OZONEATION OF LOW
MOLECULAR WEIGHT COMPOUNDS

by

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STATEMENT BY AUTHOR

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SIGNED

APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

RAYMOND A. SIERKA
Professor of Civil Engineering
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ABSTRACT

The ozonation of aqueous solutions of four low molecular weight organic acids, two alcohols, an aldehyde, and a ketone was studied. Emphasis was placed on butyric acid. Parameters generally known to effect the rate of organic destruction were separately evaluated. These variables included oxidant concentration, temperature, mixing intensity and pH.

The results indicated that the most influential parameters were pH, temperature, mixing and oxidant concentration, in that order.
CHAPTER 1

INTRODUCTION

Developed during the early 1960's as a practical method of renovating brackish water, reverse osmosis has also found application in wastewater treatment (1-3). In essence, it is a technique of separating solvent molecules from a mixture of organic and/or inorganic molecules, in both the soluble and solid states. The separation is performed using a semi-permeable anisotropic membrane. Separation occurs in a reverse osmosis module when pressure is applied, in excess of the osmotic pressure, to a solution containing an undesirable solute. The membrane selectively permits solvent molecules to pass through it while rejecting totally, or in part, the unwanted species.

To date, the prime membrane material developed is cellulose acetate, a hydroxylic polymer made up of long chains of β-glucoside units. This type of film is approximately 4 mils (100µ) thick, consisting of an 0.25µ outer layer of tightly packed and organized polymer chains backed by a progressively less dense layer. The thicker porous layer is made up of polymer chains forming larger pores. This is due to the decreasing crystallinity and crosslinking of the chains in the thicker layer (4).
The polymer chains in the rejecting dense layer have carbonyl groups that hydrogen bond to the polar solvent molecules that bridge across adjacent chains. The small pores between the parallel chains are thus filled, preventing ions and other non-hydrogen bonding substances from entering. The solvent molecule is then pushed through the pores and on to carbonyl group sites within the thicker, but less dense layer by the aforementioned applied pressure (5).

While cellulose acetate membranes perform well with colloidal, bacterial, inorganic and macromolecular organic solutions, many organic materials are not well rejected (6-7). During laboratory tests of a Schleicher and Schuell Company porous cellulose acetate membrane, Sourirajan noted that only 13% to 30% of the solutes in 0.5M aqueous solutions of isobutyl alcohol, methyl ethyl ketone, acetic acid, propionic acid, and butyric acid are rejected as compared to 75% for a 0.5M NaCl solution (8). It has been proposed that the amount of organic solute that is rejected depends upon its molecular size, and that the failure of the membrane to reject organic molecules indicates that the highly polar organic molecules act in an analogous manner as water molecules. That is, small low molecular weight organic molecules, by hydrogen bonding with the carbonyl groups, can pass through it.
Generally, activated carbon has been utilized to remove organics in low concentration from wastewater. Adsorption onto the carbon is a result of one of two characteristic properties for a given solvent-solute system. The solute may be lyophobic (solvent-disliking) or may have a high affinity for the solid (9). However, activated carbon does not adsorb highly polar, low molecular weight organic acids and alcohols to any appreciable degree (10).

It appears that oxidizing the dissolved organics to the end products of carbon dioxide and water would be the preferred method of removing them from reverse osmosis treated wastewater. The most powerful and practical oxidant capable of oxidizing these low molecular weight compounds is ozone.

The parameters affecting ozone's ability to efficiently oxidize organic material in dilute aqueous solutions have not been completely studied (11-13). This paper will investigate those parameters that are believed to have a significant influence on ozone's oxidation of materials that are not rejected well by the reverse osmosis membrane. The parameters to be studied will include mixing, oxidant concentration, temperature and pH.
Ozone was first noted by the ancient Greek civilization both during and after electrical storms, when they sensed a peculiar odor in the atmosphere. They called this phenomena "Ozein", meaning "having an odor" (14). Ozone's pungent odor was again noted in the vicinity of electrical machines by M. Van Marum in 1785 (15, p. 28). In 1801 Cruickshank observed the same odor in the gas formed at the anode during electrolysis of water (16, p. 410). Schonbein, in 1840, recognized the odor as that peculiar to a new gas, which he called "ozone", a derivation of the Greek label (15, p. 28).

Utilizing the observations noted by the aforementioned, Siemens constructed the first ozone generator in 1857 (16). However, the chemical composition of the artificially produced gas was not defined until 1872 when B Brodie established that ozone is the triatomic molecule of oxygen (17).

Using Brodie's analysis that ozone is an allotropic form of oxygen, researchers have learned that stray electrons accelerating from a high voltage source collide with oxygen molecules that are present in the atmosphere
surrounding the electrode. Some of these electrons have sufficient energy to penetrate these molecules producing additional free electrons or high-energy unstable molecules which quickly breakdown into free radicals—single oxygen atoms. Most of these single atoms combine with other oxygen molecules present to form molecules of ozone. The length of time necessary for this reaction has been measured in ten-millionths of a second (18).

Employing special laboratory techniques, ozone has been generated and separated from the gaseous mixture in which it was created. Furthermore, it has been made to exist in liquid and solid form. Many of the properties of both forms have been measured.

Ozone's melting point is -314.5°F (-192.5°C), while its density is 1.728 g/cc at -325.8°F (-196.6°C). In the solid form it exhibits a dark blue color. As a liquid, ozone has a boiling point of -169.4°F (-111.9°C), while its density varies from 1.316 g/cc at -148°F (-100°C) to 1.574 g/cc at -297.4°F (-183°C). Its color is the same dark blue as the solid form. Of special interest is the fact that liquid ozone is easily exploded, whether it is in a pure form or mixed with oxygen. Explosions are propagated by minute amounts of matter, changes in pressure on the liquid, electric sparks or sudden changes in temperature (16).
As a gas, pure ozone has a density, at standard conditions, of 2.144 g/l. Its color is light blue. It is 10 to 12 times more soluble in water than oxygen, but due to its low partial pressure, only a few mg/l can be held in solution (19). Although it is not considered to be explosive, ozone gas decomposes rapidly to elemental oxygen as heat energy is introduced to it. At 518°F (270°C) ozone converts back to oxygen as rapidly as it is created (20).

Depending upon its surroundings, it decomposes back to singlet oxygen atoms that quickly unite with other ozone molecules, causing them to break apart into O₂ molecules. This is best illustrated in the following equations:

\[ M + O_3 \leftrightarrow O_2 + O^* + M -24.6 \text{ Kcal} \]

\[ O^* + O_3 \rightarrow 2O_2 + 93 \text{ Kcal} \]

\[ O^* + O^* \rightarrow O_2 \]

where M represents a suitably weighted sum of all the substances (including ozone) present in the gas phase (21). These equations are generally held to be correct by researchers in this area of ozone technology.

One explanation that describes the mechanism of ozone's decomposition in pure water has been supported by iodometric and spectrophotometric determinations. The
mechanism is described by the following equations (22).

\[ \text{O}_3 + \text{H}_2\text{O} \rightarrow \text{HO}_3^+ + \text{OH}^- \] (1)
\[ \text{HO}_3^+ + \text{OH}^- \rightarrow 2\text{HO}_2 \] (2)
\[ \text{O}_3 + \text{HO}_2 \rightarrow \text{HO} + 2\text{O}_2 \] (3)
\[ \text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \] (4)

It is postulated that when ozone is dissolved into an aqueous solution containing organic material, reaction products of ozone and water in turn react with the organic material, as well as with each other (11). It may be possible that the \( \text{OH}^- \) radical formed in equation (1) reacts with the organic molecule \( R \) as follows:

\[ \text{RH} + \text{OH}^- \rightarrow R^- + \text{H}_2\text{O} \]

Utilizing the \( \text{O}_2 \) formed in equations (3) or (4),

\[ R^- + \text{O}_2 \rightarrow \text{RO}_2^- \]

and

\[ \text{RO}_2^- + \text{RH} \rightarrow \text{ROOH} + R^- \]

then

\[ 2\text{ROOH} \rightarrow \text{H}_2\text{O} + \text{RO}^- + \text{RO}_2^- \]

and

\[ \text{ROOH} \rightarrow \text{RO}^- + \text{OH}^- \]
The chain terminating reactions would be

\[ 2 \text{RO}^- \rightarrow \text{Products} \]
\[ \text{RO}^- + \text{R}^- \rightarrow \text{Products} \]
\[ 2\text{R}^- \rightarrow \text{Products} \]

The application of ozone to aqueous solutions containing organic material must be done as efficiently as possible. Ozone is expensive to produce, and will continue to be so, considering the rising cost in producing electricity. There is very little cost information available concerning the ozonation of water to be used for industrial reuses. Much of the literature cited relates to treating domestic water supplies or conditioning domestic wastewater prior to its reuse (23).

The parameters which affect the efficiency of ozone utilization in oxidizing solutions include pH, temperature and ozone-organic concentration ratios. These parameters separately affect the rate of reaction between ozone and organic material (11-13). In some instances the effects may be mutually enhancing, in other instances, they might be acting in opposition to each other, thus negating the desired oxidation. For example, it is fairly well known that heat energy introduced into an oxidation reaction enhances the rate at which the
reaction occurs. However, heat generally reduces the saturation level of a gas in a liquid so that one would expect less opportunity for ozone to come into contact with the dissolved organic material.

An ozonator's production rate is a function of its electrical energy input and gas supply. When the electrical energy input is adjusted to its maximum value, a given ozone generator will produce a maximum concentration by weight of ozone in a specific gas flow. As that specific gas flow is increased, the total amount of ozone produced also increases but at a diminished rate. Therefore the concentration of ozone in the gas flow leaving the ozonator progressively decreases. Generally, when the concentration of one of the reactants decreases, the rate of reaction changes in a similar manner. Although the concentration by weight is reduced, the total amount of ozone produced per unit of time is increased due to the increase in gas flow. It is difficult to state what will be the overall net effect on the organic oxidation by varying the concentration and amount of ozone available.

Finally the pH of the solution has been known to influence the rate of decomposition of ozone (11-13). It has already been discussed that the decomposition products of the reaction of ozone with water appear to react with the organic material as well as with each other (12). If
the pH is varied, it is uncertain if ozone's decomposition rate will increase more than its rate of reaction with the organics, if both rates will increase equally, or if the decomposition rate will be less than the rate of reaction with the organics.

In summation, it is considered necessary to investigate the parameters pH, temperature and oxidant concent­rate associated with the oxidation by ozonation of low molecular weight organics from the effluent of a reverse osmosis unit. Only after the relationship is clearly established among parameters, can an intelligent attempt be made to optimize the use of ozone to destroy highly polar low molecular weight compounds not rejected by reverse osmosis.
CHAPTER 3

EXPERIMENTAL PROCEDURE

Experiments were performed involving the ozonation of aqueous solutions of several low molecular weight organic compounds that are not well rejected during the reverse osmosis process. Equipment, materials, analytical tests and operating conditions are described in this chapter.

Apparatus

A transparent lucite cylinder, having an inside diameter of 3.5 in. (8.9 cm) and 12.0 in. (30.5 cm) depth was converted into a gas-sparged, axially-mixed reactor. This reactor contained the 0.04 ft$^3$ (1.2 l) batches that were used in all trials. Two baffles, each approximately 0.4 in. (1.0 cm) wide were installed opposite each other within the cylinder to within 0.5 in. (1.2 cm) of the cylinder's bottom. The baffles eliminated a mixing vortex that was observed prior to their installation.

The cylinder's closed end had taps for gas feeding and batch draining. A diffuser plate having approximately 19 holes/in.$^2$ (3 holes/cm$^2$) each averaging .08 in. (0.2 cm) in diameter was installed 0.25 in. (0.6 cm) above the
cylinder's closed end. Ozone gas was fed through 0.38 in. (1.0 cm) Tygon tubing which had an easily broken connection to allow instant introduction or cessation of ozone to the diffuser.

A 316 stainless steel propeller, attached to a variable speed Talboys D.C. motor, was positioned to rotate at 1.0 in. (2.5 cm) above the cylinder's diffuser so that immediate turbulence and bubble size reduction would occur. Mixing speed was varied from 0 to 3000 RPM.

A Welsbach T-23 ozone generator set at 110 volts produced an oxygen-ozone gas mixture at flow rates from 0 to 0.15 scfm (250 l/hr) discharging at 2.0 psig (.14 Kg/M²). Pure oxygen feed gas was chilled by routing it through a 9.1 in.³ (150 cm³) bubbler that was surrounded by crushed ice. This minimized decomposition of ozone during its momentary contact with the electric discharge heat. Chilled water, fed to the generator's water jacket, removed heat that would otherwise buildup in the unit. A standard laboratory hood vented excess or unwanted ozone. A schematic diagram for the reactor system is shown in Figure 1.

Other experimental equipment used included a Mettler balance, a Beckman Expandomatic pH meter, a Strobotac Type 1531-A timing light, a Precision Warburg Apparatus, heating plates and Pyrex reflux condensers.
Figure 1. Gas-Sparged, Axially Mixed Batch Reactor Apparatus
Materials

All chemicals used were American Chemical Society Reagent Grade. Distilled deionized water was used to prepare each batch solution of the low molecular weight organic compounds studied.

Analytical Tests

Analytical determination of the reaction of ozone with organic material was the Chemical Oxygen Demand (COD) Test as described in the 13th Edition of Standard Methods for the Examination of Water and Wastewater (24). Ozone concentrations in the liquid batches were determined using a procedure also detailed in Standard Methods (24). The percent weight of ozone emitted by the ozonator was measured using the procedure described by Belew (25).

Reactor Conditions

Mixing Speeds

Prior to beginning the investigations related to varying the oxidant concentration, reactor temperature and solution pH, the optimum batch mixing speed was experimentally determined. The optimum batch mixing speed maximized the effect that turbulence has in reducing the thickness of the stagnant film that exists at the gas-liquid interface according to the two-film theory of gas transfer to a liquid. The rate of dissolution of ozone
was then primarily limited to the rate of molecular diffusion through the stagnant film (26).

Solutions of butyric acid, one of the carboxylic acids that are not well rejected by the reverse osmosis membrane, were equally prepared and ozonated for two hours at a pH of 10.0, a temperature of 72°F (22°C), and an ozone-oxygen gas mixture application of 0.03 scfm (50 l/hr). Each 1.2 liter batch was mixed at a different speed as measured by the Strobotac timing light.

Samples of approximately $1.06 \times 10^{-3} \text{ft}^3$ (30 cm$^3$) volume were drawn from the reactor at the end of the first 15, 30, 60, 90 and 120 minutes of each ozonation. A COD analysis for each sample, $0.71 \times 10^{-3} \text{ft}^3$ (20 cm$^3$), was made employing the dilute reagent technique. At the time the samples were permanently drawn from the reactor, an additional separate $1.77 \times 10^{-3} \text{ft}^3$ (50 ml) volume was momentarily drawn, then returned to the reactor after determining its pH value. This procedure was used during all other phases of the experimentation.

**Oxidant Concentrations**

The variance in concentration by weight of ozone supplied to identical solutions of butyric acid was studied using the same methods and procedures described in the experiment to determine optimum mixing speed. However, in this experiment the mixing speed was held constant at
1500 RPM while a different gas flow rate from 0 to 0.15 scfm (250 l/hr) emitted from the ozonator during each ozonation experiment.

**Temperature Variations**

Temperature effects were measured as the change in COD resulting after identical butyric acid solutions were prepared and ozonated as described in the previous experiments. The gas feed flow rate was held constant at 0.15 scfm (25 l/hr) while the temperature was maintained at 63°F (17°C), 95°F (35°C) and 110°F (43°C) for separate batch ozonations.

Changing the temperature of the solutions was accomplished by surrounding the lucite reactor with a water bath containing 20 ft (6.1 m) of 1/2 inch copper coil. Heated or chilled water from a Warburg Apparatus was continuously repumped through the coil. Figure 2 illustrates the process apparatus.

**pH Variations**

The same experimental conditions used to study the oxidant concentration effects on butyric acid solutions were used to study the effect of pH variance except that the gas flow rate was kept constant at 0.015 scfm (25 l/hr) while the pH was varied from 4.3 to 12.0.
Figure 2. Controlled Temperature Bath
Data related to the pH effect on ozone's ability to dissolve in distilled water was obtained using the same conditions just described. Approximate dissolved ozone values and pH readings were measured during the ozonation of distilled water adjusted initially to different pH levels.

**C₁ - C₄ Compounds**

The final experiments dealt with the comparison of oxidation rates of four low molecular weight carboxylic acids, two alcohols, a ketone and an aldehyde that were reported not to be rejected by the reverse osmosis process (8).

Solutions of each material were prepared and ozonated in the same manner as in the experiments related to pH effect, except that all solutions were initially adjusted to a pH of 10. The materials used were formic, acetic and propionic acid, isobutyl alcohol, normal butyl alcohol, methyl ethyl ketone and butyraldehyde.

An additional ozonation of formic acid solution was performed except that the generator voltage was zero; that is, no ozone was produced, and the duration of the solution's exposure to the pure oxygen was only one hour instead of two. This experiment concluded the procedure used to obtain the analytical data.
In a step-wise fashion, reaction parameters were studied to find the optimum response for the oxidation of butyric acid solutions. First the effect of mixing speed was ascertained. Next the effect of oxygen-ozone gas feed concentration and flow rate was determined. With these two conditions fixed, the parameters of temperature and pH were studied. Using the above findings the oxidations of four carboxylic acids, two alcohols, an aldehyde and a ketone were compared.

**Effect of Mixing**

Figure 3 depicts the percent COD remaining as a function of ozonation time and mixing intensity for a butyric acid solution with an initial COD of 70-80 mg/l. Each rate of oxidation was obtained by calculating the slope of the line that best fits each set of data. The slope of each line increased as the mixing RPM was increased. However, the rate at which the slopes increased progressively decreased with increasing mixing speeds, as shown in Figure 4.
Figure 3. Effect of Mixing Speed on the Oxidation of Butyric Acid
Figure 4. Limitation Effect of Mixing Speed on the Oxidation of Butyric Acid
For mixing speeds greater than 1500 RPM, the change in oxidation rate was negligible. This effect indicates that ozone's oxidation capability was limited by its rate of dissolution since, according to the two-film theory:

\[ \frac{dO_3}{dt} = K (C_s - C_t) \]

where \( dO_3 \) = rate of ozone dissolution

\[ K = \text{mass transfer coefficient} \]

\[ K \propto \frac{a}{\delta} \]

\( C_s = \text{saturated concentration of ozone in solution} \)

\( C_t = \text{concentration of ozone in solution at a given time} \)

\( a = \text{interfacial area for transfer} \)

\( \delta = \text{film thickness} \)

At the mixing speed of 1500 RPM, the interfacial area for transfer of the ozone gas approached its maximum value. For this experimental system, the stagnant film thickness also approached its minimum value. Because a higher mixing rate would have very little effect on \( K \), the mixing speed of 1500 RPM, in this experimental system, was used for the remainder of the experiments.
Effect of Oxidant Concentration

The tabulations in Table I list the experimental determinations of ozone concentrations (% wt) that emanated from the Welsbach T-23 ozonator when different oxygen flow rates were used. Also tabulated are calculated values of the ozone production rate for each oxygen flow rate used. A maximum ozone concentration of approximately 5.67% by weight occurred when the oxygen flow rate was approximately 0.015 scfm (25 l/hr). The maximum ozone production rate of this particular ozonator was approached when its production rate was 8,210 mg/hr.

TABLE I
OZONE PRODUCTION

<table>
<thead>
<tr>
<th>Oxygen Supply Rate (l/hr)</th>
<th>Ozone Concentration (% wt)</th>
<th>Ozone Production Rate (mg/hr)</th>
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<tr>
<td>12.5</td>
<td>5.06</td>
<td>1,355</td>
</tr>
<tr>
<td>25.0</td>
<td>5.67*</td>
<td>3,050</td>
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<tr>
<td>37.5</td>
<td>4.84</td>
<td>3,870</td>
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<td>7,410</td>
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<td>200.0</td>
<td>1.87</td>
<td>8,025</td>
</tr>
<tr>
<td>250.0</td>
<td>1.53</td>
<td>8,210</td>
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</table>

*Optimum characteristic of the ozonator
Figure 5 shows the effect that oxygen-ozone feed flows to the gas sparged reactor had on the rate of oxidation, $\frac{d \delta \text{(COD)}}{dt}$, of aqueous butyric acid solutions having a COD of 70 mg/l. The oxidation rate increased when the oxygen-ozone feed flow was increased from 0.0075 scfm (12.5 l/hr) to 0.015 scfm (25 l/hr). When the oxygen-ozone feed flow was increased above 0.015 scfm (25 l/hr) to 0.03 scfm (50 l/hr), no significant change occurred in the oxidation rate. However, Figure 6 shows that as the oxygen-ozone feed flow was increased beyond 0.03 scfm (50 l/hr) through 0.15 scfm (250 l/hr) the oxidation rate of the butyric acid solution progressively decreased.

This relationship is probably due to the fact that the reactor residence time of the oxygen-ozone feed gas had decreased. Since the velocity of the oxygen-ozone feed gas was directly proportional to its flow, as the velocity increased it took less time to pass through the reactor. Therefore, there was insufficient time for ozone to be transported to the liquid phase where it decomposed prior to its oxidation of butyric acid.

Figure 7 shows that when the oxygen-ozone feed flow was greater or less than 0.15 scfm (25 l/hr) during the first thirty minutes of oxidation, a lesser rate of oxidation occurred. Table I shows that the maximum ozone concentration was produced at 0.15 scfm (25 l/hr).
Figure 5. Effect of Low Oxygen-Ozone Feed Flows on the Oxidation of Butyric Acid
Figure 6. Effect of High Oxygen-Ozone Feed Flows on the Oxidation of Butyric Acid
Figure 7. Effect of Different Durations of Oxygen-Ozone Feed Flows on the Oxidation of Butyric Acid
The oxygen-ozone gas feed flow of 0.15 scfm (25 l/hr) is associated with both the maximum ozone concentration possible and the maximum oxidation achieved. Since it appeared that the ozone concentration affected the oxidation rate for the reactor conditions used, its associated oxygen-ozone feed flow of 0.015 scfm (25 l/hr) was maintained throughout the remainder of the experiments.

**Effect of Varying Temperature**

Figure 8 illustrates the effect on the oxidation rate of four identical batches of butyric acid solution maintained at four different temperatures during their ozonation. The figure shows that the oxidation rate of the butyric acid solutions increased as the temperature increased.

Figure 9 is an Arrhenius plot of the data shown in Figure 8 where:

\[
K_m = \ln \left( \frac{(COD)_{in}}{(COD)_{out}} \right) \frac{\text{time (min)}}{\text{time (min)}}
\]

It shows that the oxidation rate constant varied linearly as temperature of the reaction was changed. Hewes and Davidson noted the same relationship when they ozonated secondary domestic sewage at different temperatures (12). These variations in the reaction rate as a
Figure 8. Effect of Solution Temperature on the Oxidation of Butyric Acid
Figure 9. Arrhenius Plot for Butyric Acid
function of temperature can be expressed by the Arrhenius equation written in the logarithmic form:

$$\log_{10} K_m = \log_{10} A_f - \frac{E}{2.303 RT}$$

where $K_m$ is the rate constant, $A_f$ is the Arrhenius frequency factor, $E$ is the activation energy, $R$ is the universal gas constant, and $T$ is the absolute temperature.

The plot of the data shown in Figure 9 is linear, with the slope of the line equal to $\frac{E}{2.303 RT}$ and the intercept on the $\log_{10} K_m$ axis is equal to $\log_{10} A_f$.

The slope $= -6550$, and the $\log_{10} K_m$ intercept is calculated to be $18.0 \text{ min}^{-1}$.

$$-E = (-6550) (2.303)(1.98) \text{ or } E = 29,800 \text{ cal/mole}$$

and $\log_{10} A_f = 18.0 \text{ or } A_f = 1 \times 10^{-18} \text{ min}^{-1}$.

The high activation energy obtained indicates the system was reaction-rate controlled and not mass transfer limited. The complete rate expression for the oxidation of butyric acid is

$$-d(C_3H_7\text{COOH}) + 10^{-18} e^{-29,800/ft} C_3H_7\text{COOH} \text{ moles l}^{-1}\text{min}^{-1}$$

Although the temperature of an aqueous butyric acid solution affected its rate of oxidation by ozone, the effect diminished when approximately 10% of the butyric
acid remained, as indicated in Figure 10. Similar data involving the oxidation of treated sewage was reported by Wynn et al. (13). It appears that this effect occurred because the probability of a singlet oxygen radical contacting a butyric acid molecule decreased when the organic concentration decreased. Simultaneously, the probability of a singlet oxygen radical combination increased due to the constant ozone production.

As shown in Table II, the solubility of ozone in water decreases as the water's temperature is increased (1). However, this effect did not greatly negate the positive effect that temperature had on ozone's oxidation of butyric acid solution, as Figure 8 shows.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Bunsen Coefficient (xB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.375</td>
</tr>
<tr>
<td>20</td>
<td>0.285</td>
</tr>
<tr>
<td>30</td>
<td>0.200</td>
</tr>
<tr>
<td>40</td>
<td>0.145</td>
</tr>
</tbody>
</table>

The investigations of pH effect on the ozonation of butyric acid solutions were performed at 72°F (22°C) as
Figure 10. Effect of Solution Concentration on the Oxidation of Butyric Acid
were the studies comparing the oxidation of different low molecular weight compounds.

**Effect of Varying pH**

Figure 11 relates the effect of varying the pH of butyric acid solutions, prepared and ozonated according to the parameters described on p. 16. As the solution's initial pH was increased prior to each ozonation, its rate of oxidation increased. This general concept that ozone's oxidation of an organic substance is pH dependent has been noted by others (11-13). It was generally postulated that the increased oxidation rates were catalyzed by the increase in hydroxyl ions to the solution (12).

Although Figure 11 indicates that no oxidation occurred during the two hour ozonation of the unaltered butyric acid solution, its COD increased approximately 10% at the end of that duration. Because foaming occurred throughout the entire first experimental ozonation period, the possibility of contamination of the batch or reactor equipment was considered. Therefore, everything that came into contact with the solution was carefully cleaned with detergent and a fresh sample was prepared and ozonated. The same foaming effect was again observed along with almost identical data indicating an increase in COD as ozonation continued. It is possible that the butyric acid was partially oxidized to peroxypbutyric acid,
Figure 11. Effect of Initial pH on the Oxidation of Butyric Acid
C₃H₇CO₃H, in a manner similar to that described by Swern (27). Peroxybutyric acid may have resulted when some hydrogen peroxide, formed as a result of ozone's decomposition, combined with the butyric acid in the presence of the concentrated sulfuric acid used in the COD test. The nature and proportion of products resulting from the decomposition of peroxybutyric acid depends on two different decomposition pathways. According to the pathway chosen, some of the products formed may have a higher COD than the original compound.

The pH adjusted batches of butyric acid did not foam at any time during ozonation. Due to the change in pH, the amount and variety of ozone's decomposition products may have changed so that very little peroxybutyric acid was formed. Therefore, the ozonation of butyric acid resulted in the expected manner of COD reduction.

Table III lists the pH values determined during ozonation of aqueous butyric acid solutions adjusted to a different initial pH level. While the pH of the unaltered solution did not change during the two hour run, the pH of the following four samples was lowered. It appeared that the hydroxyl ions introduced by addition of sodium hydroxide were utilized for ozone's reaction with the butyric acid.
TABLE III
CHANGE IN INITIAL pH ADJUSTMENTS

<table>
<thead>
<tr>
<th>Time of Sample</th>
<th>Sample pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>0 min</td>
<td>4.3</td>
</tr>
<tr>
<td>15 min</td>
<td>4.3</td>
</tr>
<tr>
<td>30 min</td>
<td>4.3</td>
</tr>
<tr>
<td>60 min</td>
<td>4.3</td>
</tr>
<tr>
<td>90 min</td>
<td>4.3</td>
</tr>
<tr>
<td>120 min</td>
<td>4.3</td>
</tr>
</tbody>
</table>

*Unaltered aqueous butyric acid solution

When the pH was adjusted initially to 12.0, a pH reduction to 11.8 occurred during the first 30 minutes, which was the time it took to destroy 80% of the butyric acid. After this period the pH remained at 11.8 and only 15% more butyric acid was oxidized, indicating that the rate of butyric acid removal was dependent on the presence of the hydroxyl ions. The fact that 5% of the butyric acid remained after two hours of highly pH-catalyzed ozonation is an indication that the ozone decomposed then recombined as oxygen much more rapidly than it reacted with the butyric acid.

Figure 12 depicts the effect pH had on the saturation of ozone in distilled water batches adjusted to pH
Figure 12. Effect of Initial pH on the Dissolution of Ozone in Distilled Water
4.3, 5.0 and 6.3. For each pH level, dissolved ozone concentrations were obtained after ozonating identically prepared batches for increasing intervals of time up to a maximum interval of two hours. Using the optimum mixing speed of 1500RPM, it required approximately 10 minutes for each individually adjusted batch to reach a saturated value. As the hydroxyl ion concentration was increased, the saturated dissolved ozone concentration decreased, and the time required to reach saturation increased. This effect is more pronounced in Figure 13, which shows a saturation level of only 6 mg/l was obtained after thirty minutes of ozonation when the initial pH of the distilled water was adjusted to 10.0.

Figure 14 depicts the approximate saturation levels of ozone in distilled water as a function of the water's pH. Additional saturation values were obtained for pH 5.7, 11.1 and 12.0 after one batch of distilled water at each pH had been ozonated for an interval of two hours. There was no measurable amount of ozone in the batches adjusted to pH 11 and 12. However, a slight color change was evident during the collection of ozone from the pH 11.1 sample indicating that a very slight amount of ozone was present, perhaps only 0.1 mg/l.

The saturated values indicated in Figure 14 are only relative values of the ozone residual existing in
Figure 13. Effect of pH 10 on the Dissolution of Ozone in Distilled Water
Figure 14. Effect of Initial pH on the Saturation of Ozone in Distilled Water
distilled water one minute after the cessation of ozone application. During the time interval it required to determine the ozone residual in each batch a different amount of ozone had decomposed. As the pH of the batch increased, the amount of ozone collected decreased. Therefore, the measured ozone saturation values are progressively less accurate for the higher values of pH.

Stumm studied the decomposition of ozone in aqueous solutions varying in pH from 7.6 to 10.4 at 58.3°F (14.6°C) (19). His information indicates that the ozone saturation value decreased so rapidly at pH 10, its value could not be determined accurately. However, using his data, the measured ozone saturation value after one minute for a distilled water batch at pH 8 was determined to be within 10% of its actual value. This indicated that for pH values less than 7.6, the measured saturation value is almost equal to the actual saturation value. Because the measured saturation value decreased from 18 mg/l to 9 mg/l as the pH was varied from 4.3 to 6.2, it is indicative of the limiting effect of pH on ozone saturation values in water.

While Figure 11 indicates that ozone's oxidation rate increased when the initial pH was increased, Figure 14 shows that the concentration of ozone available had decreased when the pH was increased. These results
express the idea that ozone's oxidation rate is dependent on pH more than it is dependent on its concentration. However, the optimum concentration, as determined in the prior experiments concerning oxidant concentration, is also a contributing factor.

Although ozone's oxidation rate is dependent more on pH than concentration it was shown in Table III that an excessive initial pH adjustment to the butyric acid solution created an excessive final pH in the oxidized solution. However, at pH 10 the increased oxidation rate utilized most of the excessive hydroxyl ions so that a final pH of approximately 7.0 resulted. It appears then, that an approximate pH value of 10.0 would be the optimum to use in the ozonation of aqueous butyric acid solution.

Comparing C₁ - C₄ Carboxylic Acids

The results of the ozonation of aqueous solutions of formic, acetic, propionic and butyric acids are shown in Figure 15. The formic acid was the easiest of these four acids to oxidize to carbon dioxide and water because its molecular bonding structure is the least complex of the four acids. The order of difficulty in oxidizing acetic and propionic acid followed the expected trend. However, the oxidation rate for the most complex acid studied, butyric acid, fell between formic and acetic
Figure 15. Comparative Effect on the Ozonation of C₁ - C₄ Carboxylic Acids
acid. It is postulated that this result is due to the partial oxidation products and the relative ease of their oxidation to carbon dioxide and water.

Because formic acid oxidized so rapidly, it was suspected the oxygen-ozone mixture merely stripped it out of solution, rather than oxidized it. Therefore, an identical batch was "ozonated" for one hour with the ozone generator electrically shut off. In effect, the solution was exposed to pure oxygen and mixing only. As Figure 16 demonstrates, the oxygen did not strip the formic acid out of solution. Rather it tended to increase the original COD by almost 10%, indicating a slight oxidation of other ingredients within the stock formic acid, (89.7% assay), that was used to produce the solution. The ozone in the first run, however, did effect a 99% removal in 15 minutes.

Comparing Butane Compounds

Figure 17 shows the comparison of the oxidation of products of the butane structure, namely, normal butyl alcohol, isobutyl alcohol, methyl ethyl ketone, butyraldehyde and butyric acid. It was found that butyric acid was easiest to oxidize followed by the alcohols, then the ketone and the aldehyde. According to Feiser and Feiser, ozone is a more specific reagent for the double bond which characterizes the structure of the acid (28).
Figure 16. Effect of Oxygen Without Ozone on the Oxidation of Formic Acid
Figure 17. Effect of Ozonation on Butane Structure
Therefore, ozone does not attack the alcohols as well because their structure is composed of single bonds.

It is postulated that the reason for the low oxidation of the butyraldehyde is that it was immediately converted to a ketone, which is resistant to oxidizing agents, according to Feiser and Feiser (28).
CHAPTER 5

CONCLUSIONS

The following conclusions are made concerning the results obtained after studying the effect of mixing speeds, oxidant concentrations, temperature and pH on the ozonation of aqueous solutions of highly polar low molecular weight organic compounds. These conclusions apply to only the particular experimental conditions that were used and the particular compounds that were selected.

1. Ozone's oxidation capability is limited by its rate of molecular transfer across the stagnant liquid film into the bulk liquid. The interfacial area of the transferring ozone gas was maximized while the stagnant film thickness approached its minimum value when the batch mixing speed was 1500 RPM.

2. The maximum rate of oxidation of butyric acid is dependent on the maximum concentration of ozone in the applied oxygen-ozone gas mixture. This concentration is 5.67% by weight when the oxygen supply rate was 0.015 scfm (25 l/hr).

3. Butyric acid's oxidation rate is temperature responsive, according to the linear relationship observed
in the Arrhenius plot. An activated energy of 29.8 Kcal/mole was determined.

4. The negative effect of ozone's decreasing solubility does not greatly affect ozone's ability to oxidize butyric acid as the butyric acid solution temperature is raised.

5. Solution pH affects ozone's ability to oxidize butyric acid. As each solution pH was increased from 4.3 to 12.0, the oxidation rates increased.

6. Ozone's saturation level in distilled water is adversely affected by the pH of the solution.

7. In solution, the decomposition of ozone into singlet oxygen atoms is rate-controlled by the pH of the solution.

Suggested Future Research

1. It is suggested that the experiments should be repeated using a Total Organic Carbon (TOC) analyzer instead of the COD analytical test. A better explanation may be possible for the partial oxidations of some of the materials studied.

2. The actual solutions emanating from a reverse osmosis membrane should be ozonated using the optimum parameters noted during the studies of the synthetic solutions. This would validate the step-wise optimized procedure employed.
3. A study should be made comparing the effects, if any, of different sources of the catalytic hydroxyl ions, such as, potassium hydroxide, calcium hydroxide and ammonium hydroxide. The cost of these catalytic agents may vary appreciably.
LIST OF REFERENCES


19. Stumm, W., "Ozone as a Disinfectant for Water and Sewage." Boston Society of Civil Engineers, 45, 1, 72 (1958).


