ENGINEERING EVALUATION AND CONTROL OF TOXIC AIRBORNE EFFLUENTS

Volume I

SINGLE DROPLET STUDIES OF SURROGATE HAZARDOUS WASTE INCINERATION

by

N.W. Sorbo and D.P.Y. Chang
Department of Civil Engineering
University of California
Davis, CA 95616

R.R. Steeper
Combustion Research Facility
Sandia National Laboratory
Livermore, CA 94550

C.K. Law
Department of Mechanical Engineering
University of California
Davis, CA 95616

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Mr. Joseph Pantalone
Contract Officer

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CONTENTS

	Page
Disclaimer	ii
Acknowledgements	iii
Contents	iv
Figures	v
Tables	vi
Nomenclature	vii
Glossary of Terms	viii
A. Introduction	1
B. Background	4
1. The Physics of Droplet Gasification	4
2. The Effect of Chlorine on Combustion Reactions	10
C. Experimental Methods	13
1. Description of Single Droplet Experimental Apparatus	13
2. Experimental Data Collected	15
3. Standard Operating and Analysis Procedures	18
4. Data Quality	19
D. Experimental Results and Discussion	20
1. Alkanes and Monochloroalkanes	20
2. Tetrachloroethane and Nonane	28
3. Tetrachloroethane and Alkanes	38
4. Tetrachloroethene and Octane	48
5. Chlorobenzenes	53
E. Research Implications for CARB	56
F. Summary and Conclusions	59
G. Future Work	62
References	63

LIST OF FIGURES

1. Schematic of burning droplet. 5

2. Gasification profile of a typical burning droplet. 7

3. Schematic of experimental apparatus. 14

4. Gasification profiles of hexadecane and 1-chlorohexane droplets in an oxidizing environment. 21

5. Gasification rate constants for n-alkane and 1-chloro-alkane droplet studies. 27

6. Gasification profile of tetrachloroethane droplets injected into oxidizing and inert environments. 30

7. Gasification profile of droplets of 75% tetrachloro-ethane + 25% nonane by volume (v/v) injected into an oxidizing environment. 33

8. Gasification profiles of droplets of 25%, 80%, 100% tetrachloroethane (v/v) in nonane injected into an oxidizing environment. 35

9. Gasification rate constants of tetrachloroethane/nonane droplet mixtures in oxidizing and inert environments. 36

10. Gasification profiles of droplets of 85% (v/v) tetra-chloroethane/alkane mixtures in oxidizing environments. 40

11. Gasification rate constants of droplets of 85% (v/v) tetrachloroethane/alkane mixtures and n-alkanes in oxidizing environments. 41

12. Sampling history of droplets of 85% tetrachloroethane (v/v) in alkanes in oxidizing environments. 43

13. Sampling history of droplets of 50% tetrachloroethane (v/v) in heptane in an oxidizing environment. 46

14. Gasification profile of tetrachloroethene droplets injected into oxidizing and inert environments. 49

15. Gasification rate constants of tetrachloroethene/octane droplet mixtures in oxidizing and inert environments. 52

LIST OF TABLES

1. Experimental results for n-alkane gasification studies. 23
2. Experimental results for 1-monochloroalkane droplet studies. 26
3. Summary of TECA/nonane droplet gasification results. 32
4. Summary of TECA/alkane droplet gasification results. 39
5. Summary of PERC/octane droplet gasification results. 50
6. Summary of chlorobenzene droplet gasification results. 54

NOMENCLATURE

B = a heat transfer number, given by
$B = \{c_P*(T-T_S) + Y_O*Q_C/\sigma\}/Q_V$

C = ratio of inter-drop distance to drop diameter

D = droplet diameter at time t, (μm)

K = gasification rate constant, subscript c for combustion (i.e., in an oxygen containing environment), v for vaporization, units of (mm^2/s)

ρ_G = gas density, (g/cc)

ρ_L = liquid density of the droplet at the boiling point, (g/cc)

α_G = thermal diffusivity of gas, (cm^2/s)

c_P = specific heat of gas, (cal/(g*K))

t = time, (s)

T_{amb} = ambient temperature, (K or ^oC)

T_S = surface temperature of droplet, (K or ^oC)

Y_O = oxygen mass fraction far from droplet

σ = stoichiometric fuel-to-oxygen mass ratio

Q_C = heat of combustion, HHV, (kcal/g)

Q_V = heat of vaporization at boiling point, (kcal/g)

ACRONYMS

CHC = chlorinated hydrocarbon
DCBZ = 1,2-dichlorobenzene
DE = destruction efficiency
DRE = destruction and removal efficiency
HC = hydrocarbon
HHV = higher heating value
HWI = hazardous waste incinerator/incineration
MCBZ = monochlorobenzene
MOD = minimum observed diameter
PERC = tetrachloroethene (perchloroethylene)
PIC = product of incomplete combustion
POHC = principal organic hazardous constituent
ROSE = residual organic substance emission
TCBZ = 1,2,4-trichlorobenzene
TCE = trichloroethylene
TECA = 1,1,2,2-tetrachloroethane

Glossary of Terms

burning (droplet) - Gasification of a droplet as a result of a flame surrounding the droplet. The gasification rate constant of a burning droplet K_c is about 0.1 mm^2/s larger than the gasification rate constant of a vaporizing droplet. Can occur only in oxidizing environments.

D^2-Law - The model of the spherically-symmetric, isobaric, diffusion-controlled, flame-sheet combustion or vaporization of an isolated, single-component fuel droplet with a constant and uniform temperature T_s.

diffusion flame - A flame with a three-zone structure consisting of a hot flame (reaction) zone separating a fuel-rich zone and an oxidizer-rich zone.

extinction (droplet) - The disappearance or extinction of the flame surrounding a burning droplet, as evidenced by an abrupt change in the gasification profile of the droplet. The droplet diameter at extinction is called the extinction diameter.

flame - A spatial domain in which rapid and exothermic reactions take place often (but not necessarily always) emitting light.

"flame" - Gases or particles (soot) which emit light but are not necessarily accompanied by rapid and exothermic reactions.

flame sheet - The surface at which all combustion reactions occur; often defined to be infinitesimally thin.

flame-streak - The section of light resulting from high frequency passage of droplets surrounded by "flames" falling through the chamber and visible with the naked eye.

gasification (droplet) - The transformation of the liquid in the droplet to vapor or gas surrounding the droplet either through burning or vaporization.

gasification profile - The plot of the droplet diameter squared (D^2) versus time.

ignition (droplet) - The appearance of a flame around the droplet determined by observation.

inert environment - A hot environment ($\approx$1400 K) containing no oxygen.

minimum observed diameter (MOD)- The droplet diameter of the smallest droplet for each experimental run. The MOD is not necessarily the smallest droplet that could be observed which could be as small as 30μm.

oxidizing environment - A hot environment (≈1400 K) containing about 18.4% by volume O_2 (21% O_2 dry basis).

premixed flame - A flame which has the reactants mixed prior to their arrival to the reaction zone.

ROSE - The term residual organic substance emission (ROSE) is being used in this report to refer to those organic compounds which are in the feed, e.g. POHCs, but not completely destroyed by the combustion process; those compounds which are possibly reformed or newly formed in the incinerator (not limited to the USEPA definition of product of incomplete combustion, PIC, which requires appearance in "Appendix VIII"); and those compounds which represent products <u>other than inorganic combustion products</u> such as CO, CO_2, H_2O, HCl, or Cl_2.

Stefan flow - A convective flow in a constant-pressure system generated as the result of net diffusive velocities of the species present.

thermophoresis (or thermal diffusion) - The tendency for species to diffuse under the influence of a temperature gradient.

vaporizing, vaporization (droplet) - Gasification of a droplet as a result of a hot environment surrounding the droplet and <u>not</u> a flame. Vaporization can occur in oxidizing environments with fuels which do not burn or in inert environments for all fuels.

A. Introduction

Implementation of federal and state regulations controlling the treatment and disposal of hazardous wastes has stimulated interest in hazardous waste incineration. Many hazardous wastes are chlorinated hydrocarbon liquids and are candidates for incineration in spray-fired combustors. Proper design of incinerators to handle these materials depends on an understanding of their vaporization and combustion characteristics. Because of the complexities inherent in hazardous waste incinerators (HWIs), a thorough understanding of the destruction of chlorinated hydrocarbons (CHCs) in full-scale HWIs has not been possible. This realization has motivated the need to conduct laboratory and pilot-scale studies of portions of the HWI problem.

Pilot-scale HWIs have been used to study the destruction efficiency (DE) of chlorinated hydrocarbons (CHC) as a function of combustor operating conditions (Kramlich et al., 1984; La Fond et al., 1985; Waterland, 1984; Wolbach, 1984; Chang, 1988). While insights have been gained regarding factors influencing DE, quantitative predictions of DE in full-scale HWIs have not been possible because of the uncertainty in the scaling of turbulent mixing effects. Numerous premixed CHC flame and non-flame studies (Bose and Senkan, 1983; Chang, et al., 1986; Gupta and Valeiras, 1984; Frenklach et al., 1986; Dellinger et al., 1984; Graham et al., 1986; Senser et al., 1987) have been conducted, but we are aware of only one group that has studied CHC diffusion flames (VanDell and Shadoff, 1984). These studies have been used to determine the structure, kinetic mechanisms, sooting behavior and speed of CHC flames as well as to determine mechanisms of CHC thermal decomposition in hot, non-flame environments. This report describes an experimental study involving the gasification (burning and vaporization) of single droplets of various CHCs, a diffusion flame phenomenon.

Despite the development of newer technologies, spray combustion is still the preferred method of HWI (Oppelt, 1987). Because sprays are made up of individual droplets it is not unreasonable to expect some correlation between the burning of individual droplets and the burning of sprays. In the field of spray combustion, there has been considerable discussion on the role of group burning vs. individual droplet burning. The ratio of inter-drop distance to drop diameter, C, has been found to be an important parameter which governs whether a spray burns as a group or as individual droplets. For droplets far apart ($C > 10$) individual droplet behavior is expected. For very dense sprays ($1 < C < 5$), there are intense interaction effects between droplets. However for most sprays ($C = 10$) single droplet vaporization theory still applies (Correa and Sichel, 1982). Thus single droplet burning can be used to describe spray combustion when droplets are far apart, and droplet vaporization effects can be used to describe vaporization which occurs in the spray interior.

Single droplet burning can also be used to describe the combustion of large oversized droplets which can be produced as a result of an atomizer failure. Calculations show that if a small number of these large "rogue droplets", escape the core of the spray region and fail to burn completely outside of the flame envelope, reduced incinerator DE may result (Mulholland et al., 1986). Experimental results have also shown that the production of large droplets results in a decreased DE (Kramlich et al., 1984; Chang et al., 1988). Single droplet burning characteristics can therefore be used to describe burning of these "rogue droplets". Finally, because droplet gasification has been well studied for many conventional fuels and mixtures (Law, 1982), the physical insight gained from these studies can be applied to the additional chemical complexities associated with CHC combustion.

There were four major goals to this project: 1) to quantify single droplet gasification characteristics such as burning rate, vaporization rate, and extinction diameter, for a variety of pure and multicomponent mixtures of CHCs and HCs; 2) to determine factors which govern the extinction of the flame surrounding a burning droplet, e.g., the role of chlorine atoms or bulk heating value effects; 3) to determine if droplet extinction can account for the DE of principal organic hazardous constituents (POHC) observed in full and pilot-scale studies; 4) to investigate the development of a single droplet incinerability ranking methodology which could complement existing incinerability ranking methodologies.

This report is divided into five parts: Background, Experimental Apparatus, Experimental Results and Discussion, Research Implications, Summary and Conclusions and Future Work.

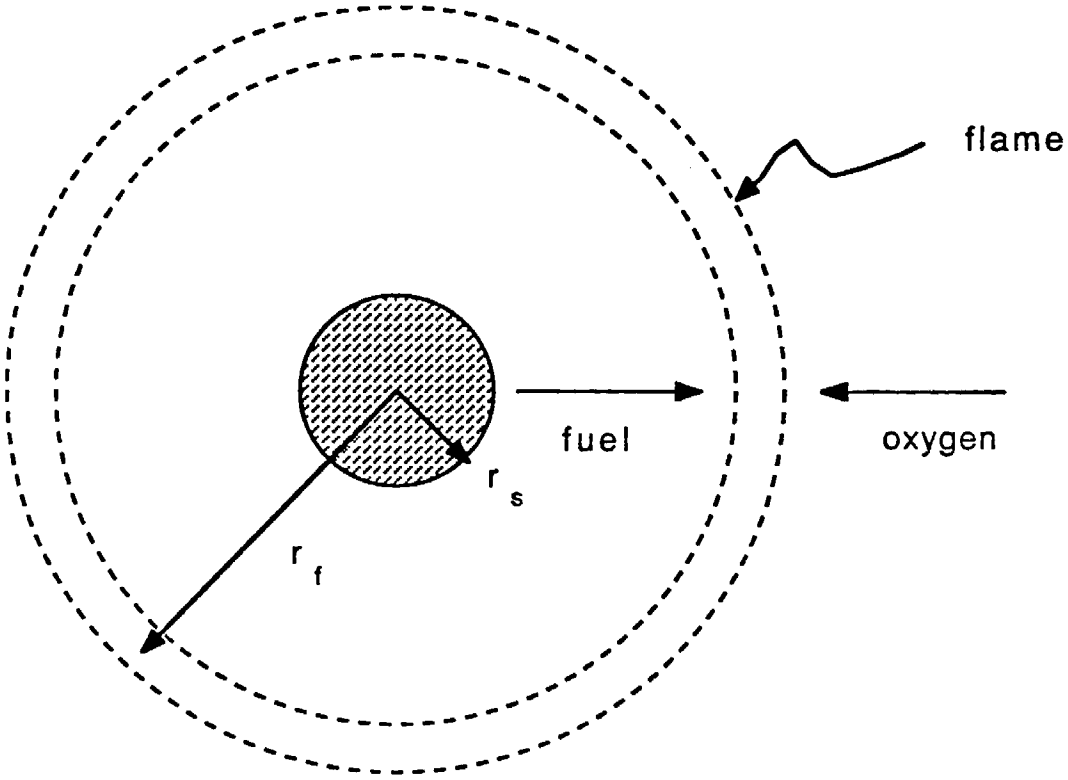
B. Background

Background for droplet gasification, as it relates to the combustion and vaporization of CHCs, is presented in two parts; one deals with the physics of droplet gasification and the other with the effects of chlorine on combustion reactions.

1. The Physics of Droplet Gasification:

Droplet gasification has been studied extensively over the past thirty years. As a result there exists a thorough understanding of how droplets are gasified in both oxidizing and inert (no oxygen) environments. A schematic diagram of a burning droplet is presented in Figure 1. In a steady burning mode, a liquid droplet is surrounded by a) an inner zone, containing vaporized fuel, pyrolysis and combustion products, b) a thin flame region, which is a source of heat and combustion products, and a sink for fuel and oxygen, and c) the surrounding air which is the source of oxygen for combustion reactions and of heat for vaporization. It is immediately apparent that the fuel and oxygen are separated by the flame. Because the fuel and oxygen must be transported by diffusion to the flame region for a reaction to take place, the flame surrounding a liquid droplet is called a diffusion flame. Thus the fuel and oxidizer are mixed in the flame or reaction region. In contrast, the fuel and oxidizer in premixed flames are mixed prior to the reaction region. The thickness of both diffusion and premixed flames is governed by the rate of chemical reaction; high rates of reaction result in thin flames and low rates of reaction lead to thicker flames.

When a fuel droplet is injected into a hot oxidizing chamber, droplet burning may occur. If the droplet diameter squared, D^2, is plotted against the droplet time, we obtain a droplet gasification profile shown in Figure 2 (a hypothetical profile with arbitrary units shown). The gasification profile



r_f = radius of flame
r_s = radius of fuel droplet

Figure 1. Schematic of burning droplet.

represents the time rate of change of the droplet surface area (proportional to D^2) and is used to characterize the size history of a burning and/or vaporizing droplet. The gasification profile shown in Figure 2 consists of a non-linear preheat region, a linear steady-burning region, and a linear vaporization region. Droplets in the preheat region undergo droplet heating and an increasing rate of vaporization, followed by fuel vapor ignition. After ignition, the gasification rate increases until a steady-state condition is reached at time = 30 on Figure 2. The non-linear behavior in the preheat region is due to the compensating effects of droplet heating, causing expansion of the droplet, and droplet gasification, which tends to decrease the size of the droplet. Thus the profile in the preheat region is flatter than the profile in the steady-burning region.

The steady-burning region is characterized by a linear gasification profile. A theory developed in the 1950s (Godsave, 1953; Spalding, 1953;, Goldsmith and Penner, 1954; Wise et al., 1955) called the D-squared law (D^2-Law) describes the steady-state behavior of droplet gasification. However, droplet gasification is never at steady-state (because the droplet is continually losing mass and its diameter is shrinking). Instead, a quasi-steady state assumption is made; the changes in the droplet occur about 1000 times slower than changes in the gas phase, thus we can assume that the gas phase processes are quasi-steady state with respect to the liquid phase processes.

The gasification profile in the vaporization region of Figure 2 is also linear. Thus we can think of droplet vaporization and droplet gasification as similar processes occurring at different rates. That is, in the burning region of the gasification profile, the droplet surface "sees" the flame, which is quite hot. Heat is transferred from the hot flame to the droplet surface, which causes rapid gasification. In the vaporization region, there is no flame surrounding the droplet so the droplet surface "sees" the ambient temperature which is frequently cooler

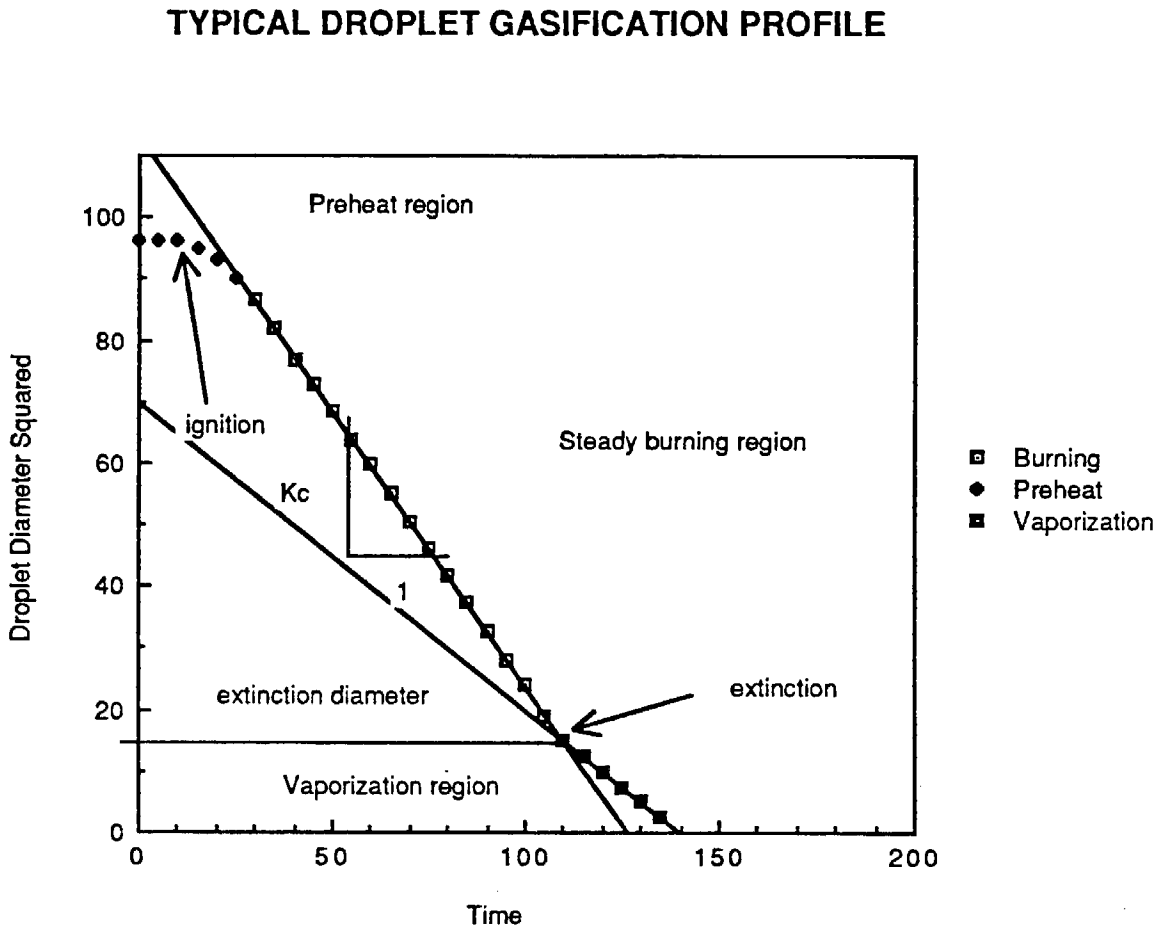


Figure 2. Gasification profile of a typical burning droplet.

than the flame temperature. Thus the heat transfer rate to the droplet surface is slower, causing a slower gasification rate and a flatter gasification profile. Nevertheless both burning and vaporizing droplets can be described by the same "law", the D^2-Law, which states that the time rate of change of droplet diameter squared is constant. Stated mathematically:

(1) $$d(D^2)/dt = -K$$

(2) $$K = 8*\rho_G*\alpha_G/(\rho_L)*\ln[1+B],$$

where $B = \{c_P*(T_{amb}-T_S) + Y_O*Q_C/\sigma\}/Q_V$. is a heat transfer number,

D = droplet diameter at time t,

K = gasification rate constant, subscript c for combustion, v for vaporization,

ρ_G = gas density,

ρ_L = liquid density of the droplet at the boiling point,

α_G = thermal diffusivity of gas,

c_P = specific heat of gas,

T_{amb} = ambient temperature,

T_S = surface temperature of droplet,

Y_O = oxygen mass fraction far from droplet,

σ = stoichiometric fuel-to-oxygen mass ratio,

Q_C = heat of combustion, HHV,

and Q_V = heat of vaporization at boiling point.

The D^2-Law is a model which describes the spherically symmetric, isobaric, diffusion-controlled, flame-sheet combustion of an isolated, single-component fuel droplet with a constant and uniform droplet surface temperature. Despite the restrictive assumptions of the D^2-Law, it will be used to represent multi-

component droplet burning with a finite rate of reaction with droplet heating, i.e. not a flame sheet.

The D^2-Law can also be used to represent droplet vaporization. In this case, Q_C in Equation (2) is set equal to zero; that is there is no enthalpy release due to combustion. It is also important to note that K in Equation (2) has a logarithmic dependence on B so that K depends weakly on T_{amb} and Q_C, which are relatively easy to obtain, and strongly on α_G which is quite difficult to evaluate, due to the large gradient in temperature and species between the droplet surface and the flame.

In the steady-burning region of the droplet profile, the gasification rate is diffusion-limited, i.e., it is independent of the chemical reaction rate occurring in the reaction zone. However, as the droplet becomes smaller, the rate of diffusion of heat away from the droplet increases. At some critical diameter, the chemical reaction rate can no longer supply heat fast enough to keep up with the increased diffusion rate. Thus some of the reactants are not converted to products, resulting in reactant "leakage" through the reaction zone and a drop in the flame temperature. As shown in Equation 3

$$(3) \quad W_r \sim [F]*[O]*A*\exp\{-E_a/(RT)\}$$

where F = fuel concentration

O = oxidizer concentration

A = pre-exponential factor

Ea= activation energy of the reaction

R = gas constant

T = absolute temperature,

and the chemical reaction rate W_r depends exponentially on T. Thus a small decrease in T results in a large decrease in W_r. As a result of this process, at some finite diameter, the flame

around the droplet is extinguished. Thus the extinction diameter represents the droplet diameter at which a flame can no longer exist around a droplet. The droplet extinction diameter is important because gasified fuel molecules/particles no longer pass through the hot reaction zone of a flame. Rather they are simply vaporized.

Evidence of droplet extinction can be seen by examining the droplet gasification profile for a break in the slope. Therefore, at time, t = 110 in Figure 2, droplet extinction occurs. Beyond time, t = 110, the droplet vaporizes until its disappearance.

Because most liquid hazardous wastes are mixtures of two or more compounds, it is important to note aspects important to multicomponent droplet gasification. There are three important factors which directly control the gasification rates of multi-component droplets. The first involves the relative concentrations and volatilities of the liquid constituents. The second takes into account miscibility of the liquid constituents and the ideality of the mixture, which affect the phase change and thereby the surface vapor pressure characteristics. The third factor includes liquid-phase mass diffusion and intensity of mixing within the liquid. This factor influences the rate at which the liquid components are brought to the surface, where gasification occurs.

2. The Effect of Chlorine on Combustion Reactions

The presence of chlorine in CHCs makes many of these compounds incineration resistant. This resistance to burning is caused by two factors: 1) low heats of combustion caused by the substitution of hydrogen atoms by chlorine atoms on a CHC molecule, and 2) retardation of the reaction rate by inhibition of the crucial $H + O_2 \rightarrow OH + O$ reaction. The first factor is obvious; by substitution of a hydrogen atom by a chlorine atom on

a hydrocarbon molecule, the heating value of the molecule is reduced resulting in a lower flame temperature. This factor was the basis for EPA's incinerability ranking scale which ranked the incinerability of compounds based on their heating value. Although it has been shown that an incinerability ranking scale based on the heating value does not predict the incinerability observed in full-scale HWI tests (Dellinger et al., 1985), it will continue to be used by EPA until a better incinerability ranking scale is promulgated.

To understand how chlorine inhibits the reaction rates of flames, it is necessary to analyze the reaction mechanisms of chlorine containing species in flames. Most of the early work on flame inhibition by chlorinated compounds was conducted in the study of fire retardants, many of which are halogenated compounds. Based on this research, it is generally accepted that radical scavenging of OH, O, and H radicals by halogens is the major mechanism of flame inhibition. The OH, O, and H radicals are needed to propagate the flame and they are produced primarily by the chain branching reactions (a) to (c):

$$H + O_2 \rightarrow OH + O \qquad (a)$$

$$O + H_2 \rightarrow OH + H \qquad (b)$$

$$O + H_2O \rightarrow OH + OH \qquad (c)$$

Based on atmospheric-pressure flames of trichloroethylene (TCE) flames a two-step oxidation scheme has been proposed Bose and Senkan, 1983). The first step involves the partial oxidation of TCE to CO, HCl and either H_2O or Cl_2:

$$C_xH_yCl_z + \{x/2+(y-z)/4\}O_2 \rightarrow xCO + zHCl + \{(y-z)/2\}H_2O \qquad (d)$$

for $z < y$, and

$$C_xH_yCl_z + \{x/2\} \rightarrow xCO + yHCl + \{(z-y)/2\}Cl_2. \qquad (e)$$

The second stage involves the HCl and Cl_2 inhibited oxidation of CO by the following overall reaction:

$$CO + \{1/2\}O_2 \text{ --> } CO_2. \qquad (f)$$

Reactions (d) through (f) represent global reactions and not elementary reaction steps. Based on a detailed study of the mechanism of TCE combustion Chang, W.D. et al., 1986b, it was found that Cl was the most important radical intermediate and participates in scavenging of H atoms from the system by rapid reactions such as:

$$RCl + H \text{ --> } R + HCl \qquad (g)$$

$$Cl_2 + H \text{ --> } HCl + Cl \qquad (h)$$

$$HCl + H \text{ --> } H_2 + Cl \qquad (i)$$

Reactions (g) to (i) then inhibit the very important chain branching reaction (a), which in turn lowers the concentration of OH and O radicals, further reducing the reaction rate by inhibition of reactions (b) and (c). Thus, from the mechanism described above, it is clear how chlorine in flames can affect the reaction rate and therefore the destruction efficiency of flames. The reader will be referred to reaction (i) in subsequent discussions of tetrachloroethane/alkane combustion.

C. Experimental Methods

In this section a description of the experimental apparatus is given, a list of data collected is given, standard operating and analysis procedures are presented, and data quality is discussed.

1. Description of Single Droplet Experimental Apparatus

The experimental apparatus was a laminar down-flow reactor in which single droplets were injected into the post combustion region of a laminar flat-flame burner. Figure 3 shows a schematic of the experimental apparatus, which is similar to that of Wang et al. (1984) and consists of five main components: 1) the droplet generator, 2) the chamber, 3) the microscope/-camera/strobe system, 4) the droplet synchronization circuit, and 5) the liquid-phase sampling probe.

Monodisperse droplets were created by a droplet generator based on the ink-jet printing technique (Carnahan and Hou, 1975) in which liquid was drawn into a cylindrical piezoelectric crystal fitted with a glass nozzle. A square wave pulse was applied to the piezoelectric causing it to contract and force the liquid through the glass nozzle. The droplet size and spacing were controlled by the frequency, pulse width, and voltage on the droplet generation circuit and the nozzle size. The droplets, with diameters varying between 200 and 300 μm and droplet Reynolds numbers of about 1, were injected into a chamber, heated by combustion products of a methane/O_2/N_2 flat-flame burner. The methane/O_2/N_2 flat-flame burner was operated to produce two different environments: 1) an oxidizing environment with an O_2 concentration of about 18.5% (21% O_2 dry basis), and 2) an inert environment with no oxygen. The gas temperature in the reactor decreased linearly between 1475 and 900 K along the 25 cm length of the chamber. The size history of the droplets was determined

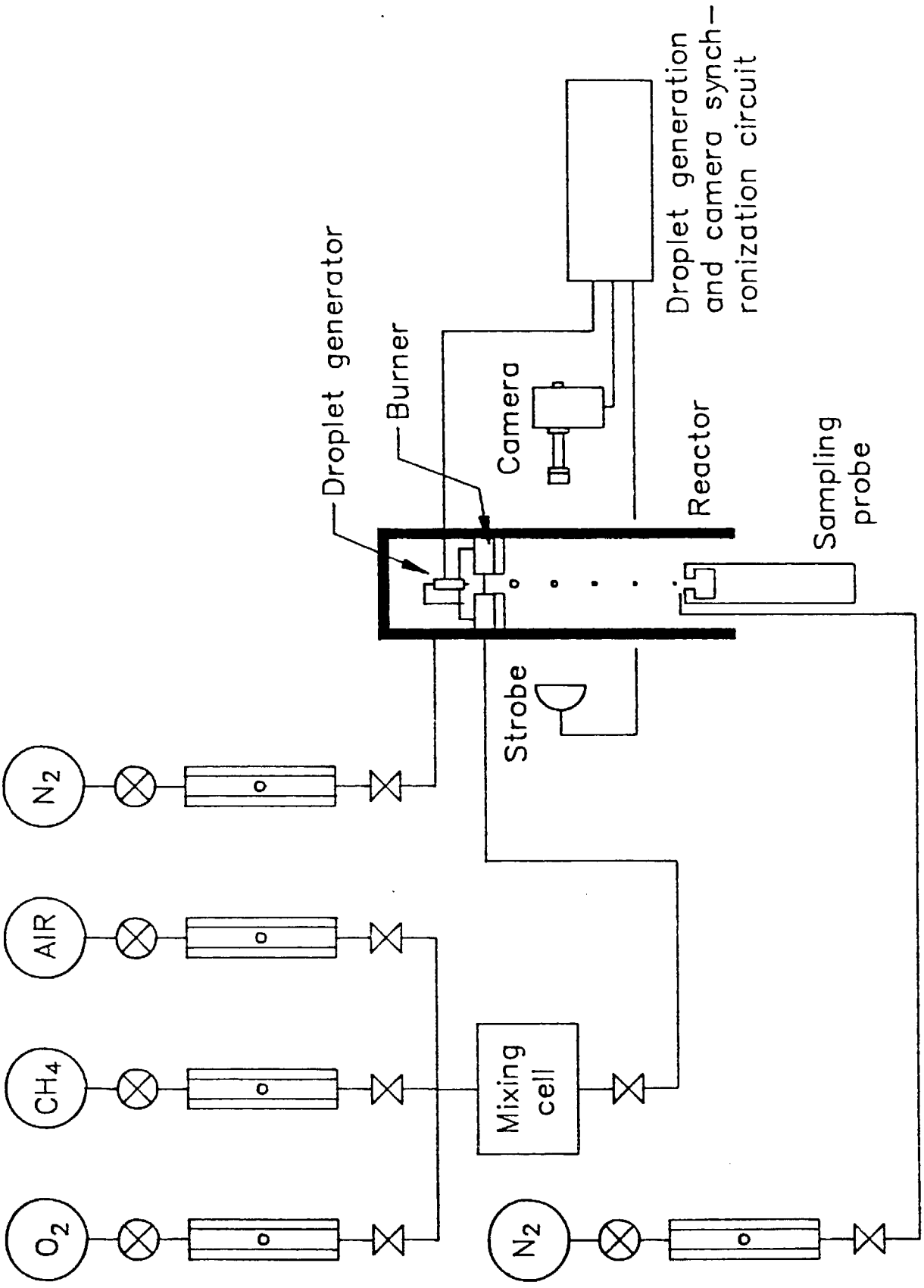


Figure 3. Schematic of experimental apparatus.

by use of photomicrography. Liquid-phase samples of the droplets were obtained using a sample probe inserted into the reactor.

2. Experimental Data Collected

The experimental data collected for this experiment consisted of a) droplet image size, b) flame characteristics, c) synchronization circuit values, d) chamber conditions, and e) liquid-phase sample data.

a) Droplet image size - The size of the droplet at any point in its lifetime was obtained by synchronizing strobe flash, droplet ejection, and camera shutter opening. The image was recorded on black and white 35 mm film (TMAX and TRI-X, ASA 400). The droplet images on the film were sized using a low power sizing microscope (30X, dissecting microscope) fitted with an appropriate ocular micrometer. The overall magnification factor for the experimental system (droplet - camera microscope at a given magnification with a given eyepiece - droplet diameter) was obtained by taking a photograph of a grid of known dimensions (254 μm square) and measuring the dimension on the sizing microscope. Thus a magnification factor was established between the known image size, the photographic microscope, and the sizing microscope. The quality of each droplet image varied. Three levels of image quality, "sharp", "average", and "fuzzy", were established. The precision on "sharp" images was +/- 1/2 division on the sizing microscope ocular micrometer (SMOM). Images of average sharpness or "average" image were determined to be within +/- 1 SMOM division while "fuzzy" images were determined to within +/- 2 SMOM divisions. Based on a calibration factor of about 5 μm per SMOM division, the following levels of accuracy were established for droplet images: "sharp" images: +/- 2.5 μm, "average" images: +/- 5 μm, "fuzzy" images: +/- 10 μm. During image sizing, a symbol (s for "sharp", no symbol for "average", f for "fuzzy") was placed next to the measurement to provide a permanent record of the image quality. The images were "fuzzy" because of poor camera/microscope focus and/or unwanted droplet movement. With practice the camera microscope focus was minimized and "fuzzy" images were indicative of unstable droplet behavior. Unstable droplet generation was manifested by the production of satellite droplets (small droplets produced with the desired droplet), shaking of the droplet image (greater than 5 droplet diameters), or relative movement of the droplet images up or down the chamber. Because the entire basis of the single droplet experiments rests on the assumption that droplets can be repeatably generated with no relative movement, the image quality was indicative of the quality of the droplet

generator tuning. Thus the image quality served as a quality control indicator on the droplet generator tuning. It should be noted that as the droplets became smaller (usually near extinction), focusing of the camera microscope became more difficult due to droplet "bounce" resulting from microcurrents in the chamber. Thus fuzzy images near the flame extinction diameter were not necessarily indicative of poor droplet stability. The minimum droplet size that could be observed using this experimental system varied between 30 to 50 μm depending on the photographic microscope resolution, droplet stability and microscope focusing.

b) Flame characteristics - "Flames" are usually associated with hot, rapidly reacting gases of about 1500 K or greater which luminesce or radiate light. However hydrogen gas "flames" emit no visible light. There are also "cool flames" which have a low exothermicity (Williams and Sheinson, 1973). In this report, a "flame-streak" is defined as the presence of visible light, regardless of its origin. Characteristics of a flame-streak such as starting point, ending point, and color, were determined in a dark room with a dark-adapted eye. Because of difficulties in determining whether a droplet was burning or not, we define "burning" as the production of a luminous gas around a droplet that can be seen with the naked eye, in a darkened room, and that has a gasification rate significantly (> 0.1 mm^2/s) above the vaporization rate (the gasification rate of droplets injected into a non-oxidizing environment).

c) Droplet ignition, extinction and minimum observed diameter - Droplet ignition was defined to occur at the point at which a luminous image or flame-streak appeared around the droplet. Because of the appearance of luminous gases around droplets that are not burning, we cannot define droplet extinction as the lack of a visible flame. Droplet extinction was therefore determined to occur at the break in the gasification profile (e.g., see t = 110 in Figure 2). The minimum observed diameter (MOD) is the droplet diameter of the smallest droplet observed for each experimental run (see t = 135 in Figure 2).

d) Synchronization Circuit Parameters - The synchronization circuit was used to i) produce the square wave pulse for droplet generation, ii) synchronize the droplet pulse with the strobe flash, and iii) synchronize the droplet pulse and strobe flash with the camera shutter opening. The circuit has the following parameters: frequency (high and low), pulse width (wide and narrow), strobe delay, strobe double exposure, and pulse voltage (direct, divide by 3, divide by 10). All parameters can be read from knob values on the front of the circuit box. To aid in data gathering, an analog signal output for frequency, voltage, and delay is available. All circuit parameters are calibrated using an oscilloscope, previously calibrated to

industry standards. The tolerances for each circuit parameter are as follows: frequency (high): +/- 0.03 Hz, frequency (low): +/- 0.01 Hz, pulse width (wide): +/- 0.03 ms, pulse width (narrow): +/- 0.001 ms, strobe delay: +/- 0.03 ms, strobe double exposure: +/- 0.001 ms, pulse voltage (direct): < +/- 0.09 V, pulse voltage (divide by 3): < +/- 0.03 V, pulse voltage (divide by 10): < +/- 0.009 V.

e) Chamber Conditions - The chamber conditions of interest are flow rate, chamber gas mixture composition (principally dependent upon oxygen), and temperature. The gas mixture composition in the chamber was determined by the combustion of the burner premixture. The components of the burner premixture were air, methane, oxygen, and nitrogen, which were metered by rotameters that have been calibrated with a wet test meter. The tolerances for the gas premixture are: air: +/- 0.1 lpm (liter per minute), methane: +/- 0.05 lpm, oxygen: +/- 0.1 lpm, nitrogen: +/- 0.1 lpm, purge (nitrogen): +/- 0.005 lpm. Based on the overall flowrate at operating conditions, the chamber flowrate tolerance was about +/- 0.1 %. Because the chamber oxygen concentration is very important in determining the burning rate and extinction of droplets, the oxygen concentration and carbon dioxide concentration were checked frequently with a Fyrite analyzer (calibration tolerance is +/- 0.1%).

The temperature in the chamber was measured by performing a thermocouple traverse on the centerline and 1 cm off centerline of the chamber. The chamber temperature profile is a function of the mixture composition and temperature transients due to chamber heating. The temperature traverse for any given mixture composition and purge rate was conducted after the relative temperature changes in the chamber became less than 5 ^{o}C per 10 minutes. Because of the relatively low chamber temperatures, the thermocouples were not corrected for radiation or conduction losses.

f) Liquid Phase Sampling Data - The liquid phase history of the droplet stream was determined by using the sample probe shown in Figure 3. The liquid phase sample probe consists of a water cooled probe body and a glass sample vial. The sample vial was placed in the sample probe, which was positioned in the chamber to intercept the droplets. The sample was taken until sufficient liquid was collected, usually about 0.5 ml. Thus a sampling period at any point in the droplet history required a sampling period of 20 to 60 minutes, during which mass losses of less than 5% per hour were observed, while for multicomponent mixtures the composition changed less than 3% during a typical sampling period. After the sample was collected, the sample vial was removed from the probe and subsequently analyzed by GC/FID. Each sample vial was scrubbed and rinsed with acetone. The opening of the sample probe, which was made of aluminum, was scrubbed and washed with acetone.

3. Standard Operating and Analysis Procedures

The standard operating procedure for this series of experiments is presented in this section. The analysis procedures for determination of each experimental parameter have been discussed. The standard operating procedure used to obtain burning/vaporization rate and extinction diameter data was:

a) Warm up the chamber until the temperature change is less than 5 ^{o}C per 10 minutes. This occurred about 45 minutes after lighting the burner.

b) Obtain stable droplets. Note: this is the key aspect of this experiment.

c) Put tuned droplet generator into the chamber and start injection of droplets.

d) Wait 5 minutes before taking any data.

e) For each mixture at experimental condition, the frequency, voltage, and pulse width are to remain fixed throughout. However in some cases these parameters may be adjusted to stabilize the droplet stream during the experiment without greatly affecting the results. Adjustment of these parameters is a last resort before the experiment was scrapped and constituted grounds for elimination of the data obtained. At each location along the droplet streak, the physical location (Z value) and strobe delay are recorded as well as any notable events such as droplet ignition, droplet extinction, flame color, start of unstable droplets, etc. The goal is to take as many data points as quickly as possible. In most cases (except for very slowly gasifying fuels or very large droplets), at least one datum was taken every centimeter. One datum consisted of at least 2 photographs and the location and strobe delay information.

f) After a complete traverse of the droplet streak had been completed, 4 to 5 "re-run" points were taken. Re-run points were repeated data points which served as a confirmation of the droplet stability. Thus if the re-run points fall on the same line as the original data, then a good data run with respect to droplet stability was predicted. If the re-run points did not fall on the original data, then the experimental data were rejected.

4. Data Quality

The data quality issue that has not yet been discussed deals with the determination of a burning or vaporization rate constant. It has been shown that the gasification of droplets (both pure and multicomponent mixtures) can be described quite well by the classical D^2-Law which states that under steady conditions the droplet diameter squared varies linearly with time. Even under ideal conditions the D^2-Law cannot be applied to all areas of the droplet lifetime. As shown in Figure 2, there exists both a non-linear preheat zone as well as a linear vaporization zone, which differ from the gasification in the steadily burning zone. Thus for each experiment that had steady droplets, good photographic images, and proper chamber conditions, the experiment was termed a "good" experimental run and a gasification (burning or vaporization) rate constant K was assigned that best fitted the linear portion of the gasification profile. The gasification rate constant, K, is the slope of a best fit linear regression of droplet diameter squared versus time through the steady burning region of the droplet lifetime. Other factors such as unstable droplets, incorrect oxygen concentration, or transient temperature conditions eliminated an experiment from consideration. In most cases, multiple runs of each compound or mixture at each operating condition were performed. An overall K for each compound or mixture at each operating condition represents the average of all "good" experimental runs. The range of all "good" experimental runs is also reported.

D. Experimental Results and Discussion

The experimental results are presented and discussed in six sections: alkanes and monochloroalkanes, tetrachloroethane (TECA) and nonane, TECA and alkanes, tetrachloroethene (PERC) and octane, and chlorinated benzenes.

1. Alkanes and Monochlorinated Alkanes:

A series of experiments using alkanes and monochloroalkanes were conducted to compare the effects of light chlorine content on the burning rate of alkanes. Although monochloroalkanes are not thought of as hazardous wastes, understanding of their combustion/vaporization behavior in contrast to that of n-alkanes is useful.

The gasification profile of a typical n-alkane, hexadecane, in an oxidizing environment is shown in Figure 4. There exists a non-linear preheat region, between time, t = 0 and t = 40 ms, which is indicative of droplet heating. As shown in Figure 4, the steady-burning region occurs between t = 40 and t = 140 ms. At t = 140 ms droplet extinction occurs at a droplet diameter of about 50 μm. Some of the experimental data collected for this project shows much "noise" in the early part of the droplet life-time that cannot be attributed to the droplet heating phenomenon. This "noise" is a result of the droplet entering the burning chamber with a stream of cool nitrogen gas used to purge the generator chamber (shown in Figure 3) of oxygen. Heating and mixing of the purge nitrogen gas and the hot combustion gases results in microturbulence which is responsible for the "noise" observed at the beginning of the droplet lifetime.

The flame-streaks of n-alkane droplets injected into a hot oxidizing environment were all thin and blue in color. N-alkane droplets injected into a vaporizing environment produced no visible flame streak.

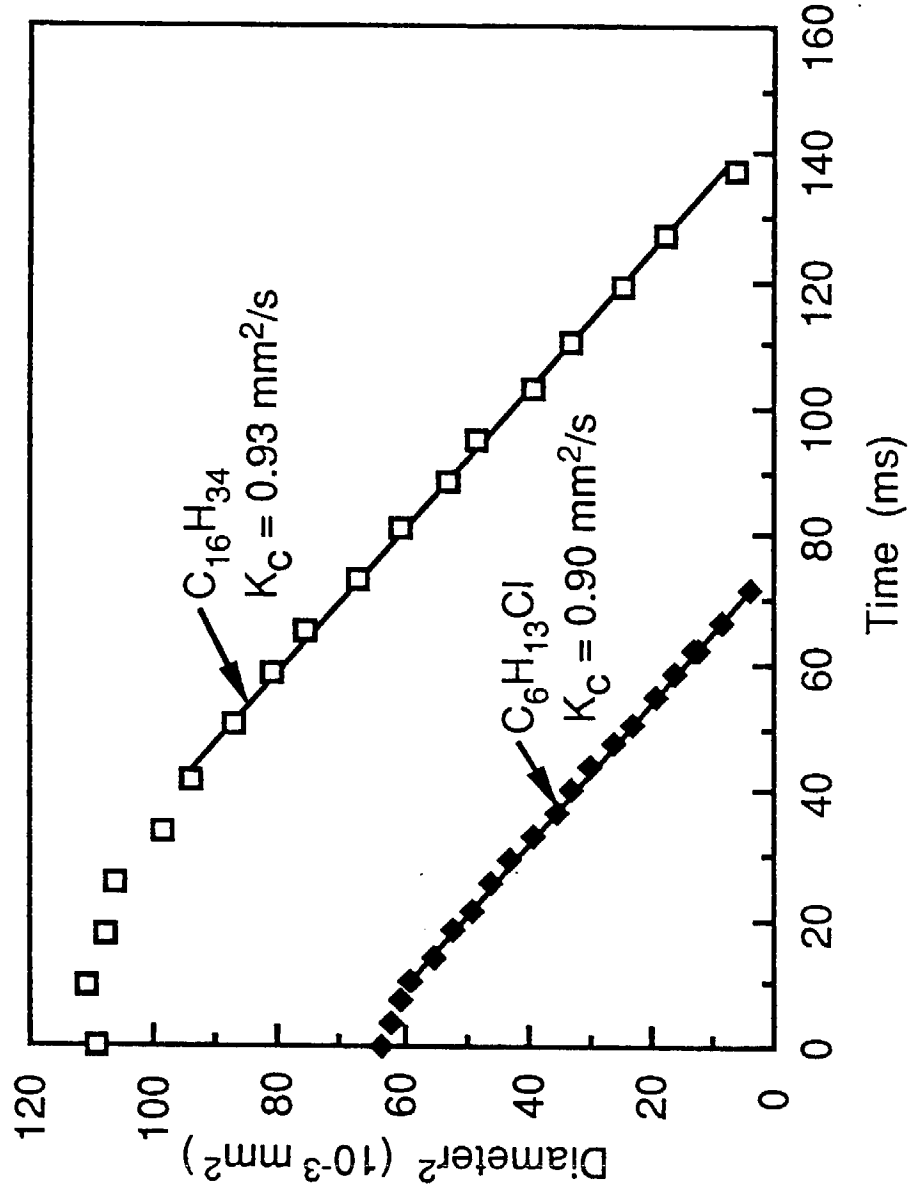


Figure 4. Gasification profiles of hexadecane and 1-chlorohexane droplets in an oxidizing environment.

The experimental results for the n-alkane burning rate studies are presented in Table 1. All data considered to be "good", as defined previously, are presented. Exceptionally good data are indicated with a "*". The mean values +/- 1 standard deviation of burning or vaporization rates are used for comparison with other fuels. The alkane results were obtained from work done for this project as well as work conducted by other researchers (Lee, 1987).

A gasification profile of a typical monochloroalkane 1-chlorohexane is also shown in Figure 4. It is similar in shape to the burning rate profile of n-hexadecane, such that it has a non-linear preheat region followed by a steady-burning region described by the D^2-Law. Droplet extinction occurs at Time = 72 ms at a diameter of 50 μm.

The flame streak appearance of gasifying monochloroalkane droplets differed from that of the n-alkanes. Monochloroalkane droplets injected into an oxidizing environment produced a "flame-streak" with three distinct regions: 1) an "initial blue flame" region, which was blue in color (similar color as observed in n-alkane burning) and which lasted less than 5% of the droplet lifetime, 2) a "sooty yellow flame" region, bright yellow in color lasting 50 to 60% of the droplet lifetime, and 3) a "terminal blue flame" region lasting through the end of the flame-streak. The transition between the "initial blue flame" and the "sooty yellow flame" was abrupt while the transition between the "sooty yellow flame" and the "terminal blue flame" was gradual. The appearance and disappearance of "sooty yellow flames" in the burning of monochloroalkanes can be explained as follows after the work of (Randolph and Law, 1986). Soot precursors are formed from pyrolyzed fuel molecules in the high temperature region between the droplet surface and the flame surrounding the droplet. High molecular weight species are transferred toward the droplet surface by thermophoresis, where they grow by coalescence with each other and by reaction with the

Table 1

EXPERIMENTAL RESULTS FOR N-ALKANE GASIFICATION STUDIES

Compound	Carbon #	HHV (kcal/g)	Run ID	Kc (mm2/s)	Kv (mm2/s)	MOD (um)	Comments
octane	8	11.53	AH-2ALB	1.04	-----	36	
			3/1/87-1	1.06	-----	25	
			3/16/87-3B	1.00	-----	90	
			9/19/87-12	0.88	-----	63	
			10/10/87-12	0.91	-----	43	
			10/10/87-34	0.98	-----	47	
			mean	.98 +/- .07	-----		
nonane	9	11.50	1/3/87-12	0.93	-----	-----	
			3/18/87-12	0.94	-----	67	
			3/18/87-3	0.92	-----	78	
			3/18/87-4	0.99	-----	45	
			3/18/87-5	1.00	-----	39	
			mean	.96 +/- .04	-----		
decane	10	11.47	1/13/86	0.97	-----	109	*
			59	0.91	-----	44	
			60	0.94	-----	66	
			61-61	0.94	-----	64	
			64-65	0.90	-----	47	
			66	0.91	-----	52	
			69-70	0.92	-----	66	
			70	0.99	-----	47	
			76-77	0.97	-----	47	
			77-78	0.94	-----	58	
			mean	.94 +/- .03	-----		
undecane	11	11.45	11/10/86ALB	0.93	-----	69	
dodecane	12	11.43	6/9/86ALB	0.95	-----	36	
tetradecane	14	11.40	10/11/87-12	0.94	-----	49	
hexadecane	16	11.38	10/12/86-ALB	0.94	-----	44	
			12/31/86-1	1.00	-----	-----	
			2/14/87-12	0.93	-----	80	
			2/14/87-2	-----	0.62	181	
			3/6/87-1	0.94	-----	34	*
			1/3/88-34	0.98	-----	85	
			1/3/88-45	0.95	-----	67	*
			mean	0.96 +/- .03	0.62		

MOD = minimum observed diameter, micrometers

* = exceptionally good data

outwardly diffusing fuel vapor. At steady state, the growing soot particles exist in a thin shell between the surface of the droplet and the flame. The location of the soot shell is determined by the balance between the outwardly directed Stefan flow and the inwardly directed thermophoretic force. However, the flame around a burning droplet changes sizes continually; first growing then shrinking. In the early stages of the droplet lifetime the soot precursors are consumed by the flame and therefore no soot is observed in the "initial blue flame". As the flame around the droplet rapidly grows, there is sufficient time for soot to form, and thus the "yellow sooty flame" is observed. Finally, as the flame size shrinks, the soot precursors are consumed and thus no yellow flame is observed near the end of the droplet lifetime. The appearance of "yellow sooty flames" in the combustion of chlorinated hydrocarbons is not unexpected. Gardner et al. (1966) studied the effect of adding various chlorinated hydrocarbons to hydrocarbon diffusion flames and found that soot production was proportional to the proportion of chlorine added to the flame. As noted by Senkan et al. (1983), the soot promoting influence of chlorinated hydrocarbons on conventional hydrocarbons are due to: 1) the relatively weak C-Cl bond strengths compared to the C-C and C-H bonds, 2) the lower enthalpies of combustion of chlorinated hydrocarbons, which results in lower flame temperature, and 3) the H, OH, and O radical scavenging characteristics of chlorine species.

Monochloroalkanes injected into an inert, i.e., non-oxidizing, environment showed a "dirty-yellow flame-streak". Note that because no oxygen was present in the inert environment, the "dirty-yellow flame-streak" cannot signify the presence of an oxidizing flame, rather only the presence of soot or some pyrolyzed molecule. The duller yellow color of this "flame-streak" is probably the result of a much lower temperature of the soot particles, resulting in a less intense and longer wavelength radiation.

A summary of all monochloroalkane data collected for this project is presented in Table 2. Note that the spread in the data, as indicated by the standard deviation in the mean K_C column is about +/- .02 mm^2/s, except for C_5 and C_{16}. The rather large spread, +/- .03 mm^2/s, in the data at C_5 is due to the difficulty in generating stable droplets for fuels with low boiling points. The large data spread for the C_{16} data is unknown, but may be due to the presence of fuel contaminants.

A graphical summary of a comparison of the burning and vaporization rates of n-alkanes and monochloroalkanes is presented in Figure 5. The trend for the n-alkane droplet burning rate constants reported in the literature is one of decreasing burning-rate with carbon number (Wang, 1984). The results of this study show a less dramatic change; a small decrease from C_8 to C_9 followed by a relatively constant rate for all fuels greater than C_9. The monochloroalkane results show a slight increase in K_C for C_5 to C_7, followed again by a relatively constant K_C for all fuels greater than C_8. As shown in Figure 5 the burning rate for the C_5 to C_7 monochlorinated alkanes is below similar values for n-alkanes. However, for a carbon number of 8 or greater, both the n-alkane and monochlorinated alkanes have similar burning rates. The vaporization rate results for both the n-alkanes and the monochloroalkanes are between 0.5 and 0.6 mm^2/s. The monochloroalkane results presented in Table 2 do not exhibit earlier droplet extinction than the n-alkane droplets. Thus the presence of one atom of chlorine substituted on the molecule did not cause early flame extinction.

Table 2

MONOCHLOROALKANE BURNING/VAPORIZATION RATE DATA SUMMARY

Compound	Carbon #	HHV (kcal/g)	Run ID	Kc (mm2/s)	Kv (mm2/s)	MOD (um)	Comments
chloropentane	5	6.96	3/9/87-1	0.96	-----	108	
			3/9/87-2	0.87	-----	47	*
			3/9/87-3	----	0.58	65	
			3/9/87-4	0.91	-----	45	
			9/11/87-3	0.93	-----	113	*
			9/11/87-12	0.88	-----	52	*
			9/12/87-2	0.90	-----	53	
			9/12/87-3	0.94	-----	33	
			mean	.91 +/- .03	0.58		
chlorohexane	6	7.37	3/12/87-23	0.90	-----	61	*
			3/12/87-34	0.93	-----	39	
			3/12/87-45	-----	0.63	107	
			9/14/87-12	0.95	-----	45	
			9/14/87-23	0.93	-----	36	
			9/14/87-3	-----	0.59	36	
			9/14/87-45	0.89	-----	24	
			mean	.92 +/- .02	0.61		
chloroheptane	7	7.69	1/30/87-2	-----	0.53	130	
			2/2/87-12	0.92	-----	99	*
			2/2/87-23	0.93	-----	48	*
			mean	.93 +/- .01	0.53		
chlorooctane	8	7.96	9/7/87-1	0.94	-----	32	*
			9/7/87-2	0.94	-----	43	
			9/7/87-3	0.90	-----	39	
			9/7/87-34	-----	0.59	96	
			mean	.93 +/- .02	0.59		
chlorodecane	10	8.36	1/23/87-12	0.93	-----	32	*
			1/23/87-23	0.94	-----	46	
			1/23/87-3	-----	0.59	63	
			mean	.94 +/- .01	0.59		
chlorododecane	12	8.65	8/22/87-12	0.92	-----	68	
			8/22/87-34	0.94	-----	63	
			mean	.93 +/- .01	-----		
chlorotetra-decane	14	8.87	1/19/87-12	0.91	-----	46	*
			1/19/87-3	-----	0.63	66	
			9/19/87-56	0.91	-----	50	*
			9/19/87-678	0.92	-----	30	
			mean	.91 +/- .02	0.63		
chlorohexa-decane	16	9.04	8/21/87-3	0.98	-----	141	
			9/8/87-23	0.93	-----	39	
			9/8/87-3	-----	0.51	209	
			9/21/87-12	0.88	-----	39	
			9/21/87-34	0.94	-----	34	
			mean	.93 +/- .04	0.51		

MOD = minimum observed diameter, micrometers

* = exceptionally good data

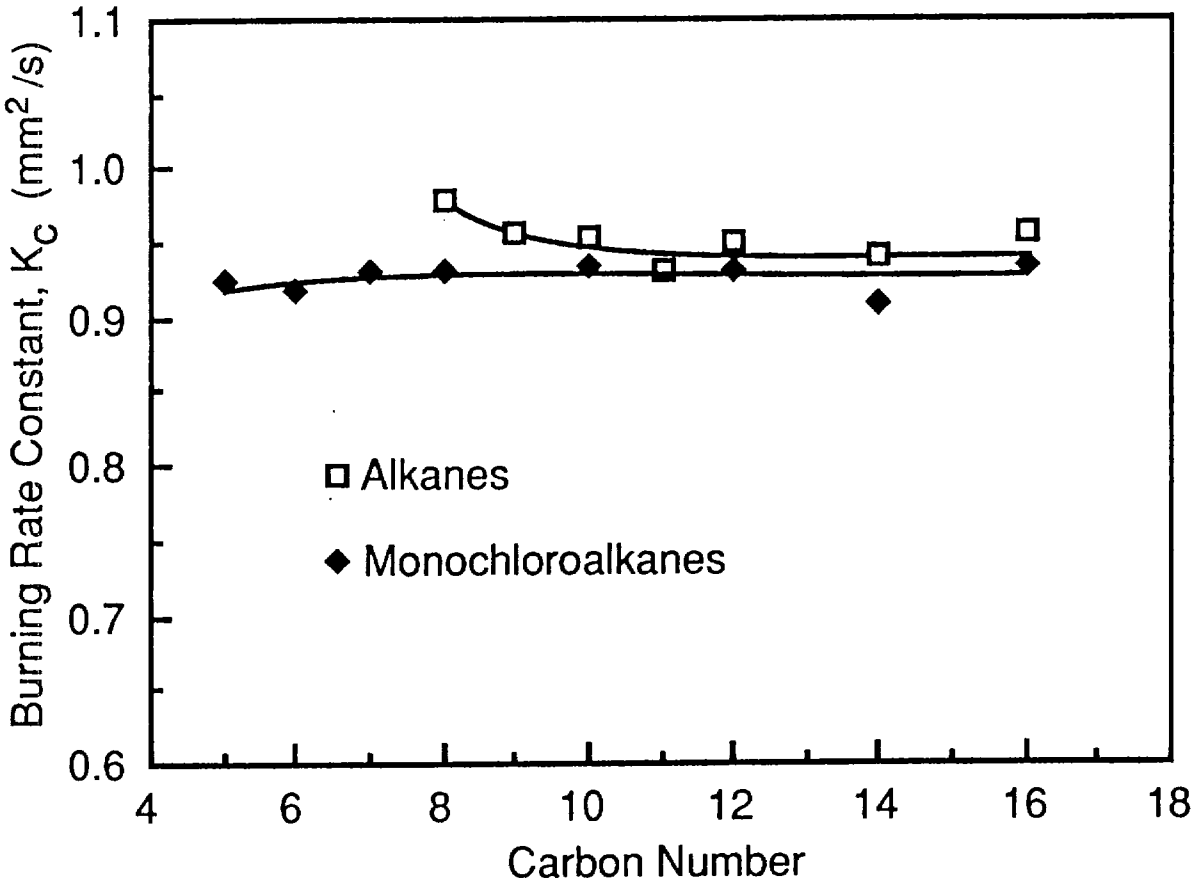


Figure 5. Gasification rate constants for n-alkane and 1-chloroalkane droplet studies.

2. Tetrachloroethane and Nonane:

The second group of experiments involved the study of the burning characteristics of mixtures of 1,1,2,2-tetrachloroethane (TECA) and nonane. This group of experiments was motivated by the results presented in Figure 6 which show gasification profile data for droplets injected into hot oxidizing and inert environments. The profiles for both sets of data coincide, from which it can be inferred that droplets of TECA do not burn.

The "flame" observations of gasifying TECA droplets are interesting. TECA droplets injected into an inert chamber environment produced a "dirty yellow flame", similar to that noted for monochloroalkane droplets gasifying in an inert environment. However, when TECA was injected into a hot oxidizing environment, a very-faint, blue-green "flame-streak" was observed. A possible explanation for the difference between the two observations is presented below.

To determine what factors might affect the blue-green TECA "flame", a separate series of experiments was conducted. First, TECA droplets were injected into a cold oxidizing chamber. The burner was ignited, the room was darkened, and the color and length of the blue-green "flame" was noted. After observing the flame for about a minute so as to let the eyes fully adapt to the darkness, the end of the "flame" was noted and the lights were turned on. A thermocouple was then placed in the chamber at the location of the end of the "flame", and a temperature reading was taken. These readings were taken periodically over the next 70 minutes. It was found that the end of the TECA "flame" moved down the length of the chamber as it heated. The gas temperature in the vicinity of the end of the TECA "flame" was about 600 ^{o}C. Thus the presence of a visible TECA "flame" was a function of chamber temperature.

A second observational test of TECA droplets in an oxidizing environment was conducted immediately after the test described above. The oxygen flowrate to the methane/air/oxygen flat flame burner was gradually reduced to zero; changing the chamber oxygen concentration from 18.4% to 4.7%. Because no additional gases were added to compensate for the reduced oxygen flow, the chamber flowrate was reduced by about 7% and the temperature probably increased, but was not measured. The results of this test were that the blue-green color of the TECA "flame" remained unchanged throughout the decreasing oxygen concentration, but that the end of the "TECA" flame seemed to get wider and fuzzier (less distinct). This observation suggests that the oxygen concentration does not have an effect on the color of the TECA "flame" in the ranges tested. However, this observation is not conclusive because the increase in temperature may have increased the reaction rate of the blue-green emitter to sufficiently offset the decrease in oxygen concentration.

The final experiment with TECA droplets in an oxidizing environment demonstrated that by increasing the purge rate flow, the TECA "flame" would be moved down the chamber. Thus the size of the droplet or quantity of TECA seemed to influence the presence of a visible "flame".

Based on the results from Figure 6, TECA "flames" have little or no exothermicity (no substantial increase in temperature from oxidation reactions), are visible only above 600 ^{o}C, are not affected by a change in oxygen concentration between 18 and 5%, and are more easily seen in larger droplets. From the above data one is led to the conclusion that the blue-green TECA "flame" is not a "flame" in the usual sense, but rather a "cool" luminous gas that emits blue-green light.

To further analyze the source of the blue-green light, it is necessary to review the spectroscopy of flames. In a study of burning mixtures of CHCs and HCs with hydrogen, Gaydon and

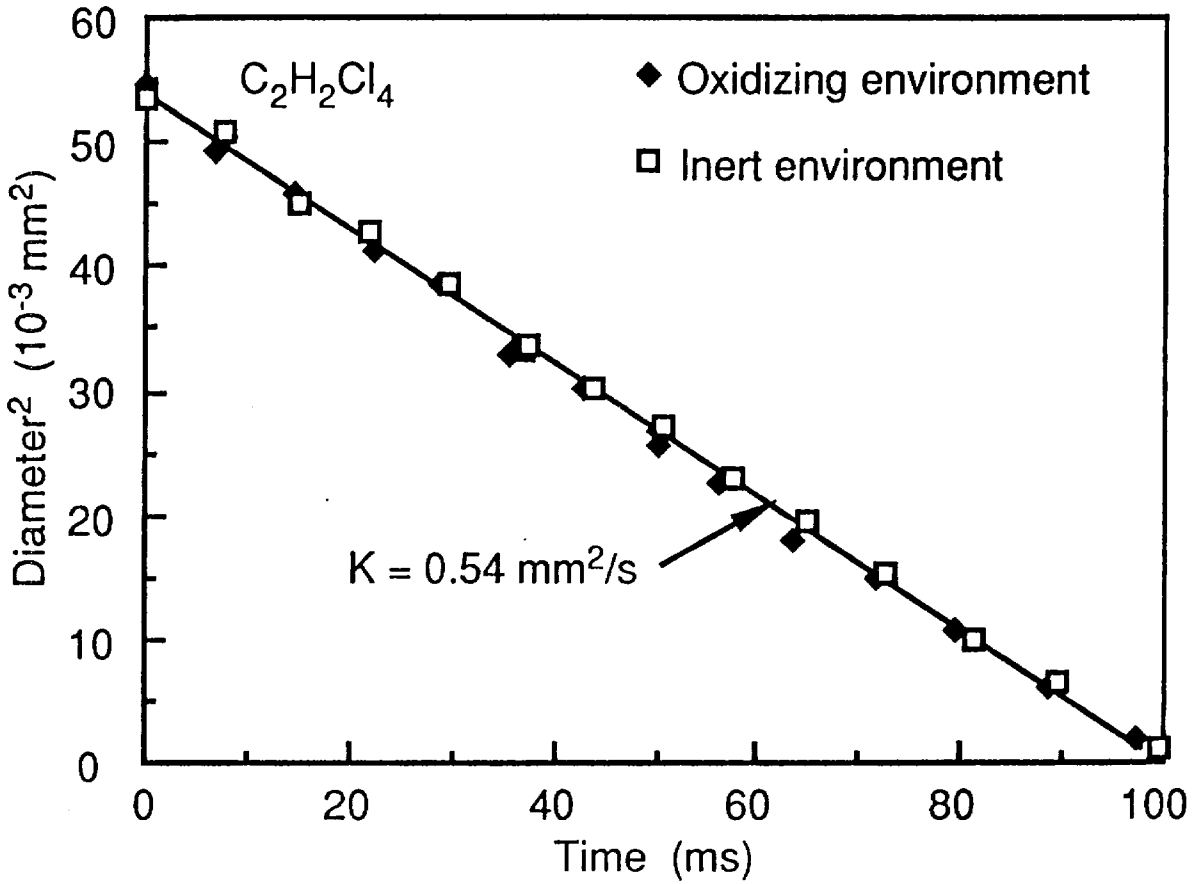


Figure 6. Gasification profile of tetrachloroethane droplets injected into oxidizing and inert environments.

Wolfhard (1950) observed that atomic hydrogen acting on organic halides produced C_2-emission (two carbon atoms) with subsequent polymerization to carbonaceous products. In this reaction, halogen atoms are stripped from the organic molecules by combination with H atoms, and the skeletonized molecules polymerize (Lewis and von Elbe, 1987). Since C_2 emits strongly at 5165 (Gaydon, 1957), which is in the blue-green region of the visible light spectrum, a small number of excited C_2 radicals could be causing the blue-green emission from the TECA droplets. Alternatively, an emission from some other unidentified species could serve as the explanation.

Heavily chlorinated species are among those that must be treated by HWI. The above results demonstrated that such species cannot be burned as pure compounds. For this reason, mixtures of CHCs and HCs were studied. Droplets of various mixtures of TECA and nonane, a n-alkane with the same volatility as TECA, were burned. Because TECA and nonane have the same volatility, the fuel mixture which is vaporized from the droplet surface and which participates in the gas phase reactions has about the same composition as that of the liquid mixture. Furthermore, this composition does not change with time as the gasification proceeds (Randolph et al., 1986).

A tabular summary of the TECA/nonane droplet gasification results is presented in Table 3. Figure 7 shows D^2 versus time data for a 75% TECA + 25% nonane (by volume) mixture (Run ID# 12/8/86-12). It is seen that the first two-thirds of the droplet lifetime resembles that of hexadecane and 1-chlorohexane. At about 70 ms, however, there is a sudden change in slope, from 0.88 mm^2/s to 0.56 mm^2/s. A separate experiment for the same mixture undergoing pure vaporization yields a vaporizing rate constant K_V = 0.55 mm^2/s. We conclude that the instant at which the slope abruptly changes represents the occurrence of droplet extinction. The fact that the flame extinguishes as the droplet's size becomes smaller is anticipated on the basis of the

Table 3

SUMMARY OF TETRACHLORDETHANE/NONANE DROPLET RESULTS

% TECA in nonane (by volume)	Cl/H (mole ratio)	HHV (kcal/g)	Run ID	Kc (mm2/s)	Kv (mm2/s)	Dext (um)	MOD (um)	Comments
100	2.00	1.89	10/31/86-2	---	0.50	---	71	
			2/12/87-1	0.54	---	---	45	*
			2/12/87-12	---	0.53	---	34	*
			2/12/87-23	0.54	---	---	45	*
			12/20/87-12	0.54	---	---	105	
			12/20/87-23	0.55	---	---	89	
			12/20/87-34	0.54	---	---	107	*
			12/20/87-45	0.46	---	---	200	high purge
			mean	0.54 +/- .01	0.52 +/-.02	---		
95	1.51	2.19	11/1/86-1	0.52	---	141	41	*
			11/3/86-1	---	0.47	---	115	
			11/3/86-2	---	0.48	---	32	
			2/5/87-123	0.65	---	173	42	
			2/5/87-34	---	0.56	---	114	
			mean	0.59 +/- .09	0.50 +/-.05	157 +/- 23		
90	1.19	2.50	12/29/86-123	0.63	---	180	61	
			12/29/87-123	0.63	---	169	58	*
			12/29/87-45	0.61	---	163	100	*
			mean	0.62 +/- .01	---	171 +/- 9		
85	0.96	2.82	11/23/86-1	0.68	---	187	59	
			11/23/86-2	---	0.53	---	102	
			11/24/86-1234	0.63	---	130	38	*
			mean	0.66 +/- .04	0.53	159 +/- 40		
80	0.79	3.16	11/23/86-4	---	0.53	---	32	
			12/5/86-1	0.78	---	183	98	
			12/7/86-23	0.78	---	190	56	*
			12/7/86-34	0.72	---	170	25	
			mean	0.76 +/- .03	0.53	181 +/- 10		
75	0.66	3.51	12/8/86-12	0.87	---	110	48	*
			12/8/86-34	0.83	---	123	39	
			11/9/86-2	---	0.55	---	147	
			mean	0.85 +/- .03	0.55	117 +/- 9		
50	0.28	5.53	1/26/87-1	0.92	---	---	49	
25	0.10	8.10	3/1/87-1	0.90	---	---	73	
			3/1/87-2	---	0.55	---	55	
			mean	0.90	0.55	---		
0	0.00	11.50	Table 1	0.96 +/- .04	---	44	---	

MOD = minimum observed diameter

* = exceptionally good data

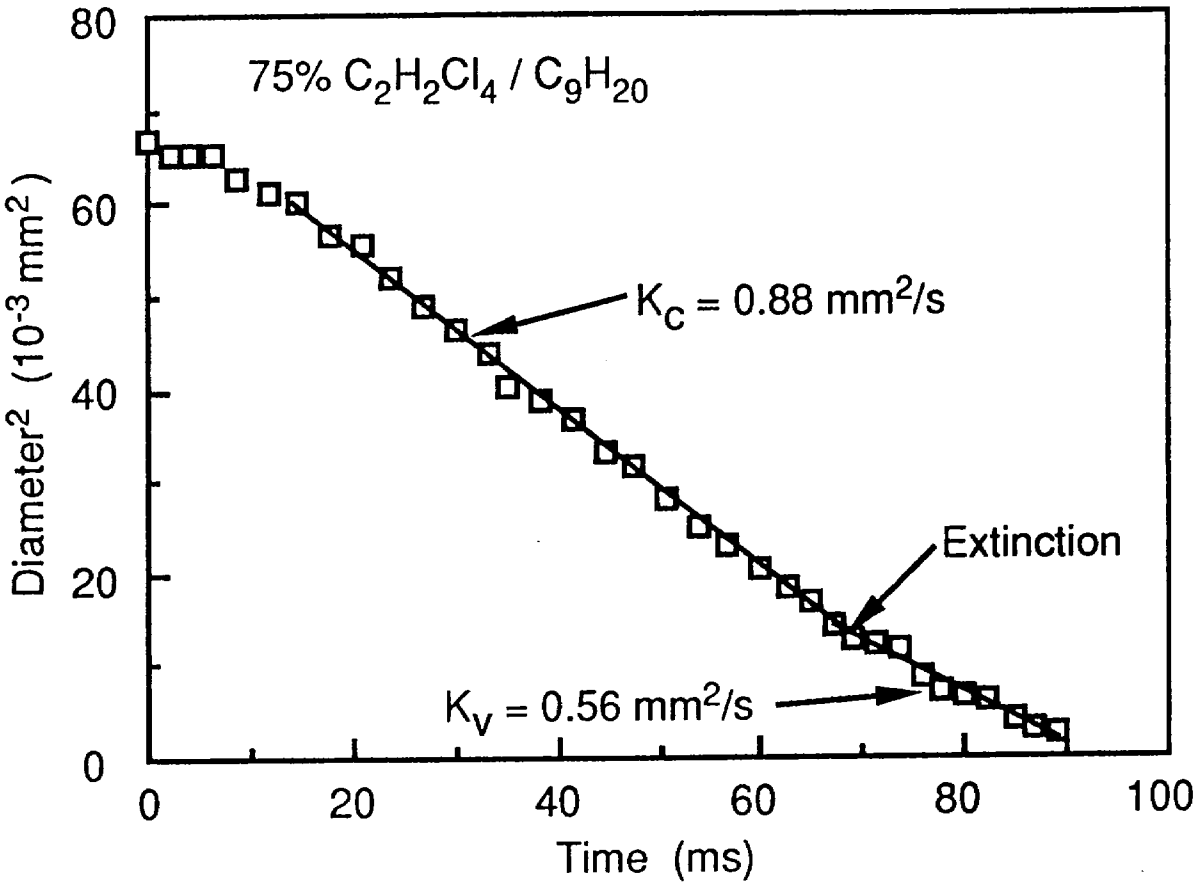


Figure 7. Gasification profile of droplets of 75% tetrachloroethane + 25% nonane (by volume) injected into an oxidizing environment.

continuous reduction in the droplet Damkohler number, which varies with the square of droplet diameter (Law, 1975).

Figure 8 compares the burning rate profiles of three concentrations of TECA/nonane mixtures. The burning profiles have been translated in time so that the onset of steady-burning occurs at time, t = 0. In addition the diameters have been scaled in such a way as to have a common starting diameter, but to retain the original slope. Thus the portion of the droplet lifetime corresponding to preheating is not shown. The 25% and 100% TECA/nonane data are quite linear throughout the observable droplet lifetime while the 80% data show droplet extinction occurs at a droplet diameter of about 190 μm.

Based on the data shown in Figure 8, a burning rate constant can be defined for the period of steady burning, after the droplet preheat region and before droplet extinction (if any). Figure 9 compares the burning rate constant, K_C, so determined, together with the separately measured K_V, for TECA/nonane mixtures of various concentrations. The composition of the curve in Figure 9 can be divided into two distinct regions, a burning rate plateau with a relatively constant K_C for TECA/nonane mixtures between 0% and 75%, and a region in which the droplets are not burning, TECA/nonane mixtures > 90%. It is significant that a mixture of 75% TECA by volume (K_C = 0.85 mm^2/s) burns almost as rapidly as pure nonane (K_C = 0.96 mm^2/s) despite a very large difference in mixture heating value; 2.80 kcal/g (LHV) for the 75% TECA/nonane mixture versus 11.41 kcal/g for pure nonane. (It should be noted that the calculation of the heating value of a highly chlorinated molecule normally assumes formation of some molecular chlorine, whereas in a system with an excess of hydrogen atoms, such as occurs in the droplet burner apparatus, hydrogen chloride can be formed from the water vapor from the methane-/air combustion. This would lead to a larger LHV.) Despite the relatively rapid burning rate of the 75% TECA/nonane mixture, early droplet extinction was noted (Dext = 117 +/- 9 μm).

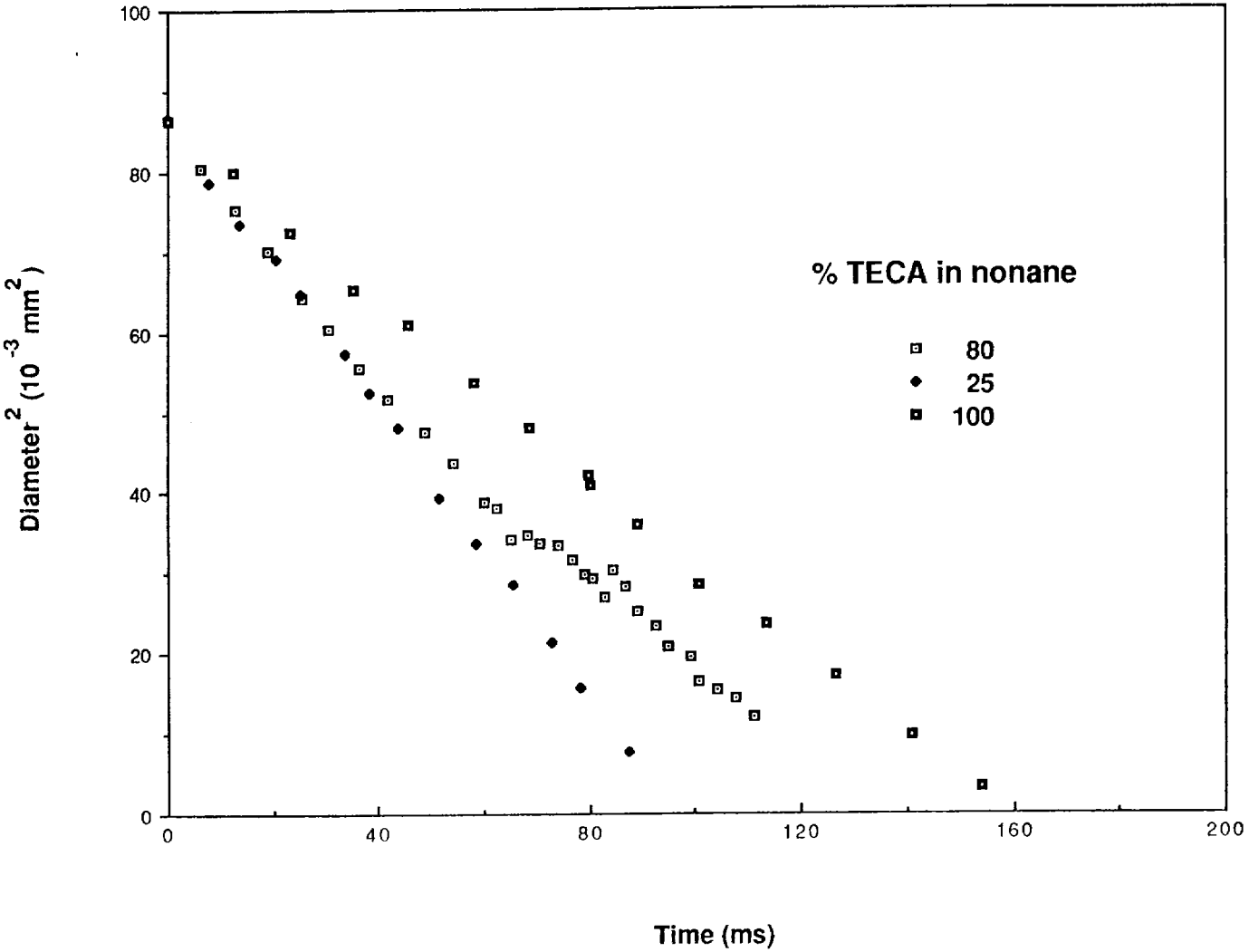


Figure 8. Gasification profiles of droplets of 25%, 80%, 100% tetrachloroethane (by volume) in nonane injected into an oxidizing environment.

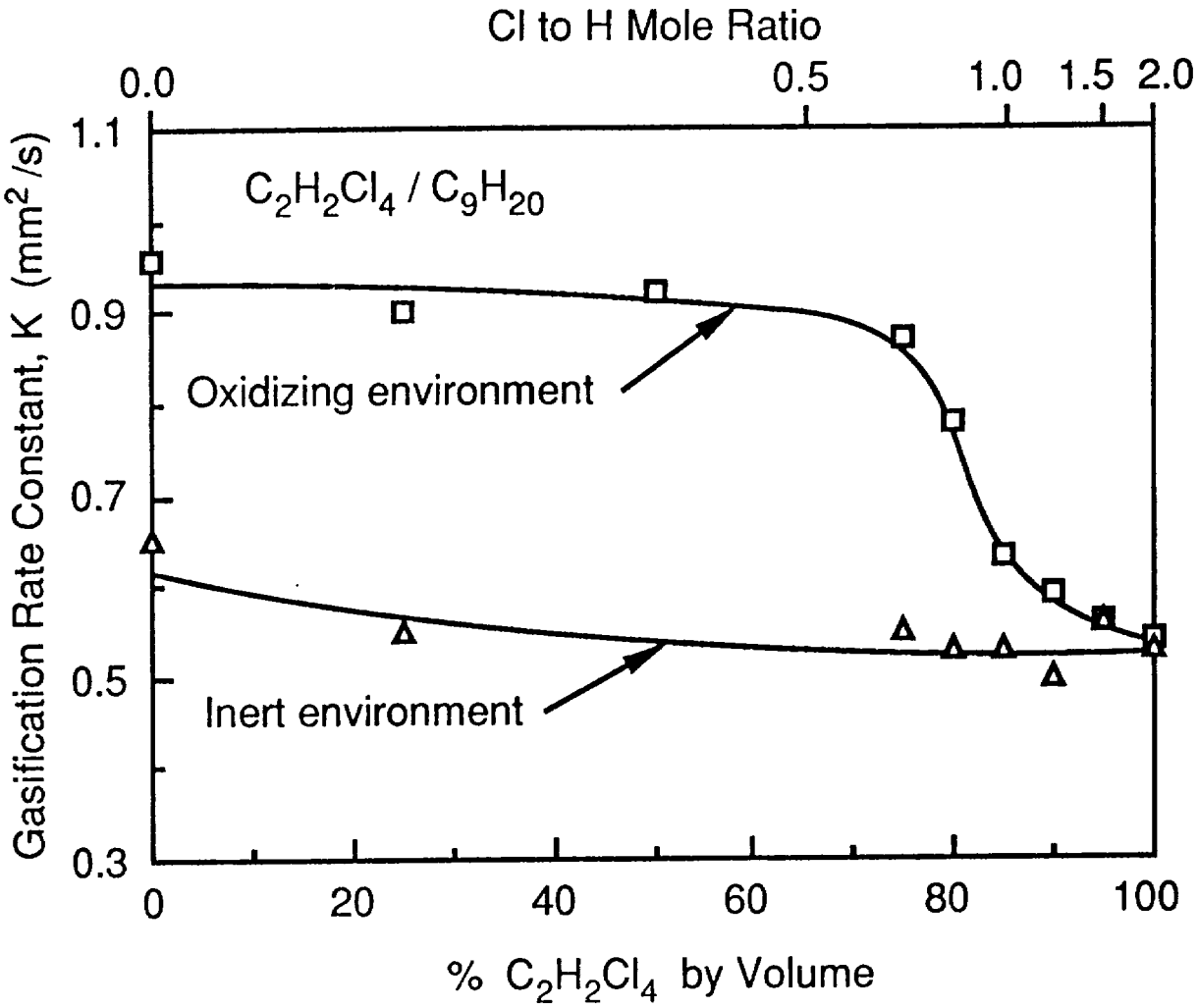


Figure 9. Gasification rate constants of tetrachloroethane/nonane droplet mixtures in oxidizing and inert environments.

For mixtures containing greater than 75% TECA, the burning rate dropped rapidly to the vaporization rate with increasing concentration of TECA. The drop in the burning rate could be due to a heat of combustion effect and/or a kinetic effect. In the latter case the inhibition of chlorine-containing species, e.g., Cl_2, Cl or HCl, on H radicals in the flame becomes an important consideration. [See reactions (g) through (i) on page 12.] In this regard it is of interest to note that the Cl/H mole ratios were 0.66, 0.79, 0.96, and 1.19 for the 75, 80, 85, and 90% TECA mixtures respectively. These results indicate that for TECA/-nonane mixtures, droplet combustion is inhibited when the Cl/H mole ratio approaches or becomes greater than unity.

3. Tetrachloroethane and Alkanes:

Mixtures of TECA and n-alkanes (TECA/alkanes) were examined next to determine the effect of volatility differential on the burning of TECA in droplet form and a summary of the results is presented in Table 4. Based on previous work (Randolph et al., 1986) the gasification process was expected to be governed either by volatility differences, resulting in batch distillation behavior, or liquid-phase diffusional resistance, resulting in a diffusion-limited, steady-state gasification processes.

Figure 10 shows the burning rate profiles of four mixtures of 85% TECA (by volume) in heptane, nonane, dodecane and hexadecane. For clarity, only the steady-burning region of the gasification profile is shown. In addition, to accurately compare burning-rate data of the mixtures with different initial diameters, the data have been shifted in time so that the onset of steady-burning occurs at the same droplet diameter. The TECA/nonane mixture is a mixture of equal volatility as discussed previously. The addition of high volatility heptane to TECA results in a gasification profile which is flatter than that of the TECA/nonane mixture. Addition of lower volatility alkanes, dodecane and hexadecane, to TECA results in a gasification profile which is steeper than that of the TECA/nonane mixture. Early droplet extinction is also observed in the TECA/nonane gasification profile.

To facilitate the comparison of the effects of mixture volatility on gasification rate, the average K_C's of TECA/alkane mixtures (from Table 4) are contrasted with the average K_C's of n-alkanes (from Table 1) in Figure 11. The K_C for the TECA/-alkane mixture increases with increasing number of carbon atoms in the added alkane. By comparing the relatively flat n-alkane burning-rate curve shown in Figure 5 to the steep TECA/alkane burning-rate curve in Figure 11, we conclude that the increase in the TECA/alkane burning-rate with increasing alkane chain length

Table 4

SUMMARY OF TETRACHLORDETHANE/ALKANE DROPLET RESULTS

TECA/alkane mixtures (by vol.)	T-boil of alkane (K)	Run ID	Kc (mm2/s)	Kv (mm2/s)	Dext (um)	MOD (um)
85% TECA/heptane	371	2/13/87-12	0.47	---	---	96
		2/13/87-34	0.47	---	---	107
		mean	0.47	---	---	---
85% TECA/nonane	424	Table 3	0.66 +/- .04	0.53	159 +/- 40	---
85% TECA/dodecane	489	1/30/87-34	0.77	---	---	72
		1/30/87-5	---	0.53	---	44
		mean	0.77	0.53	---	---
85% TECA/hexadecane	560	12/10/86-12	0.88	---	---	41
		12/10/86-234	0.88	---	---	44
		12/17/86-4	0.87	---	---	191
		12/17/86-5	0.85	---	---	65
		12/17/86-6	0.86	---	---	48
		mean	0.87 +/- .01	---	---	---
50% TECA/heptane	371	12/16/87-234	0.86	---	156	138

MOD = minimum observed diameter, micrometers

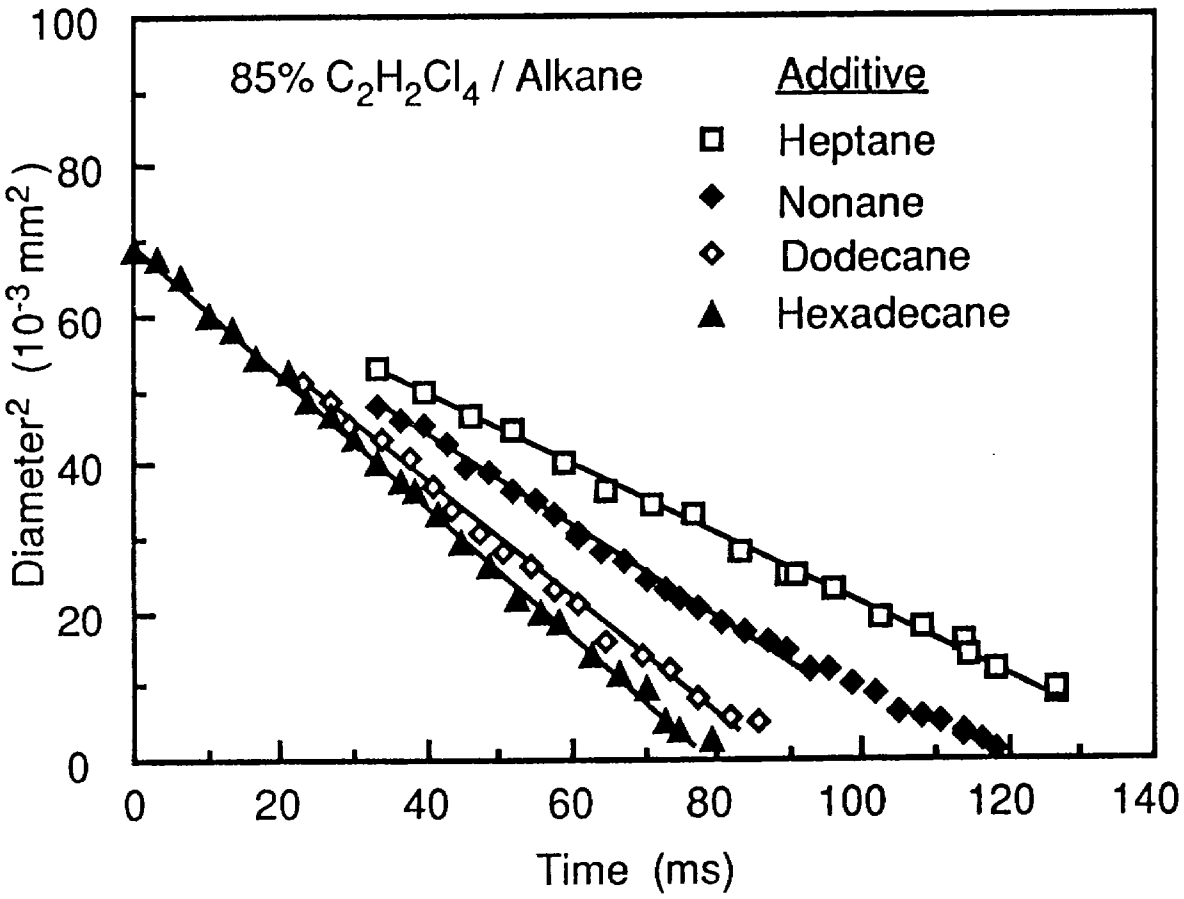


Figure 10. Gasification profiles of droplets of 85% (by volume) tetrachloroethane/alkane mixtures in oxidizing environments.

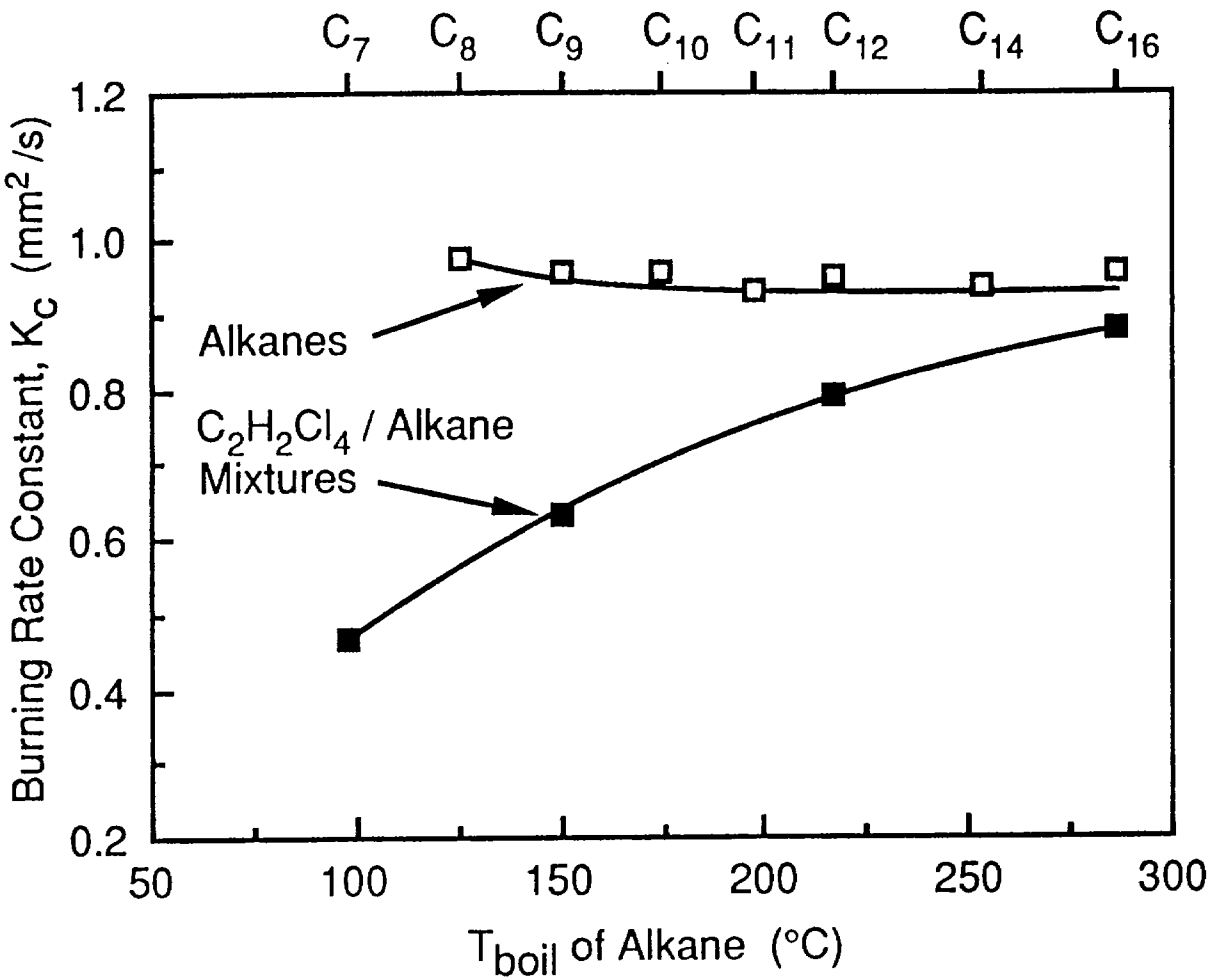


Figure 11. Gasification rate constants of droplets of 85% (by volume) tetrachloroethane/alkane mixtures and n-alkanes in oxidizing environments.

was not due to differences in the burning-rates of the alkanes added to TECA. Based on the work of Randolph et al. (1986) and Makino and Law (1988), the change in the TECA/alkane burning curve is hypothesized to be the result of differential distillation processes, liquid-phase diffusional resistance, and gasification rate.

To verify this hypothesis, we conducted liquid-phase droplet sampling of TECA/heptane, TECA/nonane, and TECA/hexadecane mixtures. Droplets were sampled at various stages in their lifetimes and analyzed by gas chromatography. The results, presented in Figure 12, show the variation of TECA droplet concentration as a function of a non-dimensional D^2-time $(1 - (Ds/Dso)^2)$, where Dso is the ignition diameter. Note that the droplet composition at t = 0 does not necessarily equal the initial droplet composition because of the existence of a small amount of vaporization which can occur as the droplet leaves the nozzle and enters the chamber. The TECA/nonane curve shows a rise in the TECA concentration from 85% to 90% during the sample period. Because the TECA/nonane mixture is an equal volatility mixture, we did not expect the TECA/nonane mixture to change significantly. Two possible explanations are given for the slight increase observed. "Leakage" of TECA through the flame could create a gas-phase TECA concentration gradient much less than the gas-phase nonane concentration gradient, resulting in a higher TECA partial pressure at the droplet surface, and therefore a lower rate of transport away from the surface. However, this mechanism for TECA enrichment is inconsistent with the concept of early thermal decomposition of TECA by four-centered HCl elimination. Non-ideal solution behavior of the TECA-nonane mixtures is a more likely explanation for the observed results.

The TECA/heptane curve rises to 100% TECA very rapidly. The TECA/hexadecane curve drops off steadily throughout the droplet lifetime, until a rapid drop occurs near droplet extinction. The small TECA concentration at D^2-time = 0.88 on the TECA/hexadecane

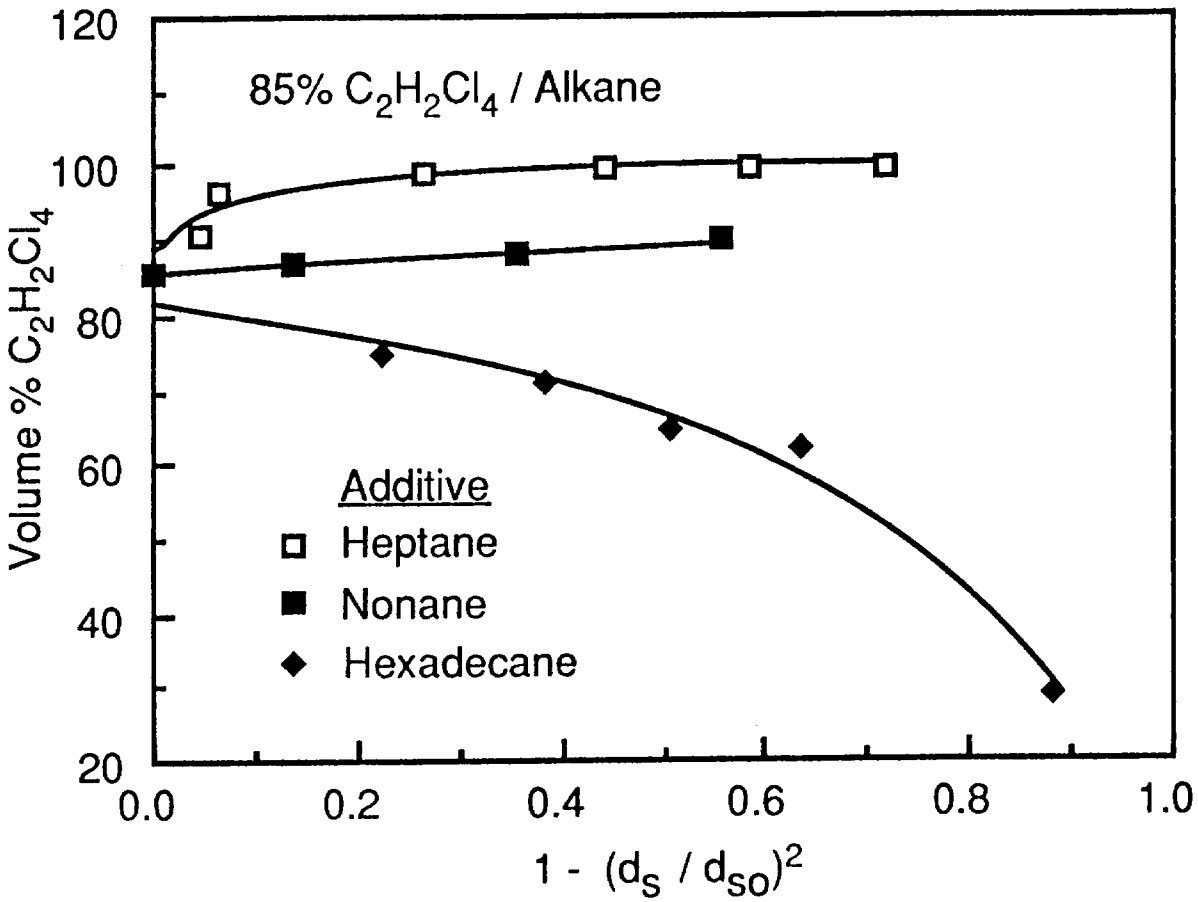


Figure 12. Sampling history of droplets of 85% tetrachloroethane (by volume) in alkanes in oxidizing environments.

curve in Figure 12 could have been caused by sampling uncertainties, which are higher for the long sampling periods needed to collect smaller droplets.

The sampling results presented in Figure 12 are in agreement with the current state of understanding (Randolph et al., 1986, Makino and Law, 1988), that multicomponent droplet gasification is controlled by liquid-phase mass diffusion, droplet surface regression rate (gasification rate), and volatility differential between components. That is, after start of gasification, much of the volatile component in the surface layer is preferentially gasified because of the short diffusion distance to the surface of the droplet. Subsequent behavior depends on the surface regression or gasification rate. If the surface regresses rapidly, then the volatile component in the droplet interior remains trapped there because of the relatively slow rate of mass diffusion. Thus, a thin surface concentration layer persists and the volatile component remains part of the droplet composition. Therefore, for fast gasification rates or slow liquid phase diffusion, a "diffusion-limit" is approached. However, for a slower rate of surface regression or gasification, there is more time to transport volatile components to the droplet surface. Thus the droplet continually loses the more volatile component. As the surface regression rate approaches zero, the volatile components have an infinite amount of time to reach the surface, independent of the liquid-phase diffusion. Thus a "distillation limit" is approached.

Upon close examination of the TECA/heptane curve in Figure 12, we note the rapid rise in TECA concentration. However the effectiveness of liquid-phase diffusional resistance was not tested because of the slow gasification rate ($K = 0.49\ mm^2/s$). To determine the effect of gasification rate on the history of TECA/alkane droplets, a mixture of 50% TECA in heptane droplets were sampled in an oxidizing environment. The mixture burned well ($K_C = 0.86$ mm2/s) but had a rather large extinction diameter

of 158 μm. The sample history, presented in Figure 13, shows a rapid rise in the TECA concentration, characteristic of distillation processes and not of liquid-phase diffusional processes.

Thus for all mixtures tested, The TECA/heptane and TECA/hexadecane curves confirm the results of Randolph et al. (1986), that the more volatile component leaves the droplet preferentially. Thus batch-distillation processes and not liquid phase diffusional resistance govern the burning of TECA/alkane droplets.

With the sampling results shown in Figure 12, an explanation can be given for the data appearing in Figure 11. When TECA/-heptane droplets are injected into the chamber, the higher volatility heptane rapidly leaves the droplet. Therefore, the droplet becomes enriched with the non-burning TECA and ultimately, burning is inhibited. Our results show that the concentration in the TECA/nonane droplets does change slightly throughout the droplet lifetime. After ignition, the TECA/nonane droplets become enriched with TECA. As the droplet diameter becomes smaller, droplet extinction becomes more likely due to a reduced droplet diameter and a decreased chemical reaction rate resulting from the enrichment of TECA in the droplet. Both of these effects increase the extinction Damkohler number (Law, 1975) and extinction is promoted.

Upon injection of TECA/hexadecane droplets into the combustion chamber, TECA is preferentially gasified resulting in enrichment of the droplet with the rapidly burning hexadecane. The gasification of large quantities of TECA early in the TECA/-hexadecane droplet lifetime explains the observed ignition delay of TECA/hexadecane droplets. The enrichment of the droplet with hexadecane further explains why the burning-rate of a TECA/-hexadecane droplet is almost as large as the burning-rate of the pure hexadecane droplet over the range of compositions tested.

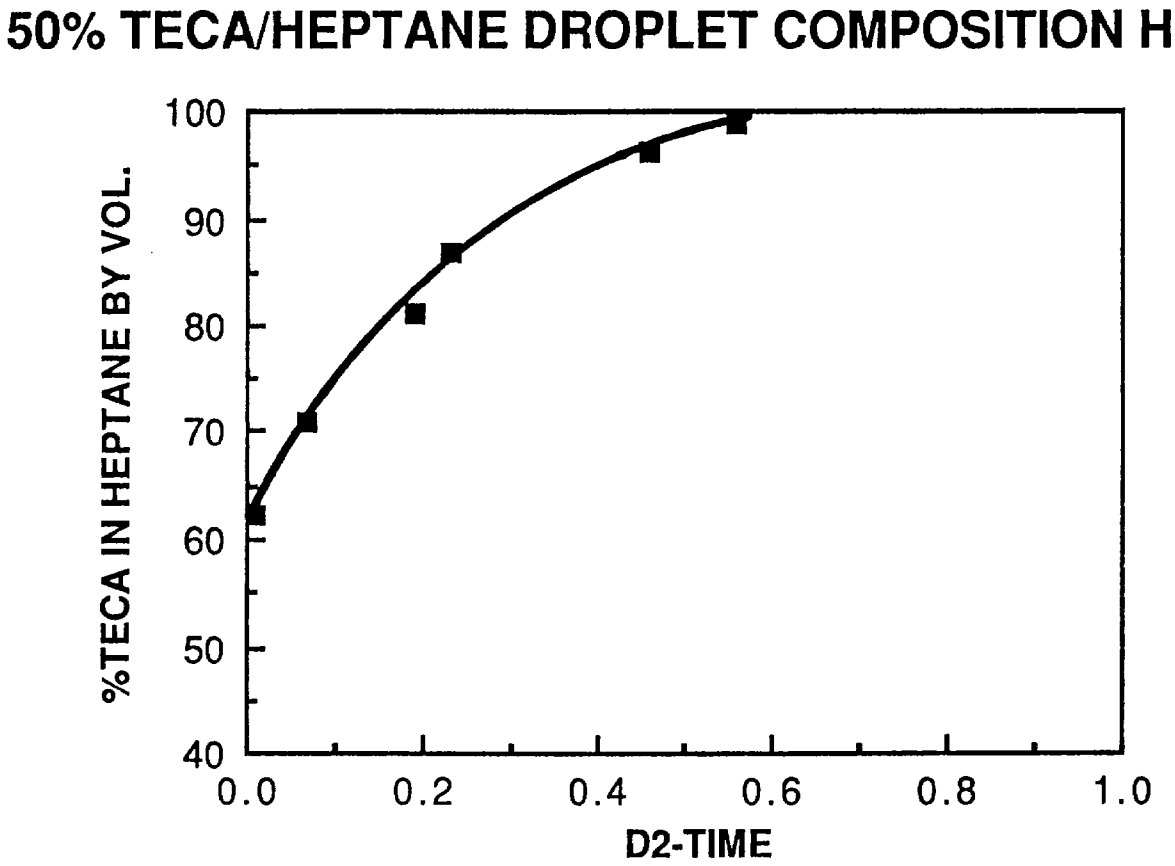


Figure 13. Sampling history of droplets of 50% tetrachloroethane (by volume) in heptane in an oxidizing environment.

For example, at a D^2-time of 0.23 the TECA concentration in the TECA/hexadecane droplet is less than 74%. The large change in the TECA concentration of the TECA/hexadecane droplet does not produce a corresponding large change in the burning-rate, as evidenced by the flat TECA/nonane burning-rate profile for 0% to 75% TECA/nonane mixtures shown in Figure 9. Based on the results from Figure 12, the slope of the TECA/hexadecane burning profile in Figure 10 is expected to increase with time. The acceleration in burning-rate would cause the profile to be concave down. The magnitude of the change in burning-rate is expected to be small and therefore unlikely to be distinguished from the "experimental noise" of the data.

At the end of the lifetime of a TECA/hexadecane droplet, it has become enriched with hexadecane, which delays extinction and promotes more complete burnout of the droplet. This effect may be important in formulating blending strategies for hazardous waste incineration. That is, to reduce the adverse affects associated with production of oversize droplets in a spray combustor, a low volatility alkane could be blended to promote the complete burnout of any oversize droplet in the combustion chamber.

4. Tetrachloroethene and Octane:

A study of the gasification characteristics of mixtures of tetrachloroethene (PERC) and octane is presented in this section. This group of experiments was motivated by the results shown in Figure 14, i.e., gasification profiles of pure PERC droplets injected into oxidizing and inert environments. The gasification rate constants for the oxidizing and inert environments are approximately equal, 0.56 and 0.59 mm2/s, respectively. We conclude that pure PERC droplets do not burn. It is of interest to note that no "flame-streak" was observed from the droplets of pure PERC injected into an oxidizing environment, in contrast to the observations of pure TECA droplets in an oxidizing environment, producing the "blue-green flame" discussed earlier. One might infer from this observation that either, a) PERC does not breakdown under these conditions, or b) the break-down products of PERC do not emit visible radiation.

To burn droplets of PERC, it must be mixed with a fuel that burns well. As discussed in Section 3, mixture volatility differences can influence the droplet gasification characteristics significantly. In order to control the gas phase mixture composition and eliminate differential volatility effects, octane (B.P. = 125 ^{o}C) was blended with PERC (B.P. = 121 ^{o}C) to form an equal volatility mixture.

The results of the PERC/octane gasification studies are presented in Table 5. Multiple K_C's of the same mixture are averaged and uncertainties of +/- 1 standard deviation are reported. For the PERC/octane droplet mixtures of 91% PERC shown in Table 5, there is a dependence of K_C on the nitrogen purge rate. (Nitrogen gas was used to purge the generator chamber of combustible gases to prevent explosions.) The purge rate also acted to accelerate the droplet velocity beyond its initial velocity exiting the droplet generator. Thus the higher the

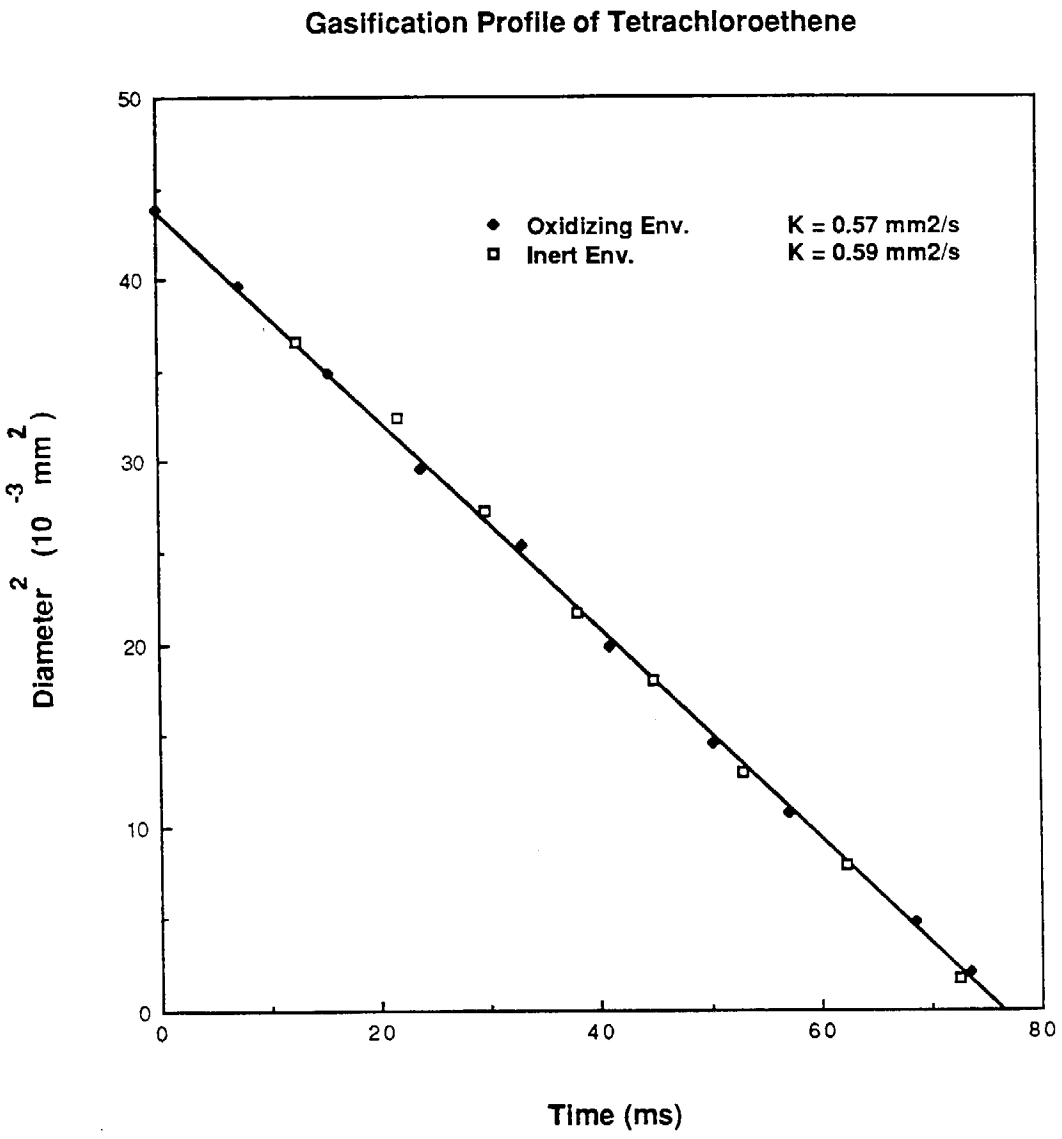


Figure 14. Gasification profile of tetrachloroethene droplets injected into oxidizing and inert environments.

Table 5

TETRCHLOROETHENE/OCTANE GASIFICATION RATE SUMMARY

%PERC in Octane (by vol)	Cl/H mole ratio	HHV (kcal/g)	Run ID	Kc (mm2/s)	Kv (mm2/s)	Dext (um)	MOD (um)	Purge setting	Comments
100	---	1.19	9/11/87-1	0.55	---	---	37	9	
			9/11/87-12	0.57	---	---	46		
			9/11/87-2	---	0.59	---	41		
			mean	0.56 +/- .01	0.59	---	---		
91	3.5	1.63	11/14/87-12	0.67	---	105	91	5	
			11/14/87-23	0.85	---	127	68	1	
			11/14/87-4	0.73	---	99	55	4	
			mean	0.75 +/- .09	---	110 +/- 15	---		
90	3.0	1.69	11/3/87-12	0.76	---	148	58	5	
88	2.5	1.79	10/22/87-12	1.00	---	136	74	1	
			10/22/87-23	0.83	---	130	86		
			10/22/87-34	0.86	---	207	139		
			mean	0.85 +/- .02	---	158 +/- 43			
85	2	1.92	10/9/87-1	0.83	---	---	27	9	
			10/9/87-12	0.83	---	---	32		
			10/9/87-3	0.85	---	---	27		*
			mean	0.84 +/- .01	---	---	---		
81	1.5	2.15	10/8/87-1	0.84	---	---	27	9	
			10/8/87-12	0.83	---	---	41		
			10/8/87-3	0.83	---	---	34		
			mean	0.83 +/- .01	---	---	---		
73	0.96	2.61	10/6/87-1	0.91	---	---	49	9	
			10/6/87-2	0.90	---	---	109		
			10/6/87-3	0.82	---	---	49		
			mean	0.88 +/- .05	---	---	---		
59	0.50	3.61	11/16/87-1	0.99	---	---	43	11	*
			11/16/87-12	0.96	---	---	46		
			11/16/87-23	---	0.59	---	27		
			mean	0.98 +/- .02	0.59	---	---		
0	0	11.53	Table 1	0.98 +/- .08	---	---	---		

MOD = minimum observed diameter, microns

* = exceptionally good data

purge rate, the higher the droplet velocity. As noted in Table 5, higher purge rates correspond to lower K_C's, for the 91% PERC mixture, and vice versa. This is expected because the droplets spend less time in the high temperature region near the top of the burner. The dependence of K_C on purge rate is observed only for mixtures which do not burn strongly (K_C < 0.8 mm2/s), i.e. the K_C for octane is not sensitive to changes in purge rate.

For the 88% PERC mixture shown in Table 5, Run #10/22/87-12 was not included in the average for that mixture composition because a) it was abnormally high compared with the other two values, b) the droplet images for this run were poor, making determination of droplet sizes difficult, and c) the omission or inclusion of this point does not affect the conclusions. Average values of each mixture were plotted as a function of volume percent PERC and presented in Figure 15. The shape of the oxidizing branch of Figure 15 is similar in shape to the TECA/nonane gasification rate constant curve shown in Figure 9 with the following exceptions: a) PERC/octane mixtures burn strongly until a critical concentration of 88% PERC is reached, while the critical TECA concentration is 75% by volume, b) the Cl/H ratio at the critical PERC and TECA concentrations is 2.5 and 0.66, respectively, and c) the Q_Cs at the critical PERC and TECA concentrations are 1.79 and 3.13 kcal/g, respectively. These observations suggest that PERC and TECA behave entirely differently from one another in an oxidizing flame environment. A hypothesis for the difference in behavior in flames for PERC and TECA is formulated below.

The region of interest for PERC and TECA behavior in the flame environment is in the fuel-rich pyrolysis zone, between the droplet surface and the flame, as shown in Figure 1. PERC molecules are relatively difficult to thermally decompose (Taylor and Dellinger, 1987). Thus PERC molecules can approach the flame zone quite closely before they begin to decompose. Once decomposition begins, the chlorine species liberated can scavenge H

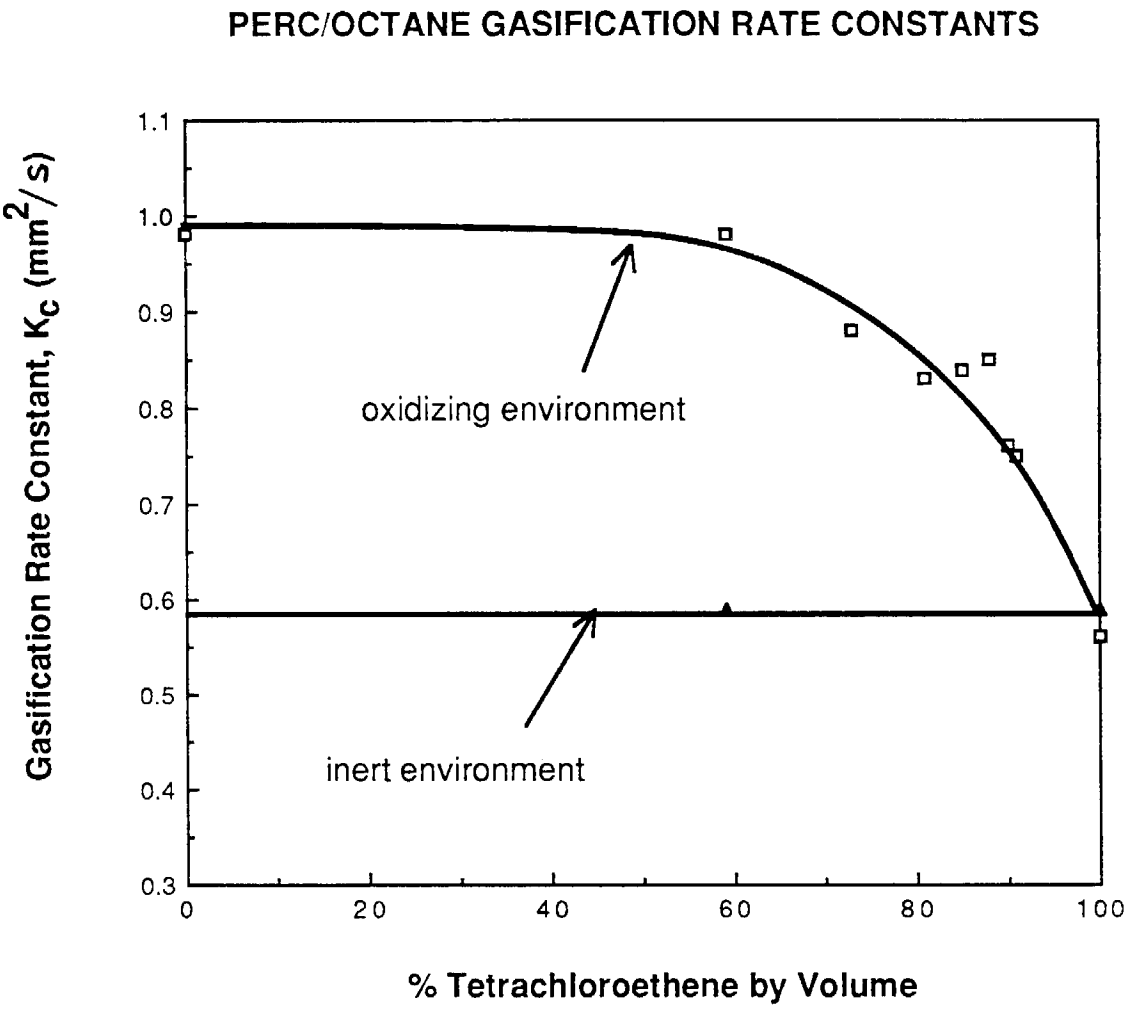


Figure 15. Gasification rate constants of tetrachloroethene/octane droplet mixtures in oxidizing and inert environments.

radicals and inhibit flame propagation. (See Equations (g), (h) and (i) for examples.) However, at high temperatures in, or very near the flame, the chain branching reactions (a), (b), (c) dominate the radical scavenging reactions. Thus, once in the flame, the high flame temperatures (adiabatic flame temperature of about 2300 K), are sufficient to destroy PERC efficiently.

In contrast, TECA, like all chloroalkanes (except perchlorinated alkanes) is subject to an endothermic decomposition reaction via a four-center elimination of HCl molecules (Senkan, 1982; Tsang, 1982) at a relatively low temperature. (The four-center elimination reaction can occur when there are adjacent Cl and H atoms which do not share the same carbon atom. The products of this reaction are a chlorinated ethene and HCl.) The molecular elimination reaction requires about 20 kcal/mol and has been calculated to occur at temperatures as low as 373 K (Semenov, 1952). If we follow the TECA molecule as it leaves the droplet surface, it is subject to an endothermic decomposition early in its gas-phase history. This breakdown could inhibit the flame in two ways: a) by cooling down the reactants, thereby slowing down the rate of reaction, or b) scavenging H radicals with HCl the primary decomposition product (see Equation [i], page 12). Experimental confirmation of this hypothesis was beyond the scope of this project, but will be pursued under a follow-on study under U.S. EPA Cooperative Research Agreement #CR-814869-01-0.

5. Chlorobenzenes:

The final group of compounds examined under this contract were the chlorobenzenes: monochlorobenzene (MCBZ), 1,2-dichlorobenzene (DCBZ), and 1,2,4-trichlorobenzene (TCBZ). A summary of the chlorobenzenes droplet gasification results is presented in Table 6. Gasification rates for each experiment as well as an arithmetic average with an uncertainty of +/- 1 standard

Table 6

SUMMARY OF CHLOROBENZENE DROPLET GASIFICATION RESULTS

Compound	Cl/H (mole ratio)	HHV (kcal/g)	Run ID	Kc (mm2/s)	Kv (mm2/s)	Dext (um)	MOD (um)
chlorobenzene	0.2	6.60	10/31/87-1	0.92	---	---	46
			10/31/87-2	0.89	---	---	43
			10/31/87-3	0.90	---	---	38
			mean	0.90 +/- .02	---	---	---
1,2-dichlorobenzene	0.5	4.57	10/29/87-2	0.85	---	---	35
			10/29/87-3	0.85	---	---	29
			10/29/87-4	0.86	---	---	43
			mean	0.85 +/- .01	---	---	---
1,2,4-trichlorobenzene	1.0	3.40	9/10/87-12	0.78	---	---	96
			9/10/87-234	0.79	---	70	36
			9/10/87-5	---	0.50	---	168
			mean	0.79 +/- .01	0.50	---	---

MOD = minimum observed diameter, micrometers

deviation are reported. The uncertainties in the K_C's are small; less than +/- 0.02 mm^2/s. The K_C results indicate fairly strong burning with the expected decrease in K_C with increasing chlorine substitution on the benzene ring. The flames observed for these droplets were very sooty, so much so that the contrast between the liquid droplet and the strobe flash was significantly reduced due to soot luminosity. Soot production was so extensive that a soot trail could be seen in the wake of the droplet. The extinction diameters for both MCBZ and DCBZ were at the limit of the optical system's ability to distinguish the droplet from the background. The extinction diameter of TCBZ droplets was 70 μm.

E. Research Implications for CARB

The implications of the results of this study are discussed in this section. The droplet research has been structured so that the feasibility of ranking incinerability of compounds, based upon single droplet gasification characteristics of pure compounds and their mixtures with HC fuels, could be evaluated. The droplet gasification data provide four types of results: a) gasification rate data, b) droplet flame extinction data, c) droplet composition history of the liquid phase, and d) observations of visible emissions from gases or particles surrounding gasifying droplets. A practical single droplet incinerability ranking scale would need to be based upon single droplet gasification rate and droplet extinction data, parameters that can be readily quantified.

A major problem with using measured parameters from droplet experiments to rank incinerability of compounds is that stable drops must first be generated and then they must be burned. The droplet generation procedures used for this project limit the compounds suitable for making droplets to those liquids with boiling points greater than about 90 ^{o}C. Unfortunately, many interesting compounds have boiling points below the droplet generation threshold. Furthermore, addition of compounds with higher boiling points to CHC's with lower boiling points creates a droplet mixture with a volatility differential. The data developed during this study has demonstrated that volatility differential causes the droplet composition to change constantly, which complicates ranking. Solid compounds would need to be dissolved or melted in order to be used with the droplet method.

A second problem with using droplets as a method to rank the incinerability of compounds is that the compounds must be capable of being burned. For example, the gasification rates for pure TECA and PERC were about the same, providing a superficial indication that they might behave similarly in a flame environment.

However differences in the appearance of the "flame-streaks" of these two compounds were observed, yielding visual evidence of a difference. Qualitative observations of this type are difficult to include in an incinerability ranking scale. To observe a definitive difference in the burning rates between TECA and PERC, readily combustible fuels of the same volatility would need to have been added to reveal the differences previously noted between the two compounds. However, multicomponent droplet studies are time consuming and are not conducive to the evaluation of a large number of compounds. Nevertheless, as a result of the TECA/nonane and PERC/octane studies, valuable insights into the destruction mechanisms of TECA and PERC in a flame environment were obtained.

The most serious drawback of attempting to use droplet-burning studies in an incinerability ranking scale is that there does not appear to be a simple relationship among droplet parameters that can be used to predict POHC DE. For example, by most incinerability ranking methods TECA would be considered relatively more easily destroyed than PERC. Yet the droplet burning results demonstrate that for the same relative mixture composition, PERC/octane mixtures can sustain a flame with relatively greater amounts of chlorine in the mixture. One cannot infer that TECA is more difficult to destroy than PERC from the above results, i.e., it is believed that the TECA was undergoing decomposition more readily than PERC, possibly even more completely before the flamelet surrounding the droplet extinguished. However, examination of the droplet data suggests that TECA interferes more readily with the maintenance of a flame than does PERC. Pilot-scale studies of an atomization failure condition in a turbulent flame reactor (TFR), have provided a tantalizing bit of data, possibly confirming the single droplet results (Chang, 1988). Chang observed that the concentrations of certain PICs such as benzene were slightly greater for a chloropentane/TECA/heptane mixture than for a PERC/TCBZ/heptane mixture fired under essentially the same conditions and overall

chemical composition. However, the DE of the chloropentane and TECA was observed to be over an order-of-magnitude greater than for PERC and TCBZ. The single droplet results suggest that TECA and by implication chloropentane (because it is also a chloroalkane) are easily destroyed and form HCl and chlorinated ethene PICs. The HCl can subsequently scavenge H atoms, reducing the concentration of OH radicals needed to attack the benzene ring. On the other hand PERC seems to be resistant to decomposition and may not interfere with the combustion process as readily. Thus the TFR results are consistent with the droplet results.

As a practical matter, it must be concluded that single droplet studies cannot be usefully applied as an incinerability index. However, the single droplet studies have yielded valuable insights into the importance of mixture volatility differential, possible chemical reactions occurring near the flame-zone and how they could affect not only the behavior of single droplet gasification, but also spray combustion situations operating in an atomization failure condition.

F. SUMMARY AND CONCLUSIONS

A summary of the experimental results and conclusions are presented below.

1. Droplets of alkanes, monochloroalkanes, tetrachloroethane (TECA), TECA/alkane mixtures, tetrachloroethene (PERC), PERC/octane mixtures, chlorobenzene, 1,2-dichlorobenzene, and 1,2,4-trichlorobenzene were generated and injected into a heated chamber of about 1400 K in two different environments; an oxidizing environment and an inert environment. These experiments provided information on droplet burning rates, extinction characteristics, and some qualitative features of the flames surrounding the droplets, all of which were used to explain how single droplets burn.

2. The classical D^2-Law can be used to describe the steady gasification region of single droplets. The gasification constant obtained from droplets injected into oxidizing and inert environments is called a burning or vaporization rate constant, respectively.

3. The burning rate constants of n-alkanes decreased for C_8 and C_9 and were relatively constant for all fuels greater than C_9. The burning rates of monochloroalkanes increased slightly for C_5 to C_7 monochloroalkanes and remained relatively constant for C_7 or greater. The burning rates for the C_5 to C_7 monochloroalkanes were slightly lower than the C_5 to C_7 burning rates for n-alkanes. The vaporization rates of n-alkanes and monochloroalkanes were approximately equal. The droplet extinction diameters of monochlorinated alkane droplets and n-alkane droplets were similar, from which it is concluded that the presence of a single chlorine atom in monochloroalkane molecules does not cause early flame extinction.

4. Droplets of pure TECA injected into a hot oxidizing environment did not burn (no observable net exothermicity) but decomposition, as evidenced by a blue-green emission from the gases surrounding the TECA droplets, was observed.

5. To burn TECA in the droplet form, n-alkanes were added to TECA. The TECA/nonane mixture was an equal volatility mixture while the TECA/heptane, TECA/dodecane, and TECA/hexadecane were mixtures with volatility differentials.

6. TECA/nonane mixtures burned strongly ($K_C > 0.8$ mm^2/s) for TECA concentrations less than a critical value of 75% by

volume. The Cl/H mole ratio and Q_C at the critical TECA concentration were 0.66 and 3.13 kcal/g, respectively.

7. TECA/nonane mixtures with greater than 90% TECA burned very weakly, if at all.

8. The addition of 15% by volume hexadecane to TECA caused the mixture to burn almost as well as pure hexadecane droplets and yielded small extinction diameters. Thus the addition of small quantities of low volatility alkanes to TECA promoted the rapid and complete burning of the droplet mixture.

9. Liquid-phase droplet sampling was conducted on 85% TECA/heptane, 85% TECA/nonane, 85% TECA/hexadecane, and 50% TECA/heptane mixtures to determine the liquid-phase compositional history of the droplets at various stages in their lifetimes. Both the 85% TECA/heptane and the 50% TECA/heptane showed a rapid loss of the higher volatility heptane. For the 85% TECA/nonane droplet, a slight increase in the TECA concentration was observed. The 85% TECA/hexadecane droplets showed a loss of the higher volatility TECA throughout the droplet lifetime. Thus for all cases except 85% TECA/nonane mixtures (nearly equal volatility), the higher volatility component of the mixture was lost throughout the droplet lifetime.

10. Droplets of pure tetrachloroethene (PERC) injected into a hot oxidizing environment did not burn (no observable exothermicity). Based on the lack of any observable light emission, either PERC did not decompose or the decomposition products did not emit visible light, c.f., TECA.

11. To burn PERC, octane was added to PERC to form an equal volatility mixture. PERC/octane mixtures burned strongly ($K_C > 0.8$ mm^2/s) for PERC concentrations less than a critical value of 88% by volume PERC. The Cl/H mole ratio and the Q_C at the PERC concentration were 2.5 and 1.79 kcal/g, respectively.

12. The TECA/nonane and PERC/octane results suggest that the thermal stability of molecules as well as the Cl/H or Q_C govern the burning characteristics of single droplets.

13. Monochlorobenzene, 1,2-dichlorobenzene, and 1,2,4-trichlorobenzene droplets burn strongly with an expected decrease in K_C with increasing chlorine substitution, but produced very sooty flames. The extinction diameter of 1,2,4-trichlorobenzene was slightly larger than the minimum observable by our experimental system, indicating a slightly

earlier extinction than for other chlorobenzenes. For trichlorobenzene the Cl/H ratio is unity.

14. Single droplet burning studies are not feasible for use as a means of ranking the incinerability of compounds because: a) there does not appear to be a simple relationship between POHC DE observed in pilot-scale spray studies and the results of droplet burning studies, b) droplet burning studies are very time consuming and are not conducive to examination of large numbers of compounds, and c) experimental constraints currently limit the range of compounds to those with moderately high boiling points (> 90 ^{o}C) and therefore omit important higher volatility compounds.

15. Single droplet studies are valuable in examining effects of mixture volatility differentials and chemical reactions occurring near the flame zone. Further they can be used to describe spray combustion processes in an atomizer failure mode.

G. FUTURE WORK

The work described in this report will be continued as part of a cooperative agreement with the EPA (CR-814869-01-0). Some of the plans for future work as part of the EPA cooperative agreement are described below.

1. Test the volatility differential concepts derived from the droplet-burning results: see to what extent they apply to spray combustion in pilot-scale combustors. For example if a low volatility hydrocarbon is added to a high volatility waste, does the mixture burn more completely in the spray combustor? Does the combustion of these mixtures in spray combustors affect the flame-holding capability of the combustor? Is the DE of these mixtures affected by the atomizer performance?

2. Droplet burning experiments may be continued with: a) tertiary mixtures of low volatility hydrocarbon, medium volatility waste, and high volatility hydrocarbon; b) mixtures which induce microexplosion (a rupture of the droplet causing extremely fine droplets to be formed). These mixtures may then be burned in a combustor to determine if these blending strategies improve the DE of the waste in a spray situation.

3. Determine if mixtures of pentachloroethane and chloroheptane, which are equal volatility mixtures and which should decompose at low temperatures via a four-center HCl elimination process, have similar droplet-burning characteristics to the TECA/nonane mixtures described in this report. Our current understanding suggests that these mixtures should have similar droplet burning characteristics. If the pentachloroethane/chloroheptane results are similar to the TECA/nonane results, then our hypothesis on the importance of thermal stability of the molecule will be strengthened.

4. Conduct gas phase sampling of the gases surrounding the burning droplet at extinction to determine PIC formation. Establish if the PICs formed at droplet extinction correlate with PICs observed in pilot-scale spray studies when operating under atomizer failure mode (producing large oversize droplets).

REFERENCES

Bose, D. and S.M. Senkan (1983). "On the Combustion of Chlorinated Hydrocarbons I. Trichloroethylene." Combust. Sci. and Tech. 35, 187.

Carnahan, R.D. and S.L. Hou (1975). "Ink Droplet Printing Devices." Presented at the IEEE/IAS 10th Annual Meeting.

Chang, D.P.Y., M.K. Richards and G.L. Huffman (1988). "Spray Combustion Studies of Surrogate Hazardous Waste Incineration." Draft Final Report for U.S. EPA Cooperative Research Agreement No. CR-813333-01-1.

Chang, W.D., S.B. Karra, and S.M. Senkan (1986). "Development of Detailed Chemical Kinetic Models for the High Temperature Oxidation of Chlorinated Hydrocarbons." Combust. Sci. and Tech. 49, 107.

Correa, S.M. and M. Sichel (1982). Nineteenth Symposium (International) on Combustion, p. 981.

Dellinger, B., J.L. Graham, D.L. Hall, and W.A. Rubey (1985). "Examination of Fundamental Incinerability Indices for Hazardous Waste Destruction." EPA Proceedings of the Twelfth Annual Research Symposium on Incineration and Treatment of Hazardous Wastes, p.160.

Dellinger, B., J.L. Torres, W.A. Rubey, D.L. Hall and J.L. Graham (1984). Hazardous Waste 1, 137.

Frenklach, M., J.P. Hsu, D.L. Miller, and R.A. Matula (1986). "Shock-Tube Pyrolysis of Chlorinated Hydrocarbons: Formation of Soot." Combustion and Flame 64, 141.

Gardner, F.H., R. Long, A. Graham and J. Badaksian (1966). Sixth Symposium (International) on Combustion, The Combustion Institute, p. 802.

Gaydon, A.G. (1957). The Spectroscopy of Flames, Chapman & Hall Ltd., p. 235.

Gaydon, A.G. and H.G. Wolfhard (1950). Proc. Roy. Soc. (London) A201, 570.

Godsave, G.A.E. (1953). Fourth Symposium (International) on Combustion, p. 818.

Goldsmith, M. and S.S. Penner (1954). Jet Propul. 24, 245.

Graham, J.L., D.L. Hall and B. Dellinger (1986). Environ. Sci. Technol. 20, 703.

Gupta, A.K. and H.A. Valeiras (1984). Combust. Flame 55, 245.

Kramlich, J.C., M.P. Heap, W.R. Seeker and G.S. Samuelsen (1984). Twentieth Symposium (International) on Combustion, 1991.

La Fond, R.K., J.C. Kramlich, W.R. Seeker and G.S. Samuelsen (1985). J. Air Poll. Control. Assoc. 35, 658.

Law, C.K. (1982). Prog. Energy Combust. Sci. 8, 171.

Law, C.K. (1975). Combust. Flame 24, 89.

Lee, A. (1987). U.C. Davis, Personal communication.

Lewis, B. and G. von Elbe (1987). Combustion, Flames and Explosions of Gases, 3rd ed., Academic Press, p. 577.

Makino, A. and C.K. Law (1988). "On the Controlling Parameter in the Gasification Behavior of Multicomponent Droplets." To appear in Combust. Flame.

Mulholland, J.A., R.K. Srivastava and J.V. Ryan (1986). "The Role of Rouge Droplet Combustion in Hazardous Waste Incineration." EPA Proceedings of Twelfth Annual Research Symposium on Incineration and Treatment of Hazardous Wastes.

Oppelt, T. (1987). J. Air Poll. Control Assoc. 37, 558.

Randolph, A.L. and C.K. Law (1986). "Influence of Physical Mechanisms on Soot Formation and Destruction in Droplet Burning." Combust. Flame 64, 267.

Randolph, A.L., A. Makino and C.K. Law (1986). "Liquid-Phase Diffusional Resistance in Multicomponent Droplet Gasification." To appear in Proceedings of the Twenty-First Symposium (International) on Combustion, The Combustion Institute.

Semenov, N.N. (1952). "The Chain Mechanism of the Decomposition of Halogenated Paraffins." U.S. AEC-tr-3976 (translated from Russian) from Uspekhi Khimii, Vol XXI, No. 6, pp. 641-713.

Senkan, S.M. (1982). "Combustion Characteristics of Chlorinated Hydrocarbons." in Detoxication of Hazardous Waste, Exner, J.H. ed., Ann Arbor Science, pp. 61-91.

Senkan, S.M., J.M. Robinson and A.K. Gupta (1983). "Sooting Limits of Chlorinated Hydrocarbon-Methane-Air Premixed Flames." Combust. Flame 49, 305.

Spalding, D.B. (1953). Fourth Symposium (International) on Combustion, 847.

Senser, D.W., V.A. Cundy and J.S. Morse (1987). Combust. Sci. Tech. 51, 209.

Taylor, P.H. and B. Dellinger (Nov., 1987). "A Thermal Stability Based Ranking of Hazardous Organic Compound Incinerability." Presented at the International Symposium on Incineration of Hazardous, Municipal and other Wastes, Palm Springs, CA.

Tsang, W. (1982). in Detoxication of Hazardous Waste, Exner, J.H. ed., Ann Arbor Science, pp. .

VanDell, R.D. and L.A. Shadoff (1984). Chemosphere 13, 1177.

Wang, C.H., X.Q. Liu and C.K. Law (1984). Combust. Flame, 56, 175.

Waterland, L. R. (1984). "Pilot-Scale Investigation of Surrogate Means of Determining POHC Destruction." Proceedings of the 77th Annual Meeting of the Air Pollution Control Association, Paper No. 84-9.1.

Williams, F.W. and R.S. Sheinson (1973). "Manipulation of Cool and Blue Flames in a Winged Vertical Tube Reactor", Combust. Sci. Tech. 7, 85.

Wise, H., J. Lorell and B.J. Wood (1955). Fifth Symposium (International) on Combustion, p. 132.

Wolbach, C. D. (1984). "Parametric Experimentation with a Pilot-Scale Boiler Burning Hazardous Compounds." EPA Proceedings of the Tenth Annual Research Symposium on Incineration and Treatment of Hazardous Waste, p. 76.