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Project Summary

Testing and Evaluation of On-Farm Alcohol Production Facilities

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This report gives the results of a sampling and analysis program managed by the Industrial Environmental Research Laboratory in Cincinnati, Ohio (IERL-Ci), to characterize the air emissions, water effluents, and solid residuals from two on-farm ethanol production processes sampled in June 1980.

Gaseous emissions, both vented and ambient, were analyzed in the field for CO_2, O_2, and hydrocarbons, including some 21 alcohols and aldehydes. CO_2 was the only compound identified in the vents. No significant increase in concentration of CO_2 was found in the ambient air. No other significant air emission problems were identified.

Liquid and solid samples of the feedstock, make-up water, distillation feed, byproduct, beer bottoms, product, and washout water were analyzed in the laboratory for priority pollutants, metals, herbicides and pesticides, and other standard chemical parameters (e.g., Biological Oxygen Demand, Chemical Oxygen Demand). The most significant result was the identification of very high Biological Oxygen Demand, Chemical Oxygen Demand, Total Organic Carbon, and Total Suspended Solids levels in both process and waste streams. The streams were also acidic (i.e., pH less than 4). The levels of priority pollutants were below current promulgated Resource Conservation and Recovery Act standards, but some metals exceeded selected state standards.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The objective of this program was to test and characterize the effluents and emissions from two farm-scale (approximately 6,000 gallons/year) ethanol production facilities. The two sites were in Kansas (Site A) and Nebraska (Site B). In both cases, the feedstock was corn and the enzymes used were a carbohydrate enzyme (brand name Taka-therm) and a glucohydrolase enzyme (brand name Diazyme L-100). Surfuric acid was added as a pH control.

During the batch sampled at Site A, the process produced 126 gallons of 88.6 percent (177 proof) ethanol from the 75 bushels of ground grain (56 pounds per bushel) or a yield of 1 5 gallons of anhydrous ethanol per bushel of ground grain. Ten thousand and four hundred pounds of byproduct for animal feed and 950 gallons of beer bottoms as waste were computed from a mass balance based on measured quantities and composition analysis. Section 5 of the full report contains a detailed analysis of these effluents.

During the batch sampled at Site B, the process produced about 13 gallons of approximately 73.6 percent (147 proof) ethanol from the 15 bushels of ground grain (56 pounds per bushel) or a yield of 0.6 gallon of anhydrous ethanol per bushel of grain A total of 3,350 pounds of byproduct for animal feed and 145 gallons of beer bottons as waste were computed from a mass balance based on measured quantities and composition analysis. The Analytical Results section of the full report contains a detailed analysis of these effluents.

The gaseous emissions, both vented and ambient were sampled using an extractive system. The sample gas was also split into two streams: one going to a total hydrocarbon monitor and the other to a gas chromatograph. The total hydrocarbon instrument monitored total hydrocarbons in the gas stream while the gas chromatograph speciated the components of the gas stream. Table 1 lists the compounds screened for by the gas chromatograph. The gas velocity in the vent was measured by using a hot wire anemometer flow measuring device. The sensing probe was inserted upstream of the gas sampling probe. Liquid and solid samples were taken of each of the solid and liquid effluents at the appropriate points.

Methodologies used for organics analysis are based on EPA Methods, the FDA Pesticide Analytical Manual, and *Standard Methods for the Examination of Water and Wastewater* 14th Ed. APHA, AWWA, WPCF. Aqueous samples were analyzed according to Table 2 and solid samples were analyzed according to Table 3.

Analytical methodologies used for the general chemistry analyses were based on *Standard Methods for the Examination of Water and Wastewater* 14th Ed. APHA, AWWA, WPCF, and *Methods for the Analysis of Water and Wastes*, EPA, March 1979. Aqueous samples were analyzed according to Table 4. The analytical procedures for high solid samples were basically the same as for the liquid samples (Table 4).

Metals were determined by atomic absorption spectrophotometry. Samples were digested with nitric acid. Mercury was determined by the cold vapor technique. Other metals were determined by either flame or graphite furnace atomization of the acid digest.

Analytical Results

The laboratory and field analytical results are presented and discussed in this section. A brief description of the quality control procedures is also included. The actual results for precision, accuracy, and recovery experiments are given in Appendix A of the full report.

The laboratory analytical sample matrix is shown in Table 5. Table 6 gives the ethanol content in the various streams.

The data are organized as follows:

- Conventional parameters
- Metals, cyanide, and phenols

Table 1. *Species Screened for by Gas Chromatograph*

Alcohols	
Methanol	*2-methyl 2-propanol*
Ethanol	*1-pentanol*
1-propanol	*2-pentanol*
2-propanol	*3-pentanol*
1-butanol	*2-methyl 1-butanol*
2-butanol	*3-methyl 1-butanol*
2-methyl 1-propanol	*2-methyl 2-butanol*
Aldehydes	
Formaldehyde	*Valeraldehyde*
Propionaldehyde	*Isovaleraldehyde*
Butyraldehyde	*Furfuraldehyde*
Isobutyraldehyde	

Table 2. *Aqueous Samples*

Analysis	*Method*
Extractable organics by GCMS	*EPA 625*
Volatile organics analysis (purge and trap)	*EPA 624*
Herbicides	*Standard Method 509B*

Table 3. *Solid Organic Analyses*

Analysis	*Method*	*Note*
Pesticides	*FDA 211 13e*	
Herbicides	*FDA 222.13c*	
Volatile organics analysis (purge and trap)	*EPA 624*	*Dilute with organic-free water*
Base/neutral and acid fraction	*EPA 625*	*Soxhlet Extraction*

Table 4. *Aqueous General Chemical Analyses*

Analysis	*Method*
BOD_5	*5-day incubation, sample analyzed for oxygen depletion*
COD	*Acid dichromate reflux, back titrate with ferrous ammonium sulfate*
TOC	*Conversion to CO_2, infrared quantitation*
Total suspended solids	*Gravimetric, 105°C, weigh residue on filters*
Total solids	*Gravimetric, 105°C, weigh residue*
Phenols	*Distill, amino antipyrine color, $CHCl_3$ extraction.*
Cyanides (total)	*Distill, barbituric acid colorimetry*
Ammonia	*Distill, followed by nesslerization*
Nitrate	*Brucine colorimetric*
Sulfate	*Turbidimetric*
Phosphorous	*Nitric/sulfuric acid digest, ascorbic acid colorimetry*
Specific conductance	*Wheatstone bridge conductivity*
Metals	*Atomic absorption spectrophotometry following acid digestion. Analysis by cold-vapor flameless AA (Hg), flame and graphite furnace analyses as appropriate for others*
pH	*Electrometric*
Total Kjeldahl nitrogen	*Sulfuric acid mercuric oxide digestion, distillation, nesslerization*

Metals: Al, Sb, As, Ba, Be, Bi, Cd, Ca, Cu, Cr, Fe, Pb, Mg, Mn, Hg, Ni, Se, Ag, Tl, Ti, and Zn

- Priority pollutants
  - Acid compounds
  - Base/neutral compounds
  - Volatile organics
  - Pesticides and herbicides

The process waste streams (beer bottoms and washout water) exhibited certain common characteristics of high BOD_5, COD, TSS and TOC, and low pH (acidic).

Solids and oxygen demand were extremely high but decreased over time through the system. The analytical values for Site B are probably on the low side because of the warming of the samples in transit. Laboratory analyses indicated that most of the substances contributing to oxygen demand were biodegradable.

The discharge of the materials high in free and bound nutrients (i.e., nitrogen and phosporous) stimulate biological activity. All process streams exhibit this characterization. Nutrients are an important limiting factor in the growth of all plants. With all other factors being equal, the rate and profuseness of plant growth is proportional to the amount of nutrient available. A high concentration of nutrients will produce rapid plant growth first becoming apparent as algae bloom. The term "bloom" is used when the concentration of individual species exceeds 500 individuals per milliliter of water.

The results from the metals analyses indicate that the corrosivity (low pH) problem might be significant. Metals (Ca, Cu, Fe, Mg, Mn, and Zn) detected at significant levels tended to increase in concentration through the system; however, the metals did tend to concentrate in the byproduct even though the pH of the byproduct and liquid streams were similar. The sources of metals throughout the process included the valves and general piping, squeezer trough, distillation columns, and holding and settling tanks. The low pH of the process streams may be leaching metals from equipment, the majority of which were not stainless steel. The increasing levels of copper, iron, manganese, and zinc through the process are indicative of this problem.

Only traces of a few priority pollutant organics, herbicides or chlorinated pesticides, were detected in any of the samples. Except for the pesticides and herbicides, these traces of compounds seemed to be contamination problems in the laboratory rather than actual residues of the compounds. In the winter when doors would be closed, it would be advisable to vent fermentation tank and product tank emission to the outdoors to prevent dangerous accumulations of CO_2 and ethanol in the work place.

Conclusions and Recommendations

The overall results indicate several areas of concern regarding the environmental impacts from on-farm alcohol production. Although primary concern should be with those normal discharges from the process, one must additionally be concerned with the "dumping" of poor batches and disposal of the solid materials other than by byproduct use, i.e., as a feedstock.

For the process liquid and solid streams, these concerns include high oxygen demand, high nutrient content, metals in the process streams and wastes, low pH (acidity), herbicide and/or pesticide residues from feed grain (but this would be highly dependent upon the feed grain supplier and the area of use). Regarding air emissions, particularly during the winter months, the only apparent concerns are venting of CO_2 for safety reasons from the fermenter off-gas and ethanol vapor from the product tank to the outdoors.

Finally, a treatability study should be performed on all effluents and off-specification process waste to determine appropriate waste treatment methods and obtain treatment design criteria.

Table 5. *Analytical Matrix*

Site	Sample type	BOD_5	COD	TOC	pH	Conductivity	TSS	TS	Phenol	Cyanide	NH_3 TKN	NO_3	SO_4	PO_4	Metals[a]	VOA	BN/A	Pesticides	Herbicides	E+OH
A	Make-up water	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			
	Feed grain																	X	X	
	Distillation feed	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X
	Beer bottoms	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X
	Washout water	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X
	Byproduct				X			X	X	X	X	X	X	X	X		X			X
	Product																			X
	Cooker runoff				X															X
B	Make-up water	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			
	Feed Grain																	X	X	
	Distillation feed	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X
	Beer bottoms	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X
	Washout water	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X
	Byproduct				X			X	X	X	X	X	X	X	X	X	X			X
	Product																			X
	Soil				X						X	X		X						
	Soil control				X						X	X		X						

[a] *Al, Sb, As, Ba, Be, Bi, Cd, Ca, Cu, Cn, Fe, Pb, Mg, Mn, Hg, Ni, Se, Ag, Ti, Tl, Zn*

Table 6. Analysis Results — Percent Ethanol by Gas Chromatography[a]

Sample type	Site A	Site B
Distillation feed	6.9	3.9
Beer bottoms	0.9	2.4
Washout water	1.2	1.1
Byproduct	0.08[b]	0.08[b]
Cooker mash runoff	Less than 0.5	--
Product	87.0 (88.6)[c]	71 0 (73.6)[c]

[a]Accuracy estimated at ±10 percent.
[b]Percent by weight.
[c]Numbers in parentheses are results from hydrometer tests.

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The complete report, entitled "Testing and Evaluation of On-Farm Alcohol Production Facilities," (Order No. PB 84-215 789; Cost: $11.50, subject to change) will be available only from:
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