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ODOR CONTROL STUDIES
I ODOR CONTROL TECHNOLOGY
A REVIEW
AND BIBLIOGRAPHY
II CATALYTIC OXIDATION OF
ODOROUS COMPOUNDS

A Thesis
Submitted to the Faculty of Graduate Studies Through
the Department of Chemical Engineering as Partial Fulfillment
of the Requirements for the Degree of Master of
Applied Science at the
University of Windsor

by

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ABSTRACT

A comprehensive review of odor control methods, as well as results of an experimental study on catalytic oxidation of pure odorants, are presented in this thesis.

In the first section, the existing literature on odor control techniques is classified and reviewed. Methods used for odor classification, detection and measurement are presented as the basic background for the evaluation of control methods. Each technique of odor removal is described in terms of its principle of operation, equipment details, and experimental results reported in the literature. Effects of parameters such as flow rates, temperatures and pressure drops on odor removal efficiencies are examined. Comparative results are summarized in tabular fashion for easy reference. Analytical methods used to derive the reported results are also described. Finally, an economic comparison of the control methods for a variety of industrial applications is presented.

In the second section, experimental results from a study of the catalytic oxidation of twenty-two pure odorants of industrial relevance are presented. The oxidation was carried out in an integral flow reactor with a platinum catalyst. The temperature of oxidation varied from 80°C to 461°C, at a space velocity of 83,481 hr^{-1}. It was found that twenty-one of the twenty-two odorants oxidized successfully with complete or nearly complete odor removal. Wide differences in the ease of oxidation, as indicated by the required preheat temperatures, are noted.

For two of the odorants, propionic acid and amyl alcohol, the experimental data were analyzed to establish the relative importance of mass transfer and kinetic rate steps. It was found that at low temperatures, external mass transfer is relatively unimportant but its importance increased rapidly with temperature. For all the experimental conditions investigated, intraparticle diffusion was estimated to be an important factor in determining the overall rate of oxidation. Low effectiveness factors and high kinetic coefficients were obtained, indicating rather high catalytic activity. It was also established that a high potential for savings in fuel requirements exists in odor control by catalytic oxidation systems.

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PART ONE

ODOR CONTROL TECHNOLOGY A REVIEW AND BIBLIOGRAPHY

I. INTRODUCTION

The most frequent complaints to environmental agencies are those concerning "offensive" odors. These odors are not, in general, extremely hazardous to the health of individuals but are capable of producing nausea, vomiting, headache, loss of appetite, hindrance of breathing, upset stomach, disturbed sleep, interference with enjoyment of property, and other problems.

Industrial odors constitute a highly significant portion of these "offensive" odors, thereby contributing to existing air pollution problems.

In this section of the thesis, a comprehensive review of odor control techniques is presented. The objective of this review was to obtain an appreciation of technical as well as economic potentials and limitations of major odor control methods.

In Chapter II, classification, detection and measurement techniques for odors are discussed. In Chapter III, the odor control techniques in present use are described. The results from literature are presented in tabular form for easy reference. Chapter IV gives a comparison of the relative economics of the control techniques for a variety of industrial applications.

II. CLASSIFICATION, DETECTION AND MEASUREMENT OF ODORS

A. Classification

The most common chemical types of odorants are compounds (both organic and inorganic) that contain nitrogen, sulphur, oxygen or one of the halogens in their molecular configurations. Ranking of odorant classes on the basis of increasing average odor threshold results in the following descending order [36, 61]:

i. Sulphides and mercaptans (sulphur-containing compounds)

ii. Amines and N-heterocyclics (nitrogen-containing compounds)

iii. Aldehydes, ketones and acids (oxygen-containing compounds)

iv. Esters, alcohols and chlorinated compounds (oxygen- or chlorine-containing compounds)

v. Hydrocarbons (compounds containing carbon and hydrogen only).

By reviewing the scientific and technical literature published over the past fifteen years, Hopton and Laughlin [36] established an inventory of the odor sources generally considered to be of major importance in an industrialized environment. They identified the primary odor-producing industries together with their chemical classes of odorants.

Underwood [77], in reviewing existing odor literature, presents a comprehensive classification of industrial odorous emissions.

B. Detection

Detection of odors is made by the human nose and is, therefore, subjective. Even when the specific chemical nature of an odorant is known, the concentration may be considerably lower than the detection limit of any available instrumental or chemical measuring technique and hence may only be detected subjectively [36].

The sensation of smell results from inhalation of specific chemical compounds which are said to possess odor. Most gases and vapors that are not normal constitutents of air are odorous in certain concentration ranges [61]. Many attempts have been made in the literature to correlate odorous characteristics of molecules to their physical and chemical properties, but for purposes of air pollution control, detection using sensory methods is the only practical technique.

C. Measurement

Odor measurement methods can be grouped into two major categories: sensory methods and analytical methods. Sensory methods are subjective because they rely on the human olfactory system. However, at present only the human nose is versatile enough to measure the four attributes of odors, which are intensity, quality, detectability and acceptability.

All measurements of odors by the human olfactory system with respect to detectability and intensity involve dilution of the odorous gas. The threshold detection or recognition of an odorant is expressed as the number of dilutions required to render it odorless [36]. The methods used include olfactometers, odor panels, ASTM syringe method and others.

Instrumental techniques (analytical methods) include gas chromatography, spectrophotometric methods in the infrared, ultraviolet or visible portions of the electromagnetic spectrum, conductometric, coulometric, amperometric, or other electrochemical methods, and various other chromatographic or spectrometric methods. Often a combination of two or more approaches is employed [61].

III. ODOR CONTROL TECHNIQUES

A. Absorption

Absorption (or scrubbing) units can be used for odor abatement if the odorous components are soluble, emulsifiable, condensable or react chemically in the solution. Water is the most widely used scrubber liquid to which bases, acids or oxidizing agents may be added. The scrubber unit provides a means for intimate contact between the odorants and the washing medium. Various arrangements such as spray chambers, packed towers, tray towers, jet or Venturi units are available.

The effectiveness of absorption for odor removal is dependent on the following [15]:

i. temperature differential between the gas and the liquid
ii. boiling point and volatility of the odorous components
iii. moisture content of the gas stream
iv. degree of gas-liquid contact
v. relative heat capacity and volatility of the absorbing liquid

Absorption of odors by the liquid is governed by the mechanisms of mass transfer including the transport of odorous molecules by diffusion and turbulence. The rate of removal depends on [15]:

i. gas-liquid interfacial area
ii. concentration gradients
iii. solubility of the odorous gas in the absorbing liquid
iv. diffusion rate of the odorous molecules in the gas phase

The rate and capacity of absorption of odors by the scrubbing liquid is often increased by chemical reaction of the odorants in the liquid phase. A large number of odor scrubbing operations involve mass transfer with chemical reaction. Some results of laboratory odor reduction tests using potassium permanganate as a scrubbing solution are given in Table 1 [1]. These results show that, for many of the compounds studied, odor reduction is most effective with $KMnO_4$ solutions at higher pH. Anderson and Adolf [1] explained this result in two-fold fashion: (i) at higher pH the rates of permanganate reactions generally increase (ii) as some of the compounds studied are ketones, the higher pH encourage enolization, and in this form, these compounds are more readily attacked by $KMnO_4$. Odor measurements were made using the syringe technique (ASTM Method D-1359-57). Gas chromatographic analysis was also performed and the results corresponded closely to the syringe results. For all compounds except butanol, a sample size of 1 ml was used with a Porapak Q column in a Beckman GC-5. Further laboratory work on chemical scrubbing has been reported by

Compounds	Odor Units Before Scrubbing	Odor Units After Scrubbing (no $KMnO_4$ used)			Odor Units After Scrubbing ($KMnO_4$ used)		
		pH 9	pH 11	pH 12	pH 9	pH 11	pH 12
Acrolein	3,200	-	-	-	200	200	200
Acrylonitrile	1,600	180	-	-	12	4	1
1,3 Butanediol	16	-	-	-	2	2	2
1-Butanol	200	200	200	-	50	40	30
Butyraldehyde	25,600	-	20,000	20,000	32	40	20
Isobutyraldehyde	64	-	-	-	10	20	20
Butyric Acid	409,600	-	-	-	100	100	8
Diethylamine	512	-	50	-	32	40	20
Ethyl Sulphide	25,600	-	-	-	80	64	2
Ethyldisulphide	25,600	-	-	-	2	50	2
Heptaldehyde	12,800	-	-	-	400	300	400
Indole	3,200	-	-	-	512	2	2
Methanol	16	-	-	-	8	2	2
Methyl Ethyl Ketone	160	8	8	6	8	72	18
Methyl Isobutyl Ketone	240	240	160	120	80	52	6
Phenol	1,280	1,800	1,600	-	2	0	0
n-Propyl Sulfide	160,000	-	-	160,000	800	3,000	800
Skatole	32	-	-	-	2	2	2
Valeraldehyde	25,600	8,000	1,600	-	3	4	3

TABLE 1: Results of Laboratory Odor Reduction Tests [1]

Dickerson and Murthy [15] and Doty et al [17]. This work on scrubbing of odorants believed to be constituents of rendering plant odors was performed under a grant from the Environmental Protection Agency. Table 2 [15] summarizes the results from this study. It was found that the reagent concentration did not materially effect odor removal efficiency except for permanganate and hypochlorite solutions, both of which are oxidizing reagents.

In industrial practice, success in odor removal by scrubbing depends largely upon identifying the odorants and finding a scrubber liquid that reacts rapidly and completely with these substances. Removal is also a function of other variables such as residence time, available contact area and the design of scrubbing device. The various types of scrubbers are described in the following sections.

1. Spray Towers

Spray towers can be used to cool gas streams prior to further treatment or can, perhaps, be used when partial reduction in emissions would be sufficient. These towers generally have a low pressure drop, high liquid consumption

	Valeraldehyde	Dipropyl Sulphide	Amyl Alcohol	Trimethyl Amine	Butyric Acid	Butanediol	Tertbutyl Amine	Heptadiene	Dimethyl Disulphide
Water	30	0	80-90	80-90	-	-	>90	0	10
NaOCl (1%)	10	>90	80	>90	-	-	-	20	50
H_2O_2 (3%)	>90	0	75	-	-	-	>90	0	slight
$KMnO_4$ (3%)	30	10-25	40-80	>90	-	-	-	25	20-75
Sodium Bisulphite (5%)	>90	10	75	-	-	-	-	-	-
HCl (5%)	0	0	80	>90	-	-	-	-	-
NaOH (5%)	10-30	0	0-60	0	>90	>90	90	-	-

TABLE 2: Scrubber Removal Efficiencies (In Percent Removed) of Various Chemicals on Different Odorants [15]

and are usually the least expensive. The number of transfer units is limited in this type of device.

This class of scrubber consists of a vertical tower in which the liquid is distributed in droplets for contacting the odorous stream. Figure 1 shows general configuration of a countercurrent tower.

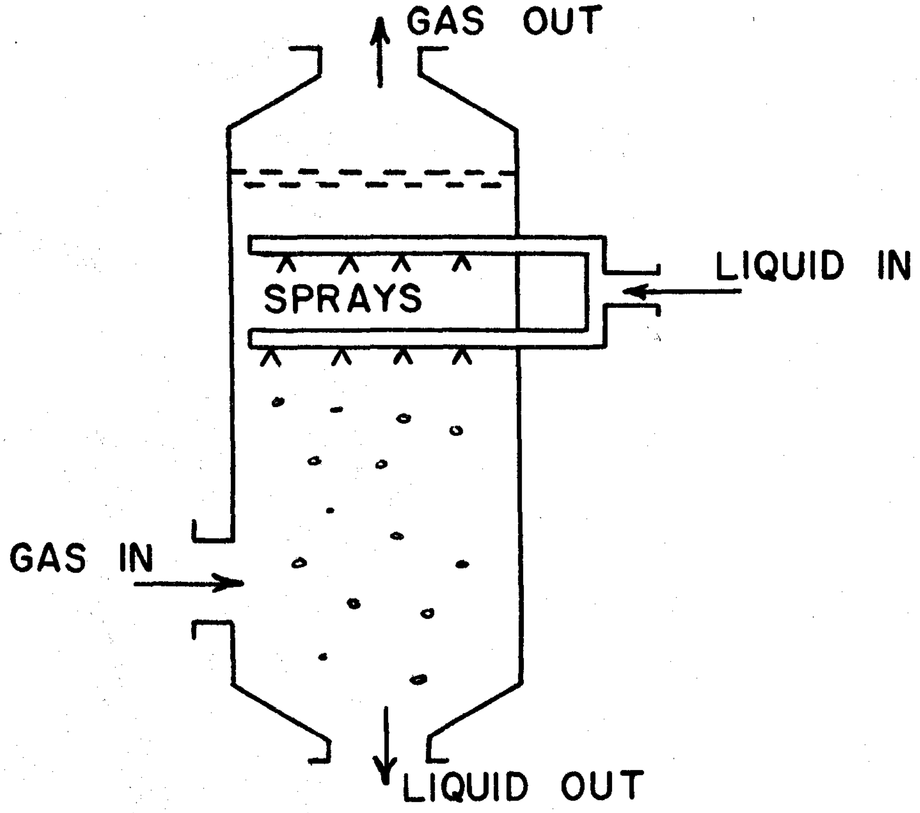

FIGURE 1. Spray Tower

Spray towers may operate in the countercurrent mode (as in Figure 1) or in the cocurrent mode in which case the gaseous stream and the liquid stream travel in the same direction. Also, the spray scrubber may be aligned vertically (Figure 1) or horizontally.

Removal efficiencies of 85% have been reported [17] by one rendering plant at a cost of $0.16/1000 cfm-hr. Their novel spray scrubbing system is reported to control odor at approximately one-fourth of the cost of other available equipment. Doty et al [17] present computer programs which estimate scrubber costs for a series of air flow rates and odor reduction ratios for the rendering industry.

2. Cross-Flow Scrubbers

Figure 2 is a simplified diagram of a cross-flow scrubber. As can be seen, the liquid and the gas interact at right angles. The main advantages are low pressure drop,

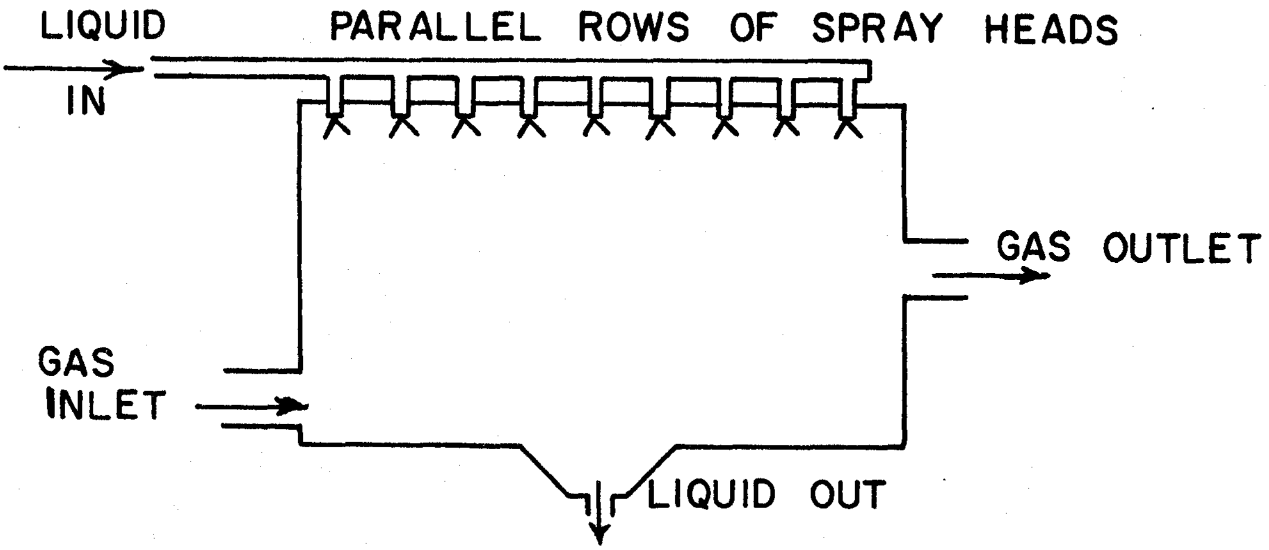

FIGURE 2: Cross-Flow Spray Scrubber

high particle collection capability and low potential of flooding the scrubber. The design of cross-flow scrubbers is rather complex and therefore it is hard to predict their performance. Cross-flow scrubbers may be operated without packing or with any standard tower packing or baffles.

3. Plate Scrubbers

The plate scrubber consists of a vertical hollow tower fitted transversely with several plates as shown in Figure 3. Gas passing through the openings in each plate mixes with the liquid flowing over it to give effective mass transfer. Some plates have baffles above the holes for effective removal of particulates from the gas stream. Plate scrubbers are used for scrubbing both particulate and gaseous pollutants.

4. Packed Towers

This type of scrubber is the most common device found in industry today for gas absorption. The tower consists of a hollow chamber packed with suitable materials such as Raschig rings, Berl saddles, Tellerettes, Pall rings,

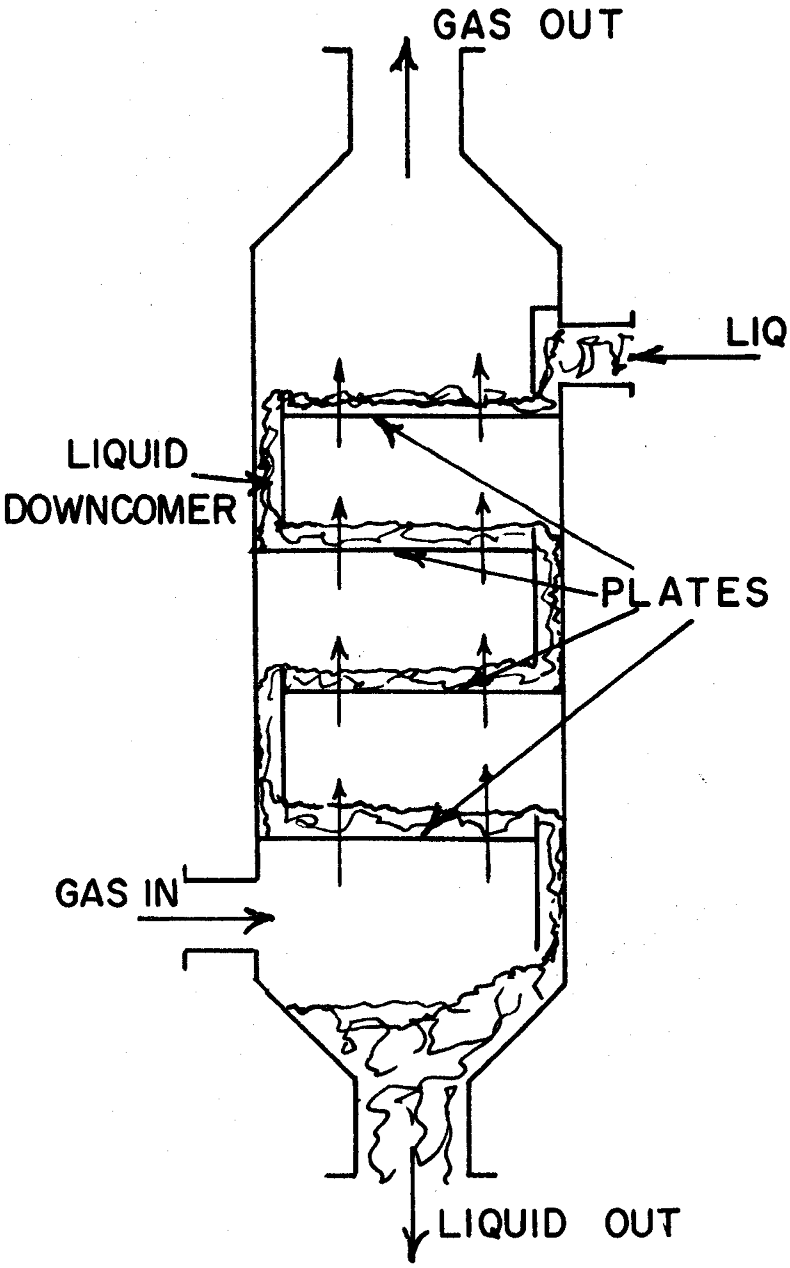

FIGURE 3: Plate Scrubber [13]

Intalox saddles or Lessig rings [15, 36]. The odorous gas flows countercurrent to the liquid flow. The liquid is distributed into films by the packing so as to offer maximum surface contact area between the gas and the liquid.

The design methods for packed bed absorbers are well established and available in published literature [71].

In the rendering odor study referred to earlier, a packed bed scrubber, six inches in diameter and two feet high, was used to establish removal efficiencies for nine pure odorants [17]. Table 3 gives details of tests made on dimethyl disulfide using pure water, water containing permanganate and water containing hypochlorite as scrubbing solution.

Scrubbing Reagent	Liquid Flow Rate gpm	Air Flow Rate cfm	Odorant Concentration from Chromatograph, µg/ml	
			Scrubber Inlet	Scrubber Outlet
		15	0.40	
			0.28	
Water	0.6	15		0.22
$KMnO_4$	0.6	15		0.12
$KMnO_4$	0.6	15		0.08
			0.08	
		15	1.5	
			1.4	
Water	0.6			1.2
NaOCl, 2.5%	0.6			0.64
			0.17	

TABLE 3: Scrubbing of Dimethyl Disulfide Using a Packed Scrubber [17]

The design methods for packed bed scrubbers are well developed and are based on the considerable literature on gas-liquid mass transfer. However, design for absorption with chemical reaction is usually accomplished under some simplifying assumptions such as stipulation of a fast reaction. The design procedures for scrubbers have been put into computer models by Doty et al [17]. Their computer projections of costs of odor control by scrubbing and other methods are discussed in Chapter IV.

5. Impingement Scrubbers

Impingement scrubbers use baffles and a water surface. The gas is forced to turn on the water surface by the baffles, thereby increasing mixing. These types of scrubbers are generally used to remove large particles and to cool the gas stream. Such devices are very simple and require virtually no maintenance [36]. These types of scrubbers come in different designs and sizes (see Reference [36]).

Results obtained using a pilot size air cleaner are given in Table 4 [24]. The unit used was basically a four stage reactor absorber. The first stage was a wetted double-impingement screen which removed particulate matter and absorbed some gases. The next two wetted stages contained fibrous packing with large wetted surface areas for gas absorption. The final stage was a dry fibre filter which prevented liquid carryover, as shown in Figure 4. Each stage had a design air flow capacity of 270 cfm with the design

Gas Flow Rate (cfm)	Absorber Resistance inches w.g.	Caustic Added (gph)	Chlorine Added (ppm)	Gas Temp.		%Odor Reduction
				Entry (°F)	Exit (°F)	
278	5.5	0	0	210	111	18
278	6.0	0.75	0	210	110	91
278	5.9	0.75	1.9	210	112	91
288	5.6	0.75	5.7	204	110	95
280	5.3	0.75	9.0	204	108	94
318	9.3	0.75	8.5	204	116	96
318	9.3	0.75	4.7	204	116	95

TABLE 4: Pilot Test Results of Gas and Vapor Removed From Spent Grain Dryers [24]

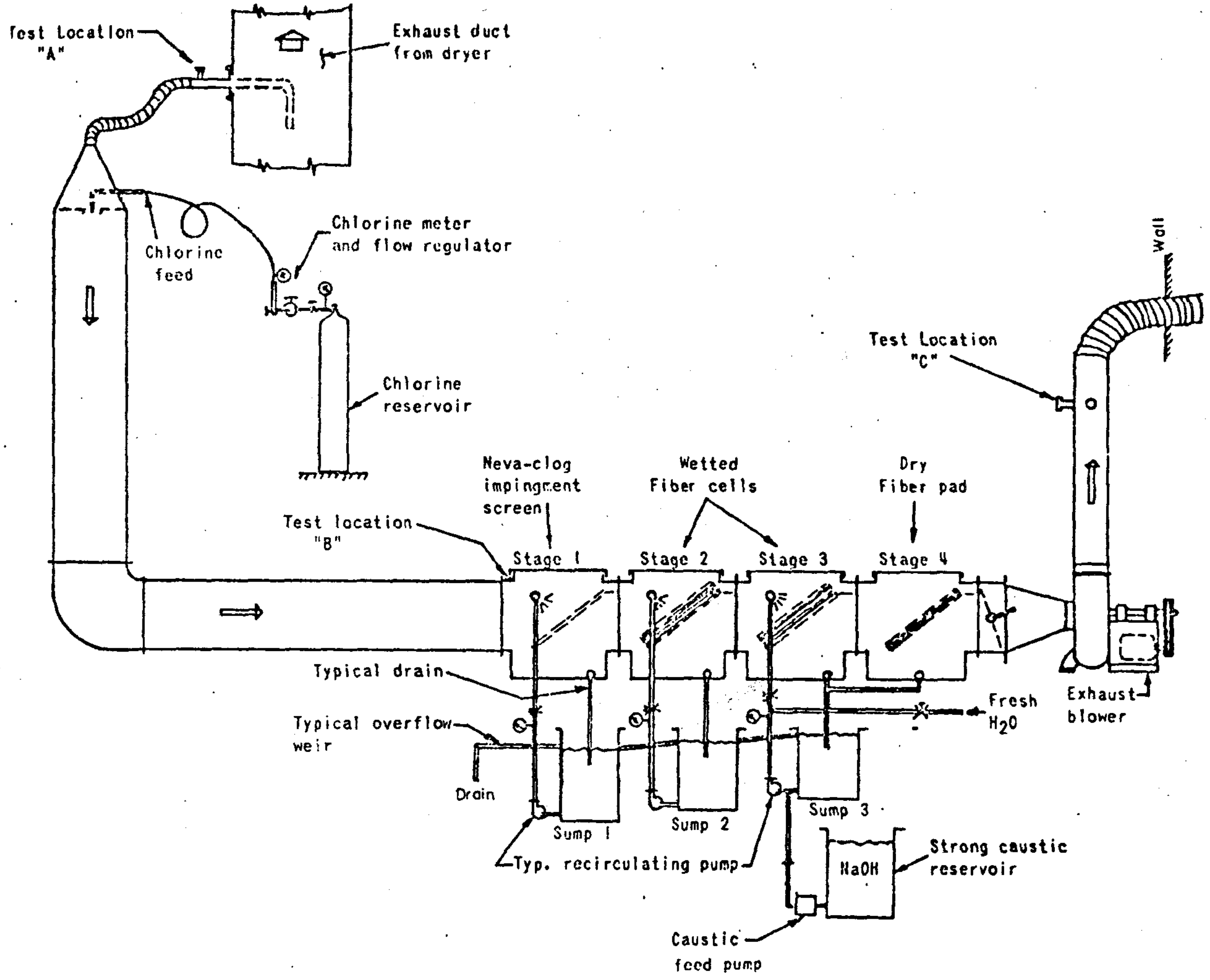

FIGURE 4: Pilot Reactor Absorber [24]

liquid flow rate on each stage being 3 gpm/sq. ft of face area. In all cases, 20% NaOH was added to the last wet stage at a rate of 0.75 gph to maintain a pH of 11-12. Chlorine was added at various dosages before the gas entered the first impinger. A Varian gas chromatograph with a 6-ft packed column containing 5% ethylene glycol phthalate on Chemisorb W was used to separate several compounds contained in the dryer offgases. A flame ionization detector, which is specially sensitive to carbon molecules in organic compounds, was used to determine up and downstream concentrations. It can be seen from Table 4 that a combination of caustic and chlorine treatments results in high odor removal efficiencies.

6. Venturi Scrubbers

It is reported [15, 36] that these scrubbers are generally most effective for use as particle removal devices or for odor removal where the odorous pollutant is associated with particles or condensibles. Because of the high pressure drops associated with Venturi devices, power costs are very high. Particle collection generally increases with pressure drop [15]. Details of Venturi scrubbers may be found in the literature [15, 36, 46].

There are generally two types of Venturi scrubbers: the High Energy Venturi, where fans are used to draw the dirty gas through a fine water spray and the Ejector Venturi, which uses the high velocity of the atomized water to cause a self induced draft to draw the gas through the system.

Experimental results obtained using an Ejector Venturi on various vapors are illustrated in Table 5 [46]. It is interesting to note that a large variety of gaseous pollutants may be removed by this method. However, no mention is made as to how these removal efficiencies were arrived at, i.e. measurement techniques, experimental set-up, are not indicated.

7. Developmental Scrubbers

a. PEPCON Scrubber

The PEPCON (Pacific Engineering and Production Company of Nevada) system works on an electrolytic basis producing oxidizing substances such as sodium hypochlorite and ozone which react with the odorous components. Reference [12] gives more details as to the engineering aspects of this

Gas	No. of Stages	Scrubbing Medium	Scrubbing Efficiency % Removal (up to)
SiF_4	2	water	97
HCl	1	water	99
NO_2	1	water	30
NH_3	1	water	97
HF	1	water	95
HNO_3	1	water	97
SO_2	1	caustic	98
H_2S	2	caustic	85
I_2	1	caustic	99.9
Cl_2	2	caustic	99

TABLE 5: Ejector Venturi Efficiencies [46]

scrubber. Figure 5 is a simplified diagram of the PEPCON system.

Table 6 [12] shows operating specifications for two typical systems utilized for the control of hydrogen sulphide. Removal efficiencies are not reported; consequently many questions regarding the operational characteristics of these scrubbers remain unanswered.

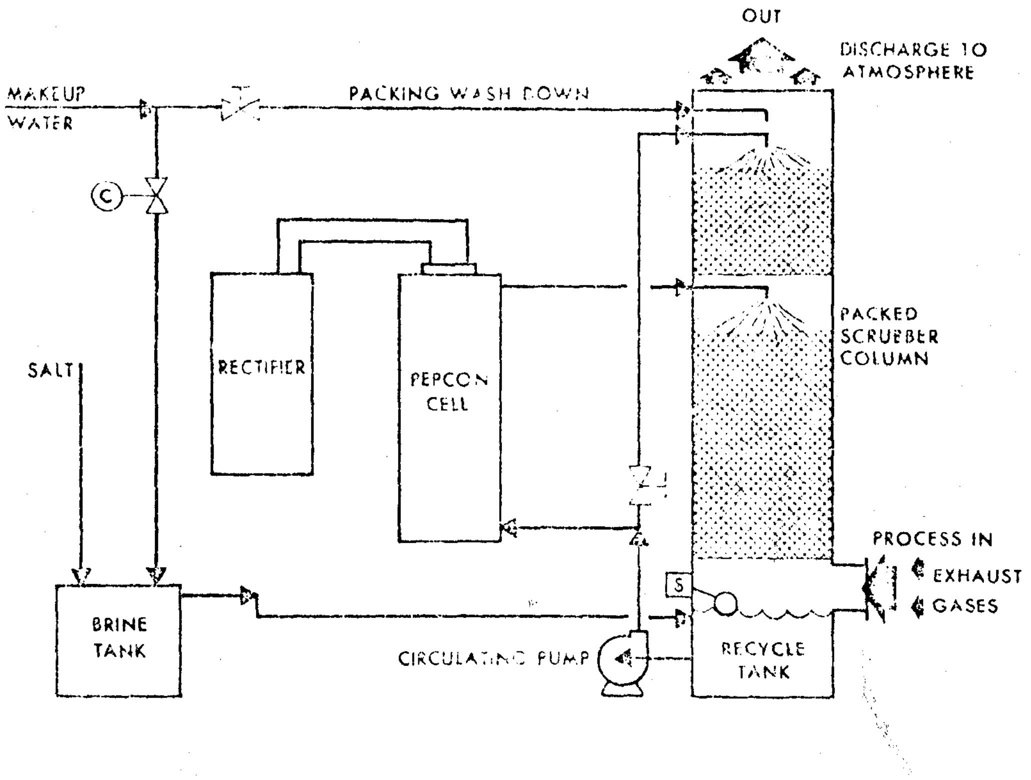

FIGURE 5: PEPCON System Flow Diagram [18]

Capacity (Gas Volume cfm)	1000	30,000
Capacity (ppm H_2S)	0-15	0-100
Power Required (power for pumps not included)	0.5 KW (max.)	60 KW (max.)
Salt Required (sea water can be used)	50 lb/wk	1500 lb/day
Area Required (rectifier area not included)	4' x 4'	10' x 20'
Height	8' (max.)	24' (max.)
Weight	750 lbs	7550 lbs
Pressure Drop Through Tower	1.5" H_2O	5.0" H_2O

TABLE 6: PEPCON Systems [12]

b. Virotrol Scrubber

The Virotrol scrubber is a four chambered baffled box into which two sprayheads are placed. The scrubbing solution is offered as a mist through which the odorous gas must pass. The spent solution is then drained through the bottom of the scrubber as can be seen in Figure 6 (Solid lines show air movement, dotted lines show chemical spray. Numbers indicate order of passage).

Experimental results obtained from this device utilizing 0.5% potassium permanganate as the scrubbing solution are given in Table 7 [1]. The syringe technique (ASTM Method D-1359-57) was used to measure odor units before and after scrubbing. Three samples were used in these experiments:

i. a mixture of butanol, butyraldehyde, methylisobutyl ketone, and butyl acetate

ii. old uncleaned lobster shells which when heated produce an odor characteristic of a fish processing plant

iii. beef bones, fat and blood which were aged and cooked to simulate odors from a rendering process.

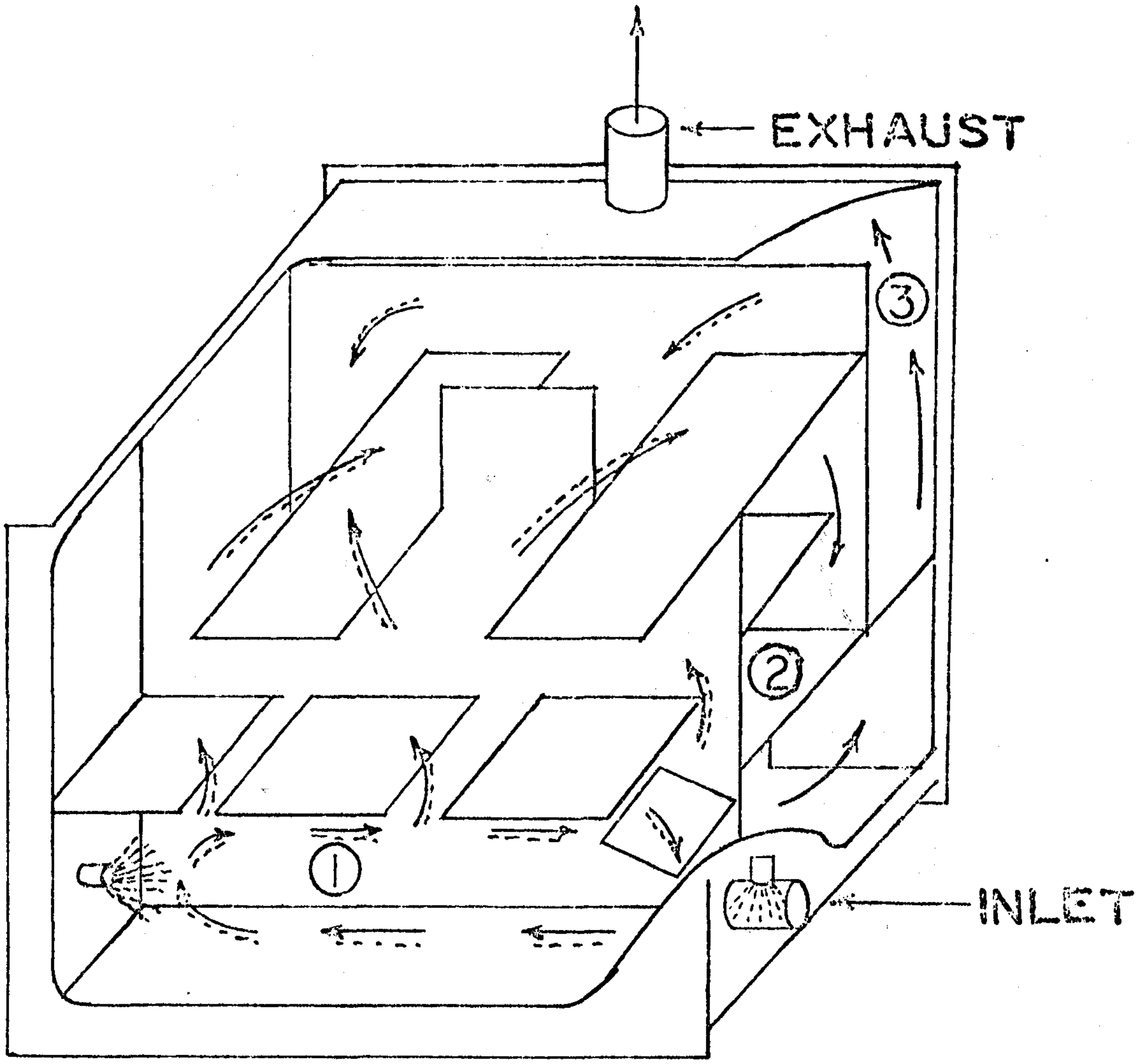

FIGURE 6: Virotrol Scrubber [1]

Samples	Odor Units Before Scrubbing	Odor Units After Scrubbing at	
		pH 9	pH 11
C_4 mixture	200	8	8
lobster shells	1,600	2	8
beef blood, bones	100	10	8

TABLE 7: Odor Reduction Using Virotrol Scrubber [1]

c. The Dustraxtor

High and Li Puma [33] have used the Zurn Air System Dustraxtor for the control of rendering plant and associated odors. The results reported are very subjective in nature because no descriptive diagram of the system has been presented. They used ten different chemicals in water as the absorbing liquid and reported that calcium hypochlorite at 0.2% Cl_2 concentration gave the best results. An air dilution method was used to prepare odor concentrations.

B. Oxidation

Complete combustion has been generally accepted as being the best method of deodorizing most foul smelling gases, although it is not always the most economical [8]. Many odorous gases are organic compounds and may be completely incinerated to odorless products such as carbon dioxide and water. Because of the energy crisis and fuel shortage, the economics of this technique are usually unattractive. However, some odorous materials themselves may be utilized as fuels. For complete combustion of odors, four conditions are essential [61]:

i. there must be sufficient oxygen
ii. there must be thorough mixing
iii. temperature must be high enough
iv. sufficient time must be allowed for the oxidation to be complete.

There are three combustion techniques in use. They are:

i. thermal oxidation (also called afterburning or direct-flame incineration)
ii. direct combustion (or flaring) and,
iii. catalytic oxidation.

The design methods for the combustion techniques are not as well established as those for scrubbing. None the less, the scientific principles that form the basis of their application are by no means recent. Each of the three combustion techniques is now discussed in detail.

1. Thermal Incineration

Thermal incineration takes place in a gas or oil-fired combustion chamber where the odorous gases are heated to their combustion temperature and thoroughly mixed for a sufficient time to ensure that the oxidation reaction goes to completion. Normal operating temperatures range from 1000 to 1600°F. Flame detention times are usually 0.3 seconds or longer. Figure 7 [8] is a simplified diagram of an incineration process. In thermal incineration the gas

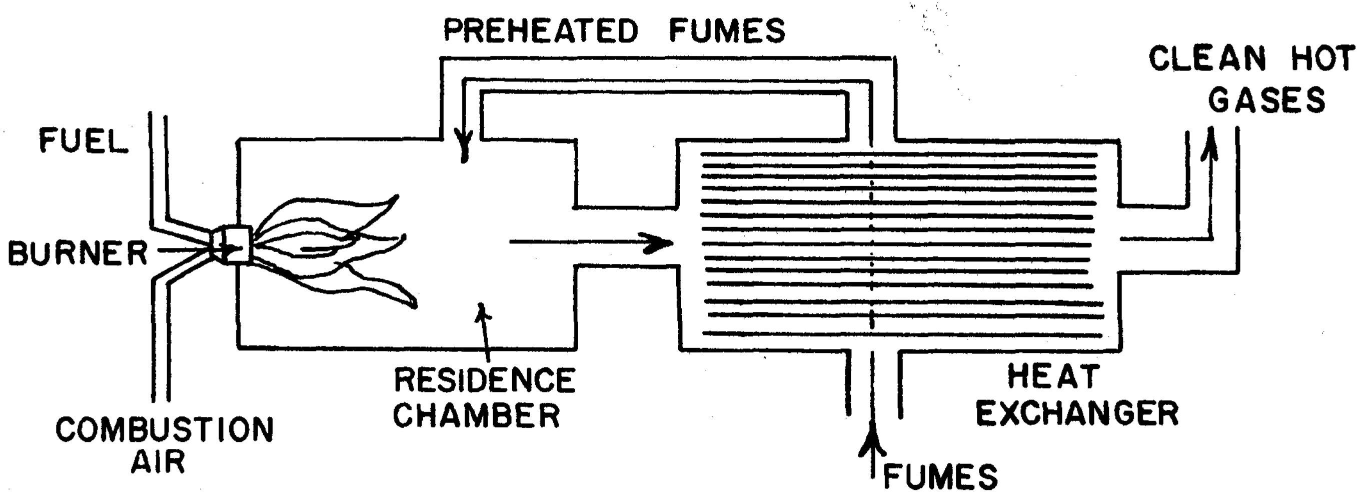

FIGURE 7: Thermal Incinerator with Heat Recovery [8]

stream is not actually passed through the burner. In many instances the gases are dilute; that is, the quantity of combustibles is very small and the heating value is very low - approximately 1 to 15 Btu/ft^3 compared to 100 Btu/ft^3 for direct-flame incinerators [8]. Examples of thermal incinerators are afterburners designed to eliminate odors from incomplete combustion processes. Heat recovery is usually employed to minimize fuel costs. Another method to conserve fuel and save money is to re-circulate odorous air streams into boiler furnaces. Care should be taken to prevent odor blowback and corrosion in the boiler tubes.

Thermal incineration has been applied to several odor producing processes. Table 8 [83] and Table 9 [84] illustrate results obtained utilizing thermal incineration in the Wire Enameling Industry. As can be seen from Table 8, four tests were made to determine the percent conversion of hydrocarbons at different combustion chamber temperatures. The strong odor from the wire enameling process was eliminated at temperatures of 1260 and 1300°F and was weak at 1100°F [83]. The hydrocarbon source was directly from the stack. Analysis was performed using the Beckman 109A hydrocarbon analyzer.

Test No.	Temperatures (°F)		Hydrocarbon (ppm)		%Conversion
	In	Out	In	Out	
1	400	900	1400	480	66
2	400	1100	1410	300	78
3	400	1260	1420	130	91
4	400	1300	1400	110	92
NOTE: 80-120 ppm Hydrocarbon in area surrounding oven.					

TABLE 8 : Wire Enameling Oven (Thermal Incineration) [83]

Test No.	Stream In	#1-Out Gas Fuel	#2-Out Oil Fuel	#3-Out Oil Fuel	#4 Cat. Unit
Temp. °F	660	1365	1365	1290	1094 (cat. preheat)
H/C (ppm)	1360	6	8	16	92
CO (ppm)	565	272	90-180	1050	450
% efficiency (H/C only)	-	99.6	99.4	98.8	93.2
% efficiency (L.A. Rule 66)*	-	99.6	99.4	63.0	93.2
O_2(%)	18.8	15.2	15.0	-	-
NO_2 (ppm)	-	4	5	-	-

* See Glossary for Definition

TABLE 9: Wire Enameling Oven Effluent [84]

The conversion substantially increased as the incineration outlet temperature was increased. Waid [84] reported the results reproduced in Table 9. Results for thermal incineration were compared to data from catalytic units to determine the comparative fuel economies, which are given in reference [84]. Hydrocarbon concentrations were determined as in reference [83]. Waid also reports that a 97% efficiency was obtained using thermal incineration on a paint drying oven effluent (Table 10). In this work, hydrocarbon concentrations were determined using the Beckman 109A hydrocarbon analyzer while carbon monoxide concentrations were determined using the Beckman 215A infrared CO analyzer. As can be seen in Table 10, the outlet temperature corresponds closely to those shown in Table 8. It is noted that since the

	IN	OUT
Temperature, °F	700°	1240°F
Hydrocarbons, ppm	750	9-22
Carbon Monoxide, ppm	25	25
Conversion of Hydrocarbons	97%	

TABLE 10: Paint Bake Oven Odor Removal [84]

carbon monoxide concentration did not increase, the hydrocarbons were being completely converted to carbon dioxide as a product and were not being partially oxidized to carbon monoxide.

Doty [17] and Sullivan [69] report results obtained in the rendering and food processing industries. Using the ASTM syringe dilution method to measure odor units/min, efficiencies of 50-99.99% are reported for afterburner temperatures of 1200°F [69]. Waid [83] also lists operational parameters for thermal incinerators of the "short flame line type combustifume burner" and "tunnel-type burner" designs. Temperatures for 90% removal of hydrocarbons were 1050-1250°F and 1200-1350°F respectively while residence times were 0.3-0.8 seconds and 0.5-1.0 seconds respectively.

2. Direct Combustion or Incineration

Direct combustion incinerators are used when the fumes are combustible (high organic content) and need little or not additional air for combustion. This is the least costly form of incineration because the contaminant is used as the fuel. Waste stream fumes should have at least 100 Btu/ft^3 heating value for incineration to be applicable. The fume to air ratio must lie between the lower and upper flammable limits.

Figure 8 is a diagram of a typical direct-flame incinerator.

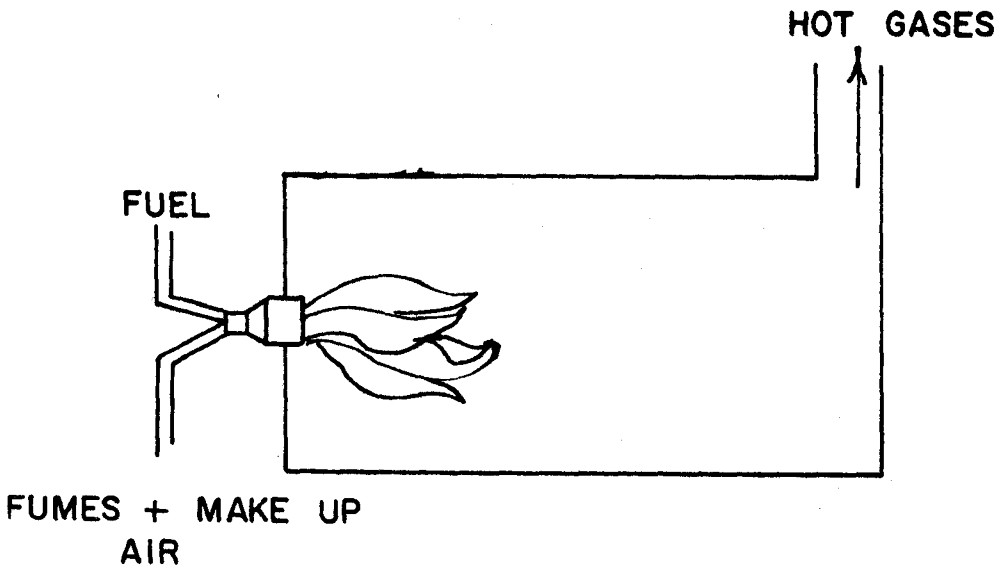

FIGURE 8 : Direct Flame Incinerator

Hopton and Laughlin [36] reported efficiencies from various industries for the direct-flame incinerator. Table 11 shows that efficiencies vary greatly from negative values to as high as 98%. Odor concentrations as reported in odor units/scf were based on the syringe dilution method. Incinerator temperatures varied from 1000°F to 1500°F. Hopton and Laughlin also reported percentage reductions for a variety of contaminants emitted from paint bake ovens. As can be seen in Table 12 the odor reduction

Application	Average Odor Concentration (Odor Units/scf)		Exhaust Gas Flow (scfm)	Incinerator Temperature (°F)	% Reduction
	Inlet	Outlet			
Wire Enameling	1300	2100	-	1000	-61
Oven portable unit	2500	350	-	1200	86
Field Test	1300	70	-	1400	97
Glass Fiber	550	625	14,000	1009	-14
Curing Oven	255	25	14,000	1352	90
Field	380	53	14,000	1250	86
Abrasive Wheel	800	10	-	1200	98
Curing Oven (Lab. Test)	1600	32	-	1400	98
Test #1					
Auto. Paint	260	14	-	1350	95
Bake Oven	170	10	-	1450	94
Test #2	650	10	-	1350	98
	680	18	-	1450	97
Hard Board Curing	1000	40	-	1400	96
Oven Lab Test	1400	15	-	1500	98

TABLE 11: Control of Odors by Direct Flame Incineration [36]

Type of Coating Applied	Class of Solvent Used (Aromatics Plus)	Afterburner Temperature (°F)	Reduction Obtained (%)			
			Odor	Particulates	Combustibles	Aldehydes
Vinyl	Ketones	1100	15	58	-	(1.3X)*
		1200	40	70	-	18
		1400	98.8	87	-	57
Enamel	Mineral Spirits	1100	(2.5X)*	(1.2X)*	-	(1.6X)*
		1200	42	1.5	-	(1.1X)*
		1400	99.2	74	-	81
Vinyl #53	Ketones	1100	0	-	(1.2X)*	-
		1200	90	-	1.5	-
		1300	86	-	34	-
		1400	98.3	-	95	-
Varnish #127	Aliphatics Mineral Spirits	1100	-	-	29	-
		1200	-	-	38	-
		1300	-	-	39	-
		1400	-	-	69	-
Varnish (alkyd resin)	Alcohols Aromatics Aliphatics	1100	(1.7X)*	-	41	-
		1200	40	-	48	-
		1300	98.3	-	75	-
		1400	98.6	-	95	-
Varnish (alkyd amine)	Mineral Spirits Aromatics	1200	-	-	60	-
		1300	-	-	79	-
		1400	-	-	92	-

*Increase in odor strength (multiply inlet concentration by this amount)

TABLE 12: Direct-Flame Afterburner for Paint Bake Oven [36]

(reported in per cent) generally increased as the afterburner temperature was increased from 1100°F to 1400°F. The removal of combustible gases also increased as the temperature was increased. It is interesting to note that some concentrations increased rather than decreased. At higher temperatures, however, a reduction was noted. Concentrations of the various parameters measured were determined using a variety of techniques. Odor concentrations were determined by the Los Angeles County Air Pollution Control District's Standard Method*. The details of the method are not provided. Particulate matter, combustible gases and aldehydes were determined by the APCD Source Test Method, the CCIR Method, and the APCD 5-46 method respectively [36].

3. Catalytic Oxidation

A flow schematic for a catalytic oxidizer is shown in Figure 9. Reaction does not take place in the presence of the flame, however a flame is used to preheat the fumes. The oxidation reaction takes place directly upon the surface of the catalyst, which is normally composed of

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* See Glossary for definition

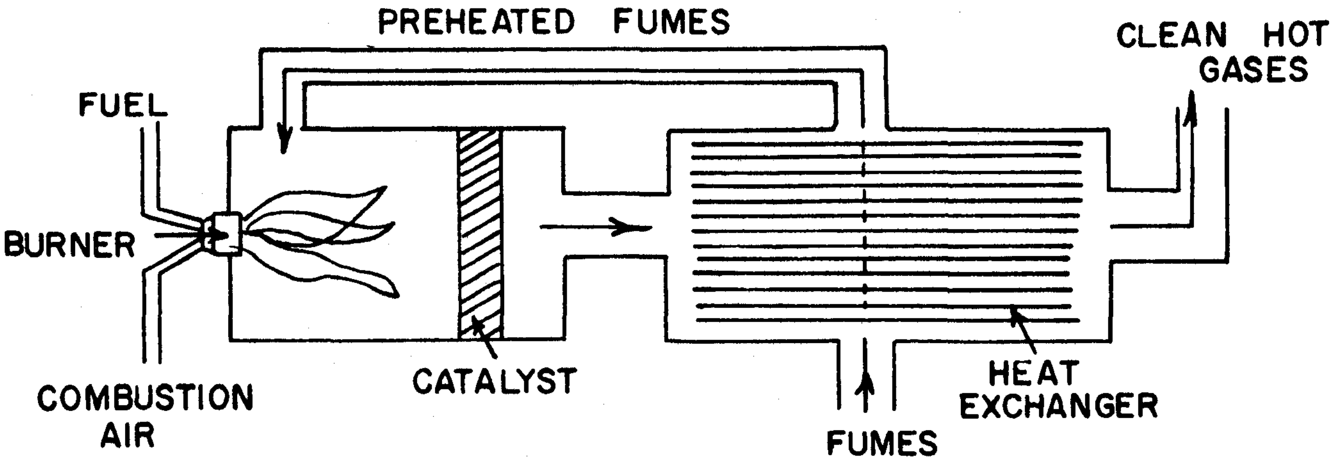

FIGURE 9: Catalytic Oxidizer with Heat Recovery

precious metals such as platinum or palladium. The waste gas must be preheated before this contact with the catalyst. The temperature upstream of the catalyst is characteristically 600-900°F and 800-1000°F downstream. The increase across the catalyst is due to the exothermic catalytic oxidation reactions.

Waste streams containing elements or metals damaging to catalyst activity must be avoided. These species include mercury, lead, tin, zinc, fluoride, chloride and bromide. Dust, soot, mud, or rust may also cause loss of activity, but this can usually be reversed by simple washing of the catalyst [36].

Basic design requirements are the same for catalytic and thermal systems. One must provide

i. thorough mixing of combustibles with air
ii. enough heat input to raise the temperature of the gas stream to the required level
iii. proper flow distribution, and
iv. sufficient residence time for the odorous gases to oxidize completely.

Catalytic combustion is often used to destory odors from diesel exhausts, nitric acid plant tail gases, paint solvents, chemical manufacture, food processing, coating ovens, and coke oven emissions [36, 61].

Actual operating data on the use of catalytic oxidizers are usually lacking in current literature. Doty [17] presents a "print-out" of a computer program which shows design and cost estimates for odor removal in the rendering industry at a variety of reduction ratios and flow rates. The temperature of oxidation is 800°F, but no actual operating results are quoted. Cheremisinoff [8] gives a limited amount of actual operating data, although the analytical methods used are not mentioned. Brown and Taylor [7] report organic concentration reductions of 60-80% using a rhodium on alumina catalyst in experiments performed at Ford's Windsor Foundry. The concentration of organics was determined using a gas chromatograph with flame ionization detector. The chromatograph was calibrated in the laboratory using natural gas in air, therefore, results reported are in terms of parts per million of methane required to give the same peak height. Table 13 shows the results obtained.

Temperature and Flow Rate	Inlet Concentration (ppm)	Outlet Concentration (ppm)	% Organics Removed
700°C, 17 cfh	1900	750	60
620°C, 17 cfh	3000	1000	67
620°C, 24 cfh	3800	1300	66
800°C, 3 cfh	2100	350	83

TABLE 13: Catalytic Oxidation of Cupola Emissions [7]

The 'Cataban Process' achieves hydrogen sulphide removal by liquid phase catalytic oxidation to elemental sulphur in the presence of air or oxygen [56]. A fine crystalline suspension is formed and easily removed from the catalyst solution by mechanical means. Cataban, the catalytic agent, is 2-4% ferric iron in chelated form. It is stable in the pH range of 1.0 - 11.0 at temperatures ranging from "room" to 260°F. Removal efficiencies of up to 100% are reported by Meuly [56]. Typical temperatures are 25-80°C for upwards of 99.6% removal at a pH of 7.8 and residence time of 4 seconds.

C. Adsorption

Activated carbon or charcoal is the most widely used substance for odor abatement of organic gases and vapors. It is most effective for gases with molecular weights over 45 or vapors with boiling points above 32°F. In general, if inlet air temperatures exceed 150°F, then cooling should be considered to enhance adsorption. As the retentive capacity of the carbon is reached, traces of the vapors are found in the exit stream. This is called the breakthrough point.

For an odor source containing many chemicals, most of the exit vapors at the breakthrough are from the more volatile chemicals since the higher boiling constituents replace them in the carbon bed [36].

When carbon is being reactivated, hot air can be used to carry the pollutants to an incinerator. A vacuum is used if there is a recovery system. If neither of these are used, regeneration is accomplished thermally by steam stripping. It usually requires about 5-10 lbs of steam to remove 1 lb of solvent from a carbon bed [36].

There are many types of beds used for adsorption. These include the fixed bed, rotating fixed bed, fluidized bed and others.

Experimental and operational results have been reported by many workers. Faulkner, Schuliger and Urbanic [22] report benzene removal for 23 hours with less than 0.008 ppm. breakthrough. After two additional hours, however, the breakthrough was 0.1 ppm. The bed depth was six inches with an air flow rate of 7700 bed volumes/hr and the inlet concentration of benzene was 150 ± 10 ppm. Urbanic and Lovett [79] did extensive research using activated carbon for the control of paint bake oven emissions. They found that in excess of 90% of all organics of C_3 or greater are removed from the oven exhaust. For these tests, gas chromatographic procedures were used for analysis. The space velocity was about 20,000 hr^{-1} at a temperature of 100°F.

As a rule of thumb, when contact time is doubled, the loss (100 minus efficiency) through the carbon bed is cut to 1/10. That is, if a charcoal bed is 2 feet thick, with a velocity of 50 ft/min and with initial efficiency of 99% and contact time of 2.4 sec, doubling the contact time to 4.8 sec (either by doubling the bed depth or halving the velocity) would reduce the loss from 1% to 1/10 of 1% making the efficiency 99.9% instead of 99.0 [2].

Adsorbents such as potassium permanganate and permanganated alumina have also been tried for odor control. Hopton [37] reports efficiencies of more than 99.5% for hydrogen sulphide from an effluent gas stream at a Union Carbide plant, using sawdust filters impregnated with potassium permangante. Before treatment, the effluent stream contained an average of 100 ppm of both H_2S and CS_2. It was passed through a 2.5 inch deep filter at a flow rate of 10.5 cfm producing a pressure drop of 10 inches of water across the filter. Analyses were performed using wet chemical methods (absorption in alkaline cadium sulphate solution and a standard colorimetric method) and by gas chromatography. Natusch [57] also did some work using activated manganese dioxide impregnated in sawdust. For the removal of H_2S, the efficiency and capacity of $Mn0_2$/sawdust is superior to that of activated carbon. For an inlet H_2S concentration of 80 ppm, the $Mn0_2$/Sawdust will adsorb 0.075 gm/gm as opposed to 0.00425 gm/gm for the activated carbon.

Although the MnO_2/sawdust adsorber is readily prepared, it is not commercially available and must be discarded after use. Also, if MnO_2/sawdust is allowed to dry, ignition will occur at 100°C [57]. Turk et al [76] compared activated carbon and permanganated alumina with regard to their effectiveness in reducing odor levels of air streams containing olefin, ester, aldehyde, ketone, amine, sulphide, mercaptan, decomposed crustacean shell vapor and stale tobacco vapor. In all cases, the odor-reducing effect of the activated carbon was much better than that of the permanganated alumina.

D. Dispersion and Dilution

Dilution or dispersion of an odor, through an elevated source such as a stack, will obviously result in odor-free air as the odorant concentration is reduced below the olfactory threshold level [61]. Dilution may be achieved by

i. increasing the height of the vent or stack through which the odorant is discharged

ii. increasing the velocity of the gas, which is actually equivalent to increasing the "effective height" of the stack

iii. increasing the temperature of the gases so as to make them more buoyant.

Dilution is not a truly reliable technique because unusual weather conditions may cause difficulties or a perceptive individual may detect an odor below the median threshold level. There may also be a "synergistic" effect between constituents in the effluent stream which may result in a lower odor threshold than those of the component substances.

Wohlers [89] used Sutton's Equation to estimate the dilution of original effluent with air as shown in Table 14. Sutton's equation is as follows:

$$C = \frac{2M}{\pi C_y C_z U X^{(2-n)} \exp[h^2/-C_z^2 X^{(2-n)}]} \qquad (1)$$

where

C = dimensionless unit representing the dilution of the original effluent with air

X = distance downwind from the stack, meters

h = height of the stack, meters

U = wind velocity, m/sec

M = volumetric gas exhaust rate, m^3/sec

C_y = horizontal diffusion coefficient, $m^{n/2}$

C_z = vertical diffusion coefficient, $m^{n/2}$

n = a pure number (stability parameter)

	Dilution Ratios [equal to 1/C, equation (1)]			
Distance From Stack (feet)	Petroleum Coking Operation	Kraft Paper Mill	Onion and Garlic Dehydration Plant	Rotogravure Press Plant
328	90,000	1,900	72	142
656	1,900	990	25	483
1,312	1,400	1,980	83	1,600
2,624	2,900	6,000	300	5,400
5,248	8,600	28,000	1,500	18,300
10,496	28,000	76,000	4,000	62,000
20,992	89,000	244,000	13,000	204,000
41,984	310,000	840,000	45,000	700,000
83,968	1,020,000	2,850,000	154,000	2,300,000
167,936	3,310,000	9,400,000	530,000	7,500,000
335,872	11,200,000	35,500,000	1,900,000	25,300,000

Values of the Parameters Used in Equation (1)

C_y	0.3	0.44	0.46	0.4
n	0.25	0.20	0.20	0.25
M(cfm)	10^5	80,000	10^6	21,000
C_z	0.3	0.34	0.33	0.2
U(mph)	15	12	8	8
h(ft)	150	115	0	0

TABLE 14: Dilution Estimates of Original Effluent with Air [89]

The odor measurements at the stacks* did not agree with the calculated dilutions at the distances in the field where the odors were noted. Data for the kraft mill, onion-garlic dehydration and the rotogravure operation showed a wide variance between the measured and calculated odor threshold values, whereas the petroleum coking plant data were in good agreement. Odor intensity or odor threshold measurements were made with a Fair-Wells Osmoscope**. This piece of equipment assumes the validity of the Weber-Fechner law which states that equal differences in sensation are produced by constant fractional increments in stimulus. The threshold differences are usually logarithmic differences or ratios. The accuracy of the osmoscope is questionable as it is possible to make a maximum error of 100%. Comparison of reported threshold values showed errors of ± 25%. Also, the Sutton Equation is only as good as the constants used in the calculations.

Hardison and Steenberg [30] give typical dilution ratios for the worst conditions with respect to ground level location, wind speed and turbulence level. These are presented in Table 15. These ratios were calculated using the

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* Gas Samples for odor intensity were taken from the exhaust stacks

**Fisher Scientific Company, Pittsburgh, Pa.

Bosenquet-Pearson method and the Carey-Halton plume rise formula with ambient discharge temperatures. Better dispersion is attained if the gas is discharged at higher temperatures.

Stack Height (feet)	Gas Flow (cfm)			
	5,000	20,000	50,000	200,000
20	1,386.5	569.1	315.9	129.6
50	4,501.7	1,847.4	1,025.4	420.8
100	10,969.8	4,501.7	2,498.6	1,025.4
200	26,731.4	10,969.8	6,088.6	2,498.6
400	65,139.6	26,731.4	14,837.0	6,088.6
600	109,679.0	45,008.9	24,981.7	10,251.8

TABLE 15: Dilution Ratios at Critical Conditions (For Discharge of Air at Ambient Temperatures) [30]

Turk [73] also reports results obtained using dispersal methods. Large discrepancies were found when odor travel was compared from four different plants with calculations of stack-gas dilutions using Sutton's equation. One extreme example cited was of the odor from a kraft-paper mill. The average dilution required to threshold was 32:1 while the maximum was 64:1. The minimum calculated dilution of stack effluent was 990:1, predicting that no odors should be detected. Actual field surveys over a six month period showed that the odor could be detected at distances of even eight miles, where the calculated dilution would be 840,000:1. Also, occasional reports of the odor were received from a distance of forty miles!

From the above it can be seen that dilution or dispersion is not a reliable method of controlling odor. Furthermore, not a single report appears in the literature in which outdoor travel from a specified source is successfully predicted using presently available theoretical equations.

E. Process Changes and Production Modifications

These abatement methods are too often overlooked, yet they should be among the first considered. Chemical processes are so diverse that it is difficult to suggest specific remedies. Quite often, however, re-use or recycling of emissions, substitution of odorless solvents or reactants for odorous ones, better equipment maintenance and adjustment of process temperatures, residence times, or other conditions can significantly reduce or completely eliminate odor production. Sometimes even slight process changes minimize odor generation and are more effective and more economical than existing control equipment [61].

IV. RELATIVE ECONOMICS OF ODOR CONTROL METHODS

In literature, the cost data are presented in many different ways, depending on the author and the industrial application studied. In addition, the data cited apply for a variety of operating conditions. The available information is classified in Table 16 according to the industry type.

A. Distilling

First et al [24] and Horlander [38] present data accumulated while removing odor from a distillery spent grain drying operation using the reactor-absorber previously discussed in Section III.A.5. While obtaining efficiencies of odor removal as high as 96%, operating costs were $30,500 per year based on around the clock operation and a capacity of 28,000 cfm at 200°F. These costs included that of water, chemicals and electricity. Horlander [38] also estimates that an incinerator would have cost $295,000 per year to achieve the same results at 1600°F (gas cost at 40¢ per thousand cubic feet).

B. Corn Processing

Sohr and Co-workers [65] investigated odor control in the corn processing industry. It was found that chemical

Section	Industry	Control Method(s) Reported	Author and Reference
A	Distilling	Reactor-Absorber	First et al [24] Horlander [38]
B	Corn Processing	Chemical Scrubbing, Incineration	Sohr [65]
C	Removal of H_2S	Permanganate Impregnated Sawdust	Hopton [37]
D	Pulp and Paper	1. Recovery Furnace, Liquid Scrubbing, Solid Adsorption, Black Liquor Oxidation	Cooper [10]
		2. Turbulent Contact Absorber	Bhatia et al [4]
E	General	1. Catalytic Oxidation Direct Flame Oxidation	Hein [31]
		2. Adsorption, Thermal Oxidation, Catalytic Oxidation, Absorption, Condensation	Cross et al [12]
F	Rendering (Theoretical Models)	Two-stage Horizontal Scrubber, Countercurrent Packed Tower Scrubber, Direct-fired Incinerator, Catalytic Bed Afterburner, Carbon Bed Adsorption	Doty et al [17] Hopton and Laughlin [36]

TABLE 16 : Literature on Cost of Odor Control Methods

absorption using potassium permanganate in a packed bed scrubber gave good results when operated in an acidic medium. Three plant operations were investigated: fiber drying, gluten drying and germ drying. Table 17 shows Sohr's results. Operating costs include chemicals, power and average maintenance expenses. The chemical absorption costs were derived from actual installation economics. A comparison with incineration is made. Incineration costs were derived from vendor material, technical seminars, actual proposals and actual installations. Also, for incineration, fuel was figured at a cost of $0.75/1000 scf and power was computed at $0.0089/hp/hour. Because the data presented for incineration are theoretical, no actual removal efficiencies or odor reductions are reported. Therefore, it is difficult to establish if incineration could provide the removal efficiencies obtained via absorption. Based on the work of Sohr and co-workers however, it appears that scrubbing is the most economical method of odor control in this application.

C. Removal of H_2S

Hopton [37] reported results obtained using permanganate impregnated sawdust for odor control. He compared the economics of the above method and incineration for the removal of

	Chemical Absorption	Incineration		
		Direct	In/Heat Recovery	With Heat Recycle
Fiber				
Installed Equipment Cost per cfm	2.34	6.43	8.54	10.81
Operating Cost, dollar per hr per 1000 cfm	0.31	2.02	1.12	0.56
% Odor Removal	93-97	-	-	-
Gluten				
Installed Equipment Cost per cfm	2.04	6.43	8.54	10.32
Operating Cost, dollar per hr per 1000 cfm	0.24	1.84	0.97	0.45
% Odor Removal	95	-	-	-
Germ				
Installed Equipment Cost per cfm	2.18	6.43	8.54	10.32
Operating Cost, dollar per hr per 1000 cfm	0.26	1.97	1.03	0.48
% Odor Removal	99	-	-	-

TABLE 17: Capital Investment and Operating Costs for Corn Processing Industry [65]

hydrogen sulfide. A preliminary cost estimate of \$100,000 per year is given. This includes installation, operational and maintenance costs but does not include disposal of spent filters. Approximately 80% of this cost is attributed to the annual permanganate requirements. Incineration was estimated to cost \$250,000/year for comparable results (99% removal of H_2S), of which \$230,000 is estimated for fuel. No unit costs were given and the type of incineration process was not stipulated.

D. Pulp and Paper

Cooper [10] presents data for odor control in the pulp and paper industry. The basis for his investigation was the reduction of total reduced sulphur (TRS) for a 500 tons per day Kraft Recovery Furnace. Table 18 summarizes the results presented. The cost effectiveness was defined by Cooper as "the amount of reduced sulphur prevented from being emitted to the atmosphere per unit amount of total expenditure", ie.

$$\text{Cost eff} = \frac{\text{Benefit}}{\text{Cost}} = \frac{\text{lb TRS Prevented}}{\text{\$ Expenditure}} = \frac{\text{lb TRS/TP Prevented}}{\text{\$/TP Expended}}$$

where

TP = Ton of pulp

TRS = Total reduced sulphur

Category	Item	Unit	Indirect Contact Evaporator		Stack Gas Controls		Black Liquor Oxidation	
			New Furnace	Existing Retrofit	Liquid Scrubbing	Solid Adsorption	SBLO-Air[1]	WSBLO-MO[2]
Economics	Capital Cost	($)	7,500,000	2,700,000	2,900,000	680,000	400,000	30,000
	Total Cost	($/Year)	835,000	307,000	450,000	184,800	74,000	93,300
	Unit Cost	($/TP)[3]	4.64	1.71	2.5	1.02	0.41	0.52
Emissions	Amount Exhausted	(lbs/TP)[4]	0.04	0.17	0.26	0.51	0.13	0.21
	Amount Prevented	(lbs/TP)	10.61	10.43	10.39	10.14	10.52	10.44
Cost Effectiveness			2.30	6.10	4.15	9.95	25.70	20.00

1. Strong Black Liquor Oxidation Using Air
2. Weak and Strong Black Liquor Oxidation Using Oxygen
3. (TP) = Tons Pulp Produced
4. (lbs/TP) = Pounds Sulphur per Tons Pulp Produced

TABLE 18: Cost Effectiveness of Alternative Total Reduced Sulfur Odor Control Measures for a Southeastern U.S. 500 TPD Kraft Recovery Furnace [10]

From a cost effectiveness point of view, Cooper's results indicate that black liquor oxidation is the most economical method of control.

Bhatia et al [4] have developed a new scrubbing technique for the removal of TRS from Kraft recovery flue gases. This method utilizes an alkaline suspension of activated carbon and is called a Turbulent Contact Absorber (TCA). It is reported that a removal of TRS of greater than 85% is achieved at an operating cost of $0.40 to $1.70/ton of pulp produced. Because of the reasonable capital investment required ($700,000 to $1,500,000), the TCA scrubbing process would be an attractive alternative to the installation of a new recovery furnace [4].

E. General

Hein [31] compares catalytic and direct-flame oxidation for general odor removal. Table 19 summarizes the operating costs of these two methods. These data clearly show that a substantial decrease in the cost is attainable with heat recovery. Also, by concentrating the odorant to 1/4-th of its lower explosion limit, a lower operating cost may be realized.

Heat Recovery Provided	Calorific Value of the Gas	Operating Cost, dollars per hour per 1000 cfm	
		Catalytic	Direct-Flame
None	Nil	0.72	1.21
None	1/4 LEL*	0.24	0.73
1/2 of Input	Nil	0.52	0.79
1/2 of Input	1/4 LEL	0.05	0.33

*LEL - lower explosion limit

TABLE 19: Estimated Operating Costs for Incineration [31]

According to the estimates presented by Hein, catalytic oxidation appears to be much more economical than direct-flame incineration.

Cross et al [12] have discussed various odor control techniques. It is stated that "there is no payout on equipment installed to control odor emissions. The operating cost exceeds the recovery value of the pollutants". Cross et al also point out that any discussion of air pollution economics should include the cost of:

i. equipment from the manufacturer

ii. installation of equipment, pumps, foundations, etc.

iii. operation

iv. maintenance .

Cross has presented a table of "generalized" odor control costs. Five of these are quoted in Table 20. No mention is made of odor removal efficiency, unit costs (power, fuel, etc), type of catalyst or any other operational variables. However, it is clear that Cross believes that absorption is the most economical method of control from both installed cost and operation cost point of view.

Control Process	Installed Cost ($/scfm)	Operation and Maintenance ($ (hr) (scfm)	Total Cost $/(year) (scfm)
Adsorption	4-10	3-4.5	3.5-5.8
Thermal Incineration	9-11	1.8-2	3-3.5
Catalytic Oxidation	8-10	1-3.5	3-4.8
Absorption	1.7-2.0	0.35-0.5	0.55-0.75
Condensation	4-9	0.25-1	0.80-2.3

TABLE 20 : Generalized Costs for Odor Pollution Control [12]

F. Rendering

Doty et al [17] compared potential and known odor control methods for rendering plants based on available literature data and the reports of performance and costs from member companies in the Fats and Protein Research Foundation. Their study indicated that the commercially available control equipment was not designed on a reliable basis, partly because of the lack of quantitative data on specific odorous constituents of rendering plant emissions.

Although the experimental work concentrated on scrubbers, the design analysis was extended to several types of incinerators, scrubbers and carbon beds. A computer design program was written for each control method (except carbon beds). This program can be used for preliminary estimates of the cost of each method for the particular conditions of any rendering plant. The design basis for the computer program is considered more closely below.

1. Countercurrent Packed Tower Scrubber

The design procedure for countercurrent packed scrubbers is based on the following:

i. reagents react rapidly with the odorants once they reach the liquid phase

ii. rate of removal is controlled by mass transfer from the gas to the liquid.

The design equation used is based on the assumption of a fast reaction in the liquid phase. It has the form

$$Z = \frac{G_M}{k_g a P_T} \ln \frac{Y_o}{Y_e} \qquad (2)$$

where

a = wetted surface area of the packing, ft^2/ft^3

Z = height of tower, ft

G_M = molar flux, lb-mole/(hr ft^2)

k_g = gas phase mass transfer coefficient, lb-mole/(atm hr ft^2)

P_t = total pressure, atm

Y_o = mole fraction of pollutant in the gas phase at the inlet

Y_e = mole fraction of pollutant in the gas phase at the exit

The gas phase mass transfer coefficient for particle packings such as rings and saddles is calculated from the following empirical equation [71]:

$$\frac{G_M}{k_g\ aP_T} = \frac{0.837}{a} \left[\frac{d_s G}{\mu_G(1-\varepsilon_o)}\right]^{0.36} Sc^{2/3} \qquad (3)$$

where

d_s = diameter of a sphere of the same surface as a single packing, ft

G = mass flux, lb/(hr ft^2)

μ_G = gas viscosity, lb/(ft)(hr)

ε_o = porosity of wetted packing

Sc = Schmidt number = $\dfrac{\text{viscosity (lb/(ft hr)}}{\text{density (lb/ft}^3\text{) diffusivity (ft}^2\text{/hr)}}$

The cost data have been entered in the form of equations based on published correlations for installed costs of equipment, unit costs for power, fuel and maintenance, amortization and operating costs. To use the program, the user specifies the air flow capacity, the desired odor removal, and the unit cost of items such as electricity. The program performs a series of design calculations to find the optimum liquid flow rate and column diameter.

An example of typical computer results is those obtained for pentanal (valeraldehyde). These are given in

Table 21. Odor is controlled by using two scrubbers in series. These calculations are based on the assumption that two scrubbing liquids can be found that will, between them, remove all important odors. It was found economical to use the maximum gas rate that the column can handle without flooding and the maximum liquid recirculation rate for which experimental correlations are available. Doty et al [17] state that at these conditions, the cost of scrubbing is less than the cost of incineration. However when the odorant concentration gets as high as 1000 ppm, the chemical cost for removal gets too high and incineration then looks better.

2. Two Stage Horizontal Spray Scrubber

A new type of spray scrubber, which was designed by the Air Conditioning Corporation, Greensboro, North Carolina, has been installed in a number of rendering plants and found to give satisfactory odor reduction. Table 22 presents results of calculations done with the computer design program. These data are for a two-stage unit.

The success of this scrubber depends on the use of low air velocities so that the droplets (size approximately 400μm) remain in the scrubber for a second. Each drop is assumed to act independently of others in the design procedure used.

Flow (CFM)	Odor Reduction Ratio	Flow Rates (lb/hr sq ft)		Packing Depth (ft)	Tower Diameter (ft)	Pressure Drop (in-H_2O)	Costs			
		Liquid	Gas				Investment ($)	Chemicals ($/Year)	Total Operating ($/Year)	$/1000 CFM hr
1,000	100	569	7500	5.2	3.2	0.46	8,200	7	2,370	0.49
	1,000	570	7500	7.8	3.2	0.69	12,180	72	3,450	0.69
	100,000	570	7500	12.9	3.2	1.15	20,120	7,200	12,600	2.50
5,000	100	570	7500	5.1	7.1	0.49	22,600	35	7,200	0.29
	1,000	570	7500	7.7	7.1	0.74	33,600	350	10,400	0.41
	100,000	571	7500	12.8	7.1	1.23	55,600	35,000	50,000	2.00
25,000	100	571	7500	5.1	15.8	0.49	67,400	175	24,800	0.19
	1,000	571	7500	7.7	15.8	0.74	99,800	1,750	35,200	0.28
	100,000	571	7500	12.8	15.8	1.23	164,680	175,000	225,000	1.80

TABLE 21: Cost Summary for Two Packed Scrubbers in Series.

Odor Reduction (Inlet/Outlet)	Scrubber Height (ft)	Flow Rates		Power Required		Annual Costs ($)		Unit Cost $/(1000 cfm)(hr)
		Gas (cfm)	Liquid (gpm)	Fan (hp)	Pump (hp)	Chemicals[1]	Total[2]	
1000/1	3.8	25,000	607.3	16.8	198.8	700	20,919	0.17
1000/1	5.8	38,000	923.1	25.6	303.4	1064	31,332	0.16
1000/1	10.0	66,000	1603.3	44.4	531.9	1848	53,589	0.16
1000/1	15.2	100,000	2429.3	67.3	815.0	2800	80,568	0.16
1000/1	22.8	150,000	3644.0	100.9	1242.5	4200	120,453	0.16
100/1	17.4	150,000	2780.9	100.9	937.4	4200	99,867	0.13
10/1	10.9	150,000	1751.8	100.9	582.4	4200	75,532	0.10

Length of scrubber is 29 ft, based on 5500 hrs per year of operation

1. Chemical cost based on effluent concentration 0.01 ppm by volume. Typical chemical cost based on reaction by NaOH at 20¢/lb

2. Includes amortization costs, power costs, maintenance costs, and quoted chemical costs.

TABLE 22: Design and Cost Summary for a Two Stage Horizontal Spray Scrubber [17]

The design equation used is the same as that for a packed scrubbing tower. The mass transfer coefficient, however, is predicted from penetration theory based on the transient diffusion of the odorant through the gas layer adjacent to each drop according to

$$k_g = \frac{2}{RT}\sqrt{\frac{\mathcal{D}}{\pi\theta_c}}$$

where

k_g = mass transfer coefficient, $\frac{\text{lb-mole}}{(\text{hr})(\text{ft}^2)(\text{atm})}$

T = temperature of the gas stream, °R

$\mathcal{D}$ = diffusivity of odorant vapor in air, ft^2/hr

θ_c = contact time of drops in scrubber, hr

R = gas constant, 0.730 $(\text{ft}^3)(\text{atm})/(\text{lb-mole})(°\text{R})$

3. Direct-Fired Incineration

A design procedure for incineration by direct-flame has been developed [17]. The rate is assumed to be governed by an overall combustion reaction, the rate constants for which are determined on an elementary reaction assumption. The program is able to explore and optimize the operating conditions to find the design having minimum annual cost. Cost data are supplied to the program as input parameters with amortization and operating costs included.

The combustion reaction is considered to be first-order with respect to both the pollutant and oxygen. For first-order kinetics and a constant volume reactor

$$k = \frac{\ln\left(\frac{C_o}{C_e}\right)}{t_R} \qquad (5)$$

where

k = reaction rate constant, $\sec^{-1}$

C_o = concentration of odorant at inlet, moles/litre (or consistent units)

C_e = concentration of odorant in effluent, moles/litre

t_R = residence time of the pollutant, sec

The constants A and ΔE in the Arrhenius equation for k were provided by a rendering company. Thus reaction rates could be evaluated from

$$k = A \exp\left[-\Delta E/RT\right] \qquad (6)$$

where

ΔE = 9560 cal/gm mole

A = 1900 $\sec^{-1}$

k = reaction rate constant, $\sec^{-1}$

R = 1.987 cal/gm mole °K

T = temperature, °K

The two independent variables in the incinerator design, reactor volume and mean gas temperature, determine the extent of oxidation of pollutants. A separate design calculation was done for each of several reactor volumes and the design having minimum cost was picked. For each chosen reactor volume, there is a temperature which will give the desired reduction of odorant concentration. This temperature is determined by substituting the desired reduction ratio and the contact time corresponding to the reactor volume into the Arrhenius equation which gives the effect of temperature on the reaction rate. The calculation for the heat requirement is done in two parts: a flame calculation and a heat balance on the mixing process. The reactor volume is based on the actual flow rate and the assumed residence time.

The installed cost is expressed in terms of volume and is estimated from correlations of data found in the literature. Fuel, fan power and maintenance costs are all included in the operating cost. Table 23 summarizes the results obtained using this program for various flows and reactor temperatures.

4. Catalytic Bed Afterburner

Because of the relatively high operating temperatures used in the direct-flame incinerator, the use of a catalyst to reduce the energy requirements offers a potential advantage. As much as 90% of the operating cost of the

Flow (cfm)	Reduction Ratio Odor Concentration	Temp. (°F)	Residence Time, (sec)	Volume (cu ft)	Investment ($)	($/Year)	Total Operating ($/Year)	Total Operating Costs, $ per hour per 1000* cfm
1,000	100	1069	0.7	33	12,500	3,150	6,400	1.28
	1,000	1186	0.7	36	13,000	3,570	6,950	1.39
	100,000	1236	1.0	52	15,200	3,753	7,703	1.55
5,000	100	1069	0.7	164	24,500	15,700	22,540	0.90
	1,000	1082	1.0	237	28,500	16,000	23,800	0.95
	100,000	1111	1.5	362	34,000	16,500	25,700	1.03
25,000	100	1069	0.7	885	49,500	87,000	103,000	0.83
	1,000	1082	1.0	1276	57,600	88,500	106,500	0.85
	100,000	1111	1.5	1952	68,800	91,300	112,300	0.90

TABLE 23: Direct-Fired Incinerator Cost Summary

* Based on 5,000 hours operation per year

direct-flame incinerator is made up of fuel costs.

Catalysts cause a faster rate of reaction which allows incineration to occur at lower temperatures. The rate of a catalytic reaction depends in part on diffusion through the pores. For certain types of catalysts pore diffusion can be neglected. In Doty's program, the controlling factor is assumed to be the mass transfer to the gross surface of the catalyst. According to Doty et al [17], it is necessary to preheat the raw plant effluents to approximately 800°F before they are treated by the catalytic unit. Design of the preheater by the computer program is the same as for the direct-fired incinerator, as a direct-flame preheater was assumed.

Mass transfer characteristics are given only for a reactor using a honeycomb type of catalyst support with flow in the longitudinal direction. This catalyst may be obtained in 1 ft^2 units of short length and may be stacked. The mass transfer equation used, with mass transfer controlling, is

$$\ln \left(\frac{Y_o}{Y_e}\right) = \frac{k_g a}{G_M} P_T Z \qquad (7)$$

where

Y_o = mole fraction of odorant entering catalyst bed

Y_e = mole fraction of odorant in effluent air stream

k_g = mass transfer coefficient, lb moles/(hr ft^2 atm)

a = external surface area of the catalyst, ft^2/ft^3

G_M = molar flux, lb moles/(hr ft^2)

P_T = total pressure, atm

Z = length of the reactor, ft

Flow through the honeycomb passages can be treated like flow in a pipe. For $4{,}000 < Re < 6{,}000$; $6 < Sc < 3{,}000$, mass transfer is correlated by a standard j-factor, according to

$$j_D = \frac{k_g \, P_{BM}}{G_M} \, Sc^{2/3} = 0.023 \, (Re)^{-0.17} \qquad (8)$$

where

j_D = Colburn j factor, dimensionless [71]

P_{BM} = log mean pressure of non-diffusing gas, atm

Sc = Schmidt number, $\dfrac{\text{viscosity lb/(ft hr)}}{\text{density (lb/ft}^3\text{) diffusivity (ft}^2\text{/hr)}}$

Re = $\dfrac{\text{diameter of tube (ft) velocity (ft/hr) density (lb/ft}^3\text{)}}{\text{viscosity (lb/(ft hr)}}$

The final design equation uses equations (7) and (8) as follows

$$\ln \left(\frac{Y_o}{Y_e}\right) = \frac{0.092\ Z}{d(Re)^{0.17}(Sc)^{2/3}} \qquad (9)$$

where

Z = length of catalytic bed, in.

d = diameter of tubular catalyst honeycomb, in.

Capital costs include the cost of housing for the catalyst bed, insulation, a fan and motor. A typical catalyst price is \$450/ft^3 of bed required [17]. Total annual costs were estimated and include amortization, fuel, fan, power and maintenance.

Table 24 summarizes design and cost calculations for three different flow rates and four different reduction ratios. The temperature has been lowered from 1200°F for the direct-fired incinerator to 800°F for the catalytic bed unit, thereby decreasing the fuel cost. Only if the plant effluent gas is already partly heated will a catalytic incinerator show an economic advantage over the direct-fired incinerator. The gaseous effluents from rendering plants are typically 120°F to 140°F which is not enough heat to affect

Flow Rate (CFM)	Odor Reduction Ratio (Inlet/Outlet)	Space Velocity (1/Hr)	Reynolds Number	Schmidt Number	Pressure Drop (in. H_2O)	Horse-Power Required	Installed Cost ($)	Annual Operating Cost ($)	Operating Costs, $ per hour per 1,000 cfm*
1000	10/1	72013	589	2.53	28.12	105.4	10,053	5637	1.13
	100/1						10,721	6048	1.21
	1000/1						11,388	6459	1.29
	100000/1						12,723	7282	1.46
5000	10/1	72013	589	2.53	28.12	527.2	23,770	21,562	0.86
	100/1						27,108	23,618	0.94
	1000/1						30,446	25,674	1.03
	100,000/1						37,123	29,786	1.19
25,000	10/1	72013	589	2.53	28.12	527.2	62,128	93,628	0.79
	100/1						78,818	103,909	0.83
	1000/1						95,509	114,189	0.91
	100,000/1						128,889	134,749	1.09

TABLE 24: Summary of Cost Estimates for Catalytic Afterburner

*Based on 5,000 hours of operation per year the heat economy. Also, it may be necessary to scrub out fatty particles which may interfere with the catalyst. This would lower the inlet temperature even more.

5. Carbon Bed Adsorption

Although a design and cost computer program was not developed for carbon adsorption, Doty et al [17] performed a sample calculation to treat 100,000 cfm of ventilation air containing about 10 ppm of odorant. It was assumed that a 100-fold reduction was sufficient. Data available on the capacity of carbon for isopropyl alcohol was used. Odorous materials of higher molecular weight and less polarity will be more readily adsorbed, and therefore this is a safe method of design. It was calculated that for 100,000 cfm and a 16-hr day, a bed of 208 ft^3 was required. Major costs include installed cost of bed and equipment, fan costs and regeneration costs. The unit cost calculated is \$0.11/(1000 cfm)(hr). The cost to reduce odor of a process stream would be much greater than that for ventilation air, mainly because of increased regeneration requirements.

6. Summary of Costs

Hopton and Laughlin [36] summarized Doty's cost estimates as shown in Table 25. As can be seen, scrubbing appears to be more economical than incineration under most flow and odor reduction conditions. Incineration gets the nod only when high odor reduction ratios are desired. The fuel savings benefit derived by utilizing catalytic incineration as opposed to direct-fired incineration is lost because of the added investment cost for the catalyst bed and additional fan cost due to pressure drop through the bed. It is concluded that catalytic incineration is not promising for this application. Also, it is noted that spray scrubbing rivals carbon adsorption for application to ventilation air.

Flow Rate cfm	Odor Levels		Operating Cost per hour per 1000 cfm				Carbon Adsorption
			Incineration		Scrubbing		
	In	Out	Direct	Catalytic	Packed Tower	Spray	
1000	10	1	-	1.13	-	-	-
1000	100	1	1.28	1.21	.49	-	-
1000	1,000	1	1.39	1.29	.69	-	-
1000	100,000	1	1.55	1.46	2.50	-	-
5000	10	1	-	.86	-	-	-
5000	100	1	.90	.94	.29	-	-
5000	1,000	1	.95	1.03	.91	-	-
5000	100,000	1	1.03	1.19	2.00	-	-
25,000	10	1	-	.79	-	-	-
25,000	100	1	.83	.83	.19	-	-
25,000	1,000	1	.85	.91	.28	.17	-
25,000	100,000	1	.90	1.08	1.80	-	-
38,000	1,000	1	-	-	-	.16	-
66,000	1,000	1	-	-	-	.16	(.23)*
100,000	100	1	-	-	-	-	.11
100,000	1,000	1	-	-	-	.16	-
150,000	10	1	-	-	-	.10	-
150,000	100	1	-	-	-	.13	-
150,000	1,000	1	-	-	-	.16	-

* Ontario Research Foundation Estimate (36)

TABLE 25: Odor Control Costs For Rendering Industry

V. COMMENTS

The literature review presented in the previous chapters is indicative of continuing activity in the field of odor control. It is apparent that scrubbing, particularly chemical scrubbing, has received the most attention in the past. The relatively low capital and operating costs for scrubbing make it a very attractive control technique for many industrial situations. However, as a control method scrubbing is not always the ideal. Its applicability is far from universal. Also, scrubbing is an incomplete disposal method because the pollutant now ends up in water.

Incineration methods are recognized to be more or less ultimate disposal techniques for many odorants of industrial origin. The major deterrent in wider use of incineration methods is their high energy cost. The data on energy savings that may be possible by heat recycle in incineration systems are not extensive. Most of the reported work on costs of incineration methods is of the computer model variety, with its unavoidable limitations as to general applicability.

There is undoubtedly much scope for techniques such as catalytic oxidation in odor control. The lower temperature requirements for catalytic oxidation should result in important energy savings. Due to lower temperatures, equipment life will also be extended.

The second part of this report describes an experimental investigation aimed at establishing the general scope of catalytic oxidation as an odor control technique.

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APPENDIX I

Glossary of Terms

GLOSSARY OF TERMS

1. Odor Threshold (as defined by ASTM E253-67T)

(a) Detection Threshold:

The minimum physical intensity detected by a subject where he is not required to identify the stimulus but just detect the existence of the stimulus.

(b) Recognition Threshold:

The minimum physical intensity detected by a subject where he is required to identify the stimulus in some manner.

2(a) Odor Concentration (ASTM Method D1391-57)

The number of cubic feet that 1 ft^3 of sample will occupy when diluted to the odor detection threshold. It is a measure of the number of odor units in 1 ft^3 of the sample. It is expressed in odor units per cubic foot.

(b) Odor Unit (AST, Method D1391-57)

One cubic foot of air at the odor threshold.

3. Los Angeles Air Pollution Control District Rule 66 (L.A. Rule 66)

The requirements of L.A. Rule 66 is that

$$\frac{\underset{\text{"IN"}}{\text{Hydrocarbons}} - [\underset{\text{"OUT"}}{\text{Hydrocarbons}} + (\underset{\text{"OUT"}}{\text{CO}} - \underset{\text{"IN"}}{\text{CO}})]}{\underset{\text{"IN"}}{\text{Hydrocarbons}}}$$

be ninety percent or higher.

4. Los Angeles Standard Method for Odor Measurement

(Danielson [13]): As per ASTM Method D1391-57

PART TWO

CATALYTIC OXIDATION
OF ODOROUS COMPOUNDS

I. INTRODUCTION

This section of the report presents results of an experimental investigation on the catalytic oxidation of odors.

Oxidation is generally accepted to be a complete method for organic odor destruction particularly for compounds containing only carbon, hydrogen and oxygen. The combustion products from complete oxidation of such compounds are odorless and not considered to be air pollutants. Of the three most common oxidation techniques, direct-flame, thermal and catalytic, discussed in detail in Part One, catalytic oxidation is becoming quite popular due to the lower fuel requirements and consequently lower operating costs.

The applications for air oxidation as a control technique for odoriferous emissions are many and are distributed throughout all aspects of industry. These include the food processing, chemical processing, petroleum refining, the pulp and paper industries and many others.

The major objective of this investigation was to test the applicability of catalytic oxidation to a spectrum of pure odorous compounds which have been identified in industrial environments. The catalyst selected was platinum on an alumina carrier. Many sources have stated that this type of catalyst is effective for the oxidation of organic odorous compounds. An experimental flow reactor system was constructed and operated to obtain data for a large variety of odorants at various oxidation temperatures. The space velocity was kept constant and consistent with the values reported to be in industrial use. The oxidation temperatures were varied by selection of different preheat temperatures. Odor reduction was measured by the ASTM Syringe Dilution method. Twenty-two pure odorous compounds were investigated. The selection was based on their reported presence in industrial environments.

Based on the results obtained, kinetic calculations were performed to determine the effect of mass transfer and intraparticle resistance on the observed oxidation rates. The effectiveness factors for the catalyst, kinetic coefficients, activation energies, heats of reaction and heat recycle levels were evaluated to establish a complete picture of the potential of catalytic oxidation systems.

II. LITERATURE SURVEY

There are several ways to eliminate odors in any specific air pollution situation. However, when high efficiencies are required (or are anticipated as future requirements) and the problem involves combustible compounds, oxidation is generally agreed to be the most complete solution. Oxidation of hydrocarbons, for example, is the only method of air pollution control which does not require a secondary treatment facility. The combustion of organic air pollutants that do not contain nitrogen or sulfur converts pollutants into harmless end products (carbon dioxide and water vapor) which can be vented directly into the atmosphere.

Three methods of combustion are in common use: catalytic, thermal and direct-flame incineration. A comparison of these methods has already been presented in Part One. A more detailed review of available literature on the catalytic oxidation of odors is now presented.

A. Catalytic Oxidation

What is a catalyst? Searles [16] defines a catalyst as "a substance that can increase the rate of a chemical reaction, under given conditions of temperature and pressure, without its own composition or chemical nature being changed in the process". Edwards [6] defines a catalyst as "an agent that accelerates a chemical reaction but is unchanged by it". The presence of a catalyst allows the chemical reaction to take place at practical levels of temperature and concentration. With a catalyst of high activity, oxidation can proceed at temperatures half those necessary to achieve the same conversion efficiency using thermal incineration.

Oxidation catalysts used for air pollution control are of the surface type [6]. This means that oxidation takes place at the surface of the catalyst where the combustibles and oxygen come into contact with each other. The catalytic surface reaction is believed to take place between adsorbed atomic oxygen and the pollutant molecule [6].

A catalyst suitable for air pollution control applications has to be active at relatively low temperatures and stable under both reducing and oxidizing conditions. Platinum alloys and/or combinations of platinum and alumina have found favor because they are stable up to 750°C and are resistant to poisoning by most elements, notable exceptions being lead and phosphorous [16]. Searles [16] states that platinum is the preferred metal for the oxidation of a wide range of organic molecules that give rise to air pollution problems.

Most catalysts require a support material. A good support for oxidizing catalysts should have a high geometric surface area and a configuration that minimizes pressure drops. An example of recent developments in support design are honeycombs (monoliths). The monoliths are obtained in units of one foot thickness which are connected in series to produce the catalyst beds. Typical monoliths have surface areas as high as 384 ft^2/ft^3 with pressure drops 1/20-th of conventional pelleted beds [16].

Typical temperatures used in catalytic oxidation are 260°C to 540°C. These temperatures are usually attained by preheating the feed to the catalytic reactors. The preheater is therefore needed to raise the temperature of the gas stream high enough to initiate the oxidation reaction. The preheat temperature is a variable depending on the compounds being oxidized and the process conditions. Preheat temperatures of about 260°C (500°F) are sufficient for catalytic oxidation of most odorous combustibles, while temperatures as high as 455°C (900°F) may be required for the more stable compounds [9, 21]. Gilpin [8] reports that a minimum preheat of 260°C was required with the Oxycat$_{TM}$ system which consists of alumina and platinum alloy catalyst. The actual temperatures of the oxidation reaction also vary widely. Von Bergen [20] states that odorous air passed through a catalytic device may be oxidized at temperatures of 260°C-426°C (800°F). Bethea [2] reports a rendering operation eliminated offensive odors by using platinum-palladium on nichrome ribbon at 370°C-425°C. Another rendering operation achieved 90-95% odor reduction at 385°C-400°C. Cheremisinoff [4] and Edwards [6] report temperatures generally between 260°C-455°C.

After the catalytic reaction has begun, the heat of reaction generated is usually sufficient to sustain the oxidation process. It is quoted [9, 21] that the temperature is increased by 55°F for each BTU/ft^3 of combustible gas entering the reactor and that the stream must be less than 1/4 of the lower explosion limit (LEL). Hein [9] and Yocom and Duffee [21] state that most industrial hydrocarbon streams have a calorific value of about 12 BTU/ft^3, which is sufficient to sustain catalytic combustion for those hydrocarbon gases that have catalytic ignition temperatures below 350°C. Von Bergen [20] says that self-sustaining catalytic combustion is attainable normally if concentrations range between 15-20% of the LEL. Below 5% of the LEL, sustained oxidation is generally unfeasable.

In odor control applications, complete, or nearly complete combustion is normally required because partial combustion products may be more odorous than the original compounds. For example, oxidation of butanol is known to proceed through the following stages [20]:

$$\underset{\text{(mild odor)}}{\text{Butanol}} \xrightarrow{O_2} \underset{\text{(bad odor)}}{\text{Butyraldehyde}} \xrightarrow{O_2} \underset{\text{(very bad odor)}}{\text{Butyric Acid}} \xrightarrow{O_2} \underset{\text{(odorless)}}{CO_2 + H_2O}$$

For catalytic oxidation systems, as with any other technique used for air pollution control, there are cost considerations which must be weighed against the benefits achieved. The most readily accepted catalytic processes are those which yield usable heat with the possibility of writing off the investment with the heat savings [20]. The hot exit gas stream may be used to raise the temperature of the inlet gases to a satisfactory temperature level. Alternately the hot exit gases may be utilized to heat the plant area and offices, or perhaps used as a heat source for another part of the process. Searles [16] states that 50% of the heat of a hot gas stream could be transferred to the inlet gas stream utilizing a heat recycle process with the Honeycat$_{\text{TM}}$ system. The limiting operational cost for catalytic systems is the cost of heating the entering stream minus the value of heat leaving the catalytic process. The relatively high investment cost for the catalyst bed and the additional fan cost due to the pressure drop through the bed can generally be compensated for by the lower operating costs due specifically to the lower fuel requirements [4]. Searles [16] believes that even in the most hostile environment that can be imagined where the catalyst lasts less than three months, the operating costs are no more than those for thermal incineration. With a catalyst life of one year or more, the cost benefits of operating a catalytic incineration system can be considerable. Edwards [6] states that the most common useful life of an oxidation catalyst is about 15,000 hours and Von Bergen [20] reports service life of over 23,000 hours. Because the catalyst is coated with precious metal, it is inclined to be self-cleaning, thereby reducing regeneration requirements.

Catalytic combustion systems are gaining in popularity for a number of emission control applications. These include the food processing, chemical processing and metal finishing industries.

B. Selection of Odorants for the Experimental Study

The odorous compounds used in this investigation were selected on the basis of their apparent presence in industrial environments. Table 1 lists the twenty-two compounds

	Odorant and Formula	Associated Industry
1.	Acetone $(CH_3CO\ CH_3)$	Poultry Kraft Mills
2.	Acrolein (CH_2CHCHO)	Varnish Cookers, Diesel Engines
3.	Amyl Alcohol $(CH_3CH_2C(CH_3)OHCH_3)$	Swine, Rendering Plants
4.	Benzene (C_6H_6)	
5.	n-Butanol $(CH_3(CH_2)_3OH)$	Swine, Beef Cattle
6.	Iso-Butanol $(CH_3CH_2CHOHCH_3)$	
7.	Butyraldehyde $(CH_3(CH_2)_2CHO)$	Swine
8.	Butyric Acid $(CH_3(CH_2)_2COOH)$	Rendering, Flues and Gelatins
9.	Trans-Cinnameldehyde $(C_6H_5CHCHCHO)$	
10.	Crotonaldehyde $(CH_3CHCHCHO)$	
11.	Cyclohexanone $(CO(CH_2)_4CH_2)$	
12.	Ethyl Acetate $(CH_3COOC_2H_5)$	Beef Cattle, Dairy Cattle
13.	n-Hexane (C_6H_{14})	Petroleum Refining
14.	3-Meth yl-2-Butanone $(CH_3COCH_2CH_3)$	
15.	Phenol (C_6H_5OH)	Petroleum Refining, Diesel Engines, Mineral Wool Production
16.	Propionic Acid (CH_3CH_2COOH)	Glues and gelatins
17.	Iso-propyl Acetate $(CH_3COOCH(CH_3)_2)$	Beef Cattle, Dairy Cattle
18.	Pyridine (NCHCHCHCHCH)	Fish Processing, Petroleum Refining
19.	Toluene $(C_6H_5CH_3)$	
20.	Triethylamine $((CH_3CH_2)_3N)$	Swine, Dairy Cattle, Rendering Plants
21.	Valeraldehyde $(CH_3(CH_2)_3OH)$	Swine, Beef Cattle
22.	Vinyl Acetate $(CH_3COOCHCH_2)$	Resin Kettles

TABLE 1: Odorous Compounds Used in the Experimental Work

used, and the industries with which they are associated. The association of these compounds with specific industries is done on the basis of Schroeder's work [15].

The physical properties of these chemicals are given in Appendix I, and the reported odor threshold data are given in Appendix II.

III. EXPERIMENTAL EQUIPMENT

The experimental equipment was constructed with the objective of investigating vapor phase air oxidation of pure odorous compounds over an active platinum catalyst.

The odor levels were measured by ASTM Technique D1391-57 at the reactor inlet and outlet. A description of the experimental set up and the major individual components of the system is given below. The specifications of all equipment used are given in Appendix VII.

A. Flow Diagram

The experimental equipment consisted of an air feeding system, chemical injection system, a preheater and a reactor. Figure 1 is a schematic of the experimental arrangement.

Compressed air at 40 psig from the laboratory air line was passed through a pressure regulator to reduce the pressure to about 30 psig, and then, through an air filter to remove impurities such as oil or dirt. The liquid odorant was injected into the air line by means of a motor driven syringe device. This unit had a variable speed control which permitted variation of the amount of chemical injected into the system (see B-2 for details). A liquid trap was used as a means of preventing liquid from entering the system.

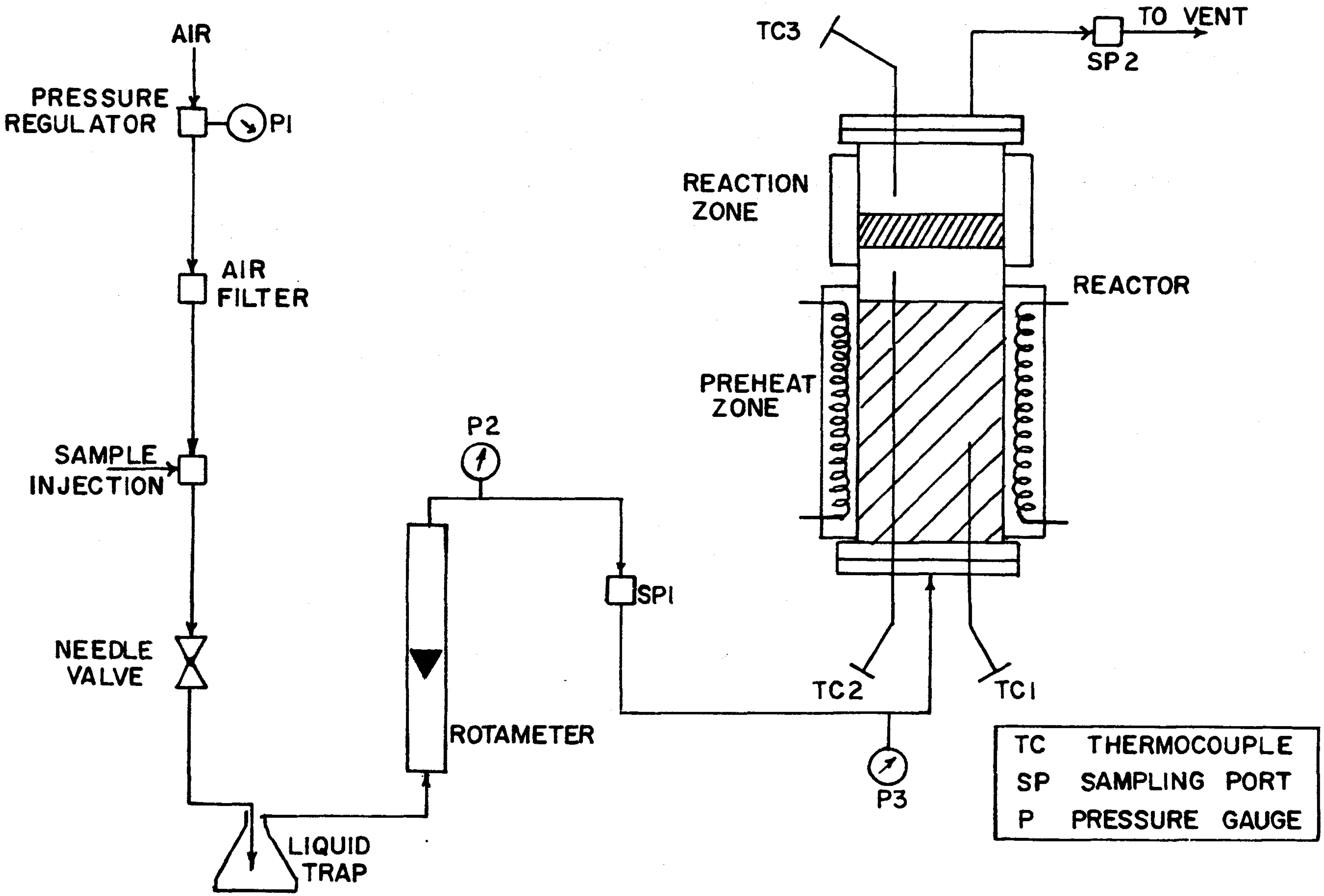

FIGURE 1 : FLOW DIAGRAM OF EXPERIMENTAL EQUIPMENT

The air flow was monitored by means of a rotameter. Air pressure was measured at the exit of the rotameter. The flow through the rotameter was regulated by means of a needle valve.

The air containing the odorant was introduced into the preheat zone of the reactor. The preheater, an electrically heated portion of the column packed with 1/8" ceramic spheres, served two purposes. It thoroughly mixed the air-odorant stream while evenly distributing the flow, and it also brought the air stream to a constant pre-determined temperature. The preheat section temperature was regulated with a temperature controller. The hot gases now entered the catalyst bed. No heat was supplied to the bed which was well insulated. The temperature was measured at the inlet to the bed and at the exit of the bed with ungrounded chromel-alumel thermocouples (TC-1 and TC-3). Pressure was measured by 0-30 psig Matheson pressure gauges. The gases were then vented to a fume hood.

B. Details of Equipment

1. Reactor

The reactor was constructed from a 14 inch section of 2 inch standard pipe (1 5/8 inch I.D.). The ends of the pipe were welded to 300 psig welding neck flanges and matching blind flanges. The details of the reactor are shown in Figure 2. Teflon gaskets, 1/10-millimeter thick, 2-inch I.D. and 5-inch O.D. were used to obtain leakproof joints. A 1 5/8-inch diameter basket constructed of stainless steel with 5 inch long arms was welded to the top blind flange to hold the catalyst bed in place. One 1/8-inch Swagelok fitting was constructed on the top flange and two 1/8-inch Swagelok fittings were constructed on the bottom flange for thermocouple placement. A 1/4-inch tube was welded to the centre of the top flange to serve as an exit and a 3/8-inch tube was welded to the centre of the bottom flange. The bottom tube was connected to a 1/4-inch piece of tubing, 5 inches long and pinched at the end with 1/8-inch holes drilled into it, which served as a diffuser.

The column was packed to a height of 7 inches with 1/8-inch ceramic spheres. A thermocouple was inserted in the bottom flange to measure the exit temperature from the preheat bed. A controlling thermocouple was inserted through the bottom flange to "mid-bed". The basket containing 1/8-inch by 1/8-inch catalyst pellets packed to a thickness of 1 3/8-inch was lowered into place. A measuring thermocouple was then placed through the top flange to monitor the temperature of the gas as it left the catalyst bed.

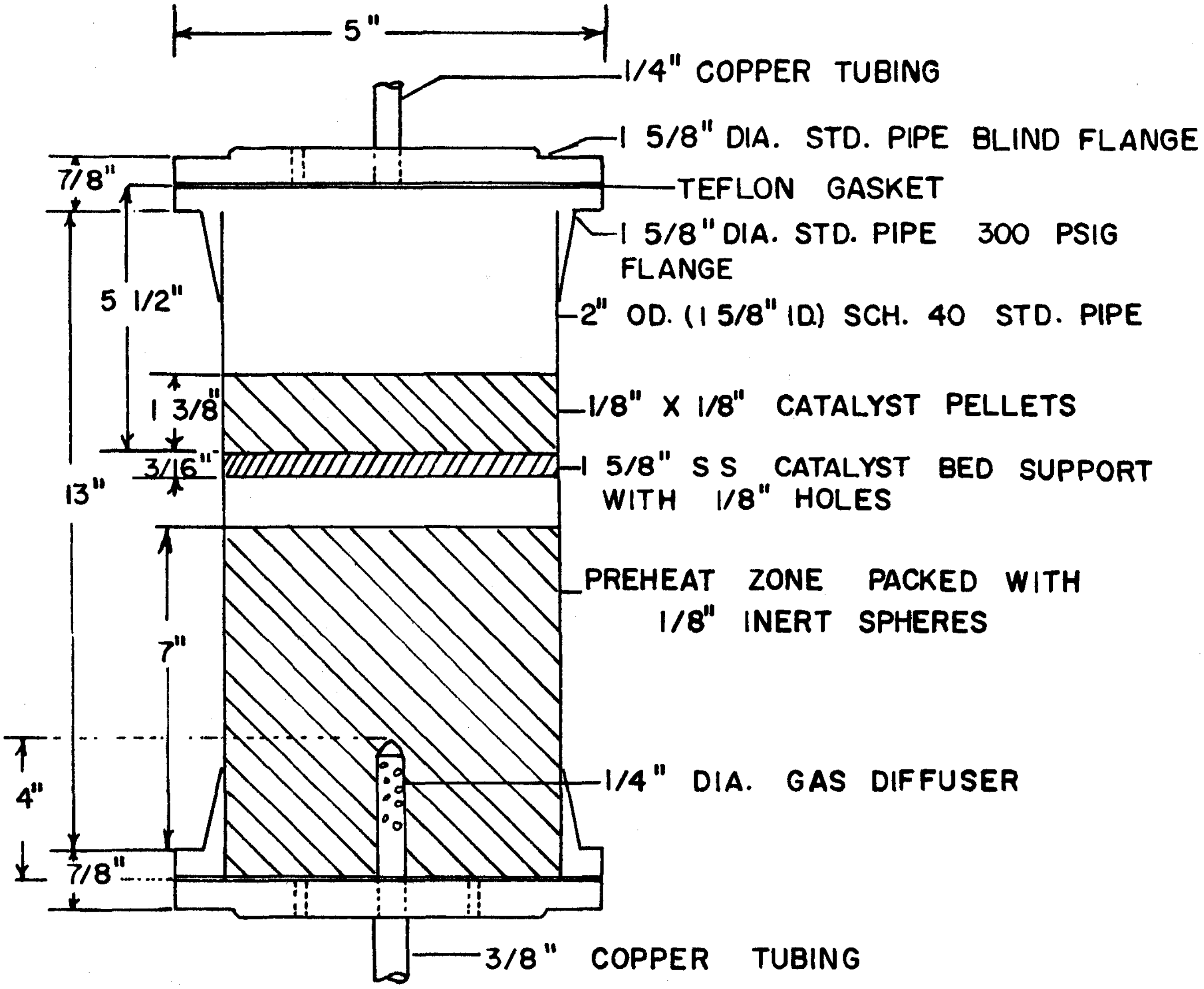

FIGURE 2 : REACTOR COLUMN

The preheater was heated by means of a beaded resistance wire. Specifications of the heater are given in Appendix VII.

2. Odorant Injection System

This system consisted of a motor, gear reducing devices, variable speed control, syringe and syringe harness. A counter was also installed to record the number of revolutions per minute of the motor.

The number of revolutions per minute could be varied from 2.5/min (setting of 0 on the Ratiotrol) to 35/min (setting of 100). The gear reduction from the motor to the syringe drive was 100 to 1. From calibration it was found that one count on the counter was equivalent to 0.00708 ml of liquid. The syringe needle entered the flow system by way of a Swagelok 'T' with a Teflon septum in the high portion of the 'T'. The minimum injection rate was 0.018 ml/min and the maximum rate was 0.248 ml/min.

C. Catalyst

The catalyst used was a commercial grade platinum catalyst supported on gamma alumina, supplied by Girdler Chemical, Inc., Louisville, Kentucky, U.S.A. (Product designation T-309B). The pellets used were 1/8-inch by 1/8-inch cylinders. The catalyst had a surface area of 190 m^2/gm as per manufacturer's quotation. It was chosen because platinum type catalysts have demonstrated high potentials in previous works on the catalytic oxidation of odors [6, 16]. The physical properties of the catalyst are given in Appendix I.

D. Analytical Equipment

The inlet and exit streams were analyzed using the ASTM D1391-57 method for the Measurement of Odors in Atmospheres (Dilution Method). The details of this method are given in Appendix VI.

IV. EXPERIMENTAL PROCEDURE

A. Calibration Procedures

1. Calibration of the Rotameter

The air rotameter was calibrated directly by using a previously calibrated temperature compensated dry test meter (Rockwell bellows-type). The dry test meter was at 1 atmosphere, therefore, volumetric flows were at standard conditions (14.7 psia and 60°F). The calibration curve is given in Appendix IV.

2. Calibration of the Injection System

The odorant injection system was calibrated by setting the syringe in place and allowing the system to operate at Ratiotrol settings of 0 to 100. The number of revolutions were counted at each setting by means of a counter. The calibration curve is given in Appendix IV.

3. Calibration of Temperature Measurement

The Hewlett-Packard 7100B Strip Chart Recorder utilizing two 17500 A Modules was calibrated using a Leeds-Northrup Millivolt Potentiometer. A known voltage was carried to the recorder and internal calibration was performed. The chromel-alumel thermocouples of the ungrounded type were connected to the recorder. The millivolt readings from the thermocouple were then translated into temperature using standard tables. The temperature reference used was ambient.

4. Calibration of the Pressure Gauges

The pressure gauges were calibrated using a dead weight tester. The indicated gauge pressure was compared to a column of mercury. The calibration curve is given in Appendix IV.

B. Experimental Technique

The thermocouples were placed in the preheat section of the reactor as in Figure 2. The 1/8-inch ceramic spheres were packed to a depth of seven inches. The catalyst tray was then put in place and the catalyst was loaded to a depth of 1.3 inches. The exit thermocouple (TC 3) was then put in place. The column was now assembled and placed in the system.

The air flow was started and a constant rate established. The preheater was then turned on and allowed to reach a predetermined steady temperature by means of the temperature controller. The preheater took approximately one hour to stabilize at 200°C.

The odorous material was injected into the system at a constant rate. The system was then allowed to run until a position of dynamic equilibrium (with respect to inlet odor concentration and temperature) could be attained. The system was allowed to run long enough at these conditions to permit several odor measurements from the inlet and exit sample ports. The reactor temperatures were frequently checked. The preheat temperature was then increased and allowed to stabilize. Samples were again withdrawn and measured for odor. This procedure was continued until no odor was detected at the exit of the reactor.

In order to shut down the reactor, the odorant feed was shut-off and the air and heater were allowed to run so as to flush out the reactor (until no odor was noticed at the exit). This usually required approximately one hour. The heater was then turned off and the air was still allowed to flow at a reduced rate until the system was at room temperature.

The syringe used for odor injection was allowed to soak in a soapy solution between runs to insure that no odor was left from the previous experiment.

V. DISCUSSION OF RESULTS

A. The Experimental Results

The important aspects of experiments performed on the twenty-two (22) pure odorants are presented in Tables 2 and 3. The complete details of the experiments are given in Appendix III. In this appendix, results of replicate runs performed for many of the odorants are also included. The reproducibility of the observations was, in general, excellent.

In all of the experimental work reported here, the odor measurements were carried out by the ASTM method (D1391-57). This method is the current standard. Even when and if other methods, based perhaps on dynamic olfactometry, become more acceptable, the odor regulations will remain based on direct sensory perception. There has been much recent work on chemical fingerprinting of odors but it seems unlikely that purely analytic procedures will be able to replace sensory methods in the near future. One difficulty with the analytic methods using, for example, gas chromatography, is that even if the odorants themselves may be identified and measured quantitatively, the products from the odor control unit may not be so easy to analyze.

CATALYST:	Pt on Gamma Alumina (0.5% by weight)
Weight of Catalyst Used:	43.6 gm
Size of Catalyst Pellets:	1/8 inch by 1/8 inch
Bed Thickness:	1.3 inches
FLOW RATES:	1.49 SCFM
SPACE VELOCITY (based on above):	83,481 hr^{-1}
RESIDENCE TIME:	0.043 sec
CATALYST LIFE TIME:	Catalyst was still active after approximately 130 hours of operation

TABLE 2: Experimental Conditions

Odorant and Formula	Temperatures (°C)		Concentrations (ou/ft^3)		Percent Odor Removal
	Preheat Exit	Reaction Bed Exit	Inlet	Exit	
Acetone CH_3COCH_3	164	231	2	5*	(-)
	215.5	268	2	1	50
	268.5	342	2	0	100
Acrolein CH_2CHCHO	195	277	50	20	60
	232	293.5	50	5	90
	273	341.5	50	0	100
Amyl Alcohol (Tert) $CH_3CH_2C(CH_3)OHCH_3$	136.5	236	50	25*	50
	196	319	50	10	80
	264	389.5	50	5	90
	337	444	50	2.5	95
	401	486.5	50	0	100
Benzene C_6H_6	152	208	20	10	50
	242.5	340	20	1	95
	313	410	20	0	100
Butanol (Normal) $CH_3CH_2CH\ OH\ CH_3$	196	253.6	100	20*	80
	233	297.5	100	20	80
	266	316	100	10	90
	319	366	100	1	99
Butanol (Iso) $(CH_3CH_2CH_2CH_2OH)$	166.5	285.5	200	500*	(-)
	185.5	308	200	500*	(-)
	250	369	200	200*	0
	301	412	200	100*	50
	355	459.5	200	50*	75
	415	500	200	0	100
Butyraldehyde $CH_3(CH_2)_2CHO$	138.5	190.5	200	250*	(-)
	156	264	200	100	50
	211	317	200	40	80
	240.5	342	200	20	90
	326	410	200	1	>99
Butyric Acid $CH_3(CH_2)_2COOH$	134	164.5	50	25	50
	167	192	50	20	60
	193.5	221.5	50	2	96
	222	271	50	0	100

TABLE 3: Results

continued ...

Odorant and Formula	Temperatures (°C)		Concentrations (ou/ft^3)		Percent Odor Removal
	Preheat	Reaction	Inlet	Exit	
Cinnamaldehyde	182	234.5	100	25	75
(Trans)	213	270	100	5	95
$C_6H_5CHCHCHO$	280	335	100	1	99
Crotonaldehyde	132	194	250	100	60
$CH_3CHCHCHO$	200	278	250	50	80
	256	323	250	25	90
	328	399.5	250	20	92
	359	424.5	250	5	98
	381	443	250	1	>99
Cyclohexanone	132	199	250	200	20
$CO(CH_2)_4CH_2$	193	289.5	250	50	80
	248	364.5	250	20	92
	331	420	250	20	92
	385	463	250	1	>99
Ethyl Acetate	103	145	100	250*	(-)
$CH_3COOC_2H_5$	158	208	100	333*	(-)
	222	320	100	200*	(-)
	258	391	100	50*	50
	301	422	100	33*	67
	372.5	481	100	5	95
	393	495	100	0	100
Hexane (normal)	80	80	20	20	0
$CH_3(CH_2)_4CH_3$	123	185	20	10	50
	170	281.5	20	1	95
	193	300	20	0	100
3-Methyl-2-Butanone	133	220	20	100*	(-)
$CH_3COCH_2CH_3$	196.5	329	20	50*	(-)
	252.5	373.5	20	20*	0
	330	437.5	20	10*	50
	339.5	482.0	20	0	100
Phenol	134	134	200	200	0
C_6H_5OH	104.5	221	200	100	50
	217	295.5	200	50	75
	284	355	200	25	87.5
	368	427.5	200	1	>99

TABLE 3; Results

continued ...

Odorant and Formula	Temperature (°C)		Concentration (ou ft^3)		Percent Odor Removal
	Preheat	Reaction	Inlet	Exit	
Propionic Acid	120	156	250	250*	0
CH_3CH_2COOH	181	268	250	200	20
	243	325	250	100	60
	268	357	250	50	80
	323	389	250	2.5	99
	350	419	250	1.0	>99
Propyl (Iso) Acetate	114	156	50	50*	0
$CH_3COOCH(CH_3)_2$	184	286.5	50	25	50
	256	355.5	50	20	60
	330	423	50	0	100
Pyridine	109	139	500	500**	0
$\overline{NCHCHCHCHCH}$	165	210	500	333**	33
	233	309	500	250**	50
	326.5	407	500	100**	80
	391	462	500	25**	95
	463	510	500	0	100
Toluene	96	96	50	50	0
$C_6H_5CH_3$	120	190.5	50	25	50
	130	246.5	50	20	60
	149	326	50	5	90
	165.5	336	50	0	100
Triethylamine	110	110	100	100	0
$(CH_3CH_2)_3N$	145	162	100	67	33
	168	227	100	50	50
	233	347	100	100***	(-)
	301	403	100	100***	(-)
	389.5	469	100	100***	(-)
	451	100	100	100***	(-)
Valeraldehyde	152	250	500	250	50
$CH_3(CH_2)_3CHO$	179	292.5	500	100	80
	206.5	323.5	500	50	90
	293	394	500	10	98
	315	419	500	1	>99

TABLE 3: Results

continued ...

Odorant and Formula	Temperature (°C)		Concentration (ou ft^3)		Percent Odor Removal
	Preheat	Reaction	Inlet	Exit	
Vinyl Acetate	132	219	200	250*	(-)
$CH_3COOCHCH_2$	185	306	200	100	50
	251	356.5	200	20	90
	333	429	200	1	>99

*Odor at the outlet was of a different nature (more sour) than at the inlet

**Odor different (apparently of a cyanide nature)

***NO_x type odor, reddish brown color in exit, discoloration of tygon tubing observed.

TABLE 3: Results

In subsequent kinetic treatment of data reported in Table 3, odor reduction level is assumed to correspond directly to the conversion level for the odorant. This one-to-one correspondence is not necessarily always true, because if intermediate oxidation products are present in the exit from the catalyst bed, they will affect the odor thresholds. The correct correspondence between odor reduction and conversion can only be established if much analytical work using chromatography is performed. This approach seems self-defeating. Nonetheless, to gain some insight into this matter, one of the odorants was tested for 'before' and 'after' peak heights in a gas chromatographic set up. The odorant used was valeraldehyde with the conditions corresponding closely to runs 3 and 5 for this chemical in Table 3. Table 4 compares odor reduction by the ASTM method to peak height reduction for comparable conditions of oxidation*. For valeraldehyde, the correspondence between the two methods seems excellent. As pointed out earlier, the same correspondence may not always be assumed to hold for all situations.

*The gas chromatographs are included in Appendix III.

Odorant: Valeraldehyde					
Temperatures		Odor Reduction by ASTM (%)	Temperatures		Peak Height Red'n (%)
Preheat Exit	Reactor Bed Exit		Preheat Exit	Reactor Bed Exit	
206.5	323.5	90	203	312	91.3
315	419	>99	311.5	404	100.0

TABLE 4: Comparison of ASTM Results to Gas Chromatograph Results

An examination of the results presented in Table 3 reveals that catalytic oxidation is a workable control technique for all but one of the twenty-two chemicals. The sole exception is triethylamine, which, upon oxidation, produced an odor worse than the original.

There are wide differences in the ease with which odors are destroyed for the other twenty-one chemicals. For all the odorants, the oxidation becomes, not surprisingly, more efficient as the preheat temperature is raised. However, for some of the chemicals such as acetone, acrolein, tert-amyl alcohol, benzene, n-butanol, butyraldehyde, butyric acid, trans-cinnamaldehyde, crotonaldehyde, cyclohexanone, n-hexane, toluene, valeraldehyde and vinyl acetate, relatively low preheat temperatures (250°C and lower) are sufficient to yield more than 90 percent odor reduction. For some other odorants, such as iso-butanol, ethyl acetate, 3-methyl-2-butanone, and pyridine preheat temperatures lower than 250°C are virtually worthless in that more odorous intermediates are generated at these low temperatures.

The results presented in Table 3 substantiate the claim of energy savings advanced for catalytic oxidation systems in the literature studies. The necessary energy requirements are a function of the required reaction temperature. In an industrial application, an acceptable odor level must be decided upon first and then appropriate conditions for oxidation can be selected. It must therefore be determined what odor level is acceptable to the surrounding community. Depending on the desired removal efficiency, the necessary preheat temperature can be read from Table 3. For example, to achieve an odor reduction of 90% for a gas stream containing butyraldehyde, butyric acid and valeraldehyde, a preheat temperature of 240°C is indicated.

In addition to the results reported in Table 3, three runs were also made using a typical distillery odor. The odor was produced by bubbling air through an aqueous solution of syrup obtained from the grain drying operation of Hiram Walker and Sons, Limited. Inlet concentrations remained constant at 10 ou/ft^3. At a preheat temperature of 262°C, the odor was completely destroyed. The exit gas stream temperature was 301°C. At preheats of 203°C and 235°C, the odor reduction was 50 percent and 75 percent respectively, with corresponding exit temperatures of 247°C and 267°C.

B. Kinetic Analysis of Experimental Results

The experimental results obtained in this investigation are for flow, temperature and composition conditions likely to be encountered in industrial set ups. As such, therefore, they do not attempt to minimize conversions or transfer resistances for the sake of analytic convenience. The data obtained correspond to integral (high conversion) rather than differential reactors. Furthermore, the reactor is operated adiabatically, rather than isothermally. Complete kinetic analysis of such data is tedious, and perhaps not called for, since a different experimental strategy can and should be used if such information is desired. None the less the data reported in Table 3 can be analyzed to determine the relative importance of various resistances to the progress of the reaction. From a design point of view, such information is extremely significant.

In order to carry out the above objective, the following equations of mass and energy balances across the catalytic reactor are written:

Mass Balance on 'A': $F_{Ao} dX_A = -r_A dW$ (1)

where

F_{Ao} = odorant flow rate, $\frac{\text{lb moles A}}{\text{hr}}$

X_A = fractional conversion, $(C_{Ao} - C_{Ab})/C_{Ao}$

r_A = reaction rate, $\frac{\text{lb moles A formed}}{\text{(lb cat hr)}}$

W = mass of catalyst, lb catalyst

C_{Ao} = initial concentration of species A, $\frac{\text{lb moles A}}{\text{ft}^3}$

C_{Ab} = bulk concentration of A at any reactor position, $\frac{\text{lb moles A}}{\text{ft}^3}$

Energy Balance on 'A': $d(Q\rho H) = (\Sigma - r_j \Delta Hr_j)dW$ (2)

where

Q = volumetric flow rate, ft^3/hr

ρ = density, lb/ft^3

H = enthalpy of reaction mixture, Btu/lb

ΔHr_j = heat of reaction, Btu/lb-mole, for reaction j

If a single reaction is assumed to occur, only one mass balance equation, together with the energy balance has to be considered. The temperature rises across the reactor as reported in Table 3 can be compared to predicted adiabatic temperature rises as per the energy balance. This comparison was made for two of the runs from Table 3 and the resulting close agreement indicated that the reactor was indeed operating in an adiabatic fashion.

A detailed kinetic analysis of results reported in Table 3 is made difficult by the fact that the rate of reaction, r_A, which is the unknown, is a function of both concentration and temperature. Therefore, a trial and error approach involving simultaneous integration of equations 1 and 2 is necessary for establishing the rate parameters.

The rate analysis can be considerably simplified if temperature variations across the bed are ignored and a mean temperature is used for data reduction. The dangers of such an approximation are self-evident, and though the mean bed temperature approach is utilized in the following analysis, the results obtained should be interpreted with caution due to this temperature assumption.

The mean bed temperature assumption allows one to ignore the energy balance and work solely with the mass balance Equation 1. The general approach is to try different forms of r_A, corresponding to different rate assumptions, in Equation 1. The detailed procedure utilized is as follows:

i. Calculate from physical property data (Appendix V) and from experimental flow conditions, the Reynold and Schmidt numbers

ii. The external mass transfer coefficient, k_{m_A}, is calculated from the equation

$$k_{m_A} = \frac{j_D G \, Sc^{-2/3}}{\rho_G} \tag{3}$$

according to [17]

where

k_{m_A} = external mass transfer coefficient, ft/hr

G = mass flux, $lb/(hr\ ft^2)$

ρ_G = gas density, lb/ft^3

j_D = mass transfer correlation coefficient, dimensionless

Sc = Schmidt number, $\mu_G/\rho_G \mathcal{D}_{AB}$, dimensionless

$\mathcal{D}_{AB}$ = bulk diffusivity, ft^2/hr

μ_G = gas viscosity, lb/(ft hr)

iii. Assuming mass transfer control, the size of the catalyst bed can be predicted using the equation

$$\left(\frac{W}{F_{Ao}}\right)_{calc.} = \int_0^{X_{Ae}} \frac{dX_A}{k_{m_A}\, a_m\, C_{Ao}\, (1-X_A)} \tag{4}$$

where

$\left(\frac{W}{F_{Ao}}\right)_{calc.}$ = predicted value of $\frac{W}{F_{Ao}}$ assuming mass transfer controls, $\frac{\text{(lb catalyst hr)}}{\text{(lb mole A)}}$

X_{Ae} = fractional conversion at exit

a_m = external area of catalyst, ft^2/lb

C_{Ao} = initial concentration of species A, $\frac{\text{lb moles A}}{ft^3}$

A comparison of predicted and experimental $\left(\frac{W}{F_{Ao}}\right)$ values reveals how good the mass transfer control assumption is for the particular run.

iv. On the assumption that chemical reaction and internal diffusion within the catalyst particle are rate controlling a "lumped" kinetic coefficient, ηk_1, assuming first order kinetics of oxidation is calculated according to

$$\left(\frac{W}{F_{Ao}}\right)_{exp} = \int_0^{X_{Ae}} \frac{dX_A}{\eta k_1\, C_{Ao}\, (1-X_A)} \tag{5}$$

where

$\left(\frac{W}{F_{Ao}}\right)_{exp}$ = experimental value of $\frac{W}{F_{Ao}}$, $\frac{\text{(lb catalyst hr)}}{\text{lb mole A}}$

ηk_1 = "lumped" kinetic coefficient, ft^3/(lb catalyst hr)

η = effectiveness factor, dimensionless

k_1 = kinetic coefficient, ft^3/(lb catalyst hr)

The values of log ηk_1 are plotted versus 1/T in order to evaluate the activation energy

v. Assuming that <u>neither mass transfer nor chemical reaction controls</u>, a new value of ηk_1 is calculated using

$$r_A = -k_{m_A} a_m (C_{Ab} - C_{As}) \tag{6}$$

and also;

$$r_A = -\eta k_1 C_{As} \tag{7}$$

Combining Equations 6 and 7 to eliminate C_{As} yields:

$$r_A = -\eta k_1 \left(\frac{k_{m_A} a_m C_{Ab}}{\eta k_1 + k_{m_A} a_m}\right) \tag{8}$$

where

r_A = reaction rate, lb mole A/(hr lb catalyst)

C_{Ab} = C_{Ao} $(1-X_A)$, lb mole A/ft^3

C_{As} = concentration of A at catalyst surface

The integral now becomes:

$$\left(\frac{W}{F_{Ao}}\right)_{\text{exp.}} = \int_0^{X_{Ae}} \frac{dX_A}{\left[\dfrac{k_{m_A} a_m}{1 + \dfrac{k_{m_A} a_m}{\eta k_1}}\right] C_{Ao}(1-X_A)} \tag{9}$$

from which value of ηk_1 may be extracted.

The values of log ηk_1 are plotted against 1/T for activation energy determination.

vi. Individual values of η and k_1 are now determined to establish the relative importance of intraparticle diffusion by utilizing the Thiele modulus equation

$$\phi_c = \frac{V_p}{S_p}\sqrt{\frac{\rho_p k_1}{\mathfrak{D}}} \qquad (10)$$

as given by [17]

where

ϕ_c = Thiele modulus, dimensionless

V_p = particle volume, cm^3

S_p = external area of catalyst, cm^2

ρ_p = density of particle, gm/cm^3

k_1 = kinetic coefficient, $cm^3/(gm\ sec)$

$\mathfrak{D}$ = corrected effective diffusivity, cm^2/sec

For cylinders with two sealed ends, the value of V_p/S_p is $r_c/2$. For cylinders with both ends open, the diffusion process is two dimensional making the Thiele type analysis invalid. For this situation a good approximation may be achieved by considering open ended cylinders to be equivalent to spheres of comparable dimensions. Therefore, for further calculations, the 1/8" x 1/8" cylindrical catalysts pellets used in this investigation are assumed equivalent to 1/8" diameter spheres, for which V_p/S_p is equal to $r_c/3$.

a. The Knudsen diffusivity is evaluated from

$$(\mathfrak{D}_k)_A = 9.7 \times 10^3\ a\ (\frac{T}{M_A})^{1/2} \qquad (11)$$

according to [17]

where

$(\mathcal{D}_k)_A$ = Knudsen diffusivity for species A, cm^2/sec

a = pore radius, cm

T = temperature, °K

M_A = molecular weight of A, gm/gm mole

The pore radius is calculated from

$$a = \frac{2\ V_g}{S_g} \tag{12}$$

where

V_g = pore volume, cm^3/gm

S_g = total surface area including pores, cm^2/gm

These values were supplied by the manufacturer and are given in Appendix I.

b. The effective diffusivity is calculated from

$$\mathcal{D}_e = \frac{1}{\left(\frac{1 - y_A\alpha}{\mathcal{D}_{AB}}\right) + \left(\frac{1}{(\mathcal{D}_k)_A}\right)} \tag{13}$$

where

$\mathcal{D}_e$ = effective diffusivity, cm^2/sec

y_A = mole fraction of species A

$\alpha = 1 - \sqrt{\frac{M_A}{M_B}}$

M_A = molecular weight of A, gm/gm mole

M_B = molecular weight of air, gm/gm mole

$\mathcal{D}_{AB}$ = bulk diffusivity of species A through B, cm^2/sec

c. The corrected effective diffusivity is determined by

$$\mathcal{D} = \frac{\varepsilon \mathcal{D}_e}{\delta} \tag{14}$$

where

$\mathcal{D}$ = corrected effective diffusivity, cm^2/sec

ε = porosity of the particle, dimensionless

δ = tortuosity factor, dimensionless

The value of the porosity is calculated from:

$$\varepsilon = \rho_p V_g \tag{15}$$

By assuming a value of ϕ_c, values of η may be determined using a plot of ϕ_c versus η.

vii. Since ηk_1 has been calculated in step v, values of η and k_1 can be determined by simple trial and error. The trial and error procedure is however not necessary for large values of ϕ_c ($\phi_c > 5$) because the value of η may be approximated by

$$\eta = \frac{1}{\phi_c} \qquad (16)$$

as indicated by [17].

If B is the value of ηk_1 calculated corresponding to step v (<u>neither controls assumption</u>) it follows that

$$(\eta k_1)_{calc.} = \beta \qquad (17)$$

and

$$k_1 \left(\frac{1}{\phi_c}\right) = \beta \qquad (18)$$

and

$$\frac{k_1}{\frac{r_c}{3}\sqrt{\frac{\rho_p k_1}{\mathcal{D}}}} = \beta \qquad (19)$$

Therefore, the values of k_1 and η can be directly determined. The calculated values of $\log k_1$ are plotted versus 1/T to provide the "true" activation energy.

The above procedure may be followed for all the data reported in Table 3. Tables 5 and 6 show the values

Run	T_{Avg} (°C)	$(\frac{W}{F_{Ao}})$ exp. $\frac{\text{(lb catalyst hr)}}{\text{lb mole A}}$	Re	j_D	Sc	k_{m_A} (ft/hr)	$(\frac{W}{F_{Ao}})$ calc. $\frac{\text{(lb catalyst hr)}}{\text{lb mole A}}$	$(\eta\, k_1)$ ft^3/(lb catalyst hr)	
							mass transfer controls assumption	chemical reaction and internal diffusion control	neither controls
Propionic Acid									
1	138.0	403.36	107	0.130	1.74	715.40	0	0	0
2	224,5	403.36	95	0.140	1.67	944.24	21.09	317.93	335.45
3	284.0	403.36	87	0.152	1.64	1148.70	78.89	1446.87	1798.54
4	312.5	403.36	85	0.155	1.63	1235.74	134.82	2659.99	3995.47
5	356.0	403.36	80	0.161	1.63	1366.39	371.16	8095.30	101,424.80
6	384.5	403.36	78	0.165	1.62	1456.73	541.41	12,592.20	-
Tert-Amyl Alcohol									
1	186.2	319.52	99	0.140	1.92	772.17	56.89	885.44	1077.25
2	257.5	319.52	90	0.145	1.91	918.09	127.20	2353.71	3914.92
3	326.7	319.52	83	0.160	1.88	1146.51	163.27	3772.84	7717.00
4	390.5	319.52	77	0.168	1.87	1327.40	201.40	5388.29	14,575.69
5	443.7	319.52	74	0.170	1.85	1460.02	456.31	13,427.94	-

TABLE 5: Summary of Kinetic Calculations

Run	T_{Avg}	$(\eta\ k_1)_{theor.}$ $ft^3/(lb\ catalyst\ hr)$ neither controls	$\mathfrak{D}$ ft^2/hr	k_1 $ft^3/(lb\ catalyst\ hr)$	η
Propionic Acid					
1	138.0	0	0.0086	-	-
2	224.5	335.45	0.0096	3108.8	0.11
3	284.0	1795.54	0.0102	85,702.7	0.02
4	312.5	3995.47	0.0105	408,569.3	0.01
5	356.0	101,586.37	0.0108	42.55×10^8	3.99×10^{-4}
6	384.5	-	0.0111	-	-
Terty-Amyl Alcohol					
1	186.2	1077.25	0.0085	36,440.3	0.030
2	257.5	3914.92	0.0090	460,555.1	0.009
3	326.7	7717.00	0.0096	1.65×10^6	0.005
4	390.5	14,575.69	0.0102	5.44×10^6	0.003
5	443.7	-	0.0106	-	-

TABLE 6: Values of η and k_1 Calculated From Experimental Data

obtained following this procedure for two of the odorants, propionic acid and tert-amyl alcohol. The following comments may be made on the basis of the results presented in Tables 5 and 6:

a. On the basis of the poor agreement between $(\frac{W}{F_{Ao}})_{exp.}$ and $(\frac{W}{F_{Ao}})_{calc.}$, the assumption of <u>external mass transfer control</u> is not valid for either odorant at the lower range of temperature. In fact, at the lowest temperature levels, the assumption of <u>chemical reaction and internal diffusion control</u> is more appropriate as can be seen by comparing values of ηk_1 reported in the last two columns of Table 5*.

b. As temperature is progressively increased, the relative importance of mass transfer resistance increases as indicated by the improving agreement between $(\frac{W}{F_{Ao}})_{exp.}$ and $(\frac{W}{F_{Ao}})_{calc.}$ shown in Table 5. At the highest temperature levels with both odorants, a design equation corresponding to <u>mass transfer control</u> [Equation 4], is the

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*Doty [5], in his design procedures, uses the assumption of mass transfer control. Presumably, he intends his procedure to be applicable only for high temperature conditions.

correct one to use. A value of $(\frac{W}{F_{Ao}})_{calc.}$ higher than $(\frac{W}{F_{Ao}})_{exp.}$ is obtained for runs 6 and 5 for propionic acid and tert-amyl alcohol respectively. This is an anomoly and reflects basic uncertainties in conversion figures when the reactions approach completion. For these two runs it is not possible to arrive at physically realistic ηk_1 for the neither controls assumption.

c. The dependence of ηk_1 values on temperature is shown in Figures 8 and 9, Appendix V. The activation energies corresponding to the chemical reaction and internal diffusion control assumption are 15,000 and 6,100 cal/gm mole for propionic acid and tert-amyl alcohol respectively. The neither controls assumption activation energy values are 23,458 and 3,654 cal/gm mole.

d. The catalyst pellet operates basically in the Knudsen diffusivity range for all practical purposes. The values of ϕ_c are all high, allowing one to use an inverse approximation for effectiveness factor [Equation 16]. The low values of η, shown in the last column of Table 6, indicate high intraparticle resistance to progress of the reaction. The fact that acceptable rates are still obtained is indicative of the high activity of the platinum catalyst.

e. The dependence of the "true" kinetic constant, k_1, on temperature is shown in Figure 10, Appendix V. The resulting values of "true" activation energy are 44,100 cal/gm mole for propionic acid and 13,864 cal/gm mole for tert-amyl alcohol. A comparison with the apparent activation energies corresponding to Figures 8 and 9, Appendix V, shows the influence of intraparticle diffusion on the activation energy. The reduction in activation energy due to intraparticle diffusion has been observed with many catalytic systems.

VI. CONCLUSIONS

The following conclusions may be drawn from the experience gained during this investigation:

i. From the experimental results obtained, it is apparent that catalytic oxidation of odors does indeed show promise. The applicability of the method for a wide variety of odorants and operating conditions is obvious.

ii. The catalyst used in this study, Pt on alumina, was in operation for over 130 hours with a number of different compounds with no apparent loss of activity*. Analysis of the experimental results showed that although the effectiveness factor, η, of the catalyst was low, the values for the kinetic coefficient, k_1, were extremely high, which indicates a high catalytic activity. No poisoning was apparent, even when nitrogenous compounds were passed through the catalytic bed.

iii. The application of results of this investigation to the industrial situations is apparent. Consider, as an example, an industrial air stream at 40,000 scfm containing 0.00107 mole fraction of propionic acid. By using the experimental value of W/F_{Ao} of 403.36 $\frac{(\text{lb catalyst hr})}{\text{lb mole}}$ and a catalyst density of 90 lb/ft^3, a charge of 30.4 ft^3 of catalyst is

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*The actual life time for the catalyst, not established in this study, would have to be at least 15,000 hours for economic viability [6].

necessary. Alternately, using the residence time of 0.043 seconds, a charge of 28.7 ft^3 is arrived at. Therefore, assuming that a charge of 30 ft^3 is required, and a cost of $450/$ft^3$ [4,5], the catalyst cost is $13,500.

iv. The energy saving potential of the catalytic technique is also rather obvious. By using the same parameters as in the above example, the cost of fuel to raise the gases from 25°C to 357°C (reaction temperature) is calculated to be $311,472/year or $1.08/(1000 scfm hr), but if the hot exit stream is used to raise the feed temperature, energy costs are reduced to $88,560/year or $0.31/(1000 scfm hr). The details of these calculations are given in Appendix V. In general, lower preheat requirements for catalytic systems should lead to substantial savings in fuel requirements.

v. The results obtained in the present work are sufficiently promising to suggest that further investigations be undertaken. In particular, one could examine the effects on odor reduction levels of

a. changes in space velocities

b. changes in catalyst composition and support.

In addition, work could be done with odors that are either synthetic mixture of pure odorants or are in fact actual odors from industrial sources.

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APPENDIX I

Catalyst Properties
and
Physical Properties
of the Odorants

A. Physical Properties of the Catalyst

Type:	Platinum Oxidation Catalyst Girdler Chemical, Inc., P. O. Box 337, Louisville, Kentucky 40201, U.S.A.; Girdler T-309B
Support:	Gamma Alumina
Pt Content:	0.5%
Surface Area:	190 m^2/gm
Size:	1/8 inch x 1/8 inch pellets (cylindrical)
Pore Volume:	0.05 cc/gm (Hg Porosimeter)
Pore Diameter:	1.2 - 0.035 Microns (Hg Porosimeter)
Mean Crystalline Size:	64 Å
Void Space:	67% (random packing)
CCl_4 Pore Volume:	0.27 at 800Å, 0.25 at 140Å

B. Physical Properties of Odorants [14]

1. Acetone ($CH_3CO\ CH_3$)

Other names:	dimethyl ketone, ketone propane, propanone
Molecular weight:	58.08
Melting Point:	-94.6°C
Boiling Point:	56.48°C
Flash Point:	0°F
Lower Explosion Limit:	2.6%

Upper Explosion Limit:	12.8%
Density:	0.7972 at 15°C
Autoignition Temperature:	1000°F
Vapor Pressure:	400 mm at 39.5°C
Vapor Density:	2.0
Threshold Limit Values (ACGIH[1]):	1000 ppm in air, or 2400 mg/m^3 of air
Fire Hazard:	dangerous when exposed to heat or flame

2. Acrolein (CH_2CHCHO)

Other Names:	propenal, acrylic aldehyde, allyl aldehyde, acralaldehyde
Molecular Weight:	56.06
Melting Point:	-87.7°C
Boiling Point:	52.5°C
Flash Point:	<0°F
Density:	0.841 at 20°/4°C
Autoignition Temperature:	unstable (532°F)
Lower Explosive Limit:	2.8%
Upper Explosive Limit:	31%

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[1] American Conference of Government and Industrial Hygienists

Vapor Density:	1.94
Threshold Limit Value (ACGIH):	0.1 ppm in air, or 0.25 mg/m^3 of air
Fire Hazard:	dangerous when exposed to heat or flame; can react vigorously with oxidizing materials
Explosion Hazard:	unknown

3. Tert-Amyl Alcohol $(CH_3CH_2(CCH_3)OHCH_3)$

Other Names:	dimethyl ethyl carbinol, 2-methyl-2-butanol
Molecular Weight:	88.15
Melting Point:	-11.9°C
Boiling Point:	101.8°C
Flash Point:	67°F
Density:	0.809 reference not specified
Autoignition Temperature:	819°F
Vapor Pressure:	10mm at 17.2°C
Vapor Density:	3.03
Fire Hazard:	dangerous when exposed to heat or flame, can react with oxidizing materials

4. Benzene (C_6H_6)

Other Names:	benzol, phenyl hydride, coal naphtha
Molecular Weight:	78.11
Melting Point:	5.51°C
Boiling Point:	80.093°C-80.094°C
Flash Point:	12°F
Density:	0.8794 at 20°C
Autoignition Temperature:	1044°F
Lower Explosion Limit:	1.3%
Upper Explosion Limit:	7.1%
Vapor Pressure:	100 mm at 26.1°C
Vapor Density:	2.77
Threshold Limit Value (ACGIH):	25 ppm in air, 80 mg/m^3 of air
Fire Hazard:	dangerous when exposed to heat or flame, can react vigorously with oxidizing materials
Spontaneous Heating:	No
Explosion Hazard:	moderate, when its vapor is exposed to flame. Use with adequate ventilation

5. Butanol ($CH_3CH_2CH_2CH_2OH$)

Other Names;	butyl alcohol
Molecular Weight:	74.12
Boiling Point:	117.5°C
Lower Explosion Limit:	1.4%
Upper Explosion Limit:	11.2%
Freezing Point:	-88.9°C
Flash Point:	84°F
Density:	0.80978 at 20°/4°C
Autoignition Temperature:	689°F
Vapor Pressure:	5.5mm at 20°C
Vapor Density:	2.55
Threshold Limit Values (ACGIH):	100 ppm in air or 303 mg/m^3 of air
Fire Hazard:	Dangerous when exposed to flame or heat
Spontaneous Heating:	No
Explosion Hazard:	Moderate when exposed to flame, can react with oxidizing materials.

6. Iso-Butanol ($CH_3CH_2CHOHCH_3$)

Other Names;	isopropyl carbinol, 2-methyl-propanol-1, iso-butyl alcohol
Molecular Weight:	74.12
Boiling Point:	107.9°C
Flash Point:	82°F
Lower Explosion Limit:	1.7%
Upper Explosion Limit:	10.9% at 212°F
Freezing Point:	-108°C
Density:	0.805 at 20°/4°C
Autoignition Temperature:	800°F
Vapor Pressure:	10 mm at 21.7°C
Vapor Density:	2.55
Threshold Limit Value (ACGIH):	100 ppm in air, 300 mg/m^3 of air
Fire Hazard:	moderate, when exposed to heat or flame
Explosion Hazard:	moderate, in form of vapor when exposed to heat or flame

7. Butyraldehyde ($CH_3(CH_2)_2CHO$)

Other Names:	butanal, butyric aldehyde, n-butyl aldehyde
Molecular Weight:	72.1
Melting Point:	-100°C

Boiling Point:	75.7°C
Flash Point:	20°F
Density:	0.817 at 20°/4°C
Autoignition Temperature:	446°F
Vapor Density:	2.5
Lower Explosion Limit:	2.5%
Fire Hazard:	dangerous when exposed to heat or flame, can react with oxidizing materials
Spontaneous Heating:	No

8. Butyric Acid ($CH_3(CH_2)_2COOH$)

Other Names:	butanoic acid, n-butyric acid, ethyl acetic acid, propyl formic acid
Molecular Weight:	88.11
Melting Point:	-7.9°C
Boiling Point:	163.5°C
Flash Point:	161°F
Freezing Point:	-5.5°C
Density:	0.959 at 20°/20°C
Autoignition temperature:	846°F
Vapor Pressure:	0.43 mm at 20°C
Vapor Density:	3.04
Lower Explosion Limit:	2%

Upper Explosion Limit: 10%

Fire Hazard: moderate when exposed to heat or flame, can react with oxidizing material

Spontaneous Heating: No

9. Trans-Cinnamaldehyde ($C_6H_5CHCHCHO$)

Other Names: cinnamic aldehyde, 3-phenyl propenal, cinnamyl aldehyde, β-phenylacrolein

Molecular Weight: 132.17

Density: 1.048 - 1.052

Melting Point: -7.5°C

Boiling Point: 253°C

10. Crotonaldehyde ($CH_3CHCHCHO$)

Other Names: 2-butenal, crotonic aldehyde, β-methylacrolein

Molecular Weight: 70.09

Boiling Point: 104°C

Freezing Point: -76°C

Flash Point: 55°F

Lower Explosion Limit: 2.1%

Upper Explosion Limit: 15.5%

Density: 0.853 at 20°/20°C

Vapor Density:	2.41
Threshold Limit Value (ACGIH):	2 ppm in air, 6 mg/m^3 of air
Fire Hazard:	dangerous, when exposed to heat or flame, can react with oxidizing materials
Spontaneous Heating:	No

11. Cyclohexanone ($CO(CH_2)_4CH_2$)

Other Names:	ketohexamethylene, pimelic ketone
Molecular Weight:	98.14
Melting Point:	-45.0°C
Boiling Point:	155.6°C
Lower Explosion Limit:	1.1% at 100°C
Flash Point:	111°F
Density:	0.9478 at 20°/4°C
Autoignition Temperature:	788°F
Vapor Pressure:	10 mm at 38.7°C
Vapor Density:	3.4
Threshold Limit Value (ACGIH):	50 ppm in air, 200 mg/m^3 of air
Fire Hazard:	moderate when exposed to heat or flame, can react vigorously with oxidizing materials
Explosion Hazard:	slight, in its vapor form, when exposed to flame
Spontaneous Heating:	No

12. Ethyl Acetate ($CH_3COOC_2H_5$)

Other Names:	acetic ether, ethyl ester, ethyl ethanoate
Molecular Weight:	88.10
Melting Point:	-83.6°C
Boiling Point	77.15°C
Lower Explosion Limit:	2.5%
Upper Explosion Limit:	9.0%
Flash Point:	24°F
Density:	0.8946 at 25°C
Autoignition Temperature:	800°F
Vapor Pressure:	100 mm at 27.0°C
Vapor Density:	3.04
Threshold Limit Value (ACGIH):	400 ppm in air, 1400 mg/m^3 of air
Fire Hazard:	dangerous, when exposed to heat or flame, can react vigorously with oxidizing material
Spontaneous Heating:	No
Explosion Hazard:	dangerous, upon exposure to heat or flame

13. n-Hexane ($CH_3(CH_2)_4CH_3$)

Other Names:	hexyl hydride
Molecular Weight:	86.17

Boiling Point:	68.7°C
Lower Explosion Limit:	1.2%
Upper Explosion Limit:	7.5%
Freezing Point:	-95.6°C
Flash Point:	-7°F
Density:	0.6603 at 20°/4°C
Autoignition Temperature:	500°F
Vapor Pressure:	100 mm at 15.8°C
Vapor Density:	2.97
Threshold Limit Value (ACGIH):	500 ppm in air, 1760 mg/m^3 of air
Fire Hazard:	dangerous, when exposed to heat or flame
Spontaneous Heating:	No
Explosion Hazard:	moderate when exposed to heat or flame, can react vigorously with oxidizing materials

14. 3-Methyl-2-Butanone ($CH_3COCH_2CH_3$)

Other Names:	ethylmethyl ketone
Molecular Weight:	72.1
Boiling Point:	79.57°C
Freezing Point:	-85.9°C
Lower Explosion Limit:	1.8%
Upper Explosion Limit:	10%

Flash Point:	22°F
Density:	0.80615 at 20°/20°C
Vapor Pressure:	71.2 mm at 20°C
Autoignition Temperature:	960°F
Vapor Density:	2.41
Threshold Limit Value (ACGIH):	200 ppm in air, 590 mg/m^3 of air
Fire Hazard:	dangerous, when exposed to heat or flame, can react with oxidizing materials
Spontaneous Heating:	No
Explosion Hazard:	moderate, when exposed to flame

15. Phenol (C_6H_5OH)

Other Names:	carbolic acid, phenic acid, phenylic acid
Molecular Weight:	94.11
Melting Point:	40.6°C
Boiling Point:	181.9°C
Flash Point:	175°F
Density:	1.072 (reference not specified)
Autoignition Temperature:	1319°F
Vapor Pressure:	1mm at 40.1°C
Vapor Density:	3.24

Threshold Limit Value (ACGIH):	5 ppm in air, 19 mg/m^3 of air (can be absorbed through the skin)
Fire Hazard:	moderate, when exposed to heat or flame, reacts with oxidizing materials
Spontaneous Heating:	No

16. Propionic Acid (CH_3CH_2COOH)

Other Names:	methylacetic acid
Molecular Weight:	74.1
Melting Point:	-22°C
Boiling Point:	141°C
Density:	0.992 (reference not specified)
Vapor Pressure:	10 mm at 39.7°C
Vapor Density:	2.56
Flash Point:	130°F
Fire Hazard:	moderate, when exposed to heat or flame

17. Iso-Propyl Acetate ($CH_3COOCH(CH_3)_2$)

Molecular Weight:	102.13
Melting Point:	-73°C
Boiling Point:	88.4°C
Lower Explosion Limit:	1.8%
Upper Explosion Limit:	7.8%

Freezing Point:	-69.3°C
Flash Point:	40°F
Density:	0.874 at 20°/20°C
Autoignition Temperature:	860°F
Vapor Pressure:	40 mm at 17.0°C
Vapor Density:	3.52
Threshold Limit Value (ACGIH):	250 ppm in air, 950 mg/m^3 of air
Fire Hazard:	dangerous, when exposed to heat or flame
Spontaneous Heating:	No
Explosion Hazard:	moderate, when exposed to heat or flame, can react vigorously with oxidizing materials

18. Pyridine ($\overline{\mathrm{NCHCHCHCHC}}\mathrm{H}$)

Molecular Weight:	79.10
Boiling Point:	115.13°C
Lower Explosion Limit:	1.8%
Upper Explosion Limit:	12.4%
Freezing Point:	-42°C
Flash Point:	68°F
Density:	0.982
Autoignition Temperature:	900°F

Vapor Pressure:	10mm at 13.2°C
Vapor Density:	2.73
Threshold Limit Value (ACGIH):	5 ppm in air, 15 mg/m^3 of air
Fire Hazard:	dangerous when exposed to heat or flame
Spontaneous Heating:	No
Explosion Hazard:	severe, in form of vapor, when exposed to flame or spark

19. Toluene ($C_6H_5CH_3$)

Other Names:	methylbenzene, phenylmethane, toluol
Molecular Weight:	92.13
Melting Point:	-95°C to -94.5°C
Boiling Point:	110.4°C
Flash Point:	40°F
Lower Explosion Limit:	1.27%
Upper Explosion Limit:	7.0%
Density:	0.866 at 20°/4°C
Autoignition Temperature:	947°F
Vapor Pressure:	36.7 mm at 30°C
Vapor Density:	3.14
Threshold Limit Value (ACGIH):	200 ppm in air, 750 mg/m^3 of air

Fire Hazard:	moderate, when exposed to flame
Spontaneous Heating:	No
Explosion Hazard:	moderately dangerous, when heated, it emits toxic fumes, can react vigorously with oxidizing materials

20. Triethylamine ($(CH_3CH_2)_3N$)

Molecular Weight:	101.19
Melting Point:	-114.8°C
Boiling Point:	89.5°C
Flash Point:	20°F
Density:	0.7229 at 25°/4°C
Vapor Density:	3.48
Lower Explosion Limit:	1.2%
Upper Explosion Limit:	8.0%
Threshold Limit Value (ACGIH):	25 ppm in air, 100 mg/m^3 of air
Fire Hazard:	dangerous, when exposed to heat or flame
Explosion Hazard:	unknown, can react with oxidizing materials

21. Valeraldehyde ($CH_3(CH_2)_3CHO$)

Other Names:	valeral, pentanal, amylaldehyde, valeric aldehyde
Molecular Weight:	86.13
Density:	0.8095 at 20°/4°C
Boiling Point:	102 - 103°C
Freezing Point:	-91°C
Flash Point:	54°F
Vapor Density:	3.0
Fire Hazard:	dangerous when exposed to heat or flame

22. Vinyl Acetate ($CH_3COOCHCH_2$)

Molecular Weight:	86.05
Melting Point	-100.2°C
Boiling Point:	73°C
Flash Point:	18°F
Density:	0.9335 at 20°C
Autoignition Temperature:	800°F
Vapor Pressure:	100 mm at 21.5°C
Lower Explosion Limit:	2.6%
Upper Explosion Limit:	13.4%
Vapor Density:	3.0

Fire Hazard: highly dangerous when exposed to heat or flame

Spontaneous Heating: No

Explosion Hazard: unknown, can react with oxidizing materials

APPENDIX II

Threshold Data for Odorous Compounds Used

	Odorant	Media	Type	Value	Reference
1	Acetone	air	recognition	100 ppm	11
		air	recognition	100 ppm	18
2	Acrolein	air	recognition	0.21 ppm	11
		air	recognition	0.21 ppm	18
		air	detection	1.8 ppm	18
		air	detection	0.038 mg/ℓ	18
		air	detection	4.1 x 10^{-6} g/ℓ	18
3	Amyl Alcohol (Tert) - no data presented				
4	Benzene	air	recognition	4.68 ppm	11
		air	detection	0.0088 mg/ℓ	18
		air	recognition	4.68 ppm	18
5	Butanol (normal)	air	detection	2.86 x 10^{-9} moles/ℓ	18
		air	detection	1.1 x 10^{-13} molecules/cc	18
6	Butanol (Iso)	-	detection	0.0075 ppm	18
7	Butyraldehyde	air	detection	0.0022 mg/ℓ	18
8	Butyric Acid	air	recognition	0.001 ppm	11
9	Cinnamaldehyde (Trans) - no data presented				
10	Crotonaldehyde	air	detection	0.021 mg/ℓ	18
		air	detection	0.13 ppm	18
		air	detection	0.0375 g/ℓ	18
11	Cyclohexanone	air	detection	1.23 x 10^{-5} mg/ℓ	18

continued ...

Odorant	Media	Type	Value	Reference
12 Ethyl Acetate	air	detection	0.686 mg/ℓ	18
	air	detection	0.006 mg/ℓ	18
	air	detection	5.0 ppm	18
13 Hexane (normal) - no data presented				
14 3-Methyl-2-Butanone	air	recognition	10.0 ppm	11
	air	recognition	10.0 ppm	18
15 Phenol	air	recognition	0.047 ppm	11
	air	detection	1.0 ppm	18
	air	recognition	0.047 ppm	18
16 Propionic Acid - no data presented				
17 Propyl (Iso) Acetate - no data presented				
18 Pyridine	air	recognition	0.021 ppm	11
	air	detection	0.032 mg/ℓ	18
	air	detection	0.23 ppm	18
	air	detection	7.4×10^{-4} mg/ℓ	18
	air	recognition	0.021 ppm	18
	air	detection	0.0037 mg/ℓ	18
	air	detection	7.4×10^{-7} g/ℓ	18
	air	detection	0.03 ppm	18
19 Toluene (from coke)	air	recognition	4.68 ppm	11
(from petroleum)	air	recognition	2.14 ppm	11
	air	recognition	4.68 ppm	18
	air	recognition	2.14 ppm	18
20 Triethylamine - no data presented				
21 Valeraldehyde - no data presented				
22 Vinyl Acetate - no data presented				

TABLE 7: Odor Threshold Data of Odorants Used [11, 18]

APPENDIX III

Experimental Data

Odorant	Pressures (psig)		Temperatures (°C)		Ratiotrol Setting	Concentration (ou/ft^3)		Percent Odor Removal
	Rotameter Exit (p2)	Reactor Inlet (p3)	Preheat Exit	Reactor Bed Exit		Inlet	Exit	
Acetone	4.0	3.2	164	231	100	2	5*	(-)
	4.5	3.7	215.5	268	100	2	1	50
	4.6	3.9	268.5	342	100	2	0	100
Acrolein	4.1	3.3	195	277	25	50	20	60
	4.3	3.5	232	293.5	25	50	5	90
	4.5	3.7	273	341.5	25	50	0	100
Tert-Amyl Alcohol	4.9	3.7	136.5	236	100	50	25*	50
	5.1	4.0	196(192)	319(313)	100	50(50)	10(10)	80(80)
	5.6	4.5	264(262)	389.5(387)	100	50(50)	5(5)	90(90)
	5.8	4.7	337(337)	444(441)	100	50(50)	2.5(215)	95(95)
	6.0	4.8	401(395)	486.5(480)	100	50(50)	0(0)	100(100)
Benzene	4.1	3.3	152(145)	208(199)	85	20(20)	10(10)	50(50)
	4.7	3.9	242.5	340	85	20	1	95
	4.9	4.1	313	410	85	20	0	100
n-Butanol	4.3	3.5	196	253.6	70	100	20*	80
	4.7	3.8	233(235)	297.5(298)	70	100(100)	20(20)	80(80)
	4.8	3.9	266(261.5)	316(329)	70	100(100)	10(10)	90(90)
	5.0	4.1	319(320)	366(370)	70	100(100)	1(1)	99(99)
Iso-Butanol	4.5	3.7	166.5	285.5	70	200	500*	(-)
	4.7	3.9	185.5	308	70	200	500*	(-)
	4.9	4.1	250	369	70	200	200*	0
	5.2	4.4	301	412	70	200	100*	50
	5.5	4.7	355	459.5	70	200	50*	75
	5.7	4.9	415	500	70	200	0	100
Butyraldehyde	4.0	3.2	138.5	190.5	70	200	250*	(-)
	4.3	3.5	156(160)	264(265)	70	200(200)	100(100)	50(50)
	4.5	3.8	211(210)	317(316)	70	200(200)	40(40)	80(80)
	4.6	3.9	240.5(251.5)	342(355)	70	200(200)	20(20)	90(90)
	5.0	4.1	326	410	70	200	1	>99

TABLE 8: Experimental Data

continued ...

Butyric Acid	4.0	3.2	134	164.5	70	50	25	50
	4.4	3.6	167(175)	192(200)	70	50(50)	20(20)	60(60)
	5.0	4.1	193.5	221.5	70	50	2	96
	5.2	4.4	222	271	70	50	0	100
Trans-Cinnamaldehyde	4.15	3.35	182	234.5	80	100	25	75
	4.3	3.5	213	270	80	100	5	95
	4.7	4.0	280	335	80	100	1	99
Crotonaldehyde	3.8	3.0	132	194	80	250	100	60
	4.4	3.6	200	278	80	250	50	80
	4.9	4.1	256	323	80	250	25	90
	5.2	4.4	328	399.5	80	250	20	92
	6.0	5.1	359	424.5	80	250	5	98
	6.1	5.1	381	443	80	250	1	>99
Cyclohexanone	4.5	3.7	132	199	70	250	200	20
	4.7	3.8	193(190.5)	289.5(288)	70	250(250)	50(50)	80(80)
	5.1	3.9	248(245)	364.5(365)	70	250(250)	20(20)	92(92)
	5.4	4.2	331(329.5)	420(420.5)	70	250(250)	20(20)	92(92)
	5.7	4.8	385	463	70	250	1	>99
Ethyl Acetate	3.8	3.0	103	145	100	100	250*	(-)
	4.0	3.2	158	208	100	100(100)	333*	(-)
	4.7	3.9	222(220)	320(320)	100	100(100)	200*(200*)	(-)(-)
	5.2	4.4	258(260)	391(394.5)	100	100(100)	50*(50*)	50(50)
	5.3	4.5	301	422	100	100	33*	67
	5.7	4.9	372.5	481	100	100	5	95
	5.7	4.9	393	100	100	100	0	100
n-Hexane	3.75	2.9	80	80	70	20	20	0
	3.9	3.1	123(125)	185(190)	70	20(20)	10(10)	50(50)
	4.5	3.7	170	281.5	70	20	1	95
	4.6	3.8	193	300	70	20	0	100
3-Methyl-2-Butanone	4.1	3.2	133	200	100	20	100*	(-)
	4.8	3.9	196.5	329	100	20	50*	(-)
	5.1	4.3	252.5	373.5	100	20	20*	0
	5.4	4.6	330	437.5	100	20	10*	50
	6.3	5.2	399.5	482	100	20	0	100

TABLE 8: Experimental Data

continued ...

Phenol	3.9	3.1	134	134	90	200	200	0
	4.2	3.4	164.5(165)	221(220.5)	90	200(200)	100(100)	50(50)
	4.5	3.7	217(215)	295.5(296)	90	200(200)	50(50)	75(75)
	4.8	4.0	284	355	90	200	25	87.5
	4.9	4.1	368	427.5	90	200	1	>99
Propionic Acid	3.5	2.6	120	156	50	250	250*	0
	4.0	2.8	181(182)	268(269)	50	250(250)	200(200)	20(20)
	4.3	3.1	243(245)	325(324)	50	250(250)	100(100)	60(60)
	4.5	3.3	268	357	50	250	50	80
	4.7	3.5	323(320)	389(385)	50	250(250)	2.5(2.5)	99(99)
	4.9	3.7	350	419	50	250(250)	2.5(2.5)	99(99)
Iso-Propyl Acetate	3.9	3.1	114	156	100	50	50*	0
	4.5	3.7	184	286.5	100	50	25	50
	5.0	4.3	256	355.5	100	50	20	60
	5.3	4.5	330	423	100	50	0	100
Pyridine	3.2	2.4	109	139	70	500	500**	0
	3.4	2.6	165	210	70	500	333**	33
	3.8	3.0	233(240)	309(310.5)	70	500(500)	250**(250**)	50(50)
	4.3	3.5	326.5(331.5)	407(408.5)	70	500(500)	100**(100**)	80(80)
	4.5	3.8	391	462	70	500	25**	95
	4.8	4.0	463	510	70	500	0	100
Toluene	3.8	3.0	96	96	100	50	50	0
	4.1	3.3	120(126)	190.5(190)	100	50(50)	25(25)	50(50)
	4.3	3.5	130(138.5)	246.5(247)	100	50(50)	20(20)	60(60)
	4.7	3.9	149	326	100	50	5	90
	4.7	3.9	165.5	336	100	50	0	100
Triethylamine	3.7	3.0	110	110	70	100	100	0
	4.1	3.5	145	162	70	100	67	33
	4.7	4.0	168(165)	227(224.5)	70	100(100)	50(50)	50(50)
	4.7	4.2	233(234.5)	347(356)	70	100(100)	100**(100**)	0(0)
	4.9	4.2	301	403	70	100	100**	0
	5.2	4.6	389.5	469	70	100	100**	0
	5.4	4.7	451	510	70	100	100**	0

TABLE 8: Experimental Data

continued ...

Valeraldehyde	4.3	3.5	152	250	70	500	250	50
	4.5	3.7	179	292.5	70	500	100	80
	4.75	3.5	206.5	323.5	70	500	50	90
	5.2	4.5	293	394	70	500	10	88
	5.4	4.7	315	419	70	500	10	>99
Vinyl Acetate	3.8	3.0	132	219	100	200	250*	(-)
	4.5	3.8	185 (190)	306 (310.5)	100	200 (200)	100 (100)	50 (50)
	4.9	4.1	251	356.5	100	200	20	90
	5.3	4.5	333	429	100	200	1	>99

T. Pressures are corrected to calibration (Appendix IV). Pressure at outlet to reactor remained constant at 0.9 psig.

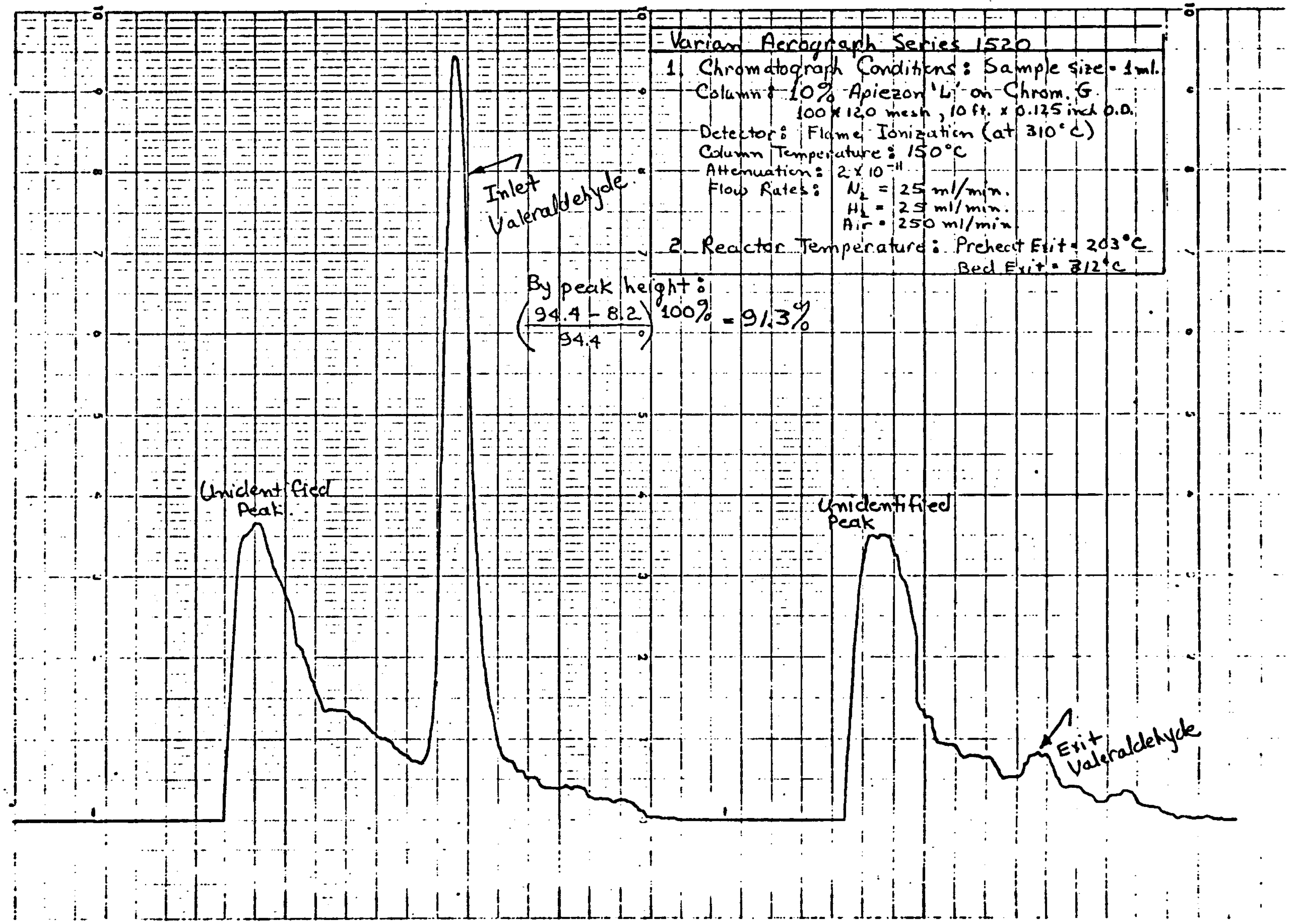
* - Odor of a different nature than at inlet, usually more sour and sharp

** - Odor of a cyanide nature

*** - Odor characteristic of NO_x

( ) - Replicate runs

TABLE 8: Experimental Data



Varian Aerograph Series 1520

1. Chromatograph Conditions: Sample size = 1 ml.
Column: 10% Apiezon 'L' on Chrom. G
100 x 120 mesh, 10 ft. x 0.125 inch O.D.
Detector: Flame Ionization (at 310°C)
Column Temperature: 150°C
Attenuation: 2×10^{-11}
Flow Rates: N_2 = 25 ml/min.
H_2 = 25 ml/min.
Air = 250 ml/min
2. Reactor Temperature: Preheat Exit = 203°C
Bed Exit = 312°C

By peak height:

$$\left(\frac{94.4 - 8.2}{94.4}\right) 100\% = 91.3\%$$

FIGURE 3: Chromatogram for Valeraldehyde at 203°C Preheat Temperature

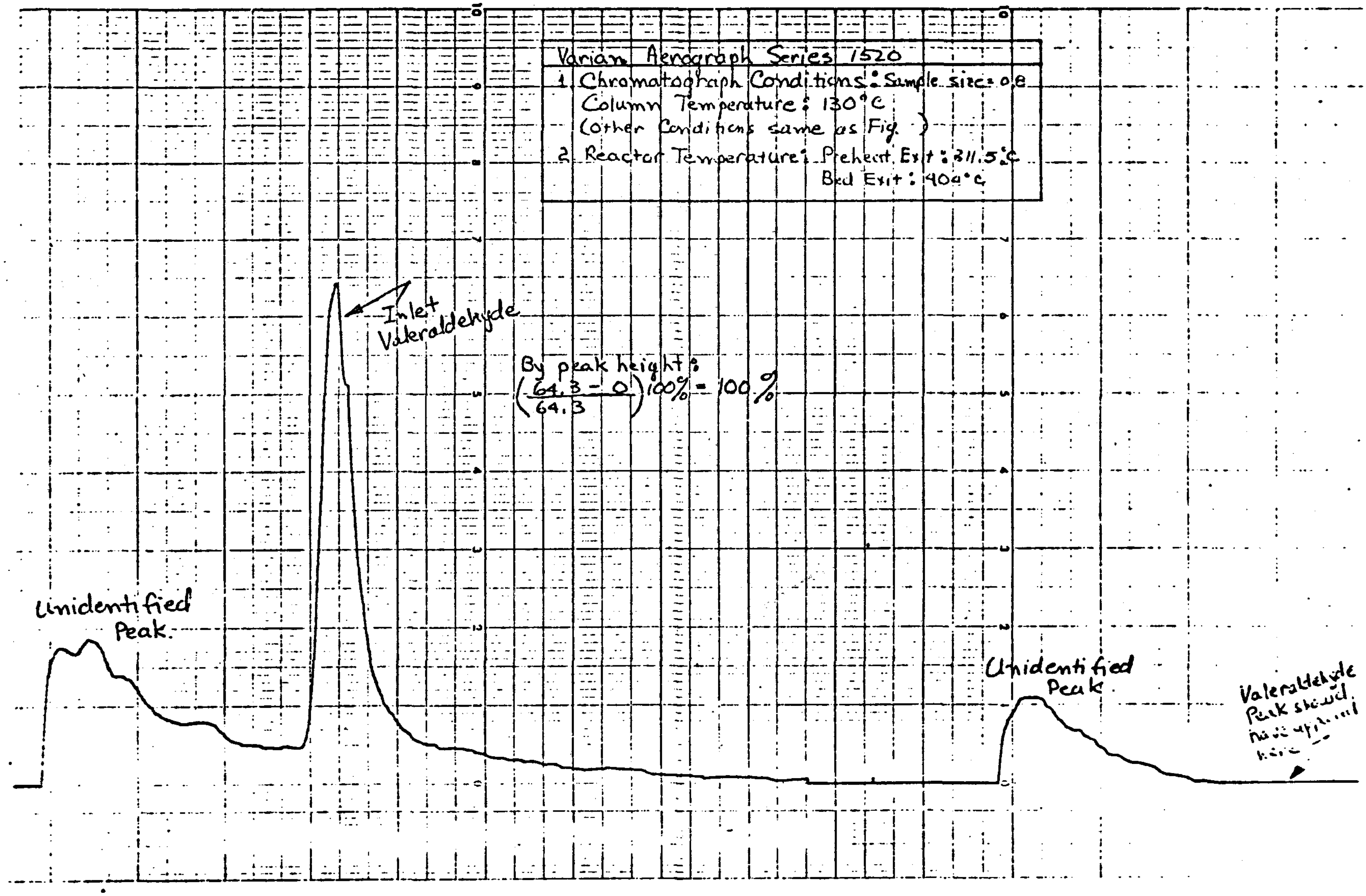


FIGURE 4: Chromatogram for Valeraldehyde at 311.5°C Preheat Temperature

APPENDIX IV

Calibration Curves

Rotameter Setting	Q scfm by Dry Test at 60°F and 14.7 psia	W lb/min	Rotameter Pressure (psig)
10	0.477	0.0364	0.33
15	0.651	0.0497	0.85
20	0.845	0.0645	1.45
25	1.036	0.0790	2.13
30	1.243	0.0948	3.05
35	1.450	0.1106	4.3
40	1.686	0.1286	5.75
45	1.956	0.1492	7.65
50	2.214	0.1689	9.95
55	2.525	0.1927	14.0
60	2.813	0.2146	17.0

TABLE 9: Rotameter Calibration Data

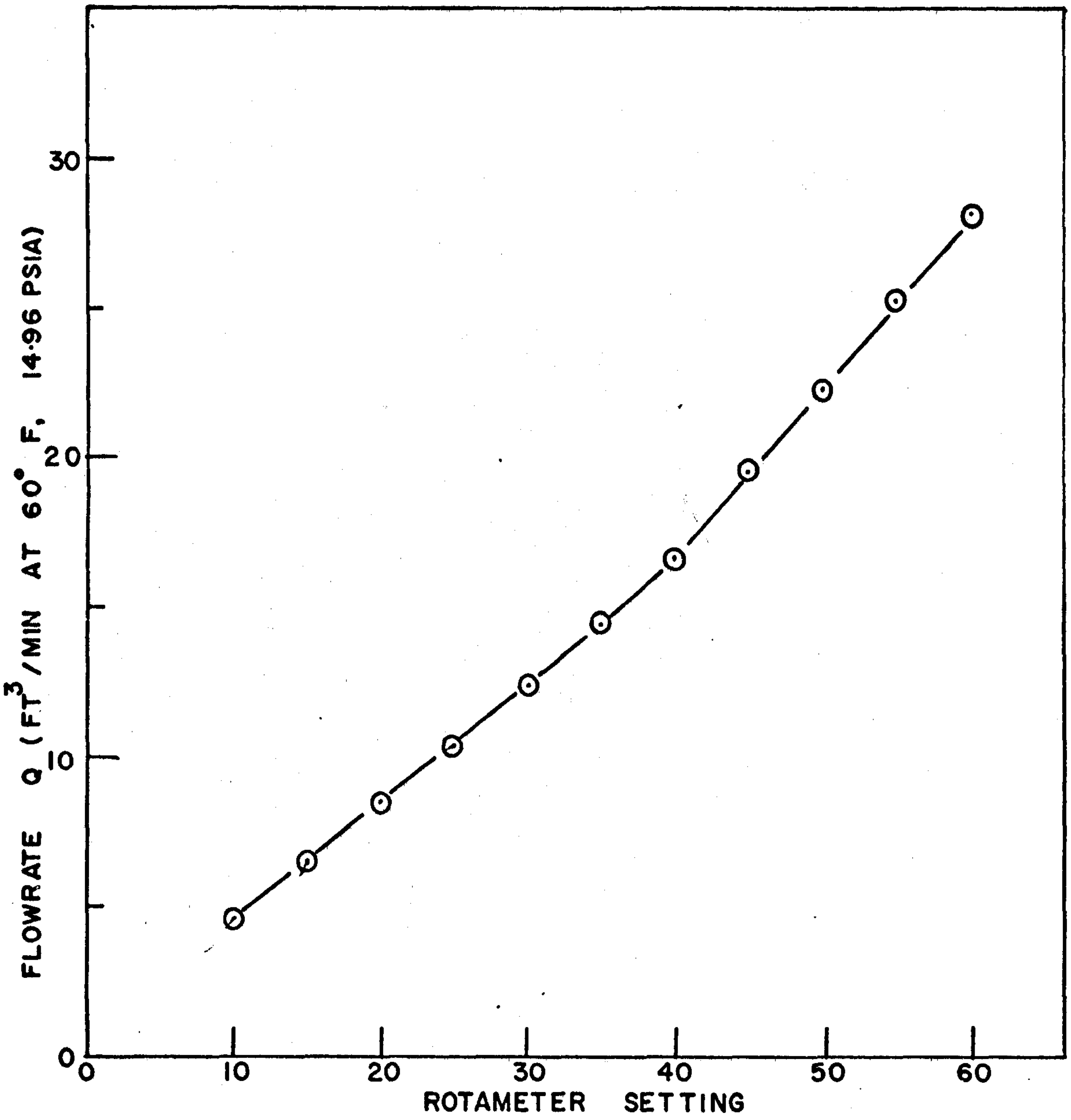


FIGURE 5 ROTAMETER CALIBRATION CURVE

Actual Pressure (Gauge Tester) (psi)	Gauge 2 (P2) (psi)	Gauge 3 (P3) (psi)
0	0	0
0.5	0.47	0
1.0	1.19	0.17
1.5	1.75	0.69
2.0	2.19	1.5
2.5	2.69	2.0
3.0	3.19	2.5
3.5	3.69	3.19
4.0	4.19	3.625
4.5	4.69	4.19
5.0	5.16	4.75
6.0	6.125	5.875
7.0	7.09	7.125
8.0	8.09	8.25
9.0	9.06	9.31
10.0	9.94	13.0
15.0	16	30.0
20.0	20.1	30.0

TABLE 10: Calibration Data for Pressure Gauges

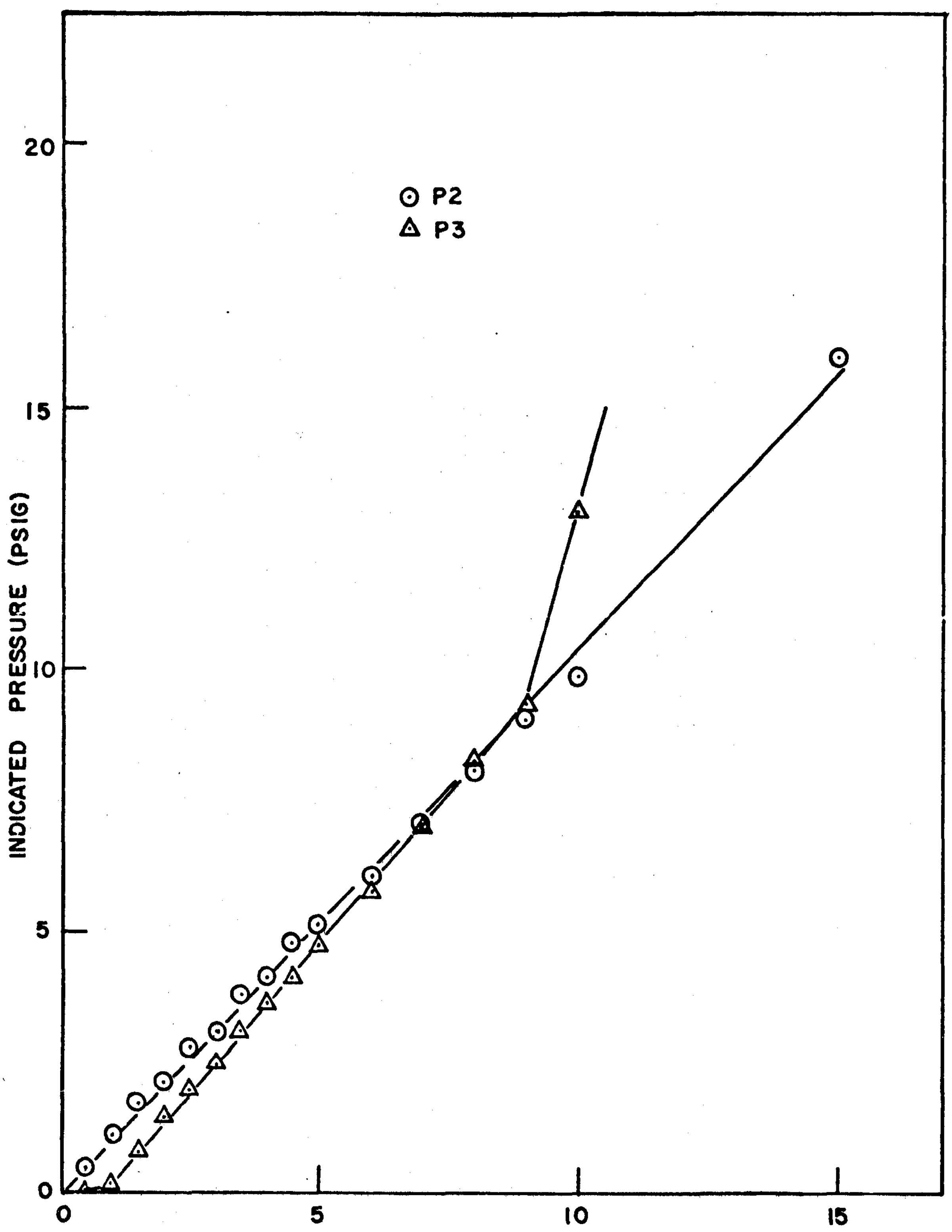


FIGURE 6 PRESSURE GAUGE CALIBRATION CURVES

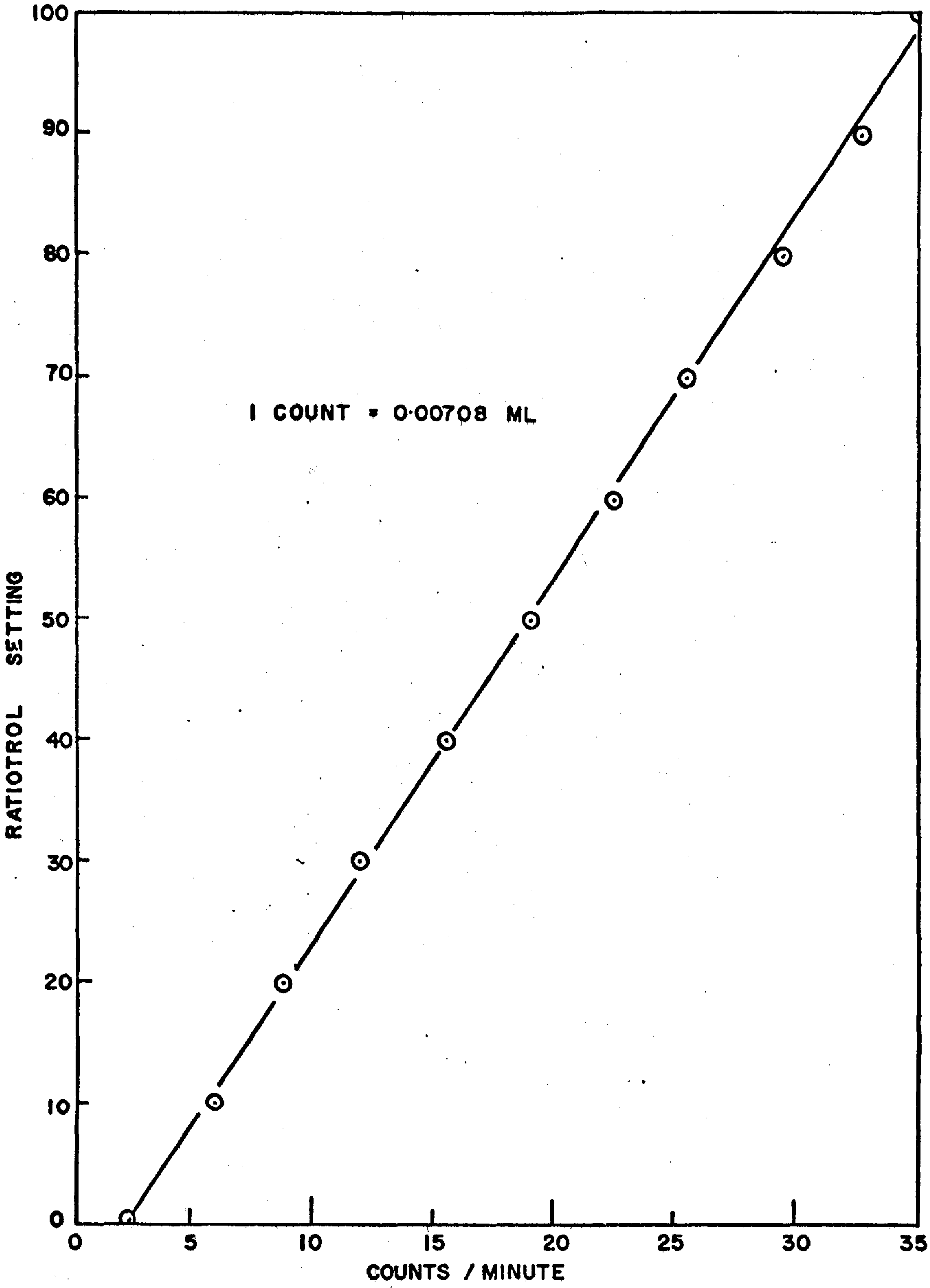


FIGURE 7 RATIOTROL CALIBRATION

APPENDIX V

Sample Calculations

1. Determination of Space Velocity at Standard Conditions (60°F and 14.7 psia)

Rotameter Setting = 36

Q_{STD} = corresponding flow = 1.49 scfm (from calibration curve)

A = cross-sectional area of reactor = 0.0144 ft^2

b = thickness of catalyst bed = 1.33 inches = 0.111 ft

ε = void space = 0.67

$$v = \text{velocity} = \frac{1.49\ \text{ft}^3/\text{min}}{0.0144\ \text{ft}^2} = 103.47\ \text{ft/min} = 1.725\ \text{ft/sec}$$

Considering the void space, velocity becomes:

$$v = \frac{1.725\ \text{ft/sec}}{0.67} = 2.574\ \text{ft/sec}$$

Thickness of the bed is 0.111 ft, therefore, residence time, t is:

$$t = \frac{b}{v} = \frac{0.111\ \text{ft}}{2.574\ \text{ft/sec}} = 0.043\ \text{sec}$$

Space velocity is equal to:

$$v_s = \frac{1}{t} = \frac{1}{0.043\ \text{sec}} = 23.189\ \text{sec}^{-1} = 83{,}481\ \text{hr}^{-1}$$

2. Determination of Physical Properties

The following calculations correspond to the 2nd run for propionic acid.

a. Average Pressure

P at inlet = 2.8 psig

P at exit = 0.9 psig

or P_{AVG} = 1.85 psig = 16.55 psia = 1.13 atm

b. Gas Viscosity

From Crane [7], using the chart on page A-5, at a temperature of 224.5°C (436.1°F), viscosity is 0.0265 centipoise or 0.0641 lb/(ft hr).

c. Gas Density

From Crane [7], using the correlation

$$\rho_G = \frac{2.7\ P\ S_G}{T}$$

where

ρ_G = density of the gas, lb/ft^3

P = absolute pressure, psia

S_G = specific gravity of gas with reference to air

T = temperature, °R

Using the values:

$T = 896.1°R$

$S_G = 1.0$

$P = 16.546$ psia

we get $\rho_G = 0.0499$ lb/ft^3

d. Gas Mass Flux

Rotameter setting is 36, which corresponds to 1.49 scfm. Density at the standard conditions (14.696 psia and 60°F) is

$$\rho_{GSTD} = \frac{2.7\ P\ S_G}{T} = 0.0763\ \mathrm{lb/ft^3}$$

Using the equation:

$$G = \frac{Q\ \rho_G}{A}$$

where

G = mass flux; lb/(hr ft^2)

Q = gas volumetric flow, ft^3/hr.

ρ_G = gas density, lb/ft^3

A = column cross-sectional area, ft^2

and substituting

$Q_{STD} = 89.4$ ft^3/hr

$\rho_{GSTD} = 0.0763$ lb/ft^3

$A = 0.0144$ ft^2

we arrive at $G = 473.7$ lb/(hr ft^2)

e. Diffusivity

The Enskog-Chapman correlation [17] is used. The equation is:

$$\mathcal{D}_{AB} = 0.0018583 \frac{T^{3/2} \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2}}{P_t \, \sigma_{AB}^2 \, \Omega_{AB}}$$

where

$\mathcal{D}_{AB}$ = diffusivity coefficient, cm^2/sec

T = temperature, °K

M_A = molecular weight of species A, gm/gm mole

M_B = molecular weight of species B, gm/gm mole

P_t = total pressure, atm

σ_{AB} = collision diameter for the molecular pair A-B

Ω_{AB} = collision integral, which could be unity if the molecules were rigid spheres, and is a function of $k_B T / \varepsilon_{AB}$ for real gases

k_B = Boltzmann's constant
= 1.3805×10^{-16} erg/(molecule °K)

ε_{AB} = Lennard-Jones potential energy function for the molecular pair AB

First calculate σ_{AB}, where

$$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$$

$$\sigma_B(\text{air}) = 3.617\ \text{Å}$$

$$\sigma_A(C_3H_6O_2) = 1.18\ V_b^{1/3}$$

where

V_b = molecular volume per mole, cm^3/gm mole

V_b is estimated by adding incremental atomic volumes, using the values from Smith [17]

3 Carbons = 3(14.8) = 44.4

6 Hydorgen = 6(3.7) = 22.2

2 Oxygen in acids = 2(12) = 24.0

Sum of increments = 90.6

or

$$V_b = 90.6\ cm^3/\text{gm mole}$$

Using

$$\sigma_A = 1.18\ V_b^{1/3}$$

$$\sigma_A = 5.3\ \text{Å}$$

Now $$\sigma_{AB} = \frac{3.617 + 5.3}{2} = 4.46\ \text{Å}$$

Now to calculate Ω_{AB}, from Smith [17]:

$$\frac{\varepsilon_B}{k_B} = 97°K \text{ for air.}$$

Using the correlation in Reid and Sherwood [12],

$$\frac{\varepsilon_A}{k_B} = 0.75\ T_c$$

where

T_c = critical temperature, °K.

For propionic acid

$$T_c = 612.7°K\ [12]$$

Therefore

$$\varepsilon_A/k_B = (0.75)(612.7°K) = 459.525\ °K$$

From Smith [17]

$$\varepsilon_{AB} = (\varepsilon_A \varepsilon_B)^{1/2}$$

$$\frac{\varepsilon_{AB}}{K_B} = 211.13\ °K$$

Using T = 224.5°C = 497.5°K

$$\frac{k_B T}{\varepsilon_{AB}} = \frac{k_B (T)}{211.13\ k_B} = \frac{497.5}{211.13} = 2.36$$

Using Table 11-1, Reid and Sherwood [12]:

$$\text{at} \quad \frac{k_B T}{\varepsilon_{AB}} = 2.36, \quad \Omega_{AB} = 1.019$$

Substituting into equation

$$\mathcal{D}_{AB} = 0.0018583 \, \frac{T^{3/2} \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2}}{P_t \, \sigma_{AB}^2 \, \Omega_{AB}}$$

where

$$T^{3/2} = (497.5)^{3/2} = 1.11 \times 10^4$$

$$\left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2} = \left(\frac{1}{28.95} + \frac{1}{74.1}\right)^{1/2} = 0.219$$

$$P_t = 1.13 \text{ atm}$$

$$\sigma_{AB}^2 = (4.46)^2 = 19.89$$

$$\Omega_{AB} = 1.019$$

Therefore $\mathcal{D}_{AB} = 0.1972 \text{ cm}^2/\text{sec} = 0.7673 \text{ ft}^2/\text{hr}$

f. Volumetric Flow Rate at Column Conditions

Using the equation:

$$Q = \frac{GA}{\rho_G}$$

where

Q = volumetric flow rate, ft^3/hr

G = mass flux, $lb/(ft^2\ hr)$

A = cross-sectional area, ft^2

ρ_G = gas density at column conditions, lb/ft^3

Values are:

G = $473.7\ lb/(ft^2\ hr)$

A = $0.0144\ ft^2$

ρ_G = $0.0499\ lb/ft^3$

Therefore

$$Q = \frac{(473.7)(0.0144)}{(0.0499)} = 136.7\ ft^3/hr$$

g. <u>Concentration of Gas Stream Entering the Reactor</u>

Using the equation

$$C_{Ao} = F_{Ao}/Q$$

where

C_{Ao} = concentration of odorant in the gas stream, $\frac{lb\ moles\ A}{ft^3}$

F_{Ao} = number of moles of A entering in the gas stream per unit time, $\frac{lb\ moles\ A}{hr}$

Q = volumetric flow rate, ft^3/hr

It is assumed that all the liquid entering goes into the gas phase.

Ratiotrol setting = 50

From the calibration curve, (Appendix IV), this corresponds to 19 counts/minute on the counter. One count = 0.00708 ml.

$$\text{Therefore feed rate} = (0.00708 \frac{\text{ml}}{\text{count}})(\frac{19 \text{ counts}}{\text{min}})$$

$$= 0.1345 \frac{\text{ml } C_3H_6O_2}{\text{min}}$$

Density = 0.992 gm/cm^3 (Appendix I)

$$F_{AO} = \frac{0.1345 \frac{\text{ml}}{\text{mt}}\ 0.992 \frac{\text{gm}}{\text{ml}} \frac{1}{454} \frac{\text{lb}}{\text{gm}} * 60 \frac{\text{mt}}{\text{nr}}}{74.1 \text{ lb/lb mole}}$$

$$= 2.38 * 10^{-4} \frac{\text{lb mole A}}{\text{hr}}$$

Therefore

$$C_{Ao} = \frac{2.38 \times 10^{-4} \frac{\text{lb mole A}}{\text{hr}}}{136.7 \text{ ft}^3/\text{hr}}$$

$$= 1.74 \times 10^{-6} \frac{\text{lb moles A}}{\text{ft}^3}$$

h. The foregoing calculations have been completed for the experimental runs for propionic acid and tert-amyl alcohol. All calculations were performed using the same correlations and equations. Table 11, summarizes these results.

3. Determination of Flow Constants, Mass Transfer and Reaction Rate Constants (using second run for Propionic Acid)

a. Reynolds Number

Reynolds number for the flow through packed beds may be defined by [17]

$$Re = \frac{d_p G}{\mu_G}$$

where

Re = Reynold number, dimensionless

d_p = equivalent diameter, ft

G = mass flux, lb/(hr ft^2)

μ_G = gas viscosity, lb/(ft hr)

First we must calculate the equivalent diameter for 1/8 inch by 1/8 inch cylindrical pellets according to [17]

$$\pi d_p^2 = \pi d L + \frac{2\pi d^2}{4}$$

where

d = diameter of cylinder, ft

L = length of cylinder, ft

d_p = equivalent diameter, ft

Run #	T_{AVG} (°C)	$\frac{1}{T}$ (10^{-3} °K)	P_{AVG} (atm)	μ_G (lb/fthr)	ρ_G (lb/ft^3)	$\mathcal{D}_{AB}$ (ft^2/hr)	G (lb/ft^{2}hr)	Q (ft^3/hr)	C_{A_o} *10^6 ($\frac{\text{lb moles}}{\text{ft}^3}$)	X_{A_e}
Propionic Acid										
1	138	2.4	1.11	0.0569	0.0595	0.5512	473.7	114.6	2.08	0
2	224.5	2.0	1.13	0.0641	0.0499	0.7673	473.7	136.7	1.74	0.2
3	284	1.8	1.14	0.0692	0.0451	0.9371	473.7	151.2	1.57	0.6
4	312.5	1.7	1.14	0.0716	0.0429	1.022	473.7	159.0	1.50	0.8
5	356	1.6	1.15	0.0757	0.0403	1.150	473.7	169.3	1.41	0.99
6	384.5	1.5	1.16	0.0779	0.0389	1.235	473.7	175.4	1.36	1.0 (0.999)*
Tert-Amyl Alcohol										
1	186.25	2.2	1.16	0.0610	0.0556	0.5729	473.7	122.7	2.45	0.5
2	257.5	1.9	1.17	0.0673	0.0486	0.7253	473.7	140.4	2.14	0.8
3	326.75	1.7	1.18	0.0731	0.0434	0.8967	473.7	157.2	1.91	0.9
4	390.5	1.5	1.19	0.0784	0.0395	1.062	473.7	172.4	1.74	0.95
5	443.75	1.4	1.19	0.0823	0.0823	1.215	473.7	186.4	1.61	1.0 (0.999)*

* Value used in calculations

TABLE 11: Physical Properties and Operating Conditions

appropriate substitution leads to

$$d_p = 0.0128 \text{ ft}$$

Using $d_p = 0.0128$ ft

$$G = 473.7 \text{ lb/(ft}^2\text{hr)}$$

$$\mu_G = 0.0641 \text{ lb/ft hr}$$

$$Re = \frac{(0.0128)(473.7)}{0.0641} = 94.6 \text{ or } 95$$

b. j_D Factor

From Figure 10-2, p. 364 in Smith [17] the value is

$$j_D = 0.14 \text{ at } Re = 95$$

c. Schmidt Number

Using the definition

$$Sc = \frac{\mu_G}{\rho_G \mathscr{D}_{AB}}$$

where

Sc = Schmidt number, dimensionless

μ_G = viscosity of gas, lb/(ft hr)

ρ_G = density of gas, lb/ft^3

$\mathscr{D}_{AB}$ = diffusivity, ft^2/hr

Using previously calculated values

$$Sc = \frac{(0.0641)}{(0.0499)(0.7673)} = 1.67$$

d. External Mass Transfer Coefficient

Using the equation

$$k_{m_A} = \frac{j_D G Sc^{-2/3}}{\rho_G}$$

where

k_{m_A} = external mass transfer coefficient, ft/hr

j_D = correlation factor, dimensionless

G = mass flux, lb/(hr ft^2)

ρ_G = gas density, lb/ft^3

Sc = Schmidt number, dimensionless

we get

$$k_{m_A} = \frac{(0.14)(473.7)}{(0.0499)} (1.67)^{-2/3}$$

$$k_{m_A} = 944.24 \text{ ft/hr.}$$

e. Experimental Value of W/F_{Ao}

W = amount of catalyst = 43.6 gm = 0.096 lb

F_{Ao} = amount of odorant entering system per hour

From previous calculations

$$F_{Ao} = 2.38 \times 10^{-4} \ \frac{\text{lb mole A}}{\text{hr}}$$

Therefore $\frac{W}{\cdot F_{Ao}} = \frac{0.096 \text{ lb}}{2.38 \times 10^{-4} \frac{\text{lb mole}}{\text{hr}}} = 403.36 \frac{\text{lb catalyst hr}}{\text{lb mole A}}$

f. Calculation of W/F_{Ao} Under Mass Transfer Control Assumption

On the assumption that mass transfer controls, the following equation [17] may be used:

$$\left(\frac{W}{F_{Ao}}\right)_{calc} = \int_{0}^{X_{Ae}} \frac{dX_A}{k_{m_A} a_m C_{Ao}(1-X_A)}$$

where

$\left(\frac{W}{F_{Ao}}\right)_{calc.}$ = predicted value of $\frac{W}{F_{Ao}}$ assumimg mass transfer controls, $\frac{\text{lb catalyst hr}}{\text{lb mole A}}$

X_A = fractional conversion

X_{Ae} = fractional conversion at exit

a_m = external area of catalyst, ft^2/lb

k_{m_A} = external mass transfer coefficient, ft/hr

C_{Ao} = initial concentration of odorant, $\frac{\text{lb moles A}}{\text{ft}^3}$

We must first calculate a_m [17]:

$$a_m = \frac{(\pi dh) + 2\left(\frac{\pi d^2}{4}\right)}{\left(\frac{\pi d^2 h}{4}\right)(\rho_p)}$$

where

$d = h = .0104$ ft.

$\rho_p = 89$ lb/ft^3 (density of particle)

Therefore $a_m = 6.44$ ft^2/lb

$$\left(\frac{W}{F_{Ao}}\right)_{calc.} = \frac{-\ln(1 - X_{Ae})}{k_{m_A} a_m C_{Ao}}$$

$$\left(\frac{W}{F_{Ao}}\right)_{calc.} = \frac{-\ln(1-0.2)}{(944.24)(6.44)(1.74 \times 10^{-6})} = \frac{0.22314}{0.0106}$$

$$\left(\frac{W}{F_{Ao}}\right)_{calc.} = 21.09 \ \frac{\text{lb catalyst hr}}{\text{lb mole A}}$$

g. <u>Calculation of "lumped" Kinetic Coefficient</u>

(i) Assuming <u>chemical reaction control</u>, the "lumped" kinetic coefficient, ηk_1, may be calculated assuming first order kinetics of oxidation. The equation used is [17]

$$\left(\frac{W}{F_{Ao}}\right)_{exp} = \int_{0}^{X_{Ae}} \frac{dX_A}{\eta k_1 C_{Ao} (1-X_A)}$$

where

$\left(\frac{W}{F_{Ao}}\right)_{exp}$ = experimental value of $\frac{W}{F_{Ao}}$

ηk_1 = "lumped" kinetic coefficient, $\frac{\text{ft}^3}{(\text{lb catalyst hr})}$

or

$$\left(\frac{W}{F_{Ao}}\right)_{exp} = \frac{-\ln(1-X_{Ae})}{\eta\, k_1\, C_{Ao}}$$

or

$$\eta k_1 = \frac{-\ln(1-X_{Ae})}{(F_{Ao})_{exp}\, C_{Ao}}$$

$$\text{Therefore, } \eta k_1 = \frac{-\ln(1-0.2)}{(403.36)(1.74 \times 10^{-6})}$$

$$\eta k_1 = 317.93 \text{ ft}^3/\text{lb hr}$$

(ii). Assuming neither mass transfer nor chemical reaction controls, the "lumped" kinetic coefficient is again calculated. The rate of reaction can be written as

$$r_A = -k_{m_A}\, a_m\, (C_{Ab} - C_{As})$$

and

$$r_A = -\eta\, k_1\, C_{As}$$

Substituting to eliminate C_{As} (concentration on the catalyst surface) yields

$$r_A = -\eta\, k_1 \left(\frac{k_{m_A}\, a_m\, C_{Ab}}{\eta\, k_1 + k_{m_A}\, a_m}\right)$$

where

$$C_{Ab} \;=\; \text{bulk concentration} = C_{Ao}\,(1-X_A)$$

The design equation now becomes

$$\left(\frac{W}{F_{Ao}}\right)_{exp} = \int_0^{X_{Ae}} \frac{dX_A}{\left(\dfrac{k_{m_A} a_m}{1 + \dfrac{k_{m_A} a_m}{\eta\, k_1}}\right) C_{Ao}\,(1-X_A)}$$

$$\left(\frac{W}{F_{Ao}}\right)_{exp} = \frac{-\ln\,(1 - X_{Ae})}{\left(\dfrac{k_{m_A} a_m}{1 + \dfrac{k_{m_A} a_m}{\eta\, k_1}}\right) C_{Ao}}$$

$$\eta k_1 \;=\; 335.45 \text{ ft}^3/(\text{lb catalyst hr})$$

4. Apparent Activation Energy

Using the equation

$$(\eta k_1) = k_o \exp\,[-E_{APP}/RT]$$

where

ηk_1 = "lumped" kinetic coefficient, ft^3/(lb catalyst hr)

T = temperature, °K

R = gas constant, 1.987 $\frac{\text{cal}}{\text{gm mole °K}}$

E_{APP} = apparent activation energy, $\frac{\text{cal}}{\text{gm mole}}$

k_o = apparent frequency factor, $\text{ft}^3/(\text{lb catalyst hr})$

we get

$$\ln (\eta k_1) = \ln k_o - E_{APP}/RT$$

The slope of the curve of $\ln (\eta k_1)$ versus $1/T$ is the value $-E_{APP}/R$, therefore

$$[\ln(\eta k_1)]_2 - [\ln (\eta k_1)]_1 = \frac{E}{R} [- \frac{1}{T_2} + \frac{1}{T_1}]$$

Therefore

$$E_{APP} = \frac{yR}{[-\frac{1}{T_2} + \frac{1}{T_1}]}$$

where

$$y = [\ln (\eta k_1)]_2 - [\ln (\eta k_1)]_1$$

(a) For the situation of <u>chemical reaction control</u>; the values from Figure 8 for propionic acid and tert-amyl alcohol give

(i) Propionic acid

$(\eta k_1)_1$ = 10,000 $\text{ft}^3/(\text{lb catalyst hr})$

$(\eta k_2)_2$ = 1,000 $\text{ft}^3/(\text{lb catalyst hr})$

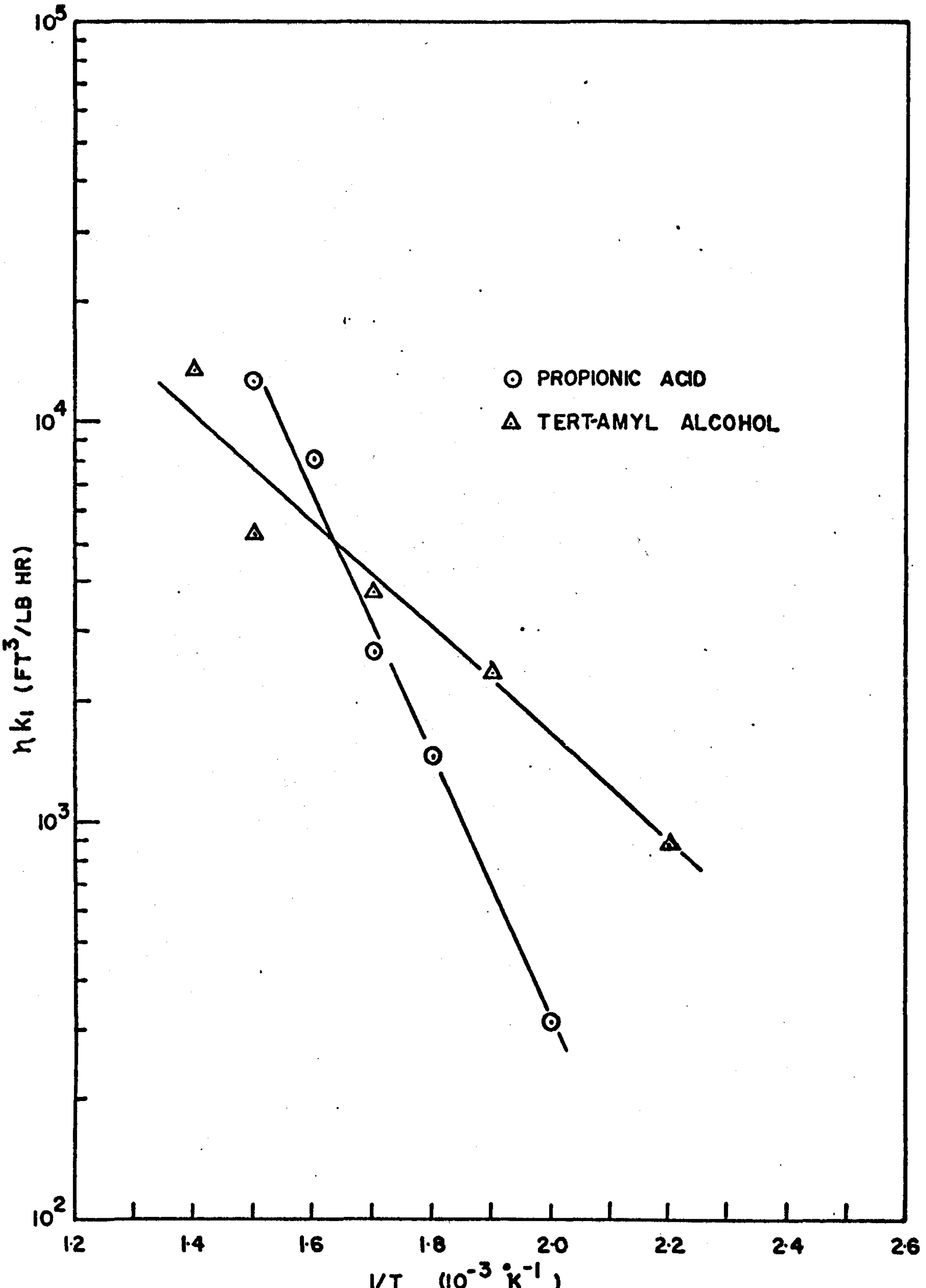


FIGURE 8 PLOT OF ηk_1 VERSUS 1/T BASED ON CHEMICAL REACTION CONTROL ASSUMPTION

$(\frac{1}{T})_1 = 1.545 \times 10^{-3}\ °K^{-1}$

$(\frac{1}{T})_2 = 1.85 \times 10^{-3}\ °K^{-1}$

$\ln (10,000) = 9.2103$

$\ln (1,000) = 6.9077$

$$E_{APP} = \frac{(6.9077 - 9.2103)\ 1.987\ \frac{\text{cal}}{\text{gm mole °K}}}{[(-1.85 \times 10^{-3}) + (1.545 \times 10^{-3})]\ °K^{-1}}$$

$$E_{APP} = \frac{(-2.3026)(1.987\ \frac{\text{cal}}{\text{gm mole}})}{-0.305 \times 10^{-3}}$$

$$E_{APP} = 15,000\ \frac{\text{cal}}{\text{gm mole}}$$

(ii) Tert-Amyl Alcohol

Because the data are more scattered than those for propionic acid the value of E_{APP} will not be as precise as that for propionic acid

$(\eta k_1)_1 = 10,000\ ft^3 (\text{lb catalyst hr})$

$(\eta k_1)_2 = 1,000\ ft^3\ (\text{lb catalyst hr})$

$(\frac{1}{T})_1 = 1.41 \times 10^{-3}\ °K^{-1}$

$$\left(\frac{1}{T}\right)_2 = 2.16 \times 10^{-3}\ {}^\circ K^{-1}$$

$$\ln(10{,}000) = 9.2103$$

$$\ln(1{,}000) = 6.9077$$

$$E_{APP} = \frac{(-2.3026)(1.987\ \frac{cal}{gm\ mole\ {}^\circ K})}{[(-2.16 \times 10^{-3}) + (1.41 \times 10^{-3})]\ {}^\circ K^{-1}}$$

$$E_{APP} = 6100\ \frac{cal}{gm\ mole}$$

(b) For the situation where <u>neither controls</u> the data from Figure 9 are used

(i) Propionic Acid

$$(\eta k_1)_1 = 100{,}000$$

$$(\eta k_1)_2 = 1{,}000$$

$$\left(\frac{1}{T}\right)_1 = 1.52 \times 10^{-3}\ {}^\circ K^{-1}$$

$$\left(\frac{1}{T}\right)_2 = 1.91 \times 10^{-3}\ {}^\circ K^{-1}$$

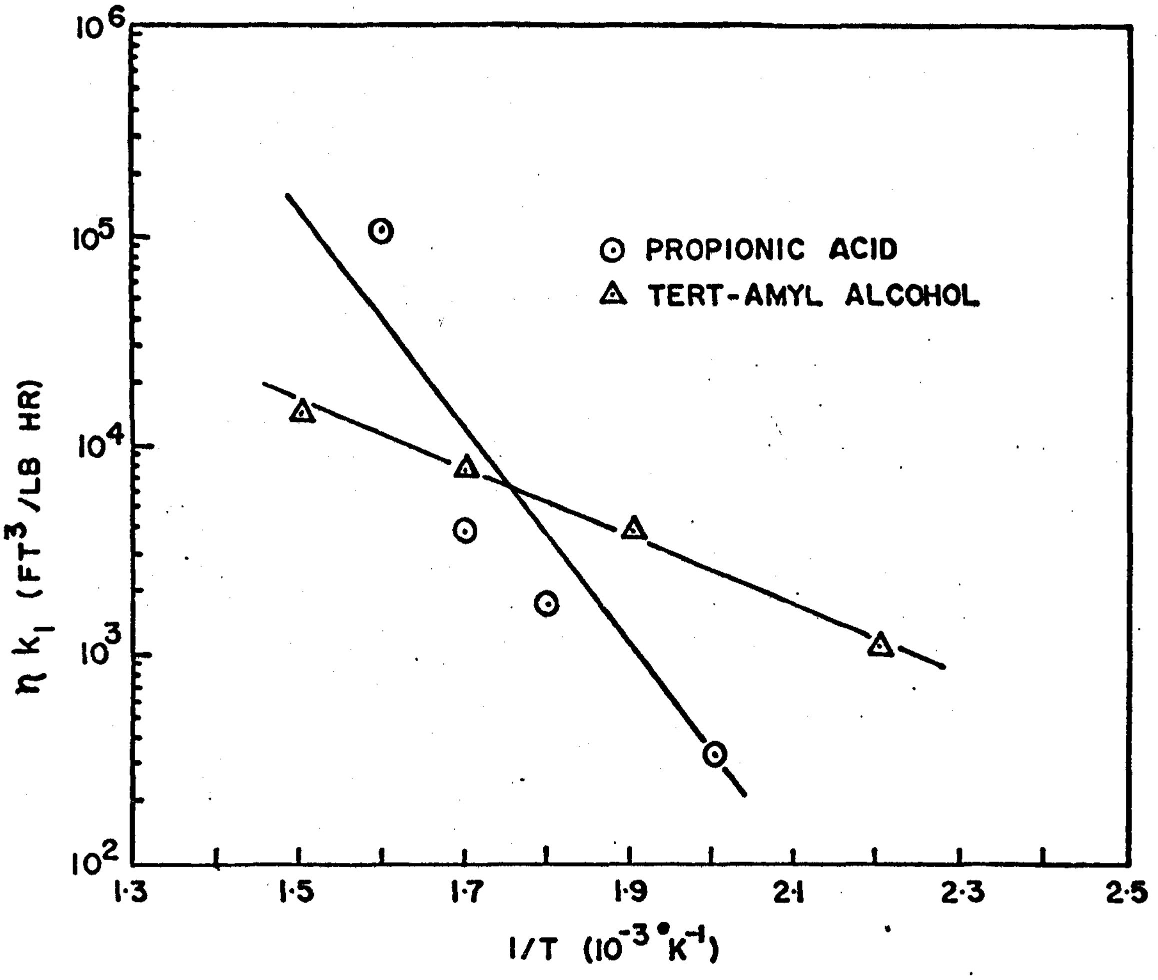


FIGURE 9 PLOT OF ηk_1 VERSUS 1/T BASED ON NEITHER CONTROLS ASSUMPTION

$$E_{APP} = \frac{(-4.6043)(1.987 \frac{cal}{gm\ mole\ °K})}{-(3.9 \times 10^{-4})\ °K^{-1}}$$

$$E_{APP} = 23,458 \frac{cal}{gm\ mole}$$

(ii) Tert-Amyl Alcohol

$(\eta k_1)_1$ = 10,000 ft^3/(lb catalyst hr)

$(\eta k_1)_2$ = 2,000 ft^3/(lb catalyst hr)

$(\frac{1}{T})_1 = 1.625 \times 10^{-3}$ °K

$(\frac{1}{T})_2 = 2.5 \times 10^{-3}$ °K

ln (10,000) = 9.2103

ln (2,000) = 7.6009

$$E_{APP} = \frac{(-1.6094)(1.987 \frac{cal}{gm\ mole\ °K})}{-(8.75 \times 10^{-4})\ °K^{-1}}$$

$$E_{APP} = 3654 \frac{cal}{gm\ mole}$$

5. Determination of Knudsen Diffusivity, Effective Diffusivity and the Corrected Diffusivity

a. Knudsen Diffusivities

Equation used is

$$(\mathcal{D}_K)_A = 9.7 \times 10^3 \, a \left(\frac{T}{M_A}\right)^{1/2}$$

where

$(\mathcal{D}_K)_A$ = Knudsen diffusivity, cm^2/sec

a = pore radius, cm

T = temperature, °K

M_A = molecular weight of species A, gm/gm mole

To arrive at pore radius, we use the equation

$$a = \frac{2 V_g}{S_g}$$

where

V_g = pore volume, cm^3/gm

S_g = surface area, cm^2/gm

Use the values supplied by the manufacturer,

V_g = $0.26 \ cm^3/gm$

S_g = $190 \ m^2/gm = 1.9 \times 10^6 \ cm^2/gm$

Therefore

$$a = \frac{2(0.26)}{1.9 \times 10^{6}} = 2.74 \times 10^{-7} \text{ cm}$$

$$M_A = 74.1, \text{ gm/gm mole}$$

$$T = 497.5°K$$

Therefore

$$(\mathcal{D}_K)_A = (9.7 \times 10^3)(2.74 \times 10^{-7})(\frac{497.5}{74.1})^{1/2}$$

$$(\mathcal{D}_K)_A = 0.0069 \text{ cm}^2/\text{sec} = 0.0268 \text{ ft}^2/\text{hr}$$

b. Effective Diffusivity

The equation used is

$$\mathcal{D}_e = \frac{1}{(\frac{1 - \alpha y_A}{\mathcal{D}_{AB}}) + (\frac{1}{(\mathcal{D}_K)_A})}$$

where

$\mathcal{D}_e$ = effective diffusivity, cm^2/sec

$\alpha = 1 - \sqrt{\frac{M_A}{M_B}}$

y_A = mole fraction of species A (odorant)

$\mathcal{D}_{AB}$ = bulk gas phase diffusivity, cm^2/sec

$(\mathcal{D}_K)_A$ = Knudsen diffusivity, cm^2/sec

Now

$$\alpha = 1 - \sqrt{\frac{74.1}{28.95}} = -0.6$$

$$y_A = 0.00107$$

Therefore

$$\mathcal{D}_e = \frac{1}{\left(\frac{1 - (-0.6)(0.00107)}{0.1972}\right) + \left(\frac{1}{0.0069}\right)}$$

$$\mathcal{D}_e = 0.0067 \text{ cm}^2/\text{sec}$$

c. <u>Corrected Diffusivity</u>

Equation used is

$$\mathcal{D} = \frac{\mathcal{D}_e \varepsilon}{\delta}$$

where

$\mathcal{D}$ = corrected diffusivity, cm^2/sec

ε = porosity of the particle, dimensionless

δ = tortuosity factor, dimensionless

Since

$$\varepsilon = \rho_p V_g$$

where

$\rho_p = 89 \text{ lb/ft}^3 = 1.42 \text{ gm/cm}^3$

$V_g = 0.26 \text{ cm}^3/\text{gm}$

therefore

$$\varepsilon = (1.42)(0.26) = 0.37$$

Assuming $\delta = 1.0$

then

$$\mathcal{D} = \frac{(0.0067)(0.37)}{1.0} = 0.0025\ \text{cm}^2/\text{sec} = 0.0096\ \text{ft}^2/\text{hr}$$

d. Effectiveness Factors and Actual Kinetic Coefficients

The Thiele Modulus, $\phi_c = \frac{r_c}{3}\sqrt{\frac{\rho_p\, k_1}{\mathcal{D}}}$

where

r_c = radius of the cylinder, cm

From initial trial and error, it becomes apparent that ϕ_c is large. Smith [17] states, that for $\phi_c > 5$, the following correlation may be used

$$\eta = 1/\phi_c$$

We have calculated values of ηk_1 corresponding to the <u>neither controls</u> assumption. These values are used for the next set of calculations.

Since $(\eta k_1) = \beta$

but $\eta = \frac{1}{\phi_c}$

therefore

$$\frac{k_1}{\phi_c} = \beta$$

where

β = experimental value of ηk_1 <u>(neither controls)</u>

or

$$\frac{k_1}{\frac{r_c}{3}\left(\frac{\rho_p k_1}{\mathcal{D}}\right)^{1/2}} = \beta$$

Using these values:

β = 335.45 ft^3/(lb catalyst hr) = 5.81 cm^3/(gm catalyst sec)

$\mathcal{D}$ = 0.0025 cm^2/sec

ρ_p = 1.42 gm/cm^3

$\frac{r_c}{3}$ = 0.053 cm

it follows that

$$\frac{k_1}{0.053\left(\frac{1.42\ k_1}{0.0025}\right)^{1/2}} = 5.81$$

or

$$\frac{k_1^{1/2}}{0.053\left(\frac{1.42}{0.0025}\right)^{1/2}} = 5.81$$

$$k_1 = 53.86\ \frac{\text{cm}^3}{\text{gm sec}} = 3108.80\ \text{ft}^3/(\text{lb catalyst hr})$$

Consequently

$$\eta = \frac{5.81}{53.86} = 0.11$$

e. The foregoing calculations have been completed for the experimental results obtained using propionic acid and tert-amyl alcohol. Table 6 summarizes the results of these calculations.

6. Activation Energies Based on Actual k_1

As previously calculated the equation used has the form

$$E_{APP} = \frac{R[(\ln k_1)_2 - (\ln k_1)_1]}{[-\frac{1}{T_2} + \frac{1}{T_1}]}$$

a. For propionic acid, use the slope of the line from Figure 10. Typical values are

$$(k_1)_1 = 10^8 \text{ ft}^3/(\text{lb catalyst hr})$$

$$(k_1)_2 = 10^4 \text{ ft}^3/(\text{lb catalyst hr})$$

$$(\frac{1}{T})_1 = 1.535 \times 10^{-3} \; {}^\circ K^{-1}$$

$$(\frac{1}{T})_2 = 1.95 \times 10^{-3} \; {}^\circ K^{-1}$$

$$\ln (10^8) = 18.4207$$

$$\ln (10^4) = 9.2103$$

$$E = 44{,}100 \; \frac{\text{cal}}{\text{gm mole}}$$

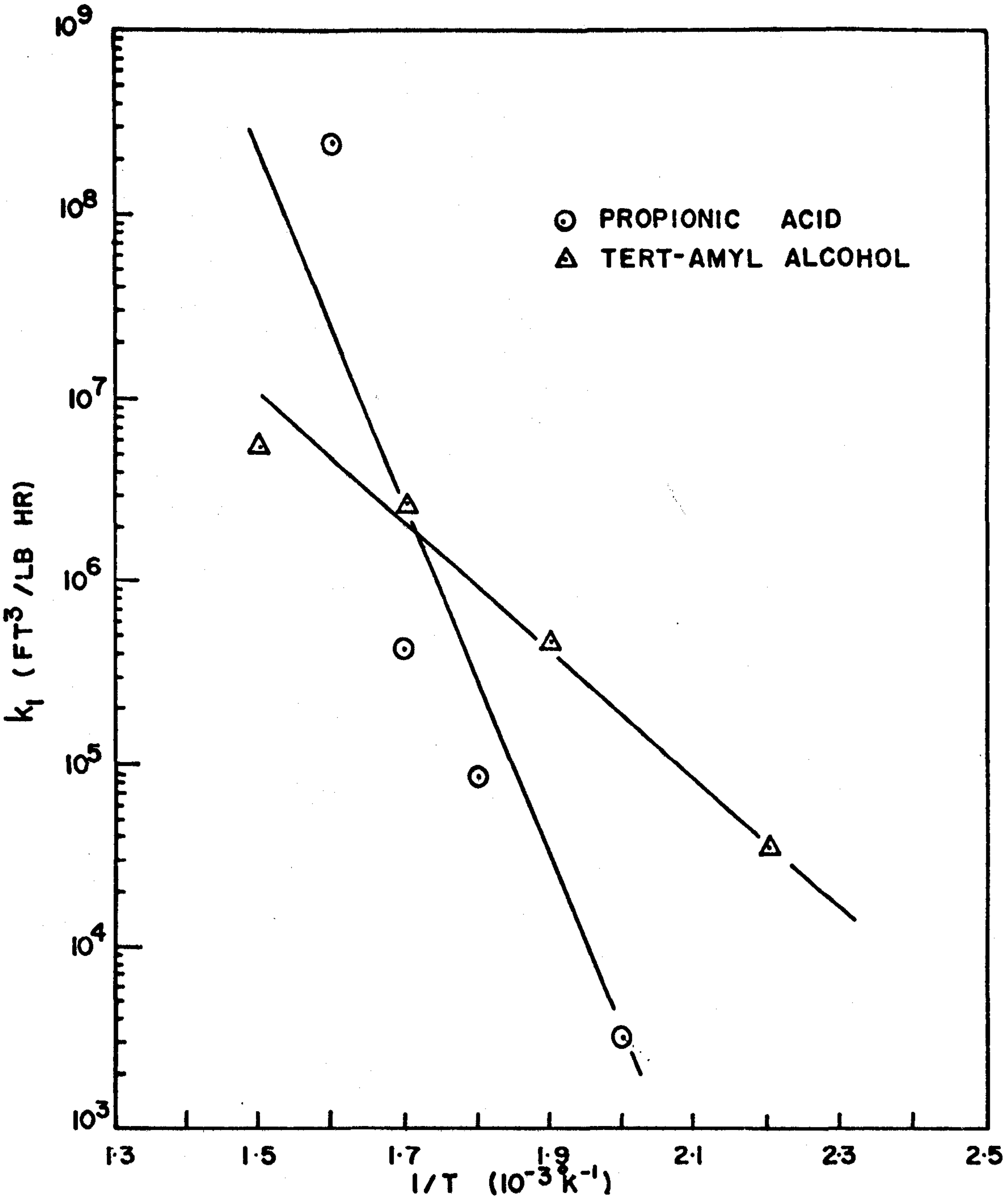


FIGURE 10 PLOT OF k_1 VERSUS 1/T

b. For tert-amyl alcohol, the values are

$(k_1)_1 = 10^7 \text{ ft}^3/(\text{lb catalyst hr})$

$(k_1)_2 = 10^5 \text{ ft}^3/(\text{lb catalyst hr})$

$(\frac{1}{T})_1 = 1.51 \times 10^{-3}\ {}^\circ K^{-1}$

$(\frac{1}{T})_2 = 2.17 \times 10^{-3}\ {}^\circ K^{-1}$

$\ln(10^7) = 16.118$

$\ln(10^5) = 13.815$

Therefore $E = 13{,}863.8 \ \frac{\text{cal}}{\text{gm mole}}$

7. Heat of Reaction

Assume that this is an ideal gas, therefore, there is no effect of pressure on the heat of reaction. The reaction for the oxidation of propionic acid is

$$CH_3CH_2COOH + 3.5\ O_2 \longrightarrow 3\ CO_2 + 3\ H_2O$$

The heats of formation at 298°K are taken from Table 3-202 in Perry's Chemical Engineers' Handbook, Fifth Edition, McGraw-Hill Book Company, New York.

$CH_3CH_2COOH_{(g)}$ = -108.75 kcal/gm mole

$O_{2(g)}$ = 0.00 kcal/gm mole

$CO_{2(g)}$ = -94.052 kcal/gm mole

$H_2O_{(g)}$ = -57.7979 kcal/gm mole

Using the equation from Smith [17]

$$\Delta H_R{}^\circ = \Sigma(\Delta H_f{}^\circ)_{products} - \Sigma(\Delta H_f{}^\circ)_{reactants}$$

Therefore

$$\Delta H^\circ_R = [(3)(-94.052)+(3)(-57.7979)]-[(3.5)(0.00) + (1.0)(-108.75)]$$

$$\Delta H^\circ_R = [(-282.156) + (-173.394)] - [0 + (-108.75)]$$

$$\Delta H^\circ_R = -346.8 \frac{kcal}{gm\ mole} \text{ at } 298°K$$

To calculate the heat of reaction at the reaction temperature of 497.5°K, we use [17]:

$$\Delta H_R{}^T = \Delta H^\circ_R + \int_{T_o}^{T} \Delta\bar{C}_p \, dT = \Delta H^\circ_R + \Delta\bar{C}_p \, (T-T_o)$$

where

$$\Delta\bar{C}_p = \Sigma \, (n \, \bar{C}_p)_{products} - \Sigma(n \, \bar{C}_p)_{reactants}$$

The values of the average heat capacities were found, in Smith [17], to be

$$\bar{C}_{p_{C_3H_2O_6}} = 26.25 \text{ cal/gm mole °K}$$

$$\bar{C}_{p_{O_2}} = 3.5 \text{ cal/gm mole °K}$$

$$\bar{C}_{p_{CO_2}} = 5.2 \text{ cal/gm mole °K}$$

$$\bar{C}_{p_{H_2O}} = 4.6 \text{ cal/gm mole °K}$$

Therefore

$$\Delta\bar{C}_p = [(3)(5.2) + 3(4.6)] - [(1)(26.25) + (3.5)(3.5)]$$

$$\Delta\bar{C}_p = [15.6 + 13.8] - [26.25 + 12.25]$$

$$\Delta\bar{C}_p = -9.1 \text{ cal/gm mole °K}$$

Therefore

$$\Delta H_R^T = -346.8 + (-9.1)(199.5)\ 10^{-3}$$

$$\Delta H_R^T = -346.8 - 1.816 = -348.6 \quad \frac{\text{kcal}}{\text{gm mole}}$$

8. Sample Calculation for Pressure Drop Through the Column

The pressure drop through the column was characteristically in the order of 2.0-4.0 psig. This large drop was believed to be due to the presence of the gas diffuser at the gas stream inlet. The following calculation is presented to give an estimate of the pressure drop due to the material in the column.

The Ergun equation is used [19] in the form

$$\frac{\Delta P}{Z}\left(\frac{g_c' \, \varepsilon^3}{(1-\varepsilon)} \frac{d_p \, \rho_G}{G^2}\right) = \frac{150\ (1-\varepsilon)}{Re} + 1.75$$

where

ΔP = difference in pressure, lb_f/ft^2

Z = length of column, ft

g_c' = conversion constant, $4.18 \times 10^8 \ \frac{lb_{mass} ft}{lb_{force} hr^2}$

ε = fraction of void in a dry packed bed, dimensionless

d_p = equivalent diameter, ft

ρ_G = density of the gas, lb/ft^3

G = gas mass flux, $lb/(ft^2 hr)$

Re = Reynolds number

Using the values previously calculated for the second run with propionic acid:

a. For the catalyst bed

ε = 0.67

d_p = 0.0128 ft

ρ_G = 0.0499 lb/ft^3

G = 473.7 lb/ft^2 hr

Re = 95

$$\frac{\Delta P}{Z}\left[\left(\frac{4.18 \times 10^8)(0.67)^3(0.0128)(0.0499)}{(1-0.67)(473.7)^2}\right]\right] = \frac{150(1-0.67)}{95} + 1.75$$

$$\frac{\Delta P}{Z}\left(\frac{80{,}299.196}{74{,}049.26}\right) = 2.271$$

$$\frac{\Delta P}{Z}(1.084) = 2.271$$

$$\frac{\Delta P}{Z} = 2.09 \; \frac{lb_f/ft^2}{ft}$$

where

Z = 1.3 inches = 0.108 ft

Therefore

ΔP = (2.09)(0.108) = 0.226 lb$_f$/ft^2

or ΔP = 0.0016 lb$_f$/in^2

b. For the preheat section

ε = 0.67

d_p = 0.0104 ft

$$\rho_G = 0.0499 \text{ lb/ft}^3$$

$$G = 473.7 \text{ lb/ft}^2\text{hr}$$

$$Re = 95$$

$$\frac{\Delta P}{Z}\left[\frac{(4.18 \times 10^8)(0.67)^3(0.0104)(0.0499)}{(1-0.67)(473.7)^2}\right] = \frac{150(1-0.67)}{95} + 1.75$$

$$\frac{\Delta P}{Z}\left(\frac{65243.10}{74049.26}\right) = 2.271$$

$$\frac{\Delta P}{Z} = 2.58 \ \frac{\text{lb}_f/\text{ft}^2}{\text{ft}}$$

where

$Z = 7.0$ inches $= 0.583$ ft

Therefore $\Delta P = (2.58)(0.583) = 1.505 \text{ lb}_f/\text{ft}^2$

or $\Delta P = 0.0105 \text{ lb}_f/\text{in}^2$

c. For the whole column

$\Delta P = (0.0105 \text{ psi}) + (0.0016 \text{ psi}) = 0.0121 \text{ psi}$

9. Effect of Heat Recycle on the Economics of Catalytic Oxidation

For this calculation, a typical industrial flow rate of 40,000 scfm of air is used. The odorant in question is propionic acid with a mole fraction of 0.00107. From experimental results, a preheat temperature of 268°C will be required for a removal efficiency of 80% (based on odor units). The reactor exit will be at 357°C. The flow scheme to be used is illustrated in Figure 11.

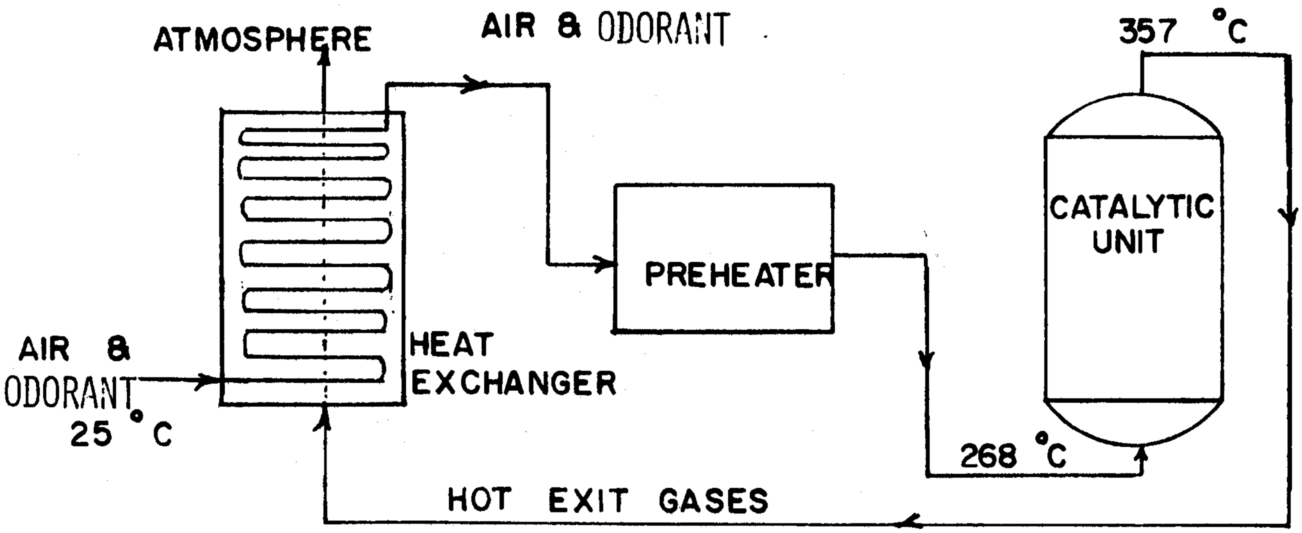


FIGURE 11: Proposed Heat Recirculation System

The basis used through this procedure is 298°K. The values of the empirical constants for the molal heat capacities at constant pressure, obtained from Hougen, Watson and Ragatz*, are given in Table 12. Because of the low

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*Hougen, O. A., Watson, K. M. and Ragatz, R. A., Chemical Process Principles, Part I, John Wiley and Sons, Inc., New York, 2nd Ed., p. 255 (1956).

From

$$\Delta H = \int_{T_1}^{T_2} \left(n_{O_2}\ C_{p_{O_2}}\right) dT + \int_{T_1}^{T_2} \left(n_{N_2} C_{p_{N_2}}\right) dT$$

substitution of the values for the heat capacity constants and

$$n_{O_2} = 0.21 \quad \text{and} \quad n_{N_2} = 0.79$$

the heat content of the exit gases per mole may be calculated as follows:

$$\Delta H_1 = 0.21 \int_{298}^{630} [(6.117)+(3.16 \times 10^{-3})T + (-1.005 \times 10^{-6})T^2]\ dT$$

$$+ 0.79 \int_{298}^{630} [(6.457)+(1.389 \times 10^{-3})T + (-0.069 \times 10^{-6})T^2] dT$$

Integrating

$$\Delta H_1 = 0.21\ \left[6.117T + \frac{(3.167 \times 10^{-3})T^2}{2} - \frac{(1.005 \times 10^{-6})}{3} T^3\right]_{298}^{630} +$$

$$0.79\ \left[6.457T + \frac{(1.389 \times 10^{-3})T^2}{2} - \frac{(0.069 \times 10^{-6})T^3}{3}\right]_{298}^{630}$$

$$\Delta H_1 = 0.21\ [2030.84 + 488.5 - 74.87] + 0.79\ [2143.72 + 214.25 - 5.41]$$

$$= 2371.86 \text{ cal/gm mole of air}$$

Now, the flow rate is 40,000 scfm. But 1 lb mole of an ideal gas at 0°C, 760 mm Hg occupies 359.05 ft^3. Assuming standard conditions of 760 mm Hg and 60°F, and using the ideal gas law

$$\frac{359.05\ ft^3}{V_2} = \frac{492°R}{520°R}$$

$$V_2 = 379.48\ ft^3$$

Therefore, 1 lb mole will occupy 379.48 ft^3 at 1 atm and 60°F. Consequently, the molar flow rate is

$$\frac{40{,}000\ ft^3/min}{379.48\ ft^3/lb\ mole} = 105.41\ \frac{lb\ moles}{min} = 47855\ \frac{gm\ moles}{min}$$

Thus the heat output in the gas stream, q_E, is

$$q_E = (2371.86\ \frac{cal}{gm\ mole})(47{,}855\ \frac{gm\ moles}{min})$$

$$q_E = 113{,}500\ \frac{kcal}{min}$$

Assuming that the exit gases transfer 50% of their heat to the incoming gases [16], the amount of energy available to heat the incoming gases, q_I, is

$$q_I = (0.5)(113{,}500\ \frac{\text{kcal}}{\text{min}}) = 56{,}752 \quad \frac{\text{kcal}}{\text{min}}$$

What temperature could the feed gases then be raised to, using this heat? By trial and error, this temperature is found to be approximately 200°C.

Therefore, the amount of heat required to raise the inlet gas stream from 200°C to a preheat temperature of 268°C is

$$\Delta H_2 = 0.21\ [6.117T + \frac{(3.167 \times 10^{-3})T^2}{2} - \frac{(1.005 \times 10^{-6})T^3}{3})]_{473}^{541}$$

$$+ 0.79\ [6.457T + \frac{(1.389 \times 10^{-3})T^2}{2} - \frac{(0.069 \times 10^{-6})T^3}{3}]_{473}^{541}$$

ΔH_2 = 490.38 cal/gm mole

It follows that the amount of heat required in the preheater, q_{P_1}, is

$$q_{P_1} = 23{,}467 \quad \text{kcal/min}$$

Assuming the use of natural gas to heat the gas streams (the heat of combustion of methane is 191.759 $\frac{\text{kcal}}{\text{gm mole}}$) the amount of methane required to provide q_{P_1} is

$$\frac{23{,}467 \quad \text{kcal/min}}{191.759 \ \text{kcal/gm mole}} = 122.38 \ \frac{\text{gm moles}}{\text{min}}$$

This is equivalent to

$$(0.270 \ \text{lb moles/min})(379.48 \ \frac{\text{ft}^3}{\text{lb mole}})$$

$$= 102.46 \ \text{ft}^3/\text{min} \quad \text{of methane}$$

Assuming a natural gas price of $2.00/1000 scf, the cost of heating the inlet stream from 200°C to 268°C is

$$C_1 = (\frac{102.46}{1000})(\$2.00) = \$0.205/\text{min}$$

Assuming 300 operating days per year

$$C_{\text{annual}} = \$88{,}560/\text{year}$$

Now, if no heat recycle was used, the amount of heat required to raise the gas stream from 25°C to 268°C in the preheater is

$$q_{P_2} = 82{,}297 \quad \frac{\text{kcal}}{\text{min}}$$

Amount of natural gas needed will be

$$= \frac{82{,}297 \quad \frac{\text{kcal}}{\text{min}}}{191.759 \ \text{kcal/gm mole}} = 429.17 \ \frac{\text{gm moles}}{\text{min}}$$

$$= 0.95 \ \frac{\text{lb moles}}{\text{min}}$$

Therefore, the cost would be

$$C_2 = \left(\frac{(0.95)(379.48)}{1000}\right) \$2.00 = \$0.721/\text{min}$$

or

\$311,472/year

Therefore, the saving in energy cost resulting from heating the incoming gas by exchange with the hot exit gas is

$$\left(\frac{311{,}472 - 88{,}560}{311{,}472}\right) 100 = 71.57\%$$

APPENDIX VI

ASTM Procedure
D 1391-57

Measurement of Odor In Atmospheres (Dilution Method)

STANDARD METHOD FOR MEASUREMENT OF ODOR IN ATMOSPHERES (DILUTION METHOD)[1]

This standard is issued under the fixed designation D 1391: the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope and Application

1.1 This method covers the determination of the odor concentration in the atmosphere and in gases discharged from industrial process operations, and for determining the odor emission rate from a stack or vent. It establishes a quantitative concept of odor, whereby the relative quantities of odor from two or more different sources, or from the same sources under different operating conditions, can be compared.

1.2 This method is intended as a quick, practical way of measuring odor concentrations. It depends upon the human olfactory sense, and is subject to the variations of this sense, from person to person, or from hour to hour in the same person. Accuracy and reproducibility of results can be increased by increasing the number of observers; this can be varied to suit the purposes of the test.

2. Summary of Method

2.1 A sample of the atmosphere or gas whose odor is to be measured is diluted with odor-free air until a dilution is achieved in which the odor can barely be perceived. The ratio of the total volume of this diluted sample (sample volume plus volume of diluting air) to the volume of original sample in the diluted sample, is a measure of the concentration of odor in the original sample.

2.2 The technique described assumes that the odor concentration is to be measured without regard to the material or materials that cause the odor, or the concentration of these causants in the sample. It does not take into account the character of an odor.

3. Definitions

3.1 odor unit-one cubic foot of air at the odor threshold

3.2 odor concentration-the number of cubic feet that 1 ft^3 of sample will occupy when diluted to the odor threshold. It is a measure of the number of odor units in 1 ft^3 of the sample. It is expressed in odor units per cubic foot.

3.3 odor emission rate-the number of odor units discharged from a stack or vent per minute. It is the product of the odor concentration of the discharge gas, and the volume rate of discharge, in cubic feet per minute.

4. Interferences

4.1 Extraneous odors and lingering taste effects interfere with this test. The area for the test must be clean, free of odors, and quiet. Hands and clothing of the observer, and equipment used in the test, must be clean and free from odor. Smoking, chewing of tobacco or gum, or eating should not be indulged in for at least 30 minutes prior to the determination of odor concentration.

4.2 Poor physical condition of the observer may interfere with this test. The observer must be free of "colds" or other physical conditions affecting the sense of smell. No observer shall carry out odor tests for longer than 15 minutes at a time, and he shall rest a like period before resuming such tests.

4.3 Not all observers are capable of carrying out this test. A group of at least twice the number of observers required shall be screened to select the most sensitive individuals for observers. A suitable screening test consists of a "triangle" test in which two identical samples and one odd sample, such as vanillan, vanillan, and methyl salicylate, each dissolved in the odorless diluent, benzyl benzoate, are presented to the observer in increasingly dilute concentrations, starting with a 1.0 percent solution. The observer is scored on his ability to distinguish the odd odorant from the two identical ones as the dilution increases. The members of the group with poorest olfactory perception shall be eliminated by this test, and the individuals with better olfactory perception shall be selected as observers.

5. Apparatus

5.1 Sampling Syringe-Two or more 100-ml Luer-type hypodermic syringes.

5.2 Dilution Syringe-One or more 100-ml Luer-type hypodermic syringes (identical to sampling syringes).

5.3 Transfer Syringe-Two or more 2-ml Luer-type hypodermic syringes and one 100-ml Luer-type hypodermic syringe.

5.4 Transfer Needle-A fitting for connecting the transfer syringe with the sampling and dilution syringes. It is made from two standard 25-gage BD[2] hypodermic needles, 1 1/2-in (38 mm) long. The mating head of one needle is cut off at a point where its inside bore is equal to the outside diameter of the needle shaft. This mating head is slid over the second needle, with the mating opening toward the tip of the needle, and silver-soldered in place (Fig. 1).

5.5 Syringe Caps-One Luer syringe cap for each syringe.

5.6 Odor-Free Room, maintained at comfortable temperature and humidity conditions.

6. Reagent

6.1 Odor-Free Air

7. Sampling

7.1 Fill two sampling syringes with the air or gas whose odor concentration is to be measured, by pushing the plunger all the way in, inserting the tip into the atmosphere to be sampled, and pulling the plunger out to the 100-ml mark. Place caps over the tips of the syringes, and transfer them to the odor-free room for the determination of odor concentration.

8. Procedure

8.1 Thoroughly scrub all syringes and transfer needles with an unperfumed detergent. Rinse thoroughly in odor-free tap water, wipe dry with a clean cloth, and allow to dry in the test room atmosphere for at least 15 minutes.

8.2 Dilution samples shall be prepared only by an assistant to the observer, and given to the observer for smelling. In preparing the dilution, place the transfer needle on the transfer syringe, remove the cap from the sampling syringe, and with the transfer syringe empty, insert the transfer needle tip into the sample syringe, and tightly connect the two syringes together. Withdraw the desired volume, V_s, of the sample into the transfer syringe. Withdraw the needle from the sampling syringe, and recap the latter. Insert the transfer needle tip into the dilution syringe, partially filled with odor-free air; and inject the sample volume, V_s, into the dilution syringe. Withdraw the transfer needle from the dilution syringe, fill the dilution syringe to the 100-ml mark with odor-free air, cap it, and allow it to stand for at least 15 sec to allow mixing by diffusion. The diluted sample is then ready for testing by the observer. If volumes of V_s of 2 ml or less are required, use the 2-ml transfer syringe. If volumes greater than 2 ml are required, use the 100-ml transfer syringe. If volumes less than 0.2 ml are required for V_s, make an intermediate dilution of 1 + 9 by drawing 0.2 ml of sample into a clean 2-ml syringe, filling it with odorfree air to the 2 ml mark, and injecting a portion of the intermediate dilution into the dilution syringe; for such tests, the sample volume, V_s, will be one tenth of the volume of the intermediate dilution used.

8.3 Without prior knowledge of the degree of sample dilution, uncap the dilution syringe and insert the tip of the syringe into one nostril. Suspend breathing for a few seconds, and during this period expel the 100-ml diluted sample into the nostril at a uniform rate over 2 to 3 sec. Record whether odor is perceived in the diluted sample. If odor is perceived, purge the dilution syringe with odor-free air until odor can no longer be detected in it. If the syringe cannot be purged of odor, clean it in accordance with 8.1 or use another clean syringe for the next dilution.

8.4 To establish order of magnitude of odor concentration of the sample, prepare samples having dilution ratios of 1 + 9, 1 + 99, 1 + 999 and 1 + 9999 in random order in accordance with 8.2. Note the greatest dilution at which odor is perceived.

8.5 Based on the results obtained in accordance with 8.4, prepare a series of dilutions in the range between the greatest dilution in which odor was perceived and the next greatest dilution in which odor was perceived and the next greatest dilution. The order of dilutions should be random, and at least one out of any four consecutive dilutions should be a "scramble" dilution, in no way related to the fundamental trend. The "scramble" dilution may range from no odor to one considerably above the threshold concentration. In this manner, the observer is assured that he cannot anticipate what the next concentration will be; he must concentrate only on whether he perceives the odor on any given sample.

8.6 Proceed in accordance with 8.5 until the difference between the greatest dilution at which odor is consistently perceived and the next greatest dilution measured is less than 50 percent of the greatest dilution at which it is consistently perceived.

8.7 If the sample being analyzed is from a stack or vent, and the odor emission rate from the stack or vent is desired, determine the average velocity of discharge from the stack or vent, in feet per minute.[3] Determine the inside cross-sectional area of the duct or stack in square feet.

9. Calculations

9.1 Calculate the odor concentration, in terms of odor units per cubic foot, as follows:

$$C = 100/V_s$$

where

C = odor concentration, odor units/ft^3

V_s = milliliters of original sample present in the most dilute sample in which odor is perceptible (8.6), and

100 = milliliters of diluted sample (8.6)

9.2 Calculate the odor emission rate, in terms of odor units per minute, as follows:

$$E = CVA$$

where

E = odor emission rate, odor units/min

C = odor concentration, odor units/ft^3, as determined in 9.1

V = velocity of stack or vent discharge, ft/min, as determined in 8.7, and

A = inside cross-sectional area of stack or vent, ft^2, as determined in 8.7.

10. Precision and Accuracy

10.1 The precision and accuracy of this method depend on the number, physical condition, experience, and skill of the observers. Any single observer should be able to attain results that are reproducible within ± 50 percent, on any given day. Where greater accuracy is desired, for any given test, more observers should be used, and their results averaged.

1. This method is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres. Current edition effective September 30, 1957. Originally issued 1956. Replace D 1391 - 56 T

2. Available from Becton-Dickinson and Co., Rutherford, N.J.

3. Methods for determining the average velocity of discharge from stacks or vents may be found in the Heating, Ventilating, and Air-Conditioning Guide, 33rd Edition, published by the American Society of Heating and Air-Conditioning Engineers, 1955, Chap. 17, p. 415.

APPENDIX VII

Equipment Specifications

Equipment Specifications

1. Air Filter

Make:	Webster
Type:	Model W04-4 M4
Maximum Pressure:	250 psig at 125°F
Filter Screen:	Ceramic Filter

2. Pressure Regulator

Make:	Moore
Type:	91F-60
Delivery Pressure Gauge:	60 psig
Inlet Hose Connection:	Reinforced rubber hose

3. Large Air Rotameter

Make:	Fisher and Porter
Type:	6704R1523/1
Tube No.:	FP-1/2-27-G-10/83
Scale:	9.5 inches
Capacity:	180 SCFH at 14.7 psia & 70°F

4. Thermocouples

Make: Thermo-Electric of Canada

Type: Chromel-Alumel

Junction: W-4 ungrounded

Accuracy: ± 0.070 mV

5. Temperature Controller

Make: Thermo-Electric of Canada

Model: 3242200-04238-1

Range: 0-674°C

Set Point Accuracy: ± 0.25% F.S.

Repeatability: 0.1% F.S.

6. Preheater Heater

Make: Marsh Beaded Heater

Type: Resistance wire

Capacity: 600 W at 115V

7. Temperature Recorder

Make: Hewlett Packard

Type: 7100B Strip Chart Dual Pen

Modules: 17500 A-10 spans from 5mV-100V with 1 megohm input resistance at null on all spans

Response Time: 0.5 seconds for full scale

Power: 115 or 230 V ± 10%, 60 HZ, 65 volt-amperes

Accuracy: ± 1/2% or ± 1°C whichever is greater

8. Chemical Feed System

Make:	Boston Gear Works
Type:	Ratiotrol, Series E, Precision Motor, Speed Control
Range:	2.5 rpm - 35 rpm
Gear Reduction:	100 to 1
Syringe:	Monoject Disposable
Injection Port:	3/8" Swagelok 'T' with plastic Septum

9. Pressure Gauges

Make:	Matheson
Type:	Serial No. 14131
Range:	0 - 30 psig

10. Chemicals

Some of the odorous compounds used in the experiments came from Canadian Laboratory Supplies Limited (Canlab), Toronto, Ontario. Other chemicals were obtained from the laboratory supplies of the Chemical Engineering Department and the Department of Chemistry. All chemicals were laboratory grade (99+% purity).

VITA AUCTORIS

1947	Born in Edmonton, Alberta, Canada
1966	Completed High School at Ross Sheppard Composite High School, Edmonton
1968	Received Technical Diploma in Chemical Technology, Northern Alberta Institute of Technology, Edmonton
1972	Received Bachelor of Science in Chemical Engineering from the University of Alberta, Edmonton
1972-73	Technical Representative with Alchem Limited, Edmonton
1973-74	Project Engineer with Environment Canada, Environmental Protection Service, Air Pollution Control Section, Edmonton
1976	Presently a candidate for the degree of Master of Applied Science in Chemical Engineering at the University of Windsor, Windsor, Ontario, Canada