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DETOXIFICATION AND DISPOSAL OF HAZARDOUS
ORGANIC CHEMICALS BY PROCESSING
IN SUPERCRITICAL WATER

Final Report

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A new process for the destruction of hazardous waste makes use of supercritical water (SCW) as the medium for a rapid and highly efficient oxidation reaction. Destruction efficiencies of 99.99% and greater have been achieved for a broad spectrum of organic chloride compounds and solvents. This report presents the results of bench scale tests of the SCW system on a variety of compounds which yielded information on destruction efficiency, performance capacity, reaction kinetics, fate of inorganic heteroatoms and system corrosion.

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Foreword

The results of studies on the use of supercritical water as the medium for oxidation and destruction of chemical wastes, conducted by MODAR, Inc. for the U.S. Army Research and Development Command under contract number DAMD17-80-C-0078 are presented in this Final Report. An addendum to this document contains limited rights data which is restricted through May 31, 1990.

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- 1 -

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

- 4 -

I. EXECUTIVE SUMMARY

Existing methods of disposal of toxic and hazardous wastes are expensive and energy intensive. MODAR has developed a new process that is capable of destroying highly toxic wastes with efficiencies of 99.99 to 99.999%. The overall effect of the MODAR process is the recovery of energy along with the disposal of wastes. In particular:

- organic components are converted rapidly and efficiently to carbon dioxide and water;

- inorganic components form salts or oxides which are only slightly soluble under process conditions and may be separated as solids;

- organic heteroatoms such as Cl, S, and P form mineral acids such as HCl, H_2SO_4 and H_3PO_4 which can be neutralized and separated as salts or removed as an aqueous solution in the liquid effluent;

- water is recovered in a highly purified form;

- wastes are treated in an enclosed system so that escape of pollutants to the environment is eliminated;

- the heat of combustion of the wastes is recovered in the form of supercritical water, from which power can be generated by conventional supercritical turbines.

The MODAR process is based on the unusual properties exhibited by water as a supercritical fluid. For reasons which will be described below, organic substances are completely soluble in supercritical water (SCW). In addition, most organic molecules reform to compounds of lower molecular weight under these conditions. SCW reforming takes place at relatively mild temperatures (375-450°C) and at high pressures (above 220 atm). In the MODAR process, the products of SCW reforming are then oxidized under SCW conditions at temperatures in the range of 450°-550°C. This step of the process is generally related to wet air oxidation (WAO). The major differences and advantages of SCW oxidation are: (i) complete solubility of organics and oxygen (or air) in SCW, which eliminates two-phase flow; (ii) rapid oxidation of organics and very short residence time; and (iii) recovery of the heat of combustion in the form of supercritical water, which can be used as a source of high temperature process heat or for generating power.

Finally, above 450°C, the solubilities of inorganic salts in water become extremely small. Since the products of SCW oxidation are above this temperature, any inorganic salts present in the feed will precipitate.

- 5 -

MODAR was formed in 1980 to establish the feasibility of this new SCW oxidation process concept and then to make the technology commercially available in the marketplace. Funding from private sources and from Federal sponsors has been utilized to further the technical development of the process. The SCW oxidation process has been reduced to practice with outstanding technical results. A bench scale development program, described herein, has been used to prove process feasibility. Using a continuous flow system that processes about 20 gal/day of wastewaters (including up to 1 gal/day of organic components), a broad spectrum of organic chlorides and solvents has been destroyed with efficiencies exceeding 99.99%. For example, PCBs and pesticides such as DDT and Lindane have been destroyed with 99.99% carbon destruction efficiency at 500-550°C and with resident times of less than 60 seconds. Dinitrotoluene (DNT) and 4,4'-dichlorobiphenyl (DCBP), which were used as feeds for kinetic studies, were both oxidized with 99.99% carbon destruction efficiency under optimum conditions of reactor temperature (>550°C) and excess oxygen. The kinetic data which have been obtained provide the basis for reactor design in larger scale systems which will retain these desirable features. The bench scale system is very completely instrumented. Material balance closures and other quality assurance checks show that the data which have been generated are sound.

Bench scale experiments have also provided insight into corrosion and heteroatom separation. Accelerated corrosion testing has demonstrated that Hastelloy C-276 and Inconel-625 appear to be unaffected by our environment, even under unusually severe conditions. There are several candidate approaches to heteroatom separation/removal which are promising, although none of them has been tested or demonstrated as part of this project. Finally, preliminary economic analyses provide estimates of processing costs for large scale operation costs which are competitive with conventional thermal oxidation techniques, even without credit for power recovery in the SCW system.

Further development and commercialization of SCW systems for waste processing with thermal recovery is now underway. Specifically, MODAR has taken steps toward the design, fabrication, operation, and field testing of a larger scale unit. The objective of this latest effort is construction, operation, and demonstration of a SCW oxidation system for processing 1000-1500 gal/day of wastewaters, including up to 50 gal/day of toxic organic wastes. This demonstration unit represents the next step in MODAR's process development program, which will subsequently lead to development of systems with capacities of 1, 10 and 100 ton/day of organic waste. The demonstration unit will be transportable; larger units will be both mobile (at 1 ton/day) and stationary (at 10 and 100 ton/day) and will recover the energy liberated by the oxidation

reaction. For the 10 and 100 ton/day systems, estimated costs are:

	10 ton/day	100 ton/day
Capital cost	$5M	$15M
Processing costs	$2.40/gal of organic waste*	$.50/gal of organic waste

*Note that this cost is based on a 100% organic waste. For an aqueous waste containing only 10% organic compounds these costs would drop to $0.25/gal in the 10 ton/day system and $0.055/gal in the 100 ton/day system.

II. BACKGROUND

Disposal of hazardous and toxic chemicals has received widespread publicity over the past decade. The 1976 Resource Conservation and Recovery Act (RCRA), and the 1980 Comprehensive Emergency Response, Compensation and Liability Act (Superfund) gave EPA the authority to regulate the disposal of hazardous wastes "cradle to grave" and to provide for the design and implementation of clean-up at existing waste disposal sites. The controversy which has developed over the implementation of RCRA and Superfund serves to highlight the degree of public interest and the difficulty in solving some of the problems they pose.

The guidelines that are evolving for disposal of toxic and hazardous wastes will clearly limit future options. Potentially acceptable techniques include incineration, chemical and biochemical degradation, "controlled" landfilling and solidification. However, the more we know about each of these conventional approaches, the more cumbersome and costly the regulatory approach becomes. For example, controlled incinerators to dispose of toxic wastes not only require extensive air pollution control equipment to remove acid vapors as well as particulate emissions, but they also require extensive testing to determine principle organic hazardous constituents (POHCs), products of incomplete combustion (PICs) and destruction and removal efficiency (DRE). Both the incinerator and air pollution control systems are expensive and energy-intensive. Certification is rigorous, expensive and time consuming.

For highly toxic wastes, such as materials containing 2,3,7,8-tetrachlorodibenzodioxin, even high temperature incineration has been found to be inadequate (Bumb, et al., 1980). In fact, there is no technology on the market today that can assure adequate destruction of such wastes. Obviously, what is needed is a new approach, a new technology which can solve such problems and still be simple to regulate.

- 7 -

Through research in a recently explored area of thermodynamics, MODAR has developed a new process that is capable of destroying highly toxic wastes with efficiencies of 99.99 to 99.999%. The process is a new approach to treatment; it is aimed at recovering resources from waste material. Organic components are converted to carbon dioxide and water, with potential recovery of the heating value; inorganic components may be removed as solids or aqueous solutions of mineral acids; water is recovered in a highly purified form. The wastes are treated in an enclosed system so that escape of pollutants to the environment is eliminated, reducing regulatory concern. Furthermore, there are a minimal number of processing steps, so that the capital investment should compare very favorably with available processes. The most significant feature of this new approach is that it can be cost-effective. When the organic content of the waste is greater than about 2% in a wastewater, the SCW process is fuel self-efficient. For organic contents of 10% or more, power recovery becomes possible, leading to energy credits which will offset costs of waste processing.

The MODAR process is based, in part, on a discovery made in 1975 by M. Modell and co-workers at M.I.T. In the course of investigating the effects of treating aqueous solutions of organics at high temperatures and pressures, it was found that complex organic substances can be dissolved and broken down into low molecular weight products when treated under conditions where water is supercritical (i.e. above $374^{\circ}C$ and 220 atm). The discovery is the basis of U.S. Patent No. 4,113,446, (Modell, et al 1978), originally assigned to M.I.T. and now exclusively licensed to MODAR.

In 1979, Modell carried this work one step further. He proposed a new method of destroying wastes by dissolving both organic material and oxygen in supercritical water (SCW), and then carrying out the oxidation in the supercritical water medium. MODAR was formed in 1980 to establish the feasibility of this new SCW oxidation process. Under Modell's supervision as President and Technical-Director of MODAR, the SCW oxidation process has now been reduced to practice with outstanding technical results. In addition, preliminary economic analyses indicate that the process is potentially much less expensive in processing costs, including capital recovery than high temperature incineration. Patent coverage has been obtained and a patent covering SCW oxidation (U.S. Patent No. 4,338,199, July 6, 1982) has been issued. This report describes the progress to date in developing this process concept into a commercial reality.

III. INTRODUCTION AND SCOPE

A. Scope of the Program

This program was undertaken to study the feasibility of supercritical water (SCW) oxidation for the destruction of toxic and hazardous chemical wastes. The specific goals were these:

1) to design and construct a bench-scale system for conducting SCW oxidation experiments.
2) to use the bench-scale system to establish the technical feasibility of SCW oxidation.
3) to obtain design data for commercial scale operation, and
4) to analyze the economics of several scales of commercial processing.

The bench-scale system is described in detail in IV. A, B, and C. The technical feasibility of SCW oxidation was demonstrated by the successful destruction of a wide variety of compounds and mixtures. By variations in process conditions such as temperature, oxygen concentration, carbon concentration and residence time, design data were generated. Three test compounds, methyl ethyl ketone, 4,4'-dichlorobiphenyl and 2,4-dinitrotoluene, were used as feed materials for these experiments. The data from individual runs show that extremely high destruction efficiencies can be obtained with SCW oxidation. Analytical and process quality assurance procedures, such as material balance closures, were implemented throughout the program. In addition, corrosion and heteroatom separation have been studied and will be discussed below.

Using the knowledge gained from these experiments, preliminary process designs and cost estimates were made f r commercial-size units of 1 and 100 tons per day of organic waste. A brief description of ongoing work to further the development of the process, based on the results of this program, is provided.

B. Technical Concepts

In the supercritical region, water exhibits unusual properties that are far different from normal liquid water (See VIII. A. for a detailed discussion). The density of supercritical water ($0.05-0.5$ g/cm^3) is low enough and the temperature high enough to essentially eliminate hydrogen bonding. In the near critical region, the dielectric constant is diminished to ca. 3 to 10 (versus 80 at 20°C) and water becomes an excellent solvent for

organic substances. At temperatures above $500^{\circ}C$, the dielectric constant is less than 2, and inorganic salts become only sparingly soluble and act as weak electrolytes (i.e. are present as molecules rather than as ions). Thus, solubility characteristics in supercritical water are the inverse of those in normal liquid water.

About $350^{\circ}C$, water reacts with organic materials in a way that leads to the formation of low molecular weight products (See VIII. B). Whereas many organic compounds tend to form high molecular weight chars at temperatures below $350^{\circ}C$, at supercritical conditions the same organics are reformed to gases (e.g. CO, H_2, CH_4, CO_2) and volatile organic liquids (alcohols, aldehydes, furans) -- without producing any char.

The products of SCW reforming can be subjected to oxidation while still under supercritical conditions (See VIII. C). It is well-known that aqueous solutions of organics will undergo oxidation at temperatures of 200 to $300^{\circ}C$. This phenomenon is the basis of the conventional wet oxidation or Zimpro process, which is operated under subcritical conditions. The wet oxidation process requires residence times of 20 minutes to 1 hour to achieve destruction efficiencies which are, at best, mediocre (typically 70 to 95% reduction in total organic carbon). On the other hand, under supercritical conditions the residence time required for oxidation is extremely small (less than 60 seconds), which reduces the required oxidizer vessel volume. In addition, oxygen is completely miscible with supercritical water and, therefore, the oxidation can be conducted under homogeneous (i.e., single phase) conditions. Thus, oxidation under SCW conditions is an efficient means of ultimate disposal of organics.

When toxic or hazardous organic chemicals are subjected to SCW oxidation, carbon is converted to CO_2 and hydrogen to H_2O. The chlorine atoms from chlorinated organics are liberated as chloride ions. Similarly, nitro-compounds should be converted to nitrogen, sulfur to sulfates, phosphorus to phosphates, etc. In other words, heteroatoms should usually form oxy-acid anions. Upon addition of the appropriate cations (e.g. Na^+, Mg^+, Ca^{++}), inorganic salts can be formed.

Finally, above some minimal concentration of organics (as low as 2% with a suitable process flowsheet), the heat of oxidation is sufficient to bring the supercritical stream to temperatures in excess of $550^{\circ}C$. At these conditions, inorganic salts have extremely low solubilities in water (See VIII. A). Thus, inorganic salts will be precipitated and can be separated from the aqueous

phase. After removal of inorganics the resulting aqueous phase is a highly purified stream of water at high temperature ($>500^\circ$C) and high pressure (3700 psia). As such, it can be used as a source of high-temperature process heat or fed to conventional supercritical steam turbines for generating electricity.

C. The MODAR SCW Oxidation Process

The MODAR process for hazardous waste destruction makes use of water in its supercritical state (SCW) as the reaction medium for carrying out the destruction of organic materials by oxidation. Key to the success of the process is the fact that gases, including oxygen (or air), and organic substances are completely soluble in SCW whereas inorganic salts exhibit greatly reduced solubilities under process conditions. Thus, it becomes conceptually possible to carry out "combustion" reactions by dissolving organic substances and oxygen in SCW bringing them into intimate contact in a single-phase medium at temperatures and molecular densities which allow the conventional oxidation reactions to proceed rapidly and essentially to completion. In fact, one would expect these conditions to be more favorable for carrying the combustion reactions to completion than those of conventional incineration processes where volatilization and mass transport of reaction species are limiting factors. Furthermore, the reduced solubility of salts makes possible the direct removal of undesirable reaction products through precipitation.

A proposed schematic flowsheet for the MODAR process described above is given in Fig. 1. The process would consist of the following steps:

1) The toxic or hazardous waste, blended with water to provide a mixture of ca. 10 wt% organics, is pressurized and heated quickly to supercritical conditions to avoid char formation. Heating is attained by mixing the feed with superheated SCW which is generated in a subsequent step.

2) Air or oxygen is pressurized and mixed with the feed. Since the water is still supercritical, the oxidant is completely miscible with the solution (i.e. the mixture is a single, homogeneous phase). Organics are oxidized in a controlled but rapid reaction. The oxidizer vessel may contain a fixed or fluidized bed, depending upon the inorganic content of the feed. The "kindling" temperature for the oxidation is on the order of $200-250^\circ$C for readily

- 11 -

FIGURE 1. SCHEMATIC OF THE MODAR SCW OXIDATION PROCESS

FEED

MAKEUP WATER

FEED SLURRY TANK

FEED PUMP

EDUCTOR

OXIDIZER SALT SEPARA- TOR

SALT

SUPERHEATED SCW

EXPANDER TURBINE

HIGH PRESSURE STEAM (WITH CO_2 + N_2)

AIR OR OXYGEN

OXIDANT COMPRESSOR
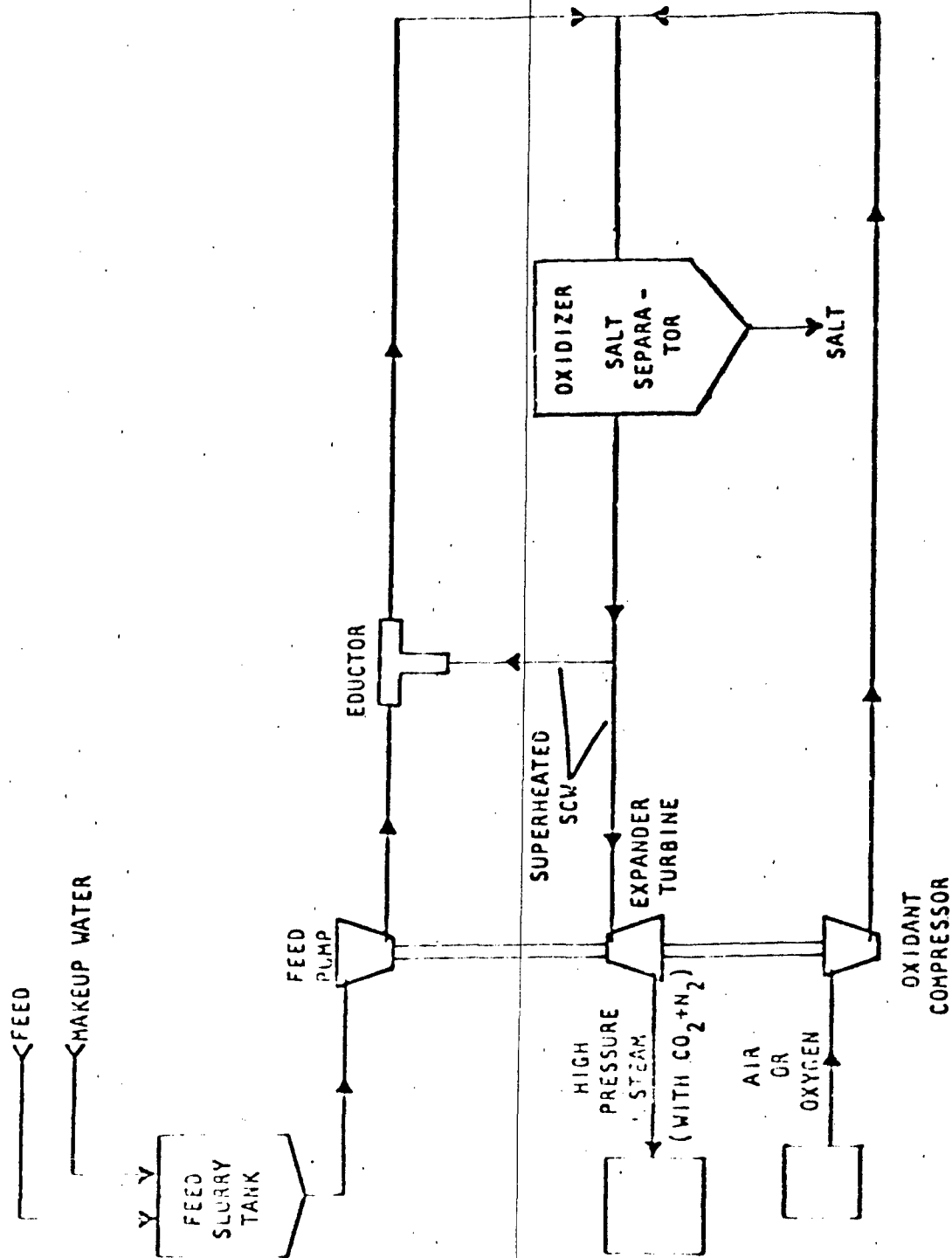
oxidized constituents (H_2, CO, C_2 + hydro-carbons), while more refractory compounds (e.g. CH_4) may require $300-400°C$. Since the oxidizer operates adiabatically, the heat released by combustion of readily oxidized components is sufficient to raise the fluid phase to temperatures where all organics are oxidized rapidly. Typically, the heat of combustion is sufficient to raise the oxidizer effluent to at least $550°C$.

3) For feeds which contain or produce inorganic salts the oxidizer vessel also functions as a gravity salt separator.

4) A portion of the superheated SCW is recycled to an eductor upstream of the SCW oxidizer. This operation provides for sufficient heating of the feed to bring the oxidizer influent to supercritical conditions.

5) The remainder of the superheated SCW is available for power generation or use as high-pressure steam. A portion of the available energy is used to generate the power required to pressurize feed and oxidant. Note that the energy required to pressurize the oxidant is recovered in the expansion of the products of combustion in the superheated SCW turbine. Thus, the method of oxidation is analogous to that of a gas turbine.

As a waste destruction process, the MODAR concept has several advantages over conventional processes. The chemical reactions which occur are carried out in a closed system and, thus, it is possible to maintain total physical control of waste materials from storage, through the oxidation process, to the eventual discharge of the products of combustion and any associated wastes. This feature, consistent with the EPA definition of a "Totally Enclosed Treatment Facility" (TETF), provides positive assurance of environmental protection. In addition, bench-scale results indicate essentially complete destruction of chemically stable materials (such as PCB's) at projected costs which are well within those presently associated with hazardous waste operations. Finally, the process can be adapted to a wide range of feed mixtures and scales of operation.

IV. APPARATUS AND PROCEDURE

A. Equipment.

The MODAR bench-scale system, with a throughput capacity of about 20 gal/day, including 1 gal/day of organic waste, was designed

- 13 -

to establish the technical feasibility of the key concepts of SCW oxidation. It is a continuous flow system which simulates the operational design of larger, commercial-scale systems. Although the system's components have been under constant study and occasional modification since the beginning of the program, it has always incorporated three essential features of the commercial-scale system design:

(i) Rapid heat-up of feed to SCW conditions for dissolution of organics without charring;

(ii) Dissolution of oxygen (or air) in the reaction mixture to form a single phase at a temperature high enough to "kindle" the oxidation reaction; and

(iii) Production of a superheated reactor effluent (T > 550°C) with sufficient thermal energy for use as a recycle stream for preheating of feed.

A typical schematic of the SCW oxidation bench-scale system is shown in Figure 2. The waste, in the form of a liquid, is pumped to operating pressure. Pure water is also pumped to pressure, heated and then mixed with the pressurized feed. Oxidant is compressed and mixed with the hot feed solution and passed into a tubular reactor. The reactor effluent is cooled and depressurized. Liquid and vapor effluent streams are separated and analyzed.

a. Feed System. Distilled water is treated with a Barnstead Nanopure A purification system equipped with four cartridges: two mixed-resin cartridges using cation and strong base anion resins for deionization, one cartridge for removal of organics and chlorine, and one cartridge containing a 0.2 micron filter for removal of submicron particulates. Water with a resistance as high as 18 megohm-cm can be obtained.

American Lewa diaphragm pumps are used to pressurize the water and waste. These pumps are equipped with ruby balls and tungsten carbide seats in the check valves and are rated for 5000 psig. The water is pumped from a polypropylene Nalgene bottle through a 50 cc burette, which is used to measure flowrate. The waste is pumped from a 1000 cc Teflon reservoir through a 10 cc pipette, which is used to measure flowrate. When waste is not being pumped (e.g. during start-up and shut-down), a three-way ball valve allows switching to water contained in another Nalgene bottle.

Bottled oxygen is compressed with an Aminco (the brand name is now Superpressure) motor-driven diaphragm compressor. It has a compression

Figure 2. Schematic of the Bench-Scale SCW Oxidation System
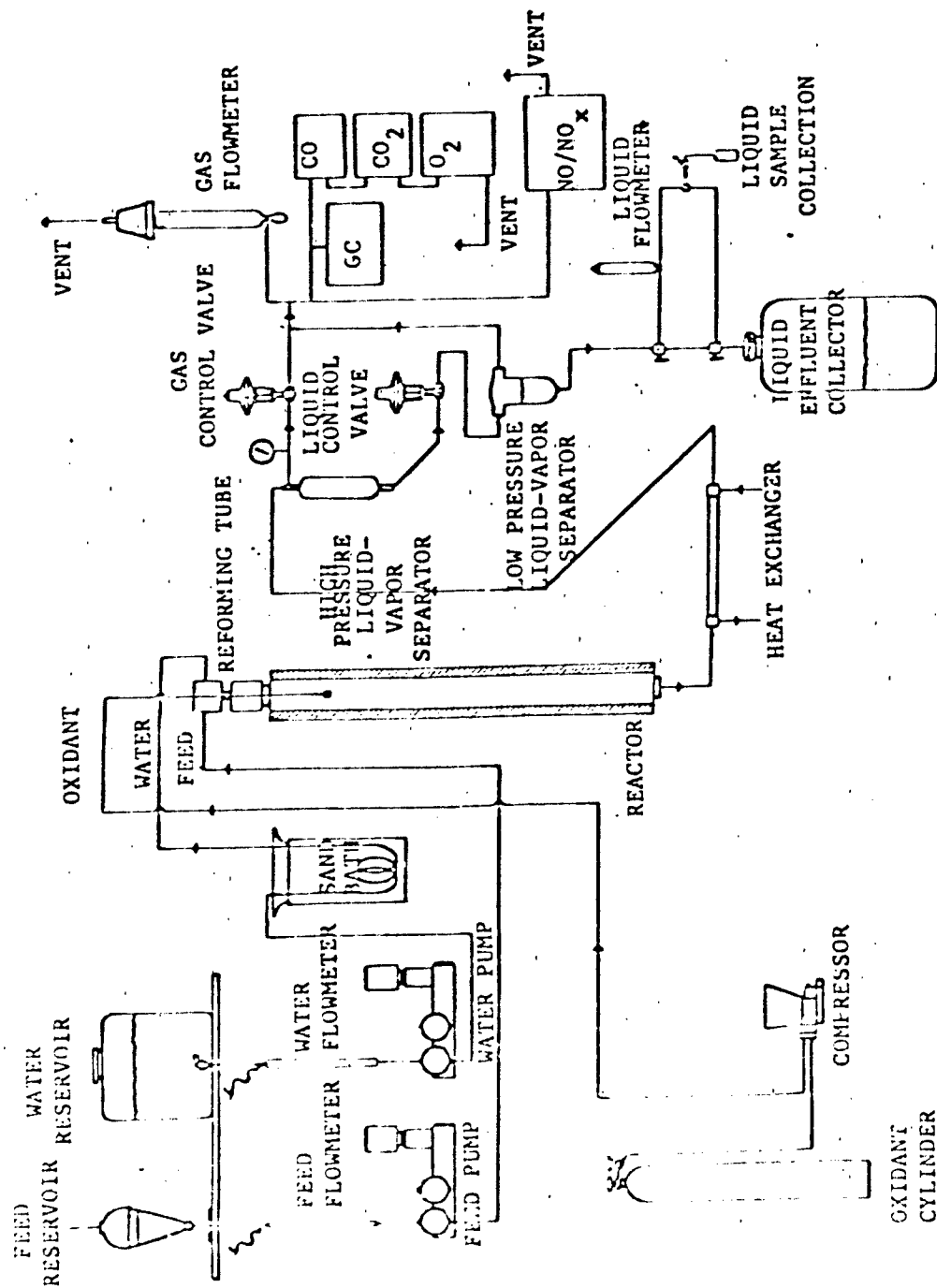
ratio of 14:1 and a 10,000 psi pressure rating. Wetted materials are 316SS for the valves and 302SS for the diaphragm.

b. Preheating and Mixing. A new feed system design has been developed so as to avoid char formation that usually occurs in heating organics above 200°C (Modell, et al., 1978). The pressurized waste feed is mixed with superheated water to bring the feed to reaction conditions very rapidly. This feed injection method has been found to eliminate char formation in the feed system.

Distilled water from the single diaphragm pumphead is passed through 20 ft. of 1/4" high-pressure 316SS coil in a sand bath. The distilled water is superheated to a temperature high enough to bring the mixture of waste and water to the desired operating temperature.

The waste is mixed with water in a 9/16" high-pressure tee and the mixture of waste and water is passed through a short section of 3/8" high-pressure tubing. This tube is designated as the "reforming tube" in Figure 2 because the organic waste is solubilized and reformed therein. This mixture is then fed to the reactor. Oxidant is fed to the reactor in a separate line and is dispersed into the mixture of waste and water, all at supercritical conditions.

c. Reactor System. The reactor was made from Hastelloy C-276 and rated at 5000 psi at 538°C (1000°F). Hastelloy C-276 was chosen as the material of construction because it is the material used under the more severe conditions of wet air oxidation. Corrosion tests (Jagow, 1972; Nelson and Van Kirk, 1979) suggested that it is the best material when compared with Ebrite 26, MP35N, Inconel 625, zirconium, Zircaloy 2, Elgiloy, tantalum, and Tantalum 40% Colombium. The reactor is 0.88" i.d. by 3' long. The seal is a modified Bridgeman single end.

The reactor effluent passes through a tube-in-tube countercurrent heat exchanger. The cooled effluent then enters a high pressure vapor-liquid separator, operated by two control valves (as shown). The gaseous effluent is mixed with the gases from the low pressure separator and the mixed flow is measured by a gas flowmeter. Samples are analyzed periodically by an on-line system described below. Analyses are performed for volatile organics, CO, H_2, CO_2, NO_x, N_2O and O_2.

d. Low Pressure Phase Separation. The liquid effluent from the high pressure separator is fed to a low pressure gas-liquid separator where gases which were dissolved at high pressure are released and returned to the gas capture system. The liquid effluent from the separator is measured on-line for pH and then collected. Liquid

- 16 -

effluent samples are taken every half hour and analyzed as discussed below.

e. Temperature Measurement. Temperatures are monitored with type K thermocouples. There are a total of eight thermocouples: in-line in the water from SCW heater; in-line in the feed-water cross; in-line in the oxygen-water cross; top, middle and bottom of the reactor on the exterior surface; in-line after the reactor; and in-line after the heat exchanger.

f. System Control and Data Storage. Temperatures, pressures and separator liquid levels are controlled by an Analog Devices MACSYM 2 microcomputer. This microcomputer is also used for data acquisition from all thermocopules, pressure tranducers, flowmeters, pH meter and process gas analyzers.

B. Procedures. The independent operating variables which control the degree of oxidation/destruction are: (i) temperature, (ii) residence time (iii) oxygen concentration and (iv) carbon concentration. The bench scale system is designed to operate as a continuous flow reactor under steady-state conditions. The operating procedure is to set values or each of these independent variables, to allow the system sufficient time to reach steady state, and then to sample and analyze the liquid and vapor effluent for partially oxidized and residual organic materials.

The typical procedures for a run are as follows:

a. Start-up Procedure.

1. Turn on the process control computer.
2. Calibrate the GC before run and zero all process analyzers.
3. Turn on heat exchanger cooling water.
4. Turn on pumps (with water only) to flowrates specified for the run.
5. Adjust the pressure to the pressure specified for the run.
6. When the system reaches operating pressure, turn on heaters and heating tapes using the process computer.
7. Measure influent and effluent flowrates and check the system for leaks.
8. When the system reaches operating temperature, take a blank liquid sample.
9. Turn on the oxidant compressor to the flowrate specified for the run.
10. When all operating variables have reached the desired values, switch feed from deionized water to the feed under study.

b. Operating Procedure.

1. Set the data logging time so a printout of temperatures, pressures and flowrates is done periodically.
2. Take a GC of gas effluent every 20 minutes.
3. Take 4-40 cc liquid samples every 30 minutes for total carbon, pH and Cl⁻ analysis.
4. Take 50 cc liquid samples for GC/MS analysis every 30 minutes.

C. Analyses. The following techniques were used for the analyses of the effluent streams: total organic carbon analysis (TOCA), pH, inorganic chloride and nitrate electrodes, and gas chromatography/mass spectrometry (GC/MS) on liquid effluent; gas chromatography (GC) and process gas analyzers on the gaseous effluent. A detailed discussion of the instrumentation and the methods of operation, calibration, etc. is presented in the Section VIII. D. Classical quality assurance techniques were used to make sure that analytical results were valid. These include blanks, "unknowns" and calibration samples. A discussion of the procedures is not provided in this report, but the data from each run do include the results of material balance closure calculations which depend on flow and analytical measurements. The fact that these balances closed quite well indicates that the chemical analyses are within acceptable limits of accuracy for the purposes of this program.

V. RESULTS AND DISCUSSION

A. Preliminary Screening Experiments. Upon completion of the construction of the bench-scale system, this series of tests was conducted to shake down the system. The test compounds, which were chosen for their low toxicity, were dextrose (as an aqueous solution), cyclohexane, benzene, methyl ethyl ketone (MEK), and a solution of biphenyl in cyclohexane (18 wt% biphenyl). In reports on the results of these and later tests, a consistent set of terms is used. These are defined in Table 1.

A summary of the "screening test" results is given in Table 2. Note that in the early experiments, the temperature is given as a range. These values represent the inlet and outlet fluid temperatures (i.e. in-line before and after the reactor; see Fig. 2). In these early tests, the reactor furnace was not well suited to the task of controlling the temperature, as there was a sizable heat leak from the bottom of the reactor (corrected after run 6).

Dextrose (i.e. glucose) is a relatively easy compound to oxidize and, therefore, represented a suitable choice for the first experiments. The destruction efficiency of 99.6% observed in run 3 is typical for the oxidation of this sugar, even at temperatures as low

- 18 -

TABLE 1. DEFINITION OF TERMS

Temperature (^{o}C) = Unless otherwise stated, temperature is that of the external surface of the reactor.

Residence Time (min)[1] = Volume of reactor divided by volumetric flow rate of water input plus water from oxidation of feed, assuming density of water equals 0.3.

Organic Carbon In (ppm) = Carbon content of organic/water feed mixture as it enters the reactor.

Organic Carbon Out (ppm) = Total carbon in liquid effluent after sparging or total carbon minus inorganic carbon.

Destruction Efficiency (%) = $$\frac{(\text{Organic Carbon In} - \text{Organic Carbon Out}) \times 100}{\text{Organic Carbon In}}$$

Combustion Efficiency (%) = $[CO_2/(CO_2 + CO + CH_4)] \times 100$ concentrations in the effluent vapor, as measured by GC analysis.

Excess Oxygen (%) = $$\frac{(\text{Oxygen Input}) - (\text{Stoichiometric oxygen requirement}) \times 100}{\text{Stoichiometric oxygen requirement}}$$

Organic Chloride Nitrogen In (ppm) = Chloride/Nitrogen content of organic/water feed mixture, as it enters the reactor

Organic Chloride Out (ppm) = Residual organic chloride as determined by GC/MS.

Organic Chloride Conversion (%) = $$\frac{(\text{Organic Chloride In} - \text{Organic Chloride Out}) \times 100}{\text{Organic Chloride In}}$$

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[1] In general, values cited for residence time are in excess of the true value. This is due to the assumption of the 0.3 g/cc density. In all experiments where the temperature is 400°C or greater the density of the reactor fluid is less than 0.3 (ranging to as low as 0.1 at 600°C)

TABLE 2. PRELIMINARY SCREENING TESTS

Run No.	3	4a	4b	5a
Feed Material	Dextrose	Cyclohezane		Biphenyl + Cyclohezane
Temperature ($^{\circ}$C)	440-400	435-390	445-390	450-393
Residence Time (min.)	6-8	6-8	6-8	6-8
Carbon Analysis				
Organic In (ppm)	20,000	21,400	21,400	28,700
Organic Out (ppm)	80	1,200	5.8	50
Destruction Efficiency (%)	99.6	94.4	99.97	99.8
Combustion Efficiency (%)	95.3	79.2	99.5	99.4
Gas Composition				
O_2	7.5	1.5	24.8	3.8
CO_2	88.3	73.7	74.3	95.1
CH_4	0.3	1.2	0.4	0.2
H_2	<.5	3.2	–	–
CO	4.1	18.2	–	0.4

5b	6	11a	9a	11b	9b
Biphenyl + Cyclohexane	Benzene	MEK	MEK	MEK	MEK
450-393	90-320	430	440	460	460
6-8	3	4.2	4.4	4.2	3.2
28,700	36,900	21,300	23,200	21,900	24,930
7.5	540	108	28.0	7.9	4.8
99.97	98.5	99.49	99.88	99.96	99.98
99.8	98.4	96.1	100.	100.	100.
17.7	9.3	71.7	29.33	42.4	44.61
81.8	87.9	11.4	73.14	42.2	45.84
0.1	0.2	-	-	-	-
-	0.08	-	-	-	-
0.1	1.2	-	-	-	-

as $400^{\circ}C$. Note that the combustion efficiency of 95.3% is the result of incomplete oxidation of CO (4.1% in gaseous effluent). In general, we have found that CO oxidation is not complete at $400^{\circ}C$ and that residual CO concentration is sensitive to the amount of excess oxygen.

The feed for run 4 was cyclohexane. The results of run 4a are typical of those experiments which are run lean in oxygen. In general, the removal of organics from liquid effluent is good as is evidenced by high destruction efficiency (94.4% in run 4a), but the combustion efficiency is low. Thus, the conversion of feed materials to low molecular weight vapors and gases appears to occur rapidly, while oxidation of gaseous species such as CO and CH_4 seems to be rate-limiting. Comparison of run 4b, in which excess oxygen is present, with 4a shows that the rate of oxidation of the gaseous species is sensitive to the oxygen concentration, as would be expected for the rate-limiting step.

In run 5, a solution of biphenyl in cyclohexane was used as the feed. Comparison of run 5b with 4b, both of which had excess oxygen, shows that oxidation of aromatic hydrocarbons is as efficient as that of aliphatics, even at moderate temperatures of 400 to $450^{\circ}C$.

Run 6, with benzene feed, was conducted at a higher flowrate and, thus, shorter residence time. Due to insufficient temperature control, the reactor effluent was below the critical temperature of water. Even so, the destruction and combustion efficiencies were reasonable.

In runs 9 and 11, with MEK feed, a new reactor furnace had been built and temperature control was improved substantially. Comparison of the results of these runs show that at 3 to 4 min. residence time, MEK destruction efficiency increased by one to two nines (i.e. 99.49% to 99.98%) with a $30^{\circ}C$ rise in temperature (430 to $460^{\circ}C$). The ease with which MEK is oxidized under CCW conditions led us to choose MEK as the solvent for subsequent tests with chlorinated hydrocarbons.

B. Preliminary Study of the Oxidation of Chlorinated Organics. This series of tests was conducted to determine the ease or difficulty of oxidizing organic chlorides and whether any byproducts of concern would be formed. In particular, these exploratory experiments were used to define the conditions under which high destruction efficiencies could be achieved.

The feed materials and compositions for each run in this series are given in Tables 3a and 3b. Chronologically, we began this series with a model compound, dichlorodiphenyl trichloroethane (DDT), and progressed to more complex mixtures.

TABLE 3a. COMPOSITION OF FEED MIXTURES FOR RUNS 10 - 12

		wt % in feed	wt % Cl in feed
Run 10			
DDT	$C_{14}H_9Cl_5$	10.3	5.157
MEK	C_4H_8O	89.7	–
		100.0	5.157
Run 11			
DDT	$C_{14}H_9Cl_5$	4.32	2.133
MEK	C_4H_8O	95.68	–
		100.0	2.133
Run 12			
1,1,1-trichloroethane	$C_2H_3Cl_3$	1.01	0.806
1,2-ethylene dichloride	$C_2H_2Cl_2$	1.01	0.739
1,1,2,2-tetrachlorehylene	C_2Cl_4	1.01	0.866
o-chlorotoluene	C_7H_7Cl	1.01	0.282
1,2,4-trichlorobenzene	$C_6H_3Cl_3$	1.01	0.591
biphenyl	$C_{12}H_{10}$	1.01	–
o-xylene	C_8H_{10}	5.44	–
MEK	C_4H_8O	88.48	–
		100.0	3.285

TABLE 3b. COMPOSITION OF FEED MIXTURES FOR RUNS 13 - 15

		wt % in feed	wt % Cl in feed
Run 13			
hexachlorocyclohexane	$C_6H_6Cl_6$	0.69	0.497
DDT	$C_{14}H_9Cl_5$	1.00	0.493
4,4'-dichlorobiphenyl	$C_{12}H_8Cl_2$	1.57	0.495
hexachlorocyclopentadiene	C_5Cl_6	0.65	0.505
MEK	C_4H_8O	$\frac{96.09}{100.0}$	$\frac{-}{1.99}$
Run 14			
PCB 1242	$C_{12}H_XCl_{4-6}$	0.34	0.14
PCB 1254	$C_{12}H_XCl_{5-8}$	2.41	1.30
transformer oil	$C_{10}-C_{14}$	29.26	-
MEK	C_4H_8O	$\frac{67.99}{100.0}$	$\frac{-}{1.44}$
Run 15			
4,4'-dichlorobiphenyl	$C_{12}H_8Cl_2$	3.02	.96
MEK	C_4H_8O	$\frac{96.98}{100.0}$	$\frac{-}{0.96}$

- 24

A summary of the results for this series is given in Tables 4a and 4b. Note that the compounds identified by GC/MS analysis are identified by letters at the bottom of Tables 4a and 4b; the structures are given in Table 5. Using the methods described in Section VIII. D.4 (p. 80) the mass spectra were searched for each of the compounds shown in Table 5; only those found in one experiment or another are given in Tables 4a and 4b. In other words, compounds, A,D,G,I,J,L and P were not present in the test results shown in Tables 4a and 4b. It should be especially noted that chlorinated dibenzo-p-dioxins were never found in any of our effluents, even though their mass spectra were specifically searched for. Detection limits for the GC/MS runs were 0.1 ppb.

The results of run 10, with a solution of DDT in MEK as the feed, illustrate an important generality that we have observed in other cases. As discussed in the preceding subsection, 440°C and a substantial excess of oxygen are sufficient to oxidize the MEK solvent rather well. On the other hand, the carbon destruction efficiency for run 10 is only 97.6% We conclude that the DDT solute is more resistant to oxidation than the MEK solvent, which, of course, is not surprising. However, one may be surprised by the finding that the organic chloride conversion is 99.99%. It appears that the chlorinated aromatics are readily decomposed by reforming and/or oxidation, although they are not completel oxidized at 450°C within three or four minutes residence time.

The results of run 11, as shown in Table 4a, are representative of one of our most important findings: In the neighborhood of 500°C, organic chlorides can be destroyed by SCW oxidation with efficiencies above 99.99%. In run 11, at 505°C, both carbon destruction efficiency and organic chloride conversion exceed 99.99%. Comparison of run 11 with run 10, both with a DDT/MEK feed, show that the increase of 50 to approximately 60°C is more than sufficient to enhance carbon destruction efficiency by two nines (97.6 to 99.993%).

The feed for run 12 consisted of a mixture of five organic chlorides (Table 3a), two of which were aromatic chlorides (o-chlorotoluene and 1,2,4-trichlorobenzene). Once again, the carbon destruction efficiency exceeded 99.99%. The reported organic chloride conversion is 99.997%. However, we must keep in mind that organic chlorides more volatile than dichloromethane (the extractant for GC/MS analysis) would not have been identified by our present analytical methods. Head space analysis of the liquid effluents or purge-and-trap analysis of the gaseous effluent would be required to determine the extent of conversion of compounds such as chlorinated ethanes and ethylenes. On the other hand, other experiments have shown that low molecular weight organic chlorides are readily oxidized under these conditions.

TABLE 4a. OXIDATION OF ORGANIC CHLORIDES
RUNS 10, 11, 12

Run No.	10	11	12
Temperature (^{o}C)	446	505	495
Residence Time (min.)	2.6	3.7	3.6
Carbon Analysis			
Organic Carbon In (ppm)	23,300	26,700	25,700
Organic Carbon Out (ppm)	558	2.0	1.0
Destruction Efficiency (%)	97.6	99.993	99.996
Combustion Efficiency (%)	90.2	100.	100.
Gas Composition			
O_2	48.5	25.58	32.84
CO_2	38.6	59.02	51.03
CH_4	0.1	–	–
H_2	–	–	–
CO	4.1	–	–
Excess Oxygen (%)	76.2	31.7	47.3
Chloride Analysis			
Organic Chloride In (ppm)	1,855	876.	1266.
Organic Chloride Out (ppm)	.447	.023	.037
Organic Chloride Conversion (%)	99.98	99.997	99.997
GC/MS Effluent Analysis			
Compound B (ppb Cl)	32	–	–
C	127	–	–
E	89	–	9
F	–	18	12
H	81	–	–
K	118	5	16
M	–	–	–
N	–	–	–
O	–	–	–

TABLE 4b. OXIDATION OF ORGANIC CHLORIDES
RUNS 13, 14, 15

Run No.	13	14	15
Temperature (^{o}C)	488	510	500
Residence Time (min.)	3.5	3.7	4.4
Carbon Analysis			
Organic Carbon in (ppm)	24,500	38,500	33,400
Organic Carbon Out (ppm)	6.4	3.5	9.4
Destruction Efficiency (%)	99.97ͻ	99.991	99.97
Combustion Efficiency (%)	100.	100.	100.
Gas Composition			
O_2	37.10	10.55	19.00
CO_2	46.86	70.89	70.20
CH_4	-	-	-
H_2	-	-	-
CO	-	-	-
Excess Oxygen (%)	57.9	10.5	19.8
Chloride Analysis			
Organic Chloride In (ppm)	748.	775.	481.
Organic Chloride Out (ppm)	<.028	.032	.036
Organic Chloride Conversion (%)	99.996	99.996	99.993
GC/MS Effluent Analysis			
Compound B (ppb Cl)	-	-	-
C		-	-
E	-	14	-
F	18	-	-
H	<4	-	-
K	<5	6	-
M	0.2	-	-
N	0.3		36
O	-	12	-

- 27 -

It should be noted that chlorinated compound K, which is DDE (see Table 5), was found in the liquid effluent of run 12, although the concentration was minute (16 ppb). It is extremely difficult to accept the hypothesis that the DDE was formed by reaction or rearrangement of any of the chlorinated organics in the run 12 feed. We are more apt to believe that we had cross-contamination of samples from the low pressure, room temperature portion of our bench-scale system (i.e., the apparatus downstream of the high pressure vapor-liquid separator in Fig. 2). To prevent cross-contamination, an acetone wash system was installed before run 16.

The feed for run 13 was a mixture of four non-volatile chlorinated organics, including hexachlorocyclohexane (Lindane) and 4,4'-dichlorobiphenyl (a model PCB compound), both of which should be relatively stable. As shown in Tables 4b, the carbon destruction and chlorine conversion efficiencies were very good, the latter being somewhat higher than the former.

The feed for run 14 was a mixture of spent transformer oil, containing two PCB's, which was diluted with MEK. Once again, both carbon destruction and chlorine conversion exceeded 99.99%. Note that the residual organic chlorides identified by GC/MS (compounds E,K and O) are all DDT-related species. Thus those trace quantities are probably cross-contaminants from run 13. It should also be noted that for run 14, mass spectra were searched for all chlorinated biphenyls. That is, we specifically looked for trace quantities of tri-, tetra-, penta- and hexa-chlorobiphenyl, in addition to the mono- and di-chloro species (compounds M and N in Table 5). At the detection limit of < 10 ppb, none of these chlorinated biphenyls were found. If we discount compounds E, K and O as cross-contaminants, then the chlorinated biphenyl conversion efficiency is >99.9994%.

Run 15 was an experiment with a model PCB 4,4'-dichlorobiphenyl (DCBP). This material was chosen for study of reaction kinetics, as discussed in subsection V.D., below. The results obtained in run 15, at $500^{\circ}C$, were excellent once again.

C. Performance Capacity. Possibly the key question in any analysis of the desirability of SCW oxidation (vis a vis competing processes) is that of determining how well it can perform as a destruction system. We feel that the body of data available now is sufficient to make it clear that the process works substantially better in this regard than conventional combustion/incineration techniques. With the operation conditions optimized, the destruction efficiencies for methyl ethyl ketone (MEK) were 99.99-99.999%. These data and the kinetic analysis outlined below indicate that commercial designs can be developed to provide for the destruction of carbon-containing feeds to any desired degree.

Table 5. Compounds Searched by GC/MS Analysis

A: Cl—⟨ ⟩—OH

B: Cl—⟨ ⟩—CHO

C: Cl—⟨ ⟩—CO - CH₃

D: Cl—⟨ ⟩—COOH

E: Cl—⟨ ⟩—CO—⟨ ⟩—Cl

F: Cl—⟨ ⟩—CO CO—⟨ ⟩—Cl

G: (CH₂ bridged dichloro fluorene structure)

H: (O bridged dichloro structure)

I: CHCl (dichloro diphenyl ethylene structure)

J: CH₂ (dichloro diphenyl ethylene structure)

K: CCl₂ (dichloro diphenyl ethylene structure)

L: Isomer of I.

M: Cl—⟨ ⟩—⟨ ⟩

N: Cl—⟨ ⟩—⟨ ⟩—Cl

O: CCl₃ (dichloro diphenyl structure)

P: (dichloro dibenzo dioxin structure)

Notes: p-Isomers are assumed, based on the position of the chlorine atoms in the starting materials.

Compound F – No authentic MS

Compound G – No MS available in literature

- 29 -

D. Special Kinetic Studies. A series of tests has been run in
order to gain further insight into the reaction kinetics of organic,
substances combusted by oxygen in the SCW medium. In addition to
providing a basis for the prediction of what residence time is necessary
to produce a given destruction efficiency at higher temperatures, we
should gain additional theoretical ins`ght into reaction mechanisms
under these conditions.,

In order to determine the kinetics of a reaction, one must operate
under conditions in which the reaction is significantly less than
complete. Thus, we set up a matrix of temperatures and residence times
which, we had hoped, would result in conversions less that 99%. In
order to provide meaningful results, the organic feed concentration was
reduced to about 1 wt% carbon in water so that the reactor would
approach isothermal conditions.

Data were taken for three feedstocks, methly ethyl ketone (MEK), 3%
4,4'dichlorobiphenyl (DCBP) in MEK, and 3% 2,4-dinitrotoluene (DNT) in
MEK.

From experimental data, rate constants were calculated for both
first order and second order mechanisms. These results were not
definitive, mechanistically, but they do augment the available data base
for the process and emphasize the conclusion that high destruction
efficiencies are consistently obtained at temperatures of 500°C or
above. A more quantitative discussion of these experiments may be found
in an addendum, "Detoxification and Disposal of Hazardous Organic
Chemicals by Processing in Supercritical Water, Limited Rights Data".

E. Partial oxidation and reforming of 2,4-dinitrotoluene. This
series of tests was undertaken to determine the effect of temperature
and oxygen concentration on the fate of DNT-nitrogen. For these tests,
the DNT concentration was considerably higher than that used in the DNT
kinetics experiments described in subsection D, above.

The first experiment in this series, high concentration MEK only
(Run 68), was done to establish a baseline for the remainder of the
series, and as expected we had very high efficiencies, above four
nines. The next experiment (Run 69) was with 12 wt% DNT in MEK as
shown in Tables 6a and 6b. The destruction and combustion efficiencies
were both higher than the run with MEK only. For the first time in a
DNT run we were able to obtain a good closure of the nitrogen balance.
Also in this series (Run 70A) we were able to operate with a very small
amount of excess oxygen and still maintain efficiencies of four nines or
better. In fact as one lowered the oxygen input to just below the

- 30 -

TABLE 6a. OXIDATION AND REFORMATION OF DNT
Runs 68-70b

Run No.	68	69	70A	70B
Feed Material	MEK	12%DNT/MEK	12%DNT/MEK	12%DNT/MEK
Oxidant	O_2	O_2	O_2	O_2
Residence Time (min)	1.2	1.2	1.2	1.2
Temperature (^{O}C)				
Avg. Wall	584	580	574	570
Excess O_2	27.5	21.0	4.5	-1.7
Carbon Analysis				
Organic In (ppm)	17959	17612	17439	17439
Organic Out (ppm)	1.0	0.7	0.1	66.9
Destruction Efficiency	99.9947	99.9959	99.9992	99.6164
Combustion Efficiency	>99.99	>99.99	>99.99	98.5128
Carbon Out-Liquid (%)	5.4	3.9	3.0	4.6
Carbon Out-Gas (%)	104.2	14.1	101.2	102.2
C Balance Total (%)	109.6	108.0	104.2	106.8
Nitrogen Analysis				
N In (ppm)	-	513	508	508
N as Nitrate (ppm)	-	35	10	4
N as Nitrite (ppm)	-	20	-	-
N Out Liquid (%)	-	10.8	2.0	0.8
N Out Gas (%)	-	94.9	93.8	110.1
N Balance (%)	-	105.7	95.8	110.9
Gas Composition (%)				
O_2	28.25	23.26	6.89	0.53
CO_2	71.15	75.76	93.83	98.30
CH_4	0.00	0.00	0.00	0.00
H_2	0.00	0.00	0.00	0.35
CO	0.00	0.00	0.00	1.48
N_2	0.11	0.35	0.47	0.51
N_2O	0.00	0.52	0.62	0.61
NO	0.00	0.00	0.00	0.45
C_2H_6	-	-	-	-
C_2H_4	-	-	-	-
C_3	-	-	-	-
C_4	-	-	-	-
C_5	-	-	-	-
C_6	-	-	-	-

TABLE 6b. OXIDATION AND REFORMATION OF DNT
Runs 72-75B

Run No.	72	73	75A	75B
Feed Material	10%DNT/MEK	12%DNT/MEK	12%DNT/MEK	12%DNT/MEK
Oxidant	None	None	O_2	O_2
Residence Time (min)	2.2	2.2	1.1	1.1
Temperature (^{O}C)				
Avg. Wall	402	509	479	577
Excess O_2	-100.00	-100.00	-50.0	-49.1
Carbon Analysis				
Organic In (ppm)	19874	18222	17275	18360
Organic Out (ppm)	13664	12291	4462	4906
Destruction Efficiency	31.2466	32.550	74.1713	73.2783
Combustion Efficiency	8.7985	4.5876	43.5893	46.2343
Carbon Out-Liquid (%)	75.5	78.3	34.8	33.9
Carbon Out-Gas (%)	2.5	13.3	78.3	76.
C Balance Total (%)	78.0	91.6	113.1	110.2
Nitrogen Analysis				
N In (ppm)	471	432	409	435
N as Nitrate (ppm)	-	-	-	-
N as Nitrite (ppm)	-	-	-	-
N Out Liquid (%)	14.0	20.5	-	-
N Out Gas (%)	8.8	33.6	24.0	40.3
N Balance (%)	22.8	54.1	24.0	40.3
Gas Composition (%)				
O_2	0.05	0.00	0.14	0.04
CO_2	9.22	6.47	45.91	50.96
CH_4	29.29	20.33	10.20	10.23
H_2	1.56	3.75	4.35	3.19
CO	43.29	37.19	39.67	33.46
N_2	3.67	3.64	0.33	0.59
N_2O	0.00	0.00	0.00	0.00
NO	-	-	-	-
C_2H_6	1.76	9.35	0.57	1.27
C_2H_4	8.73	24.53	3.70	5.87
C_3	0.55	1.50	0.13	0.21
C_4	0.11	0.35	0.03	0.10
C_5	0.00	0.03	0.10	0.00
C_6	0.00	0.54	0.00	0.04

stoichiometric amount needed for complete oxidation (Run 70B)
destruction efficiencies of about 98% were still maintained. This is an
indication that the amount of oxygen needed to operate a system cleanly
may be just a few percent above the stoichiometric amount needed for
complete oxidation. When oxyen input is lowered to 50% (Runs 75A & B)
of the amount needed for complete oxidation, we get approximately 77% of
the carbon out in the gas phase compared to nearly 100% in complete
oxidation experiments. The makeup of the gas shifts from mostly CO_2
in complete oxidation to a mixture, in partial oxidation, of CO_2, CO
and hydrocarbons up to C_6 in length. The liquid analyses, done by GC,
of extracts for these runs were extremely difficult because of the large
number of compounds present in the liquid. Those compounds that were
identified are presented in Table 7.

The final runs in this series were the reforming tests (Runs 71, 72
and 73). No data are tabulated for run 71. This was the MEK baseline
reforming test and we could not obtain any gaseous effluent from the
system. In fact, it appeared as if the MEK was not reforming in this
run. With 10% DNT added, we could account for 2.5% of the carbon out
in the gas phase at $402^{\circ}C$. At $509^{\circ}C$, the carbon in the gas phase
was 13.3% of the total carbon out. If one looks at the gas product
distribution of the two temperatures, it can be seen that the $500^{\circ}C$
run has significantly more ethylene and ethane than the $400^{\circ}C$ run.
Not only was more gas produced at $500^{\circ}C$, the gas composition changed.
In the liquid analysis of these runs, it can be seen that at higher
temperature the products seem to be of lower molecular weight. It seems
likely that some recombination reactions may have taken place in either
the sample vial or actually in the reactor.

F. Oxidation Using Air. Using air as the oxidant rather than pure
oxygen may be advantageous in commercial applications. To determine the
feasibility of using air, experiments wre conducted using air instead of
oxygen, but with all other conditions the same. When the air
experiments in Table 8 are compared with their oxygen counterparts, the
results show similar, high destruction efficiencies for both air and
oxygen. In two cases, the air had a somewhat higher destruction
efficiency and in two cases it was somewhat lower. Of course, the gas
effluent is diluted several fold by nitrogen when air is used. Based on
these results, SCW oxidation appears to be equally effective with air as
with pure oxygen. Nitric oxide and nitrogen dioxide were not formed.
This is very likely due to the relatively low temperature of the system
(compared to peak temperatures in a typical combustion zone).

G. Heteroatom Removal Concepts. The conceptual approach to handling
heteroatoms (any element other than C, H, O, or N) has been to rely on
data which show that many salts are essentially insoluble in SCW at
temperatures in the neighborhood of $500^{\circ}C$. Thus, if suitable cations

TABLE 7. DNT REFORMATION PRODUCTS

Run No.	69	70B	72	73
			Concentration	
	PPB	PPM	PPM	PPM
Component Name				
1. Unidentified		0.54	7.30	65.88
2. Aniline		0.02	17.98	457.00
3. Benzonitrile		0.06	6.77	31.00
4. Phenol	0.27	3.32	5.10	131.00
5. Unidentified		0.02		
6. o-Cresol	0.20	0.02	7.07	
7. p-Cresol	0.27	0.15	9.25	
8. o-Toluidine		0.01		46.00
9. p-Toluidine		0.04		31.00
10. Nitrophenol	0.24		12.00	
11. Nitrotoluene				
12. Quinoline (iso?)		0.09		
13. Methyl (iso?) Quinoline				28.00
14. Indole		0.09	14.19	27.00
15. Methyl-tetrahydronaphthalene		0.06		313.00
16. Acrylaniline		0.03		41.80
17. Dinitrobenzene	1.50	0.12	126.15	10.80
18. Dinitrophenol	0.58	0.03	36.12	13.80
19. Dinitrotoluene	0.92	0.08	259.48	
20. Dinitrocresol	0.25			

TABLE 8. OXIDATION WITH AIR

Run No.	34	35	36	37
Feed Material	MEK	DCBP/MEK	MEK	DCBP/MEK
Oxidant	AIR	AIR	AIR	AIR
Temperature (^{O}C)	519	510	456	456
Residence Time	1.4	1.4	1.4	1.4
Excess O_2 (%)	20.1	17.0	13.9	18.3
Carbon Analysis				
Organic In (ppm)	9,206.	9,839.	9,583.	9,624.
Organic Out (ppm)	2.5	0.2	6.7	44.4
Destruction Efficiency (%)	99.97	99.998	99.93	99.54
Combustion Efficiency (%)	>99.99	>99.99	99.70	98.84
Carbon Balance Closure (%)	102.45	103.96	105.48	105.16
Cl in (ppm)	0	142	0	139
Gas Composition				
O_2	3.85	3.34	2.85	3.74
CO_2	13.59	14.09	14.17	13.69
CH_4	0.00	0.00	0.00	0.01
H_2	0.04	0.04	0.05	0.04
CO	0.00	0.00	0.04	0.15
N_2	73.31	73.31	73.30	73.12

- 35 -

are present, the reaction products of typical heteroatoms (i.e. HCl, H_2SO_4, H_3PO_4, H_4SiO_4, etc.) can, in concept, be precipitated as their corresponding salts produced by acid-base neutralization. Carbonates ($CaCO_3$ or $MgCO_3$) and hydroxides (NaOH) have been viewed as candidate additives (as sources of the needed cations), since after the neutralization reaction they would not introduce any new compounds into the system.

It should be noted that a wide variety of other inorganic compounds should be removed by similar mechanisms. For example, arsenic is apt to appear as H_3AsO_4 and may react with the proposed cation additives to form calcium and magnesium arsenates. It is likly that most of the metals, such as tungsten and molybdenum, that would be converted to oxy-acids are apt to be removed effectively with one or more of the proposed additives. In some cases, the exhausted scavengers may be loaded with compounds of sufficient commercial value to warrant their use as byproducts of the oxidation process. As an example, if tungsten is present in the effluent, it is apt to be precipitated as $CaWO_4$. The separation of metals from the scavengers would, of course, depend on the particular metals and on their concentrations.

The collection of inorganic solids from the oxidizer effluent is primarily a hardware design problem. A number of possible methods and devices have been considered, although none has been investigated experimentally as part of this work. Two possibilities, gravity separators and cyclones, which utilize inertial forces, have subsequently been tested for use in solids removal systems.

The first tests were conducted using a combination reactor/solid separator. This was a large volume vessle which relied on gravity to separate the solids from the fluid stream. The salt, NaCl for these tests, was either dissolved in the feed or produced by neutralizing the HCl produced from oxidation of a chlorinated hydrocarbon with NaOH. The solid would theoretically fall to the bottom of the vessel while the fluid stream exited from the top or side. In practice it was impossible to collect substantial amounts of solid in the vessle without plugging either the inlet, the outlet, or both. The problem seemed to be one of localized fluid mechanics in the settler and the agglomeration behavior of the particles. As they formed the salts were apparently sticky and adhered to the hot reactor surface immediately on contact. The removal of salt from the fluid stream was essentially complete, however, with the NaCl concentration in the effluent liquid about 100 ppm, the level predicted from the solubility of NaCl in supercritical water.

For the next tests the reactor and solid separator were separated. The oxidation reaction took place in a tubular reactor, designed to keep

- 36 -

the salts moving at high velocity as they formed. The reactor effluent entered a cyclone in which inertial forces caused the solids to separate while the fluid phase exited at the top. The approach appeared successful with low efficiency cyclones, but as the cyclone efficiency was improved the plugging problems increased. A major modification to the feed injector nozzle had been made while the cyclone tests were being conducted and the reactor/gravity solid separator approach was retested with excellent results. This is the configuration which has been in use for all major experiments involving salt separation on the bench scale and which will be tested on the demonstration unit.

H. Corrosion Study. The bench-scale process development program for the SCW oxidation process has been operating for more than eighteen months. Over that period of time the bench-scale reactor has been operated for more than 2000 hours at a fairly wide range of temperatures and concentrations of oxygen and chloride ion. Since corrosion was a key concern when the process first came under consideration, MODAR has taken advantage of every opportunity to study the behavior of the materials of construction under process conditions. Dr. Ronald Latanision (MIT Corrosion Laboratory) of the MODAR Technical Advisory Board and the technical staff of the Stellite Division of the Cabot Corporation have provided useful advice and technical support to MODAR in this aspect of the program.

Reactor corrosion studies have involved the exposure of clip-supported, pre-stressed coupons of candidate reactor materials to the reactor environment during the course of the bench-scale experimental program. Since no corrosion was observed after several hundred hours of exposure during the initial reactivity and kinetic study programs, a period of more intense exposure was carried out. Chloride levels of 5000 and 10,000 ppm were created by oxidizing trichloroethylene at about 550°C. A complete microscopic and metallurgical study of the exposed coupons indicates that overall corrosion at reactor conditions is not a problem for the materials under study, Hastelloy C-276 and Cabot Alloy 625.

Considerable corrosion activity was, however, observed in the area of the system where the reactor effluent was cooling down into the subcritical region. After intensive study it was determined that this corrosion was mainly due to cavitation erosion, although chloride (and probably oxygen) levels are important contributory factors. Cavitation erosion is likely the result of entering the two-phase region (thermodynamically) with fairly high fluid velocities in the tubing and fittings. Several approaches to dealing with this problem present themselves and it is not expected to be an impediment to the development of the process. The absence of corrosion in the reactor itself is not particularly surprising. The low dielectric constant of water and the resultant absence of ionized species at these conditions can be expected to interfere with electrochemical attack.

- 37 -

VI. CONCLUSIONS

Tests with the bench-scale system were undertaken in May, 1980 with the objectives of: (i) demonstrating the technical feasibility of applying the process to a wide range of waste constituents and (ii) gathering kinetic and other data necessary to design a large, demonstration-scale system.

A thorough description of prior and continuing work under the bench-scale testing program has been presented in this report. Typically, extremely high conversions of feed carbon to gaseous carbon dioxide have been observed. Mixed feeds have ranged from 2 to 6 percent carbon, by weight, and destruction efficiencies have generally ranged from the high nineties to "four or five nines" (99.99+%), with most results being toward the higher conversion end, unless experiments were deliberately designed to yield kinetic data (hence requiring less than complete conversion). As we have grown more experienced in operating the unit and its attendant sampling and analytical systems, we have experienced good material balance closure (generally within a few percent). Mass spectrometric analysis of liquid samples has been extremely favorable; residual organic chloride concentrations can be reduced to the 10 ppb range. On balance, the process has performed better than initially anticipated.

The results to date make it clear that the chemistry and kinetics of the system behave pretty much as our initial concepts anticipated they would. The process should be able to successfully treat any and all organic wastes and efficiently render them harmless. The remaining technical objectives at the bench-scale level, corrosion testing and salt (heteroatom) separation, have been studied in the laboratory and reported herein. The results of these studies have convinced us that neither of these potential problems will present an obstacle, technically or economically, to the further development of the process.

Further development of the SCW oxidation process is being pursued in order to be able to make systems commercially available at the earliest possible date. Bench-scale studies will be continued to test process improvements and run "treatability" tests on candidate waste streams. The design, fabrication, operation, and field testing of a larger scale unit will also be undertaken. A fifty-fold scale-up in waste throughput is achievable, and will allow the resolution of all remaining technical issues, as well as provide the design data necessary to eventually move to large scale commercial units.

VII. FUTURE PLANS

A. Technical Review/Process Analysis

As discussed in the preceding section, the bench-scale development program has achieved essentially all of its technical objectives. High destruction efficiencies can be attained for essentially all carbon-containing wastes. Corrosion and heteroatom removal were not totally resolved at the end of the testing program, but solutions with current technology appeared available. The remaining questions at the end of the development program were questions of scale-up and commercialization, i.e., operating experience (reliability, controllability, etc.) and economics of construction/operation at various levels of scale.

Conceptual designs and preliminary economic analyses of systems with larger capacities and using potentially available technologies are presently being evaluated. A 10 TPD unit, using air as the oxidant has been designed and costed. The process flowsheet for this unit is similar to that shown in Figure 1, except that only partial recovery is contemplated via feed/product heat exchange. The unit generates approximately 9000 pounds/hour of 150 psig by-product steam for other uses in the manufacturing/production facility in which the SCW oxidation unit is situated. The SCW unit destroys 10 tons of organic waste per day, or 900,000 gallons per year for a 330 stream-day year. Capital costs (Table 9) are estimated at approximately $5M dollars, with the largest capital cost item the air compressor. Estimates of annualized operating costs yield projected processing costs in the range of $2.40/gallon of organic, or 25 cents/gallon of wastewater containing 10 percent organic wastes.

A schematic of the largest system we envision, at 100 TPD capacity, is shown in Figure 3. At these large throughputs, we can take advantage of the very sizable economics of scale. For example, air compression can be accomplished by the axial compressor stages built into gas turbines. The process design of Fig. 3 employs two gas turbines in series, each having a compression ratio of 8. Gas turbine #1 is commercially available. (For example, a Sulzer Bros. Type 3 turbine can accommodate air at the flow rate required for 100 TPD and has a net power rating of 5.8 MW). Gas turbine #2 of Fig. 3 is envisioned to be a 500 HP engine used for powering small aircraft. Although such units are readily available in the required size range, we would need to modify the housing to withstand pressures up to 65 atm. We anticipate that the gas turbines will comprise the largest single cost in a 100 TPD system.

The economic analysis for this 100 TPD system has not been completed. However, based upon what we know about the cost of gas

Table 9.   PROJECTED COSTS FOR 10 TPD CAPACITY

Annual capacity: 10TPD x 330 DPY = 3300 TPY
                                   = 900,000 gal/year

CAPITAL COST ESTIMATE

Tanks, Pumps, Eductor
Heat Exchanger, Reactor & Instrumentation
Separators, Let-Down Units, Start-Up Furnace
Air Compressor
Contingencies

Capital Cost Estimate $5320
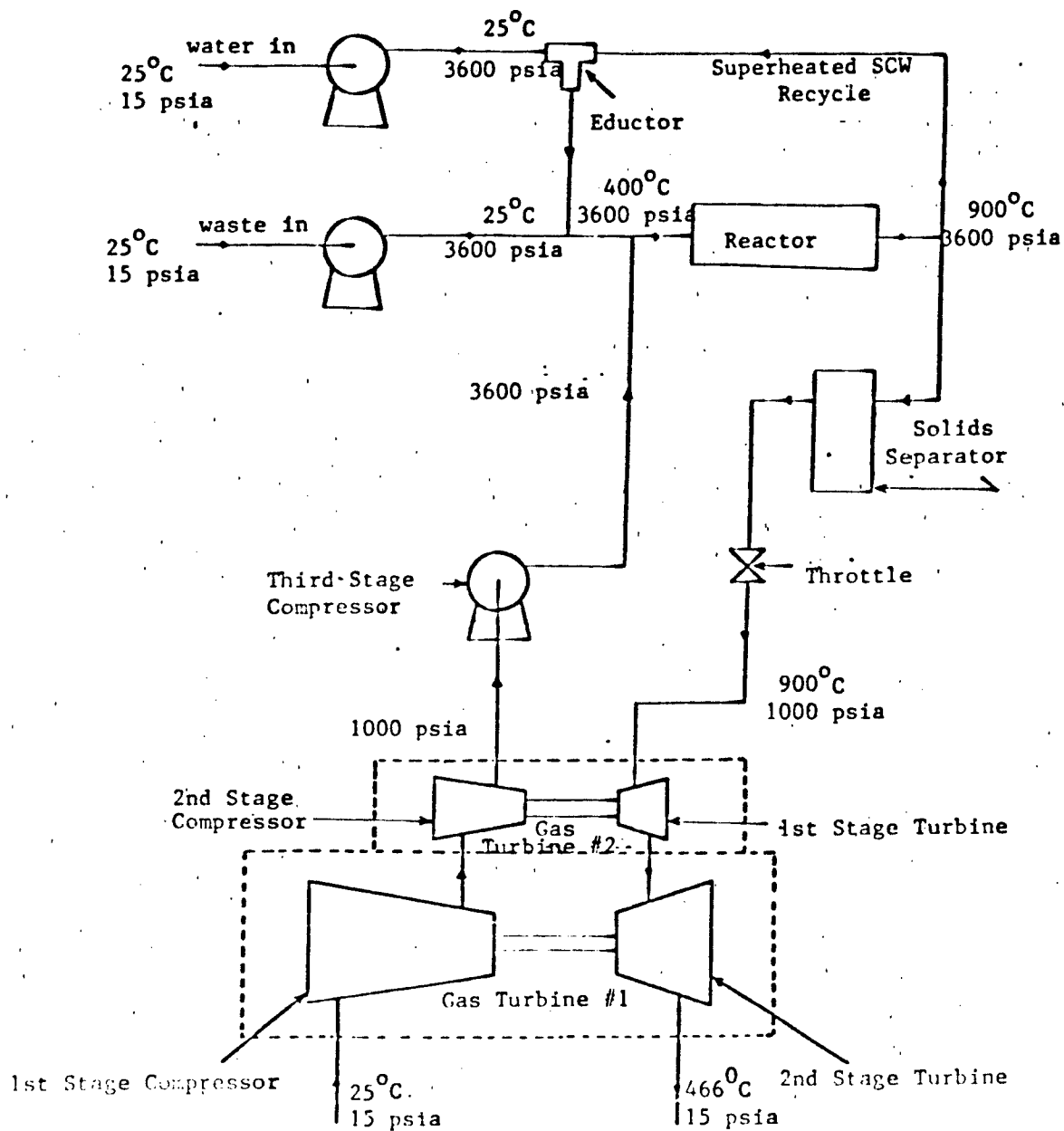
PROCESSING COSTS

Chemicals and Utilities (Elec: 4c/KWH; H_2O = 5.5c/MGAL)
Operating Labor and Plant Overhead
Maintenance (5% CCE)
By-Product Steam Credit ($6.00/M LBS)
Cost of Capital (25% CCE)

Total Operating Cost $2143

Unit Cost/Gallon Organic $2.38
Unit Cost/Gallon Wastewater
   at 10% Organic Content $0.26

Figure 3. Schematic of 100 TPD Waste Treatment System
With Gas Turbines

turbines, we anticipate that such system could be priced for sale at approximately 15 million dollars. Projected annualized processing costs including the costs of capital recovery would be about $.50/gallon organic or 5.5 cents/gallon of wastewater containing 10 percent organic.

Large scale systems (e.g. 10 to 100 ton/day capacity) will compete with incinerators and containment sites for the larger volume waste treatment market. Cost, reliability, and controllability are seen to be key factors in the success of the process in this area. These central processing units would utilize air as the oxidant and would recover process-generated energy to drive air compressors and generate salable electricity or steam. Figure 4 presents a cost comparison between SCW destruction and conventional liquid injection incineration, for the case of dilute organic wastes in a wastewater (2-30% concentration). These results, which are typical, are encouraging in that they suggest that there will be a number of large-scale applications for which the MODAR SCW oxidation system will be preferred over other technologies. This factor, coupled with the present regulatory strategy, which minimizes land disposal, appears to suggest a bright future for this technology in years to come.

B. Process Development Strategy

Over the long term, MODAR intends to build, license, or otherwise make available in the marketplace systems for both mobile and fixed-site applications. We have in mind eventually carrying out a large-scale demonstration as the final stage in process developme t. Naturally, however, we are also interested in entering the marketplace as soon as possible, and we anticipate that smaller, mobile systems will be our initial commercial product.

It makes good technical (as well as business) sense for MODAR to proceed as rapidly as possible to a demonstration of a small mobile system, with capacity 1000 gal/day of wastewater, or 50 gal/day organic waste. The classical approach to process development requires moving upward in scale incrementally (bench to pilot to semi-works, etc.) and in this case the business objectives are consistent with good technical practice. A unit at this scale will allow us to pin down the fluid mechanical aspects of the process as well as permit tests to (i) demonstrate process feasibility and reliability on a variety of "real world" wastes, (ii) allow careful characterization of effluent streams to be made, and (iii) provide the data necessary to develop refined economic analyses. The results of a demonstration at this scale will provide the data base necessary to design a full-scale demonstration incorporating energy recovery and also to move into the marketplace with products and services built around the mobile system.

The present program to build and evaluate the SCW demonstration units is described in outline form below. The program consists of four tasks,

- 42 -

FIGURE 4

COMPARISON OF INCINERATION AND SCW OXIDATION
PROCESSING COSTS
FOR TREATMENT OF DILUTE ORGANIC WASTES

FEED: 100 TPD ORGANIC IN WATER

BASIS:

- ORGANIC HEATING VALUE 13,500 BTU/LB
- PROCESSING COST INCLUDES:
  - CAPITAL RECOVERY AT 35%/YR, EARLY 1981 $.
  - POWER COST OR RECOVERY AT 4¢/KWH.
  - ENERGY COST OR RECOVERY AT $5.50/MM BTU.
- 365 DAYS/YR, 24 HRS/DAY

Liquid Injection
Incinerator/Chemical
Scrubber

MODAR SCW
SYSTEM

PROCESSING COST ($/TON OF ORGANIC)

WEIGHT PERCENT ORGANIC IN WATER FEED
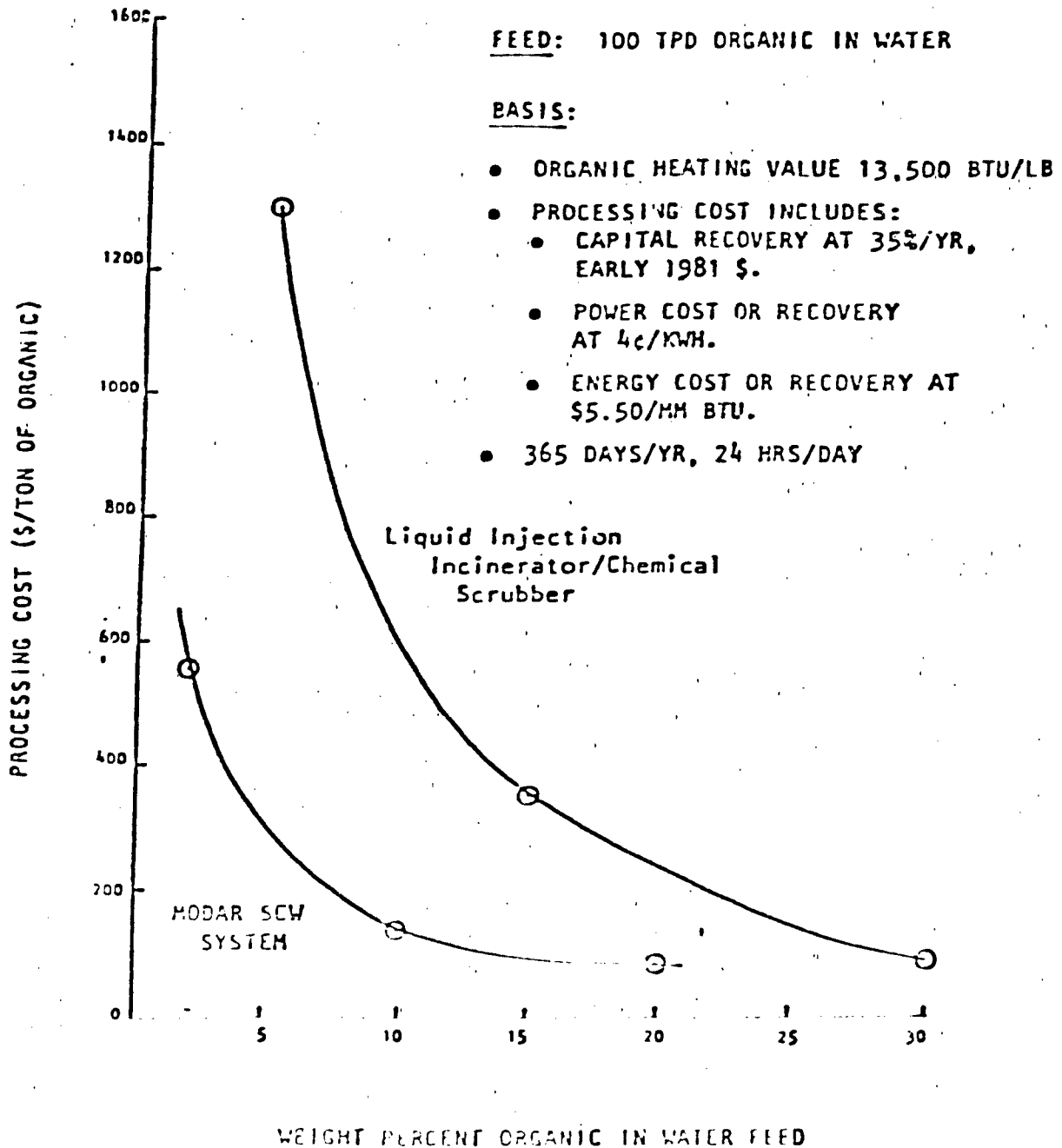
conducted in sequence:

Task A is concerned with the design, equipment procurement
and fabrication of a skid-mounted system, designed to process
1000 gal/day of wastewaters, including 50 gal/day of organic
wastes.

Task B is concerned with the in-house testing and evaluation
of the system as fabricated. It will include defining an
appropriate start-up protocol, conducting preliminary tests
with several model compounds, and finally testing destruction
efficiency of several mixtures at design flow rates.

Task C is an actual field demonstration of the unit on site.
It involves transportation of the unit to the site, repetition
of the preliminary tests, short duration tests with the site-
specific waste and a long term (at least twenty days) test run,
at design capacity with the waste material.

Task D is the analysis of all test results and preparation of
a final report.

VIII. APPENDIX

A. Properties of Supercritical Water

The supercritical region can best be visualized with the aid of a temperature-density diagram, as shown in Fig. 5. The critical point (C.P.), which lies on the vapor-liquid saturation dome, occurs at $374^\circ C$ and 0.3 g/cm^3. The supercritical region lies above $374^\circ C$ and $450^\circ C$, and densities from 0.2 to 0.7 g/cm^3. In this region, the density varies very rapidly with 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 shown in Fig. 6 (Quist and Marshall, 1965; Franck, 1970). In the near critical region, the dielectric constant ranges between 2.5 and 15, which corresponds to that of a polar organic liquid under normal conditions. The unusually high dielectric constant of normal liquid water (80) is the result of strong hydrogen bonding. The lower values in the supercritical regime are indicative of a greatly reduced extent of hydrogen bonding. This is not surprising, since hydrogen bonds are very short-range forces, and since the supercritical fluid has a significantly lower density than the normal liquid (Franck, 1976).

Supercritical water SCW behaves very much like a polar organic solvent. Organic materials, which are only sparingly soluble in water at room temperature, become completely miscible with water in the supercritical regime. For example, the solubilities of benzene, pentane, heptane and 2-methyl pentane in water are shown in Figs. 7 to 10 (Connolly, 1966). Consider the case of benzene, Fig 7. At $260^\circ C$ (curve a), the solubility is fairly independent of pressure at about 7-8 wt% benzene, which is already far higher than that at $25^\circ C$ (.07 wt%). Above $260^\circ C$, the solubility increases with temperature; at $287.5^\circ C$ (curve c) a maximum appears in the range of 200-250 atm. The maximum is very pronounced at $295^\circ C$ (curve d). At $300^\circ C$ the solubility curve splits into two branches (curve e); between these two branches at 200 to 500 atm. benzene and water are miscible in all proportions. The lowest temperature at which complete miscibility first occurs is called the critical solution temperature (CST). For benzene, it is around $300^\circ C$ (Connolly, 1966; Rebert and Kay, 1959). The other aliphatic hydrocarbons shown in Figs. 8 to 10 require somewhat higher temperatures for complete miscibility: $351-353^\circ C$ (Connolly, 1966).

Another way to demonstrate miscibility is by examining the critical curve in a pressure-temperature-concentration diagram. The schematic shown in Fig. 11 is approximately correct for many organic-water binary systems, such as benzene-water. The critical point of water is presented by CP_h and that of the hydrocarbon by CP_1. The dashed curve in Fig. 11, beginning CP_h, is the upper branch of the critical curve; to the left of this branch, the system may separate into two fluid phases, whereas to the right of it (at higher temperatures) a
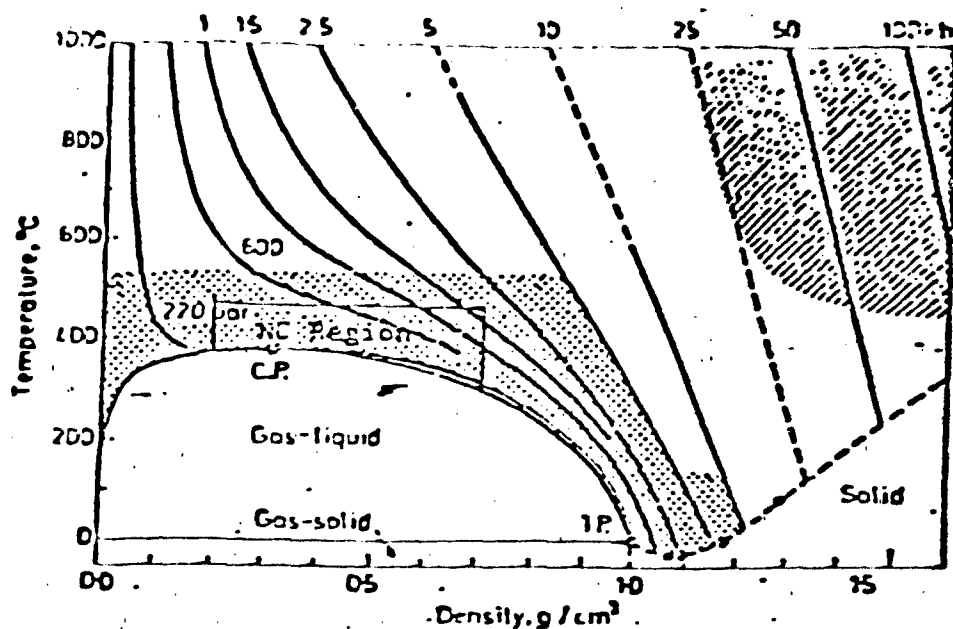
Figure 5 . Temperature/density diagram of water. Full lines: measured isobars. Dashed lines: interpolated isobars. Cross-hatched zone: viscosity and dielectric constants determined. Single shading: ionic conductance determined. (Franck, 1970)
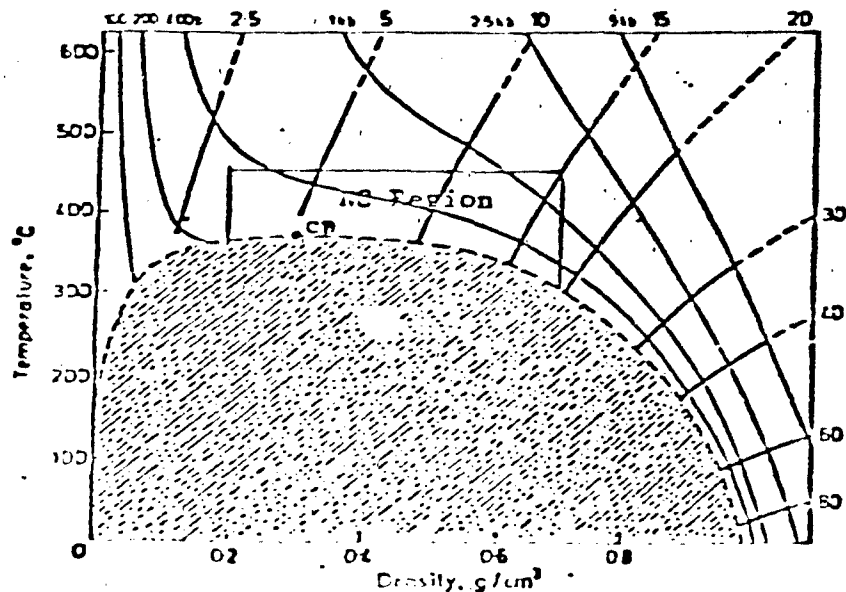

Figure 6.   Dielectric constant of water as a function of temperature
and density ——: Measured   ----: Calculated ——:
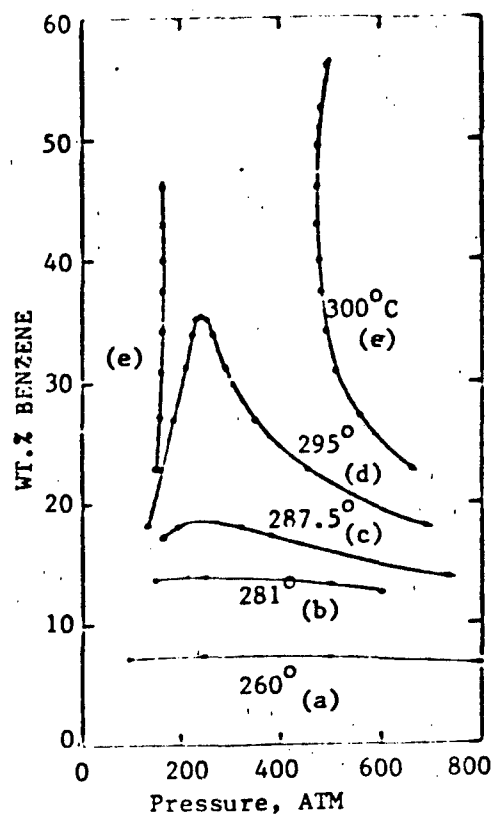isobars.

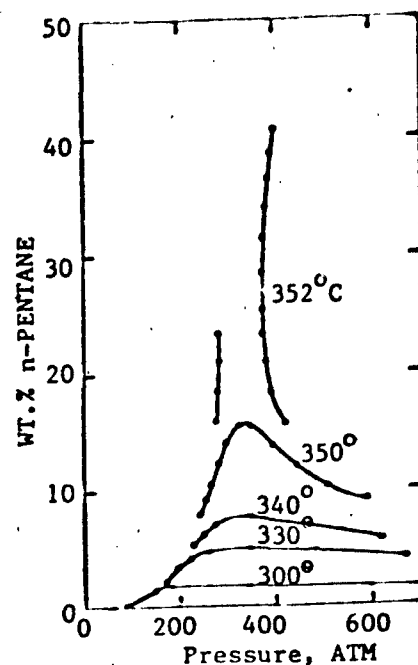(Franck, 1970)

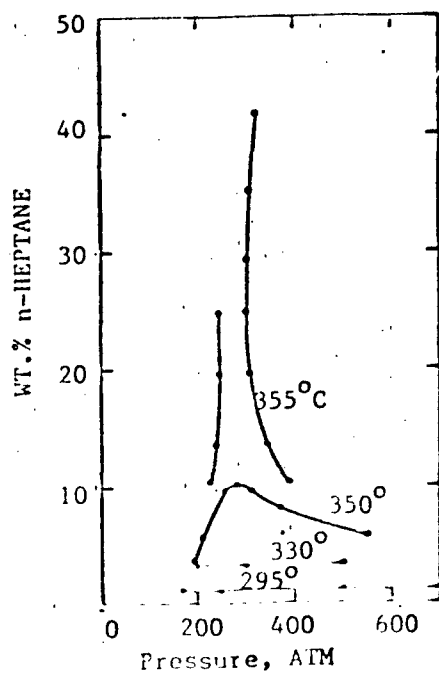Figure 7. Solubility of benzene in water

Figure 8. Solubility of n-pentane in water

Figure 9. Solubility of n-heptane in water
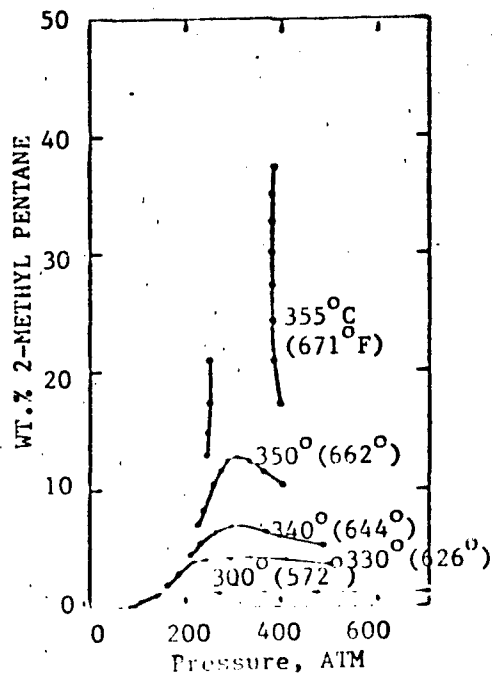
Figure 10. Solubility of 2-methyl pentane in water

Connolly (1966)
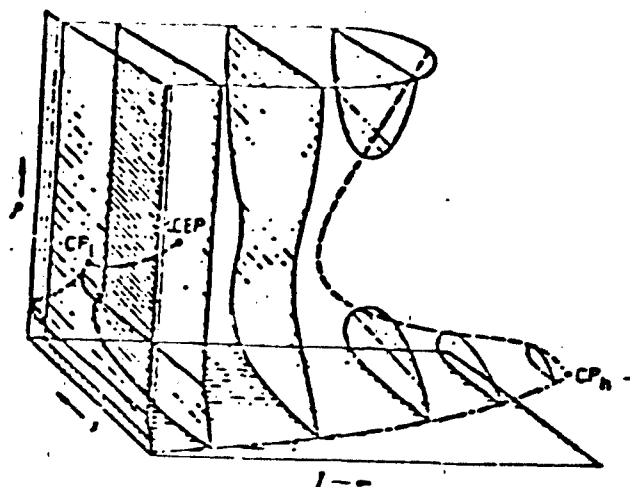
Figure 11. Schematic pressure-composition-temperature-diagram of a binary system with interrupted critical curve.

CP_l and CP_h: Critical points of the lower and higher boiling pure components.

LCEP: Lower critical end point.

Branches of the critical curve: _ _ _ _ _ _ _

(Franck, 1976)
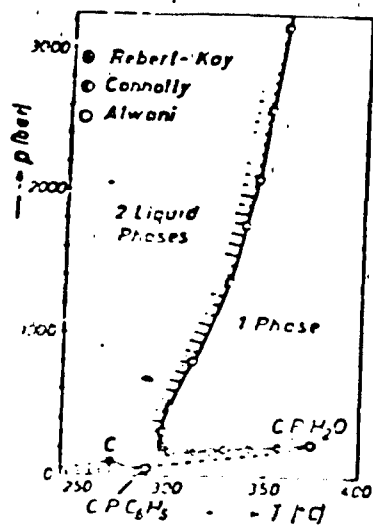
Figure 12. P-T projection for the benzene-H_2O system.
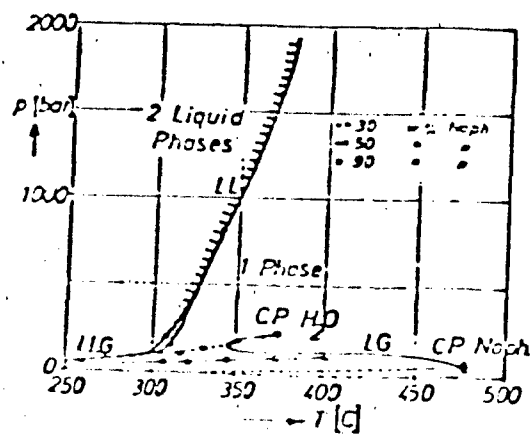
Figure 13. P-T projection for the naphthalene-H_2O system.

- 48 -

homogeneous phase exists at all temperatures and concentrations. In other words, to the right of the critical curve, the components are completely miscible. The projection of the critical curve, in pressure-temperature space, is shown in Figs. 12 and 13 for benzene-water and naphthalene-water, respectively. In both cases, it can be seen that above the critical temperature and pressure of water, the organics are completely miscible with water (unless extremely high pressures are involved). Although the number of organic-water systems that have been studied in this detail is very limited, it is clear that water is an excellent solvent for some of the least soluble organics at room temperature. We would anticipate that other organics behave similarly. Indeed, we have found that substances as complex as wood can be completely solubilized in SCW as described in the next section.

The behavior of SCW as a solvent for inorganic salts is as unusual as that for organics. While water becomes an excellent solvent for organic substances about 300-375°C, it becomes a very poor solvent for inorganic salts about 450°C. For example, the solubilities of salts in water from 200 to 450°C are shown in Figure 14 (Marshall, 1975). Most salts show gradually increasing solubilities over this range. (The exceptions are K_2SO_4, Na_2SO_4, Na_3PO_4, Na_2CO_3 and Li_2SO_4.) When temperatures are increased above this range, the solubilities drop precipitously. For example, the solubilities of a number of common salts in this higher temperature range are shown in Figs. 15 and 16 (Martynova, 1976). NaCl, which has a solubility of 35-40 wt% at lower temperatures, drops to 10^5ppb or 100 ppm at 500°C; $CaCl_2$, with a solubility of over 70 wt% at subcritical temperatures, drops to less than 10 ppm at 500°C.

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 is shown in Fig. 17 as a function of temperatures and water density (Marshall, 1976). At 400-500°C and densities in the range of 0.35, the dissociation constant is of the order of 10^{-4}. Thus, strong electrolytes become weak electrolytes.

The properties of water as a function of temperature are summarized in Fig. 18. We see that water goes through a complete reversal in solubility behavior toward organic and inorganic substances through the temperature range of 300-500°C. Below this range, the pattern is similar to normal liquid water; low organic and high inorganic solubility. Within the range of 375 to 450°C there is a high solubility of both organic and inorganic substances. Above this range, inorganic salts are practically insoluble, and organic substances are completely miscible.
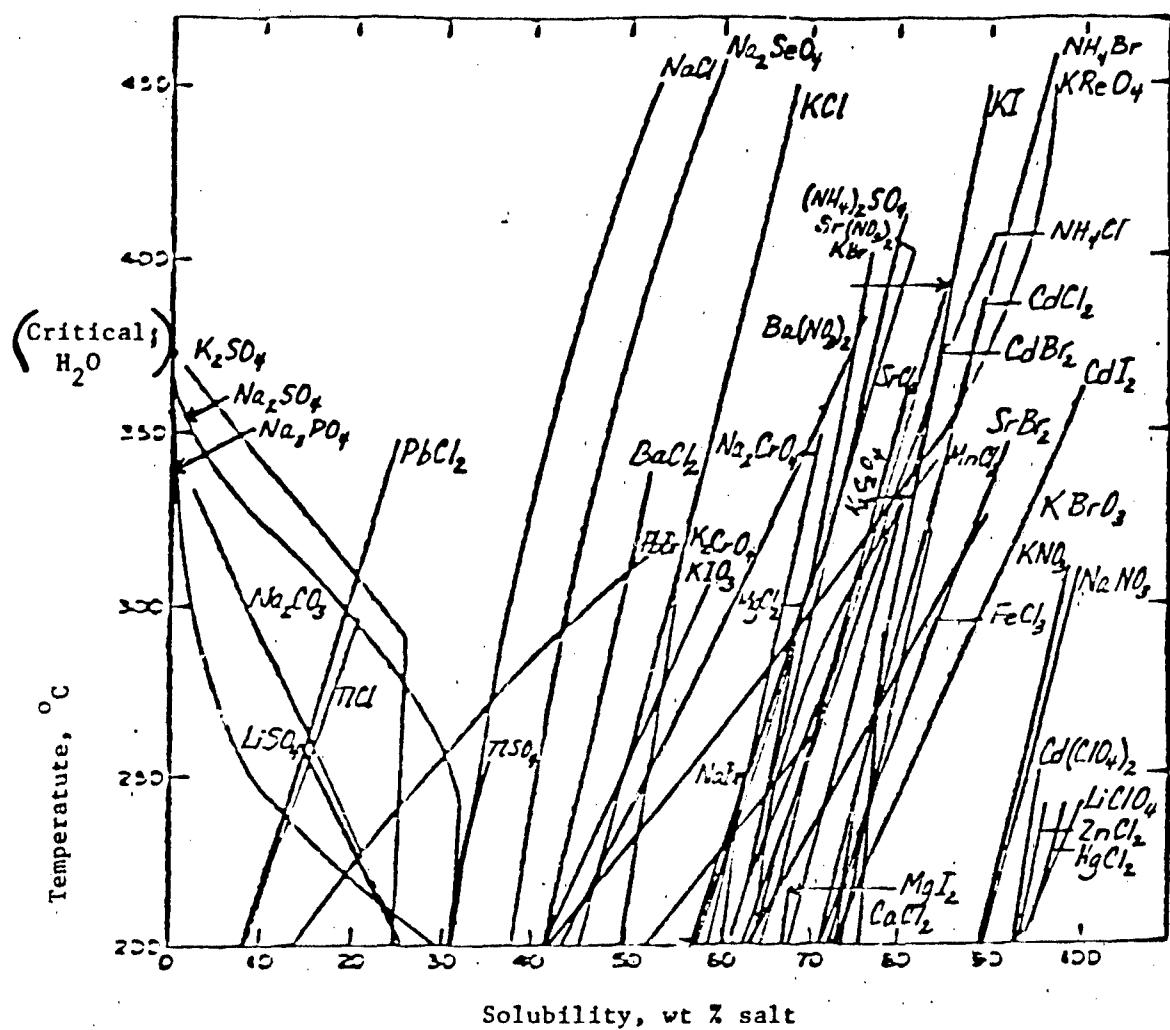
- 49 -

Figure 14. The solubilities of salts in water solution at
temperatures from 200 to 450°C. A graphic summary
of many published solubilities of salts showing a
quantitative comparison of the different behaviors
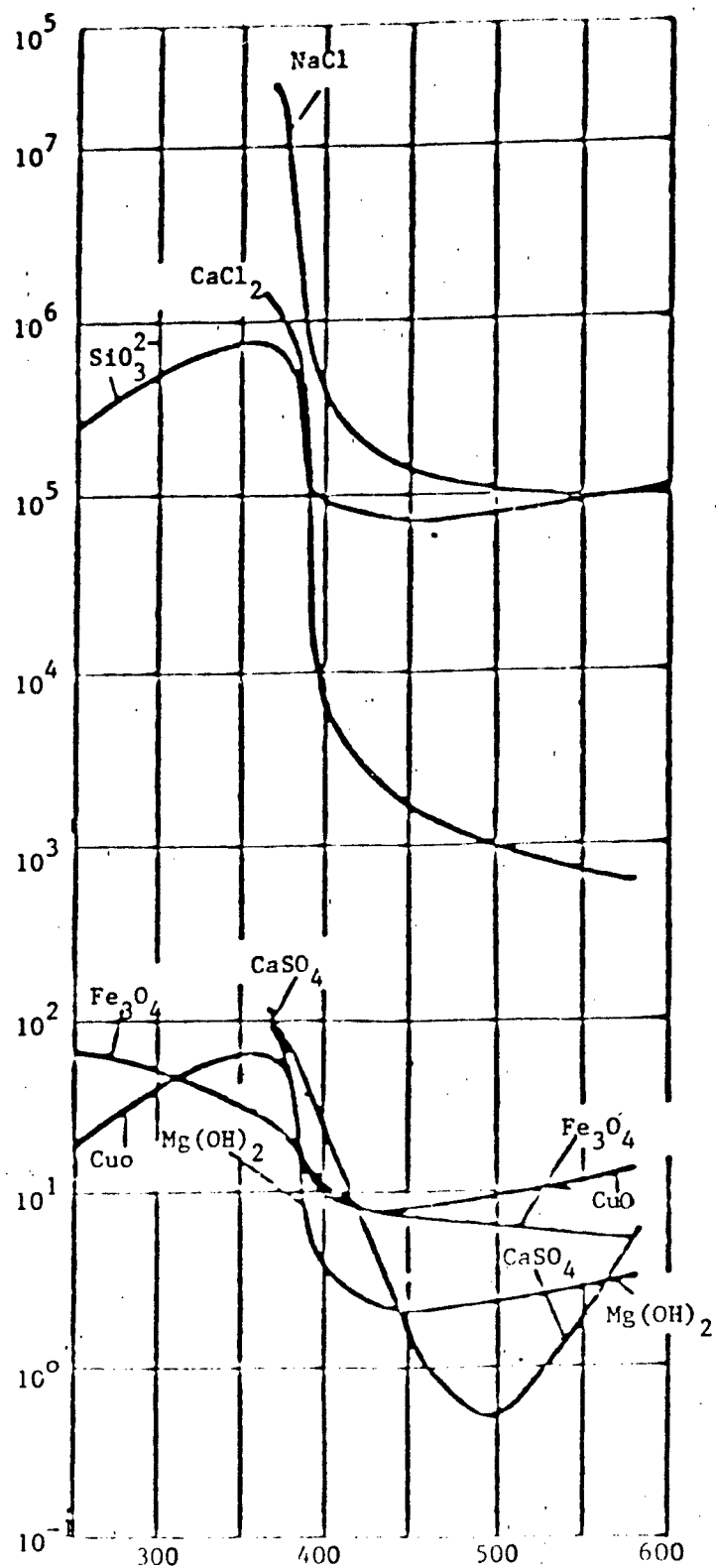and trends.

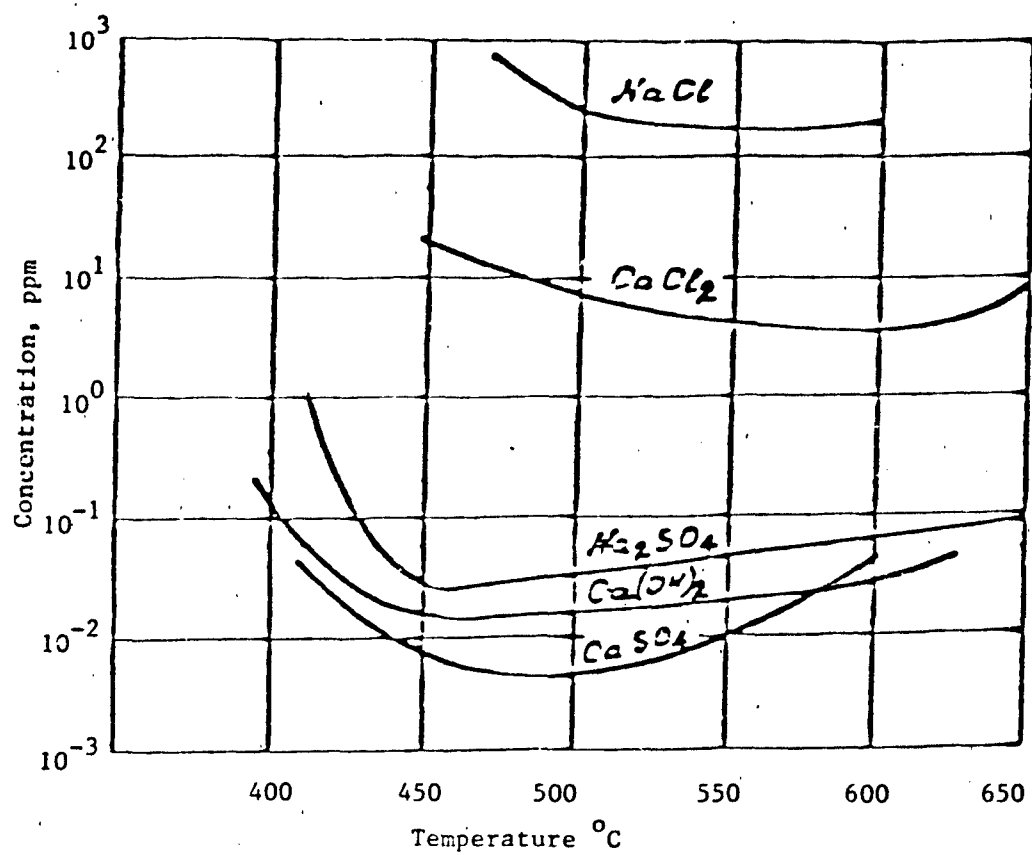Figure 15. Solubility Curves for some salts and metal oxides at 250 bars.

- 51 -

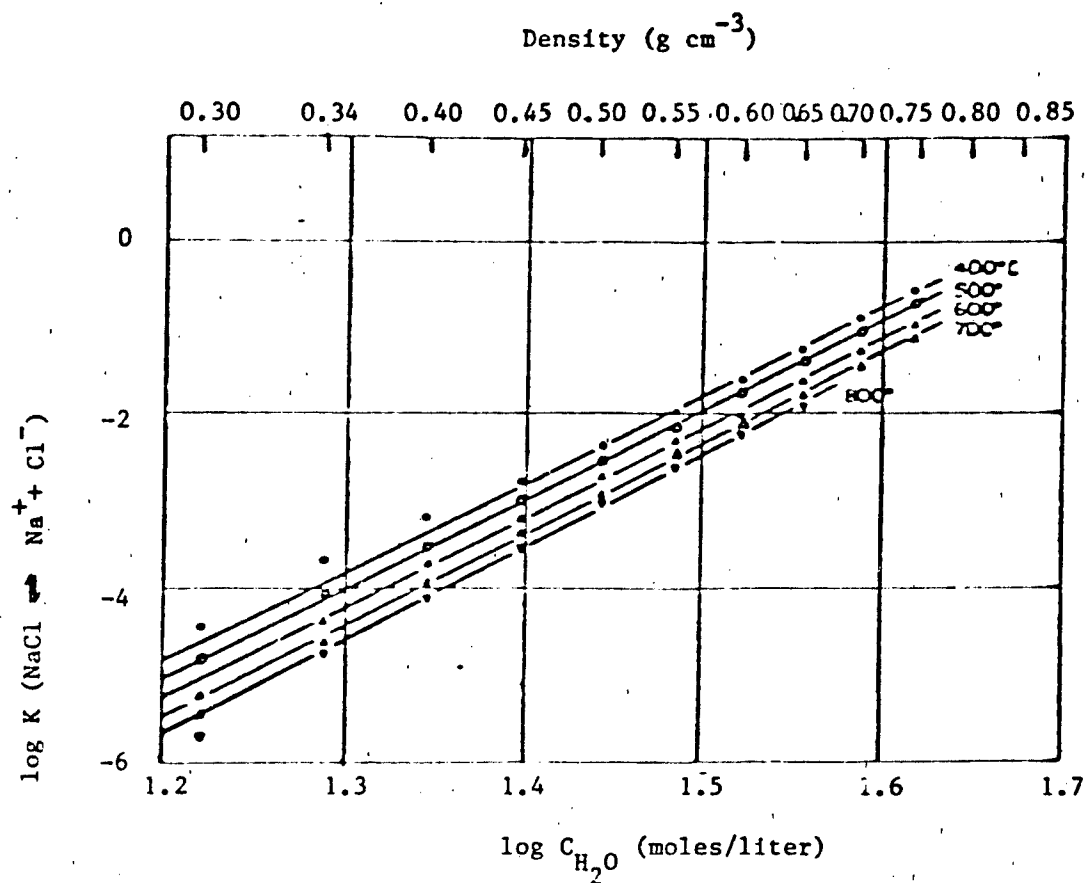Figure 16. Solubility curves for various salts at 300 bars over the temperature range 400-600°C.

Figure 17. Log K (molar units) for the equilibrium
NaCl = Na$^+$ Cl$^-$ as a function of the logarithm
of the Molar Concentration of water at
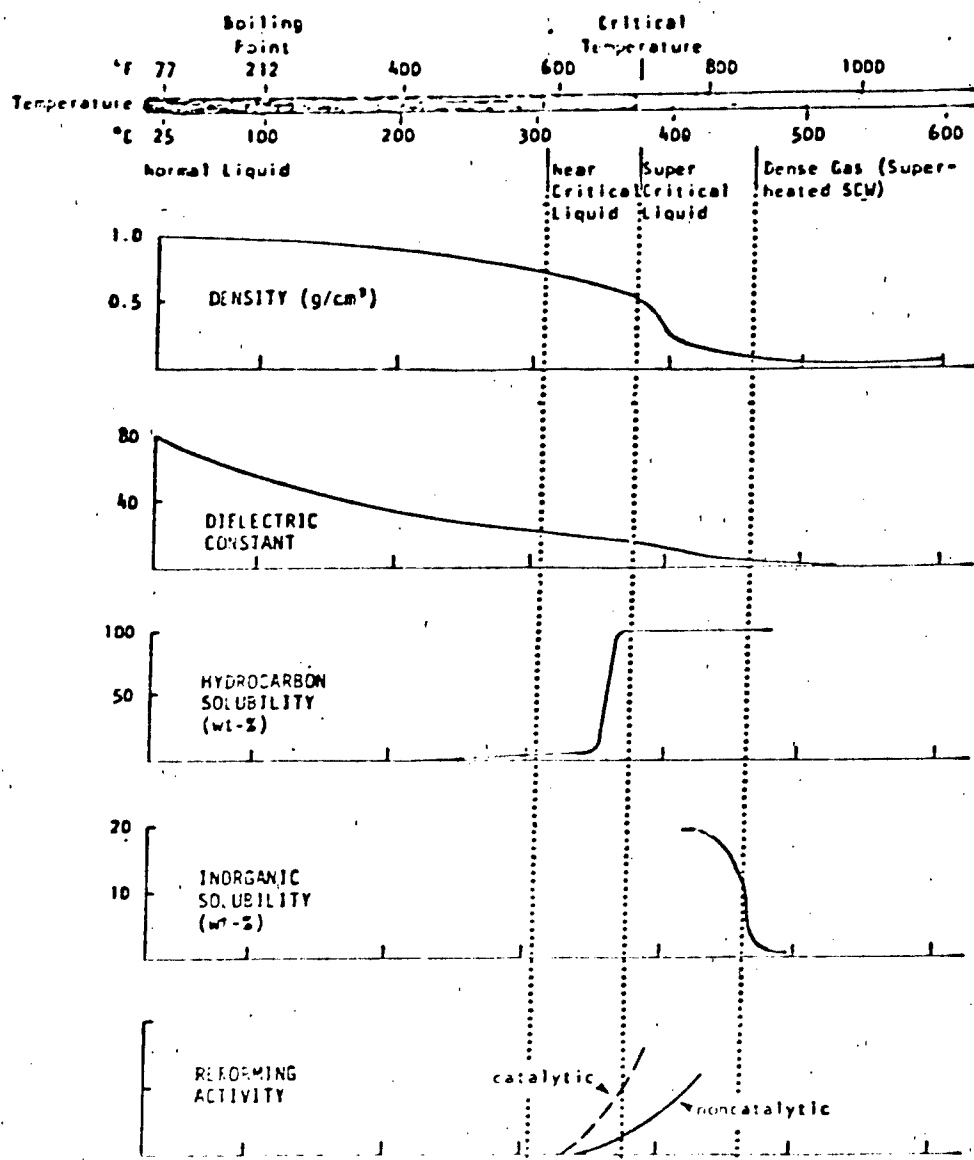temperatures from 400 to 800°C.

Figure 18. The properties of water. (Data for the pressure range of 200 to 300 atm.)

B. Decomposition and Reforming of Organics in Supercritical Water

It has long been known that steam will react with organic compounds at moderate to high temperatures and near-ambient pressure. At high temperatures (>800°C), organics are reformed with steam to CO and H_2. This reaction is the basis of the first step in many coal gasification processes under development today. At moderate temperatures (350 to 450°C), naphtha and other light hydrocarbons react with steam in vapor-phase, solid catalyzed reactions to form, predominantly, CH_4 and CO_2.

Over the past eight years, Modell and others conducted a research program at M.I.T. on the reactions of organics with water in the subcritical liquid phase and in the supercritical fluid region. These prior studies were aimed at developing processes for converting organic wastes, as well as coal, to liquid and gaseous fuels. Some results of the prior work are described here because they are pertinent to the program.

The reactions of cellulose (a major constituent of organic wastes) and glucose (one of the major products of cellulose hydrolysis) with water were studied in a batch, high-pressure autoclave reaction (see Figure 19). The autoclave was charged with water and heated to the desired temperature. A concentrated solution of feed, held between valves A and B, was then rapidly injected into the reactor. Liquid and vapor samples were collected at various intervals of time. At the completion of the run, the reactor was cooled down to ambient temperature and any solids that may have formed were collected and analyzed.

The results of a series of runs with a glucose feed at subcritical temperatures (150, 200 and 300°C) are shown in Figs. 20 to 22. The distribution of carbon as glucose, liquid products and solid are presented as a function of time. The formation of gaseous products was negligible under these conditions. From comparison of Figs. 20 to 22, it can be seen that (i) glucose reacts very rapidly at 300°C and (ii) a char forms, with increasing rate of formation at increasing temperatures. From GC/MS analysis of the liquid products and chemical analysis of the char, it was concluded that the char forms by condensation polymerization of liquid intermediates (Amin, et al, 1975). The mechanism appears similar to glucose pyrolysis in the absence of water.

When the temperature and pressure were raised to the critical conditions of water, a rather startling discovery was made: no char was formed. The products were entirely liquid organics and a gaseous mixture of CO, H_2, CO_2, CH_4 and light hydrocarbons. The discovery is the basis of U.S. Patent No. 4,113,446 (Modell, et al, 1978).
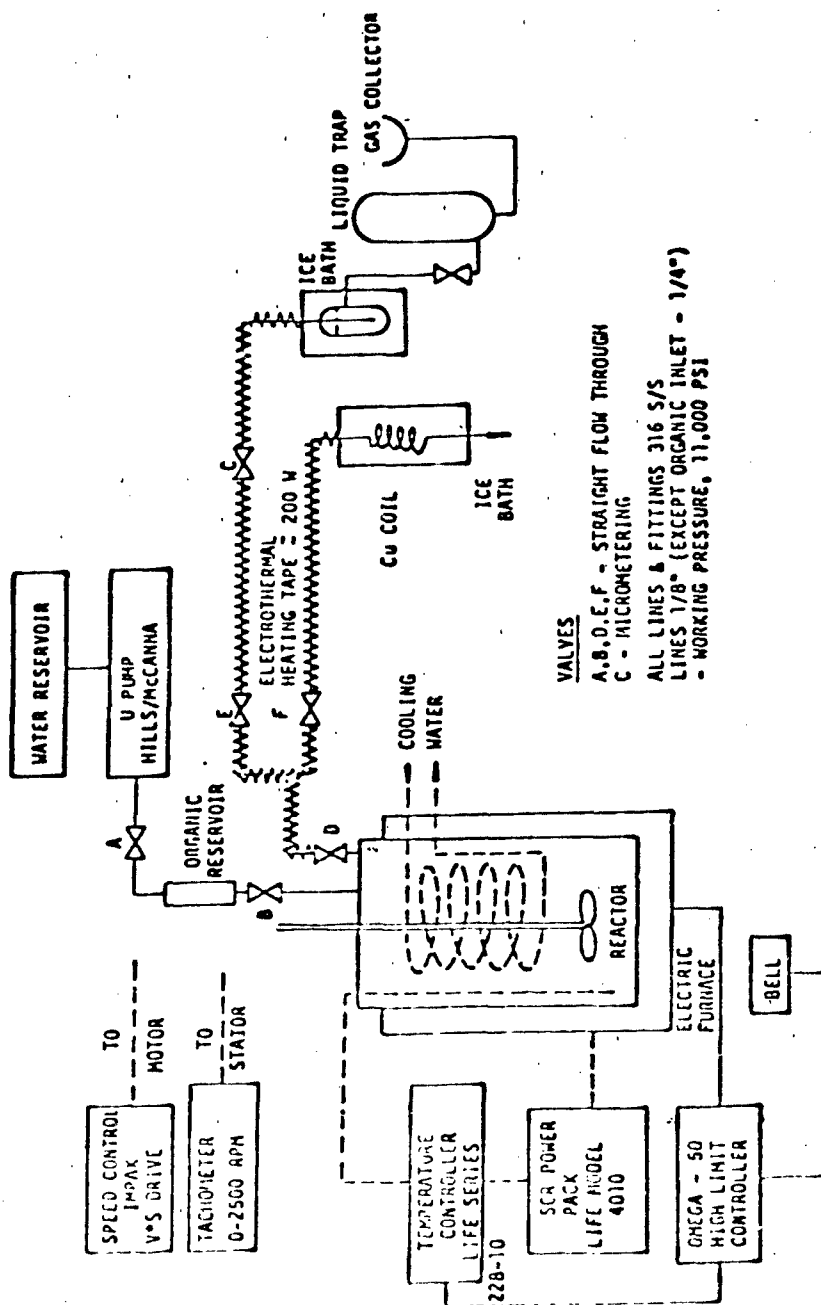
- 55 -

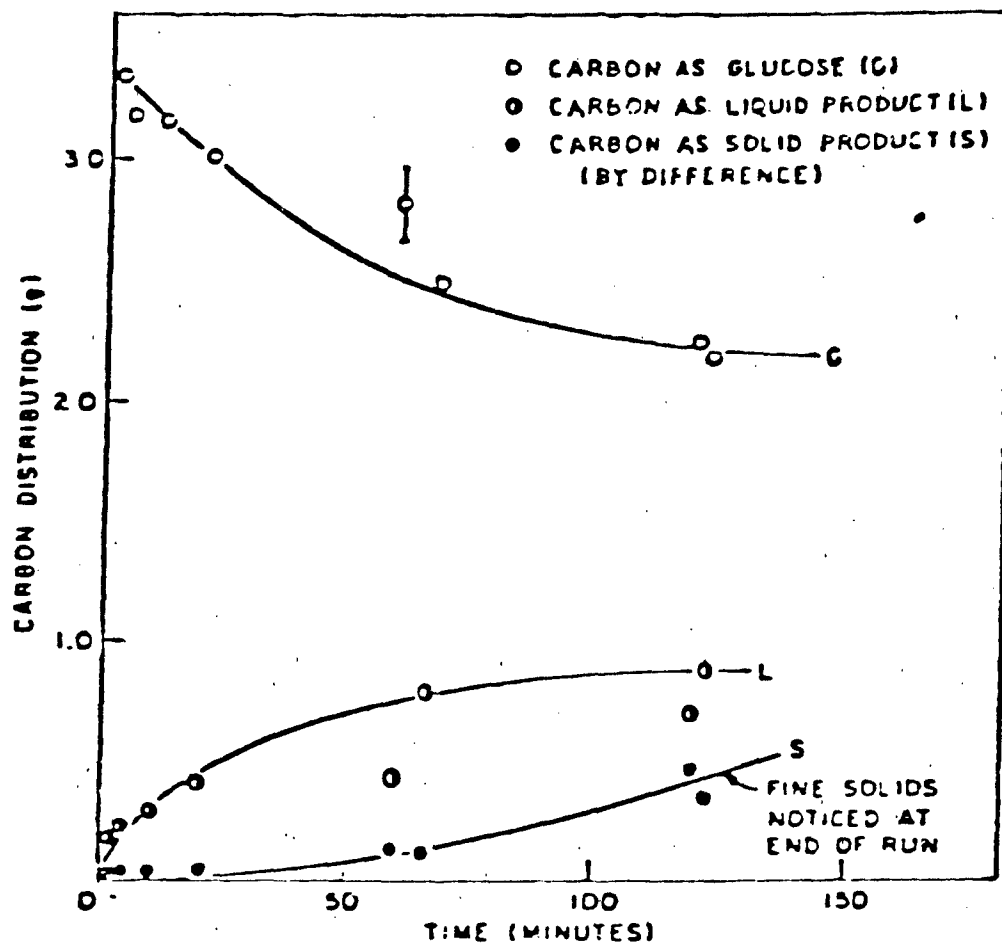Figure 19. EXPERIMENTAL APPARATUS

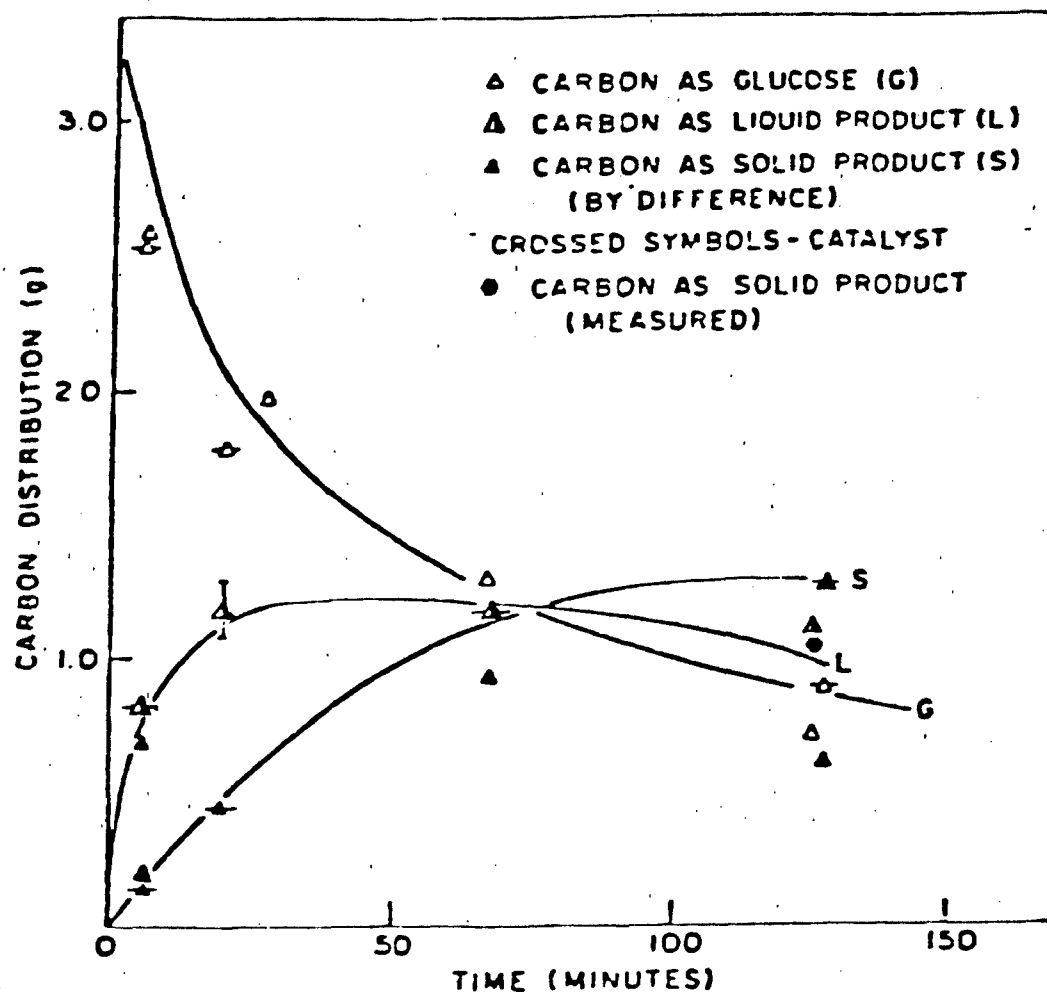Figure 20. Product Distribution at 150°C.
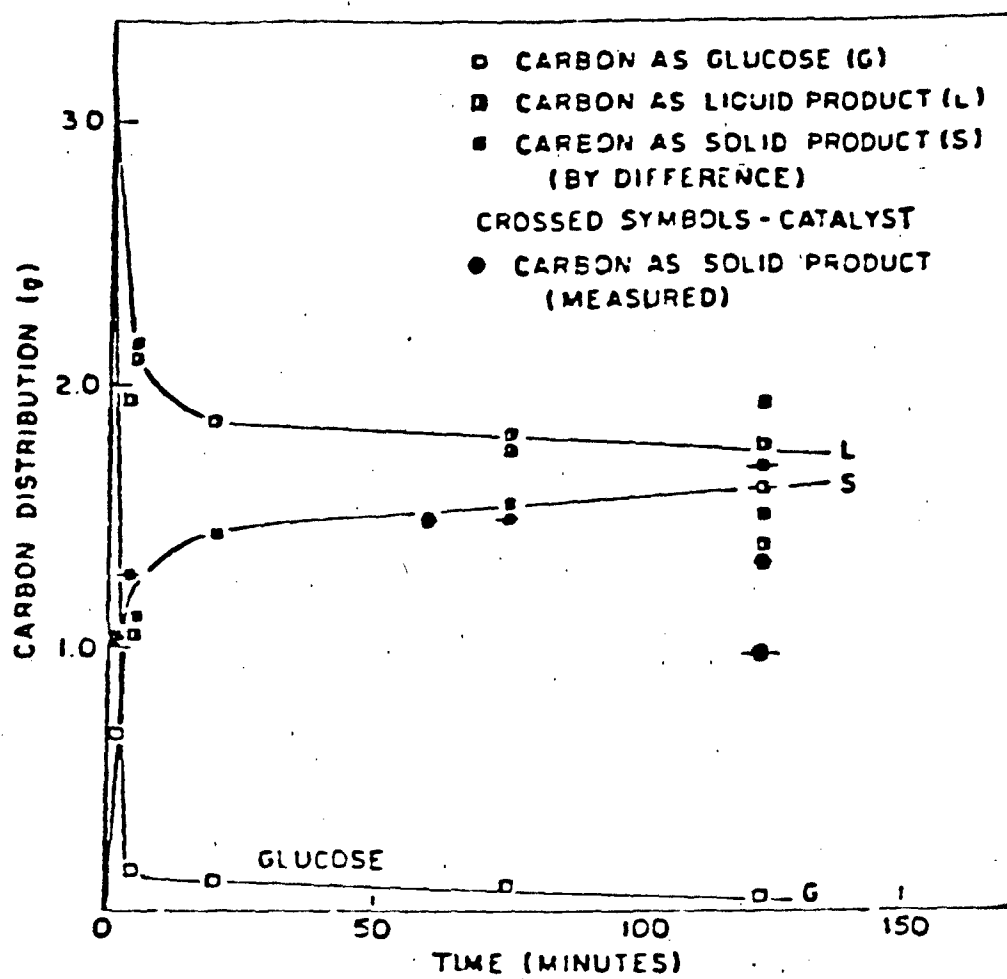
Figure 21. Product Distribution at 200°C.

Figure 22. Product Distribution at 300°C.

A number of experiments were subsequently conducted with a variety of organics in the near critical and supercritical region of water. Some of the results are given in Table 10. With dilute solutions of glucose (4 g carbon in 300 g water), no char is found. To determine if the absence of char is related to temperature alone or to critical density, run 34 was made under the same conditions as runs 26 and 35, except that the pressure was set at 150 atm. At this subcritical pressure, the water phase is a gas-like fluid (<0.1 g/cm^3). Since appreciable char was formed in run 34, it was concluded that the critical density is a necessary condition for avoiding char formation. In run 36, with a more concentrated glucose feed, the solid phase was a low-melting tar which is very likely soluble in SCW but precipitates out upon cooling. The only other cases in which solid was observed were in runs 37 and 39 with polyethylene feed. Those solids, which analyzed as CH_2, appeared to be porous beads of unreacted polyethylene.

The absence of char under the critical conditions of water is believed to be related to the high solubility of organics in SCW. In the case of carbohydrates, the char-forming reactions are thought to be products of condensation polymerization of intermediates. For such a polymerization reaction, a poor solvent would enchance the rate by allowing hydrophobic molecules to cluster. On the other hand, a good solvent such as SCW would provide maximum dispersion of the intermediates and thereby minimize the tendency for polymerization.

A series of runs was conducted with maple sawdust (in 3 mm x 1/2 mm needles) as feed. The batch reactor of Fig. 19 was used without the addition of catalysts. As shown in Table 11, five runs were made at constant temperature and varying residence time (5 to 60 min). The feed concentration varied by a factor of ten because an unpredictable amount of the feed was left in the organic reservoir.

In all of the runs with maple sawdust, the feed material was completely solubilized; the product once again did not contain a char. These results are very significant in light of the complex nature of the feed material.

At a residence time of 5 min, the percent of carbon gasified (16.8%) was substantially higher than that of glucose (without catalyst) at 60 min residence time (8.2%; Table 10, run 23). Increasing residence time of maple sawdust reforming increased gasifications significantly. At 30 to 60 min over a third of the feed carbon appears as gaseous products. (The percent gasification in run M-3 is suspect because the amount of feed was very small and, therefore, the calculated results are subject to a large uncertainty.)

The gas composition did not vary appreciably with residence time. It was very rich in CO, with significant amounts of H_2 and CH_4. The quality of the gas as a fuel is reflected in the high heating values, as

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Table 10

Results at Critical (647 K; 22MN/M^2)

% ORIGINAL CARBON IN

Run No.	Catalyst	Reaction Time (Mins.)	Carbon Initially In (g)	Final Liquid Phase	Final Gas Phase	Solid Phase	Carbon Closure %
GLUCOSE							
23	None	60	4	77.7	-8.2	--	85.9
21	Ni	60	4	86.8	10.0	--	96.8
28	M	10	4	70.0	11.0	--	81.0
26	M	30	4	65.0	20.2	--	85.2
35	M	30	4	70.8	23.3	--	94.1
34*	M	30	4	27.75	3.4	(68.85)[a]	--
36	M	30	12	60.4	9.5	8.5	78.4
CELLULOSE							
27	M	30	1.42	77.4	18.3	--	95.7
HEXONOIC ACID							
32	M	30	5.75	82.6	2.8	--	85.4
POLYETHYLENE							
37	M	30	3.22	25.6	2.3	62.4	90.3
39	M	180	3.22	27.0	4.0	62.7	93.7
UREA							
31	M	30	0.9	77.7	11.1	--	88.8
NITROGEN BALANCE							
			2.1	95.2	--	--	95.2

a   by difference

*   operating pressure was 15.2 MN/M^2

Ni   C11-2S-04 nickel catalyst (Catalysts and Chemicals)

Carbon Closure = [(carbon in products)/(original carbon)]100

M = catalyst mix

2g each of: G91B, G90B, C11-2S-04, 22-6HA, 11-3, Co/Mo, Pt/Al_2O_3

(C:H:O) Ratio Solid	H_2	CH_4	CO_2	CO	C_2^+
--	25.8	1.3	34.4	38.5	—
--	30	1.5	42	37	--
—	25.7	1.0	31.6	41.6	--
--	45.1	3.2	38.5	12.5	0.7
—	43.13	2.9	40.6	12.6	0.74
$CH_{0.8}O_{0.2}$	23.21	0.5	65.1	11.24	—
$CH_{1.12}O_{0.3}$	20.38	1.1	42.48	36.07	—
—	14.5	1.5	19.7	64.2	0.13
—	67.61	0.8	31.6	≤ 5.0	—
$CH_{2.0}$	26.6	2.54	65.87	≤ 5.0	—
$CH_{2.0}$	35.75	3.73	54.43	≤ 5.0	1.2
—	—	—	100	—	—

NITROGEN BALANCE

--	--	--	--	—	—

TABLE 11. RESULTS OF REFORMING MAPLE SAWDUST AT 377°C

Run No.	Reaction Time (min)	Carbon in Feed (g)	Gas Composition					% Carbon as:		Higher Heating Value of Gas		
			H₂	CO	CH₄	CO₂	C₂⁺	Gas	Extracted Liquid	Btu lb gas	Btu 10³ft³	% of feed
M-1	5	.59	8.3	79.2	2.3	10.1	-	16.8	1.1	4,250	314	15.5
M-2	15	.96	17.9	69.4	3.7	9.1	-	18.1	1.5	4,940	322	19.4
M-3	30	.10	15.9	65.5	5.1	13.0	0.5	(88.3)	-	4,810	325	(92.9)
M-4	30	.67	5.0	82.4	2.9	9.6	0.1	33.1	0.6	4,240	323	30.1
M-5	60	.29	16.8	57.2	5.6	19.6	0.9	39.5	6.2	4,490	311	40.2

- 64 -

shown in the last 3 columns of Table 11. The last column represents the percentage of feed heating value that is recovered in the gaseous product. (A heating value of 5,600 Btu/lb. was used for the maple sawdust feed.)

Since no char was produced in reforming maple sawdust, the liquid phase contained all of the organic materials that were not recovered as gaseous products. In an attempt to analyze the liquid phase composition, samples of liquid product were extracted with methylene chloride, concentrated by evaporation, and analyzed by GC/MS. A large number of components were found, the majority of which were alcohols, aldehydes and furan-derivatives. However, the fraction of feed carbon that was contained in the methylene chloride concentrate was small, ranging from 0.6 to 6.2% (column 10, Table 11). In subsequent tests, we have found that the major portion of the liquid products are very volatile and, thus, they most probably evaporated as the methylene chloride extract was being concentrated. Although we have not yet identified these organic liquid products, the fact that they are very volatile implies that they should be readily separable from water using relatively conventional means (e.g., flashing, steam-stripping or distillation). Production of liquid fuels by SCW reforming thus appears to be a viable process.

In summary, the prior work at M.I.T. has shown that SCW reforming of complex organic materials offers the potential of decomposing organic wastes to gases and volatile organic liquids. Organic structures are solubilized and broken down into lower molecular weight organics and gaseous fuels without the formation of char. Processing takes place in a system closed to the environment and, therefore, virtually eliminates contamination of the atmosphere.

C. Oxidation of Organics in Supercritical Water

In the temperature range of 200 to 300°C, many organics are susceptible to oxidation in the aqueous phase. The process, commonly called wet air oxidation (WAO), is show schematically in Fig. 23 (Wilhelmi and Knopp, 1979). The feed and oxidizing agent are pressurized to reaction conditions (1500 to 2500 psia), heated to operating temperature and then fed to a reactor for a residence time of 0.5 to 1 hr. The process is usually effective for removing 70 to 95% of the initial COD. The residual COD is primarily due to innocuous aliphatic acids (e.g. acetic acid), which are by-products of oxidation of more complex molecules, and which are oxidized very slowly under WAO conditions. Recent studies have shown WAO to be effective in removing over 99.9% of a variety of toxic organic chemicals (e.g. 2.4-dinitrotoluene, hexachlorobenzene, pentachlorophenol).
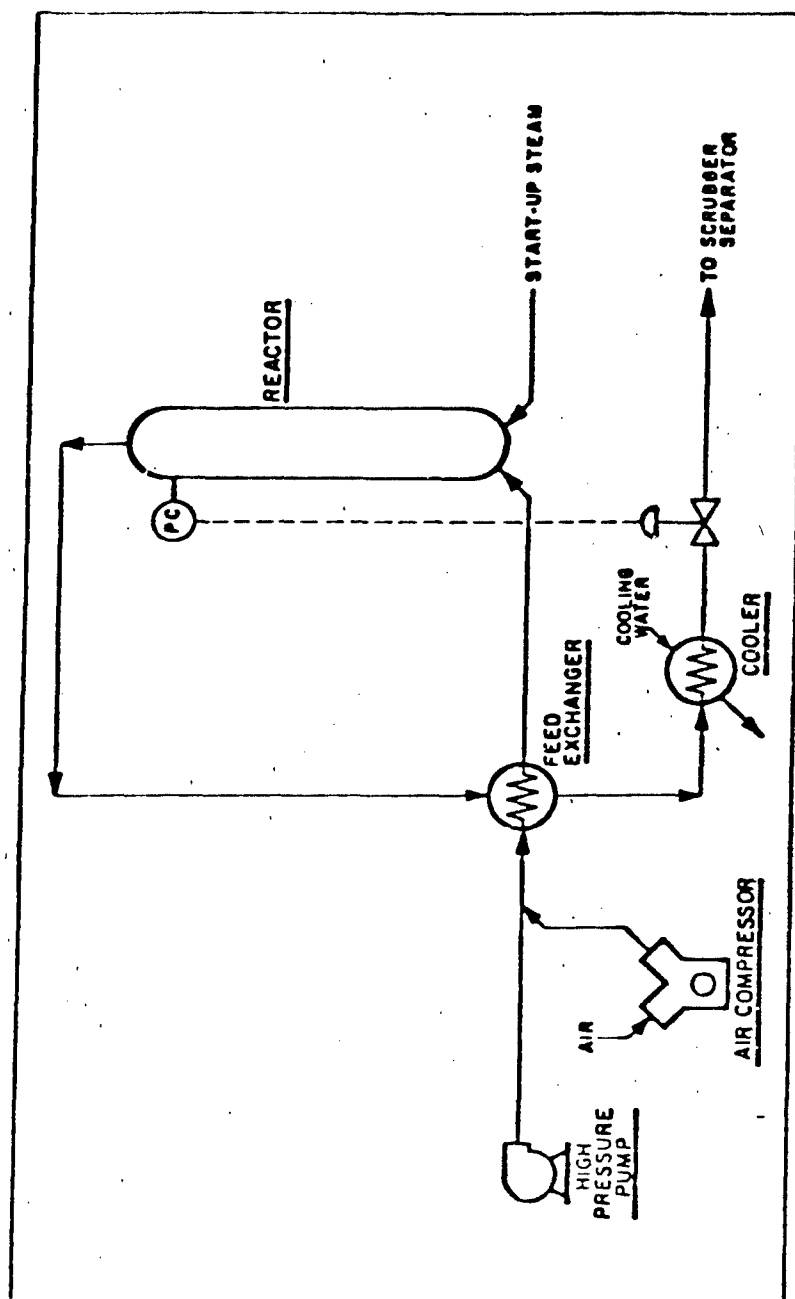
FIGURE 23. Basic Flowsheet of the Wet Air Oxidation Process

Although WAO can be an effective waste treatment process, it is costly in terms of capital equipment and inefficient in recovery of the heat of combustion. The process suffers from a number of limitations. Under the conditions in which oxygen or air are mixed with the feed, the solubility of the gas in water is considerably less than that required for complete combustion. For example, the solubility of oxygen in water is shown in Figs. 24 and 25. Nitrogen solubility in water is shown for comparison in Figs. 26 and 27 (Pray, et al. 1952). For a feed containing 5 wt% hydrocarbon, 15 wt% oxygen is required for comp'ete combustion. By extrapolation of Fig. 24, at $250^{\circ}C$ ($482^{\circ}F$) a partial pressure of oxygen in excess of 25,000 psia would be required to dissolve enough oxygen in the water to allow for complete combustion. Since this pressure is clearly not practical, a two-phase (water-gas) mixture must be fed to the WAO reactor. As a consequence, the reactor must have provisions for agitation so as to avoid excessive mass transfer resistance between the phases. The reactor is an expensive item because it must operate at high temperature and high pressure with a relatively large volume to provide a residence time of 0.5 to 1 hr. 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.

In addition to requiring a large capital investment, WAO is inefficient in recovering the energy of combustion of the organic components of the waste feed. Because the reaction is relatively slow, the products do not reach as high a temperature as could be attained by adiabatic combustion. As a consequence, the heat released by combustion and which resides in the reactor exit stream is available at a rather low temperature.

The MODAR concept for oxidation of organics is an improvement upon WAO and represents a breakthrough in enhanced efficiency and reduction in capital investment. In the MODAR process, the oxidation is conducted under supercritical conditions. The major advantages of operating supercritically are:

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

- rapid oxidation of organics, which approaches adiabatic combustion as well as high outlet temperatures, and very short residence times.

- complete oxidation of organics, which eliminates the need for auxiliary off-gas processing;
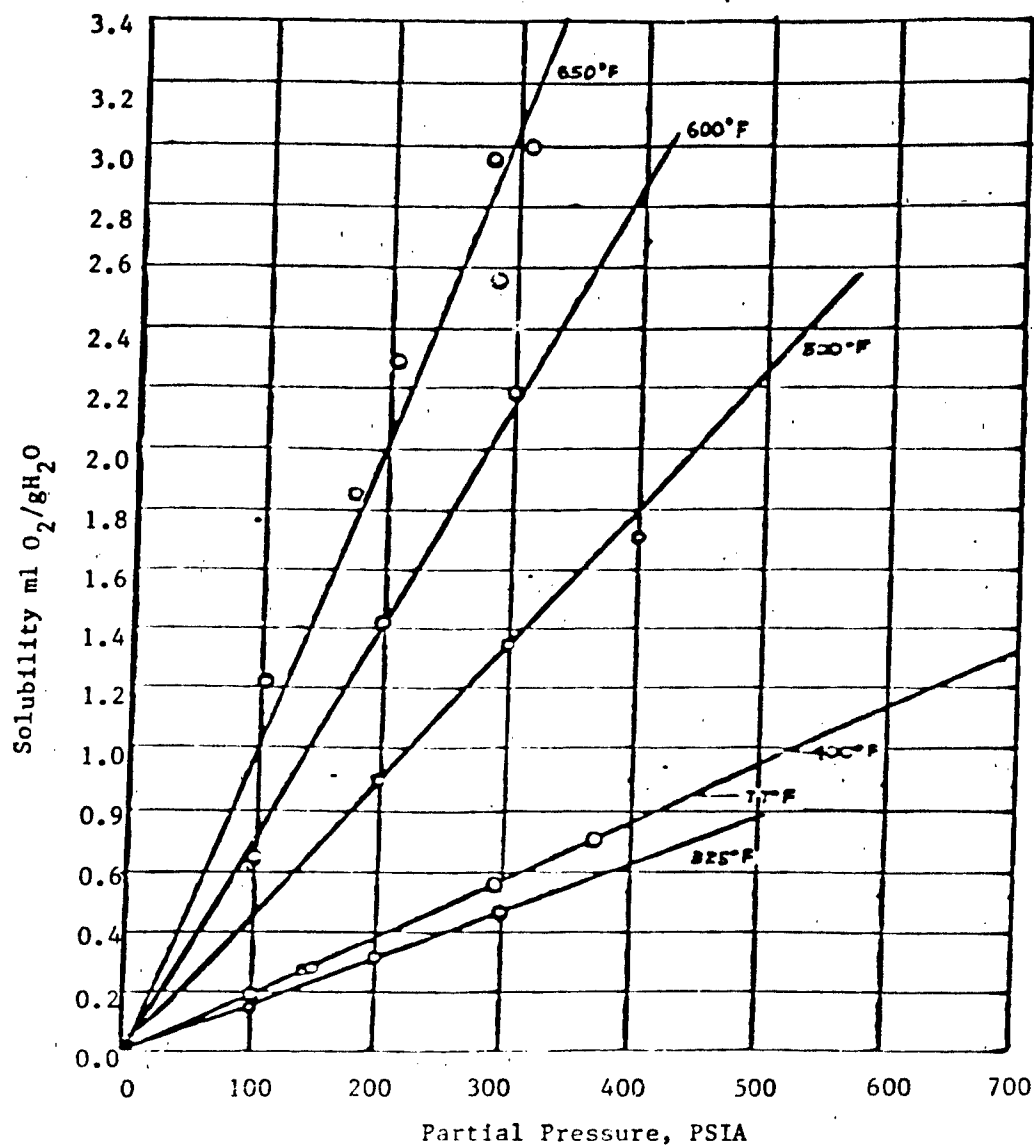
- 67 -

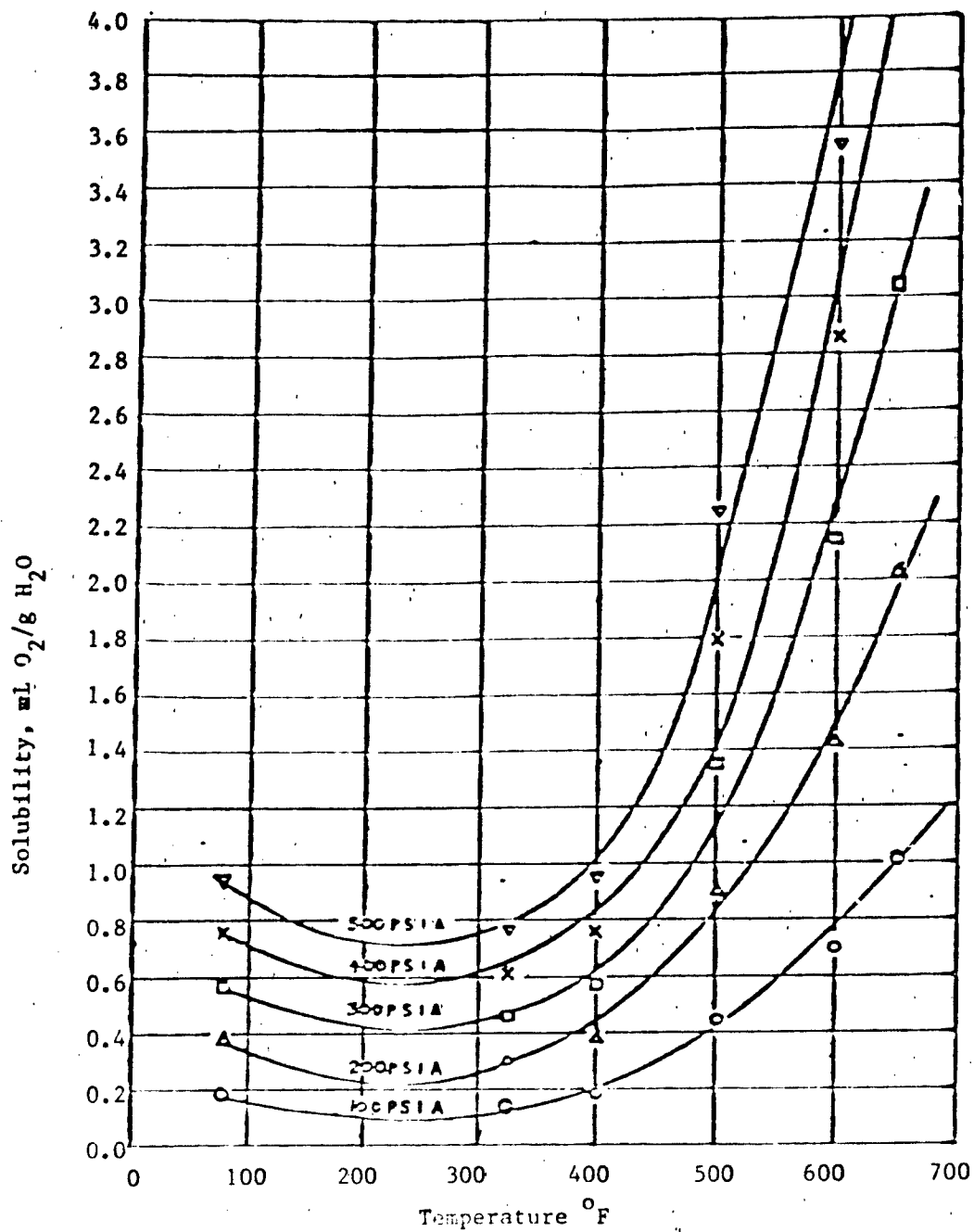Figure 24. Solubility of Oxygen in Water with Varying Pressure.

Figure 25.   Solubility of Oxygen in Water with Varying
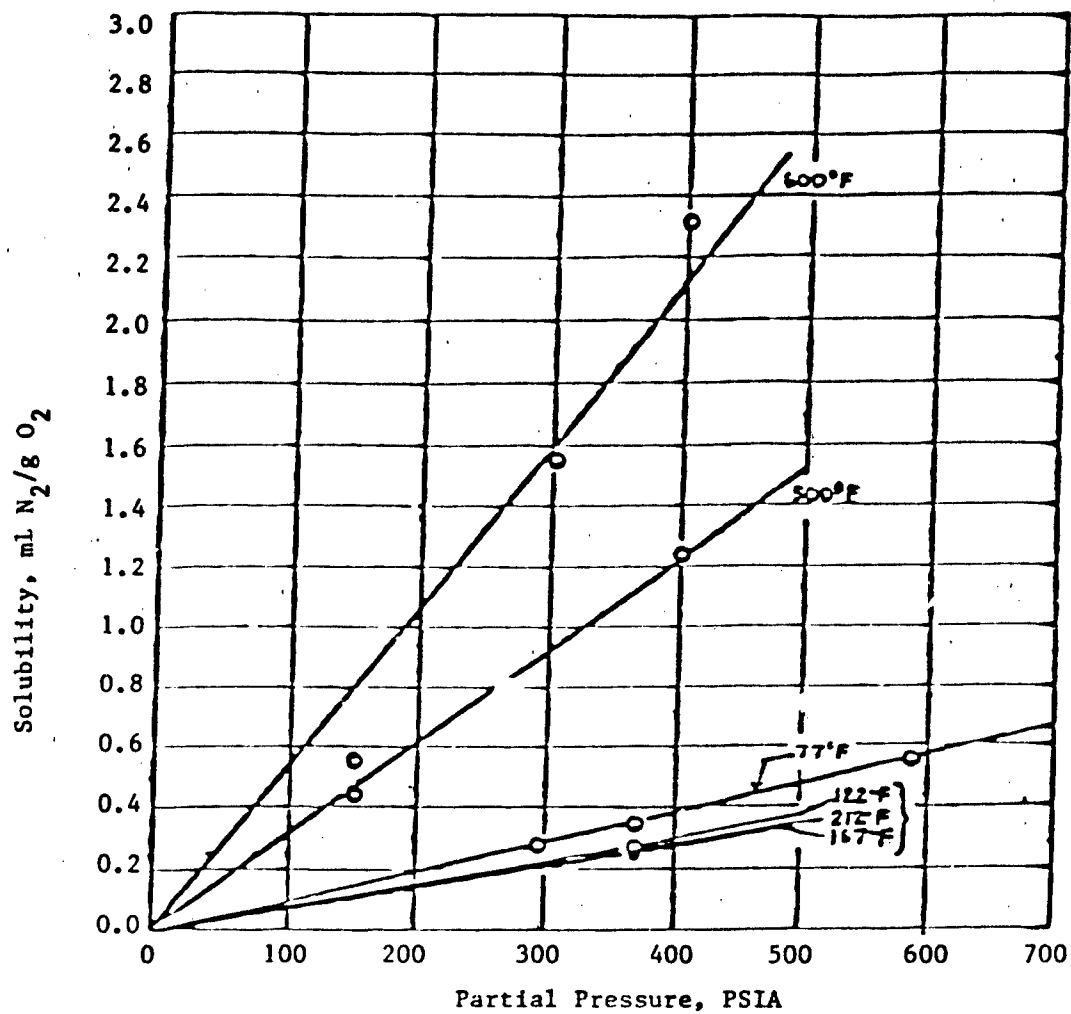Temperature.

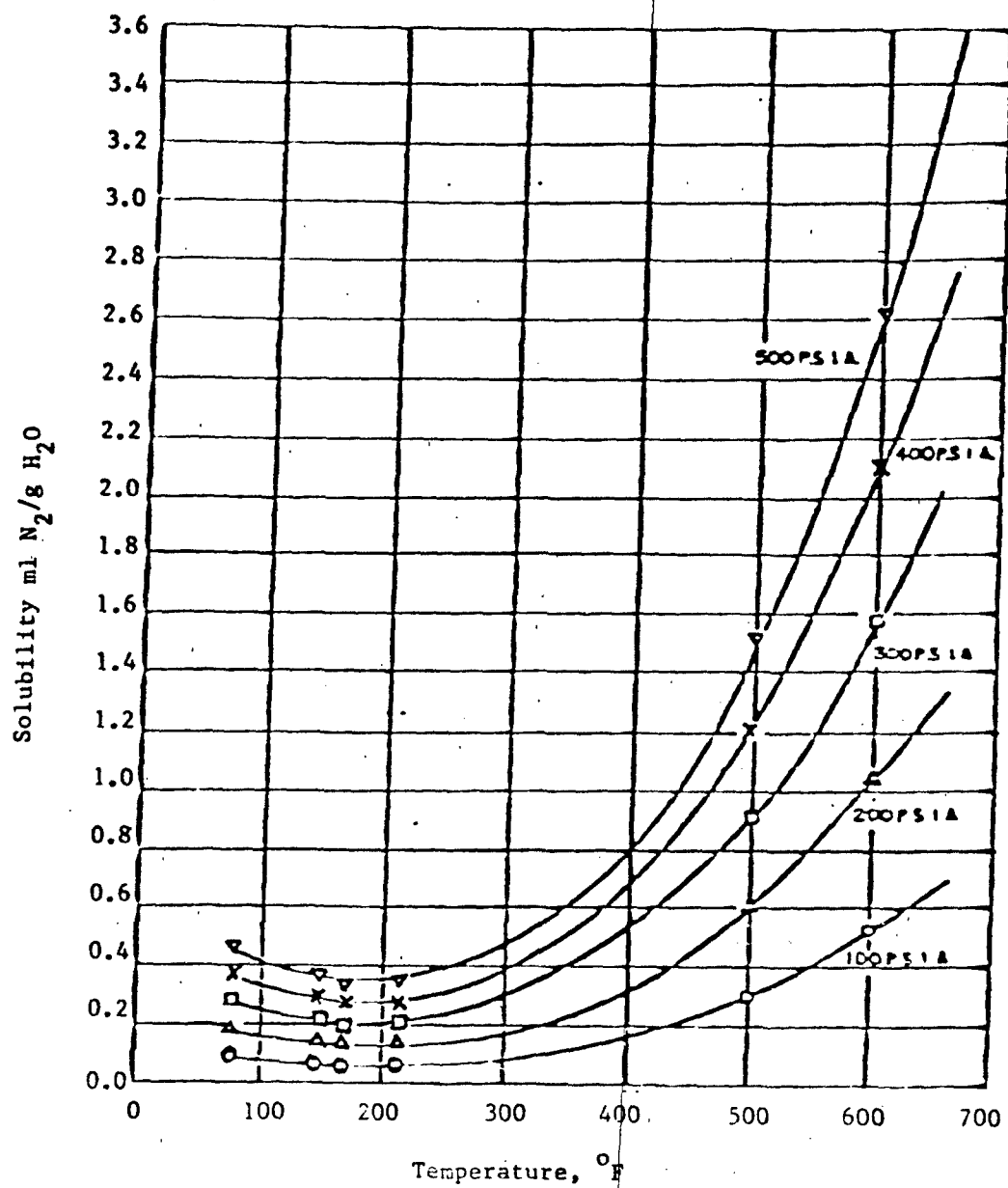Figure 26. Solubility of Nitrogen in Water with Varying Pressure.

Figure 27. Solubility of Nitrogen in Water with Varying Temperature.

. removal of inorganic constituents which will precipitate out
of the reactor effluent because the outlet temperature is
above 450-500°C; and

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

In the MODAR oxidation process, the oxidant (air or oxygen) is mixed
with waste stream under supercritical conditions. The solubility of
oxygen in supercritical water has not been reported in the literature.
However, oxygen and nitrogen solubilities are comparable (see Figs. 24 -
27) and nitrogen solubility has been reported. Above 375°C it has
been found that nitrogen is miscible in all proportions with water and,
therefore, it is likely that oxygen is miscible in all proportions with
SCW. In other words, by operating supercritically, it is possible to
dissolve as much oxygen in water as is needed for complete oxidation of
organics. By this means, the feed to the oxidizer is simply
homogeneous, single phase mixture of organics, oxidant and water. The
elimination of two-phase flow simplifies the oxidizer design by
eliminating the need for mechanical stirring. In fact, the oxidizer can
be a tubular reactor or fluidized bed, either of which contains no
moving parts.

The rate of oxidation under SCW conditions is substantially faster
than that under WAO conditions (<1 min vs. 0.5 to 1 hr). While the
density of the aqueous process stream may be as much as an order of
magnitude less, the oxidizer vessel volume is still significantly less
than that required for WAO. Since the oxidation process is very rapid,
reactions in the oxidizer vessel will approach adiabatic operation. In
other words, the heat losses from the oxidizer vessel are negligible and
the oxidizer effluent contains essentially all of the heat of
oxidation. The outlet temperature of the oxidizer is determined by the
concentration of organics in the SCW/feed mixture. For example, when
this mixture contains 5 wt% organics and enters the oxidizer vessel at
400°C, the oxidizer outlet temperature will be on the order of 550 to
600°C. This temperature range is more than sufficient to drop
inorganic solubility to very low levels. Therefore, inorganics are
precipitated out during oxidation.

After removal of solids from the oxidizer effluent, the fluid phase
is a mixture of water, carbon dioxide and nitrogen (if air is used as
the oxidant) at high temperature (550-600°C) and high pressure (3700
psia). As shown in Fig. 2, part of this stream is tapped off to mix
with fresh feed. In this manner, incoming feed is heated rapidly to the
SCW conditions required for reforming.

- 72 -

D. Details of Chemical Analysis Procedures

1. **Gas Chromatography and Gaseous Effluent.** The gas chromatograph is manufactured by Carle Instruments and is designed for the analysis of twenty-five components (Fig. 28). This instrument has a specially designed Hydrogen Transfer System (HTS) and a dual Thermal Conductivity Detector (TCD), which give it the capability for sensitive and linear determination of hydrogen and other components with a single injection. All components except hydrogen are measured in a thermal conductivity detector with helium. Hydrogen is eluted with the helium carrier gas, but is then transferred via the HTS into a nitrogen carrier before measurement. Dual, independent TCD's are used for the two carriers but they are wired into the same bridge circuit. Thus all peaks are in the same direction, and since hydrogen is separated by the system before measurement, the signal is not coincident with any other component of the sample. The output from the GC is monitored by a Perkin-Elmer Sigma 10 Data Station which plots, integrates, reports, calibrates and stores data from the analyses. The total time of the analysis may vary from 13 to 45 minutes depending on the components of interest.
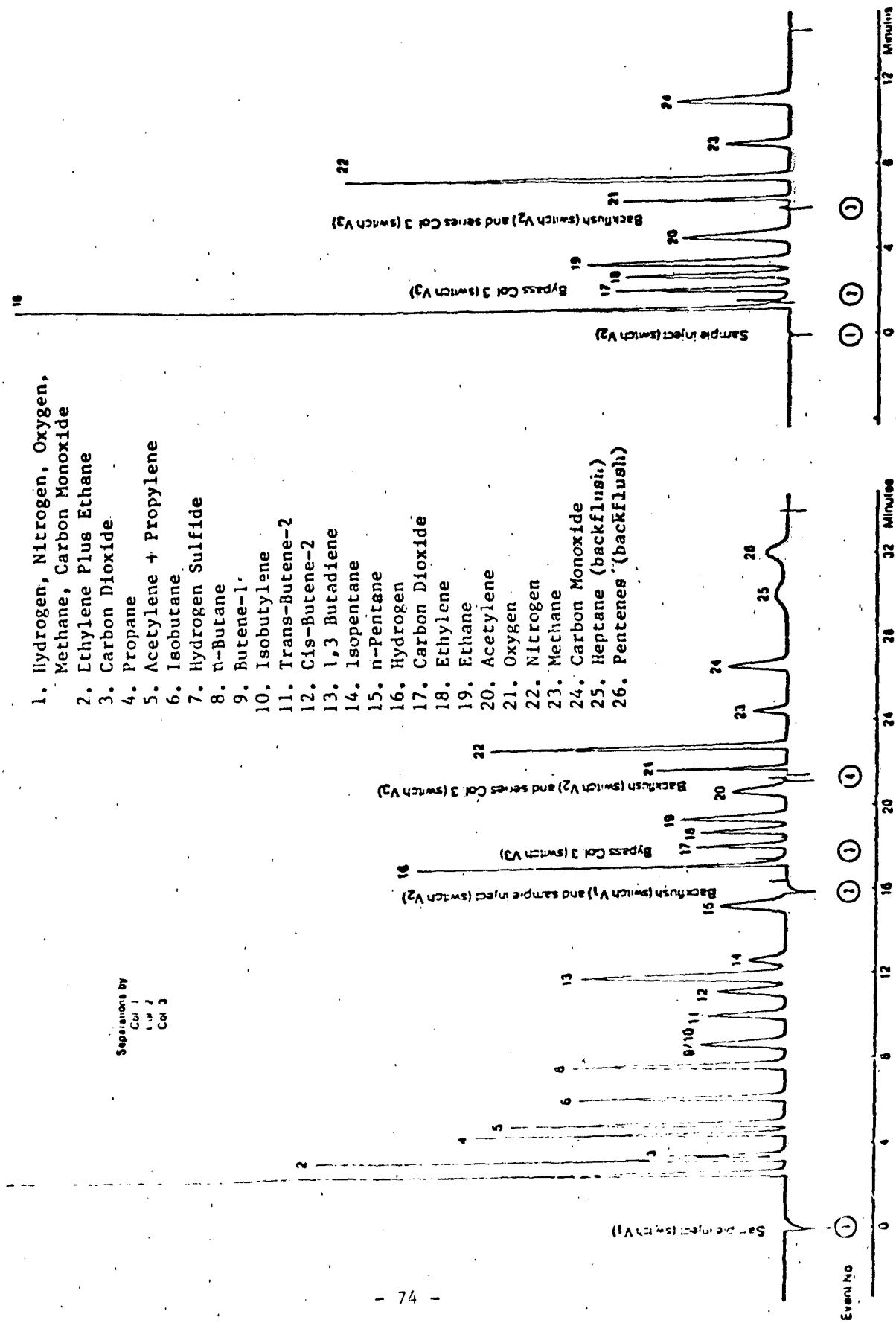
2. **Process Analyzers.** The Model 864/5 Beckman Infrared Analyzers automatically and continuously determine the concentration of carbon monoxide and carbon dioxide in the flowing mixture. The analysis is based on a differential measurement of the absorption of infrared energy. The instrument has a wide range of applications, subject only to the limitation that the analysis involves a single component which must absorb infrared energy at a wavelength for which no other component of the mixture absorbs.

The Model 755 Beckman Oxygen Analyzer provides continuous readout of the oxygen content of a flowing gas stream. The determination is based on measurement of the magnetic susceptibility of the gas sample. Oxygen is strongly paragmagnetic while other common gases with a few exceptions are weakly diamagnetic.

These instruments provide direct readouts on their front panels and are directly connected to the Analog Devices MACSYM to give direct readings to the computer.

3. **TOC Analysis of the Liquid Effluent** The Beckman 915B Total Organic Carbon Analyzer (TOCA) is used for the liquid effluent stream. The analysis is done by subtracting inorganic carbon (IC) concentration from the total carbon (TC) concentration to give total organic carbon. Alternatively, the sample is acidified and sparged to remove carbonates and then analyzed for total carbon. The operating principle of the TC channel is that all organic carbonaceous material, together with any inorganic bicarbonates and carbonates, will be completely converted into

- 73 -

Figure 28. Sample Chromotographs with Available Options

1. Hydrogen, Nitrogen, Oxygen, Methane, Carbon Monoxide
2. Ethylene Plus Ethane
3. Carbon Dioxide
4. Propane
5. Acetylene + Propylene
6. Isobutane
7. Hydrogen Sulfide
8. n-Butane
9. Butene-1
10. Isobutylene
11. Trans-Butene-2
12. Cis-Butene-2
13. 1,3 Butadiene
14. Isopentane
15. n-Pentane
16. Hydrogen
17. Carbon Dioxide
18. Ethylene
19. Ethane
20. Acetylene
21. Oxygen
22. Nitrogen
23. Methane
24. Carbon Monoxide
25. Heptane (backflush)
26. Pentenes (backflush)

carbon dioxide (CO_2) when a sample is subjected to a temperature of approximately 950°C in the presence of a suitable oxidizing catalyst (Fig. 29).

After the conversion, a continuous flow of carrier gas conveys the CO_2 to the flow-through sample cell of an infrared analyzer sensitized for detection of CO_2. Before entry of the gaseous sample into the cell, water vapor is condensed and removed to ambient dewpoint levels.

The signal output from the infrared analyzer is routed through microprocessor circuitry to provide direct readout in ppm of carbon in the injected sample.

The IC concentration is determined by injecting a second sample into the inorganic carbon channel. Here, the temperature is maintained at 155°C. No catalyst is present; instead, quartz chips, coated with phosphoric acid, are contained in a quartz reaction chamber. Inorganic carbon compounds, such as bicarbonates and/or carbonates, react with the acid to form CO_2 according to the following acid/base reactions:

(Bicarbonates) $HCO_3^- + H_3PO_4 \rightarrow CO_2 + H_2O + H_2PO_4^-$

(Carbonates) $CO_3^= + H_3PO_4 \rightarrow CO_2 + H_2O + HPO_4^=$
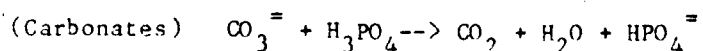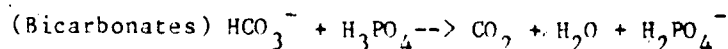
Because of the relatively low temperature and the absence of a catalyst, none of the organic carbon present is converted into CO_2.

Once the value of the inorganic carbon peak is obtained, it can be subtracted from the total carbon value previously established. The resulting difference is the total organic carbon concentration of the sample.

Where TIC levels are very low, (typically 0.5 to 2.0 ppm), the two channel difference method is usually unsuitable because of the relatively high CO_2 concentrations in our liquid effluent. Thus, it is necessary to remove the inorganic carbon by acidifying the sample to about pH 2, followed by sparging with a stream of clean, CO_2-free air.

4. GC/MS Analysis of the Liquid Effluent. The liquid effluent sample is mixed with an approximately equal amount (40-50 ml) of dichloromethane and vigorously shaken for a few minutes. After the phases have settled, an aliquot (5-30 ml) of the dichloromethane phase is withdrawn and concentrated to 1.0 ml in a Kuderna-Danish apparatus. It is blown down further with a flow of dry nitrogen to 0.1-0.5 ml. One microliter of this solution is injected into a stand-alone gas chromatograph and an appropriate aliquot (1-2 ul, depending on the concentration of the solution as judged from the GC experiment) is injected into the GC/MS system.
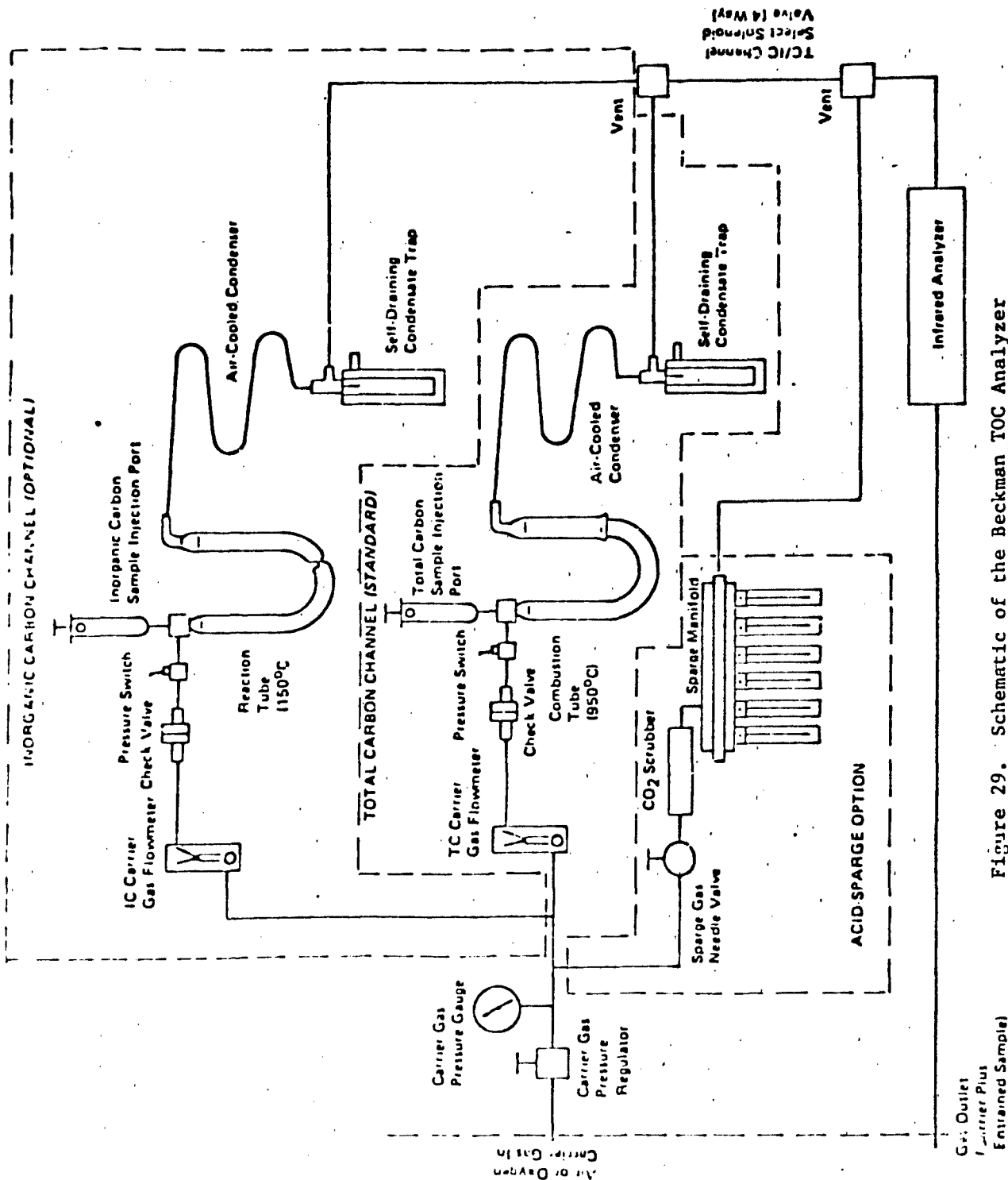
Figure 29. Schematic of the Beckman TOC Analyzer

A Varian 3700 gas chromatograph, equipped with flame ionization detector and automatic integrator, is used for stand-alone GC analysis. Columns are 15 m fused quartz coated with either SE-30 or SE-52. It is held at 45° for 1 min and then heated at 6°/min to 300^oC. A dual pen recorder records simultaneously at 2 mV full scale and one other sensitivity, either 20 or 50 mV full scale.

Another Varian 3700 gas chromatograph is coupled to a Varian-mat 212 double focusing mass spectrometer via an open-split interface. The conditions on the gas chromatograph are the same as on the corresponding stand-alone GC run. The mass spectrometer is scanned from M/Z of 30 through 500 at cycle times ranging from 2.0 to 2.8 seconds (but is constant for each separate set of experiments). The resolution of the mass spectrometer is set to 1:1000.

The GC/MS is interfaced to a Varian-mat SS-200 data system. It is based on a PDP 11/34 equipped with 80 K core, two discs totalling 5 M words capacity and a magnetic tape drive. Data can either be processed and evaluated on this data system or transferred via tape to a PDP 11/45 computer with 120 K core, a tape drive and a 350 M byte disc. This computer contains all the mass spectrometry data processing and evaluation programs developed at M.I.T. over the years.

The data are searched for compounds of interest either by inspection of the mass spectra at GC-peaks in the proper retention areas or by plotting mass chromatograms of the characteristic masses of the compounds (e.g. M/Z of 154, 188, 222, 256, 290, 358, 392 and 426 for biphenyl through octachlorobiphenyl), followed by inspection of the mass spectra of these maxima.

Alternatively, the data can be transferred to the PDP-11/45 and selected mass spectra compared with the NIH/EPA/MSDC mass spectral library or automatically microfilmed for easier visual inspection.

As a search for tetrachlorodibenzodioxins and tetrachloro-dibenzofurans, the mass chromatograms of M/Z 320 and 304, respectively, are plotted and the mass spectra at any maximum in the plot are inspected for the characteristic M/Z 320, 322, 324, 326, 328 pattern (304, 306, 308, 310, 312 for TCDF). If an indication of one of these compounds were found the entire spectrum of the compounds in the chromatographic peak would be compared to the authentic spectra.

After identification of the components of interest, their concentration is estimated from the stand-alone GC trace. Peak heights are determined and converted to nanograms by use of known amounts of standard solutions.

It should be noted that when partial oxidation experiments were made, some of the GC's of the liquid samples were very complex. The

effort of identification and quantitation was mainly directed towards those components related to the feed, and to detection of dioxins and dibenzofurans.

5. Inorganic Chloride Concentration of the Liquid Effluent. Chloride was determined with an Orion Model 407 specific ion meter provided with a chloride electrode Model 94-17. This device allows free chloride in aqueous solution to be measured quickly, simply and accurately. The ionic strength is maintained about 0.1 M by addition of 2 ml per 100 ml of an ionic strength adjuster (ISA).

6. pH of the Liquid Effluent. The pH was measured with an Orion Digital pH/mV Meter Model #601A and a combination reference/pH electrode from Fisher Scientific (Model # 3-639-94).

7. Nitrate Concentration of the Effluent. Nitrate was measured by an Orion ion specific electrode: Model 93-07m attached to an Orion Model 407 specific ion meter. The ionic strength of standards and samples was adjusted to a minimum of 0.12 molar with ammonium sulfate solution. Electrode operation, maintenance and calibration procedures were performed on a regular basis, conforming with good laboratory practice.

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