

Source Test and Evaluation Report
Alcohol Facility for Gasohol Production

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SOURCE TEST AND
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ALCOHOL FACILITY FOR
GASOHOL PRODUCTION

Final Report

by

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This document was prepared to provide IERL-Ci with information concerning the requirements for the environmental characterization of an alcohol plant. It should prove useful as a guide in future sampling efforts conducted for the alcohol industry. In addition, this study was conducted to furnish IERL-Ci with environmental data from a commercial facility currently providing anhydrous ethanol for Gasohol. This information can be used to determine the environmental impacts from large-scale alcohol plants. Further information concerning this subject can be obtained from Robert Mournighan of the Advanced Energy Systems Branch, Energy Pollution Control Division.

David G. Stephan
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ABSTRACT

This study defines the requirements for environmental sampling and analysis of alcohol-producing facilities capable of supporting a Gasohol industry and applies these requirements to the environmental characterization of an alcohol plant. This document includes a conceptual design of a grain alcohol plant using a coal-fired boiler that is projected to be typical of future plants which will support a Gasohol industry. Environmental control options are also discussed based on a comparison of alcohol plant stream compositions with environmental regulations. The results of this study provide preliminary information on the environmental consequences of large-scale fermentation ethanol plants which will provide alcohol for Gasohol.

This study was conducted by Radian Corporation, McLean, Virginia, under the direction of Mr. Gilbert J. Ogle, Program Manager. The program was carried out under EPA Contract No. 68-03-2667.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AA	-- atomic absorption
BOD	-- biochemical oxygen demand
COD	-- chemical oxygen demand
M ³	-- cubic meters
DDG	-- distiller's dried grains
DS	-- dissolved solids
FID	-- flame ionization detection
GC	-- gas chromatography
HHV	-- higher heating value
kJ	-- kilojoules
kPa	-- kiloPascals
kw	-- kilowatts
MS	-- mass spectroscopy
ND	-- not detected
OVA	-- organic vapor analyzer
PM	-- particulate matter
ppb	-- parts per billion
ppm	-- parts per million
SS	-- suspended solids
TDS	-- total dissolved solids
THC	-- total hydrocarbon
TOC	-- total organic carbon
TS	-- total solids
TSS	-- total suspended solids
VDS	-- volatile dissolved solids
VSS	-- volatile suspended solids

micro

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We also wish to thank the management and operating staff of Midwest Solvents' alcohol facility in Atchison, Kansas for their assistance and cooperation in preparing this document and in conducting the sampling effort. The efforts of Mr. James Mandia, U.S. EPA Region VII; Mr. Bruce Newton, IPP/NAFC; Dr. William Telliard, Effluent Guidelines Division, U.S. EPA; Ms. Yvonne Garbe, Office of Solid Waste, U.S. EPA; Mr. David Markowordt, Office of Air Planning and Standards, U.S. EPA; Mr. Mike Malloy, Aerospace Corporation; and Mr. Bill Kubby, Acurex Corporation in the review of this document are also appreciated.

SECTION 1

INTRODUCTION

OBJECTIVE

The objectives of this program are to define the requirements for environmental sampling and analysis of alcohol-producing facilities which are developing to support a Gasohol industry, and to apply these requirements to a demonstrated sampling and analysis effort at a selected alcohol plant.

Background

Ethanol has been used as a fuel mixed with gasoline or alone as early as the 1930's. Prior to World War II, over 4 million cars ran on alcohol fuels. The market for alcohol fuels, however, diminished as gasoline became inexpensive and plentiful. A systematic investigation of large-scale use of alcohol as a gasoline substitute began only with the advent of the energy crunch in 1973.

Today the term Gasohol (1) has been coined to describe a blend of 90 percent unleaded gasoline and 10 percent agriculturally derived ethanol, although ethanol can be used in concentrations up to 20 percent in gasoline without carburetor modification. Alcohol is an attractive alternative liquid fuel since it can be synthesized from renewable biomass sources. As a near-term gasoline substitute, ethanol can help alleviate the oil import problem and reduce the balance of trade deficit while providing a market for farm surpluses or wood and wood residues. There are many political and economic factors which favor the development of a gasohol industry; however, there are also some uncertainties about the industry which should be investigated. One of these is the environmental impact of large-scale alcohol-producing facilities.

Radian Corporation has conducted a program to define requirements for environmental sampling and analysis of alcohol-producing facilities which are developing to support a Gasohol

(1) "Gasohol" is a registered trademark of the Nebraska Agricultural Products Industrial Utilization Committee.

industry, and has applied these requirements to the environmental characterization of an alcohol plant. This program was carried out under Work Directive S1003 of EPA Contract No. 68-03-2667. Four interim reports were previously submitted to EPA under this project.

Approach

To address the first objective, the determination of sampling and analytical requirements for facilities capable of providing alcohol for Gasohol, the following tasks were conducted:

- Task 1 - Data collection;
- Task 2 - Process evaluation;
- Task 3 - Review of environmental regulations; and
- Task 4 - Assessment of control technology and requirements.

In the first task, state-of-the-art technology was summarized to identify commercial or pilot plant facilities typical of those which would support a Gasohol industry. Information on ethanol and methanol processes utilizing a variety of biomass materials was collected from technical publications and journals as well as from contacts with project officers of government agencies and industrial personnel. A bibliography (page 134) was assembled containing the sources of information for this task and was submitted as the first interim report for this program.

To address the second task, the information gathered on alcohol technology was assessed to identify several existing alcohol beverage plants which employ processing steps similar to those which might be utilized in future alcohol fuel plants. Flow diagrams, processing steps, mass balances, and emissions sources were identified for these plants. These data were presented in a second interim report and are included in Appendix A. A detailed mass and energy balance for an alcohol fuel plant considered to be typical of future alcohol facilities supporting a Gasohol industry, also presented in the interim report, has been updated and included in Section 3.

Task 3 consisted of a review of federal and state environmental regulations which might be applicable to fermentation ethanol facilities. This information is presented in Section 4; supporting data is provided in Appendix B.

In Task 4, a comparison of the environmental regulations identified in Task 3 with alcohol stream compositions was made to

define the environmental control requirements necessary for compliance. A discussion of this analysis and designation of the probable control technologies to be implemented are presented in Section 5. The information in Sections 4 and 5 comprised the third interim report for this project.

To conduct the sampling and analysis of an alcohol plant, the second objective of this program, a site-specific sampling plan, was formulated based on the sampling and analytical requirements determined in the previous tasks. These sampling requirements and test plan constituted the fourth interim report of this program and are presented in Sections 6 and 7, respectively.

A brief discussion of the sampling trip (which highlights any deviations made in the test plan during sampling and analysis) is included in Section 8. The results and conclusions from the sample analyses are presented in Section 2.

SECTION 2

CONCLUSIONS AND ANALYTICAL RESULTS OF AN ALCOHOL PLANT ENVIRONMENTAL CHARACTERIZATION

CONCLUSIONS AND RECOMMENDATIONS

The sampling and analytical requirements for the environmental characterization of an ethanol-producing facility include:

- A quantification of the pollutants present in effluent streams such as pesticides, ammonia, benzene, and metals in the solid waste streams and by-products; solids, organics, metals, pH, pesticides and benzene in the liquid effluents; and criteria pollutants, hydrocarbons, and benzene in the air emissions.
- A determination of the effectiveness of environmental control modules such as condensers on distillation columns and vacuum lines; cyclones, scrubbers, or other mechanical collectors on stacks or dryer exhausts; and biological treatment on distillery wastewaters.
- A characterization of selected internal process streams to determine the fate of pesticides or benzene losses in an alcohol plant.

Table 1 presents a summary of the analytical parameters and methods of analyses necessary to conduct an environmental characterization of an alcohol plant.

As a result of the research conducted in this program, it was determined that:

- Alcohol facilities have the potential to cause environmental problems from the discharge of liquid effluents or air emissions if these streams are not properly treated or controlled.
- Untreated distillery wastewaters are acidic and high in biochemical oxygen demand (BOD), chemical oxygen demand (COD), and suspended solids (SS).
- Uncontrolled exhausts from by-product distiller's dried grain (DDG) dryers are high in particulate loading.

TABLE 1. ANALYTICAL PARAMETERS AND METHODS FOR ALCOHOL
PLANT PROCESS AND EFFLUENT STREAMS

<u>Analytical Parameters</u>	<u>Stream</u>	<u>Analytical Method</u>
<u>Gases</u>		
NO _x	boiler flue gases, dryer off gases	EPA Method 7
SO ₂	boiler flue gases, dryer off gases	EPA Method 6
CO ₂	boiler flue gases, dryer off gases	Orsat analyzer
particulates	boiler flue gases, dryer off gases mechanical collectors	EPA Method 5
hydrocarbons	boiler flue gases, dryer off gases fermentation vents, all condenser vents	GC w/FID
benzene	dehydration column and stripping column condenser vents	GC w/FID
<u>Liquids</u>		
solids	makeup water, barometer condensate, cooling tower and boiler blowdown, fermenter wash water, wastewater, treatment influent and effluent	EPA 160.1, 160.2, 160.3, 160.4
organics	all effluent streams of concern except boiler blowdown	BOD (EPA 405.1) COD (EPA 410.1) TOC (EPA 415.1)
metals	makeup water, cooling tower and boiler blowdown, wastewater treatment influent and effluent	AA
pH	all effluent streams	pH meter (EPA 150.1)
benzene	makeup water, dehydration column and stripping column bottoms, wastewater treatment influent and effluent streams	GC/MS
pesticides	fermenter wash water, flash cooler condensate, cooker feed, fermenter outlet, wastewater influent and effluent	GC/MS
sulfates	makeup water cooling tower blowdown, wastewater treatment influent and effluent	Gravimetric
<u>Solids</u>		
pesticides	biological sludge, by-product grains, feedstock grains	GC/MS
ammonia	biological sludge, by-product grains, feedstock grains	EPA 350.2
benzene	biological sludge, by-product grains, feedstock grains	GC
metals	biological sludge, by-product grains, feedstock grains	AA

- NO_x, SO₂ and particulate emissions from fuel oil or coal combustion for steam generation can be a major environmental problem at an alcohol plant.
- Solid waste streams, which can be eliminated through recycle and inclusion in the by-products, pose no serious environmental problems as they are innocuous.

The conclusions listed below are based on the analytical results (see Section 2 - Results) obtained from the environmental characterization of an alcohol plant:

Solid Wastes and By-Products

- The analysis of benzene, pesticides, and ammonia in the DDG, animal feed, and biosludge streams revealed that no major environmental problems would be associated with the discharge or utilization of solid wastes from this alcohol plant due to the presence of these compounds.
- Pesticides identified on feedstock grains were apparently destroyed during feedstock preparation (i.e., cooking) as no traces of pesticides were found in the solid wastes or wastewater effluent streams.

Wastewaters

- Dissolved solids (DS), the major contributor to total solids (TS) came from the makeup city water and well water, not the fermentation process.
- Barometric condensate, evaporator condensate, and fermenter wash water were the only significant sources of suspended solids (SS) at the alcohol plant.
- Benzene does not appear to be a major wastewater problem for this facility, which employs a benzene dehydration unit, as it was detected at levels less than 60 ppb in the wastewater.
- All wastewater streams from fermentation and distillation were acidic; they could be an environmental problem if not neutralized prior to discharge.
- Extended aeration and clarification reduced high concentrations of suspended solids (SS), BOD, COD, total organic carbon (TOC), and ammonia in the wastewater from this distiller to acceptable discharge levels.

- The plant records for this alcohol plant show that excursions in the biological treatment system may occur due to occasional spills or mechanical problems. Additional aeration facilities or equilization basins can be employed to avoid the discharge of poorly treated wastewaters due to upsets in the current system.
- Most of the 14 priority pollutants detected at very low levels (less than 40 ppb) in the wastewaters from this facility were found to be contaminants from equipment or the on-site laboratory and not products or by-products of alcohol production.
- Total solids (TS) concentration in the bottoms from the solvent extractor, rectifier, fusel oil column, stripping column, and dehydration column were very low due to upstream removal in the beer still.

Air Emissions

- Condensers, the only pollution abatement devices for hydrocarbons on the vent lines, provided adequate control for hydrocarbon emissions.
- Sulfur dioxide and nitrogen oxide emission levels were low as expected for a facility using natural gas. Combustion of fuel oil or coal could present greater environmental problems.
- The analysis for particulate emissions from the cyclones on the dryers showed this facility to be in compliance. However, particulate emissions have a high potential to be an environmental problem for alcohol plants which dry their by-product grains or use coal or No. 6 fuel oil for steam generation.

It must be emphasized that the above conclusions are based on a single environmental characterization. Additional sampling and analysis should be conducted at other plant sites to confirm these initial conclusions.

Recommendations--

Recommendations for further research to ensure that alcohol plants supporting the Gasohol industry pose no major environmental problems include:

- (1) Gas chromatography/mass spectroscopy (GC/MS) analysis of pesticide levels in the flash cooler condensate and the feed stream to the fermenter to confirm the fate of pesticides in alcohol synthesis;

- (2) Environmental characterization of other distilleries which utilize different feedstocks, processing equipment, fuel sources, and wastewater treatment methods;
- (3) Evaluation of other pollution control technologies to control emissions and effluents;
- (4) Performance of area monitoring for hydrocarbons to determine worker safety information; and
- (5) Analysis for priority pollutant metals should be conducted for the by-product stream to determine whether these species could build up in concentration when landfarmed or landspread.

Results--

The analytical results of the sampling effort are presented below for each of the solid, liquid, and gas streams sampled.

Solids--Table 2 reveals the concentration of benzene, pesticides, and ammonia (measured as nitrogen content) in the animal feed, distiller's dried grains (DDG), and biological sludge from wastewater treatment. The benzene level of the streams was quite low. No pesticides were detected in any of these streams. The detection limit for biological sludge (5 percent solids) was lower than that for DDG (95 percent solids) since the GC analysis was conducted using a liquid sample. The nitrogen content of these streams was also low.

As expected, a variety of pesticides was found in the feedstock grain. Gas chromatography indicates the presence of nine commonly used pesticides in concentrations of 0.003 ppm to 16.2 ppm as shown in Table 3. The gas chromatography analytical technique applied in this screening effort involved matching elution of the peaks from the gas chromatography column with standard values established for these compounds. The precision and accuracy of this analytical method is limited due to interferences between pesticides and other compounds in the sample. However, this method is sufficient to indicate the presence of pesticides. The concentration of pesticides can be confirmed in future work by using gas chromatography analysis in conjunction with mass spectroscopy as in the priority pollutant analysis.

Liquids--Table 4 presents the analytical results for all liquid stream parameters. Each pollutant's parameters will be discussed separately in the following paragraphs.

Total Solids (TS)--The concentration of TS varied from 13 to 2,735 ppm. The lowest values were for the flash cooler condensate and evaporator condensate while wastewater treatment

TABLE 2. ANALYTICAL RESULTS/SOLIDS

<u>Analytical Parameters</u>	<u>Streams</u>		
	<u>Animal Feed</u>	<u>DDG</u>	<u>Biological Sludge</u>
Benzene ⁽¹⁾ (ppb)	2.9	15.2	16.2
Pesticides	ND ⁽²⁾	ND ⁽³⁾	ND ⁽⁴⁾
Ammonia (ppm N)	135	135	50

-
- (1) Average of two determinations
 (2) Detection limit was 10 ppb
 (3) Detection limit was 40 ppb
 (4) Detection limit was 1 ppb

TABLE 3. PESTICIDE LEVEL IN FEEDSTOCK GRAIN

<u>Pesticide Measured</u>	<u>Concentration (ppm)</u>
p, p'-DDT	16.2
Endrin	1.0
DDD and/or β -Endosulfan	0.1
Dieldrin and/or p, p'-DDE	0.35
α -Endosulfan	0.06
Heptachlor and/or β -BHC	0.04
Aldrin and/or Δ -BHC	0.008
Heptachlor Epoxide	0.007
α -BHC	0.003

TABLE 4. ANALYTICAL RESULTS FOR LIQUID STREAMS

<u>Analytical Parameter (ppm)</u>	<u>City Water</u>	<u>Cooker Feed</u>	<u>Flash Cooler Condensate</u>	<u>Fermenter Outlet</u>	<u>Solvent Extractor Bottoms</u>	<u>Rectifier Bottoms</u>	<u>Fusel Oil Column Bottoms</u>	<u>Dehydration Column Bottoms</u>	<u>Stripping Column Bottoms</u>	<u>Barometric Condensate</u>
Sample Date	8/16	8/16	8/18	8/17	8/18	8/18	8/18	8/18	8/18	8/16
Total Solids	547		13		161	113	221	(1)		2330
Total Dissolved Solids	547		8		161	113	218		<1	
Volatile Dissolved Solids	120									
Total Suspended Solids	<1		4.5		<1	<1	3	<1	<1	100
Volatile Suspended Solids	<1									
BOD	<1		1880		1570	1440	97		16	3204
TOC	2.9				533	563	36		11	1790
pH (average)	7.46		3.36		4.41	4.67	7.09		4.11	2.61
Benzene (ppb)	10.8							59.4	5.7	
Ammonia (as N)	<1									
Pesticides		(2)	ND	ND		ND				(3)
Sulfate	190									
Copper	<0.1									
Iron	0.2									
Iodine	<2									

(1) Sample not available for analysis.

(2) Endrin 4.7 ppb; α -Endosulfan 93.8 ppb; Aldrin and/or β -BHC 37 ppb.(3) DDD and/or β -Endosulfan 9.3 ppb.

ND Not Detected (<1 ppb).

(continued)

TABLE 4. (continued)

Analytical Parameter (ppm)	Evaporator Condensate		Cooling Tower Blowdown		Fermenter Wash Water	Well Water		Wastewater Treatment Influent	Wastewater Treatment Effluent		Boiler Blowdown
Sample Date	8/16	8/17	8/16	8/17	8/18	8/16	8/17	8/16	8/16	8/17	
Total Solids	136	74	1450	1350	841	617	640	1200	326	313	2735
Total Dissolved Solids	68	64	1260	1160	648	599	619	671	309	304	2730
Volatile Dissolved Solids	68	64	364	356		177	86	301	139	130	
Total Suspended Solids	68	10	191	192	193	18	21	530	17	9	5
Volatile Suspended Solids	67	10	183	190	173	4	5	525	11	9	
BOD	3160	(3)	831	(3)	323	2	(3)	93	3	(3)	
COD			1090	(3)				2600	20	(3)	
TOC	1230	(3)	340	(3)	126	3.5	(3)	828	7	(3)	
pH (average)	2.91	2.73	5.30	5.10	6.13 ⁽¹⁾	7.18	7.03	4.32	7.16	6.84	11.53
Benzene (ppb)			2.7	3.0		3.7	3.2	5.0	6.6	27.9	
Ammonia (as N)					<1	<1	(3)	42	<1	(3)	
Pesticides		ND	ND	ND	ND			ND	ND	ND	
Sulfate			520	450		47	55	47	49	52	
Copper			0.024	0.64		<0.05	<0.05	0.95	0.68	<0.05	0.19
Iron			8.5	10		8.1	8.0	19	0.35	0.27	0.35
Iodine			<2	<2	22	<2	<2	<2	<2	<2	

(1) One determination only.

(2) Results for 8/17 suspect due to disruption of normal operation.

(3) Analysis conducted after sample preservation expiration.

ND Not Detected (<1 ppb).

influent, cooling tower blowdown, and barometric condensate values were relatively high. Since the beer still removes most of the solids from the alcohol/water streams, the solids concentration in all subsequent columns such as the solvent extractor, rectifier, and fusel oil column was also low. Solids in the wastewater treatment effluent were also much lower than in wastewater treatment influent due to biological action.

Total Dissolved Solids (TDS)--The range for TDS was less than 1 ppm (stripping column bottoms) to 2,730 ppm (boiler blowdown). High TDS levels in the boiler blowdown and cooling tower blowdown are due to the build-up of impurities and water treatment chemicals caused by the evaporation of water. Total dissolved solids were the major contributor to total solids in all of the streams analyzed.

Volatile Dissolved Solids (VDS)--The concentration of VDS varies from 64 ppm to 364 ppm. As expected, VDS constitute all of the dissolved solids for the evaporator condensate stream and a large portion of the dissolved solids for the wastewater treatment influent. The dissolved solids for remaining streams were less than one-third VDS.

Total Suspended Solids (TSS)--Wastewater treatment influent, cooling tower blowdown, fermenter wastewater, and barometric condensate streams were relatively high in suspended solids. TSS concentration for city water, flash cooling condensate boiler blowdown, and the bottoms from the solvent extractor, rectifier, dehydration column, fusel oil column, and stripping column were near or below the detection limit (1 ppm). Low levels of suspended solids were also found in the well water, wastewater treatment effluent, and evaporator condensate streams.

Volatile Suspended Solids (VSS)--Most of the suspended solids found were VSS. In every stream analyzed, except the well water, VSS comprised 75 to 100 percent of the total suspended solids, which means that most of the suspended material was organic in nature.

Biochemical Oxygen Demand (BOD)--Levels of BOD range from 4 ppm (city water) to 3,204 ppm (barometric condensate). Generally, streams which were found to be high in solids were also high in BOD. These include barometric and evaporator condensate, cooling tower blowdown, fermenter wastewater, and wastewater treatment influent. Exceptions were the flash cooler condensate and column bottoms from the solvent extractor and rectifier which have low solids content but high BOD. However, these streams were also high in dissolved organic compounds (based on TOC analysis) which also contribute to high BOD values. The BOD for wastewater treatment effluent and well water was very low.

Chemical Oxygen Demand (COD)--Analysis for COD was conducted for three streams: cooling tower blowdown, wastewater treatment influent, and wastewater effluent. The values for the first two streams were very high. The COD for the wastewater effluent was low, indicating good performance from biological treatment.

Total Organic Carbon (TOC)--Measurements of TOC vary from 3 to 1,790 ppm. The TOC concentration for city water, stripping column and fusel oil column bottoms, well water, and wastewater treatment effluent was low. For the remaining eight streams, the TOC level was one-third to two-thirds the BOD concentration, indicating that organic compounds such as ethanol or fusel oils account for a large portion of the BOD.

pH--The liquid streams exhibited a pH range of 2.6 to 11.5 with most of the streams being acidic. These include condensate from the barometric condensers, evaporator, and flash cooler; column bottoms from the solvent extractor, rectifier, and stripping column; cooling water blowdown; fermenter wastewater; and wastewater treatment influent stream. Acidity in these streams is due to the addition of sulfuric acid during fermentation to retard bacterial growth. Boiler water blowdown was the only basic stream. The high pH of this stream was due to pH requirements for boiler water. Relatively neutral streams include city water, well water, fusel oil column bottoms, and wastewater effluent streams.

Benzene--Benzene concentration was reported in the range of 2.7 to 59.4 ppb for the liquid streams. These values are near the detection limit for benzene and have limited accuracy.

Ammonia--Ammonia concentration, analyzed as ppm nitrogen, was below the detection limit for all streams except wastewater treatment influent. Biological treatment reduced this level to less than 1 ppm in the wastewater effluent.

Pesticides--Gas chromatography indicated the presence of pesticides in only two streams: feed to the cooker and barometric condensate. The presence of pesticides in the cooker feed was expected since traces were found on the feedstock grain. The existence of these compounds in the condensate stream, however, was not expected since the pesticides are believed to be destroyed during the cooking process. As mentioned earlier, mass spectroscopy can be used with GC analysis to confirm the presence of pesticides in the streams.

Sulfates--Relatively high concentrations of sulfates were present in the cooling tower blowdown and city water makeup stream. The other streams tested (well water and wastewater treatment influent and effluent streams) contained moderate amounts of sulfates. The source of sulfates for the process

streams was most likely from the addition of sulfuric acid for pH control and from the city water makeup stream.

Copper--The concentration for copper was low in all of the streams, ranging from less than 0.01 ppm in the city water to 0.95 ppm in the wastewater treatment influent stream.

Iron--The concentration of iron varied from 0.2 ppm to 9.0 ppm. High levels of iron were found in the cooling tower blowdown, well water, and wastewater treatment influent streams. Iron level in the wastewater treatment effluent, boiler blowdown, and city water was very low.

Iodine--The concentration of iodine in all streams except the fermenter wash water was below the detection limit (less than 2 ppm). The analysis indicates the fermenter wash water streams had an iodine level of 22 ppm, which compares favorably with the 25 ppm concentration that plant personnel reported to be using for cleaning and disinfection.

Priority Pollutant Analysis--

Tables 5 through 9 present the results of priority pollutant analysis of the cooling tower blowdown, wastewater treatment influent, and wastewater effluent stream. The general types of priority pollutant compounds for which GC/MS analysis was conducted include total cyanides, total phenols, volatiles, pesticides, acid compounds, and base/neutral compounds. Analysis for metals was conducted using atomic absorption.

Metals, Total Cyanide, Total Phenol--Table 5 presents the results of priority pollutant analysis of metals, total cyanide, and total phenol. The results indicate ppb levels of all the parameters. If present, beryllium, lead, mercury, selenium, silver, thallium, and total cyanide values were below their detection limits. The wastewater treatment effluent streams have the lowest concentration of the parameters detected; all species except chromium, copper, and total phenols are highest in the cooling tower blowdown stream.

Volatiles--GC/MS analysis indicated the presence of five volatile priority pollutants at concentrations of 15 µg/l or less in the streams tested (Table 6). Chloroform and methyl chloride were detected in the cooling tower blowdown, and benzene and methylene chloride were detected in the wastewater treatment influent and effluent streams. The chloroform, methyl chloride, and methylene chloride were likely to be contaminants from the laboratory as they are common reagents used in routine analysis. Toluene, also present in the wastewater treatment influent stream, was probably associated with the benzene used in dehydration operations.

TABLE 5. ANALYTICAL RESULTS FOR PRIORITY POLLUTANTS
METALS, TOTAL CYANIDE, AND TOTAL PHENOL

Analytical Parameter (ppb)	Stream		
	Cooling Tower Blowdown	Wastewater Influent	Wastewater Effluent
Antimony	18 \pm 3	10.0 \pm 5	4.5 \pm 0.4
Arsenic	7.5 \pm 1.5	2.4 \pm 0.1	0.4 \pm 0.2
Beryllium	4 \pm 1	<1	<1
Cadmium	2.5 \pm 0.4	1.0 \pm 0.1	0.3 \pm 0.1
Chromium	4.4 \pm 0.1	7.0 \pm 0.4	1.2 \pm 0.1
Copper	24	950	680
Lead	<5	<5	<5
Mercury	<0.2	<0.2	<0.2
Nickel	4 \pm 2	4 \pm 2	<0.5
Selenium	<0.3	<0.3	<0.3
Silver	0.72 \pm 0.02	<0.06	<0.06
Thallium	<2	<2	<2
Zinc	750 \pm 10	270 \pm 10	<50
Total Cyanide	<20	<20	<20
Total Phenol	56	84	7.5

TABLE 6. PRIORITY POLLUTANT ANALYSIS: VOLATILES (µg/l)

	Stream		
	Tower Blowdown	Wastewater Influent	Wastewater Effluent
Acrolein	ND	ND	ND
Acrylonitrile	ND	ND	ND
Benzene	ND	1.6	1.1
Carbon tetrachloride	ND	ND	ND
Chlorobenzene	ND	ND	ND
1,2-Dichloroethane	ND	ND	ND
1,1,1-Trichloroethane	ND	ND	ND
1,1-Dichloroethane	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	ND
1,1,2,2-Tetrachloroethane	ND	ND	ND
Chloroethane	ND	ND	ND
bis (Chloromethyl) ether	ND	ND	ND
2-Chloroethylvinyl ether	ND	ND	ND
Chloroform	5.7	ND	ND
1,1-Dichloroethylene	ND	ND	ND
1,2-trans-Dichloroethylene	ND	ND	ND
1,2-Dichloropropane	ND	ND	ND
1,3-Dichloropropylene	ND	ND	ND
Ethylbenzene	ND	ND	ND
Methylene chloride	ND	15.	6.1
Methyl chloride	3.3	ND	ND
Methyl bromide	ND	ND	ND
Bromoform	ND	ND	ND
Dichlorobromomethane	ND	ND	ND
Trichlorofluoromethane	ND	ND	ND
Dichlorodifluoromethane	ND	ND	ND
Chlorodibromomethane	ND	ND	ND
Tetrachloroethylene	ND	ND	ND
Toluene	ND	1.6	ND
Trichloroethylene	ND	ND	ND
Vinyl chloride	ND	ND	ND

ND = Not Detected (<1 µg/l)

Pesticides--No traces of the 25 commonly used pesticides were detected in the cooling tower blowdown or wastewater treatment influent and effluent streams as shown in Table 7.

Acid Compounds--Table 8 reveals that four different acidic priority pollutants were detected in the streams sampled at concentrations of 36 $\mu\text{g/l}$ or lower. The cooling tower blowdown stream contained 2,4-dimethylphenol, pentachlorophenol, and phenol, while the wastewater treatment influent contained 2-nitrophenol and phenol. Sodium pentachlorophenolate is commonly used to help reduce bacterial growth during fermentation; in the acidic environment of the fermenter, it may degrade to pentachlorophenol. Phenol is a by-product in the fermentation process and is typically found in small amounts along with the fusel oils and aldehydes. The source of 2,4-dimethylphenol and 2-nitrophenol is unknown. No acid compounds were detected in the wastewater effluent stream.

Base/Neutral Compounds--Bis (2-ethylhexyl) phthalate, di-n-butyl phthalate, and diethyl phthalate were detected in all three streams at concentrations of 30 $\mu\text{g/l}$ as shown in Table 9. The presence of phthalates was likely due to contamination from tubing or other plastic materials which use these compounds as plasticizers. Anthracene and phenanthrene were detected at the 1.5 $\mu\text{g/l}$ level in the wastewater influent stream; the source of these compounds is unknown.

Gases--

Sampling data and analytical results for air effluent streams from the alcohol plant are presented in Tables 10 through 12.

Total Hydrocarbons and Benzene--Table 10 presents the results of total hydrocarbon and benzene analysis for the air effluent streams measured as ppm methane. The stream with the highest concentration of hydrocarbons was the condenser vent on the stripping column. Benzene accounts for about 95 percent of the hydrocarbons in this stream, which is not remarkable since the vent lines from the separator and benzene storage tank are also connected to this vent. The condenser vent on the dehydration column also had a high concentration of hydrocarbons, half of which was benzene. Although these vents had high concentrations of hydrocarbons, the total emissions from these sources were small due to the low gas flow rates from the vents.

The streams with the lowest concentrations of hydrocarbons were the vent on the dryer cyclone and the fermenter vent. The flow rates of these streams were relatively large, however, and the mass emission from these sources was of the same magnitude as the mass emissions from the stripping column and the dehydration

TABLE 7. PRIORITY POLLUTANT ANALYSIS: PESTICIDES ($\mu\text{g/l}$)

	Stream		
	Tower Blowdown	Wastewater Influent	Wastewater Effluent
Aldrin	ND	ND	ND
Dieldrin	ND	ND	ND
Chlordane	ND	ND	ND
4,4'-DDT	ND	ND	ND
4,4'-DDE	ND	ND	ND
4,4'-DDD	ND	ND	ND
α -Endosulfan	ND	ND	ND
β -Endosulfan	ND	ND	ND
Endosulfan sulfate	ND	ND	ND
Endrin	ND	ND	ND
Endrin aldehyde	ND	ND	ND
Heptachlor	ND	ND	ND
Heptachlorepoxyde	ND	ND	ND
α -BHC	ND	ND	ND
β -BHC	ND	ND	ND
γ -BHC	ND	ND	ND
σ -BHC	ND	ND	ND
PCB-1242	ND	ND	ND
PCB-1254	ND	ND	ND
PCB-1221	ND	ND	ND
PCB-1232	ND	ND	ND
PCB-1248	ND	ND	ND
PCB-1260	ND	ND	ND
PCB-1016	ND	ND	ND
Toxaphene	ND	ND	ND

ND = Not Detected ($<1 \mu\text{g/l}$)

TABLE 8. PRIORITY POLLUTANT ANALYSIS: ACID COMPOUNDS (µg/l)

	Stream		
	Tower Blowdown	Wastewater Influent	Wastewater Effluent
2,4,6-Trichlorophenol	ND	ND	ND
p-Chloro-m-cresol	ND	ND	ND
2-Chlorophenol	ND	ND	ND
2,4-Dichlorophenol	ND	ND	ND
2,4-Dimethylphenol	36.0	ND	ND
2-Nitrophenol	ND	10.0	ND
4-Nitrophenol	ND	ND	ND
2,4-Dinitrophenol	ND	ND	ND
4,5-Dinitro-o-cresol	ND	ND	ND
Pentachlorophenol	4.2	ND	ND
Phenol	4.5	7.0	ND

ND = Not Detected (<1 µg/l)

TABLE 9. PRIORITY POLLUTANT ANALYSIS: BASE/NEUTRAL
COMPOUNDS ($\mu\text{g}/\text{l}$)

	Stream		
	Tower Blowdown	Wastewater Influent	Wastewater Effluent
Acenaphthene	ND	ND	ND
Benzidine	ND	ND	ND
1,2,4-Trichlorobenzene	ND	ND	ND
Hexachlorobenzene	ND	ND	ND
Hexachlorobenzene	ND	ND	ND
bis(2-Chloroethyl) ether	ND	ND	ND
2-Chloronaphthalene	ND	ND	ND
1,2-Dichlorobenzene	ND	ND	ND
1,3-Dichlorobenzene	ND	ND	ND
1,4-Dichlorobenzene	ND	ND	ND
3,3'-Dichlorobenzidine	ND	ND	ND
2,4-Dinitrotoluene	ND	ND	ND
2,6-Dinitrotoluene	ND	ND	ND
1,2-Diphenylhydrazine (as azobenzene)	ND	ND	ND
Fluoranthene	ND	ND	ND
4-Chlorophenyl phenyl ether	ND	ND	ND
4-Bromophenyl phenyl ether	ND	ND	ND
bis(2-Chloroisopropyl) ether	ND	ND	ND
bis(2-Chloroethoxy) methane			
Hexachlorobutadiene	ND	ND	ND
Hexachlorocyclopentadiene	ND	ND	ND
Isophorone	ND	ND	ND

ND = Not Detected ($<1 \mu\text{g}/\text{l}$)

(continued)

TABLE 9. (continued)

	Stream		
	Tower Blowdown	Wastewater Influent	Wastewater Effluent
Naphthalene	ND	ND	ND
Nitrobenzene	ND	ND	ND
N-Nitrosodimethylamine	ND	ND	ND
N-Nitrosodiphenylamine	ND	ND	ND
N-Nitrosodi-n-propylamine	ND	ND	ND
bis(2-Ethylhexyl) phthalate	30	22	10
Butyl benzyl phthalate	ND	ND	ND
Di-n-butyl phthalate	2.5	5.5	1.6
Di-n-octyl phthalate	ND	ND	ND
Diethyl phthalate	2.8	7.5	1.5
Dimethyl phthalate	ND	ND	ND
Benzo(a)anthracene	ND	ND	ND
Benzo(a)pyrene	ND	ND	ND
3,4-Benzofluoranthene	ND	ND	ND
Benzo(k)fluoranthene	ND	ND	ND
Chrysene	ND	ND	ND
Acenaphthylene	ND	ND	ND
Anthracene	ND	1.5	ND
Benzo(ghi)perylene	ND	ND	ND
Fluorene	ND	ND	ND
Phenanthrene	ND	1.5	ND
Dibenzo(a,h)anthracene	ND	ND	ND
Indeno(1,2,3-c,d)pyrene	ND	ND	ND
Pyrene	ND	ND	ND
2,3,7,8-Tetrachloro- dibenzo-p-dioxin	ND	ND	ND

ND = Not Detected ($<1 \mu\text{g/l}$)

TABLE 10. TOTAL HYDROCARBON AND BENZENE ANALYSIS AND SAMPLING DATA

Stream/Parameter	Sample Date	Sample Time	Gas Temp. (°C)	Pipe or Duct (ID-cm)	Avg. Gas Velocity (M/s)	Avg. Gas Flow Rate (Dry M ³ /hr)	Avg. Concentration (ppm CH ₄)	Emissions (kg CH ₄ /hr)
Fermenter Vent THC	8/18	1603-1708				2,960 ⁽¹⁾	95.7	0.19
Beer Still Condenser Vent THC	8/18	1734-1836	65.6	10.8	12,800	74	219	.011
Solvent Extractor Condenser Vent THC	8/18	1214-1325	48.9	10.2	1,460	9.4	1,710	.011
Rectifier Condenser Vent THC	8/18	1845-1936	37.8	10.8	<90	--	1,530	--
Fusel Oil Column Condenser Vent THC	8/18	1103-1207	79.4	10.8	1,140	4.6	973	.003
Dehydration Column Condenser Vent THC Benzene	8/17	1412-1512 1548-1555	37.8	5.1	1,335	2.5	29,900 17,000	0.050 0.027 ⁽²⁾
Stripping Column Condenser Vent THC THC Benzene	8/17	1200-1232 1320-1348 1817-1825	37.8	5.1	1,370	2.5	55,400 55,200 52,900	.095 .095 0.090 ⁽³⁾
Cyclone Vent on Dryer THC	8/17	0912-1003	98.9	158.8	55,600	63,960	7.7	0.33

(1) Total gas flow rate from all fermenters based on hourly plant production.

(2) This is equivalent to 0.31 kg/hr benzene.

(3) This is equivalent to 0.98 kg/hr benzene.

TABLE 11. ANALYTICAL RESULTS AND SAMPLING DATA FOR
AMMONIA, SULFUR DIOXIDE, AND NITROGEN OXIDE

Stream/ Analytical Parameter	Sample Time & Date	Gas Vol. Sampled (M ³)	Total Wt. of Species Collected (µg)	Gas Phase Con- centration (ppm)	Gas Flow Rate (M ³ /hr)	Emission (kg/hr)
Farmenter Vent	8/17					
NH ₃ #1	1613-1740	0.40	<430 ⁽¹⁾	<1.5	2,970	<0.003
NH ₃ #2	1744-1910	0.42	<430 ⁽¹⁾	<1.5	2,970	<0.003
Cyclone Effluent (Dryer)	8/18					
NH ₃ #1	13-05-1455	1.0	2,420	3.27	63,960	.15
NH ₃ #2	1911-2038	0.82	700	1.19	63,960	0.051
SO ₂ #1	1114-1244	0.86	<650 ⁽¹⁾	<0.3	63,960	<0.050
SO ₂ #2	1739-1907	0.76	<650 ⁽¹⁾	<0.3	63,960	<0.050
NO _x #1	1020	0.0013	67.5	26.1	63,960	1.4 ⁽²⁾
NO _x #2	1022	0.0014	29.4	10.7	63,960	0.58 ⁽²⁾
NO _x #3	1433	0.0013	21.9	8.3	63,960	0.50 ⁽²⁾
NO _x #4	1558	0.0012	79.1	32.7	63,960	1.7 ⁽²⁾

(1) Detection Limit

(2) lb/hr of NO₂

TABLE 12. PARTICULATE MATTER ANALYSIS AND DRYER CYCLONE
EFFLUENT SAMPLING DATA

	Particulate Sample #1 8/16	Particulate Sample #2 8/16
Sampling Time	1114-1455	1739-2038
Gas Volume Metered (M^3)	2.0	1.8
Standard Gas Volume (M^3)	1.9	1.7
Average Flue Gas Velocity (M/s)	14.0	14.1
Average Flue Gas Temp. ($^{\circ}C$)	98.9	88.3
Stack Pressure (kPa)	102	102
Flue Gas Composition		
H_2O	19.2	20.4
CO_2	5.0	5.1
O_2	6.5	0.5
CO	0	0.6
N_2	69.3	73.4
Flue Gas Molecular Weight	27.14	26.80
Flue Gas Total Flow (Actual M^3)	1,670	1,670
(M^3 /hour)	63,390	64,240
Duct Diameter (M)	1.6	1.6
Flue Gas Grain Loading (grams/ M^3)	0.04	0.02
Filter Weight Gain (grams)	0.02589	0.01741
Probe Wash Weight Grain (grams)	0.05749	0.02198
Particulate Flow Rate (kg/hour)	2.8	1.5
Sample Percent Isokinetic	110.9	108.9

column. The flow rate from the condenser vent for the rectifier was too low and variable to measure. The hydrocarbon concentrations and emissions for the condenser vents on the beer still, solvent extractor, and fusel oil column were very low.

Ammonia--Samples were taken from the fermenter vent and the dryer cyclone effluent stream for ammonia analysis. As Table 11 illustrates, the ammonia concentration in both streams was very low and total emissions from both streams were less than 0.8 kilograms per hour.

Sulfur Dioxide and Nitrogen Oxide--Table 11 also presents the SO_2 and NO_x results for the dryer cyclone effluent stream. The SO_2 concentration was below the detection limit. Nitrogen oxide concentrations were below 35 ppm, which corresponds to an emission of less than 1.8 kilograms per hour NO_2 .

Particulate Matter--Table 12 presents the results of particulate matter analysis along with sampling data for the effluent stream for the dryer cyclone (flue gas). Particulate emissions were calculated to be 1.4 to 2.7 kilograms per hour with particulate loading measured at 0.02 to 0.04 grams per M^3 . Also presented in this table is the composition of the flue gas.

SECTION 3

ALCOHOL PROCESS EVALUATIONS/CONCEPTUAL DESIGN

This section presents a conceptual design of a fermentation alcohol plant likely to support a Gasohol industry.¹ The major unit operations of the facility are identified and a schematic flow diagram is presented to show internal stream routing. This diagram also forms the framework for mass balances around the major pieces of equipment. Included in the conceptual design discussions are a list of assumptions and a summary of the energy requirements. In light of the rapid political and technological changes presently occurring in the Gasohol field, however, prediction of even the major processing steps must be considered tentative.

Stream flow rates are based on actual plant data while properties were taken from the literature. From this design, estimates were prepared for the sources, levels, and flow rates of potentially hazardous emissions and effluent streams generated by a future alcohol plant.

FERMENTATION ETHANOL PRODUCTION

Before discussing the more complicated flow diagram prepared for the conceptual alcohol plant design, a simplified model containing processing units necessary for any fermentation ethanol process will be described. Figure 1 depicts a generalized flow scheme for a fermentation alcohol facility and illustrates the four essential steps to produce anhydrous ethanol:

- Feedstock preparation;
- Fermentation;
- Distillation; and
- Dehydration.

¹Flow diagrams and mass balances have also been prepared for three existing fermentation ethanol plants. This information has been presented in a previous report and is reiterated in Appendix A of this document.

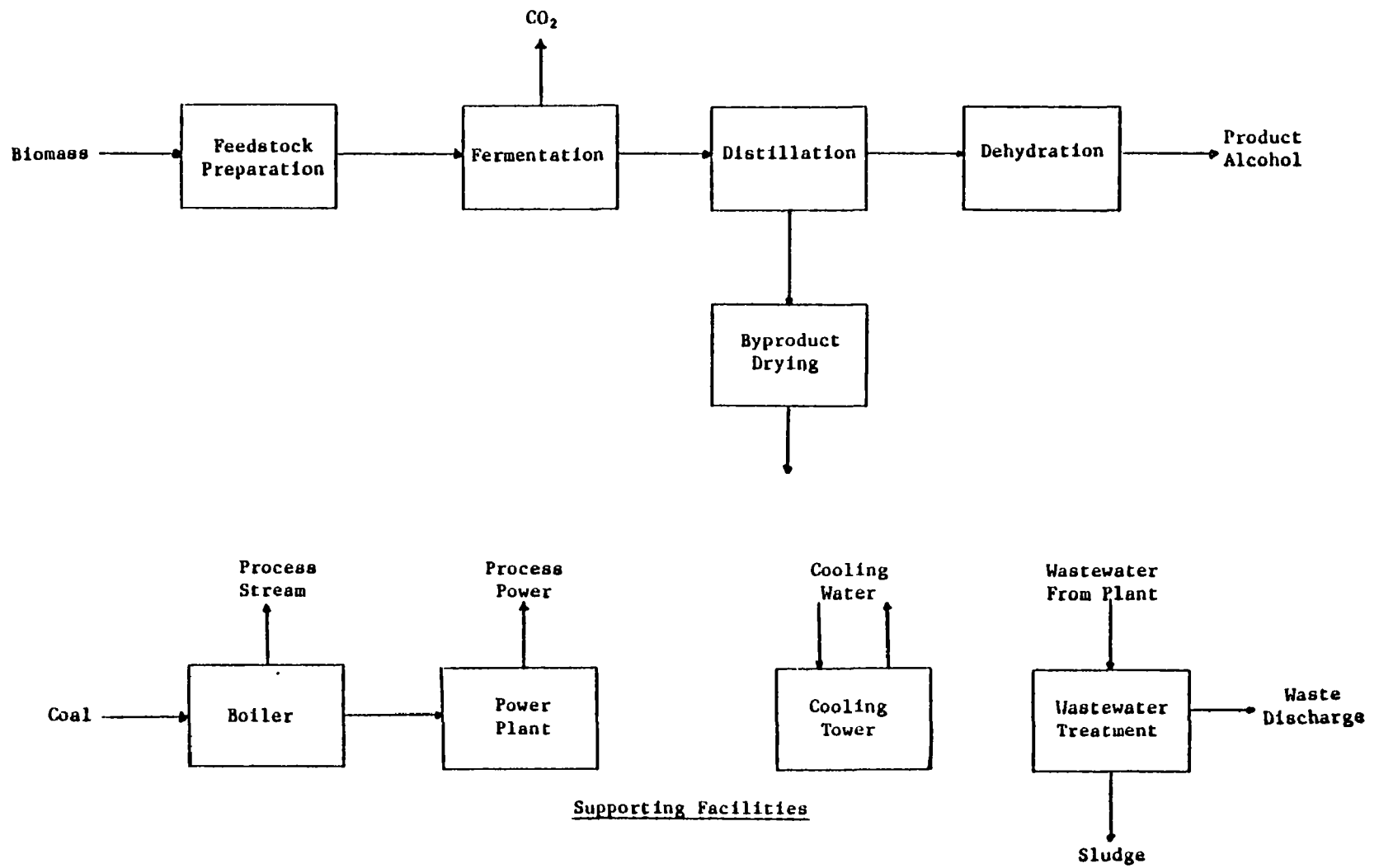


Figure 1. Flow diagram for an alcohol facility.

The first two steps include biological processes. The feedstock preparation step consists of breaking down the starch (polymer of sugar molecules) of the biomass into individual sugar molecules. This includes grinding, cooking, and enzyme conversion. In the next step, fermentation, the yeast converts the sugar to ethanol and carbon dioxide according to the equation below:



The third step, distillation, removes unreacted feedstock material such as protein, fibers, oils, and a small amount of sugar; it also concentrates the solution by separation from water. A portion of the unreacted material can be recycled to fermentation, but most is dried and sold as a by-product (animal feed). Dehydration removes nearly all the remaining water; this step is necessary to produce a fuel product.

Supporting facilities necessary for any plant include the equipment for the steam and power generation required by the process, a cooling tower, and a wastewater treatment system.

Conceptual Design of an Alcohol Fuel Plant

Although the five facilities currently providing ethanol for Gasohol are converted alcohol beverage plants, in the next 5 to 10 years most of the necessary capacity will be generated by "grassroots" facilities using, for the most part, conventional fermentation technology. A conceptual design was developed to reflect such a facility that might be built in that time period.

After a short discussion of the criteria used in selecting the flow scheme, a list of assumptions used to develop the mass and energy balances is presented. Following the mass balance sheets and the flow diagrams is a summary of the overall mass and energy inputs and outputs of the plant. This subsection concludes with a discussion of the environmental impact of an alcohol facility, including an estimate of the probable emission factors according to their sources, flow rates, and levels of pollutants.

Criteria Used for Selection of Processing Steps--

The logical basis for any consideration of a fermentation alcohol plant is the established distillery industry. As cited previously, however, distinct differences exist between fuel grade and a beverage grade alcohol product. These differences lie primarily in the purity and water content of the alcohol. Significant alterations of the processing equipment and procedures required for fuel grade ethanol will result from these operating conditions in the distillation sequence and additional separation columns which are unnecessary in an alcohol fuel

plant. On the other hand, ordinary distillation techniques are unable to remove the 4 to 5 percent water in aqueous alcohol; even this small amount of water in ethanol/gasoline mixtures causes phase separation. To produce anhydrous (water-free) ethanol for fuel use, the remaining water must be extracted using a third component. Other process changes are also possible and are included in the plant design.

More modern equipment has also been incorporated into the conceptual design. For example, low moisture (less than 9 percent) distiller's dried grains (DDG) can be efficiently dried by a pneumatic dryer using air directly heated by combustion flue gases. The moisture laden effluent air is then scrubbed for reduction of particulates and SO₂ before being vented to the atmosphere. Each processing step or procedure was selected as an attempt to reflect the probable construction and operation of a future grassroots fuel alcohol facility.

Assumptions--

The assumptions made in developing a conceptual design were carefully chosen to reflect current or planned practices in the alcohol industry. These assumptions may be grouped into material balance, power and steam production, and emissions-related assumptions.

Material Balance Assumptions--

- (1) Throughput for the plant is 198 cubic meters per day of absolute alcohol, or 6,516 kilograms per hour for an annual production of 436,200 cubic meters per year at an 80 percent operating rate.
- (2) Corn is the feedstock.
- (3) An anhydrous product (less than 0.3 percent water) will be produced.
- (4) Fusel oils and aldehydes will remain in the product alcohol, nominally at concentrations of 1.25 percent.
- (5) A standard distiller's yeast (Saccharomyces cerevisiae) is selected for reaction in the batch fermentation process.
- (6) Fungal amylase is the saccharifying enzyme used to hydrolyze the starch.

- (7) By-products are CO_2 , which can be vented or collected and sold, and an animal feed supplement known as distiller's dried grains (DDG).
- (8) A cooling tower for recirculation of plant cooling water is assumed; a temperature rise of 17°C in the water used for plant cooling equipment is typical.
- (9) In the assessment of alcohol plant emissions, the environmental load is a strong function of the energy required. This is because a large portion of the total plant effluents are generated from heat and power production. In general, many more heat recovery techniques, particularly in the distillation section, could be implemented to lessen the energy requirements. Because of the great variety of these heat recovery procedures, no attempt was made to include more than basic conservation techniques in this initial design.
- (10) In general, heat losses, unless conjectured to be significant, were neglected in making the energy balances.

Power Production--

- (1) Saturated process steam is produced at 1,035 kPa (181°C) and 297 kPa (121°C).
- (2) The cleanup required from a coal-fired boiler would offer great incentive for the use of oil-fired units in the near term. The current policy, however, is that grassroots plants must have coal-firing capability. Therefore, an Illinois No. 6 coal is used as the main fuel source for steam and power production. The following is the ultimate analysis (as-received basis) of the coal:

C	66.3 wt %
H ₂	4.5
O ₂	7.5
N ₂	1.3
Ash	11.7
S	2.7
H ₂ O	5.8
HHV	5,580 kJ/kg

- (3) A spreader stoker coal furnace is used with a boiler efficiency of 80 percent (heat losses of 20 percent).
- (4) Total air at 145 percent of theoretical air is used in firing the coal. Complete combustion is assumed.
- (5) Bottom ash from the spreader stoker boiler is assumed as 35 percent of the total ash in the coal feed.
- (6) For the fuel service to the dryer furnace, a No. 2 distillate fuel oil was selected of the following composition:

C	8.2 wt %
H	12.5
O	Nil
N	0.02
S	0.3
Ash	Nil
HHV	9,270 kJ/kg

- (7) Excess air (60 percent relative humidity and 27°C dry bulb) of 10 percent is used to fire the fuel oil. Complete combustion is assumed.
- (8) A flue gas temperature of 427°C and heat losses of 20 percent are assumed.

Emissions--

- (1) Emission factors for the coal-fired boiler and the oil-fired dryer furnace are adopted from both combustion calculations and the EPA report, "Compilation of Air Pollutant Emission Factors," AP-42 (third edition).
- (2) On-site wastewater treatment using extended aeration as the biological treatment process was chosen. Effluent sludge is to be recycled to the dryer for inclusion with the DDG.
- (3) Cooling water blowdown is assumed at 10 percent of the total cooling water requirement.

Flow Diagnosis of an Alcohol Facility

A conceptual design of an alcohol facility that might support a Gasohol industry appears in Figures 2 and 3. Supporting data is given in Tables 13 and 14.

The process begins by grinding shelled corn in a hammer mill before dilution with water and recycled stillage from the beer still bottoms. Steam is injected to raise the temperature, which aids in solubilizing the mash, thus forming a more suitable substrate for enzymatic hydrolysis. Retention times in the range of 1 to 2 minutes are maintained in the continuous pipeline pressure cooker. The cooked material is cooled to 63°C by evaporating some of the water under vacuum.

Fungal amylase is added in the conversion tank as the hydrolytic enzyme that breaks down the starches to fermentable sugars. Use of the amylase is a notable difference from conventional beverage plants; both federal regulations and final product flavor require distillers to use enzyme directly derived from the malting of barley.

After the cooked mash is cooled to 27°C, it is introduced into the batch fermentation vessels. Yeast is added and the temperature controlled at 27°C in the water-jacketed reactors. The low strength fermented mash (10 percent alcohol) is pumped to the beer still overhead heat exchanger where the feed is heated to 93°C. The heated stream is introduced into the top of the beer still. This column separates the solids and much of the water from the alcohol.

Because the final product is ethanol for fuel, the aldehyde column and the fusel oil purification column(s) found in beverage grade alcohol plants may be eliminated. The overheads from the beer still are fed to the rectifier, where 95 percent alcohol is produced. Fusel oils (mostly amyl alcohols) are removed from the lower part of the column and added to the feed to the dehydration unit. Again, this is permissible in a fuel grade plant because fusel oil contamination does not affect the combustion of ethanol. Water is removed at the rectifier bottoms and sent to wastewater treatment.

Dehydration of the alcohol is necessary to produce an anhydrous product suitable for blending as a motor fuel. Benzene has been selected as the drying agent, although other solvents have been investigated (notably ethyl ether). The overheads from the benzene dehydration column which are cooled in a separator form two layers. The water/alcohol-rich bottom layer containing residual solvent is routed to the benzene recovery column where the benzene is separated and recycled to the dehydration column. The benzene/ethanol-rich top layer is recirculated to the benzene de-

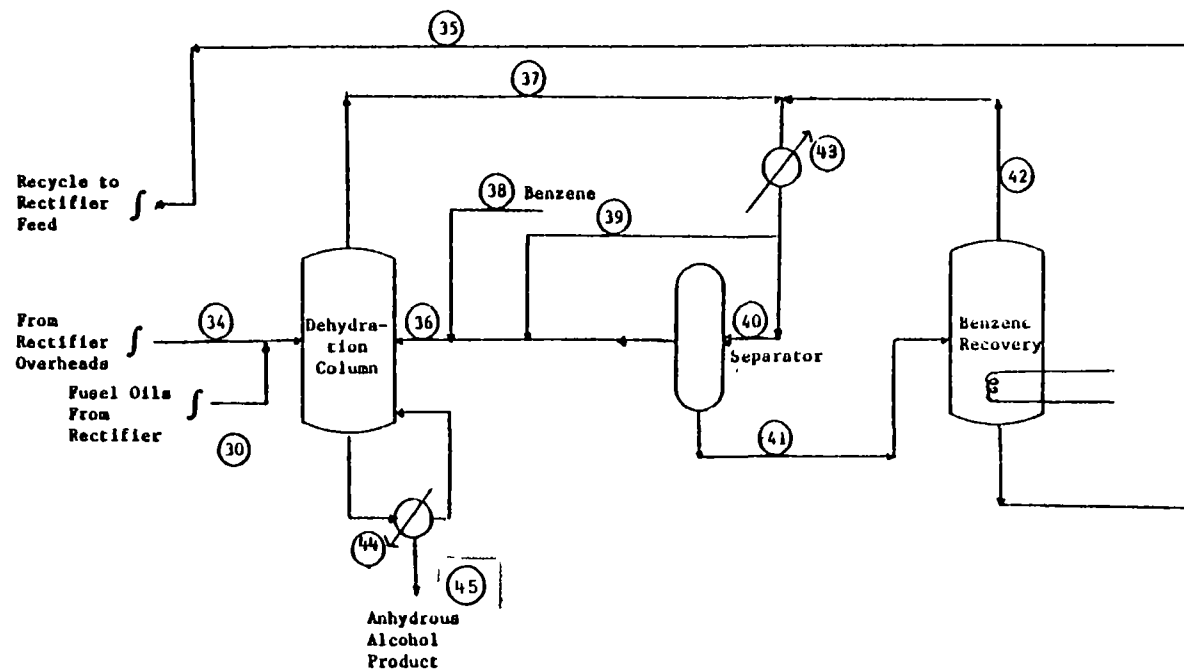


Figure 2. Flow diagram for conceptual design.

Figure 2. Flow diagram for conceptual design.
(continued)

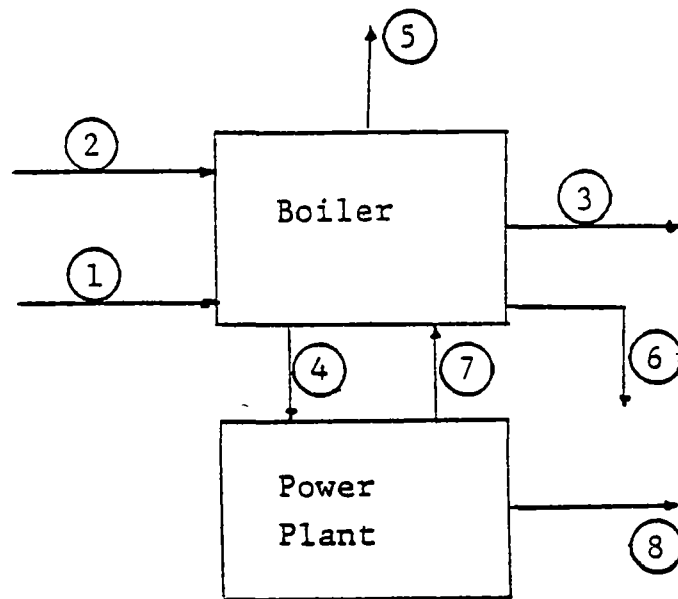


Figure 3. Steam and power generation.

TABLE 13. MASS AND ENERGY BALANCES FOR CONCEPTUAL DESIGN

<u>Stream</u>	<u>Origin and Destruction</u>	<u>Composition</u>	
		<u>kg/hr</u>	<u>Wt%</u>
1	Corn to hammer mill	21,320	
2	Makeup water to cooker (from flash condensate)	23,450	
3	Steam to cooker	12,500	
4	Saccharifying enzyme to conversion tank	2,130	
5	Cooling water to direct-cooled condenser	162,950	
6	Condensate from flash cooler to cooling water system	146,500	
7	Cooker mash to conversion tank	59,950	
7a	Cooling water to mash cooler	97,580	
8	Yeast slurry to fermenter	9,430	
	yeast	4,350	46
	water	5,080	54
8a	Converted mash to fermenter	62,100	
9	CO ₂ from fermentation	6,360	
9a	Cooling water to fermenter jacket	75,000	
10	Beer from beer well to beer still	65,160	
	ethanol	6,520	10
	water	51,730	79.4
	solids	6,930	10.6
11	Steam injected into beer still	3,850	
12	Cooling water for overhead condenser	136,360	
13	Beer still overheads to rectifier	8,150	
	ethanol	6,520	80
	water	1,550	19
	fusel oils	82	1
14	Beer still bottoms to centrifuge	60,860	
	water	53,930	88.6
	solids	6,930	11.4
15	Centrifuge cake to dryer	15,820	
	water	10,270	65
	solids	5,550	35
16	Thin liquids from centrifuge to evaporator	45,050	
	water	43,640	96.9
	solids	1,410	3.1

(continued)

TABLE 13. (continued)

<u>Stream</u>	<u>Origin and Destruction</u>	<u>Composition</u>	
		<u>kg/hr</u>	<u>Wt%</u>
17	Recycle thin stillage to cooker	14,770	
	water	14,320	96.9
	solids	454	3.1
18	Steam to multi-effective evaporator (@ 30 psig)	7,810	
19	Cooling water to evaporator condenser	161,450	
20	Evaporator return to cooling water system	168,950	
20a	Water to secondary treatment	20,500	
21	Cake from evaporator to dryer	1,850	
	water	915	49.5
	solids	935	50.5
22	No. 2 fuel oil to dryer furnace	1,070	
23	Combustion air (10% excess)	16,770	
24	Hot flue gas from furnace to dryer	92,820	
25	Distillers dried grain	7,120	
	water	640	9.0
	solids	6,480	91.0
26	Dryer off gases to scrubber	103,730	
	water	10,860	10.5
	air	92,860	89.5
27	Makeup water to scrubber	Fluctuates	
28	Wastewater to treatment system	12,440	
29	Vent gas to stack	10,695	
	water	14,180	13
	air	92,800	87
30	Fusel oils from rectifier to dehydration column	70	
31	Bottoms from rectifier to WW treatment (water)	1,550	
32	Steam to rectifier reboiler (150 psig)	9,080	
33	Cooling water from rectifier condenser	280,100	
34	190 proof ethanol to dehydration column	7,140	
	ethanol	6,860	96
	water	780	4

(continued)

TABLE 13. (continued)

<u>Stream</u>	<u>Origin and Destruction</u>	<u>Composition</u>	
		<u>kg/hr</u>	<u>Wt%</u>
35	Recycle from benzene recovery to rectifier	630	
	ethanol	340	54.4
	water	290	45.6
36	Reflux to dehydration column	4,480	
	ethanol	600	13.4
	water	90	2.1
	benzene	3,790	84.5
37	Overheads from dehydration column	5,710	
	ethanol	945	18.5
	water	380	7.4
	benzene	3,785	74.1
38	Benzene makeup	Variable	
39	Bypass reflux	520	
	ethanol	95	18.5
	water	40	7.4
	benzene	390	74.1
40	Feed to separator	4,630	
	ethanol	860	28.5
	water	340	7.4
	benzene	3,430	74.1
41	Feed to benzene recovery	670	
	ethanol	350	52.0
	water	290	43.1
	benzene	32	4.9
42	Overheads from benzene recovery	45	
	ethanol	9	19.2
	water	3	7.1
	benzene	33	72.7
43	Cooling water to dehydration condenser	45,450	
44	Steam to dehydration reboiler	1,610	
45	Anhydrous ethanol production	6,520	

TABLE 14. INPUTS AND OUTPUTS FOR STEAM AND POWER GENERATION

<u>Stream</u>	<u>Description</u>	<u>Flow Rate (kg/hr)</u>	<u>T(°C)</u>	<u>H(kj/kg)</u>
1	Coal feed to main boiler	4,770	Ambient	HV-5,580
2	Combustion air	62,090	Ambient (27° and 60% RH)	
3	Process steam, saturated			
	at 150 psia	27,045	181	570
	at 30 psia	7,815	121	557
4	Steam to drive power plants	5,000	18	570
5	Flue gas from main boiler	67,550	180	
	CO ₂	11,590		
	H ₂ O	3,000		
	SO ₂	258		
	NO _x	40		
	O ₂ (excess)	4,555		
	N ₂	47,820		
	Unburned hydrocarbons	7		
	Fly ash	366		
6	Bottom ash from main boiler	1,090		
7	Power required in main boiler	76 kw		
8	Process power	976 kw		

hydration column as reflux. Aqueous alcohol from the benzene recovery unit bottoms is also recycled to the rectifier feed for water removal.

By-product CO₂ recovered from fermentation may be purified through a scrubbing train and sold; producers may choose to vent this stream to the atmosphere. Trace amounts of alcohol vapor may be present in this stream when vented.

Beer still slops are centrifuged for the removal of the majority of the solids. A portion of the centrate (thin stillage) is recycled and the remainder evaporated in a multi-effect evaporation unit for further removal of the solids. The wet cake (35 percent) from the centrifuge is mixed with the evaporated solids and augered to a flash drying system; hot flue gases and air pneumatically convey the granular material through the vertical drying duct, vaporizing most of the surface moisture. A cyclone is used for solids separation and the dried material is collected and sold as distiller's dried grains (DDG). The flue gas stream, still carrying some entrained solids, is sent to a wet centrifugal scrubber for solids removal before ventilation to the stack. The scrubbing liquor is recycled, with a continuous blowdown piped to the wastewater treatment system.

Two support furnaces are required in this alcohol plant. An oil-fired furnace provides the hot gases to the dryer, and main process steam is generated in a coal-fired spreader stoker boiler. It should be noted that combustion products from these units form the bulk of the air emissions.

The wastewater treatment system is shown in Figure 4 with supporting data contained in Table 15. An extended aeration-activated sludge system was selected including secondary sedimentation, recycle of some solids, and recirculating the remaining effluent sludge to the flash drying system for addition to the animal feed by-product. A more extensive discussion of the plant's air, water, and solid effluents is found in the Emissions section.

Discussion of Conceptual Design

Based on the alcohol production rate of 190 M³ per day (57,820 M³ per year at an 80 percent operating rate) of anhydrous alcohol, Table 16 presents the overall inputs and outputs to the alcohol facility. As discussed earlier in the Assumptions section, energy consumption in the plant was calculated assuming the application of only minimal heat recovery techniques. The resulting energy and utility requirements are presented in Table 17.

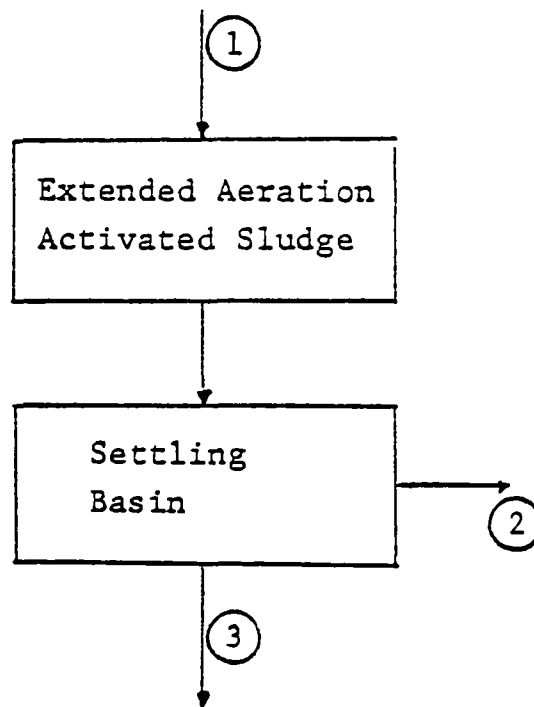


Figure 4. Wastewater treatment facility.

TABLE 15. MASS BALANCE FOR WASTEWATER TREATMENT SYSTEM

<u>Stream</u>	<u>Origin and Description</u>	<u>Flow Rate</u>
1	Wastewater from plant	2,400 M ³ /day
2	Treated water to river	2,270 M ³ /day
3	Sludge (50 percent solids) to landfarming	45 kg/hr

TABLE 16. INPUTS AND OUTPUTS OF AN ALCOHOL FACILITY

<u>Material</u>	Input or Output <u>g/M³ Ethanol</u>	<u>Total</u> <u>(kg/hr)</u>
<u>INPUT</u>		
Corn @ 56 lb/bu	37	21,330
Enzyme	3.7	2,130
Yeast	7.6	4,350
Benzene	Enough to Replace Losses	
Coal	8.3	4,770
Oil	1.9	1,070
<u>OUTPUT</u>		
Alcohol (100%)	11.2	6,520
Carbon Dioxide	11.0	6,360
Distiller's Dried Grains	12.4	7,120
Sludge	0.79	45

TABLE 17. ENERGY AND UTILITY REQUIREMENTS

<u>Utility Required</u>	<u>By-Product Drying</u>	<u>Distillation</u>	<u>Cooking, Grinding, Fermentation</u>	<u>Auxiliaries</u>	<u>Steam Generation Requirements</u>	<u>Total Per M³</u>	<u>Total Per Hour</u>
Btu	117 kJ/M ³	51 kJ/M ³	45 kJ/M ³	0.7 kJ/M ³	21 kg/M ³	61,900 kJ	134,748,000 kJ
Steam							
(Saturated @ 1,035 kPa)		25.3 g/M ³	21.7 g/M ³	---	8.6 g/M ³	13.8 g	32,050 kg
(Saturated @ 207 kPa)	13.8 g/M ³	0	0	---			7,800 kg
Fuel Oil (No. 2 distillate)	1.9 g/M ³	----	----	---		1.08 lb	1,070 kg
Electric Power	0.9 j/M ³	0.08 j/M ³	0.5 j/M ³	0.2 j/M ³	0.6 j/M ³	23 j	1,306 kw
Cooling Water	19.6 M ³ /M ³	55.9 M ³ /M ³	40.8 M ³ /M ³	---	19.1 M ³ /M ³	135.9 M ³	1,116 M ³
Coal (Illinois No. 6)							4,560 kg

The required steam and power are generated by the combustion of coal. Some designs have attempted to use the stover (corn-stalks, husks, and cobs) associated with corn production as a fuel source, thereby improving the net energy balance. This seems unlikely due to the cost of collection and transportation as well as solids handling problems at the plant. Removal of stover from the original field also increases the fertilizer requirement and mandates more stringent land erosion control. For these reasons and the federal requirement that energy sources in grassroots facilities be non-fuel oil-fired, a steam and power plant firing an Illinois No. 6 coal was selected.

A recirculating cooling water system was selected with the following operating parameters:

- Permissible temperature rise of 17°C;
- Ten percent blowdown rate;
- Maximum temperature of 32°C permissible in water returned to process; and
- Pumping requirements of 265 kw/1,000 M³/p.

In addition to coolers and condensers located in the process, cooling water is required in the power plant for heat exchangers on 0.12 M³/S/kw generated. The power plant turbines also require 3.83 kilograms steam per kilowatt hour. Finally, the boilerhouse auxiliary equipment (pumps, fans, etc.) consume 212 kilowatt hours for every 1,000 kilograms of steam generated. These data and the total requirements are presented in Table 18.

Long-Term Developments Which Might Affect the Design--

Every attempt was made to design a facility that would be representative of plants supporting a Gasohol industry. Many other processing steps, routes, or procedures currently or potentially available could be implemented. Areas of research include:

- Continuous fermentation under vacuum;
- Elimination of the rectifying column;
- Use of various extraction solvents; and
- Alternate feed stock sources.

Continuous Fermentation--Two routes for continuous fermentation are currently proposed. One pathway employs a series of continuous stirred tank reactors and yeast centrifuges for

TABLE 18. TOTAL UTILITY REQUIREMENTS

<u>Utility</u>	<u>Process Rate</u>	<u>Utility Generation Requirement</u>	<u>Amount Consumed in Generation of Utilities</u>	<u>Total Rate</u>
<u>Steam</u>				
1,035 kPa	27,050 kg/hr	3.8 kg/kwh	500 kg/hr	32,050 kg/hr
207 kPa	7,800 kg/hr		0 kg/hr	7,800 kg/hr
<u>Electricity</u>				
	976 kw	265 kw/1,000 M ³ /s	253 kw	1,300 kw
		2.2 kwh/1,000 kg steam	76 kw	
<u>Cooling Water</u>				
	960 M ³ /s	0.12 M ³ /s	160 M ³ /s	1,100 M ³ /s

recycling the active yeast to the process. The most significant problems include difficulty in separation of the yeast by mechanical means from the unconverted mash and low levels of output alcohol concentration necessitated by its toxic effects on the yeast.

The latter problem is also the major deterrent to a scheme that uses a packed column; the bed material provides a fixed substrate for attachment of the yeast. Researchers have suggested development of a high alcohol tolerance organism or a series of intermediate product draws as methods of circumventing the toxicity problem.

The second pathway is continuous fermentation under vacuum (4 to 5 kPa) that eliminates the need for costly distillation steps. Product alcohol is vaporized as it is formed in the fermentation vat. Supportive research at Cornell University (41) indicates that the energy savings achieved by using the heat from the exothermic fermentation reaction to distill off the alcohol is offset by the pumping requirements necessary to maintain the reduced pressure and bring the CO₂ off gas up to atmospheric pressure. However, capital costs for the vacuum fermentation scheme are lower than for conventional batch fermentation with distribution. The development of a thermophilic yeast strain viable at temperatures of 40°C to 50°C would mean lower vacuum requirements and would be one way to circumvent these problems. Vacuum fermentation technology has been developed in Switzerland and is soon to be tested here in the United States.

Elimination of the Rectifying Column--Some experimentation is currently underway in eliminating the rectifying column by increasing the height of the beer still and introducing an intermediate reboiler. Relaxation of the product quality requirements in fuel grade ethanol presents the major impetus for this option.

Use of Various Solvents for Extraction--Benzene is one of the many solvents suitable for the azeotropic distillation of an ethanol-water system. Other solvents are also under intensive investigation - ethyl ether, hexane, or a gasoline cut. The latter is of particular interest because less solvent recovery is necessary. The component ratios required in the feed to the dehydration column for proper operation are less rigid for a system using a gasoline cut. Further, the energy consumption is also lessened. However, safety, cost, and transportation questions have yet to be answered.

Alternate Feedstock Sources--Other sources of biomass are continually being researched as raw materials for fermentation processes. These include agricultural and forestry wastes, high starch terrestrial or aquatic "energy" crops, and urban and industrial wastes. The most promising sources of feedstocks for

fermentation ethanol plants in the next decades appear to be forest, agricultural, and urban wastes. Because the infrastructure for collection and transportation of urban wastes already exists, an economic incentive favoring the use of this source exists. None of these, however, are likely to supply alcohol plants in the near future.

ENGINEERING AND DESIGN

At this level of design, little peripheral equipment was included. These units will only slightly increase the total energy consumption. In addition, plant layout and location, which would also impact the engineering design, are beyond the scope of this report.

Emissions

Based on the conceptual design, the major streams of environmental concern were identified and quantified according to air, water, and solid waste impacts.

Air--

Values of air emissions for the alcohol facility appear in Table 19. The principal air pollutants from this plant are generated from the main boiler coal combustion. As indicated earlier, the selection of a coal-fired boiler was influenced by federal guidelines for the construction of new facilities. However, the substantially higher costs associated with firing coal, due primarily to handling and cleanup operations, discourages manufacturers from using it as the principal fuel source. The emissions from an oil-fired furnace would be significantly different from the values presented in Table 19.

Data on the emissions from the dryer furnace, which fires a No. 2 distillate fuel oil, can also be found in Table 19. After contacting the wet grain stream, the moisture-laden air and flue gases first pass to the dryer cyclone and then to a wet cyclone scrubber for final removal of particulates. Most of the water condenses in the scrubber and hence serves as makeup water for the recirculating scrubber liquor. Based on the operating parameters of such a system, the outlet criteria pollutant concentrations were determined to assess compliance with the relevant regulations. Such regulations for a medium size industrial furnace (10.5 to 264 million kj per hour) have not yet been developed under New Source Performance Standards (NSPS). The more stringent standards for utility size furnaces (less than 264 million kj per hour) were then examined as a guideline. As shown in Table 19, the scrubber air effluent easily meets each appropriate standard.

TABLE 19. AIR EMISSIONS FOR AN ALCOHOL FACILITY

<u>Stream</u>	<u>Quantity Generated kg/hr</u>	<u>Ultimate Disposition</u>
Fermentation Vent		
CO ₂	6,360	Condensed and sold, or vented to the atmosphere
Hydrocarbons	Trace	
Main Boiler - Coal-Fired (129 x 10 ⁶ kj/hr)		
Flue Gases:	67,550	Requires a mechani- cal collector/wet scrubber system
CO ₂	11,610	
H ₂	3,030	
N ₂	47,820	
O ₂	4,455	
NO _x	40	
SO ₂	260	
Fly ash	360	
Unburned hydrocarbons (no control applied)	7	
Dryer Furnace - Oil-Fired (48 x 10 ⁶ kj/hr)		
Flue Gases - Scrubber Outlet:	107,050	Vent to atmosphere
CO ₂	17,730	
H ₂	14,200	
N ₂	73,180	
O ₂	1,840	
SO ₂	6	
NO _x	2.5	
Particulates	0.3	
Benzene Fugitive Emissions	NDA	

Fugitive emissions of benzene from the dehydration section are considered to be minimal if an equipment maintenance schedule is instituted and proper housekeeping procedures followed.

Wastewater--

Table 20 presents data on wastewater streams generated by the alcohol facility. The stillage, which includes sludge recycled from the on-site wastewater treatment plant, is dried for sale as cattle feed. This process not only eliminates a potent waste stream from the treatment plant but also produces a saleable by-product.

The cooling tower blowdown is the largest volume influent to the treatment plant. This stream carries 63 percent of the total solids loading; however, only 8 percent of the total BOD load is introduced by this waste stream. The analysis of this stream varies widely depending on the makeup water source, the materials of construction used in the cooling water system, and the process condensates which are added to the system.

The strength of the evaporator condensate is a strong function of the type of evaporation scheme used. In this design, the condensate represents 2 percent and 32 percent of the solids and BOD loadings, respectively. Although it is a low pH stream (3.9), the dilution factor is large enough to prevent any acidity problems for the wastewater treatment plant.

The plant and equipment washes contribute a significant portion to the wastewater system. This stream represents 23 percent of the total BOD load. This large portion is characteristic of washes used in any food or grain processing equipment especially for batch-type vessels. Instruction in conservation-oriented housekeeping procedures should be conducted to avoid high volumes of wash waters. Much of this water can be reused after settling and removal of solids.

Bottom water from the rectifying column, though high in BOD concentration, is a small volume stream. This stream, as well as the boiler blowdown and sanitary sewage, contributes only minor loadings to the treatment plant.

The wastewater treatment system employed is an extended aeration-activated sludge unit. This technology was selected primarily because it reflects current operating practices in the beverage grade alcohol industry. Mean cell residence times of 20 to 30 days (sludge age with hydraulic retention time of 18 to 36 hours) are typical for this type of unit. Further discussion of this and other systems may be found in the control technology evaluation section of this report.

TABLE 20. SUMMARY OF INFLUENT WASTEWATER CHARACTERISTICS

<u>Stream</u>	<u>Quantity Generated</u>		<u>Total Solids</u>		<u>Suspended Solids</u>		<u>BOD</u>			<u>pH</u>
	<u>kg/day</u>	<u>M³/day</u>	<u>ppm</u>	<u>kg/day</u>	<u>ppm</u>	<u>kg/day</u>	<u>ppm</u>	<u>kg/day</u>	<u>% of Total</u>	
Scrubber Blowdown	300,000	300	2,600	780	760	228	1,040	310	31	5.0
Cooling Tower Blowdown	2,684,000	2,690	800	2,150	14	38	30	80	8	8.0
Boiler Blowdown	65,500	65	100	6	5	0.3	0	0	0	7.0
Evaporator Condensate	492,700	490	130	64	12	6	650	320	32	3.9
Plant & Equipment Washes	349,000	350	1,050	368	400	140	650	227	23	6.0
Rectifier Water	37,150	37	240	9	40	1.5	1,250	46	5	5.0
Sewerage Infiltration	65,500	65	NDA		NDA		NDA			NDA
Sanitary Sewage	43,600	44	750	33	200	9	200	9	1	NDA
Total Wastewater	4,037,450	4,041	843	3,410	104	422.8	246	990	100	NDA

NDA - No Data Available

Solids--

Solid wastes data are presented in Table 21. Collected fly ash from the particulate control devices installed with the main boiler may be in a slurry if a wet scrubber is used, or dry if mechanical or electrical collectors are employed. This stream will often be landfilled. Fly ash may be reinjected also. Bottom ash from the main boiler bed is sluiced off into a sedimentation tank or pond. This material is very coarse and settles rapidly. The overflow may be discharged without further treatment. The dust from coal handling would either be injected into the boiler or included with the fly ash for landfill disposal. The grain dust would probably be recycled to the grain milling operation. Land disposal of sludges from sanitary sewage and excess activated sludge will probably continue.

TABLE 21. SOLID WASTES GENERATED
BY AN ALCOHOL FACILITY

<u>Stream</u>	<u>Quantity Generated kg/hr</u>	<u>Ultimate Disposal</u>
Sludge (effluent from wastewater treatment)	46	Recycled to dryer
Power Generation Fly Ash	360	Landfilled
Bottom Ash - Main Boiler	195	Slurried and ponded on-site or contracted out; overflow from pond discharged
Collected Coal Dust	NDA	Landfilled
Collected Grain Dust	NDA	Recirculated
Miscellaneous Plant Wastes	NDA	Incinerated or contracted

NDA: No Data Available

SECTION 4

REVIEW OF ENVIRONMENTAL REGULATIONS

In keeping with the objectives of Task 3 in the Work Plan, this section identifies the federal and state environmental regulations which may affect the alcohol industry. The results are utilized to determine the minimum pollution control technology requirements which are discussed in Section 5, Control Technology Requirements. The Methodology section contains a discussion of the methodology selected to analyze the regulations. An analysis of the applicable regulations according to air, water, and solid waste is reported in the Air Regulations, Federal Regulations, and State Regulations sections.

METHODOLOGY

To identify pertinent emission standards and appropriate pollution control requirements for air, water, and solid wastes from the alcohol industry, it is necessary to:

- Characterize the air, water and solid waste streams; and
- Review federal and state environmental regulations.

Characterization of the waste streams was done in a previous section of this report and a summary of the results is provided in the Appendix Table B-1. Also, a summary of the major emission sources and corresponding pollutants based on the calculations in Section 3 is given in Table 22.

Federal and state environmental laws were reviewed for regulations specific to the alcohol industry as well as for major emission sources and pollutants produced in an alcohol facility. Implementing regulations for the following federal environmental laws were reviewed: the Clean Air Act of 1970 as amended through 1977; the Water Pollution Control Act Amendments of 1972 (as amended by the Clean Water Act of 1977 and other amendments through 1978); the Resource Conservation and Recovery Act of 1976. Air, water, and solid waste regulations promulgated by the states of Colorado, Illinois, Iowa, Kansas, Missouri and Nebraska were reviewed. These states were chosen because they either produce or have plans to produce alcohol for blending in Gasohol in the near future. Also, regulations from other states considering alcohol production were reviewed to confirm that the above states' emissions standards for the alcohol industry are representative.

TABLE 22. ALCOHOL PLANT WASTE STREAMS

<u>AIR EMISSIONS</u>	
<u>Stream</u>	<u>kg/hr</u>
Main Boiler Flue Gases	67,550
NO _x	40
SO ₂	260
Fly Ash	360
Unburned Hydrocarbons	7
Coal Dust	NDA
Grain Dust	NDA
Dryer Flue Gases	92,840
NO _x	3
SO ₂	6
Particulates	32
Fermentation Vent	
CO ₂	6,360
Hydrocarbons	NDA
Fugitive Emissions	NDA
<u>WASTEWATER</u>	
Influent to Wastewater Treatment	168,180
Scrubber Blowdown	12,400
Cooling Tower Blowdown	111,800
Boiler Blowdown	2,730
Evaporator Condensate	20,590
Plant & Equipment Washes	14,550
Rectifier Water	1,550
Sewerage Infiltration	2,730
Sanitary Sewage	1,820

(continued)

TABLE 22. (continued)

<u>WASTEWATER</u>	
(continued)	
	<u>kg/hr</u>
Total BOD	226 ppm
Total Solids	843 ppm
Total Suspended Solids	104 ppm
<u>SOLID WASTE</u>	
Sludge from Biological Treatment	46
Power Generation	
Fly Ash	360
Bottom Ash	195
Dust (Coal & Grain)	NDA
Plant Wastes (boxes, trash, etc.)	NDA

NDA - No Data Available

Air Regulations

After reviewing the Clean Air Act and its amendments, the Standards of Performance for New Stationary Sources, and the appropriate states' air regulations, it was found that there are no air regulations which specifically address the fermentation alcohol industry.

Table 22 and Table B-1 show that the major potential sources of air pollution will be the following:

- Criteria pollutants from combustion processes (steam generation, process heaters);
- Dust from coal handling and grain drying;
- Organic vapors from fermentation vent; and
- Uncondensed organics from distillation overheads, flash cooler, and evaporators.

Fugitive emissions of benzene and other volatile organics may also be a potential source; however, if proper maintenance and housekeeping procedures are followed, these emissions will be small.

Emission standards do exist for sources such as fossil fuel-fired steam generators, incinerators and grain elevators; these generic standards will probably be applied to this equipment as it is found in the alcohol industry. General emission standards which may potentially affect the industry will also be applied to particulate matter and sulfur dioxide generation. Pertinent federal and state regulations are addressed in detail in the paragraphs below.

Federal Regulations--

Table 23 gives the specific federal standards of performance for fossil fuel-fired steam generators, incinerators, and grain elevators. These are the only sources of air emissions found in the alcohol industry which fall under federal regulation. These standards are applicable unless superseded by more stringent state regulations.

Other federal regulations or standards which could affect the degree of emissions control required include the maintenance of National Ambient Air Quality Standards (NAAQS) which are summarized in Table B-2. Compliance with Prevention of Significant Deterioration (PSD) requirements is also necessary. The PSD regulations include both an ambient air increment analysis, presented in Table B-3, and a control technology review which requires

TABLE 23. EPA AIR REGULATIONS ON STANDARDS OF PERFORMANCE
FOR NEW STATIONARY SOURCES

<u>Source</u>	<u>Applicability</u>	<u>Emission Standards</u>		
		<u>Particulate Matter</u>	<u>SO₂</u>	<u>NO_x</u>
Fossil-Fuel- Fired Steam Generators	<264 x 10 ⁶ kJ/hr Heat Input	0.05 kg/10 ⁶ kJ	0.38 kg/10 ⁶ kJ (liquid fuel)	0.14 kg/10 ⁶ kJ (liquid fuel)
			0.58 kg/10 ⁶ kJ (solid fuel)	0.34 kg/10 ⁶ kJ (solid fuel)
Incinerators	45,450 kg/day		0 18/M ³ (1)	
Grain Elevators (2)	Dryers	0% Opacity		
	Any Process Emission	0.02 g/M ³ (0% Opacity)		
	Truck or Railcar Unloading Station	5% Opacity		
	Railcar Loading Station	5% Opacity		
	Truck Loading Station	10% Opacity		
	Any Grain Hand- ling Operation	0% Opacity		

(1) Corrected to 12 percent CO₂.

(2) There are also particulate emission standards for barge or ship loading and unloading stations which have not been listed here.

best available control technology for major sources of pollution. For a particular alcohol plant to be classified as a major stationary source under the PSD regulations, it must emit, or have the potential to emit, 250 tons or more per year of any air pollutant regulated under the Clean Air Act and its amendments.

State Regulations--

The flue gas from the fossil-fuel-fired steam generator is the largest single source of air emissions from an alcohol plant. Table 24 presents a summary of the required fuel combustion emission standards of each chosen state as a function of the actual heat input. A more detailed account of air regulations for the states can be found in Table B-4 of the Appendix.

Another major source of particulate matter emissions stems from grain handling and drying. Illinois and Iowa have specific regulations governing emissions from these sources as shown in Table 25. Particulate emissions from grain handling and drying for the other four states will be controlled by the most stringent of the following regulations: Particulate Emission Standards for Process Emission Sources (Table B-5) and/or State Air Regulations for Fugitive Dust and Ground Level Particulate Concentrations (Table B-6).

In addition to the grain handling and drying air emissions, the particulate matter emission requirements listed in the above tables will also regulate particulate emissions from any other process or fugitive emission source. Table 26 gives particulate emission requirements for incinerators and emission limitations for volatile organic compounds in the states of Colorado and Illinois.

Finally, it should be noted that the National Ambient Air Quality Standards or the states' ambient air quality standards (Table B-7), if more stringent than any of the above regulations, must be maintained at all times.

Water Regulations

As with air emissions, no specific regulations which govern the waste stream effluents for the alcohol industry were found. Table 22 and Table B-1 show that the major volumes of wastewater are from the process condensates and the cooling water blowdown, while the major pollutants of concern are organic suspended solids. An analysis of the stillage that forms the major component of these organic solids appears in Table B-8.

Federal Regulations--

Although no federal effluent guidelines have been established for the alcohol industry, effluent guidelines and standards do exist for grain mills and sugar processing if either of these operations takes place on-site. However, because they do not

TABLE 24. SUMMARY OF STATE AIR REGULATIONS FOR FUEL BURNING EQUIPMENT⁽¹⁾

	State	% Opacity	Ringlemann Chart	Particulate ⁽²⁾ Emissions (kg/10 ⁶ kj)		Sulfur Dioxide ⁽²⁾ Emissions (kg/10 ⁶ kj)	
				Coal	Oil	Coal	Oil
69	CO	20		0.07	0.07	0.6	0.9
	IL	30		0.05	0.05	0.9	0.5
	IA	40	2	0.29	0.29	2.9	1.2
	KS	20		0.16	0.16		
	MO	20	1	0.12	0.12	3.8	3.8
	NB	20	1	0.16	0.16	1.2	1.2

(1) Specific air quality zones exist within each state which might mandate different emissions requirements (see Table B-4).

(2) Basis for emission standards is a heat input of roughly 132×10^6 kj.

TABLE 25. SUMMARY OF STATE AIR REGULATIONS FOR GRAIN HANDLING AND DRYING

<u>State</u>	<u>% Particulate Removal Required</u>						<u>Allowable Particulate Emissions (mg/M³)</u>
	<u>Through-Put (35,300 M³/Yr)</u>	<u>Cleaning & Separating</u>	<u>Major Dump Pit Area</u>	<u>Internal Transferring Area</u>	<u>Load-Out Area</u>	<u>Dryers</u>	
Illinois ⁽¹⁾	≤2	90	90	90	90	90	
	>2	98	98	98	98	98	
Iowa ⁽²⁾	Any						0.23

(1) These regulations do not apply to grain annual throughputs of less than 10,590 M³.

(2) For any grain handling or processing, 0.1 grain/SCF is the maximum amount of particulate matter allowed in the exhaust gas.

TABLE 26. STATE AIR REGULATIONS FOR INCINERATORS
AND VOLATILE ORGANIC MATERIAL

State	Incinerator			Storage		Volatile Organic Material Emissions Criterion			
	New or Existing Sources	Charge Rate (kg/hr)	Particulate Emissions (g/M ³)	Capacity (M ³)	Control Efficiency %	Emissions Condition	Allowable Emissions		% Removal Required
							(kg/day)	(kg/hr)	
CO	New	Any	0.23			Heated in Presence of Oxygen	6.8	1.4	85
	Existing	Any	0.35 ⁽²⁾			Any Other	18.2	3.6	85
	Either	Any	0.35 ⁽³⁾						
IL	All Sources	910-27,270 >27,270	0.18 0.12	152	85-90	Any		3.6 ⁽⁴⁾	
	Remaining Existing Sources	---	0.46						
	Remaining New Sources	---	0.23						
IA	All Sources	<450 ≥450	0.81 0.46						
KS	All Sources	<90 2,730 >2,730	0.69 0.46 0.23						
MO	All Sources	<90 ≥90	0.69 0.46						
NB	All Sources	<910 ≥910	0.46 0.23						

(1) Effluent gases are corrected to 12 percent dioxide.

(2) Emission limitations for incinerators in designated air pollution control areas.

(3) Emission limitations for incinerators outside designated air pollution control areas.

(4) Emissions of organic material in excess of those shown are allowable if such emissions are controlled by one of the following methods: (a) Flame, thermal or catalytic incineration so as either to reduce such emissions to 10 ppm equivalent methane (molecular weight 16) or less, or to convert 85 percent of the hydrocarbons to carbon dioxide and water; or (b) A vapor recovery system which adsorbs and/or absorbs and/or condenses at least 85 percent of the total uncontrolled organic material that would otherwise be emitted to the atmosphere; or (c) Any other air pollution control equipment approved by the Agency capable of reducing by 85 percent or more the uncontrolled organic material that would be otherwise emitted to the atmosphere.

apply directly to the alcohol industry, these regulations have not been included in this report.

Secondary treatment of industrial wastes may be required if the wastes are discharged into navigable waters and contain biochemical oxygen demand (BOD) and suspended solids (SS). Since many alcohol production waste streams are high in BOD and SS, secondary treatment,--as a minimum,--will probably be required. Federal effluent standards for secondary treatment are shown in Table 27.

If an alcohol facility uses a publicly owned treatment works (POTW) for disposal of its wastes, pretreatment of the wastes will almost certainly be required. Specific pretreatment standards depend on waste characteristics and POTW requirements. Therefore, only the following general pretreatment requirements can be given:

- No pollutants which create fire or explosion hazards may be discharged to a POTW;
- No discharge which will cause corrosive structural damage--no discharges with pH less than 5.0;
- No solid or viscous pollutants discharged in amounts which will cause obstruction to the flow in sewers;
- No discharges of any pollutant, including oxygen demanding pollutants (BOD, etc.), released in a discharge of such volume or strength as to cause interference in the POTW; and
- No discharges of waste heat in amounts which will inhibit biological activity in the POTW that result in interference; in no case will heat be discharged in such quantities such that the temperature at the treatment works influent exceeds 40°C (104°F) unless the works is designed to accommodate such heat.

Only the latter two provisions are areas of potential concern for an alcohol facility.

Notwithstanding any of the above regulations, the EPA administrator can establish effluent limitations for a source or sources interfering with the attainment or maintenance of any promulgated water quality standards.

State Regulations--

In reviewing the state water regulations, none were found specific to the alcohol industry. Table 28 lists the effluent limitations for BOD, SS, and pH for the states reviewed. All of these emissions limitations are directly applicable to the

TABLE 27. FEDERAL EFFLUENT QUALITY STANDARDS
FOR SECONDARY TREATMENT

	<u>BOD</u> <u>(mg/l)</u>	<u>SS</u> <u>(mg/l)</u>	<u>pH</u>
30-Day Average	30	30	6-9
7-Day Average	45	45	6-9
Percent Removal Efficiency Required (30-Day Average)	85	85	---

TABLE 28. SUMMARY OF STATE WATER REGULATIONS POTENTIALLY GOVERNING THE ALCOHOL INDUSTRY

State	Control Technology Required	Discharging ⁽¹⁾ To Public Facilities	pH	Effluent Criteria SS (mg/l)		BOD (mg/l)		% Removal Required	
				7-Day Average	30-Day Average	7-Day Average	30-Day Average	SS	BOD ₅
Colorado	BMP	Pretreatment Required	6-9	45	30	45	30	85	85
Illinois ⁽²⁾	BDT	Pretreatment Required	5-10		37		30		
Iowa	BMP	Pretreatment Required		45	30	45	30	85	85
Kansas	BPCT	Pretreatment Required	6-9		30		30	85	85
Missouri ⁽³⁾	BPCT	Pretreatment Required						85	85
Nebraska	BPCT	Pretreatment Required						85	85

- (1) Pretreatment criteria are governed by EPA's Pretreatment Standards (40 CFR 128) and by specific public treatment works requirements in order to meet effluent limitations and/or water quality standards.
- (2) No more than 5 percent of the samples collected shall exceed 2.5 times the numerical limits prescribed by this rule.
- (3) The 85 percent reduction requirement for SS and BOD₅ was not specifically stated in Missouri's regulations. This is the degree of control expected to be required and represents BPCT for this type of facility.

NOMENCLATURE: SS = Suspended solids
 BMP = Best management practices
 BDT = Best degree of control
 BPCT = Best practical control technology
 BOD₅ = 5-Day biochemical oxygen demand

wastewater being generated at an alcohol plant. It can be seen that an 85 percent reduction in BOD and SS is required.

As was previously stated in the federal regulations, pre-treatment standards for effluents discharged to a POTW are dependent upon the wastes being discharged and the specific requirements of the POTW.

In all cases, the state water quality standards must be maintained. Therefore, emission limitations can be set by the state for any pollutant for which there is a water quality standard and the commensurate emission reduction required can be more severe than the amounts mandated at the federal level.

Solid Wastes Regulations

The major components of the solid wastes generated at an alcohol plant which fires coal are bottom ash from the main boiler; fly ash, coal dust, and grain dust from particulate controls; and wastewater sludge containing organic species such as protein, oils, starch, and yeast. The sludge may also contain traces of ethanol, fusel oils, and pesticides. At this time, the levels of pesticides present in the solid wastes is unknown. It is expected, however, that the pesticides will be present at the ppb level.

Federal Regulations--

It is believed that most distillers will dispose of less than 100 kilograms (220 pounds) per month of hazardous wastes (including benzene and pesticides). In this event, they must comply with Section 250.29 (persons who dispose of less than 100 kilograms per month of hazardous waste, retailers, and farmers) of the proposed Resource Conservation and Recovery Act regulations. In general, this provision requires that any hazardous waste generated, no matter how small the quantity, be disposed of either in:

- A solid waste facility which has been permitted or otherwise certified by the state as meeting the criteria pursuant to Section 4004 of RCRA; or,
- A treatment, storage, or disposal facility permitted by the administrator pursuant to the requirements of Section 3005 (Permits for Treatment, Storage, and Disposal of Hazardous Waste), or permitted by an authorized state program pursuant to Section 3006 (Guidelines for Authorized State Hazardous Waste Programs) of RCRA.

State Regulations--

No specific regulations were found for disposal of industrial solid wastes from the alcohol industry. The following general requirements were given for disposal of solid wastes for all the states reviewed:

- Permit to construct disposal site required:
 - Site selection has to be approved
 - Engineering design criteria for site have to be met
- Permit to operate is required:
 - Operating plans and processing facilities design and operation must meet specific criteria and be approved.
 - Site and facilities are to be inspected before operation can commence
- Regulations developed for storage and transportation of wastes;
- Special operating permit (or approval) is required for disposal of hazardous wastes; and,
- Sites must be environmentally sound; they must be designed to comply with all air and water laws (or any other environmental regulations that would apply).

SECTION 5

CONTROL TECHNOLOGY REQUIREMENTS

In this section, alcohol process effluent streams are compared with environmental regulations to determine the environmental control requirements necessary for alcohol plants which would support a large-scale Gasohol industry. These control requirements are defined in terms of the component to be controlled, level of control required, and the source and characteristics of the stream to be controlled. Control options are identified with an emphasis on alcohol plants which utilize grain as a feedstock and employ coal-fired boilers for power. The criteria which are used to evaluate the control options are:

- Development Status;
- Applicability;
- Performance;
- Capital Cost and Operating Cost; and
- Secondary Pollutants.

AIR EMISSIONS

As mentioned in Section 4.2, the major sources of air pollution from an alcohol plant are:

- Criteria pollutants from combustion processes (steam generation, process heaters);
- Dust from coal handling and grain handling and by-product drying;
- Hydrocarbon emissions from fermentation vent, distillation overheads, flash cooler, evaporators, storage; and
- Fugitive air emissions.

Criteria Pollutants

Combustion of fossil fuels such as coal or oil to provide the relatively large amount of energy used in alcohol production

results in significant quantities of criteria pollutants such as NO_x , SO_2 , and particulates. Table 29 illustrates the levels of these pollutants when a No. 6 Illinois coal is used in a coal-fired boiler.

Federal new source performance standards (NSPS) currently apply only to combustion sources having gross heat inputs greater than 264×10^6 kj per hour, a level somewhat larger than expected in alcohol plants. However, EPA is currently preparing proposed NSPS for smaller sources (industrial boilers).

A comparison of the estimated air emissions in Table 29 with the state regulations (Table 24) reveals the following:

- NO_x is not a major problem (no NO_x standards were applicable for the states examined);
- SO_2 control is needed in Colorado, Illinois, Nebraska; and,
- Particulate control up to 98.5 percent removal is needed in all states.

In situations where NO_x control is necessary, there are two general methods of control for large stationary sources: combustion modifications and flue gas treating (FGT). Presently, combustion modifications are commercially available technology while FGT technology is just emerging from the developmental stages. Although FGT control is more efficient, it is also more expensive. Combustion modifications such as staged combustion, flue gas recirculation, and low air firing, which reduce NO_x emissions by about 30 percent, should be sufficient for NO_x control.

Flue gas desulfurization (FGD) is a technology for the reduction of SO_2 emissions from coal or oil combustion. Although there are several processes termed regenerable which are reaching commercialization, throwaway systems (where sulfur is disposed in a landfill or ponded) are more common; only throwaway systems can be commercial in terms of regular application to non-prototype systems.

The installation of FGD equipment on coal-fired boilers in alcohol plants is highly unlikely due to high capital cost and operating expenses, secondary pollution, and availability of low-sulfur coal or fuel oil. The capital cost of a lime/limestone system for the conceptual alcohol plant (probably the least expensive control option), is estimated to run from 5 to 10 million dollars, or about 25 percent of the cost of the rest of the alcohol plant. Also, the operating expenses may cost the distiller about \$.03 per liter ethanol, which does not include

TABLE 29. BOILER EMISSIONS AND ENVIRONMENTAL
CONTROL REQUIREMENTS

	SO_2 ⁽²⁾ <u>(kg/hr)</u>	Particulate ⁽³⁾ Matter <u>(kg/hr)</u>
Uncontrolled ⁽¹⁾ Boiler <u>Emissions</u>	260	360

<u>State</u>	<u>Permissible Emissions (kg/hr)</u>	<u>% Removal Required</u>	<u>Permissible Emissions (kg/hr)</u>	<u>% Removal Required</u>
Colorado	68	74.0	8.0	97.9
Illinois	103	61.1	5.7	98.5
Iowa	341	0.0	34.0	90.8
Kansas			18.7	94.9
Missouri	455	0.0	14.2	96.2
Nebraska	142	46.0	18.7	94.9

(1) Basis 132 MM kj/hr heat input; using Illinois No. 6 coal with heating value = 5,610 kj/kg, 2.7% S, 11.7% ash.

(2) All S in coal assumed to form SO_2 .

(3) Sixty-five percent of ash in coal is converted to fly ash for a Spreader Stoker Boiler.

the cost of sludge disposal. The throwaway systems such as the lime or limestone processes generate sludge that must be disposed of in ponds or in landfills. Leaching from these disposal sites can potentially pollute ground or surface waters. Finally, the use of low-sulfur coal that exists in western states which have the most strict SO₂ regulations would make FGD unnecessary. Fuel oil might be an alternative in other areas where low-sulfur coal might be unavailable.

A comparison of environmental regulations with the flue gas emissions from a coal-fired boiler reveals that particulate control (fly ash) will be a major problem for the distiller. Many control devices exist for controlling particulate matter, such as fabric filters (baghouses), wet scrubbers, electrostatic precipitators (ESP), and inertial separators. Table 30 presents a brief characterization of each of these control options. In most applications, inertial separators (which include impingement, cyclone, or mechanical centrifugal separators) will not be efficient enough to be considered, except as pre-collectors to control devices which can remove fine particulates. Electrostatic precipitators will also be uncommon in alcohol production facilities due to their high capital cost. Wet scrubbers will provide adequate control for some states, but might be avoided due to the large quantities of liquid waste generated by these control devices. Therefore, baghouses are probably the best alternative for particulate control from coal-fired boilers when high efficiency removal is necessary.

Dust from Coal Handling, Grain Handling, and By-Product Drying

The handling of coal and grain, as well as by-product drying (DDG production) will pose another particulate control problem for the distiller. The control options for these particulates are similar to those for fly ash particulate control. Use of ESP's and wet scrubbers has been limited in existing facilities due to high cost, explosion hazards, and desirability of having a dry by-product.

Though cyclones are very common in grain handling industries, only low or medium efficiency separators are used due to the increased operational cost and maintenance associated with high-efficiency multiple cyclones. In many cases, cyclone exhausts are routed through filter cloth to remove fine particulates. Baghouses (using cotton sateen) are ideal for areas with strict regulations for particulate control and should be used on all systems except by-product drying.

Wet scrubbers are the best alternative for exhaust gases from direct-contact DDG dryers because these dryer particulates will easily cake on fabric filters and severely decrease their

TABLE 30. PARTICULATE MATTER CONTROL OPTIONS

	<u>Fabric Filters</u>	<u>Wet Scrubbers</u>	<u>Electrostatic Precipitators</u>	<u>Inertial Separators</u>
Development Status	Commercially available, widely used	Commercially available, widely used	Commercially available, widely used	Commercially available, widely used
Applicabil- ity	Excellent for collection of fly ash and dust from coal hand- ling (1)	Extensively used for pro- cess and combustion sources	Standard con- trol devices for the elec- tric utility industry (2)	Most widely used partic- ulate matter control devices; ade- quate for controlling dust from materials handling and fly ash
Performance	High effi- ciency (>99.9), 90% effi- cient for submicron particles	>95% effi- ciency for 1 micron or smaller	High effi- ciency (>99%) for submicron particles	79-90% removal effi- ciency, not for fine particulate control
Capital Cost (3)	Relatively high	Moderate	Very high	Low
Operating Cost	Moderate	Relatively high (4)	Moderate (5)	Low
Secondary Pollutants	Solid waste	Liquid waste	Solid or liquid waste	Solid waste

(1) Fabric weave and finish can be designed for special applications.

(2) Submicron particle removal requires very high energy inputs.

(3) High maintenance cost.

(4) Collection of very high or very low resistivity particles is difficult.

(5) All control options are rated on the same basis: 10,000 acfm, 24°C gas temperature, non-corrosive gas, 7,000-hour operating time, and mid-1977 base data.

effectiveness. The liquid waste from the wet scrubbers will not pose a disposal problem since it can simply be sent to wastewater treatment.

Hydrocarbon Emissions

Sources of hydrocarbon emissions from an alcohol facility (other than from combustion) include the vents from:

- Distillation columns;
- Flash cooler;
- Evaporators;
- Vacuum ejectors; and
- Fermenters.

Illinois and Colorado are the only states which have regulations governing hydrocarbon emissions from these types of sources, the latter state requiring 85 percent removal (see Table 25). Since the hydrocarbon streams from the first four sources are too dilute to be economically recovered and do not have a high recoverable market value, the simplest and most effective control for these hydrocarbons would be direct flame incineration, or flares. Most flares are sized to operate at efficiencies between 95 and 99 percent, although higher efficiencies can be obtained. In the event the emissions are too dilute for direct combustion, the vent streams could be utilized as the air feed to process burners (e.g., DDG drying). Thus, the distiller can control these hydrocarbon emissions and at the same time decrease fuel requirements.

In many existing alcohol plants, the CO₂ stream from the fermenter, which is more than 99 percent CO₂ and water vapor with traces of organics, is vented to the atmosphere. Although not a significant source of pollution, modern distillers may prefer to collect and condense the CO₂ since a good market currently exists. If a distiller chooses to recover CO₂, all impurities can easily be removed from the CO₂ stream prior to cryogenic recovery by passing the vent gas through a water scrubber to condense the water vapor and any organic vapors present in the CO₂ stream. The blowdown from the water scrubber can be routed to wastewater treatment.

As shown in Table 26, the State of Illinois requires that volatile hydrocarbon emissions (i.e., alcohol emissions) from storage facilities of 150 M³ (40,000 gallons) or more must be controlled by 85 to 90 percent. Since this quantity amounts to less than 1 day's production, compliance must be maintained by

the distiller. Floating roofs or internal floating covers can be employed to control storage emissions. These devices reduce tankage emissions by eliminating the vapor space above the product surface. Efficiencies for floating roof tanks and internal floating covers are 85 and 95 percent, respectively.

Fugitive Air Emissions

Fugitive dust emissions can be caused by several activities occurring at alcohol production facilities:

- Unpaved roads
 - Personnel and maintenance vehicles
 - Raw material or waste hauling vehicles
- Windblown dust
 - Unpaved, bare ground
 - Waste piles (bottom ash)
 - Raw material piles (coal, grain)
- Materials handling
 - Front-end loaders, etc.
 - Conveyor systems.

Control of fugitive dust is aimed primarily at preventing or confining the emissions rather than collecting afterwards. Commonly used dust control methods are listed in Table 31. In the case of conveyor controls (confinement by hoods), an induced air flow draws the entrained dust through a conventional control device for removal and disposal. The other controls are purely preventive in nature.

Fugitive hydrocarbon emissions have two principal sources: leaks and evaporation from open surfaces. Unlike fugitive dust, which arises in a diffuse way over an area, many fugitive hydrocarbon losses occur from specific points such as valves or flanges. However, these sources are so numerous in most plants processing hydrocarbon liquids that the emissions can be considered diffuse for practical purposes.

Fugitive hydrocarbons are prevented by maintenance and design. Consequently, there are no specific recommendations for their control. The methods below are frequently applicable:

- Confinement, diversion, and flaring;
- Dual seals;

TABLE 31. FUGITIVE DUST CONTROL METHODS

<u>Source</u>	<u>Control Method</u>	<u>Control⁽¹⁾ Efficiency</u>
Unpaved Roads	Reducing Vehicle Speeds	25-40%
	Wetting	50%
	Paving	85%
Windblown Dust	Wetting	50%
	Confining (Covers or Enclosures)	100% ⁽²⁾
Materials Handling	Wetting	50%
	Confining (Hoods over Conveyors with Air Pickups at Transfer Point)	80%

(1) Because control efficiency is highly dependent on dust characteristics, meteorological parameters and other factors, these figures represent only very rough estimates.

(2) This control efficiency only applies while the cover is in place.

- Sparing of critical pumps, compressors, and valves;
- Use of surface condensers rather than direct-contact units (barometric or low-level jet); and
- Use of outages for repairs and a systematic preventive maintenance program.

WASTEWATER TREATMENT

The first step in assessing the wastewater control technology requirements is to delineate the treatment objectives. Most of these objectives have already clearly been defined by the Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500) and other state laws. A survey of the applicable federal and state regulations, previously presented in Section 4 of this report, will provide the framework for identification of the necessary control technologies.

The next step is to examine the influent wastewater characteristics to determine the degree of treatment required to comply with existing regulations. A summary of these characteristics generated from the conceptual design of an alcohol facility is presented in Table B-1.

A comparison of the pertinent regulations regarding the pollutant loadings shows the necessity for nearly 88 percent removal of the influent BOD to 30 ppm (30-day average), and 85 percent removal of the suspended solids. No significant pH problems are anticipated, but nonetheless, care should be exercised when using alkali washes for equipment cleanup. Each of the above criteria will be used to guide the selection of the appropriate control systems.

It should be noted that dissolved inorganics, primarily from boiler and cooling water blowdown and the ash sluicing system if a coal-fired boiler is used, are not specifically regulated; however, discharges of metal ions which would violate water quality standards will require control. Also, pretreatment regulations will require control of toxic substances which could inhibit or even stop activity in a biological wastewater treatment process. The levels of these pollutants in wastewater from a distillery are a function of the following:

- Makeup water ion concentration;
- Materials of construction;
- Degree of ion concentration per cooling or boiler water cycle; and

- Hydraulic detention time in cooling water or boiler water cycles.

These parameters vary widely depending primarily on location, internal plant water reuse, and other plant operating procedures. Should these potential pollutants occur in sufficient amounts, a suitable control technology would be required. However, past experience in the alcohol industry has shown these levels to be below the concentration necessitating treatment, and therefore, no dissolved inorganic control technologies will be discussed.

Suspended Solids Treatment

The suspended solids are first treated by preliminary screening and sedimentation for removal of the coarse solids. This screening often involves the passage of wastewater across an inclined wedgewire screen. Sedimentation is a general process usually denoting the gravity settling of the suspended solids in a holding tank. Air flotation and flocculation are also candidate treatment processes for suspended solids reduction, but these involve higher operating costs due to the requirements for chemical addition.

The suspended solids portion of the effluent from this pretreatment system are mostly volatile and are treated using the biological oxidation processes outlined in the following section. The nonvolatile portion is settled in the biotreatment unit with the biological floc. Final clarification may be necessary to meet the standard of 30 ppm suspended solids (30-day average) in the final effluent.

Dissolved Organics

The core of an efficient distillery wastewater treatment system is the biological oxidation process. Table 32 outlines the key operating parameters of four possible classes of biotreatment processes which might be implemented in an alcohol facility. Some of the specific treatment processes might not provide sufficient BOD removal, which is the primary selection criterion. Obviously, the capital and operating costs will also form important selection criteria for the alcohol producer; these vary widely and hence are described only qualitatively in this table. A short description of each treatment process likely to be included in a future fuel alcohol wastewater treatment system follows.

Existing facilities are often equipped with either a high rate trickling filter system or an extended aeration activated sludge unit. Associated with the former is a reasonable resistance to shock loading and an ability to process consistently high

TABLE 32. OPERATING PARAMETERS OF WASTEWATER TREATMENT SYSTEMS

PROCESS	Mean Cell Residence Time d, days	Hydraulic Retention Time d, h	Food to Micro-organism Ratio (kg BOD applied/ kg MLSS d)	Volumetric Loading (kg BOD ap- plied/m ³ d)	Recycle Ratio	BOD Removal Eff. %	Shock Loading Ability	Capital Cost	Operating Cost
1 Activated Sludge								Moderate	High
Conventional	5-15	4-8	0.2-0.4	0.3-0.6	0.25-0.5	85-95	Poor		
Continuous stirred-tank reaction	5-15	3-5	0.2-0.6	0.8-2.0	0.25-1.0	85-95	Good		
Modified Aeration	0.2-0.5	1.5-3	1.5-5.0	1.2-2.4	0.05-0.15	60-75	Poor		
Contact Stabilization	5-15	(0.5-1.0) ⁽¹⁾ (3-6) ⁽²⁾	0.2-0.6	1.0-1.2	0.25-1.0	80-90	Poor		
Extended Aeration	20-30	18-36	0.05-0.15	0.1-0.4	0.75-1.50	75-95	Good		
2 Aerated Lagoons	3-6			Not Applicable	None	75-95	Good	Low	Moderate
3 Trickling Filter		4-12						High	Moderate
Low rate	Intermittent Sloughing			0.08-0.41	Minimum	80-85	Poor		
High rate	Continuous Sloughing			0.41-4.8	Always	65-80	Excellent		
4 Anaerobic Digestion	10-30	15-20		1.6-6.4 kg VS ₅₅ /m ³ d	None	45-75	Variable	Moderate	Moderate

(1) Contact unit

(2) Solids acclimation unit

organic loadings. Recently, concern over the effluent quality from a trickling filter has caused some operators to construct an extended aeration unit.

The microorganisms in extended aeration operate in the endogenous respiration phase, during which the substrate for biological activity includes cellular protoplasm in addition to dissolved organics in the wastewater. This results in a more highly polished effluent with good settling properties. The long retention times involved limit this system to wastewater flows of about 1 million gallons a day. Only small volumes of sludge are wasted; this material can be recycled for drying and inclusion in the by-product animal feed, landfarmed or used as fertilizer. For a more detailed discussion of these processes refer to Wastewater Engineering: Treatment/Disposal/Reuse.

Another alternative to wastewater treatment is to omit by-product stillage drying and route this waste stream along with other high BOD and SS waste streams (i.e., flash cooler condensate, rectifier bottoms, and solvent-recovery bottoms) to an anaerobic digester. In practice, the streams are usually concentrated using centrifugation; the thin liquids are recycled to the cooker or fermenter. Since the resulting waste stream has a relatively high concentration of solids, it is considered a solid waste stream and will be discussed in a later section.

An aerated lagoon is also a candidate treatment process for plant wastes. This option differs from extended aeration primarily because no sludge is recycled. Proper operation of the lagoon is required for prevention of odors and leaching of harmful pollutants.

The primary difficulty of control technology assessment for industrial wastewater systems is the wide variability in the influent wastewater characteristics. Pilot plant studies are almost always required for a design suitable for a particular application. However, a combination of the technologies discussed above in a complete system could be designed for compliance with the pertinent regulations.

SOLID WASTE TREATMENT AND DISPOSAL

Several types of solid or semi-solid (i.e., sludge) wastes will be generated from alcohol production facilities. Some are directly produced in the alcohol process while others are formed in power generation when coal-fired boilers are utilized. These solids include:

- Power generation bottom ash;
- Power generation fly ash from particulate controls;

- Grain dust from particulate controls on grain handling;
- Coal dust from particulate controls on coal preparation and/or pretreatment;
- Wastewater treatment sludge - biological system; and
- By-product stillage.

Treatment and land disposal of these wastes must be carried out in an environmentally acceptable fashion to prevent contamination of surface and ground waters.

For bottom ash and fly ash, landfill is the best disposal technique available to the distiller. Special precautions must be taken to ensure that the water table is below the landfill site. Also, in some cases, provisions must be made for leachate collection and treatment to avoid contamination of ground waters.

Other particulates from an alcohol plant include grain dust from grain handling and milling and coal dust from coal handling and pulverizing. The grain dust collected can be recycled to grain milling operations and will not present a disposal problem for the distiller. Likewise, coal dust can be routed to the boiler and burned as fuel to eliminate this source of solid waste.

The sludge from biological wastewater treatment in an alcohol plant can be converted to a valuable by-product such as fertilizer or animal feed. Techniques available to the distiller for sludge processing include:

- Centrifugation and drying;
- Drying beds; and
- Landfarming.

Since the sludge from wastewater treatment is innocuous, it is possible to return it to the dryer for DDG production. The sludge is centrifuged first to remove excess water; the supernatant is returned to wastewater treatment. This scheme eliminates a solid waste disposal problem while increasing the yield of a valuable by-product.

Drying beds, which consist of filtration media made of sand and gravel, are the most widely used sludge dewatering method in the United States. Water is removed by evaporation or drainage (the collected filtrate is usually returned to the treatment plant). The method should be restricted to well-digested sludge since raw sludge is odorous, attracts insects, and does not dry

satisfactorily when applied at reasonable depths. Climatic conditions such as precipitation rate, air temperature, humidity, and wind velocity are very important in determining effectiveness. The dewatered sludge is removed mechanically or manually and can be used as fertilizer.

Landfarming involves applying the wastes in the soil of a properly engineered site and using the microbes naturally present in the soil to decompose the organic fraction of wastes. It is an effective sludge disposal method when pollution preventative practices are exercised. Application rates, soil conditions, water runoff, percolation, and odor must be monitored and controlled. Rototillers are usually employed to till the soil to obtain maximum dewaterability and aeration. This method is particularly advantageous if large land area is located in proximity to the alcohol plant.

Much research is currently underway to develop new approaches to fermentation by-product processing. One process under intensive investigation is anaerobic digestion of the wet by-product stillage. One reason this process is of interest is that methane produced from this reaction could provide a significant portion of the plant's energy requirements. Further, speculation has been made that the market for the dried by-product (DDG) may diminish as the number of alcohol plants substantially increases. Anaerobic digestion would provide an additional incentive for fuel alcohol producers because of the assurance of an on-site use for a produce whose supply, in the advent of a large-scale Gasohol industry, might otherwise far exceed the demand. The digested sludge from this control option can be used as cattle feed or fertilizer.

SECTION 6

SAMPLING AND ANALYTICAL REQUIREMENTS FOR AN ALCOHOL FACILITY

To determine the sampling and analytical requirements necessary to conduct an environmental characterization of a fermentation ethanol plant, the following steps must be taken:

- Identification of characterization objectives;
- Process analysis;
- Sampling procedure review and selection;
- Analytical procedure review and selection, and
- Identification of data evaluation requirements.

CHARACTERIZATION OBJECTIVES

The objectives of an environmental characterization of an alcohol plant are:

- To delineate the identities of pollutants in the gaseous, liquid and solid waste streams;
- To determine the effectiveness of environmental control modules; and
- To characterize selected internal process streams which affect the plant emissions and effluents.

To satisfy the first objective, an effluent characterization must be completed. This entails the measurement of one or more pollutants in one or more of plant effluent streams.

To address the second objective, a control module characterization must be conducted which investigates the operating performance of one or more pollutant control elements. The characterization test involves sampling both the input and the effluent streams of selected modules.

To fulfill the third objective, process module characterizations must be completed. These characterizations carry the stream analysis at least one module further back into the process

than the control module. Process module characterization defines the effect of analytical and process parameters of process modules on the performance of control modules.

PROCESS ANALYSIS

A thorough analysis of process equipment and operating parameters is required for accuracy and efficiency in determining the sampling and analytical requirements. The process streams which should be investigated and the analytical parameters which should be measured are presented in the paragraphs below along with the criteria for their selection. A portion of the information considered in this review may differ from one alcohol facility to the next; therefore, the general requirements presented here will require modification according to a site-specific process analysis.

To conduct an environmental characterization of an alcohol plant, the selection criteria for plant process streams should include:

- The objectives of the characterization;
- The pollutants present; and
- Material balance considerations.

For the most part, the selection of analytical parameters is based on regulatory considerations. Two general types of regulations determine the pollutants to be analyzed: pollutant discharge limitations and ambient pollutant standards. Such regulations may exist at the federal, state or local levels, and will not necessarily be identical. Consequently, regulations applicable to the specific location of an alcohol plant should be reviewed when selecting analytical parameters. A summary of applicable state and federal environmental regulations for fermentation ethanol plants is presented in Section 4 of this report. Other criteria which are also important are:

- The need to close material balances for chemical species;
- The need to analyze for materials which have adverse effects on control modules; and
- The usefulness of some analytical parameters as sensitive indicators of control or process module performance.

A process description of the fermentation alcohol plant is presented in Section 3, Alcohol Process Evaluation. The major processing units are:

- Milling, cooking, and fermentation;
- Distillation and dehydration;
- By-product processing;
- Steam production; and
- Environmental control systems.

The emissions and effluent sources from these processes are discussed below and summarized in Table 33.

Milling, Cooking, and Fermentation

Gaseous emissions from these processing steps include grain dust from handling and the vented stream(s) from fermentation, which often include carbon dioxide and low concentrations of ethanol, aldehydes, and water. Liquid effluents typically generated are wash waters (which are alkali and high in biodegradable organic compounds) and condensate from flash cooling equipment. Residual pesticides from washing of the grain during handling and processing could be present. Collected grain dust forms the only significant solid waste generated from these processing steps.

Distillation and Dehydration

Air emissions from the distillation/dehydration sequence will include fugitive emissions, noncondensables (CO₂, N₂, O₂, etc.) and light hydrocarbons from the vents on condensers. Bottoms from the rectifying and dehydration columns make up the liquid effluents for this process sequence. These streams have a high biochemical oxygen demand (BOD) and could also be contaminated with benzene. No solid wastes are directly associated with distillation and dehydration.

By-Product Processing

Dryer flue gases are the major source of air emissions from by-product processing if direct contact dryers are employed. The components of these gases are highly dependent on the type of fuel fired in the combustion furnace associated with the dryer. Generally, criteria pollutants (SO_x, NO_x, particulates, unburned hydrocarbons, CO, ozone) might be present, although some, especially ozone, will be very low in concentration. Liquid effluents requiring treatment include condensate from the evaporator and wash waters from the various units used in this drying section. No solid wastes are generated from by-product processing since all can be incorporated into the by-product distiller's dried grains.

TABLE 33. EMISSION AND EFFLUENT SOURCES

Section of Operation	Gaseous Emissions	Liquid Effluents	Solid Wastes
Milling, Cooking and Fermentation	<ul style="list-style-type: none"> - mechanical collectors for milling operations (particulates) - fermentation vents (CO₂, hydrocarbons) 	<ul style="list-style-type: none"> - wash waters (dissolved and suspended solids, organics, pesticides, alkalal) - flash cooling condensate (dissolved and suspended solids, organics) 	<ul style="list-style-type: none"> - grain dust from mechanical collectors (pesticides)
Distillation and Dehydration	<ul style="list-style-type: none"> - condenser vents on columns (benzene and other volatile organics) 	<ul style="list-style-type: none"> - rectifier bottoms (organics) - dehydration bottoms (benzene and other organics) 	<ul style="list-style-type: none"> - none
By-product Processing	<ul style="list-style-type: none"> - dryer flue gases (NO_x, SO₂, CO, hydrocarbons, particulates) - barometric and evaporator condenser vents (hydrocarbons) 	<ul style="list-style-type: none"> - evaporator condensate (dissolved and suspended solids, organics) 	<ul style="list-style-type: none"> - grain dust from direct-contact dryer (pesticides)
Steam Production	<ul style="list-style-type: none"> - flue gases (NO_x, SO₂, CO, particulates) 	<ul style="list-style-type: none"> - sludging systems (inorganics) - boiler blowdown (inorganics) - cooling water blowdown (dissolved and suspended solids, organics) 	<ul style="list-style-type: none"> - coal dust, fly ash, bottom ash from coal fired boiler (inorganics)
Environmental Control System	<ul style="list-style-type: none"> - evaporation from biological treatment ponds (benzene and other organics) 	<ul style="list-style-type: none"> - scrubber blowdown (dissolved and suspended solids, organics) 	<ul style="list-style-type: none"> - biological sludge from wastewater treatment (pesticides, benzene, NH₃, metals)

Steam Production

Coal, oil or natural gas are the most common source of fuel in the alcohol industry. Of course, many more environmental obstacles must be addressed for the combustion of coal than of the other two sources. Nonetheless, air emissions from the combustion of any of these fuels can contain criteria pollutants. Solid wastes could include collected coal dust, fly ash, and bottom ash from coal-fired furnaces. Sluicing systems and boiler blowdown are two major sources of liquid effluents. These streams may be high in total dissolved solids and trace elements. Further, priority pollutants could appear in the sluice system. Finally, if a recirculating cooling water system is operating at the plant, another effluent will arise from blowdown of this system.

Environmental Control System

Environmental control systems potentially include:

- Wastewater treatment system;
- Wastewater pretreatment system for pretreating plant effluents prior to off-site treatment at a municipal or publicly owned treatment facility;
- Wet scrubbers for flue gas cleaning;
- Mechanical collectors;
- On-site solid waste disposal (landfill or landfarm);
- Fermentation vent collection system, and
- Tank farm control equipment.

If present, a wastewater treatment system handling the plant effluents on-site is the major control module requiring environmental sampling. In keeping with the previously stated objectives, characterization of plant scrubbers and mechanical collectors should also be conducted. Aqueous scrubber blowdown streams will be contaminated with organic vapors, NH_3 , H_2S , SO_2 , etc. The wastewater treatment system could produce odors and volatile organics as air emissions. Outfall to the receiving body constitutes the principal liquid effluent, and the solid waste is commonly comprised of excess activated sludge. If this sludge undergoes land disposal, leaching characteristics become important. Aqueous scrubber blowdown streams or slurries from mechanical collectors will be contaminated with dissolved and suspended solids, organic vapors, NH_3 , H_2S , SO_2 , and other pollutants.

SAMPLING PROCEDURES

The careful selection and execution of sampling procedures is the most critical step in producing reliable characterization data. Samples must accurately represent composition of the stream samples and must be compatible with the analytical techniques applied. Factors which must be considered in order to maintain sample integrity and provide a representative sample include:

- Spatial and temporal variations in stream composition;
- Changes in sample composition following removal from a stream;
- Limitations of the analytical techniques; and
- Requirements for accuracy.

Spatial variations in composition can be averaged by compositing aliquots collected over the cross section of a flowing stream or throughout the volume of a static storage vessel or pile. However, it is best to avoid these variations by selecting a sampling location where the material is well mixed.

Temporal variations can occur for a variety of reasons, ranging from stratification in the material source stream to process operation fluctuations. They can be averaged by compositing aliquots collected over a period covering all process cycles or characterized in detail by analysis of each aliquot.

Preserving the sample integrity throughout the collection, transport, and analysis sequence is of utmost importance. For instance, many alcohol plant effluents contain highly biodegradable compounds whose concentration is to be measured. Unless stored at reduced temperatures (about 4°C) to decrease biological activity, a determination of the biochemical oxygen demand (a measure of the biodegradable organic concentration) will be inaccurate.

Both manual and continuous sampling are available techniques for the characterization of an alcohol facility. The methods and type of test plan discussed in this report are oriented toward the intermittent manual techniques. This focuses the sampling program described herein on short-term compliance verification and permit support analysis.

Gases

The major sources of emissions and the components of these sources are presented in Table 33. In addition to identifying

the chemical components of the stream, the selection, design, and execution of sampling procedures for gas streams requires knowledge of the following:

- Stream physical conditions;
- Reactivity of stream components relating to both sample stability and safety considerations; and
- Physical arrangement of the piping or ducting containing the stream.

The temperature and pressure of the gases from the condenser vents, the fermenter vents, and the mechanical collector exhausts are near ambient conditions and warrant no special sampling procedures related to these physical parameters. Since the flow from condenser vents is often variable in an alcohol plant, continuous monitoring devices should be used when possible. The presence of high concentrations of water vapor in streams such as the exhaust from the cycles on the by-product dryer may interfere with collection devices. In these instances, the gases can be passed through a drying column or osmotic membrane to remove the moisture prior to collection. Well-documented procedures exist for sampling flue gas species such as EPA Method 7 for NO_x and EPA Method 5 for particulates.

In regard to safety, the emission of volatile hydrocarbons in alcohol plants dictates that only explosion-proof sampling methods are to be employed. This means that battery-operated pumps and samplers, grab techniques, or impingers must be used. Also, since benzene emissions are suspended from the condenser vents on the dehydration column and stripping column, respirators should be worn when sampling in these areas.

The appropriate stream and piping must be examined for accessibility. If no sampling port is available, location and construction of a port is required. Method 1, promulgated by the EPA, presents criteria for selecting a gas stream sampling point.

Liquids

Many liquid effluents from an ethanol plant are relatively high in biodegradable organics. Preservation techniques such as chilling to inhibit biological breakdown of organics is necessary to maintain the integrity of the samples. Also, some analytical parameters such as metals, ammonia, chemical oxygen demand (COD), total organic carbon (TOC), cyanides, and phenol require the addition of acids or bases as a pre-analytical preparation. Since settling may occur enroute to analysis for some samples high in suspended solids, these should be filtered on-site for analysis

later. Table 34 presents a summary of the preservation and preparation techniques as well as time limits for analysis associated with liquid stream parameters.

The preferred sampling points for liquid streams are existing valves, either in-line or on a side stream. These valves provide a ready source from the stream and should be used when compatible with the objectives of the test program. Many alcohol plants are equipped with such valves as part of their routine sampling program for quality control purposes. Other points of easy access are outflow orifices where the liquid streams flow into ponds, tanks, or other open surfaces. Open or noncontained streams may be sampled at any point compatible with accuracy requirements. The major restriction in selecting sampling points is stream homogeneity. It may be necessary to have sampling valves installed, to ensure a well mixed sample. Sampling should be done just downstream from points of turbulence, such as elbows or pump-discharge lines.

In selecting sampling methods for liquids, the analytical techniques planned must also be considered. For example, glass containers must be used when sampling for pesticides, benzene, phenols, base/neutrals, and purgeables since plastic containers may provide interference during analysis. Samples may be taken at regular intervals over the duration of the test and then either analyzed individually or combined to provide an averaged sample. If possible, the test duration should be long enough to cover normal process variations.

Solids

There are two general techniques of sampling methods for solids: grab sampling and grab-and-composite sampling. Although the collecting methods are the same, the grab-and-composite sampling is the more precise technique. Conveyed solids such as grain or coal may be representatively sampled by compositing over a period of time. When solids such as by-product grains, bottom ash or collected fly ash are stored in piles or silos, stratification can occur and obtaining a representative sample can be difficult. Core sampling can overcome this problem in a static storage pile or container.

ANALYTICAL METHODS

The purpose of an analytical method is to provide qualitative and/or quantitative data for the analytical parameters identified in the test plan. Factors affecting the selection of analytical techniques include:

- Compatibility with sampling procedure;

TABLE 34. LIQUID SAMPLE PRESERVATION AND PREPARATION TECHNIQUES (148)

	<u>Preservation Technique</u>	<u>Preparation Technique</u>	<u>Analysis Time Limit</u>
Dissolved and Suspended Solids	Cool, 4°C	Filter	7 days
BOD	Cool, 4°C		24 hours
Sulfates	Cool, 4°C		7 days
Iodine	Cool, 4°C		24 hours
COD	Cool, 4°C	Acidify to pH <2 with H ₂ SO ₄	7 days
NH ₃	Cool, 4°C		24 hours
TOC	Cool, 4°C		Filter, acidify to pH <2 with H ₂ SO ₄
Pesticides	Cool, 4°C		
pH		On-Site Measurement	6 hours
Benzene	Cool, 4°C		
Priority Pollutants (149)			
Purgeables	Cool, 4°C		
Base/Neutrals	Cool, 4°C		
Cyanides	Cool, 4°C	pH >12 with NaOH	24 hours
Phenols	Cool, 4°C	Acidify to pH <4 H ₃ PO ₄	24 hours
Metals	Cool, 4°C	Filter, acidify to pH <2 with HNO ₃	6 months

- Expected concentration level and required detection limits;
- Presence of interfering species;
- Accuracy and precision requirements;
- Requirements of the established quality control program; and
- Time, equipment and cost limitations.

Modern technology has provided the analyst with a wide range of analytical tools, ranging from classical "wet-chemical" techniques to sophisticated instrumental methods. Each analytical parameter of interest can be identified and/or quantified by one or more of these procedures. The selection of the optimum approach from the available alternatives requires all the skills of a well-trained professional. Table 35 presents a summary of analytical methods which can be used to measure the parameters identified in the previous sections.

DATA EVALUATION PROCEDURES

The data acquired during the environmental characterization of a fermentation alcohol facility may be critical to the successful development of the Gasohol industry. This information may form the basis for future environmental regulations which might evolve as the Gasohol industry grows. Sound statistical methods used in program design and data correlation will ensure the acceptance of the data and provide a sound basis for regulation, control and environmentally acceptable operation.

Statistical methods have primary uses in three areas of the environmental characterization:

- Checking the reliability of collected data, establishing confidence intervals for the data, and comparing means (averages) for data collected at different times;
- Evaluating the quality control performance of the sampling and analysis program; and
- Determining cause-and-effect relationships between variables, analyzing the sources of variability in collected data, and assessing the extent to which variables are correlated.

Sample collection technique affects the data characteristics, each one having different ramifications on statistical treatment of data. Four types of sample collection techniques

TABLE 35. ANALYTICAL TECHNIQUES FOR AN
ENVIRONMENTAL CHARACTERIZATION

<u>Analytical Parameter</u>	<u>Analytical Technique</u>
<u>Gases</u>	
Total hydrocarbons	Gas chromatograph (GC) with flame ionization detector (FID)
Benzene	GC with FID
Ammonia	Colorimetric method (nessleri- zation) or titration with H_2SO_4
Particulates	EPA Method 5
Carbon Monoxide, Oxygen	Orsat Analyzer
Sulfur Dioxide	EPA Method 6
Nitrogen Oxides	EPA Method 7
<u>Liquids</u>	
Total Solids	Evaporate sample to dryness @ $105^{\circ}C$ and record weight
Total Dissolved Solids	Filter sample, evaporate fil- trate to dryness @ $105^{\circ}C$, record weight loss
Volatile Dissolved Solids	Ignite filtrate from TDS in an oven @ $550^{\circ}C$, record weight loss
Total Suspended Solids	Filter sample, evaporate filter paper residue to dryness @ $105^{\circ}C$, record weight
Volatile Suspended Solids	Ignite dried residue from TSS in an oven @ $550^{\circ}C$, record weight loss
Biochemical Oxygen Demand (BOD)	Analyze for dissolved O_2 , incu- bate @ $20^{\circ}C$ for 5 days in the dark, record reduction in dis- solved O_2
Chemical Oxygen Demand (COD)	Oxidize sample with $K_2Cr_2O_7$ in a 50% H_2SO_4 solution @ reflux temperature, use Ag_2SO_4 cata- lyst and Hg_2SO_4 (to remove chloride interference), record excess dichromate

(continued)

TABLE 35. (continued)

<u>Analytical Parameter</u>	<u>Analytical Technique</u>
<u>Liquids (continued)</u>	
Total Organic Carbon (TOC)	Oxidize sample in a high-temperature furnace, measure CO ₂ produced with infrared analyzer
pH	On-site analysis with pH instrument
benzene	GC analysis or GC with mass spectroscopy (MS)
pesticides	Extraction followed by GC or GC/MS
sulfates	Gravimetric or Turbidimetric methods
ammonia	Buffer with a borate solution to pH of 9.5, use colorimetric or titration method for analysis
metals	Atomic absorption spectroscopy
iodine	Amperometric titration
<u>Solids</u>	
benzene	Heat solids and withdraw overhead vapors with a syringe, analyze vapors with GC
pesticides	Extract from solid and use GC or GC/MS
ammonia	Acidify sample, distill into boric acid solution, use colorimetric or titrimetric techniques
sulfates	Extract from solids with HCl, add H ₂ O ₂ , use barium-thorin titration (EPA Method 5)
metals	Oxidize organic matter with low temperature asher, dissolve with HClO ₄ , use atomic absorption

are continuous monitoring, manual sampling (periodic or intermittent), composite sampling, and totalizing.

Data from continuous monitors place no constraints on the statistical data analysis. When used with an automatic data logging system, they greatly increase the possible applications of statistical analysis because:

- More information can be handled than is possible by human data recorders;
- Data can instantaneously be placed in the proper formats for statistical analysis; and
- Preliminary on-site analysis of data is feasible in many cases.

In the case of manual sampling, the frequency or number of samples collected during the characterization test is important. The limitations of each sampling and analytical method must be considered in selecting both the variables to be evaluated and the statistical methods to be used. Also, for manual sampling and analysis methods, the test plant should ensure that the final data logging procedures are in formats which minimize data transfer and the possibility for error.

Compositing is an averaging technique in which sample aliquots are collected over a relatively long period of time and either combined to obtain an average sample for analysis or retained as separate entities for analysis. In the first case, a composite sample is collected, while in the latter, a composite average is developed after analysis is completed. The latter technique should be used at least initially to ensure that sufficient aliquots are collected to yield a good average sample.

Totalizers are counting devices used to indicate the generation of consumption of some entity. In some cases, such as coal totalizers in power plants, data (sample) collection is merely the reading of a meter and the frequency is at the discretion of the test plan designer.

Quality Control

A quality control program is intended to prevent the propagation of bias through the sampling/analysis/evaluation chains of the test program. The statistical methods commonly used in maintaining a quality control program are relatively simple and should be performed in the field to ensure rapid feedback of information when a loss of control is indicated. The most common types of analysis are correlation tests and regression tests used

for estimating data variability and the maintenance of control charts. The features of correlation analysis are summarized below:

- Gives a quantitative assessment of the extent to which two parameters are linearly related;
- Requires only that data for the two parameters be collected in pairs; and
- Cannot be used by itself to study cause-and-effect relationships between variables.

In comparison, regression analysis offers the following features:

- Provides an estimate of error in the data generation chain;
- Provides an estimate of the dependence of one variable on one or more other variables;
- Can be used to develop a simulation model of a process or process module;
- Requires that only the dependent variables be influenced by error; and
- Is difficult to use in field tests when more than one independent variable is involved.

Quality control charts have several potential uses:

- To determine acceptable levels of data quality;
- To achieve the acceptable levels; and/or
- To maintain the acceptable levels.

These charts can be used for such quality control data as: replicate samples, isokinetic sampling rates, EPA sampling train calibration factors, and "spiked" sample recovery results. For most applications, control limits are set at three standard deviations for replicate results.

In regard to maintaining quality assurance during analysis, the following procedures are recommended:

- Duplicate testing;
- Frequent calibration of analytical equipment with standards and spiked samples;

- Analyzing blanks;
- Monitoring with quality control charts;
- Conducting daily GC/MS system performance evaluations;
and
- Distilling standards to confirm distillation efficiencies
and reagent purity.

SECTION 7

TEST PLAN

This test plan consists of a set of procedures which will accomplish the objectives outlined below. This plan is based on the general sampling and analytical requirements outlined in Section 6, but has been modified for a particular alcohol plant.

OBJECTIVES AND SCOPE

The objectives of the environmental characterization of a fermentation ethanol plant for this test plan are:

- A delineation of the identities and amounts of pollutants in gaseous, liquid, and solid waste effluent streams;
- A determination of pollutant removal performance of existing control modules; and
- A determination of the fate of pesticides and benzene in the process route.

To satisfy the first objective an effluent characterization was completed in which every effluent stream (gas, liquid, or solid) from the plant was reviewed to determine whether it contained pollutants.

To address the second objective, a control module characterization was conducted where the influent and effluent streams of each pollution control device was sampled.

To complete the third objective, internal streams suspected of containing the hazardous compounds were scheduled to be sampled to determine where these substances are destroyed or emitted from the alcohol facility.

PROCESS ANALYSES

A thorough analysis of process equipment and operating parameters was made in this section to assure accuracy and efficiency. This analysis consisted of the following steps:

- Identification of process streams to be sampled and their important analytical parameters;

- Selection of a process stream-analytical parameter matrix;
- Identification of the process operating parameters which should be monitored prior to and during execution of the test plan;
- Selection of the sets of operating conditions for which characterizations will be made; and
- Designation of the stream and analytical parameter combinations for which data from other sources (plant records and operating personnel) will be adequate.

Process Description

To address the first two steps, the process flow diagram for the alcohol facility (Figure 5) was broken down into nine components and each stream sampled was identified with a number for future reference. A brief description of each component is presented and the analytical parameters of interest for each stream are summarized according to process unit (Table 36) and in a sampling matrix (Tables 37 through 39).

A general description of an alcohol facility has been given in Section 3. The particular plant sampled does differ from the conceptual plant in several ways. One major difference in this plant is its operation in conjunction with a protein extraction unit which removes some of the protein, oils, and starch and provides a high-sugar content feedstock for the alcohol process. Since this processing scheme is not an integral part of a typical alcohol plant, it was not included in the characterization. The alcohol plant also derives part of its feedstock from on-site dry milling operations; this unit, which is typical of most alcohol plants, was considered within the scope of the characterization.

In the conceptual design, the source of steam was from a coal-fired boiler. Steam for this plant is produced from an on-site boiler which uses natural gas 9 months of the year and No. 6 fuel oil for the remaining 3 months. At the time of sampling, natural gas was the source of fuel for the boiler. Since no electricity is generated on-site, the fuel requirements are determined strictly by process heat needs.

Another deviation from the "typical" alcohol facility is that the flue gases from the boiler are routed to the direct contact dryer where water is removed from the by-product distiller's dried grains (DDG). The dried gases are then sent to cyclones for particulate removal. Thus, there are no direct boiler furnace emissions from the alcohol plant.

Figure 5. Alcohol plant flow diagram.

TABLE 36. ALCOHOL PLANT EFFLUENT SOURCES AND EMISSIONS

Process Unit	Gaseous Emissions	Liquid Effluents	Solid Wastes
Grain Preparation	None	None	Grain Dust, Chaff and Dirt Recycled
Cooking and Cooling	Condenser Vent (hydrocarbons)	Flash Cooler Condensate (dissolved and suspended solids, organics)	None
Conversion and Fermentation	CO ₂ Stream (hydrocarbons)	Fermenter Wash Water (dissolved and suspended solids, organics, alkali, iodine)	None
Distillation	Condenser Vent (hydrocarbons)	None	None
Purification	Condenser Vent (hydrocarbons)	Solvent Extractor and Fusel Oil Column Bottoms (dissolved and suspended solids, organics)	None
Rectification	Condenser Vent (hydrocarbons)	Rectifier Column Bottoms (dissolved and suspended solids, organics)	None
Dehydration	Condenser Vents and Vent on Separator (Benzene and other hydrocarbons)	Stripping Column Bottoms (Benzene, Ethanol, Fusel Oils, and other organics)	None
By-Product Processing	Evaporator Condenser Vent (hydrocarbons) Cyclone Off-Gases NO _x , SO ₂ , CO, particulates)	Evaporator and Barometric Condensate (dissolved and suspended solids, organics)	Grain Dust collected by cyclone (recycle to dryer)
Wastewater Treatment	Fugitive emissions (organics)	Treated Effluent from Wastewater Treatment	Screened solid and biological sludge (recycled to dryer)

TABLE 37. SAMPLING/ANALYTICAL MATRIX - SOLIDS

Analytical Parameters	Stream Number	Grain	DDG	Animal Feed	Biological Sludge
		1	22	26	32
Benzene			X	X	X
Pesticides		X	X	X	X
Ammonia			X	X	X

TABLE 38. SAMPLING/ANALYTICAL MATRIX - GASES

Analytical Parameters	Stream Number	<u>Cyclone Grain Preparation</u>		<u>Condenser Vent</u>	Fermenter Vent	<u>Condenser Vent</u>		
		Inlet	Outlet	Flash Cooler		Beer Still	Solvent Extractor	Rectifier
		2	3	6	8	10	12	14
Total Hydrocarbons				X	X	X	X	X
Ammonia					X			
Particulates		X	X					

(continued)

TABLE 38. (continued)

Analytical Parameters	Stream Number	Condenser Vents		Separator Vent	Condenser Vent	Cyclone		Condenser Vent
		Fusel Oil Column	Dehydration Column		Stripping Column	Dryer Inlet	Dryer Outlet	Evaporator
		16	18	19	20	23	24	28
103 Total Hydrocarbons		X	X	X	X		X	X
Benzene			X	X	X			
Ammonia							X	
Particulates						X	X	
Carbon Monoxide							X	
Sulfur Dioxide							X	
Nitrogen Oxides							X	

TABLE 39. SAMPLING/ANALYTICAL MATRIX - LIQUIDS

Analytical Parameters	Stream Number	City Makeup Water	Milled Grain (Cooker Feed)	Flash Cooler Condensate	Fermenter Outlet	Solvent Extractor Bottoms	Rectifier Bottoms	Fusel Oil Column Bottoms	Dehydration Column Bottoms
		4	5	7	9	11	13	15	17
Total Solids		X		X		X	X	X	X
Total Dissolved Solids		X		X		X	X	X	X
Volatile Dissolved Solids		X							
Total Suspended Solids		X		X		X	X	X	X
Volatile Suspended Solids		X							
BOD		X		X		X	X	X	
COD									
TOC		X		X		X	X	X	
pH		X		X		X	X	X	
Benzene		X							X
Ammonia		X							
Pesticides			X	X	X		X		
Sulfates		X							
Copper		X							
Iron		X							
Iodine		X							

(continued)

TABLE 39. (continued)

Analytical Parameters	Stream Number	Stripping Column Bottoms	Barometric Condensate	Evaporator Condensate	Cooling Tower Blowdown	Fermenter Wash Water	Well Water	WW Treatment Influent	WW Treatment Effluent	Boiler Blowdown
		21	25	27	29	30	31	33	34	35
Total Solids			X	X	X	X	X	X	X	X
Total Dissolved Solids		X	X	X	X	X	X	X	X	X
Volatile Dissolved Solids				X	X		X	X	X	
Total Suspended Solids		X	X	X	X	X	X	X	X	X
Volatile Suspended Solids				X	X	X	X	X	X	
BOD		X	X	X	X	X	X	X	X	
COD					X			X	X	
TOC		X	X	X	X	X	X	X	X	
pH		X	X	X	X	X	X	X	X	
Benzene		X			X		X	X	X	
Ammonia						X	X	X	X	
Pesticides				X	X	X		X	X	
Sulfates					X		X	X	X	
Copper					X		X	X	X	X
Iron					X		X	X	X	X
Iodine					X	X	X	X	X	

In addition to a beer still and a rectifier, this plant has a solvent extractor and a fusel oil column to aid in separating higher alcohols and other impurities from the ethanol product. These units would not be necessary in an alcohol plant designed solely for fuel production.

Finally, in the alcohol plant sampled, all solid waste, grain dust, wastewater treatment sludge, and screened solids are recycled to the dryer for DDG production. Therefore, no solid waste requiring disposal is generated from this alcohol plant.

Analytical Parameter Selection

Grain Preparation--

The first unit in the alcohol product route is grain preparation. As Figure 6 shows, whole grain is pulverized using hammer mills. The chaff and dirt which is shaken loose and grain dust which is collected by cyclones is sent to the dryer for DDG production. The milled grain is then slurried with water and sent to the cooker.

Analytical parameters which were scheduled for evaluation included particulate concentration in the influent and effluent streams for the cyclones and pesticide levels in the whole grain and in the feed stream to the cooker. Also, the makeup water to grain preparation was tested for total solids (TS), total dissolved solids (TDS), volatile dissolved solids (VDS), total suspended solids (TSS), volatile suspended solids (VSS), BOD, TOC, pH, benzene, ammonia, pesticides, sulfates, copper, iron, and iodine to establish baseline data for these parameters.

Cooking and Cooling--

In the next step, flour from the protein extraction unit and the milled whole grain is gelatinized and solubilized in the cooker. The cooked grain then passes to the flash cooling equipment which consists of a series of vacuum chambers where heat is removed by evaporating some of the water from the slurried grain. (Refer to Figure 7).

Although the overhead condensate was expected to have a low BOD and contain a relatively small amount of solids, this stream was tested for these parameters as well as for pH. Also, the flash cooker condensate was monitored for the presence of pesticides. Finally, the vent on the flash cooler condenser was measured for total hydrocarbons.

Conversion and Fermentation--

Figure 8 presents a schematic diagram of conversion and fermentation. Enzyme is added to the solubilized starch in the converter tank where the starch is broken down into component sugar molecules. The yeast then metabolizes the sugar into

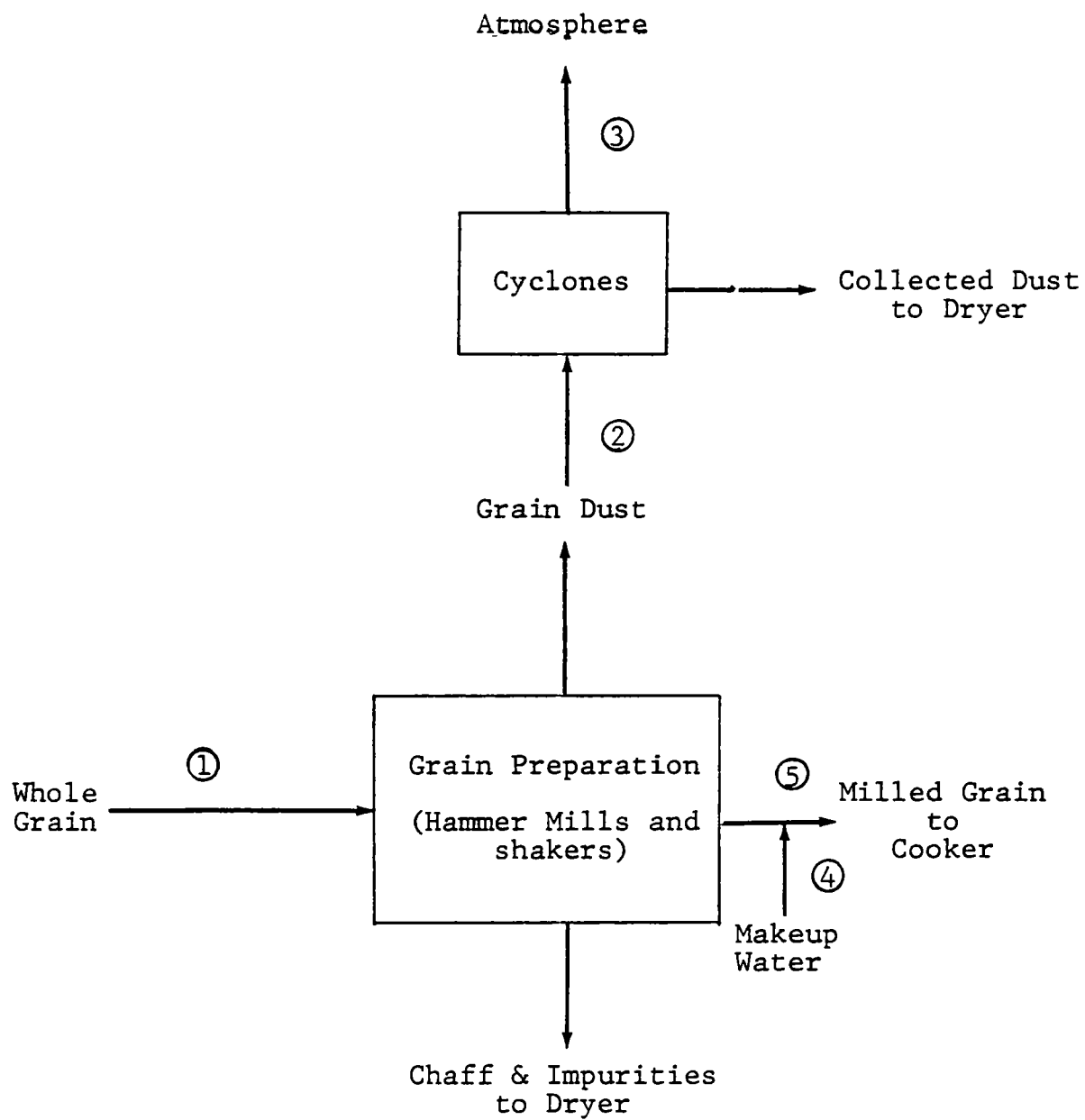


Figure 6. Grain preparation.

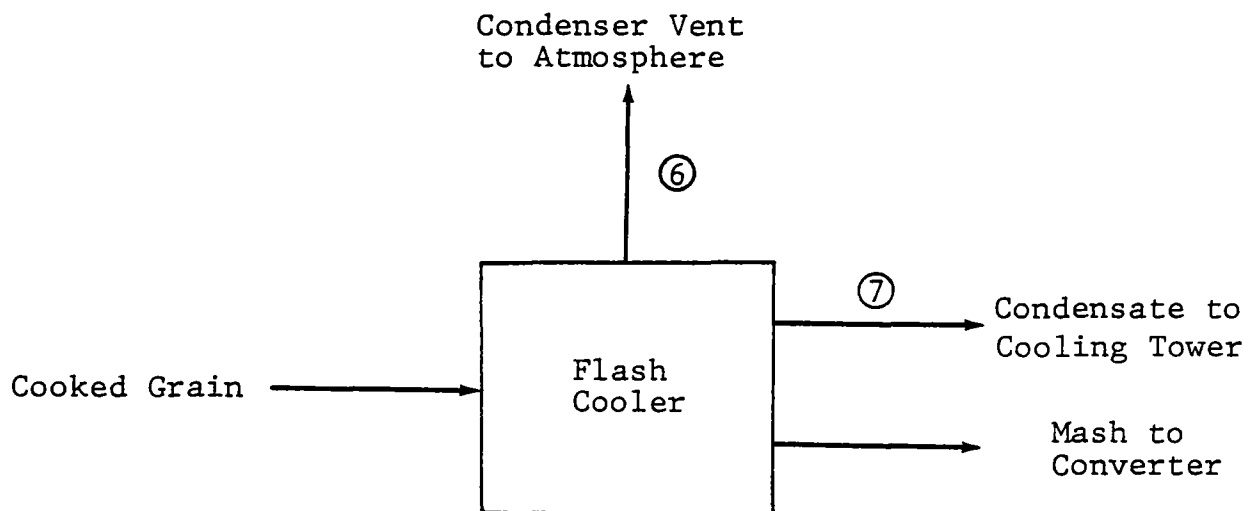
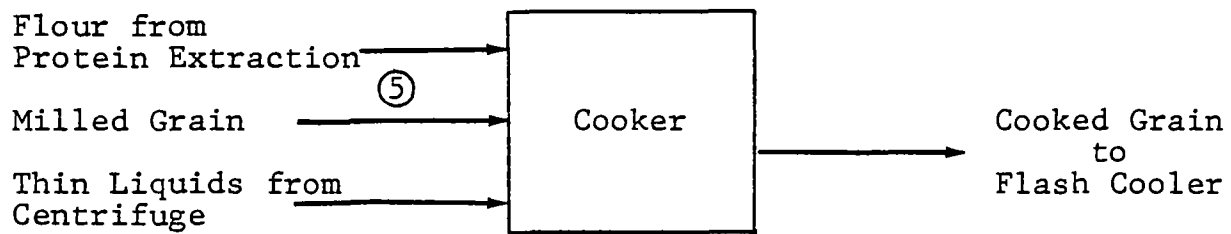


Figure 7. Cooking and cooling.

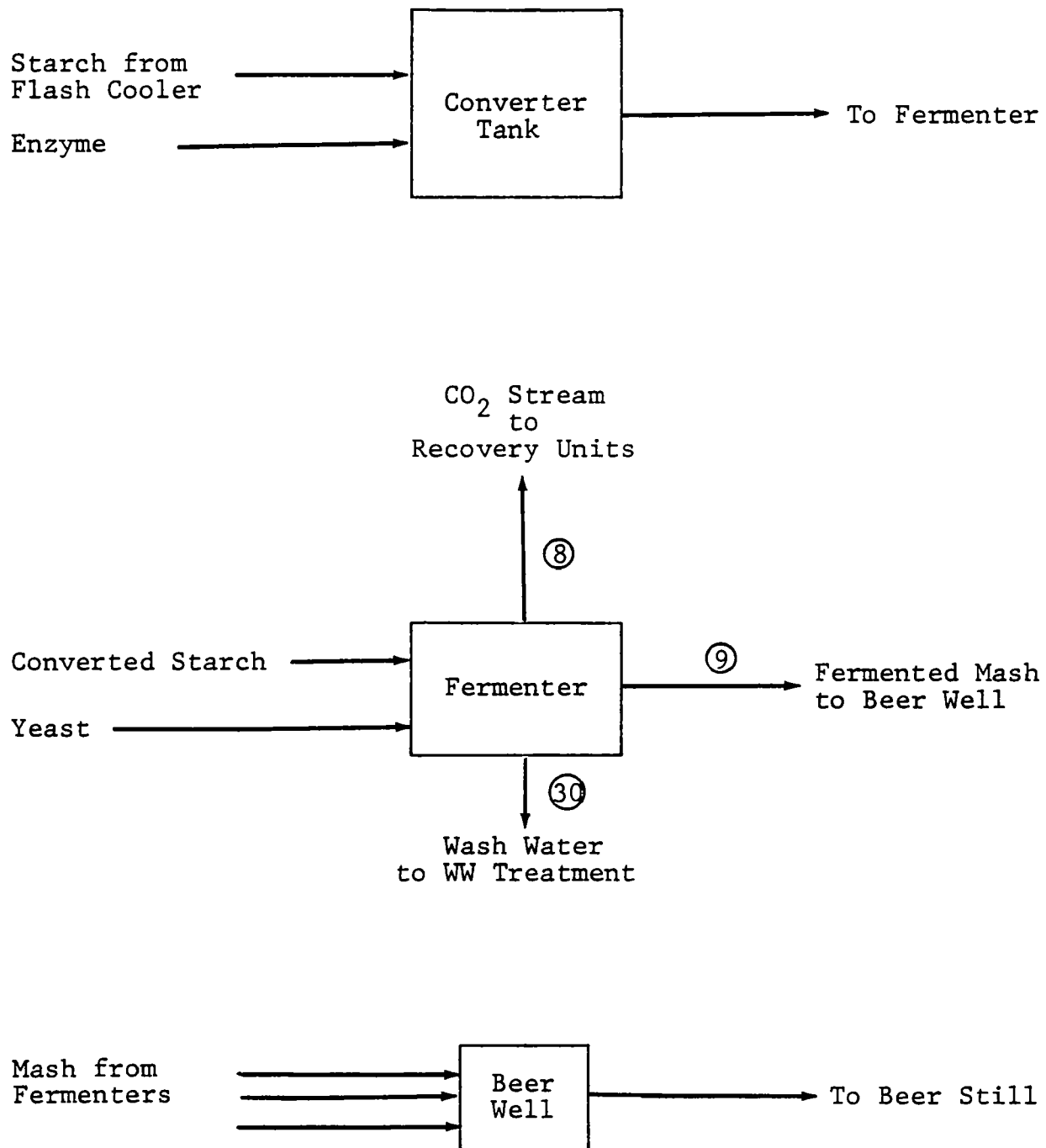


Figure 8. Conversion and Fermentation.

ethanol and carbon dioxide in the fermenter. The fermented mash is routed to a holding tank (called the beer well) prior to distillation.

The carbon dioxide stream contains small amounts of ethanol and water vapor along with traces of other organic compounds such as acetaldehyde and furfural, which are by-products of fermentation. This stream was scheduled to be sampled for ammonia and total hydrocarbon content. Since the fermenters are washed after each batch with a 25 ppm iodine solution, the wash water was tested for this element in addition to TS, TDS, TSS, BOD, TOC, pH, ammonia, and pesticides. To help trace the fate of pesticides, the fermenter output stream to the beer well was also screened for pesticides.

Distillation--

In the beer still, the fermented mash is separated into an alcohol-rich overhead stream and an aqueous bottoms streams containing a high level of solids. These solids are comprised largely of yeast cells, protein, and fibers.

As Figure 9 indicates, the only effluent stream that is not routed to another process unit is the vent on the overhead condenser. This stream was tested for total hydrocarbons.

Purification--

As Figure 10 illustrates, purification involves the addition of water to aid in the separation of higher alcohols (fusel oils) and aldehydes from ethanol.

The aqueous bottoms from the solvent extractor and fusel oil column which are sent to wastewater treatment were tested for TS, TDS, TSS, BOD, TOC, and pH. Also, the vents on the overhead condensers from these columns release volatile organics. These vent streams were analyzed for total hydrocarbon content. The fusel oils extracted during purification are sold as by-products and were not examined.

Rectification--

In the rectifier, the aqueous alcohol stream from the solvent extractor is concentrated to 95 to 96 percent ethanol. Residual impurities such as fusel oils are also removed in this column. (See Figure 11).

The vent on the overhead condenser was analyzed for total hydrocarbons and the rectifier bottoms was analyzed for TS, TDS, TSS, BOD, TOC, pH, and pesticides.

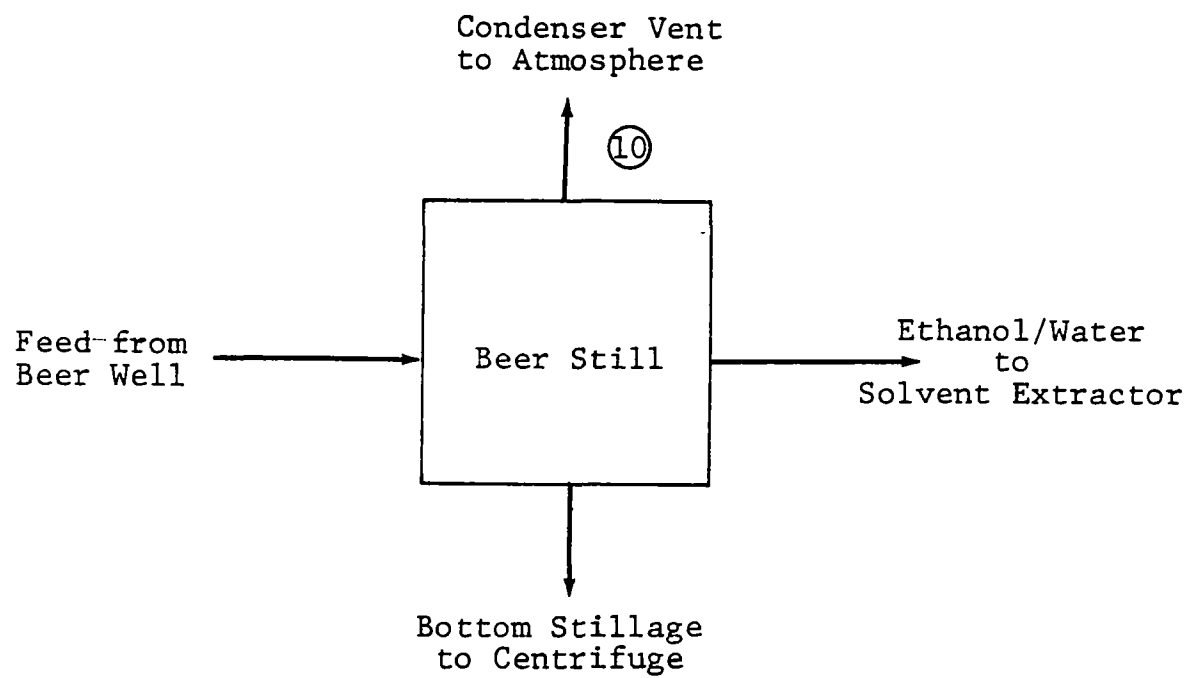


Figure 9. Distillation.

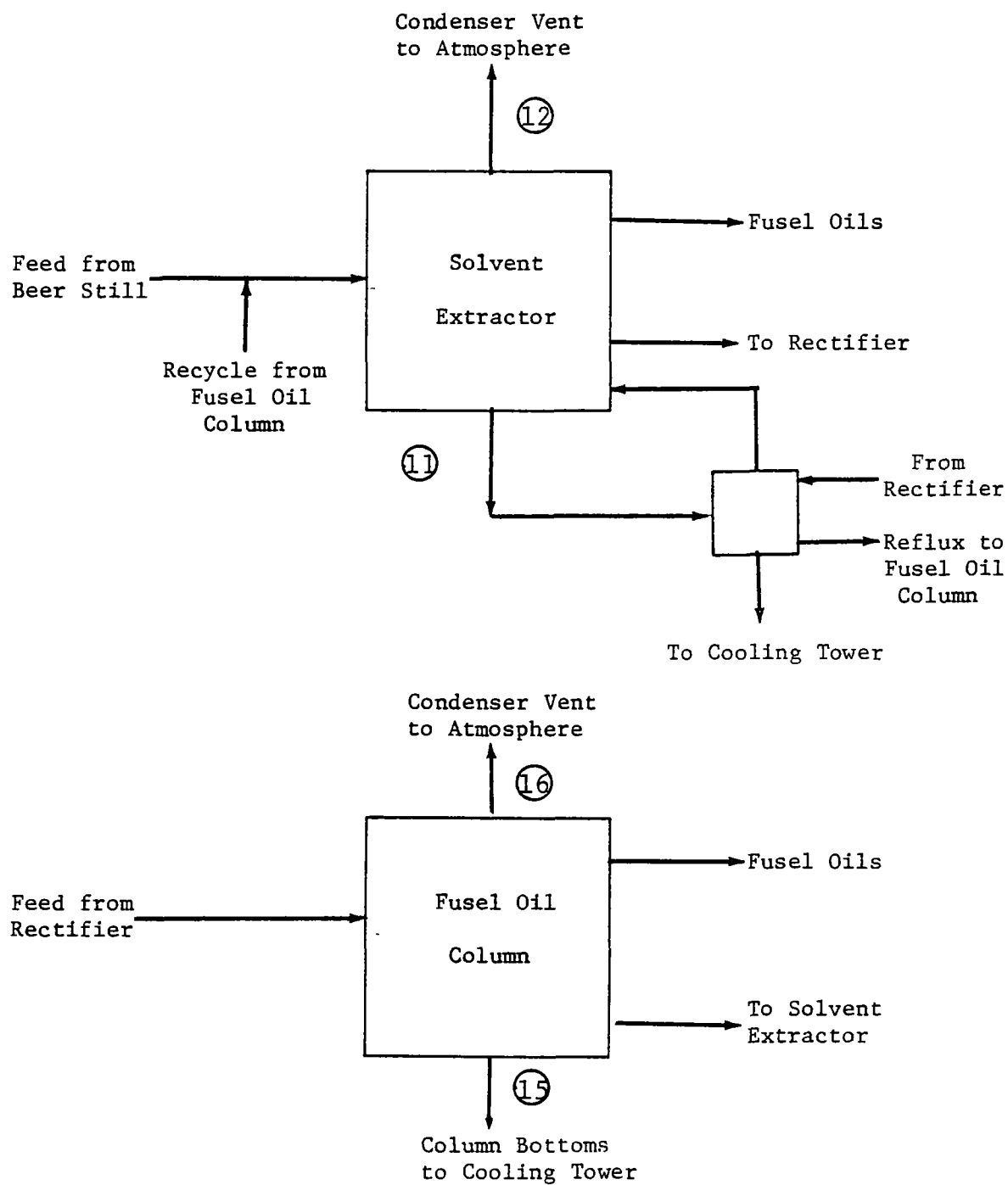


Figure 10. Purification.

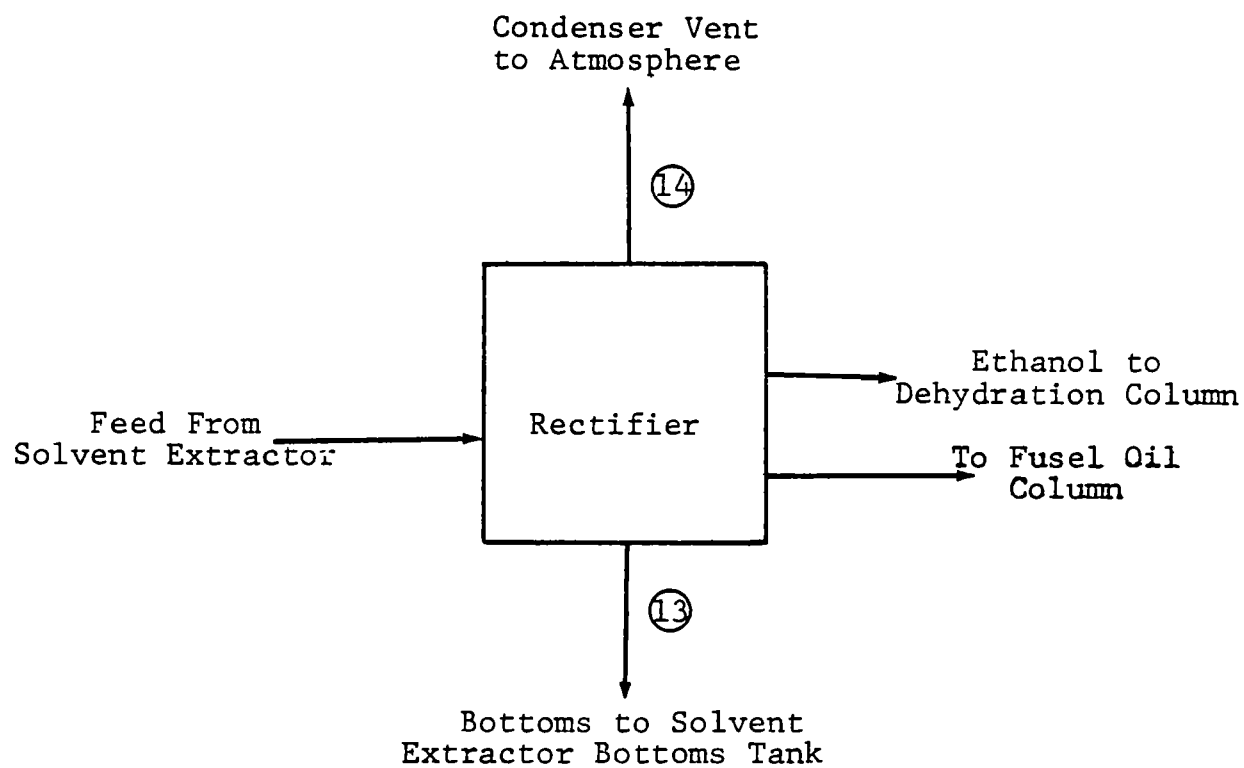


Figure 11. Rectification.

Dehydration--

In the dehydration sequence illustrated in Figure 12, benzene is used to form a ternary azeotrope with the ethanol/water feed to the dehydration column. Addition of the proper amount of benzene causes nearly all of the water and benzene to leave the top of the column while ethanol is withdrawn from the bottom of the column. A chilled separator and a stripping column are used to remove water from the dehydration column overhead stream (via the stripping column bottoms) and recycle benzene back to the dehydration column.

Ethanol withdrawn as bottoms from the dehydration column was analyzed for TS, TDS, TSS, and benzene. The water stream from the stripping column may also contain benzene and other organic compounds. In addition to benzene, this stream was analyzed for TS, TDS, BOD, TOC, and pH. Air emissions from the vents on the overhead condensers and the separator were analyzed for benzene and total hydrocarbon content.

By-Product Processing--

As Figure 13 shows, the water in the bottoms stillage from the beer still is removed using centrifuges, multi-effect evaporators, and a direct-contact dryer.

Three streams associated with the evaporators were examined for pollutants, including the overhead condensate, barometric condensate from the vacuum ejectors, and air emissions from condenser vents. The overhead and barometric condensate were tested for TS, TDS, VDS, TSS, VSS, BOD, TOC, and pH. The vent streams on the condensers for the evaporators were analyzed for total hydrocarbons.

Particulate emissions are the major concern for the direct-contact dryer. Particulate levels will be checked in the inlet stream as well as in the effluent stream from the cyclone to determine the pollutant removal performance of this control module. Because boiler flue gases are used in drying, SO_2 , CO , and NO_x levels were monitored in the exhaust from the dryer cyclones.

Wastewater Treatment--

Cooling tower blowdown (which is comprised of condensate from the evaporators, the flash cooler, and the barometric condensers as well as the bottoms from the solvent extractor, the rectifier, and the stripping columns), and equipment wash water are routed to a sludge pit where they are diluted with well water as Figure 14 reveals. This wastewater, along with thin liquids from the centrifuged wastewater biosludge, is passed through screens to remove large particles and fibers and then routed to extended aeration ponds and clarifiers for biological treatment.

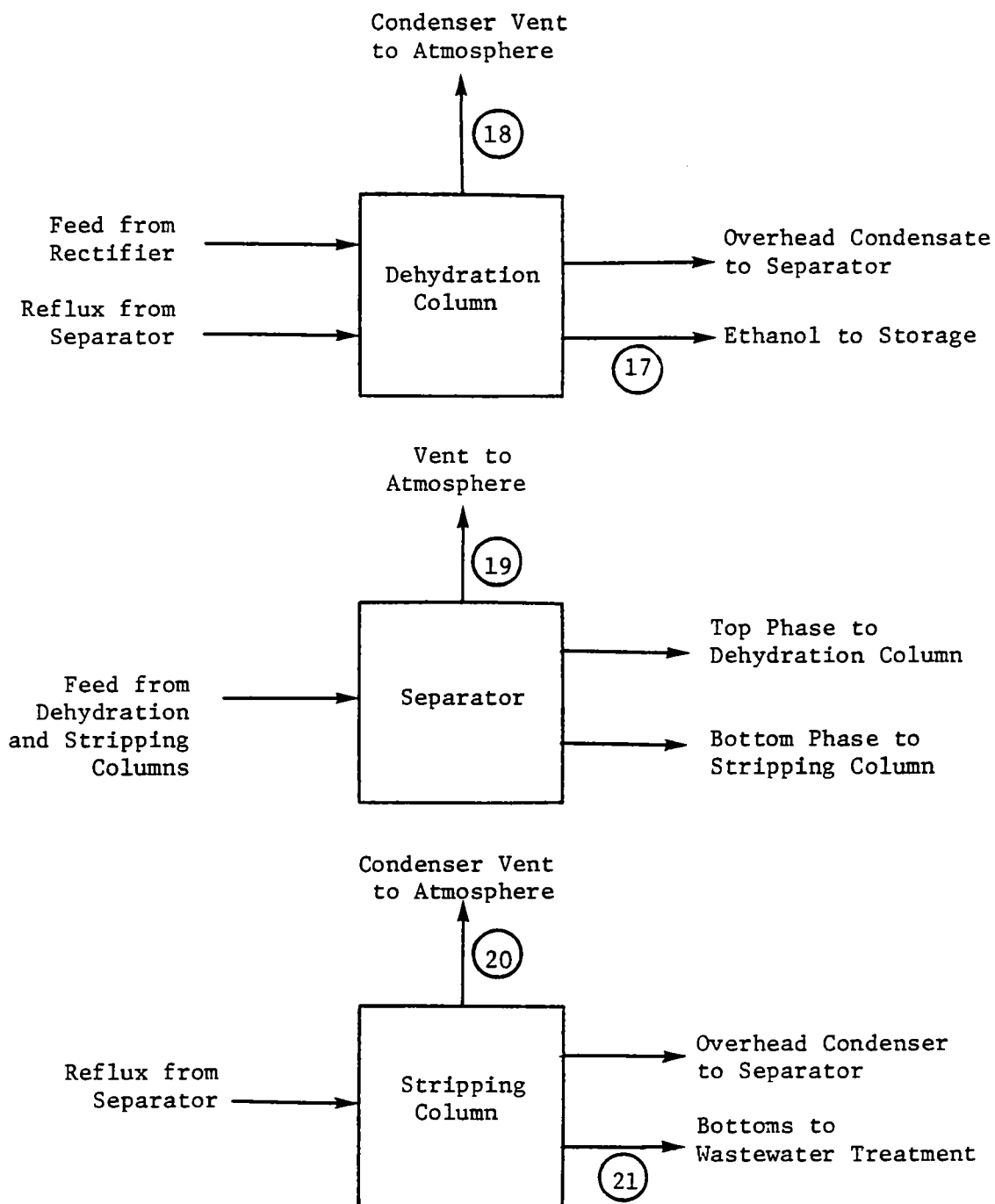


Figure 12. Dehydration.

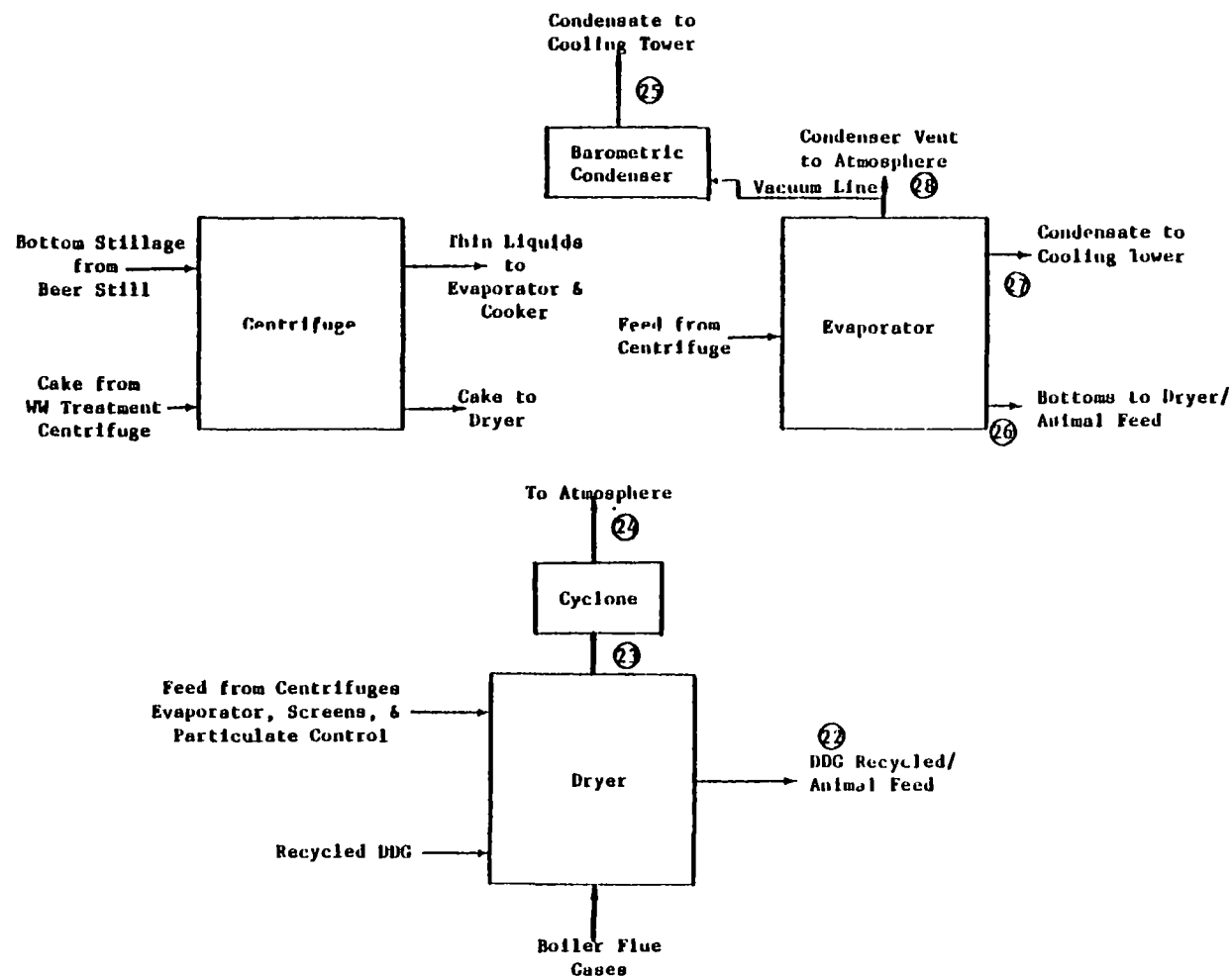


Figure 13. By-product processing.

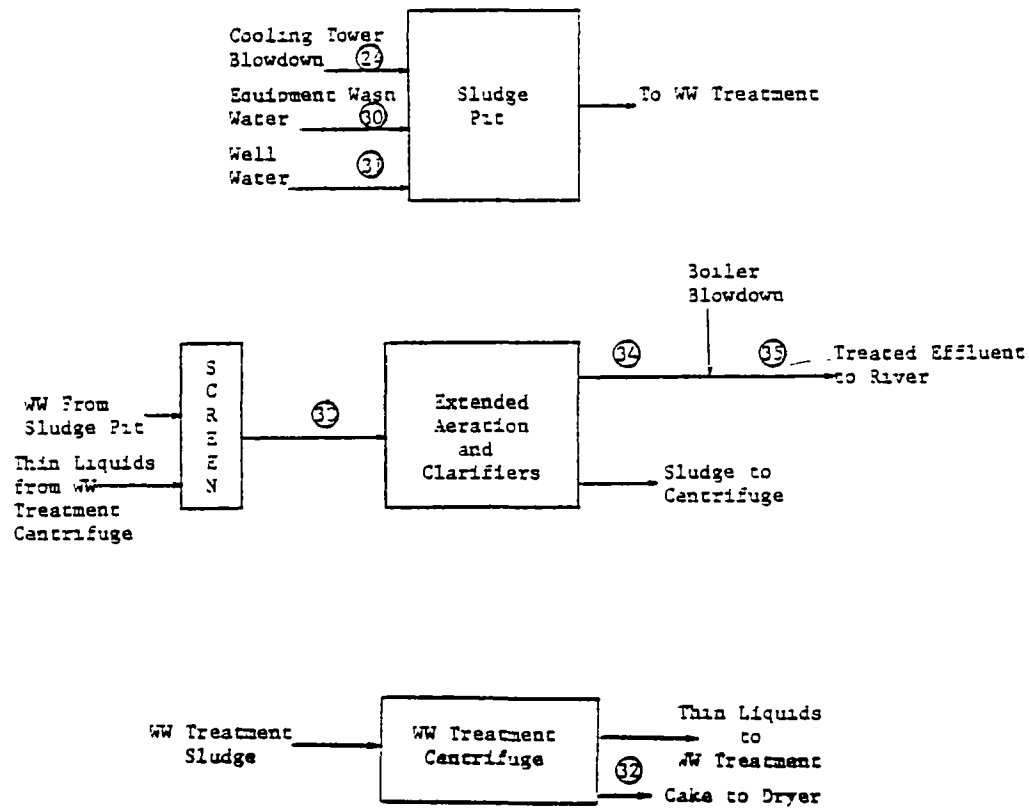


Figure 14. Wastewater treatment.

Untreated blowdown from the boiler is added to the treated effluent prior to discharge into the river. All solid waste from this system is sent to the dryer for inclusion in the DDG product.

The cooling tower blowdown stream was tested for TS, TDS, VDS, TSS, VSS, BOD, COD, TOC, pH, benzene, pesticides, sulfates, copper, iron, and iodine due to the quantity and types of streams which make up the feed to the cooling towers. The blowdown stream was also screened for priority pollutants.

The well water was analyzed for TS, TDS, VDS, TSS, VSS, BOD, TOC, pH, benzene, ammonia, sulfates, copper, iron, and iodine.

To determine the pollutant control performance of the wastewater treatment system, both the influent and effluent streams were tested for TS, TDS, VDS, TSS, VSS, BOD, COD, TOC, pH, benzene, ammonia, pesticides, sulfates, copper, iron, and iodine. Both influent and effluent from wastewater treatment were screened for priority pollutants according to EPA protocol. Also, boiler blowdown which is added to the treated effluent stream from the clarifier was tested for TS, TDS, TSS, copper, and iron.

Finally, the cake from the centrifuged biosludge stream which is recycled to the dryer was analyzed for benzene, pesticides, and ammonia.

Sampling/Analytical Matrix

A sampling/analytical matrix is a convenient means of displaying the set of sampled streams and analytical parameters. Such a matrix clearly indicates the analytical parameters to be measured in each sampled stream. The sampling/analytical matrices for solid, gaseous, and liquid streams for the alcohol plants sampled are presented in Tables 37, 38, and 39, respectively.

Operating Parameters

A major purpose of the process analysis is to identify process variables which have significant effects on stream analytical parameters. Process variables which are important in an alcohol plant include: feedstock composition, production rate, control module operating parameters, and other basic operating parameters (e.g., temperatures, flow rates, pressures).

Once the principal determinants of stream analytical parameters have been established, the sets of operating conditions to be characterized can be selected. If cause-and-effect phenomena are to be statistically analyzed, the tested sets of operating conditions must be based on a valid experimental design.

In this alcohol plant characterization, sampling will be conducted only at steady state or "normal" operating conditions. However, it is believed that only a few analytical parameters would be significantly affected by the changed conditions.

Existing Process Data--

Due to time and budget restraints, data on several streams may be taken from plant records as collected by operating plant personnel or regional EPA personnel. No data will be used unless it has been collected in an acceptable manner and certified by regional EPA personnel.

Sampling Procedures

Sampling procedures may be grouped into two basic categories: manual methods and continuous sampling. The manual methods are generally more flexible, more easily executed, and more labor intensive. Continuous automated techniques are more complicated and more capital intensive. Section 6.3, Sampling Procedures, presents a detailed discussion concerning the selection of sampling techniques. This section, along with the process analysis and site visit, was used to determine:

- Approximate sampling location for each sampled stream;
- Sample collection procedures for each location and analytical parameter; and
- Handling and preservation techniques for each sample.

Some important considerations in finalizing the specifications include:

- Possible last-minute process or equipment modification;
- The steps for ensuring needed cooperation between plant operator, sampler, sample handler, and analyst in a field test situation;
- Revisions to approved regulatory agency test methods or agency approval of more convenient test methods; and
- Health and safety ramifications of the proposed port locations and sampling methods (e.g., toxic or explosive gases, high internal pressures and/or temperatures, elevated or exposed positions).

The following sections discuss the techniques chosen for the collection of material from the solid, liquid, and gas streams which were identified in the previous section. Also presented in

this section is the tentative test schedule for the sampling effort.

Solids--

There are two general techniques for sampling methods for solids: grab sampling and grab-and-composite sampling. Although the sample collecting methods are identical, grab-and-composite sampling is the more precise technique. In this method, the grab samples are collected periodically over the duration of the test and then composited to form a single sample. The grab-and-composite technique will be used to collect all solid samples in the characterization.

Three of the solid streams (whole grain, grain dust, and DDG) are sufficiently dry and free-flowing to be collected using the shovel technique. Since these streams are believed to be relatively homogeneous, there should be no problems in obtaining a representative sample. Samples will be collected in clean, 1-liter containers every 2 hours for an 8-hour period and then composited.

The quantity of material collected in this sampling method will yield much larger quantities than are needed for analysis. The technique that will be used to reduce the sample size without affecting the distribution of componential samples is called the coning and quartering method. This method consists of shaping the sample into a conical pile which is then sharply divided into quarters. Two opposite portions are combined and the composite is then further reduced by again coning and quartering. This is repeated until a sample of the desired 1-liter size is obtained.

The remaining two streams (animal feed and wastewater treatment sludge) have a high concentration of water and cannot be collected and handled as the above streams. Instead, samples from these streams can be collected in 200-ml portions every 2 hours for 8 hours and then composited to obtain the desired 1-liter sample.

Although no preservation techniques are necessary for the solid samples, all will require preliminary treatment or preparation prior to analysis. This includes:

- Pulverizing the whole grain;
- Vaporatization of ethanol, fusel oils, and benzene;
- Solvent extraction for pesticides;

- Acidification and distillation of ammonia; and
- Acid extraction for sulfates.

Liquids--

All liquid streams which will be sampled are single phase, homogeneous streams. Furthermore, none of the streams will be sampled at high temperatures or pressures. These conditions greatly simplify the sampling techniques as well as reduce health and safety concerns.

The sampling points for most of the liquid streams are existing in-line valves. These valves provide a ready source from the stream and are currently used by the plant personnel for sampling. The valves pertaining to liquid streams which contain ethanol are sealed by the Bureau of Alcohol, Tobacco, and Firearms personnel. Permission to break these seals and their surveillance will be obtained prior to sampling.

Other sampling points which will be used are outflow orifices where liquid streams flow into ponds, tanks, or other open surfaces. Liquid streams to be sampled from these plants include the influent and effluent streams from wastewater treatment, boiler blowdown, and fermenter wash water.

Many of the analytical parameters which will be monitored in the liquid streams have special preservation or preparation requirements. These requirements are presented in Table 40 along with the time limits in which analysis must be conducted to assure accurate test results.

Each liquid sample submitted for analysis will be the composite of five 200-ml samples taken every 2 hours over an 8-hour period. The actual test schedule is presented later in this section.

Gases--

All gas stream sampling will be conducted at atmospheric conditions and at moderate temperatures (20-150°C). There is one restriction that limits equipment choice: all sampling methods must be explosion proof. To meet this restriction, battery-operated hand pumps and samplers and grab sample techniques will be used. Also, since the gas flow on condenser vents is expected to be variable, the vent streams will be monitored continuously for 1-hour periods.

Most of the gas samples will require pretreatment, which consists of absorption in liquids or on solids. The sampling methods to be used for each parameters are presented below in more detail.

Total hydrocarbons--To sample the vents and cyclone outlet stream on the dryer for total hydrocarbons, one end of a tube will be inserted into the vent lines or dryer exhaust and the other end of the tube will be connected to an organic vapor analyzer. This instrument, which has a direct read-out, will be used for continuous monitoring.

Benzene--The collection method for benzene will consist of extending one end of a tube into the vent or cyclone exhaust and connecting the other end to a personal sampler (a hand-held, battery-operated sampler). Two in-line glass tubes containing granulated charcoal (capacity is 6 liters per set of tubes) will be used in series to absorb the benzene. The benzene is eluted from the charcoal using carbon disulfide.

Ammonia--The samples for ammonia analysis will be collected using a series of two Smith-Greenburg impingers containing a 5 percent solution of sulfuric acid.

Particulates--Particulate matter will be withdrawn isokinetically from the cyclone exhaust streams and collected on a heated glass fiber filter in accordance with EPA Method 5.

Carbon monoxide--For the collection of CO, a tube will be inserted in the cyclone outlet stream and connected to an Orsat analyzer. A hand pump will be used to convey the dryer off gases through the tube to the analyzer for on-site analysis.

Sulfur dioxide--The sample for sulfur dioxide will be collected using a series of two Smith-Greenburg impingers containing a 3 percent hydrogen peroxide solution. (EPA Method 6)

Nitrogen oxide--A grab sample will be collected for nitrogen oxide analysis using an evacuated flask containing a dilute sulfuric acid/hydrogen peroxide-absorbing solution. This technique is in accordance with EPA Method 7.

TEST SCHEDULE

A sampling schedule is necessary to ensure that all necessary samples will be collected during the available time period without the use of excessive manpower. At this time, four test team members are scheduled for 3 days to complete the test plan requirements. The tentative schedule devotes the first day to setting up the equipment and collecting one full set of liquid samples. Duplicate samples for selected liquid streams as well as multiple samples of gas and solid streams will be collected the following 2 days.

Before the test schedule will be finalized, another survey of all sample locations will be made prior to the arrival of the test team to help avoid any problems which might arise. Other considerations which will affect the final sampling schedule are:

- The expected plant operating schedule;
- Preparation (set-up) time requirements for sampling and any required on-site sample recovery and analysis; and
- Personnel and equipment availability.

Sampling frequency and timing involve decisions concerning how often to sample and when to sample, respectively. Sampling frequency constraints include the sampling technique itself, plant operational variations, quality control requirements, and data evaluation needs.

All solid, liquid, and gas streams (except for the gas streams from the condenser vents) will be sampled every 2 hours over an 8-hour period and composited. The condenser vent streams have variable gas flows and will be monitored continuously over 1-hour periods which should be sufficiently long to average out normal process variations.

The stipulations of the quality control program and of data evaluation will be incorporated into the sampling frequency. Multiple samples will be taken from selected streams on consecutive days in order to make an estimate of the analytical and process variability of the data.

The general timing for samples is established largely by the plant operating schedule. The most important factor in final timing of the sample collection is that for any sampling, the plant should be given sufficient time to stabilize at the prescribed conditions (i.e., steady state).

Revisions in test plan content or scheduling may result due to:

- Changes to the plant operating schedule as a result of equipment failures or changing objectives;
- Identification of problems in sampling and analytical methods;
- Feedback of data from the quality control and data evaluation programs which indicate a problem with quality control in a sample-analysis-evaluation chain; or

- Revisions of program scope arising from preliminary characterization results.

Analytical Techniques

The selection of at least tentative analytical procedures is required prior to sample collection to ensure the continuity of an integrated sampling/preservation/analytical scheme. The considerations used in selecting the particular analytical technique for the test effort were:

- Expected concentration level and required detection limits;
- Presence of interfering species;
- Accuracy and precision requirements;
- Requirements of the quality control program; and
- Time, equipment, and cost limitations.

In the following paragraphs, a brief account of the analytical methods chosen and preliminary treatments or preparations required for the test effort is presented. The methods and pre-treatments for the parameters are organized into sections corresponding with solid, liquid, and gas streams.

Solids--

Benzene--The solid sample is heated in a glass container which is rotated in a hot oil bath. Then the overhead vapors are withdrawn using a syringe and injected into a gas chromatograph for analysis. The detection limit for benzene using this technique is about 1 ppm.

Pesticides--The method for pesticide analysis involves extracting the pollutant from the solid sample and submitting it for gas chromatograph analysis using an EPA-documented technique. The detection limit for pesticides is 10 ppb or less using this method.

Ammonia--The concentration of ammonia in solid samples is determined by acidifying the sample, distilling the ammonia into a boric acid solution, then using colormetric or titrimetric techniques. The detection limit for this method is about 1 ppm.

Sulfates--The sulfates are extracted from the solids using an acidic medium (HCl). Next, hydrogen peroxide is added to this extract to convert all the oxidized sulfur species to sulfate.

Then, an analysis for sulfates is performed by the barium-thorium titration method as specified in EPA Method 6. The detection limit for sulfates in the liquid medium is about 5 ppm.

Liquids--

Total solids--To analyze for total solids content, an aliquot of the sample is evaporated to dryness at 105°C and weighed on a Mettler balance. An alternative to analysis for total solids is to report it as the sum of total dissolved solids and total suspended solids.

Total dissolved solids--To determine the amount of dissolved solids, an aliquot of the sample is filtered and the filtrate is then evaporated to dryness at 105°C and weighed.

Volatile dissolved solids--The residue that is obtained from drying the filtrate of the total dissolved solids sample is ignited at 550°C in an oven. The weight loss is then reported as volatile dissolved solids.

Total suspended solids--An aliquot of the sample is filtered and the residue collected on the filter is dried to a constant weight at 105°C.

Volatile suspended solids--The residue collected on the filter and dried to a constant weight for total suspended solids determination is ignited at 550°C in an oven. A glass fiber filter without an organic binder is used and the weight loss is reported as volatile suspended solids.

Biochemical oxygen demand (BOD)--An aliquot of the sample is analyzed for dissolved oxygen (membrane electrode method) and then incubated at 20°C for 5 days in the dark. The sample is then analyzed again for dissolved oxygen. The reduction in the dissolved oxygen concentration is a measure of the BOD.

Chemical oxygen demand (COD)--The organic and oxidizable inorganic matter in the sample are oxidized by potassium dichromate in a 50 percent sulfuric acid solution at reflux temperatures. Silver sulfate is used as a catalyst and mercuric sulfate is used to remove chloride interference. The excess dichromate is analyzed to provide a measure of the COD.

Total organic carbon (TOC)--This test is performed by injecting a known quantity of sample into a high-temperature furnace. The organic carbon is oxidized to carbon dioxide in the presence of a catalyst. The carbon dioxide that is produced is quantitatively measured by means of an infrared analyzer. Acidification and aeration of the sample prior to analysis eliminates errors due to the presence of inorganic carbon.

pH--The pH of the liquid samples is measured using a laboratory pH instrument having a glass electrode in combination with a reference potential electrode.

Benzene--The analysis for benzene is conducted using standard gas chromatographic techniques. The detection limit for benzene using this method is approximately 100 ppb.

Pesticides--The pesticides are extracted from the liquid streams and submitted for GC analysis according to documented EPA methods; the detection limit is 10 ppb.

Sulfates--Analysis for sulfates is performed using the Gravimetric Method. Sulfate is precipitated as barium sulfate in a hydrochloric acid medium by the addition of barium chloride. A precipitate is formed (BaSO_4) and filtered, washed with hot water, ignited, and weighed. The detection limit is estimated to be 10 ppm.

Ammonia--An aliquot of the sample is buffered with a borate solution to a pH of 9.5 in order to decrease the hydrolysis of cyanites and organic nitrogen compounds. Next, the sample is distilled into a solution of boric acid. The ammonia in the distillate is determined colorimetrically by nesslerization or titrimetrically with standard sulfuric acid with the use of a mixed indicator. (The choice is dependent on the ammonia concentration).

Copper and iron--Analysis for these elements is performed using atomic absorption spectroscopy. The detection limits for copper and iron are 0.05 ppm.

Iodine--An amperometric titration method is used for the analysis of iodine in liquid waste streams. The detection limit for iodine using this technique is 7 ppm.

Gases--

Total hydrocarbons--An organic vapor analyzer (OVA) which consists of a portable GC with a flame ionization detector will be used to measure total hydrocarbon content of the vapor streams from the condenser vents as well as the vents on the separator and fermenter. The instrument will be calibrated using different concentrations of a hydrocarbon species (Methane). Total hydrocarbon content will be ready as ppm methane.

Benzene--As mentioned in Section 7.3, this organic compound is collected on granulated charcoal contained in a series of glass tubes. The sample will be eluted from the charcoal using carbon disulfide. The carbon disulfide effluent was analyzed for benzene using a gas chromatograph with a flame ionization detector. The detection limit for this method is estimated at 1 ppm.

Nitrogen oxide--The grab sample collected for nitrogen oxide analysis is subjected to a colorimetric method using the phenol-disulfonic acid (PDS) procedure. This technique is in accordance with EPA Method 7 and can be used to determine all nitrogen oxides except nitrous oxide. The detectability limit for this method is 2 to 400 mg per M³.

DATA EVALUATION

This section presents the general approach for the analysis of data which should be employed to verify the reliability of collected data, to evaluate the quality control performance of the sampling and analysis program, and to analyze the sources of variability in collected data.

Sample collection techniques affect the data characteristics, which, in turn, affect the statistical treatment of the data. The collection techniques applied to this sampling program will include continuous monitoring, manual sampling (periodic or intermittent) and composite sampling. A description of these techniques and their effects on statistical treatment of data is presented in Section 6.5. Estimates of data variability to be included in the test effort will include standard deviation and confidence intervals.

Quality Control

To provide assurance that the collection of samples will be both accurate and precise, the quality control program conducted on-site included the following elements:

- Calibration of both sampling and on-site analytical equipment to establish accuracy;
- Replicate sampling to establish the limits on precision;
- The use of alternative (replicate) sampling analysis methods and correlation analysis of the results as judged necessary by the sampling team leader to confirm accuracy; and
- The establishment of a chain of responsibility for data generation, which extends from sample collection to sample recovery to sample analysis. (This will be done by means of a strict record-keeping system which includes a master log for tracking samples).

The quality control program which was implemented to ensure accurate and precise analytical results consisted of:

- Calibration of analytical equipment with standards and spiked samples (for all analyses except solids determination);
- Duplicate testing (all analyses);
- GC/MS system performance evaluation (for priority pollutant analyses except metals);
- Analysis of blanks (organics analyzed by purge and trap technique and metals); and
- Distillation of standards to confirm distillation efficiency and reagent purity (cyanides and phenols).

SECTION 8

SAMPLING AND ANALYSIS OF AN ALCOHOL FACILITY

A brief account of the sampling trip is presented in this section. Highlighted are the deviations which occurred from the test plan described in Section 7. Included are any omissions or additions in the sampling effort as well as changes in sampling procedures or analytical methods. These deviations are discussed in terms of the solid, liquid, and gas streams sampled.

TEST PLAN DEVIATIONS

Solid Streams

No problems were encountered concerning the collection, preparation, or analysis of the solid stream samples. All samples were collected during the second and third days of the sampling effort.

Liquid Streams

The first day of the sampling effort for liquid streams was devoted to preparations such as labeling sampling containers, administering acid or base preservation chemicals, weighing filter papers, and devising a daily sampling schedule. To formulate this schedule, the location and accessibility of all the streams were reviewed which resulted in the addition of several streams to the sampling effort. These streams included:

- The well water makeup stream to the sludge pit since it is a major portion of the input to the wastewater treatment system; and
- The feed stream to the cooker for pesticide analysis in order to better follow the fate of pesticides in the alcohol process.

Also, it was believed impossible to sample the fusel oil column bottoms and the solvent extractor bottoms because they are mixed shortly after leaving the columns. Closer inspection of this system revealed the existence of sampling ports upstream of the point where the column bottoms are combined. Therefore, each of these streams was sampled separately.

During the course of the sampling effort, two modifications were made to the sampling techniques:

- Although the alcohol plant was known to have three cooling towers, it was assumed the water quality from each was similar and that one would be randomly chosen for sampling. However, plant personnel advised that the water from one tower in particular was considerably different from the other two towers. Since two additional liquid streams had already been added to the sampling effort, time did not permit for each cooling tower to be sampled separately. Therefore, blowdown from all three cooling towers was composited to obtain a representative sample of the total cooling tower blowdown.
- Similarly, samples were composited from two multi-effect evaporators which also differed in effluent water quality.

The liquid streams chosen for the first day of sampling included the well water, evaporator condensate, cooling tower blowdown, influent and effluent streams from wastewater treatment, city water, and barometric condensate. For quality control purposes, the first five of these streams were chosen to be sampled again on the following day. Unfortunately, the liquid samples from the second day of sampling (17 August) were delivered 2 days late by the shipper. Time permitted for the priority pollutant samples to be recollected, but not for the duplicate liquid streams. Parameters from these five streams which must undergo analysis within 24 hours to ensure their integrity are BOD, TOC, COD, and ammonia (see Table 40). The results for these parameters must be considered suspect and have been omitted from the results.

The normal operation of the wastewater treatment system was disrupted due to a pipe failure the morning of the second sampling day (17 August). Repairs were made within 2 hours and sampling efforts were resumed for the wastewater treatment system. However, the concentrations measured for many of the parameters in the wastewater influent were abnormally high, indicating several more hours were necessary for treatment operations to stabilize. Therefore, values for these samples have been deleted from the results.

Gas Streams

The air effluent stream sampling was begun on the second day after calibrating instruments, setting up sampling equipment, and confirming sampling port locations for these streams. The first parameters measured were particulate matter from the cyclone effluent stream which is associated with by-product dryers.

TABLE 40. PRESERVATION AND PREPARATION REQUIREMENTS FOR LIQUID STREAM PARAMETERS (148)

<u>Analytical Parameter</u>	<u>Preservation Technique</u>	<u>Preparation Technique</u>	<u>Analysis Time Limit</u>	<u>Quantity^(*) Collected</u>
Total Dissolved Solids	Cool, 4°C	Filter	7 days	200 ml
Volatile Suspended Solids	Cool, 4°C	Filter	7 days	
Total Suspended Solids	Cool, 4°C	Filter	7 days	
Volatile Suspended Solids	Cool, 4°C	Filter	7 days	
BOD	Cool, 4°C		24 hours	200 ml
Sulfates	Cool, 4°C		7 days	
Iodine	Cool, 4°C		24 hours	
COD	Cool, 4°C	Acidify to pH <2 with H ₂ SO ₂	7 days	200 ml
NH ₃	Cool, 4°C		24 hours	
TOC	Cool, 4°C	Filter, acidify to pH <2 with H ₂ SO ₄	24 hours	200 ml
Pesticides	Cool, 4°C			200 ml (glass)
pH		On-Site Measurement	6 hours	200 ml
Cu, Fe		Acidify to pH <2 with HNO ₃		200 ml
Benzene	Cool, 4°C			glass vial (no air)
Priority Pollutants				
Purgeables	Cool, 4°C			2 glass vials
Base/Neutrals	Cool, 4°C			750 ml (glass)
Cyanides	Cool, 4°C	pH 2 with NaOH	24 hours	200 ml
Phenols	Cool, 4°C	Acidify to pH <4 with H ₃ PO ₄	24 hours	200 ml (glass)
Metals		Filter, acidify to pH <2 with HNO ₃	6 months	200 ml

(*) Every 2 hours for an 8-hour period.

Mechanical difficulties were encountered with the organic vapor analyzer (OVA) that day which prevented further sampling. Repairs were made in time to sample the fermenter vent for ammonia, the dryer cyclone effluent stream for total hydrocarbons (THC), and the condenser vents on the dehydration column and stripping column for benzene and THC the following day. On the last day, the dryer cyclone effluent stream was sampled for ammonia, NO_x, and SO₂; the fermenter vent and condenser vents on the beer still, solvent extractor, rectifier, and fusel oil column were sampled for THC.

There were several changes made in the collection and analysis of air effluents. Inspection of the facility revealed that the cyclones on the grain milling operations were in a closed-loop system, thus preventing the collection of samples from the cyclone inlet or outlet stream. Also, the condenser vent on the flash cooler and the cyclone inlet for the by-product grain dryer were physically inaccessible to the sampling team. In addition, the separator vent and condenser vent for the stripping column shared the same vent line as the benzene makeup storage tank. Total air emissions from these three sources are identified as stripping column condenser vent effluents.

Six of the gas streams contained significant concentrations of water and it was necessary to remove this water prior to total hydrocarbon (THC) analysis. These streams included the cyclone outlet stream on the dryer, solvent extractor, rectifier, and fusel oil column. The water was removed from the stream by use of a Perma-Pure® dryer which contains an osmotic membrane that passes water vapor from the sample stream. The THC concentration measured is therefore on a dry-gas basis.

The gas velocity of the dryer cyclone effluent was measured at 22 points in the duct using an "S-type" pilot during the two collection periods for particulate matter. The flow rate was determined on a dry basis by removing the measured moisture content from the process flow. The moisture content of the stream was determined by weighing the impingers before and after the runs, and then comparing the gain in weight with the metered gas volume.

The gas velocity of the carbon dioxide stream from the fermenter vent could not be measured. Values for the flow rate were taken from plant records.

Gas velocities of the remaining streams (condenser vents on the beer still, solvent extractor, fusel oil column, rectifier, dehydration column and stripping column) were measured using a self-contained and direct-reading velocimeter.

The temperatures of all the streams except the fermenter vent were measured using a dial thermometer. Since these streams were atmospheric vents, the measured gas temperatures and atmospheric pressure were used in calculations to determine flow rates at standard conditions.

Gas velocity measurements were made at each vent except the fermenter vent over two 1-minute periods. Readings were taken every 5 seconds over 1-minute intervals. This was done twice and the two values were averaged to provide the flow rate. The accuracy of these measurements is questionable, due to the very erratic flow natures of the vents. Also, the flow rate from these vents can be in either direction. The velocimeter registered a zero reading if a reverse flow was occurring.

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APPENDIX A

FLOW DIAGRAMS AND MASS BALANCES FOR SELECTED ALCOHOL PLANTS

PROCESS EVALUATIONS

After reviewing the data collected in Task I, three alcohol facilities were chosen for further study based on the following criteria:

- Product Type (methanol or ethanol);
- Development status;
- Product quality (beverage or fuel grade);
- Plant design and availability of data.

Product Type

Based on information gathered concerning alcohol processes, it was concluded that methanol/gasoline mixtures were inferior to ethanol/gasoline mixtures for large-scale use as motor fuel. Examples of some problems methanol/gasoline mixtures entail are:

- Methanol/gasoline mixtures have low tolerances for water and exhibit phase separation at the ppm level of water contamination. Ethanol/gasoline mixtures can tolerate twice as much water as methanol/gasoline mixtures.
- Methanol has relatively low energy content (about half that of gasoline). Ethanol contains approximately 2/3 the Btu content of gasoline.
- Addition of methanol to gasoline substantially increases the Reid Vapor Pressure (RVP) of the resulting mixture and might cause vapor lock. Ethanol does not increase RVP as much as methanol.
- Significant quantities of methanol in motor fuel might necessitate carburetor modifications since it burns leaner (and thus may cause performance deficiencies such as stalling, hard starting, and lean surge). Ethanol can be utilized in concentrations up to 20 percent without carburetor modifications.

Ethanol from grain or other biomass materials has the support of an influential political force which will spur its use as a motor fuel component. For example, the 1978 Energy Bill removed the 4¢/gallon federal tax from gasohol (mixtures containing 10 percent ethanol and 90 percent unleaded gasoline) which amounts to a subsidy of 40¢/gallon ethanol. As of October 1979, 16 states have removed all or part of their state gasoline tax for gasohol and legislation is in the works for four additional states. These subsidies make gasohol prices competitive with premium unleaded gasoline at the pump.

Thus, further efforts in this project will concentrate on ethanol rather than methanol due to ethanol's superior performance as a motor fuel and to political and economic factors.

Development Status

The literature search conducted in Task I revealed the existence of numerous bench-scale facilities that explore novel ethanol synthesis techniques at universities and private laboratories around the country; however, no pilot units utilizing new technologies to manufacture fuel grade ethanol are expected to be operational before 1980. Therefore, only commercial fermentation ethanol plants using established processing technology could be considered. Among the existing facilities examined, special attention was focused on those containing processing units which are likely to be incorporated into future alcohol fuel plants that would support a gasohol industry.

Product Quality

For the purposes of this report, two grades of alcohol will be considered, fuel and beverage. Due to the phase separation induced by water contamination of ethanol/gasoline mixtures, fuel alcohol must be nearly water-free (anhydrous) in the absence of blending agents. Also, according to government regulations imposed by the Bureau of Alcohol, Tobacco, and Firearms (ATF), ethanol fuel must be denatured to be exempt from the beverage tax (\$21/gallon 100 percent ethanol). Beverage alcohol is rarely concentrated above 95 percent and is very low in impurities.

The removal of contaminants and subsequent improvement of the potability of beverage grade alcohol is energy intensive. Existing beverage alcohol plants may consume up to three times as much energy as future fuel grade alcohol plants that are properly designed for energy conservation. Therefore, economics dictates that alcohol facilities supporting the gasohol industry will produce a fuel grade ethanol. The fuel grade ethanol is not expected to differ significantly in engine performance compared to beverage grade ethanol of higher purity.

Four fermentation alcohol plants in the United States are currently manufacturing anhydrous, denatured ethanol. These facilities formerly produced beverage grade alcohol, but have recently added a dehydration unit along with several processing modifications to increase operating efficiency. Two of these facilities have been chosen for further study and are included in Section 3. Other beverage alcohol plants in the U.S. are planning to add a dehydration unit to their facility and will also provide ethanol for use in gasohol.

Plant Design and Data Availability

Although there are no grassroots facilities specifically designed to support a gasohol industry, the plants considered in Section 3 have many processing steps which are expected to be present in future fuel grade alcohol plants. The three plants chosen for further study in Section 3 will be discussed below in terms of their advantages and disadvantages with regard to operating schemes and data availability.

Plant I has been converted from a beverage plant to a fuel plant and with the modification planned (removal of purifying columns and perhaps continuous fermentation), will closely resemble a grassroots ethanol fuel plant. Because the waste streams from the alcohol plant are combined with wastewater from other on-site processes, proper sampling of this facility would be difficult.

Plant II has added a benzene dehydration unit and begun production of anhydrous ethanol; however, no other process modifications are currently under consideration. This plant has a segregated wastewater treatment system which recycles wastewater sludge back to the alcohol process, thereby eliminating a solid waste disposal problem and increasing by-product output (distiller's dried grains and solubles). This plant was chosen for the sampling effort.

The third plant is the most modern ethanol facility in North America. However, the facility is strictly a beverage plant and has no plans for any modification which might alter the quality of their product. Nevertheless, the plant could provide useful data concerning processing steps they would have in common with a grassroots ethanol fuel plant.

Alcohol Plant I--

Figure A-1 presents a flow diagram representing a beverage ethanol plant which has been converted to an ethanol fuel plant. Table A-1 gives the flow rates and compositions of the process streams illustrated in Figure A-1 for Plant I.

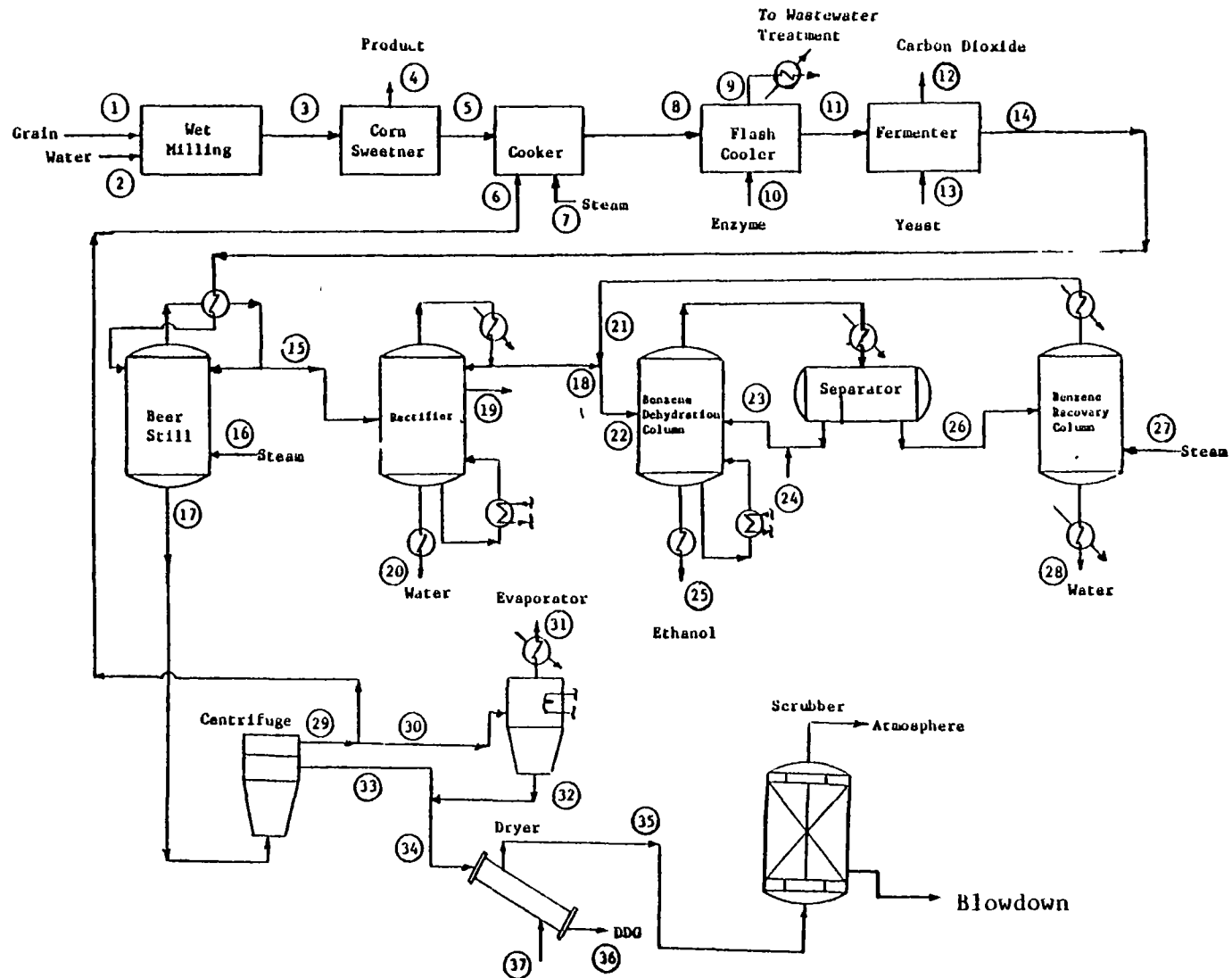


Figure A-1. Flow diagram for plant I.

TABLE A-1. MASS BALANCES PLANT I

<u>Stream</u>	<u>Origin & Destination</u>	<u>Component</u>	<u>Stream Composition</u>	
			<u>lb/hr</u>	<u>Wt %</u>
1	Grain from storage to wet milling	whole grain	50,400	100.0
2	Water (from cooling water) to wet milling	water	235,200	100.0
3	Milled grain from wet milling fed to corn sweetener plant	milled grain water	50,400 235,200	17.6 82.4
4	Product from corn sweetener	starch, protein oils water	23,400 109,200	17.6 82.4
5	Partially saccharified starch with protein to cooker	starch/protein water	27,000 126,000	17.6 82.4
6	Stillage from beer still to cooker	solids water	4,430 84,270	5.0 95.0
7	150# steam to cooker	water	35,740	100.0
8	Mash from cooker to flash cooler	solids water	31,430 210,270	13.0 87.0
9	Condensate from flash cooler to wastewater treatment	water	126,930	100.0
10	Saccharifying enzyme to flash cooler	enzyme	2,570	100.0
11	Mash from flash cooler to fermenter	solids water	34,000 119,080	22.2 77.8
12	Carbon dioxide from fermenter	carbon dioxide	13,725	100.0
13	Yeast makeup to fermenter	yeast	4,000	100.0
14	Beer from fermenter to beer still	solids water ethanol	11,470 117,550 14,335	8.0 82.0 10.0
15	Overhead condensate from beer still and feed to rectifier	ethanol water fusel oils	14,335 3,400 165	80.0 19.0 1.0

(continued)

TABLE A-1. (continued)

<u>Stream</u>	<u>Origin & Destination</u>	<u>Component</u>	<u>Stream Composition</u>	
			<u>lb/hr</u>	<u>Wt %</u>
16	Steam to beer still	water	49,915	100.0
17	Beer still bottoms to centrifuge	solids	11,470	6.5
		water	163,900	93.5
18	Rectifier overhead condensate	ethanol	14,335	96.0
		water	600	4.0
19	Fusel oils from rectifier	fusel oil	105	65.0
		water	60	35.0
20	Rectifier bottoms to ww treatment	water	2,800	100.0
21	Overhead condensate from benzene recovery column	ethanol	752	77.2
		water	47	4.8
		benzene	175	18.0
22	Feed to benzene azeotrope column	ethanol	15,087	94.8
		water	647	4.1
		benzene	175	1.1
23	Top layer from separator including benzene makeup to benzene azeotrope column	ethanol	1,253	13.5
		water	158	1.7
		benzene	7,855	84.8
24	Benzene makeup to benzene azeotrope column	benzene	40	100.0
25	Ethanol from benzene azeotrope column	ethanol	14,335	100.0
26	Bottom layer from separator to benzene recovery column	ethanol	752	47.8
		water	647	41.1
			175	11.1
27	Steam to benzene recovery column	water	550	100.0
28	Bottoms from benzene recovery column to wastewater treatment	water	1,150	100.0
29	Supernatant from centrifuge to evaporator or cooker	solids	8,320	5.0
		water	158,050	95.0
30	Supernatant from centrifuge to evaporator	solids	3,890	5.0
		water	73,780	95.0

(continued)

TABLE A-1. (continued)

<u>Stream</u>	<u>Origin & Destination</u>	<u>Component</u>	<u>Stream Composition</u>	
			<u>lb/hr</u>	<u>Wt %</u>
31	Condensate from evaporator overhead to wastewater treatment	water	66,550	100.0
32	Evaporator bottoms to dryer	solids	3,890	35.0
		water	7,230	65.0
33	Centrifuge cake to dryer	solids	3,150	35.0
		water	5,850	65.0
34	Dryer feed from centrifuge and evaporator	solids	7,040	35.0
		water	13,080	65.0
35	Water vapor from dryer to scrubber	water	12,470	100.0
36	Distiller's dried grains and solubles from dryer	solids	7,040	92.0
		water	610	8.0
37	Hot dry air from oil or natural gas fired burner	flue gas	80,000	100.0

Modifications which have been made include the addition of a benzene dehydration unit and removal of purifying columns. The major impurities (primarily higher alcohols, also called fusel oils) are removed in a sidestream from the rectifier. If these fusel oils are not removed from the distillation column, they will build up in the rectifier and upset proper operation. Since this plant produces fuel grade ethanol, the fusel oils can be combined with the finished product.

Other alterations being considered by this plant include enlarging the beer still to include rectification (eliminating the need for a separate rectifier) and utilizing continuous fermentation (still a developing technology) to increase production.

Alcohol Plant I operates in conjunction with a corn sweetener plant which utilizes some of the protein, oils, and starch and provides a high sugar content feedstock for the alcohol process. This situation is ideal since the corn sweetener products are of relatively high value and a portion of unfermentable material is removed from the alcohol plant feedstock.

The wastewater treatment facilities for Plant I are typical for a fermentation alcohol plant and include extended aeration and clarifiers. The wastewater from the alcohol plant is combined with the wastewater from other on-site processes and, therefore, a material balance could not be prepared for the treatment facility.

Alcohol Plant II--

The flow diagram and material balances for Alcohol Plant II are presented in Figure A-2 and Table A-2, respectively.

Alcohol Plant II is a beverage plant which produces neutral grain spirits; a benzene dehydration unit has been added to one of their distillation trains to produce anhydrous ethanol. The addition of a dehydration unit is the only modification presently planned by this facility which intends to remain primarily in the beverage alcohol market. The dehydration units of Plant I and II are similar except that Plant II routes the Benzene Stripping Column overheads to the separator while Plant I returns this stream to the Benzene Dehydration Column. The method employed by Plant II is superior because it takes advantage of density and solubility differences of ethanol, water, and benzene to promote separation while the Plant I relies more on energy-intensive distillation.

Alcohol Plant II has a unique wastewater treatment facility which routes sludge from the extended aeration pond to the dryer for inclusion in the by-product feed. This essentially eliminates solid waste disposal problems.

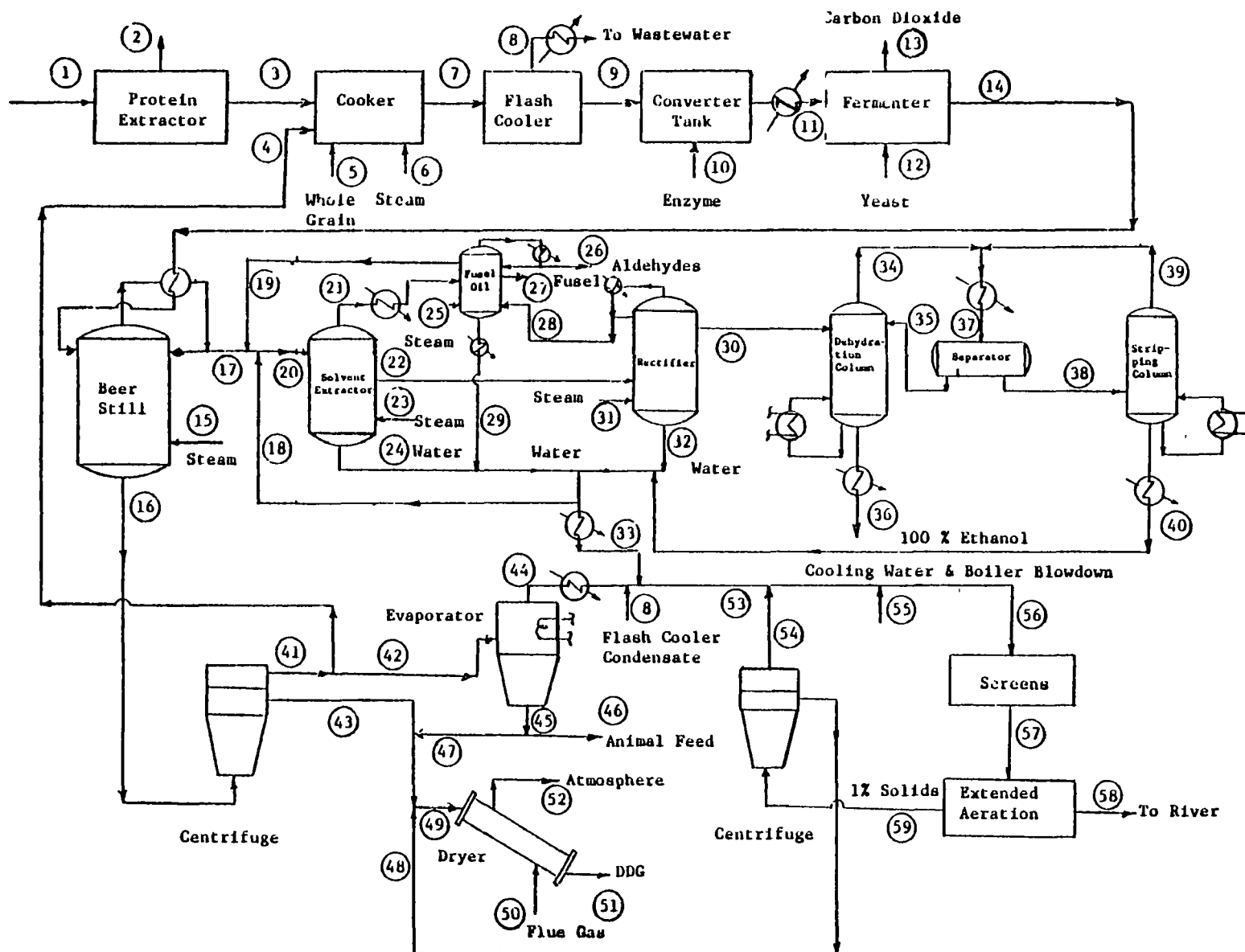


Figure A-2. Flow diagram for Plant II.

TABLE A-2. MASS BALANCES PLANT II

<u>Stream</u>	<u>Origin & Destination</u>	<u>Component</u>	<u>Stream Composition</u>	
			<u>lb/hr</u>	<u>Wt %</u>
1	Flour and water from wet milling	flour	139,950	75.0
		water	46,650	25.0
2	Product from protein extractor	protein, starch,		
		oils	21,770	25.0
		water	65,320	75.0
3	Flour feed from protein extractor to cooker	flour	24,880	25.0
		water	75,630	75.0
4	Stillage from centrifuge	solids	1,370	4.0
		water	32,880	96.0
5	Whole grain, fresh feed to cooker	grain	2,750	100.0
6	Steam to cooker	water	27,100	100.0
7	Mash from cooker to flash cooler	solids	29,000	17.7
		water	134,610	82.3
8	Flash cooler condensate to wastewater treatment	water	27,100	100.0
9	Mash from flash cooler to converter tank	solids	29,000	21.2
		water	108,010	78.8
10	Saccharifying enzyme to converter tank	enzyme	2,500	100.0
11	Cooled mash from converter tank to fermenter	solids	31,500	22.5
		water	108,010	77.5
12	Yeast to fermenter	yeast	4,500	100.0
13	Water from fermenter	water	13,725	100.0
14	Mash from fermenter to beer still	water	105,500	81.0
		ethanol	14,335	11.0
		solids	10,450	8.0
15	Steam to beer still	water	39,400	100.0
16	Beer still bottoms to centrifuge	solids	10,450	7.0
		water	138,800	93.0
17	Beer still overheads to solvent extractor	ethanol	14,335	70.2
		water	6,000	29.3
		fusel oils	100	0.5

(continued)

TABLE A-2. (continued)

<u>Stream</u>	<u>Origin & Destination</u>	<u>Component</u>	<u>Stream Composition</u>	
			<u>lb/hr</u>	<u>Wt %</u>
18	Recycled process water to solvent extractor	water	175,000	100.0
19	Alcohol stream from fusel oil column to solvent extractor	ethanol	7,664	95.0
		water	335	4.2
		fusel oil	70	0.8
20	Total feed to solvent extractor	ethanol	21,999	10.8
		water	181,335	89.1
		fusel oils	170	0.1
21	Solvent extractor overheads to fusel oil column	ethanol	1,964	70.0
		water	701	25.0
		fusel oils	140	5.0
22	Alcohol stream from solvent extractor to rectifier	ethanol	20,035	10.0
		water	180,585	89.9+
		fusel oils	30	150 (*)
23	Steam to solvent extractor	water	5,800	100.0
24	Solvent extractor bottoms to wastewater treatment/recycle	water	6,215	100.0
25	Steam to fusel oil column	water	4,100	100.0
26	Overheads from fusel oil column	aldehydes	15	37.5
		water	25	62.5
27	Fusel oil side stream from fusel oil column	fusel oil	85	70.8
		water	35	29.2
28	Rectifier overheads to fusel oil column	ethanol	5,700	95.0
		water	270	4.5
		fusel oil	30	0.5
29	Fusel oil column bottoms to ww treatment/recycle	water	4,676	100.0
30	Rectifier alcohol sidestream to benzene dehydration column	ethanol	14,335	95.0
		water	750	5.0
31	Steam to rectifier	water	13,900	100.0

(*) ppm

(continued)

TABLE A-2. (continued)

<u>Stream</u>	<u>Origin & Destination</u>	<u>Component</u>	<u>Stream Composition</u>	
			<u>lb/hr</u>	<u>Wt.-%</u>
32	Rectifier bottoms to treatment/recycle	water	193,465	100.0
33	Distillation columns bottoms to wastewater treatment	water	30,106	100.0
34	Benzene dehydration column overheads to separator	ethanol	2,393	18.5
		water	957	7.4
		benzene	9,585	74.1
35	Separator top layer to benzene dehydration column	ethanol	2,393	19.6
		water	207	1.7
		benzene	9,585	78.7
36	Benzene dehydration column bottoms (product)	ethanol	14,335	100.0
37	Total separator feed overheads from benzene recovery column and benzene dehydration column	ethanol	3,349	23.6
		water	1,029	7.3
		benzene	9,807	69.1
38	Separator bottom layer to benzene recovery column	ethanol	956	47.8
		water	822	41.1
		benzene	222	11.1
39	Benzene recovery column overheads to separator	ethanol	956	76.5
		water	72	5.8
		benzene	222	17.7
40	Benzene recovery column bottoms to wastewater treatment/recycle	water	750	100.0
41	Supernatant from centrifuge to cooker or evaporator	solids	5,392	4.0
		water	129,408	96.0
42	Supernatant from centrifuge to evaporator	solids	4,022	4.0
		water	96,528	96.0
43	Centrifuge cake to dryer	solids	5,058	35.0
		water	9,392	65.0
44	Evaporator overhead condensate to wastewater treatment	water	90,495	100.0
45	Evaporator bottoms to dryer or animal feed	solids	4,022	40.0
		water	6,033	60.0

(continued)

TABLE A-2. (continued)

<u>Stream</u>	<u>Origin & Destination</u>	<u>Component</u>	<u>Stream Composition</u>	
			<u>lb/hr</u>	<u>Wt %</u>
46	Animal feed from evaporator	solids	800	40.0
		water	1,200	60.0
47	Evaporator bottoms to dryer	solids	3,222	40.0
		water	4,833	60.0
48	Centrifuge cake (wastewater treatment) to dryer	solids	50	0.5
		water	960	99.5
49	Total dryer feed	solids	8,330	35.4
		water	15,185	64.5
50	Boiler flue gas to dryer	air	162,260	92.7
		water	12,780	7.3
51	Distiller's dried grains and solubles from dryer	solids	8,330	92.0
		water	725	8.0
52	Dryer off gas to atmosphere	air	162,260	85.6
		water	27,240	14.4
53	Total process water	solids	55	227 (*)
		water	243,250	99.9—
54	Centrifuge supernatant wastewater treatment to wastewater treatment	solids	5	0.1
		water	4,550	99.9
55	Cooling water and boiler blowdown	water	660,250	100.0
56	Total feed to wastewater treatment screens	solids	60	66(*)
		water	908,050	99.9+
57	Wastewater from screens to extended aeration	solids	60	66(*)
		water	908,050	99.9+
58	Treated wastewater from extended aeration	solids	5	5.5(*)
		water	902,550	99.9—
59	Solids from wastewater treatment to centrifuge	solids	55	1.0
		water	5,500	99.0

(*) ppm

Similar to Alcohol Plant I, Alcohol Plant II employs processing units upstream from the cooker to remove protein, oils, and fiber from the alcohol plant feedstock.

Alcohol Plant III--

The flow diagram and mass balances for Plant III, a whiskey distillery, are presented in Figure A-3 and Table A-3, respectively.

The operators of this particular plant are primarily concerned with product quality and no modifications are planned which would alter this quality. The flow diagram clearly shows the additional processing units such as the purifying, aldehyde, and fusel oil columns which typify such a facility.

There are no process units upstream of the cooker to remove unfermentable materials as in Plants I and II. This, again, is to preserve product quality. It also improves the value of the Distiller's Dried Grains and Solubles (DDGS) which contain higher amounts of proteins, oil and fiber.

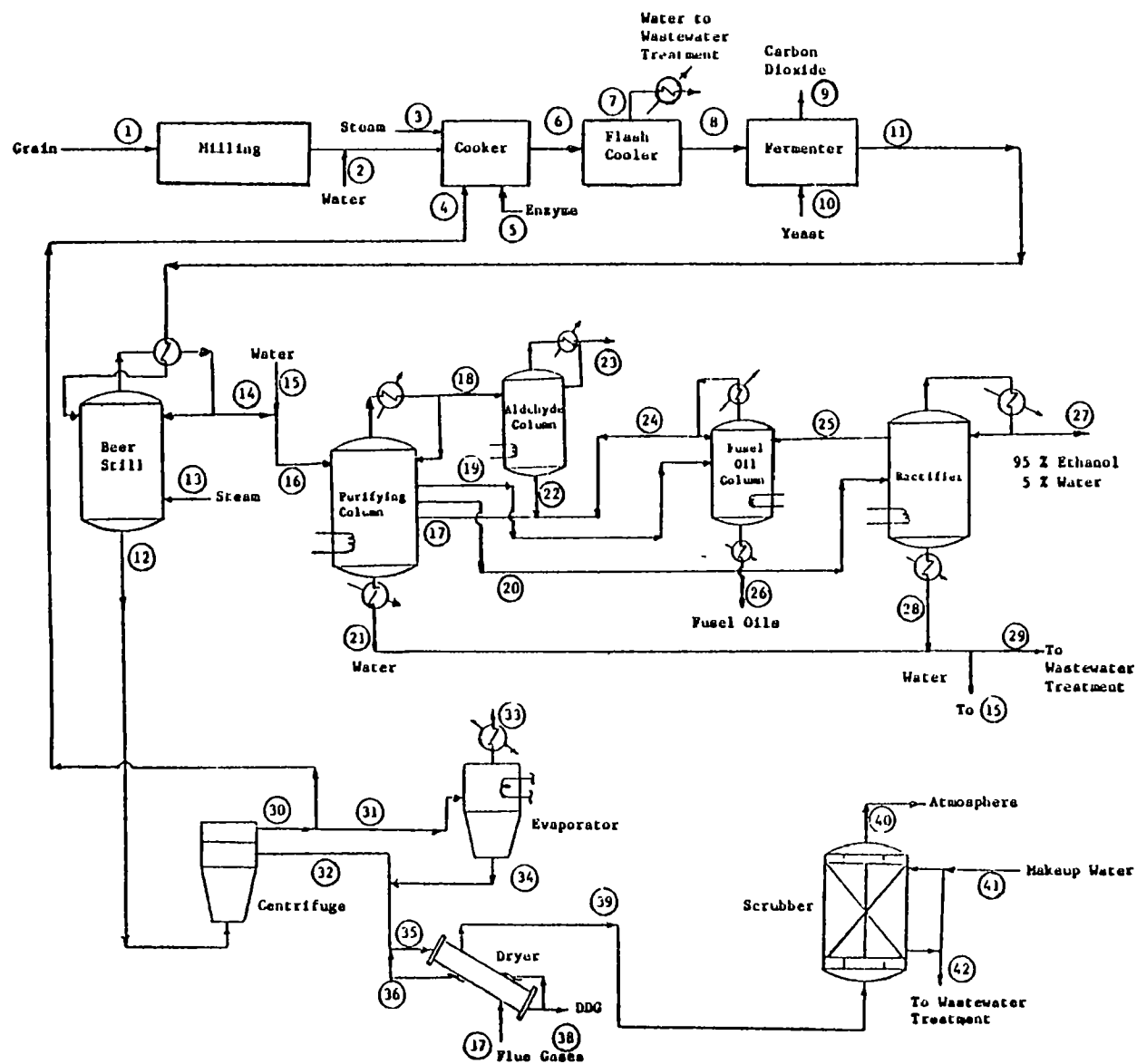


Figure A-3. Flow diagram for Plant III.

TABLE A-3. MASS BALANCES FOR PLANT III

<u>Stream</u>	<u>Origin & Destination</u>	<u>Component</u>	<u>Stream Composition</u>	
			<u>lb/hr</u>	<u>Wt %</u>
1	Grain from storage to milling	grain	28,360	100.0
2	Process water to cooker	water	85,080	100.0
3	Steam to cooker	water	28,150	100.0
4	Stillage to cooker	solids	1,135	3.0
		water	36,680	97.0
5	Enzyme to cooker	enzyme	2,500	100.0
6	Mash from cooker to flash cooler	solids	32,000	17.6
		water	149,910	82.4
7	Flash cooler condensate to wastewater treatment	water	13,910	100.0
8	Mash from flash cooler to fermenter	solids	32,000	19.0
		water	136,000	81.0
9	Carbon dioxide from fermenter	carbon dioxide	13,900	100.0
10	Yeast to fermenter	yeast	5,235	100.0
11	Mash from fermenter to beer still	ethanol	14,335	9.0
		water	132,250	83.0
		solids	12,750	8.0
12	Beer still bottoms to centrifuge	solids	12,750	7.0
		water	169,400	93.0
13	Steam to beer still	water	37,150	100.0
14	Beer still overheads to purifying column	ethanol	14,335	79.9
		water	3,460	19.2
		fusel oils	140	0.9
15	Process water to purifying column	water	179,350	100.0
16	Total fresh feed to purifying column	ethanol	14,335	7.2
		water	182,830	92.7
		fusel oils	140	0.1
17	Aldehyde and fusel oil columns feed to purifying column	ethanol	4,560	85.4
		water	765	14.3
		fusel oils	15	0.3
18	Purifying column overheads to aldehyde column	ethanol	1,015	82.9
		water	185	15.1
		aldehydes	25	2.0

(continued)

TABLE A-3. (continued)

<u>Stream</u>	<u>Origin & Destination</u>	<u>Component</u>	<u>Stream Composition</u>	
			<u>lb/hr</u>	<u>Wt %</u>
19	Purifying column fusel oil sidestream to fusel oil column	ethanol	1,880	76.1
		water	470	19.0
		fusel oil	120	4.9
20	Alcohol/water sidestream from purifying column to rectifier	ethanol	16,000	66.0
		water	8,220	34.0
		fusel oil	10	413(*)
21	Purifying column bottoms to wastewater treatment	water	174,720	100.0
22	Aldehyde column bottoms to column	ethanol	1,015	86.0
		water	160	13.6
		aldehydes	5	0.4
23	Aldehyde column overheads	aldehydes	20	44.4
		water	25	55.6
24	Fusel oil column overheads to purifying column	ethanol	3,545	85.2
		water	605	14.5
		fusel oil	10	0.3
25	Rectifier sidestream to fusel oil column	ethanol	1,665	89.5
		water	185	1.0
		fusel oil	10	0.5
26	Fusel oil column bottoms	fusel oil	120	70.0
		water	50	30.0
27	Rectifier overheads	ethanol	14,335	95.0
		water	750	5.0
28	Rectifier bottoms to wastewater treatment	water	7,285	100.0
29	Wastewater from purifying column and rectifier	water	2,655	100.0
30	Supernatant from centrifuge to cooker and/or evaporator	solids	4,780	3.0
		water	154,615	97.0
31	Centrifuge supernatant to evaporator	solids	3,645	3.0
		water	117,935	97.0
32	Centrifuge cake to dryer	solids	7,970	35.0
		water	14,795	65.0

(*) ppm

(continued)

TABLE A-3. (continued)

<u>Stream</u>	<u>Origin & Destination</u>	<u>Component</u>	<u>Stream Composition</u>	
			<u>lb/hr</u>	<u>Wt. %</u>
33	Evaporator condensate to wastewater treatment	water	114,290	100.0
34	Evaporator bottoms to dryer	solids	3,645	50.0
		water	3,645	50.0
35	Total dryer feed	solids	39,335	65.0
		water	21,180	35.0
36	Dryer recycle stream	solids	27,720	91.0
		water	2,740	9.0
37	Boiler flue gases to dryer	air	102,570	92.7
		water	8,080	7.3
38	Distillers' dried grains and solubles	solids	11,615	91.0
		water	1,150	9.0
39	Dryer off-gases to scrubber	air	102,570	80.2
		water	25,370	19.8
40	Scrubber off-gases to atmosphere	air	102,570	91.4
		water	9,640	8.6
41	Make-up water to scrubber	water	15,730	100.0
42	Spent scrubber liquor to wastewater treatment.	water	15,730	100.0

APPENDIX B

SUPPORTING DATA FOR SECTION 3

ENVIRONMENTAL REGULATIONS

TABLE B-1. CHARACTERIZATION OF THE EFFLUENTS FROM AN ALCOHOL FACILITY

<u>Stream</u>	<u>Quantity Generated</u>		<u>Total Solids</u>		<u>Suspended Solids</u>		<u>BOD</u>			<u>pH</u>
	<u>lb/day</u>	<u>gal/day</u>	<u>ppm</u>	<u>lb/day</u>	<u>ppm</u>	<u>lb/day</u>	<u>ppm</u>	<u>lb/day</u>	<u>% Total</u>	
Scrubber Blowdown	657,000	78,800	2,600	1,708	760	499	1,040	683	31	5.0
Cooling Tower Blowdown	5,904,000	709,000	800	4,723	14	83	30	177	8	8.0
Boiler Blowdown	144,000	17,300	100	14	5	1	0	0	0	7.0
Evaporator Condensate	1,084,000	130,100	130	141	12	13	650	705	32	3.9
Plant & Equipment Washes	768,000	92,200	1,050	806	400	307	650	499	23	6.0
Rectifier Water	81,720	9,810	240	20	40	3	1,250	102	5	5.0
Sewerage Infiltration	144,000	17,300	NDA		NDA		NDA			NDA
Sanitary Sewage	<u>96,000</u>	<u>11,500</u>	<u>750</u>	<u>72</u>	<u>200</u>	<u>19</u>	<u>200</u>	<u>19</u>	<u>1</u>	<u>NDA</u>
Total	8,880,000	1,066,000	843	7,484	104	925	246	2,185	100	

NOTES: NDA - No data available.

(continued)

TABLE B-1. (continued)

<u>SOLID WASTES</u>		<u>AIR EMISSIONS</u>	
<u>Stream</u>	<u>Quantity Generated lb/hr</u>	<u>Stream</u>	<u>Quantity Generated lb/hr</u>
Sludge (effluent from wastewater treatment)	100	Fermentation Vent	
Power Generation Fly Ash	814	CO ₂	14,000
Bottom Ash - Main Boiler	430	Hydrocarbons	trace
Collected Coal Dust	NDA	Main Boiler - Coal-Fired (123x10 ⁶ Btu/hr)	
Collected Grain Dust	NDA	Flue Gases (with no control applied)	148,600
Plant Wastes (trash, boxes, etc.)	NDA	CO ₂	25,500
		H ₂ O	6,600
		N ₂	105,200
		O ₂	9,800
		NO _x	86
		SO ₂	567
		Fly ash	798
		Unburned hydrocarbons	16
		Dryer Furnace - Oil-Fired (46x10 ⁶ Btu/hr)	
		Flue Gases - Scrubber Outlet:	235,500
		CO ₂	39,000
		H ₂ O	31,250
		N ₂	161,000
		O ₂	4,050
		SO ₂	13
		NO _x	5.5
		Particulates	0.7
		Fugitive Emissions	NDA

Notes: NDA - No data available.

TABLE B-2. SUMMARY OF NATIONAL AMBIENT
AIR QUALITY STANDARDS

<u>Pollutant</u>	<u>Averaging Time</u>	<u>Primary Standard</u>	<u>Secondary Standard</u>
Particulate Matter	Annual (Geometric Mean)	75 $\mu\text{g}/\text{m}^3$	60 $\mu\text{g}/\text{m}^3$
	24-Hour*	260 $\mu\text{g}/\text{m}^3$	150 $\mu\text{g}/\text{m}^3$
Sulfur Oxides	Annual (Arithmetic Mean)	80 $\mu\text{g}/\text{m}^3$	---
	24-Hour*	365 $\mu\text{g}/\text{m}^3$	---
	3-Hour*	---	1300 $\mu\text{g}/\text{m}^3$ (0.5 ppm)
CO	3-Hour*	10 mg/m^3 (9 ppm)	10 mg/m^3 (9 ppm)
	1-Hour*	40 mg/m^3 (35 ppm)	40 mg/m^3 (35 ppm)
NO ₂	Annual (Arithmetic Mean)	100 $\mu\text{g}/\text{m}^3$ (0.05 ppm)	100 $\mu\text{g}/\text{m}^3$ (0.05 ppm)
Photochemical Oxidants	1-Hour*	240 $\mu\text{g}/\text{m}^3$ (0.12 ppm)	240 $\mu\text{g}/\text{m}^3$ (0.12 ppm)
Hydrocarbons (Non-Methane)	3-Hour** (6 to 9 a.m.)	160 $\mu\text{g}/\text{m}^3$ (0.24 ppm)	160 $\mu\text{g}/\text{m}^3$ (0.24 ppm)

*The expected number of days per calendar year on which the ozone level exceeds the given level must be less than or equal to 1

**Not to be exceeded more than once per year.

TABLE B-3. AMBIENT AIR INCREMENTS

<u>Pollutant</u>	<u>Maximum Allowable Increase (Micrograms Per- Cubic Meter)</u>
<u>CLASS I</u>	
Particulate Matter:	
Annual Geometric Mean	5
24-hr Maximum	10
Sulfur Dioxide:	
Annual Arithmetic Mean	2
24-hr Maximum	5
3-hr Maximum	25
<u>CLASS II</u>	
Particulate Matter:	
Annual Geometric Mean	19
24-hr Maximum	37
Sulfur Dioxide:	
Annual Arithmetic Mean	20
24-hr Maximum	91
3-hr Maximum	512
<u>CLASS III</u>	
Particulate Matter:	
Annual Geometric Mean	37
24-hr Maximum	75
Sulfur Dioxide:	
Annual Arithmetic Mean	40
24-hr Maximum	182
3-hr Maximum	700

TABLE B-4. STATES' AIR REGULATIONS FOR FUEL BURNING EQUIPMENT.

State	% Opacity	Ringelmann Chart	New or Existing Source	Heat Input (10 ⁶ Btu/hr)	Particulate Emissions (lbs/10 ⁶ Btu)		Sulfur Dioxide Emissions (lbs/10 ⁶ Btu)		Nitrogen Dioxide Emissions (lbs/10 ⁶ Btu)	
					Coal	Oil	Coal	Oil	Coal	Oil
CO	20		All Sources	0.10	0.50 ¹					
				1.00	0.50					
				10.00	0.27					
				100.00	0.15					
				250.00	0.12					
				500.00	0.10					
			New Sources	<250.00			1.20	0.30		
				≥250.00			0.40	0.30		
IL ²	30		Existing CMA ³	any	0.10	0.10			1.00 ⁴	
			Existing ⁵	≤10.00 ⁶	1.00	0.10			1.00 ⁴	
				100.00	0.19	0.10			1.00 ⁴	
				≥250.00	0.10	0.10			1.00 ⁴	
			New	any	0.10	0.10				
				≤250.00			1.30	1.00 ⁴		
			Existing-Met	Any			1.30			
			Existing	Any			6.00			
			New	≥250.00					0.70	0.30
			Existing ⁵	≥250.00					0.90	0.30

¹ Interpolation of the data for fuel burning equipment shall be by use of the following equations

$$\begin{aligned}
 PE &= 0.5 & \text{for } FI \leq 1.0 \\
 PE &= 0.5 (FI)^{-0.26} & \text{for } 1.0 < FI \leq 500.0 \\
 PE &= 0.1 & \text{for } 500.0 \leq FI
 \end{aligned}$$

where: PE = Particulate emissions in pounds per million Btu heat input.
FI = Fuel input in million Btu per hour.

² Emission standard for CO is 200 ppm basis 50 percent excess air for all sources with heat input > 10.00x10⁶ Btu/hr.

³ CMA - Located in the Chicago major metropolitan area.

⁴ This represents the amount of emissions allowable when residual fuel oil is burned. If distillate fuel oil is used, SO₂ emissions cannot exceed 0.3 lbs SO₂ per million Btu of heat input.

⁵ Located outside the Chicago major metropolitan area.

⁶ Interpolation of the data for heat input values greater than 10 million Btu per hour but smaller than 250 million Btu per hour shall be calculated by the following equation:

$$S_s = \frac{5.18}{(H_s)^{0.715}}$$

where: S_s = allowable emission standard in pounds per million Btu of actual heat input.
H_s = Actual heat input, million Btu per hour.

⁷ SO₂ emission standards for fuel combustion sources located in the Chicago, St. Louis, and Peoria major metropolitan areas (MMA), and any other MMA which has an annual arithmetic average sulfur dioxide level greater than 45 ug/m³

⁸ Nitrogen dioxide emission standards for fuel combustion sources located in the Chicago and St. Louis MMA.

(continued)

TABLE B-4. (continued)

State	Opacity	Ringelmann Chart	New or Existing Source	Heat Input (10 ⁶ Btu/hr)	Particulate Emissions (lb/10 ⁶ Btu)		Sulfur Dioxide Emissions (lb/10 ⁶ Btu)		Nitrogen Dioxide Emissions (lb/10 ⁶ Btu)	
					Coal	Oil	Coal	Oil	Coal	Oil
IA	40	2	Existing SMSA ⁹	Any	0.60					
			Existing	Any	0.30		6.00 ¹⁰	2.50		
			New	≤150.00	0.60		6.00	2.50		
				150.00-250.00	0.20		6.00	2.50		
				>250.00	0.10		1.20	1.20		
KS	20 ¹¹		All Sources	≤10.00	0.60 ¹²					
				50.00	0.41					
				100.00	0.35					
				250.00	0.28		1.50	1.50	0.90	0.30
				500.00	0.24		1.50	1.50	0.90	0.30
VB	20	1	All Sources	≤10.00 ¹²	0.60					
				50.00	0.41					
				100.00	0.35					
				250.00	0.28					
			All Sources	Any			2.50			

⁹Inside any standard metropolitan statistical area.

¹⁰Four sources located in the following counties: Black Hawk, Clinton, Des Moines, Dubuque, Jackson, Linn, Louisa, Muscatine and Scott.

¹¹The 20 percent opacity regulation is for new equipment; the percent opacity limitation for existing equipment is 40 percent.

¹²The allowable particulate emission rate for equipment having intermediate input between 10 million Btu and 10,000 million Btu may be determined by the formula:

$$A = \frac{1.026}{I^{0.233}}$$

where: A = The allowable particulate emission rate in lb/hr/10⁶ Btu.
I = The total heat input in 10⁶ Btu/hr.

(continued)

TABLE B-4. (continued)

State	% Opacity	Ringelmann Chart	New or Existing Source	Heat Input (10 ⁶ Btu/hr)	Particulate Emissions (lbs/10 ⁶ Btu)		Sulfur Dioxide Emissions (lbs/10 ⁶ Btu)		Nitrogen Dioxide Emissions (lbs/10 ⁶ Btu)	
					Coal	Oil	Coal	Oil	Coal	Oil
MO	20	1	Existing- Met ¹³	<10.00 ¹⁴	0.60					
				50.00	0.40					
				100.00	0.33					
				250.00	0.26					
			New-Met ¹³	<10.00 ¹⁵	0.40					
				50.00	0.24					
				100.00	0.19					
				250.00	0.15					
			All-Kmet ¹⁶	>0.35				8.00		
			All-Slmet ¹⁷	<2000.00				2.30		
			Existing	≤10.00 ¹⁸	0.60					
				50.00	0.46					
				100.00	0.40					
				250.00	0.28					
			New	≤10.00 ¹⁹	0.60					
				50.00	0.348					
				100.00	0.275					
				250.00	0.20					
			All Sources	>0.35				8.00		

¹³Fuel burning equipment emission standards in the Kansas City and St. Louis metropolitan areas.

¹⁴The allowable particulate emission rates for heat inputs between 10 million Btu and 5,000 million Btu per hour are determined by the following equation:

$$E = 1.09 (Q)^{-0.159}$$

where: E = Maximum allowable particulate emission rate in pounds/million Btu of heat input.

Q = heat input in millions of Btu per hour.

¹⁵The allowable particulate emission rates for heat inputs between 10 million and 1,000 million Btu per hour are determined by the following equation:

$$E = 0.80 (Q)^{-0.181}$$

where: E and Q are the same as above.

¹⁶Sulfur dioxide emission limitations for the Kansas City metropolitan area.

¹⁷Sulfur dioxide emission limitations for the St. Louis metropolitan area.

¹⁸The allowable particulate emission rates for heat inputs between 10 million and 10,000 million Btu per hour are determined by the following equation:

$$\log Y = -0.23299 \log X + 1.4091$$

where: Y = Allowable emission rates in pounds/million Btu of heat input.

X = Heat input in Btu per hour.

¹⁹The allowable particulate emission rates for heat inputs between 10 million and 2,000 million Btu per hour are determined by the following equation:

$$\log Y = -0.3382 \log X + 2.1454$$

where: Y and X are the same as above.

TABLE B-5. PARTICULATE EMISSION STANDARDS FOR
EMISSION SOURCES

<u>State</u>	<u>Particulate Emission Standards</u>	
CO	Process Weight Rate (lbs/hr)	Emission Rate (lbs/hr)
	50	0.03
	100	0.55
	500	1.53
	1,000	2.25
	5,000	6.34
	10,000	9.73
	20,000	14.99
	60,000	29.60
	80,000	31.19
	120,000	33.28
	160,000	34.85
	200,000	36.11
	400,000	40.35
	1,000,000	46.72

Interpolation of the data in this table for the process weight rates up to 60,000 lbs/hr shall be by use of the equation:

$$E = 3.59 P^{0.62} \quad P \leq 30 \text{ tons/hr}$$

and interpolation and extrapolation of the data for process weight rates in excess of 60,000 lbs/hr shall be by use of the equation:

$$E = 17.31 P^{0.16} \quad 30 \text{ tons/hr} \leq P$$

where: E = Emissions in pounds per hour.

P = Process weight rate in tons per hour.

(continued)

TABLE B-5. (continued)

State	<u>Particulate Emission Standards</u>			
	Process Weight Rate (lbs/hr)	Emission Rate (lbs/hr)	Process Weight Rate (lbs/hr)	Emission Rate (lbs/hr)
IA ⁴	100	0.55	16,000	16.5
	200	0.88	18,000	17.9
	400	1.40	20,000	19.2
	600	1.83	30,000	25.2
	800	2.22	40,000	30.5
	1,000	2.58	50,000	35.4
	1,500	3.38	60,000	40.0
	2,000	4.10	70,000	41.3
	2,500	4.76	80,000	42.5
	3,000	5.38	90,000	43.6
	3,500	5.96	100,000	44.6
	4,000	6.52	120,000	46.3
	5,000	7.58	140,000	47.3
	6,000	8.56	160,000	49.0
	7,000	9.49	200,000	51.2
	8,000	10.4	1,000,000	69.0
	9,000	11.2	2,000,000	77.6
	10,000	12.0	6,000,000	92.7

Interpolation of the data in this table for process weight rates up to 60,000 lbs/hr shall be accomplished by the use of the equation:

$$E = 4.10 P^{0.67}$$

and interpolation and extrapolation of the data for process weight rates in excess of 60,000 lbs/hr shall be accomplished by the use of the equation:

$$E = 55.0 P^{0.11} - 40$$

where: E = Rate of emission in lbs/hr
P = Process weight in tons/hr

⁴Does not apply to grain handling; also, if the director determines that a process complying with the emission standards in this table is causing or will cause air pollution in a specific area of the state, an emission standard of 0.1 grain/SCF of exhaust gas may be imposed.

(continued)

TABLE B-5. (continued)

StateParticulate Emission StandardsIL¹

Process Weight Rate (lbs/hr)	Emission Rate (lbs/hr)		Process Weight Rate (lbs/hr)	Emission Rate (lbs/hr)	
	Existing Sources ²	New Sources ³		Existing Sources ²	New Sources ³
100	0.55	0.55	50,000	35.40	14.00
200	0.87	0.77	60,000	40.00	15.60
400	1.40	1.10	70,000	41.30	17.00
600	1.83	1.35	80,000	42.50	18.20
800	2.22	1.58	90,000	43.60	19.20
1,000	2.58	1.75	100,000	44.60	20.50
1,500	3.38	2.40	200,000	51.20	29.50
2,000	4.10	2.60	300,000	55.40	37.00
4,000	6.52	3.70	400,000	53.60	43.00
6,000	8.56	4.60	500,000	61.00	48.50
8,000	10.40	5.35	600,000	63.10	53.00
10,000	12.00	6.00	700,000	64.90	58.00
20,000	19.20	8.70	800,000	66.20	62.00
30,000	25.20	10.80	900,000	67.70	66.00
40,000	30.40	12.50	1,000,000	69.00	67.00

¹Does not apply to grain handling and drying or corn wet milling.²Interpolated and extrapolated values of the data in this table for process weight rates up to 30 tons per hour shall be determined by using the equation:

$$E = 4.10 p^{0.67}$$

where: E = Allowable emission rate in lbs/hr

P = Process weight rate in tons/hr

and interpolated and extrapolated values of the data for process weight rates in excess of 30 tons per hour shall be determined by using the equation:

$$E = 55.0 p^{0.11} - 40$$

³Interpolated and extrapolated (up to process weight rates of 450 tons per hour) values of the data in this table shall be determined by using the equation:

$$E = 2.54 p^{0.534}$$

and interpolated and extrapolated values of the data of this table for process weight greater or equal to 450 tons per hour shall be determined using the equation:

$$E = 24.8 p^{0.16}$$

(continued)

TABLE B-5. (continued)

State	<u>Particulate Emission Standards</u>			
	Process Weight Rate (lbs/hr)	Emission Rate (lbs/hr)	Process Weight Rate (lbs/hr)	Emission Rate (lbs/hr)
KS	100	0.551	16,000	16.5
	200	0.877	18,000	17.9
	400	1.40	20,000	19.2
	600	1.83	30,000	25.2
	800	2.22	40,000	30.5
	1,000	2.58	50,000	35.4
	1,500	3.38	60,000	40.0
	2,000	4.10	70,000	41.3
	2,500	4.75	80,000	42.5
	3,000	5.38	90,000	43.6
	3,500	5.96	100,000	44.6
	4,000	6.52	120,000	46.3
	5,000	7.58	140,000	47.8
	6,000	8.56	160,000	49.0
	7,000	9.49	200,000	51.2
	8,000	10.4	1,000,000	69.0
	9,000	11.2	2,000,000	77.6
	10,000	12.0	6,000,000	92.7
	12,000	13.6		

Interpolation of the data in this table for other process weights shall be accomplished by use of the following equations:

$$\text{Process weights} < 30 \text{ ton/hr, } E = 4.1 P^{0.67}$$

$$\text{Process weights} > 30 \text{ ton/hr, } E = 55 P^{0.11} - 40$$

where: E = Rate of emissions in lbs/hr
P = Process weight in ton/hr

(continued)

TABLE B-5. (continued)

State MO ⁵	<u>Particulate Emission Standards</u>			
	<u>Process Weight Rate (lbs/hr)</u>	<u>Emission Rate (lbs/hr)</u>	<u>Process Weight Rate (lbs/hr)</u>	<u>Emission Rate (lbs/hr)</u>
	2,000	4.10	30,000	25.2
	2,500	4.76	40,000	30.5
	3,000	5.38	50,000	35.4
	3,500	5.96	60,000	40.0
	4,000	6.52	70,000	41.3
	5,000	7.58	80,000	42.5
	6,000	8.56	90,000	43.6
	7,000	9.49	100,000	44.6
	8,000	10.4	120,000	46.3
	9,000	11.2	140,000	47.8
	10,000	12.0	160,000	49.0
	12,000	13.6	200,000	51.2
	16,000	16.5	1,000,000	69.0
	18,000	17.9	2,000,000	77.6
	20,000	19.2	6,000,000	92.7

Interpolation of the data in these two tables for process weight rates up to 60,000 lbs/hr shall be accomplished by use of the equation:

$$E = 4.10 P^{0.67}$$

and interpolation and extrapolation of the data for process weight rates in excess of 60,000 lbs/hr shall be accomplished by use of the equation:

$$E = 55.0 P^{0.11} - 40$$

where: E = Rate of emission in lbs/hr
P = Process weight rate in tons/hr

⁵Does not apply to corn wet milling drying processes; these processes must be equipped with control equipment to remove not less than 99.5 percent by weight of all particulate matter in the dryer discharge gases.

(continued)

TABLE B-5. (continued)

State	<u>Particulate Emission Standards</u>			
	Process Weight Rate (lbs/hr)	Emission Rate (lbs/hr)	Process Weight Rate (lbs/hr)	Emission Rate (lbs/hr)
NB	100	0.551	16,000	16.5
	200	0.877	18,000	17.9
	400	1.40	20,000	19.2
	600	1.83	30,000	25.2
	800	2.22	40,000	30.5
	1,000	2.58	50,000	35.4
	1,500	3.38	60,000	40.0
	2,000	4.10	70,000	41.3
	2,500	4.76	80,000	42.5
	3,000	5.38	90,000	43.6
	3,500	5.96	100,000	44.6
	4,000	6.52	120,000	46.3
	5,000	7.58	140,000	47.8
	6,000	8.56	160,000	49.0
	7,000	9.49	200,000	51.2
	8,000	10.4	1,000,000	69.0
	9,000	11.2	2,000,000	77.6
	10,000	12.0	6,000,000	92.7
	12,000	13.6		

Interpolation of the data in this table for process weight rates up to 60,000 lbs/hr shall be accomplished by use of the equation:

$$E = 4.10 P^{0.67}$$

and interpolation and extrapolation of the data for process weight rates in excess of 60,000 lbs/hr shall be accomplished by use of the equation:

$$E = 55.0 P^{0.11} - 40$$

where: E = Rate of emission in lbs/hr
P = Process weight rate in tons/hr

If two or more units discharge into a single stack, the allowable emission rate will be determined by the sum of all process weights discharging into the single stack.

TABLE B-6. STATE AIR REGULATIONS FOR FUGITIVE DUST AND
GROUND LEVEL PARTICULATE CONCENTRATIONS

<u>State</u>	<u>Regulations</u>
CO	<p>No person shall emit or cause to be emitted from any source of fugitive dust whatsoever, any particulate matter which:</p> <ul style="list-style-type: none"> • at or from the source of said emission is of such a shade or density on the property of emission origination so as to obscure an observer's vision to a degree in excess of 20 percent opacity, or • is visibly transported off the property of emission origination and remains visible to an observer positioned off said property when sighting along a line which does not cross the property of emission origination.
IL	<p>No person shall cause or allow the emission of fugitive particulate matter from any process, including any material handling or storage activity, that is visible by an observer looking generally toward the zenith at a point beyond the property line of the emission source.</p> <p>No person shall cause or allow the emission of fugitive particulate matter from any process, including any material handling or storage activity, in such a manner that the presence of such particulate matter shown to be larger than forty (40) microns (mean diameter) in size exists beyond the property line of the emission source.</p>
IA	<p>No person shall allow, cause or permit any materials to be handled, transported or stored: or a building, its appurtenances or a construction haul road to be used, constructed, altered, repaired or demolished, with the exception of farming operations or dust generated by ordinary travel on unpaved public roads, without taking reasonable precautions to prevent particulate matter in quantities sufficient to create a nuisance, as defined in Section 657.1 of the Code, from becoming airborne.</p>

(continued)

TABLE B-6. (continued)

State

Regulations

KS

The provisions of other emission control regulations, notwithstanding, no person shall cause or permit the handling, transport-- or storage of any materials or any other use of a premise in a manner which has been demonstrated to allow sufficient quantities of particulate matter to become airborne to cause a ground level particulate concentration at the property line equal to or exceeding 2.0 milligrams per cubic meter above background concentrations of any time period aggregating more than 20 minutes during any hour.

MO

No person may cause or permit the handling or transporting or storage of any material in a manner which allows or may allow particulate matter to become airborne in such quantities and concentrations that it remains visible in the ambient air beyond the premises where it originates or that its presence may be found beyond the premises where it originates, it has particulate matter shown to be larger than forty (40) microns in size and which results in at least one complaint being filed with the executive secretary.

No person shall cause, suffer, or permit the emission of any particulate matter so as to cause concentrations of particulate matter at any inhabited place to exceed any one of the following:¹

<u>Pollutant</u>	<u>Concentration</u>	<u>Remarks</u>
Suspended Particulates	80 micrograms per cubic meter	6-month geometric mean
(High volume sampler)	200 micrograms per cubic meter	2-hour arithmetic averages for not less than five two-hour sampling periods within any one year. No more than 3 samples shall be taken during any 24-hour period.
Soiling Index	0.4 COH/1000 lineal feet	6-month geometric mean
(AISI paper tape sampler)	1.0 COH/1000 lineal feet	8-hour arithmetic average

¹This regulation shall apply throughout the state of Missouri except in the City of St. Louis, and St. Charles, St. Louis, Jefferson, Franklin, Clay, Cass, Buchanan, Ray, Jackson, Platte, and Greene Counties.

(continued)

TABLE B-6. (continued)

<u>State</u>	<u>Regulations</u>
NB	Handling, Transporting, Storing. No person may cause or permit the handling or transporting or storage of any material in a manner which may allow particulate matter to become airborne in such quantities and concentrations that it remains visible in the ambient air beyond the premises where it originates.

TABLE B-7. STATES' AMBIENT AIR QUALITY STANDARDS¹

State	Sulfur Dioxide		Carbon Monoxide		Nitrogen Dioxide	Photochemical Oxidants	Nonmethane Hydrocarbons	Particulates	
	Primary µg/m ³	Secondary µg/m ³	Primary mg/m ³	Secondary mg/m ³	Annual Arithmetic Mean (AAM) µg/m ³			Primary µg/m ³	Secondary µg/m ³
CO	Category I II III		9 ppm-8 hr		0.05 ppm	0.08 ppm	0.24 ppm	Nondesignated areas 150-24 hr Designated areas 180-24 hr	
	AAM	2 10 15							
	24 hr max	5 50 100							
	3 hr max	25 300 700							
IL	0.03 ppm- AAM 0.14 ppm- 24 hr	0.50 ppm- 3 hr	9 ppm-8 hr 35 ppm-1 hr		0.05 ppm-AAM	0.08 ppm	0.24 ppm	75-ACM 260-24 hr	60-ACM 150-24 hr
IA	80-AAM 365-24 hr	1300-3 hr	9 ppm-8 hr 35 ppm-1 hr		100	160	160	75-ACM 260-24 hr	60-ACM 150-24 hr
MO	53-AAM 365-24 hr 1300-3 hr	53-AAM 365-24 hr 1300-3 hr	9 ppm-8 hr 35 ppm-1 hr		100	160		60-ACM 150-24 hr	60-ACM 150-24 hr
NB	80-AAM 365-24 hr	1300-3 hr	9 ppm-8 hr 35 ppm-1 hr		100	160	160	75-ACM 260-24 hr	60-ACM 150-24 hr

¹Kansas has no Ambient Air Quality Standards for SO₂, CO, NO_x, photochemical oxidants, nonmethane hydrocarbons, or particulates.

TABLE B-8. ANALYSIS OF BEER STILLAGE

pH	4.1
Total Solids, ppm	47,345
Suspended Solids, ppm	24,800
BOD, ppm	34,100
Volatile Solids, ppm	43,300
Total Nitrogen, wt%	0.045
Calcium	Trace
Magnesium (as MgO), ppm	88
Iron, ppm	3
Copper, ppm	1

Sources: 14 and 30.