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Physical And Chemical Properties
Of Combustion Generated Soot

Reza Toossi
(Ph.D. Thesis)

May 1978

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Prepared for the U.S. Department of Energy under Contract No. W-7405-ENG-48

Physical and Chemical Properties of
Combustion Generated Soot

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	vii
ACKNOWLEDGMENT	ix
LIST OF FIGURES	x
LIST OF TABLES	xv
NOMENCLATURE	xvi
CHAPTER 1: INTRODUCTION	1
CHAPTER 2: BURNER STUDIES	4
2.1 Introduction	4
2.2 Temperature Distribution in the Porous Burner	6
2.2.1 Mathematical Model	6
2.2.2 Limiting Cases	11
2.2.3 Results and Discussion	12
2.3 Design and Construction	18
2.4 Apparatus	22
2.5 Measurement of Flame Temperature	24
2.6 Heat Losses to the Burner	26
2.7 Effects of Inert Gas Shroud	32
2.8 Determination of Burning Velocity	35
2.9 Conclusion	38
CHAPTER 3: PARTICULATE SAMPLING APPARATA	41
3.1 Introduction	41
3.2 Combustion Chamber	43

3.3	Sampling Probe	43
3.4	Dilution System	45
3.4.1	Boundary Layer Diluter	46
3.4.2	Determination of Dilution Ratio	49
3.5	Sample Allotment	49
3.6	Particle Collection System	52
CHAPTER 4: PARTICULATE SAMPLING RESULTS		
4.1	Operating Conditions	53
4.2	Size Distributions	53
4.2.1	Number, Surface, and Volume Distributions	53
4.2.2	Humidity Effects	63
4.2.3	Residence Time	65
CHAPTER 5: CHEMICAL COMPOSITION AND PROPERTIES		69
5.1	Introduction	69
5.2	Chemical Characterization	70
5.2.1	Surface Analysis	70
5.2.2	Bulk Analysis	82
CHAPTER 6: REACTION STUDIES IN A PLUME OF COMBUSTION PRODUCTS		84
6.1	Introduction	84
6.2	Mathematical Formulation	85
6.2.1	Governing Equations	86
6.2.2	Dimensionless Parameters	90
6.2.3	Initial Conditions	92
6.3	Solution and Results	93
6.4	Catalytic Conversion of SO ₂ in the Plume . . .	96
CHAPTER 7: CONCLUSIONS		105

APPENDIX A: CARBON IN FLAMES	108
A.1 Formation	108
A.2 Effects of Controllable Parameters	109
A.2.1 Pressure	109
A.2.2 Temperature	109
A.2.3 Composition	110
A.2.4 Electrical Field	111
A.3 Characterization of Soot	113
A.3.1 Size Distribution	113
A.3.2 Structure	114
APPENDIX B: ACETYLENE PURIFICATION SYSTEM	115
APPENDIX C: THERMOCOUPLE DESIGN AND TEMPERATURE CORRECTIONS .	118
C.1 Thermocouple Construction	118
C.2 Temperature Corrections	120
APPENDIX D: PARTICULATE LOSSES	124
D.1 Anisokinecity	124
D.2 Losses in the Sampling Tube	125
D.3 Coagulation Losses	128
APPENDIX E: ANCILLARY APPARATA	131
E.1 Particle Analysis	131
E.1.1 Number: Condensation Nuclei Counter .	131
E.1.2 Size: Electrical Aerosol Size Analyzer	131
a. Principle of operation	131
b. Sampling requirements	132
c. Data reduction	132
d. Error analysis	135

E.1.3 Mass: Carbon Analyzer	135
E.2 Gas Analysis — Condensation Dewpoint Hygrometer	136
APPENDIX F: ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS (ESCA)	137
REFERENCES	139

ABSTRACT

The physical and chemical properties of soot particles generated by an acetylene-air, premixed flame stabilized on a well-characterized, water cooled, porous, flat flame burner are analyzed over a wide range of operating parameters. From a preliminary analysis of the temperature distribution in the porous disk, it is concluded that burner performance is optimum for an aspect ratio < 0.3 , Péclet number < 0.5 , and Biot number < 1.0 . To characterize the soot generated in combustion systems as a function of combustion parameters, the temperature, velocity, and burner heat losses are measured over the stable range of burner operation. The flat flame achieved with this burner is uniform in temperature over the entire flame disk within a few percent of the maximum flame temperature. In separate experiments, hot film indicates that the cold flow gas velocity assessment is uniform within $\sim 10\%$ over the entire porous disk.

Particle size distribution measurements by an Electrical Aerosol Size Analyzer indicate two submicron modes, one centered at $\sim 80 \text{ \AA}$ and another which occurs only in luminous flames at high equivalence ratios at $\sim 500 \text{ \AA}$. The former is thought to be generated by the primary premixed flame, while the latter comes from the secondary diffusion flame. Scanning electron micrographs show particles which are approximately spherical. The chemical composition of soot collected on different filter media is determined by X-ray photoelectron spectroscopy (ESCA) and X-ray fluorescent techniques. Two oxygenated species, as yet

unidentified but here designated as O_I and O_{II} , adsorbed on carbon particles, are recognized. The ratios of atomic concentrations O/C and O_I/O_{II} are determined as a function of flame parameters. These ratios decrease as the flame equivalence ratio increases but remain constant at equivalence ratios > 2.0 . It appears that chemical properties of soot particles are highly affected by the precise mixture of the reactants when $\phi \leq 2.0$, but physical coagulation processes dominate at higher equivalence ratios.

The rate of heterogeneous oxidation of SO_2 in a plume containing combustion-generated carbon particles is also studied. Water vapor and oxygen concentrations along with particle size and concentration are found to have controlling influences on the oxidation of SO_2 . An analysis is presented in which integrated forms of species, momentum, and energy equations are solved to predict concentration histories along the trajectory of a reacting plume of combustion products.

ACKNOWLEDGMENTS

The author wishes to gratefully acknowledge the assistance of many of the faculty of the Mechanical Engineering Department and staff of the Atmospheric Aerosol Research group at the Lawrence Berkeley Laboratory for their contribution and guidance in this research. Professor P. J. Pagni, thesis advisor, has provided the overall guidance necessary for successful completion of this work. Dr. T. Novakov, head of the Atmospheric Aerosol Research group at Lawrence Berkeley Laboratory, encouraged me and provided much technical assistance throughout this research. Discussions with the Atmospheric Aerosol Research group staff, especially Drs. S. G. Chang, R. L. Dod, and P. J. Bekowies, are greatly appreciated.

The author wishes to convey his thanks and appreciation to Mr. R. C. Schmidt and Mr. H. A. Brendel for their assistance in building the experimental facilities necessary for completion of this work. Mr. J. Holthuis made a special effort in the construction of the burner. Finally the help given by Ms. Cecil Grant and Ms. Jeanne Sheriff in editing and Ms. Linda Wroth for typing the text is appreciated.

This research was supported under grants from the National Science Foundation-RANN, the U.S. Department of Energy, and the National Bureau of Standards.

LIST OF FIGURES

Fig. 2-1.	Model of flow-through porous disk: gas flows through the disk and is ignited at the top. The temperature at the lower surface is taken to be that of the average inlet and outlet water temperature	8
Fig. 2-2.	Nondimensional temperature distribution in the porous disk for $Bi = 0.0$ (insulated rim)	13
Fig. 2-3.	Effect of Peclet number on surface temperature for $Bi = 0.0$	15
Fig. 2-4.	Dimensionless surface temperature in the porous disk for different aspect ratios ($Pe = 0.1$, $\theta_w = -0.05$	17
Fig. 2-5.	Schematic of the burner. A mixture of reactant gases enter opening F and flow through the sintered disk A. Water is flowing through coil H to cool the burner. Gas shroud enters at E and flows into the annulus between point C and D. The outlet of the cooling coil is insulated by jacket G	19
Fig. 2-6.	Stability map of the flat flame burner for propane/air mixture	21
Fig. 2-7.	Schematic diagram of the experimental apparatus. Fuel and air are mixed and burned 2-3 millimeters above the disk	23
Fig. 2-8.	Radial temperature distribution of a flame of acetylene/air mixture. Temperatures are not corrected for radiation and convection losses. (a) $\phi = 1.0$, $\bar{S}_{25} = 21$ cm/sec; (b) $\phi = 0.7$, $\bar{S}_{25} = 21$ /cm/sec	25
Fig. 2-9.	Maximum flame temperature of an acetylene/air mixture as a function of equivalence ratios for different total reactant flow rates	27
Fig. 2-10.	Heat transferred to the burner as a function of burning velocity for lean acetylene/air flame. Solid lines are calculated heat losses based on adiabatic flame temperature, Q_T' ; dashed lines are experimental values, Q_B	31

Fig. 2-11.	Velocity distribution across the burner. O is with shroud; • is without shroud; lines at right represent the position of the inner and outer diameter of the main burner and shroud	33
Fig. 2-12.	Effect of a shroud of argon gas on temperature distribution across a flame of propane/air mixture. Operating conditions are $\phi = 1.2$, $\bar{S}_{25} = 10.2$ cm/sec, and velocity in the shroud is 10.2 cm/sec	34
Fig. 2-13.	Dependence of burning velocities on composition for acetylene/air mixtures at 1 atmosphere pressure . . .	37
Fig. 2-14.	Burning velocities of lean acetylene/air mixtures	49
Fig. 2-15.	Burning velocities of rich flame of acetylene/air mixtures. Burning velocities smaller than 5 cm/sec are not reported here because of lack of accurate flow-measurement device	40
Fig. 3-1.	Schematic of experimental setup. A mixture of dry purified air and acetylene is metered and then burned, producing a flat flame. Part of the combustion product is sampled at different locations and diluted before analysis	42
Fig. 3-2.	Sampling probe	44
Fig. 3-3.	Boundary layer diluter system	44
Fig. 3-4.	Equilibrium concentration of product of combustion of C_2H_2 -air flame, $T = 300^\circ K$	47
Fig. 3-5.	Sample allotment system. a) Size distribution for b) Filter collection	50
Fig. 4-1.	SEM of acetylene/air flame soot collected on different filter substrates. SEM accelerating potential = 20 kV. a) Blank 1 μm pore size Millipore filter, $M = 5000\times$; b) Soot at $\phi = 1.94$ on 1 μm Millipore, $M = 10600\times$, sampling time 10 minutes; c) Same as b), but $M = 42400\times$; d) Soot at $\phi = 1.40$ on 0.8 μm Nuclopore, $M = 8000\times$, sampling time is 6 hours; e) Soot at $\phi = 1.94$ on 1.0 μm fluoropore filter, $M = 9200\times$, sampling time 2 minutes; f) Same as e), but $M = 36800\times$	54

Fig. 4-2.	Number distribution of the C_2H_2 -air post-flame soot at different equivalence ratios. Sampling conditions are $RH = 70\%$ after dilution, $T = 298^\circ K$, and $\dot{V} = 37.2$ lpm at STP	57
Fig. 4-3.	Surface distributions of the C_2H_2 -air flame calculated from number distributions plotted in Fig. 4-2	58
Fig. 4-4.	Volume distributions of the C_2H_2 -air flame calculated from number distributions plotted in Fig. 4-2	59
Fig. 4-5.	Soot volume fraction for acetylene/air flame soot as determined from size distribution	61
Fig. 4-6.	Comparison of the total number of particles per cm^3 of undiluted product gases at STP detected with CNC and EASA. Sampling conditions are $RH = 70\%$, $T = 298^\circ K$, and $\dot{V} = 37.2$ lpm at STP	62
Fig. 4-7.	Particle concentration (number/ cm^3 of the product at STP) as a function of relative humidity in the sampled gas. Dilution ratio was kept constant and equal to 16.4. Total flow rate of the reactants is $\dot{V} = 37.2$ lpm at STP	64
Fig. 4-8.	Particle number concentration as a function of total residence time in the system for an acetylene/air flame, with $\phi = 1.9$, $RH = 70\%$, and $\dot{V} = 37.2$ lpm at STP. The dashed line is the predicted concentration due to coagulation losses. It is assumed that particles are monodispersive and are $100 \text{ \AA}$ in diameter initially.	66
Fig. 5-1.	Wide scan (XPS and Auger) of an acetylene/air flame ($\phi = 1.94$, $\bar{S}_{25} = 23.6$ cm/sec) soot collected on a silver filter	71
Fig. 5-2.	Change in peak intensities as a function of exposure time in vacuum	73
Fig. 5-3.	X-ray photoelectron spectra near $C(1s)$ for carbon species for an acetylene/air flame soot sample collected on a silver-membrane filter.	75
Fig. 5-4.	Same as Fig. 5-3, but at binding energies close to the $O(1s)$ binding energy	76

Fig. 5-5.	Deconvolution of the typical oxygen band to two bands of symmetric profile: each band has a nearly Gaussian shape. The two species are designated as $O_I(1s)$ at maximum peak binding energy of 534.3 eV, and $O_{II}(1s)$ at maximum peak binding energy of 532.4 eV	77
Fig. 5-6.	Change of ratio of atomic concentration as a function of equivalence ratio. It is seen that chemical composition of Nuchar is similar to the fine soot particles generated close to the threshold limit of flame luminosity	79
Fig. 6-1.	Coordinate system. ρ , T , and u are the potential density, absolute temperature, and velocity; b is half the plume diameter, and v is wind velocity	87
Fig. 6-2.	Plume trajectory. The dotted line is the centerline. Note the periodic nature of the plume due to the stratification. The plume eventually stabilizes at its maximum rise	94
Fig. 6-3.	Dimensionless plume rise as a function of non-dimensional distance from the stack	95
Fig. 6-4.	Dimensionless temperature and velocity distribution inside the plume as a function of distance downstream of the stack. U_x is the component of velocity in the horizontal x direction	97
Fig. 6-5.	Nondimensional concentration of different species vs. distance traveled downstream from the stack. Nondimensional concentration profiles are $w_1 = 5.55 \times 10^{-5}$, $w_2 = 2.82 \times 10^{-5}$, $w_3 = 17.33$	102
Fig. 6-6.	a) Sulfate concentration; and b) fraction converted in the plume as a function of distance downstream of the stack. $T_0 = 293^\circ K$, $T_1 = 290.6^\circ K$, $T_2 = 388.0^\circ K$, $w_1 = 5.55 \times 10^{-5}$, $w_2 = 2.82 \times 10^{-5}$, $w_3 = 17.33$	104
Fig. B-1.	XPS spectra of a) nonpurified acetylene soot (top spectra); and b) purified acetylene soot (bottom spectra). An order of magnitude reduction in phosphorus and ammonium complex and a significant increase in sulfate is observed	116
Fig. C-1.	Thermocouple	119
Fig. C-2.	Emissivity of the Pt-Pt-10% Rh thermocouple as a function of temperature	122

Fig. D-1.	Diffusion losses as a function of particle diameters for different total flow rates	127
Fig. D-2.	Coagulation losses as a function of particle diameters for different initial concentrations	130
Fig. E-1.	Minimum number of detectable particles by EASA instrument at each size range	133

LIST OF TABLES

Table 3-1.	Required dilution ratios for several equivalence ratios and given sampling conditions	48
Table 5-1.	Summary of the ESCA analysis of particulates collected on silver filters	80
Table 5-2.	Bulk analysis of soot samples from an acetylene-air flame ($\phi = 1.9$, $\bar{S}_{25} = 19.6$, R.H. = 70%, and $T = 65^\circ\text{F}$ at the sampling point)	83
Table 6-1.	Summary of the literature results for plume trajectory for limiting cases	98
Table 6-2.	Plume trajectory for Figures 6-5, 6-6	101
Table D-1.	Penetration through the sampling system	128

NOMENCLATURE

a	aspect ratio
b	plume radius (m)
Bi	Biot number
c_p	specific heat at constant pressure (cal/g °K)
C_j	concentration of pollutant j (g/m ³)
d	diameter (cm)
D	diffusion coefficient (cm ² /sec)
E	activation energy (kcal/mole)
F_i	buoyancy flux (cm ⁴ /sec ³)
Fr	Froud number
f_v	soot volume fraction
g	gravitational acceleration (m/sec ²)
h	thermal conductance (cal/sec·cm ² ·°C)
H	plume height (m)
k	rate constant (m ⁶ /g ²)
k_0	coagulation constant
ℓ_b	buoyancy scaling length (m)
ℓ_m	momentum scaling length (m)
L	length (m)
$\dot{m}$	mass flow rate (g/sec)
M	molecular weight (g/mole)
n	molecularity

n	number density (number/cm ³)
N	number of species
Nu	Nusselt number
p	penetration
Pe	Péclet number
Pr	Prandtl number
q	heat flux (cal/sec)
$\dot{Q}$	rate of heat loss (or emission)(cal/sec)
$\dot{Q}'$	rate of heat loss per cm ³ of fuel (cal/cm ³ ·sec)
r	radial distance
r_p	particle radius
r_e	thermal resistivity (ohms)
R	velocity ratio
R	radius (cm)
Re	Reynolds number
s	distance along plume trajectory (m)
S	stratification parameter
S_u	burning velocity (cm/sec)
$\bar{S}_{25}$	velocity of unburned gas measured at 25°C and 1 atm (cm/sec)
t	time (seconds)
T	temperature (°K)
Ta	Taylor number
u, v	velocity (cm/sec)
$\dot{V}$	volume flow rate (liters/min)
w_j	reaction rate for species j (g/m ³ ·sec)
x, z	horizontal and vertical coordinates (m)

α, β	entrainment constants
Γ_j	flux of species j (g/sec)
δ	standoff distance (cm)
ϵ	entrainment rate (m^2/sec)
ϵ	emissivity
ϕ	equivalence ratio
λ	thermal conductivity ($\text{cal}/\text{sec}\cdot\text{cm}\cdot^\circ\text{C}$)
ρ	density (g/m^3)
ρ^*	potential density (g/m^3)
ω	Brunt Vaisalla frequency (sec^{-1})
θ	angle
σ	Stefan Boltzmann constant
ν	kinematic viscosity (cm^2/sec)

Subscripts

0	surface condition, initial condition
1	soot (or carbon)
2	SO_2
3	water vapor
ad	adiabatic
ϵ_L	centerline
cond	conduction
f	fuel
fl	flame
i	stack
m	maximum

p	particle
Rad	radiation
s	sulfate
w	water (liquid)
∞	smbient

CHAPTER 1

Introduction

In this study, the physical and chemical properties of combustion-generated soot particles are investigated over a wide range of the pertinent combustion parameters. Soot generated by an acetylene-air flame stabilized on a well-characterized cooled porous premixed flat flame burner is analyzed for size, distribution, concentration, chemical composition, and chemical reactivity. This information is of considerable importance to both industry and environmental pollution studies. Only recently these questions have evoked a great interest among environmentalists because it was shown that soot particles are not only a major source of air pollution in themselves [1] but that they also affect the rate of NO_x , CO, and hydrocarbon formation [2,3]. Furthermore, soot particles are efficient catalysts for sulfur dioxide oxidation in polluted air [4,5].

The catalytic properties of the soot particles and their abundance in the ambient air call for a thorough understanding of the properties of these particles. It is demonstrated that most of these particles are primary [6] and therefore the heterogeneous gas-particle reaction mechanism might be even more, or at least as, important as the gas phase photochemical or the solution chemical mechanisms. Since the rates of these heterogeneous reactions depend strongly on specific surface area, fine soot particles generated in nonluminous or slightly luminous "clean" flames may be important in these reactions.

Most of the literature on the properties of soot particles deals with the initiation and characterization of the soot particles within the flame, or the soot emitted by flames as carbon black. The characterization is usually done by measuring the amount of scattered light or by probing the gases and analyzing deposits with an electron microscope (e.g., Howard et al. [7]). These techniques do not reveal much information about the properties of soot particles from "nonsooty" flames. The question of what happens to the nuclei after they leave the flame remains unanswered. This task is carried out in this study by developing a well-controlled apparatus for soot generation and by analyzing the soot samples over a wide range of parameters. Some of these parameters, such as total flow rate, heat removal rate, and equivalence ratio, are important during the course of a reaction inside the flame; while other parameters, such as residence time, humidity content, and amount of dilution control the rate of growth of soot particles during their transport. Chemical reactions which are directly affected by the presence of these particles are also of interest. This task is particularly difficult because combustion, fluid mechanics, transport, and chemical processes play important roles in the formation and characterization of soot particles. Collaboration between the Mechanical Engineering Department of the University of California at Berkeley and the Atmospheric Aerosol Research Group of the Lawrence Berkeley Laboratory facilitated this inquiry.

The research consisted of three parts: 1) design of a soot generation system, 2) characterization of the soot produced, and 3) modeling of transport in a reacting plume. Chapter 2 explains the design of a

porous plate flat flame burner. Flame temperature, burning velocity, and rate of heat removal from the burner over the stable range of flames are determined. The stability of the burner depends on the rate of heat removal by the porous disk and the surface temperature distribution. Effects of burner size, sintered material, and combustion regime on the nonuniformity of disk temperature are also considered in Chapter 2. Chapter 3 is devoted to an experimental system design and sampling. Particle number and size distribution were measured by commercial equipment and by scanning electron micrographs and reported in Chapter 4. X-ray photoelectron spectroscopy analyses of these particles are discussed in Chapter 5. Chapter 6 describes mathematical modeling of the plume dispersion from tall stacks under neutral and stable ambient conditions with laminar cross wind when chemical reactions are present. As a specific example, transport of pollutant gases from a coal-fired power plant is considered. A brief summary of known properties of soot particles produced in flames and the effect of combustion parameters on soot production is given in Appendix A. Appendix B describes the acetylene purification system, and Appendix C describes the thermocouple design. Appendixes D, E, and F consider the particulate losses, data reductions, and laboratory instrumentation used in this work.

CHAPTER 2

Burner Studies

2.1 Introduction

A water-cooled porous premixed flat flame burner is designed and characterized in the range of stable flames for acetylene and propane. A model is presented to evaluate the effects of geometry and material on some aspects of the burner performance. Flat flame burners have long been used to investigate combustion processes because the flame stabilized on these burners has uniform temperature, burning rate, and chemical composition. Powling [8] in his pioneer work used glass beads followed by a matrix of rolls of alternately plain and corrugated metal tapes to achieve the uniform distribution of the premixed reactants. The use of metal gauze was necessary for flame stability. The burner was not cooled, and therefore a stable flame was limited to a narrow range of mixture conditions near the lean limit of combustion.

Botha and Spalding [9] were able to stabilize the flame at higher velocities and for richer mixtures by providing a cooling jacket at the rim. In Hoelscher-Biedler's burner [10], stabilization was achieved by means of a baffle placed in the hot exhaust product gases. Further improvements were made by Kaskan [11], who designed a burner in which heat was removed uniformly by a cooling coil imbedded in the porous sintered disk. After passing through the disk, the gas velocity was not found to be uniform over the entire surface. Therefore the one-dimensional nature of these flames was limited to only certain regions

on the burner surface where gas velocities were uniform.

Diffusion flat flames were also obtained by a proper design of the burner. Wolfhard [12] used a diaphragm to separate fuel and oxidizer. The sudden removal of the diaphragm and concurrent ignition resulted in a flat wedge of combustion products at the interface. A counterflow diffusion burner [13] was designed in which fuel and oxidizer were flown through two separate jets facing each other. Each of the two jets was similar in construction to the premixed burners of reference 8.

Diffusion flames generally have a greater tendency to smoke than premixed flames. Chemical reactions in diffusion flames are not chemically rate controlled. The characteristic reaction time is much less than the characteristic diffusion time, and therefore diffusion is rate controlling. Thermal decomposition of fuel takes place in the preheating zone while it diffuses to the reaction front. The result is a high concentration of hydrocarbon radicals which cause formation of soot [14]. In premixed flames, oxygen and fuel are intimately mixed before reaction. The soot formation reaction rate in such flames must compete with the most rapid oxidation reactions for the carbon atoms. The result is a lower tendency toward soot formation and smaller size soot particles (40 to 100 Å in premixed flames, compared with 1100 to 1300 Å in diffusion flames [14]).

Since the finer soot particles are expected to have larger specific surface sites for small mass loadings, the soot generated by premixed flames might be a better catalyst in the heterogeneous gas-particle reaction. It is resolved that a premixed flat flame burner would be suitable in this study.

2.2 Temperature Distribution in the Porous Burner

A one-dimensional flat flame is defined as one which has uniform temperature and velocity in the radial and tangential directions. Theoretically this is possible only when the temperature and velocity of the reacting gas exiting the porous disk are uniform. The temperature of the gas at each point is the same as the disk temperature within a few pore diameters of the disk [15]; therefore it is necessary for a flat flame burner to have little or no radial temperature gradient across the porous disk. Furthermore, radiation losses from the flame will be uniform under these conditions. A model is presented to investigate temperature nonuniformity in a porous disk burner similar to the one used here.

2.2.1 Mathematical Model

The basic assumptions are:

1. A steady-state condition is present.
2. The temperature of the gas is the same as the temperature of the disk at each point within the disk.
3. The cooling water maintains the entire plane of the coil assembly at a constant temperature T_w equal to the average of the inlet and outlet water temperatures.
4. Fluid properties such as density, specific heat, and viscosity are constant.
5. The average velocity at the point of exit is the same as the incoming gas velocity and is equal to the total flow rate divided by the disk surface area; i.e., details of the jets and pores are ignored.

6. Emissions from the surface are negligible compared with the radiation from the flame. Conduction in the preheating zone is also negligible.

Preliminary analyses showed that the temperature distribution in the portion of the disk below the cooling coil is not of interest to this analysis. The temperature in this region is nearly linear in the direction parallel to the burner axis between the water temperature and the incoming gas temperature. Since these two temperatures differ by only a few degrees, the temperature gradient is negligible and this heat loss can be neglected. Under the above assumptions, the energy equation for an element within the sintered disk of Figure 2-1 becomes:

$$\lambda \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial z^2} \right] - \rho c_p v \frac{\partial T}{\partial z} = 0 \quad (2-1)$$

ρ , c_p , and v are density, specific heat, and velocity of the incoming gas respectively. λ is the thermal conductivity of the porous media.

Boundary conditions are:

$$\text{at } z = 0 \quad T = T_w \quad (2-2a)$$

$$\text{at } z = L \quad \lambda \frac{\partial T}{\partial z} = \dot{q}_{fl}'' \quad (2-2b)$$

$$\text{at } r = r_0 \quad \lambda \frac{\partial T}{\partial r} = h(T_0 - T) \quad (2-2c)$$

$\dot{q}_{fl}''$ is the heat flux from the flame by radiation and conduction. h is conductance at the burner periphery defined as

$$h = \frac{1}{\Sigma R_n}$$

where ΣR_n is total thermal resistance at the rim and is the sum of the

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Fig. 2-1. Model of flow-through porous disk: gas flows through the disk and is ignited at the top. The temperature at the lower surface is taken to be that of the average inlet and outlet water temperature.

internal resistance of the inner and outer rim and flow resistance of the shroud gas flow. For a thin rim, $t \ll r_0$,

$$\sum R_n = \frac{2t}{\lambda_s} + \frac{1}{\bar{h}_{sh}} + \frac{1}{\bar{h}_0}$$

where λ_s = thermal conductivity of the tube

t = thickness of the tube

$\bar{h}_0$ = unit surface conductance over the exterior surface

$\bar{h}_{sh}$ = unit surface conductance in the shroud.

For the laminar flow of the gas in a short duct, $\bar{h}_{sh}$ can be approximated by the Pohlhausen equation for flow over a flat plate [16]:

$$\bar{h}_{sh} = \frac{Re_D \cdot Pr}{4} \left(\frac{D}{L}\right)^2 \ln \left[1 - \frac{2.654}{Pr^{0.167} (Re_D \cdot Pr \cdot D/L)^{0.5}} \right]^{-1}$$

Introducing the dimensionless quantities $\bar{z} = z/L$, $\bar{r} = r/r_0$

$$Pe = \frac{(\rho c_p) g \nu L}{\lambda}, \quad a = \frac{L}{r_0}, \quad \bar{T} = \frac{T - T_0}{q_{fl} L / \lambda}, \quad Bi = \frac{hr_0}{\lambda}, \quad \text{and} \quad \theta_w = \frac{T_w - T_0}{q_{fl} L / \lambda},$$

the governing equations and their boundary conditions become

$$a^2 \left[\frac{1}{\bar{r}} \frac{\partial}{\partial \bar{r}} \left(\bar{r} \frac{\partial \bar{T}}{\partial \bar{r}} \right) \right] + \frac{\partial^2 \bar{T}}{\partial \bar{z}^2} - Pe \frac{\partial \bar{T}}{\partial \bar{z}} = 0 \quad (2-3)$$

$$\bar{z} = 0 \quad \bar{T} = \theta_w \quad (2-4a)$$

$$\bar{z} = 1 \quad \frac{\partial \bar{T}}{\partial \bar{z}} = 1 \quad (2-4b)$$

$$\bar{r} = 1 \quad \frac{\partial \bar{T}}{\partial \bar{r}} = -Bi \cdot \bar{T} \quad (2-4c)$$

The above set of differential equations with nonhomogeneous boundary conditions can be written in terms of the superposition of the two

equations with homogeneous boundary conditions. Assuming a product solution

$$\theta = R(\bar{r}) \cdot Z(\bar{z})$$

for each case and solving by the method of separation of variables after some manipulation, the final results will be

$$\begin{aligned} \bar{T}(\bar{r}, \bar{z}) = \exp\left(\frac{Pe}{2} \bar{z}\right) & \left\{ \sum_{n=1}^{\infty} C_{n1} \sinh(\alpha_n \bar{z}) J_0(\xi_n \bar{r}) \right. \\ & \left. + \sum_{n=1}^{\infty} C_{n2} [\cosh(\alpha_n \bar{z}) - E \cdot \sinh(\alpha_n \bar{z})] J_0(\xi_n \bar{r}) \right\} \end{aligned} \quad (2-5)$$

where

$$E = \frac{\alpha_n \sinh(\alpha_n) + \frac{Pe}{2} \cosh(\alpha_n)}{\alpha_n \cosh(\alpha_n) + \frac{Pe}{2} \sinh(\alpha_n)}$$

$$\alpha_n^2 = (a \xi_n)^2 + \left(\frac{Pe}{2}\right)^2$$

$$C_{n1} = \frac{2Bi}{(\xi_n^2 + Bi^2)} \cdot \exp\left(-\frac{Pe}{2}\right) \left\{ \alpha_n \cosh(\alpha_n) + \frac{Pe}{2} \sinh(\alpha_n) \right\}^{-1} \cdot \frac{1}{J_0(\xi_n)} \quad (2-5a)$$

$$C_{n2} = \frac{2Bi}{(\xi_n^2 + Bi^2)} \cdot \frac{\theta_w}{J_0(\xi_n)} \quad (2-5b)$$

and ξ_n 's are the roots of the following equation:

$$\xi_n J_1(\xi_n) - Bi J_0(\xi_n) = 0 \quad (2-6)$$

Here J_n is the Bessel function of first kind of order n .

2.2.2 Limiting Cases

a) $Bi \rightarrow \infty$, *highly conducting rim*. In this case the boundary condition at the rim, Eq. (2-4e), becomes

$$\bar{T}(\bar{r}) = 0 \quad (2-7)$$

The solution given by Eq. (2-5) is still valid for the new set of boundary conditions, but the constants C_{n1} and C_{n2} are given by:

$$C_{n1} = \frac{2}{\xi_n} \cdot \exp(-Pe/2) \left\{ \alpha_n \cosh(\alpha_n) + \frac{Pe}{2} \sinh(\alpha_n) \right\}^{-1} \cdot \frac{1}{J_1(\xi_n)} \quad (2-8a)$$

$$C_{n2} = \frac{2}{\xi_n} \cdot \frac{\theta_w}{J_1(\xi_n)} \quad (2-8b)$$

Here ξ_n 's are the roots of [69, p. 142]

$$J_0(\xi_n) = 0 \quad (2-9)$$

b) $Bi \rightarrow 0$, *a perfectly insulated rim*. Heat conduction in this case is one dimensional, and the governing equations and the corresponding boundary conditions become:

$$\lambda \frac{d^2 T}{dz^2} - \rho c_p v \frac{dT}{dz} = 0 \quad (2-10)$$

$$\text{at } z = 0 \quad T = T_w \quad (2-11)$$

$$z = L \quad \lambda \frac{dT}{dz} = q_{f1}'' \quad (2-12)$$

If we define $T' = \frac{T - T_w}{\frac{q_{f1}'' L}{\lambda}}$ as the new nondimensional temperature, with

other variables as previously defined, the equations in dimensionless form become

$$\frac{d^2 T'}{d\bar{z}^2} - Pe \frac{dT'}{d\bar{z}} = 0 \quad (2-13)$$

$$\text{at } \bar{z} = 0 \quad T' = 0 \quad (2-14a)$$

$$\text{at } \bar{z} = 1 \quad \frac{dT'}{d\bar{z}} = 1 \quad (2-14b)$$

The solution is:

$$T'(z) = \frac{\exp(Pe \cdot \bar{z}) - 1}{Pe \cdot \exp(Pe)} \quad (2-15)$$

The surface temperature becomes uniform at

$$T'_s = \frac{1}{Pe} [1 - \exp(-Pe)] \quad (2-16)$$

while the profile through the porous disk is linear for most Pe as discussed in the next section.

2.2.3 Results and Discussion

Numerical calculations have been made to determine the temperature distribution in the disk over a wide range of parameters. Dimensionless temperature distribution in the disk as a function of height is plotted for the ideal limiting case $Bi = 0.0$ in Figure 2-2. This figure indicates an approximately linear temperature profile in the disk when the Péclet number is less than 0.5, the upper limit range for most practical cases ($0.005 < Pe < 0.5$). The temperature increases linearly from T_w at the plane of the coil to the surface of the burner. When $Bi = 0$, dimensionless surface temperature is calculated by Eq. (2-16) and is

XBL 784-721

Fig. 2-2. Nondimensional temperature distribution in the porous disk for Bi = 0.0 (insulated rim).

plotted in Figure 2-3. For small Péclet numbers, the nondimensional surface temperature changes little from unity. Assuming

$$T'_s = \frac{T_s - T_w}{\frac{q_{fl}'' L}{\lambda}} = 1$$

$$\text{we have } T_s = T_w + \frac{q_{fl}'' L}{\lambda_s} \quad (2-17)$$

This equation shows that surface temperature of the disk can easily be found for the ideal burner only if heat flux from the flame is known. Unfortunately, these losses cannot always be estimated easily to a high degree of accuracy. Assuming convective losses are unimportant,

$$q_{fl}'' = q_{rad}'' + q_{cond}'' \quad (2-18)$$

Assuming unit shape factor between the disk and the flame, the radiation heat flux can be written as

$$q_{rad}'' = \sigma \epsilon_{fl} (T_{fl}^4 - T_s^4) \approx \sigma \epsilon_{fl} T_{fl}^4 \quad (2-19)$$

Values of flame emissivity ϵ_{fl} are very difficult to estimate and can vary from 0.01 to 0.3 in flame thermal radiation [17]. An accurate estimate of this variable can be made only if detailed temperature and composition profiles are known throughout the reaction zone. Assuming conduction is significant only in the direction of the reaction coordinate, conduction loss can be written to the first approximation as

$$q_{cond}'' \approx \bar{\lambda}_g \frac{T_{fl} - T_g}{\delta} \quad (2-20)$$

where $\bar{\lambda}_g$ is the average thermal conductivity of the reactant gases in the preheating zone, T_g is the surface temperature, and δ is the standoff

Fig. 2-3. Effect of Péclet number on surface temperature for $Bi = 0.0$

distance. Standoff distance itself is a function of combustion parameters, such as nature of the reactants, burning rate, and pressure; and therefore it has to be measured experimentally. Also it is seen from Eq. (2-20) that conduction losses can be estimated only if the surface temperature T_s is known a priori. Therefore, it is concluded that a trial-and-error approach must be used to calculate surface temperature from the set of equations, (2-17) to (2-20).

When the burner rim is not insulated ($Bi \neq 0$), the temperature distribution is no longer one dimensional, and it changes in the radial direction. The disk surface temperature is plotted in Figure 2-4 for various boundary conditions and different aspect ratios. As the Biot number increases, surface temperature deviates from the one-dimensional case and the effect of the rim boundary condition becomes more pronounced. At the limiting case of $Bi \rightarrow \infty$, surface temperature at the edge drops sharply to the ambient condition. When $Bi = 1$, surface temperature at the edge drops only 10% from its maximum temperature at the center.

Detailed calculations show that temperature distribution remains practically unchanged when the aspect ratio is small ($a < 0.3$). Figure 2.4 also shows that disk maximum temperature is independent of the Biot number for small aspect ratios ($a < 0.3$). Thus the graphs of Figure 2-2 also represent the centerline temperatures of the disk for small aspect ratios, irrespective of their rim boundary conditions.

Ideally burners with small aspect ratios are more uniform in temperature than larger ones. However, shorter disks might not be so efficient as taller disks in smoothing the flow; and therefore velocity

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Fig. 2-4. Dimensionless surface temperature in the porous disk for different aspect ratios ($Pe = 0.1$, $\theta_w = -0.05$).

nonuniformity might increase, which in turn reduces temperature uniformity. Increase in burner diameter requires a much larger flow rate of reactants and therefore should be limited. The optimum value of the aspect ratio depends therefore on the individual burner design and the effectiveness of the porous disk in smoothing the flow field; but it should be kept below 0.3 for the reasons discussed above. The upper limits for Péclet and Biot numbers are set at 0.5 and 1.0 respectively. These requirements can be met by selecting a highly thermally conductive material for the porous disk and by insulating the rim.

2.3 Design and Construction

The schematic of the burner is shown in Figure 2-5. A fuel-air mixture enters the burner at F and is distributed over the cross section of the burner by the sintered disk A. The flat flame stabilizes a few millimeters downstream of the disk. The cooling water is supplied to the burner by a 3.2-mm (1/8" O.D.) copper tubing H at a constant head. Gases providing the atmospheres, other than air, are supplied to inlet E at the base. Sintered disk B insures flow uniformity of these gases. The construction of the burner was carried out in the following steps: The copper tubing was rolled in a helical manner with rings of equal spacing and imbedded in the sintering mold, ensuring that the plane of the coil was parallel with the burner surface, so a temperature gradient would not occur.

The assembly was sintered using tin-coated atomized copper powder (61 A, powder manufactured by Alcan Metal Powder) with a particle size of 30-100 mesh size (0.15 - 0.18 mm diameter). During sintering, the tin

XBL 781-36

Fig. 2-5. Schematic of the burner. A mixture of reactant gases enter opening F and flow through the sintered disk A. Water is flowing through coil H to cool the burner. Gas shroud enters at E and flows into the annulus between point C and D. The outlet of the cooling coil is insulated by jacket G.

coating bonds the particles together and diffuses into the copper to form bronze. The choice of powder was based on optimization of the corrosion resistance to reactant gases, heat capacity, pressure drop, and permeability. Sintering was carried out under an argon atmosphere for 20 minutes at 840-860°C, the temperature range specified by the manufacturers for achieving sufficient diffusion, acceptable metallurgical bonding, uniform density, and for avoiding surface oxidation. The sintered porous disk was subsequently gold plated to prevent corrosion and oxidation by combustion gases. The annular ring B was sintered in a similar manner. Next, the sintered disks were pressure fitted between two brass tubings, C and D, as shown in Figure 2-5. A stainless steel tubing jacket G was provided on the water outlet to minimize heat losses to the ambience.

A burner constructed in this manner can be stabilized over a wide range of equivalence ratios and flow rates. Figure 2-6 shows the stability map for a propane-air flame. There is a similar map for an acetylene-air flame, but these results are not reported because of a leak found at the burner edge. When the mixture is ignited, the flame takes different shapes, depending on the flame velocity and equivalence ratio. For each total flow rate, there is a certain equivalence ratio below which the mixture cannot be ignited. As the flame becomes richer, the lifted flame becomes more stable until it stabilizes as a flat flame. For a very rich mixture, the flame eventually becomes conical, and finally soot formation is started. Figure 2-6 shows that for propane flames at high flow rates (> 15 lpm), these limits are well defined and independent of flow rates. Flames can be stabilized for flow rates

XBL 784-728

Fig. 2-6. Stability map of the flat flame burner for propane/air mixture.

greater than those reported here, but experimental difficulties limited the maximum flow rates to 40 lpm.

2.4 Apparatus

A schematic diagram of the experimental apparatus is shown in Figure 2-7. The air supply from commercially compressed cylinders is dried by passing it through a bed of silica gel dessicator. A 10-gallon surge tank was found to be effective in eliminating flow fluctuations. A commercial, 99.6% pure acetylene supplied by Matheson Gas Products was used as fuel. The flow rates of the fuel and air were metered separately through rotameters within $\pm 0.5\%$ full scale and mixed in a mixing tee before entering the burner. The temperature and pressure of the reactant gases were measured by means of pressure gauges and thermocouples and the flow rates were corrected to standard ambient conditions (60°F, 1 atm). The cooling water was filtered to remove particle contaminants in the water. Flow rates and inlet and outlet temperatures of the water were then monitored.

The thermocouple sensors were shielded by stainless steel tubing to prevent possible corrosion by water. Two very fine screens were provided in the cooling coil 0.5 cm upstream of the thermocouple. This was done to disturb the fully developed temperature profile which would otherwise be established in the coil. For each equivalence ratio, a mixture of fuel and air was ignited, and the flow rates adjusted until the flame became flat. After each adjustment, at least 10 minutes were allowed for conditions to become steady before any measurements were taken.

XBL 7710-2056

Fig. 2-7. Schematic diagram of the experimental apparatus. Fuel and air are mixed and burned 2-3 millimeters above the disk.

2.5 Measurement of Flame Temperature

Temperature is an important factor in controlling the behavior of a combustion regime. Knowledge of detailed temperature distribution inside a flame is particularly necessary because the chemical reactions inside a flame are strongly temperature dependent. Theoretical calculations are not usually sufficient for estimating the flame temperature with the needed accuracy because of the various heat losses from the flame. Also, the imperfection in design and construction of the burner results in nonideal flame behavior. In this section the temperatures of the flames of acetylene-air and propane-air mixtures are measured for the range of equivalence ratios and total reactant flow rates which produce stable flat flames. Temperature distributions across the flame surface are measured to evaluate flame uniformity.

A 75- μ m thick platinum, platinum-10% rhodium thermocouple was used. Details of design and construction of the thermocouple are given in Appendix C. The two-holed ceramic tube which supported the thermocouple was mounted on a Brinkman micromanipulator which allowed thermocouple movement in all directions. Care was taken to hold the thermocouple in a plane parallel to the burner disk to help reduce temperature gradient across the junction and therefore minimize conduction losses. Typical graphs of temperature distribution at any given radial direction are given in Figure 2-8 for acetylene-air flames. The flame surface (plane of maximum temperature) was seen to be uniform within 3% from the maximum flame temperature (1784°K uncorrected for acetylene flame at $\phi = 1.0$ and $\bar{s}_{25} = 21$ cm/sec; maximum flame temperature measured in this study). The flame temperature drops sharply at the edges of the flame where

XBL 781 - 54

Fig. 2-8. Radial temperature distribution of a flame of acetylene/air mixture. Temperatures are not corrected for radiation and convection losses.
 (a) $\phi = 1.0$, $\bar{S}_{25} = 21$ cm/sec;
 (b) $\phi = 0.7$, $\bar{S}_{25} = 21$ cm/sec.

mixing with the cool ambient air occurs.

Flame surface nonuniformity was studied by comparing temperature distribution measured in two different ways: first, maximum flame temperatures were obtained at several regularly spaced points of the burner by traversing the thermocouple up and down along to the reaction coordinate to locate the maximum flame temperature; second, maximum temperature was found at the centerline of the burner and then the thermocouple was traversed in the plane parallel to the burner surface. These two techniques resulted in a maximum of 2% difference over 90% of the flame surface area.

In another set of experiments, the effect of total flow rates on the flame temperature was investigated and summarized in Figure 2-9. An increase in the total flow of the gas mixture (increase in reactant gas velocity) causes an increase in flame temperature. The phenomenological analysis of a flame wave [18] indicates an increase in standoff distance when the flow rate of reactants is increased. This, in turn, reduces heat conduction to the burner surface. Cooling water will be less effective in cooling the flame, and the result is a higher flame temperature.

2.6 Heat Losses to the Burner

Heat loss to the porous flame holder is the main factor in stabilization of the flame. After ignition, a flame is formed which travels upstream if the flame speed of the mixture exceeds the stream velocity, or downstream if the stream velocity is less than the flame speed. In the latter case, the flame will move toward the plate until an energy balance is achieved.

XBL7710-2051

Fig. 2-9. Maximum flame temperature of an acetylene/air mixture as a function of equivalence ratios for different total reactant flow rates.
($\diamond \dot{V} = 45$ lpm; $\square \dot{V} = 35$ lpm; $\triangle \dot{V} = 25$ lpm; $\nabla \dot{V} = 15$ lpm)

The amount of heat lost to the plate depends on the flow velocity of the reactants and can be measured calorimetrically. As flow velocity is decreased, the flame attempts to flash back, and moves closer to the heat sink. If still stable, it finds a new position where greater heat loss has reduced its burning velocity to the reduced flow velocity.

Many attempts have been made to relate burner heat losses to the fundamental combustion parameters such as flame temperature and flame burning rate. However, the results have not always been consistent. Botha and Spalding [9] assumed that heat loss from the flame to the burner was the only heat lost by the flame. Therefore adiabatic flame velocities of mixtures of propane-air gases were obtained by extrapolation of the graphs of heat loss versus flow velocity to zero heat loss. Identical results were found when the burner diameter was increased from 25 to 50 millimeters.

Edmondson, Heap, and Pritchard [19,20] used a burner similar to Spalding's but in a different environment. Different values of heat extraction rate resulted in different values for burning velocities, all of which were lower than those found in alternative methods. Furthermore, increase in burner diameter removed heat more efficiently in the rich methane-air flames [21], and the corresponding flame temperatures and flame velocities were higher. It was therefore concluded that other heat losses exist and must be included. Kaskan [22] showed that nonthermal radiation in an air-hydrogen flame is negligible. He also calculated heat losses due to incomplete combustion at maximum temperature by measuring product concentrations and recombining them to produce water vapor. These losses were also insignificant. Egerton [23]

used an uncooled burner and found that there were no parts of the reactants which escaped complete combustion, and the unburned gases were eventually burned in the vortices generated at the rim [24]. However, the experimental setup and reactant mixture conditions have not been discussed in Egerton's work, and it is not possible therefore to determine under what conditions the conclusion will prevail. Yumlu [25] studied the effects of entrainment on the measured flame temperature of a lean H_2-O_2 mixture. A mass spectrometer was used to analyze flame composition. Traces of nitrogen present in ambient air and unburned hydrogen were found. Measured H_2 and N_2 concentrations increased with an increase in equivalence ratio and a decrease in total flow rate. The discrepancy between measured and calculated temperatures was greater for leaner and slower-burning flames.

The discrepancies in the conclusions derived by different authors suggest that different forms of heat loss are significant for each system. To investigate the significance of such unknown losses in the burner designed, a comparison was made between the heat losses to the burner and the total heat losses from the flame. Assuming combustion products are at chemical equilibrium at the maximum temperature, the energy balance leads to the following equation:

$$\int_{T_Q}^{T_{ad}} M c_p dT = Q_T \quad (2-21)$$

where c_p = specific heat of products (cal/gr $^{\circ}$ K)

T_Q = measured flame temperature ($^{\circ}$ K)

T_{ad} = adiabatic flame temperature ($^{\circ}$ K)

M = molecular weight of products (gr/mole of product)

Heat losses per unit volume of the fuel are a more suitable parameter because the heat of combustion is defined per unit volume of fuel. Since one mole of acetylene reacts with 2.5×4.76 moles of air at stoichiometric conditions, then Q'_T , defined as total heat lost per cm^3 of fuel, becomes

$$Q'_T = \frac{1}{22400} \left(1 + \frac{2.5 \times 3.76}{\phi} \right) \int_{T_Q}^{T_{ad}} M c_p dT \quad (2-22)$$

ϕ is the equivalence ratio. T_Q can be obtained from graphs of Figures 2-14 and 2-15. Values of M , c_p , and T_{ad} were taken from the equilibrium calculations of acetylene-air flame.

Measured heat lost to the burner for different flow rates and equivalence ratios are calculated using the following:

$$Q'_B = \frac{\dot{m}_W c_{pW} (T_{out} - T_{in})}{\dot{V}_f}$$

where Q'_B = heat removal rate from the burner (cal/cc fuel)

$\dot{m}_W$ = mass flow rate of cooling water (gr/min)

c_{pW} = specific heat of water (cal/gr $^\circ$ K)

T_{in}, T_{out} = water temperature at inlet and outlet of the coil ($^\circ$ K)

$\dot{V}_f$ = volume flow rate of fuel (cc/min)

Figure 2-10 shows the plot of Q'_B and Q'_T for different flow rates and equivalence ratios. These plots show a very good agreement between the values at high flow rates. Discrepancies increase for richer flames and flames of slower-burning rates. It is thus concluded that heat

XBL 7710-2052

Fig. 2-10. Heat transferred to the burner as a function of burning velocity for lean acetylene/air flame. Solid lines are calculated heat losses based on adiabatic flame temperature, Q'_T . Dashed lines are experimental values, Q'_B .

losses to the burner are the only major loss for high flow rates and all other heat losses can be neglected. For lower flow rates and richer flames, however, the heat losses other than those to the burner are important. These heat losses are probably due mainly to the diffusion of ambient air and incomplete combustion at the plane of maximum temperature.

2.7 Effect of an Inert Gas Shroud

The effects of a shroud of inert gas on velocity and temperatures near the edges were investigated. Velocity measurement was made by a hot film probe anemometer when cold air was flown through the burner assembly (Figure 2-11). Velocity was uniform within 7% over the entire burner except at the edges. At the edges velocity dropped sharply to zero when no gas passed through the shroud. When argon gas was introduced in the shroud, at a velocity equal to that of the main flow, the velocity was raised at the edge due to the reduced shear forces.

The effect of the inert shroud gas on the flame temperature at the edges was also investigated. Figure 2-12 shows the temperature distribution of an acetylene-air flame at equivalence ratio of 1.10. With the shroud gas, the temperature drops move rapidly at the edges. An increase in flame temperature is also recognized close to the flame edge. The changes in temperature distribution are believed to be due to the different diffusion coefficients of the combustion gases and the inert shroud gas (argon here). When there is no shroud, the fluid mechanic shear layer causes mixing of hot product gases with cool ambient gas, producing a region of raised temperature beyond the burner rim.

XBL 784-719

Fig. 2-11. Velocity distribution across the burner.
○ is with shroud; ● is without shroud.
Lines at right represent the position of the
inner and outer diameter of the main burner
and shroud.

XBL 784-736

Fig. 2-12. Effect of a shroud of argon gas on temperature distribution across a flame of propane/air mixture.
○ without the shroud
● with the shroud
Operating conditions are $\phi = 1.2$, $\bar{S}_{25} = 10.2$ cm/sec, velocity in the shroud is 10.2 cm/sec.

With a shroud, this macroscopic mixing is reduced significantly, and the temperature falls sharply at the rim as shown in Figure 2-12. The temperature increase near the edge of the flame disk can be explained by the species composition of the shroud. The argon gas used here decreases the thermal diffusivity in the region near the burner rim. This causes a reduction in the rate of heat extraction, which in turn shifts the flame to become more adiabatic.

2.8 Measurement of Burning Velocity

The burning velocities of a mixture of acetylene-air, measured by a variety of experimental methods, are reported by several authors and summarized by Williams and Smith [26]. These results are widely scattered, and they vary somewhat with the method of measurements. Rallis [29] measured the laminar burning velocity of acetylene-air flow by a constant volume bomb and found its dependence on the pressure. Linnett et al. [30] used the soap bubble method for velocity measurement. A soap bubble is filled with the reactant gas mixture. A spark at the center starts a flame which spreads through the bubble. The speed of travel is determined photographically. The flame speed is defined as the burning speed divided by the expansion ratio as determined by the ratio of initial and final bubble size. Linnett recognized that the values of flame speeds measured in this manner for the rich flame were higher than those reported by other methods, but he was not able to explain the sources of discrepancy. Flame propagation velocity through a tube is found by the ratio of flow velocity by surface area as

XBL 784-725

Fig. 2-13. Dependence of burning velocities on composition for acetylene/air mixtures at 1 atmosphere pressure.

- Ref 28,
- Ref 29,
- ◇ Ref 30,
- △ Ref 31,
- Ref 32,
- × this work

determined from the flame area photographs by Friedman [32]. Their results agree well with the results reported in this work and are plotted in Figure 2-13 along with other reported data.

For ideally flat flames, burning velocities are obtained by dividing the volumetric flow rate by the flame area. The flame area was taken to be equal to the area of the burner disk. Assuming that the combustion products behave as ideal gases and that pressure remains constant during the reaction, flame velocities are then normalized to values measured at 25°C according to the relation $S_{25} = S \cdot 298/T$, where S is the flame velocity and T is the incoming reactant gas temperature in degrees Kelvin.

Thermal theories of flame propagation proposed by Semenov [27], which assume the flame is controlled by a single overall reaction rate in the form of Arrhenius rate, find the following relation for the burning velocity of a combustible mixture:

$$S_u^2 = \frac{\text{const}}{E^{n+1}} \exp(-E/RT_f)$$

where $n = 1$ for unimolecular and $n = 2$ for bimolecular reactions. Slopes of the plot of the logarithm of the burning velocity against the reciprocal of the maximum flame temperature give the values of $E = 53 \pm 5$ kcal/mole°K for activation energy. The discrepancy in the value of E calculated in this manner is probably due to the fact that the rate of acetylene oxidation cannot be represented by a simple overall reaction rate.

Adiabatic burning velocities can be calculated by extrapolating the data to adiabatic flame temperature calculated in equilibrium (Figs.

XBL 7710-2054

Fig. 2-14. Burning velocities of lean acetylene/air mixtures. Points marked $\odot$, $\triangle$, $\square$, are extrapolated to corresponding adiabatic flame temperature.

XBL 7710-2053

Fig. 2-15. Burning velocities of rich flame of acetylene/air mixtures. Points indicated $\odot, \ominus$ are extrapolated to corresponding adiabatic flame temperatures. Burning velocities smaller than 5 cm/sec are not reported here because of lack of accurate flow-measurement device.

2-14 and 2-15). The maximum burning velocity of 150 cm/sec at an equivalence ratio of 1.2 was obtained in this manner and agrees with other reported data (see Fig. 2-13). The occurrence of maximum burning velocity and flame temperature at the rich side of the stoichiometric ratio can be attributed to the high heat of formation of acetylene.

2.9 Conclusion

According to the criteria assigned by the analytical study of temperature distribution in the burner disk, a burner was designed and constructed which can be stabilized over a wide range of equivalence ratios and flow rates. Flame temperatures were measured and found to be uniform within 2% at the flame front. Heat losses to the burner were measured and were shown to be the only losses at high flow rates. Discrepancies at low flow rates are attributed to dilution by and diffusion with ambience. Detailed measurement of the flow fields and concentration of products is needed for a thorough understanding of the shroud gas effects. Burning rates were measured and concur with reported data.

CHAPTER 3

Particulate Sampling Apparata

3.1 Introduction

A schematic of the experimental apparata used in this study is shown in Figure 3-1. A mixture of fuel and air is ignited to produce a flat flame. The gas supply system for the burner is described in section 2.4. The products of combustion are confined to a chamber which is sealed from the ambient air. A portion of the combustion products is drawn through a sampling tube and is diluted for analysis. The temperature of the hot undiluted gases is measured by a glass thermometer at the probe entrance. An exhaust manifold is provided at the top of the chamber. The pressure differential across an orifice is measured at the exhaust manifold to assure a slight positive pressure inside the chamber. This is important to prevent the flow of dirty room air into the system.

A boundary layer diluter is used to eliminate particle deposition on sampling tube walls. Dilution air is provided by recycling part of the sample back to the dilution chamber. A rotary vane GAST pump is used for recycling the diluent. To check the pump for leaks, a series of tests are conducted and the flow rates of incoming and outgoing air are compared. No leak was detected.

The humidity of the diluent is controlled in the following manner. The recycled sample is distributed through a tee arrangement between a bubbler system and a tower of a molecular sieve dryer and is then mixed

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Fig. 3-1. Schematic of experimental setup. A mixture of dry purified air and acetylene is metered and then burned, producing a flat flame. Part of the combustion product is sampled at different locations and diluted before analysis.

again. Total flow rate is determined by the amount of dilution required and is measured by a rotameter. An absolute filter is necessary to remove the particulates while a column of Ascarite removes the carbon monoxide and carbon dioxide contaminants. Before each run, the purity of filtered diluent air is checked by a Condensation Nuclei Counter. The sample allotment system follows the dilution system and is explained in section 3.5.

3.2 Combustion Chamber

The chamber is made of a 1.7-mm thick stainless steel tube 65 cm in length and 15 cm in diameter. Four sampling ports, 12 mm in diameter, are provided in the chamber at 10, 20, 30, and 40 cm above the base. Four other 6-mm openings are provided for the introduction of additive gases or measurement devices. A 6.4-mm plexiglass window is used to observe the flame. The base is sealed by an 11.5-cm O-ring and then clamped to the burner base to prevent dilution of burned gases with room air. All O-rings are from Viton and could tolerate very high temperatures.

3.3 Sampling Probe

Figure 3-2 shows the sampling probe designed for this study. The probe is made of 1.25-mm thick, 8-mm diameter stainless steel tubing. The nozzle angle, 15° , was chosen in accordance with the results of Whitley and Reed [33], who tested different probes for the most accurate sampling results. The nozzle is 40 mm long before bending 90° , to allow particles to enter the nozzle parallel to its axis. This reduces

Fig. 3-2. Sampling probe.

XBL 7710-2058

Fig. 3-3. Boundary layer diluter system.

inertial deposition losses within the nozzle. A 4-mm orifice is placed and welded 200 mm downstream of the bend. Two 3-mm pressure taps were installed 4 mm on each side of the orifice. Calculations show (see section D.1) that at the orifice the nondimensional product $Ta \cdot Re_p \leq 1$ for even the worst cases in this study, and therefore particles follow the stream lines and losses are negligible. Here Ta is Taylor number, and Re_p is Reynolds number, based on the particle radius defined in section D.1. No deposit was observed at the wall of the orifice.

3.4 Dilution System

The sample extracted from the chamber should be diluted prior to its entry into counting and collecting devices for the following reasons:

1. Dilution is an easy means of bringing the sample to the required temperature and relative humidity.
2. Counting devices are usually designed for samples of atmospheric pressure and temperature conditions. Hot combustion gases have to cool before being sent into these instruments. Direct cooling of these gases produces condensation of water and other vapors generated in the combustion processes. Condensation cannot be allowed since it is accompanied by a major loss of particulate matter.
3. In many cases when the flame is sooty, a high concentration of nuclei or particulate matter will cause rapid clogging of the sensing devices. Also the detection limits of many of these instruments are far below the average concentration in the undiluted samples.
4. Flow requirements for some of these instruments are beyond total flow of the burned combustion products.

The rate of dilution is calculated to bring the sample gas to a certain temperature and humidity by using the equilibrium data of Figure 3-4, given in Table 3-1.

3.4.1. Boundary Layer Diluter

The basic principle of the boundary layer diluter (BLD) is shown in Figure 3-3 and discussed by Mitchell and Silverman [34]. A boundary layer of clean air is introduced along the tube to keep the particle-laden flow away from the wall. Porous ceramic tubing 20 mm in diameter was coaxially placed in a stainless steel chamber 150 mm in length and 68 mm in diameter. Two O-rings were provided at both ends to prevent leakage of the diluent gas. For occasional cleaning purposes, a stainless steel cap was used at one end to provide access inside the diluter.

Clean filtered gas is introduced from a 12.7-mm tube into the space between the outer jacket and the porous cylinder. This gas then flows through the cylinder to establish a layer of clean gas between the contaminated stream and the wall of the porous cylinder. The sample is gradually diluted as it passes through the unit. The laminar boundary layer prevents deposition of the particles on the surface. The linear relation between the pressure drop across the ceramic wall and the flow is laminar. For the flow rates of interest to this study (50-100 liters/minute of dilution air), however, the Reynolds number, based on the tube diameter, was always above 5000, indicating that the flow at the exit was turbulent, which assists in mixing the effluent.

XBL 784-724

Fig. 3-4. Equilibrium concentration of product of combustion of C_2H_2 -air flame, $T = 300^\circ K$.

Table 3.1 Required dilution ratios for several equivalence ratios and given sampling conditions.

ϕ	x_{H_2O}	M	W	Dilution ratio			
				100%RH at 60°F	50%RH at 60°F	20%RH at 60°F	5%RH at 60°F
.8	.056	29.42	.0343	3.1	6.2	13.3	30.0
1.0	.066	29.14	.0408	3.7	7.4	15.8	35.7
1.2	.071	28.59	.0447	4.0	8.2	17.4	39.1
1.4	.071	27.90	.0458	4.1	8.3	17.8	40.0
1.6	.065	27.19	.0430	3.9	7.8	16.7	37.6
1.8	.054	26.51	.0367	3.3	6.7	14.3	32.1
2.0	.039	25.88	.0271	2.4	5.0	10.5	23.7

M = molecular weight of product

ϕ = equivalence ratio

w = humidity ratio of the product

$$w = x_{H_2O} \frac{18}{M}$$

x_{H_2O} = mole fraction of water vapor

w' = humidity ratio of conditioned sample

$$\text{then RH} = \frac{w}{w'}$$

3.4.2 Determination of Dilution Ratio

The dilution ratio can be found easily from flow rate measurements. If $\dot{V}$ is the flow rate of recycled gas and $\dot{V}'$ is the flow rate through the probe, then the dilution ratio is $(\dot{V} + \dot{V}')/\dot{V}$ where $\dot{V}$ is determined by adding the flow rates through all the analyzers. Alternatively, the dilution ratio is frequently checked by monitoring carbon monoxide and carbon dioxide as tracer gases. The dilution ratio is the ratio of concentration of the tracer gases before and after dilution. Figure 3-4 shows that CO_2 is a good tracer gas for lean flame mixtures, while CO is more convenient for rich flame conditions. The concentration of CO_2 gas was determined by injecting the samples extracted by septums (Fig. 3-1) into a gas chromatograph. A carbon monoxide Mine Safety Analyzer was used in CO measurements.

3.5 Sample Allotment

The sampling flow system and instruments used for gas and particulate analysis are shown in Figure 3-5a. The sample's temperature and dew point are measured before it is distributed among different sampling instruments. A dew point measurement is made by drawing 1 lpm of sample through a 1/4" stainless steel tubing. "Plastic" tubing is avoided because of the hygroscopic nature of the material.

Insoluble carbon contaminants as well as the condensate reduce the amount of light to the photoconductor. The sensor should be cleaned occasionally to avoid this error. A Condensation Nuclei Counter (Rich Model 100, Environment One) and an Electrical Aerosol Size Analyzer (Model 3110, Thermosystems, Inc., St. Paul, Minnesota) are used for

XBL 781 - 55

Fig. 3-5. Sample allotment system. a) Size distribution for
b) Filter collection.

measuring the total number of particulates and their size.

The sample is drawn at the rate of 4 lpm while 46 lpm of air are supplied from the room for the required collecting rod sheath flow. The temperature of the incoming sample is kept below 100°C. At higher temperatures outgassing of Teflon tubings used in the instrument results in erroneous particulate counts. When the aerosol concentration is low, the sample requirements restrict the amount of dilution air which can be added to the probed sample (see Appendix E). Condensation might occur under these conditions. The humidity of the sample is reduced by diverting the samples through a diffusional dryer by a stopcock (Fig. 3-5a). The diffusional dryer consists of a 50-cm plexiglass tubing with a diameter of 5 cm. A fine screen is rolled to make a 1-cm diameter tubing located coaxially with the plexiglass tubing. The shell assembly is filled with silica gel dessicator. Two Teflon fittings seal the screen between two caps. Since water vapor has a much larger diffusion coefficient than solid carbon particles, the particles follow the streamline, whereas the water vapor diffuses radially and consequently is absorbed by the dessicant. The loss of particles through the dryer is measured by both counting particles with and without the use of a dryer. Results are corrected for these losses. The voltage output of the analyzer is recorded by a strip chart recorder and could be read directly from a digital counter.

One-fourth-inch copper tubing was used for sampling 3 lpm of flow for the CNC. Tubing was heated to 100°C with a heating tape when needed. The output of the CNC is recorded on a different chart recorder and is proportional to the total number of particles per cubic centimeter of

sample. The principles of operation of these units and detailed descriptions of data handling are given in Appendix E.

3.6 Particle Collection System

In another set of experiments, carbonaceous particulates from the flame were collected on different filter media for electron microscopy and elemental analysis. The choice of filter material depended on the type of analysis made. Nuclepore and Fluoropore filters were used for electron micrography. Total carbon analysis was done using a quartz filter. Millipore filters were suitable for X-ray fluorescence spectroscopy while ESCA analysis could be done only if a nonorganic substrate were used. Silver filters were used in ESCA analysis.

A constant flow air sampler (Sierra Instruments, Model 250-10) was used to draw samples from the combustion chamber. Sample mass flow rate was maintained constant, irrespective of filter loading by a solid-state motor speed controller. Flow rates of 10-30 standard liters per minute (SLPM) were used. Rotor and housing of the carbon vane vacuum pump were nickel plated to stand high temperature and mixture content of the sample. Twenty-five-millimeter stainless steel filter holders were used on the main sample line (Fig. 3-5b). Sample collection was started when the sample lines reached their equilibrium temperature and humidity. For each run the whole system was cleaned thoroughly of carbon deposits for the next run.

CHAPTER 4

Particulate Sampling Results

4.1 Operating Conditions

A total of 132 experiments were carried out to investigate the effects of different parameters on the formation and size distribution of post-flame particulate carbon. Independent variables under consideration were temperature, humidity, fuel/air mixture ratio, residence time, and total flow rates. With the apparatus built for this study, relative humidities from 30 to 90% and residence times from 20 to 55 seconds were attained. Experiments were carried out for the equivalence ratios from 1.2 to 2.0; richer or leaner mixtures produced particles whose concentrations were beyond the instruments' scope of sensitivity. The particle generation of a very lean flame is below minimum detectable limits (see Appendix E, Fig. E-1). Very rich "sooty" flames are so "dirty" that they cause the instrument to clog very rapidly. For such high concentrations, the coagulation process is very rapid and the correction factors due to these losses are difficult to estimate.

4.2 Size Distribution

4.2.1 Number, Surface, and Volume Distributions

Scanning electron micrographs (SEM) of the particles collected on a variety of filters are shown in Figure 4-1. Flames with equivalence ratios smaller than luminosity threshold limit generate very few particles that could be collected on the filter. A very long sampling time

(a)

(b)

(c)

XBB 781-1000

(d)

(e)

XBB 781-1001

(f)

Fig. 4-1. SEM of acetylene/air flame soot collected on different filter substrates. SEM accelerating potential = 20 kV.

- a) Blank 1 μm pore size Millipore filter, $M = 5000\times$.
- b) Soot at $\phi = 1.94$ on 1 μm Millipore, $M = 10600\times$, sampling time = 10 minutes.
- c) Same as b), but $M = 42400\times$.
- d) Soot at $\phi = 1.40$ on 0.8 μm Nuclopore, $M = 8000\times$, sampling time = 6 hours.
- e) Soot at $\phi = 1.94$ on 1.0 μm fluoropore filter, $M = 9200\times$, sampling time = 2 minutes.
- f) Same as e), but $M = 36800\times$.

or a large flow rate was needed to collect sufficient particles on the filter to be detected easily by an electron microscope. Figure 4-1d shows particles of the order of $100 \text{ \AA}$ for the acetylene-air mixture flame at an equivalence ratio of 1.4 and 19.6 cm/sec reactant gas velocity on a Nuclepore filter. Gaseous combustion products for the luminous flames were observed to attack Nuclepore filters. For this reason Nuclepore filters were not used when the flame was luminous. Silver membrane filters have a complicated structure which is not easily distinguishable from the particles collected on the filter. Quartz fiber filters are very unstable in high vacuums. Millipore and Fluoropore filters thus proved to be most suitable. Figure 4-1a shows the SEM for a blank Millipore filter. Figures 4-1b, c, d, and f represent the particles collected by flames at equivalence ratios of 1.94 for different sampling times and filter substrates. Particles as big as 0.3 microns are distinguishable.

Figures 4-2, 4-3, and 4-4 show the number, surface, and volume distribution of the particles generated by flames at different equivalence ratios as measured by an Electrical Aerosol Size Analyzer (EASA). The points marked represent actual experimental results, while the solid lines are plotted to fit the experimental data. The positions of peaks at maximum are indicated by fine solid bars. The principle of operation and a procedure for data reduction and error analysis are given in detail in Appendix E.

For flames with equivalence ratios smaller than 1.84, the particle production rate is much smaller than the rate for richer flames. Only particles within a very small size range (peak at $\sim 55\text{-}70 \text{ \AA}$ and $\sigma_g = 1.1$)

XBL 784-730

Fig. 4-2. Number distribution of the C_2H_2 -air post-flame soot at different equivalence ratios, $\square$ ($\phi = 1.2$), $\triangle$ ($\phi = 1.4$), ∇ ($\phi = 1.6$), $\times$ ($\phi = 1.84$), $\diamond$ ($\phi = 1.9$), $\circ$ ($\phi = 2.0$). Sampling conditions are R.H. = 70% after dilution, $T = 298^\circ\text{K}$, $\dot{V} = 37.2$ lpm at STP.

XBL 784-731

Fig. 4-3. Surface distributions of the C_2H_2 -air flame calculated from number distributions plotted in Fig. 4-2.

XBL 784-732

Fig. 4-4. Volume distributions of the C_2H_2 -air flame calculated from number distributions plotted in Fig. 4-2.

are observed. When a flame becomes luminous ($\phi = 1.84$), distribution is bimodal. The first mode consists of particles less than $80 \text{ \AA}$ ($\sigma_g = 1.4$), and the second mode of particles at around $500 \text{ \AA}$ ($\sigma_g = 1.9$). The bimodal nature of size distribution is closely related to the rapid transition between luminous and nonluminous flames.

Whitby et al. [35] found two submicron nuclei modes in their studies of aerosol size and concentration of a propane-air diffusion flame. The first mode was observed at about $0.008 \text{ \mu m}$, and the second mode at about $0.05 \text{ \mu m}$. When the air was not filtered, another mode at 0.1 to $0.5 \text{ \mu m}$ was observed, which was called the accumulation mode. The first nuclei mode was hygroscopic and was believed to be formed by the conversion of sulfur in the fuel into sulfuric acid. The second mode was strongly dependent on the air-fuel ratio, which was thought to be carbon.

It is interesting to note that the bimodal distribution of acetylene-air flame soot particles is similar to the bimodal distribution found in the diffusion propane flame by Whitby's group. This might indicate that soot generated by different combustion systems has similar properties.

The soot volume fractions are calculated as a function of the equivalence ratio for the acetylene-air flame and are plotted in Figure 4-5. On the same figure is shown the soot volume fraction found by Wersberg et al. [36] in an acetylene-oxygen flame at equivalence ratio of 3.0 at 20 mm Hg pressure. Although the experimental conditions in their work and the work reported here are quite different, the agreement is satisfactory.

The total number of particles can be found by adding the particle concentrations at each size range. These are shown in Figure 4-6.

XBL 784-737

Fig. 4-5. Soot volume fraction for acetylene/air flame soot as determined from size distribution. □, this work; ○, Wersborg et al. [72]; ▨ represents the range of equivalence ratio at which the onset of carbon formation could be detected with certainty [71].

XBL 784-723

Fig. 4-6. Comparison of the total number of particles per cm³ of undiluted product gases at STP detected with ● CNC and ◆ EASA. RH = 70%, T = 298°K, and $\dot{V}$ = 37.2 lpm at STP.

Alternatively, the total particle concentration is measured by the Condensation Nuclei Counter. An effort was made to dilute the sample to reduce particle concentration below the nonlinear range of the CNC. However, for very rich flames ($\phi > 1.84$) this was not possible, and therefore the results are less accurate. Unfortunately, no data are available to estimate the errors associated with the nonlinear scale. Periodic calibration of the instrument with an independent technique is needed. Liu [37] states that factory calibration of the CNC instrument is good only within a factor of three. The change in magnitude of the error with size is not discussed in his studies. Another reason for the inconsistency between EASA and CNC results is the 30 Å diameter limit of detection for the CNC, which is lower than the 60 Å diameter limit of detection for the EASA. Therefore CNC readings are usually higher than EASA readings.

4.2.2 Humidity Effects

The effect of humidity at the sampling point on the measured particle concentration has been investigated and is shown in Figure 4-7. The humidity is changed by adjusting the ratio of diluent passed through the dryer and bubbled through the water, and by keeping the dilution ratio constant and equal to 16.4. Relative humidity is calculated by measuring the dewpoint and dry bulb temperature at the sampling point. The temperature of the sample gas before dilution always remained above 100°C, and therefore the relative humidity was usually low. Relative humidities below 30% could not be attained because of the limitation of the recycling gas pump's capacity. Relative humidities higher than 90%

XBL 784-729

Fig. 4-7. Particle concentration (number/cm³ of product at STP) as a function of relative humidity in the sampled gas. Dilution ratio was kept constant and equal to 16.4. Total flow rate of the reactants is $\dot{V} = 37.2$ lpm at STP.

were very difficult to control because these higher humidities could easily result in condensation. When condensation occurred, CNC counts increased beyond the range of instrument sensibility ($> 10^7$ particles cm^{-3}), and it took several hours for the instrument to stabilize.

The rate of particle collection is nearly independent of relative humidity from 30 to 70%; after that point it increased rapidly. Fissan [38] measured the particle production rate from a mixture of blue propane-air premixed flame. The particle production rate increased from 40,000 to 110,000 particles cm^{-3} when the relative humidity of the chamber increased from 70 to 100%. Similar results were also observed at lower humidities. Quantitative comparison of these results with the results reported in this study cannot be made since the experimental setup and the combustion parameters of the two projects differ greatly. However, the results reported in these studies show that humidity plays an important role in the particle formation process. Without flame, particles are not observed; but with a flame, particle concentration increases markedly with humidity. Based on these observations, it is believed that the flame provides nuclei which are largely hygroscopic; and therefore, in the presence of water, they grow to particles large enough to be detected by the particle counters.

4.2.3 Residence Time

The effect of residence time on particle number distribution is investigated by sampling from the different sampling ports on the chamber and by using different lengths of sampling tubes (Fig. 4-8). Residence time is defined as the time over which the combustion products leave the

XBL 784-735

Fig. 4-8. Particle number concentration as a function of total residence time in the system for an acetylene/air flame, $\phi=1.9$, $RH=70\%$, and $\dot{V} = 37.2$ lpm at STP. The dashed line is the predicted concentration due to coagulation losses. It is assumed that particles are monodisperse and are $100 \text{ \AA}$ in diameter initially.

flame and travel to the particle sample collection device. The observed sharp decrease in particle concentration with residence time could not be generated by losses to the tube wall alone, and therefore coagulation processes are also important. Figure 4-8 shows a typical plot of number concentration as measured with the Condensation Nuclei Counter. Uncertainties in the EASA results for small size particles do not allow quantitative representation of the effect of residence time on size distribution.

In general coagulation losses should be calculated by considering the polydisperse size distribution given in Figure 4-2, using the coagulation constants for particles of different sizes [94]. The process is tedious and requires detailed calculations; however, a good estimate of coagulation losses is possible by assuming the particles are monodisperse and 100 Å in diameter. Initial particle number density is taken to be equal to the measured number concentration. It should be noted that particle diameters are smaller than 100 Å when they leave the flame, but they coagulate rapidly to 100 Å in the sampling tube. The drop in particle number density by coagulation is given by Eq. D-5 as:

$$N = \frac{N_0}{1 + K_0 N_0 \Delta t}$$

where $K_0 = 4\pi d_p D$ is the coagulation constant. d_p is particle diameter and D is the binary diffusion coefficient. Assuming initial particle concentration $N_0 = 8 \times 10^7$ particles·cm⁻³ and $d_p = 10^{-6}$ cm, then $D = 5.24 \times 10^{-4}$ cm²/sec and $K_0 = 6.57 \times 10^{-4}$ cm³/sec.

The dashed line in Figure 4-8 shows the predicted number

concentration under these conditions. The agreement is good. In conclusion, these results show that coagulation is an important mechanism in determining particle size distribution. Residence time should be monitored carefully to estimate the losses and true size distribution at the time of production.

CHAPTER 5

Chemical Composition and Properties

5.1 Introduction

Soot, defined somewhat arbitrarily, is the combustion-produced, air-suspendable carbonaceous particles relevant to air pollution. Most work in the past, however, has dealt with carbon blacks and charcoal (activated carbon). The differences between soot and other carbonaceous species are related to particle size, surface-to-volume ratio, total surface area, amount of surface oxygen complexes, and their bonding structure [39]. Different oxygen-containing functional groups have been postulated to exist on the carbon surface [40-51]. The relative amounts of these complexes and their structure depend on the thermal history of the carbon particles. For example, when activated carbon is heated to 350°C, it shows acidic properties; but if heated to 1000°C [47,51], this same sample becomes basic. It has been suggested that these surface oxygen complexes may influence the chemical properties and catalytic reactivity of the carbon particles. The differences in the catalytic adsorptive properties of soot and activated carbon are believed to be qualitative rather than quantitative. Because of the many different parameters affecting particle production in combustion sources and the possible differences in their physical and chemical properties, elaborate studies of soot particles are needed to find the quantitative differences between soot and activated carbon.

The remainder of this chapter deals with these studies and a comparison of acetylene-flame soot properties with those of activated carbon (Nuchar). Elemental analyses and chemical reactivity of soot will be discussed.

5.2 Chemical Characterization

5.2.1 Surface Analysis

Samples collected under different flame and sampling conditions were analyzed for their surface properties using X-ray photoelectron spectroscopy (XPS) to determine their oxidation state as well as their chemical composition. The fundamental principles of this method are given in Appendix F.

All samples were collected on 1.2- μ m pore diameter silver membrane filters. Silver filters are more stable under X-ray and are less susceptible to charging effects. Figure 5-1 shows the species detected on an acetylene-air flame soot sample ($\phi = 1.94$, $\bar{s}_{25} = 23.6$ cm/sec, 15-minute collection time at 15 lpm STP) over a wide range of binding energies as determined by ESCA. The principle of operation of ESCA is given in Appendix F. The binding energies of the two peaks with the strongest intensity correspond to those of C(1s) and O(1s). Because of the nonmonochromized nature of the X-rays produced by Al(K $_{\alpha}$) used in the spectrometer, another peak designated C(1s)K $_{\alpha 3,4}$ is seen in the spectrum. Ag(3d) has a doublet at binding energies of about 172 and 167 eV. Two Auger peaks corresponding to transitions C(K $_1$ L $_{23}$ L $_{23}$) and O(K $_1$ L $_{23}$ L $_{23}$) are also easily recognized. Trace metals are not detected at this sensitivity level.

XBL 781-35

Fig. 5-1. Wide scan (XPS and Auger) of an acetylene/air flame ($\phi = 1.94$, $\bar{S}_{25} = 23.6$ cm/sec) soot collected on a silver filter.

The specific intensities (intensity/unit time) of the ESCA spectrum of the species under investigation change with the time of exposure of the sample to vacuum. A thin film of oil from the diffusion pump is formed on the sample. The thickness of the film increases with exposure time. Since the ESCA technique is restricted to surface analysis, the sample should be exposed for as short a time as possible. However, this is limited in practice since the good resolution of the peak intensities is usually lost for short-period scanning. Figure 5-2 shows the change in the insensitivity of different species as a function of exposure time for the same sample used in obtaining the spectra of Figure 5-1. A reduction in silver and sulfur intensity results in a corresponding increase in carbon intensity. The oxygen intensity remains constant. Linear extrapolation to zero time is made for an evaluation of the true intensities.

The spectral data are numerically analyzed in the following manner: the intensities for species j are normalized for the number of scans and the scanning time per each channel and are then corrected for incomplete coverage according to

$$I_j^t = I_j^o - \alpha I_j^{bl}$$

I is the intensity at each channel normalized to counts/second. Superscripts t , o , and bl correspond to true, raw, and blank values respectively. α is the fraction of the filter surface not covered by exhaust particulates and is assumed to be equal to the ratio of the silver peak intensities of the sample to that of the blank filter normalized to carbon.

XBL 781-7040

Fig. 5-2. Change in peak intensities as a function of exposure time in vacuum. ($\phi = 1.94$, $\bar{S}_{25} = 23.6$ cm/sec, collection time = 15 minutes at 15 lpm STP.)

Finally a base line is drawn and the background is subtracted. A value of 285.0 eV was assigned to the C(1s) peak. Displacement of binding energy due to charging effect is calculated as the difference between observed carbon peak binding energy and 285.0. Oxygen and sulfur spectra are shifted by this value.

The effect of flame richness (equivalence ratio) on the composition of the soot was investigated in a series of experiments. Chapter 3 describes the experimental setup. In all the experiments, the total flow rate, temperature, and humidity at the sampling point were kept constant. Collection time varied for the different samples, however. It was adjusted to allow for formation of enough deposit to cover the filter substrate. This was checked by comparing the intensity of the silver peak for the sample with that of a blank filter. In most cases, a surface coverage of better than 98% of the filter face area was obtained. In a few cases where total coverage was not obtained, corrections were made to subtract the unexposed filter background. Figures 5-3 and 5-4 show spectra of C(1s) and O(1s) for several equivalence ratios. The dotted lines are the raw data from the spectrometer. The dashed lines represent the net peaks.

Analysis of the spectra of Figure 5-4 shows that an oxygen peak can be deconvoluted into two well-defined symmetric profiles as shown in Figure 5-5. These oxygenated complexes are designated as O_I and O_{II} . The position and full band width at half maximum peak intensity (FWHM) of the carbon and oxygen spectra are:

Fig. 5-3. X-ray photoelectron spectra near C(1s) for carbon species for an acetylene/air flame soot sample collected on a silver membrane filter. a) $\phi = 1.84$; b) $\phi = 1.94$; c) $\phi = 2.2$; d) $\phi = 2.4$. The dotted line is the actual spectrum. The broken line represents the same spectrum after background subtraction. The scale on the left of the ordinate shows the net peak intensity of the corrected spectrum.

Fig. 5-4. Same as Fig. 5-3 but at binding energies close to the O(1s) binding energy.

XBL 781 - 34

Fig. 5-5. Deconvolution of the typical oxygen band to two bands of symmetric profile: each band has a nearly Gaussian shape. The two species are designated as $O_I(1s)$ at maximum peak binding energy of 534.3 eV, and $O_{II}(1s)$ at maximum peak binding energy of 532.4 eV.

<u>Complex</u>	<u>Peak Binding Energy</u>	<u>FWHM</u>
C(1s)	285.0 eV	1.71 ± .01 eV
O _I (1s)	534.3 eV	2.3 ± .05 eV
O _{II} (1s)	532.4 eV	1.75 ± .10 eV

Relative atomic concentration of these two oxygen complexes (O_{II}/O_I) and the oxygen-to-carbon ratio (O/C) are plotted against the equivalence ratio in Figure 5-6 and are given in Table 5-1. Here the atomic concentration is defined as the ratio of the area under peak for each species to its atomic sensitivity. Values of atomic sensitivity assumed in these calculations are 60.8 for C(1s) and 80.0 for O(1s) [52].

The change in ratio of O_{II}/O_I and (O/C) for different flame conditions may be indicative of the very different reactive properties of soot generated under different combustion environments. The chemical structure and functional groups of these two oxygen complexes cannot be determined solely on the basis of their binding energies. More work is needed to identify these complexes.

The plots of Figure 5-6 represent two distinctive regions of soot production. In the first region ($1.84 < \phi < 2.0$), the rapid decrease of O_{II}/O_I and O/C ratios with the equivalence ratio indicates that the large particles detected at the richer side of this region are not the result of coagulation of fine particles generated under leaner conditions; otherwise the O_{II}/O_I and O/C ratios would have remained the same. This fact was further studied by comparing two samples collected under identical conditions except for the length of the sampling tube. One of

XBL 784-733

Fig. 5-6. Change of ratio of atomic concentration as a function of equivalence ratio. It is seen that chemical composition of Nuchar is similar to the fine soot particles generated close to the threshold limit of flame luminosity.

Table 5.1. Summary of the ESCA analysis of particulates collected on silver filters.

Sample number	ϕ	Area under peak			Atomic concentration			Percent coverage	O/C	O_{II}/O_I
		C	O _I	O _{II}	C	O _I	O _{II}			
1	1.84	4029	1160	615	50.0	14.5	7.69	53	0.44	0.53
2	1.89	7997	716	277	131.5	9.00	3.46	100	0.095	0.38 ^a
3	1.89	8313	763	339	136.7	9.54	4.24	98	0.100	0.44 ^b
4	1.89	8650	784	348	142.3	9.8	4.35	96	0.099	0.44 ^c
5	1.94	5231	470	137	86.0	5.88	1.71	49	0.088	0.29 ^d
6	1.94	8205	619	225	135.0	7.74	2.81	100	0.078	0.36 ^e
7	2.00	5375	322	51	88.4	4.03	0.64	61	0.053	0.16 ^d
8	2.00	8563	472	81	140.8	5.90	1.01	100	0.049	0.17 ^f
9	2.10	2828	151	20	46.5	1.89	.25	100	0.046	0.13 ^b
10	2.10	7530	377	57	123.8	4.71	.71	100	0.044	0.15 ^c
11	2.20	8356	326	77	137.4	4.08	0.96	100	0.037	0.13
12	2.40	2341	121	15	38.5	1.51	0.19	100	0.044	0.12
13	Nuchar	6162	794	376	101.3	9.93	4.70	100	0.144	0.47

^a 35 min sampling time

^d 5 min sampling time

^b 8 sec residence time

^e 15 min sampling time

^c 28 sec residence time

^f 10 min sampling time

the samples was collected at a much longer residence time to ensure coagulation. Similar O_{II}/O_I and O/C ratios were found for samples 3 and 4, and samples 9 and 10 also verify this point.

For flames with an equivalence ratio larger than 2.0, the curve of O/C and O_{II}/O_I becomes flat. It is concluded that coagulation of the particles is the major mechanism for inducing particle growth of very rich flames ($\phi > 2.0$). Under these conditions, the total mass of the particles remains unchanged.

To compare the composition of Nuchar with that of soot, Nuchar deposited on a silver filter was analyzed with ESCA. The deposit was prepared by placing the Nuchar powder in a sealed jar and sucking the content onto the filter with a vacuum pump. The analyses show that Nuchar behaves similarly to soot generated near the threshold limit. These results are also indicated on the plot of Figure 5-6.

Several other experiments were conducted where the relative humidity in the dilution chamber was changed. The differences between their behavior was negligible and were within the limits of experimental uncertainties. These observations indicate that relative humidity does not affect the soot formation mechanism but influences only the physical properties of particles, such as size distribution.

Catalytic reactivities of soot particles in SO_2 oxidation are investigated. SO_2 gas at a concentration of 10 ppm is introduced downstream of the flame just after the entrance of the products into the sampling probe. Little conversion to sulfate is observed. This result contrasts with the earlier experiments by Novakov [4], who found strong conversion when a flame of propane-air was stabilized on a Bunsen

burner. Unlike the experimental setup used in this study, ambient air was allowed to enter the system. The ambient air provided the necessary oxygen atoms for the oxidation of SO_2 to SO_3 , which can easily absorb water to produce sulfuric acid. More work is needed for the quantitative measurement of the rate of SO_2 oxidation.

5.2.2 Bulk Analysis

X-ray fluorescent and combustion methods are used for bulk analysis. The combustion method measures the CO_2 concentration in combustion products obtained by burning carbon collected on the quartz fiber filters in the oxygen atmospheres (see section E-1.3). The x-ray fluorescent technique [70] determined the amount of light elements and trace metal contaminants from the soot sample collected on 1.0- μm Millipore filters.

These techniques complement ESCA since ESCA analyzes only the outer 50-150 Å of the exposed particles, e.g., if particles collected are 1 micron in size, ESCA analyzes only the outer 0.5-1.5%. In addition, the bulk analyses provide concentrations of species present on the filter not available from ESCA, which gives only the ratio of elemental concentrations and the identities of the species present.

In Table 5-2, the bulk analysis results are summarized for two parallel samples collected from an acetylene-air flame on quartz and Millipore filters. These results are corrected for different flow rates through the samples. Conditions under which samples were collected are also given.

Table 5-2. Bulk analysis of soot samples from an acetylene-air flame.
($\phi=1.9$, $\bar{s}_{25}=19.6$, R.H.=70%, and $T=65^{\circ}\text{F}$ at the sampling point)

Combustion:	Carbon = $120 \pm 5 \mu\text{g}/\text{cm}^2$ of filter area
XRF:	Sulfur = $185 \pm 18 \text{ ng}/\text{cm}^2$ of filter area
	Chlorine = $583 \pm 26 \text{ ng}/\text{cm}^2$ of filter area

Samples were analyzed for other elements and trace metals such as Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Hg, As, Se, Br, Pb, Rb, Sr, Cd, Sn, Sb, and Ba. Concentrations of all of these were below $5 \text{ ng}/\text{cm}^2$, the detection limit of the XRF analyzer.

CHAPTER 6

Reaction Studies in a Plume of Combustion Products

6.1 Introduction

Theoretical prediction of the spatial distribution of pollutant concentrations emitted by tall power plant stacks is important to studies of the impact of such plants on the neighboring environment. Prediction is of special importance in regions close to the stack where the plume is hot and experimental measurements are difficult. Much work has been done on the dispersion of chemically inert pollutants during their flight. When chemical reactions inside the plume become important, mathematical formulation of the combined transport and chemistry becomes so complex that analytical results can only be obtained if major simplifications are made or if the chemistry or transport is ignored. More assumptions are needed if the plume contains solid particles and liquid droplets. In the real plume of a smoke stack, gaseous, liquid, and solid pollutants exist. These pollutants react chemically and are transported by various mechanisms to neighboring locations. In many cases, particulates in the plume are fine soot particles. These particles follow the streamlines of the gaseous pollutants and therefore can be treated like gases. Of interest here is the spatial distribution of pollutants such as carbon, SO_2 , and sulfate formed as the result of SO_2 oxidation in the presence of carbon catalysts.

In recent years several authors have tried to solve the diffusion

equations for the reacting pollutants. Gaseous reactions have recently been considered in a few photochemical smog models. Freiberg [53] has studied the iron-catalyzed oxidation of SO_2 in water droplets in a dispersing plume. Seinfeld et al. [54-56] found the numerical solution to the diffusion equation when a chemical reaction is present. Other authors [57,58] have used a similar approach for different reaction schemes. Since these authors have ignored ambient entrainment and buoyancy effects, their solution is not valid close to the stack where buoyancy is dominant and reactions are fast. To properly account for the changes in concentrations, velocity, temperature, and their interreactions, continuity, momentum, energy, and species equations must be solved simultaneously. Such a procedure is used for a nonreacting plume by Hoult et al. [59]. Conservation equations are written and the trajectory of the plume and the dispersion of inert chemical species are found. This work has been extended for a reacting plume by including the species conservation equation of the reacting elements. As a special case, section 6.4 describes the catalytic oxidation of SO_2 to sulfuric acid on soot particles in a coal-fire dispersing stack plume under the condition that the condensation of H_2O does not occur during the adiabatic expansion and the transport of the plume.

6.2 Mathematical Formulation

The present model is an extension of the work of Hoult, Fay, and Fourney [59] on a chemically reacting plume. Analytical solutions can be found for special cases [60-62]. The basic assumptions in the model are:

1. Flow velocity perpendicular to the plume trajectory is neglected.
2. Plumes are ejected from stacks which are sufficiently high and have enough source strength to ensure that the intensity of atmospheric turbulence is much less than that associated with the turbulent plume.
3. Velocity, density, and pollutant concentration profiles are similar in all sections normal to the plume. The validity of this assumption is verified experimentally by Ooms [63].
4. Boussinesq's approximation is valid; i.e., density variation affecting inertia is neglected. This assumption is valid when the initial fractional density difference $\frac{\rho_\infty - \rho_1}{\rho_\infty}$ is smaller than 0.5 [64].
5. Molecular transport compared with turbulent transport is neglected.

The coordinate system is shown in Figure 6-1. v is the cross wind velocity, assumed constant with z for simplicity; u , ρ , and c_j 's are velocity, density, and species concentration respectively. The plume centerline makes an angle θ with the horizontal. s is the distance along the plume axis from the stack and b is the plume radius. s and θ are related to the Cartesian coordinate as

$$z = \int_0^s \sin \theta \, ds \quad (6-1)$$

$$\text{and } x = \int_0^s \cos \theta \, ds \quad (6-2)$$

6.2.1 Governing Equations

Conservation of mass along the plume path is written

$$\frac{d}{ds} \int u dA = \epsilon \quad (6-3)$$

XBL 7710-2048

Fig. 6-1. Coordinate system. ρ , T , and u are the potential density, absolute temperature, and velocity; b is half the plume diameter, and v is wind velocity.

$$\text{where } \epsilon = 2\pi b[\alpha |u - v\cos\theta| + \beta |v\sin\theta|] , \quad (6-3a)$$

α and β are entrainment parameters. Values of α and β are assumed constants in the calculations. Strictly speaking, the value of β changes as the plume travels. By definition

$$\beta \equiv \frac{v \frac{d}{dx} (\pi b^2)}{2\pi b v \left(\frac{dz}{dx}\right)} = \frac{db}{dz}$$

Values for β were found so theoretical calculations gave the same values of finite plume rise as the observed field data [59]. The value of $\beta = 0.9$ give minimum rms error.

The momentum equation in the s direction balances acceleration, momentum entrained, and buoyancy.

$$\frac{d}{ds} \int u^2 dA = \frac{g \sin\theta}{\rho_1} \int (\rho_\infty - \rho) dA + \epsilon v \cos\theta \quad (6-4)$$

The transverse momentum equation balances centrifugal force, momentum entrained, and buoyancy.

$$\frac{d\theta}{ds} \int u^2 dA = \frac{g \cos\theta}{\rho_1} \int (\rho_\infty - \rho) dA - \epsilon v \sin\theta \quad (6-5)$$

In the above equations, ρ is replaced by ρ_1 , the density at the stack height. Assuming the concentration of reacting pollutants is small enough so that reaction heat is much smaller than the stack emission heat, the energy equation can be written as

$$\frac{d}{ds} \int \rho u c_p (T - T_\infty) dA = \rho_\infty \epsilon c_p (T - T_\infty)$$

$$\text{or: } \frac{d}{ds} \int \rho u \left(\frac{1}{\rho} - \frac{1}{\rho_\infty} \right) dA = \rho_\infty \varepsilon \left(\frac{1}{\rho} - \frac{1}{\rho_\infty} \right)$$

It is assumed that the atmosphere is linearly stratified in density, so that

$$\rho = \rho_\infty + \frac{d\rho_\infty^*}{dz} z$$

where $d\rho_\infty^* = \left(\frac{\partial \rho^*}{\partial S} \right)_{p=p_1} dS$ is the potential density (S is entropy).

Using the last two equations and substituting (6-1) for z , the energy equation is reduced to

$$\frac{d}{ds} \int (\rho_\infty - \rho) u dA = \sin \theta \frac{\rho_\infty}{\rho} \left(\frac{d\rho_\infty^*}{dz} \right) \quad (6-6a)$$

far from the stack $\rho \approx \rho_\infty$

$$\frac{d}{ds} \int (\rho_\infty - \rho) u dA = \sin \theta \left(\frac{d\rho_\infty^*}{dz} \right) \quad (6-6b)$$

Close to the stack

$$\rho_1 - \rho_\infty \approx \rho_1 \frac{T - T_\infty}{T_1}$$

Conservation of chemical species j can be written as

$$\frac{d}{ds} \int C_j u dA = \varepsilon C_{j,\infty} + \int w_j'' dA \quad j = 1, \dots, N \quad (6-7)$$

In this equation, C_j is the concentration inside the plume. $C_{j,\infty}$ is background ambient concentration, w_j'' is the rate of production of species j , and N is the number of species examined.

Equations (6-1) to (6-7) can be solved numerically for (N+4) unknowns ρ , u , b , θ , C_1 , C_2 , ..., C_N .

Initial parameters are values of the above parameters at the stack.

6.2.2 Dimensionless Parameters

The characteristic length scales ℓ_m and ℓ_b and a characteristic frequency ω are defined [61] for nondimensionalization of governing equations:

$$\ell_b \equiv \frac{F_i}{v^3} = \frac{u_i b_i}{v^3} \left| \frac{\rho_1 - \rho_i}{\rho_1} \right| g \quad (6-8)$$

is the buoyancy length scale. πF_i is the buoyancy efflux which can be evaluated as

$$F_i \equiv \frac{\dot{Q}_i}{\pi \frac{\rho_i}{g} C_p T_1} = u_i b_i \left(\frac{\rho_1 - \rho_i}{\rho_1} \right) g \quad (6-9a)$$

$$\text{at the stack } F_i = u_i b_i^2 \left(\frac{T_i - T_1}{T_1} \right) g \quad (6-9b)$$

$$\ell_m = b_i \frac{u_i}{v} = b_i R \quad (6-10)$$

measures the scale of a pure jet (zero initial buoyancy). R is defined as the velocity ratio $R = u_i/v$.

$$\omega = - \frac{g}{\rho_0} \frac{d\rho_0^*}{dz} \quad (6-11)$$

is the Brunt-Vaisalla frequency. ω^{-1} is the characteristic time for the oscillation of a plume about its equilibrium position in the atmosphere

(plume rise z). The following dimensionless groups are defined:

$S = \frac{v}{\omega \ell_b}$ Stratification (or stability) parameter is the ratio of flow time an element of plume requires to reach its final height to the flow time required for the plume to be bent appreciably in a cross wind.

$R = \frac{u_i}{v}$ Velocity ratio.

$Fr = R \sqrt{\frac{\ell_m}{\ell_b}} = \frac{u_i}{\sqrt{g \left(\frac{T_i - T_1}{T_1} \right) b_i}}$ The ratio of inertia force to buoyancy force.

$$\bar{\rho} = \frac{\rho - \rho_\infty}{\rho_i - \rho_1}, \quad \bar{T} = \frac{T - T_\infty}{T_i - T_1}, \quad \bar{C}_j = \frac{C_j - C_{j,\infty}}{C_{j,i} - C_{j,\infty}}, \quad \bar{W}_j = \frac{C_{j,\infty}}{C_{j,i} - C_{j,\infty}}$$

$$\bar{b} = \frac{b}{\ell_b S}, \quad \bar{s} = \frac{s}{\ell_b S}, \quad \bar{x} = \frac{x}{\ell_b S}, \quad \bar{z} = \frac{z}{\ell_b S}, \quad \bar{u} = \frac{u}{v}$$

$$\bar{\omega}_j'' = \omega_j'' \frac{\ell_b S}{v(C_{j,i} - C_{j,\infty})}$$

Assuming a top hat profile for u , ρ , and C_j 's (i.e. constant values inside the plume in a direction perpendicular to the trajectory and zero elsewhere), the governing equation will be reduced to ordinary differential equations under these conditions; and the following groups will appear as natural nondimensional parameters:

$$m = \bar{b}^2 \bar{u}$$

$$k = \bar{b} \bar{u}$$

$$f' = \bar{b}^2 \bar{u} \bar{\rho} \frac{R^5 S}{Fr^4}$$

$$\Omega = \frac{Fr^2}{R^2 S}$$

$$n_j = \bar{b}^2 \bar{u} \bar{c}_j$$

$$\text{then } \bar{b} = \frac{m}{k}, \quad \bar{u} = \frac{k^2}{m}, \quad \text{and} \quad \bar{c}_j = \frac{n_j}{m}.$$

Conservation equations reduce to:

$$\text{geometry:} \quad \begin{cases} \frac{d\bar{x}}{d\bar{s}} = \cos \theta \\ \frac{d\bar{z}}{d\bar{s}} = \sin \theta \end{cases}$$

$$\text{mass:} \quad \frac{dm}{d\bar{s}} = \bar{\varepsilon} \quad \text{where} \quad \bar{\varepsilon} = \frac{2m}{k} \left\{ \alpha \left| \frac{k^2}{m} - \cos \theta \right| + \beta \left| \sin \theta \right| \right\}$$

$$\text{momentum:} \quad \begin{cases} \frac{dk^2}{d\bar{s}} = f' \frac{m}{k} \sin \theta + \bar{\varepsilon} \cdot \cos \theta \\ \frac{k^2 \theta}{d\bar{s}} = f' \frac{m}{k^2} \cos \theta - \bar{\varepsilon} \cdot \sin \theta \end{cases} \quad (6-12)$$

$$\text{energy:} \quad \frac{df'}{d\bar{s}} = -m \sin \theta$$

$$\text{species:} \quad \frac{dn_j}{d\bar{s}} = \bar{\varepsilon} \bar{w}_j + \bar{\omega}_j'' \frac{m^2}{k^2} \quad j = 1, \dots, N$$

6.2.3 Initial Conditions

Initial conditions are specified by values of the dependent parameter at the stack, $s=0$, i.e.:

$$\bar{x} = \bar{z} = 0, \quad m = m_i = \frac{\Omega^2}{R}, \quad k = k_i = \Omega, \quad n_j = n_{j,i} = \frac{\Omega^2}{R}, \quad \theta_i = \frac{\pi}{2}, \quad f = f'_i \quad (6-13)$$

To account for conservation of energy rather than conservation of buoyancy at the stack, f'_i evaluated based on buoyancy conservation

$$f'_i = \bar{b}_i^2 \bar{u}_i \bar{\rho}_i \frac{R^5 S}{Fr^4} = \frac{\rho_i}{S} \sim \frac{\rho_\infty - \rho_i}{\rho_i}$$

must be multiplied by $\frac{T_i}{T_1}$ to make $f'_i \sim \frac{T_i - T_\infty}{T_1}$; therefore $f'_i = \frac{\bar{\rho}_i}{S} \frac{T_i}{T_1}$.

6.3 Solution and Results

The set of (N+4) first order ordinary differential equations given in Eq. (6-12) and the (N+4) initial conditions stated in Eq. (6-13) gives a complete description of a turbulent plume in a laminar cross flow. These sets of equations were solved using Gear-Hindmarsh integration routine for different reaction mechanisms. However, the results of plume trajectories, temperature, and velocity profiles are independent of the mechanism. Figure 6-2 shows the plume trajectory. The same plot is redrawn on the log-log scale on Figure 6-3.

The periodic nature of the plume trajectory can be explained on physical grounds. When a piece of air mass expands adiabatically to a new position, it cools. However, if the temperature decrease is less than the atmospheric laps rate, the air mass is colder than the ambient air and it is driven back to its original position. Under these conditions, the restoring force is balanced by the acceleration, so:

$$\rho \frac{g}{T} \frac{d\theta}{dz} \Delta z = \rho \frac{d^2 \Delta z}{dt^2}$$

$\frac{1}{T} \frac{d\theta}{dz}$ represents the change in density per meter of rise and $\theta = T + 0.0098 z$

-94-

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Fig. 6-2. Plume trajectory. The dotted line is the centerline. Note the periodic nature of the plume due to the stratification. The plume eventually stabilizes at its maximum rise.

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Fig. 6-3. Dimensionless plume rise as a function of nondimensional distance from the stack.

is the potential temperature. The solution of this equation leads to the general form for a harmonic oscillation with frequency $\omega = \frac{g}{T} \frac{d\theta}{dz}$. These results are compared with the analytical results for limiting cases done by Fay et al. [61] and are summarized in Table 6-1. Maximum plume height occurs at $\frac{x_m}{\ell_b S} = \pi$, half the period of oscillation.

A plot on nondimensional temperature and plume velocity in the plume is given in Figure 6-4. Numerical calculation shows temperature and velocity oscillation are similar to the trajectory behavior; however, the amplitude is so small that this behavior cannot be shown in graphs. Practically, when the plume rises to the equilibrium rise at $\bar{x} = 1$, temperature and velocity in the plume approach their ambient value. The entrainment rate decreases, and the plume expands very slowly. Transport becomes negligible, and chemical reactions can be considered as they occur in a static batch reactor.

6.4 Catalytic Conversion of SO₂ in Plumes

Studies of catalytic oxidation of SO₂ on soot particles have been made in the past few years. Novakov et al. [4] showed that soot particles can act as a catalyst for the conversion of SO₂ on a propane-air flame soot. Furthermore, activated charcoal behaved in a similar manner. Recently, Chang, Brodzinsky, Toossi, Markowitz, and Novakov [5] measured the rate of oxidation of SO₂ in aqueous solutions containing suspended carbon or soot particles. The sulfate formed can be extracted from the surface of the particles, and soot is regenerated. Studies of the surface structure of Nuchar and soot particles, reported in the last chapter, also indicate a similarity between soot and activated carbon.

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Fig. 6-4. Dimensionless temperature and velocity distribution inside the plume as a function of distance downstream of the stack. U_x is the component of velocity in the horizontal x direction.

TABLE 6-1. Summary of the literature results for plume trajectory for limiting cases.

Trajectory [Ref.]	Parameter limit	Predicted trajectory
Plume rise near the stack [59]	$\frac{z}{l_m} \ll 1$	$\frac{z}{l_m} = \left(\frac{R}{\alpha R + \beta} \right)^{1/2} \left(\frac{x}{l_m} \right)^{1/2}$
Plume rise far from the stack [60] (buoyancy controlled)	$\frac{x}{l_b S} \gg 1$	$\frac{z}{l_b} = \left(\frac{3}{2\beta^2} \right)^{1/3} \left(\frac{x}{l_b} \right)^{2/3}$
Plume rise far from the stack [62] (no buoyancy)	$\frac{z}{l_m} \gg 1$ $Fr \rightarrow \infty$	$\frac{z}{l_b} = \left(\frac{3}{\beta^2} \right)^{1/3} \left(\frac{x}{l_m} \right)^{1/3}$
Maximum plume rise with uniform stratification [62]	$\frac{x_m}{l_b S} = \pi$	$\frac{z_m}{l_b} = \left(\frac{6S^2}{\beta^2} \right)^{1/3}$
Equilibrium plume height for downwind from the stack [59]	$\frac{x}{l_b S} \gg 1$	$\frac{z_\infty}{l_b} = 1.53 \left(\frac{S}{\beta} \right)^{2/3}$

Yamamoto et al. [65] have investigated the catalytic oxidation of SO_2 on activated carbon in the presence of O_2 and H_2O vapor. Their experiments simulated conditions in the scrubbing process where the temperature and concentration of SO_2 and H_2O are much higher and O_2 is lower than in the plume and ambient atmosphere. The rate of reaction was found to be first order with respect to SO_2 provided the concentration of SO_2 was less than 0.01%, and square root with respect to the concentration of O_2 and H_2O vapor. The activation energy varied from -4 to -7 kcal/mole between 70° and 150°C, depending on the origin of the activated carbon. The catalytic activity of carbon particles depends on the particles' surface chemical and physical composition [50]. The effect of the physical properties of activated carbon, such as surface area and micro and macro pore volumes, on the rate of oxidation of SO_2 was also investigated by Sugiyama et al. [66]. Their results show that when the rate is constant for a given activated carbon, the reaction initially occurs on the surface of both micropores and macropores. When the amount of accumulated H_2SO_4 reaches about 10 wt % of the carbon, the rate gradually decreases with reaction time until the micropore volume is filled up by H_2SO_4 . The reaction on the macropores continues with a constant but much slower rate than initially.

According to the results given by Yamamoto et al. [67], the rate expression until the amount of H_2SO_4 formed reaches 10 wt % of the carbon can be written as follows:

$$\frac{d(C_s)}{dt} = \frac{98}{64} \frac{d(C_2)}{dt} = C_1 C_2 C_{\text{O}_2}^{0.5} C_3^{0.5} (K_1 + K_2) e^{-E_a/RT} \quad (6-14)$$

where C_1 , C_2 , C_3 , and C_{O_2} are the concentrations of carbon, SO_2 , water vapor, and O_2 ; k_1 and k_2 are the rate constants on the surface of the micro- and macropores respectively. E_a is the activation energy assumed to be -6000 cal/gr·mole. The reaction rate of the coal base-activated carbon obtained by Yamamoto et al. [67] has the following physical properties: micropore volume, 0.4 ml/g; micropore radius, 7.4 Å; macropore volume, 0.40 ml/g; macropore radius, 2.2 μ; BET surface area, 894 m²/g; and particle diameter, 0.25 mm. Although the reaction was studied between 70° and 150°C, the activation energy determined is assumed to be valid at ambient temperature and that the rate at this temperature can be obtained by extrapolation. The calculated reaction rate constant ($k_1 + k_2$) for this carbon is equal to 4.242 m⁶/gr² sec. This rate constant value was used in the computation. Assuming the oxygen concentration in the plume is the same as that in the air

($C_{O_2} = 0.20$), equation (6-14) becomes

$$w_s'' = \frac{d(C_s)}{dt} = 6.38 \times 10^{-10} C_1 C_2 C_3 \exp(6000/RT) \quad (6-15)$$

where R is the universal gas constant 1.987 cal/g·mole, °K.

$$\text{Noting } w_3'' = w_1'' = 0$$

$$w_2'' = -\frac{64}{98} w_s''$$

The species equations can be written as

$$\frac{dn_1}{ds} = \bar{\epsilon} \bar{w}_1$$

$$\frac{dn_s}{ds} = \bar{n} \left(\frac{n_1}{m} + \bar{w}_1 \right) \left(\frac{n_2}{m} + \bar{w}_2 \right) \left(\frac{n_3}{m} + \bar{w}_3 \right)^{1/2} \frac{m^2}{k^2}$$

$$\frac{dn_2}{d\bar{s}} = \bar{\epsilon}\bar{W}_2 - \frac{64}{98} \frac{dn_s}{d\bar{s}}$$

$$\frac{dn_3}{d\bar{s}} = \bar{\epsilon}\bar{W}_3$$

Here $\bar{\eta} = 6.38 \times 10^{-10} (C_{1,i} - C_{1,\infty})(C_{3,i} - C_{3,\infty})^{1/2} \frac{l_b S}{v} \exp\left(\frac{3000}{T}\right)$

n_s is defined as $n_s = \bar{b}^2 u \bar{C}_s$ where $\bar{C}_s = \frac{C_s}{C_{2,i} - C_{2,\infty}}$. It is assumed no sulfuric acid is present in the smoke stack and the ambient background concentration is zero. Other parameters used in plume calculations and conditions at the stack exit are summarized in Table 6-2.

TABLE 6-2. Plume parameters for Figures 6-5, 6-6.

Velocity ratio [68]	R	3.333
Froud no. [68]	Fr	3.148
Stability parameter [68]	S	18.14
Buoyancy efflux [68]	f_1'	0.0704
Soot conc. at stack	$C_{1,i}$	0.36 g/m ³
SO ₂ conc. at stack	$C_{2,i}$	2.84 g/m ³
H ₂ O conc. at stack	$C_{3,i}$	11.0 g/m ³
Ambient soot conc.	$C_{1,\infty}$	2×10^{-5} g/m ³
Ambient SO ₂ conc.	$C_{2,\infty}$	8×10^{-5} g/m ³
Ambient H ₂ O conc.	$C_{3,\infty}$	10.4 g/m ³ (80% R.H.)
SO ₂ flux at stack [68]	Γ_2	1500 g/sec

6.5 Results and Discussion

Nondimensional concentrations of soot particles and sulfur dioxide as a function of nondimensional distance from the stack are plotted in Figure 6-5.

At distances far enough downstream, the concentrations approach

XBL 7710-10243

Fig. 6-5. Nondimensional concentration of different species vs. distance traveled downstream from the stack. Nondimensional concentration profiles are $w_1 = 5.55 \times 10^{-5}$, $w_2 = 2.82 \times 10^{-5}$, $w_3 = 17.33$.

ambient conditions. The ambient SO_2 concentration is above the carbon particulate concentration in this example. The concentration of sulfate formed in the plume is shown in Figure 6-6. On the same graph, the percentage of the total conversion as a function of distance downstream of the stack is given. Conversion rate is defined as the ratio of the total mass flux of sulfuric acid formed across the plume and the flux of sulfur dioxide at the stack exit. The results show that although total conversion of SO_2 increases with time, the concentration of H_2SO_4 reaches a maximum in the plume only a short distance downstream from the stack. The predicted conversion rate accounts for only a small fraction of the total sulfate present in the atmosphere. However, recent studies [52] of the catalytic oxidation of SO_2 on carbon in aqueous suspension shows that their conversion rate is much faster (4.4% per hour). It is therefore concluded that some liquid water condensed on the particles is needed before a catalytic reaction is started. More experiments are planned to investigate the effect of relative humidity and the conditions under which carbon particles can act as nuclei for water condensations.

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Fig. 6-6. a) Sulfate concentration; and b) fraction converted in the plume as a function of distance downstream of the stack. $T_0 = 293^\circ\text{K}$, $T_1 = 290.6^\circ\text{K}$, $T_i = 388.0^\circ\text{K}$, $w_1 = 5.55 \times 10^{-5}$, $w_2 = 2.82 \times 10^{-5}$, $w_3 = 17.33$.

CHAPTER 7

Conclusions

Based on primary analysis of the temperature distribution of the burner disk, a laminar premixed flat flame burner was designed. The burner is then characterized for a range of operating parameters in which the flame is stable. When the flame is flat, temperature, velocity, and heat extraction rates are measured experimentally for an acetylene-air flame between equivalence ratios of 0.6 and 1.4 and reactant flow rates of 15 to 45 lpm (STP). Adiabatic flame velocities are found by extrapolating the values of heat extraction rates vs. flow velocities to zero heat losses. The effect of a flow of an inert gas shroud on the flame stability is studied.

With richer flames (e.g., $\phi > 1.4$ at 30 lpm total reactant flow rate), the flame becomes conical. At an even larger equivalence ratio ($\phi \approx 1.84$), the flame becomes luminous and carbon is formed at greater rates.

Size distribution of the particles is determined by commercial size analyzers and by a scanning electron microscope. The effects of humidity in the dilution chamber and residence time of the particle passing through the system before detection are investigated. Samples are collected on filter substrate and are analyzed for surface and bulk analysis using X-ray photoelectron spectroscopy and X-ray fluorescent technique.

To investigate the effect of soot particles from a combustion

source on air quality, a model is presented for reaction studies in a plume of combustion products. The effects of entrainment, buoyancy, and cross wind are included. As a specific example, the rate of SO_2 conversion in the plume when soot particles act as a catalyst is calculated.

The following conclusions have been drawn from the results of the theoretical and experimental studies presented in this dissertation:

1. The acetylene-air or propane-air flame stabilized on this burner is uniform in temperature over the entire flame disk within a few percent of the maximum flame temperature (e.g., 2% for an acetylene-air flame at $\phi = 1.0$ and $\bar{s}_{25} = 21$ cm/sec). Velocity is uniform within ± 8 to 12% when the flow velocity changes from 6 to 30 cm/sec.

2. The adiabatic flame velocity of an acetylene-air mixture occurs at an equivalence ratio of ≈ 1.2 and is equal to 165 cm/sec. This value of flame velocity is in good agreement with the results achieved by other techniques [28-32].

3. Based on numerical analysis of temperature distribution in the porous disk, it is concluded that temperature uniformity will be achieved if the disk aspect ratio is less than 0.3. Values of 0.5 and 1.0 are suggested as the upper limit for a Péclet number and a Biot number. Under these conditions, the surface temperature drop at the edges is always less than 10% of the maximum surface temperature.

In analyzing the physical and chemical properties of soot, these conclusions are made:

1. In general, two modes of particle size are observed. When the flame is richer than the threshold limit of flame luminosity, the first mode consists of particles smaller than $100 \text{ \AA}$, peaked around $80 \text{ \AA}$, while

the second mode is located at 500 Å. A nonluminous blue flame generated particles only in the first mode, and therefore the distribution is unimodal. It is postulated that when the flame is nonluminous, it burns as a premixed flame and therefore better mixing of the reactants prior to reaching the combustion zone results in small size particles. In richer luminous flames where reactants diffuse through the reaction front without being burned, the flame behaves like a diffusion flame, and therefore a second mode is seen in the size distribution.

2. The number of particles generated increases rapidly when the relative humidity in the sample train is larger than 70%. Therefore, there appears to be a large number of fine nuclei, which grow in the presence of water to sizes detectable by the instruments.

3. Chemical analyses of samples reveal the presence of two different oxygenated species adsorbed on carbon particles. The chemical structure of these species is not known yet. The relative atomic concentration of these species and the ratio of total oxygen-to-carbon changes when the equivalence ratio is smaller than 2.0. With richer flames ($2.0 < \phi < 2.4$), this dependence disappears. It is thus concluded that the chemical composition of soot generated varies with different conditions. These observations might also indicate a dependence of particle size on the chemical properties of soot particles.

4. Oxidation of SO_2 to sulfate in the presence of soot particles is possible only when enough oxygen is present to oxidize SO_2 to SO_3^- .

5. X-ray fluorescence analysis of the particulates did not reveal any detectable amount ($< 5 \text{ ng/cm}^2$ filter) of trace elements.

APPENDIX A

Carbon in Flames

A.1 Formation

The detailed mechanism of carbon formation in flames is unknown. It is suggested that carbon is formed by a series of complex chain reactions maintained by free radicals which lead to polymerization and thermal decomposition of fuel [71]. Wersborg, Fox, and Howard [72] divided the process of carbon formation into three parts: (1) the nucleation of radicals and charged heavy hydrocarbons, (2) the depletion of heavy hydrocarbons by decomposition of the hydrocarbons on the surface of the nuclei, and (3) the agglomeration to large particles. Thomas [73] postulated different paths for aliphatic and aromatic fuels. Aliphatic compounds break down into simpler alkyl and olefin radicals before they build up into large conjugated polyene and polybenzoid radicals, whereas aromatic fuels can readily form radicals which polymerize into large soot particles.

Carbon formation usually occurs for equivalence ratios lower than those predicted by equilibrium calculations. This is because residence time is much smaller than characteristic chemical reaction time. Equilibrium is not attained and fuel decomposes faster than it is oxidized; therefore, soot is generated in equivalence ratios as low as 1.3 [74,75].

The onset of soot generation is defined as the equivalence ratio at which the flame becomes luminous, i.e., the presence of carbon particles can be detected by the eye. It does not rule out the presence of fine soot particles at leaner flames. The onset of soot formation,

defined in this manner, varies with the flame geometry, i.e., whether the flame is flat, conical, or cellular; and the onset is therefore not only a characteristic of fuel.

The position of carbon luminosity in different hydrocarbon flames depends on the relative rate of the diffusion of the fuel and the oxidizer to the reaction front. Oxygen diffuses much more rapidly toward the edges of a small concentration gradient than hydrocarbons having more than four carbon atoms; thus there is partial enrichment on the top of the cone. In acetylene-type flames, the diffusion rate of light hydrocarbons is not very different from that of oxygen; this ensures more uniform enrichment of the fuel and therefore more uniform carbon luminosity in the flame [71].

A.2 Effect of Controllable Parameters

A.2.1 Pressure

As the pressure increases, the rate of carbon formation increases. At higher pressures, the chemical reaction is accelerated; therefore, combustion is initiated earlier and more fuel is burned in the fuel-rich region. The coagulation rate is increased because it is directly proportional to the collision frequency of the particles.

An increase in pressure does not change the onset of soot formation if the flow velocity (and accordingly the temperature) remains unchanged [76], but the onset is shifted to leaner fuel if mass flow remains constant [77,78].

A.2.2 Temperature

In general, a higher flame temperature seems to suppress soot

formation near the threshold limit. For very rich flames, on the other hand, it increases the amount of soot deposited [14]. It is believed that near the threshold limit, a higher temperature helps completion of the oxidation of carbon. In very rich flames, a high temperature accelerates the pyrolysis reaction so that it dominates the oxidation rate of soot.

The effects of change in the flow velocity, the burning rate, and the air/fuel ratio of some additives can be explained most readily by studying their effects on the flame temperature. For example, increasing the cold gas velocity has the corresponding effect of increasing the temperature because of decreased heat losses to the burner.

A.2.3 Composition

The ratio of fuel to oxidizer is an important parameter in the onset of carbon formation. In premixed flames, increasing the oxygen concentration may promote the rate of attack of larger molecules and give a more uniform distribution of oxygen among carbon atoms, which suppresses soot formation. The effect of oxygen concentration on soot in diffusion flames was studied by Chakaborty [79]. The reaction zone was shifted to the fuel side of the flames with an increase in the oxygen index. The temperature increases throughout the reaction zone, which in turn promotes pyrolysis of the fuel; but at the same time, particles passing through this zone were consumed more rapidly. Concentration of radical species such as O and OH in the reaction zone increased, and possibly these radical species could have prevented the formation of soot particles by diffusing to the hot pyrolysis zone. Therefore, whether or

not soot is produced depends on which processes predominate.

Dilution of the oxidizers with nitrogen, for a given fuel-oxygen mixture, promotes the formation of carbon. Hence it seems that dilution of premixed combustion gases with considerable amounts of exhaust gases would probably reduce the efficiency of oxygen in suppressing the formation of carbon. This effect is somewhat different from the effect of the diluents in diffusion flames, and might be explained by considering the role of nitrogen in preventing the huge surrounding supply of oxygen from penetrating and reacting with fuel.

A.2.4 Electric Field

The marked changes in the nature of the soot generated in luminous flames when an electric field is applied imply that the particles present in the flame are charged. Whether these particles are positively or negatively charged depends on two mechanisms: (1) thermionic emission, which removes electrons from the surface and results in a positively charged surface, and (2) attachment, which changes to the sign of local flux.

The negative ions in the flame are generally thought to be electrons whose mobilities are about a thousand times greater than those of positive ions. In a steady state, the concentration of a species is inversely proportional to its mobility. In the presence of an electric field, the probability of meeting a positive particle is much greater than that of meeting a negative particle. Experiments carried out by Weinberg show that an appreciable fraction of carbon particles are charged positively. This has been shown in a study of a premixed

flame [80]. A field was applied between the brass plates (cathode) and the flat flame burner matrix (anode). Carbon was generally deposited at a much greater rate on the negative electrode. However, it was shown, this increase is only in volume, not mass, and is accompanied by a change in density. The effect of the field is to build loose, fluffy, and bulky agglomerates. This study shows that the total weight of the deposit on the bulky agglomerate occurs when the plate is charged. Reversing the field causes the flame to be distorted toward the burner mouth. In this case only a little soot is deposited on the top plate, and it grows in the form of long filaments on the matrix and burner rim.

Wersberg [72] uses a water cooled flat flame burner for measurement of local concentration and mass distribution of charged particles. His data show that the mass and size of charged species increase with distance above the burner.

The effects of electrical changes on diffusion flames were also investigated in an ethylene counterflow flat diffusion flame [80]. Irrespective of the direction of the field, the weight of the soot collected was 2% less than the weight with no field. The flame changed in appearance from yellow to blue. The particle sizes were reduced from about $1100 \text{ \AA}$ to less than $100 \text{ \AA}$ when a strong field was applied. However, in a small field and under certain conditions, it was possible to hold the positively charged particles in the reaction zone against the gas flow so that their time of passage through the carbon-forming region was increased. This situation resulted in rapid growth of large particles.

A.3 Characterization of Soot

A.3.1 Size Distribution

In general, diffusion flames and slow-burning premixed flames release particles in the larger size range, while fast-burning premixed flames yield smaller particles. Particles in the range of 50 to 2500 Å are detected in flames [14].

Studies of carbon formation in premixed hydrocarbon flames at reduced pressure [81] show that carbon particles become detectable at ~ 40 Å, a short distance behind the oxidation zone. In the region where the polyacetylene concentration decreases, the size of the particles increases by agglomeration of smaller particles, and the number density of carbon particles goes down. At a greater distance above the flame, the size of the particles increases while the number of particles decreases; but the total mass of carbon remains constant. Samples were extracted by a cooled quartz probe in these experiments, while similar experiments carried out by Wersborg, Fox, and Howard [82] used a molecular beam sampling technique. Particles as small as 15 Å were collected on a grid.

Fissan, Kittelson, and Whitby [38] used a laminar premixed propane flame stabilized on a 1/4-inch copper tubing in a relatively controlled environment. Particle concentration increased markedly with humidity. At a given humidity change in equivalence ratio from a blue premixed flame to a yellow pure diffusion flame, minor changes in the particle concentration occur. Synergistic effects are seen if clean filtered dilution air is replaced by dirty room air; i.e., the particle concentration is much greater than could be accounted for by the difference

between clean and dirty ambience. This is explained by a higher humidity in the flame and exhaust gases which causes nuclei and particles in the air to grow.

A.3.2 Structure

The properties of flame-generated soot are remarkably similar irrespective of the type of flame, i.e., premixed or diffusion, the nature of fuel, and the other conditions under which they are formed [83]. X-ray diffraction studies show that the particles have a basically graphitic structure. Each particle of soot consists of a large number of these small crystallites of around 20-30 Å in size [7]. Soot has some hydrogen atoms which vary from more than 50% of the number of carbon atoms to almost none (up to 4% by weight) [73,81].

APPENDIX B

Acetylene Purification System

X-ray photoelectron spectroscopy analysis (ESCA) of samples collected showed little or no particulate sulfate present. It has been shown that the combustion of sulfur-containing fuels produces some particulate sulfate [4]. The presence of a considerable amount of phosphate phosphorous in the samples led us to believe that phosphine present in the acetylene was being oxidized to produce phosphate. Since the concentration of phosphorous compounds in most fuels is very small, these reactions are not important to environmental studies.

A typical ESCA spectrum of the sample collected from the system is shown for ranges of binding energies of interest (Fig. B-1a). Intensities are plotted in arbitrary units and normalized to the C(1s) peak. Stronk peaks at binding energies of 137 and 402 eV agree in energy with the N^{-3} and P^{+5} peaks from ammonium phosphate powder. No sulfate was observed. It is therefore concluded that the oxidation of phosphorous competed with the sulfur oxidation reactions. To validate this hypothesis, it was necessary to remove the phosphine compounds from the fuel. Acetylene was passed through a column of Purifi (Purifi Company, Mason, Ohio 45040) made of a Pyrex tubing 50 cm long and 12.5 cm in diameter. Purifi, used commercially as an acetylene purifier, consists of ferrous oxides, tetrahydrate copper sulfate, manganese oxides, and mercuric chloride, which is carried in diatomaceous earth. The

XBL 784-727

Fig. B-1. XPS spectra of a) nonpurified acetylene soot (top spectra), and b) purified acetylene soot (bottom spectra). An order of magnitude reduction in phosphorus and ammonium complex and a significant increase in sulfate is observed.

purifying capacity of the material is greatly increased by the moisture content of the gas. To obtain maximum efficiency, acetylene was bubbled through water before entering the Purifi bed. The added moisture was then removed by a column of Dririte which followed the Purifi bed.

The acetylene thus purified was believed to be phosphine free, at least to a few hundred ppb. However, it was found that acetylene purified in this manner contained some acidic species. These species caused rapid corrosion of the burner disk. To overcome this difficulty, acetylene was passed through a column of activated carbon, followed by a column of Ascarite (NaOH on asbestos). This increased the lifetime of the burner although the corrosion effects were not completely eliminated. Therefore, it is suggested that stainless steel burners be used in conducting such reaction studies.

ESCA analyses of the particulate material collected from the purified acetylene (Fig. B1-b) showed an order of magnitude reduction in collected ammonium phosphate and an increase in particulate sulfate.

APPENDIX C

Thermocouple Design and Temperature Corrections

C.1 Thermocouple Construction

A platinum, platinum-10% rhodium thermocouple was used to measure the flame temperature (Fig. C-1). This thermocouple was constructed according to suggestions given by Fristrom and Westenberg [84] and by Kaskan [11].

The fine wire was 75 μm in diameter, while 250- μm -diameter wire was used for supports in the Y-shaped assembly. A 15-cm double-holed ceramic tube, 0.32 cm in diameter, and two 0.6-cm long single-holed ceramic tubes were cemented together with saureisin adhesive cement to hold the support wires in place and thus put the finer wire in tension. The thermocouple junction was carefully butt welded so that the bead diameter remained only slightly larger than the lead wire (approximately 0.012 cm). Then the thermocouple was coated with a thin layer of fused quartz at 1850°K to eliminate catalytic reaction and contamination of the bare platinum wires with hot combustion gases.

Much finer lead (0.0005 cm in diameter) had been used [11] to measure the temperature profile across the reaction zone. However, since only maximum flame temperature was of interest here, local perturbation by the thermocouple wire was not very important, and wires 0.0075 cm thick gave adequate accuracy.

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Fig. C-1. Thermocouple

C.2 Temperature Corrections

The steady state energy equation for thermocouple wire can be written:

$$\lambda \frac{d^2 T}{dx^2} + \frac{4h}{d} (T_{fl} - T) - \frac{4\sigma\epsilon}{d} (T^4 - T_0^4) = 0 \quad (C-1)$$

where x = distance along the wire

λ = thermal conductivity of thermocouple wire

d = diameter of thermocouple wire

ϵ = emissivity of thermocouple wire

T = temperature of thermocouple

T_{fl} = flame temperature

T_0 = enclosure's black body temperature

h = heat transfer coefficient

In this equation the radiation exchange between wire and combustion gases is neglected. However, this is not a good assumption for a sooty flame where the absorption of radiant energy by soot particles is important. For such an instance, another term should be added to the above energy equation. When there is no thermal conduction along the wire (small temperature gradient between bead and support junction), the first term is zero and radiation corrections are calculated from:

$$\Delta T_{rad} = T_{fl} - T = \frac{\sigma\epsilon}{h} (T^4 - T_0^4) = \frac{\sigma \cdot d}{Nu} (T^4 - T_0^4) \frac{\epsilon}{\lambda} \quad (C-2)$$

The heat transfer coefficient is estimated in using Kramer's equation quoted by Hinze [85]:

$$Nu = \frac{hd}{\lambda} = 0.42 Pr^{0.2} + 0.57 Pr^{0.33} Re^{0.5} \quad 10^{-2} < Re < 10^4 \quad (C-3)$$

Kaskan used the following equation to evaluate h:

$$Nu = \frac{hd}{\lambda} = 0.8 Re^{0.25} \quad (C-4)$$

Using Eq. (C-4) gave radiation corrections which are 15-20% higher than those found by Eq. (C-3). In these calculations gas viscosity and gas thermal conductivity were assumed to be the same as air at the thermocouple temperature. Emissivity of the thermocouple wire can be calculated from a theoretical expression derived by Davisson and Weeks [86] based on electromagnetic theory:

$$\begin{aligned} \epsilon = 0.751 (T \cdot r_e)^{1/2} - 0.632 (T \cdot r_e) + 0.670 (T \cdot r_e)^{3/2} \\ - 0.607 (T \cdot r_e)^2 \end{aligned} \quad (C-5)$$

where $r_e = \frac{4T}{\lambda} \times 10^{-10}$ is the electrical resistivity of the wire.

Bradley and Entwistle [87] calculated and measured the emissivity for silica-coated platinum wire using the above equation. The emittance is close to the uncoated wire emissivity at high temperature. At lower temperatures the emittance is increased as a consequence of the high absorption at the longer wavelength.

Using experimental data by Bradley and Mathews [88] for the thermal conductivity of pt-pt-10% Rh junction alloy, emissivity is calculated from Eq. C-5 and is plotted in Figure C-2. A surprisingly simple relationship is derived if the value of the thermal emissivity is divided by the thermal conductivity data reported:

XBL 781 - 42

Fig. C-2. Emissivity of the Pt - Pt - 10% RH thermocouple as a function of temperature.

$$\frac{\varepsilon}{\lambda} = 3.20 \pm 0.05 \quad \quad \quad 800 < T < 2000 \quad \quad \quad (C-6)$$

Therefore the constant value of $\frac{\varepsilon}{\lambda} = 3.2 \text{ ft} \cdot \text{sec} \cdot ^\circ\text{K} \cdot \text{Btu}^{-1}$ is used in calculating the temperature corrections given by Eq. C-2).

APPENDIX D

Particulate Losses

A successful sampling system must meet the following four requirements: (1) obtainment of a representative sample; (2) preservation of the compositional characteristics of a sample while preparing it for the analyzer; (3) transportation of the sample quickly enough to minimize corrections on the analyzed sample; and (4) accurate measurement of the species of interest. The first requirement is met if the sample is homogeneous. When particles are present, the sampling must be done isokinetically. The second requirement can be satisfied with a probe which is nonreactive to flue gases. The third requirement calls either for a shorter sampling time or a higher flow velocity. The last and most important requirement is to have reliable sampling equipment over a wide range of operating conditions. This is discussed in Appendix E.

D.1 Anisokinicity

An isokinetic sample is obtained when the velocity of the sample equals that of the main stream. Anisokinicity arises when the trajectory of the particulate is different from that of the gas due to the higher inertia of solid phase. Theoretical analysis of errors due to anisokinetic sampling was done by Badzioch [89] and Vitols [90]. It can be shown [91] that particles follow the stream line when $Ta \cdot Re_p \lesssim 1$, where $Re_p = \frac{u \cdot r_p}{\nu}$ is the Reynolds number based on particle radius r_p and gas kinematic viscosity ν . $Ta = \frac{\rho_p \cdot r_p}{\rho_g R}$ is the Taylor number. ρ_p is particle

density, ρ_g is gas density, and R is the radius of the sampling probe. In our probe design, $R = .5$ cm, $\bar{u} = 120 - 1200$ cm/sec, $\rho_g = 10^{-3}$ g/cm³, $\rho_p = 1$ g/cm³, and $\nu = .1$ cm²/sec. Calculations show that errors due to anisokinecity become important for particles bigger than 13 microns ($r_p = 6.5 \times 10^{-4}$ cm), for $\bar{u} = 120$ cm/sec, and particles bigger than 4 microns ($r_p = 2 \times 10^{-4}$ cm) when $\bar{u} = 1200$ cm/sec. Since the particles found in our flame are all submicron particles, anisokinecity is unimportant for our sampling.

D.2 Losses in the Sampling Tube

Once the representative sample enters the probe nozzle, the particles in the gas are subject to different losses to the wall of the tube. The significant losses are due to gravitational settling, inertial impaction, reentrainment of particles, coagulation, and Brownian and turbulent eddy diffusion. Gravitational settling, inertial impaction, and reentrainment of particles are important only for particles bigger than 15 μ m. Davies [92,93] shows that turbulent eddy diffusion is important only for particles larger than 1-3 microns. On the other hand, Brownian diffusion is important only for particles smaller than 1-3 microns.

The diffusional deposition losses to the walls of a circular tube for a laminar flow are given by Gormley and Kennedy and can be found in Fuchs [94] (p. 204) as follows:

$$p = 1 - 2.56\mu^{2/3} + 1.2\mu + .177\mu^{4/3} + \dots \text{ for } \mu \leq .01 \quad (D-1)$$

$$p = 0.819 \exp(-3.657\mu) + .097 \exp(-22.3\mu) + .032 \exp(-57\mu) + \dots \\ \text{for } \mu > .01 \quad (D-2)$$

where $p = \frac{\bar{n}}{n_0}$ = particle penetration

$\bar{n}$ = average particle concentration at each point

n_0 = initial particle concentration

$$\mu = \frac{D L}{R^2 \bar{u}}$$

D_p = diffusion coefficient of the particle (cm^2/sec)

L = length of the tube (cm)

R = tube radius (cm)

$\bar{u}$ = average flow velocity in the tube (cm/sec)

The diffusion coefficients are functions of particle radius and are calculated using Einstein's equation.

Diffusion losses are considered those of the sampling probe ($T = 300^\circ\text{C}$, $L = 30$ cm, $R = .67$ cm) and the sampling line ($T = 25^\circ\text{C}$, $L = 120$ cm, $R = .67$ cm). $P = P_{\text{probe}} \times P_{\text{line}}$.

The range of flow rates used in our experiments varied between 8 ℓpm in size distribution measurements (Chapter 4) and 55 ℓpm when particulates were collected on the filter (Chapter 5).

The results are summarized in Table D-1 and plotted in Figure D-1.

Fig. D-1. Diffusion losses as a function of particle diameters for different total flow rates; solid dot = 55 lpm, and hollow dot = 8 lpm.

XBL 784-734

Table D-1. Penetration through the sampling system.

Microns d_p	cm^2/sec $D_{25^\circ\text{C}}$	cm^2/sec $D_{300^\circ\text{C}}$	$\dot{V}=8 \text{ lpm}$			$\dot{V}=55 \text{ lpm}$		
			P_{probe}	P_{line}	P	P_{probe}	P_{line}	P
.004	3.23(-3)	6.21(-3)	.936	.845	.791	.982	.971	.954
.01	5.24(-4)	1.00(-3)	.981	.969	.951	.995	.991	.986
.02	1.35(-4)	2.60(-4)	.992	.987	.979	.998	.996	.994
.04	3.59(-5)	6.90(-5)	.997	.995	.992	.999	.998	.997
.10	6.82(-6)	1.33(-6)	1.000	.998	.998	1.000	.999	.998
1.0	2.79(-7)	5.27(-7)	1.000	1.000	1.000	1.000	1.000	1.000

D.3 Coagulation Losses

The model of Smoluchowski (see Fuchs [94], p. 288) is used to estimate losses due to coagulation. We assume that:

1. The particles are spherical and monodispersed.
2. The fluid is dilute; i.e., the probability of multiple coagulation is negligible.
3. The coefficient of relative diffusion of the two particles is equal to twice the diffusion coefficient of each.
4. The particles adhere at every collision.

The basic coagulation equation is

$$\frac{dn}{dt} = -k_0 n^2 \quad (\text{D-3})$$

where $k_0 = 4\pi d_p D$ is the coagulation constant, d_p is the particle diameter, and D is the diffusion coefficient for one of the particles.

Integrating Eq. (D-3) gives

$$\frac{1}{n} = \frac{1}{n_0} + k_0 t \quad (\text{D-4})$$

$$\text{or } n = \frac{n_0}{1+k_0 n_0 t} \quad (\text{D-5})$$

$$\text{and } p = \frac{n}{n_0} = \frac{1}{1+k_0 n_0 t} \quad (\text{D-6})$$

t is the total residence time of the particles from the time they leave the flames (~ 5 seconds). Since the diffusion coefficient is a function of temperature, coagulation losses are calculated separately in the chamber, probe, and sampling line before they are added together. Figure D-2 shows the penetration of particles for different initial concentrations. n_0 is the concentration of particles at the flame front. A dilution factor of 20 is assumed when coagulation losses in the sampling line are considered.

XBL 781 - 46

Fig. D-2. Coagulation losses as a function of particle diameters for different initial concentration.

- $\times$ $n_0 = 10^5$ particles/cm³
- $\bullet$ $n_0 = 10^6$ particles/cm³
- $\circ$ $n_0 = 10^7$ particles/cm³
- $\square$ $n_0 = 10^8$ particles/cm³

APPENDIX E

Ancillary Apparata

E.1 Particle Analysis

E.1.1 Number: Condensation Nuclei Counter

A Condensation Nuclei Counter (CNC) (Rich Model 100, Environment One Corp.) is used to measure the total number of particles in the sample. The instrument measures particles as small as .001 micron in the concentration range of 10 to 10^7 particles per cubic centimeter with a response time of 1 to 2 seconds. It operates by suddenly cooling the sample under adiabatic expansion and causing the relative humidity to rise to 300%. Water condenses on the nuclei to form drops 5 microns in size, which then attenuate the light. The light signal is proportional to the number of particles present. The efficiency of the particle counter decreases for particles smaller than .01 microns. Below this size a much higher degree of saturation is needed for the particles to become effective as condensation nuclei [95]. Calibration matrix is not available for these size ranges; therefore corrections for diffusion losses inside the sampling tube do not have statistical significance.

E.1.2 Size: Electrical Aerosol Size Analyzer

a. Principle of operation: The electrical aerosol size analyzer determines the size of submicron particles larger than $100 \text{ \AA}$ by measuring the electrical mobility of unipolarly charged particles. The particles are neutralized through a krypton 85 neutralizer (Thermo-

System, Inc.) and then uniformly charged before entering the precipitator section where they are electrostatically precipitated on a collector rod. The voltage across the collector rod determines the particles which can escape the field without being precipitated. These particles are detected by an electrometer sensor. Changing the collector voltage will result in a different electrometer current. The difference between these two currents is an indication of the number of particles in a certain size range. A detailed description of the instrument can be found elsewhere [96,97].

b. Sampling requirement: Instrument sensitivity, defined as the ratio of the electrometer current to the number of particles, is a function of particle size [97]. The detection limit of the instruments therefore depends on the sensitivity of the electrometer in measuring current flow. The noise current of the electrometer is about 10^{-15} amp. These data may be used to determine the minimum number of particles in each cubic centimeter of the sample that can be detected with such an electrometer for a signal-to-noise ratio of 2 to 1. The result of such a calculation is given in Figure E-1. These results show that particles larger than $80 \text{ \AA}$ in diameter can be detected when at least 10^5 particles are present in a cubic centimeter of sample. In all the measurements done by EASA, the dilution ratio was set in order to maintain a concentration of approximately 10^5 particles/cc at the lowest channel.

c. Data reduction: The electrometer output currents are used to evaluate the number, surface area, and volume distribution of an aerosol sample using the sensitivity matrix according to the procedure outlined

XBL 781 - 52

Fig. E-1. Minimum number of detectable particles by EASA instrument at each size range.

in the users' manual. In calculating the surface and volume distribution, it is assumed that the particles are spherical with a diameter D_{pi} , the average of the sizes detectable by each channel. The values of sensitivity given are for monodisperse aerosols and therefore the distributions determined in this manner are good only to the first approximation.

The cumulative number plots (cumulative number fraction $\leq D_p$ versus $\log D_p$) of the aerosols generated by our experimental system appeared to be linear, indicating distributions can be represented by a logarithmic normal fit. The polydispersity of the aerosol can best be represented by its geometric standard deviation which for the log-normal distribution is calculated from the equalities

$$\sigma_g = \frac{84.13\% \text{ size}}{50\% \text{ size}} = \frac{50\% \text{ size}}{15.87\% \text{ size}}$$

The fact that particles are not monodisperse was taken into consideration, and the values of σ_g for each mode calculated in this manner were used to correct particle size distribution. Recently, polydisperse instrument sensitivities were reported by Liu and Pui [98] that take into consideration the fact that a specific particle size is sensed in neighboring channels as well as in its own channel. In a computer program written by Liu and Kapadia [37], values of σ_g , for which chi-square of the current differential in adjacent channels minimizes, are calculated. Corresponding sensitivities are used to calculate number, surface, and volume distributions.

Results were represented in the form of $dN/d(\log \bar{D}_p)$ per cubic centimeter of air as a function of $\bar{D}_p$ on a log-log scale. The advantage is that the area under the curve corresponds to the total number of

particles per cubic centimeter rather than to the probability of finding a particle in the corresponding size range.

d. Error analysis: Errors involved in size measurement with EASA are due to sampling losses to the tube and analyzer current fluctuations. If S is the sensitivity of the analyzer, ΔI is the difference between the currents of the adjacent channels, and P is the penetration of the particles for size range ΔD_p . Then we have

$$\Delta N_p = \frac{S}{P} \Delta I \quad (E-1)$$

$$\Delta S_p = \Delta N_p \cdot \pi D_p^2 \quad (E-2)$$

$$\Delta V_p = \Delta N_p \cdot \frac{\pi D_p^3}{6} \quad (E-3)$$

where ΔN_p , ΔS_p , and ΔV_p are corresponding numbers, surfaces, and volumes in the particular size range. Let σ_1 and σ_2 be standard deviations of the current measurement in the two channels. Then the standard deviation of ΔN_p becomes (Wilson [99], p. 272):

$$\sigma_N = \frac{S}{P} (\sigma_1^2 + \sigma_2^2) \quad (E-4)$$

From this it follows that

$$\sigma_S = \pi D_p^2 \sigma_N \quad (E-5)$$

$$\sigma_V = \frac{\pi D_p^3}{6} \sigma_N \quad (E-6)$$

E.1.3 Mass: Carbon Analyzer

The total carbon particulate matter (carbonate and noncarbonate) is

determined by measuring the CO_2 released by complete combustion in an oxygen environment. The particulates collected on a pre-fired carbon-free quartz fiber filter are put into a porcelain boat and heated to 920°C in a tube furnace in an O_2 environment in the presence of CuO catalyst. At this temperature all carbon is oxidized to carbon dioxide. CO_2 was then frozen in dry nitrogen maintained at -165°C to -175°C while other interferences such as H_2 , O_2 , and N_2 passed through the trap. Water was removed by a dry ice-methanol bath at -78°C upstream from the liquid nitrogen trap. CO_2 was removed by heating the trap and was flushed into a gas chromatograph for analysis. Helium was the carrier gas.

The gas chromatograph was calibrated against the known amount of pure graphite. The output of the GC was corrected for combustion and trapping efficiencies before being transformed into units of micrograms of carbon per squared centimeter of filter face area. Mass loading determined in this manner was accurate within 2-3%. For further discussion of this technique, refer to Belsky [100].

E.2 Gas Analysis -- Humidity: Condensation Dewpoint Hygrometer

A dewpoint hygrometer (Model 1200 AP, General Eastern, Inc.) was used to measure the dewpoint of the gas sample by cooling the surface of a mirror until condensation occurred. The specular component of the light from the mirror was detected by a photodetector. The photodetector was built in an electrical bridge circuit so that the specular detector was fully illuminated when the mirror was clear. When dew was formed on the mirror, the photodetector measured the reduced light. An accuracy of better than $\pm 0.5^\circ\text{C}$ can be achieved with this unit.

APPENDIX F

Electron Spectroscopy for Chemical Analysis (ESCA)

X-ray photoelectron spectroscopy (also known as XPS or ESCA) is a powerful tool for both surface elemental analysis and determination of the oxidation state of the element studied. Extensive reviews of the subject can be found in Siegbahn et al. [101] and Carlson [102], and therefore only a brief description of the technique will be given here. The method consists of the measurement of kinetic energies of photoelectrons expelled from a sample irradiated with monoenergetic X-rays. The kinetic energy of a photoelectron expelled from a subshell i , E_{kin} , is found as the difference between X-ray photon energy ($h\nu$) and the binding energy of the electron in that subshell (E_i).

The electron binding energies are characteristic of each element. However, these energies are not a property solely of the atom, but also of its chemical environment, i.e., of the molecular structure. When the valence state of an atom is changed and a chemical bond is formed, the corresponding redistribution of the electrical charge valence shell is sensed by all the core electrons and can cause a "chemical shift" in electron binding energies. Such chemical shifts can be predicted with a simple model in which valence electron orbitals form a valence shell of electrical charge and the core electrons reside in the center of this shell. When an atom is bound to other molecules, the charge is added to or removed from the valence shell and the electrical potential inside

the valence shell is changed. The potential energy of the inner electrons is increased or decreased depending on whether a charge is added or removed. The binding energy of an inner electron, i.e., the energy required to transfer it to infinite distance from the atom, is therefore changed by the same amount. Binding energies will be greater than the binding energy of the neutral atom if the effective charge is positive, i.e., for oxidized species, and lower if the effective charge is negative, i.e., for reduced species.

The photon source commonly used is Mg or Al $K\alpha$ X-rays because of their characteristic narrow $K\alpha$ X-ray natural band width. The contribution to the photoelectron spectrum from continuous radiation is unnoticeable in general, since the Bremsstrahlung spectrum is distributed over several kilovolts while the $K\alpha$ X-rays are centered in a peak of about 1 volt FWHM. An AEI-ES 200 ESCA spectrometer used in our studies uses $K\alpha$ X-rays generated by impingement of electrons emitted from a tungsten filament on an aluminum anode.

An alternative nonradiative process (Auger transition) can bring excited atoms to ground state. In this case the readjustment to an inner shell will take place by having one electron from a less tightly bound orbital fill the hole. The de-excitation energy is consumed to eject a second electron into the continuum, the kinetic energy of which is the difference between this de-excitation energy and its binding energy. Auger spectroscopy becomes very useful in surface studies of light elements where the X-ray fluorescence yield is small. Two such processes are identified as $C(K_1L_{23}L_{23})$ and $O(K_1L_{23}L_{23})$ in a typical sample of acetylene-air flame and are shown in Figure 5-1. The notation used is $1 \equiv S_{1/2}$, $2 \equiv P_{1/2}$, and $3 \equiv P_{3/2}$.

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.