DEVELOPING OZONE DISPERSION AND REACTION MODELS AND CONDUCTING A THERMODYNAMIC STUDY FOR SAFETY EVALUATIONS OF AN INDOOR AIR POLLUTION ABATEMENT PILOT PLANT.

by

Surya Rao

Thesis submitted to the faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

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Approved:

Donald L. Michelsen (Chairman)

Dr. William L. Conger

Dr. Andrea M. Dietrich

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Dr. Donald L. Michelsen, Chairman.
Chemical Engineering

(ABSTRACT)

A Dispersion model for ozone inside the rectangular duct of
an indoor air quality pilot plant was simulated. Using this
the concentration profiles of ozone at several points
downstream of ozone insertion were simulated and they
matched well with experimental results. Recommendations for
future work are cited.

A thermodynamic study was conducted to check the levels of
concentration in which certain toxic compounds could be
present due to the oxidation of pre-determined chlorinated
compounds. STANJAN, a package which solves for equilibrium
concentrations using the element potential method, was used.
Recommendations for future work are cited.

A Reaction model was developed for the global oxidation
reactions occurring in the catalyst bed which is situated
downstream of the ozone insertion. Once this was done, the
effect of moisture and temperature were studied
qualitatively and recommendations for further work are
cited.
Acknowledgments

On the completion of my Thesis I would like to extend my sincere feelings of gratitude to my advisor Dr. D Michelsen, who was a constant source of support and help and without whose able guidance I could not have completed my thesis in so short a time. I would like to thank Dr. Don Van der vaart for helping me with the completion of my thesis. The Union Carbide unit which worked on the pilot plant in Blacksburg deserves my thanks for providing me with the requisite data.

I thank my room-mate Mr. Nagendra Prasad for his tremendous help and support. Last but not the least Mr. Lokesh Juneja deserves special mention for helping me with my thesis and for making my stay in Blacksburg memorable.

Surya Rao
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CHAPTER 1: INTRODUCTION

Building sickness, as defined by Molhave\textsuperscript{1}, basically consists of symptoms which are common among the general populace but are more wide-spread among workers in some buildings than in others. These symptoms are found to deteriorate while in the building and get better, away from the building according to Molhave\textsuperscript{2}. Studies of different buildings have shown that there are less symptomatic workers in naturally ventilated buildings as compared to sealed air conditioned buildings.

The symptoms most commonly complained of are headaches, tiredness and lethargy. Apart from these more common symptoms, dryness of the nose, or running/blockage of the nose or, irritation of the eyes are also quite prevalent among "sick" building inhabitants, according to Molhave\textsuperscript{1}.

Volatile organic compounds (VOCs), particulates with and without biomatter and smoke are some of the identified causes of indoor air sickness. The organic indoor pollutants were categorised by a working group of the World Health
Organization into 4 categories based on their boiling points. The category which had boiling points ranging from 50°C to 260°C was called the VOC's. Most of the dissolved or vaporised organics come in this category.

The most common source of the VOC's are the building materials and the furniture materials, according to a study conducted by Fanger et al. Ventilation systems could also be a possible source of contaminants due to the presence of fungi, algae, bacteria etc., which thrive on the moisture present in the ventilation ducts. Smoking produces a wide range of gases and vapors as well as significant fine particulate matter. Also, industrial necessities like copy machines and printing machines contribute to the presence of volatile organic compounds in working places.

The VOC's affect the membranes in the nose, eyes, ears and throat. Also the tissues of exposed body parts like hands, neck, face etc are affected by the surface reactions occurring on them. The effects of VOC's may show adaptation like perception of the odors or might increase with exposure.

The impact of this attention worldwide has been an awakening to these issues and their possible treatment in the United
States with U.S. EPA as the lead organization. The treatment effectiveness of activated carbon, ultra filtration and light-activated catalyzed systems continue to be studied. With the increased attention several years ago, Union Carbide set up an Indoor Air Pollution Abatement Pilot Facility at Virginia Tech at their Prices' Ford Research Center. The thrust of setup was to evaluate the use of ozone catalyzed treatment to destroy VOC's.

The pilot plant consisted of an approximately 75-100 ft duct with a 2"x4" cross-section, through which the polluted indoor air is passed along with ozone which is inserted into the mainstream through distributor tubes. The air was polluted by injecting pollutants such as benzene. Ozone acts as an oxidising agent for the VOCs (volatile organic compounds). Further down the duct, there are catalyst beds onto which both the VOC's and the ozone are adsorbed. The adsorbed ozone oxidises the VOC's to less toxic compounds. The treated air plus any excess ozone pass through a carbon bed in which the ozone is destroyed. The pilot plant was operated on an once through basis.
The Ozone dispersion model

The aim of the first part of the thesis was to develop a computer simulated dispersion model to determine the ozone concentrations at different lengths downstream of the ozone addition points and to obtain an estimate of where along the duct the ozone concentration would reach a steady-state. The results were compared with previously collected ozone dispersion measurements from the pilot plant setup. This estimate could serve as a tool to assess where the oxidation beds must be placed for satisfactory performance.

The Thermodynamic study

The second part of the thesis was to conduct a thermodynamic study of the system in order to identify compounds that could be formed during the oxidation process and their probable equilibrium concentrations. The reason to conduct this study is based on the concern that the presence of chlorinated compounds in the vicinity of the air-quality plant could result in their oxidation thus leading to the production of toxic compounds. This concern is highlighted by Dr. Donald Michelsen, Department of Chemical Engineering,
in his memo dated November 19, 1990, to Dr. George Keller at Union Carbide, see Appendix 4.

Tri chloroethylene was selected for this study. The aim of this part of the thesis is to check if toxic compounds could be formed by oxidation of chlorinated compounds and if so could they be present in levels above the recommended threshold values.

For conducting this study, a computer package called 'STANJAN' was used. This package, amenable to running on personal computers, uses the concept of element potentials to calculate the equilibrium concentrations of pre-selected products. STANJAN is widely used for solving combustion problems.

The Reaction Model

The aim of the third part of the thesis was to develop a model to simulate the reactions on the catalyst beds and to qualitatively study the effect of moisture and temperature on the rates of the reactions. The two reactions taken into consideration were the oxidation of VOCs with ozone and the decomposition reaction of ozone. For this purpose the Langmuir-Hinshelwood approximation was used for adsorption
and surface reactions. Langmuir isotherms are assumed for the VOCs and ozone.

In summary, the objective of this thesis and the work that went into it is to obtain a computer simulated dispersion model to calculate ozone concentrations at various lengths downstream of ozone insertion, a thermodynamic study to check for the formation of toxic compounds and a reaction model to simulate the global reactions in the catalyst bed and to qualitatively study the effect of moisture and temperature on the reactions. The three parts of the theses are explained in more detail in the next three chapters.
CHAPTER 2: BACKGROUND

Relevance of this work

Indoor air quality is becoming an increasingly important issue today with highly stringent standards to be met to ensure the safety of the workers in working environments. A building is called "sick" if its inhabitants complain of symptoms which deteriorate while in the building and tend to disappear when away from it, according to Molhave\textsuperscript{1}. The afore-mentioned symptoms might be present even in people who work in healthy environs, but are generally more wide-spread among the inhabitants of the "sick" building.

Symptoms

The most common symptoms are tiredness, lethargy and headache. Nausea could also grouped above as one of the more common symptoms. Dryness, running or blockage of the nose or eyes are grouped together with thirst, dryness of the skin and symptoms of asthma (chest tightness, wheeze and breathlessness) are grouped separately by Molhave\textsuperscript{1}. One of
the most common symptoms is lethargy which may improve tremendously while away from the building. The abundance of lethargy in sick buildings has been verified by the large number of cases wherein workers required a few additional couple of hours of sleep apart from their regular nights sleep.

Headache is also a frequent occurrence in workers in sick buildings. Workers are generally found to complain of ache across both sides of the forehead and sometimes in the back of the neck. Migraine is not generally found among the building sickness symptoms. Blocked nose, sore eyes and dry throat have been confirmed by medical interview to be work-related.

**Volatile Organic Compounds (VOC's) and health effects:**

From a number of small-scale studies\textsuperscript{4,5,6,7} it has become evident that the concentration of many organic compounds in indoor air is higher than in the outdoor air. A working group\textsuperscript{8} of the World Health Organization (WHO) categorized the organic indoor pollutants into four groups based upon their boiling-point ranges, although no sharp distinction exists between the four categories. The other three groups exist in either liquid form or as particulates.
According to this group volatile organic compounds were those having a boiling-point range with a lower limit between 50°C and 100°C and an upper limit between 240°C and 260°C, where the higher values refer to the polar compounds.

Sources of VOC's

VOCs are frequent air contaminants in non-industrial environments. Both building materials and furniture materials are known to emit VOCs, according to Fanger et al. Ventilation systems transport outdoor pollutants to the indoor environment in the form of fungi, algae, bacteria and other particles. All human activities are possible sources for volatile organic compounds. Activities such as smoking are sources of offending gases and vapors. Industrial necessities such as copy machines, printing machines etc. are other sources for VOCs (Molhave, 1, 21). From studies conducted it is fairly common knowledge that 50 to 300 volatile organic compounds are found in most non-industrial environments. Each compound seldom exceeds a concentration of 50μg/m³, which is 100 to 1000 times lower than relevant occupational threshold values (TLV's).
Effect of VOC's

The toxic effects of volatile organic compounds may be classified under effects common to most VOCs and special effects caused by only a few compounds.

Common Effects

Usually the tissues affected by the volatile organic compounds are mucousal membranes in the eyes, nose, throat; skin in face, neck and hands; upper and lower airways. Surface reactions occurring on tissues exposed to the air seem to be the reason for the most frequent effects, according to Molhave\(^1\). The effects are reversible and vanish shortly after stop of exposure.

The effects which are most frequent are acute. They may, like perception of odors, show adaption. Other effects may be sub-acute in which case they may be expected to increase with exposure like headaches. The acute effects may be divide into three classes, according to Molhave\(^1\). The first is primary perceived stimulation caused by the air pollution of the sensory system.

The second effect consists of observed or perceived secondary biochemical changes in skin and other tissue
exposed to the polluted air. These may be caused either directly by the exposure or by perceivable changes in tissue.

The third class consists of observable changes in human behavior. The sub-acute changes may be observed as headaches and other weak subjective nervous related effects or weak inflammatory-like reactions.

In conclusion it may be noted that several comprehensive biological models have been put forward to illustrate the effect of low level volatile organic compounds. Also several health criteria have been suggested to ensure prevalence of hygienic conditions at work places.

Clearly, Indoor Air quality is an increasingly important issue today with standards to be met at work places to alleviate pollution in working environments. An Indoor Air Quality Pilot plant was set up at Prices' Fork, Blacksburg, by Union Carbide for experimental testing and to determine the efficiency and costs of such a venture.

The Ozone Dispersion Model

The purpose of this model is to simulate ozone dispersion
in a rectangular duct. Since the flow of the ozone is in the turbulent regime and since no turbulent models can be conveniently used a plug flow model was used. For the purpose of solving for concentrations of ozone at different points along the duct, a package called PDETWO which solves two dimension non-linear partial differential equations was used. This package was created by Melgaard and Sincovec - see Appendix 1. Essentially what this package does is to solve the continuity equation for ozone.

The ozone is introduced through two ozone insertion tubes and serves as an oxidant to oxidize the pollutants in the indoor air. So it is essential to know the dispersion profile of ozone in order to verify experimental estimates of required duct length for the ozone to attain uniform concentration. The results obtained from the ozone dispersion model were compared with the experimental values of the ozone concentrations measured at various positions along the duct.

**Experimental System to be Modelled**

The experimental system consists of a rectangular duct with a 2ft x 4ft cross-section. Indoor air to be processed flows through the duct. Ozone is introduced by means of an ozone
distributor which branches into two tubes. Thus ozone is introduced at a fourth and three-fourths of the vertical height of the duct. The steady-state concentration of ozone desired is 5ppm. The flowrate of air is 3500 cfm through the duct and the ozone flows through the distributor at 60 cfm. The Re# of the air stream is 1.32x10^5 which is much above the upper limit (Re# = 2100) for laminar flow.

As shown in Figure 1, the X axis is along the breadth or the horizontal width of the duct, the Y axis is along the vertical width of the duct and the Z axis downstream from the ozone insertion points. So essentially the package solves the continuity equation for ozone at specified lengths downstream of the ozone insertion, at different values of Z. The ozone concentration is constant along the X axis and varies only with the Y axis.

The Package

The PDETWO package is widely used for solving systems of non-linear partial differential equations using the Finite Difference technique. A software interface is required to solve time-dependent coupled systems of nonlinear partial differential equations (PDEs), which are defined over a two-dimensional rectangular region. The software interface
Figure 1. Schematic diagram of the duct.
employs the method of lines technique whereby centered differencing with respect to the two spatial variables results in a system of time dependent ordinary differential equations (ODEs), which can then be solved using one of the readily available modern ODE integrators. A routine is also described to be used in conjunction with the software interface for the efficient generation of the jacobian matrix. The software interface to be supplied by the user should consist of input parameters to the package. These parameters include:

1) The mesh spacing
2) The initial conditions
3) The boundary conditions
4) The dispersion coefficients

The package solves for time dependent differential equations a simplified version of which is given below.

\[
\frac{du}{dt} = \frac{d}{dx}[D(x)\frac{du}{dx}] + \frac{d}{dy}[D(y)\frac{du}{dy}] \ldots \ldots \ldots (1)
\]

Since the package solves for time dependent nonlinear partial differential equations and since the ozone dispersion is to be studied in a steady state condition
(i.e., when nothing changes with time), the $z$ variable is substituted for the time variable. This results in an equation of the sort of eq(1) which can be solved by PDEtwo. The final continuity equation is essentially the same as equation (1) except that the concentration variable takes the place of $u$ and $(z)$, the distance travelled down the duct, take the place of the time variable. See Appendix 1 for details.

Assumptions Made

To simplify the problem certain assumptions were made.

1. The flow in the duct is assumed to be at steady-state and hence ozone concentration doesn't depend on time.

2. The ozone introduced is assumed to flow initially only in the direction of the flow of air. All other velocity components of the ozone are neglected. In the actual setup the ozone flows out in the direction opposite to the direction of the air-stream and then makes a U-turn to flow along with the air-stream.

3. Since the flow inside the duct is turbulent, the velocity is assumed to be constant.
4. The ozone dispersion coefficients in the X and Y directions are assumed to be equal and constant throughout the duct.

The Thermodynamic Study Using 'STANJAN'

In studies conducted by Atkinson, it was found that many organics do not get oxidized completely to CO₂ and H₂O. There are a lot of intermediates which are also formed. The thermodynamic study was completed with the aim of checking whether the presence, through spill, of certain chlorinated compounds might result in the production of hazardous chemicals as a result of them being drawn in with air to a low temperature ozone catalytic oxidation treatment.

'STANJAN' employs the method of element potentials (Appendix 2) to calculate equilibrium conditions given the initial number of moles of the reactants. Early development of the method was done by Powell¹¹ and it was revised and put to use for solving combustion -equilibrium problems by Reynolds¹²,¹⁴. Element potential is analogous to Chemical potential in the sense that just as chemical potential is defined for a species, element potential is defined for an element. The method of element potentials uses theory to relate the mole fractions of each species to quantities called element potentials. There is one element potential
for each independent atom in the system, and these element potentials, plus the total number of moles in each phase, are the only variables that must be adjusted. There are many other advantages to the element-potential method such as the easy accessibility of the thermochemical data which is all that the user must have to solve for the equilibrium concentrations of the products given reactant concentrations. This particular method was chosen over many other available methods for determining equilibrium concentrations, because of the following reasons.

If one uses the concept of equilibrium constants, then it is necessary to identify the set of reactions that take place and to determine the associated equilibrium constants. One then to solve a set of non-linear algebraic equations for the mole fraction of each species. This is a difficult task if the system is large. Other methods based on the minimization of the Gibbs function adjust the moles of each species, consistent with atomic constraints, until the minimum Gibbs function state is found. Again, there are many variables involved, and great care must be taken to be sure that all moles are non-negative. When there are important rare species in the system, this can be a very difficult task. Taking all these factors into consideration the relatively new method of element potentials was used.
because of its many advantages.

The program, called 'STANJAN' because of its roots at Stanford and its connection with the JANNAF thermochemical data tables, is an interactive program designed for use with either desktop or mainframe computers. The basic data are taken from the JANNAF tables, and data for a selection of species accompany the program.

All expected products have to be fed to the package. In this simulation tri chloroethylene (TCE) is used as the chlorinated compound since it is a major component of many cleaning fluids. Twenty possible reaction products were decided upon and these were also inputted to the package. The 20 products and their threshold level values (TLV) are given in Table 1. In running the equilibrium program, oxygen is assumed to pass through and to be unreactive and serve as a diluent like nitrogen. The physical properties at 25° used in the 'STANJAN' program are shown on Table 2.

In the first part of this study, TCE concentrations of 5 and 10 ppm were used and the ozone concentration was varied from 2.5ppm to 10ppm. At these concentrations, the equilibrium concentrations of all the 20 compounds were obtained using 'STANJAN' to see if the concentrations of any of the
**Table 1**

*Expected Products From Ozonation of TCE*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Common Name</th>
<th>Threshold Limit Values (TLV) in ppm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂=CHCl</td>
<td>Vinyl Chloride</td>
<td>5.0</td>
</tr>
<tr>
<td>CHCl=CHCl</td>
<td>1,2-dichloroethene</td>
<td>200.0</td>
</tr>
<tr>
<td>CHCl=CCl₂</td>
<td>Trichloroethene</td>
<td>50.0</td>
</tr>
<tr>
<td>CCl₂=CCl₂</td>
<td>Perchloroethene</td>
<td>50.0</td>
</tr>
<tr>
<td>CCl₄</td>
<td>Carbon Tetrachloride</td>
<td>5.0</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>Chloroform</td>
<td>10.0</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>Dichloromethane</td>
<td>100.0</td>
</tr>
<tr>
<td>CH₃Cl</td>
<td>Chloromethane</td>
<td>50.0</td>
</tr>
<tr>
<td>COCl₂</td>
<td>Phosgene</td>
<td>0.1</td>
</tr>
<tr>
<td>CH₂COCl</td>
<td>Acetyl Chloride</td>
<td>--</td>
</tr>
<tr>
<td>Cl₂</td>
<td>Chlorine</td>
<td>1.0</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>Acetic acid</td>
<td>10.0</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrogen chloride</td>
<td>5.0</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
<td>--</td>
</tr>
<tr>
<td>CH₂CO</td>
<td>Ketene</td>
<td>0.5</td>
</tr>
<tr>
<td>H₂CO</td>
<td>Formaldehyde</td>
<td>2.0</td>
</tr>
<tr>
<td>O₃</td>
<td>Ozone</td>
<td>0.1</td>
</tr>
<tr>
<td>O₂</td>
<td>Oxygen</td>
<td>--</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
<td>5000.0</td>
</tr>
<tr>
<td>N₂</td>
<td>Nitrogen</td>
<td>--</td>
</tr>
</tbody>
</table>
Table 2

Thermochemical properties of the 20 compounds considered in the thermodynamic evaluation of the Indoor Air Quality plant

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molar mass</th>
<th>Enthalpy of formation (Kcal/mol)</th>
<th>Entropy cal/mol/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl=CH₂</td>
<td>62.5</td>
<td>8.52</td>
<td>63.16</td>
</tr>
<tr>
<td>CHCl=CHCl</td>
<td>96.9</td>
<td>0.90</td>
<td>69.28</td>
</tr>
<tr>
<td>CHCl=CCl₂</td>
<td>98.96</td>
<td>-1.86</td>
<td>77.70</td>
</tr>
<tr>
<td>CCl₂=CCl₂</td>
<td>165.83</td>
<td>-2.89</td>
<td>81.60</td>
</tr>
<tr>
<td>CCl₄</td>
<td>153.82</td>
<td>-24.60</td>
<td>74.13</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>119.38</td>
<td>-24.67</td>
<td>70.74</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>84.93</td>
<td>-22.12</td>
<td>64.65</td>
</tr>
<tr>
<td>CH₃Cl</td>
<td>50.48</td>
<td>-19.34</td>
<td>56.12</td>
</tr>
<tr>
<td>CH₃COCl</td>
<td>78.50</td>
<td>-58.26</td>
<td>70.60</td>
</tr>
<tr>
<td>COCl₂</td>
<td>98.92</td>
<td>-52.34</td>
<td>67.83</td>
</tr>
<tr>
<td>Cl₂</td>
<td>70.91</td>
<td>0.00</td>
<td>53.37</td>
</tr>
<tr>
<td>HCl</td>
<td>36.46</td>
<td>-22.08</td>
<td>44.72</td>
</tr>
<tr>
<td>CH₂CO</td>
<td>42.04</td>
<td>-11.41</td>
<td>59.24</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>60.05</td>
<td>-103.41</td>
<td>67.58</td>
</tr>
<tr>
<td>H₂CO</td>
<td>30.03</td>
<td>-25.97</td>
<td>52.34</td>
</tr>
<tr>
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<td>-94.14</td>
<td>51.13</td>
</tr>
<tr>
<td>H₂O</td>
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<td>-57.85</td>
<td>45.17</td>
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<td>49.08</td>
</tr>
<tr>
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<td>+34.14</td>
<td>57.16</td>
</tr>
<tr>
<td>N₂</td>
<td>28.00</td>
<td>0.00</td>
<td>45.84</td>
</tr>
</tbody>
</table>
possible products went up to levels beyond the recommended TLVs. The assumption being made here is that only ozone is being adsorbed onto the catalyst surface and not the other products which are formed by ozone decomposition.

In the second part of this study, the effect of moisture was investigated. At concentrations of 5ppm TCE and 5ppm ozone, the H₂O concentration was varied from 0 to 10ppm and the equilibrium concentrations of the products was obtained.

More on the theory of element potentials and its usage in 'STANJAN' is given in Appendix 2.

The Reaction Model

In this part of the dissertation, the aim was to develop a model to simulate the reactions in the catalyst bed and to qualitatively study the effect of moisture and temperature on the two reactions. The reactions under consideration are the oxidation of the VOCs and the decomposition of ozone. Since very little data is available, statistical estimates of system parameters is not possible. Also since the exact nature of the reactions taking place in the catalyst bed are unknown, global reaction rate expressions were assumed. The rate constants were varied to approximate 50% and 10%
conversion of ozone and the VOCs Langmuir-Hinshelwood\textsuperscript{9} model was used for the describing the adsorption isotherms and the surface reactions. The rate expressions once formulated were found to constitute a system of first-order non-linear differential equations which could be solved numerically. The presence of moisture was later incorporated into the rate expressions in an effort to study its effect. The effect of temperature is studied by solving the system of equations at 59°F and at 77°F.

In summary, this part of the dissertation, rate expressions for the catalytic oxidation of the VOCs were simulated using representative values from more traditional catalytic system\textsuperscript{10} and due to extremely scarce data, conversions of ozone and VOCs are assumed to be 50% and 10% respectively. Then the rate constants were varied and conversions numerically calculated to see what the approximate rate constants could be to achieve the required conversions of VOCs and ozone. Then the effects of moisture and temperature were studied qualitatively.
CHAPTER 3: PROCEDURE

The Ozone Dispersion Model

The development of the Ozone Dispersion model is done using the package PDETW0. This package is widely used for solving problems where a system of non-linear differential equations have to be solved simultaneously, for instance in determining the temperature profile in a plate subjected to convective heating. See Appendix 1.

Input Parameters to the Package

1. Mesh Size

The mesh size is input to the package as NX and NY, the number of points the horizontal and vertical axis of the grid comprise of. These parameters are to be adjusted so that appropriate nodes correspond to points where the ozone is being injected into the air-stream. Also initial estimates can be made using coarse meshes but to obtain accurate results finer meshes are required. More information on meshes and their generation is given in a subsequent section.
2. Initial Conditions

The initial conditions have to be supplied to the package. Since ozone is introduced through two tubes, the initial conditions should specify where in the initial mesh the ozone is introduced and also the concentration at which it is introduced. The initial conditions used for this problem can be shown in pictorial form as follows.

\[ \begin{array}{cccccccccccccc}
1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 & 13 \\
\hline
1 & * & * & * & * & * & * & * & * & * & * & * & * \\
2 & * & * & * & * & * & * & * & * & * & * & * & * \\
3 & * & * & * & * & * & * & * & * & * & * & * & * \\
4 & --0-0-0-0-0-0-0-0--0--0--0--0--ozone insertion \\
5 & * & * & * & * & * & * & * & * & * & * & * & * \\
6 & * & * & * & * & * & * & * & * & * & * & * & * \\
7 & --*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-*-**-CENTER LINE. \\
8 & * & * & * & * & * & * & * & * & * & * & * & * \\
9 & * & * & * & * & * & * & * & * & * & * & * & * \\
10 & --0-0-0-0-0-0-0-0--0--0--0--0--ozone insertion \\
11 & * & * & * & * & * & * & * & * & * & * & * & * \\
12 & * & * & * & * & * & * & * & * & * & * & * & * \\
13 & * & * & * & * & * & * & * & * & * & * & * & * \\
\end{array} \]

Figure 2

Layout of Mesh For Flow Simulation
As shown above, for instance using a 13x13 mesh we have (NX-1), 12 mesh spacings in the x direction and (NY-1), 12 mesh spacings in the y direction. Since ozone is introduced at a fourth and three-fourths of the duct height, we have in our mesh ozone coming in through mesh numbers 4 and 10. At all points corresponding to meshes 4 and 10 in the vertical direction we have initial concentration which is set constant for each run. At all other points we have ozone concentration equals zero.

3. Boundary Conditions

The boundary conditions that were specified for this problem were that the fluxes of ozone at each of the four walls was zero. The package allows for the incorporation of both the Newmann and the Dirichlet boundary conditions by specifying just three parameters $A, B$ and $C$ in both the horizontal and the vertical boundary conditions (BCs). By appropriate values given to these parameters we make the fluxes at each of the walls equal to zero.

Boundary conditions are:

at $x = 0, x = 1$ \hspace{1cm} $dc/dx = 0$

at $y = 0, y = b$ \hspace{1cm} $dc/dy = 0$
4. Dispersion Coefficients

The dispersion coefficients in the horizontal and vertical directions have to be specified to the package. These are the parameters $D(x)$ and $D(y)$ which appear in eq(1). They can be functions of $x$ and $y$ but in our case the assumption is made that they remain constant and equal to each other. These are to be specified as $D_H$ and $D_V$ to the package.

Calculation of Dispersion Coefficients

Using correlations of radial dispersion coefficients for gases as a function of Reynolds number as plotted by Carberry J.J\textsuperscript{10}, the dispersion coefficients are estimated. First the Reynolds number is calculated. Then using the plot of $Re_s$ vs $D_r/r$ the appropriate value of $D_r/r$ is calculated. The $Re_s$ for the system is approximately $1.32 \times 10^5$ and the transition between the laminar and turbulent regimes occurs at $Re_s = 2100$. Then once the kinematic viscosity($r$) is known, the dispersion coefficient is calculated. The kinematic viscosity of air used for this purpose was $0.1552$ cm$^2$/sec and the corresponding value of the dispersion coefficient ($D_r$) calculated was $233$ cm$^2$/sec and this is inputted to the package as $D_x$ and $D_y$.  

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The Model

Essentially the continuity equation for ozone is used to model the concentration profile of ozone as it flows down the duct. The equation is as follows:

\[ V \frac{dc}{dz} \frac{d}{dx} [D_x \frac{dc}{dx}] + \frac{d}{dy} [D_y \frac{dc}{dy}] \]

\[ \text{---(2)} \]

where

\[ V_z = \text{velocity of flow along the z direction.} \]
\[ D_x = \text{dispersion coefficient along the x axis.} \]
\[ D_y = \text{dispersion coefficient along the y axis.} \]
\[ C = \text{concentration of ozone as a function of x, y, and z.} \]

The X axis is along the horizontal width of the duct, the Y axis is along the vertical height of the duct and the Z axis is along the length of the duct downstream of the ozone insertion and hence in the direction of flow of air.

Mesh Generation

PDETW0 essentially solves for the time dependent differential equations of the type shown in equation \( \text{(4)} \).
In this equation, the time coordinate is substituted by the Z coordinate which is the axis along the length of the duct. The variable 'u' in equation (4) is replaced by the concentration variable 'c'. At each plane where the concentration profile of ozone is to be calculated, a mesh is constructed. Using the initial conditions and the boundary conditions supplied to the package, values for the ozone concentration are calculated using finite difference approximations. Each node in the mesh is equivalent to a point and thus concentrations are calculated at each node. Using the initial conditions specified, the package calculates concentration values at the next mesh, at each and every node. The meshes were constructed in such a way that they correspond closely to the cross-section of the duct. Different mesh sizes were used to see how the error diminishes with increasing mesh size.

The experimental system was equipped with apparatus to determine concentrations at four planes perpendicular to the axis of the duct, i.e., at four lengths downstream of the ozone insertion. To compare the theoretical and experimental values of the concentration profile, the concentration values were obtained at the exact same four planes using the computer model, too.
A 10x10 mesh was used in the very first trial. The problems observed with this mesh size was that the concentration was seen to be accumulating near the walls at \( Y = 0.0 \) and \( Y = 2.0 \). Also the steady state concentration of 5ppm was obtained at a significantly larger distance from the point of ozone insertion than was observed experimentally. Then a 5x5 mesh was used to simulate a fourth of the duct and the results obtained were extrapolated over the whole duct. This gave considerably better results than the original 10x10 mesh. But this was surprising since finer the mesh better are the approximations made by the package. Therefore this gave rise to the idea that if odd number of meshes were used better results could be expected because even distribution about the center line would result. Thereafter meshes 13x13 and 17x17 were used and as expected good results were obtained. Since there was no concentration variance observed along the X axis, later meshes used consisted of only 10 nodes in the X direction.

Later on mesh grids of 25 x 10 were used so that 24 divisions were obtained in the X direction and this was suitable for simulating one division along the X axis for every inch along the width of the duct. This gave results not very much better than the 13 x 13 or 17 x 17 meshes but it made mapping the grid onto the cross-section of the
duct much easier.

A 73x73 mesh was then used and as expected it gave much better results than the 13x13, 17x17, 25x25 meshes. The disadvantage was that computer time was excessive. With the 73x73 meshes, the computer took as much as 6-7 hours for solving the package. With the 25x25 meshes, however, the process was much quicker and generally took about 15-20 minutes. The final steady state concentration of 5 ppm was achieved in both the experimental and the computer simulated models at about the same length down the duct, but the concentration profile in the experimental set-up seemed to be doing better than the simulated model in the initial stages. In other words, the mixing of ozone into the airstream accelerates faster in the experimental set-up but the mixing in the simulated model catches up with the experimental results well in time before reaching the steady state concentration of 5 ppm.

After this was done, an effort was made to incorporate the initial turbulence generated in the experimental system due to the backward thrust of ozone when it is first inserted. To do this, the number of points through which ozone is inserted into the duct was increased in the computer simulated model. Essentially, the ozone which was coming
initially out of 2 points out of a total of 25, was made to come out of 6, 10, 14 and 18 points out of 25. In other words, instead of assuming that the ozone came out through just two points along the width of the duct, it was assumed to be coming out of 18 points out of a total of 25. This approximation gave results which compared really well with the experimental values within the allowable range of 2-5%.

The Thermodynamic Study using 'STANJAN'

About the package 'STANJAN'

The package 'STANJAN' is used for the purpose of interactively determining the equilibrium concentrations of the 20 toxic compounds that might be formed if some liquid like cleaning fluid containing TCE (tri-chloroethylene) is spilt in the vicinity of the indoor air pollution abatement device. See Appendix 2 for description of thermodynamics.

Implementation of 'STANJAN'

First of all, the list of all compounds had to be decided upon. Initially only about 5-6 compounds were used but later on the list was expanded to accommodate 20 possible compounds. Since the study was initially for considering the outcomes of spilt TCE, a majority of the 20 compounds were
compounds containing Cl₂ and those that were toxic and had a low TLV (threshold level value). The compounds that were chosen for the final study along with their TLV's and thermochemical data are listed in Table 1 and Table 2 respectively.

The thermochemical data for the compounds was obtained from a compilation of physical and chemical reference data\textsuperscript{13}. The reactants in the system were O₃ and TCE. The runs were conducted using 'STANJAN' at concentrations of O₃ varying from 2.5-10.0 ppm keeping the TCE concentration constant at 5ppm and 10.0 ppm. The final concentrations of all the 20 compounds corresponding to all the different combinations of the input parameters are obtained. O₂ is assumed as acting like an inert gas. For the compounds which are more toxic than the rest like, COCl₂, CHCl₃, CCl₄, HCl and Cl₂ plots of their concentration versus the ozone concentration were plotted at both the fixed values of TCE concentration, 5ppm and 10.0ppm of TCE. The plots are shown in figures 9 through 16.

Since moisture was bound to be present in the vicinity of the operating system and since H₂O was not considered as a reactant in the previous study, the next step was to incorporate moisture in the system and to see its effects.
So again the runs were conducted varying the water concentration from 0 ppm to 10.0ppm and observing how the concentrations of all the possible final products changed with water concentration. The plots of both types of runs, with and without moisture are presented along with the results and discussions in figures 17 through 20.

A further explanation of the method of element potentials and 'STANJAN' is shown in the Appendix 2.

About the Model

In this part of the dissertation the aim is to develop a model to simulate the reactions taking place in the catalyst bed and to study the effect of moisture and temperature on the two reactions. The reactions to be modelled are the oxidation of the VOCs and the decomposition of ozone. The reactions are as follows:

1. The oxidation of the VOC's by ozone.

\[ \text{VOC's} + \text{O}_3 \rightarrow \text{oxidized products}. \]

2. The decomposition of ozone.
The Langmuir-Hinshelwood model is used to describe the adsorption of $O_3$ and the VOCs and also the surface reaction. Langmuir isotherms are assumed for generating the rate expressions for the disappearance of the VOC's and the ozone. The final rate expressions are as follows:

$$\frac{dC_{VOCs}}{dt} = \frac{-k_1 \cdot K_{VOCs} \cdot K_3 \cdot C_{O3} \cdot C_{VOCs}}{(1 + K_{VOCs} \cdot C_{VOCs} + K_3 \cdot C_{O3})^2}$$

$$\frac{dC_{O3}}{dt} = \frac{-k_2 \cdot K_3 \cdot C_{O3}}{(1 + K_{VOCs} \cdot C_{VOCs} + K_3 \cdot C_{O3})}$$

Since the aim is to determine the conversion of the VOC's and the ozone as a function of the distance traversed across the catalyst bed, the following transformation can be used.

$$u = \frac{dx}{dt} = 0.25 \text{ m/s}$$

where $x$-the axial distance traversed from the beginning of the catalyst.
t = the time elapsed since the air stream entered
the catalyst bed.

u = the superficial velocity of the air-stream
through the catalyst = 0.25 m/s

Now, using the above relation between x and t, equations (3)
and (4) can be re-written as,

\[ \frac{dC_{VOCs}}{dx} = \frac{\alpha \cdot C_{VOCs} \cdot C_{O3}}{(1 + \beta \cdot C_{O3} + \Omega \cdot C_{VOCs})^2} \]  

(5)

\[ \frac{dC_{O3}}{dx} = \frac{-\sigma \cdot C_{O3}}{(1 + \beta \cdot C_{O3} + \Omega \cdot C_{VOCs})} \]  

(6)

where \[ \alpha = k_1 \cdot K_{O3} \cdot K_{VOCs} / u \]
\[ \sigma = k_2 \cdot K_{O3} \]
\[ \beta = K_{O3} \]
\[ \Omega = K_{VOCs} \]

Now, equations (5) and (6) constitute a system of first
order non-linear differential equations which can be solved
numerically for instance, by using one of the IMSL routines.
Input parameters

The parameters that are needed to be inputted to the package are \( \alpha, \sigma, \beta \) and \( \Omega \) as well as the initial conditions. The equations to be substituted in the package are as in (5) and (6).

\[
\text{at } x = 0, \quad C_{O_3} = 5 \text{ ppm.}
\]

\[
C_{\text{VOCs}} = 1 \text{ ppm.}
\]

Now, since very little data is available, statistical estimation of the system parameters is impossible. Therefore, values representative of traditional (non ozone enhanced) catalytic oxidation systems were used. Also, the conversions of \( O_3 \) and the VOCs were assumed to be 50\% and 10\% respectively. Then, only the rate constants \( k_1 \) and \( k_2 \) were varied to approximate the assumed conversions. It is hoped that through such a model some qualitative aspects of the process may be identified.

Effect of Moisture

Water, if present in the system, could act as an inhibitor. The effect of the presence of moisture can be studied by
incorporating water into the Langmuir-Hinshelwood model. Including water gives us the following rate expressions:

\[
d\frac{C_{\text{VOCs}}}{dx} = \frac{-\alpha \cdot C_{\text{VOCs}} \cdot C_{\text{O3}}}{(1 + \beta \cdot C_{\text{O3}} + \Omega \cdot C_{\text{VOCs}} + \delta \cdot C_{\text{H2O}})^2} \tag{7}
\]

\[
d\frac{C_{\text{O3}}}{dx} = \frac{-\sigma \cdot C_{\text{O3}}}{(1 + \beta \cdot C_{\text{O3}} + \Omega \cdot C_{\text{VOCs}} + \delta \cdot C_{\text{H2O}})} \tag{8}
\]

where \(\delta\) = adsorption equilibrium coefficient of \(\text{H}_2\text{O}\) on the catalyst surface. With the help of equations (7) and (8), the effect of moisture can be easily studied by using the model, if the adsorption equilibrium coefficient of water on the catalyst surface is known.

**Effect of Temperature**

The effect of temperature will also be studied by solving the equations (5) and (6) at \(59^\circ\text{F}\) and \(77^\circ\text{F}\) to see if it affects the selectivity of the ozone decomposition reaction in anyway.
The IVPAG routine from the IMSL library was used for numerically solving the system of first-order, non-linear differential equations. The IVPAG routine utilizes the Gears backward difference method for solving the system of equations. The program which was used to interface the IVPAG routine can be easily obtained from the IMSL manual. See Appendix 3 for a limited identification of the IVPAG program.
CHAPTER 4: RESULTS AND DISCUSSIONS

The Ozone Dispersion model

The objective with respect to the ozone dispersion model was well realised in the sense that, using a package and inputting relevant details by way of a driver program, a computer simulated concentration profile of the ozone was obtained which matched very well with the experimental readings. By trial and error method, the meshes were generated and the initial conditions were manipulated such that the simulated dispersion profile of ozone matched, within allowable limits, with the data that was collected earlier from the pilot plant.

Comparing the experimental and the theoretical results

First of all it has to be understood that the plots of the concentration profile plotted from the experimental values and those plotted from the computer simulated values are different with respect to the axes they are plotted against.

The values obtained from the experiments are plotted with
ozone concentration in the vertical Y axis and the breadth of the duct on the X axis. The simulated values are plotted with ozone concentration on the Y axis and the width of the duct on the X axis. Now, it is obvious why the technique that was opted for plotting experimental points was not opted for the computer simulation points. If the same technique would have been applied to the predicted concentrations as well, then all points on the X axis would have the same concentration and the dispersion along the width of the duct could not have been properly visualised.

After realising that two plots with different axes had to be compared, the best way to do it was to compare the deviation from the average concentration of the plots and/or the range of maximum-minimum concentration values for the two plots. The plots of the experimental runs were obtained from the Union Carbide Corporation for the purpose of comparing them with the simulated values. Their plots are shown in figure 3. The experimental values were measured at the top, middle and the bottom of any given plane were the measurements were to be conducted. So the average values of the top, middle and the bottom survey were calculated and another set
Figure 3. Development of Ozone Distribution with downstream position.
of concentration profiles were generated. The range of the maximum and minimum values were then calculated for both the experimental and computer simulation profiles for comparison. The concentration plots obtained from the computer model values and the comparison between the maximum-minimum range are shown in Figures 4 through 8 and Table 3 respectively.

As shown in Table 3, the range of maximum - minimum at 14.5 inches, according to the simulated plots is about 3.35. The same range for the experimental values is about 3.7 for the 18/25 mesh grid. But for later distances along the duct where concentrations were measured the computer model values did better than the experimental values in terms of overall mixing and dispersion. At 60 inches the experimental values varied over a region of 1.5 ppm, whereas the theoretical values varied over a region of 0.6 ppm. The concentration of ozone converges to a value above 5ppm. This is because accuracy of calculations for a 25x25 mesh grid is not as much as, for instance, a 73x73 mesh grid. The simulated concentration profiles for using the 73x73 grid is shown in figure 8. The accuracy of calculations is good in this case as can be seen by the ozone concentration converging at
Figure 4. Simulated Vertical Concentration Profiles at 14.5" down the duct.
Figure 5. Simulated Vertical Concentration Profiles at 60" down the duct.
Figure 6. Simulated Vertical Concentration Profiles at 102" down the duct.
Figure 7. Simulated Vertical Concentration Profiles at 149.5" down the duct.
Figure 8. Simulated Vertical Concentration Profiles Using the 73 X 73 mesh.
<table>
<thead>
<tr>
<th></th>
<th>14.5in</th>
<th>60in</th>
<th>102in</th>
<th>149.5in</th>
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<tr>
<td><strong>Experimental</strong></td>
<td>3.35</td>
<td>1.5</td>
<td>0.45</td>
<td>0.2</td>
</tr>
<tr>
<td><strong>Simulated values</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18/25 spread</td>
<td>3.70</td>
<td>0.6</td>
<td>0.10</td>
<td>0.0</td>
</tr>
<tr>
<td><strong>Simulated values</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2/25 spread</td>
<td>9.30</td>
<td>2.09</td>
<td>0.42</td>
<td>0.06</td>
</tr>
<tr>
<td><strong>Simulated values</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2/73 spread</td>
<td>9.93</td>
<td>1.69</td>
<td>0.33</td>
<td>0.05</td>
</tr>
</tbody>
</table>
almost 5ppm.

The good match between the experimental and computer simulated model plots shows that, although a turbulent representation of the flow of the air-stream would probably have lent more reality to the model, nevertheless a plug-flow model did a good job too in describing the concentration profile of the ozone.

The reason why the values in the first plane, at such a short distance from the ozone insertion, did not match for the experimental and the computer model values could be because of one of the assumptions made in the very beginning. The assumption that ozone is being inserted directly into the air-stream and in the direction of propagation of the air-stream was just a simplifying assumption. In actuality the ozone is inserted into the air-stream but in the opposite direction. This could have provided a great deal of initial turbulence and helped mixing in the initial stages. This is proved by the fact that when the ozone was simulated as coming out of 18 points instead of just 2, the results of the model and the experiments seemed to match pretty well.
Suggested Future Work

1. Instead of using a constant velocity throughout the duct, a velocity profile for the turbulent regime can be incorporated into the model to see how the results vary.

2. To observe quicker and better mixing of ozone before it enters the catalyst bed, the ozone insertion can be done at a bend. This too could be attempted to be modelled using the same package but with mesh points to define the bend, velocity profiles which describe the velocity at the bend and so on.

3. The same ratio of ozone insertion points to total number of points can be used with a finer mesh as it improves accuracy.

4. Instead of allowing the ozone to reach a steady-state concentration before it reaches the catalyst bed, one can see what the effect of a non-uniform concentration profile of ozone entering the catalyst bed would be.
The Thermodynamic study using "STANJAN"

Using this package, a thermodynamic study was conducted to determine if any of the compounds which could be formed would be present above the recommended safe limit, the TLV's (threshold level values). A list of 20 toxic compounds that could be present were decided upon. At first the run was conducted using 'STANJAN' at an initial condition of 5ppm of Tri-chloroethylene (TCE), for ozone concentrations varying from 2.5ppm to 10.0ppm, keeping the TCE concentration constant. At the above conditions, the equilibrium concentrations of all the 20 compounds were obtained. Similarly the run was carried out for ozone concentrations varying from 2.5ppm to 10.0ppm but this time keeping the concentration of TCE fixed at 10.0ppm.

Graphs were plotted of concentration of each of the 20 compounds against the ozone concentration at both 5ppm and 10.0ppm of TCE. The concentrations that could then be expected during the actual working of the plant were thus estimated. Now, these concentrations were compared with the Threshold Level Values available in literature. This now provided us with a list of potentially hazardous compounds and the concentrations they could be present in during
favorable conditions.

As shown in Figures 9 through 12, at 5ppm, HCl could be present in concentrations of up to 15ppm which is much above the recommended Threshold level value of HCl. Also the concentration of chlorine (Cl₂) could reach up to 7.5ppm while the recommended TLV for Cl₂ was just 1.0ppm. Another instance of where the concentration of a toxic compound was likely to get out of hand was in a situation where 5ppm TCE and about 5ppm O₃ might be present. At condition, the concentration of CCl₄ (Carbon tetrachloride) could be as high as 2.5ppm while the recommended TLV for CCl₄ was 5ppm. Figure 9 through 12 are summarized on Table 4. Also at 10.0ppm of TCE and 10.0ppm of O₃, the concentration of CCl₄ could go up to 5.01ppm which is slightly higher than the TLV. The Figures 13 through 16 are summarized in Table 5.

After these studies were conducted, the effect of moisture on the concentrations of the twenty toxic compounds was decided to be studied. The only change that had to be introduced from the earlier study was to incorporate some moisture as an initial condition of the 'STANJAN' package. This study was conducted at the following initial conditions.
Figure - 9

COCl₂ vs. Ozone at 5ppm TCE.
Figure - 10

$Cl_2$ vs. Ozone at 5ppm TCE.
Figure - 11

CHCl₃ vs. Ozone at 5ppm TCE.
Figure - 12

CCL₄ vs. Ozone at 5ppm TCE.
### Table 4

Concentrations of select compounds calculated using 'STANJAN' at different concentrations of ozone. All concentrations in ppm.

At 5 ppm TCE.

<table>
<thead>
<tr>
<th>Ozone</th>
<th>COCl₂</th>
<th>Cl₂</th>
<th>CO₂</th>
<th>CHCl₃</th>
<th>HCl</th>
<th>CCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TLV=0.1ppm</td>
<td>TLV=1ppm</td>
<td>TLV=5000ppm</td>
<td>TLV=10ppm</td>
<td>TLV=5ppm</td>
<td>TLV=5ppm</td>
</tr>
<tr>
<td>2.50</td>
<td>2.6x10⁻¹²</td>
<td>8x10⁻³⁵</td>
<td>3.75</td>
<td>1.4x10⁻⁵</td>
<td>3.75</td>
<td>4.1x10⁻⁸</td>
</tr>
<tr>
<td>3.33</td>
<td>8.6x10⁻¹¹</td>
<td>5.5x10⁻³²</td>
<td>5.00</td>
<td>2.2x10⁻⁶</td>
<td>4.99</td>
<td>3.2x10⁻⁵</td>
</tr>
<tr>
<td>5.00</td>
<td>2.9x10⁻⁹</td>
<td>9.7x10⁻¹⁸</td>
<td>7.50</td>
<td>9.8x10⁻¹⁸</td>
<td>5.00</td>
<td>2.50</td>
</tr>
<tr>
<td>6.66</td>
<td>3.8x10⁻²⁶</td>
<td>5.00</td>
<td>10.00</td>
<td>2.4x10⁻⁶⁷</td>
<td>5.00</td>
<td>3.2x10⁻³⁶</td>
</tr>
<tr>
<td>7.50</td>
<td>4.7x10⁻⁶³</td>
<td>7.50</td>
<td>10.00</td>
<td>7x10⁻¹⁴</td>
<td>1.4x10⁻¹⁴</td>
<td>4.8x10⁻¹⁰</td>
</tr>
<tr>
<td>10.00</td>
<td>4.5x10⁻⁶⁶</td>
<td>7.50</td>
<td>10.00</td>
<td>2x10⁻¹⁵⁴</td>
<td>4.4x10⁻⁹</td>
<td>4.5x10⁻¹¹⁶</td>
</tr>
</tbody>
</table>
Figure - 13

COCl₂ vs. Ozone at 10ppm TCE.
Figure - 14

Cl₂ vs. Ozone at 10ppm TCE.
Figure - 15

CHCl₃ vs. Ozone at 10ppm TCE.
Figure - 16

$\text{CCl}_4 \text{ vs. Ozone at 10ppm TCE.}$
Table 5

Concentrations of select compounds calculated using 'STANJAN' at different concentrations of ozone. All concentrations in ppm.

At 10 ppm TCE.

<table>
<thead>
<tr>
<th>Ozone</th>
<th>COCl₂</th>
<th>Cl₂</th>
<th>CO₂</th>
<th>CHCl₃</th>
<th>HCl</th>
<th>CC₁₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>TLV=0.1 ppm TLV=1 ppm TLV=5000 ppm TLV=10 ppm TLV=5 ppm TLV=5 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.50</td>
<td>1.2×10⁻¹⁶</td>
<td>6.6×10⁻⁴⁶ 8×10⁻¹⁰⁵ 3.1×10⁻¹⁸</td>
<td>5.5×10⁻¹⁴ 5.0×10⁻¹⁹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.33</td>
<td>2.2×10⁻¹⁶</td>
<td>7.4×10⁻⁴⁶ 2×10⁻¹⁰⁴ 2.7×10⁻¹⁸</td>
<td>5.5×10⁻¹⁴ 4.7×10⁻¹⁹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.00</td>
<td>6.3×10⁻¹⁴</td>
<td>1.6×10⁻³⁴ 7.50</td>
<td>4.0×10⁻⁰⁶ 7.50</td>
<td>1.1×10⁻⁰⁷</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.66</td>
<td>1.9×10⁻¹²</td>
<td>9.3×10⁻³² 10.00</td>
<td>6.3×10⁻⁰⁶ 10.00</td>
<td>7.7×10⁻⁰⁵</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.50</td>
<td>2.5×10⁻¹¹</td>
<td>1.8×10⁻²⁹ 11.25</td>
<td>5.4×10⁻⁶ 10.00</td>
<td>1.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.00</td>
<td>5.9×10⁻¹¹</td>
<td>1.9×10⁻¹⁷ 15.00</td>
<td>2×10⁻¹⁷ 10.00</td>
<td>5.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Ozone Concentration fixed at: 5 ppm.
TCE Concentration fixed at: 5 ppm.
H₂O concentration varying from: 0 ppm to 10.0 ppm.

It was generally observed, as can be seen in Figures 17 through 20, that more the moisture present in the system lesser of the toxic compounds like COCl₂ (phosgene), CCl₄, Cl₂ and CHCl₃ (chloroform) were formed. Only HCl was found to be formed much above its recommended Threshold level value of 5 ppm, and its concentration increased with the amount of moisture present.

In summary, on completing the thermodynamic study using 'STANJAN', one can conclude that there are at least 3-4 instances where highly toxic compounds could be formed in levels much higher than the recommended threshold level values, if some liquid like cleaning fluid containing chlorinated compounds like TCE were inadvertently spilled in the vicinity of the operating indoor air quality system even at concentrations of 5-10 ppm, highly toxic compounds might be formed. Another point that could raise concern is that the concentrations predicted by 'STANJAN' using the method of element potentials is based on infinite contact time and so it only predicts the equilibrium concentrations. The study
Figure - 17

$\text{COCl}_2$ vs $\text{H}_2\text{O}$ @ 5ppm TCE, 5ppm Ozone.
Figure - 18

CHCl₃ vs H₂O @ 5ppm TCE, 5ppm Ozone.
Figure 19

Cl₂ vs H₂O & 5 ppm TCE, 5 ppm Ozone.
Figure - 20

CCl₄ vs H₂O @ 5ppm TCE, 5ppm Ozone.
Table 6.

Concentrating of select compounds calculated using 'STANJAN', at different concentrations of \( \text{H}_2\text{O} \). All concentrations in ppm.

At 5ppm of \( \text{O}_3 \) and TCE.

<table>
<thead>
<tr>
<th>( \text{H}_2\text{O} )</th>
<th>COCl(_2)</th>
<th>CHCl(_3)</th>
<th>HCl</th>
<th>Cl(_2)</th>
<th>CO(_2)</th>
<th>CCl(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TLV=0.1ppm TLV=10ppm TLV=5ppm TLV=1ppm TLV=5000ppm TLV=5ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.50</td>
<td>2.2x10(^{-9})</td>
<td>9.8x10(^{-16})</td>
<td>10.0</td>
<td>9.8x10(^{-16})</td>
<td>8.75</td>
<td>1.25</td>
</tr>
<tr>
<td>5.00</td>
<td>1.1x10(^{-25})</td>
<td>5.7x10(^{-32})</td>
<td>15.0</td>
<td>5.7x10(^{-32})</td>
<td>10.0</td>
<td>2.86x10(^{-33})</td>
</tr>
<tr>
<td>6.66</td>
<td>7.9x10(^{-51})</td>
<td>4.8x10(^{-68})</td>
<td>15.0</td>
<td>3.26x10(^{-46})</td>
<td>10.0</td>
<td>1.35x10(^{-83})</td>
</tr>
<tr>
<td>7.50</td>
<td>5.2x10(^{-51})</td>
<td>2.6x10(^{-68})</td>
<td>15.0</td>
<td>2.6x10(^{-46})</td>
<td>10.0</td>
<td>5.9x10(^{-84})</td>
</tr>
<tr>
<td>10.00</td>
<td>2.6x10(^{-51})</td>
<td>9.1x10(^{-69})</td>
<td>15.0</td>
<td>1.8x10(^{-46})</td>
<td>10.0</td>
<td>1.5x10(^{-84})</td>
</tr>
</tbody>
</table>
does not take into account the kinetics of the reaction. Hence the study cannot predict whether the concentration levels will be approached from above or below. In other words, at 5ppm TCE and 5ppm O₃, the predicted concentration of COCl₂ which is $10^{-8.54}$, could be approached from either above 0.1ppm (TLV of COCl₂) or from below it. The degradation of TCE in the presence of helium, oxygen and water has been studied in a gas-phase photo-catalytic oxidation reactor using a TiO₂ catalyst (18). The reaction has resulted in the formation of hydrogen chloride, carbon monoxide, carbon dioxide, molecular chorine, dichloractyl chloride and phosgene. Possible mechanism for formation of phosgene are given. Similarly, unpublished studies by Woody (19) on the degradation of TCE using a UV catalyzed TiO₂ surface has shown that as much as 60% of the 100 to 300 ppm TCE could be transformed to phosgene in a system containing 1000 to 3000 ppm of water vapor. Changes in the catalyst system markedly decreased phosgene formation. Its formation is at least partially a function of the kinetic breakdown pattern. Finally a discussion took place following the paper presented by Anderson at the I and EC Special Symposium presented by ACS in Fall 1993, (20). He indicated that he had found no phosgene in testing conducted on photoactive titania breakdown. However, he operated at higher levels of saturated water. In conclusion, the
STANJAN modeling indicated concerns for phosgene formation particularly under low water content systems, and these concerns have been verified by recent experimental testing.

Aside from TCE, there is evidence that sun catalyzed oxidation in the atmosphere can create partially oxidized toxic products. A series of citations to Atkinson's research at the University of California suggest a real concern. See Appendix 4 for a list of relevant reference.

Perhaps as significant is the effect of ozone and nitrogen dioxide on the mutagenic transformation of dilute wood smoke observed by Kamens et al, the 13 reference cited in Appendix 4, but also cited as reference 21 in the bibliography of the thesis.

The Reaction Model

As stated in the earlier chapter, the conversion of ozone and the VOC's are assumed to be 50% and 10% and the adsorption equilibrium coefficients of ozone and the VOCs are assumed to be of the order of $10^4 \text{ (sec)}^{-1}$. These values are fictitious in that they are not based on any experimental evidence. They are used here to identify certain qualitative issues of relevance to the process.
They are, however, based on values estimated for traditional catalytic oxidation.\textsuperscript{17}

Now the differential equations, the initial conditions, the adsorption equilibrium coefficients and the values for α and σ, which depends on $k_1$, $k_2$, $K_{O3}$, $K_{VOCs}$ and $u$, were obtained by the running the program in conjunction with the IMSL routine IVPAG and the conversions of ozone and the VOC's were calculated. For the 50\% and 10\% conversions of the ozone and the VOC's respectively the values of the lumped parameters α and σ are as follows:

$$\alpha = k_1 \cdot K_{O3} \cdot K_{VOCs} / u = 5 \times 10^5 \text{ dm}^{-3} \text{ (mol)}^{-1} \text{ (sec)}^{-0.2}.$$  

$$\sigma = k_2 \cdot K_{O3} / u = 2.5 \text{ (dm)}^{-1} \text{ (sec)}^{-1}.$$  

From these values of α and σ the values of the rate constants for the two reactions can also be approximated. The values for the rate constants $k_1$ and $k_2$ are calculated to be as follows

$$k_1 = 1.25 \times 10^{-2} \text{ liter.(mol)}^{-1} \text{ (sec)}^{-1}.$$  

$$k_2 = 6.25 \times 10^{-4} \text{ (sec)}^{-1}.$$
These values for the reaction rate constants are subject to the condition that the adsorption equilibrium coefficients for both the VOCs and ozone are of the order of $10^4$ (sec)$^{-1}$. So once the adsorption equilibrium coefficients for the VOCs and ozone are correctly known, the reaction rates $k_1$ and $k_2$ can be determined. Appendix 3 gives a copy of the programming used.
Effect of Moisture

After incorporating the presence of water and arriving at equations (7) and (8), the conversions of the VOCs and ozone were calculated at various relative humidities. As shown in the Figure 21, the conversion of both the VOCs and the ozone decrease with increasing relative humidities. But, the fall of ozone decomposition seems to be lower than that of the VOC oxidation. At 100% relative humidity, the ozone decomposition falls by about 65% whereas the VOC oxidation falls by about 90%. This is because the factor $\delta \cdot C_{H2O}$ which appears in the denominator of equations (7) and (8) is subject to an exponent of 2 in the VOC oxidation expression. Hence, greater the contribution of $\delta \cdot C_{H2O}$ to the denominator, greater is the drop in VOC oxidation as compared to the drop in ozone decomposition. Since the VOC oxidation is to be maximised, the indoor air quality unit should be operated at a low relative humidity or if possible in the absence of moisture. An adsorption equilibrium coefficient of $10^{-1}$ (sec)$^{-1}$ was assumed for water, due to lack of data. This assumption is not based on any experimental evidence and is fictitious. The effect of moisture is related to the value of $\delta$, which is the adsorption equilibrium coefficient of water on the catalyst
Figure 21. Reactions at 59° F and 77° F.
surface.

**Effect of temperature**

To see what the effect of temperature could be on the two reactions, the equations (5) and (6) were solved at two temperatures, 59°F and 77°F. As shown in the Figure 22, both the VOC oxidation rate and the ozone decomposition rate increased with temperature. The increase in the ozone decomposition is much more substantial compared to the decrease in VOC oxidation. The increase of both the rates with temperature is because of the fact that with temperature, the rate constants were found to increase but the adsorption equilibrium coefficients were found to decrease. So, in equations (5) and (6), $\alpha$ and $\sigma$ in the numerators increased and, $\beta$ and $\Omega$ in the denominators decreased which suggests why both the rates of ozone decomposition as well as that of VOC oxidation increased with temperature. The rate of VOC oxidation however, increases just barely as compared to the rate of ozone decomposition. This could be due to the choice of the rate constants used for the VOC oxidation and ozone decomposition. Therefore the indoor air quality unit should be operated at a temperature lower than room temperature so
Figure 22. Conversion vs. % Relative Humidity.
that the ozone decomposition can be curbed.

In summary, if the rate constants and the adsorption equilibrium coefficients that were used for the qualitative study are close to the actual values, then it is recommended that the Union Carbide Indoor Air Pollution Abatement unit be operated at temperatures much lower than the room temperature and at very low or zero relative humidities, since these conditions would tend to minimise the undesired ozone decomposition reaction and maximise the desired VOC oxidation reaction.

**Suggested further work**

(1) Since the exact nature of the oxidation reaction of the VOC's with ozone is not known, global reaction rate expressions are assumed. But if the nature of the reactions can be accurately predicted then this would lend more accuracy to the model.

(2) Also some other model for surface adsorption could be used instead of the Langmuir isotherms. If it is known that the multi-layer adsorption takes place on the surface of the catalyst, then a better model to use would probably be the
B.E.T. model.

(3) Once more data is available, statistical methods can be used to estimate the system parameters.
Conclusions

The ozone dispersion model, the thermodynamics study and the reaction model provide an overall theoretical approximation to the experimental pilot plant run by Union Carbide. Although the models discussed in this paper are only first approximations, by implementing the changes discussed in the suggested future work it could be put to better use.

In the ozone dispersion model, using a constant velocity for the air-ozone stream is the simplest way to approach such a problem. By using a turbulent velocity profile, a better simulation of the concentration velocity profile for ozone should be obtained. The ozone dispersion model could really be put to good use by Union Carbide in monitoring any pilot plant activities at Blacksburg, VA. The model should provide a first approximation for selecting points for ozone concentration. For instance, initially along the duct the concentration of ozone changes drastically with distance traversed along the duct, but the downstream concentration reaches a steady state concentration very slowly. This could help the Union Carbide team to establish the following:
1. A cut-off length after which they could place the catalyst bed.

2. The effect flow conditions and geometrical addition configurations would have on the steady state concentration of ozone.

3. The feasibility and optimization of different duct designs could be evaluated first using the ozone dispersion model. For instance, by making minor changes to the ozone dispersion model, one could get the concentrations profile of ozone for the case where ozone is introduced just before a right angled bend. The steady state concentration profile of ozone could be expected much earlier in this case and so the extra length of the duct could be saved. The modeling does, however, become much more complex if a bend is included in the simulation.

Similarly, the STANJAN model could be used to predict the breakdown path to equilibrium. A series of equilibrium studies can help to report under what ozonation conditions pretargeted toxic compounds might approach or exceed their threshold limits. Having determined problem compounds, then pilot testing could be conducted perhaps under dry and/or partially saturated air conditions to verify any tendency to form.
The reaction models, while still requiring some verification, could provide insight into how ozonation reactions could be affected by temperature and humidity conditions.
Bibliography


2. Molhave, L., (1990), Indoor Climate, Air Pollution and Human Comfort. Accepted for Toxic and Industrial Health; Special issue on total exposure assessment.

3. Fanger, P. O., J. Lauridsen, P. Bluysen, and G. Clausen, Air Pollution Sources in Office and Assembly Halls, Qualified by the Olf Unit; Energy and Building. 1988, 12, 7-19.


APPENDIX - 1

PDETWO

C THIS PROGRAM IS TO BE USED IN CONJUNCTION WITH AND AS AN INTERFACE FOR
C THE PACKAGE PDDEO, WHICH SOLVES 2-DIMENSIONAL NON-LINEAR DIFFERENTIAL
C EQUATIONS. THIS PACKAGE WAS DEVELOPED JOINTLY BY D.K. MELGARD AND
C R.F. SINCOVEC AND PUBLISHED IN THE "ACM TRANSACTIONS ON MATHEMATICAL
C SOFTWARE" 7, 1 (MARCH 1981).

C THIS PROGRAM WITH THE PDDEO PACKAGE, GENERATES CONCENTRATION PROFILES OF
C THE OZONE AT VARIOUS POINTS ALONG THE LENGTH OF THE DUCT.

C PROGRAMMER — SURYA RAO.

C

IMPLICIT REAL*8(A-H,O-Z)
INTEGER IX,NPDE,NSTEP,NX,NFE,NODE,MF,MY,NRIWK,
* - NJE,NQUSED,LY,INDEX.I,IWORK,KODE,IK,MORDER,LU,LPW,NRIWK
PARAMETER( NPDE=1, NX=73, NY=73, MF=23, MORDER=5)
PARAMETER( NODE=NPDE*XNX NY)
PARAMETER( LPW=(3*(NX+1)*NPDE-2)*NODE, LU=NODE*(MORDER+1) )
PARAMETER( NRIWK=NPDE*(NPDE*(NX+3) + 13 + NX)*NX+4+4*NODE+LPW+LU )
PARAMETER( WRNK=NODE )
COMMON /GEARS/ HUSED,NQUSED,NSTEP,NFE,NJE
COMMON /PROB/ DL,DLI,KODE
DIMENSION CI(NX, NY)
DIMENSION WORK(NRRIWK), IWORK(NRIWK), X(NX), Y(NY)

* * DEFINE THE PROBLEM PARAMETERS. *
* *
* *
WRITE (6,110)
110 FORMAT(1H1, 3X, 36HOUTPUT FROM EXAMPLE 1. ELLIPTIC PDE/)

INDEX=1
T0=0.0
H=0.1D-06
EPS=0.1D-06
DX = 2.0/(DFLOAT(NX)-1.0)
DY = 1.0/(DFLOAT(NY)-1.0)
DO 120 IX=1,NX
120 XIX=DFLOAT(IX)*DX
INORK(1) = NPDE
INORK(2) = NX
INORK(3) = NY
INORK(4) = MORDER
INORK(5) = NRIWK
INORK(6) = NRIWK

* AT POINTS P1 AND P2 THE OZONE IS BEING INTRODUCED. *
* *
* *
P10 = (((NY-1)/4)+1)
P1I = P10 - 1
P12 = P10 - 2
P13 = P10 - 3
P14 = P10 - 4
P15 = P10 + 1
P16 = P10 + 2
P17 = P10 + 3
P18 = P10 + 4
P20 = ((3×(NY-1)/4)+1)
P21 = P20 - 1
P22 = P20 - 2
P23 = P20 - 3
P24 = P20 - 4
P25 = P20 + 1
P26 = P20 + 2
P27 = P20 + 3
P28 = P20 + 4

*DEFINE THE INITIAL CONDITION AT POINTS P1 TO P28 WHERE THE OZONE IS
*INTRODUCED THE CONCENTRATION IS SPECIFIED AT ALL OTHER POINTS THE
*C CONCENTRATION OF OZONE IS ZERO INITIALLY, THAT IS, IN THE INITIAL MESH

DO 160 IY = 1,NY
   DO 160 IX = 1,MX
      IF(IY.EQ.P10.OR.IY.EQ.P11.OR.IY.EQ.P12.OR.IY.EQ.P13.OR.IY.EQ.P14
        .OR.IY.EQ.P26.OR.IY.EQ.P27.OR.IY.EQ.P28) THEN
         CI(IX,IY) = (5.00×NY/18.0)
      ELSE
         CI(IX,IY) = 0.0
      ENDIF
   160 CONTINUE

*THE WRITE STATEMENT FOR THE INITIAL CONCENTRATION OF THE OZONE.

C WRITE (6,170) NODE,T0,H, EPS, MF, C1
C 170 FORMAT(/6H NODE,13.4H T0, 13,4H EPS, MF ,
C    ICE1//16H INITIAL VALUES /10(/3H ,.10E11.2))
C 129 CONTINUE

*SET UP THE LOOP FOR CALLING THE INTEGRATOR AT DIFFERENT TOUT VALUES*

I = 1
DO 260 J=1,6
   IF (I .EQ. 1) TOUT = .001
   IF (I .EQ. 2) TOUT = .365
   IF (I .EQ. 3) TOUT = 1.512
   IF (I .EQ. 4) TOUT = 2.57
   IF (I .EQ. 5) TOUT = 3.767
   IF (I .EQ. 6) TOUT = 6.500
   WRITE (6,200) TOUT
   200 FORMAT (/6H TOUT, E15.6)
** CALL THE INTEGRATOR **
CALL DRIVEP (NODE, TD, H, C1, TOUT, EPS, MF, INDEX, WORK, IWORK, X, Y)

* CHECK ERROR RETURN *
* IF (INDEX .NE. 0) GOTO 1000 *

* OUTPUT THE RESULTS *
* IF (NY .EQ. 25) INCR = 1
* IF (NY .EQ. 49) INCR = 2
* IF (NY .EQ. 75) INCR = 4
* IF (NY .EQ. 97) INCR = 5
* IF (NY .EQ. 11) INCR = 1
* DO 219 IX = 1, NX
  DO 219 IY = 1, NY
  IF (C1(IX, IY) .LT. 0.0) C1(IX, IY) = -1 * C1(IX, IY)

  219 CONTINUE
  WRITE (6, 220) HUSED, NUSED, NSTEP, NFE, NJE
  FORMAT (/, 7H HUSED, 2E10.4, 7H ORDER, I3, 7H NSTEP, I6, 5H NFE, I5,
  5H NJE, I5)
  WRITE (6, 230) (C1(IX, IY), IX=1,111, IY=1, NY, INCR)
  230 FORMAT (79H U VALUES, /*13H, 11E11.4))

* CALCULATIONS FOR MAXIMUM, MINIMUM AND AVERAGE CONC. VALUES. *

C MAX = 0.0
C MIN = C1(1,1)
C CTOT = 0.0
* DO 240 IX = 1, NX
  DO 240 IY = 1, NY
    CTOT = CTOT + C1(IX, IY)
    IF (C1(IX, IY) .GT. CMAX) CMAX = C1(IX, IY)
    IF (C1(IX, IY) .LT. CMIN) CMIN = C1(IX, IY)

  240 CONTINUE
  CAVG = CTOT/NODE
  WRITE (6, 250) CAVG
  FORMAT (/, 42H TOTAL CONC. AT THIS LENGTH DOWN THE DUCT //
  3H, E11.4))
  WRITE (6, 251) CMIN
  251 FORMAT (/, 43H MINIMUM CONC. AT THIS LENGTH DOWN THE DUCT //
  3H, E11.4))
  WRITE (6, 252) CMAX
  252 FORMAT (/, 43H MAXIMUM CONC. AT THIS LENGTH DOWN THE DUCT //
  3H, E11.4))
  WRITE (6, 253) CAVG
  253 FORMAT (/, 43H AVERAGE CONC. AT THIS LENGTH DOWN THE DUCT //
  3H, E11.4))
  I = I+1

  260 CONTINUE
C
1000 STOP
END

******************************************************************************
SUBROUTINE BNDRYV (T,X,Y,U,AV,BV,CV,NPDE)
******************************************************************************

C
C DEFINE THE VERTICAL BOUNDARY CONDITIONS
C
REAL T,U,X,Y,AV,BV,CV
IMPLICIT REAL*8(A-H,O-Z)
INTEGER NPDE
COMMON /PROB/ DL,DLI,KODE
DIMENSION U(NPDE),AV(NPDE),BV(NPDE),CV(NPDE)
******************************************************************************
* VERTICAL BC COEFFICIENTS. *
******************************************************************************
AV(1) = 0.0
BV(1) = 1.0
CV(1) = 0.0
RETURN
END

******************************************************************************
SUBROUTINE BNDRYH (T,X,Y,U,AH,BH,CH,NPDE)
******************************************************************************

* * DEFINE THE HORIZONTAL BOUNDARY CONDITIONS
******************************************************************************
IMPLICIT REAL*8(A-H,O-Z)
INTEGER NPDE
COMMON /PROB/ DL,DLI,KODE
DIMENSION U(NPDE),AH(NPDE),BH(NPDE),CH(NPDE)

AH(1) = 0.0
BH(1) = 1.0
CH(1) = 0.0
RETURN
END

******************************************************************************
SUBROUTINE DIFFH (T,X,Y,U,DH,NPDE)
******************************************************************************

* * DEFINE THE HORIZONTAL DIFFUSION COEFFICIENTS
******************************************************************************
IMPLICIT REAL*8(A-H,O-Z)
INTEGER NPDE
COMMON /PROB/ DL,DLI,KODE
DIMENSION U(NPDE),DH(NPDE,NPDE)

DH(1,1) = 0.009856
RETURN
END
SUBROUTINE DIFFV (T,X,Y,U,DV,NPDE)

* DEFINE THE VERTICAL DIFFUSION COEFFICIENTS *

IMPLICIT REAL*8(A-H,O-Z)
INTEGER NPDE
COMMON /PROB/ DL,DLI,KODE
DIMENSION U(NPDE),DV(NPDE,NPDE)

DV(1,1) = 0.009856

RETURN
END

SUBROUTINE F(T,X,Y,U,UX,UY,DUXX,DUYY,DUDT,NPDE)

* DEFINE THE PDE *

IMPLICIT REAL*8(A-H,O-Z)
INTEGER NPDE
COMMON /PROB/ DL,DLI,KODE
DIMENSION U(NPDE),UX(NPDE),UY(NPDE),DUXX(NPDE,NPDE),
* DUYY(NPDE,NPDE),DUDT(NPDE)

DUDT(1) = DUXX(1,1) + DUYY(1,1)

RETURN
END
COMPUTED PROPERTIES.

<table>
<thead>
<tr>
<th>INDEPENDENT ATOM</th>
<th>POPULATION</th>
<th>ELEMENT POTENTIAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1.000000000E-03</td>
<td>7.8529E+01</td>
</tr>
<tr>
<td>H</td>
<td>5.000000000E-04</td>
<td>-5.6608E+01</td>
</tr>
<tr>
<td>Cl</td>
<td>1.500000000E-03</td>
<td>-5.3045E+01</td>
</tr>
<tr>
<td>O</td>
<td>1.000000000E-03</td>
<td>-2.1713E+02</td>
</tr>
<tr>
<td>N</td>
<td>1.999960000E+02</td>
<td>-1.1534E+01</td>
</tr>
</tbody>
</table>

Products at $T = 298.15$ K  $P = 1.000E+00$ atmospheres.

Phase 1: Molal mass = 28.00 Kg/kmol.

<table>
<thead>
<tr>
<th>species</th>
<th>mol fracn</th>
<th>mass fracn</th>
<th>mols*</th>
</tr>
</thead>
<tbody>
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<td>.999E+00</td>
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</table>

* Species mols for the atom population in mols.

Mixture properties: molal mass = 28.000 kg/kmol
$T = 298.15$ K ; $P = 1.0133E+05$ Pa ; $V = 8.7373E-01$ m³/kg.
$U = -.8871E+05$ J/kg ; $H = -.1758E+03$ J/kg ; $S = .6850E+04$ J/kg-K

Made 0 (T,P) iterations; 3 equilibrium iterations; v 3.89 IBM-pc.
COMPUTED PROPERTIES.

<table>
<thead>
<tr>
<th>INDEPENDENT ATOM</th>
<th>POPULATION</th>
<th>ELEMENT POTENTIAL</th>
</tr>
</thead>
<tbody>
<tr>
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<td>7.8529E+01</td>
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<td>H</td>
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<tr>
<td>Cl</td>
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<td>O</td>
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</tr>
<tr>
<td>N</td>
<td>1.999950000E+02</td>
<td>-1.1534E+01</td>
</tr>
</tbody>
</table>

Products at $T = 298.15 \, K$ $\quad P = 1.000E+00$ atmospheres.

Phase 1: Molal mass = 28.00 Kg/kmol.

species mol fracn mass fracn mols*

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
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<tbody>
<tr>
<td>CHCl=CH$_3$</td>
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<td>.120E-26</td>
<td>5.389E-26</td>
</tr>
<tr>
<td>CHCl=CHCl</td>
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<td>Cl$_2$</td>
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<td>HCl</td>
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<td>9.999E+01</td>
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</table>

* Species mols for the atom population in mols.

Mixture properties: molal mass = 28.000 kg/kmol
$T = 298.15 \, K$ $\quad P = 1.0133E+05 \, \text{Pa}$ $\quad V = 8.7373E-01 \, \text{m}^3/\text{kg}$.
$U = -.8871E+05 \, \text{J/kg}$ $\quad H = -.1758E+03 \, \text{J/kg}$ $\quad S = .6850E+04 \, \text{J/kg-K}$

Made 0 ($T,P$) iterations; 3 equilibrium iterations; v 3.89 IBM-pc.
COMPUTED PROPERTIES.

<table>
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<th>INDEPENDENT ATOM</th>
<th>POPULATION</th>
<th>ELEMENT POTENTIAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1.00000000E-03</td>
<td>1.7226E+01</td>
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<td>H</td>
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<td>N</td>
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Products at $T = 298.15 \text{ K}$ $\quad P = 1.000E+00$ atmospheres.

Phase 1: Molal mass = 28.00 Kg/kmol.

<table>
<thead>
<tr>
<th>species</th>
<th>mol fracn</th>
<th>mass fracn</th>
<th>mols*</th>
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<td>0.999E+00</td>
<td>9.999E+01</td>
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</table>

* Species mols for the atom population in mols.

Mixture properties: molal mass = 28.000 kg/kmol
$T = 298.15 \text{ K} \quad P = 1.0133E+05 \text{ Pa} \quad V = 8.7373E-01 \text{ m}^3/\text{kg}$.
$U = -.8879E+05 \text{ J/kg} \quad H = -.2624E+03 \text{ J/kg} \quad S = .6850E+04 \text{ J/kg-K}$

Made 0 (T,P) iterations; 1 equilibrium iterations; v 3.89 IBM-pc.
APPENDIX - 2

The Element-Potential Method For Chemical Equilibrium Analysis

Introduction

The element-potential method for chemical equilibrium analysis is a powerful tool which is not very widely used for the reason that is almost unknown. The problem of solving for equilibrium values can be solved in various ways. If the concept of equilibrium constants is used, then it is necessary that the set of reactions that take place be identified first. Then it is necessary to determine the the equilibrium constants of the reactions that have been identified. In many cases both the above steps may be difficult if not impossible and in may other cases the trouble might not be worthwhile. Other methods involve minimization of the Gibbs free energy. The mols of the different species are adjusted till the minimum Gibbs function is realised. Here also there are many functions
involved and great care must be taken to see that the mols are non-negative.

The method of element-potentials was developed early by Powell\textsuperscript{11} and a powerful numerical implementation was developed by Reynolds\textsuperscript{12}. This numerical implementation was given the name 'STANJAN'. For pre-STANJAN history of the method, see Van Zeggeren and Storey\textsuperscript{14}.

The method of element potentials uses theory to relate the mol-fractions of each species to quantities called element potentials. Each independent atom in the system has one element potential, and these element potentials together with the total number of mols in the system are the only variables to adjusted to arrive at a solution for any equilibrium related problem. The program is called STANJAN because of its roots at Stanford and its connection with the JANNAF thermochemical data tables. STANJAN is an interactive program that can be used both on desk-top computers as well as on main-frame computers.

The assumptions made by STANJAN are that the gas phase is a mixture of ideal gases and that the condensed phases are ideal solutions. For most practical purposes these are very valid assumptions.
Using STANJAN, the user specifies the species in each phase and their mol numbers and also the state parameters. STANJAN then solves for the equilibrium state using the method of element potentials. The results supply the user information about the composition of each phase and also the thermodynamic properties of the system.

The state parameters that the user can specify include
1. temperature and pressure.
2. pressure and entropy.
3. enthalpy and pressure.
4. volume and entropy.

In conclusion, STANJAN is a powerful and easy-to-use program for the computation of chemical equilibrium in single or multiple-phase systems. For more information on the how the latest numerical implementation can be used for purposes other than those mentioned above, see Reynolds$^{12}$.

**The Basic Theory of the Method of Element Potentials**

The Gibbs function of a system is:
\[ G = \sum_{j=1}^{s} \tilde{g}_{j} N_{j} \quad \ldots \ldots \ldots (1) \]

where \( g_{j} \) is the partial molal Gibbs function and \( N_{j} \) is the number of mols of the species \( j \), and \( s \) is the total number of mols in the system. Assuming that each phase in the system is either a mixture of ideal gases or an ideal solution, the partial molal Gibbs function can be written as:

\[ \tilde{g}_{j} = g_{j}(T,P) + RT \ln x_{j} \quad \ldots \ldots \ldots (2) \]

where \( g_{j}(T,P) \) is the Gibbs function of pure \( j \) calculated at the system temperature and pressure, \( x_{j} \) is the mol fraction of \( j \) in its phase, and \( R \) is the universal gas constant. The atomic population has to follow the following rule.

\[ \sum_{j=1}^{s} n_{ij} N_{j} = p_{i}, i = 1, \ldots, a \quad \ldots \ldots \ldots (3) \]

where \( n_{ij} \) is the number of \( i \) atoms present in a \( j \) molecule, \( p_{i} \) is the number of mols of \( i \) atoms in the system, and \( a \) is the number of different atom types present in the system. To find the equilibrium solution, one has to find the distribution of \( N_{j} \) that minimises \( G \) at the given \( T \) and \( P \) and subject to the atomic constraints.
Let $g_j' = g_j (T,P)/RT$ for convenience. Differentiating (1) we have:

$$d(G/RT) = \sum_{j=1}^{i} (g_j' + \ln x_j) dN_j + \sum_{j=1}^{i} \frac{\dot{N}_j}{x_j} dx_j \ldots \ldots \ldots (4)$$

The number of mols in phase $m$ are denoted by $N_m$.

$$x_j = N_j / N_{(j)} \ldots \ldots (5)$$

where $N_{(j)}$ is the number of mols in the phase having species $j$. The second summation in (4) can be re-written as:

$$\sum_{m=1}^{p} \dot{N}_m \sum_{j=1}^{i} dx_j$$

where $p$ is the total number of phases which might be present. The above expression vanishes because the mol fraction in each phase has to sum upto 1. The $dN_j$ in (4) are all not independent and an expression relating them can be obtained by differentiating (3).

$$\sum_{j=1}^{i} \eta_j d_j = 0, \ i = 1, \ldots, \alpha \ldots \ldots (6)$$
Now, we must solve for the a restricted $dN_j$ in terms of the s-a free $dN_j$ and then plug these expressions into (4) so that we can express G in terms of the independent variable $N_j$ only. To do this we can multiply (6) by lagrange multipliers $\delta_i$ and then subtract (6) from (4). After doing this we obtain:

$$d(G/RT) = \sum_{j=1}^{s} (g_j + \ln x_j) dN_j - \sum_{i=1}^{a} \delta_i \sum_{j=1}^{s} n_{ij} \dot{dN}_j$$

...(7)

These $\delta_i$'s are the multipliers that are required to drop out the set of restricted $dN_j$ from the equation. Since the $G/RT$ is required to be minimum, $d(G/RT)$ is required to be zero. Hence the coefficients of the $dN_j$ on the right hand side of the above equation can be set to zero.

$$g_j + \ln x_j - \sum_{i=1}^{a} \delta_i n_{ij} = 0$$

...(8)

From the above expression we get:

$$x_j = \exp\left(-g_j + \sum_{i=1}^{a} \delta_i n_{ij}\right)$$

...(9)

Equation (9) is the main result of the theory of element
potentials for the mixture of ideal gases and for ideal solutions. It relates the mol fraction in each phase to the \( g(T,P)/RT \), the atomic structure of the molecule and the element potentials (the lagrange multipliers \( \delta_i's \)). From (2) and (8) we see that

\[
g_j / RT = \sum_{i=1}^{a} \partial_i n_y \quad \ldots (10)\]

So we see that \( \delta_i \) represents the Gibbs function/RT per mol of atoms. Rewriting (3) as

\[
\sum_{j=1}^{i} n_y N_{ij} x_j = p_i \quad i = 1, \ldots, a \quad \ldots (11)\]

Using equation(9) which gives an expression for \( x_j \) and substituting it into (11), we get a set of equations relating the unknowns \( \delta_i \) and \( N_m \). To these set of equations we add the \( p \) equations,

\[
\sum_{j=1}^{i} x_j = 1, \quad m = 1, \ldots, p \quad \ldots (12)\]

Equations (11) and (12) must be solved simultaneously for determining the element potentials and phase mols. Mol
iteration methods must be wary of negative mols, which can never be a problem with the mol fractions which are generated by equation(9).
APPENDIX - 3

IVPAG PROGRAM

PROGRAM RXN2

INTEGER NPARAM, NEQ
PARAMETER (NPARAM = 50, NEQ = 2)

INTEGER IDO, NOUT, IMETH, INORM, IEND
REAL A(1,1), FCN, FCNJ, HINIT, PARAM(NPARAM), TOL, X, XEND
REAL Y(NEQ), P, Q, R
EXTERNAL FCN, IVPAG, SSET, UMACH

METH = 2
MITER = 3
HINIT = 1.0E-03
INORM = 2
IMETH = 1
CALL SSET (NPARAM, 0.0, PARAM, 1)
PARAM(1) = HINIT
PARAM(10) = INORM
PARAM(12) = IMETH

P = 1.0E+75
Q = 1.0E+75
R = 1.0E+05

IDO = 1
X = 0.0
Y(1) = 1.0E-06
Y(2) = 5.0E-06

TOL = 1.0E-06
CALL UMACH (2, NOUT)

WRITE (NOUT, 99998)

DO 10 IEND = 1, 10
   XEND = IEND * 0.025
   CALL IVPAG (IDO, NEQ, FCN, FCNJ, A, X, XEND, TOL, PARAM, Y)
   WRITE (NOUT, 99999) X, Y
   10 CONTINUE

IDO = 3
CALL IVPAG (IDO, NEQ, FCN, FCNJ, A, X, XEND, TOL, PARAM, Y)
99998 FORMAT (1lx, 'X', 14x, 'Y(1)', 1lx, 'Y(2)')
99999 FORMAT (4E15.5)

END

SUBROUTINE FCN (NEQ, X, Y, YPRIME)
INTEGER NEQ
REAL X, Y(NEQ), YPRIME(NEQ), P, Q, R

C
YPRI ME(1) = -5.0E+05*Y(1)*Y(1)/(1+1.0E+04*(Y(1) + Y(2)))*12
YPRI ME(2) = -2.5E+00*Y(2)/(1 + 1.0E+04*(Y(1) + Y(2)))

RETURN
END

SUBROUTINE FCNJ (NEQ, X, Y, DYP DY)

INTEGER NEQ
REAL X, Y(NEQ), DYP DY(*), P, Q, R

RETURN
END
PROGRAM RXN2

INTEGER NPARAM, NEQ
PARAMETER (NPARAM = 50, NEQ = 2)

INTEGER I0, IOUT, IMETH, INORM, IEND
REAL A(1,1), ECN, ECNJ, HINIT, PARAM(NPARAM), TOL, X, XEND
REAL Y(NEQ)
EXTERNAL FCN, IVPAG, SSET, UMACH

METH = 2
MITER = 5
HINIT = 1.0E-02
INORM = 2
IMETH = 1
CALL SSET (NPARAM, 0.0, PARAM, 1)
PARAM(1) = HINIT
PARAM(10) = INORM
PARAM(12) = IMETH

I0 = 1,
X = 0.0
Y(1) = 1.0E-04
Y(2) = 5.0E-04

TOL = 1.0E-06
CALL UMACH (2, NOUT)

WRITE (NOUT, 99993)
DO 10 IEND = 1, 10
XEND = XEND + 4.0 + 10.0
CALL IVPAG (I0, NEQ, FCN, FCNJ, A, X, XEND, TOL, PARAM, Y)
WRITE (NOUT, 99999) X, Y
10 CONTINUE

I0 = 3
CALL IVPAG (I0, NEQ, FCN, FCNJ, A, X, XEND, TOL, PARAM, Y)
99998 FORMAT (11X, X, 14X, Y(1), 11X, Y(2))
99999 FORMAT (4E15.5)

END

~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
SUBROUTINE FCN (NEQ, X, Y, YPRIME)
INTEGER NEQ
REAL X, Y(NEQ), YPRIME(NEQ)

YPRIME(1) = -1.0E-27 + Y(1)*Y(2)/(1+7.92E+05*(Y(1)+Y(2)))**2

YPRIME(2) = -1.25E-13*Y(2)/((1+7.92E+05*(Y(1)+Y(2))))

RETURN
END

~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
SUBROUTINE FCNJ (NEQ, X, Y, CYPDY)
INTEGER NEQ
REAL X, Y(NEQ), CYPDY(*)

RETURN
END
### USING IVPRK

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<tr>
<th>STEP</th>
<th>Y1</th>
<th>Y2</th>
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<td>0.000</td>
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### USING IVPAG

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<th>OUTPUT</th>
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<th>V 45</th>
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<tr>
<td>X</td>
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<td>Y(2)</td>
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<tr>
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</table>
PROGRAM RXN

INTEGER MXPARN, NEQ
PARAMETER (MXPARN = 50, NEQ = 2)

INTEGER IDO, ISTEP, NOUT
REAL FCN, FLOAT/PARAM(MXPARN), T, TEND, TOL, Y(NEQ)
EXTERNAL FCN, IVPRK, SSET, UMACH

CALL UMACH(2, NOUT)

T = 0.0
Y(1) = 1.0E-04
Y(2) = 2.0E-04

TOL = 0.00005

CALL SSET (MXPARN, 1.0, PARAM, 1)

PARAM(10) = 1.0

WRITE (NOUT, 39999) FORMAT (4X, 'ISTEP', 5X, 'DIST', 9X, 'Y1', 11X, 'Y2')

IDO = 1
DO 10 ISTEP = 1/10
THE LENGTH IS IN DECIMETERS, 10M = 4 INCHES(APPROX.)
THE LENGTH ALONG THE REACTOR IN INCHES.
TEND = FLOAT(ISTEP) * 4.00
CALL IVPRK (IDO, NEQ, FCN, T, TEND, TOL, PARAM, Y)
WRITE (NOUT, '(16.3E+2.5)') ISTEP, T, Y
10 CONTINUE

IDO = 3
CALL IVPRK (IDO, NEQ, FCN, T, TEND, TOL, PARAM, Y)
END

SUBROUTINE FCN (NEQ, T, Y, YPRIME)
INTEGER NEQ
REAL T, Y(NEQ), YPRIME(NEQ)

YPRIME(1) = -1.78E-07 - Y(1) * Y(2) / (1 + (7.92E+05 * Y(1))
+ (7.92E+05 * Y(2)) + 2
YPRIME(2) = -1.25E-27 - Y(2) / (1 + (7.92E+05 * Y(1)) +
+ (7.92E+05 * Y(2)) )

RETURN
END
\[ \begin{align*} 
C_6H_6 + O_3 & \xrightarrow{k_1} \text{products} \\
O_3 & \xrightarrow{30} \\
\gamma_1 & = -k_1 \Theta_{voc} \Theta_{O_3} \\
\gamma_2 & = -k_2 \Theta_{O_3} \\
\Theta_{O_3} & = \frac{k_{O_3} [O_3]}{1 + k_{O_3} [O_3] + k_{C_6H_6} [VOC]} \\
\Theta_{voc} & = \frac{k_{voc} [voc]}{1 + k_{O_3} [O_3] + k_{voc} [voc]} \\
\gamma_1 & = -k_1 k_{O_3} k_{voc} [O_3] [voc] \\
& \quad \div (1 + k_{O_3} [O_3] + k_{voc} [voc]) \\
\gamma_2 & = -k_2 k_{O_3} [O_3] \\
& \quad \div (1 + k_{O_3} [O_3] + k_{voc} [voc]) 
\end{align*} \]
Differential Equations:

\[ \frac{dY_1}{dt} = -K_1R_03k_{voc}Y_1Y_2 \left( \frac{1}{1 + K_03Y_2 + k_{voc}Y_1} \right)^2 \times \frac{-2.5 \times 10^{-7}Y_1Y_2}{\left[1 + 1.32 \times 10^5(Y_1 + Y_2)\right]^2} \]

\[ \frac{dY_2}{dt} = -K_2K_03Y_2 \left( \frac{1}{1 + K_03Y_2 + k_{voc}Y_1} \right)^2 \times \frac{-3.11 \times 10^{-27}Y_2}{\left[1 + 1.92 \times 10^5(Y_1 + Y_2)\right]} \]

If velocity through the reaction bed is \( V = 0.25 \text{ m/s} \), then,

\[ \frac{dY_1}{dx} = \frac{0.25 \times 0.25}{2.5 \text{ dm/s}} \]

\[ \frac{dY_2}{dx} = \frac{-1.25 \times 10^{-27}Y_2}{\left[1 + 1.92 \times 10^5(Y_1 + Y_2)\right]} \]
Influential Equations: 

$$\frac{dY_1}{dt} = -K_1 K_{03} k_{voc} \frac{Y_1 Y_2}{(1 + K_{03} Y_2 + k_{voc} Y_1)^2} \frac{-2.5 \times 10^{-7} Y_1 Y_2}{[1 + 1.92 \times 10^5 (Y_1 + Y_2)]^2}$$

$$\frac{dY_2}{dt} = -K_2 K_{03} \frac{Y_2}{(1 + K_{03} Y_2 + k_{voc} Y_1)} \frac{-3 \times 10^{-27} Y_2}{[1 + 7.92 \times 10^5 (Y_1 + Y_2)]}$$

If water flows through the reactor bed in \( U = 0.25 \text{ m/s} \), then,

$$\frac{dx}{dt} = 0.25 \text{ m/s} = 2.5 \text{ dm/s}$$

$$\frac{dY_1}{dx} = -10^{-7} \frac{Y_1 Y_2}{[1 + 7.92 \times 10^5 (Y_1 + Y_2)]}$$

$$\frac{dY_2}{dx} = -1.25 \times 10^{-27} Y_2 \frac{1}{[1 + 7.92 \times 10^5 (Y_1 + Y_2)]}$$
November 19, 1990

To: George Keller
From: Donald L. Michelsen
Subject: Ozonation Reaction Concerns

During the last month, I have been assembling and reviewing (in part) key articles on ozonation reactions—homogeneous air phase but some sunlight catalyzed. These were identified by the two groups of seniors involved in part on the project. A few articles on catalytic air (and oxygen) oxidation of organic have also been identified, but additional computer library searching seems desirable.

The kinetics of ozone reaction with various organic in dark environments without catalysts has been the subject of extensive research of the Statewide Air Pollution Research Center (SAPRC) in Riverside, California for about 15 years. Roger Atkinson is the key individual (714-787-4191 (O), 5124 (Secretary)). Their focus has been mostly concerned with depletion (disappearance of ozone not by-product formation), in the presence of numerous organic usually under dark conditions and certainly not in the presence of any oxidation catalyst. We have completed a literature search, xeroxed articles, and are in contact with Dr. Roger Atkinson (SAPRC). I have talked with him but the interpretation of literature (particularly formation of potential harmful by-products) is complex. I am also concerned with divulging classified information. There is a considerable body of literature on the catalytic oxidation of organic with air (and oxygen) at room and especially elevated temperatures. I have had several private conversations with Dr. Don van der Vaart, adjunct faculty at Virginia Tech, (804-979-8583) and collected copies of key articles. I plan to explore the oxidation of organic over catalyst in the presence of oxygen or air, but to sort out the thousands of references we must firm down potential toxic and harmful organic. A bibliography is attached and two copies of key articles are attached for UCC review. I have the original print-out from the chemical abstract search available to you upon request. Drawing from only a partial review of these articles several concerns surface.

The catalytic ozonation of cyclic chlorinated organic such as dichlorobenzene and benzyl chloride is of concern. For example, air oxidation of 1,2, DCB over V₂O₅ catalyst forms at room temperature produces maleic anhydride; 2-chloromaleic anhydride; 2,3 dichloromaleic anhydride; 1,2,3, trichlorobenzene; 1,2,4-trichlorobenzene, carbon dioxide, hydrochloric acid and water (Atalay and Alpay, 1987). With ozonation similar byproducts might be expected.
The catalytic ozonation of the short chain chlorinated paraffin such as trichloroethylene and tetrachloroethylene is hard to predict as they generally are slowly degraded by either non-catalytic ozonation or air oxidation of catalyst. However, breakdown chemistry suggests the dichlorocarbonyl and possibly vinyl chloride could be an intermediate and deserves investigation (Grossjean, 1990; Ramanathan and Spivey, 1989). The analytical problems are formidable but can we afford not to pursue them? Likely, this testing should be conducted first at UCC at South Charleston. FTIR analysis may be required; some limited analysis would be possible in the Department of Chemical Engineering. Furthermore, "A study of the OH radical reaction with allyl chloride by long path FTIR absorption spectroscopy indicated that the co-products C\text{7}CH\text{2}CHO and HCHO accounted for a 44% of the reaction..." (Tuazon et al. 1990).

The breakdown of many organic by catalytic ozonation should be complete but if any partial oxidation products are remaining HCHO (formaldehyde) and CHO or CHOCH may be present. With a low TLV for HCHO, specific analysis for formaldehyde would be desirable. Apparently FTIR works. The use of alumina adsorption followed by chromotropic acid-sulfuric acid spectrophotometric method may be feasible and provides a specific analysis for formaldehyde (NIOSH P & CAM 235).

The use of benzene for initial studies may be convenient because of considerable literature of carbon adsorption and the logical comparison which could be made. However, benzene is known to be "0" order reaction with air over catalyst at elevated temperatures. Thus, the study of benzene destruction by ozonation may be "too easy" and give a false unintended high destruction rate--atypical of other aromatics. We may be misleading ourselves.

The potential formation of harmful by-products from decomposition of nitrogen, amine, and sulfur containing organic seem less likely. However, the UCC oxidation catalyst may be subject to sulfur poisoning; some air oxidation catalysts are. A computer search of catalytic oxidation of nitrogen and sulfur containing would be appropriate. However, to sort out the huge number of citations it would be helpful if we had a number of possible suspect chemical by-products we thought might be present--as a starting point.

From talking with Atkinson we had better look at ozonation of terpenes as well. He is concerned about these reactions. I looked at copies of relevant articles, but I'm not sure what breakdown products might create problems. I felt it was not appropriate to contact him further until I cleared this with you.

Finally, there is strong evidence that dilute wood smoke (particulates) in the presence of 0.30 ppm of O\text{3} and .76 ppm NO\text{2} resulted in the higher concentration of mutagenic compounds (rev/mg) based on the salmonella trishiumurium plate incorporation assay (Ames test) (Kamens et al. 1985). Notice that Andrea Dietrich was a co-author on this paper.

In conclusion, the development of the appropriate pro-prototype should continue. However, a closer look at the breakdown chemistry at the laboratory level should continue incorporating GC/MS but also FTIR for identification of critical volatile constituents. In addition, this testing likely should consider and possibly address the formation of mutagenic compounds (Ames test) which if particularly effective for oxygenated straight chain and aromatic hydrocarbons. However, the test does not give reliable results for straight chain chlorinated organic such as TCE, PCE or vinyl chloride. These reaction and by-product
formation studies might be conducted in capillary reactors. However, UCC pilot plant with very thin catalyst beds might provide partial oxidation conditions and/or some by-pass as a function of ozone supplied and space velocity, and yield a smear of by-products.

I question seriously pushing ahead rapidly with pre-prototype testing until by-product formation as a function of operating conditions has been resolved including control logic to prevent occurrence (ever?) upon scale-up. The liability issue concerns me. Analytical protocol development could take some time.

cc:  William Conger
     Andrea Dietrich
     Pat Edwards
     Kim Harich
     Jay Miller
     Joan Rodberg
     Jim Woods
Bibliography

I. Ozonation


II. Catalytic Oxidation of Organics and Contaminant Analysis


21. Corchnoy & Atkinson: 2-Carene
Vita

The author, Surya Rao was born on October 21, 1967 to Prabharakar and Durga Rao, in Dehradun, India. After completing his schooling in Bombay, he joined the Indian Institute of Technology, Bombay with a Chemical Engineering major. He graduated in June, 1990 and later joined the Chemical Engineering Department of VPI & SU as a Masters Candidate in Fall 1990. The author plans to return to his country after obtaining his Masters in Chemical Engineering.

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Surya Rao
February, '92.