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SUPERCRITICAL WASTE OXIDATION OF AQUEOUS WASTES
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ABSTRACT

For aqueous wastes containing 1 to 20 wt% organics, supercritical water oxidation is less costly than controlled incineration or activated carbon treatment and far more efficient than wet oxidation. Above the critical temperature ($374^{O}C$) and pressure (218 atm) of water, organic materials and gases are completely miscible with water. In supercritical water oxidation, organics, air and water are brought together in a mixture at 250 atm and temperatures above $400^{O}C$. Organic oxidation is initiated spontaneously at these conditions. The heat of combustion is released within the fluid and results in a rise in temperature to $600-650^{O}C$. Under these conditions, organics are destroyed rapidly with efficiencies in excess of 99.999%. Heteroatoms are oxidized to acids, which can be precipitated out as salts by adding a base to the feed. Examples are given for process configurations to treat aqueous wastes with 10 and 2 wt% organics.

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INTRODUCTION

Aqueous wastes containing organic materials represent a major fraction of the total toxic and hazardous waste generated in the U.S. The predominant treatment methods have been deep-well injection and lagooning (including solar evaporation). These land-based disposal practices do not address ultimate destruction of the toxic components of the waste; consequently, there is increasing public concern with continued reliance on these techniques. Destruction methods, which usually cost an order of magnitude more than disposal methods, are based on oxidation of the organic content. For aqueous wastes, destruction methods include activated carbon treatment (with oxidative regeneration), incineration, wet oxidation and supercritical water oxidation.

For very dilute aqueous wastes (e.g., below 1% organic), activated carbon treatment is a viable alternative. Organics are desorbed and then oxidized during regeneration of the carbon. Since a significant fraction of the activated carbon is lost to oxidation during regeneration, fresh carbon must be added each cycle as make up. After-- burners are used to destroy vapors that may result from partial oxidation during regeneration. The major cost of carbon treatment is the cost of regenerating the carbon and

providing the make up carbon. Since the cost per gallon is nearly proportional to the organic content, carbon treatment is usually not considered for wastes containing more than 1% organic.

Incineration, on the other hand, is usually restricted for economic reasons to relatively concentrated aqueous wastes. To attain high destruction efficiencies in treating toxic waste, incineration is conducted at high temperature $(900-1100^{O}C)$ with relatively long residence time (e.g.,2 sec). With aqueous wastes, the heat required to bring the water component of the waste to these severe conditions is substantial. If the waste contains 25% organic or more, there is sufficient heating value in the waste to sustain the process. With decreasing organic content, the supplemental fuel required to satisfy the energy balance becomes a major cost. Thus, controlled incineration of aqueous wastes with less than 20% organic is only considered in extenuating circumstances.

In the range of concentrations of 1 to 20% organic, wet oxidation and supercritical water oxidation are far less costly than controlled incineration or activated carbon treatment. In wet oxidation of hazardous wastes, organics are oxidized in the aqueous phase at temperatures in the

range of 150 to 300°C and under pressures of 100 to 150 atm (1). In practice, residence times of 0.5 to 2 hr are required for removal of 50 to 95% of the initial COD. The residual organics are primarily innocuous aliphatic acids, which are by-products of oxidation of more complex molecules, and which are oxidized very slowly under wet oxidation conditions. Destruction of toxic organic chemicals (e.g., chlorophenols, nitrotoluenes) can be as high as 99.9%, but many materials are more resistant (e.g., chlorobenzenes and PCB's).

Although wet oxidation is more energy-efficient than incineration, the process suffers from a number of limitations. Under the conditions in which air and aqueous waste are mixed, the solubility of oxygen in water is considerably less than that required for complete oxidation. Thus, a two-phase mixture is present in the reactor. The reactor is an expensive item because it must operate at high temperature and high pressure with a relatively large volume to provide necessary residence time. Because the oxidation is not complete, the off-gas from the process can contain appreciable concentrations of volatile organics and may require additional treatment before release to the atmosphere.

SUPERCRITICAL WATER OXIDATION

Supercritical water oxidation of organics is an improvement upon wet oxidation and represents a breakthrough in enhanced efficiency and reduction in capital investment. The major advantages of operating supercritically are:

o enhanced solubility of oxygen and air in water, which eliminates two-phase flow;

o rapid oxidation of organics, which approaches adiabatic conditions as well as high outlet temperatures with very short residence times;

o complete oxidation of organics, which eliminates the need for auxiliary off-gas processing;

o removal of inorganic constituents, which precipitate out of the reactor effluent at temperatures above $450^{\circ}C$; and

o recovery of the heat of combustion in the form of supercritical water, which can be a source of high-temperature process heat or used to generate power in supercritical turbines.

These advantages arise primarily from the unusual properties exhibited by water under supercritical conditions.

The Properties of Supercritical Water

Above the critical temperature and pressure, the properties of water are quite different from that of the
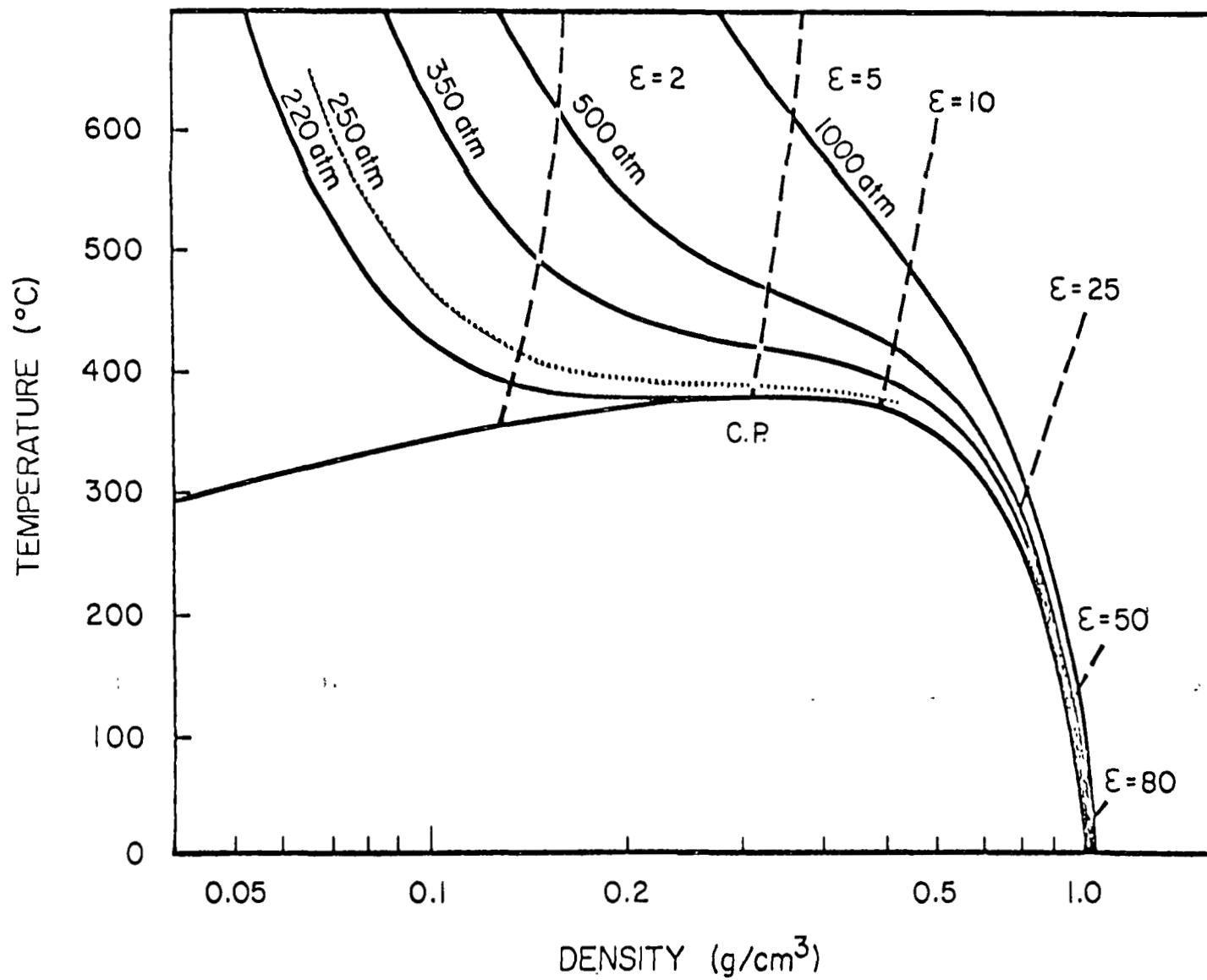
Figure 1

Temperature-density diagram for water with isobars
(solid lines) and constant dielectric constant (dashed lines)

normal liquid or atmospheric steam. For example, organic
substances are completely soluble (i.e., miscible in all
proportions) in water under some supercritical conditions,
while salts are almost insoluble under other supercritical
conditions. These solubility characteristics are strongly
dependent upon density.

A temperature-density diagram is shown in Fig. 1. The
critical point (C.P.), which lies on the vapor-liquid
saturation dome, occurs at 374°C and 0.3 g/cm^3. The
supercritical region lies above 374°C and to the right of
the 220 isobar. Near the critical point (e.g., between
300°C to 450°C and densities from 0.2 to 0.7 g/cm^3),
the density varies very rapidly with relatively small
changes in temperature at constant pressure.

Insight into the structure of the aqueous fluid in this
region has been obtained from measurements of the static
dielectric constant, which are also shown in Fig. 1 (2,3).
The dielectric constants of some common solvents are given,
for comparison, in Table 1.

The dielectric constant is a measure of the degree of
molecular association. Normal liquid water has an ξ of 80,
largely as a result of strong hydrogen bonding. The

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TABLE 1.   DIELECTRIC CONSTANTS OF SOME COMMON SOLVENTS

Carbon Dioxide	1.60
n-Hexane	1.89
Benzene	2.28
Ethyl ether	4.34
Ethyl acetate	6.02
Benzyl alcohol	13.1
Ammonia	16.9
Isopropanol	18.3
Acetone	20.7
Ethanol	24.3
Methanol	32.6
Ethylene glycol	37.
Formic acid	58.

dielectric constant of the saturated liquid decreases rapidly with increasing temperature, even though the density falls slowly. Since hydrogen bonding forces are strong only when molecules are in close proximity, small increases in density parallel relatively large decreases in short-range order resulting in a rapid decline in ε. At $130^{O}C$ ($\rho =$ 0.9 g/cm^3), the dielectric constant is about 50, which is near that of formic acid; at $260^{O}C$ ($\rho =$ 0.8 g/cm^3), the ε of 25 is similar to that of ethanol.

As density decreases further, the dielectric constant becomes less dependent upon temperature (i.e., the lines of constant ε in Fig. 1 become almost vertical). At the critical point, the dielectric constant is 5. Ramon spectra of HDO in this region indicate little, if any, residual

hydrogen bonding (4). The major contribution to $\mathcal{E}$ is now molecular association due to dipole-dipole interactions, which gradually decrease with increasing void volume.

Above 300°C, the temperature-density relationship becomes pressure-dependent (see Fig. 1). We shall follow the 250 atm isobar (which is a convenient pressure for supercritical operations). At 300°C, the $\mathcal{E}$ of about 15 is similar to that of benzyl alcohol. Proceeding above 300°C along the 250 isobar, we see $\mathcal{E}$ dropping to 10 at 400°C, 5 at 420°C and 2 at 490°C. Through the two hundred degree rise from 300 to 500°C, the dielectric constant varies from that of moderately polar to non-polar organic solvents.

While dielectric constant is not the sole determinant of solubility behavior, the solvent power of water for organics is consistent with the variation of $\mathcal{E}$, as described above. Benzene solubility in water is a good example (5,6). At 25°C, benzene is sparingly soluble in water (0.07 wt%). At 260°C, the solubility is about 7 to 8 wt% and fairly independent of pressure. At 287°C, the solubility is somewhat pressure dependent, with a maximum of 28 wt% at 200 to 250 atm. In this pressure range, the solubility rises to 35 wt% at 295°C; at 300°C, the critical point of the benzene-water mixture is surpassed.

When the mixture becomes supercritical, by definition, there is only a single phase. Thus, the components are miscible in all proportions.

Other hydrocarbons exhibit similar solubility behavior. Aliphatic hydrocarbons are somewhat less soluble in water at comparable temperatures. Thus, higher temperatures are required to reach the same solubility as that of benzene. Binary mixtures of pentane-water and heptane-water become supercritical (and, therefore, completely miscible) at about $350^{\circ}C$ (5).

The locus of critical points of binary mixtures containing water have been reported for a variety of organic substances (e.g., ethane, ethylene, n-butane, 1,3,5 trimethylbenzene, naphthalene) and gases (nitrogen, carbon dioxide, ammonia, hydrogen, argon). Except for argon, all of the compounds studied to date are completely miscible with water above $374^{\circ}C$ at 250 atm. Argon is completely miscible above $390^{\circ}C$.

For densities less than 0.7 g/cm^3, the solubility of inorganic salts in water is as unusual as that of organics. At 250 atm, the solubilities of salts reach a maximum at 300 to $450^{\circ}C$. Beyond the maximum, the solubilities drop very

rapidly with increasing temperature. For example, NaCl solubility is about 40 wt% at 300°C and about 100 ppm at 450°C; $CaCl_2$ has a maximum solubility of 70 wt% at subcritical temperatures, which drops to 10 ppm at 500°C (7). Given the fact that the dielectric constant of water is about 2 at 490°C and 250 atm (see Fig. 1), it is not surprising that inorganics are practically insoluble.

Coincident with the loss of solvating power for inorganic salts, supercritical water also loses the ability to dissociate salts. For example, the dissociation constant of NaCl at 400-500°C and densities in the range of 0.35 is of the order of 10^{-4}. Thus, strong electrolytes become weak electrolytes in supercritical water.

The properties of water, as a function of temperature, are summarized in Fig. 2. We see that water goes through a complete reversal in solubility behavior toward organic and inorganic substances through the temperature range of 350-450°C. Below this range, the pattern is similar to normal liquid water: low organic and high inorganic solubility. Within the range, there is high solubility of both organic and inorganic substances. Above this range, inorganic salts are practically insoluble, and organic substances are completely miscible.
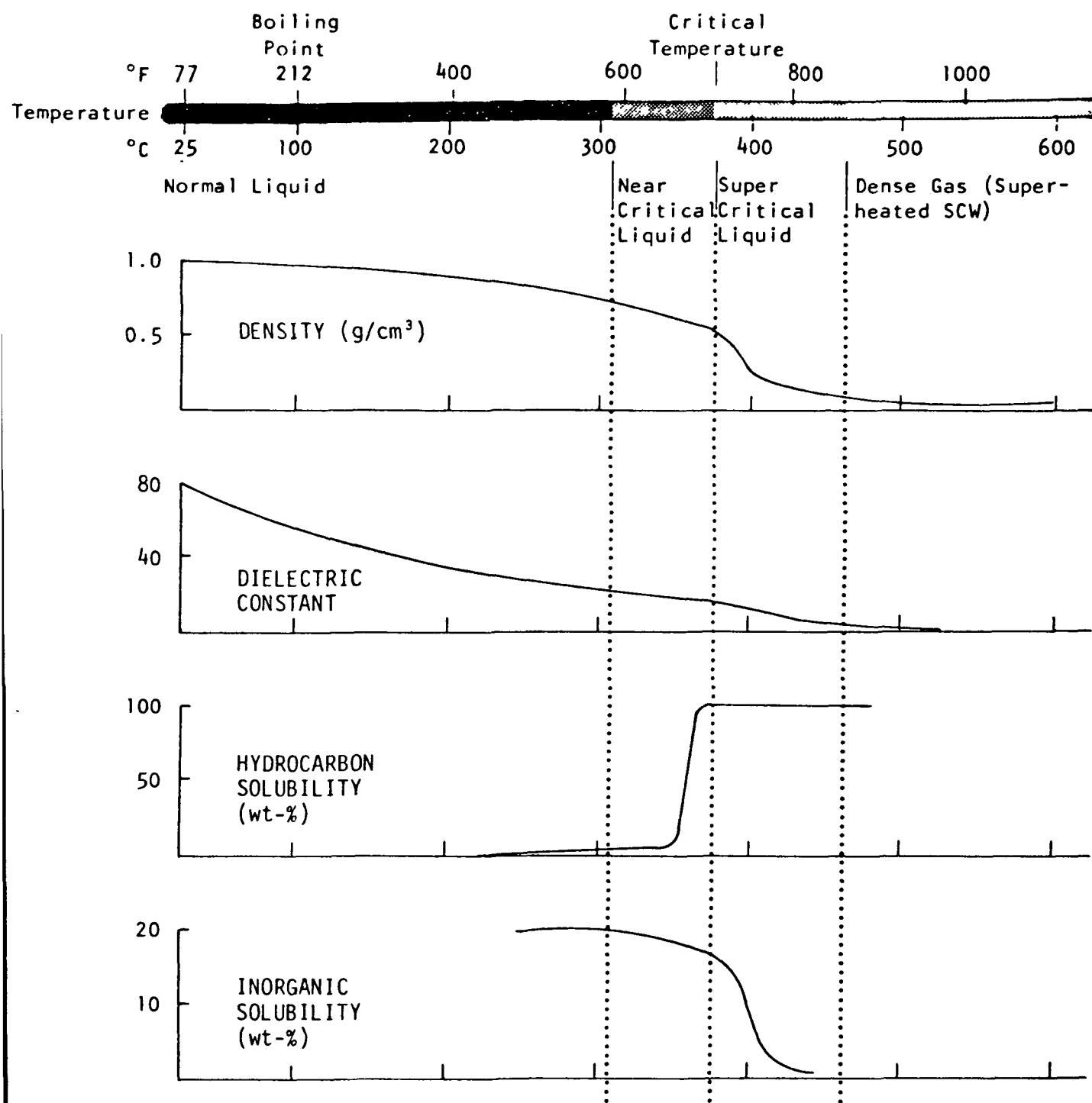
Figure 2

Properties of water at 250 atmospheres

The Effect of Temperature on Destruction Efficiency

Over the past five years, a number of studies of SCW oxidation have been conducted using a bench scale unit, which has been described previously (8,9). Reported here are results of a study of the effect of temperature on destruction efficiency. The results, shown in Table 2, are striking examples, yet quite typical of other results that have been obtained. The feed material for the tests of Table 2 were mixtures of 2,4-nitrotoluene in methylethyl ketone. All experiments were run with a residence time of 20 to 30 sec. Each column of Table 2 represents the average values of the two runs.

At the four temperatures of 404, 457, 513 and 574°C, the organic carbon destruction efficiencies were 92.5, 99.8, 99.93 and 99.998%, respectively. These results correspond to an increase in rate of over 3 orders in magnitude in the temperature range of 404 to 574°C. There is reason to believe that these results are limited not by reaction kinetics but by the rate of mixing of reactants. Rates of almost two orders of magnitude higher than the highest of Table 2 were observed when operating with a new feed intro-duction device at 630°C (i.e., destruction efficiencies were greater than 99.999% at residence times as low as 0.6 sec).

TABLE 2

THE EFFECT OF TEMPERATURE ON DESTRUCTION EFFICIENCY; OXIDATION OF DINITROTOLUENE

Run No.	44/45B	42/43	39/40	69/70A
Feed Material	3% DNT/ MEK	3% DNT/ MEK	3% DNT/ MEK	12% DNT/ MEK
Temperature ($^{\circ}$C)	404	457	513	574
Carbon Analysis				
Organic Carbon In (ppm)	9,540	9,650	9,750	17,530
Organic Carbon Out (ppm)	712	15.7	6.9	0.4
Destruction Efficiency (%)	92.5	99.8	99.93	99.998
Total Carbon Recovered (%)	99.9	98.6	100.6	106.1
Nitrogen Analysis				
Organic Nitrogen In (ppm)	64	65	65	511
Nitrogen Out-Liquid (%)	58.7[a]	10.6[a]	2.2[a]	6.4[b]
Nitrogen Out-Gas (%)	NA	23.1[c]	23.1[c]	94.4
Total Nitrogen Recovered (%)	58.7	33.7	25.3	100.8
Gas Composition (mol %)				
O_2	16.96	11.88	15.04	15.08
CO_2	70.40	88.85	81.24	84.80
CH_4	0.10	0.06	0.18	ND
H_2	1.68	0.08	0.04	ND
CO	9.63	0.29	0.35	ND
N_2	0.10	0.06	0.06	0.41
N_2O	NA	NA	NA	0.57
NO	NA	NA	NA	ND
Liquid Products Containing Nitrogen (ppm)				
Dinitrobenzene	170.4	0.187	0.0066	<1 ppb
Dinitrophenol	6.1	0.002	0.0046	<1 ppb
Dinitrotoluene	60.5	0.535	0.0087	<1 ppb
Dinotrocresol	1.2	0.024	0.0018	<1 ppb

[a] Primarily organic nitrogen in liquid products
[b] Primarily nitrate and nitrite nitrogen
[c] Molecular nitrogen

It is interesting to note the fate of organic nitrogen in the dinitrotoluene oxidation tests. At $574^{\circ}C$, the last column of Table 2, 94% of the nitrogen in the feed is recovered as N_2 and N_2O in the gaseous effluent and 6% is recovered as nitrate and nitrite ions in the liquid effluent. No NO, NO_2 or NH_3 was found in the gas phase nor was NH_3 found in the liquid phase.

In the other three columns of Table 2, the nitrogen material balance closure was poor because we did not analyze for N_2O in the gas phase and NH_3 in the liquid phase. In other experiments with dinitrotoluene, ammonia and amines were found at 400 to $500^{\circ}C$ while N_2O is the major product at 500 to $550^{\circ}C$.

In no case were NO and NO_2 formed as products of oxidation of nitrogen compounds in SCW oxidation. At 600 to $650^{\circ}C$, N_2 and N_2O are the major products, even when the feed is primarily ammonia nitrogen. The N_2O component can be readily decomposed catalytically to N_2 and O_2 and, thus, SCW oxidation of nitrogen-containing organics is far less damaging to the environment than high temperature incineration.

Figure 3

Process Schematic for Oxidation of an
Aqueous Waste with a heating value of
1750 Btu/lb
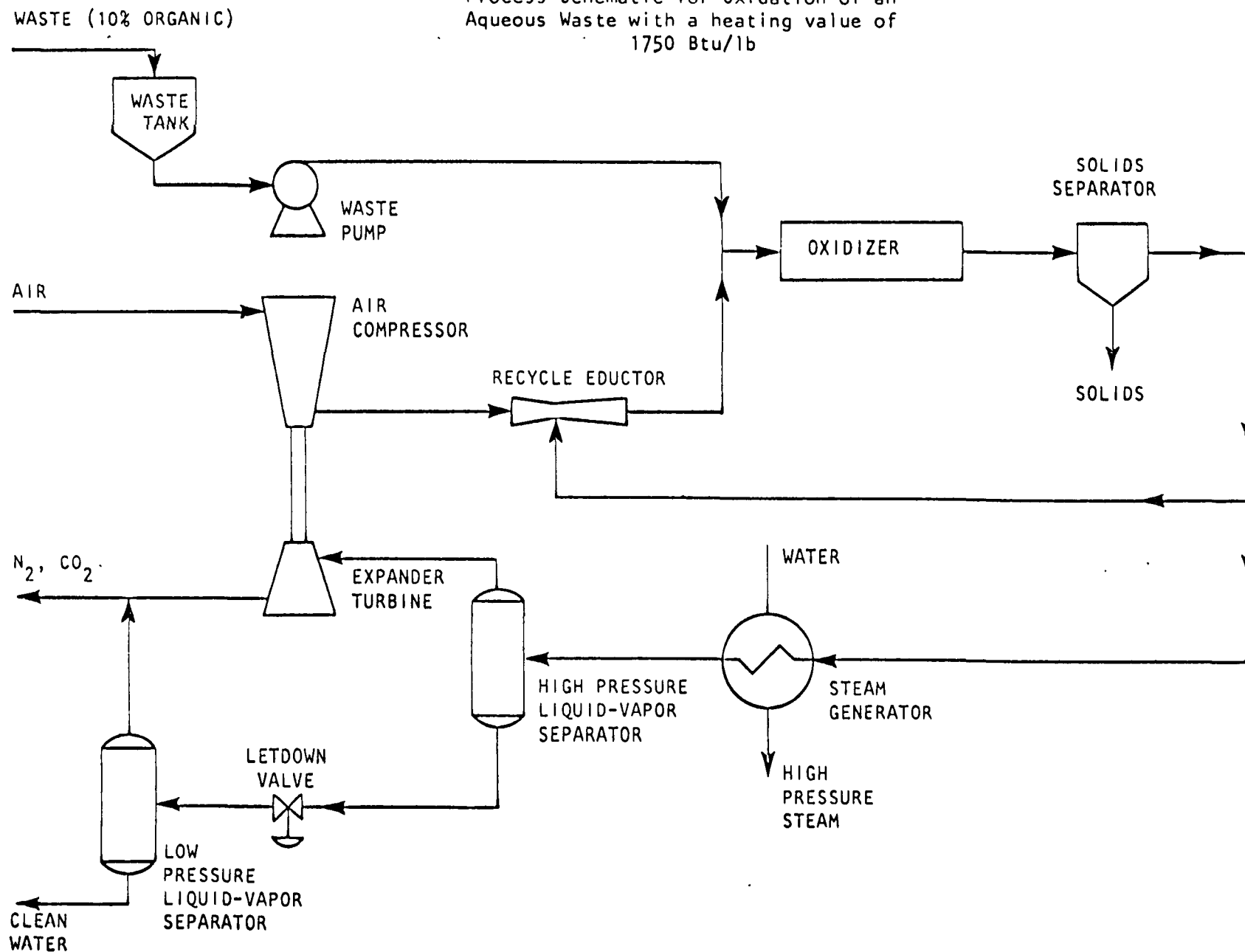
SCWO for Treatment of Aqueous Wastes

Supercritical water oxidation can be applied to wastes with a wide range of organic concentration. A schematic flowsheet for a process for treating an aqueous waste containing 10 wt% organic is given in Fig. 3. This process consists of the following steps:

1. The waste, as either an aqueous solution or a slurry, is pressurized and delivered to the oxidizer inlet. It is heated to supercritical conditions by direct mixing with recycled reactor effluent.

2. Oxygen is supplied in the form of compressed air, which is used as the motive fluid in an eductor to provide recycle of a portion of the reactor effluent. This inlet mixture is then a homogeneous phase of air, organics and supercritical water.

3. The organics are oxidized in a controlled but rapid reaction. The short residence times required allow adiabatic operation of the oxidizer. The heat released by combustion of readily oxidized components is sufficient to raise the fluid phase to temperatures at which all organics are oxidized rapidly.

4. The effluent from the oxidizer is fed to a cyclone. The solubility of inorganics is extremely

low at the reactor effluent temperatures. Inorganic salts that are originally present in the feed or which form in the combustion reactions precipitate out of the fluid phase in the oxidizer and are separated here.

5. The fluid effluent of the solid separator is a mixture of H_2O, N_2, and CO_2. A portion of this is recycled through the eductor to provide supercritical conditions at the oxidizer inlet.

6. The remainder of the effluent is available as a high temperature, high pressure fluid for energy recovery. This stream is cooled to a subcritical temperature in a heat exchanger which serves to generate low pressure or high pressure steam.

7. Now at a subcritical temperature, the mixture has formed two phases and enters a high pressure liquid-vapor separator. Practically all of the N_2 and most of the CO_2 leaves with the gas stream. The liquid consists of water with an appreciable amount of dissolved CO_2.

8. The gas stream can then be expanded through a turbine to extract the available energy as power. A portion of the power is used for compression of the inlet air.

9. The liquid from the high pressure separator is

depressurized and fed to a low pressure separator. The vapor stream is primarily CO_2 which is vented with the gas turbine effluent. The liquid stream is clean water.

The destruction efficiency (defined herein as the conversion of organic materials in the feed to final oxidation products of CO_2, H_2O and acids or oxyacids of heteroatoms and metals) is a function of reactor temperature and residence time. It has been found that a reactor effluent temperature in the range of 600 to 650°C and residence time of 5 sec are sufficient for a destruction efficiency of more than 99.999%. Higher temperatures could be used to reduce the residence time. However, at 5 sec residence time, the reactor cost is a small fraction of total capital cost and, therefore, there is not much incentive to try to reduce reactor volume by operating above 650°C.

Increasing either temperature or residence time will result in increased destruction efficiency. The oxidation kinetics appear to be approximately first order in organic concentration. Thus, in theory, doubling the reactor length and, thereby, doubling the residence time from 5 to 10 sec should result in doubling the logarithm of destruction

efficiency; in other words, 99.999% should become 99.999999999%! [Of course, the analytical techniques required to document such high destruction efficiencies are not available.]

For the process configuration illustrated in Fig. 3, the reactor exit temperature is a direct function of the heating value of the feed. To attain a temperature of 600 to 650°C, the waste should contain about 1,750 Btu/lb or 4,050 J/g, which is the heating value of an aqueous solution of about 10 wt% benzene (heat of combustion of 17,500 Btu/lb or 40.5 kJ/g) or 14 wt% ethanol (12,800 Btu/lb or 29.7 kJ/g). If the waste is more concentrated or otherwise has a higher heating value, it could be blended with more dilute waste or, if unavailable, with water. In the latter case, the added water would be recovered from the process effluent in a form which is pure enough to be used as process water in most applications.

The energy released by combustion is contained within the reactor effluent as thermal energy. As shown in Fig. 3, it could be recovered as heat in the steam generator and/or power from the expansion turbine. The energetics of the SCW oxidation process are such that the amount of power available for recovery is substantially more than that required

to compress the air and waste. The overall process is somewhat analogous to a gas turbine power cycle. However, many applications require systems which are small (by chemical process industry standards) and capital-intensive. In those cases, power recovery cannot be justified on economics and, thus, the heat of combustion and the energy input for air compression are simply recovered as steam.

For wastes with heating values below 1,750 Btu/lb, auxiliary fuel could be added to make up the required heating value. The fuel cost can be appreciable when treating a very dilute waste. In such cases, it is more economical to use a regenerative heat exchanger rather than a steam generator, as shown in Fig. 4. This process configuration differs from that of Fig. 3 by addition of a feed-effluent heat exchanger and deletion of steam generator and eductor. In this manner, the minimum heating value of the feed for autogenic operation is 350 Btu/lb (800 J/g), which is a concentration of 2 wt% benzene-equivalent. For the same heat release rate, the process of Fig. 4 can treat five times as much waste (at 2 wt%) as that of the process of Fig. 3 (at 10 wt%). This increased waste volume more than compensates for the higher capital cost due to the regenerative heat exchanger.

Figure 4

Process Schematic for Oxidation of an
Aqueous Waste with a heating value of
350 Btu/lb

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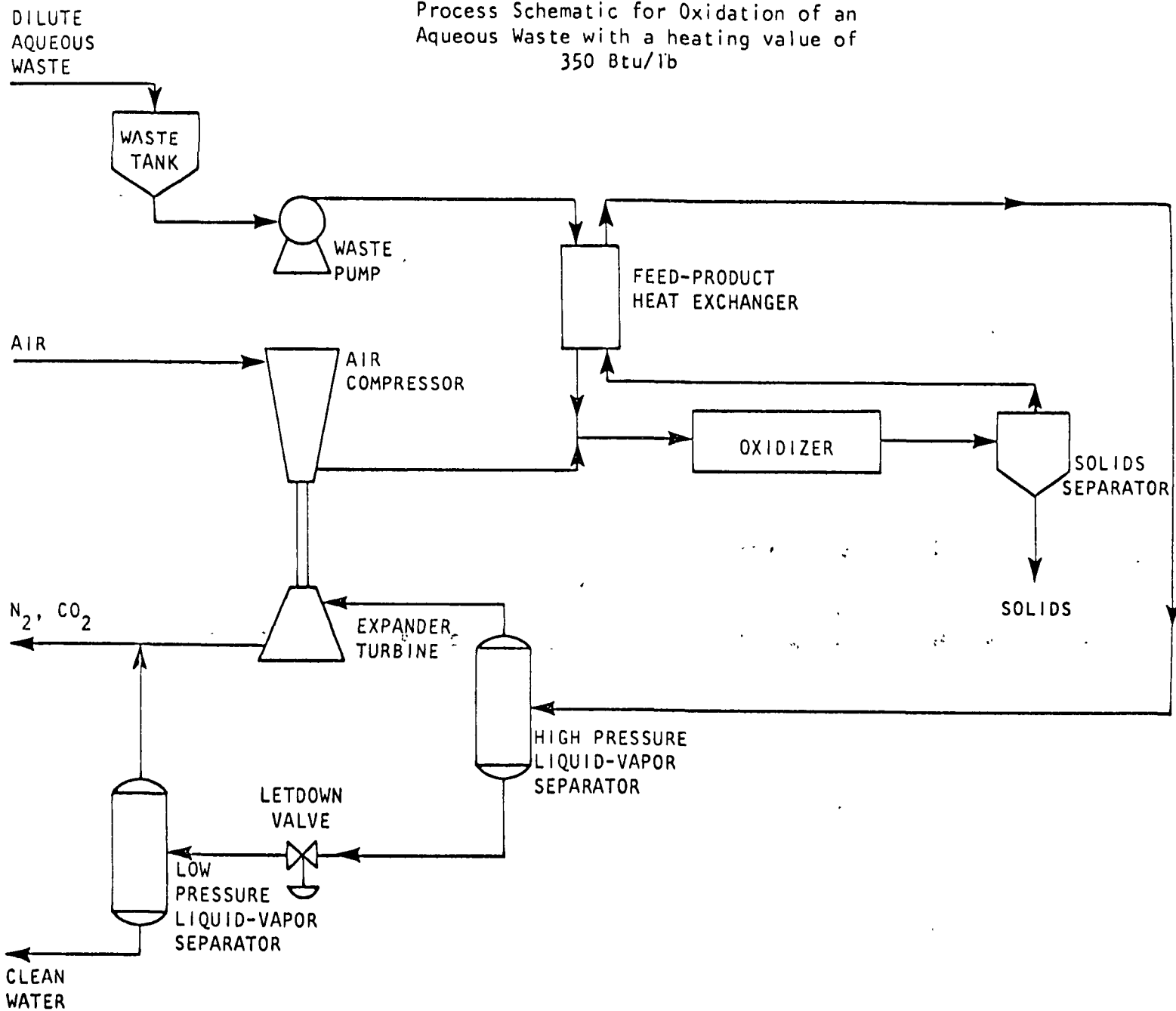
Advantages of Supercritical Water Oxidation

As a waste destruction process, SCW oxidation has several advantages over conventional processes. The chemical reactions that occur are carried out in a closed system, making it possible to maintain total physical control of waste materials from storage, through the oxidation process, to the eventual discharge of the products of combustion. This feature provides positive assurance of environmental protection. In addition, bench-scale results have demonstrated essentially complete combustion of chemically stable hazardous and toxic materials. The process can be adapted to a wide range of feed mixtures and scales of operation. Systems can be designed as skid--mounted, transportable units and as larger scale stationary units. The process is capable of generating all the power required for air compression and feed pumping and, thus, can have no net energy requirement for system operation.

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