cell removal, other than hollow fiber filtration, were considered including other types of filters, centrifugation, settling and flocculated settling.

CO is the preferred substrate for each of the bacterial isolates capable of producing ethanol from CO, CO_2 and H_2. The cell is capable of producing more cell mass on CO than CO_2/H_2, and the culture operates much more stably on CO than CO_2/H_2. This latter observation is illustrated by observing the typical CO and H_2 conversions in a CSTR operating with a mixture of CO, CO_2 and H_2. The CO conversions are often more than 90 percent, while the H_2 conversions are more typically 50-70 percent. If a process upset occurs, the H_2 conversion drops rapidly, while the CO conversion is often unaffected or is at least not affected until after the H_2 conversion falls. Because waste or fuel gases from refineries may contain little of no CO, the culture should be shown to be capable of converting CO_2 and H_2 with minimal CO.

In feeding a reactor CO_2 and H_2 under non-sterile conditions, methanogen contamination may become a problem. Methanogens convert CO_2 and H_2 to CH_4 by the equation:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (3)$$

Furthermore, methanogens grow well under similar conditions as Isolates C-01 and O-52 (anaerobic, 37°C, same vitamins and other nutrients, etc.) The reactor is operated under non-sterile conditions because contamination is not usually a problem with a high CO concentration feed. Furthermore, sterile conditions will require additional expense in the process. An effective method for removing and eliminating methanogen contamination must be developed, or the system must be operated under sterile conditions.

Finally, acetate in the recycle water is sent back to the fermenter after distillation. However, if the acetate concentration is too high, reactor upset occurs. The acetate tolerance of the culture must be identified, whereby the culture is still capable of producing ethanol from CO, CO_2 and H_2.

WATER RECYCLE

Previous water recycle studies in Year 2 showed that water from distillation could successfully be recycled back to the reactor if the cells were removed prior to distillation using a hollow fiber filter. These cells were not recycled back to the fermenter. Experiments in Year 3 were performed first with a hollow fiber filter with cell recycle, and secondly to evaluate the effect of alternative methods of removing solids on water recycle.

Hollow Fiber Filtration with Cell Recycle

A gas containing 45 percent CO, 50 percent H_2 and 5 percent CH_4 was fed to a CSTR operating at a gas retention time of 6.5 min and a liquid retention time of 16 hr. A hollow fiber filter was used to separate cells from the permeate and recycle the cells back to the reactor. The permeate from the hollow fiber filter was distilled and then sent through activated carbon prior to recycle. Previous experiments without the carbon canister in the cell recycle stream were not successful.

Figures 13-15 show experimental results from three water recycle runs. The first run was initiated at t = 3466 hr with a batch of recycle water containing 4.89 g/L acetate. During the run, the cell concentration was about 3.5 g/L and the CO and H_2 conversions were 90 and 35 percent, respectively. The ethanol concentration leaving the reactor was 17 g/L and the acetic acid concentration was about 5 g/L. A second water recycle experiment with another batch of recycle water was started at t = 3568 hr. Similar results were obtained in this study. Finally, a third water recycle experiment with another batch of recycle water was initiated at t = 3680 hr. Again, similar results were obtained. It appears that water recycle coupled with cell recycle is possible if carbon bed adsorption is used to treat the recycle water.

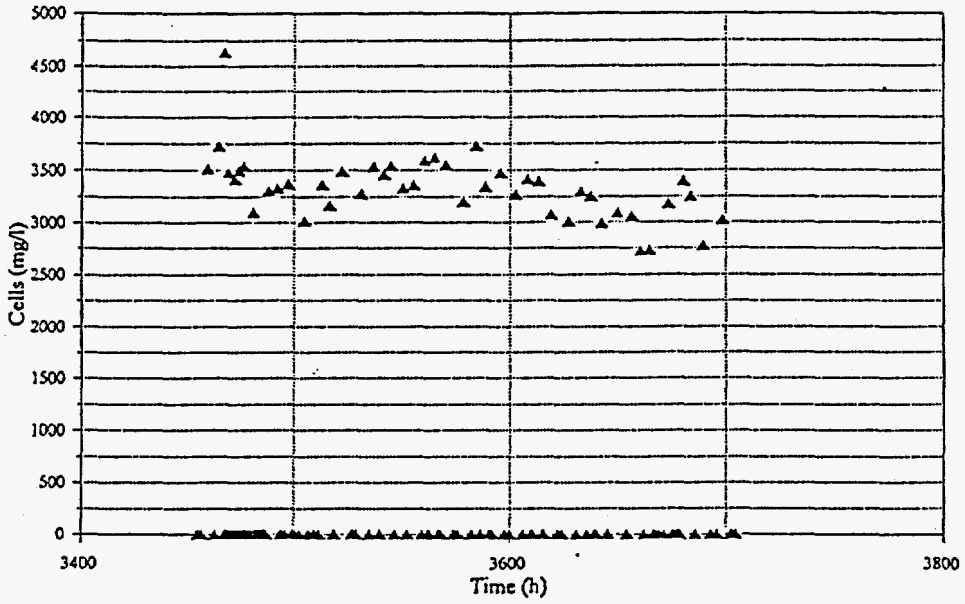


Figure 13. Cell Concentrations During the Three Water Recycle Experiments Performed in a CSTR with Hollow Fiber Cell Recycle. Water was Treated by Carbon Bed Adsorption

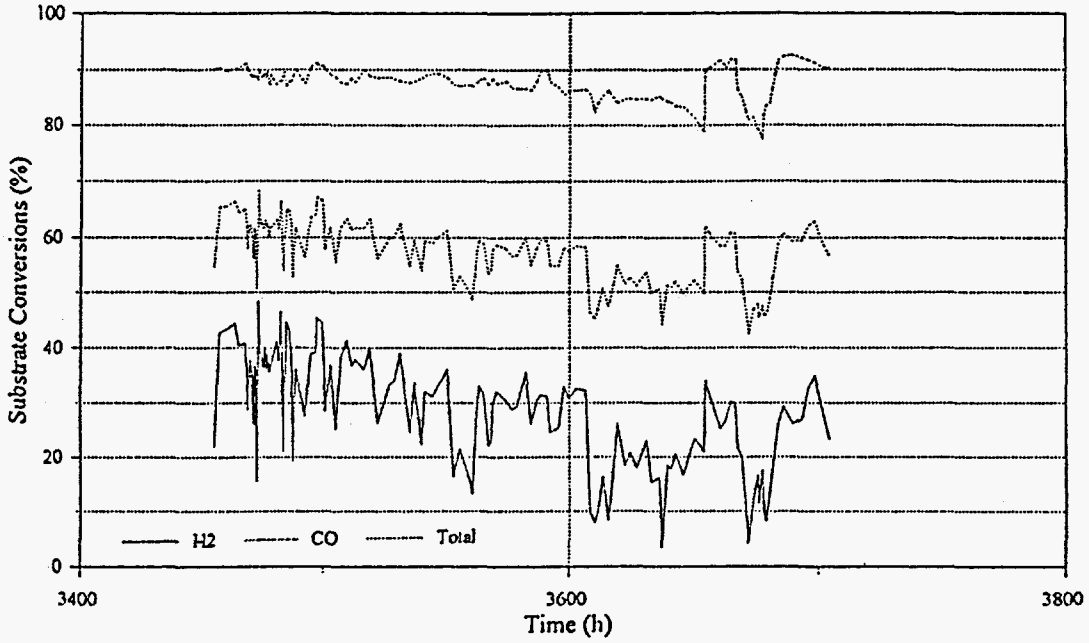


Figure 14. *Gas Conversions* During the Three Water Recycle Experiments Performed in a CSTR with Hollow Fiber Cell Recycle. Water was Treated by Carbon Bed Adsorption

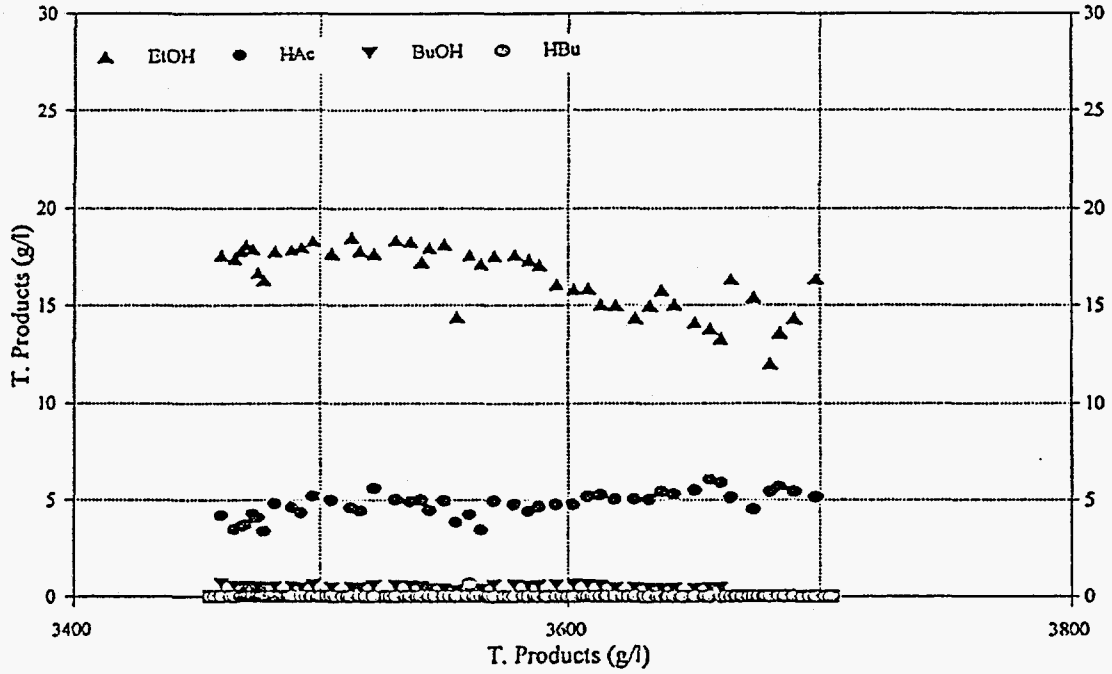


Figure 15. Total Product Concentrations During the Three Water Recycle Experiments Performed in a CSTR with Hollow Fiber Cell Recycle. Water was Treated by Carbon Bed Adsorption

Use of Flocculants for Cell Removal

A second set of experiments was performed using flocculated settling as an alternative to hollow fiber filtration. Flocculated settling will be discussed further in a later section of this report. In this experiment, a gas containing 23.6 percent H_2, 40.4 percent CO, 20.0 percent CH_4 and 16.0 percent CO_2 was used. Flocculation was used to remove cells but was not used for cell recycle. The recycled water was prepared by flocculating the cells, removing the cells by coarse filtration, carbon bed filtration of the filtrate, distillation of the filtrate to remove ethanol and autoclaving. Three recycle experiments were performed, with the results from the experiments shown in Figures 16-18.

The initial experiment was started at t = 119 hr. The recycle water contained 1.99 g/L ethanol and 3.27 g/L acetate. The reactor performed steadily for seven days. The ethanol concentration reached 24 g/L. A second pass of recycle water was started at t = 297 hr, this time containing 2.4 g/L ethanol and 3.7 g/L acetate. The reactor again performed fairly steady, with a bit of a drop in cell density and H_2 uptake. The maximum ethanol concentration was 27 g/l. The third pass was initiated at t = 452 hr with water containing 1.7 g/L ethanol and 3.5 g/L acetate. In this experiment, the H_2 conversion dropped, and a trend of decreasing CO conversion was observed. The ethanol concentration fell to 18 g/L. With the addition of fresh medium, reactor performance improved. It was suspected that there may have been a problem with nutrients in the system, although medium modification did not improve performance.

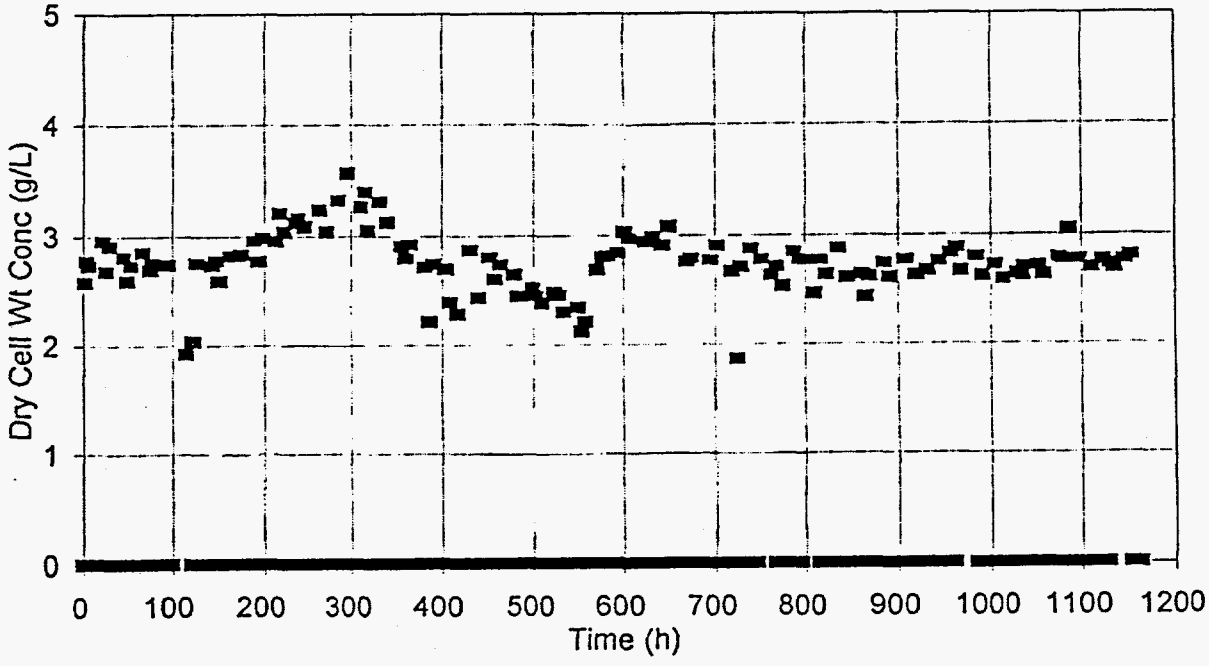


Figure 16. Cell Concentrations During the Three Water Recycle Experiments. Flocculation and Filtration Were Used to Treat the Water Prior to Recycle

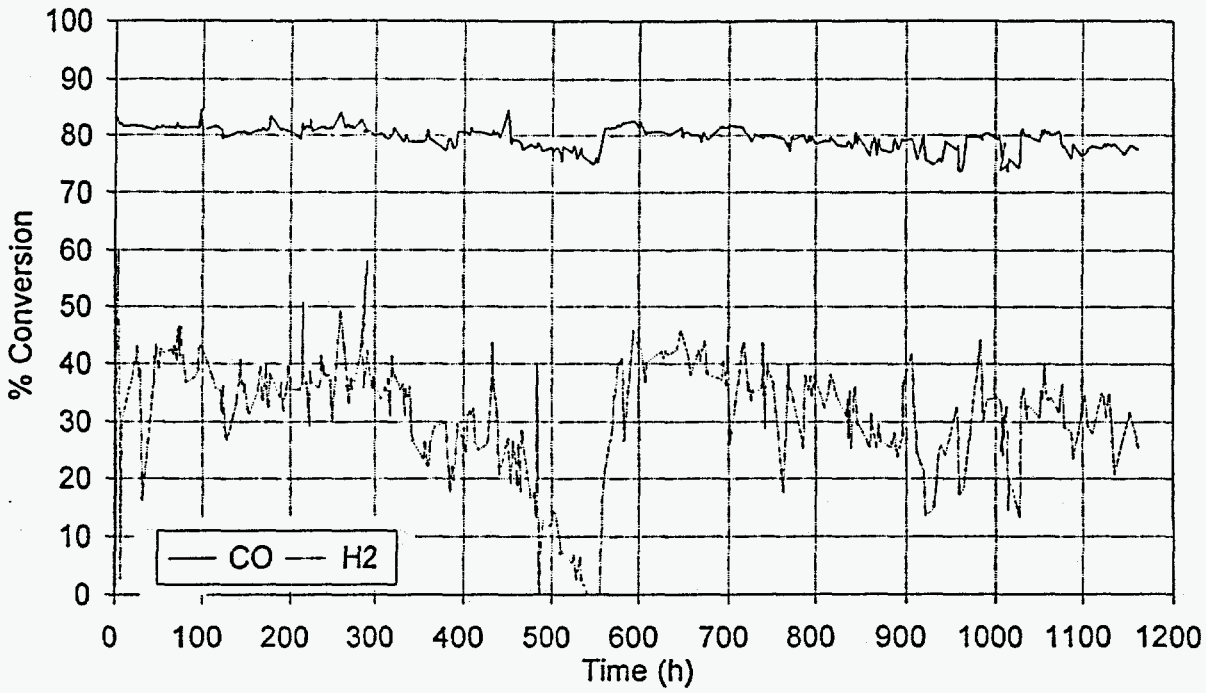


Figure 17. Gas Conversions During the Three Water Recycle Experiments. Flocculation and Filtration Were Used to Treat the Water Prior to Recycle

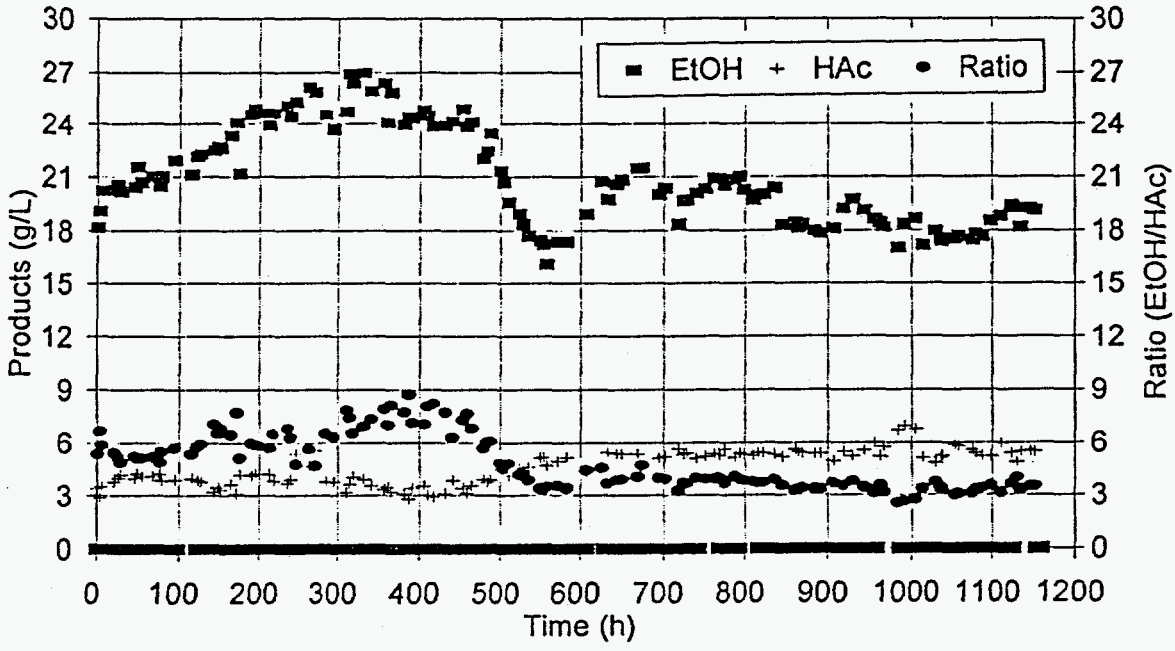


Figure 18. Product Concentrations During the Three Water Recycle Experiments. Flocculation and Filtration Were Used to Treat the Water Prior to Recycle

ALTERNATIVE METHODS FOR CELL REMOVAL

Hollow fiber filtration for cell recycle or cell removal is a very costly technology. Several alternative methods for removing cells from the fermentation broth were thus investigated including centrifugation, settling, heat assisted settling and flocculated settling. Experiments were performed in the laboratory using settling, heat assisted settling and flocculated settling. The following paragraphs discuss results from these experiments.

Cell Settling

A simple experiment was performed to estimate the settling rate of Isolate C-01. Culture broth containing cells was added to a tube and the clear liquid height measured as a function of time. Results from this test are shown in Figure 19. A maximum settling rate of about 0.03 cm/min was observed, a rate which is too slow for commercial application. It was found that if the cells were heated to 80-85°C, they settled almost completely in about 15 min which would be practical for a commercial application. The cells, of course, cannot be recycled once they are heated because cell lysis and protein denaturation occur. Cell lysis is the breaking of cells upon death of their constituent parts, and protein denaturation is the unravelling and break up of proteins usually upon heating or large pH change.

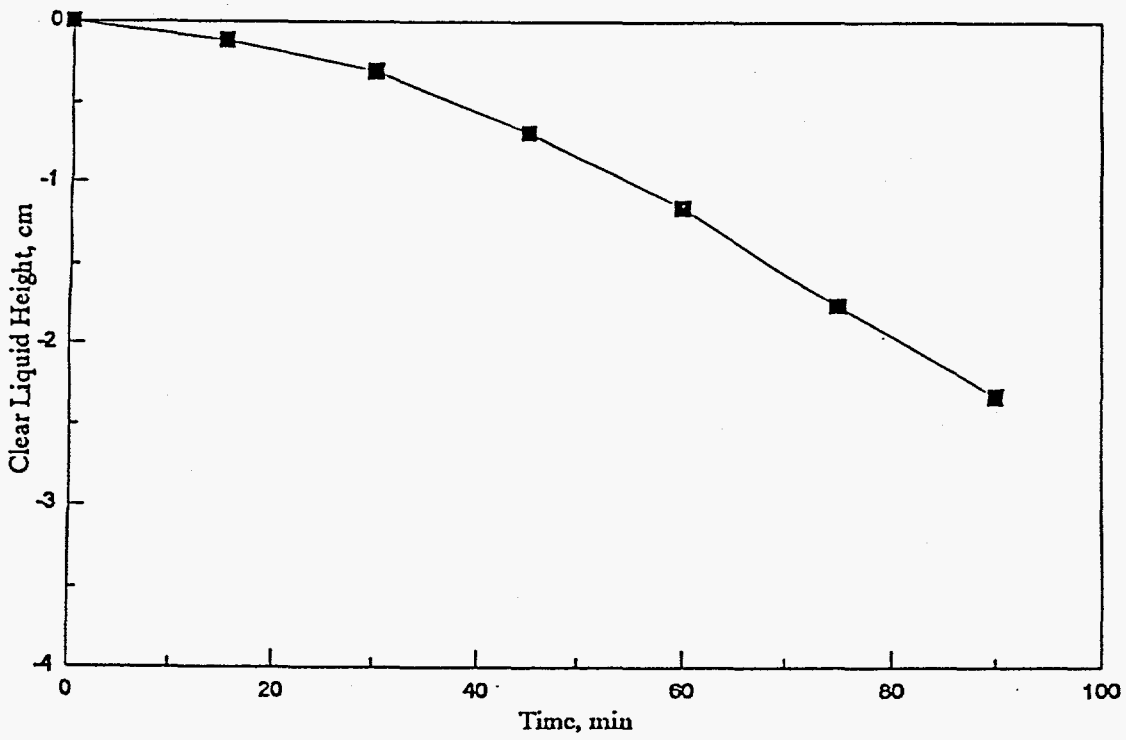


Figure 19. Simple Settling Test with Isolate C-01

A settling apparatus was connected to a CSTR using the arrangement shown in Figure 20. This apparatus was originally thought to enhance performance in much the same manner as the hollow fiber filter, but it was later discovered that the performance enhancement was due to the increased "reactor" volume by the addition of the settler. The settler was thus removed.

Flocculant Addition

Flocculants were added to the culture in an effort to enhance the settling rate. Batch studies were carried out to compare settling rates as a function of the type and concentration of flocculant, and CSTR studies were performed with the best flocculants to determine if they could be used for settling as an alternative to hollow fiber membrane cell recycle.

Batch Flocculant Testing. Eleven flocculant samples were obtained from Allied Colloids and two samples were obtained from Cytec. None of the flocculants were toxic to the culture. Percol 787 from Allied Colloids appears to be the best flocculant in terms of culture floc viability after flocculation, although several of the other flocculants also appear to be effective. A concentration of 5-10 ppm Percol 787 appears to be adequate for cell flocculation in batch culture.

CSTR Studies with Flocculant Addition. The settler shown previously in Figure 20 was reconnected to the CSTR. Percol 787 was added to the medium along with the normal concentrations of vitamins and minerals. In using 1 ppm Percol 787, no change in cell density was observed. In increasing the concentration to 5 ppm, an increase in cell density from 2.2 g/L to 2.8 g/L was observed. This concentration is still far below the 4.5-6.0 g/L levels attained in using a CSTR with hollow fiber filtration for cell recycle. Thus, the addition of Percol 787 was not sufficient as a flocculant to provide the necessary cell density in the CSTR to replace the hollow fiber membrane.

The system was modified to send the medium containing flocculant first to the settler and then to the CSTR. This change was made to ensure that the reactor agitation did not break the flocs as soon as or before they were formed. Despite numerous changes, the system did not perform well with Percol 787. The flocculant Cysep 349 was also used in a number of modified reactor-settler systems at various concentrations. These results were also not successful. It appears that the flocculant system works well to remove cells from the system (perhaps prior to distillation), but does not work well as a method of recycling cells back to the reactor.

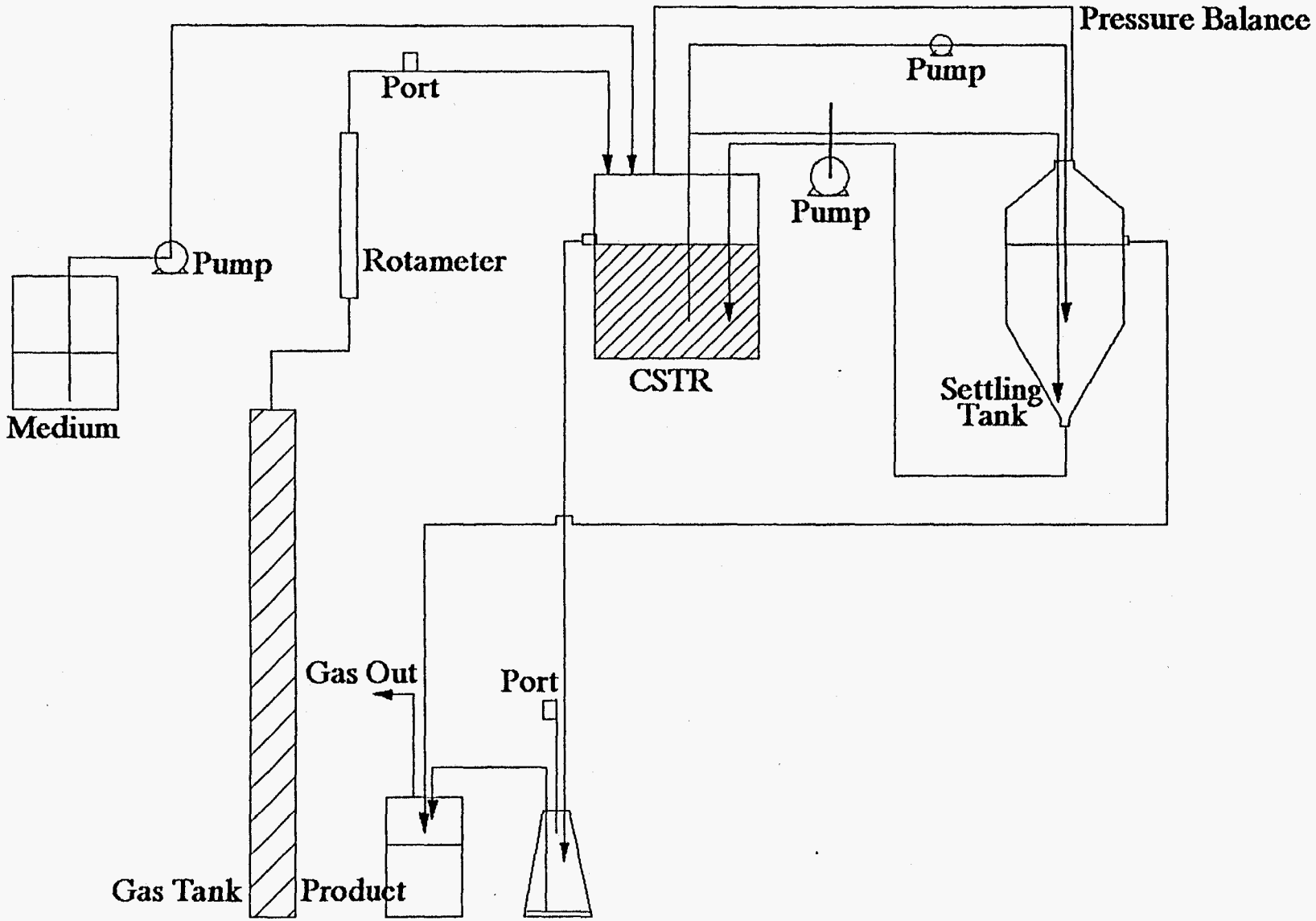


Figure 20. CSTR with Cell Settling and Recycle for Ethanol Production

CO_2/H_2 UTILIZATION

As was noted earlier, some refinery waste gas streams that may be candidates for conversion to ethanol contain little or no CO, the preferred substrate for isolates C-01 and O-52. Studies were thus initiated to determine if the cultures could use CO_2 and H_2 with either no CO or at least minimal levels of CO in the gas feed.

Although the overall stoichiometrics of Equations (1) and (2) show that either CO and water or CO_2 and H_2 may be used as substrates for ethanol production, the conversions of CO, CO_2 and H_2 had only been demonstrated previously for gas mixtures containing at least a 1:1 mixture of H_2 and CO. It is known that the cultures grow 2.5 times faster on CO and produce 2.5 times more cells on CO than H_2. It is further known that similar cultures produce acetic acid/acetate on gas mixtures containing as little as 2 percent CO in a H_2/CO_2 mixture. Finally, it is known that the culture will be more susceptible to methanogen contamination under non-sterile operating conditions when using a gas mixture with little or no CO present, a compound which is inhibitory to methanogens.

Initial attempts of growing Isolate O-52 in the CSTR on CO_2 and H_2 alone were somewhat successful in growing the culture, but resulted in only 0.6 g/L ethanol and 1.5 g/L acetic acid/acetate as products. Furthermore, methanogen contamination became a problem. Other attempts at supplementing the feed with a small amount of CO resulted in little growth and eventual culture washout. Similar results were obtained with Isolate C-01. Despite multiple inoculation attempts, the resulting product concentrations and cell density were always low. Thus, the use of a gas containing low concentrations of CO in H_2 and CO_2 in these preliminary studies was abandoned. The prudent solution to the problem is to supply the system with a gas which contains CO as well as H_2 and CO_2.

METHANOGEN CONTAMINATION

One of the major problems of running a non-sterile system for the conversion of CO, CO_2 and H_2 to ethanol is the potential for methanogen contamination, particularly in systems employing feed gases low in CO. CO acts as a contaminant (methanogen) poison, particularly in high concentrations, especially when coupled with a minimal liquid medium.

Considerable effort has gone into ridding the fermenters of methanogen contamination once it occurs. The contamination seems to occur most often when the reactor is in the start-up phase and has low concentrations of ethanol and acetate produced as products. The addition of the methane inhibitor bromoethanesulfonic acid (BESA) has been shown to be quite effective in relieving the culture of contamination. The key to BESA addition is the use of a relatively high concentration for an extended period of time, similar to the use of an antibiotic. Figure 21 shows the effects of BESA addition on the culture at various concentrations. Perhaps the best way to view the effects of methanogen contamination is to monitor the carbon balance, defined by the equations:

$$CB = COU/CO * 100 \quad (4)$$

where

$$COU = CO - CO_2 - 2.89 \times 10^{-8} X \bullet L - (E + A) \quad (5)$$

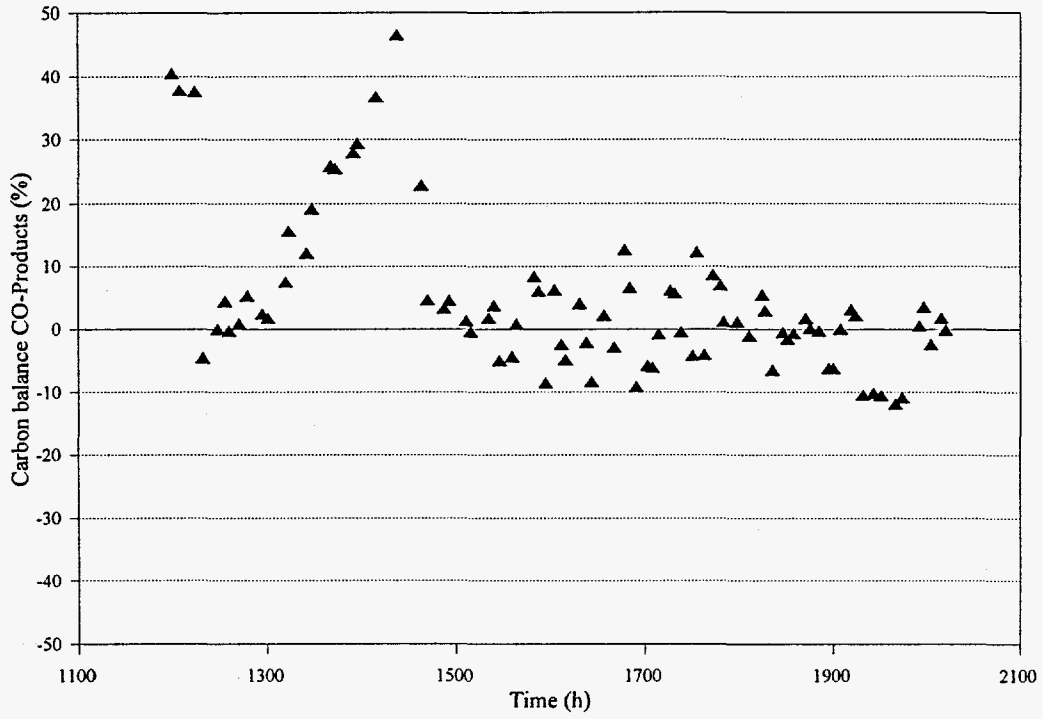


Figure 21. Controlling Methanogens with the Addition of BESA

In Equations (4) and (5),

CB = carbon balance (%)
COU = CO used in producing cells and products (mmol/min)
CO = CO uptake rate (mmol/min)
CO_2 = CO_2 production rate (mmol/min)
X = cell biomass concentration (mg/L)
L = liquid flow rate (mL/d)
E = ethanol production rate (mmol/min)
A = acetic acid/acetate production rate (mmol/min)

The constant 2.89×10^{-8} is a conversion factor in converting mg/L•mL/d to mmol/min, calculated as:

$$\left(\frac{mg}{L}\right)\left(\frac{mL}{d}\right)\left(\frac{L}{1000mL}\right)\left(\frac{d}{24hr}\right)\left(\frac{hr}{60\,\text{min}}\right)\left(\frac{L}{1000mL}\right)(0.5) = 2.89\ x\ 10^{-8}$$

The factor 0.5 represents the fact that the cells contain approximately 50 percent carbon.

Thus, the carbon balance should be zero if all of the CO taken up by the cell is converted to cell mass and products, since COU will be zero. Because gas phase composition calculations are based on methane as a tracer, the carbon balance will not be zero if methane is produced by methanogens. In analyzing the carbon balance of Figure 21, it is seen that the carbon balance, CB, was 40 percent at t = 1200 hr. BESA at a concentration of 100 ppm was added daily as a pulse to the reactor. Despite this addition, the reactor continued to be contaminated. During the period of t = 1300 to t = 1450 hr, the ethanol concentration dropped from 14 g/L to 8 g/L, and the acetate concentration increased from 2 g/L to 4 g/L. The BESA concentration was increased to 250 ppm on a daily one-shot basis at t = 1446 hr, and was continued until t = 1862 hr. At t = 1862 hr, very few methanogens were seen in the reactor, and the ethanol concentration rapidly increased to 17 g/L. This technique of adding a relatively high concentration of BESA on a daily basis for an extended period of time works well in controlling and eliminating the contaminant. Again, contamination is not a problem in reactors producing high concentrations of ethanol.

ACETATE TOLERANCE

Experiments were performed to determine the effects of acetate concentration as recycle on culture performance. Figures 22-24 show results from this experiment. Glacial acetic acid was added to the fresh medium at a concentration of 3 g/L at t = 2234 hr, at a concentration of 4 g/L at t = 2709 hr, at a concentration of 5 g/L at t = 2927 hr, at a concentration of 6 g/L at t = 3087 hr and at a concentration of 7 g/L at t = 3186 hr. The acetic acid addition was thus continuous over this time period from t = 2234 to t = 4200 hr. Little change in cell growth, product concentrations or substrate uptake was noted with the acid addition to the medium. Ethanol production increased slightly. These experiments show that up to 7 g/L of acid can be added to the reactor, while the amount recycled from distillation needs to remain at or below 5 g/L. This discrepancy is not well understood, but may indicate that cell by-products limit the concentration of acid in the recycle stream.

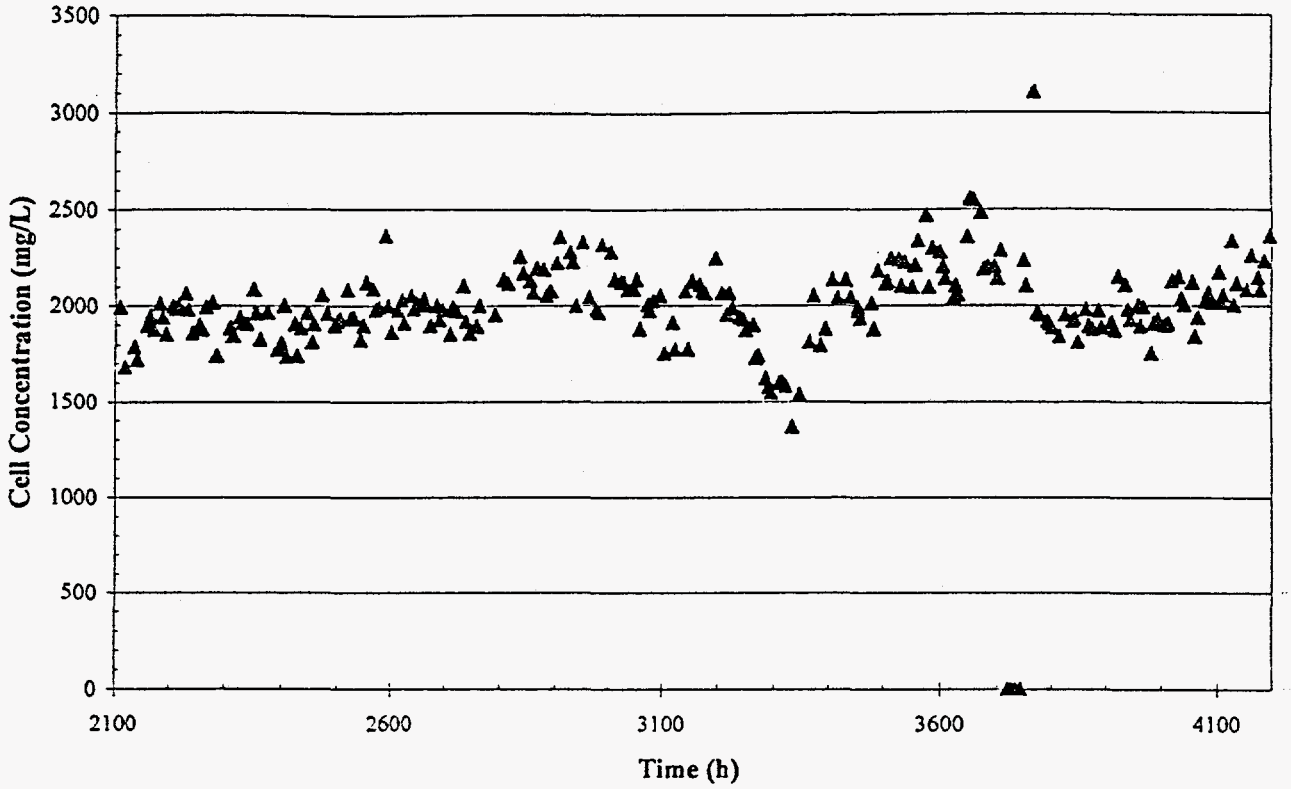


Figure 22. Cell Concentrations During the Acetate Addition Study

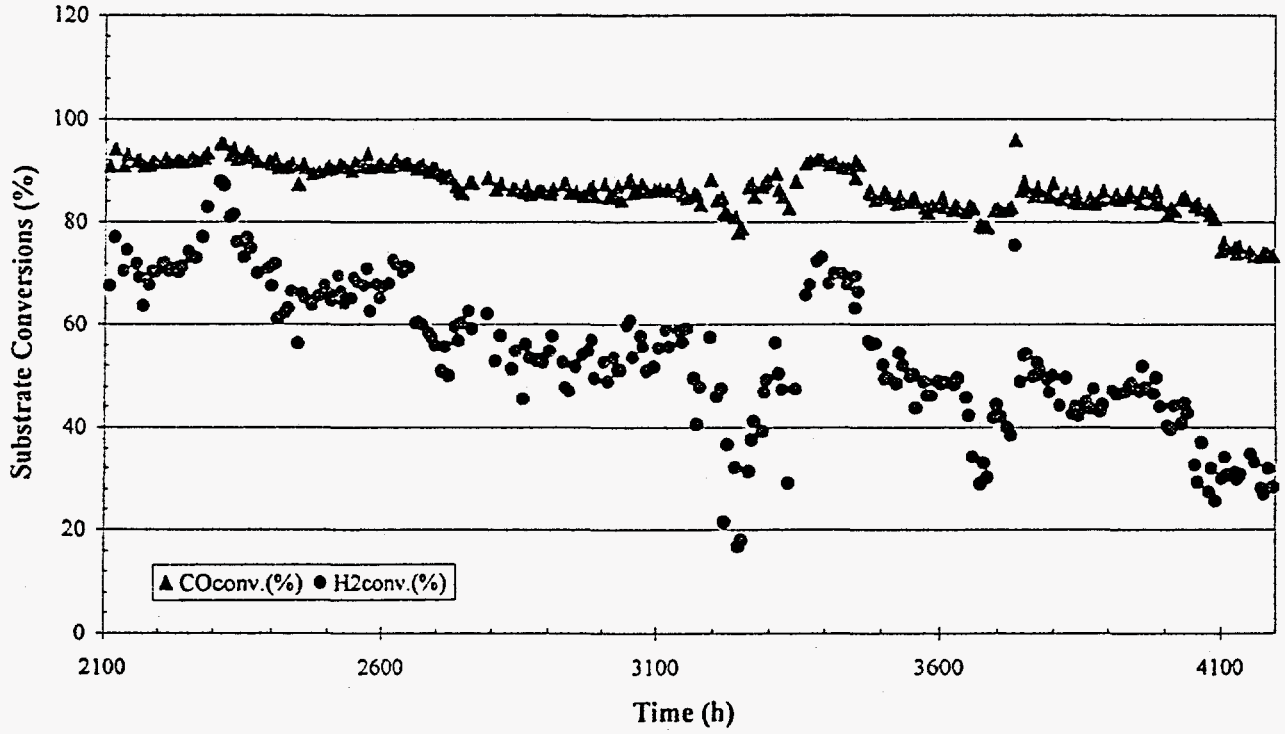


Figure 23. Gas Conversions During the Acetate Addition Studies

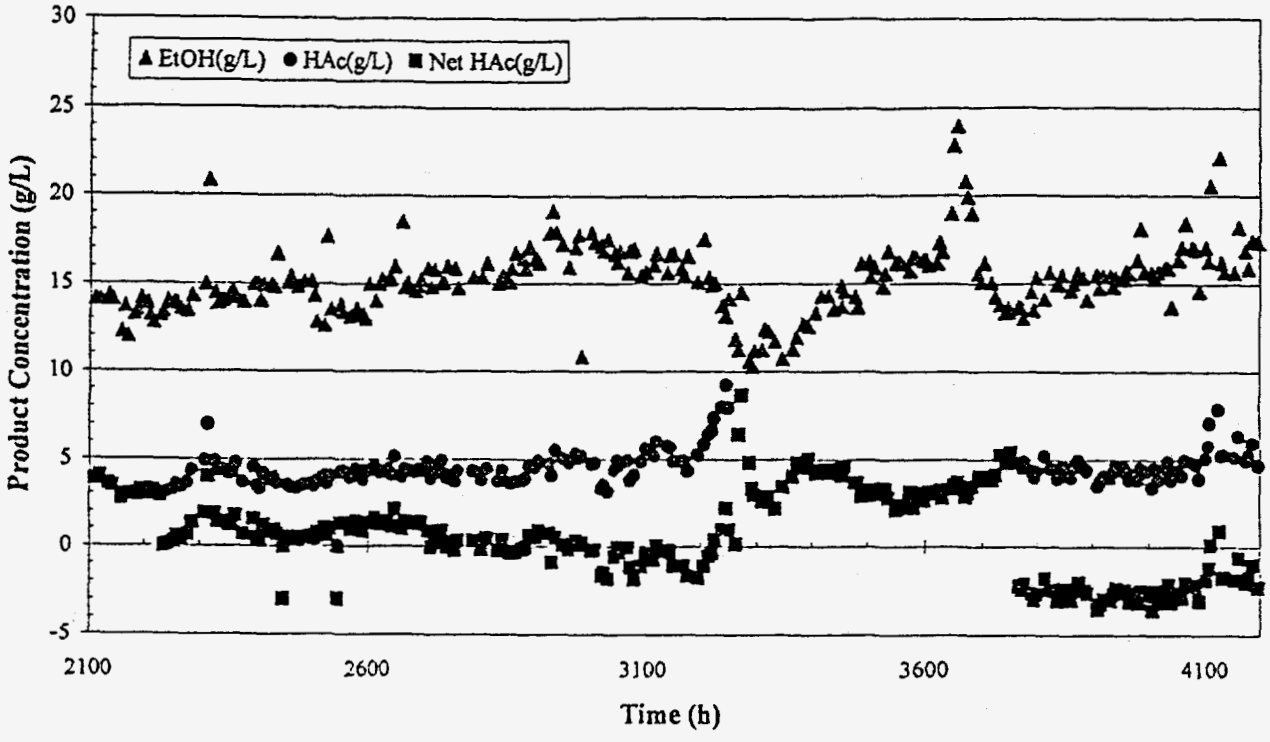


Figure 24. Product Concentrations During the Acetate Addition Studies

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 triple to 3 billion gallons per year as it replaces gasoline as the predominant liquid fuel. 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 was conducted in three phases: Phase II - Technology Development; Phase III - Engineering Development; and Phase IV - Demonstration. DOE budget constraints resulted in cancellation of Phase IV prior to construction and operation of the prototype demonstration. Phase I, Exploratory Development, had been successfully completed in the BRI laboratories prior to project initiation. The research effort has resulted in the development of two strains (Isolate O-52 and Isolate C-01) which produce ethanol from CO, CO_2 and H_2 in refinery waste gas. Fermentation of CO_2 and H_2 alone, without the presence of CO, has not been successful in preliminary experiments. Also, low concentrations of CO invite methanogen contamination, which may be removed by bromoethanesulfonic acid (BESA) addition. Results from single continuous stirred tank reactor (CSTR) laboratory tests have shown that about 20 g/L of ethanol can be produced, with less than 5 g/L acetic acid produced as a by-product. Laboratory studies performed with two CSTRs in series have yielded ethanol concentrations of 25-30 g/L with 2-4 g/L acetic as the by-product. Hollow fiber filtration of the water before distillation is sufficient to eliminate the recycle of toxic materials back to the fermenter. As an alternative, flocculation may be used to aid in removing the cells, but the filtrate must be treated by carbon bed adsorption prior to distillation and water recycle. If cell recycle is employed, again carbon bed treatment is required prior to distillation and water recycle.

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.

A detailed process design has been prepared for the construction of a prototype unit to produce 2.63 lb/hr of ethanol from refinery waste gas containing 21.5 percent H_2, 20.0 percent CO, 9.5 percent CO_2, 4.0 percent CH_4 and 45.0 percent N_2 at 2.72 atm. The design includes plant layouts, piping diagrams, equipment sizing and cost estimates, P&IDs, a computer I/O list, and an instrument list. It is estimated that the total equipment cost will be about $250,000, and the total estimated cost of the facility, including engineering and construction costs will be $1.4 million.

Ernst and Young/Wright Killen was selected to identify industrial partners for this project. EY/WK prepared economic projections which were quite favorable. Several companies had been contacted and had expressed interest when the project was cancelled.

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