

Environmental Sanitation Reviews

No. 16, September 1985



Environmental Sanitation Information Center Asian Institute of Technology P.O. Box 2754 Bangkok 10501, Thailand

ENVIRONMENTAL SANITATION INFORMATION CENTER

Dr. David Donaldson	Regional Advisor in Water Supply and Sanitation, Pan American Health Organization, Washington, D.C., U.S.A.
Dr. Mary Elmendorf	Consulting Anthropologist, Sarasota, Florida, U.S.A.
Dr. Richard Feachem	Head, Department of Tropical Hygiene, London School of Hygiene and Tropical Medicine, London, U.K.
Prof. Ivanildo Hespanhol	Professor of Sanitary Engineering, Dept9. de Engenharia Hidráulica e Sanitária, Univer- sity of São Paulo, São Paulo, Brazil.
John Kalbermatten*	Senior Advisor, Energy, Water and Tele-communications Department, The World Bank, Washington, D.C., U.S.A.
Prof. Raymond C, Loehr	H.M. Alharthy Centennial Professor, Civil Engineering Department, University of Texas, U.S.A.
Dr. Harvey F. Ludwig	Consulting Engineer, SEATEC International, Bangkok, Thailand.
Prof. J. Matsumoto	Faculty of Engineering, Department of Civil Engineering, Tohoku University, Sendai, Japan.
Prof. T. Matsuo	Department of Urban and Sanitary Engineering, The University of Tokyo, Tokyo, Japan.
Dr. Michael G. McGarry	Vice-President, Cowater International, Ottawa, Ontario, Canada.
Prof. Daniel A. Okun	Kenan Professor of Environmental Engineering/Emeritus, School of Public Health, University of North Carolina, Chapel Hill, North Carolina, U.S.A.
John Pickford	WEDC Group Leader, University of Technology Loughborough, Leics, U.K.
Witold Rybczynski	Associate Professor, School of Architecture, McGill University, Montreal, Quebec, Canada.
Prof. Hillel Shuval	Director, Environmental Health Lab., Hebrew University, Haddusah Medical School, Jerusalem, Israel,
Dr. B.B. Sundaresan	Director, National Environmental Engineering Research Institute (NEERI), Nagpur, India.
Prof. N.C. Thanh	Professor of Environmental Engineering, Department of Environment and Water Re- sources, CEFIGRE, Valbonne, Cedex, France.
Prof. T. Viraraghavan	Faculty of Engineering, University of Regina, Regina, Saskatchewan, Canada.
*Advisory role only.	

 Ş	T	A	١F	F	
 2	l	F	ł	r	

	Mr. H.A. Vespry (Canada)	Director
	Dr. K. Hanaki (Japan)	Technical Advisor
	Ms. Sein Mya (Burma)	Senior Information Scientist
Ì	Ms. Helen B. Cruda (Philippines)	Information Scientist
	Ms. Penchun I. (Thailand)	Secretary
1	Ms. Orawan K. (Thailand)	Secretary
1		

-ACKNOWLEDGEMENTS-

ENSIC gratefully acknowledges the financial support it receives from the International Development Research Centre (IDRC) of Canada; the Government of Australia; the Canadian International Development Agency (CIDA) and the Asian Institute of Technology (AIT). It is also indebted to the AIT Regional Computer Center (RCC) for the use of its computer facilities.

MANAGEMENT OF ETHANOL PRODUCTION WASTES:

A REVIEW OF AVAILABLE INFORMATION

by

Raymond C. Loehr

H.M. Alharthy Centennial Professor, Civil Engineering Department, University of Texas, Austin, U.S.A.

Manotosh Sengupta

Research Scientist, Central Board for the Prevention and Control of Water Pollution, Department of Environment, New Delhi, India

6158 340 85mA

H.F. Ludwig (Reviewer)

Editorial Board Member, ENSIC & Consulting Engineer, SEATEC International, Bangkok

> ENVIRONMENTAL SANITATION INFORMATION CENTER BANGKOK, THAILAND SEPTEMBER, 1985

JOIN ENSIC

You will receive. . .

Environmental Sanitation Abstracts (3 issues per year) Environmental Sanitation Reviews (3 issues per year) A Quarterly Newsletter - ENFO

The ENSIC publications will be made available through subscribed membership of the Center without any extra charge for the publications.

MEMBERSHIP FEES	US\$	US\$
Members from	Individual	Institutional
Developed Countries ¹	45	85
Developing Countries ²	25	45
AIT Alumni, All Countries	(15% discount) (include air-mailing of E	- ENFO and surface-mailing
	of all other ENSIC pub	
¹ Europe, North America, Australia, Japa	an, New Zealand, Middle East.	
² All other countries.		

To get all your copies by air-mailing add:

Asia	12
Africa, Europe, Oceania	19
Americas	27

Payment can be made by bank draft, cashier's cheque or UNESCO coupons, payable to:

"Environmental Sanitation Information Center"

REFERENCE SERVICE

ENSIC members can use the Center's References at the rate of US\$ 3.00/hour.

DOCUMENT SUPPLY

*Including su	face mailing charge	0.20/page	(for Developed Countries)
		0.15/page	(for Developing Countries)
*Air-mailing e	extra charge:		
	Asia	0.05/page	
	Africa, Europe, Oceania	0.08/page	
	Americas	0.10/page	
Microfiches (60 pag	jes per fiche)	3.00/fiche	(Air-mailed)
Binding			

* A service fee of US\$ 5.00 is charged for each AIT publication (Theses, Reports, etc.)

Contents

I	GLOBAL INTEREST		
II	ETHANOL PRODUCTION PROCESSES	2	2
	2.1 Background	:	2
	2.2 Synthetic Method	2	2
	2.3 Fermentation	3	3
	2.3.1 General	5	3
	2.3.2 Sugar Containing Raw M	aterial - Molasses 4	1
	2.3.3 Starch Containing Raw M	iaterial – Corn 5	5
	2.4 Support Facilities	2	9
111	ETHANOL PRODUCTION WASTE CHAR.	ACTERISTICS 10)
	3.1 Wastewater	10)
	3.2 Solid Waste	13	3
	3.3 Environmental Impact of Ethanol	Wastes 13	3
	3.4 Detailed Characteristics	14	ł
IV	TREATMENT AND DISPOSAL OF ETHA	NOL WASTE 23	3
	4.1 In-Plant Source Control	23	3
	4.2 End of Pipe Control Methods	20	ô
	4.3 Solid Waste Treatment and Dispo	sal 37	7
v	RECOVERY AND REUSE	39	9
	5.1 Production of Biomass and Bioch	emicals 39	9
	5.2 Stillage as an Animal Fed	31	9
VI	SUMMARY AND CONCLUSIONS	40	0
	ACKNOWLEDGEMENTS	41	Ł
	REFERENCES	4:	2
	APPENDIX	46	ô

Management of ethanol production wastes: A review of available information

by

Raymond C. Loehr Manotosh Sengupta

I. GLOBAL INTEREST

Petroleum-based fuels have been a desirable energy source because of their ease of handling and relatively low cost. As the cost of such fuels increases, alternative fuels become of interest. The fact that the production, distribution and economics of petroleum-based fuels are subject to political and other interruptions also causes interest in other fuels. Production of biomass alcohol is one of the available options.

Appreciable use of alcohol fuels occurs in many countries. Brazil is reported to have reduced its consumption of imported petroleum from 83% in 1979 to 68% in 1982 (NRC, 1983). The production and use of ethanol was a factor that caused this decrease.

Worldwide, over 40 nations have blended alcohol (usually ethanol) into their fuel base. In countries such as Czechoslovakia, France, Germany, and Sweden, the use of 10 to 25% alcohol blends has been mandatory. Prior to World War II, more than 4 million European automobiles used alcohol fuel. World War II enhanced the use of alcohol as a fuel source, particularly in Europe. By 1944 the U.S. was producing close to 600 million gallons of alcohol. After the war and through the 1960s, alcohol was rarely used for automotive purposes. However, in the 1970s rising energy prices renewed interest in the production of ethanol for fuel.

While progress has been achieved in the technology of ethanol production, relatively less emphasis has been given to the environmental effects of the wastes obtained during production. These wastes require economic and environmentally sound management. This article discusses:

- (a) ethanol production from different biomass feedstocks,
- (b) waste sources and characteristics, and
- (c) feasible treatment and management alternatives.

The information in this article results from a detailed review of the published literature. Due to the difficulty of obtaining data on waste management at ethanol production plants in developing countries, the article relies primarily on information from the United States and Europe.

All units of measurement and cost figures are reported as in the literature from which they were derived, and no attempt has been made to convert them into a uniform base. A table for metric unit conversion is given in Appendix.

II. ETHANOL PRODUCTION PROCESSES

2.1 Background

One of man's first biochemical activities was to ferment grains and fruit juices. The resultant dilute ethanol was used for human consumption and medicinal purposes. More recently, distillation processes increased the ethanol concentration and produced almost pure ethanol. The chemical and physical characteristics of ethanol are presented in Table 2.1. Both synthetic and fermentation methods can be used to produce ethanol.

Characteristics	
Chemical:	
Formula	CH₃CH₂OH
Molecular weight	46.1
% Carbon (by weight)	52.1
% Hydrogen (by weight)	13.1
% Oxygen (by weight)	4.7.
C/H ratio	4.0
Physical:	
Specific gravity	0.8
Liquid density (lb/ft ³)	49.3
Boiling point (°F)	173
Freezing point (°F)	-173
Solubility in water	Infinite
Surface tension (dyne/cm ²)	23
Dielectric constant	24.3
Viscosity at 68°F (cp)	1.17
Thermal:	
Lower heating value (Btu/gal.)	73,560
Higher heating value (Btu/gal.)	84,400
Heat of vaporization (Btu/gal.)	3,378
Specific heat (Btu/lb - °F)	0.60
Autoignition temperature (°F)	685
Flash point (°F)	70

Table 2.1. Summary of ethanol characteristics (SERI, 1980).

2.2 Synthetic Methods

Most industrial grade ethanol is produced by synthetic methods. The primary synthetic process is the sulphuric acid process, as given in eq. (1).

chemical sulphuric natural gas ----- C₂H₄ ----- CH₃CH₂OH ...(1) processing (ethylene) acid plus (ethanol) catalyst

2.3 Fermentation

2.3.1 General

Sugar, starch and cellulosic containing biomass can be fermented to ethanol. Potential raw materials are listed in Table 2.2. The production of alcohol by fermentation of biomass follows the general steps indicated in Fig. 2.1.

Ethanol from sugar based raw material is produced worldwide. The coversion of starches to ethanol is a common practice, especially in the tropics. Commercially viable methods for conversion of cellulose to ethanol are not yet available (ANL, 1980).

Plants	Typical crop vield	Potential ethanol yield		
i idiita	(ton/ha/yr*)	(liters/ton)	(liters/ha/yr)	
Sugar Based				
Sugar cane* *	50 — 90	70 90	3,500 - 8,000	
Sugar beet (Beta vulgaris)	15 — 50	90	1,350 - 5,500	
Sweet sorghum (Sorghum bicolor)	45 – 80	60 - 80	1,750 - 5,300	
Nipa palm*** (Nipa fouticans)		_	2,300 - 8,000	
Cultivated palm	_	-	8,000	
Starch based				
Cassava (Manihot esculenta)	10 - 65	170	1,700 - 11,050	
Sweet potato (Ipomoea batatas)	8 - 50	167	1,336 - 8,350	
Irish potato (Solanum tuberosum) Sago palm (Metroxylon sagu and	10 – 25	110	1,110 - 2,750	
Metroxylon rumphii)	15 boles/ha/yr	_	1,350	
Cereal Grains				
Wheat (Triticum aestivum)	1.5 2.1	340	510 - 714	
Maize (Zea mays)	1.7 – 5.4	360	600 - 1,944	
Rice (Oryza sativa)	2.5 – 5.0	430	1,075 - 2,150	
Barley (Hordeum vulgare)	1.2 – 2.5	250	300 - 625	

Table 2.2. Potential raw materials for alcohol production (NRC Report, 1983)

* Metric 'ton'.

** About 1 ton sugar produces 300 kg molasses and 245 liters alcohol.

*** A potential biomass for production of alcohol in swampy saline tracts of Southeast Asia and the Pacific.

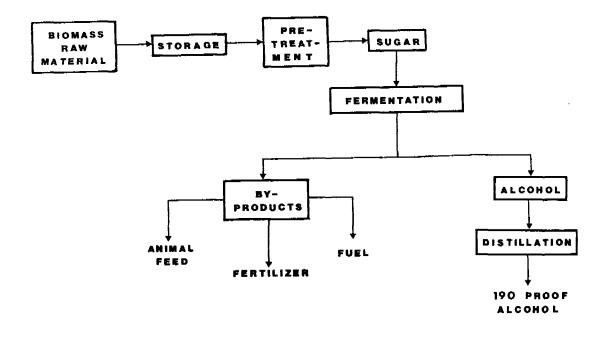


Fig. 2.1 Production of alcohol from biomass

2.3.2 Sugar Containing Raw Material - Molasses

Process Description

The general process steps involved in the production of ethanol from molasses are shown in Fig. 2.2. The molasses are diluted to about a 12-20% sugar content which is then acidified with sulfuric acid and nitrogen and phosphorus are added. In a typical fermentation, a batch is inoculated with yeast and allowed to ferment for 12-60 hours at 30°C. About 7 to 10% ethanol results in the final product or "beer."

The ethanol is separated in a two to three column distillation system to concentrate the ethanol to about 95%. Subsequent azeotropic distillation is used when absolute alcohol is required. The first distillation column is essentially a stripping column that removes most of the water along with other constituents from the ethanol, which then undergoes concentration and rectification in additional distillation columns (Fig. 2.2). The material removed in the first column contains the principle components of distillery wastewater and is generally known as stillage. Other terms used for this waste are "slops," and "vinasse." If the yeasts are not separated for recycle or for their food value, the stillage will also contain spent yeast cells.

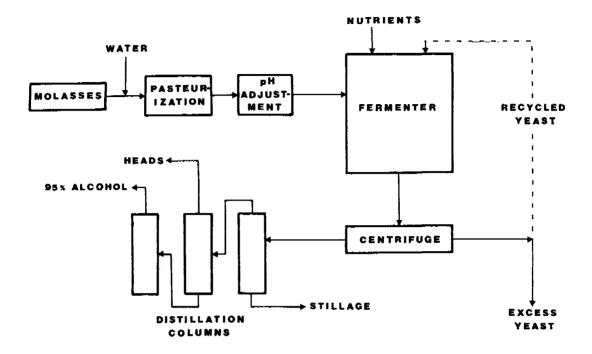


Fig. 2.2 Processes involved in the production of alcohol from molasses

Waste Generation

In a molasses-based ethanol production plant, both solid and liquid wastes are produced. The solid wastes, such as bottom ash and particulate matter, are generated primarily from combustion processes used to supply steam and electricity to the plant. The wastewater results from cleaning the molasses tanks, and from stillage, fermenter and condenser cooling water, fermenter wastewater and floor washings. The characteriscits of these wastes are described in Section 3.

2.3.3 Starch Containing Raw Material - Corn

General

Ethanol may be manufactured from any carbohydrate source such as corn or other grains. The production of 190-proof (95%) ethanol and anhydrous alcohol from corn follows steps similar to those involved in the production of beverage alcohol from grains. The general flowsheet of ethanol production from corn is shown in Fig. 2.3.

Enzymatic Hydrolysis (ANL, 1980)

Malt-germinated barley is a source of the enzymes diastase and maltase. The grain starch is hydrolyzed by these enzymes into simple sugars (saccharification). As there can be problems associated with the production and use of malt-derived enzymes,

.

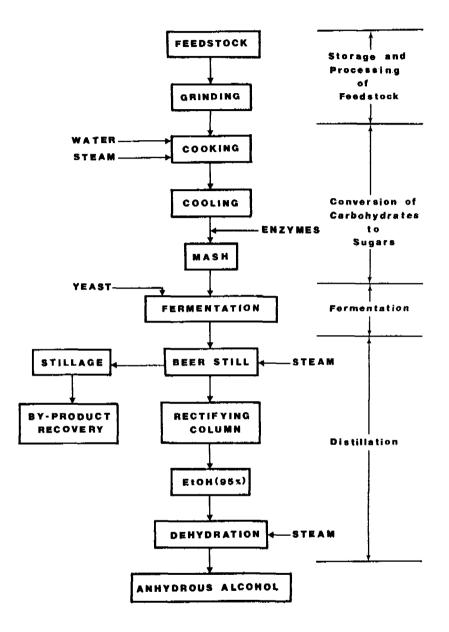


Fig. 2.3 Major steps involved in the production of alcohol from corn

commercial enzymes produced by fungal and bacterial processes (e.g., alpha- and gluco-amylase) are used for the enzymatic hydrolysis. In the saccharitication process, the temperature is kept at about 90° C.

These enzymes hydrolyze the starch molecule in a structurally specified manner resulting in the production of dextrose until the enzyme reaches a branch in the starch molecule, whereupon a dissaccharide is produced. Under the best conditions, a dextrose yield of about 98.5% can be achieved. The general reactions involved in this process are shown of Fig. 2.4.

The relatively slow rate of the enzyme reaction can be increased by utilizing a small quantity of acid, which reduces viscosity but has little other impact on the dextrose yield. A dilute acid solution (approx. 0.1 N) is used and is followed by the addition of the enzymes.

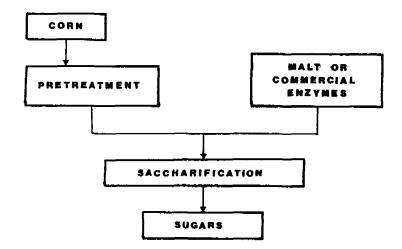


Fig. 2.4 Enxymatic hydrolysis of corn

Acid Hydrolysis

The starch also can be hydrolyzed by mineral organic acids, resulting in saccharides of variable polymerization and products of degradation. Acid-catalyzed hydrolysis can produce about 85% fermentable sugar from starch. The reaction steps are represented in eq. (2)

enzyme or acid

$$(C_6H_{10}O_5)n + nH_2O -----nC_6H_{12}O_6 ...(2)$$

starch water (catalyst) (sugar)

The reactions occur under pressure with mineral acid, either in batches or in a continuous process.

Fermentation and Distillation

Fermentation requires two to five days depending on the operating temperature and can occur in vats arranged to permit the filling, fermenting, emptying, cleaning and sterilization required for the batch process. Heat is generated and the temperature is controlled at 32-35°C for satisfactory completion of the reaction. In the fermentation, sugars are converted by yeast into nearly equal weights of ethanol and carbon dioxide.

Process Details

Alcohol production from corn results from a series of steps (Fig. 2.3) that includes cleaning of the raw product, milling, cooking, fermentation and distillation. The corn is cleaned using vibrating screens, airjets to remove dust and lighter particles and magnetic separators to remove metal objects.

In milling, the outer hull of cellulose is broken, exposing the starch within the corn kernel. Impact or hammer mills are generally used. Wet milling also is practiced. After milling, the grain is slurried with water to facilitate handling.

Cooking involves the gelatinization and hydrolysis of the starch to simple sugars in the presence of enzymes. The hydrolysis step requires 20 to 35 gallons (26 to 132 liters) of water per bushel (35.24 liters) of corn. The mash is heated by direct steam injection to gelatinize and liquify the starch. It is then cooled and pumped to the enzymatic hydrolysis process. Before fermentation, the mash is cooled to about 25° C so as not to inhibit the yeast.

The yeast required for the fermentation is normally produced by a separate process and is rarely reused, because yeast characteristics can change or contamination can occur. Temperature, pH, and nutrient levels are controlled. The residence time for a batch fermentation is greater than one day and results in a product stream that contains from 10-12% alcohol. The product stream also contains about 6 to 8% solids which are mostly fibers and dead yeast cells. The alcohol is separated and concentrated by distillation to 190-proof alcohol (95%). For fuel-grade ethanol, further concentration to a purity in excess of 99% is required. The azeotrope of ethanol and water is broken by adding a dehydrating agent such as benzene to form a tertiary mixture that allows separation of the ethanol under proper temperature and pressure (EPA, 1979; Radian Corporation, 1981). Anhydrous ethanol is withdrawn from the dehydration column bottom. The column heads (Fig. 2.2) contain a mixture of benzene, ethanol and water. This mixture is routed to a separator where two layers are formed - a benzene-ethanol rich top layer containing a small amount of water and a water-ethanol rich bottom layer containing some residual benzene. The ethanol-water layer is sent to a benzene recovery column to strip the benzene, and the ethanol is recycled to the dehydration column. The benzene-alcohol layer is also routed to the dehydration column. The bottoms from the dehydration column are with-drawn for further treatment.

Waste Generation

In a grain-based alcohol production plant both solid and liquid wastes are generated. The solid wastes generally are grain dust from feedstock preparation, stones, twigs, and mold clumps from grain handling and cleaning, and bottom ash and

particulate matter from the combustion process used to supply steam and electricity to the alcohol plant.

Wastewaters result from cleaning the enzyme reactors, fermenters and other plant equipment, from stillage, from condensate returns, from evaporators, coolers, condensers and other heat exchangers, and from boiler and cooling tower blowdowns.

2.4 Support Facilities

The support facilities necessary for any ethanol plant include equipment for steam and power generation, a cooling tower, and a wastewater treatment system. The boiler used in the ethanol plant is usually either coal or oil fired.

III ETHANOL PRODUCTION WASTE CHARACTERISTICS

This section highlights:

(a) the characteristics of the waste generated from the ethanol production unit processes and from the ethanol plant as a whole and

(b) the probable impact of these wastes on the environment.

3.1 Wastewater

The sources of wastewater from an ethanol plant are condensate from the cooking and cooling units, from the rectifier and beer still bottoms, and from evaporator condensate and washwater. Fig. 3.1 illustrates the sources of wastewater from different unit processes.

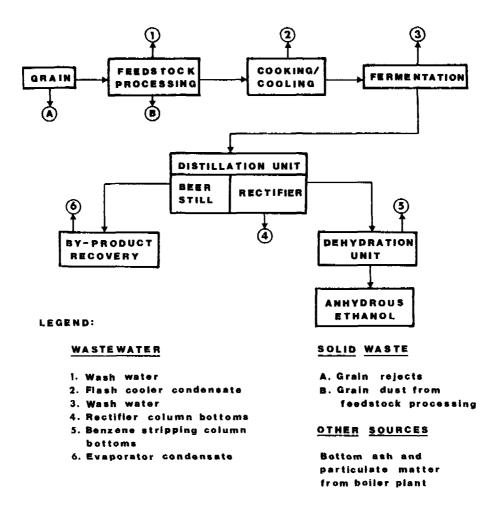


Fig. 3.1 Sources of waste during the production of ethanol

The extent to which each of the wastewater sources contributes to the total plant raw waste load varies. Table 3.1 presents the approximate volume of wastewater generated from each of the processes in grain-based ethanol plants having a production capacity greater than 18.25 x 10^6 L/yr (greater than 18,250 m³/yr). The table includes wastewaters generated from the evaporator condensate of a corn-based ethanol plant by-product recovery system.

Source of wastewater generation	Approx. volume generated m ³ /10 ³ kg grain** (% of total wastewater)
A. Unit process:	
Cooking and cooling:	
— flash water condensate	0.3 - 1.0 (11 - 36%)
Distillation:	
 beer still bottoms and 	
rectifier bottoms	0.43 – 1.4 (7 – 28%)
Dehydration:	
 – solvent stripping column/or 	
dehydration column	0.002 (1%)
By-product recovery:	
 evaporator condensate 	2.2 – 4.1 (50 – 77%)
B. Clean-up waters	0.04 - 0.45 (1 - 7%)

Table 3.1 Volume of pollutants generated at grain based ethanol plants* (ESE, 1974 and EPA, 1981, Plants in the United States.)

* In terms of ethanol production, about 2.5 US gallons (9.46 liters) of 200-proof ethanol are produced per bushel of corn (SERI, 1980). This is approximately 100 gallons (378.5 liters)/1000 kg of corn.

** Based on a plant having a production capacity greater than 19 X 10⁶ liters/yr.

In a molasses-based ethanol plant, the process generally excludes a by-product recovery system. In these ethanol plants, the stillage is the main fraction of the waste load. In a molasses-based plant, the sources of wastewater are stillage, fermenter and condenser cooling water and fermenter washwater. The cooling water generally is a low BOD waste and is recycled back to the process. The stillage has a volume that ranges from 135 to 1800 m³/d (Dubey, 1974). Fermenter washwater is approximately 5% of the stillage volume. Thus, stillage contributes about 95% of the total volume of the wastewater. This indicates why treatment of stillage receives such a high emphasis at ethanol plants.

Ethanol is produced commercially in both small-scale 2 to 4×10^{6} L/yr (0.5 to 1×10^{6} gal./yr) and larger plants greater than 4×10^{7} L/yr (1×10^{7} gal./yr). The composition and the volumes of the wastewater from these plants vary with the type of process, the quality of the incoming water and the location of the facility. The volumes of wastewater generated from ethanol plants per unit of ethanol production are summarized in Table 3.2. The wastewater to ethanol ratio varies widely (6.9-33.7) and does not appear to be a function of plant size.

Plant code	Feedstock	Ethanol production (m³/d)	Wastewater production (m ³ /d)	Ratio <u>m³ wastewater</u> m³ ethanol
A03	Corn	200	2,400	12.1
A06	Corn	24	170	6.9
A10	Molasses	21	340	16.2
E02	Molasses	30	760	25.0
E04	NA	25	400	15.7
E05	NA	52	830	16.0
E06	NA	43	610	14.2
E07	NA	47	570	12.0
E08	Corn	32	610	19.1
E09	Corn	230	7,650	33.7
E11	NA	45	1,100	24.4
E12	NA	44	820	18.6
E 13	NA	90	1,320	14.7
E15	Corn	23	380	16.2
E17	Corn	23	380	16.5
E18	Corn	23	350	15.3
E19	Corn	118	1,550	13.1

Table 3.2. Production and wastewater generation for beverage and ethanol-for-fuel plants in the USA (EPA, 1981)

NA - Information not available.

The volume of stillage from sugar-based ethanol plants is also large. The stillage is produced at a rate of about 12-13 L/L of ethanol and is high in alkali salts and BOD (Sweeten et al., 1982; Dock et al., 1981). Each gallon (3.78 liters) of ethanol produced results in a raw waste yield of about 3500 grams of BOD in a sugar derived ethanol plant (ANL, 1980).

The wastes from the feedstock, saccharification, fermentation, stillage separation and evaporation processes are included in the above estimate. The volume of liquid waste generated from ethanol plants is in the range of 12 to 55 L/L of ethanol produced with an average flow of 33 L/L of ethanol (ANL, 1980). The BOD ranges between 14,400 and 20,400 mg/L before by-product recovery. Hira <u>et al</u>⁵ (1983) reported that the wastewater production from 13 small-and medium-scale ethanol and rum distillers' plants produced wastewater volumes ranging between 1.14 x 10⁷ and 7.5 x 10⁷ L/yr.

3.2 Solid Waste

The solid wastes from corn-based ethanol plants are:

- (a) grain dust from feedstock preparation and by-product processing,
- (b) rejects during grain handling,
- (c) sludge from the wastewater treatment system, and
- (d) bottom ash and particulate matter from the plant boilers.

In addition, the scrubbing of the stack gas from the plant boilers will contribute scrubber sludges and collected fly ash to the solid waste. The total amount of solid waste generated from the plant boiler will depend on the coal composition and the nature of any air pollution control system. The solid waste production estimated by several studies is presented in Table 3.3.

Plant size (liter/yr)	D	Solid wastes (kg/yr)				
	Raw Material	Wastewater sludge	Ash	Dust	Scrubber*** waste	
7.57 X 10 ⁷	Corn	NA	4.9 X 10 ⁶ (0.06)*	NA	NA	
8.33 X 10 ⁷	Corn	NA	1.64 X 10 ⁷ (0.19)	2.18 X 10 ⁶ (0.03)	4.5 X 10 ⁷ (0.54)	
7.57 X 10 ⁷	Corn	7.30 X 10⁵ (0.01)	3.86 X 10 ⁷ ** (0.51)	NA	-	
1.89 X 10 ⁸	Corn	4.49 X 10 ⁶ (0.02)	7.03 X 10 ⁶ (0.4)	2.86 X 10 ⁶ (0.15)	NA	
2.27 X 10 ⁸	Corn	3.26 X 10⁵ (0.001)	1.72 X 10 ⁷ (0.078)	NA	NA	

Table 3.3. Summary of the solid wastes produced from ethanol plants in the U.S.A. (Hira et. al, 1983)

* Number in parenthesis indicates the kg of solid waste produced per liter of ethanol production.

** Includes scrubber wastes.

*** Waste generated during scrubbing the stack gas from the plant boilers.

NA No data available.

3.3 Environmental Impact of Ethanol Wastes

The wastewater from ethanol plants consists primarily of organic materials, has a high BOD_5 , COD and solids content, and a pH that is related to the chemicals used for cleaning. These wastes have a high pollution potential. The disposal of the

untreated waste to surface waters may kill fish. Verma and Dalala (1976) studied the survival of two species of fish when treated with diluted stillage at different temperatures and pH values (Table 3.4). The LC₅₀ value indicates the percent of waste in the water that killed 50% of the fish in the test within 96 hours.

The solid waste, particularly sludges, can be used for animal feed, but can create environmental problems if not properly handled. In Brazil, the ethanol production from sugar cane in 1983 was about 5 million m³. The environmental impact in terms of water pollution was stated to be equivalent to the wastes from a population of 77 million (Costa-Ribeiro ε Costello-Branco, 1979). In India, from 70 distilleries with a total alcohol production capacity of 270 million liters, the waste was estimated to be about 4000 million kg, causing pollution of surface waters (Sundaram ε Pachaiyappam, 1975).

Fish species	Experimental protocol	Findings
Puntius sophore	Alkalinity — 160 mg/L Dissolved oxygen — 7.2 mg/L pH 6.2 — 6.5	$LC_{50} = 8.1\%$ waste at $20 = 24^{\circ}C$ $LC_{50} = 6.3\%$ waste at $30 = 34^{\circ}C$
Mystus vittatus	As above pH 6.1 — 6.4	LC _{so} 11.15% waste at 20 - 24°C LC _{so} 10% waste at 30 - 34°C

Table 3.4. Effect of stillage on fish life (Verma & Dalala, 1976)

3.4 Detailed Characteristics

Wastewater

The characteristics of ethanol plant wastewater depend on the process, nature of feedstock and by-product recovery practices. Plant size and location also may influence the wastewater characteristics.

The two major raw materials used for alcohol production from biomass are:

- (a) molasses from cane or beet sugar, and
- (b) starchy material such as corn grain.

The spent wash from molasses-based ethanol production is a viscous liquid with an unpleasant smell. It is acidic with a pH as low as 4.5, the BOD is in the range of 50,000-60,000 mg/L, and the total solids content exceeds 10% by weight. These solids contain a high fraction of inorganics. The characteristics of spent wash from different sources are noted in Table 3.5.

Characteristics	India	Brazil	Cuba	Hawaii	Australia
рН	3.8 - 4.5	4 5.7		_	4.6
Sp. gravity	1.05		1.03	1.05	-
Water (%)	88 - 93	-	93.7	88.8	- 1
Volatile and organic matter (g/L)	40 - 60	63.4	43	84	4 – 4.9*
Crude ash (%)	3 – 5	19.2	2.04	2.8	
Total solids (%)	7 – 12	-	6.31	11.2	4.8 - 6.3
Total nitrogen (g/L)	0.9 - 1.5	1.2	0.8	1.4	3.3 - 4.4*
Phosphorus as $P_2 O_5$ (g/L)	0.1	0.2	-	_	- 1
Potash (K_2O) (g/L)	5 – 20	7.8	5.2	8.6	[_
Lime (g/L)	2.6 - 4.0	-	1.5	3,2	-
BOD ₅ (g/L)	35 45			_	_
COD (g/L)	65 - 95		_	_	45 - 50

Table 3.5. Characteristics of molasses-based ethanol industry spent wash (Sundaram and Pachaiyappam, 1975; Sheehan and Greenfield, 1980; Philip and Panicker, 1964; Braun and Huss, 1982.)

* Organic solids (% W/V)

** gNH₃/L

The waste characteristics are related to the feedstock. The characteristics of the wastewater from ethanol plants using different teedstocks are summarized in Table 3.6.

There is a difference in the wastewater BOD (8.7-60 g/L) with different feedstocks (Basu, 1975; Kishore et al., 1979; Hiatt et al., 1973; Bhaskaran, 1964). Mosasses-based ethanol plant wastewater is characterized by a high, biodegradable, dissolved solids content of which up to 50% may be present as reducing sugars, a high ash content, a high temperature, and a low pH. The wastewater from grain-based ethanol plants has much less ash than the wastewater from molasses-based ethanol plants (Table 3.6). The suspended solids content of the corn-based waste is mainly due to spent grains.

A summary of the stillage characteristics from five small-scale (less than 2×10^{b} L/yr) corn-based ethanol plants is presented in Table 3.7. The variation among the plants is due to differences in plant size and the process scheme used. Small-scale alcohol plants also may have large amounts of pollutant due to poor housekeeping.

Characteristics of wastewater produced from different unit processes are summarized in Table 3.8 in terms of conventional, non-coventional, and priority pollutants (potentially toxic organics and metals). BOD values are high in the flash cooler condensate, rectifier bottoms (distillation unit), evaporator condensate, and washwater. The pH of flash cooler condensate, rectifier bottoms, and dehydration unit wastewater is acidic, whereas the pH of evaporator condensate is alkaline. The washwater contains a wide range of pH (4-12), suspended solids (63-1180 mg/L), and oil and grease (25-137 mg/L). In flash cooler condensate, the BOD is related to the entrainment of dissolved organic substances in flashed vapor.

	Distillery type					
Characteristics*	Mollases		Grain		Wine	
	Range	Average	Range	Average	Range	Average
pН	3.5 - 5.7	4.2	3.8 - 7.5	5.4	3.9 – 4.5	4.1
Temperature (°C)	80 ~ 105	94	42 - 95	73	-	-
Total solids	21 140	78	20.5 - 47.3	33.8	24 – 125	62
Volatile solids	40 100	59	24 - 36	29	-	29
Suspended solids	1 13	5	_	11.4	0.2 0.9	0.6
Dissolved solids	25 110	57	-	_	_	22
Crude fiber				10	-	-
Ash	16 40	29	-	3.6	-	
Volatile fatty acids (as acidic acid)	0.7 - 5.5	2.2	1.8 – 2.4	2.1	-	0.75
Reducing sugars	14 45.0	26	10.9 - 30.5	24.0	-	_
Fats and oils	-	_	_	2.9	_	_
Total nitrogen	0.6 - 8.9	1.8	0.2 - 1.9	1.0	0.4 - 1.0	0.7
Organic nitrogen	0.6 - 8.7	1.9	1.4 2.1	1.7	_	
Ammoniacal nitrogen	0.04 - 0.89	0.3	0.01 - 0.09	0.05	0.01 - 0.05	0.03
Sodium (Na ₂ O)	0.13 - 2.51	1.0	_	_	-	1.3
Potassium (K ₂ O)	4.8 22.59	10.7	_	_	_	16.5
Calcium (CaO)	1.26 - 6.70	3.5	_		-	1.3
Magnesium (MgO)	0.66 - 2.35	1.6	_	_	_	2.3
Phosphorus (P)	0.026 - 0.33	0.2	0.039 - 0.087	0.063		1.2
Silicate (SiO ₂)	_	1.5	_	—		0.5
Chloride (CF)	0.68 – 7.39	3.8	_	_	-	1.3
Sulphate (SO ₄ =)	1.56 - 6.60	4.4	-	-		3.6
Total iron (Fe ²⁺)	0.001 - 0.120	0.07	_		— ·	—
Copper (Cu ²⁺)	0.004 - 0.03	0.014	-	-	ļ _ ,	
Zinc (Zn ²⁺)	0.027 – 0.225	0.11	-	-	- 1	_
COD	15 — 176	78	-	-	- 1	-
BOD₅	7 95	36	15 – 340	22	- 1	12

Table 3.6. Characteristics of wastewater from different ethanol plants (Sheehan and Greenfield, 1980.)

* All figures are in grams per liter except pH and temperature,

	Ethanol production facility					
Parameter (mg/L)	No. 1	No. 2	No. 3	No. 4	No. 5	
BOD₅	28,400	20,800	38,600	54,400	43,100	
COD	36,800	23,100	60,500	98,700	58,400	
тѕ	12,200	35,000	52,000	40,400	39,460	
vs	9,870	29,900	49,000	38,270	30,980	
TKN	266	361	224	532	546	
$NO_2 + NO_3 - N$	0.45	2.6	0.25	0.08	<0.5	
$NH_4 = N$	4.5	10	31.5	0.37	0.05	
SO₄	300	NA	466	388	299	
PO₄	400	NA	477	544	700	
Ag	<0.002	NA	<0.02	0.01	0.00	
As	<0.015	NA	0.005	NA	<0.00	
Ba	0.09	NA	0.30	NA	0.39	
Çd	0.01	NA	0.006	0.006	0.2	
Cr	0.02	NA	0.006	0.02	0.0	
Ca	0.13	NA	0.17	0.15	0.3	
Hg	<0.002	NA	NA	0.0015	0.00	
Pb	0.05	NA	0.03	0.04	0.1	
Zn	4.41	NA	5.2	13.8	5.0	

Table 3.7. Stillage characteristics from small-scale ethanol plants (Hira et_al., 1983.)

NA — No data available.

The stripping column bottoms from the dehydration unit contained organics such as methylene chloride and benzene, as well as Cr, Cu and Zn. The data indicate that potentially toxic organics and metals do not occur in the wastewater in high concentrations.

The characteristics of the raw wastewater from 13 small- and medium-scale ethanol facilities are summarized in Table 3.9. The conventional pollutant concentrations were greater than those typical of domestic sewage. The pH value varied from 3-13. Of the 101 potentially toxic organics tested, only 11 were present. Benzene, bis (2 ethylhexyl) phthalate, methylene chloride and phenolics were present in the range of 18-236 g/L. Except for copper, nickel, lead and zinc, the metals in the raw wastewater were in low concentrations. Among the non-conventional parameters, COD, TOC, and total volatile solids were present in high concentrations.

Compound	Flash cooler condensate (cooking and cooling unit)	Distillation unit (rectifier bottom)	Dehydration unit	Evaporator condensate	Washwater
Conventional pollutants BOD₅ (total), mg/L Oil and grease, mg/L pH Total suspended solids, mg/L Toxic organic pollutants, µg/L*	13 — 1900 — 3.4, 7.2 5, 30	1440, 300 - 4.7, 6.2 <1.0	26, 16 3.9, 4.1 <1.0, 1.0	628, 2550 — 7.95 —	48 — 1760 137, <25 4 — 12 63 — 1,180
Benzene Bis (2-ethylhexyl) Phthalate Butyl benzyl phthalate Chloroform Ethylbenzene Methylene chloride Pentachlorophenol Phenol Phenol Toluene Trichloroethylene	None >10	>10 - - >10 - - >10 - - - - -	5.7**, 59.4*** - - 22 - <0.01 -	- 6, 13.5 74 - 34, 17.5 150 - - - 16	None >10
Metals, μg/L**** Antimony (total) Arsenic (total) Beryllium (total) Cadmium (total) Chromium (total) Copper (total) Copper (total) Cyanide (total) Lead (total) Mercury (total) Nickel (total) Selenium (total) Silver (total) Thallium (total) Zinc (total)	<10		 4.0 6 10	- 9.7, 1.5 17, 1.0 862, 9.5, 80 - 160, 13.5 - 168, 17 - - 36, 26	None >10

Table 3.8. Pollutants in the wastewater generated from different sources at ethanol plants (EPA, 1981.)

 Priority pollutant organics with at least one maximum concentration >10 μg/L. Average concentrations are listed.

** Benzene from stripping column.

*** Wastewater stream from dehydration column.

**** Metals with a least one analysis above the detection limit (dl) for that metal. Average concentrations are listed.

2	Untreat	ed wastes
Compound	Mean	Max
Conventional pollutants		+
BOD ₅ (total), mg/L	1,400	5,250
Coliform, colonies/100 ml	2,600	24,000
Oil and grease, mg/L	186	1,560
pH	-	13
Total suspended solids, mg/L	400	3,930
Γoxic organic pollutants, μg/L		
Benzene	65	1,000
Bis (2-ethylhexyl) Phthalate**	18	72
Butyl benzyl phthalate	13	220
Chloroform**	27	390
Ethylbenzene	1	11
Methylene chloride**	30	100
Pentachlorophenol**	4	47
Phenol**	33	190
Phenolics (total) * *	236	1,240
Toluene	10	94
Trichloroethylene	7	92
letals, µg/L***		
Antimony (total)	4	10
Arsenic (total)	3	8
Beryllium (total)	1	8
Cadmium (total)	6	17
Chromium (total)	17	36
Copper (total)	342	1,210
Cyanide (total)	9	10
Lead (total)	54	189
Mercury (total)	0	1
Nickel (total)	71	270
Selenium (total)	5	43
Silver (total)		3
Thallium (total)	11 164	47 590
Zinc (total)	104	590
onconventional parameters, mg/L		
Chlorine (total)	0	0
COD	2,620	6,690
Dissolved solids	1,660	5,170
Kjeldahl nitrogen (total)	24	97
MO alkalinity (CaCO ₃)	400	2,180
$NH_3 - N$ (ammonia)	21	94
Nitrite (total)	0	0
Phosphate (PO_4)	24	5
Settleable solids (ml/L)		27
Temperature (°C)	35	44
Total acidity (CaCO ₃) Total error carbon (TOC)	180 850	680 2,150
Total organic carbon (TOC)	820	
Total solids Total volatile solids		3,270
Total volatile solids Volatile supported solids	1,010 120	2,480 150
Volatile suspended solids	120	100

Table 3.9. Pollutants in ethanol production wastewater* (Hira et. al., 1983.)

* Combined wastewater from 13 small and medium-scale ethanol production facilities.

** Found at two or more plants in untreated waste.

*** Metals with at least one analysis above the detection limit for that metal.

Some ethanol production facilities utilize termentable substrates other than molasses and grain. These feedstocks can include sugar beets, potatoes and sorghum. The wastes from such a facility using culled potatoes have been analysed and a summary is presented in Table 3.10. This facility produces approximately 1 million gallons (3787 m^3) of ethanol per year.

The wastewater characteristics (Table 3.10) show a high oxygen demand and a low pH. In addition, the wastes contained significant concentrations of aluminum, cadmium, calcium, chromium, copper, iron, manganese, mercury, titanium and zinc. These metals occurred as a result of leaching from the process equipment, and from inorganic chemicals used in the process and for cleaning. Lotal and fecal coliform bacteria were found in high concentrations in the sluice water and the cooker washwater.

Parameter	Range
BOD	780 — 107,000 mg/L
COD	4.600 — 216,000 mg/L
Total organic carbon	1,600 – 57,500 mg/L
Total suspended solid	880 – 35,000 mg/L
На	2.7 – 6.8

Table 3.10. Wastewater characteristics from an ethanol production facility using potatoes as a feedstock (Kuby et al., 1984.)

Solid Waste

A large portion of the solid waste, except sludge, ash and sulfur-containing matter, is either recycled and reused in the process or is processed and sold as animal feed. The sludge also can be recycled to the dryer after treatment and then mixed with by-products such as distillers' dry grain (DDG), provided the facility does not combine sanitary waste and process water. The decision to reuse or treat the solid waste depends on its characteristics.

Detailed characteristics of the solid mash separated before the distillation unit in a corn-based small-scale ethanol plant are noted in Table 3.11. The nutritional characteristics of solid vinasses have been determined and are summarized in Table 3.12 and 3.13.

Other solid waste generated from the ethanol plant consists of ash and sulfur containing waste material. Because of the lack of data, characterization cannot be provided.

Command .	Separated so	olid mash
Compound	Site A	Site B
General		
ρΗ	3.9	3.4
Kjeldahl nitrogen (total)	1.65%*	1.16%*
NH ₃ -N (mg/kg)	34.0	66.0
Nitrate (total) (mg/kg)	5.0	13.0
Phosphate as P (mg/kg)	1,250	910.0
Total solids	33.0%*	21.0%*
Toxic organic pollutants (non delected) Metals (Total), mg/kg**		
Aluminum	<1.0	<10.0
Antimony	<0.2	<0.2
Arsenic	<0.2	<0.2
Beryllium	<0.2	<0.2
Cadmium	<0.02	<0.02
Calcium	220	230
Chromium	0.5	<0.5
Copper	3.2	5.1
Iron	92.0	128.0
Lead	<3.0	<3.0
Magnesium	270	210
Mercury	<0.02	<0.02
Nickel	<1.0	<1.0
Selenium	<0.2	<0.2
Zinc	6.7	16.7
Cyanide	<0.1	<0.1

Table 3.11. Pollutants in the solid mash from a solid/liquid separator before fermentation at two com-based ethanol plants. (EPA, 1980)

* Percent by weight.
** mg/kg dry weight.

Deverenters* (%)	Feedstock used		
Parameters* (%)	Sugar cane	Sugar beets	
Ash	30.0	29.0	
Crude protein (N X 6.25)	10.0	36.0	
Crude lipid	0.2	0.3	
Crude fibre	Tr.**	Tr.**	
Potassium	9.0	5.5	
Sodium	0.7	4.0	
Magnesium	0.7	1.2	
Calcium	3.2	0.7	
Iron	0.1	0.2	
Sulphate	8.0	0.6	
Chloride	_	4.3	

Table 3.12. Characteristics of concentrated vinasses (Robertiello, 1982.)

* All values are expressed as % on a dry matter basis.

** Trace.

Amino acid	Feedstoo	k used
	Cane	Beet
Lysine	0.10	0.31
Histidine	0.02	0.16
Arginine	0.04	0.38
Ornithine	_	0.73
Aspartic	0.83	0.89
Threonine	0.11	0.14
Serine	0.12	0.65
Gilutamic	0.29	9.09
Proline	0.37	_
Glycine	0.10	0.56
Alanine	0.20	1.61
Valine	0.09	0.64
Methionine	0.08	0.11
Isoleucine	0.11	0.65
Leucine	0.12	0.59
Tyrosine	0.08	0.21
Phenylalanine	0.09	0.19

Table 3.13. Amino acids in vinasses (% dry matter). (Robertiello, 1982.)

IV TREATMENT AND DISPOSAL OF ETHANOL WASTE

This section discusses treatment and disposal approaches for ethanol production wastes. The appropriate waste management approaches must be an integral part of the overall plant management, and a wide variety of approaches can be considered (Fig. 4.1).

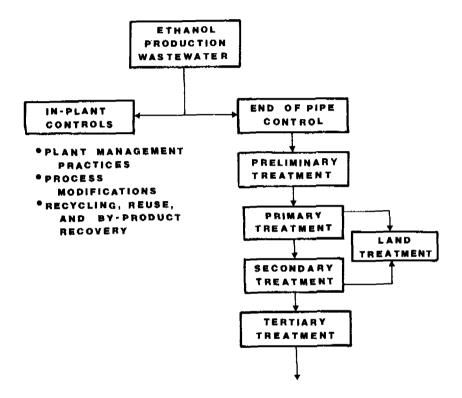


Fig. 4.1 Ethanol production wastewater treatment alternatives

4.1 In-plant Source Control

Wastewater generation is a function of the process and management practices followed in the production facility. In-plant source controls such as improved plant management practices, process modifications, recycle and by-product recovery, and source separation can reduce the raw waste load that will require treatment.

Plant Management Practices

Plant management practices such as spill controls, washwater control and water conservation are possible source control methods. Spills and overflows may result from tank overflow, loss of cooling and heating in the distillation unit, pump malfunction or operator error. Spills can be separated and contained by a centralized sump or a spill lagoon. The sump may be designed so that the spill can be recycled to the distillation column for ethanol recovery or pumped to the wastewater treatment facility. Liquid from the spill lagoon can gradually be pumped to the wastewater treatment system to protect the treatment system from large load and flow variations.

Common in-plant controls which may be used to reduce wastewater generation include:

- (a) The installation of central cleanup system units (valved or triggered hoses). These systems generate a controlled-pressure supply of hot or warm water containing detergent and reportedly clean better with less water (ESE, 1974).
- (b) The elimination of unnecessary water use. The installation of valves to reduce water usage and the use of automatic shut-off valves.
- (c) The use of low-volume, high pressure systems on all water sprays.
- (d) The utilization of freshwater in the latter stages of production, and the reuse of process water in the earlier stages. The recycling of water for reuse in feedstock preparation (e.g., washing, mashing, etc.).
- (e) The utilization of non-contact waters (e.g., water from mash cooling and distillation column cooling) for other plant uses.
- (f) The recycling of stillage to reduce the volume of waste to be treated and to remove some of the organics and inorganics. If the sugar-based ethanol plant is associated with a sugarmili, there is a possibility of using stillage as a portion of the cane washwater 'Sheehan & Greenfield, 1980). Stillage can also be utilized for the dilution of molasses.

Process Modification

The quantity of wastewater generated per liter of alcohol production depends on plant management practices and on the equipment used in the process. Possible process modifications that can reduce the waste load include:

- (a) The installation of automatic controls for evaporator operation at optimum levels of liquid/solid separation. This will increase the performance of the evaporator and decrease the waste loads in the evaporator condensate.
- (b) The replacement of barometric condensate systems used in cookers, coolers and evaporators with surface (non-contact) condensers. The cooling water added to the condensate increases the hydraulic load to the wastewater treatment system. The barometric condensate can amount to as much as 28% of the total BOD load (ESE, 1974).
- (c) The use of re-boilers rather than live steam for heating the distillation column (ESE, 1974).

By-Product Recovery

The conversion and fermentation of agricultural crops yield other products in addition to ethanol and carbon dioxide. If these by-products are removed from the wastewater, the pollutant load can be reduced significantly. Depending on the

feedstock and the process used, the stillage from the bottom of the "beer" still (Fig. 2.2) may be recovered as a by-product. By-products and their possible uses are noted in Table 4.1.

Feedstocks	By-product	Remarks
Mollasses	Yeast cell and fertilizer ingredients e.g., K_2O	Used as a fodder yeast, reduces BOD _s 40-50%
Low protein sugar crops	Fuel and fertilizer ingredients e.g., K_2O	Used as fuel due to low feeding value, reduces organic loading.
Starch feedstock, e.g., grain	Animal and human feed	DDG used as animal feed, corn gluten used as human feed, reduces organic load.

Table 4.1.	By-product recovery from stillage of different feedstocks
	(SERI, 1980).

The wastewater from the bottom of the "beer" column contains a suspension of spent grain and dilute alcohol. The solids can be removed from the alcohol solution and concentrated by screening or centrifuging, pressing and drying to produce distillers' dry grain (DDG). The extracted liquid can be concentrated with multiple-effect evaporators to syrup containing approximately 35% dissolved solids. This can be mixed with the dehydrated solids and the mixture dried in a rotary dryer. The production of DDG is about 1.0 kg/L of alcohol produced. The energy requirement is generally high to recover the by-product. Kalter et al. (1980) reported that 46% of the total plant input energy is required for by-product recovery. The flow diagram for by-product recovery from a corn-based distillery wastewater is shown in Fig. 4.2.

Besides animal feed production, recovery of fertilizer nutrients (mainly potassium) from the distillery wastewater has been proposed (Chakrabarty, 1963; Paul, 1972). In the early sixties Chakrabarty (1963) conducted studies on the recovery of potash, methane and vitamin B_{12} from distillery wastes. At the Mohan Meakin Breweries Ltd., Lucknow, India, the evaporator concentrate was pumped to the top of an incinerator where it passed down inclined baffle plates countercurrent to the hot gasses. The resulted "spent waste coke" was burned. The ash had a high potash content (37% potassium oxide), some calcium (9%) and was mixed with nitrogen and phosphate compounds to produce a well-balanced mixed fertilizer. In Europe, Sastry & Mohanras (1964) reported that stillage incineration produced ash containing 35% potassium oxide and 2% phosphorus pentoxide. Others used the same methodology to extract fertilizer ingredients from stillage (Gupta et al., 1968; Dubey, 1974; Jackman, 1977).

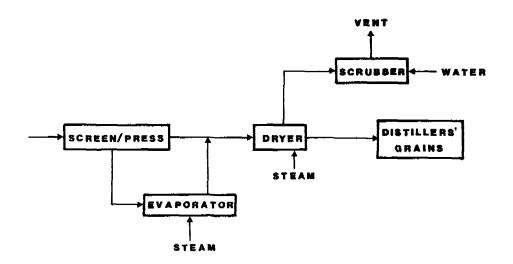


Fig. 4.2 By-product recovery from corn based ethanol production wastewater

4.2 End of Pipe Control Methods

Preliminary Treatment Methods

The raw wastewater should receive preliminary treatment such as screening, equalization and neutralization to achieve effective primary and secondary treatment. Rapid changes in wastewater flow and concentration may cause problems in a wastewater treatment plant. Equalization controls such fluctuations and is practiced in ethanol-for-fuel plants and beverage alcohol plants in the USA (Radian Corporation, 1981). Neutralization also can occur in equalization basins. Coarse screens can be used after bar screens to achieve suspended solids removals of 5-25%.

Primary Treatment

The most widely used primary waste treatment process in the ethanol industry is sedimentation. The removal of settleable solids reduces the oxygen requirements of subsequent biological processes and reduces the solids loadings to secondary sedimentation tanks.

A properly designed primary sedimentation tank can generally remove about 50-70% of the suspended solids and 25-40% of the BOD₅ in domestic sewage. However, no information is available regarding the performance of primary sedimentation units with ethanol production wastewaters.

Chemical coagulation and precipitation can increase solids removal in primary treatment. However, this process is not widely used in ethanol wastewater treatment systems.

Biological Treatment

Ethanol production wastewater requires a high degree of treatment before discharge. A typical treatment process scheme will include preliminary treatment, primary clarification and biological treatment (secondary treatment) as given in Fig. 4.1. The ethanol-for-fuel-industry and the ethanol beverage industry in the United States use the biological treatment options identified in Table 4.2 (Radian Corporation, 1981).

Secondary treatment options	% Plants using the noted technology to treat at least part of their wastewate				
Activated sludge	21				
Aerated Lagoon	63				
Stabilization ponds	42				
Trickling filter	16				
Rotating biological contactor	16				

Table 4.2. Secondary treatment options for ethanol industry wastewater in the USA (EPA, 1981).

Table 4.3 outlines key operating parameters of some of the biological treatment processes. Capital and operating costs are important selection criteria. These vary widely and are described only qualitatively.

(a) Activated Sludge

In most treatment systems, activated sludge treatment follows dilution of the raw stillage. Table 4.4 summarizes the operating information and the performance of such processes as identified in the literature.

Efficient performance of activated sludge plants (greater than 85% BOD removal) with ethanol wastewater has been reported in several studies. Burkhead et al. (1968) treated grain distillery evaporator condensate (BOD₅, 266-564 mg/L) by activated sludge at a loading rate of 0.29 kg BOD_5/m^3 .d and achieved 91.5% BOD₅ removal with added nutrients, pH adjustment and using an acclimated sludge. Sheehan and Greenfield (1980) reported that low loading rates (less than 0.15 kg BOD_5/kg MLSS.d) were used in Japan to achieve greater than 85% BOD_5 removal. With grain distillery evaporator condensate (860 mg BOD_5/L), Thomas et al. (1974) obtained 99% BOD removal with an organic loading rate 0.3 kg BOD_5/kg MLSS.d and a hydraulic retention time of 33 hours.

Note: Some of the ethanol plants adopted a combination of treatment methods and the total does not sum to 100 percent (sample population of 25 plants).

Operating cost	High				Moderate	Moderate		Moderate
Capital cost	Moderate				Low	High		Moderate
Shock loading ability	Pror	Fair	Fair	Good	Good	r Fair	Excellent	Variable
BOD removal efficiency (%)	8505	60-75	06-08	75-95	75–95	80-85	65-80	45-75
Recycle ratio	0 75_0 5	0.05-0.15	0.25-1.0	0.75-1.5	None	Minimum	Always	None
Volumetric Ioading (kg BOD _s /m ³ .d)	03-D6	1.2-2.4	1.0-1.2	0.1-0.4	ł	0.080.41	0.414.8	1.6–6.4 (kg VSS/m ³ . d)
Food Microorganism ratio (kg BOD/kg MLVSS. d)	50	1.5-5.0	0.2-0.6	0.05-0.15	1	1	I	I
Hydraulic retention time (h)	a	1.5-3	0.5-1ª, 3-6 ^b	18–36	ļ	4-12	ļ	15–20
Mean.cell residence time (days)	ų ų	0.2-0.5	5-15	20–30	3.6	I	ļ	10–30
Process	1. Activated sludge	Modified aeration	Contact stabilization	Extended aeration	2. Aerated lagoon	3. Trickling filter Low rate	High rate	 Anaerobic digestion (conventional)

^aContact unit. ^bSolids stabilization unit.

Waste	Initial BOD₅ (mg/L)	Organic loading (kg BOD₅/m³.d)	Hydraulic retention time (h)	MLSS (mg/L)	BOD removal (%)
Distillery wastewater	-	_	_	_	27 – 72
Rum stillage and domestic sewage (1:10)	_	_		_	28
Grain distillery evaporator condensate	266 564	0.29	_	2000 – 7000	91.5
Alcohol distillery waste	_·	<0.15*	_	-	>85
Grain distillery evaporator condensate	860	0.3*	33	3,000	99
Distillery wastewater		1.043 (COD)	23.0		85–90 (COD)

Table 4.4. Activated sludge treatment of ethanol production wastewater. (Sheehan and Greenfield, 1980).

*Refers to kg BOD/kg MLSS.d

(b) Lagoons

An aerated lagoon can be an attractive alternative for the treatment of ethanol plant wastewater. The required effluent quality can be achieved by adding a polishing lagoon to the aerated lagoon to remove suspended solids. Aerated lagoons can also be used in combination with an anaerobic lagoon or an oxidation pond to achieve the desired overall treatment efficiency.

The performance of combined systems are summarized in Table 4.5. Rao (1972) reported data for two lagoons in series. The initial anaerobic lagoon operated at loadings of 0.6-1.05 kg BOD_/m³.d and retention time of 38 to 66 days, respectively. The BOD_removal in the anaerobic lagoon ranged from 55 to 95%. The aerobic lagoon operated at loadings of 0.07 to 0.82 kg BOD_/m³.d and retention time of 24 to 43 days. The overall BOD₅ removal efficiency ranged from 84 to 92%. Temperatures during operation varied between 18° and 27°C. The overall performance of a combined aerated lagoon and stabilization pond at a beverage alcohol plant in the USA (ESE, 1974) was 96 and 73% BOD₅ and TSS removal respectively.

The oxidation ditch is similar to the aerated lagoon in that a surface aerator is used to supply the oxygen. When anaerobic lagoon effluent was treated in an oxidation ditch (Sundaram and Pachaiyappam, 1975) at an organic loading of 0.12 kg BOD per kg MLVSS, a BOD reduction of 98% was achieved.

(c) Trickling Filter

The trickling filter is an attached-growth biological process used by a few beverage alcohol plants for secondary treatment and is applicable for the treatment of wastewater from the ethanol production industry.

Waste characteristics	Treatment combination	Depth (m)	Organic loading (kg BOD ₅ / m ³ . d)	Retention time (days)	% BOD _s removal (%)	Reference
Distillery wastewater	Anaerobic lagoon + Aerobic lagoon	1.8 0.9	0.6–1.06 0.07–0.82	38–66 24–43	55—95 84—92	Rao (1972)
Beverage alcohol industry waste and sewage	Aerated lagoon + Stabilization pond + Chlorination	3.0 1.5			96	ESE (1974)
Anaerobically treated distillery wastewater	Oxidation ditch	1.0–1.5	0.12 kg BOD/kg MLVSS	_	98	Sundaram and Pachaiyappam (1975)

Table 4.5	. Performance of	of combined	processes	treating et	thanol	wastewaters
-----------	------------------	-------------	-----------	-------------	--------	-------------

Both low-rate rock filters and high-rate trickling filters have been evaluated for the treatment of distillery waste. Typical results are summarized in Table 4.6. Successful treatment by both low- and high-rate filters has been achieved. Callely <u>et</u> al. (1977) noted the advantage of high-rate filters. During the treatment of grain distillery wastes, conventional filters were able to operate at a loading rate of only 0.15 kg $BOD_5/m^3.d$, using a recycle ratio of 3:1. Using plastic media, it was possible to load the system to 1.72 kg $BOD_5/m^3.d$ and achieve 66% BOD_5 removal.

Trickling filters can be combined with other processes to increase the BOD removal. A 97% BOD reduction was achieved in a beverage alcohol plant in the USA when the treatment system consisted of two trickling filters in series followed by an aerated lagoon and two subsequent polishing ponds (ESE, 1974).

(d) Rotating Biological Contactors (RBC)

The rotating biological contactor (RBC) or biodisc has been used at several beverage alcohol facilities in combination with other treatment facilities. Several studies investigated the performance of RBCs with distillery wastewater. Results are summarized in Table 4.7.

Thomas & Koehrsen (1974) used RBCs for the treatment of grain distillery wastewater. After grit removal, the stillage passed through an aerated equalization tank. The effluent was treated by an RBC at a loading rate of 0.035 kg $BOD_5/m^3.d$. The overall BOD_5 removal was more than 92%. Antonie (1976) reported that 82 to 96% $BOD_5/m^3.d$. The treatment system consisted of an aerated lagoon followed by an RBC and a stabilization pond. This system, at a beverage alcohol industry in the United States, achieved overall BOD_5 and TSS reductions of 97 and 73% respectively (Radian Corporation, 1981).

Waste characteristics	Type of filter	lnitial BOD₅ (mg/L)	Organic Ioading (kg BOD₅/m³.d)	Recycle ratio	BOD₅ removal (%)
Rum distillery waste		405	0.05	_	00
(1% in sewage)	Low rate	485	0.95	3	96
Distillery wastewater	Low rate	—	0.45	4	93
Grain distillery evaporator condensate	Low rate		0.66 — 1.49	3 – 11	33 – 77
Distillery waste	Low rate	20,000	-	32	95
Whiskey distillery waste	High rate	1,000	—	-	98
Rum distillery waste (10% in domestic sewage)	Low rate Low rate	<u>-</u>	11.78 (COD) 5.37 (COD)	0.68 2	33.2 (COD) 46.4 (COD)
Molasses spent wash (1% in domestic sewage)	Two stage	485	0.96	3	≈95
Grain plant evaporator condensate	High rate	_	1.5	_	70
Grain distillery waste	High rate		1.7	3	66

Table 4.6. Biofiltration of stillage (Sheehan and Greenfield, 1980.)

Table 4.7. RBC treatment of ethanol wastewater (Thomas, 1974; Antonie, 1976; EPA, 1981.)

Waste characteristics	Initial	Organic	BOD	TSS
	BOD	loading	removal	removal
	(mg/L)	(kg BOD _s /m³.d)	(%)	(%)
Grain distillery evaporator condensate	-	0.035	>92	_
Distillery wastes	(i) 600—1000	0.0380.109	96-82	-
	(ii) 1300	0.109	<82	-
Beverage alcohol wastewater	—	_	50	10

(e) Anaerobic Processes

Numerous studies have reported the advantages and performance of anaerobic digestion processes with ethanol wastes. Anaerobic treatment is commonly considered as a single or only treatment process for ethanol wastes. It should be recognized, however, that anaerobic processes may be best used as the first step in the overall biological treatment of such wastes. Used in this manner, anaerobic processes can provide a major reduction in the pollutant load of these wastes and thus reduce the size, energy requirements, and costs of subsequent aerobic processes.

Typical results that have been obtained using mesophilic and thermophilic anaerobic processes for ethanol production wastes are identified in Tables 4.8 and 4.9.

Table 4.8 indicates the wide range of initial BOD_5 , raw materials and distillery wastes that have been used in these studies. The need for dilution was investigated by Radhakrishnan et al. (1969) in a mesophilic digester using molasses stillage. In spite of the dilution, as long as the organic loading was about the same (3.0 to 3.6 kg $BOD_5/m^3.d$), the BOD_5 removals were approximately 80%. At a specified hydraulic loading, the BOD_5 removal increased as feed concentration decreased.

Like other decomposable organic matter, distillery waste produces methane during anaerobic digestion. Boruff and Buswell (1932) digested distillery effluent at thermophilic temperatures and at loadings between 2.8 and 8.5 kg $BOD_5/m^3.d$. Biogas production was 3 to 7 L/L of digester. The gas contained about 54% methane. Buswell and Le Bosquet (1936) achieved 99% BOD_5 reduction with distillery waste. Biogas production was 685 L/kg of volatile solids fed. With blackstrap molasses stillage, Jackson (1966) reported 60% BOD_5 removal with 10 days retention time by thermophilic digestion. Gas production was 2.54 L/L of digester per day.

In Japan, about ten distilleries have produced methane from their waste using thermophilic and mesophilic anaerobic digestion (Ono, 1964). Ammon (1964) reported that methane recovery from distillery waste was a general practice in Germany. In India, Chakrabarty (1963) reported that 60% methane was generated by mesophilic anaerobic digestion of distillery wastes. Based on these results it was estimated that a distillery producing 100,000 gpd (455 m³/d) spent wash with an average BOD of 40,000 mg/L could obtain about 432,000 ft³ (12096 m³) of biogas per day with a total BTU of 276.5 x 10⁶ (291.7 kJ). This is the equivalent of about 6.6 tons of furnace oil having a BTU of 18,600/lb. By-product recovery in the form of the methane gas produced during anaerobic treatment could be used as an energy source within the alcohol plant.

Other anaerobic processes such as the upflow anaerobic sludge blanket process (Lettinga et al., 1980; Pipyn et al., 1979); the contact process (van den Berg & Lentz, 1977; Donelly, 1978) and the anaerobic filter (Witt et al., 1979; Braun & Huss, 1982) can also be used for the treatment of ethanol production wastes. Braun & Huss (1982) reported that anaerobic filter treatment is a potential process for molasses distillery slops without pretreatment or dilution. The performance of anaerobic filters under different operating conditions are summarized in Table 4.10.

Waste characteristics	Initial BOD (mg/L)	Organic loading (kg BOD ₅ /m ³ .d)	Hydraulic retention time (day)	BOD _s removal (%)
South African distillery waste	700	0.7	1.0	93
South African distillery waste	-	-	—	85
14% rum distillery waste at 28°C	_	-	_	87
German alcohol/yeast waste -				2
50% stillage/50% domestic sewage	10,000	-	_	80
Diluted distillery waste	-	8.8 (VS)	3.75	55 (TOC)
Cane molasses distillery waste	-		12	70
Cane molasses distillery waste	{			1
using 2 digesters in series	-	0.74	(i) 40	- 1
			(ii) 20	99
Cane molasses distillery waste				}
using 1 digester	-	max. 3.8	-	92
Distillery/yeast plant waste	-	2.4	-	96
Distillery spent washwater	-	6.7-11	8–12	90–95
Alcohol/compressed yeast plant waste	-	2.0	—	70
Molasses stillage (100%)	-	3.0	10.0	80
Molasses stillage (40%)	-	3.6	5.0	81.7
Molasses stillage (27%)	-	3.3	6.7	79.3
Distillery waste (33%)	-	1.9	5.0	89
Wine distillery waste	-	3.2	6.9	97.3
Malt distillery waste	25,000	4.0	6.2	95.6
Beet molasses distillery waste				
(continuous)	-	3.0	10.0	80.6
Beet molasses distillery waste				
(high rate)	32,000	3.2	10.0	95.9
Cane molasses stillage (65%)	65,000*	11.6 (min.)	5.6	72*
Cane molasses stillage (100%)	100,000*	5.9	16.7	71.9
Rum distillery waste – sludge recycle	33,000 - 55,000	0.09-1.2	35 - 221	60-80
Molasses distillery waste	15,000	1.8–2.4	-	9580
Cereal brewery stillage	22,620*	1.5	15	55* max
Cereal brewery stillage	22,620*	2.8	8.0	35*
Rum distillery waste – sludge recycle	55,000*	3.9	13.9	80*
Rum distillery waste plus yeast		_		
extract — sludge recycle	55,000*	9.9	5.5	80*
Wine stillage — sludge recycle	12,320	1.2	10.0	98.8
Concentrated yeast waste sludge				
recycle	3,0006,000	-	10.0	85

Table 4.8. Mesophilic anaerobic digestion of stillage (Sheehan and Greenfield, 1980)

* Value refers to COD measurement. (i) and (ii) refers to first and second digester respectively.

Waste characteristics	Initial BOD (mg/L)	Organic loading (kg BOD₅/ m³.d)	Hydraulic retention time (day)	BOD ₅ removal (%)	Methane generation (L/L of stillage)	Reference
Distillery waste	17,000 —	2.8 8.5	6 2	72 (VS) 58 (VS)	3 - 7	Boruff et al. (1932)
Distillery waste & trickling filter	15,000	max 2.4		99	685 (L/kg)	Buswell et al. (1936)
Distillery/yeast plant waste	-	6.43		96	-	Ono (1964)
Blackstrap molasses distillery waste	_	-	10	60	2.54	Jackson (1966)
Distillery waste (16.7%)	-	4.25	-	70	-	Sonoda et al. (1968)
Distillery waste (33.3%)	-	15.30	-	70	-	Sonoda et al. (1968)
Beet molasses distillery waste (continuous)	-	4.0 - 1.0	7 – 25	84 — 92	_	Basu (1975)
Beet molasses distillery waste (high rate)	-	2.0 - 3.5	10	87 – 97	-	Basu (1975)

Table 4.9. T	hermophilic anaerobic digestion of stillage
--------------	---

Table 4.10. Anaerobic filter treatment of distillery slops (Braun and Huss, 1982).

Waste characteristics	Initial COD (mg/L)	Volumetric Ioading (kg VS/m ³ .d)	Hydraulic retention time (day)	COD removal (%)	Gas production (m ³ /m ³ .d)
Molasses distillery slops					
a. without iron addition	45,000— 50,000	30	1.6	47	13
b. addition of 2 g/L FeSO ₄ .7 H ₂ O	45,000 50,000	40	1.3	50	18
c. addition of 4 g/L FeSO ₄ .7 H ₂ O	45,000 50,000	50	1.1	34	20

~

Tertiary Treatment

Tertiary treatment of ethanol production wastewater may be needed in certain cases. Granular-media filtration, air flotation and land application can be applicable with ethanol-for-fuel wastewater. However, neither granular-media filtration nor air flotation has been widely used for this purpose.

At one ethanol plant in the United States, air flotation was used to remove algae and SS from aerated lagoon effluents. Only in the beverage alcohol industry has land treatment been used. Two grain distilling plants have treated their wastewater by the slow rate (SR) process. Additional details about the land application of distillery wastes are discussed in a subsequent section.

Processes such as reverse osmosis, electroflocculation and electrosmosis have been studied but are not considered as viable treatment alternatives for ethanol wastes (Dubey, 1974; Sastry & Mohanrao, 1964).

Land Application

The application of alcohol industry wastewater to land has been used in many countries. This process recycles the organic matter and nutrients through a cropland system as the wastewater is treated by the biological, physical and chemical mechanisms in the soil. The rate of stillage application, crop grown, yield and performance of land treatment systems are summarized in Table 4.11.

High stillage loads applied to soil can deteriorate cane quality (Bajpai and Dua, 1972) and develop soil salinity problems (Monterio, 1975). To overcome these difficulties, Seehan & Greenfiled (1980) reported a desirable maximum loading of about $35-50 \text{ m}^3/\text{ha}$. In an Australian study an upper limit of $12 \text{ m}^3/\text{ha}$ was noted (Seehan and Greenfield, 1980). In India, Bajpai and Dua (1972) conducted a detailed study on the fertilizer value of spent wash using sugar cane as the test crop. The irrigation of diluted (20%) spent wash, up to an application rate of 200 kg N/ha, increased sugar cane yield. Higher rates (300 kg N/ha) adversely affected the yield, the cane quality, and the nitrogen in the soil.

In Brazil, extensive studies have been undertaken (Planalsucar, 1980, 1982) to evaluate the land application of vinasse using commercial sprinkler systems. The application had a positive effect on agricultural yields. Initial results indicated that for clayey soils, the threshold dosage of potassium applied through vinasse was approximately 400 kg K₂O/ha while for sandy soils, the threshold rate was about 600 kg K₂O/ha. Other studies have indicated that the minimum dosage of K₂O using sprinkler irrigation is 200 kg/ha and the ideal dosage is about 400 kg/ha.

The practical utilization of vinasse must take the following into account:

- the type and natural fertility of soils,
- the nutrient concentration in the vinasse,
- the crop species to be grown, and
- the climate and precipitation patterns.

Table 4.11. Land application of distillery wastes (Sheehan and Greenfield, 1980).

·							
Country	Brazil	NA	ъ	NA	NA	NA	Australia
Experience	Yield increase, overdose causes fly breeding	Higher applications may cause odor problems	J	38% yield increase	Increased cane yield and reduced weeds	45 – 100% yield increase	Yield was equal with K ₂ O treated slop; ash content juice was slightly higher
Concentrated or diluted stillage	Concentrated	Concentrated	Concentrated	Concentrated	AN	diluted to 25% solids	NA
Supplemental fertilizer or lime	٩	* 4 Z	Lime	N,P,K	۲Z	Ą	٩ N
Irrigation period	Once in 4 yrs.	per day	two week interval	NA	ΨN	Per year	AN
Application rate (m ³ /ha)	650–5,830 (based on pH of soil)	3 3	50	382 - 419	185	200	6.4 - 12.9
Crop grown	Sugar cane	Sugar cane	NA	Sugar cane	Sugar cane	Grass, maize and fodder	Sugar cane

* Information is not available.

In Brazil, theoretically, the application of 100 m^3 of mixed vinasse is sufficient to replace the mineral tertilization of one hectare of sugar cane. Sprinkler irrigation of vinasses was indicated to be five times less costly than furrow or truck irrigation and five to six times less costly than mineral fertilization of the crop.

4.3 Solid Waste Treatment and Disposal

Various solid or semi-solid wastes are generated at ethanol plants (Section 3.2). Some result from the ethanol production while others are formed during power generation when coal fired boilers are utilized. Fig. 4.3 indicates the treatment and disposal options for the solid wastes from ethanol production facilities.

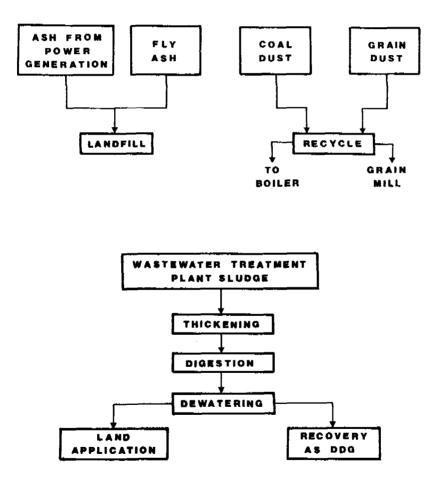


Fig. 4.3 Treatment and disposal options for the solid waste trom ethanol production

Treatment and land disposal of the solid wastes must be carried out in an environmentally acceptable manner to prevent surface and ground water contamination. For bottom ash and fly ash, landfills may be the best available disposal option. Other particulates from an alcohol plant include grain dust from grain handling and coal dust from coal handling and pulverizing. The grain dust can be collected and recycled to grain milling operations, while coal dust can be recovered and burned as fuel.

Biological treatment processes generate sludge which also needs proper handling and disposal. This can be done by thickening, stabilization by digestion, dewatering and possible reuse. A molasses-based ethanol plant in the United States (Radian Corporation, 1981) used aerobic digestion for the stabilization of excess activated and primary sludge mixtures. A disadvantage of aerobic digestion is the power requirement for the needed oxygen. Vacuum filtration, centrifugation or drying beds can be a part of a sludge treatment system. Vacuum filtration can achieve a solids content of up to 20-30%. At higher solids content, the sludge is easily handled as cake. A solids centrifuge is able to achieve a solids content of 10-35% solids. Sludge at this concentration is semi-solid and can be trucked to landfills. Sludge-drying lagoons provide a non-mechanical means of dewatering the waste biological sludge, and are the most widely used sludge-dewatering method in the United States.

The biological sludge from ethanol wastewater treatment can be returned to the dryer for DDG production and used as animal feed. This can be a preferred option for the ethanol producer utilizing corn grain as a feedstock. For low-protein stillage produced from sugar cane, the common practice is stabilization and/or disposal.

After dewatering, the sludge that is not recovered is sent to ultimate disposal. The most common options are landfills and land application. In the United States, about 6% of the ethanol fuel plants in operation use land application as the sludge disposal alternative (Radian Corporation, 1981).

V RECOVERY AND REUSE

Recovery and reuse of constituents in the waste is another possibility to reduce the pollution load. Many possibilities exist for the utilization of residues resulting from the processing of agricultural products (Loehr, 1984), such as is done in the production of alcohol. The more feasible approaches for ethanol production wastes have been the production of biomass and biochemicals and the use of stillage as animal feed.

5.1 Production of Biomass and Biochemicals

There is some interest in the production of biomass and biochemicals from ethanol production residue. At present, most of the possibilities are in laboratory or pilot plant stages of evaluation.

Stillage can be used to produce yeast. During this process, 40-50% of the stillage BOD is reduced. <u>Candida utilis</u> and <u>Candida tropicalis</u> have received the most attention. The yield of yeast depends on the concentration of substrate and nutrients, and on the pH, temperature and retention period.

The use of stillage to produce algae (<u>Chlorella pyrenoidosa</u> and <u>Chlorella vulgaris</u>) and fungi (<u>Penicillium</u> and <u>Aspergillus</u> foetidus NRRL 337) resulted in substantial reduction of BOD₅ (Hang, et al., 1977; Seehan & Greenfield, 1980). Distillers' solubles have been used in the media for commercial antibiotic production (Sundaram & Pachaiyappam, 1975). Production of a feed riboflavin and vitamin B concentrate and the production of feed B₁₂ concentrate containing an antibiotic using screened stillage as the basic media has occurred (Sundaram & Pachaiyappam, 1975).

5.2 Stillage As An Animal Feed

The nutritional value of the stillage has been recognized (Rastogi & Krishna, 1963; Dubey, 1974; Robertiello, 1982). Due to their high nutritional value, concentrated sugar beet vinasses may be utilized in animal feeds (Robertiello, 1982). The high potash content in such material is considered as a deterrent because it can cause diarrhea (Lewiki, 1978). The K/Ca ratio of the animal feed should be maintained in the desirable range to avoid animal health problems. Dubey (1974) noted the low calcium content in stillage and suggested that CaCO₃ be added before it is used as cattle feed. Mixing dry stillage with forage has been proposed. Production of animal feed consisting of beet pulp with 7-20% fodder yeast grown on stillage was reported (Seehan & Greenfield, 1980).

Many studies have quantified the effect of stillage as a cattle food supplement. During a cattle feeding trial experiment, the daily weight gains were observed to be 50-80 g higher when stillage (1.5 kg of 72-74% stillage) was used in place of molasses (Sheehan & Greenfield, 1980). It was also reported that dairy cows fed 91% straw and 9% stillage per day supplemented with protein gave 1 kg of extra milk per kg of stillage fed to them. Cattle feeding costs were reduced by 13-23% by using feed containing 53% stillage (Seehan & Greenfield, 1980).

Stillage digestibility is approximately 50-60% (Lewiki, 1978) and can be up to 10% of a ruminant diet but only 2-3\% of pig diets. The above studies indicate that stillage and DDG (dry distillers' grain) can be used as a cattle food supplement.

VI SUMMARY AND CONCLUSIONS

There continues to be global interest in the production of ethanol for fuel from biomass. The wastes resulting from the ethanol production must be treated in an economic and environmentally sound manner.

Depending on the feedstock used, there can be different processes used for ethanol production. In starch-derived ethanol production plants, the processes include grain processing, starch to sugar conversion, cooking and cooling, solid mash separation and by-product recovery. Somewhat different processes are used in sugar-based ethanol plants.

Similar types of solid wastes (bottom ash, particulate matter from the boiler plant, sludge from wastewater treatment plants) are generated in both types of ethanol plants. In addition, corn based plants generate solid wastes such as grain dust, solid mash from the separator or DDC from the by-product recovery unit.

The sources of wastewater in a molasses-based ethanol plant are stillage, fermenter and condenser cooling water, fermenter washwater and the washwater from cleaning equipment and floors. In corn-based plants, the additional sources of wastewater are flash cooler condensate from cooking and cooling units and evaporator condensate from the by-product processing units. In both these types of plants, non-contact cooling and boiler blowdown are generated.

In most cases, the cooling waters are the main fraction of the hydraulic load at the ethanol plants. The cooling waters are either recycled in the process or discharged separately. The extent to which each of the remaining sources contribute to the total plant raw waste load varies, and is a function of design and process parameters, such as the choice of feedstock, the form and extent of by-product recovery or extraction, water reuse and recycling and the desired product quality. The approximate hydraulic loads from the major unit processes, based on data from three grain ethanol plants, are 50-77% from evaporator condensate, 11-36% from flash cooler condensate of cooking and cooling units and 7-28% from distillation units. In a molasses-based ethanol plant, the stillage quantity ranged between 135-1800 m³/d while fermenter washwater may be only 5% of this value.

The wastewater flow rate varies with the plant production capacity. The wastewater flow rate per unit of ethanol produced varies from 7 to 34 and is a function of the feedstocks and the process scheme used for ethanol production.

The quantity of solid wastes from the supporting facilities can also vary widely; 1-20 g sludge, 60-510 g ash and 30-150 g dust per liter of ethanol production.

Among the process waste streams, flash cooler condensate (cooking and cooling unit), distillation bottoms, and evaporator condensate have high concentrations of BOD and a low pH (except for evaporator condensate). The washwater contains a high concentration of $BOD_{_{2}}$, TSS, and a wide variation in pH (4-13).

Out of 101 potentially toxic organics evaluated, only 11 appeared to be present in significant amounts (greater than 10 mg/L). Except for copper, nickel, lead and zin, metals were in low concentrations.

The concentrations of conventional pollutants appeared higher in molasses-based ethanol plant wastewater than in corn-based plant wastewater. Higher concentrations of inorganics occurred in the wastewater from the molasses-based plants.

A number of treatment, disposal and utilization methods for ethanol plant waste are possible. These methods include in-plant control methods, physical, chemical, and biological treatment processes, and land treatment. By-product recovery processes, such as yeast production and the use of separated solids for animal feed, are also possible.

This review indicates that:

- 1. Ethanol production plant have the potential to cause environmental problems if the wastes from such plants do not receive proper treatment or disposal.
- Cooling tower blowdown is a major wastewater volume. The blowdown should be separated from other wastewaters or reused in the process.
- 3. The characteristics of the wastewaters depend on the feedstocks and the processes used. The evaporator condensate, flash water condensate and washwater in a corn-based ethanol plant having a by-product recovery system are the main sources of the organic load. In a molasses-based ethanol plant, distillation bottoms and washwater are the main sources of the organic load.
- 4. The solid wastes are generated primarily from the supporting facilities. Grain dust and the solid mash generated from corn-based ethanol plants can be used as by-products.
- 5. The available data indicates that with proper design and operation of the treatment facilities, high pollutant removals can be achieved.
- 6. If adequate land is available, land treatment can be a feasible treatment method either alone or in combination with other processes.
- Recycle and reuse of the ethanol plant wastewater can reduce the pollutant load.
- Recovery of the by-products (DDG, animal feed, yeast fodder, fertilizers) from ethanol wastewater is an option that will reduce the pollutant load.
- 9. Solid wastes can be disposed of by landfilling, recycling or by-product use.

ACKNOWLEDGEMENT

While assisting in the preparation of this article, Dr. Sengupta was a visiting Senior Scientist at Cornell University and was supported by a World Health Organization (WHO) Fellowship. The assistance provided by the WHO is gratefully acknowledged.

REFERENCES

- Acruex Corporation (1980) "Testing and Evaluation of On-Farm Alcohol Production Facilities." Contract No. 68003-2567, LESC Task 4032, U.S. Environmental Protection Agency.
- Ammon, F.K.V. (1964). Discussion on the paper "Utilization of Materials Derived from Treatment of Wastes from Molasses Distilleries" by T.R. Bhaskaran. <u>Proceedings</u> of the 2nd International Conference on Water Pollution Research, Tokyo. pp. 100-104.
- ANL Argonne National Laboratory (1980). "Alcohol Production from Agricultural and Forestry Residuals, A Technology Assessment of Solar Energy System." Report No. DOE/EV-0108 UC-58b, U.S., Department of Energy, Washington, DC.
- Antonie, R.L. (1976). "Fixed Biological Surfaces--Wastewater Treatment." CRC Press, Cleveland. p. 109.
- Bajpai, P.D. & Dua, S.P. (1972). "Studies on the Utility of Distillery Effluent (spent wash) for Its Manurial Value and Its Effect on Soil Properties." <u>Indian Sugar</u>, pp. 687-689.
- Basu, A.K. (1975). "Characteristics of Distillery Wastewater." J. Water Poliut. Control Fed., 47(8): 2184-2190.
- Bhaskaran, T.R. (1964). "Utilisation of Materials Derived from Treatment of Wastes from Molasses Distilleries." <u>Advances in Water Pollution Research</u>, 2. Edited by Baars, J.K., Pergamon Press, New York, pp. 85-104.
- Boruff, C.S. & Buswell, A.M. (1932). "Power and Fuel Gas from Distillery Wastes," Ind. Eng. Chem., 24(1): 33-36.
- Braun, R. & Huss, S. (1982). "Anaerobic Filter Treatment of Molasses Distillery Slops." Water Res., 16(7): 1167-1171.
- Burkhead, C.E.; Lessig, C.A., Jr. & Richardson, T.R. (1968). "Biological Treatment of Distillery Waste." <u>Proceedings, 23rd of Industrial Waste Conference.</u>, Purdue University, Lafayette, Ind. pp. 795-797.
- Buswell, A.M. & Le Bosquet, M. (1936). "Complete Treatment of Distillery Wastes." Ind. Eng. Chem., 28(8): 795-797.
- Callely, A.G.; Forster, C.F. & Stafford, D.A. (eds.) (1977). "Treatment of Industrial Effluents." Hodder & Stoughton, London.
- Chakrabarty, R.N. (1963). "Potash Recovery -- A Method of Disposal of Distillery Wastes and Saving Foreign Exchange." Symposium on Ethyl Alcohol Production Technique, New Delhi, India. Noyes Development Corp., N.Y. (1964). pp. 93-97.

- Dock, J.S. et al. (1981). "Environmental Control Perspective for Ethanol Production from Biomass," <u>Proceedings of the Energy from Biomas and Wastes V Symposium</u>, Institute of Gas Technology, Lake Buena Vista, Florida. pp. 1015-1038.
- Donelly, T. (1978). "Industrial Effluent Treatment with the Bioenergy Process." Proc. Biochem., 13(6): 14-16.
- Dubey, R.S. (1974). "Distillery Effluents -- Treatment and Disposal." <u>Sugar News</u> Annl., 6: 9-26.
- EPA U.S. Environmental Protection Agency (1979). "Proceedings of the Environmental Evaluation of Gasobol Production and Health Effects." Report No. EPA-907/9-79-005.
- ESE Environmental Science Engineering (1974). "Draft Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Beverages Segment of the Miscellaneous Foods and Beverages Point Scource Category." Effluent Guideline Division, Environmental Protection Agency, Washington, D.C.
- Gupta, S.C.; Shukla, J.P. & Shukla, N.P. (1968). "Recovery of Crude Potassium Salts From Spent Wash of Molasses Distilleries by Fluidized Incineration." <u>Proceedings, 36th Annual Convention Sugar Technology Association</u>. India, pp. xxxxii-1 - xxxxiii-7.
- Hang, Y.D.; Splittstoesser, D.F.; Woodams, E.E. & Sherman, R.M. (1977). "Citric Acid Fermentation of Brewery Waste." J. Food Sci., 42(2): 383-384.
- Hiatt, W.C.; Carr, A.D. & Andrews, J.F. (1973). "Anaerobic Digestion of Rum Distillery Wastes." <u>Proceedings</u>, 34th Industrial Waste Conference, Purdue University. pp. 966-976.
- Hira, A.U.; Mulloney, J.A., Jr. & D'Alessio, G.J. (1983). "Alcohol Fuels from Biomass." Environ. Sci. Technol., 17(5): 202-213.
- Jackman, E.A. (1977). "Distillery Effluent Treatment in the Brazilian National Alcohol Program." Chem. Eng. (London), 319: 239-242.
- Jackson, C.J. (1966). "Fermentation Waste Disposal in Great Britain." Proceedings, 21st Industrial Waste Conference, Purdue University, Lafayette, Ind., pp. 19-32.
- Kalter, R.J. et al. (1980. "Ethanol Production in Northern New York: Technical and Economic Feasibility." ERDA Report 80-22. Department of Agricultural Economics, Cornell University, Ithaca, N.Y.
- Kishore, K.; Jain, A.K.; Shanker, G. & Shukla, S.D. (1979). "Utilization of Distillery Waste." Chem. Age India, 30: 823-826.

- Kuby, W.; Nackord, S. & Wyss, W. (1984). "Testing and Evaluation of an Alcohol <u>Production Facility Using Potatoes as a Feedstock.</u>" Industrial Environmental Research Laboratory, Environmental Protection Agency, Cincinnati, OH.
- Lettinga, G.; Van Velsen, L; de Zeeuw, W. & Homba, S.W. (1980). "The Application of Anaerobic Digestion to Industrial Pollution Treatment." <u>Proc. 1st Int. Symp.</u> <u>Anaerobic Digestion</u>. Edited by Stafford <u>et al</u>., Applied Science Ltd., London. <u>pp. 167-186</u>.
- Lewiki, W. (1978). "Production, Application and Marketing of Concentrated Molasses-Fermentation Effluent (Vinasses)." Proc. Biochem., 13(6): 12-13.
- Loehr, R.C. (1984). "Pollution Control for Agriculture," second edition. Academic Press, New York, NY.
- Longdong, D. (1969). "Purification of Wastes from a German Yeast Plant." Proceedings, 24th Industrial Waste Conference, Purdue University, Lafayette, Ind., pp. 770-788.
- Monterio, C.E. (1975). "Brazilian Experience With the Disposal of Wastewater from the Cane Sugar and Alcohol Industry." Proc. Biochem., 10(9): 33-41.
- NRC National Research Council (1983). "<u>Alcohol Fuels: Options for Developing</u> Countries." National Academy Press, Washington D.C.
- Ono, H. (1964). Formal Discussion on Paper by Bhaskaran, T.R. Proc. 2nd Int. Conf. Water Poll. Res., Tokyo. Edited by Baars, J.K., Pergamon, Oxford, pp. 100-104.
- Paul, B.B. (1972). "By-Product Industry Based on Distillery Effluent for Manufacture of Chicken and Cattle-Feed and Mixed Fertilizers. <u>Chem. Age of India</u>, 23: 875–878.
- Philip, V. & Panicker, P.K.N. (1964). "Alcohol Distillery Stillage -- Utilization and Disposal." Chem. Age India, 15: 177-181.
- Pipyn, P.; Verstraete, W. and Ombregt, J.P. (1979). "A Pilot Scale Anaerobic Upflow Reactor Treating Distillery Wastewaters." Biotechnol. Lett., 1: 495-500.
- Planalsucar. (1980, 1982). "Programa Nacional de Melohoramento da Cana-de-Acucar," Annual Report, Ministry of Industry and Commerce, Brasilia, Brazil.
- Radhakrishnan, I.; De S., B. & Nath, B. (1969). "Evaluation of Loading Parameters for Anaerobic Digestion of Cane Molasses Distillery Waste." J. Wat. Pollut. Control Fed., Part 2, 41(11): R431-R440.
- Radian Corporation (1981). "Draft Development Document for Proposed Effluent Limitations Guidelines New Source Performance Standards and Pretreatment Standards for Ethanol-for-Fuel Point Source Category." U.S. Environmental Protection Agency.
- Rao, B.S. (1972). "A Low-Cost Waste Treatment Method For the Disposal of Distillery Waste (Spent Wash)." Water Res., 6(11): 1275-1282.

Rastogi, M.K. & Krishna, M.C.R. (1963). "Preparation and Properties of a Protein Digest Made From Distillery Sludge." <u>Symposium of Ethyl Alcohol Production</u> <u>Technique</u>, New Delhi, India. Noyes Development Corp., N.Y. (1964), pp. 98-104.

- Robertiello, A. (1982). "Upgrading Agricultural and Agro-Industrial Waste: The Treatment of Distillery Effluents (Vinasses) in Italy." <u>Agric. Wastes</u>, 4(5): 387–395.
- Sastry, C.A. & Mohanrao, G.J. (1964). "Treatment and Disposal of Distillery Wastes." Symp. on Ethyl Alcohol Production Technique, New Delhi, India. Noyes Development Corporation, N.Y. pp. 88-92.
- Scarberry, R.M.; Papai, M.P. & Braun, M.A. (1979) "Source Test and Evaluation Report. Alcohol Facility for Gasohol Production." Radian Cooperation for U.S. EPA, NTIS No. PB82-237041.
- SERI Solar Energy Research Institute (1980). "Fuel from Farms -- A Guide to Small Scale Ethanol Production." SERI/SP451-519, UC-61.
- Sheehan, G.J. & Greenfield, P.F. (1980). "Utilization, Treatment and Disposal of Distillery Wastewater." Water Res., 14: 257-277.
- Sonada, Y. & Tanaka, M. (1968). "Anaerobic Digestion of Low Concentration Wastes. 1. Continuous Digestion Tests of Some Industrial Wastes." <u>J. Ferment. Technol.</u>, 46: 789-795.
- Sundaram, S.S. & Pachaiyappam, V. (1975). "Distillery Wastes Disposal and By-Product Recovery." Chem. Age of India, 26: 139-155.
- Sweeten, J.M. et al. (1982). "Nutrient Recovery and Pollution Control from Ethanol Stillage", Proceedings of the Energy from Biomass and Wastes VI Symp., Inst. of Gas Technology, Lake Buena Vista, FL.
- Thomas, J.L. & Koehrsen, L.G. (1974). "Activated Sludge Bio-Disc Treatment of Distillery Wastewater." EPA-660/2-74-014.
- Van den Berg, L. & Lentz, C.P. (1977). "Food Processing Waste Treatment by Anaerobic Digestion." <u>Proceedings, 32nd Industrial Waste Conference</u>, Purdue University. pp. 252-258.
- Verma, S. R. and Dalala, R.C. (1976). "Toxicity of Distillery Waste to <u>Puntius</u> <u>Sophore</u> (Ham) and <u>Mystus vittatus</u> (Bloch) (Piscesi caprinidae: Bagridae) Part
 Bioassay Studies and TLM Determination." <u>Acta Hydrochem. Hydrobiol.</u>, 4: 547-552.
- Witt, E.R.; Humphrey, W.J. & Roberts, T.E. (1979). "Full Scale Anaerobic Filter Treats High Strength Wastes." <u>Proceedings</u>, 34th Industrial Waste Conference, Purdue University. pp. 229-234.

APPENDIX

Multiply the U.S. custom	iary unit		To obtain the SI unit		
Name	Symbol	bγ	Symbol	Name	
Acceleration					
feet per second squared	ft/s²	0.3048	m/s ²	meters per second squared	
inches per second squared	in/s²	0.0254	m/s²	meters per second squared	
Area					
acre	acre	0.4047	ha	hectare	
acre	acre	4.0469 X 10 ⁻³	km ²	square kilometer	
square foot	ft²	9.2903 X 10 ⁻²	m²	square meter	
square inch	in ²	6.4516	cm ²	square centimeter	
square mile	mi²	2.5900	km²	square kilometer	
square yard	yd²	0.8361	m²	square meter	
Energy					
British thermal unit	Btu	1.0551	kJ	kilojoule	
foot-pound (force)	ft lb	1.3558	JJ	joule	
horsepower-hour	hp h	2.6845	MJ	megajoule	
kilowatt-hour	kŴ h	3600	kJ	kilojoule	
kilowatt-hour	k₩ h	3.600 X 10 ⁶	J J	joule	
watt-hour	Wh	3.600	kJ	kilojoule	
watt-second	Ws	1.000	J	joule	
Force					
pound force	lb _f	4.4482	N	newton	
Flow rate					
cubic feet per second	ft ³ /s	2.8317 X 10 ⁻²	m ³ /s	cubic meters per second	
gallons per day	gal/d	4.3813 X 10 ⁻⁵	L/s	liters per second	
gallons per day	gal/d	3.7854 X 10 ⁻³	m³/d	cubic meters per day	
gallons per minute	gal/min	6.3090 X 10 ⁻⁵	m ³ /s	cubic meters per second	
gallons per minute	gal/min	6.3090 X 10 ⁻²	L/s	liters per second	
million gallons per day	Mgal/d	43.8126	L/s	liters per second	
million gallons per day	Mgal/d	3.7854 X 10 ³	m³/d	cubic meters per day	
million gallons per day	Mgal/d	4.3813 X 10 ⁻²	m ³ /s	cubic meters per second	

Table A. Metric Conversion Factors (U.S. Customary units to SI Units) (After METCALF and EDDY, 1979) *

*Wastewater Engineering, Treatment, Disposal, Reuse. McGraw Hill, Inc., New York, NY, U.S.A.

Multiply the U.S. customa	ary unit			To obtain the SI unit
Name	Symbol	by	Symbol	Name
Length			-+	
foot	ft	0.3048	m	meter
inch	in	2.54	cm	centimeter
inch	in	0.0254	m	meter
inch	in	25.4	mm	millimeter
mile	mi	1.6093	km	kilometer
yard	γd	0.9144	m	meter
Mass				
ounce	οz	28.3495	g	gram
pound	lb	4.5359 X 10 ²	g	gram
pound	lb	0,4536	kg	kilogram
ton (short: 2000 lb)	ton	0,9072	Mg (metric ton)	megagram (10 ³ kilogram)
tonne (long: 2240 lb)	ton	1.0160	Mg (metric ton)	megagram (10 ³ kilogram)
Power			1	
British thermal units per second	Btu/s	1.0551	kW	kilowatt
foot-pounds (force) per second	ft-lb _f /s	1.3558	W	watt
horsepower	hp	0,7457	kW	kilowatt
Pressure (force/area)				
atmosphere (standard)	atm	1.0133 X 10 ²	$kPa (kN/m^2)$	kilopascal (kilonewtons per square met
inches of mercury (60°F)	in Hg (60°F)	3.3768 X 10 ³	Pa (N/m ²)	pascal (newtons per square meter)
inches of water (60°F)	in H ₂ O (60°F)	2.4884 X 10 ²	Pa (N/m ²)	pascal (newtons per square meter)
pounds (force) per square foot	lb _f /ft ²	47.8803	Pa (N/m ²)	pascal (newtons per square meter)
pounds (force) per square inch	lb_f/in^2	6.8948 X 10 ³	$Pa (N/m^2)$	pascal (newtons per square meter)
pounds (force) per square inch	lbs/in ²	6.8948	kPa (kN/m²)	kilopascal (kilonewtons per square met
remperature				
degrees Fahrenheit	°F	0.555(°F - 32)	°C	degrees Celsius (centigrade)
degrees Fahrenheit	°F	0.555 (°F + 459.67)	°ĸ	degrees Kelvin
Velocity				
feet per second	ft/s	0.3048	m/s	meters per second
miles per hour	mi/h	4.4704 X 10 ⁻¹	m/s	kilometers per second

Multiply the U.S. cu	stomary unit		1	To obtain the SI unit
Name	Symbol	by	Symbol	Name
Volume acre-foot cubic foot cubic foot cubic inch cubic yard gallon gallon ounce (U.S. fluid) imperial gallon	acre-ft ft ³ in ³ yd ³ gal gal oz (U.S. fluid) imp. gal	1.2335 X 10 ³ 28.3168 2.8317 X 10 ⁻² 16.3871 0.7646 3.7854 X 10 ⁻³ 3.7854 2.9573 X 10 ⁻² 4.546	m ³ L m ³ cm ³ m ³ L L L L	cubic meter liter cubic meter cubic centimeter cubic meter cubic meter liter liter liter

Table A – (C	continued)
--------------	------------