Copyright Warning & Restrictions

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be "used for any purpose other than private study, scholarship, or research." If a, user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of "fair use" that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation

Printing note: If you do not wish to print this page, then select "Pages from: first page # to: last page #" on the print dialog screen



The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

ABSTRACT

Removal of Volatile Organic Compounds (VOC's) Acetone and Ethyl Alcohol Emitted in the Manufacture of a Muti-Base Propellant

by Yih-Leu Liu

The Production Base Modernization Activity located at Picatinny Arsenal, initiated this study for the removal of the low concentrations of VOC's, acetone and ethyl alcohol emitted from the mixer operation and the forced air dry unit in the manufacture of a multi base propellant. Air pollution requirements necessitate 85 % removal of the VOC's prior to discharge of the vent gases into the atmosphere. Because of the availability of sulfuric acid, it is proposed to use 70 percent or stronger acid as the absorbing agent in a recirculating acid absorption tower.

Vapor - Liquid Equilibrium (VLE) data were measured for the three solutes, acetone, ethyl alcohol, and diethyl ether in sulfuric acid. Gas analysis was made by using a Hewlett - Packard 5700 A Gas Chromatograph, using a column, 1/8 inch diameter by 10 feet long, stainless steel, packed with 3 percent, SP - 1500, 80 / 120 carbopack B. The correlations are linear at low concentrations indicating that Henry's Law applies but flex upward at higher concentrations.

The absorption study was conducted in a two inch diameter glass column, packed to a height of 18 inches with 1/4 - inch Raschig rings. The results show that for the recirculation system, the VOC breakthrough of acetone, occurred in 4 - 5 hours for 76 percent acid but no breakthrough is detected after 24 hours for 96 percent acid. No ethyl alcohol or diethyl ether were detected in all runs made. Use of acid purge can prolong breakthrough. For 76 percent acid, the breakthrough occurred in about 21 hours for a purge rate equal to about 1 percent of the recirculation rate.

The prototype plant was simulated for the mixer unit and the forced air dry unit and data were estimated for numbers of transfer units, heights of a transfer unit, column diameters and packed heights, column pressure drops and materials of construction were specified. Water, present as humidity in the air, is a major consideration. The study indicates that 96 percent sulfuric acid is an excellent absorbent for this system.

REMOVAL OF VOLATILE ORGANIC COMPOUNDS (VOC'S) ACETONE AND ETHYL ALCOHOL EMITTED IN THE MANUFACTURE OF A MULTI-BASE PROPELLANT

by

Yih-Leu Liu

A Thesis

Submitted to the Faculty of New Jersey Institute of Technology in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemical Engineering Department of Chemical Engineering, Chemistry and Environmental Science October, 1992

 \bigcirc \langle

APPROVAL PAGE

Removal of Volatile Organic Compounds (VOC's) Acetone and Ethyl Alcohol Emitted in the Manufacture of a Muti-Base Propellant

by

Yih-Leu Liu

Dr. Deran Hanesian, Thesis Adviser Professor of Chemical Engineering, N. J. I. T.

Dr. Edward C. Roche Jr., Committee Member Professor of Chemical Engineering, N. J. I. T.

Dr. Angelo J. Perna, Committee Member Professor of Chemical and Environmental Engineering, N. J. I. T.

BIOGRAPHICAL SKETCH

Author: Yih-Leu Liu

Degree: Master of Science in Chemical Engineering

Date: October, 1992

Undergraduate and Graduate Education:

- Master of Science in Chemical Engineering New Jersey Institute of Technology, Newark, NJ, 1992
- Bachelor of Science in Chemical Engineering Tunghai University, Taichung, Taiwan, 1986

Major: Chemical Engineering

Position Held:

June, 1991 - August, 1992

Research Assistant Hazardous Substance Management Research Center New Jersey Institute of Technology Newark, New Jersey This thesis is dedicated to my parents How-Chin Liu and Chiou-Mey Liao

ACKNOWLEDGEMENT

The author wishes to express his sincere gratitude to his advisor, Professor Deran Hanesian, for his guidance, friendship, and moral support throughout this research.

Special thanks to Professors Edward C. Roche and Angelo Perna for serving as members of the committee.

The author is grateful to the U. S. Army for the funding of the research, through the National Science Foundation, and to the Hazardous Substance Management Research Center for providing further and continued help for this project.

The author appreciates the timely help and suggestions from the members of New Jersey Institute of Technology faculty, including : Mr. Bill Forster, and Mr. Bill Guzy, and the members of the Production Base Modernization Activity located at Picatinny Arsenal, including : Dr. Robert Goldberg, and Ms. Florence Elie.

And finally, the author would like to thank his parents for their full support without which he would not have accomplished very much.

TABLE OF CONTENTS

1 INTRODUCTION
2 LITERATURE REVIEW
3 ALTERNATIVE TECHNOLOGY
4 RESEARCH OBJECTIVES
5 THEORY
5.1 Countercurrent Gas Absorption with Chemical Reaction8
5.2 Estimation of H OG for Acetone - Sulfuric Acid System15
6 EXPERIMENTAL RESULTS
6.1 Vapor-Liquid Equilibrium Studies21
6.1.1 Experimental Apparatus21
6.1.2 Experimental Procedures23
6.1.3 Experimental Results24
6.2 Gas Absorption Studies
6.2.1 Experimental Apparatus29
6.2.2 Experimental Procedures35
6.2.3 Experimental Results
6.3 Simulation Of VOC Removal41
7 DISCUSSION OF RESULTS
7.1 Vapor-Liquid Equilibrium Studies46
7.2 Gas Absorption Studies
7.3 Proposed Pilot Plant
8 CONCLUSIONS AND RECOMMENDATIONS
APPENDIX
BIBLIOGRAPHY119

LIST OF TABLES

Та	ble Page
1	Reactions between Acetone and Sulfuric Acid12
2	Reactions between Ethyl Alcohol and Sulfuric Acid13
3	Reactions between Diethyl Ether and Sulfuric Acid14
4	Properties at 25 °C used in Eq. 19 to Estimate H L, acetone-sulfuric acid
5	HP 5700 A GC Operating Conditions23
6	Reagents Used in This Study23
7	Height of Column
8	Effect of Acid Concentration on N OG52
9	Proposed Pilot Plant Operating Conditions
10	HP 5700 A GC Calibration [Species In Air] Summarized Table63
11	Calibration Data for Air Flow Rotameter and Teflon Pump
12	HP 5700 A GC Calibration [Acetone In Air]78
13	HP 5700 A GC Calibration [Ethanol In Air]79
14	HP 5700 A GC Calibration [Ethyl Ether In Air]80
15	Acetone In Air Equilibrium with Mixtures of Acetone and 73 % Sulfuric Acid
16	Vapor Liquid Equilibrium Data for Acetone, and Ethanol in 76 % Sulfuric Acid
17	Vapor Liquid Equilibrium Data for Ethyl Ether in 76 %, and 96 % Sulfuric Acid
18	Temperatures of the scrubber by using 76 % Sulfuric Acid (No purging)
19	Temperatures of the scrubber by using 76 % Sulfuric Acid (Purge: 1ml / min)
20	Temperatures of the scrubber by using 96 % Sulfuric Acid (No purging)

LIST OF FIGURES

Fi	gure Page
1	Height of Transfer Unit vs. m G / L; system: Acetone - Air - Water16
2	Acetone in Air Equilibrium with mixtures of Acetone and Various Concentration of Sulfuric Acid
3	Height of Transfer Unit vs. m G / L (Intercept = 2.38)20
4	Vapor - Liquid Equilibrium Experimental Apparatus
5	HP 5700 A GC - Calibration Curve (concentration: ppm by volume)25
6	Acetone in Air Equilibrium with mixtures of Acetone and diluted Sulfuric Acid (73 %)26
7	Ethyl Ether in Air Equilibrium with mixtures of Ethyl Ether and 96 % Sulfuric Acid27
8	Ethyl Ether in Air Equilibrium with mixtures of Ethyl Ether and 76 % Sulfuric Acid
9	Acetone in Air Equilibrium with mixtures of Acetone and diluted Sulfuric Acid at Various Temperatures
10	Ethanol in Air Equilibrium with mixtures of Ethanol and diluted Sulfuric At Various Temperatures
11	Acetone in Air Equilibrium with mixtures of Acetone and concentrated Sulfuric Acid
12	Ethanol in Air Equilibrium with mixtures of Ethanol and concentrated Sulfuric Acid
13	Absorption Column Schematic Diagram
14	Sulfuric Acid concentration decline due to the moisture from Air : Wt % vs. Time
15	Duplicated Runs in the Absorption Column Using 76 % Sulfuric Acid (No purge)
16	Absorption Column Using 76 % Sulfuric Acid: VOC Recovery % vs. Time
17	Absorption Column Using 96 % Sulfuric Acid (No purge): VOC Recovery % vs. Time
18	Acetone in Air Equilibrium with mixtures of Acetone and Various Concentration of Sulfuric Acid47
19	Acetone-Sulfuric Acid system; Equilibrium constant vs. Wt % Sulfuric Acid48

20	Ether in Air Equilibrium with mixtures of Ether and Wt % Sulfuric Acid49
21	Ether - Sulfuric Acid system; Equilibrium constant vs. Wt % Sulfuric Acid50
22	Number of Transfer Units (N $_{OG}$) vs. VOC Recovery Rate [for Mixer Unit]53
23	Number of Transfer Units (N $_{OG}$) vs. VOC Recovery Rate [for FAD Unit]54
24	Proposed Pilot Plant Study Unit57
25	HP 5700 A GC - Calibration Curve (concentration: ppm by weight)62
26	Calibration Curve of Air Flow Rotameter by Wet Test Meter64
27	Teflon - Pump (Calibration Curve)

1 C = concentration of solute in the absorbent, Eq. 13 - 16 $2 C_{0}$ concentration of solute in the make - up fresh absorbent, = Eq. 13 -16 diffusivity, m^2 / hr or ft^2 / hr 3 D = diffusivity, cm^2 / s , Eq. 20 4 D = gas flow rate, kg moles $/ m^2$ -hr or lb moles $/ ft^2$ -hr 5 G = 6 G' feed gas flow rate, Eq. 8 - 12 = $7 H_{G}$ individual height of a transfer unit, gas phase, m or feet = 8 H_I individual height of a transfer unit, liquid phase, m or feet = 9 H_{OG} overall height of a transfer unit, m or feet = 10 k Ξ chemical reaction rate constant, Eq. 8 - 12 11 k' chemical reaction rate constant, Eq. 13 - 16 = 12 k_x a individual mass transfer coefficient, liquid phase, = kg moles / hr-m³-m.f. or lb moles / hr -ft³ -m.f. 13 k_v a individual mass transfer coefficient, gas phase = kg moles / hr-m³-m.f. or lb moles / hr-ft³-m.f. overall mass transfer coefficient, 14 K_v a = kg moles / hr-m³-m.f. or lb moles / hr-ft³-m.f. liquid flow rate, kg moles $/ m^2$ -hr or lb moles $/ ft^2$ -hr 15 L = 16 M molecular weight of solvent, Eq. 20 = 17 M organics-free mass of solution in the absorption system, Eq. 8 - 12 = 18 M' organics-free mass of solution in the absorption system, Eq.13 - 16 == 19 μ viscosity, cp, Eq.20 = 20 µ liquid viscosity, kg / m-hr or lb / ft-hr = 21 N OG overall number of transfer units = 22 N SC Schmidt Number $\mu / \rho D$ = =

LIST OF COMMON ABBREVIATIONS AND SYMBOLS

23	q	=	purge rate, out the system
24	q'	=	purge rate, into the system
25	ρ	=	liquid density, kg / m^3 or lb / ft^3
26	Т	-	temperature, ^o K, Eq.20
27	t		time
28	V	=	molar volume of solvent (acetone = $77.5 \text{ ml} / \text{gmole}$), Eq.20
29	¥	=	volumertic flow rate
30	х	=	2.6 for water as an associated solvent, Eq.20
31	x	=	mole fraction, solute in the liquid phase
32	у	-	mole fraction, solute in the gas phase
33	y*	=	equilibrium mole fraction in the gas phase
34	Z	=	packed height, m or ft

Subscript

Water	water content of the sulfuric solution		
Orig	original		
Moisture	humidity of air		
E	ethyl alcohol		
Acid	sulfuric acid		
Α	acetone		
2	leaving from column for gas phase and liquid phase		
entrance to column for gas phase and liquid phase			

Chapter 1 Introduction

In the manufacture of multi-base propellants, volatile organic compounds (VOC's) are emitted from the manufacturing process. Currently, air pollution requirements by states and the U.S. Environmental Protection Agency (EPA) necessitate a reduction in VOC emissions. Jake (1987) reported that an acceptable emission level is achieved if the feed organic content at the gas discharge is reduced by eighty-five percent, as was achieved at the Radford Army Ammunition Plant (RAAP) in Radford, Virginia during laboratory studies. This has not been implemented because of the presence of nitroglycerin (NG) in the vapor.

The Production Base Modernization Activity located at Picatinny Arsenal, a member organization of the Hazardous Substance Management Research Center (HSMRC) at New Jersey Institute of Technology, has requested that the HSMRC study the removal of the VOC's, acetone and ethyl alcohol, from the emissions originating in multi-base propellant production by absorption in concentrated sulfuric acid. [*Private Communication, 1991*]

The two principal areas of VOC pollution in the manufacture of the multi-base propellants are in the mixer unit and in the forced air dry (FAD) unit.

a. Mixer unit:

In the propellant blending unit, the VOC concentrations are estimated to be 450 ppm by volume acetone, 900 ppm ethyl alcohol, and 2 - 14 ppm nitroglycerin (NG), for a flow rate of about 1,000 cubic feet per minute (CFM). The bulk of the emissions are generated approximately twice a shift during a fifteen minute 'blow-down' cycle when an inert gas is passed through the mixer unit.

b. Forced air dry (FAD) unit:

The FAD unit is a batch drying unit operation. The approximate maximum concentrations of VOC's encountered in this operation are 1,200 ppm by volume acetone, 1,850 ppm ethyl alcohol and 2 - 14 ppm NG. The flow rate is about 1,500 CFM per bay (a basic propellant drying area) with four bays constituting a FAD. The VOC concentrations at the end of the 38 hour drying cycle are essentially zero.

The operating temperature varies from ambient to a maximum of 140° F (60 $^{\circ}$ C). Approximately 50% of the emissions are lost during the loading of the bay (this includes those emissions generated during transporting the propellant from the cutting area to the FAD area). [Langford, T. H. et. al., 1983]

Process propellant quantity limitations permit operating two bays simultaneously. The two remaining bays in a FAD unit are on turn-around. Hence, a gas absorption unit should have as a design basis the removal of the VOC emissions from two operating bays.

Absorption of solvents with sulfuric acid is one of the oldest methods of solvent recovery. It was first used for the recovery of alcohol and ether in the manufacture of artificial silk by the old Chardonnet process and was then widely applied in the manufacture of powder in Germany and Austria before and during World War I. The air containing alcohol and ether entered the tanks filled with sulfuric acid. The tanks were cooled from the outside by spraying with water.

At the Troisdorf powder factory near Cologne, lead towers were sprayed on the inside with sulfuric acid which was used for the absorption of the solvent. Air containing alcohol and ether entered from below in countercurrent flow relative to the sulfuric acid. The solvents were distilled from the sulfuric acid by heating to $120 \,^{\circ}$ C. Alcohol was then partly converted into ether. The yield was low; only 10 - 12 percent of solvent used for the manufacture of the powder was recovered. [Urbanski, 1967]

The U.S. Army has demonstrated the removal of acetone and ethyl alcohol from a vapor stream on a laboratory scale using concentrated sulfuric acid. [Jake, 1987] U.S. Army multi-base propellant and munitions manufacturing plants have sulfuric acid concentration facilities capable of producing 90 percent acid from 70 percent acid by vacuum evaporation. In addition, there are oleum producing facilities capable of producing 109 percent sulfuric acid from 70 percent spent acid by burning sulfur to form sulfur dioxide (SO_2), converting the SO_2 to sulfur trioxide (SO_3), followed by absorption of the SO_3 in sulfuric acid to form oleum. Because of availability, sulfuric acid would be a desirable absorbing agent into which the VOC's can be absorbed to reduce plant emissions. Other studies have also been cited extensively by Jake (1987).

Chapter 2 Literature

There is a paucity of published data for the removal of acetone and ethyl alcohol using sulfuric acid. Ormandy (1929) has studied the removal of acetone vapors from air using concentrated sulfuric acid and phosphoric acid. Other absorption agents that were used are: water, cresols, and sodium bisulfite solutions. The use of sodium bisulfite would involve absorption with chemical reaction. Generally, the concentrations of acetone used were much higher than needed for this proposed study, and ranged up to about 26,000 ppm in air. Ormandy described two laboratory experimental methods, including a description of both apparatus and analytical techniques. A flow diagram of a proposed plant was also presented by Ormandy (1929).

Robinson (1942) presented data on the recovery of diethyl ether in sulfuric acid. Vapor-liquid equilibrium data were given at various concentrations of sulfuric acid at 20 ^o C. [Robinson, 1942]

No vapor-liquid equilibrium data could be located for ethyl alcohol nor nitroglycerin (NG) using concentrated sulfuric acid as the solvent.

Jake (1987) reported on using concentrated sulfuric acid as a solvent and expanded on Oramandy's study (1929). Using a laboratory absorption bottle Jake measured break-through times as a function of the percent inlet gas solute that is removed. The concentrations of sulfuric acid ranged from 76 percent to 95 percent and solution temperature ranged from 6 $^{\circ}$ C to 37 $^{\circ}$ C. Jake concluded that concentrated sulfuric acid as solvent is superior to sodium bisulfite from the view of capital costs, and that cold sulfuric acid is an excellent absorbent.

Othmer and Scheibel (1941) studied the absorption of acetone with water in a packed gas absorption column and presented an equation for the overall mass transfer coefficient. Scheibel and Othmer (1944) studied the absorption of various ketones with water.

Leva (1953) reported the Scheibel - Othmer studies and referred to the work of Larson (1942) for the absorption of acetone with water.

Sherwood and Holloway (1940) reported that in the absorption of ammonia, when sulfuric acid was used instead of water, absorption coefficients were 50 - 70 percent greater. When water was used alone, the liquid film resistance was an appreciable fraction of the total resistance. Thus, addition of the acid reduced the liquid film resistance.

Tamir (1986) studied the absorption of acetone from air into water using a twoimpinging stream absorber. Molstad and Parsly (1950) studied the absorption of ethyl alcohol vapors from air with water in packed towers.

This study (Liu, Hanesian, Roche) was reported at the 16 $\underline{\text{th}}$ Annual Army Environmental R & D Symposium which was held in Williamsburg, VA, June 25, 1992 and will be published in the proceedings.

Chapter 3 Alternative Technology

Glycols as Absorbents: [Jake, 1987]

Previous studies (Jake, 1987) indicated that diethylene glycol (DEG) and triethylene glycol (TEG) were borderline absorbents. The DEG absorbent solution absorbed 80.5% of the total VOC's indicating DEG could possibly be used to meet the EPA requirement of 85% VOC removal. However, the DEG total VOC concentration of 0.21 wt% does not meet the economic recovery requirement of 1.4 wt%. TEG is a poor absorbent since none of the VOC's were absorbed.

Union Carbide PURASIV HR Solvent Recovery System: [Jake, 1987]

A continuous, indirectly heated VOC recovery via activated carbon (AC) adsorption provides an efficient method of removing small quantities of VOC's from gas streams. However, its use has been rejected in the past due to the incompatibility of NG with AC.

Membrane Technology: [Jake, 1987]

The process was developed by Membrane Technology and Research, Inc. [Menlo Park, CA]. Two membranes which have an active layer of silicone rubber supported on a polysulfone compound were screened for the recovery of 1,500 ppm acetone vapors. The residue stream was recycled into the feed stream resulting in a permeate concentration of 8 % acetone. Another membrane module underwent experimental testing. This module was a composite spiral - wound membrane consisting of three membrane layers : silicone rubber, Kraton, and silicone rubber. The residue was recycled resulting in a permeate concentration of 14 % acetone. The NG absorptivity on the basic membrane was 76.19 % absorbed.

Ceilcote Solvent Recovery System: [Jake, 1987]

The system [The Ceilcote Company (Berea, OH)] is a continuous, close - loop absorption process for removal of VOCs.

The absorbent fluid is a proprietary high - boiling point organic liquid. The fluid is inexpensive and does not deteriorate with age or use. However, the system uses high - pressure (400 - lb) steam which is not available in the FAD area.

In addition, the NG vapors may be condensed on the internal condenser, and, therefore, the process may not meet safety requirement.

Photocatalytic Decomposition of Nitroglycerin - contaminated Airborne VOC's:

In this study, commercially available low -pressure mercury ultraviolet light was employed onto the photoreactor which has a catalyst surface of TiO_2 and other semiconductors. It was found that the concentration of NG could be reduced to less than 0.1 ppm, and acetone and ethanol were oxidized with the formation of CO and CO₂. [Nazim Z. Muradov, Clovis A. Linkous and Ali T - Raissi, 1992]

Chapter 4 Research Objectives

The objectives of this study are:

- To measure vapor-liquid equilibrium data for the systems:
 - Acetone Sulfuric Acid
 - Ethyl Alcohol Sulfuric Acid
 - Ethyl Ether Sulfuric Acid

at concentrations of 76 percent and 96 percent and at temperature ranging from 15 °C

to 54 °C.

- To study the absorption of the VOC's, acetone and ethyl alcohol in a packed gas absorption column with recirculating sulfuric acid.
- To develop a complete, computerized material and energy balance on a prototype plant to remove VOC's from the mixer unit and FAD unit.

Chapter 5 Theory

5.1 Countercurrent Gas Absorption with Chemical Reaction

Concentrated Sulfuric Acid can be used as an absorbent of acetone and ethyl alcohol from air in a countercurrent packed gas absorption column.

In a packed gas absorption system, the packed height can be calculated from the Equation 1.

$$Z = N OG^H OG$$
 (1)

The overall number of transfer units is calculated from the Equation 2.

$$N_{OG} = \int_{y_1}^{y_2} \frac{dy}{y - y^*}$$
(2)

In the dilute region, the operating line for the column, with a slope, L/G, is a straight line and the equilibrium line with a slope, m, is also a straight line. Hence, Equation 2 reduces to Equation 3.

$$N_{OG} = \frac{\frac{y_1 - y_2}{\left[y_1 - y_*\right] - \left[y_2 - y_2^*\right]}}{\ell n \left[\frac{y_1 - y_*}{y_2 - y_2^*}\right]}$$
(3)

The overall height of the transfer unit H $_{OG}$ is related to the overall mass transfer coefficient by Equation 4.

$$H_{OG} = \frac{G}{K_{y^a}}$$
(4)

The two film theory shows that the overall resistance is the sum of two film resistances from Equation 5.

$$\frac{1}{K_{ya}} = \frac{1}{k_{ya}} + \frac{m}{k_{xa}}$$
(5)

Thus, it can be shown (Foust etal, 1980) from Equation 6, that

$$H_{OG} = H_G + H_L \frac{mG}{L}$$
(6)

The breakthrough curves for the amount of VOC removed can be developed as a function of time. Since, when the liquid phase is recirculated, an unsteady state material balance is necessary. The basic equation is :

Hence, for acetone, the component balance assuming pseudo first order kinetics is :

$$M\frac{dx_{1A}}{dt} = G_1' y_{1A} - G_2' y_{2A} - k_A x_{1A}$$
(8)

This equation reduces to

$$M \frac{dx_{1A}}{dt} + k_A x_{1A} = G'(y_{1A} - y_{2A})$$
(9)

for the dilute system with no purge rate of sulfuric acid, since $G_1' = G_2'$

Similarly, for ethyl alcohol, the component balance is :

$$M \frac{dx_{1E}}{dt} + k_E x_{1E} = G'(y_{1E} - y_{2E})$$
(10)

For runs with a sulfuric acid purge, the equation for acetone becomes :

$$M \frac{dx_{1A}}{dt} = G\left(y_{1A} - y_{2A}\right) - \left(L_{1}x_{1A} - L_{2}x_{2A}\right) - k_{A}x_{1A}$$
(11)

Since pure acid is used, x_{2A} is zero, and for dilute systems Equation 11 becomes :

$$M\frac{dx_{1A}}{dt} = G\left[y_{1A} - y_{2A}\right] - L_{1}'x_{1A} - k_{A}x_{1A}$$
(12)

A similar equation can be written for each component, ethyl alcohol, diethyl ether (inlet feed is zero). With proper purge, the transients should eventually disappear and steady state may be achieved.

The function for the concentration of sulfuric acid with time could be derived by :

$$M' \frac{dC_{acid}}{dt} = q' C_{o,acid} - q C_{acid} - k'$$
(13)

When the concentration of sulfuric acid is high, a pseudo zero order chemical reaction with a rate constant k' can be assumed.

Rearranging, Equation 13 gives,

$$M' \frac{dC_{acid}}{dt} + qC_{acid} = q'C_{o,acid} - k'$$
(14)

Similarly, the function for the concentration of water with time would be obtained by :

$$M' \frac{dC_{water}}{dt} = q' \quad C_{0,water} - qC_{water} + q'' \left[\frac{kg BDA_{in}}{min}\right] \quad H$$
(15)

where H is the absolute humidity, [g Water / kg Dry Air]

Rearranging, Equation 15 gives,

$$M' \frac{dC_{water}}{dt} + q \quad C_{water} = q' C_{0,water} + q'' \left[\frac{kg BDA_{in}}{min}\right] H$$
(16)

A search of the literature indicates that acetone, ethyl alcohol and diethyl ether will react with sulfuric acid. Jake (1987) indicated that nitroglycerin is destroyed by concentrated sulfuric acid by the formation of nitric oxide (NO_x) compounds which in turn are absorbed by the sulfuric acid.

Some of the reactions found are shown in Tables 1 - 3. These reactions were found in standard organic chemistry textbooks.

Table 1 shows the reactions of acetone and sulfuric acid. Table 2 shows the reactions of ethyl alcohol and sulfuric acid. [*Feiser*, L. F. & Feiser, M., 1957] Table 3 shows the reactions of diethyl ether and sulfuric acid. [Robinson, 1942]

Hence, absorption of VOC's in sulfuric acid reduce to a classic problem of gas absorption with chemical reactions.

Table 1. Reactions between Acetone and Sulfuric Acid





yellow crytalline solid, mp. 28 ° C, bp. 197.2 ° C

Other condensation product produced:



Mesitylene Trimethyl Benzene 1,3,5 :

low yield, colorless, mp. -44.8 ° C, bp. 164.8 ° C

Table 2 . Reactions between Ethyl Alcohol and Sulfuric Acid

$$CH_{3} - CH_{2} - OH + HO - SO_{2} - OH \xrightarrow{conc.} H_{2}SO_{4}$$

$$CH_{\overline{3}} - CH_{\overline{2}} - O - SO_{\overline{2}} - OH + H_{2}O$$

$$Ethyl Sulfuric Acid$$

$$Ethyl Hydrogen Sulfate$$

$$(T 2.a)$$

Euryr Hydrogen Sunde

Proceeds to completion with excess H_2SO_4 at 0 ° C.

H₂O reverses reaction

$$H \stackrel{H}{C} - CH_{2} - O - SO_{2} - OH \xrightarrow{170 \circ C} 96\% H_{2}SO_{4}$$

$$CH_{2} = CH_{2} + H_{2}SO_{4}$$
(T2.b)
Ethylene

$$CH_{3} - CH_{2} - O - SO_{2} - OH + HO - CH_{2} - CH_{3} \xrightarrow{}_{140 \text{ °C}}$$

$$CH_{3} - CH_{2} O + H_{2}SO_{4}$$

$$CH_{3} - CH_{2} O + H_{2}SO_{4}$$

$$(T2.c)$$

Diethyl Ether; colorless liquid, bp. 34.6 ° C

Both ethylene and diethyl ether which are byproducts at 170 ° C and 140 ° C have small differences in optimum temperature.

$$CH_{3} - CH_{2} - O - SO_{2} - OH \qquad < 140 \circ C$$

$$CH_{3} - CH_{2} - O - SO_{2} - OH \qquad Low Pressure$$

$$CH_{3} - CH_{2} - O - SO_{2} - OH \qquad Low Pressure$$

$$CH_{3} - CH_{2} - O - SO_{2} + H_{2}SO_{4} \qquad (T2.d)$$

Diethyl Sulfate; Colorless liquid; mp. -25 ° C, bp. 210 ° C

$$CH_{3}-CH_{2}-O-CH_{2}-CH_{3} + H_{2}SO_{4} \xrightarrow{20 \circ C}$$

$$CH_{3}-CH_{2}-O-SO_{2}-OH + HO-CH_{2}-CH_{3}$$

$$Ethyl Sulfuric Acid Ethyl Alcohol (T3.a)$$

Ethyl alcohol reacts with Sulfuric Acid :

$$CH_{3} - CH_{2} - OH + H_{2}SO_{4} \xrightarrow{20 \text{ °C}}$$

$$CH_{\overline{3}} - CH_{\overline{2}} - O - SO_{\overline{2}} - OH + H_{2}O$$

$$Ethyl Sulfuric Acid \qquad Water \qquad (T3.b)$$

5.2 Estimation of H OG for Acetone - Sulfuric Acid

An estimate of the H $_{OG}$ needed can be made using the data given by Othmer and Scheibel (1941). At operating conditions in the FAD unit, calculations indicate that about 74 percent of the resistance would be in the gas phase when using water. The constants in Equation 6 were determined from the Othmer's and Scheibel's data. The data are shown in Figure 1 for the acetone - air - water system. Hence, Equation 6 can be estimated to be Equation 17 for this system.

$$H_{OG} = 2.3806 + 2.9482 \frac{mG}{L}$$
(17)

For the acetone-air system, the gas film resistance should not change with the change in solvent. Sherwood and Holloway (1940) showed that the H $_{L_1}$ in Equation 6, which would change with solvent, can be estimated from Equation 18.

$$H_{\rm L} = \frac{1}{a} \left[\frac{L}{\mu} \right]^n \left[\frac{\mu}{\rho D} \right]^{\rm S}$$
(18)

Hence, using H_L for acetone - water of 2.95 from Equation 13, H_L for acetone - H_2SO_4 can be estimated by Equation 19, assuming diffusional effects only.

$$\frac{\left(H_{L}\right)_{\text{acetone}-H_{2}SO_{4}}}{\left[H_{L}\right]_{\text{acetone}-H_{2}O}} = \left(\frac{\mu_{H_{2}O}}{\mu_{H_{2}SO_{4}}}\right)^{n} \left(\frac{N_{\text{sc}_{\text{acetone}-H_{2}SO_{4}}}{N_{\text{sc}_{\text{acetone}-H_{2}O}}}\right)^{s}$$
(19)

Table 4 summarizes the data used to estimate H L, acetone-sulfuric acid.



Figure 1. Height of Transfer Unit vs. m G / L; System: Acetone-Air-Water

16

		Water		73 % Sulfuric Acid			
Viscosity, <i>cp</i>	0.95	1	11.00 ²				
Density, lb / ft^3	62.20 ³		102.36 ⁴				
Diffusivity, cm^2 / s , Act	1.22 ⁵ 782.00		Unknown 40777.00				
Schmidt Number, N _{SC}							
n = ().22; a		100;	S	=	0.5	

Table 4. Properties at 25 ° C used in Eq. 19 to Estimate H L, acetone - sulfuric acid

References :

- 1. Perry's Handbook
- 2. Kirk and Othmer Encyclopedia, Vol. I, p.196
- 3. Perry's Handbook
- 4. International Critical Table
- 5. Tyn, M.T., Culus, W.F.; J. Chem Eng & Data, 20, 3 (1975)

Actually, the value of H $_{\rm L}$, the resistance to mass transfer in the acetone - sulfuric acid system can only be estimated by this method because diffusion of acetone into sulfuric acid is not the sole factor. Rather, the absorption of acetone in concentrated sulfuric acid is in reality absorption with chemical reaction. The kinetic reaction factors must play a role. It is believed that the acetone will react rapidly as it reaches the sulfuric acid film. However, very little is known about the kinetic rate constant, its role in the resistance in the liquid film, and the rate of diffusion of the reaction products in determining the liquid film resistance. The data for Othmer and Scheibel (1941) indicted that 74 percent of the overall resistance in the acetone-water system is in the gas phase. With the equilibrium constants in the acetone - sulfuric acid system being much lower than that for acetone - water system (Figure 2), it is believed that for the case of absorption with chemical reaction of the acetone in sulfuric acid, the major resistance to mass transfer will be in the gas phase and that this will approach 100 percent.



Figure 2. Acetone in air equilibrium with mixtures of acetone and Various Concentrations of H2SO4 (Temp = 15 °C) [Ormandy, 1929]

The Wilke-Chang equation can be used to estimate the diffusivity of acetone in 73 percent sulfuric acid by Equation 20.

$$D=7.4E-8\frac{[XM]^{0.5}T}{\mu V^{0.6}}$$
(20)

Hence, Equation 20, compared for the two systems becomes

$$\frac{D_{acetone-H_2SO_4}}{D_{acetone-H_2O}} = \left(\frac{M_{H_2SO_4(73\%)}}{M_{H_2O}}\right)^{0.5} \left(\frac{\mu_{H_2O}}{\mu_{H_2SO_4(73\%)}}\right)$$
(21)

Thus, D acetone-H2SO4 (73 wt %) is calculated to be 6.424 E-06 ft² / hr and H L, acetone-H2SO4 (73 wt %) is estimated to be about, 12.64 feet, calculated from Equation 19.

For acetone - H_2SO_4 (73 wt %), Equation 6 becomes Equation 22.

$$H_{OG} = 2.38 + 12.64 \frac{mG}{L}$$
 (22)

Figure 3 shows the correlations of Equations 17 and 22.



Figure 3. Height of Transfer Unit vs. m G / L (Intercept = 2.38)

20

Chapter 6 Experimental Results

6.1 Vapor Liquid Equilibrium Studies

6.1.1 Experimental Apparatus

The experimental apparatus is shown in Figure 4. An available Hewlett Packard, 5700 A Gas Chromatograph was used with a ten foot stainless steel column, 1 / 8 inch in diameter, packed with Supelco, Catalog Number, 1 - 1813 M, 80 / 120 Carbopack B / 3 %, SP - 1500 packing. The unit contained a Model 18711 A Thermal Conductivity Detector (TCD).

The flask used for the calibration curve study had a volume of 4360 ml which was carefully measured. Known amounts of liquid organics were added with a 10 micro-liter syringe.

The recirculating blower was a Teflon Diaphragm Vacuum Pump (Cole Palmer, Catalog No. L - 07056 - 22). It has a single pump head configuration, a maximum vacuum of 25 inches of mercury, a maximum discharge pressure of 25 psi and flow rate of 0.57 cubic feet per minute.

For equilibrium studies, the 4360 ml flask was replaced with a 500 ml flask. This experimental method is a modified version of that used by Ormandy (1929). The sample loop in the Six-Way Valve was 3.0 ml.


Figure 4. Vapor - Liquid Equilibrium Experimental Apparatus

6.1.2 Experimental Procedure

Isopropyl Alcohol Methanol

Water

(A) Calibration

Known amounts of liquid organics were added to the 4360 ml flask shown in Figure 1 that had been flushed with nitrogen. The conditions used for calibration are shown in Table 5. The purity of the reagents is shown in Table 6.

Table	5.	HP	5700A	GC	Operating	Conditions
-------	----	----	-------	----	-----------	------------

Carrier Gas :	Helium at a rate of 20 ml / m	in
Oven Temperature :	80 - 110 ^o C sequencing at a	rate of 4 ^o C / min
Detector Setting :		
	Sensitivity -	6
	Attenuation -	4
	Temperature -	150 °C
Sample Circulation Rate :	0.13 cubic feet / m	in
	or 3.68 liter / m	in
Retention Time; minutes		
	Air	1.27
	Ethyl Alcohol	3.12
	Acetone	4.25
	Ethyl Ether	6.95

Table 6. Reagents Used in This Study

Sulfuric Acid. H ₂ SO ₄		Ethyl A	lcohol.	СH ₃ CH ₂ OH
Fisher Scientific Co.,		Fisher Scientific Co.,		
A 300 ^c - 212 Reagent Grade A Min. 95 % by weight Max. 98 % by weight Specific Gravity 1 Normality 3	CS .84 6	A 962 - 4 Reagent Alcohol Anhydrous Alcohol, Vol. 90 $\% \pm 1 \%$ Denaturants Added, volume Methyl Alcohol, 5 $\%$ Isopropyl Alcohol 5 $\%$		
Acetone. CH ₃ CO CH ₃		Diethyl	Ether. CH	3CH2OCH2 CH3
Fisher Scientific Co., A 18 - 4 Certified ACS		Mallincki Anhydroi	rodt UN 11 us Analytical	55 Reagent
Density 0.7854 gm / ml at 25 °	° C	Density	0.7077	gm / ml at 25 ^o C
Boiling Point 56.1 $^{\circ}$ C ± 0.1 C Denaturants Added, volume	°C	Water	0.005	%

0.01 % 0.02 %

0.3 %

Density	0.7077 gill, ill at 25
Water	0.005 %

(B) Equilibrium Studies

Known amounts of liquid organics were added to 100 ml of sulfuric acid. The concentrations of sulfuric acid which were used were 76 percent by weight and 96 percent. Initial tests were made at room temperature.

However, a large quantity of heat of mixing was observed and, hence, the acid and the organic were then both cooled to 0 $^{\circ}$ C before mixing. The system was blanketed with nitrogen and the gas phase was recirculated. The temperature of the sulfuric acid solution was controlled at the desired temperature between 15 $^{\circ}$ C and 54 $^{\circ}$ C.

After equilibrium was established, three different samples were trapped in the sample loop of the six-way valve (Figure 4) and then swept into the GC column directly. The average of these three analyses was used for the correlations. Operating conditions for the Gas Chromatograph are shown in Table 5.

6.1.3 Experimental Results

(A) Calibration

The calibration curve is shown in Figure 5 for acetone, ethyl alcohol and diethyl ether.

(**B**) Equilibrium Studies

Prior to making the equilibrium studies, the method and apparatus used were verified by comparison with previous studies. Figure 6 shows a comparison of the measurements of acetone with the data of Ormandy (1929). Agreement is excellent. Figures 7 and 8 show the data for diethyl ether compared with the data of Robinson (1942). Agreement is also excellent.

With the experimental technique established, vapor - liquid equilibrium data were developed for acetone, ethyl alcohol, and diethyl ether in 76 percent by weight sulfuric acid and 96 percent by weight acid.

Figure 9 shows the data for acetone in 76 percent by weight sulfuric acid as a function of temperature. The mole fraction of acetone in the air is far in excess of the concentration that will result in this study (1,200 ppm in the feed gas). Figure 10 shows the data for ethanol in 76 percent acid.



Figure 5. HP 5700A GC - Calibration Curve [Acetone, Ethanol, and Ethyl Ether In Air]





Figure 7. Ethyl Ether in Air equilibrium with mixtures of Ethyl Ether and 96 wt% H2SO4 [Temp = 20°C]



Figure 8. Ethyl Ether in Air equilibrium with mixtures of Ethyl Ether and dilute 76 wt% Sulfuric Acid [$T = 20^{\circ}C$]

As expected, for a given mole fraction of acetone, or ethanol in the liquid phase, the mole fraction in the vapor phase rises with the temperature.

Figures 11 and 12 show the equilibrium data for acetone and ethyl alcohol in 96 percent by weight sulfuric acid. There is no trace of acetone or ethyl alcohol in the vapor phase.

6.2 Gas Absorption Studies

6.2.1 Experimental Apparatus

The same gas chromatograph that was used for the equilibrium studies was used for the absorption studies. The flow diagram is shown in Figure 13.

The gas absorption column was made of 2 inch diameter Pyrex glass pipe packed to height of 1 foot, six inches with 1/4 - inch Ceramic Raschig rings. The top of the column was a short section of 1/4 - inch Berl Saddle packing, 5.5 inches high. The section was installed for true countercurrent absorption using fresh purge sulfuric acid.

Temperatures were measured of the input and output streams with thermocouples. Other temperatures were measured with thermometers. The sulfuric acid reservoir was a glass bottle with a capacity of about 510 ml and was cooled in an ice bath.

The recirculating pump was a Teflon Low Flow Diaphragm Pump, Cole - Parmer Catalog Number L - 07088 - 48. The pump speed (or flow) was controlled by Cole - Parmer Series 2630 power supply, variable speed controller, Cole - Parmer Catalog Number L - 02630 - 25.

All tubing, fittings, and valves were made of type 316 stainless steel or teflon.



Figure 9. Acetone In Air equilibrium with mixtures of Acetone and diluted H2SO4 at Various Temperatures



Figure 10. Ethanol In Air equilibrium with mixtures of Ethanol and dilute H2SO4 at Various Temperatures



Figure 11. Acetone in Air equilibrium with mixtures of Acetone and concentrated Sulfuric Acid



Figure 12. Ethanol in Air equilibrium with mixtures of Ethanol and concentrated Sulfuric Acid



Figure 13. Absorption Column Schematic Flow Diagram

The air to the column was filtered and controlled with a calibrated rotameter with a maximum scale reading equal to 31 liter / min. (Max = 100%) The acetone and ethyl alcohol glass reservoirs were 500 ml 3-neck flasks and flows were metered with rotameters with maximum scale rates of 2 liter / min (Max = 100%) and 6.8 liter / min (Max = 100%) respectively.

The fresh, 76 percent sulfuric acid purge was stored in a reservoir made of 2 - inch Pyrex glass pipe, 8 inches long. The flow was forced into the system by pressurizing the free space of the reservoir with 5 *psig* of helium gas. The purge was controlled through a rotameter at 1 ml / min and room temperature.

6.2.2 Experimental Procedure

The air flow was set at 15 liter / min and the nitrogen rates to the acetone and ethyl alcohol reservoirs were set at 150 ml / min and 750 ml / min respectively. The reservoirs were kept at room temperature. The air feed was heated to the desired temperature of $140 \circ F (60 \circ F)$. The feed gas and off gas were analyzed. The sulfuric acid recirculating rate was set at about 100 ml / min. The liquid and gas flow rates were set to avoid flooding and the L / G ratio was in the vicinity of the loading point.

Samples of absorber effluent gas were analyzed over a period time to determine breakthrough. For runs with a sulfuric acid purge, the purge rate was about 1 - 2 percent of the recirculation rate. After a few runs, it was noted that the packing began to settle. At this point, the column was inverted to loosen the packing and returned to its original packed height.

6.2.3 Experimental Results

The experimental results of the absorption study are shown in Figures 14 - 17. Figure 14 shows that the humidity in the laboratory air causes the sulfuric acid concentration to decline with time. The relationships are nearly all linear.

Figure 15 shows the percent VOC removed as a function of time for two duplicate runs with recirculating 76 percent sulfuric acid and no purge for acetone. The first traces of acetone appeared in the absorber gas effluent in about two hours.









Figure 15 shows the percent VOC removed as a function of time for two duplicate runs with recirculating 76 percent sulfuric acid and no purge for acetone. The first traces of acetone appeared in the absorber gas effluent in about two hours. Thereafter, the amount of acetone in the absorber gas effluent increased rapidly and, hence, the percent VOC removed dropped sharply.

Breakthrough, defined as an acceptable 85 percent removal of the VOC (Jake, 1987), occurred in about 4 - 5 hours.

Figure 15 also shows that there was no breakthrough for ethyl alcohol, and also there was no trace of diethyl ether. Figure 16 compares the data with no purge to that with a small purge rate of 1 ml / min (Recirculation rate is 100 ml / min). There was no evidence of acetone in the absorber gas effluent until about 18 hours. Thereafter, the percent removal dropped sharply as acetone began to appear in the absorber gas effluent, and breakthrough occurred in about 21 hours. There was still no evidence of ethyl alcohol nor diethyl ether in the absorber gas effluent.

Figure 17 shows the same results with 96 percent sulfuric acid for a 24 - hour run. There was no trace of acetone, ethyl alcohol, or diethyl ether with recirculation only. Purge acid was not needed during this period.

Observations were made with 76 percent acid indicating that the sulfuric acid became green in color but remained clear. This color was probably due to the corrosion of stainless steel resulting in metallic ions.

For 96 percent acid, the color first appeared light yellow (probably acetone reacting with sulfuric acid to form Di Isopropylidene Acetone [Ref. Table 1]), and then became dark brown. The reaction products of the VOC's, acetone and ethyl alcohol, with sulfuric acid were the possible causes. There was same evidence of stainless steel corrosion and this could be from unknown type 304 stainless steel parts used. The acid had no effect on the glass column, ceramic packing, or teflon parts used in the system. (pump *etc.*)

The literature (E. I. du Pont Inc.) shows various materials of construction are resistant to 76 percent and 96 percent sulfuric sulfuric acid. Type 304 stainless steel is not resistant except at concentrations greater than 100 percent. However, type 316 stainless steel is resistant at lower temperature to acid concentrations greater than 80 percent.

The process design of the VOC removal system utilizing recirculating concentrated sulfuric acid requires that a dynamic analysis be made of the acid accumulator, since the mass and energy relationships that describe the acid inventory are by definition time dependent. This is best illustrated by considering the forced air dryer (FAD) effluent air process unit which has a design air flow of 3,000 cubic feet per minute at 140 ° F. The following table summarizes the contaminants present in the effluent from the FAD unit.

3,000 cfm of Air at 140 ^o F Water and VOC Content (From the FAD Unit)

ppm (Vol)
44,000
1,200
1,850
15

A sulfuric acid concentration greater than 90 wt % is sufficient to remove all of the water vapor and at least 85 percent of the acetone, ethyl alcohol and nitroglycerin (NG) VOC's present in the FAD effluent. The design take up of the contaminants by the acid solution is summarized in the following table, and is based on the above removal factors.

3,000 cfm of Air at 140 ^o F Acid Solution Take-Up

	Lb/hr
Water	335
Acetone	25
Ethanol	31
NG	1.2

The circulation rate of the acid solution to be employed in the vapor - liquid contactor is established using as the criteria a pressure drop which will generate good vapor - liquid contacting and hence the realization of the desired removal of the volatile organic compounds from the forced air dryer unit's effluent. The removed material will accumulate with the circulating sulfuric acid.

The minimal volume of acid in the scrubbing system is set by estimating the overall holdup in the major pieces of equipment plus the associated piping. Good design practice dictates that the operating acid inventory in the acid accumulator be sufficient so that the operation of the acid circulation pump and the ancillary equipment consisting principally of an acid heat exchanger will have stable operating characteristics.

(A) Material Balance

The initial design and analysis of the circulating acid system material balance considered the following :

- The accumulated water will dilute the initial acid charge.
- The acid concentration will be maintained at a level of 95 wt % using makeup acid coupled with an acid purge.
- The acid addition and purge will be designed to maintain the minimum acid concentration, and thus the VOC's will not have steady state characteristics.
- The VOC's in the acid solution will consume negligible quantities of sulfuric acid.

The design analysis of the acid circulation system was accomplished by the development of a simulation model using BASIC for portability and rapid model development. (Appendix F) The model used a specified inventory of 2,000 gallons of 96 wt % sulfuric acid. Provisions exist to allow the initial acid inventory to have VOC's present. The minimum acid concentration was set at 95 wt %. This level was established by considering materials of construction versus acid strength. The 95 wt % acid concentration will be maintained using 98 wt % acid as makeup plus an acid purge.

The water - VOC take up by the circulating acid from the FAD air effluent was assumed to be 100 % of the water and a specified 85% removal rate for the VOC's.

The model development permits variable water and VOC content in the feed gas as well as variable recovery factors. The material balance associated with the model assumes initial operation with no acid makeup - purge. The dilution of the acid is monitored until the minimum acid concentration is achieved. When the minimum strength acid is reached, makeup acid (98 wt %) coupled with an acid purge stream is used to maintain the specified minimum acid strength. The concentration of the VOC's is continuously monitored during the acid circulation both with and without acid addition - removal.

Using an initial inventory of 2,000 gallons of uncontaminated 96 wt % sulfuric acid, it took 1.0 hour before the circulating acid reached the minimum acid level of 95 wt %. The 95 wt % acid strength was maintained utilizing an 11.5 gpm acid addition rate (98 wt % acid) coupled with an 11.9 gpm purge rate of 95 wt % acid (containing VOC's). The ability to use oleum to maintain the minimal acid level concentration was not included in the model development.

(B) Energy Balance

The energy balance associated with the VOC recovery unit model considered the following issues in accomplishing the process design of the sulfuric acid cooler :

- The entering air stream is cooled from the entering gas temperature (140 ° F) to the specified discharge temperature.
- The removed water and VOC's are condensed.
- The condensed water dilutes the sulfuric acid accompanied by a heat of reaction.
- The makeup purge acid streams are included in the acid solution energy balance.
- The unsteady state energy balance is used to establish the heat duty associated with the acid cooler under variable load conditions.

The 2,000 gallon acid inventory is initially circulated without acid addition - purge or use of the acid cooler. The VOC removal system operates only for 0.15 hours before the acid inventory experiences a temperature rise of 10 $^{\circ}$ F from the initial temperature of 80 $^{\circ}$ F to a maintainable operating temperature of 90 $^{\circ}$ F.

To sustain the operating temperature of 90 $^{\circ}$ F, 0.76 M Btu / hr must be continuously removed in a heat exchanger. When the acid inventory reaches the 95 wt % level due to water take up, the acid makeup - purge is initiated.

Under these circumstances the heat duty associated with the external heat exchanger reduces to the level of 0.56 M Btu / hr because of the addition of cold make-up acid (80° F) and the removal of energy via the acid purge stream. The two heat removal levels associated with the external acid cooler are essentially constant due to the low level of VOC's in the system.

(C) VOC Buildup in Acid Solution

The continuous circulation of sulfuric acid in contact with the FAD air effluent containing some 3,065 ppm (by volume) of VOC's does not exhibit steady state characteristics. The acid addition - purge is designed to maintain the acid concentration level at the stipulated minimum of 95 wt %.

With the water-sulfuric acid steady state material balance established, the other species present in the FAD effluent continue to have an unsteady state behavior. Even considering the VOC's present in the acid purge the VOC's continue to exhibit a buildup in the acid solution.

The following table describes the time variation of VOC's (ppm by wt). These data were obtained from the simulation model, and clearly describe a linear relationship with time

3,000 cfm of Air at 140 ° F

VOC Buildup in Acid Solution, ppm

	12 hr	24 hr	36 hr
Acetone	9,440	18,490	27,160
Ethanol	11,560	22,630	33,250
NG	460	905	1,330

The model can thus be used to characterize the VOC content in the total acid inventory with time.

With the constraint of a specified minimum acid concentration, the only manipulative parameters available to the process designer is the size of the initial acid charge and the initial loadings VOC's. The above tabular data reflects an initial acid charge 2,000 gallons void of VOC's.

Thus the hydrocarbon concentrations can only be reduced by using a larger acid charge or to totally replace the acid with a fresh charge at some predetermined interval.

Chapter 7 Discussion of Results

7.1 Vapor Liquid Equilibrium Studies

Vapor Liquid Equilibrium Data presented by Ormandy (1929) in the dilute region are shown in Figures 2 and 18. The slope of the graph in the dilute region is a measure of Henry's Law constant. Figure 2 also shows the data for acetone in water (0% sulfuric acid). Figure 18 shows that as the concentration of acid rises, the slope decreases. Figure 19 shows a correlation of equilibrium constant and sulfuric acid concentration. The graph shows that the equilibrium constant approaches zero in the vicinity of 75 percent sulfuric acid by weight for low concentrations of acetone in the liquid. This fact is verified in Figure 9 for 76 percent by weight sulfuric acid and in Figure 11 for all concentrations of acetone in 96 percent by weight sulfuric acid. Hence, using 96 percent acid removes all acetone from the vapor phase.

The same analysis was used with the Robinson (1942) data for diethyl ether. Figure 20 shows that in the dilute region, the equilibrium constant falls as the concentration of sulfuric acid rises. Figure 21 shows that the equilibrium constant approaches zero in the vicinity of 96 percent sulfuric acid but does not drop to zero. This fact is shown in Figure 7.

There are no available published data for ethyl alcohol in sulfuric acid. Figure 10 shows that at low concentrations and low temperatures, the concentration of ethyl alcohol in the vapor is nil with 76 percent sulfuric acid. In Figure 12, the data for 96 percent sulfuric acid show no trace of ethyl alcohol at all concentrations and all temperatures.

Unknowns Observed During Vapor-Liquid Equilibrium Studies:

In the studies using 76 percent sulfuric acid no unknowns appeared during the acetone and diethyl ether runs. (Appendix E) With ethyl alcohol, at high concentrations and at temperatures above 34 ° C, the methyl alcohol (CH_3OH) impurity in the reagent grade ethyl alcohol (C_2H_5OH) appeared at a retention time of 2.05 minutes and the isopropyl alcohol impurity appeared at 4.96 minutes.



Figure 18. Acetone in air equilibrium with mixtures of Acetone and Various Concentrations of H2SO4 (Temp = 15 °C) [Ormandy, 1929]



Figure 19. Acetone-Sulfuric Acid System; Equilibrium constant vs. Weight Percent Sulfuric Acid (Temp = 15 °C) [Ormandy, 1929]





With acetone in 96 percent sulfuric acid, sulfur dioxide (SO₂) was detected at the retention time of 1.92 minutes above 34 ° C. These analyses were made using a HP 5988 Mass Spectrograph coupled with a HP 5890 Gas Chromatograph. The column for this system was a 50 meters long and 0.32 mm in diameter cross-linked methyl-silicone capillary column. The carrier gas (Helium) rate was 1ml/min. Temperature sequencing was, initial temperature 30 ° C (hold 2 minutes) then increase temperature at 4 ° C/min to final temperature 160 ° C (hold 5 minutes). 2 - methyl - propanol or butenol (C₄H₈O) was detected at a retention time of 12.3 minutes using the HP 5890 only. With ethyl alcohol in 96 percent sulfuric acid, sulfur dioxide (SO₂) was detected at a retention time of 1.92 minutes. Above 54 ° C, C₄H₈O was detected along with CH₃OH and isopropyl alcohol using the HP 5890 only.

With diethyl ether and 96 percent sulfuric acid, $C_6H_{14}O_2$ (Retention Time = 13.2 minutes) and C_4H_8O (Retention Time = 12.6 minutes) were detected using the HP 5890 only.

If temperatures reach higher levels, the acetone, ethyl alcohol and diethyl ether with 96 percent sulfuric acid may yield other compounds. Sulfur dioxide (SO_2) will also be stripped out of the acid by the gas flow.

7.2 Gas Absorption Studies

Calculations for 1 - inch ceramic Raschig rings indicate that the mixer unit would require a column diameter of 2.5 feet and the FAD unit would require a column diameter of 4.5 feet. The results of calculations are summarized in Table 7 for 85 percent removal of the VOC's.

Curves were also presented for N $_{OG}$ as a function of percent VOC removal at various L / G ratios and acid strengths for both the mixer unit and FAD unit. For 73 percent acid the curves are shown in Figures 22 and 23. The results are summarized in Table 8 for 85 percent removal of the VOC's.

Table 7. Height of Column

(85 % removal, 1 inch Ceramic Raschig Rings)

$Z = N_{OG} * H_{OG}$

	Mixer Unit		FAD Unit	
	H ₂ O	H ₂ SO ₄ (73%)	H ₂ O	H ₂ SO ₄ (73%)
L = moles / hr	407	211	1220	211
G = moles / hr	137	137	411	411
CFM	1000	1000	3000	3000
ppm Acetone	450	450	1200	1200
L / G (Mass Ratio) Pressure Drop,	1.8	2.8	1.8	0.79
inches of water / ft of packing	0.8	0.45	0.6	0.25
Column Diameter, ft	2.5	2.5	4.5	4.5
N OG H OG (estimated), <i>ft</i>	1.6 3.5	0.44 7.4	1.6 3.5	0.58 7.4
Z, ft	5.6	3.3	5.6	4.3

Table 8. Effect of Acid concentration on N $_{OG}$

Mixer - 2 ft and 6 inches	in Diameter			
% H ₂ SO ₄	N OG	L/G (molar)	Pressure Drop	
			inches of water / ft of packing	
73	0.44	1.54	0.45	
65	0.64	1.73	0.50	
0	1.60	2.97	0.80	
FAD - 4 ft and 6 inches i	n Diameter			
% H ₂ SO ₄	N OG	L/G(molar)	Pressure Drop	
			inches of water / ft of packing	
73	0.58	0.51	0.25	
65	0.64	1.73	0.45	
0	1.60	2.97	0.60	





The effect of rising acid strength is to markedly reduce the N $_{OG}$ needed and, hence, this results in a shorter packed height. Since the slope of the equilibrium line becomes zero for 76 percent and 96 percent acid, the N $_{OG}$ values approach $ln (y_1/y_2)$ [Equation 3]. Hence, with these acid strengths almost any type of contacting system can remove the VOC's from air. The estimated H $_{OG}$ for the mixer unit and FAD unit are summarized in Table 7 and the required packed height is also shown. The estimated packed tower height is less for sulfuric acid over water but neither is very large.

The decline in sulfuric acid concentration on an organics free basis with time, which is shown in Figure 14, results from the humidity of the laboratory air. Humidity considerations will be a major design factor. These calculations are also dependent upon the size of the reservoir. A larger reservoir, would mean a less rapid decline in concentration with time. These data show that a purge rate of sulfuric acid will be necessary. Furthermore, if the concentrations of the purge acid were higher than 76 percent, the recirculating acid concentration can be maintained at a constant value.

Figure 15 shows that a recirculating 76 percent acid system alone cannot remove acetone sufficiently. However, the sulfuric acid did remove ethyl alcohol completely and there was no trace of diethyl ether in the absorber gas effluent. A comparison of Figures 9 and 10 shows that the equilibrium constant at room temperature for ethyl alcohol is about half that of the acetone. Hence, the ethyl alcohol is held more tightly in the liquid phase than acetone. In addition, the ethyl alcohol may react more rapidly to ethyl sulfuric acid and, hence, held more firmly in solution. Acetone reactions may be slower. Figure 16 shows that a purge rate of 1 ml / min, prolongs the breakthrough time for acetone by a factor of 4 - 5. These breakthrough times are also dependent upon the reservoir size. Higher purge rates or higher concentrations prolong breakthrough.

Figure 17 shows that 96 percent sulfuric acid appears to remove all the acetone and ethyl alcohol for the period of the study. In a totally recirculating system, some breakthrough will eventually occur because the acid concentration will fall, and, hence, the equilibrium constant will rise. These facts will eventually cause acetone to appear in the absorber gas effluent. In all runs, there was no trace ever of ethyl alcohol or diethyl ether in the absorber gas effluent. In addition, none of the products of reaction appeared in the absorber gas effluent when the GC column was raised to a temperature of about 140 $^{\circ}$ C from a previous maximum of 110 $^{\circ}$ C and the retention time was observed to 15 minutes.

Corrosion and material of construction considerations are important to keep plant investment and maintenance costs low. Type 304 stainless steel is not suitable and it may have been the major cause of the green color observed with 76 percent acid. There was no absolute control on the parts used in the experimental apparatus and, hence, it is possible that some type 304 stainless steel was used. Type 316 stainless steel is suitable in acid strengths above 80 percent by weight at lower temperatures. In the region of 96 percent acid, the temperature can rise to as high as $40 - 60^{\circ}$ C and type 316 stainless steel is still suitable. Suitability is defined as a corrosion rate of less than 0.02 inches per year.

7.3 Proposed Pilot Plant

Figure 24 shows the proposed pilot plant of the experimentation of the removal of VOC's, acetone, ethyl alcohol, and nitroglycerin from the mixer and the FAD unit. It is proposed to build the pilot plant at the actual plant site to permit actual flows from the mixer and the FAD unit to be tested.

With an on - line Gas Chromatograph the estimated cost of this pilot plant will be in the range of \$ 70,000 - \$ 80,000. All construction will be with glass, glass - lined vessels, or type 316 stainless steel.



Figure 24. Proposed Pilot Plant Study Unit
Based on the laboratory data, the operating conditions of proposed pilot plant are summarized in Table 9.

Table	9.	Proposed	Pilot Plant	Operating	Conditions
-------	----	----------	-------------	-----------	------------

Gas Feed Rate, ft ³ /min	at STP	•	3.08
Liquid Circulation Rate,	gal / min	•	0.165
Fresh H ₂ SO ₄ Feed Rate,	gal / min	:	0.003
Purge Acid Rate,	gal / min	:	about 0.003 keeping acid level constant
Nitrogen Flow to Acetone Vaporizer,	ft 3 / min	:	0.071
Nitrogen Flow to Ethanol Vaporizer,	ft 3 / min	:	0.121

Chapter 8 Conclusions and Recommendations

The conclusions of this study are:

- 1. The reactions between acetone, ethanol and sulfuric acid are observed to be exothermic reactions.
- 2. The vapor-liquid equilibrium data for using 76 % sulfuric acid show that the correlations are functions of concentration and temperature:
 - a. Concentration term: linear at low concentrations but flex upward at higher concentrations.
 - b. Temperature term: the VOC's in the vapor phase increasing as temperature raise.

But using 96 % sulfuric acid, the VOC's in the vapor phase are nil in this study.

- 3. Using 96 percent sulfuric acid in a gas absorption column can remove acetone and ethyl alcohol, with or without purge.
- 4. Using 96 percent sulfuric acid will prolong breakthrough time.
- 5. Seventy six percent acid is not as effective as ninety six percent acid.
- 6. The humidity in the air will be a major factor in the system design.
- 7. A continuous system using 96 percent sulfuric acid can be designed to remove effectively all of the acetone and ethyl alcohol from the air leaving the mixer units and the FAD units.
- 8. The proper choice of acid strength and temperature can result in use of cheaper materials of construction to keep plant cost down.

The recommendations of this study are:

- 1. Construct a pilot plant unit to study the removal of VOC's, acetone and ethyl alcohol from the mixer and the FAD units at the plant site.
- 2. Keep the temperature of sulfuric acid low.
- 3. Select glass, teflon, and type 316 stainless steel as materials of construction.
- 4. Follow the progress of nitroglycerin removal at the plant site.

- 5. Build the absorption column about 6 inches in diameter and about 5 feet high packed with half inch Ceramic Raschig rings with a smaller section 4 inches in diameter and one and half feet high to act as a countercurrent gas absorption section utilizing the fresh make - up acid feed.
- 6. The Gas Chromatograph should contain a Flame Ionization Detector (FID) which will allow better sensitivity at lower concentrations.

Appendix A Calibration Graphs

•

.



Figure 25. HP 5700A GC - Calibration Curve [Acetone, Ethanol & Ethyl Ether In Air]

TABLE 10.	HP	5700A	GC	Calibration	[Species	In Air]	(Summarized	Table)
	Acetone		PAN	Ethanol			Ethyl Ether	
Concn.	Concn.	Peak-Area	Concn.	Concn.	Peak-Area	Concn.	Concn.	Peak-Area
(ppm.m)	(ppm.v)	Percentage	(ppm.m)	(ppm.v)	Percentage	(ppm.m)	(ppm. v)	Percentage
84	42	0.006006	167	105	0.01001	114	45	0.01501
167	83	0.02236	233	147	0.01435	182	71	0.028693
209	104	0.02102	433	272	0.028013	303	118	0.040373
435	217	0.057737	650	409	0.048717	439	172	0.054037
670	334	0.091783	883	555	0.065063	606	237	0.08008
887	442	0.110433	1317	828	0.113433	879	344	0.117433
1356	676	0.1732	2000	1258	0.195533	1409	551	0.19445
1640	818	0.2222	3000	1886	0.291633	2181	852	0.300857
2478	1236	0.337667	3550	2232	0.363033	3030	1184	0.411713
3014	1503	0.410067						
3516	1754	0.474167						
Note :		Operating	Conditions	shown in	Table 5			



Figure 26. Calibration Curve of Rotameter for Air by Wet Test Meter

64



Figure 27. Teflon - Pump (Calibration Curve)

65

Table 11.	Calibration	Data for Meter	and Pump	
Rotameter for	Main - Air Flow	Teflon Pump	for H2SO4	
Scale (Max = 100)	Flow Rate (Liter / minute)	Scale (Max = 10)	Flow Rate (c.c. / minute)	
19	5.701	3	36	
32	10.297	4	103.5	
35	12.136	5	220	
48	15.036	6	481	
60	20.226	7	670	
79	25.359	8	825	
88	28.317	9	785	
97	30.891	10	520	
Note :				
Wet Test	Meter Method	Using water as	a measurement	
for the calibration	of Rotameter;	for it's a positive	displacement	
			pump.	

Appendix B Sample Calculations

1 Calibration Calculation:

Let's say we throw 12 μ L acetone liquid into a closed system:

We had a vessel of 4360 ml containing air heated at 60 ° C. According to the ideal gas law :

$$N_{air} = \frac{PV}{RT} = \frac{1 \text{ atm } * 4.360 \ \ell}{0.08205 \ \frac{\text{liter} * \text{ atm}}{\text{gmole} *^{0} \text{ K}}} = 0.1595 \text{ g-mole}$$

At room temperature, the density of acetone liquid is 0.7887 g/ml. So,

W acetone = $\rho_{acetone} * V_{liquid acetone} = 0.7887 [g/ml] * 1.2 E-02 [ml]$ = 9.4644 E -03 g

Then, the number moles of acetone (N_{acetone}) = W_{acetone} / M_{acetone} = $9.4644 \text{ E} \cdot 03 / 58.09$

= 1.629 E -04 g-mole. Assuming ideal gas behavior, molar ratio is equal to volumetric ratio at the

same temperature and pressure. Thus, the concentration (ppm. by volume) of acetone in air would be

$$C_{acetone} = [N_{acetone} / (N_{air} + N_{acetone})] * 1 E + 06$$

= [1.629 E-04 / (0.1595 + 1.629 E - 04)] * 1E + 06
= 1020.27 ppm by volume.

The mole fraction, y acetone would be 0.001020.

2 Estimation of N_{OG} for FAD unit by using 73 % H₂SO₄:

Using Equation 3 to calculate N OG.

$$N_{OG} = \frac{\frac{y_1 - y_2}{\left(y_1 - y_*\right) - \left(y_2 - y_2^*\right)}}{\ell n \left(\frac{y_1 - y_*}{y_2 - y_2^*}\right)}$$

(Eq.3)

From Table 7, the concentration of VOC was 1200 ppm (by volume) acetone. Therefore, the inlet mole fraction of acetone would be

 $y_1 = 1200 / (1200 + 1 E + 06) = 1.2 E - 03$

From Figure 18, the equilibrium curve for acetone - sulfuric acid system:

 $y^* = 2.0862 \text{ E} - 02 * x^*$. At the top of the column, $x_2 = 0$, $y_2 = 0.15 * y_1$ = 1.8 E -04 [85 % VOC Recovery].

The operating line, which has a slope, 0.51 (L/G ratio), is drawn through (x_2 , y_2).

 $y_2^* = 0$ at $x_2 = 0$. At $y_1 = 1.2 \text{ E} - 03$, from the operating line we obtain $x_1 = 2 \text{ E} - 03$. Then we go to the equilibrium curve and get $y_1^* = 4.2 \text{ E} - 05$.

Substituting all these values into Equation 3, we would get 0.576 for N $_{OG}$

3 Estimation of H OG for Acetone - 73 wt % H₂SO₄

a. Sherwood, T. K. & Holloway, F. A. L., Trans. AICHE 36, p. 39 (1940)

$$H_{L} = \frac{1}{a} \left(\frac{L}{\mu} \right)^{n} \left(\frac{\mu}{\rho D} \right)^{s}$$

For 1 "Raschig Rings: n = 0.22, a = 100, s = 0.5, thus, $\frac{\begin{pmatrix} H_L \\ acetone-H_2SO_4 \\ \hline H_L \\ acetone-H_2O \end{pmatrix} = \begin{pmatrix} \mu_{H_2O} \\ \overline{\mu_{H_2SO_4}} \end{pmatrix}^{0.22} \begin{pmatrix} Nsc_{acetone-H_2SO_4} \\ \overline{Nsc_{acetone-H_2O}} \end{pmatrix}^{0.5}$

b. Physical properties of water compared to those of sulfuric acid:

 $\mu_{\text{water}} = 0.95 \text{ cp} (25^{\circ} \text{ C}, \text{Perry's Handbook})$ $\mu_{\text{sulfuric acid}} = 11 \text{ cp} (\text{Kirk & Othmer Encyclopedia, <u>196</u>})$ $\rho_{\text{water}} = 62.2 \text{ lb/ft}^3 (\text{Perry's Handbook})$ $\rho_{\text{sulfuric acid}} = 102.36 \text{ lb/ft}^3 (\text{International Critical Tables})$ $D_{\text{acetone - water}} = 1.22 \text{ cm}^2/\text{s}$

(Tyn, MT & Culus, W. F. J of Chem Eng & Data 20, III, p. 310, 1975)

c. Estimate D acetone - sulfuric acid:

Wilke - Chang Equation

Wilke, C. R. & Chang, P.; AICHE J, 1, p. 264 (1955)

$$D=7.4E-8\frac{\left(XM\right)^{0.5}T}{\mu V^{0.6}}$$

 $D = cm^2/s$

Χ	=	2.6 for water as solvent assoc	iated so	lvents	
М	=	molecular weight of solvent,	=	76.4	g / mole
Т	=	temperature, 0 K ,		298.15	οĸ
μ	Ξ	viscosity, cp,		11	ср
V		molar volume of solute (acet	one = 7'	7.5 c.c. ,	/ gmole)

The ratio of Equation 10 for the two systems gives,

$$\frac{D_{acetone-H_2SO_4}}{D_{acetone-H_2O}} = \left(\frac{M_{H_2SO_4(73\%)}}{M_{H_2O}}\right)^{0.5} \left(\frac{\mu_{H_2O}}{\mu_{H_2SO_4(73\%)}}\right) = 0.1359$$

 $D_{acetone - sulfuric acid} = 0.1359 * 4.727 = 0.6424 \text{ ft}^2 / \text{hr}$

d. Calculations of H $_{OG}$ and H $_{L}$ acetone - water :

[Othmer, D. F. & Scheibel, E. G., Trans. AICHE, <u>37</u>, p. 211 - 225 (1941)]

From Figure 2 on p. 219, the slope of the equilibrium graph, m, is 1.148 and is the equilibrium constant for acetone - water system at room temperature.

Let's pick up Run 1 data from Table 2 on p.218 as an example to get a set of (m G / L, HOG):

(1) $G = 177 \text{ lb / hr} - \text{ft}^2 [\text{Air}];$ $L = 526 \text{ lb / hr} - \text{ft}^2 [\text{Water}]$ G/L (Molar ratio) = (177/29)/(526/18) = 0.20886m G/L = 1.148 * 0.20886 = 0.23716 (2) $K_g a = 2.26 \text{ lb mole / hr - ft}^3 - \text{atm};$ H OG = G / K_g a * P * M = 2.7006 ft [P = 1 atm; M = 29 lb / lb mole]

Then, we plotted H $_{OG}$ vs. m G / L. That would give us the equation 7.

$$H_{OG} = 2.3806 + 2.9482 \frac{mG}{L}$$

The slope of the line, 2.9482, is the H $_L$ acetone - water \cdot

e. Calculations of H_L acetone - sulfuric acid:

N sc acetone - water = $\mu_{water} / (\rho_{water} * D_{acetone - water}) = 0.00782$ N sc acetone - sulfuric acid = $\mu_{acid} / (\rho_{acid} * D_{acetone - acid}) = 0.40483$

$$\frac{\begin{pmatrix} H_{L} \\ acetone-H_{2}SO_{4} \\ \hline H_{L} \\ acetone-H_{2}O \\ \hline = (0.95/11)^{0.22} * (40477/782)^{0.5} \\ = 0.5834 * 7.195 \\ = 4.198 * 2.9482 \\ = 12.38 \\ \end{bmatrix}^{0.22} \begin{pmatrix} N_{SC} \\ acetone-H_{2}SO_{4} \\ \hline N_{SC} \\ acetone-H_{2}O \\ \hline SC_{acetone-H_{2}O} \\ \hline SC_{acetone-H_{2}O}$$

f. H $_{OG}$ as a function of m G / L for

Acetone - Water system:

$$H_{OG} = 2.3806 + 2.9482 \frac{mG}{L}$$

Acetone - 73 % sulfuric acid system:

$$H_{OG} = 2.38 + 12.38 \frac{mG}{L}$$

For m G / L = 0.4028Acetone - H₂O $H_{OG} = 3.56 \text{ ft}$ Acetone - H₂SO₄ (73 %) $H_{OG} = 7.37 \text{ ft}$

4 Estimation of the height of column for FAD unit by using 73 % H₂SO₄:

Z (height of column) = $N_{OG} * H_{OG}$ = 0.58 * 7.4 = 4.3 feet

5 Estimation of the column diameter and the pressure drop for FAD unit by using 73 % sulfuric acid:

[Warren L. Mc Cabe, Julian C. Smith, and Peter Harriott, "Unit Operation Of Chemical Engineering", McGraw - Hill Book Co., 1985]

Figure 22 - 4 on p. 621 gives correlations for estimating flooding velocities and pressure drop in packed tower. The quantities to be used in the ordinates of Figure 22 - 4 are as follows:

The average molecular weight of the entering gas is

$$29 * 0.9988 + 58.09 * 0.0019856 = 29.0806$$

$$\rho_{y} = 29.0806 * 492 / (359 * 610) = 0.065335 \text{ lb / ft}^{3}$$

$$\rho_{x} = 102.36 \text{ lb / ft}^{3} ; \qquad \mu_{x} = 11 \text{ cp}$$

$$g_{c} = 32.174 \text{ ft} - \text{lb / lb}_{f} \text{ -s} ; \qquad G_{x} / G_{y} = 0.79$$

For 1 - inch ceramic Raschig rings, $F_p = 155$ (Table 22 - 1, p. 619). Then,

$$\frac{G_x}{G_y} \frac{\rho_y}{\rho_x - \rho_y} = 0.79 \frac{0.065335}{102.36 - 0.065335} = 0.019965$$

From Figure 22 - 4, at flooding

$$\frac{G_v^2 F_p \mu_x^{0.1}}{g_c(\rho_x - \rho_y)\rho_y} = 0.20$$

The mass velocity at flooding is

$$G_{y} = \sqrt{\frac{0.20*32.174*0.065335*(102.36-0.065335)}{155*11^{0.1}}} = 0.46723 \frac{1b}{ft^{2}-s}$$

The total gas flow is 3000 * 0.065335 / 60 = 3.26675 lb / s. If the actual velocity is 44 % of the flooding velocity, the cross - section area S of the tower is

$$S = \frac{3.26675}{0.46723*0.44} = 15.8903 \text{ ft}^2$$

The diameter of the tower is

$$\frac{15.8903}{0.7854} = 4.48 \text{ ft}$$

At 44 % of the flooding velocity, $G_y = 0.46723 * 0.44 = 0.20558$ lb/ft ²-s, and the abscissa value in Figure 22 - 4 (p.621) is still 0.019965. The ordinate becomes 0.20 / 5.1653 = 0.0387. For these conditions, and from the same graph, the parameter gives the pressure drop, which is about 0.25 in. water per foot of packed height; the total pressure drop is 4.3 * 0.25 = 1.075 in. water.

6 Calculations of vapor liquid equilibrium data:

Let's take 30 ml acetone in 100 ml 76 % H2SO4 at 23 o C as an example:

a. Mole fraction of solute in the solvent (x):

$$W_{acetone} = \rho * V = 0.7887 \text{ g/ml} * 30 \text{ ml} = 23.661 \text{ g}$$

$$N_{acetone} = W/M = 23.661 \text{ g/}(58.09 \text{ g/mole}) = 0.40732 \text{ mole}$$

$$W_{sulfuric acid} = \rho * V = 1.6761 \text{ g/ml} * 100 \text{ ml} = 167.61 \text{ g}$$

$$N_{sulfuric acid} = W/M = 167.61 \text{ g/}(79.16 \text{ g/mole}) = 2.11736 \text{ mole}$$

$$x_{acetone} = N_{acetone}/(N_{acetone} + N_{sulfuric acid}) = 0.16134$$

b. Mole fraction of solute at equilibrium in the vapor phase (y):

The acetone - peak area ratio on the digital printout chromatograph is 1.335.

From the calibration curve, the acetone concentration (ppm by volume) in the air is equal to 4881.

$$y_{acetone} = N_{acetone} / (N_{acetone} + N_{air}) = 4881 / (4881+1E06) = 0.00486$$

7 Estimation of nitrogen flow rate to the VOC reservoir to get desired feed concentration:

Preparing 1850 ppm (by volume) acetone in the hot air (temp. = $60^{\circ}C$;

flow rate = 16 liter / min)

¥

Following the ideal gas law,

N_{air} = P \forall / R T = (1 * 16) / (0.08205 * 333.15) = 0.58533 mole / min. N_{acetone} = 1850 E -06 * 0.58533 = 1.083 E -03 mole / min Antoine's equation for acetone is

 $\log P_{\text{sat,acetone}} = 7.11714 - \frac{1210.595}{(T+229.664)}$

At room temperature, 25 °C, the saturation pressure of acetone is

 $P_{\text{sat,acetone}} = 10^{\left(7.11714 - \frac{1210.595}{(T+229.664)}\right)} = 211.747 \text{ mmHg} = 0.2786 \text{ atm}$

	P sat, acetone	=	$y_{acetone} * \pi$
	0.2786 atm	=	y acetone * (1 atm)
	y acetone	=	$0.2786 = N_{acetone} / (N_{acetone} + N_{nitrogen})$
		=	$1.803E - 03 / (1.803E - 03 + N_{nitrogen})$
1	Solving N _{nitrog}	en ,	gives 0.00282 moles.
]	Following Ideal Ga	s Law,	$P \neq nitrogen = N_{nitrogen} R T$
nitro	gen = (0.0))0282) ((0.0802) (298.15) / (1) = 68.9 ml / min

8 Estimation of the sulfuric acid concentration in reservoir as a function of time:

Laboratory air humidity specification:Dry bulb temperature:22 ° C ;Wet bulb temperature:13 ° C

From PSYCHOMETRIC CHART (Cat. No. 794 - 001, Carrier Corporation, 1975), the moisture content is 5.8 g water / kg dry air. And the specific volume of air is 0.836 m^3 / kg dry air.

The air flow rate is set at 17 liter / min (= 1.02 m^3 / hr). The rate of moisture brought in is

 $1.02 \text{ [m}^3 / \text{hr}\text{]} * 1.1962 \text{ [kg dry air / m}^3\text{]} * 5.8 \text{ [g water / kg dry air]}$

= 7.25 g / hr.

a . The reservoir had 510 ml sulfuric acid (96 wt %) without purge:

 $W_{total} = 510 \text{ ml} * 1.84 \text{ g/ml} = 938.4 \text{ g}$ By definition, $W_{sulfuric acid} (\text{Orig}) = 96\% * 938.4 \text{ g} = 900.864 \text{ g}$ $W_{water} (\text{Orig}) = 4\% * 938.4 \text{ g} = 37.536 \text{ g}$ After five hours, the moisture added would be 7.25 g/hr * 5 hr = 36.25 g.

$$Wt \%_{acid} = W_{acid} (Orig) / [W_{acid} (Orig) + W_{water} (Orig) + W_{moisture}] * 100 \%$$

= 900.864 / (900.864+37.536+36.25) * 100 % = 92.43 %

b. The reservoir had 510 ml sulfuric acid (96 wt %) with a purge of 5 ml / min:

After five hours, W sulfuric acid (Orig.), W water (Orig.), and W moisture would be the same as previous, 900.864, 37.536, and 36.25, respectively.

For one hour, within the 4 to 5 hour time period, the make - up 96 wt % sulfuric acid would bring in

5 ml / min * 1.84 g / ml * 60 min / hr * 1 hr = 552 g 96% acid solution.

W' make-up sulfuric acid = 529.92 g; W' make-up water = 22.08 g. The purged sulfuric acid from the circulation stream would take out

5 ml / min * 1.826 g / ml * 60 min / hr * 1 hr = 547.8 g 93% acid solution.

[for this time, the weight percent of circulation acid dropped to 93 %]

W" purged sulfuric acid = 514.932 g; W" purged water = 32.869 g

Thus, the weight percentage of sulfuric acid would be

{[Wacid (Orig.)+W 'make-up acid-W "purged acid] / [Wt. of solution]} * 100%

.

= (915.95/978.85) * 100 % = 93.57 %

Appendix C All Measured Data

TABLE 12.	HP 5700 A	GC	Calibration	[Acetone	In Air
Concentration	Acetone	Peak	Area	Percentage	Retensio
(ppm W.)	First Run	Second Run	Third Run III	Average Of Three	(min)
84	0.006006	0.006007	0.006005	0.006006	4.
167	0.02303	0.02202	0.02203	0.022360	4.
209	0.02202	0.02002	0.02102	0.021020	4
435	0.05907	0.05807	0.05607	0.057737	4.
670	0.09212	0.09211	0.09112	0.091783	4
887	0.1121	0.1101	0.1091	0.110433	4.
1356	0.1762	0.1702	0.1732	0.173200	4.
1640	0.2242	0.2212	0.2212	0.222200	4.
2478	0.3394	0.3373	0.3363	0.337667	4.
3014	0.4144	0.4044	0.4114	0.410067	4
3516	0.4765	0.4735	0.4725	0.474167	4
Note:					
(a) Carrier Gas	(He)Flow	Rate :	20 ml / min		
(b) Oven Temp	(sequenced) :	80 - 110 [°] C	with Rate:	4 °C / min	
(c) Detector Sett	ing:	Sensitivity -	6;	Attenuation -	4
(d) Sample-gas	Circulation	Reate :	0.13 ft^3 /	min	
	Temperature:		40 - 50 [°] C		

TABLE 13.	HP 5700 A	GC	Calibration	[Ethanol	In Air]
Concentration	Ethanol	Peak	Area	Percentage	Retension Time
(ppm W.)	First Run	Second Run	Third Run III	Average Of Three	(min)
167	0.01001	0.01001	0.01001	0.010010	3.19
233	0.01402	0.01401	0.01502	0.014350	3.21
433	0.028	0.02802	0.02802	0.028013	3.13
650	0.05005	0.04605	0.05005	0.048717	3.18
883	0.06507	0.06506	0.06506	0.065063	3.2
1317	0.1131	0.1131	0.1141	0.113433	3.21
2000	0.1972	0.1952	0.1942	0.195533	3.21
3000	0.2923	0.2923	0.2903	0.291633	3.23
3550	0.3714	0.3594	0.3583	0.363033	3.24
Note:	4				.
(a) Carrier Gas	(He)Flow	Rate :	20 ml / min		
(b) Oven Temp	(sequenced):	80 - 110 [°] C	with Rate:	4 °C / min	
(c) Detector Set	ting:	Sensitivity -	6;	Attenuation -	4
(d) Sample-gas	Circulation	Reate :	0.13 ft^3 /	min	
	Temperature	:	40 - 50 [°] C		

.

TABLE 14.	HP 5700 A	GC	Calibration	[Ethyl Ether	ln Air]
Concn.	Ethyl Ether	Peak	Area	Percentage	Retension Time
(ppm W.)	First Run	Second Run	Third Run	Average Of Three	(min)
114	0.01501	0.01501	0.01501	0.015010	7.23
182	0.02903	0.02903	0.02802	0.028693	7.21
303	0.04104	0.04104	0.03904	0.040373	7.22
439	0.05406	0.054	0.05405	0.054037	7.17
606	0.08108	0.08008	0.07908	0.080080	7.15
879	0.1181	0.1191	0.1151	0.117433	7.14
1409	0.197	0.19317	0.19318	0.194450	7.09
2181	0.3023	0.301	0.29927	0.300857	7.07
3030	0.41644	0.40934	0.40936	0.411713	7.05
Note :					
(a) Carrier G	as	(He)Flow	Rate :	20 ml / min	
(b) Oven Tem	p :	80 - 100 °C	with Rate :	4 °C / min	
(c) Detector S	Setting :	Sensitivity - Temp -	6; 150 °C	Attenuation -	4
(d) Sample Ga	IS	Circulation Temperature :	Rate :	0.13 ft^3 / 40 - 50 °C	min

TABLE 15. Acetone	in Air	Equilibrium	with	mixtures of	Acetone & 73% H2SO4 Temperature = 15 ° C
c.c. Acetone	Gms. Acetone	Experiment's	Data cubic meter	N.J.I.T.; 1992 of air	Ormandy's Data Trans. Inst. Of ChE
per 100 c.c. H2504	Runi	Run II		Average	published in 1929
0.5	0.12674058	0.11877304	0.13471607	0.1267432	NA
1	0.1823645	0.126746	0.1984396	0.1691834	0.13
5	0.668462	0.7242	0.732187	0.708283	NA
10	1.783766	1.927129	2.084323	1.9317393	1.8
20	4.694543	5.041431	5.018512	4.918162	4.6
30	8.921348	9.304604	8.838983	9.021645	8.5
40	15.262669	14.856573	15.48605	15.201764	14.2
Note :				<u></u>	
(a) Carrier Gas	(He) Flow	Rate :	20 ml / min	(d) Sample	Gas: Pato: 0.12 $f^{0.2}$ / min
(b) Oven Temp :	80 - 110 °C	with Rate :	4 °C / min	Temperature	: 40 - 50 °C
(c) Detector Setting :	Sensitivity: - 6 Temperature -	; Attenuation 150 °C	: - 4	(e) Retension	Time (minute): Acetone - 4.25

Table 16 .	Vapor Liquid Acetone, and	Equilibrium Ethanol in	Data 76 wt %	for H2SO4
X (mole frac.)		Y (mole frac.)	Acetone / Air	
Acetone / Acid	15 [°] C	23 [°] C	33 [°] C	54 [°] C
0.00640	0.000017	0.000017	0.000017	0.000640
0.03113	0.000017	0.000960	0.001411	0.002490
0.06039	0.000927	0.001469	0.002655	0.004740
0.11390	0.002220	0.003080	0.004674	0.011840
0.16160	0.002910	0.004860	0.007490	0.016650
0.20450	0.004640	0.007990	0.013200	0.024400

X (mole frac.)		Y (mole frac.)	Ethanol / Air	
Ethanol / Acid	15 ° C	23 [°] C	33 [°] C	54 °C
0.007270	0.00000	0.00000	0.00000	0.00000
0.035350	0.00000	0.000000	0.000000	0.000000
0.068290	0.000000	0.000000	0.000000	0.007157
0.127857	0.00000	0.000000	0.004338	0.009982
0.180260	0.000000	0.004140	0.005419	0.015540
0.268205	0.004372	0.004692	0.008180	0.030910

Table 17 .	Vapor Liquid Equilibriun in 76 wt %, and 96 wt %	n Data for Ethyl Ether Sulfuric Acid			
X (mole fraction)	76 wt % Y	Sulfuric Acid (mole fraction)			
Ethyl Ether / Acid	20 ° C				
	Ronbinson's Data	N. J. I. T. 's Data			
0.02720	0.0013158	0.0013625			
0.05300	0.0030263	0.0030616			
0.07700	0.0050000	0.0054517			
0.10000	0.0063158	0.0069852			
0.12820	0.0073684	0.0076534			

X (mole fraction)	96 wt % Y	Sulfuric Acid (mole fraction)			
Ethyl Ether / Acid	20 °C				
	Ronbinson's Data	N. J. I. T. 's Data			
0.124500	0.000964900 0.00097765				
0.242400	0.002368400 0.001935000				

Table 18.	Temperatu	res of the	scrubber	by using 76	% H2SO4	(No purge)
RUN I						
Time	Reservoir	(Temp:	°C)	Acid (T: °F)	Influent	Effluent
(hour)	Acetone	Ethanol	Acid	Circulated	Gas (T: [°] F)	Gas (T:°F)
0.5	21	21	25	80	140	100
1	21	21	25	90	145	102
1.5	21	21	23	92	145	103
2	21	21	19	90	145	104
2.5	21	21	19	95	143	105
3	21	21	19.5	92	142	105
3.5	21	21	21	95	140	105
4	21	21	22	98	145	104
4.5	21	21	22	100	142	105
5	21	21	22	100	142	105
5.5	21	21	22	100	142	105
6	21	21	22	102	143	107
6.5	21	21	20	102	142	105

RUN II

ſ

Time	Reservoir	(Temp :°C)	Acid Reser.	Acid (T: °F)	Influent	Effluent
(hour)	Acetone	Ethanol	(T: [°] F)	Circulated	Gas (T: [•] F)	Gas (T: [®] F)
1	25	25	80.5	90	141	94
2	24	24	79	98	150	103
3	24	24	78	106	145	103
4	24	24	78	106	143	108
5	24	24	76	113	143	108
6	24	24	76	115	143	110

Table 19. Temperatu res of the scrubber by using 76% H2SO4 (Purge:1ml/min)						
Time (hour)	Reservoir Acetone	(Temp: °C) Ethanol	Acid Res (T: [°] F)	Acid (T:°F) Circulated	Influent Gas (T: ° F)	Effluent Gas (T: ^o F)
1	24.5	24.5	73	80	143	87
2	24.5	24.5	73	70	149	95
3	24.5	24.5	73	75	149	101
4	24.5	24.5	73	75	145	105
5	24.5	24.5	73	75	145	107
6	23	23	74	85	140	110
7	23	23	74	95	140	109
8	23	23	74	98	141	107
9	23	23	74	100	141	108
10	23	23	72	103	140	111
11	24	24	76	104	142	113
12	24	24	72	107	145	112
13	23	23	75	108	142	113
14	23	23	72	73	142	93
15	23	23	78	78	145	95
16	23	23	69	85	145	105
17	23	23	68	85	144	104
18	22	22	72	86	142	104
19	22	22	75	92	142	105
2 0	22	22	81	93	142	104
2 1	22	22	73	100	142	106
2 2	22	22	65	104	136	107
2 3	22.5	22.5	74	70	145	85

Table 20.	Temperatu	res of the	scrubber	by using 96	% H2SO4	(No Purge)
Time	Reservoir	(Temp	: °C)	Acid (T: °F)	Influent	Effluent
(hour)	Acetone	Ethanol	Acid	Circulated	Gas (T: °F)	Gas (T: [•] F)
1	24	24	12	61	138	77
2	23	23	26	8 1	143	97
3	23	23	22	88	143	103
4	23	23	26	92	145	107
5	23	23	20	95	143	108
6	23	23	22	95	143	110
7	23	23	25	95	143	109
8	24	24	23	98	141	107
9	24	24	27	100	141	108
10	24.5	24.5	27	103	142	111
11	24.5	24.5	23	104	141	113
12	24.5	24.5	26	107	145	112
13	24.5	24.5	27	108	142	113
14	22.5	22.5	24.5	73	142	93
15	23	23	23	78	145	95
16	23	23	19	85	145	105
17	23	23	24	85	144	104
18	22	22	22	86	142	104
19	22	22	23	92	142	105
2 0	22	22	23.5	93	142	104
21	22	22	24	100	142	106
2 2	22	22	24	104	136	107
23	22.5	22.5	26	70	145	85
24	22.5	22.5	26	82	150	102
2 5	22.5	22.5	27	82	150	102

Appendix D Samples of Gas Chromatographic Output Data



RUN # 5

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0 .26	141520	ЕH	0.211	0.095
1.25	1.4893E+08	↑SH8	0.286	99.537
3.50	26888	TEP	0.378	0.818
7.24	44513 0	88	0.209	8.298
8.47	2 9346	EВ	8 2 89	0.053

YOTAL AREA= 1.4962E+08 MUL FACTOR= 1.0000E+00



MUL FACTOR= 1.6800E+00



STOP

RUN # 25

ARFAZ

ET	AREA	TYPE	ARZHT	ARE4%
0.23	7 88 68	BH	0.518	0,057
1.16	1.22752+08	↑SHH	6.236	98,889
2.05	448530	TBV	0.221	0.355
3.17	86 2 188	TVV	0.697	8 .6 99

TOTAL AREA= 1.2413E+08 MUL FACTOR= 1,0000E+00

Absorption Column: using 76 wt % H_2SO_4 without purge

[at 4 hour]





TOTAL AREA= 2.8222E+07 MUL FACTOR= 1.0000E+00



AREAN RT

RT	AREA	TYPE	AR/HT	ARE A%
й.27	367490	BH	9,741	6, 425
1.29	7.7030E+07	tshe	6, 1 53	99.525
Appendix E Unknown Peak Identification Report

Hazardous Substance Management Research Center Analysis Service Laboratory

To: Dr. D. Hanesian From: Dustin Ho Re: GC/MS analysis Date: 4/20/92

Enclose please find GC/MS analysis report for your 3 gas samples. All samples were run by HP 5988 Mass spectrometry couple with HP 5890 Gas Chromatograph. All samples were cryofocus by liquid nitrogen then injected into GC/MS analysis by using 50mx0.32mm crosslink methyl-silicone capillary column. The carry gas flow-rate is 1ml/min. The oven initial temp. is 30°C hold 2 min. then increase at 4°C/min to final temp. 160°C hold 5 min.

Sample ID Compound found

HANA1	CO2,	SO2,	C4H8O,	СЗН6О,	CHC13
HANB1	CO2,	SO2,	C4H8O		
HANCI	CO2,	C6H14	102, C4H	180	

The major compounds were found in your samples listed in above table. Chloroform was residue from previous sample due to your student was not clean gas sample cylinder properly. C3H6O was acetone. C4H8O was 2methyl propanal or butenol.

If you have any further question, feel free to contact me.

```
Dustin Ho
```

c.c. C.Brockway

Note :

HANA1 - 40 ml Acetone / 100 ml 96 wt% H_2SO_4 HANB1 - 10 ml Ethanol / 100 ml 96 wt% H_2SO_4 HANC1 - 10 wt% Ethyl Ether / 100 ml 96 wt% H_2SO_4 Appendix F BASIC Computer Program For Simulation of VOC Removal In a Gas Absorption Column

15

100 REM	Volatile organic emmisio	ons				
110 REM removal from FAD (forced Air Drier) and the MXR (Mixer) units						
120 REM	`	,				
130 REM						
140 REM	Components in the mod	el				
150 REM	# Compounds	Mol Wt (MW)	SpGr (SG)			
160 REM	$1 \qquad \text{Air}(dry)$	28 07	Spor (50)			
170 DEM	$\frac{1}{2} \qquad \text{Water}$	19 016	1 000			
170 KEW	2 Water 2 Sulfurio ani l	18.010	1.000			
100 REM	5 Sulfuric acid	98.080	1.835			
190 REM	4 Acetone	58.02	0.795			
200 REM	5 Ethanol	46.07	0.794			
210 REM	6 Diethyl ether	74.12	0.719			
220 REM	/ Nitroglycerin	227.07	1.593			
230 REM	NC+1 Total					
240 REM						
250 DIM	CF1IN(9), V1(9), CF2OU	Г, V2(9)				
260 DIM	WT(9), WTNEW(9), PPM	NEW(9), PPMLIMIT(9)				
270 DIM	RFAC(9)					
280 DIM	MASS(9)					
290 DIM	PPMOUT(9)					
300 DIM	PPMWT(9), $WTFRAC(9)$					
310 DIM	SPGR(9)					
320 DIM	WT0(9) $WTPCT0(9)$					
330 RFM	(10()), (11C10())					
340 NC-7	7					
350 NCD1						
260 DEM						
270 DEM	Malagular Weishts					
370 REM	Molecular weights					
380 DIM	ZMW(9)					
390 ZMW	(1)=28.9/: ZMW(2)=18.01	6: ZMW(3)=98.086				
400 ZMW	(4)=58.02: ZMW(5)=46.07	: ZMW(6)=74.12				
410 ZMW	7(7)=227.07					
420 REM						
430 RE	М	• • • • • • • • • • • • • • • • • • • •				
440 REM						
450 REM	Sulfuric acid (100% ac	id, 0% water)				
460 REM	SpGr = 1.835	,				
470 REM	\hat{M} ol Wt = 98.086					
480 REM						
490 REM	Sulfuric Acid:					
500 REM	Wt Pct (%)	SpGr (SG	Deg Be			
510 REM	33% (battery	acid) 1 250				
520 REM	62 18	1.230	50.55			
530 REM	77 67	1.520	50			
540 PEM	00	1.700	00			
550 PEM	02 10	1.020 (13)	C)			
560 DEM	95.19	1.033	00			
570 DEN	73 04	1.839 (15				
500 DEM	90 02	1.841 (15				
JOU KEM	98 100	1.841 (15				
JYU KEM	100	1.836 (15	C)			
OUU KEM						
010 REM	Oleum:					
620 REM	100% H2SO4	1.835				
630 RFM	10					

640 REM 20 (104.5% acid) 1.915 40 (109 % acid) 650 REM 1.983 1.992 660 REM 66 (114.6% acid) 670 REM 680 REM 690 REM 700 REM ... Gas feed 1 = Gas In710 REM 2 = Gas Out720 REM V1 and V2 = lb/hr of each component, (1)-(7) 730 REM V1cfm and V2cfm = cf/min @ specified process conditions 740 REM STP cond = 0C/32F and 760 mm Hg 750 REM 760 REM 770 REM ### DIM CF1IN(9), V1(9), CF2OUT, V2(9) 780 REM 790 REM Vin = Air vapor rate in800 REM cf/min ... cf1in(i) @ cond 810 REM lb/hr v1(i) 820 REM Tin = Temperature, F 830 REM Pin = Pressure, mm Hg RH = Inlet Relative Humidity (%) 840 REM 850 REM 860 REM Organic concentrations in Gas Feed 870 REM ppmACE = ppm acetone (by volume) 880 REM ppmEtOH = ppm ethanol (by volume) 890 REM ppmDIETHER = ppm diethyl ether (by volume) = ppm nitroglycerin (by volume) 900 REM ppmNG 910 REM 920 REM Vout = Vapor rate out, 930 REM cf/min ... cf2out(9) @ cond 940 REM lb/hr v2(9) 950 REM Tout = Temperature, FPout = Pressure, mm Hg 960 REM 970 REM 980 REM 990 REM READ record #1 1000 PRINT: PRINT 1010 REM PRINT " Air inlet rate and conditions:" 1020 REM PRINT " Air flow rate, cf/min:": INPUT VIN 1030 REM PRINT " Pressure, mm Hg:": INPUT PIN 1040 REM PRINT " Temperature, F:": INPUT TIN 1050 PRINT " Air inlet rate and conditions:" 1060 PRINT " Air flow rate, cf/min:, VIN" 1070 PRINT " PIN" Pressure, mm Hg:, 1080 PRINT " TIN" Temperature, F:, 1090 READ VIN, PIN, TIN 1100 REM 1110 PRINT: PRINT 1120 PRINT " Air inlet rate and conditions used in simulation:" 1130 PRINT " Air flow rate, cf/min:", VIN Pressure, mm Hg: ", PIN 1140 PRINT " Pressure, mm Hg: 1150 PRINT " Temperature, F: TIN 1160 REM 1170 PRINT

1171 PRINT " Input a 'CR' to continue." : INPUT CR 1180 IF (CR=9) THEN STOP 1190 CLS 1200 REM 1210 REM 1220 REM 1230 REM 1240 REM READ record #2 1250 PRINT : PRINT 1260 REM PRINT " Gas outlet conditions:" 1270 REM PRINT " Absorber pressure drop, mm Hg:": INPUT DPDPDP 1280 REM PRINT " Estimated Gas Temperature, F: " : INPUT TOUT 1290 PRINT " Gas outlet conditions:" 1300 PRINT " Absorber pressure drop, mm Hg:, DPDPDP" 1310 PRINT " Estimated Gas Temperature, F:, TOUT" 1320 READ DPDPDP, TOUT 1330 REM 1340 REM ... Assume a 25 mm Hg pressure drop through the absorption 1350 REM column if the pressure drop is greater than 50 mm Hg 1360 REM 1370 POUT=PIN-ABS(DPDPDP) 1380 IF (POUT = 0!) THEN POUT=PIN-25 1390 IF (POUT > PIN) THEN POUT=PIN-25 1400 IF (POUT < 760) THEN POUT=760: PIN=785 1410 REM 1420 PRINT: PRINT 1430 PRINT " Gas outlet conditions used in simulation:" 1440 PRINT " Pressure, mm Hg: POUT 1450 PRINT " Estimated Temperature, F:", TOUT 1460 REM 1470 PRINT: PRINT " Input a 'CR' to continue.": INPUT CR 1480 IF (CR=9) THEN STOP 1490 CLS 1500 REM 1510 REM 1520 REM 1530 REM 1540 REM READ records #3 and #4 1550 PRINT: PRINT 1560 REM PRINT " Inlet gas data:" 1570 REM PRINT " Water:" 1580 REM PRINT " Temperature of ambient air: " : INPUT TAIR Water, Relative Humidity (%):": INPUT RH 1590 REM PRINT " 1600 REM PRINT " HC concentrations:" ": INPUT PPMACE ": INPUT PPMETOH 1610 REM PRINT " Acetone, ppm by volume: 1620 REM PRINT " Ethanol, ppm by volume: 1630 REM PRINT " Nitroglycerin, ppm by volume:": INPUT PPMNG 1640 PRINT " Inlet gas data:" 1650 PRINT " Water:" 1660 PRINT " Temperature of ambient air:, TAIR" 1670 PRINT " Water, Relative Humidity (%):, RH" 1680 PRINT " HC concentrations:" 1690 PRINT " Acetone, ppm by volume:, PPMACE" 1700 PRINT " Ethanol, ppm by volume:, PPMETOH"

Nitroglycerin, ppm by volume:, PPMNG" 1710 PRINT " 1720 READ TAIR, RH 1730 READ PPMACE, PPMETOH, PPMNG 1740 REM 1750 PRINT: PRINT 1760 PRINT " Inlet gas data used in simulation:" 1770 PRINT " Water:" Temperature of ambient air: ", TAIR 1780 PRINT " 1790 PRINT " Water, Relative Humidity (%):", RH 1800 PRINT " HC concentrations:" Sulfuric acid, ppm by volume:", PPMACID 1810 REM PRINT " PPMACE 1820 PRINT " Acetone, ppm by volume: 1830 PRINT " **PPMETOH** Ethanol, ppm by volume: 1840 REM PRINT " Diethyl ether, ppm by volume:", PPMDIETHER Nitroglycerin. ppm by volume:", PPMNG 1850 PRINT " 1860 REM 1870 PPMACID=0! 1880 PPMDIETHER = 0!1890 REM 1900 CPAIR=.242 Specific heat, Btu/lb-F:" 1910 PRINT " 1920 PRINT " Air: ", CPAIR 1930 WTRHEAT=1045 1940 PRINT " Latent heat, Btu/lb:" 1950 PRINT " **WTRHEAT** Water:", 1960 REM 1970 PRINT: PRINT " Input a 'CR' to continue.": INPUT CR 1980 IF (CR=9) THEN STOP 1990 CLS 2000 REM 2010 REM 2020 REM 2030 REM Determination of specified CFM of vapor feed @ cond 2040 REM VIN = CFM @ cond of air plus water vapor (HC free) 2050 V1CFM=VIN 2060 REM ... Vapor presure data for water from Felder and Rousseau 2070 REM 2nd Edition, page 235, Table 6.1-1 2080 TDEGC=(TAIR-32!)/1.8 2090 PARG=8.10765-1750.236/(TDEGC+235!) 2100 VPWTR=10^(PARG) 2110 VPPSIA=VPWTR/760*14.696 2120 PWTR=VPWTR*RH/100 2130 PRINT "T-feed (F) = ", TAIR 2140 PRINT "T-air (F) = ", TIN 2150 PRINT " VP (mm Hg) = ", VPWTR2160 PRINT " VP (psia) = ", VPPSIA 2170 PRINT " PP-wtr (psia) = ", PWTR 2180 REM 2190 CFAIR =V1CFM*(1-PWTR/PIN) 2200 CFWTR =V1CFM*(PWTR/PIN) 2210 REM 2220 CFACID =V1CFM*(PPMACID/1000000!) 2230 CFACE =V1CFM*(PPMACE/1000000!) 2240 CFETOH =V1CFM*(PPMETOH/1000000!)

```
2250 CFDIETHER=V1CFM*(PPMDIETHER/1000000!)
2260 CFNG
            =V1CFM*(PPMNG/100000!)
2270 \text{ CF1IN}(1)=\text{CFAIR}
2280 CF1IN(2)=CFWTR
2290 CF1IN(3)=CFACID
2300 CF1IN(4)=CFACE
2310 CF1IN(5)=CFETOH
2320 CF1IN(6)=CFDIETHER
2330 CF1IN(7)=CFNG
2340 REM
2350 REM ... Sum the gas constituents ... CFM @ COND (Tin and Pin)
2360 CF1IN(NCP1)=0!
2370 FOR I=1 TO NC
2380 CF1IN(NCP1)=CF1IN(NCP1)+CF1IN(I)
2390 NEXT I
2400 REM
2410 PRINT: PRINT
2420 PRINT " Inlet gas cuft/min (@ cond) used in simulation:"
2430 PRINT "
               Air (BDA): ", \overline{CF1IN(1)}
                         ", CF1IN(2)
2440 PRINT "
                Water:
2450 PRINT
2460 PRINT "
               Sulfuric acid:", CF1IN(3)
                          ", CF1IN(4)
", CF1IN(5)
2470 PRINT "
                Acetone:
2480 PRINT "
               Ethanol:
2490 REM PRINT "
                    Diethyl ether:", CF1IN(6)
2500 PRINT "
               Nitroglycerin:", CF1IN(7)
                          ", CF1IN(NCP1)
2510 PRINT "
               TOTAL:
2520 REM
2530 PRINT: PRINT " Input a 'CR' to continue." : INPUT CR
2540 IF (CR=9) THEN STOP
2550 REM
2560 REM ... Convert the inlet gas to CFM @ STP (0C and 760 mm Hg)
2570 CF1IN(NCP1)=0!
2580 FAC=(460+32)/(TIN+460)*(PIN/760)
2590 FOR I=1 TO NC
2600 \text{ CF1IN}(I) = \text{CF1IN}(I) + \text{FAC}
2610 CF1IN(NCP1)=CF1IN(NCP1)+CF1IN(I)
2620 NEXT I
2630 REM
2640 REM
                2650 REM
2660 REM Conversion of inlet gas feed from CFM @ STP [CF1IN]
           to lb/hr [V1]
2670 REM
2680 V1(NCP1)=0!
2690 FOR I=1 TO NC
2700 V1(I)=CF1IN(I)/359.036642#*ZMW(I)*60
2710 V1(NCP1)=V1(NCP1)+V1(I)
2720 NEXT I
2730 REM
2740 REM ... Re-store actual CFM values to CF1IN(i)
2750 FAC=(TIN+460)/(460+32)*(760/PIN)
2760 FOR I=1 TO NCP1
2770 CF1IN(I)=CF1IN(I)*FAC
2780 NEXT I
```

2790 REM 2800 REM 2810 PRINT: PRINT 2820 PRINT " Inlet gas flow rate (lb/hr) used in simulation:" Air (BDA): ", V1(1) Water: ", V1(2) 2830 PRINT " 2840 PRINT " Sulfuric acid:", V1(3) 2850 PRINT " ". V1(4) 2860 PRINT " Acetone: ", V1(5)2870 PRINT " Ethanol: Diethyl ether:", V1(6) 2880 REM PRINT " 2890 PRINT " Nitroglycerin:", V1(7) 2900 PRINT " ", V1(NCP1) TOTAL: 2910 REM 2920 PRINT: PRINT " Input a 'CR' to continue." : INPUT CR 2930 IF (CR=9) THEN STOP 2940 REM 2950 REM 2960 REM 2970 REM 2980 REM ... Gas removal factors (%) used in simulation:" 2990 REM ... fraction of gas removed from the feed:" 3000 REM 1 Air = 0%3010 REM 2 Water = 100%3020 REM 3 Sulfuric acid = 100%3030 REM 4 Acetone = Input Data 3040 REM 5 Ethanol = Input Data 3050 REM 6 Diethyl ether = 100%7 Nitroglycerin = Input Data 3060 REM 3070 REM 3080 REM ... DIM RFAC(7) 3090 REM 3100 REM 3110 REM READ record #5 3120 PRINT: PRINT 3130 REM PRINT " Gas removal factors ... fraction of gas removed from the feed:" 3140 REM PRINT " Gas removal factors for" 3150 REM PRINT " ": INPUT RFAC(4) Acetone (#4), % removed: ": INPUT RFAC(5) 3160 REM PRINT " Ethanol (#5), % removed: 3170 REM PRINT " Nitroglycerin (#7), % removed:": INPUT RFAC(7) 3180 PRINT " Gas removal factors ... fraction of gas removed from the feed:" 3190 PRINT " Gas removal factors for" 3200 PRINT " Acetone (#4), % removed:, RFAC(4)" 3210 PRINT " Ethanol (#5), % removed:, RFAC(5)" 3220 PRINT " Nitroglycerin (#7), % removed:, RFAC(7)" 3230 READ RFAC(4), RFAC(5), RFAC(7) 3240 REM 3250 REM ... Define removal factors (%) for components #1, #2, #3, and #6 3260 RFAC(1)=0! 3270 RFAC(2)=100! 3280 RFAC(3)=100! 3290 RFAC(6)=100! 3300 REM 3310 REM ... Convert all removal factors from percent (%) to fractions 3320 FOR I=1 TO NC

3330 RFAC(I) = RFAC(I)/100!3340 NEXT I 3350 REM 3360 PRINT: PRINT 3370 PRINT " Gas removal factors (fractions) used in simulation:" 3380 PRINT " Air (BDA): ", RFAC(1) ", RFAC(2) 3390 PRINT " Water: 3400 PRINT " Sulfuric acid:", RFAC(3) ", RFAC(4) ", RFAC(5) 3410 PRINT " Acetone: 3420 PRINT " Ethanol: 3430 REM PRINT " Diethyl ether:", RFAC(6) 3440 PRINT " Nitroglycerin:", RFAC(7) 3450 REM 3460 PRINT: PRINT " Input a 'CR' to continue." : INPUT CR 3470 IF (CR=9) THEN STOP 3480 CLS 3490 REM 3500 REM 3510 REM 3520 REM ... Generate the gas discharge rate ... V2(i), lb/hr 3530 REM Mass removed by circulating acid ... MASS(i), 1b/hr 3540 REM ... DIM MASS(9) 3550 MASS(NCP1)=0! 3560 V2(NCP1)=0! 3570 FOR I=1 TO NC 3580 MASS(I)=V1(I)*RFAC(I) 3590 MASS(NCP1)=MASS(NCP1)+MASS(I) 3600 V2(I) = V1(I)*(1!-RFAC(I))3610 V2(NCP1)=V2(NCP1)+V2(I)3620 NEXT I 3630 REM 3640 REM 3650 REM ... Generate the gas discharge volumetric flow rate CF2OUT(i) 3660 REM CFM @ cond (Tout and Pout) 3670 FAC = 359.036642#*(TOUT+460)/(460+32)*(760/POUT) 3680 CF2OUT(NCP1)=0! 3690 FOR I=1 TO NC 3700 CF2OUT(I)=(V2(I)/60!)/ZMW(I)*FAC 3710 CF2OUT(NCP1)=CF2OUT(NCP1)+CF2OUT(I) 3720 NEXT I 3730 REM 3740 REM **3750 PRINT: PRINT** 3760 PRINT " Outlet gas cuft/min (@ cond) used in simulation:" 3770 PRINT " Air (BDA): ", CF2OUT(1) ", CF2OUT(2) 3780 PRINT " Water: Sulfuric acid:", CF2OUT(3) Acetone: ", CF2OUT(4) 3790 PRINT " 3800 PRINT " ", CF2OUT(5) 3810 PRINT " Ethanol: 3820 REM PRINT " Diethyl ether:", CF2OUT(6) 3830 PRINT " Nitroglycerin:", CF2OUT(7) 3840 PRINT " ", CF2OUT(NC+1) TOTAL: 3850 REM 3860 PRINT: PRINT " Input a 'CR' to continue." : INPUT CR

3870 IF (CR=9) THEN STOP 3880 REM 3890 REM 3900 TDEGC=(TOUT-32!)/1.8 3910 PARG=8.10765-1750.236/(TDEGC+235!) 3920 VPWTR=10^(PARG) 3930 RHOUT=CF2OUT(2)/(CF2OUT(1)+CF2OUT(2))*POUT/VPWTR*100! 3940 REM ### DIM PPMOUT(9) 3950 FAC=CF2OUT(1)+CF2OUT(2) 3960 FOR I=3 TO NC 3970 PPMOUT(I)=CF2OUT(I)/FAC*1000000! 3980 NEXT I 3990 REM 4000 REM 4010 PRINT: PRINT 4020 PRINT " Outlet gas specifications (@ cond) used in simulation:" 4030 PRINT " Relative humidity (water)" Water, RH (%):", RHOUT 4040 PRINT " 4050 PRINT " Concentrations, ppm by vol of VOC's in Air" 4060 PRINT " Sulfuric acid:", PPMOUT(3) ", PPMOUT(4) ", PPMOUT(5) 4070 PRINT " Acetone: 4080 PRINT " Ethanol: Diethyl ether:", PPMOUT(6) 4090 PRINT " 4100 PRINT " Nitroglycerin:", PPMOUT(7) 4110 REM 4120 PRINT: PRINT " Input a 'CR' to continue." : INPUT CR 4130 IF (CR=9) THEN STOP 4140 REM 4150 REM 4160 PRINT: PRINT 4170 PRINT " Outlet gas mass flow rate (lb/hr) used in simulation:" 4180 PRINT " Air (BDA): ", V2(1) ". V2(2) 4190 PRINT " Water: Sulfuric acid:", V2(3) Acetone: ", V2(4) 4200 PRINT " 4210 PRINT " ", V2(5) 4220 PRINT " Ethanol: 4230 REM PRINT " Diethyl ether:", V2(6) 4240 PRINT " Nitroglycerin:", V2(7) 4250 PRINT " ", V2(NCP1) TOTAL: 4260 REM 4270 PRINT: PRINT " Input a 'CR' to continue." : INPUT CR 4280 IF (CR=9) THEN STOP 4290 REM 4300 REM 4310 REM 4320 PRINT: PRINT 4330 PRINT " Material absorbed (lb/hr) by the circulating acid:" 4340 PRINT " Air (BDA): ", MASS(1)", MASS(2) 4350 PRINT " Water: 4360 PRINT " Sulfuric acid:", MASS(3) ** ', MASS(4) 4370 PRINT " Acetone: ", MASS(5) 4380 PRINT " Ethanol: 4390 REM PRINT " Diethyl ether:", MASS(6) 4400 PRINT " Nitroglycerin:", MASS(7)

4410 PRINT " TOTAL: ", MASS(NC+1) 4420 REM 4430 PRINT: PRINT " Input a 'CR' to continue." : INPUT CR 4440 IF (CR=9) THEN STOP 4450 REM 4460 REM 4470 REM 4480 REM 4490 REM DIM PPMWT(9), WTFRAC(9) 4500 REM 4510 REM Acid information 4520 REM Volume of acid solution, gallons ---- VOL 4530 REM water 4540 REM sulfuric acid 4550 REM 4560 REM Acid strength (water & H2SO4) ---- wtpctin 4570 REM Acid specific gravity ---- spgrin 4580 REM Temperature of acid, F ---- Tpotin 4590 REM 4600 REM Concentrations, ppm by weight 4610 REM ---- **PPMWT**(1) Air Water 4620 REM ---- PPMWT(2) 4630 REM H2SO4 ---- PPMWT(3) 4640 REM ---- PPMWT(4) Acetone Ethanol----Diethyl ether----Nitroglycerin----PPMWT(7) 4650 REM 4660 REM 4670 REM 4680 REM 4690 REM Acid stength ... lower limit ---- WTacidMIN 4700 REM 4710 REM Makeup Acid specific gravity ---- spgrADD 4720 REM 4730 REM 4740 REM READ record #6 4750 PRINT: PRINT 4760 REM PRINT " Sulfuric Acid Solution Data:" 4770 REM PRINT " Initial volume of acid solution:" : INPUT VOL 4780 REM PRINT " Acid strength (Organic Free), wt%:": INPUT WTPCTIN 4790 REM PRINT " Specific gravity (Organic Free): " : INPUT SPGRIN 4800 REM PRINT " Temperature of acid, F:" : INPUT TPOTIN 4810 PRINT " Sulfuric Acid Solution Data:' 4820 PRINT " Initial volume of acid solution: VOL" 4830 PRINT " Acid strength (Organic Free), wt% :, WTPCTIN" 4840 PRINT " Specific gravity (Organic Free):, SPGRIN" 4850 PRINT " Temperature of acid, F:, TPOTIN" 4860 REM 4870 READ VOL, WTPCTIN, SPGRIN, TPOTIN 4880 REM 4890 REM PRINT: PRINT " Input a 'CR' to continue.": INPUT CR 4900 REM IF (CR=9) THEN STOP 4910 REM 4920 REM 4930 REM READ record #7 4940 REM ... Calculate: ppmwt(2) and ppmwt(3) from acid data

```
4950 PRINT: PRINT
                   Organic concentrations in acid charge, ppm by wt:"
4960 REM PRINT "
                                          ": INPUT PPMWT(4)": INPUT PPMWT(5)
4970 REM PRINT "
                     Acetone, ppm by wt:
4980 REM PRINT "
                     Ethanol, ppm by wt:
                     Diethyl ether, ppm by wt:" : INPUT PPMWT(6)
4990 REM PRINT "
5000 REM PRINT "
                     Nitroglycerin, ppm by wt:": INPUT PPMWT(7)
5010 PRINT "
              Organic concentrations in acid charge, ppm by wt:"
5020 PRINT "
                Acetone, ppm by wt:,
                                      PPMWT(4)
5030 PRINT "
                                      PPMWT(5)"
                Ethanol, ppm by wt:,
5040 REM PRINT "
                     Diethyl ether, ppm by wt:, PPMWT(6)"
5050 PRINT "
               Nitroglycerin, ppm by wt:, PPMWT(7)"
5060 REM
5070 READ PPMWT(4), PPMWT(5), PPMWT(7)
5080 PPMWT(1)=0!
5090 PPMWT(6)=0!
5100 REM
5110 PRINT: PRINT " Input a 'CR' to continue.": INPUT CR
5120 IF (CR=9) THEN STOP
5130 REM
5140 REM
5150 REM ... Data for SPGR is defined:
5160 REM
             Water
                                 spgr = 1.000
5170 REM
             Ethanol
                                 spgr = 0.794
                                 spgr = 0.795
5180 REM
             Acetone
5190 REM
             Diethyl ether
                                 spgr = 0.719
5200 REM
             Nitroglycerin
                                 spgr = 1.593
5210 REM
5220 REM ... DIM SPGR(9)
                                      : SPGR(3) = 1.835
5230 \text{ SPGR}(1)=0!
                  : SPGR(2) = 1!
5240 SPGR(4)=.795 : SPGR(5)=.794
                                       : SPGR(6) = .719
5250 \text{ SPGR}(7) = 1.593
5260 REM
5270 REM ... Calculate the initial mass in acid drum using acid charge
5280 REM
            and specified HC concentrations in acid.
5290 FAC=62.43/7.48052
5300 ZWT=VOL*FAC*SPGRIN
5310 \text{ ZWATER}= \text{ZWT}^{(1!-\text{WTPCTIN}/100!)}
5320 ZACID=ZWT*(WTPCTIN/100!)
5330 REM
5340 REM ### DIM WT0(9), WTPCT0(9)
5350 \text{ WTO}(1)=0!
5360 WT0(2)=ZWATER
5370 WT0(3)=ZACID
5380 WT0(4) = ZWT*(PPMWT(4)/1000000!)
5390 WT0(5) = ZWT^{(PPMWT(5)/1000000!)}
5400 WT0(6)=ZWT*(PPMWT(6)/1000000!)
5410 WT0(7)=ZWT*(PPMWT(7)/1000000!)
5420 REM
5430 VOL0=VOL
5440 WT0(NC+1)=ZWT
5450 FOR I=4 TO NC
5460 WT0(NCP1)=WT0(NCP1)+WT0(I)
5470 VOL0=VOL0+WT0(I)/(FAC*SPGR(I))
5480 NEXT I
```

5490 REM 5500 REM ... Weight percent (%) based on acid-water binary." 5510 FOR I=1 TO NC 5520 REM +++ WTPCT0(I)=WT0(I)/WT0(NCP1)*100! 5530 WTPCT0(I)=WT0(I)/ZWT*100! 5540 NEXT I 5550 REM 5560 REM 5570 PRINT: PRINT 5580 PRINT " Acid storage drum ... initial loadings used in simulation" 5590 PRINT 5600 PRINT " Initial acid drum data" 5610 PRINT " = ", VOL Volume of acid (gal) = ", ZWT 5620 PRINT " Mass of acid (lb) 5630 PRINT " Total volume of solution (gal) = ", VOL0 Total mass of solution (lb) = ", WT0(NCP1) 5640 PRINT " Temperature, F = ", TPOTIN 5650 PRINT " **5660 PRINT** 5670 PRINT " Mass (lb) Wt PCT (%):" Inventory: ", WT0(2), WTPCT0(2) 5680 PRINT " Water: Sulfuric acid: ", WT0(3), WTPCT0(3) 5690 PRINT " **5700 PRINT** ", WT0(4), WTPCT0(4) ", WT0(5), WTPCT0(5) 5710 PRINT " Acetone: 5720 PRINT " Ethanol: Diethyl ether: ", WT0(6), WTPCT0(6) 5730 REM PRINT " 5740 PRINT " Nitroglycerin: ", WT0(7), WTPCT0(7) 5750 PRINT 5760 PRINT " Note: Weight % based on acid-water binary." 5770 REM 5780 PRINT: PRINT " INPUT A 'CR' to continue.": INPUT CR 5790 IF (CR=9) THEN STOP 5800 REM 5810 REM ... Return point for time analysis ... can change the following: 5820 REM (1) Minimum acid strength in storage drum (2) Makeup acid strength / specific gravity 5830 REM 5840 REM (3) Delta time step in the numerical analysis 5850 REM 5860 REM 5870 REM READ records #8, #9 and #10 5880 PRINT: PRINT 5890 REM PRINT " Minimum acid values in storage drum (HC free)" 5900 REM PRINT " Acid strength: ": INPUT WTACIDMIN 5910 REM PRINT " Specific gravity:": INPUT SPGRACIDMIN 5920 REM PRINT 5930 REM PRINT " Makeup sulfuric acid" 5940 REM PRINT " Acid strength: " : INPUT WTPCTADD Specific gravity:" : INPUT SPGRADD 5950 REM PRINT " 5960 REM PRINT " Temperature, F: ": INPUT TADDACID 5970 REM PRINT 5980 REM PRINT " Delta Time (hours) for numerical analysis", DTIME 5990 REM 6000 PRINT " Minimum acid values in storage drum (HC free)" 6010 PRINT " Acid strength:, WTACIDMIN" 6020 PRINT " Specific gravity:, SPGRACIDMIN"

6030 PRINT 6040 PRINT " Makeup sulfuric acid" 6050 PRINT " Acid strength:, WTPCTADD" 6060 PRINT " Specific gravity:, SPGRADD" 6070 PRINT " Temperature, F:, TADDACID" **6080 PRINT** 6090 PRINT " Delta Time (hours) for numerical analysis:, DTIME" 6100 READ WTACIDMIN, SPGRACIDMIN 6110 READ WTPCTADD, SPGRADD, TADDACID 6120 READ DTIME 6130 REM 6140 IF (DTIME > .1) THEN DTIME=.016150 REM 6160 REM PRINT: PRINT " Input a 'CR' to continue, or '9' to STOP.": INPUT CR 6170 REM IF (CR=9) THEN STOP 6180 REM 6190 REM 6200 PRINT: PRINT 6210 PRINT " Minimum acid values in storage drum (HC free)" Acid strength: ", WTACIDMIN 6220 PRINT " 6230 PRINT " Specific gravity:", SPGRACIDMIN 6240 PRINT 6250 PRINT " Makeup sulfuric acid:" 6260 PRINT " Acid strength: ", WTPCTADD Specific gravity:", SPGRADD Temperature, F: ", TADDACID 6270 PRINT " 6280 PRINT " 6290 PRINT 6300 PRINT " Delta Time (hours) for numerical analysis", DTIME 6310 REM 6320 PRINT: PRINT " Input a 'CR' to continue, or '9' to STOP.": INPUT CR 6330 IF (CR=9) THEN STOP 6340 REM 6350 REM 6360 REM 6370 REM ... Start of time dependent analysis on the acid storage drum 6380 REM Time step is in hours. 6390 NTIME=0 6400 JTIME=0 6410 TIME=0! 6420 MZTIME=0 6430 REM 6440 TPOT=TPOTIN 6450 REM 6460 REM 6470 REM ... See Input Data Above: DTIME=1/100 6480 REM 6490 REM $6500 \text{ REM} \dots \text{ Load drum mass variable} = WT(9)$ 6510 REM \$\$\$ DIM WT(9), WTNEW(9), PPMNEW(9), ppmlimit(9) 6520 FOR I=1 TO (NCP1) 6530 WT(I) = WT0(I)6540 NEXT I 6550 REM ### 6560 REM ### Time incrementation return point ###

6570 REM ### 6580 REM 6590 REM ... Acid loss due to consumption with organic reactions has 6600 REM not been included in the analysis (Material Balance). 6610 REM Also the associated heat of reaction has not been 6620 REM included (Heat Balance) 6630 REM 6640 FOR J=1 TO 10 6650 REM 6660 REM ... Compute drum contents (mass basis) at end to time step 6670 NTIME=NTIME+1 6680 TIME=TIME+DTIME 6690 WTPCT=WT(3)/(WT(2)+WT(3))*100! 6700 FOR I=1 TO (NCP1) 6710 WTNEW(I)=WT(I)+MASS(I)*DTIME 6720 NEXT I 6730 REM 6740 REM ... Compute concentrations of drum contents (2) and (3), acid strength 6750 REM 6760 WTPCTNEW=WTNEW(3)/(WTNEW(2)+WTNEW(3))*100! 6770 FOR I=4 TO 7 6780 PPMNEW(I)=WTNEW(I)/WTNEW(NCP1)*1000000! 6790 NEXT I 6800 REM 6810 REM 6820 REM === == if (nc>1) then go to 71206830 REM 6840 REM 6850 REM ... Component data # Component MW 6860 REM SpGr 1 Air (dry) 28.97 6870 REM 6880 REM 2 Water 18.016 1.000 3 Sulfuric acid 98.086 1.835 6890 REM 0.795 6900 REM 4 Acetone 58.02 6910 REM 5 Ethanol 46.07 0.794 6920 REM 6 Diethyl ether 74.12 0.719 6930 REM 7 Nitroglycerin 227.07 1.593 6940 REM 6950 REM 6960 REM ... [HEAT1] 6970 REM ... Sensible heat lost by incoming vapor stream [HEAT1] 6980 REM ... Cp data for air = 0.242 Btu/lb-F (Maxwell's Data Book on HC's) 6990 HEAT1=V1(NCP1)*DTIME*CPAIR*(TIN-TOUT) 7000 PRINT " heat 1 = ", HEAT 1 7010 REM 7020 REM ... [HEAT2] 7030 REM ... Latent heat removed for condensation [HEAT2] 7040 REM Latent heat data used, Btu/lb 7050 REM Water = 1045Acetone = 2307060 REM EtOH = 3907070 REM 7080 REM = 430 (WAG)NG 7090 HEAT2=(MASS(2)*1045+MASS(4)*230+MASS(5)*390+MASS(7)*430)*DTIME 7100 PRINT " heat2 = ", HEAT2

```
7110 REM
7120 REM ... [HEAT3]
7130 REM ... Heat of mixing of Water and H2SO4+H2O (Acid)
7140 REM
           Data from Perry (3rd Edition, pg 277) 100F
7150 REM
           Btu/lb
                       @ 100 wt% acid = +20
7160 REM
                        @ 90 wt% acid = -50
7170 REM
                        h(\%) = -50 + 7*(\%-90)
7180 REM
          Btu/lb of water @ 100F = 68 Btu/lb = hin2
7190 HIN1=-50+7*(WTPCT-90)
7200 HIN2=68!
7210 HINTOTAL=HIN1*(WT(2)+WT(3))+HIN2*MASS(2)*DTIME
7220 HPOT=-50+7*(WTPCTNEW-90)
7230 HPOTTOTAL=HPOT*(WTNEW(2)+WTNEW(3))
7240 HEAT3=HINTOTAL-HPOTTOTAL
7250 PRINT " heat3 = ", HEAT3
7270 REM
7280 REM ... New value of T-pot (Calculate T-detla)
7290 REM ... Compute the temperature rise
7300 REM
           Specific heat data used, Btu/lb-F=cal/g-C
           (2)+(3) Water+Acid = 0.35
7310 REM
7320 REM
           (4)
                Acetone = 0.53
7330 REM
           (5)
                EtOH
                        = 0.62
7340 REM
           (7)
                NG
                       = 0.6 (WAG)
7350 CPLIQMIX=(WT(2)+WT(3))^{*}.35+WT(4)^{*}.53+(WT(5)+WT(6))^{*}.62+WT(7)^{*}.6
7360 REM CPLIQMIX=CPLIQMIX/WT(NCP1)
7370 TDELTA=(HEAT1+HEAT2+HEAT3)/CPLIQMIX
7380 REM
7390 IF (MZTIME > 0) THEN GOTO 7450
7400 TPOT=TPOT+TDELTA
7410 PRINT " T-pot = ", TPOT
7420 IF (TPOT < 90) THEN GOTO 7590
7430 REM
7440 REM
7450 REM ... ##### Remove energy to hold T=90 F #####
7460 REM
7470 REM
7480 QOUT=(HEAT1+HEAT2+HEAT3)/DTIME
7490 PRINT " T-pot & Q-out = ", TPOT, QOUT
7500 REM
7510 IF (MZTIME > 0) THEN GOTO 7590
7520 MZTIME=1
7530 HOURS=NTIME*DTIME
7540 PRINT: PRINT " Heat Xhr started, T-pot>90F, Time (hrs) = ", HOURS
7550 PRINT: PRINT " Input a 'CR' to continue, or '9' to STOP.": INPUT CR
7560 IF (CR=9) THEN STOP
7570 REM
7580 REM
7590 REM ... Transfer drum contents into the variable "WT(i)"
7600 REM
          for next time step.
7610 FOR I=1 TO (NCP1)
7620 WT(I)=WTNEW(I)
7630 NEXT I
7640 REM
```

7650 REM 7660 IF (WTPCTNEW < WTACIDMIN) THEN GOTO 7980 7670 REM 7680 REM ... Increment "jtime" 7690 NEXT J 7700 REM 7710 REM ... Print out the ntime, time, wt%acid, and ppm HC's 7720 HOURS = NTIME*DTIME 7730 PRINT 7740 PRINT " Circulation continuing with no acid addition or purge" 7750 PRINT " n = ", NTIME, " Time, hr = ", HOURS 7760 PRINT 7770 PRINT " wt% acid = ", WTPCTNEW ppm acetone = ", PPMNEW(4) 7780 PRINT " ppm ethanol = ", PPMNEW(5) 7790 PRINT " 7800 PRINT " = ", PPMNEW(7) ppm NG **7810 PRINT** 7820 PPMHC=PPMNEW(4)+PPMNEW(5)+PPMNEW(6)+PPMNEW(7) 7830 PRINT " ppm HC's = ", PPMHC7840 PRINT 7850 PRINT " Temperature of acid = ", TPOT 7860 REM 7870 PRINT: PRINT " Input a 'CR' to continue," 7880 PRINT " or '8' to change acid min-strength / makeup" PRINT " or '9' to STOP." 7890 7900 INPUT CR 7910 IF (CR=8) THEN 5810 7920 IF (CR=9) THEN STOP 7930 GOTO 6560 7940 REM 7950 REM 7970 REM 7980 REM ... Min acid concentration reached 7990 REM ... Print out the ntime, time, wt%acid, and ppm HC's 8000 HOURS = NTIME*DTIME 8010 REM 8020 REM ... Compute storage drum volume (gallons) 8030 PPG=62.43/7.48052 8040 ZVOL=(WT(2)+WT(3))/(PPG*SPGRACIDMIN) 8050 FOR I=4 TO 7 8060 ZVOL=ZVOL+WT(I)/(FAC*SPGR(I)) 8070 NEXT I **8080 PRINT** 8090 PRINT " Min acid strength limit reached ... start purge/makeup" 8100 PRINT " n = ", NTIME, "Time, hr = ", HOURS8110 PRINT wt% acid = ", WTPCTNEW 8120 PRINT " ppm acetone = ", PPMNEW(4) 8130 PRINT " 8140 PRINT " ppm ethanol = ", PPMNEW(5)= ", PPMNEW(7) 8150 PRINT " ppm NG 8160 PRINT 8170 PPMHC=PPMNEW(4)+PPMNEW(5)+PPMNEW(6)+PPMNEW(7) ppm HC's = ", PPMHC 8180 PRINT "

8190 PRINT 8200 PRINT " Drum mass (lb) = ", WT(NCP1) 8210 PRINT " Drum volume (gal) = ", ZVOL 8220 REM 8230 PRINT: PRINT " Input a 'CR' to continue," 8240 PRINT " or '8' to change acid min-strength / makeup" 8250 PRINT " or '9' to STOP." 8260 INPUT CR 8270 IF (CR=8) THEN 5810 8280 IF (CR=9) THEN STOP 8290 REM 8300 REM 8310 REM ... Acid addition and acid purge. 8320 REM Acid addition rate ... using makeup acid 8330 REM Purge of acid ... concentration equals thoroughly mixed drum 8340 REM 8350 REM ... Calculate acid addition rate to maintain current concentration 8360 REM = 0%8370 REM 1 Air 2 Water 8380 REM = 100%3 Sulfuric acid = 100%8390 REM 8400 REM 4 Acetone = Input Data 8410 REM 5 Ethanol = Input Data 6 Diethyl ether = 100%8420 REM 7 Nitroglycerin 8430 REM = Input Data 8440 REM 8450 REM 8460 ADDACID=WTPCTADD/100 8470 ADDWTR =1!-ADDACID 8480 POTACID= WTNEW(3)/(WTNEW(2)+WTNEW(3)) 8490 POTWTR = 1!-POTACID 8500 TOP=POTACID*MASS(2) 8510 BOT=POTWTR*ADDACID-POTACID*ADDWTR 8520 REM ### PRINT " top = ", TOP: PRINT " bot = ", BOT 8530 ADDRATE=TOP/BOT 8540 PPGADD=62.43/7.48052* SPGRADD 8550 GPMADD=(ADDRATE/60)/PPGADD 8560 PRINT: PRINT " Acid addition:" Mass rate, lb/hr = ", ADDRATE Flow rate, gpm = ", GPMADD 8570 PRINT " 8580 PRINT " 8590 PRINT " = ", PPGADD lb/gal 8600 PURGE=ADDRATE+MASS(2) 8610 PPGPURGE=WT(NCP1)/ZVOL 8620 GPMPURGE=(PURGE/60)/PPGPURGE 8630 PRINT: PRINT " Acid purge:" Mass rate, lb/hr = ", PURGE Flow rate, gpm = ", GPMPURGE 8640 PRINT " 8650 PRINT " = ", PPGPURGE 8660 PRINT " lb/gal 8670 REM 8680 PRINT: PRINT " Input a 'CR' to continue," or '8' to change acid min-strength / makeup" 8690 PRINT " 8700 PRINT " or '9' to STOP." 8710 INPUT CR 8720 IF (CR=8) THEN 5810

8730 IF (CR=9) THEN STOP 8740 REM 8750 REM 8760 REM ### ### 8770 REM ### ### Time incrementation return point ### 8780 REM ### ### 8790 REM 8800 REM ... Acid loss due to consumption with organic reactions has not been included in the analysis (Material Balance). 8810 REM Also the associated heat of reaction has not been 8820 REM 8830 REM included (Heat Balance) 8840 REM 8845 REM ... Time interval set for 6 hours, assuming a time step of 0.01 hours (DTIME) 8847 REM 8850 FOR J=1 TO 600 8860 REM 8870 REM ... Compute drum contents (mass basis) at end to time step 8880 NTIME=NTIME+1 8890 TIME=TIME+DTIME 8900 WTPCT=WT(3)/(WT(2)+WT(3))*100! 8910 FOR I=1 TO (NCP1) 8920 WTNEW(I)=WT(I)+MASS(I)*DTIME 8930 NEXT I 8940 REM 8950 REM ... adjust the water ... component #2 8960 POTWTR = WT(2)/(WT(2)+WT(3))8970 WTNEW(2)=WTNEW(2)+(ADDRATE*ADDWTR-PURGE*POTWTR)*DTIME 8980 REM 8990 REM ... adjust the acid ... component #3 9000 POTACID= WT(3)/(WT(2)+WT(3))9010 WTNEW(3)=WTNEW(3)+(ADDRATE*ADDACID-PURGE*POTACID)*DTIME 9020 REM 9030 REM. adjust total drum content component # NCP1=NC+1 9040 WTNEW(NCP1)=WTNEW(NCP1)+(ADDRATE-PURGE)*DTIME 9050 REM 9060 REM ... Compute concentrations of drum contents Components (2) [Water] and 9070 REM (3) [Sulfuric acid] for wt % acid 9080 REM Components (4)-(7) use ppm by wt 9090 WTPCTNEW = WTNEW(3)/(WTNEW(2)+WTNEW(3))*100! 9100 FOR I=4 TO 7 9110 PPMNEW(I)=WTNEW(I)/WTNEW(NCP1)*1000000! 9120 NEXT I 9130 REM 9140 REM 9150 REM *** PRINT " n=", NTIME, " j=", J, " wt% acid=", WTPCTNEW 9160 REM 9170 REM ... Check HC content in the acid storage drum 9180 REM 9190 REM ### HC ppm (wt) limits in acid storage drum 9200 PPMLIMIT(1)=PPMLIMIT(2)=PPMLIMIT(3)=0! 9210 PPMLIMIT(4) = 10009220 PPMLIMIT(5) = 10009230 PPMLIMIT(6) = 1000

9240 REM == PPMLIMIT(7) = 1009250 PPMLIMIT(7) = 1000000!9260 REM 9270 REM if (ppmnew(4) > ppmlimit(4)) then goto 10220 9280 REM if (ppmnew(5) > ppmlimit(5)) then goto 10220 9290 REM if (ppmnew(6) > ppmlimit(6)) then goto 10220 9300 IF (PPMNEW(7) > PPMLIMIT(7)) THEN GOTO 10510 9310 REM 9320 REM 9330 REM ... [HEAT1] 9340 REM ... Sensible heat lost by incoming vapor stream [HEAT1] 9350 HEAT1=V1(NCP1)*DTIME*CPAIR*(TIN-TOUT) 9360 REM PRINT " heat 1 = ", HEAT 19370 REM 9380 REM ... [HEAT2] 9390 REM ... Latent heat removed for condensation [HEAT2] Latent heat data used, Btu/lb 9400 REM 9410 REM Water = 1045Acetone = 2309420 REM 9430 REM EtOH = 390= 430 (WAG)9440 REM NG 9450 HEAT2=(MASS(2)*1045+MASS(4)*230+MASS(5)*390+MASS(7)*430)*DTIME 9460 REM PRINT " heat2 = ", HEAT2 9470 REM 9480 REM ... [HEAT3] 9490 REM ... Heat of mixing of Water and H2SO4+H2O (Acid) Data from Perry (3rd Edition, pg 277) 100F 9500 REM 9510 REM (a) 100 wt% acid = +20Btu/lb (a) 90 wt% acid = -509520 REM 9530 REM h(%) = -50 + 7*(%-90)9540 REM Btu/lb of water @ 100F = 68 Btu/lb 9550 HIN1=-50+7*(WTPCT-90) 9560 HIN2=68! 9570 REM ... heat of mixing + sensible heat of "addacid" 9580 HIN3=-50+7*(WTPCTADD-90)+.34*(TADDACID-TPOT) 9590 HINTOTAL=HIN1*(WT(2)+WT(3))+HIN2*MASS(2)*DTIME +HIN3*ADDRATE*DTIME 9600 HPOT=-50+7*(WTPCTNEW-90) 9610 HPOTTOTAL=HPOT*(WTNEW(2)+WTNEW(3)) 9620 HEAT3=HINTOTAL-HPOTTOTAL 9630 REM PRINT " heat3 = ", HEAT3 9640 REM %%% heat3=0 9650 REM 9660 REM ... [HEAT4] 9670 REM ... heat4=purge*cplliqmix*(tpot-tpot)*dtime=0.0 9680 HEAT4=0 9690 REM 9700 REM ... New value of T-pot (Calculate T-detla) 9710 REM ... Compute the temperature rise 9720 REM Specific heat data used, Btu/lb-F=cal/g-C 9730 REM (2)+(3) Water+Acid = 0.35 9740 REM Acetone = 0.53(4) = 0.629750 REM (5) EtOH = 0.6 (WAG) 9760 REM (7) NG

9770 CPLIQMIX=(WT(2)+WT(3))*.35+WT(4)*.53+(WT(5)+WT(6))*.62+WT(7)*.6 9780 REM CPLIOMIX=CPLIOMIX/WT(NCP1) 9790 REM TDELTA=(HEAT1+HEAT2+HEAT3+HEAT4)/(WT(NCP1)*CPLIQMIX) 9800 TDELTA=(HEAT1+HEAT2+HEAT3+HEAT4)/CPLIQMIX 9810 REM 9820 IF (MZTIME > 0) THEN GOTO 9880 9830 TPOT=TPOT+TDELTA 9840 REM PRINT " T-pot = ", TPOT 9850 IF (TPOT < 90) THEN GOTO 10000 9860 REM 9870 REM 9880 REM ... ##### Remove energy to hold T=90 F ##### 9890 REM 9900 REM 9910 QOUT=(HEAT1+HEAT2+HEAT3+HEAT4)/DTIME 9920 REM PRINT " T-pot & Q-out = ", TPOT, QOUT 9930 IF (MZTIME > 0) THEN GOTO 10000 9940 HOURS=NTIME*DTIME 9950 PRINT: PRINT " Heat Xhr started, T-pot>90F, Time (hrs) = ", HOURS 9960 PRINT: PRINT " Input a 'CR' to continue, or '9' to STOP.": INPUT CR 9970 IF (CR=9) THEN STOP 9980 MZTIME=1 9990 REM 10000 REM ... Transfer drum contents into the variable "WT(i)" for next 10010 REM time step. 10020 FOR I=1 TO (NCP1) 10030 WT(I) = WTNEW(I)10040 NEXT I 10050 REM 10055 IF (NTIME = 600) THEN GOTO 10130 10060 IF (NTIME = 1200) THEN GOTO 10130 10065 IF (NTIME = 1800) THEN GOTO 10130 10070 IF (NTIME = 2400) THEN GOTO 10130 10075 IF (NTIME = 3000) THEN GOTO 10130 10080 IF (NTIME = 3600) THEN GOTO 10130 10082 IF (NTIME = 4200) THEN GOTO 10130 10084 IF (NTIME = 4800) THEN GOTO 10130 10088 rem 10090 REM ... Increment "jtime" 10110 NEXT J 10120 REM 10130 REM ... Print out the ntime, time, wt% acid, and ppm HC's 10140 HOURS = NTIME*DTIME10150 REM 10160 REM ... Compute storage drum volume (gallons) 10170 FAC=62.43/7.48052 10180 ZVOL=(WT(2)+WT(3))/(FAC*SPGRACIDMIN) 10190 FOR I=4 TO 7 10200 ZVOL=ZVOL+WT(I)/(FAC*SPGR(I)) 10210 NEXT I 10220 PPGMIX=WT(NCP1)/ZVOL 10230 PRINT 10240 PRINT " Circulation continuing with acid addition and purge" n = ", NTIME, "Time, hr = ", HOURS

10260 PRINT wt% acid = ", WTPCTNEW ppm acetone = ", PPMNEW(4) 10270 PRINT " 10280 PRINT " ppm ethanol = ", PPMNEW(5) 10290 PRINT " = ", PPMNEW(7) 10300 PRINT " ppm NG 10310 PRINT 10320 PPMHC=PPMNEW(4)+PPMNEW(5)+PPMNEW(6)+PPMNEW(7) 10330 PRINT " ppm HC's = ", PPMHC 10340 PRINT Drum mass (lb) = ", WT(NCP1) Drum volume (gal) = ", ZVOL 10350 PRINT " 10360 PRINT " 10370 PRINT " = ", PPGMIX lb/gal 10380 REM 10390 PRINT: PRINT " Input a 'CR' to continue," 10400 PRINT " or '8' to change acid min-strength / makeup" 10410 PRINT " or '9' to STOP." 10420 INPUT CR 10430 IF (CR=8) THEN 5810 10440 IF (CR=9) THEN STOP 10450 GOTO 8770 10460 REM 10470 REM 10490 REM 10500 REM 10510 REM ... HC concentration limit exceeded 10520 REM ... Print out the ntime, time, wt%acid, and ppm HC's 10530 HOURS = NTIME*DTIME 10540 REM 10550 REM ... Compute storage drum volume (gallons) 10560 FAC=62.43/7.48052 10570 ZVOL=(WT(2)+WT(3))/(FAC*SPGRACIDMIN) 10580 FOR I=4 TO 7 10590 ZVOL=ZVOL+WT(I)/(FAC*SPGR(I)) 10600 NEXT I 10610 PPGMIX=WT(NCP1)/ZVOL 10620 PRINT 10630 PRINT " HC concentration limit reached or simulation stopped." 10640 PRINT " Acid addition/purge maintains only the water/acid content." 10650 PRINT " HC values continue to change with time." 10660 PRINT " n = ", NTIME, "Time, hr = ", HOURS10670 PRINT 10680 PRINT " wt% acid = ", WTPCTNEW ppm acetone = ", PPMNEW(4)10690 PRINT " ppm ethanol = ", PPMNEW(5)10700 PRINT " = ", PPMNEW(7) 10710 PRINT " ppm NG 10720 PRINT 10730 PPMHC=PPMNEW(4)+PPMNEW(5)+PPMNEW(6)+PPMNEW(7) ppm HC's = ", PPMHC 10740 PRINT " 10750 PRINT 10760 PRINT " Drum mass (lb) = ", WT(NCP1) 10770 PRINT " Drum volume (gal) = ", ZVOL 10780 PRINT " lb/gal = ", PPGMIX

```
10790 REM
10800 PRINT: PRINT " Input a 'CR' to continue termination of simulation,"
10810
         PRINT "
                     or '8' to change acid min-strength / makeup"
         PRINT "
10820
                      or '9' to STOP."
10830 INPUT CR
10840 IF (CR=0) THEN STOP
10850 IF (CR=8) THEN 5810
10860 IF (CR=9) THEN STOP
10870 GOTO 8770
10880 STOP
10890 REM
10910 REM
10920 REM ... The following are the values associated with the variables
10930 REM
              that are contained in the "data" statements.
10940 REM
10950 REM READ record #1
10960 REM PRINT " Gas inlet rate and conditions:"
10970 REM PRINT "
                     Gas flow rate, cf/min:" : INPUT VIN
10980 REM PRINT "
                     Pressure, mm Hg:"
                                         : INPUT PIN
10990 REM PRINT "
                     Temperature, F:"
                                         : INPUT TIN
11000 REM read VIN, PIN, TIN
11010 DATA 3000, 780, 140
11020 REM
11030 REM
11040 REM READ record #2
11050 REM PRINT " Gas outlet conditions:"
11060 REM PRINT "
                     Absorber pressure drop, mm Hg:": INPUT DPDPDP
11070 REM PRINT " Estimated Gas Temperature, F: " : INPUT TOUT
11080 REM read DPDPDP, TOUT
11090 DATA 20, 90
11100 REM
11110 REM
11120 REM READ records #3 and #4
11130 REM PRINT " Inlet gas data:"
11140 REM PRINT "
                     Water:"
11150 REM PRINT "
                       Temperature of ambient air: ": INPUT TAIR
11160 REM PRINT "
                       Water, Relative Humidity (%):": INPUT RH
11170 REM PRINT "
                     HC concentrations:"
                       Acetone, ppm by volume: ": INPUT PPMACE
Ethanol, ppm by volume: ": INPUT PPMETOH
11180 REM PRINT "
11190 REM PRINT "
11200 REM PRINT "
                       Nitroglycerin, ppm by volume:": INPUT PPMNG
11210 REM READ TAIR, RH
11220 REM READ PPMACE, PPMETOH, PPMNG
11230 DATA 90, 95
11240 DATA 1200, 1850, 15
11250 REM
11260 REM
11270 REM READ record #5
11280 REM PRINT " Gas removal factors"
11290 REM PRINT "
                    ... fraction of gas removed from the feed:"
11300 REM PRINT " Gas removal factors for"
11310 REM PRINT "
                                              ": INPUT RFAC(4)
                     Acetone (#4), % removed:
11320 REM PRINT "
                                              ": INPUT RFAC(5)
                     Ethanol (#5), % removed:
```

```
Nitroglycerin (#7), % removed:": INPUT RFAC(7)
11330 REM PRINT "
11340 REM READ RFAC(4), RFAC(5), RFAC(7)
11350 DATA 85, 85, 85
11360 REM
11370 REM
11380 REM READ record #6
11390 REM PRINT " Sulfuric Acid Solution Data:"
11400 REM PRINT "
                     Initial volume of acid solution: "
                                                    : INPUT VOL
11410 REM PRINT "
                     Acid strength (Organic Free), wt%:" : INPUT WTPCTIN
11420 REM PRINT "
                     Specific gravity (Organic Free): " : INPUT SPGRIN
11430 REM PRINT "
                     Temperature of acid, F:
                                                    : INPUT TPOTIN
11440 REM read VOL, WTPCTIN, SPGRIN, TPOTIN
11450 DATA 2000, 96, 1.841, 80
11460 REM
11470 REM
11480 REM READ record #7
11490 REM PRINT " Organic concentrations, ppm by wt, in the acid:"
11500 REM PRINT "
                     Acetone, ppm by wt:, PPMWT(4)'
11510 REM PRINT "
                     Ethanol, ppm by wt:, PPMWT(5)"
11520 REM REM PRINT "
                          Diethyl ether, ppm by wt:, PPMWT(6)"
11530 REM PRINT "
                     Nitroglycerin, ppm by wt:, PPMWT(7)"
11540 REM read PPMWT(4), PPMWT(5) PPMWT(7)
11550 DATA 0.0, 0.0, 0.0
11560 REM
11570 REM
11580 REM READ records #8, #9 and #10
11590 REM PRINT "
                   Minimum acid values in storage drum (HC free)"
11600 REM PRINT "
                     Acid strength: " : INPUT WTACIDMIN
                     Specific gravity:" : INPUT SPGRACIDMIN
11610 REM PRINT "
11620 REM PRINT
11630 REM PRINT "
                   Makeup sulfuric acid"
11640 REM PRINT "
                     Acid strength: ": INPUT WTPCTADD
Specific gravity:": INPUT SPGRADD
11650 REM PRINT "
11660 REM PRINT "
                     Temperature, F: ": INPUT TADDACID
11670 REM PRINT
11680 REM PRINT " Delta Time (hours) for numerical analysis", DTIME
11690 REM
11700 REM READ WTACIDMIN, SPGRACIDMIN
11710 REM READ WTPCTADD, SPGRADD, TADDACID
11720 REM READ DTIME
11730 DATA 95, 1.839
11740 DATA 98, 1.841, 80.0
11750 DATA 0.01
11760 REM
11770 REM
               .....
11780 REM
11790 END
```

Bibliography

- 1. Du Pont, E. I. de Nemous and Company, Inc. "Sulfuric Acid Storage and Handling." p. 14
- 2. Feiser, L. F. & Feiser, M. "Organic Chemistry." 3rd Ed. D.C. Heath Co., Boston (1957)
- Foust, Alan S., Wenzel Leonard A., Clump, Curtis W., Maus, Louis, Anderson, Bryce, L. "Principles of Unit Operations." John Wiley and Sons, New York, N.Y. (1980)
- 4. Jake, C. A. "Volatile Organic Carbon Emissions, Phase II." Report AMXTH-TE-CR-87116, Final Report, Radford Army Ammunition, Radford, Virginia 24141-0298 February (1987)
- Lanford, T. H., Todd, J. S., Price, D. D., and Graff, A. "Modernized FAD For Multibase Propellants." Report ARLCD-CR-82053, United States Army Armament Research and Development Command, Dover, New Jersey 07081 January (1983)
- 6. Larson, M. S. Thesis, Chem. Eng. Lafayette College (1942)
- 7. Nazim Z. Muradov, Clovis A. Linkous and Ali T-Raissi "Photocatalytic Decomposition Of Nitroglycerin - Contaminated Airborne VOCs." Florida Solar Energy Center, presented in the 16 th Annual Army Environmental R & D Symposium (1992)
- 8. Ormandy, W. R. "The Recovery of Acetone Vapors From Air." Transactions of the Institute of Chemical Engineers Vol. 7 (1929): 80 84
- 9. Othmer, D. F. & Scheibel, E. G. "Acetone Absorption by Water in a Semi Commercial Packed Tower." *Trans. AICHE* <u>37</u>, (1941): 211
- 10. Private Communication, Picatinny Arsenal to HSMRC, N.J.I.T. (1991)
- 11. Robinson, Clark Shove "The Recovery Of Vapors." Reinhold Publishing Corp., New York (1942): 246 - 251
- 12. Scheibel, E. G. & Othmer, D. F. "Gas Absorption As a Function of Diffusivities and Flow Rates." *Trans. AICHE* <u>40</u> (1944): 611
- 13. Sherwood, T. K. & Holloway, F. A. L. "Performance of Packed Towers -Experimental Studies of Absorption and Desorption." *Trans. AICHE* <u>36</u> (1940): 21
- 14. Tamir, Abraham "Absorption of Acetone in a Two Impinging Stream Absorber." Chem. Engr. Sci. <u>41</u> No. 12 (1986): 3023
- 15. Urbanski, Tadeusz "Chemistry and Technology of Explosives." Pergamon Press Vol. III (1967): 603
- 16. Wilke, C. R. & Chang Pin "Correlations of Diffusion Coefficients in Dilute Solutions." AICHE Journal <u>1</u> (1955): 264