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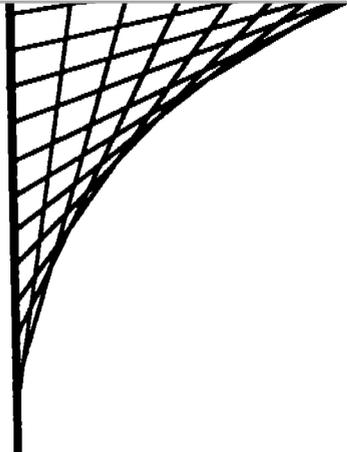
Ethanol Emissions Control from Wine Fermentation Tanks Using Charcoal Adsorption A Pilot Study

_____ by

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Contents

Section I. Introduction

Background and Purpose	1
Pilot Study	1

Section II. Equipment

Fermentation	3
Emission Control	3
Instrumentation	6

Section III. Methods

Fermentations	7
Charcoal Adsorption Unit	11
Measurements	11

Section IV. Results

Fermentations	13
Emissions	14

References	19
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Acknowledgements	19
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SECTION 1. INTRODUCTION

Background and Purpose

The mission of the Air Resources Board (ARB) is to define the health threat of air pollution and, in conjunction with county and regional air pollution control agencies, regulate its causes where necessary to achieve or maintain healthy air. For California, the ARB:

- Sets air quality standards;
- Monitors air quality;
- Provides technical expertise to help county and regional air pollution control officials set emission limits for industrial causes of air pollution; and
- Operates one of the largest air pollution research programs in the world.

The mission of the Viticulture and Enology Research Center at California State University, Fresno is to conduct research and other activities beneficial to the grape and wine industries of California. Of particular concern to the wine industry, specifically to the larger wineries of the Central Valley, is the interest of the ARB and some of the county air pollution control agencies, in ethanol emissions from wine fermentation tanks. The ARB has determined that ethanol is a reactive substance which, through its products of photolysis, contribute to the formation of smog.

When the staff of the ARB originally proposed a control rule for ethanol emissions from wine fermentation, it identified control devices and equipment that it considered feasible for compliance with the rule. The Wine Institute advocated to the Air Resources Board that a number of technical and economic issues pertaining to these devices had not been adequately addressed. To address those issues, the board then approved a voluntary, industry-funded three-tier demonstration program as suggested by the Wine Institute.

Pilot Study

First, in order to study the feasibility of the concept, a pilot study utilizing 1,412-gallon fermentation tanks affixed with three of the suggested control devices was undertaken in 1987. The control devices included a catalytic incinerator, a water scrubber, and a charcoal adsorption unit. Then, depending on the results of this initial study, a larger study would be undertaken at a commercial winery. Finally, if these results were favorable, full scale implementation of the program could be instituted at some wineries.

During the 1987 fermentation, the ARB staff also visited three operating wineries in the Fresno area that would be affected if controls become required. The three wineries were Christian Brothers (Mount La Salle Vineyards), Guild-Cribari, and Gallo. The purpose of the visits was to survey tank usage patterns and review historical fermentation tank usage patterns for 1984 through 1986. This information is needed to help determine the overall costs of emission control. Based on that survey, the ARB staff estimated that the capital cost for the three wineries is between \$3.1 million and \$25 million to install carbon adsorption systems and between \$3.7 million to \$33 million to install catalytic incineration systems. About 60 to 70 percent of those capital costs is the cost of the venting systems.

In 1987, before the fermentation period, the board also created an Ad Hoc Advisory Committee composed of ARB technical staff and wine industry representatives to jointly determine the demonstration program protocol. The committee was also to provide the board with scientific data from which to base recommendations for further implementation of the program.

In 1987, following approval of a protocol for the first phase implementation of the demonstration program, the Wine Institute and Winegrowers of California jointly funded a pilot project utilizing the enology facility at CSU, Fresno. During 1987, the efficacy of the three suggested ARB control devices was evaluated.

During the 1987 study, four fermentations were carried out; two on red must and two on clarified white juice. Ethanol emissions from each tank and into and from each control device were monitored by ARB technical staff.

Sufficient data were provided by this study for the Ad Hoc Committee to tentatively conclude that the water scrubber was not feasible due to technical problems relating to the disposal of the ethanol-laden waters, and the catalytic incinerator was not feasible due to inordinate high costs of implementation.

However, design, implementation and paucity of data obtained during this study due to operational problems associated with the charcoal adsorption unit precluded the Ad Hoc Advisory Committee from making recommendations on use of this unit to the board. As a result, the committee indicated to the board that the results of the pilot study were incomplete and recommended further experimentation to be carried out during the 1988 season.

Again, CSU, Fresno was selected to perform the experiments following an Ad Hoc Advisory Committee approved protocol for the 1988 demonstration program. The 1988 study was funded by the California Agricultural Technology Institute (CATI), the California Wine Commission through the American Vineyard Foundation and guaranteed by the Wine Institute. Several large Central Valley wineries provided logistical support. The Wine Institute retained Frederiksen Engineering (Oakland, CA) to provide design and engineering expertise.

The 1988 study focused primarily on two issues:

1. Efficiency of the emission collection hoods atop each fermentation tank vent in capturing ethanol emissions.
2. Operational efficiency of the charcoal adsorption unit.

ARB technical staff again provided for monitoring of ethanol emissions from fermentation tanks and to and from the charcoal adsorption beds.

This paper presents the results of the 1988 study on the operational efficiency of the charcoal absorption unit.

SECTION II. EQUIPMENT

Fermentation

The pilot plant installation where this work was performed is located at the CSU, Fresno enology facility. This fermentation line is provided with a bin dumper, a Demoisy Model D-8 crusher stemmer, and ancillary 3-inch diameter stainless steel must lines. Pomace pressing was performed on a Bucher RPL 18 press.

The fermentation line itself consists of four 1,412 gallon (shell volume) (1,467 nominal volume) jacketed, stainless steel fermentors (8 feet high x 5.5 feet diameter). The tanks are provided with manholes on the side at the bottom of the tank and on the conical top. In addition, each tank has a 6-inch diameter lidded hand hole on top. A 2-inch diameter vent is located at the center of the conical top. The tank shells are insulated with 3-inch thick polyurethane - aliphatic coating. Only tanks 1 and 2 were used for this experiment. Both tanks are provided with 2-inch diameter pumpover lines which extend to about 1-inch below the uppermost height of the tank shell. At this point, the pipe enters semi-tangentially into the tank to allow for as even a spray as possible. In addition, the pumpover lines are provided with a sight glass to allow for visual determination of pumpover rate and, when pumpover is not being conducted, with a means to indicate if a foamover occurs. This device permits must pumpover in what is essentially a "closed" system without the need to open either the manhole or hand hole.

Each tank is also provided with an anti-foam injector which consists of a silastic gland fitting located midway between the upper manhole and the tank vent. Each tank also has a sampling tap located 4 inches above the bottom manhole. Tank 1 was termed "reference" and tank 2 was termed "controlled." The vent of tank 1 was affixed to measuring devices to determine gas characteristics and flow. The vent of tank 2 was provided with a stainless steel capture hood which was piped to the emissions control device through 1-inch diameter piping as described below.

Cooling water (44 degrees Fahrenheit) for the tank jackets and condenser unit was provided by a 25-ton, chilled water refrigeration unit. Tank temperatures were thermostatically controlled by UE800 controllers in conjunction with Red Hat solenoid valves.

Emission Control

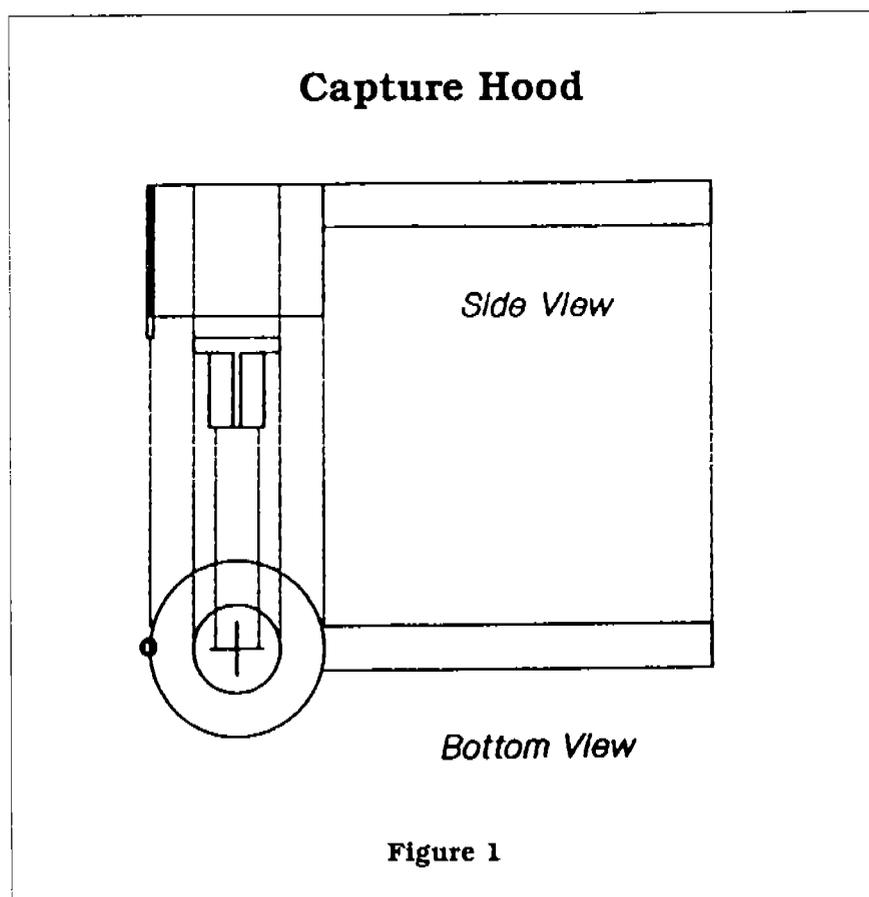
Fermentation emissions were collected from fermentation tank 2 which is fitted with a cylindrical stainless steel capture hood provided with a slitted plastic skirt that extends to the top of the tank. The purpose of this skirt is to allow some air to be drawn into the control piping. Also, this slitted skirt acts as protection should a foamover occur.

The capture hood (See Fig. 1) is connected with 1-inch stainless steel square tubing to a foamover pot. A rotameter and valve are located at the exit of this vessel. From there the line goes into a tube-in-tube chiller cooled by 44 degrees Fahrenheit water. At the exit of this chiller there is a condensate collection vessel (300 mL volume). The purpose of this chiller and condensate trap is to remove as much water as possible before passing the gas stream through a charcoal adsorption bed. The gas stream is then pumped through appropriate piping and valving into either one of two

charcoal adsorption beds enclosed in insulated 6-inch diameter x 3-foot stainless steel cylinders. After passage through the charcoal bed the stream is ducted into the atmosphere (See Fig. 2).

Each charcoal adsorption bed is also connected to a source of dry, filtered steam for purposes of regeneration. In normal operation, one bed is adsorbing volatiles while the other bed is either in the process of being regenerated or is idle.

Adsorbed volatiles freed from the charcoal upon steam regeneration are condensed into a stainless steel reservoir cooled by chilled water at 44 degrees Fahrenheit. The vent from this system is provided with an additional condenser in order to prevent the escape of volatiles into the atmosphere.



Instrumentation

The instruments for determining ethanol concentrations and gas flows out of the fermentation tanks and through the charcoal adsorption unit are listed in Table 1. The specifics of the instrumentation are noted below.

Table 1. Summary of Sampling and Analytical Methods

<u>Control to be Analyzed</u>	<u>Sampling Method</u>	<u>Analytical Method or Detection Principle</u>
Ethanol	Continuous Analyzer	FID
Gas Flows	Rotameter	Balanced Forces
Gas Volume	Positive Displacement	Positive Displacement
Gas Volume	Gas Test Meter	Expansion of Diaphragms

1. Ethanol Concentrations

Ethanol concentrations were measured with Beckman 400 flame ionization detectors (FID). The sensor is a burner. A regulated flow of sample gas passes through a flame sustained by regulated flows of zero air and hydrogen (fuel gas). Hydrocarbon compounds, such as ethanol, contained in the sample gas undergo a complex ionization producing electrons and positive ions. Polarized electrodes collect these ions, causing current to flow through electronic measuring circuitry. Current flow is proportional to the rate at which carbon atoms enter the burner.

An FID does not respond to carbon dioxide (CO₂) or water vapor which is present in the fermentation gas stream with the ethanol. An FID will respond to other hydrocarbons in the gas stream, but previous studies indicated that the concentrations of other hydrocarbons in the gas stream are insignificant relative to the concentration of ethanol.

2. Gas Flow and Volume Measurement

a. Rotameters

Rotameters measure fluid flow. They are variable-area, constant-head, rate-of-flow meters. As fluid flows upward through a tapered tube, a shaped weight within the tapered tube is lifted upward until the upward fluid force balances its weight.

b. Positive Displacement Meter

Positive displacement meters measure total gas volume. Two figure-8 shaped (two-lobed) impellers counter-rotate within a rigid casing. Gas enters and exhausts on opposite sides of the casing. The impellers are accurately produced so that a continuous seal without contact is formed at all positions during rotation. As a result the impellers rotate with very little pressure and the gas on the inlet side is effec-

tively isolated from the outlet. In rotating, an impeller traps a known specific volume of gas between its lobes and the adjacent semi-circular portion of the meter casing. Rotation of the impellers is measured by a magnetically coupled counter.

c. Test Meter

The test meter measures total volume. Gas enters one half of a double-diaphragm contained in a molded port and pan. Expansion of the diaphragm causes the metering unit to move. When one diaphragm is fully expanded, then it begins to deflate and the other diaphragm begins to expand. Expansion of the second diaphragm causes the metering unit to continue to move.

SECTION III. METHODS

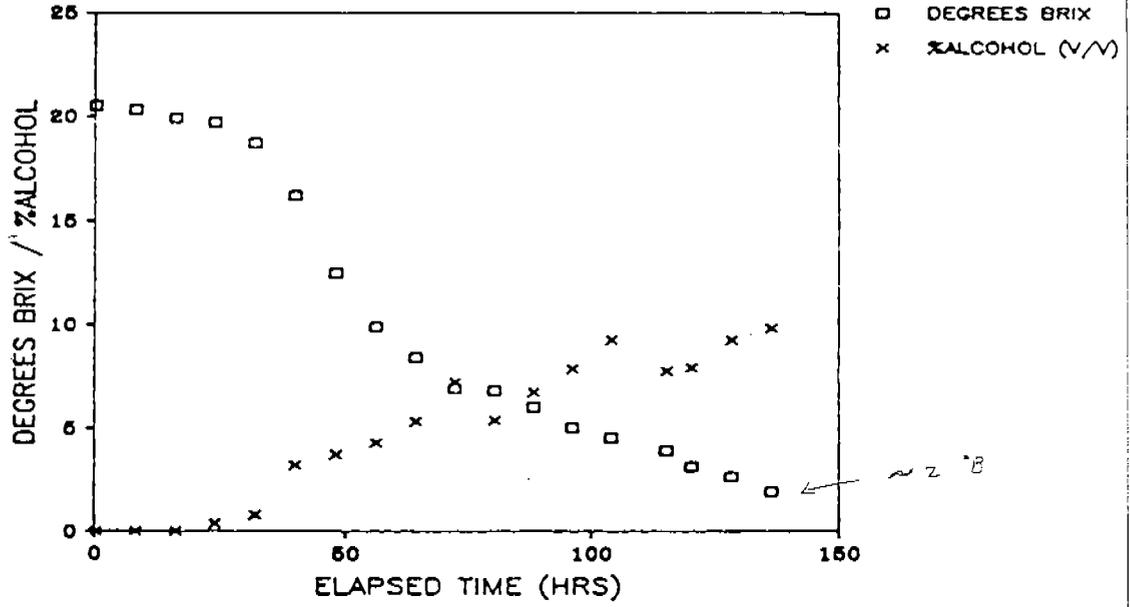
Fermentations

Four fermentations were carried out in this study as follows:

- (1) Red I - Carignane grapes from CSU, Fresno vineyard, 918 gallons per tank (65 percent fill); 80 degrees Fahrenheit nominal fermentation temperature. Started 12:00 noon September 2, 1988. (Results for Red I are not presented in this report due to problems in measuring the volume of gas vented from the reference tank and collecting the ethanol captured by the charcoal adsorption unit.)
- (2) Red II - Carignane grapes from CSU, Fresno vineyards, 918 gallons per tank (65 percent fill); 80 degrees Fahrenheit nominal fermentation temperature. Started 12:00 noon September 7, 1988.
- (3) White I - Clarified French Colombard juice (provided by Gallo Winery) (2 percent solids), 918 gallons per tank (65 percent fill); 80 degrees Fahrenheit nominal fermentation temperature. This wine was fermented as a red. Started 12:00 noon September 14, 1988.
- (4) White II - Clarified juice as above, 1130 gallons per tank (80 percent fill); 55 degrees Fahrenheit nominal fermentation temperature. Started 12:00 noon September 19, 1988.

Saccharomyces cerevisiae var. Montrachet yeast was used. Zero time for each experiment (fermentation) was inoculation time. Both "reference" and "controlled" tanks were filled simultaneously. Fermentation progress was followed by measuring Balling and alcohol content (v/v by GC) at 8-hour intervals. For purposes of this study, the fermentations were considered complete when the Balling reached 2 degrees. Fermentation progress in each case may be seen in Figures 3, 4, and 5.

Ethanol Emissions II RED WINE II - TANK 1



Ethanol Emissions II RED WINE II - TANK 2

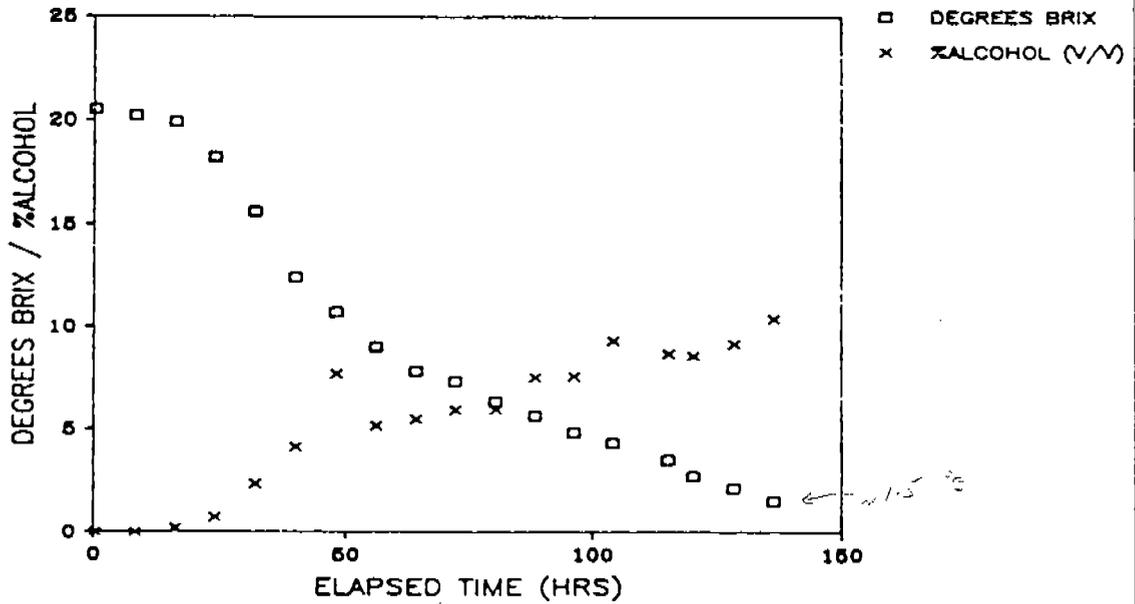
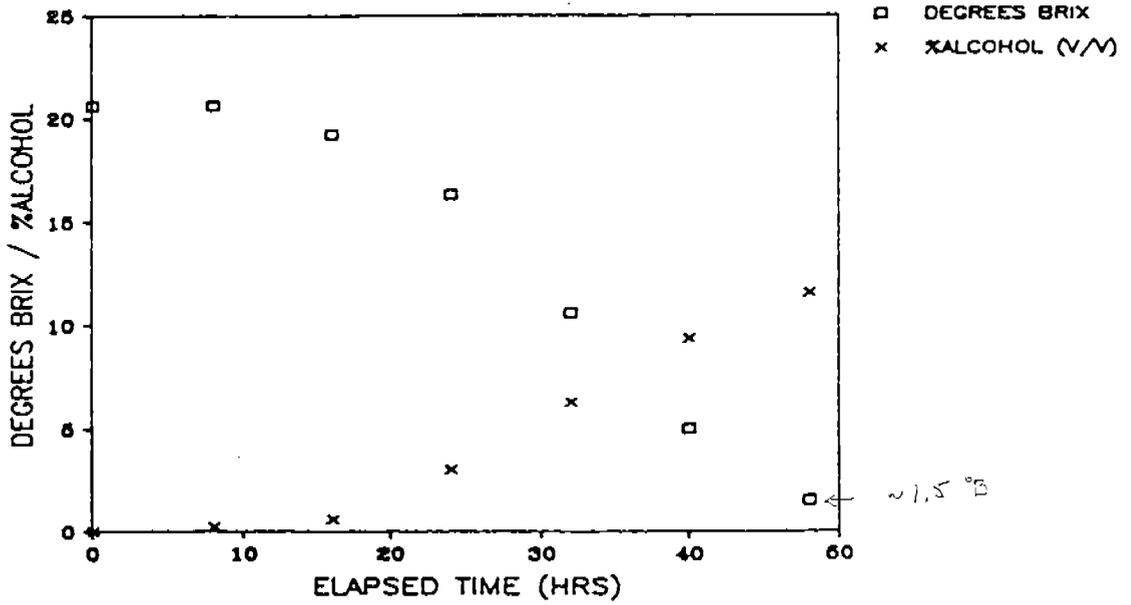


Figure 3

Ethanol Emissions II WHITE WINE I - TANK 1

85° fermentation



Ethanol Emissions II WHITE WINE I - TANK 2

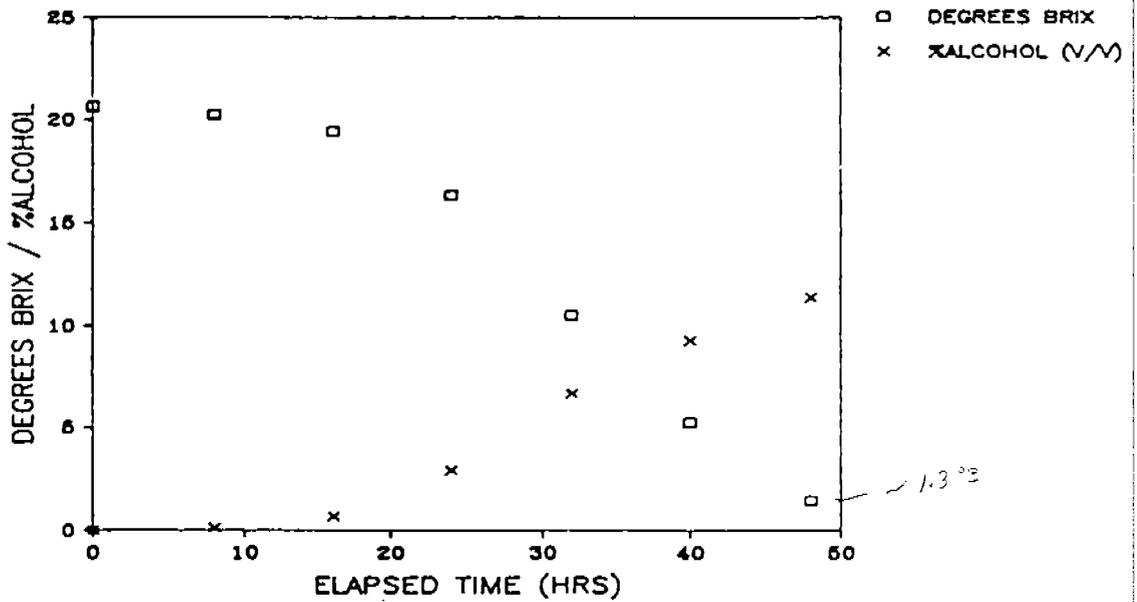
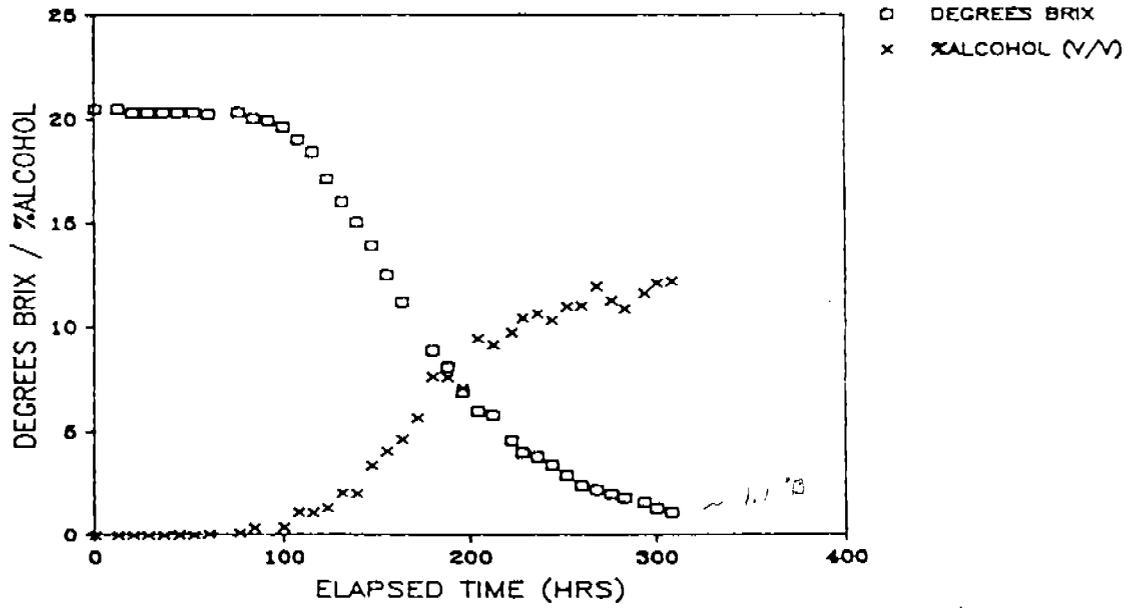


Figure 4

Ethanol Emissions II WHITE WINE II - TANK 1



Ethanol Emissions II WHITE WINE II - TANK 2

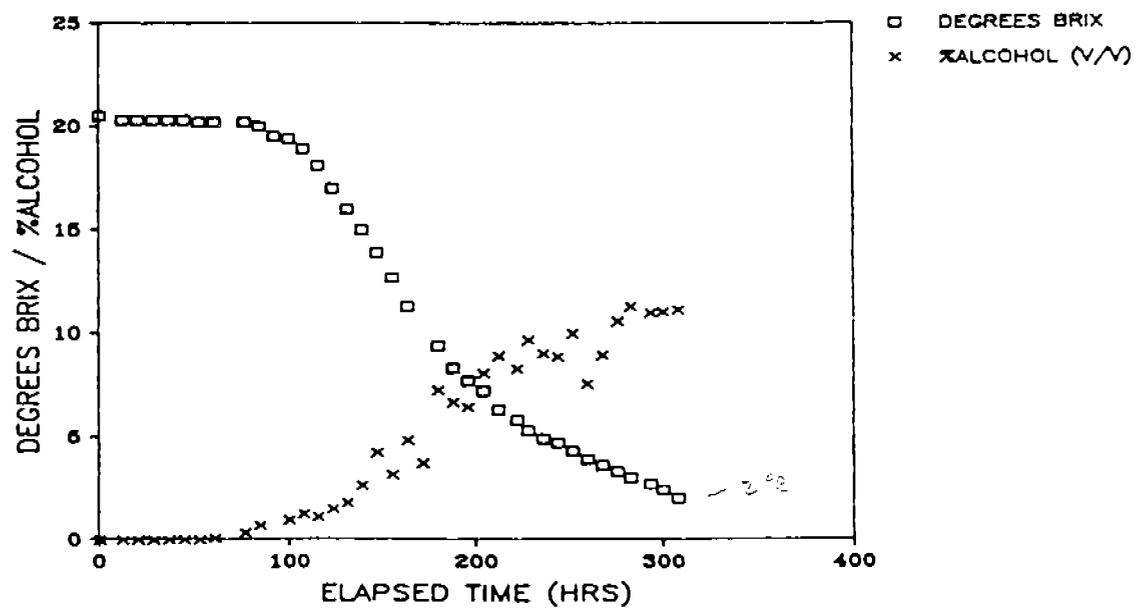


Figure 5

Charcoal Adsorption Unit

1. Adsorption Mode: Normal operation of the charcoal adsorption unit calls for one bed (column) being on the adsorption mode while the other is either being regenerated with steam or idle.

After passage through the chiller-heater (See Fig 2) the volatile stream is insufflated with a pump onto the top of the column operating in the adsorption mode. Theoretically, as the volatiles are adsorbed into this bed, the temperature of the bed should rise. Thus, temperature measurements on the bed at various heights should produce an indication as to when the bed is progressively saturated. In practice however, this method, using appropriately spaced thermocouples on the column, did not work well. Accurate determination of bed saturation was obtained by referring to the ARB-monitored hydrocarbon analyzer whose probe was located at the column vent exit. Thus, when the hydrocarbon analyzer's baseline increased to above 3 percent volatiles, the column was considered saturated and the other column placed in the adsorption mode. In this manner a minimum of volatiles were lost into the atmosphere. As expected, time to saturate a column varied depending on the progress of the fermentation.

2. Regeneration Mode: Columns (beds) which had become saturated were immediately regenerated by using dry, clean, house steam. The regeneration process, measured from the time the temperature at the inlet of the condenser rose above 175 degrees Fahrenheit, took about one hour. This time interval was determined during the experiments carried out during 1987. Any further increase in regeneration time did not result in an increase in the amount of volatiles collected, except for water.

Volatiles were condensed and collected in a stainless steel reservoir and removed immediately upon termination of the regeneration process. This aqueous solution of volatiles thus collected was stored under refrigeration in tightly stoppered bottles for alcohol analysis.

Upon completion of regeneration, the column was then thoroughly dried and cooled using a stream of air. The column, thus dried, was then ready to receive volatiles again. During a fermentation it was necessary to change back and forth several times between the two adsorption beds.

Measurements

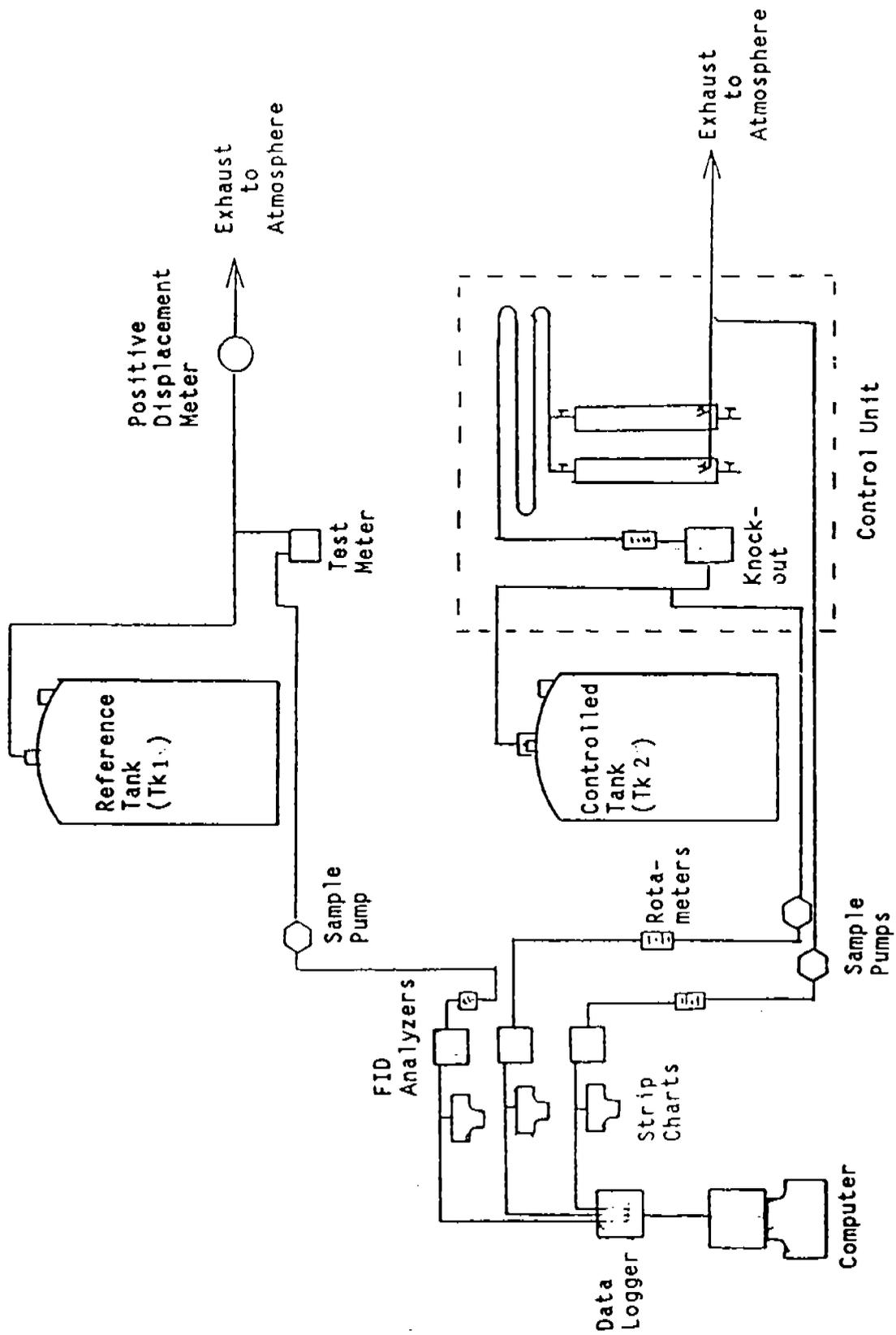
1. Fermentation:

- a. Brix/Balling: Initial Brix on the unfermented grape juice and must was taken by refractometer. After inoculation, soluble solids (Balling) were taken by hydrometry following the procedure by Zoecklein et. al., pp 22-29 (4).
- b. Ethanol: Ethanol content of the initial juice and the fermenting must was determined by alcoholimetry and by G. C., (Zoecklein et. al., pp 50-61).

2. Emissions:

Sampling was performed at the outlet of the reference tank (tank 1) and the inlet and outlet of each of the charcoal

Ethanol Emissions Sampling Setup



adsorption units (control unit) connected to the controlled tank (tank 2). Specific sampling information is given below. Figure 6 shows the sampling setup.

Figure 6

a. Gaseous Emissions

Sampling for ethanol in the fermentation tanks exhausts was performed in accordance with California Air Resources Board stationary source sampling method, "Method 100 - Procedures for Continuous Emission Stack Sampling." This test method is used for determining gaseous emissions from stationary sources.

For this particular study three gaseous hydrocarbon sampling instruments were available to sample the inlet and outlet of the charcoal control unit and the vent of the reference tank simultaneously. Total hydrocarbon concentration (mostly ethanol) was measured by an analyzer equipped with a flame ionization detector (FID). The gas samples were drawn through separate Teflon sampling lines by three sampling pumps and exhausted into the analyzers. Data from the three instruments were recorded on strip charts and a computer data acquisition system. The analyzers were calibrated at the ARB Sacramento facilities before the emissions test, and in the field before, during, and after each fermentation.

b. Flows

Flow rates into the control unit and analyzers were measured with rotameters. The analyzers and the control device required specific constant flows for optimum performance. The rotameters, at a glance, were able to indicate if the flows were correct. Any flow adjustment could be made quickly with the rotameters. The fermentation period was timed so total flows could be calculated.

A test gas meter and positive displacement meter measured total volume at a variety of flow rates. The test gas meter measured the gas from the reference tank to the analyzers. The positive displacement meter measured the amount of gas from the reference tank in excess of that needed by the sampling instruments. At the beginning and end of each fermentation, gas production from the reference tank was less than that required for the instruments. At those times the positive displacement meter was reversed to measure the dilution air going to the instruments.

Flow volumes out of the reference tank and flow rates through the control unit were periodically recorded during each fermentation.

SECTION IV. RESULTS

Fermentations

As mentioned above, all fermentations were considered complete for the purposes of this experiment when the Balling decreased to or below 2 degrees. Figures 3, 4, and 5 show progress for each fermentation. All fermentations were typical as shown by the decrease in Balling and the concomitant increase in alcohol content.

Since White Wine I was fermented as a red (80 degrees Fahrenheit), its fermentation curve is accelerated as compared to that of White Wine II which was fermented at 55 degrees Fahrenheit in the traditional manner.

Emissions

For each fermentation, ethanol emissions from both tanks and the charcoal adsorption unit are shown graphically in Figures 7 through 12. The figures for the reference tank (tank 1) show the ethanol concentrations in parts per million (ppm) for the different periods of time plus the cumulative ethanol emission in pounds. The figures for the controlled tank (tank 2) show ethanol concentrations in ppm into and out of the control unit and the cumulative ethanol emission in pounds into and out of the control unit. The controlled tank shows lower ethanol concentrations than the reference tank because dilution air is being drawn into the charcoal adsorption unit in order to maintain 7 cubic feet per minute flow through the unit.

The total mass emissions, in pounds of ethanol from both fermentation tanks for each fermentation are shown on Table 2 below. The range is between 1.60 and 4.14 pounds of ethanol.

Table 2. Ethanol Emissions (Uncontrolled)

Fermentation	Reference Tank, lbs. of Ethanol	Controlled Tank, 1/ lbs. of Ethanol
1. Red II	3.93	4.14
2. White I	3.56	3.04
3. White II	1.75	1.60

1/ Emissions from controlled tank to charcoal adsorption unit.

Table 3 below shows the total ethanol emissions into and out of the charcoal adsorption unit during each fermentation. This table also shows the control adsorption unit during each fermentation. As indicated, the control efficiency of the charcoal unit was better than 98 percent for the three fermentations.

Table 3. Control Efficiency of Ethanol Control Unit (Charcoal Adsorption)

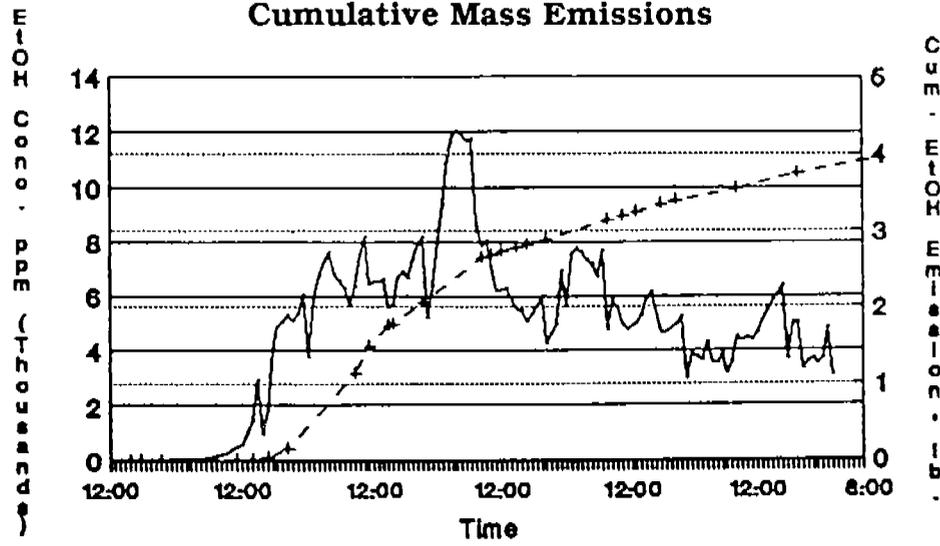
Fermentation	Ethanol In, lbs.	Ethanol Out, lbs.	Control Efficiency, 1/ %	Ethanol Collected 2/ from Control Unit lbs.
1. Red II	4.14	0.0653	98.4	4.76 <i>98.9%</i>
2. White I	3.04	0.00421	99.9	2.96 <i>99.9%</i>
3. White II	1.60	0.0311	98.1	1.89 <i>99.8%</i>

1/ Efficiency = [(In-Out)/In] * 100

2/ Ethanol collected is ethanol recovered from the charcoal adsorption unit.

Also, listed in Table 3 is the amount of ethanol collected from the charcoal adsorption unit. For all three fermentations, the amount of ethanol collected from the control does not exactly balance with the amount of ethanol calculated to enter and exhaust from the charcoal adsorption unit. For Red Wine II and White Wine II the amount of ethanol collected from the control unit is slightly higher than the amount of ethanol calculated to enter the control unit. For White Wine I the most amount of ethanol collected from the control unit was slightly less than that expected based on the amount of gaseous ethanol entering and exhausting from the charcoal adsorption unit. These differences are small and do not effect the final results appreciably at present. The reason for the differences is unknown.

Red Wine II - Reference Tank Emissions Ethanol (EtOH) Concentrations & Cumulative Mass Emissions

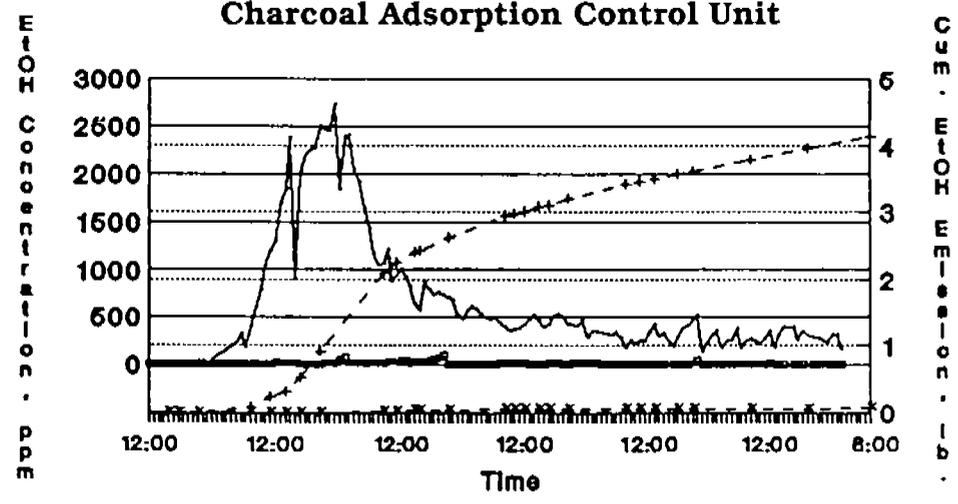


— EtOH Conc, ppm - + - Cum. Emission, lb.

(Fermented 9/7/88 thru 9/13/88)

Figure 7

Red Wine II - Controlled Tank Emissions Ethanol (EtOH) Emissions In and Out of Charcoal Adsorption Control Unit

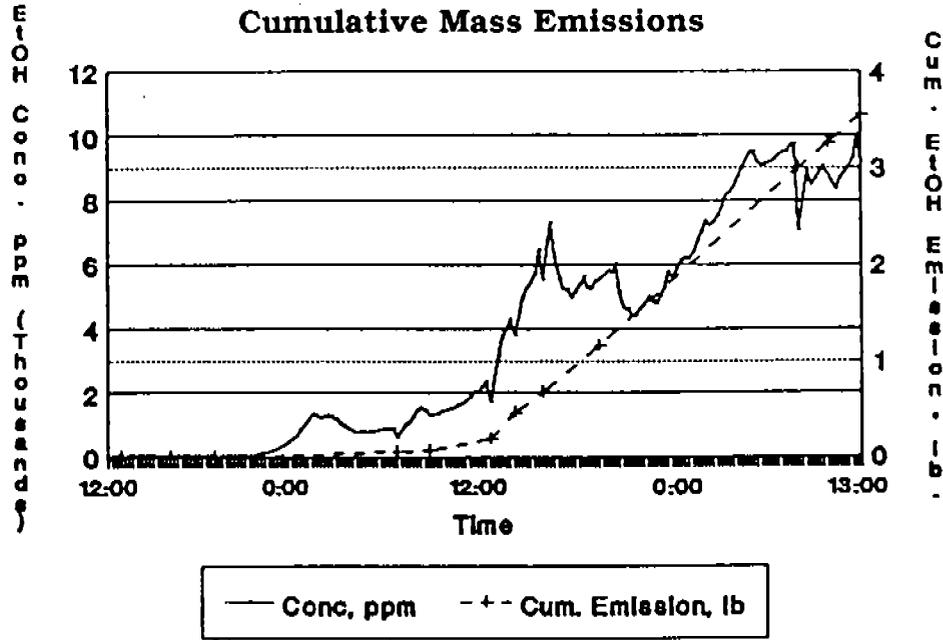


— Conc In, ppm - + - Cum. Emission In, lb
—•— Conc. Out, ppm - * - Cum. Emission Out, lb

(Fermented 9/7/88 thru 9/13/88)

Figure 8

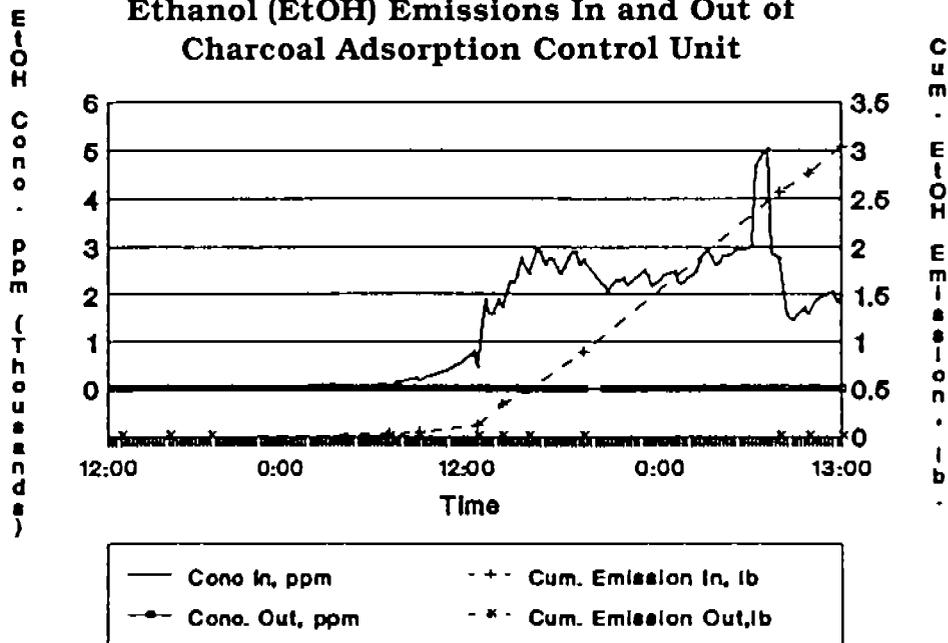
White Wine I - Reference Tank Emissions
Ethanol (EtOH) Concentration & Cumulative Mass Emissions



(Fermented 9/14/88 thru 9/16/88)

Figure 9

White Wine I - Controlled Tank Emissions
Ethanol (EtOH) Emissions In and Out of Charcoal Adsorption Control Unit



(Fermented 9/14/88 thru 9/16/88)

Figure 10

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