PLASMA ASSISTED NO_x REDUCTION IN EXISTING COAL COMBUSTORS

A Final Report

by

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Abstract

The feasibility of NO_x reduction using plasma injection has been investigated. Both numerical and experimental methods were used in the development of this new NO_x reduction technique.

The numerical analysis was used to investigate various flow mechanisms in order to provide fundamental support in the development of this new NO_x control technique. An efficient and realistic "Group" model was developed for the modeling of gas-particle turbulent flows which uses particle groups to represent the dispersed phase and considers particle dispersions within each group due to the turbulence. A factor of 20 reduction was achieved in the computational time as compared to a classical two-phase flow model. The calculations using this approach can give the information of the particle trajectories and distributions which are important for the design of the in-flame plasma injection configuration. The group model also established the necessary ground for further complete modeling of the whole process including the chemical kinetics. Numerical calculations were also performed for a turbulent gas flow field with variable properties. The results provided fundamental understanding of mixing effects encountered in the experiments at Pittsburgh Energy and Technology Center.

A small scale experimental facility was designed and constructed at the heterogeneous combustion laboratory at Carnegie Mellon University. A series of tests were conducted in this setup to investigate the potential of the ammonia plasma injection for NO_x reduction and parametric effects of this process. The experimental results are very promising. About 86% NO_x reduction was achieved using ammonia radicals produced by argon plasma within the present test range. The total percentage of NO_x reduction increases when ammonia flowrate, argon flow rate and initial NO concentration increase and when plasma power and the amount of excess air in the combustor decrease. A combined transport and reaction model was postulated for understanding the mechanism of NO_x reduction using the plasma injection.

Contents

Abstract	iii
Table of Contents	iv
List of Figures	vii
List of Symbols	x
Acknowledgments	xii
1 Introduction	1
2 Numerical Modeling of In-Flame Injection	6
2.1 Theoretical Background	6
2.2 Basic Eulerian/Lagrangian Formulation	11
2.2.1 Gas Phase	11
2.2.2 Dispersed Phase	12
2.3 Turbulent Dispersions	13
2.3.1 Center of a Group	13
2.3.2 Particles in a Group	14
2.3.3 Splitting of a Group	17
2.4 Numerical Analysis	20
2.5 Results and Discussion	21

2.5.1	General Nature:	21
2.5.2	Data Comparisons on Particle Laden Jets:	21
2.5.3	Thermal Effects	28
2.5.4	Computational Effort	29
2.6	Summary	30
3	Numerical Modeling of Downstream Injection	31
4	Experimental Background	37
5	Experimental Apparatus	39
6	Experimental Results	46
6.1	Optimum NO Reduction within the Test Range	47
6.2	Plasma Power Effect	47
6.3	Excess Air Effect	52
6.4	Argon Flowrate Effect	53
6.5	Cross Flame Injection	56
7	Discussions of Experimental Results	58
7.1	Comparison with Thermal DeNO _x	58
7.2	Combined Transport and Reaction Model	63
7.3	Comparison with PETC's Results	70
7.4	Summary	73
8	Conclusions and Future Work	75
8.1	Conclusions	75
8.2	Future Work	77
	Appendix A NO_x Control Techniques	81
	Appendix B Gaussian Distribution of Particle Dispersions	83

Appendix C	Splitting of a Group	85
Appendix D	Test Data	89
Appendix E	Air Leakage	93
Appendix F	Combustion Stoichiometry Calculations	95
Appendix G	Plasma Gun Temperature Calculations	97
Appendix H	System Efficiency Analysis	99
H.1	Analysis	99
H.2	Results and Discussion	102
H.3	The Data Used in the Calculations	109
H.4	The Efficiency Calculations for the Nitrogen Plasma	110
H.5	The Efficiency Calculations for the Ammonia Plasma	114
Appendix I	Radical Freezing Through a Supersonic Nozzle	117
Bibliography		122

List of Figures

2-1	The Schematic of the Computational Field Using the Group Approach .	16
2-2	The Splitting of a Group	19
2-3	Normalized Radial Particle Concentration Distributions	22
2-4	The Trajectories of Groups	23
2-5	Particle Distributions within Groups	24
2-6	Axial Particle Concentration Distributions at the Center Line	26
2-7	Radial Particle Concentration Distributions at $x/d=20$	27
2-8	Axial Temperature Distributions at the Center Line	28
3-1	Numerical Simulation of Downstream Injection	32
3-2	Axial Velocity Distributions at the Center Line	33
3-3	Radial Velocity Distributions at Different Axial Locations	34
3-4	Axial Temperature Distributions at the Center Line	35
3-5	Radial Temperature Distributions at Different Axial Locations	36
5-1	Overview Photograph of Entire Experimental Setup	40
5-2	Schematic of Overall Experimental Set-up	41
5-3	Schematic of Plasma Generator System	43
5-4	Photograph of the Plasma Flame	44
6-1	Percentage NO Reduction vs. NH_3 Injection Rate	48
6-2	Final Downstream NO Concentration vs. Plasma Power at a Condition of Low NH_3 Injection Rate	49

6-3	Final Downstream NO Concentration vs. Plasma Power at a Cold Condition without Fuel Combustion	50
6-4	Plasma Effects on Temperature Distributions	51
6-5	Percentage Reduction of NO vs. NH ₃ Injection Rate at Conditions of Different Excess Air in Combustion	52
6-6	Radial Temperature Distribution	54
6-7	Radial Temperature Distribution	55
6-8	Plasma Effects on NO Reduction	57
7-1	Percentage NO Reduction vs. NH ₃ Injection Rate at Conditions with or without Plasma Power	59
7-2	Percentage NO Reduction vs. NH ₃ Injection Rate at Conditions with or without Plasma Power	60
7-3	Percentage NO Reduction vs. NH ₃ Injection Rate at Conditions with or without Plasma Power	61
7-4	Performance of Ammonia Injection in the Destruction of NO _x in Combustion Products: (a) NO _x penetration data of Muzio and Arand; (b) calculated NO penetration; (c) dimensionless times for NH ₃ and NH ₂ oxidation.	62
7-5	Measurements of Temperature Field of Plasma Jet	64
7-6	Combined Transport and Reaction Model	66
7-7	Different Regions in a Plasma Jet	68
7-8	Experimental facility at PETC	71
7-9	DC Plasma Torch Nozzle Geometry and the Arc Stratification	72
C-1	Particle Distributions within Groups	86
C-2	Particle Distributions within Groups	87
C-3	Particle Distributions within Groups	88
H-1	Schematic of System Efficiency Analysis	100

H-2	Gun Efficiency vs. Mass Ratio of Argon to Nitrogen	103
H-3	Normalized Energy Requirement vs. Mass Ratio of Argon to Nitrogen . .	104
H-4	Temperature of Argon vs. Mass Ratio Ar/NH ₃	106
H-5	Gun Efficiency vs. Mass Ratio of Ar/NH ₃	107
H-6	Normalized Energy Requirement vs. Mass Ratio Ar/NH ₃	108
I-1	Nozzle Schematic	118
I-2	Pressure Drop vs. Temperature Drop at the Nozzle Exit	120
I-3	Area Ratio vs. Temperature Drop at the Nozzle Exit	121

List of Symbols

C	particle concentration
C_D	drag coefficient
C_μ	turbulence model constant
d	nozzle diameter
d_p	particle diameter
D_i	diffusion coefficient
$f(r), f_1(r), f_2(r)$	probability density distributions
h	heat transfer coefficient
k	turbulent kinetic energy
L_e	eddy characteristic size = $C_\mu^{3/4} k^{3/2} / \epsilon$
$\dot{m}$	mass flux of gas
N	number of particles in a group
r	radial coordinate
R_g	particle group size
Re	Reynolds number = $\rho(u - u_p)d_p/\mu$
S	source term in governing equations for gas phase
S_v	volumetric source strength
t_e	eddy lifetime
t_R	particle transit time
t_i	interaction time between particle and eddy
T	temperature
u	gas velocity vector
x	axial coordinate
$\bar{X}^2, \bar{Y}^2$	mean square distances
y	vertical distance
ϵ	dissipation rate of turbulence kinetic energy
μ	viscosity

μ_t	turbulent viscosity = $C_\mu \rho k^2 / \epsilon$
μ_1, μ_2	mean values in Gaussian distributions
ρ	density
τ_p	particle relaxation time
σ_ϕ	turbulent Prandtl/Schmidt numbers
σ_1, σ_2	standard deviations in the Gaussian distributions
ϕ	general variable
$\% \Delta$	total percentage of NO_x reduction

Subscripts

p	particle property
0	initial condition
i	initial condition
f	final condition

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Chapter 1

Introduction

The emission of nitrogen oxides (NO_x) from both utilities and industrial coal-fired boiler applications is of growing concern. NO_x emission can have a deleterious catastrophic influence on the environment in depleting the ozone layer and in acid deposition. The role of NO_x in acid rain and ozone chemistry has become more prominent which has been evidenced by recent studies in Europe and the United States investigating the cause of vegetation damage and deforestation [1, 2, 3, 4, 5].

Even though more strict acid rain-control legislation has already been enacted by many states and at the federal level, coal combustion as a source of electricity is expected to grow in coming years for three reasons: 1) the black mineral is cheap, 2) it is plentiful, and 3) utilities are reluctant to build new power plants. Currently, coal-fired plants generate nearly 60 percent of the utilities' output of electricity in the United States. Clearly, the rapidly growing concern over pollutant emission, coupled with the increased demand for energy, makes the NO_x control problem critical, especially for utility supplies.

NO_x emission from fossil-fuel-fired steam generators are about 90 percent or more nitric oxide (NO) and the rest nitrogen dioxide (NO_2) [6]. The NO_x level from a given fuel is a combination of two major sources:

- Thermal NO_x produced by high temperature fixation of atmospheric nitrogen (N_2) and oxygen (O_2).

- Fuel NO_x generated from the chemically-bound atomic nitrogen in the fuel's hydrocarbon molecules.

Fundamental and experimental studies have indicated that NO_x emission are generally a function of 1) fuel nitrogen content, 2) combustion temperature, 3) fuel/air mixing rates, 4) local stoichiometry, and 5) combustion sequence (reburning).

Currently, there are two basic types of NO_x control technologies: combustion modification and post combustion flue gas treatment [7]. Combustion modification techniques usually inhibit the formation of NO_x in the furnace through changes in furnace design and operation. The NO_x formation is a complex process, primarily dependent on oxygen availability and temperature during combustion. In general, lower oxygen levels and lower peak flame temperatures lead to reduced NO_x formation from fuel-bound and atmospheric nitrogen. Exploiting these phenomena is the basis for combustion modification techniques. Favorable conditions can be created by designing high temperature fuel rich and lower temperature burnout zones, or forming a secondary fuel rich, short residence and high temperature region. Typical approaches are operational modification, overfire air, low- NO_x burners, and reburning, etc (see Appendix A) [7, 8]. The combustion modification techniques have achieved a substantial degree of NO_x control. For example, low- NO_x burners can reach up to 75% reduction when combined with overfire air or reburning. However, these techniques are not effective enough in most applications. In addition, they may not be applicable to all existing boilers.

Post combustion flue gas treatment techniques remove NO_x from flue gas downstream of the boiler. The most promising approaches currently used are ammonia injection with catalytic reduction called selective catalytic reduction (SCR) and ammonia injection without catalytic reduction called selective non-catalytic reduction (SNCR) or thermal de NO_x (see Appendix A) [7, 9, 10, 11]. They employ NH_3 and NH_4 , which are decomposed from ammonia in the flue gas, to convert NO_x to elemental N_2 and H_2O . Using SCR under optimum conditions to treat flue gas from low-sulfur coal, NO_x reduction of up to 90 percent have been demonstrated [12]. Although it is the most effective, SCR has a

number of disadvantages. First of all, the effective temperature window is very narrow because the reactions necessary to reduce NO_x are highly dependent on temperature. At lower temperatures, little or no NO_x is reduced due to the slow reaction of ammonia, and the ammonia is wasted. At higher temperatures, the NH_2 oxidation becomes faster than NO reduction, allowing additional NO to be formed from the ammonia. In either case, the ammonia is not used as effectively as desired. The slip ammonia (unreacted) may react with SO_3 in the flue gas to form ammonium sulfates which precipitate onto downstream equipment, causing pluggage and corrosion. This is a particular problem with high-sulfur coals. In addition, the catalyst replacement frequency and the catalyst disposal, (which may be considered hazardous waste) are also important issues relating to the SCR operation. Lastly, SCR may not be cost effective because it requires extensive path modification and/or involves large operational costs. Therefore, new NO_x control techniques are desired to be more effective than combustion modification, less expensive and less troublesome than SCR and SNCR, and have applicability to a broad range of boiler systems.

A novel technique, which applies plasma jet in combustors or flue gases to reduce NO_x , is proposed here. The radicals generated from plasma jets of NH_3 , CH_4 , H_2O , or their mixtures, or mixtures of their components will react with the NO_x and the NO_x precursors, reducing the NO_x emission. The concept of this method is the combination of the staged combustion and ammonia injection, using the strengths of each. It is potentially cost effective for two reasons: 1) significantly less NH_3 may be required to achieve the same NO_x reduction due to the direct radical injection in comparison to the ammonia injection, and 2) instead of NH_3 , a less expensive gas (H_2O or CH_4) might potentially be used.

In the proposed technique, the plasma can be injected into the flue gas (downstream injection) or into the combustor inside or near the flame (upstream injection). The research on both downstream and upstream plasma injections are conducted in the development of this new technique. The study of the plasma injection process involves

complicated chemical and fluid mechanics processes leading to two major areas of research. The first area is chemical kinetics, which is not the domain of this thesis. The second area is concerned with thermal fluid dynamics, which is the major interest in the present study.

In the upstream plasma injection, the plasma jet is injected into the combustor inside or near the flame. The efficiency of NO_x reduction is strongly influenced by the combustor flow field, which is a turbulent two-phase reacting flow in pulverized coal combustors. In this complicated two-phase flow, one major question is how the coal particles travel and interact with hot gas. The information on particle trajectories and distributions is very important for the design of the plasma injection configuration. Numerical methods can be used to simulate the flow field and provide the necessary information for fundamental understandings. Much progress has been achieved in this area recently due to the advance of computers. However, modeling the complex physical phenomena of turbulence, chemical reaction, and interphase transport can introduce excessive computational requirements so that a numerical simulation becomes impractical. The existing two-phase computer codes, e.g. KIVA [13], need large computers, even supercomputers, and long computational times in many applications. Therefore, maintaining computational efficiency is crucial in the pursuit of even more sophisticated analysis. The major effort for developing two phase flow models has been focused on the turbulent interaction between gas phase and dispersed phase. If this interaction is modeled efficiently and realistically, the other aspects of the modeling, such as turbulence and chemical reactions can easily be incorporated using the standard approaches.

The downstream plasma injection has been experimentally studied in a large scale test facility at PETC[14]. The preliminary results were very promising, but little is known about the fundamental science of the process.

The present research, therefore, was designed to address the key issues of the plasma injection process for NO_x reduction as a first step of the development of this new technique, using both numerical and experimental methods. The following are the objectives

of this research.

Objective

1. The first part of the numerical analysis focuses on the development of an efficient and realistic model for the turbulent gas-particle flows with the consideration of turbulent particle dispersions. This model is expected to pave the ground for further complete modeling of the whole process including the chemical kinetics.
2. The attention of the second part of the numerical analysis has been given to the mixing effects of downstream plasma injection. The results of the study have been used for explaining the experimental results obtained at PETC [14].
3. The goal of the experimental study is to explore the feasibility of NO_x reduction by ammonia plasma injection in a small scale combustor, and confirm the experimental results at PETC with a different combustion facility and plasma generator.
4. Finally, the analysis of the experimental results and a postulated model are desired to explain the mechanism of plasma injection for NO_x reduction.

The numerical models in the Objective 1 and 2 are described in Chapters 2 and 3 respectively. The experimental study for the Objective 3 is detailed in Chapters 4 through 6. The analysis of the experimental results and the postulated model for the Objective 3 are given in Chapter 7. The conclusions and the future work are then given at the end of the thesis.

Chapter 2

Numerical Modeling of In-Flame Injection

2.1 Theoretical Background

In the upstream plasma injection, the plasma jet is injected into the combustor inside or near the flame. The efficiency of NO_x reduction is strongly influenced by the combustor flow field, which is a turbulent two-phase flow in pulverized coal combustors. In this two-phase flow, where pulverized coal is dispersed phase, one major question is how the coal particles travel and interact with hot gas. Numerical methods can be used to analyze the transport problem. The actual flow field involves heat and mass transfer, chemical kinetics and gas-particle interactions. The present research focuses attention on the modeling of gas-particle interactions, which is one of the most difficult problems in the modeling of two-phase flows. The objective is to develop an efficient and realistic model, which can give important information, e.g. particle trajectories and distributions, for the design of the plasma injection configuration. It will also pave the ground for whole flow simulations. The developed model can be incorporated easily in the models where the other aspects of the flow field, such as chemical kinetics, are also considered.

Computer modeling of turbulent two phase flows is becoming an increasingly viable

part of the design process, with the objective to reduce the time and cost of process development. Primarily, gas-particle flow models have been classified as two major categories: Locally Homogeneous Flow (LHF) models and Separated Flow (SF) models [15, 18, 19]. The LHF models assume that rates of transport between the phases are fast in comparison to the rate of development of the flow field as a whole, and the particles and the gas are in dynamic equilibrium state, i.e. at each point there are no slip and no relative velocities between the two phases [16, 17]. With these assumptions, the presence of liquid at high mixture fractions is the only feature that distinguishes a two-phase flow from a single-phase flow. Therefore, the gas-particle flow corresponds to a variable density single-phase flow, and the governing equations for single phase with state relationship defined for two-phase flow boundary conditions can give the solutions for the whole flow field. It provides a simple modeling approach and requires minimum information concerning injected characteristics, since initial particle size and velocity distributions play no role in computations [15, 18, 19]. However, this approach is only effective when the particle sizes are very small, the densities of the phases are almost the same, and the rate of development of the process itself is slow. These assumptions are not justified for flows in pulverized coal combustors.

The SF models consider finite rate of interphase exchange of mass, momentum and energy, which have been more desirable because of their more comprehensive nature. There are generally three types of SF models: the Continuum Formulation Model (CFM), the Continuous Droplet Model (CDM), and the Discrete Droplet Model (DDM) [15, 18].

The Continuum Formulation Model (CFM) is a very simple method, where the particle phase is conceptually smeared and distributed into the gas phase and the motion of both phases is treated as though they were interpenetrating continua [15]. This formulation results in similar governing equations in the Eulerian coordinates for both phases. The particle phase is represented using averaged quantities (average particle density and velocity, etc.). Conceptually, this formulation can be easily solved since standard numerical techniques such as derived for the gaseous phase can be used for the dispersed phase

conservation equations. In practice, however, there are many difficulties in describing the droplet phenomena, e.g. the turbulent dispersion of droplets and the interaction terms between the gas phase and liquid phase because the interfacial phenomena in sprays are not well known as they were for single droplets. When the range of particle sizes must be considered, the two fluid modeling becomes unwieldy and costly in terms of computer storage and time required. In particular, it requires small computational grids for all phases near the injector exit in order to reduce numerical diffusion errors, since the Euler coordinates are used for all the phases. Thus, this approach is primarily used to model simple situations such as monodisperse, non-vaporizing sprays, and other situations where representing the liquid phase with averaged values results in little error.

The Continuous Droplet Model (CDM) was proposed by Williams [20]. In this method, a multidimensional statistical distribution function, $f_p(r, x, v, t)$, gives a field description of droplet properties. The distribution function is treated as a continuous property of the flow, and an Eulerian transport equation for this function derived from conservation principles for the droplet phase is solved with the gas phase equations containing appropriate source term for the droplet effects [21]. Because of the complexities inherent with the formulation, the CDM has limited applications so far. For three spatial dimensions, the distribution function is a function of at least eight unknowns. When variations in drop size, concentration and temperature must be considered, the dimensions will be increased further, leading to intolerable computer storage requirements. It also requires extensive grid refinement to reduce the numerical diffusion errors in the regions where there are strong spatial gradients of properties. Therefore, the spray equation formulation may be applied when only very simple phenomena are considered, e.g., the motion of monodisperse nonevaporating droplets in two spatial dimensions.

The Discrete Droplet Model (DDM) is the most logical and common approach [15]. In this method, the entire particle flow is divided into a finite number representing clusters of discrete particles. Each cluster contains a large number of particles which have the same properties. The motion and transport through the flow field of clusters

are found using a Lagrangian formulation, a distinct advantage since numerical diffusion is minimized. Appropriate source terms are also introduced into the Eulerian gas-phase conservation equations [21, 22]. The DDM is very easy to implement and has been well established through comparison with experiments.

In the efforts for developing gas-particle flow models using the DDM approach, the major focus is on the turbulent interaction between gas phase and dispersed phase. Attempts to comprehensive modeling of turbulent particle dispersion have generally been made in two approaches [23, 24]. One is the Continuum approach, which considers the particle dispersion as a diffusion process with an appropriate particle diffusion coefficient [25, 26]. It has fallen into disfavor due to the difficulty in obtaining a gas-particle exchange coefficient and the inconvenience of incorporating the model into the Lagrangian formulation of particle cluster tracing. The other is the Lagrangian approach where the particle dispersion is modeled directly by considering the interaction between turbulent eddies and particles in trajectory calculations, which has found wider acceptance.

Among the Lagrangian models, a rather advanced one is the Stochastic Separated Flow (SSF) model, which was originally developed by Gosman and Ioannides [27] and later modified by Shuen et al. [16, 28, 29, 13]. The SSF model entails random sampling for instantaneous gas flow properties based on a two-equation turbulence model and using the resulting fluctuations in a Lagrangian computation for particle cluster motion. In a sense, this approach is an exact simulation of dispersed-phase properties. The computational results showed good agreement with measurements [23]. In the SSF approach, however, it is assumed that all the particles within a cluster are always concentrated at one point during the flight, behaving like a single particle at all times. A particle cluster is essentially a computational particle and the turbulent dispersion of particles which belong to the same cluster is not considered in the SSF method. Therefore, in order to obtain a statistically meaningful distribution, a large number of characteristic particle trajectories, and consequently, very long computational times are needed, which can increase computational requirements to unreasonable levels, even for supercomputers.

Clearly, more efficient, yet realistic, models are really desirable.

This research has developed a new "Group" approach for the modeling of turbulent gas-particle flows, which is essentially a hybrid scheme of both continuum approach and Lagrangian approach [30, 31, 32, 33, 34]. The model uses particle groups to represent a gas-particle flow and takes into account the turbulent particle dispersion within each group in the flow field. In the SSF model, however, all the particles in a cluster are assumed to stay at the center of the cluster and a Dirac delta function is essentially used for the probability density function of particle position within each cluster. The present "Group" modeling considers that each group has a dimension which grows during the flight. This growth is due to the turbulent dispersion of particles as the group travels in the Lagrangian coordinates. When the group grows to a critical size, it is split into smaller groups. The particle dispersion within a group is described by a probability density function which is a Gaussian distribution. Due to the growth of the group, only a small number of groups must be traced to provide statistically reasonable results.

The "Group" approach closely simulates a real flow, because in a real flow the particles within a group are dispersed by turbulence instead of staying at one point. This is consistent with the conceptual situation that if particles in a small region of a spray are dyed in red color, this dyed group of particles will disperse in time within the spray. The present "Group" approach essentially traces this dyed group of particles in the spray.

The concept of this "Group" approach can be incorporated into any computational program which presently employs the Lagrangian approach to trace the dispersed phase. As will be discussed in later sections, the major assumption used in the "Group" approach is that the turbulence should be isotropic in the field. This assumption is reasonable for most axisymmetric turbulent sprays which contain strong shear layers. In the shear layers of a spray, although the turbulent flow is not isotropic in the tangential direction, they are isotropic in the axial and radial directions. The present group model can be used directly for the calculations of two-dimensional axisymmetric sprays which are independent upon the tangential coordinate. This new modeling concept is expected to have more

advantages when the geometrical scale is large, where its higher computational efficiency becomes indispensable.

In the following sections, the basic formulation of this method, the effectiveness of the model, and the efficiency of the computations using this approach will be presented.

2.2 Basic Eulerian/Lagrangian Formulation

In the present study, a standard Eulerian approach is applied to the gas phase transport. The Lagrangian formulation is used to trace the motion of the center of each group. The modeling of the turbulent particle dispersion in a group is a new approach.

2.2.1 Gas Phase

The gas phase is represented by Eulerian conservation equations and the k- ϵ two equation turbulence model. The governing equations for a steady, axisymmetric turbulent flow are of the following form [27]:

$$\frac{\partial(\rho \bar{u} \phi)}{\partial x} + \frac{1}{r} \frac{\partial(r \rho \bar{v} \phi)}{\partial r} = \frac{\partial}{\partial x} \left(\frac{\mu_t}{\sigma_\phi} \frac{\partial \phi}{\partial x} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\mu_t}{\sigma_\phi} \frac{\partial \phi}{\partial r} \right) + S_\phi + S_{p\phi} \quad (2.1)$$

where the designation $\phi=1$ yields the continuity equation. The symbol ϕ also represents the mean axial and radial velocity components $\bar{u}$ and $\bar{v}$, turbulent kinetic energy k , dissipation rate of turbulent kinetic energy ϵ , and total energy E . The turbulent Prandtl number is represented by σ_ϕ and S_ϕ is a general source term, while $S_{p\phi}$ represents the particular sources due to the presence of particles. The expressions for S_ϕ and $S_{p\phi}$ pertaining to each variable are standard forms and given in [27]. The constants used in the k- ϵ two equation turbulence model are $C_\mu=0.09$, $C_1=1.44$, and $C_2=1.92$.

2.2.2 Dispersed Phase

The dispersed phase is represented by characteristic particle groups, which are described with a Lagrangian view point. The center of the group is traced as a single computational particle with its particle motion equation, which is given as follows after neglecting the virtual mass, Bassett forces, and Magnus forces.

$$\frac{d\mathbf{u}_p}{dt} = \frac{(\mathbf{u} - \mathbf{u}_p)}{\tau_r} \quad (2.2)$$

where $\mathbf{u}$ and $\mathbf{u}_p$ are the local gas and particle velocity vectors, and τ_r is the particle relaxation time.

The particle relaxation time is calculated by [28]:

$$\tau_r = \frac{4\rho_p d_p}{3\rho C_D \|\mathbf{u} - \mathbf{u}_p\|} \quad (2.3)$$

where C_D is the drag coefficient which is obtained from the following expressions:

$$C_D = 0.44 \quad \text{for } Re > 1000 \quad (2.4)$$

$$C_D = 24(1 + Re^{2/3}/6)/Re \quad \text{for } Re < 1000 \quad (2.5)$$

The position of a computational particle which represents a group center can be found by integrating:

$$\frac{d\mathbf{x}_p}{dt} = \mathbf{u}_p \quad (2.6)$$

The particle temperature is determined by an energy balance. For nonevaporating particles, the energy equation is given by:

$$\frac{\pi}{6} \rho_p d_p^3 C_p \left(\frac{dT_p}{dt} \right) = \pi d_p^2 h (T - T_p) \quad (2.7)$$

where h is the heat transfer coefficient, T and T_p are gas and particle temperatures, and C_p is the specific heat.

2.3 Turbulent Dispersions

2.3.1 Center of a Group

The turbulent effect on the trajectory of a computational particle which represents the center of a group is considered in a fashion similar to the SSF method. The motion of the center of a particle group is assumed to behave like a single particle interacting with a succession of turbulent eddies [23]. Properties within a particular eddy are uniform and determined from the gas phase analysis. The instantaneous velocity field that this computational particle experiences consists of the mean and fluctuating gas velocities. The magnitude of the fluctuating velocity component is proportional to $(2k/3)^{1/2}$ (where k is turbulent kinetic energy) by assuming that the turbulence is isotropic. The instantaneous gas flow velocities are randomly sampled when a computational particle interacts with eddies. The interaction time between the particle and the eddy is taken as the minimum of the eddy lifetime and the transit time required for the particle to cross the eddy:

$$t_i = \min(t_e, t_R) \quad (2.8)$$

where t_e is the eddy lifetime, and t_R is the particle transit time.

The eddy lifetime is calculated by [28]:

$$t_e = L_e / (2k/3)^{1/2} \quad (2.9)$$

where k is the turbulent kinetic, and L_e is the eddy characteristic size.

The formulation for the eddy characteristic size is:

$$L_e = C_\mu^{3/4} \frac{k^{3/2}}{\epsilon} \quad (2.10)$$

where, ϵ is dissipation rate of turbulence kinetic energy, and C_μ is the turbulence model constant.

The particle transit time is given by [28]:

$$t_R = -\tau_r \ln(1.0 - \frac{L_\epsilon}{\tau_r \|u - u_p\|}) \quad (2.11)$$

2.3.2 Particles in a Group

In an actual turbulent two phase flow, the particles belonging to a group are dispersed by turbulence rather than staying concentrated at one point during the flight. Conceptually, a group of particles in a two phase flow is viewed as if the particles in this group are dyed in red color. These red particles disperse in the gas-particle flow; however, we are only tracing these red drops with the assumption that there are no collisions and coalescence. According to the present model, all the particles in a group move together in an absolute coordinate and the particle dispersion is a relative motion to the center of the group. Therefore, the particle group grows from its center, and the dispersion of particles is observed from the center of the group.

Assumptions used in the group approach are given as follows:

1. Drop-to-drop collisions are neglected.
2. The turbulent flow is “locally” isotropic and homogeneous.
3. The dispersion of particles in a group is assumed to originate from a point source located at its center when this group leaves the nozzle.

Although the center of a group follows the trajectory of a single particle, the relative particle position within a group in respect to the group center at any time is random because of the turbulent gas velocity field. Therefore, the movement of particles relative to the center of the group is almost like a random walk. Theoretical considerations and experimental data suggest that the probability distributions resulting from a particle

transport by turbulent diffusion is similar to Brownian diffusion [35]. This kind of particle dispersion can be closely represented by a normal Gaussian distribution. Figure 2-1 shows a qualitative picture for the demonstration of the particle dispersion within a group.

The typical probability density function for this distribution can be given for a 2-D field as:

$$f(x, y, t) = \frac{N}{\sqrt{2\pi\bar{X}^2}\sqrt{2\pi\bar{Y}^2}} \exp\left(-\frac{x^2}{2\bar{X}^2} - \frac{y^2}{2\bar{Y}^2}\right) \quad (2.12)$$

where N is the total particle number in this group, and $\bar{X}^2$ and $\bar{Y}^2$ are the overall mean square distances in x and y directions. The $\bar{X}^2$ and $\bar{Y}^2$ are functions of time and affected by the particle size and the gas flow field. All the measurements of x and y are made from the center of the group. The total particle group size is estimated to be $6\sqrt{\bar{X}^2}$ and $6\sqrt{\bar{Y}^2}$ based on the probability theory.

It is interesting to note that Equation (2.12) is also a solution to a diffusion equation. One can prove that this distribution preserves its Gaussian form when particles encounter different eddies in the flight (see Appendix B). The overall mean square distances of Equation (2.12) can be calculated from:

$$\bar{X}^2 = \delta_{x1}^2 + \delta_{x2}^2 + \dots + \delta_{xi}^2 + \dots \quad (2.13)$$

$$\bar{Y}^2 = \delta_{y1}^2 + \delta_{y2}^2 + \dots + \delta_{yi}^2 + \dots \quad (2.14)$$

where δ_{xi}^2 and δ_{yi}^2 are the mean square displacement in each time interval δt_i which can be calculated from the turbulent diffusion theory [36, 37]:

$$\delta_{xi}^2 = u_p'^2 \delta t_i^2; \quad \delta_{yi}^2 = v_p'^2 \delta t_i^2 \quad (2.15)$$

In the Equation (2.15), u_p' and v_p' are particle fluctuating velocities. They can be calculated by the following equation, which is obtained by subtracting the mean flow Equation (2.2) with the instantaneous equation of motion for a particle:

Figure 2-1: The Schematic of the Computational Field Using the Group Approach

$$\frac{du'_p}{dt} = \frac{1}{\tau_r}(u' - u'_p) \quad (2.16)$$

where u' and u'_p are the gas and particle fluctuating velocity vectors, and τ_r is the particle relaxation time.

2.3.3 Splitting of a Group

In some cases, when a particle group grows fast, or when the traveling distance of a group is very long, the group size may become very "large" so that the splitting of the group becomes necessary in order to maintain the validity of the assumption of locally homogenous turbulent flow within the group. A typical criterion for splitting is given as follows:

$$\frac{k_e - k_c}{k_c} \geq Er \quad ; \text{ and } R_g \geq R_m \quad (2.17)$$

where, k_e kinetic energy at the edge of the group; k_c kinetic energy at the center of the group; Er is determined according to the turbulent flow field, and the value of 10% is selected in the calculations of this research; R_g is the size of the group, and R_m is the minimum size of the group for splitting, which is related to the grid size.

The following principles are imposed during splitting:

1. The total number of particles is conserved;
2. The distributions of particles within the new groups are still Gaussian, the centers of new groups are a distance apart, and an equal split is maintained.
3. After splitting, the summation of the new distributions should be as close as possible to the original distribution, but the size of the new group should be much smaller than the original one.

For simplicity in illustration, if we consider the 1-D case, the original Gaussian distribution of particles within a group is:

$$f(r) = \frac{N}{\sqrt{2\pi}\sigma} \exp\left(-\frac{r^2}{2\sigma^2}\right) \quad (2.18)$$

After the equal split, the distributions of the two new groups become:

$$f_1(r) = \frac{N_1}{\sqrt{2\pi}\sigma_1} \exp\left(-\frac{(r - \mu_1)^2}{2\sigma_1^2}\right) \quad (2.19)$$

$$f_2(r) = \frac{N_2}{\sqrt{2\pi}\sigma_2} \exp\left(-\frac{(r - \mu_2)^2}{2\sigma_2^2}\right) \quad (2.20)$$

where, N , N_1 , and N_2 are particle numbers; σ , σ_1 , and σ_2 are standard deviations; and μ_1 , and μ_2 are mean values of Gaussian distributions.

According to the principles of equal splitting (Principle 2) and total number conservation (Principle 1) imposed during splitting, there are following relationships.

$$N_1 = N_2 = N/2 \quad (2.21)$$

$$\mu_1 = -\mu_2 \quad (2.22)$$

$$\sigma_1 = \sigma_2 \quad (2.23)$$

In order to keep effective splitting, the summation of the new distributions should be as close as possible to the original distribution, but the size of the new group should be much smaller than the original one (Principle 3), the following conditions can be presented:

- All the particles within a domain of $[-c\sigma, c\sigma]$ should be conserved after splitting:

$$\int_{-c\sigma}^{c\sigma} f(r)dr = \int_{-c\sigma}^{c\sigma} f_1(r)dr + \int_{-c\sigma}^{c\sigma} f_2(r)dr \quad (2.24)$$

where, $f(r)$, $f_1(r)$ and $f_2(r)$ are Gaussian distributions.

Figure 2-2: The Splitting of a Group

- The overlapped region of the new groups are restricted in this domain:

$$\mu_1 = 3\sigma_1 - c\sigma \quad (2.25)$$

The c value is calculated to give optimal results of splitting to preserve the original distribution. From calculations for a group splitting in a homogeneous flow field, the value of c is 1.25. Then, $\mu_1 = 0.6869 \sigma$; and $\sigma_1 = 0.64 \sigma$ (see Figure 2-2). Sample demonstrations for the splitting of a group are given in Appendix C.

It should be pointed out that the group splitting involves empiricism in deciding the splitting criteria for each group. The criteria used for group splitting need be further examined. For some conditions, when the group grows slowly, or when the traveling distance is short, the splitting may not be necessary.

2.4 Numerical Analysis

To illustrate this "Group" approach, the gas phase elliptic partial differential equations together with the boundary conditions are solved using an existing finite difference computer program, TEACH-code [38, 39, 40], which is widely applied for the computation of turbulent flows. The particle-gas coupling is incorporated in the numerical procedure. In a highly dilute two-phase flow, using a one-way coupling, which neglects the particle effects on the gas phase, will eventually give the same results as that using a two-way coupling, which uses special source terms to consider the presence of particles. The ordinary differential equations governing the behavior of each computational particle are solved by a second order accurate implicit method for each computational particle. For the particle dispersion within a group, the distribution function is calculated in every time step. The integration of Equation (2.12) gives the particle numbers in the computational cells covered by a group:

$$N_{cell} = N \int_{x_1}^{x_2} \frac{1}{\sqrt{2\pi X^2}} \exp\left(-\frac{x^2}{2X^2}\right) dx \int_{y_1}^{y_2} \frac{1}{\sqrt{2\pi Y^2}} \exp\left(-\frac{y^2}{2Y^2}\right) dy \quad (2.26)$$

$$= \frac{N}{4} \left[\operatorname{erf}\left(\frac{x_2}{\sqrt{2X^2}}\right) - \operatorname{erf}\left(\frac{x_1}{\sqrt{2X^2}}\right) \right] \left[\operatorname{erf}\left(\frac{y_2}{\sqrt{2Y^2}}\right) - \operatorname{erf}\left(\frac{y_1}{\sqrt{2Y^2}}\right) \right] \quad (2.27)$$

where x_1 , x_2 , y_1 , and y_2 are the boundary position of the computational cell.

2.5 Results and Discussion

2.5.1 General Nature:

Hinze [36] developed an analytical expression for the turbulent dispersion of “marked” fluid particles. The particles were introduced into a uniform turbulent flow field at a constant rate from a point source. The concentration distribution $C(x,r)$ at position (x,r) for homogeneous and isotropic turbulence with long diffusion times is as follows [36]:

$$C(x,r) = \frac{S_v}{4\pi\mu_t|x|} \exp\left(-\frac{Ur^2}{4\mu_t|x|}\right) \quad (2.28)$$

where U is the flow velocity, μ_t is the turbulent diffusivity, and S_v is the volumetric source strength.

The Equation (2.28) is essentially of a Gaussian form. As shown in Figure 2-3, the distribution follows Gaussian form after normalization, where $\bar{C}$ equals $C/(S_v/4\pi\mu_t|x|)$ and $\bar{r}$ equals $r/(\sqrt{2\mu_t|x|/U})$. This is consistent with the present assumption of Gaussian dispersion of particles within each group.

In this “Group” model, each group follows a trajectory as shown in Figure 2-4, which is affected by the turbulent eddies along its path. Figure 2-5 displays the particle distributions within each group at two axial locations ($x=10\text{cm}$ and $x=16\text{cm}$), in order to demonstrate the particle dispersions within a group as well as the growth of the group. Whereas, the SSF model does not consider the dispersion of particles in each cluster, the new model is physically more realistic since the particle dispersion is considered.

2.5.2 Data Comparisons on Particle Laden Jets:

In order to validate the new approach, the “Group” modeling was applied to the analysis of a particle-laden jet containing fly ash particles. The preliminary results of this study were compared with the results of the SSF method and the experimental data.

Figure 2-3: Normalized Radial Particle Concentration Distributions

Figure 2-4: The Trajectories of Groups

Figure 2-5: Particle Distributions within Groups

The experimental results were reported by Yuu et al. in reference [41]. Their experimental set-up contained a jet nozzle which could provide uniform exit properties. This flow uniformity allowed a plug flow assumption to be imposed as an initial condition for the numerical calculations. The following initial conditions were specified [23]:

$$\bar{u}_0 = \frac{4\dot{m}_0}{\rho_0 \pi d^2} \quad (2.29)$$

$$k_0 = (0.02\bar{u}_0)^2; \quad (2.30)$$

$$\epsilon_0 = 2.84 \times 10^{-5} \bar{u}_0^3 / d \quad (2.31)$$

The nozzle geometry and the properties of the two-phase particulate flow were taken from reference [41] and included in the computations to enable comparisons with the experimental results. The nozzle diameter is 8mm. The particles are nearly monodisperse having a mass mean diameter of 20 μm . The flow is dilute with particle mass loadings of 0.1-0.4%. These loadings are sufficiently small, so that the particles have a negligible effect on the mean and turbulent gas phase properties. The grid of the flow field is axial system with 32×29 meshes.

The distributions of particle concentrations along the center line of the jet are shown in Figure 2-6 for the present method, the SSF approach, and the experimental results. The SSF results are presented for two different particle cluster numbers (20 and 500). For the smaller particle cluster number, the particle concentration distribution is not smooth due to statistically insufficient data. In order to obtain a reasonable agreement with the experimental results, 500 particle clusters were required as shown in the figure. Unlike the results of the SSF method, the results of the present approach are in sound agreement with the experimental results with only 15 groups. At x/d more than 15, slightly larger deviation is observed.

Figure 2-7 compares the radial distributions of particle concentration for the present approach and the SSF method. Both methods have very similar results along radial

Figure 2-6: Axial Particle Concentration Distributions at the Center Line

Figure 2-7: Radial Particle Concentration Distributions at $x/d=20$

Figure 2-8: Axial Temperature Distributions at the Center Line

direction also. Since the corresponding experimental data of radial distribution and radial initial conditions are not clearly reported in reference [41], the comparison was made only with the results of the SSF method.

2.5.3 Thermal Effects

The effect of jet temperature on the particle temperature distribution was investigated and presented in Figure 2-8. The geometry and the initial kinematic conditions were kept similar to that in reference [41]. However, the cold particles with an initial temperature of 300K were injected into hot air stream with initial temperature 800K, and were heated up by the surrounding gas due to mixing. The temperatures of gas and particles are solved by energy conservation equations. The calculations were performed for fly ash and alumina particles of the same size ($20 \mu\text{m}$). The density, ρ , and specific heat, C_p , for

fly ash are 2.0 gm/cm^3 and 1.214 j/(kgK) , respectively. These properties are 3.9 gm/cm^3 and 1.5 j/(kgK) for alumina particles.

Figure 2-8 shows the axial variation of gas and particle temperatures. The gas temperature decreases rapidly up to about 8 cm distance from the nozzle exit. Its decrease is more gradual further downstream. The average particle temperatures increase steeply for both particle materials immediately downstream of the nozzle. These temperatures show a peak for both materials, and gradually decrease. The calculated results of the "Group" model which used 15 groups for both materials are in very good agreement with the results using the SSF method with 500 particle clusters.

A comparison of the average axial temperature distribution for the fly ash and alumina particles has shown that the product of density and specific heat have a strong influence on the magnitude of particle temperature. Alumina particles heat-up and cool down more slowly than fly ash due to their higher thermal inertia. This results in a lower peak and higher downstream temperatures for alumina particles. The calculated radial average particle temperature distributions with the "Group" approach are also in reasonable agreement with the results of the SSF method. However, there are differences at large radii downstream of the injector. Since the temperature in a group was assumed to be uniform in this model, the increased group size introduces some error in the calculated temperature. This problem is expected to be solved by group splitting.

2.5.4 Computational Effort

In the calculations of particle laden jets, a 32×29 grid was used. Negligible difference was observed when the number of grids was increased to 40×40 . All calculations were performed on a Sun 386i/250 computer (5 MIPS, 25 MHz). In the calculations of particle laden jets, for the dispersed phase calculation, the computational time using SSF approach with 500 groups was 509 s, while the present study only took 53 seconds for a similar agreement with the experimental data. The reduction in computation time for the particle laden jet was about a factor of 10. This major reduction in the computation

time in the present approach is because of the significant decrease in the number of particle groups required for realistic predictions.

The group approach has also been applied to impacting sprays [33, 34], where a 36×35 grid was used. For the liquid phase calculation of $150\mu\text{m}$ diameter particles, the SSF approach took about 900 seconds with 980 groups, while the “Group” approach only took about 46 seconds for similar results. The reduction in computation time for the impacting spray was about a factor of 20. As expected, the reduction of computation time is more significant when the geometrical scale is large.

2.6 Summary

In this study, a new, efficient “Group” model was presented by incorporating the turbulent dispersion of the particles within the groups while tracing the trajectory of its center stochastically. This approach can be applied to general computational programs which employ the Lagrangian method to trace the dispersed phase. All the calculations using this approach have shown that:

- The group approach is “efficient” in the computational time because much fewer particle group numbers are required to obtain reasonable statistical results than that with the classical SSF approach so that a significant computational time reduction can be achieved.
- The group approach is “realistic”, since it considers the turbulent particle dispersion within each group.
- The group approach is very easy to implement, has wide applications, and can be incorporated into any computational program which employs the Lagrangian approach to trace the dispersed phase, and also includes heat transfer and chemical kinetics.

Chapter 3

Numerical Modeling of Downstream Injection

The effect of downstream plasma injection has been investigated experimentally in a large scale set-up at the Pittsburgh Energy Technology Center (PETC) by John Boyle [14]. Figure 3-1A shows the test section of the experimental set-up. These experiments has already given promising results showing about 90% NO_x reduction. During the tests at PETC, a rod was placed upstream of the plasma injection point perpendicular to the flow, in order to provide efficient mixing. However, it is important to have a theoretical review to recognize how the rod functions and physically explain this mixing process. Therefore, a numerical analysis was designed to support this mixing argument in the experiments at PETC. The numerical analysis is not able to simulate the exact flow field due to its complexity and some unknowns. A simplified model which closely represents the real test conditions was studied instead. The geometry of computational flow field is shown in Figure 3-1B. A step change in the computation was used to simulate the divergence effect in the test set-up. The effect of the rod at the upstream of the plasma injection was simulated by a low velocity and high temperature jet. Air was used as the working fluid. Although the computation used a simplified model, the general trend of the parametric effects and the qualitative features of physical phenomena are still

A. Schematic of Experiments at PETC

B. Geometry of Computational Flow Field

Figure 3-1: Numerical Simulation of Downstream Injection

Figure 3-2: Axial Velocity Distributions at the Center Line

simulated. The computational results can help the analysis of real tests.

The computation used an existing TEACH-code [38, 39], which is widely applied for the computation of turbulent flows. However, the original code assumed only constant fluid properties. In the present calculations, the properties (such as density, viscosity, and specific heat) strongly depend on temperature because of high temperature range. Therefore, the code was modified to take into account the variable fluid properties.

Figures 3-2 and 3-3 display the axial and radial velocity distributions, respectively. They show that there is a recirculation zone close to the exit of central jet. This recirculation is affected by velocity difference and temperature difference between outside and inside jets. A large relative velocity causes an obviously strong recirculation flow near the injector. When the temperature of the central jet increases, the axial velocity near the injector decreases due to the high density difference and high viscosity at high temperature.

Figure 3-3: Radial Velocity Distributions at Different Axial Locations

Figure 3-4: Axial Temperature Distributions at the Center Line

Figure 3-5: Radial Temperature Distributions at Different Axial Locations

Figures 3-4 and 3-5 demonstrate the axial and radial temperature distributions respectively. The temperature decreases rapidly in the recirculation zone near the injector due to the mixing effect. The radial temperature profiles gradual decay along the axial distance.

Regarding to the test conditions at PETC, the recirculation zone is generated by the rod located upstream of the injection point. This rod acts like a flame holder used in high speed combustion applications to generate a recirculation zone. The recirculation zone allows for very rapid and effective mixing of radicals. Close examination of the flame holders and the flow mixing will be critical to the general application of this process to power plants.

Chapter 4

Experimental Background

The chemical kinetics of NH_3 -derived radicals with combustion products were studied using CHEML, a general chemical kinetics routine, by Boyle [42]. The modeling results showed that the radicals of NH_3 are very effective on the NO_x reduction. At favorable conditions, one NH_3 molecular may destroy more than one NO_x molecular due to chain reactions. The NH_3 -derived radicals, NH_2 and NH , can react very quickly with NO according to the following reactions.

Both reactions (4.1) and (4.2) can be very effective and are almost independent of the temperature when the reaction temperature is below 3000K.

The radicals NH_2 and NH are generated by:

Although the basic radical-NO_x reaction process is generally identified by CHEML analysis based on an ideal thermodynamic and zero dimensional situation, an experimental investigation is necessary for the validation of the mechanism and the further development of this new technique, since the real process is complicated and affected by both fluid and chemical dynamics. The present experimentation is exploratory in nature and is mainly directed to investigate the feasibility of NO_x reduction by plasma injection and some parametric effects on the process.

Chapter 5

Experimental Apparatus

The experimental apparatus was designed and constructed in the heterogeneous combustion laboratory at CMU. Figure 5-1 shows an overview photograph of entire experimental setup, while Figure 5-2 shows the schematic of the overall set-up. It consists of three parts: combustor, plasma gun system, and measurement instruments.

The combustor is a laboratory scale device for testing the NO_x reduction system. The diameters of the combustor and the fuel injector are 15cm and 1cm respectively. The length of the combustion chamber is 150cm. A gas (methane) jet diffusion flame is established from the fuel injector at the center of the combustor. Preheated secondary air is fed into the chamber to complete the combustion. Several layers of stainless steel ball bearings, a honeycomb, and screens provide thermal stability, flow straightening, and turbulence reduction. A certain amount of NO are doped into the gas fuel jet to raise the NO concentration in the combustor for study. Viewing ports and sampling/measurement ports are available. A water spray chamber cools the gases before they exit from the system. A butterfly valve is used to adjust the suction of exhaust gases. The plasma can be injected into the early, middle and tail parts of the diffusion flame, or further downstream of the flame.

In the laboratory study, a low power plasma gun is needed to generate radicals. It is also required to be capable of operating with different types of plasma. An inductively

Figure 5-1: Overview Photograph of Entire Experimental Setup

Figure 5-2: Schematic of Overall Experimental Set-up

coupled plasma (ICP) system was found to satisfy these requirements. However, the existing ICP system was designed for mass spectroscopy analysis, which only uses argon gas and introduces some sample injection into the plasma. This system was successfully converted for the present applications. The torch box was modified and the orientation of the injection was converted from vertical to horizontal. Plasma jets of various gases or their mixtures can be generated easily. The plasma torch power ranges from 0.2 to 1.6 kW.

The schematic of plasma generator system is shown in Figure 5-3, while Figure 5-4 displays a photograph of the plasma flame. The RF generator generates RF power. The controller is used for the automatic control of the system. The matching box is responsible for the matching between the RF power delivered and the flow resistance. The plasma gun configuration is shown in detail in Figure 5-3. The assembly of tubes, called "torch", is set up in a water-cooled coil connected to the RF generator. Flowing gases are introduced into the torch, the RF field is switched on and the gas in the coil region is made electrically conductive by Tesla sparks. Then a plasma is formed, provided that the magnetic field strength is high enough and the gas streams follow a particular, rotationally symmetrical pattern. This inductively coupled plasma (ICP) is maintained by inductive heating of the flowing gas in a way similar to the inductive heating of a metallic cylinder placed in an induction coil; that is, the RF currents flowing in the coil generate axial oscillating magnetic fields, which in turn generate high frequency, annular electric currents, heating and dissociating the plasma gas. The gas flows are introduced tangentially in the tubes. The argon flow from the intermediate tube is used to produce a low-pressure area at the center of the torch and cause recirculation of the plasma giving a continuous supply of ions in the coil region. The outer gas flow is used to cool the inside walls of the outermost quartz tube and center the plasma radially in the tube. The plasma itself is anchored near the exit end of the concentric tube arrangement. The flame shape is similar to that of a Bunsen flame [43, 44].

Measurements include gas flow rates, temperatures and concentrations of NO and

Figure 5-3: Schematic of Plasma Generator System

Figure 5-4: Photograph of the Plasma Flame

NO_x . The flowrates are measured by rotameters. Chromel-alumel (Type K) thermocouples are used to measure temperatures, and placed at different axial locations of the combustor, giving both axial and radial temperature distributions. The instrument for NO and NO_x measurement is a Chemiluminescent NO/ NO_x Analyzer, Model 10AR made by Thermal Electron Corporation. The developed experimental facility provides great flexibilities in plasma injection location, type of plasma gas, plasma torch power, placement of analyzers, range of NO concentrations and flame conditions.

Chapter 6

Experimental Results

After construction of the set-up, a series of tests have been conducted. First, each component of the set-up was tested separately. Second, shakedown tests were conducted to ensure that the equipment operates at design conditions prior to the start of the reference tests. The reference tests, which include a cold test (without combustion), a hot test (with combustion), and a plasma test providing parametric characterizations of the system. Lastly, the process tests were conducted to evaluate the feasibility of NO_x reduction by plasma injection. In the process tests, operating conditions, such as plasma power, NH₃ flow rate, argon flow rate, and fuel/air ratio., were systematically varied to quantify their effects on process performance.

The evaluation of the total percentage of NO_x reduction is a primary experimental goal. The percentage is defined as the ratio of the NO_x (ppm) reduced by the plasma to the initial concentration of the NO_x (ppm) before the reduction.

$$\% \Delta = 100 \frac{[NO_x]_i - [NO_x]_f}{[NO_x]_i} \quad (6.1)$$

where, $[NO_x]_i$ is the initial NO_x concentration before the reduction, the $[NO_x]_f$ is the final NO_x concentration after the reduction, and $\% \Delta$ is the total percentage of NO_x reduction.

It was found that the amount of NO_2 in the combustor is almost zero in all the cases of tests. Therefore, the NO_x , which is the sum of the NO and NO_2 , is essentially NO .

6.1 Optimum NO Reduction within the Test Range

A parametric investigation has been undertaken to determine the influence of various parameters on the reduction of NO . The optimum test conditions were determined for the maximum NO reduction within the covered range of this study. Figure 6-1 shows the variation of NO reduction ($\%\Delta$) as a function of ammonia (NH_3) flow rate at the optimum conditions within the tested range.

According to the figure, the total percentage of NO reduction ($\%\Delta$) increases with the mass flow rate of NH_3 . At lower mass flow rates (0.2-0.8 lpm) of NH_3 , the NO reduction ($\%\Delta$) is rather sensitive to the variation of flow rate. The highest value of NO reduction achieved within the test range is 86% at the ammonia flowrate of 0.90 lpm. The trend of the curve in Figure 6-1 suggests that further increase in NH_3 flow rate would probably increase the $\%\Delta$. However, it was limited by the operation conditions of present plasma generator as will be discussed in the following sections.

6.2 Plasma Power Effect

Figures 6-2 and 6-3 display the plasma power effects on NO concentration with and without combustion respectively, where NO_f represents the final NO concentration after plasma injection. For both cases, plasma was injected downstream of the flame.

Figure 6-2 illustrates the effect of plasma power on the amount of NO at air and fuel flowrates of 155 and 13.4 lpm respectively. The dotted line in this figure denotes the initial NO concentration (550 ppm). When only argon plasma was injected without ammonia, at torch power $P_p < 400\text{W}$, there was almost no change in NO concentration. However, the NO concentration increases with the torch power when $P_p > 500\text{W}$. This effect can be seen more clearly in Figure 6-3 at a condition without combustion in which when the

Figure 6-1: Percentage NO Reduction vs. NH₃ Injection Rate

Figure 6-2: Final Downstream NO Concentration vs. Plasma Power at a Condition of Low NH₃ Injection Rate

plasma power increases, the NO concentration increases considerably if $P_p > 600\text{W}$. The reason is that the gas temperature increases with the plasma power so that the oxygen and other stable molecules in the combustor are dissociated and generate more NO. This is evidenced by the results of temperature measurements in Figure 6-4. The temperatures downstream of the plasma injection increase significantly with the plasma torch power. The temperature in the local area of the plasma injection could be much higher than that shown in the figure.

When ammonia plasma is injected together with argon, the amount of NO is reduced by ammonia radicals. The effectiveness of the NO reduction increases when plasma torch power decreases as shown in Figure 6-2. As explained before, ammonia radicals react with the additional NO produced by the local heating effect of plasma gas when the torch

No Combustion, Downstream Plasma Injection

Figure 6-3: Final Downstream NO Concentration vs. Plasma Power at a Cold Condition without Fuel Combustion

Air=195lpm, No Combustion
Downstream Injection at x=28 in.

Figure 6-4: Plasma Effects on Temperature Distributions

power is high. In addition, the plasma torch may create temperatures in the ammonia which may cause oxidation of NH_3 , producing more NO . Therefore, the plasma injection is not as effective when the torch power is high. The desired torch power should be below 300W. However, since the standard ICP plasma gun was designed for only argon gas, the introduction of the ammonia gas into the gun changes the flow resistance so that there is a limitation on the ammonia flowrate when the plasma torch power is low. This problem may be solved by changing the capacitor of the matching box of the plasma generator system so that the flow resistance and the RF power delivered can match each other at the operation conditions of low torch power and high ammonia flowrate. For the present test conditions, it was found that 400W torch power seems to be the optimal choice in

Figure 6-5: Percentage Reduction of NO vs. NH₃ Injection Rate at Conditions of Different Excess Air in Combustion

which the torch power is relatively low so that very little additional NO is generated and the amount of ammonia introduced into the plasma gun can be relatively high. This value of the plasma power was used in most of the tests. The fact that the lower the plasma power, the better the NO_x reduction implies higher NO_x reduction may be achieved at a lower power consumption.

6.3 Excess Air Effect

Figure 6-5 demonstrates the excess air effect on NO reduction for four different air flow rates at a fuel flow rate of 13.4lpm and a plasma gun power of 400W. Referring

to the figure, the air flow of 127lpm provides the stoichiometry ratio corresponding to the fuel flow rate. The air flow rates of 155, 195 and 230lpm generate 25, 50 and 75% excess air respectively. The figure reveals clearly that the smaller the amount of excess air, the higher the NO reduction by plasma injection. This result is expected because less additional NO is generated by the local heating effect of the plasma when the amount of excess air in the combustor is lower.

It should be mentioned that there may be some additional excess air sucked into the combustor from very small gaps at the plasma injection port. Therefore, the real air flow rate inside the combustor may be more than that supplied by the house air. This is similar to the "Chimney Effect". However, this does not affect the results reported above in a negative way and the general trend of the test results is correct. In other words, the present experimental data is conservative in the sense that if this excess air leakage did not exit, the total percentage of NO reduction would be higher. The amount of this type of excess air depends on the balance of the total gas flow inside the combustor and the suction of the blower. Appendix E gives some approximate calculations from the experimental data. The excess air due to the leakage ranges from 6% to 32% of the supplied total gas flow rate for the corresponding test conditions.

6.4 Argon Flowrate Effect

The following table illustrates that the total percentage of NO reduction increases significantly with argon flow rate, when the other flow conditions are the same.

Fuel(lpm)	Air(lpm)	P_p (W)	NH_3 (lpm)	Ar(lpm)	$\Delta\%$
13.4	127	400	0.13	13	3.6
13.4	127	400	0.13	21	14.3
13.4	127	400	0.26	17	14.3
13.4	127	400	0.26	21	26.8

Fuel=13.4lpm, Air=127lpm, Downstream
H=31in.(2in. above the injection point)

Figure 6-6: Radial Temperature Distribution

One possible reason for this behavior is that when argon flow increases, the penetration of the plasma jet into the main flow in the combustor is deeper so that the mixing of radicals is better. This can be observed from the temperature distributions shown in Figures 6-6 and 6-7 at a cross section about 2 inches downstream of the plasma injection location. In these figures, the axis y is the distance from the wall in the plasma flow direction. The figures show that the temperature of the flue gas in the combustor is higher and the profile is flatter when the argon flow rate is higher.

Fuel=13.4lpm, Air=127lpm, Downstream
H=31in.(2in. above the injection point)

Figure 6-7: Radial Temperature Distribution

6.5 Cross Flame Injection

Figure 6-8 shows the results of cross-flame injection on the NO reduction for both plasma and pure ammonia gases. The injection location is at $x=15\text{in}$ which is at the upper part of the flame. The fuel and air flow rates are 19.5lpm and 195lpm respectively, and the initial NO concentration is 530ppm. The figure demonstrates that plasma injection has effects on the NO reduction for this cross flame injection. However, it is not as effective as downstream injection and pure ammonia cross-flame injection (thermal deNO_x process). The possible reason is that in the diffusion flame, the outside of the flame is unburned air which is heated by plasma jet and produces more NO by oxidation, and the radicals injected from the side wall of the combustor first encounter this part of NO. Therefore, the radicals have less chance to encounter original NO in the combustor so that the effective NO reduction is not very high. However, the presented result is not sufficient to conclude that in-flame injection is not as effective. If the plasma configuration can be designed so that the plasma can be directly injected into the flame especially in the fuel rich region, the total percentage of the NO reduction may be expected to be much higher.

Cross flame Injection at $x=15\text{in.}$
Fuel=19.5lpm, Air=195lpm

Figure 6-8: Plasma Effects on NO Reduction

Chapter 7

Discussions of Experimental Results

7.1 Comparison with Thermal DeNO_x

In the downstream injection, the plasma injection is much more effective than pure ammonia injection (thermal deNO_x) on the NO reduction as shown in Figures 7-1, 7-2 and 7-3. For these figures, the fuel flow rate is the same at 13.4lpm, but the air flow rate supplied is 155lpm($\approx 25\%$ excess air), 195lpm($\approx 50\%$ excess air), and 230lpm($\approx 75\%$ excess air) respectively.

As mentioned before, both plasma injection and pure ammonia injection use radicals of NH₂ and NH to react with NO molecules. In the thermal deNO_x process, the reaction for the ammonia to be dissociated into the radicals NH₂ and NH occurs in the main stream and is highly dependent on the flow temperature. As shown in Figure 7-4, it is effective only in a very small temperature range. If the flow temperature is too cold (< 970 K), little or no NO_x is reduced, and the ammonia is wasted. Worse yet, if the gas is too hot (> 1300 K), the NH₃ can oxidize forming more NO_x [10, 11]. In the test conditions, the flow temperature in the injection section is about 920K. This temperature is not within the effective temperature range of the thermal deNO_x. In Figures 7-1, 7-2 and 7-3, the experimental results have also shown that when the excess air is reduced, the effectiveness of the thermal deNO_x increases, although it is still much less effective than

Figure 7-1: Percentage NO Reduction vs. NH₃ Injection Rate at Conditions with or without Plasma Power

Figure 7-2: Percentage NO Reduction vs. NH₃ Injection Rate at Conditions with or without Plasma Power

Figure 7-3: Percentage NO Reduction vs. NH₃ Injection Rate at Conditions with or without Plasma Power

$$z = [\text{NO}]/[\text{NO}]_i$$

$$\chi = [\text{NH}_3]_i/[\text{NO}]_i$$

θ = dimensionless NH_3
oxidation time

γ = dimensionless NH_2
oxidation time

Figure 7-4: Performance of Ammonia Injection in the Destruction of NO_x in Combustion Products: (a) NO_x penetration data of Muzio and Arand; (b) calculated NO penetration; (c) dimensionless times for NH_3 and NH_2 oxidation.

[10]

the plasma injection. This is because the flow temperature increases when the excess air decreases.

In plasma injection, the radicals (NH_2 and NH) are produced by the plasma gun and the dissociation of the plasma gas is not dependent on the flue gas temperature. Although all the ammonia may not be dissociated by the plasma gun, the heating effect of the plasma gas may increase local flow temperature into the favorable temperature range for the dissociation of NH_3 corresponding to thermal deNO_x operation, which will be discussed in detail in the following section. The dissociation of NH_3 by plasma gun also increases the efficiency of ammonia utilization.

Theoretically, the plasma temperature at the core of the plasma flame can be as high as 7000K [43]. However, the temperature of the plasma jet (free jet) decays very quickly. Figure 7-5 shows typical temperature measurement data where the plasma jet is injected into the atmosphere. At a location about 2.5 inch downstream of the nozzle exit, the temperature decreases to about 1700K. The calculations (see Appendix G) based on the measurements of the flow temperature in the combustor have also shown that the bulk mean temperature of the plasma jet is about 2000K. This temperature distribution is favorable for the generation of NH_3 radicals. According to the kinetic analysis [14], high temperatures (e.g. 6000K) are effective for generating high radical concentrations, but lower temperatures (e.g. 2000K) are desirable for longer radical lifetimes. Therefore, both thermal effects and the kinetic effects make plasma injection more effective than pure ammonia injection downstream of the flame in the combustor. When the plasma power is lower, the outside area of the core is cooler. Therefore, the freezing effect is stronger, causing higher NO_x reduction.

7.2 Combined Transport and Reaction Model

The mechanism of the plasma injection process for NO_x reduction has not been well understood yet, however, a postulation can be made at this moment. Since part of

Figure 7-5: Measurements of Temperature Field of Plasma Jet

the plasma gas is used for cooling the plasma gun, only the remaining part of the gas enters into the plasma core and is ionized or dissociated into radicals. The plasma core is anchored at the center near the exit end of the concentric torch tubes by the recirculation zone generated by the tangential flows. The strong interaction between the hot gas inside the plasma core and the cold gas outside the core at the edge of the recirculation zone results in small hot "pockets" formed in the flow field. These small "hot" pockets contain free atoms and radicals and are at very high temperature, high viscosity, low density, and high velocity. They are dispersed through the reacting medium rather like droplets from an atomizer, and free radicals survive within the pockets for appreciable distances in the downstream direction. During the transportation of a hot pocket, its radicals diffuse out of the pocket to react with the surrounding gas. The concept of this combined transport and reaction model is shown schematically in Figure 7-6. Such hot pockets have been observed experimentally in nitrogen plasma jets by Behbahani et al.[45, 46, 47]

For the present operating conditions of the plasma gun, the contents and the structure of each hot gas pocket may be very complicated. Conceptually, the following are possible.

- **Ammonia Radical pockets:** When a very small proportion of ammonia gas contacts with the plasma core, it is heated to exceedingly high temperatures. Therefore, a small ammonia radical pocket will be formed containing NH_2 , NH , and H .
- **Hot argon pockets:** A hot argon pocket encapsulates only argon atoms at very high temperature.
- **Mixed ammonia radical and hot argon pockets:** Since the ammonia and argon gas are mixed inside the tube of the plasma torch, the mixture of ammonia radicals and argon atoms may be contained in a pocket. The mixed type of hot pockets may have three different forms: 1) the argon atoms are at the center, and are surrounded by ammonia radicals, 2) the ammonia radicals are at the center with argon atoms outside, and 3) both ammonia radicals and argon atoms are mixed

Figure 7-6: Combined Transport and Reaction Model

together.

During its motion through the flow field, a hot pocket may generate more desired ammonia radicals because of diffusion and reactions with surroundings. When a hot argon pocket encounters cold ammonia molecules, these molecules may be heated up and dissociated into radicals. Therefore, the high temperature hot argon pocket becomes a mixed hot pocket with argon atoms surrounded by ammonia radicals. When an ammonia radical pocket with NH_2 , NH and H radicals travels to a colder region, the H radicals will be used to simulate the dissociation of NH_3 according to the following reaction.

This reaction is the major source of NH_2 radicals at low temperature according to the kinetic analysis [42]. When the ammonia radicals diffuse out and react with NO molecules, one of the possible reactions is:

The free H radicals generated from this reaction will encourage the decomposition of surrounding NH_3 .

Figure 7-7 shows a picture of different regions in a plasma jet. Region 1 is the core of the plasma which is the hottest area. The temperature in this region can be 7000K, or even higher. When gases enter this region, they are heated up to very high temperatures and ionized, generating hot pockets. Since the argon flow is the major portion of the plasma gases, many hot argon pockets are formed in this region. The dissociation of NH_3 in this region is mostly from the reaction (A) which is much faster than the reaction (B) at high temperatures. Region 2 is the area surrounding the plasma core and the tail of the plasma flame. This region can be called the "warm" area where the temperature ranges from 2000 to 4000K. When a hot argon pocket travels to this region and encounters ammonia gas, the NH_3 will be heated and dissociated. During the

NH₃ Dissociation:

NO Reduction:

Region	Temperature	Radicals Moleculars	Possible Reactions
①	Hot (6000 - 7000 K)	Ar, NH ₂ , NH, H	(A), (B), (C)
②	Warm (2000 - 4000K)	Ar, NH ₂ , NH, H, NH ₃ (hot argon heats up NH ₃)	(A), (B), (C)
③	Cold (800 -2000 K)	Ar, NH ₂ , NH, H, NH ₃ , NO	(B), (D), (E) and thermal deNO _x

Figure 7-7: Different Regions in a Plasma Jet

dissociation of NH_3 , some amount of free H atoms from the reaction (A) will help in turn further dissociation of ammonia according to the reaction (B). Region 3 is the rest of the area in the plasma jet which interacts with the flue gas in the combustion chamber. Temperatures here may range from 800 to 2000 K. It is this region where the reactions for NO reduction occur. When a radical pocket travels to this region and encounters NO molecules, ammonia radicals NH_2 and NH diffusing out of the pocket react with NO according to the reactions (D) and (E). Free H atoms from the reaction (E) may produce more NH_2 when they react with ammonia. Since this region covers the temperature range (around 1200K) for the effective thermal deNO_x process, when ammonia enters areas with this temperature range, thermal deNO_x will occur. As a result, stages of the chemical reaction occur at different temperatures and each stage will have a different reaction rate. To determine the temperatures at which various reactions occur depends strongly on the fluid dynamics of the plasma and the surrounding gases.

The life time of a radical relates to the distance it will diffuse from each pocket rather than its travel from the plasma gun torch. Due to the existence of hot pockets and their transport, radicals survive within the pocket and more radicals may be generated during their flight. Therefore, radicals can react with NO very effectively during their life time.

In summary, it is postulated that the plasma gun generates radicals in the form of hot pockets. These hot pockets are dispersed away from the hot regions to cold regions. During the traveling of the radical pockets, more ammonia radicals may be generated continuously because of the temperature effect, the diffusion of radicals and chemical reactions. If the NO is uniformly distributed in the flow field, the NO reduction by reactions with ammonia may happen at any location along the path of a radical pocket. The combination of the transport and the reaction of radicals allows for very effective NO_x reduction.

The combined transport and reaction model can also explain the fact that the more argon flow, the higher NO_x reduction. When the argon flow rate is higher, the frequency of the occurrence of hot pockets increases and the velocity of the pocket will be faster.

Therefore, probably more pockets will exist in the flow field, and they will be dispersed with further distance from the exit of the plasma gun, resulting in higher NO_x reduction. The optimum conditions for the NO_x reduction are the conditions in which there are many hot pockets formed, and these pockets can effectively provide effectively the desired reduction radicals NH_2 and NH due to the temperature effects, the transport and reaction of these pockets in the flow field.

7.3 Comparison with PETC's Results

The experimental work on downstream plasma injection has also been conducted in a large scale setup at Pittsburgh Energy and Technology Center (PETC) [14]. Both experiments at CMU and PETC showed close similarity on the NO_x reduction and its parametric effects, although they were performed on two different facilities and with two different plasma generators.

The schematic of the experimental facility at PETC is shown in Figure 7-8 [14]. Fuel Oil #2, containing approximately 0.6% nitrogen and 0.2% sulfur, was burned. The flue gas was doped with NO , after exiting the test combustor. A one inch diameter ceramic cylinder has been placed across the flue gas two inch distance upstream of the injection port to enhance mixing. Molecular radicals were created by a 40 kW DC plasma torch as shown in Figure 7-9 [14]. Argon, the process gas, was heated by electrical arcs between the cathode and the anode. Gases containing radical precursors (e.g. ammonia) were introduced into the argon stream from the annular gas chamber. This type of plasma generator may also provide radical pockets because of the arc stratification as shown in Figure 7-9.

The experimental results at PETC have shown that, at optimal conditions (low plasma torch power, high initial NO concentration, and appropriate flue gas temperature), about 85% to 90% NO_x reductions can be achieved, while the highest NO reduction in the present tests at CMU is about 86% at the conditions of low plasma gun power,

Figure 7-8: Experimental facility at PETC

Nozzle geometry

Arc Stratification

Figure 7-9: DC Plasma Torch Nozzle Geometry and the Arc Stratification

intermediate NO concentration, and small amount of excess air. The consistency between the test results at PETC and at CMU suggests that the process of NO_x reduction using plasma jet is independent of the combustion system and the plasma generator. The high NO_x reduction can always be achieved if the test conditions are favorable to generate radicals effectively and can provide good mixing of radicals.

7.4 Summary

A series of experimental tests were performed in order to investigate the feasibility of the plasma injection for NO_x reduction. The results were very promising. It seems that the mechanism of the process is a key issue. Very high NO reduction can be achieved in the conditions in which there is an effective production of ammonia radicals in the flow field and good transport and reaction of these radicals. The following are the conclusions from the experimental Results.

1. The downstream injection is very effective for the NO_x reduction. The highest total percentage of NO_x reduction is 86% in the present tests.
2. The lower the amount of excess air in the combustor, the higher the total percentage of NO_x reduction. This is because the excess air may cause additional oxidation, resulting more NO formation.
3. When argon flowrate increases, the total percentage of NO_x reduction increases. The high argon flow rate provides high velocity of plasma gas and high "freezing" effect of radicals so that radical pockets have wide dispersion and radicals have long life time. Therefore, high NO_x reduction can be achieved.
4. Two different plasma guns and facilities at PETC and CMU provide the similar results of NO_x reduction. This implies that NO_x reduction by plasma injection is independent of the combustion system and the plasma generator, and proves the feasibility of the plasma injection for the NO_x reduction.

5. The plasma should be injected into the fuel rich zones for the in-flame injection configuration in order to avoid the additional NO formation in the unburned air.

Chapter 8

Conclusions and Future Work

The growing concern on the NO_x emissions from power plants makes NO_x control a critical problem. The weaknesses in current NO_x control techniques necessitate more effective, less expensive and more widely applicable techniques to be developed. The feasibility of a new NO_x reduction technique by using plasma injection was investigated in this research by both numerical and experimental methods.

The general conclusions of the research accomplished are detailed below.

8.1 Conclusions

1. With the objective of developing an efficient and realistic numerical model for turbulent two phase flows to provide fundamental support in the development of this new NO_x control technique, a "Group" model with splitting was formulated. This model uses particle groups to represent the dispersed phase and considers particle dispersions within each group due to the turbulence, which is one of the most difficult problems in the modeling of turbulent two-phase flows. A factor of 20 reduction was achieved in the computational time as compared to a classical two-phase flow model. The calculations using this approach can give the information of particle trajectories and distributions which are important for the design of the

in-flame plasma injection configuration. This fundamental research also established the necessary ground for further complete modeling of the whole process including the chemical kinetics, if desired by other researchers. All the calculations using this group approach showed that:

- The group approach is “efficient” in the computational time because very small number of particle groups are required to obtain reasonable statistical results.
 - The group approach is “realistic”, since it considers the particle dispersions within each group due to flow turbulence.
 - The group approach is very easy to implement, has wide applications, and can be incorporated into any computational program which employs the Lagrangian approach to trace the dispersed phase, and also includes heat transfer and chemical kinetics.
2. Numerical calculations were also performed for turbulent gas flow field with variable properties. The results provide fundamental understanding of mixing effects in the experimental work at PETC. The calculations showed that the recirculation zone generated by a rod at the test section allows for very rapid and effective mixing of radicals.
 3. With the aim of exploring the potential of ammonia plasma injection for the NO_x reduction, a small scale experimental facility was constructed, and a series of tests were conducted. The experimental results were very promising and achieved the goal at the first stage of the development of this new technique.
 - The experimental results have indicated that the downstream plasma injection for NO_x reduction is very effective. The test results from both CMU and PETC showed a close similarity although the corresponding facilities and plasma gun generators were different.

- The downstream plasma injection has achieved 86% NO_x reduction in the optimum testing conditions within the range of test conditions of the present study. The total percentage of NO_x reduction increases when the ammonia flowrate, the argon flowrate and the initial NO concentration increase, and the plasma torch power and the amount of excess air decrease.
4. The mechanism of the process is the most important in the fundamental understanding and the development of this new technique. A combined transport and reaction model was postulated to explain the mechanism of this process. According to this postulation, the plasma gun generates radicals in the form of hot pockets. During the flight of these hot pockets, more ammonia radicals are generated due to nonhomogeneous temperature and species field, the diffusion of radicals and chemical reactions. Although ammonia radicals have very short lifetime according to the CHEML analysis based on an ideal thermodynamic and zero dimensional situation, the real life of a radical relates to the distance it diffuses from each pocket rather than its travel from the plasma gun torch. The reaction of NO reduction by ammonia radicals can happen at any location along the path of a radical pocket when radicals diffuse out of the pocket and encounter NO molecules.

8.2 Future Work

The numerical and experimental analysis have identified the potential of plasma injection for NO_x reduction at the first stage of the development of this new technique. However, in order to optimize the process and apply it to a large scale combustion system, better understandings of the basic mechanisms of this very promising process are needed. In the future research, the objective is to focus the study on examining the fluid and chemical dynamics of this advanced but not fully understood process, the low power plasma process, and testing the use of N_2 or other alternatives for the plasma carrier-gas.

Modeling of Transport and Reactions of Plasma Pockets

Based on the postulated model in this research, the analytical/computational study of the transport and reactions of plasma pockets in the fluid flow should be performed to reveal the fundamental mechanism which governs this critical process. According to the postulation, A plasma pocket undergoing dispersion in a shear layer of flow should be considered from the viewpoint of fluid mechanics. The numerical modeling can be used to analyze the shear and mixing. The variable properties should be used in the modeling because the plasma at high temperature will have a very different density and viscosity than its surroundings.

The overall modeling should consider the mass, momentum, energy and species conservation equations with variable properties and with including chemical reactions. The evolution of a plasma pocket can be traced in a Lagrangian coordinate system where the coordinates move together with the plasma pocket. Only the major species will be traced. The reactions of species over time and space can be calculated according to their local concentrations and local temperatures. The existing computer code, TEACH, which has already been modified to consider the variable properties in this research, can be used with appropriate further modifications.

Low power plasma process

The fact that the NO_x reduction increases when the plasma power decreases found in the experimental work is a pleasant surprise, because it implies better NO_x reduction may be achieved at a lower power consumption. However, in the present study, due to the difficulty of sustaining the plasma at lower powers (less than 400W), not much testing can be conducted at the low power range of the existing plasma system. More information is needed.

The existing ICP system can be modified to allow for the operation of lower power at various flow conditions by replacing a new capacitor with a wider range of coupling capability. More extensive data should be established for the low power conditions on the modified system.

Alternative Plasma Carrier-gas

The present study use argon as a carrier-gas to generate ammonia radicals. However, the argon gas is expensive and it is impractical to use a large amount of argon gas in real power plants for NO_x reduction from the viewpoint of cost effectiveness.

At low energy levels, it is desirable to use N_2 gas or even the air as carrier gas, but it needs to be studied for feasibility. Since the existing ICP system was designed only for argon gas, it has to be modified and operated for the alternative plasma carrier-gas. Parametric effects will be studied for the variation of carrier-gas flow and types of carrier-gas. The condition of combustion products will also be varied in terms of excess air, NO_x concentration, temperature, etc.

Real Applications

The developed numerical model and experimental testing and analytical results can be used in the future applications of plasma injection system for the NO_x reduction of pulverized coal combustors.

For the in-flame plasma injections, the numerical analysis of two phase combusting flows should be performed using the "Group" model developed in this research with including chemical reactions. The information on particle trajectories and distributions provided by this analysis will be helpful for the design of the plasma injection configuration. It would also be useful if the flow field can be simulated using the modified TEACH code to analyze the mixing effects of the plasma with the combusting gases.

The experimental data obtained from the laboratory will be used to identify optimal operating conditions of this innovative process in terms of NO_x reduction vs. power consumption at various conditions. This will provide valuable information for making decisions on how to apply this technology in a real system.

The evolution of plasma pockets of various sizes and temperatures at different shear flow conditions and ambient temperatures should be studied systematically. The result of this modeling will give important guidance to the criterion of the plasma generator design as well as the real engineering system design for implementing this technology in full scale system. This is very important because, so far, none of the existing plasma generators

are designed for the purpose of production of radicals in this type of applications.

Appendix A

NO_x Control Techniques

Techniques	NO _x Reduction	Notes[14]
Operational Modifications <ul style="list-style-type: none">- Low excess air- Biased firing	10-30%	Limits boil capacity and operational flexibility
Overfire Air (OFA) <ul style="list-style-type: none">- Fuel rich inner zone- Cooler burnout zone	30-50%	Significant modifications required Coal applications are questionable
Low-NO_x Burners <ul style="list-style-type: none">- Designed to inhibit NO_x- Fuel rich primary zone- Cooler burnout zone	40-60%	Not applicable as retrofits to all existing boilers. (cyclone burners:12%)
Reburning A short residence high temperature zone in which	50%	Most complicated process Requires fast burning fuel in reburn zone.

NO_x is consumed

(oil or natural gas)

Selective Catalytic Reduction 80%
SCR)

-Post combustion

-Ammonia injection

Temperature Sensitivity

Catalyst disposal

High sulfur coals cause
downstream corrosion

Selective Non-Catalytic Reduction 50%
(SNCR or Thermal De NO_x)

-Post combustion

-Ammonia injection

Temperature Sensitivity

Less efficient than SCR

High sulfur coals cause
downstream corrosion

Appendix B

Gaussian Distribution of Particle Dispersions

It has been proven that Equation (2.12) preserves its form, Gaussian function, during the process. This proof is given as follows:

There is a well known central limit theorem of the probability theory [48]. The theory states that if X_1 and X_2 are independent stochastic variables, having Gaussian distributions $N(0, \sigma_1^2)$ and $N(0, \sigma_2^2)$ respectively (where their averages are zero and their variances are σ_1^2 and σ_2^2 respectively), then their sum $X=X_1+X_2$ is also Gaussian $N(0, \sigma_1^2+\sigma_2^2)$. The average and variance of X are the sums of the averages and the variances of X_1 and X_2 . Mathematically, this theory claims that if $f_{X_1}(x_1)$ and $f_{X_2}(x_2)$ are Gaussian probability densities of X_1 and X_2 respectively, the probability density of the sum, $f_X(x)$, will be

$$f_X(x) = \int f_{X_1}(x_1)f_{X_2}(x-x_1)dx_1 \quad (B.1)$$

$$= \frac{1}{\sqrt{2\pi(\sigma_1^2 + \sigma_2^2)}} \exp\left(-\frac{x^2}{2(\sigma_1^2 + \sigma_2^2)}\right) \quad (B.2)$$

which is also a Gaussian distribution.

For the particle dispersions within a group, the probability function of particle po-

sitions is essentially a solution of a diffusion equation. It is assumed that the diffusion coefficient is constant during each time interval δt , but varies with different time intervals when particles encounter different eddies in the flight. The solution to the diffusion equation with an initial condition of a Dirac function will develop into a Gaussian distribution during a time interval δt_1 from time t_0 to t_1 . Now, consider a time interval δt_2 from time t_1 to t_2 . The final probability density will be:

$$f_X(x, t_2) = N \int \left(\frac{\exp(-\frac{x_1^2}{2(2D_1\delta t_1)})}{\sqrt{2\pi(2D_1\delta t_1)}} \right) \left(\frac{\exp(-\frac{(x-x_1)^2}{2(2D_2\delta t_2)})}{\sqrt{2\pi(2D_2\delta t_2)}} \right) dx_1 \quad (B.3)$$

where, D_1 and D_2 are diffusion coefficients. The first term in the integral is the initial condition of the diffusion equation from time t_1 to t_2 , which is a Gaussian distribution after experiencing δt_1 time of diffusion. The second term of in the integral is the Green's function of the diffusion equation. These two terms are similar and can be rewritten as

$$f_X(x, t_2) = N \int f_{X_1}(x_1) f_{X_2}(x - x_1) dx_1 \quad (B.4)$$

Equations (B.4) and (B.2) have the same form. Since the successive particle displacements are uncorrelated, Equation (B.2) can be applied to the present situation. This means the final distribution is Gaussian and can generally be written as

$$f_X(x, t) = \frac{N}{\sqrt{2\pi\bar{X}^2}} \exp(-\frac{x^2}{2\bar{X}^2}) \quad (B.5)$$

where, $\bar{X}^2 = \delta_{x1}^2 + \delta_{x2}^2 + \dots + \delta_{xi}^2 + \dots = 2D_1\delta t_1 + 2D_2\delta t_2 + \dots + 2D_i\delta t_i + \dots$

Appendix C

Splitting of a Group

In order to demonstrate the group modeling with splitting, calculations were performed for a group splitting successively in a homogeneous flow field. Figures C-1, C-2 and C-3 show the sequence of the splittings. In Figure C-1, a group is split into two at time t_1 . In Figure C-2, each new group is split into two and the total group number is four at time t_2 . In Figure C-3, after further splitting, the total group number is 8 at time t_3 . From these figures, we can see that the superposition of the new distributions after several splits closely approximates the distribution of the original group. This is due to the diffusive effects of dispersions which reduces the error along time.

Figure C-1: Particle Distributions within Groups

Figure C-2: Particle Distributions within Groups

Figure C-3: Particle Distributions within Groups

Appendix D

Test Data

Case 1 Optimum NO reduction within the Test Range (Downstream Injection)

Fuel(lpm)	Air(lpm)	P _p (W)	Ar(lpm)	NH ₃ (lpm)	[NO] _i (ppm)	[NO] _f (lpm)	%Δ
16	155	400	17	0.23	710	605	15
16	155	400	20	0.52	710	290	59
16	155	400	>20	0.78	710	120	83
16	155	400	>20	0.92	710	100	86

Case 2 Excess Air Effect on NO reduction (Downstream Injection)

Fuel(lpm)	Air(lpm)	P _p (W)	A _i (lpm)	NH ₃ (lpm)	[NO] _i (ppm)	[NO] _f (lpm)	%Δ
13.4	230	300	20	0.23	530	360	32
13.4	230	400	17	0.23	530	490	8
13.4	230	400	20	0.52	530	330	38
13.4	230	400	>20	0.78	530	240	55
13.4	230	400	>20	0.91	530	520	59
13.4	230	500	13	0.23	530	570	-8
13.4	230	800	13	0.23	530	610	-15
13.4	230	800	13	0.78	530	580	-9

13.4	195	300	20	0.23	550	360	35
13.4	195	400	17	0.23	550	490	11
13.4	195	400	20	0.52	550	340	38
13.4	195	400	>20	0.78	550	200	64
13.4	155	400	17	0.23	550	470	15
13.4	155	400	20	0.52	550	280	49
13.4	155	400	>20	0.78	550	135	76
13.4	155	400	>20	1.0	550	100	82
13.4	155	300	20	0.23	550	330	40
13.4	155	400	20	0.23	550	400	27
13.4	155	500	20	0.23	550	450	18
13.4	155	500	17	0.23	550	510	7
13.4	155	560	17	0.23	550	540	2
13.4	127	400	13	0.13	550	540	2
13.4	127	400	20	0.13	550	480	13
13.4	127	400	17	0.23	550	470	15
13.4	127	400	20	0.23	550	410	26
13.4	127	400	20	0.52	550	260	53
13.4	127	400	>20	0.78	550	120	78
13.4	127	400	>20	0.90	550	100	82

Case 3 Thermal DeNOx Effect on NO reduction (Downstream Injection)

Fuel(lpm)	Air(lpm)	P _p (W)	Ar(lpm)	NH ₃ (lpm)	[NO] _i (ppm)	[NO] _f (lpm)	%Δ
13.4	230	0	0	0.23	530	510	4
13.4	230	0	0	0.78	530	505	5

13.4	230	0	0	1.3	530	505	5
13.4	195	0	0	0.23	550	540	2
13.4	195	0	0	0.78	550	510	7
13.4	195	0	0	1.3	550	500	9
13.4	155	0	0	0.23	550	490	11
13.4	155	0	0	0.52	550	450	18
13.4	155	0	0	0.78	550	435	21
13.4	155	0	13	0.52	550	445	19
13.4	155	0	13	0.78	550	430	22
13.4	155	0	20	0.52	550	410	26
13.4	155	0	20	0.78	550	380	31

Case 4 Plasma Torch Power Effect NO reduction (Downstream Injection)

Fuel(lpm)	Air(lpm)	P_p (W)	Ar(lpm)	NH ₃ (lpm)	[NO] _i (ppm)	[NO] _f (lpm)
13.4	155	200	13	0	550	550
13.4	155	300	13	0	550	555
13.4	155	400	13	0	550	560
13.4	155	500	13	0	550	575
0	195	300	13	0	10	15
0	195	400	13	0	10	24
0	195	500	13	0	10	58
0	195	600	13	0	10	102
0	195	800	13	0	10	300

Case 5 Cross-flame Injection for NO reduction

Fuel(lpm)	Air(lpm)	P _p (W)	Ar(lpm)	NH ₃ (lpm)	[NO] _i (ppm)	[NO] _f (lpm)	%Δ
19.5	195	400	0	0.26	520	500	4
19.5	195	400	0	0.52	520	450	13
19.5	195	400	0	0.78	520	390	25
19.5	195	400	0	1.0	520	330	36
19.5	195	400	0	1.3	520	295	43
19.5	195	0	0	0.13	500	410	18
19.5	195	0	0	0.26	500	380	24
19.5	195	0	0	1.3	500	175	65

Appendix E

Air Leakage

An experimental test was conducted to evaluate air leakage from the plasma injection port due to the strong suction of the blower of the set-up. At the same combustion condition, NO concentrations were measured for two different cases: 1) the injection port was well sealed by a plate, and 2) the injection port was open to the plasma torch box in the same way as in real tests. It is assumed that the case 1 is an ideal condition in which there is no air leakage at all. Therefore, the calculations of air leakage can be made based on the comparison of the data for these two different cases. From the NO concentration measured at case 1, the amount of NO in the combustor can be calculated according to the total supplied gas flow rate, i.e. $[\text{NO}](\text{ppm}) = [\text{NO}](\text{mole number}) / [\text{total gas}](\text{mole number})$. This calculated amount of NO can then be used to calculate the total real gas flow inside the combustion chamber. Therefore, the amount of the air leakage from the injection port equals the subtraction of the total supplied gas from the total real gas. The following table gives the results of approximate calculations for a fuel flow rate of 13.4lpm and three different supplied house air flow rates of 195, 155 and 127lpm, respectively.

Supplied Air	NO at Case 1	NO at Case 2	NO Calculated	Total supplied gas
(lpm)	(ppm)	(ppm)	(lpm)	(lpm)
195	465	490	0.102	208
155	485	575	0.0968	168
127	465	610	0.0856	140

Supplied Air	Total real gas	air leakage	$\frac{\text{air leakage}}{\text{supplied air}}$	Supplied excess air	Real excess air
(lpm)	(lpm)	(lpm)	(%)	(%)	(%)
195	219	11	5	54	62
155	199	31	20	22	46
127	184	44	34	0	34

Appendix F

Combustion Stoichiometry Calculations

The combustion stoichiometry for fuel-lean combustions is:

where, ϕ is the equivalence ratio.

A. Stoichiometry Combustion without Excess Air

At the stoichiometric combustion condition, the amount of excess air is zero and ϕ equals 1. The mole ratio of air to the fuel is 9.56. The combustion stoichiometry becomes:

The composition of the combustion products includes: $Y_{CO_2} = \frac{1}{10.56} = 9.47\%$, $Y_{H_2O} = \frac{2}{10.56} = 18.94\%$, and $Y_{N_2} = \frac{7.56}{10.56} = 72\%$.

B. Fuel-lean Combustion with 25% Excess Air

At the fuel-lean combustion with 25% condition, ϕ equals 0.8. The mole ratio of air

to the fuel is 11.95. The combustion stoichiometry becomes:

The composition of the combustion products includes: $Y_{CO_2} = \frac{1}{12.95} = 7.72\%$, $Y_{H_2O} = \frac{2}{12.95} = 15.44\%$, $Y_{O_2} = \frac{0.5}{12.95} = 3.86\%$, and $Y_{N_2} = \frac{9.45}{12.95} = 72.97\%$.

C. Fuel-lean Combustion with 50% Excess Air

At the fuel-lean combustion with 50% condition, ϕ equals 0.67. The mole ratio of air to the fuel is 14.34. The combustion stoichiometry becomes:

The composition of the combustion products includes: $Y_{CO_2} = \frac{1}{15.34} = 6.52\%$, $Y_{H_2O} = \frac{2}{15.34} = 13.04\%$, $Y_{O_2} = \frac{1}{15.34} = 6.52\%$, and $Y_{N_2} = \frac{11.34}{15.34} = 73.92\%$.

D. Fuel-lean Combustion with 75% Excess Air

At the fuel-lean combustion with 75% condition, ϕ equals 0.57. The mole ratio of air to the fuel is 16.73. The combustion stoichiometry becomes:

The composition of the combustion products includes: $Y_{CO_2} = \frac{1}{17.73} = 5.64\%$, $Y_{H_2O} = \frac{2}{17.73} = 11.28\%$, $Y_{O_2} = \frac{1.5}{17.73} = 8.46\%$, and $Y_{N_2} = \frac{13.23}{17.73} = 74.62\%$.

Appendix G

Plasma Gun Temperature Calculation

When the test conditions are: fuel equals 13.4lpm, air equals 127lpm (about 0% of excess air), the flow temperature measured at the cross section about 2 in above the injection port is about 773 K, and this temperature is increased to 873 K with 400 W of plasma injection. This temperature increase is due to the heat effect of high temperature plasma gas. According to the energy balance, there is a following relationship:

$$n_t C_t (T_2 - T_1) = n_p C_{Ar} (T_p - T_\infty) \quad (G.1)$$

where, n_t is the total mole number of flow gas in the combustion chamber ($n_t \approx 160 \text{ lpm} = 7.15 \text{ mole/m}$), n_p is the mole number of plasma gas ($n_p \approx 17 \text{ lpm} = 0.76 \text{ mole/m}$), T_1 and T_2 are flow temperatures before and after plasma injection, respectively, T_p is the bulk mean temperature of plasma gas, and C_t is the specific heat of the flow mixture.

According to the stoichiometry combustion calculations in Appendix F, the specific heat of the flow mixture can be calculated by:

$$C_t = 0.0947 C_{O_2} + 0.1849 C_{H_2O} + 0.72 C_{N_2} = 35.14 \text{ J/mol/K} \quad (G.2)$$

where, C_{O_2} , C_{H_2O} and C_{N_2} are the specific heat for O_2 , H_2O and N_2 , respectively, and calculated according to the average temperature of T_1 and T_2 .

Therefore, the bulk mean plasma temperature at this condition can be obtained:

$$T_p = \frac{n_i C_i (T_2 - T_1)}{n_p C_{Ar}} + T_\infty \approx 1889 K \quad (G.3)$$

This is a approximate calculation. Since there exists air leakage at the injection port, the total mole number of the flow gas in the combustor might be higher than the above number and the resulting bulk plasma temperature should be higher than 1889 K.

Appendix H

System Efficiency Analysis

An important aspect of any control device such as in the present report is that it does not significantly tax the net generating capacity of the plant, and hence minimizes costs. This section documents the results of an efficiency analysis of the proposed device. As is seen below, depending on further testing and device analysis, the system could be quite effective.

A scheme was developed to analyze the energy requirement and the efficiency of the system, and the calculated system efficiencies were used to identify the potential for the use of the plasma jet injection to reduce NO_x . The calculation results were also used to determine the optimum operating conditions from the viewpoints of low energy requirement and high efficiency.

H.1 Analysis

A system efficiency analysis is performed for an electrical power plant where plasma assisted NO reduction is incorporated. The efficiency model for this system of plasma assisted NO reduction is shown in Figure H-1.

In the power plant, the electric power which is about 33% of the input power is converted from the energy released by high temperature combustion, which also produces

Figure H-1: Schematic of System Efficiency Analysis

NO_x emissions. A plasma gun heats and dissociates the flowing gases and generates a plasma jet. The plasma jet is injected into the combustion products to reduce NO_x.

During the whole process, part of the energy is required for heating and dissociating the gases. The remaining energy is consumed as the heat loss from the plasma gun, the mixing loss and for the other competing reactions to reduce the NO. These losses are accounted for and quantified below.

The system efficiency is evaluated by the "Normalized Energy Requirement", which is defined as the ratio of the energy input to the gun to the input power to the plant:

$$\eta = \frac{E}{W} = \frac{E_r}{W} \frac{1}{\eta_r} \frac{1}{\eta_g} \quad (\text{H.1})$$

where, W is the input power; E_r is the energy of the plasma required for reducing the NO; η_r is the reaction efficiency; and η_g is the gun efficiency.

The reaction efficiency is affected by the mixing pattern. If there are x2% mixing loss and x3% energy consumed in the reactions other than that reduce the NO, the reaction efficiency is defined by:

$$\eta_r = \frac{E_r}{E_d} = \frac{E_d - E_m - E'}{E_d} = 1 - x2\% - x3\% \quad (\text{H.2})$$

where, E_d is the dissociation energy, i.e. the energy which contributes to the creation of the desired radicals; E_m is the mixing loss in the gases; E' is the energy lost to competing reactions; X₂ is the ratio of the mixing loss to E_d; and X₃ is the ratio of the energy lost to competing reacting reactions to the E_d.

The gun efficiency is related to the dissociation energy, the heating of the gases and the heat loss from the plasma gun. Heating of the gas is unavoidable during dissociation. One way to heat the plasma gas is using high temperature Argon as a carrier gas. The temperature of the argon and the mass ratio of the argon to the plasma gas have strong effects on the gun efficiency, which can be optimized by calculations. The definition of the gun efficiency is given by

$$\eta_g = \frac{E_d}{E} = \frac{E - E_g - E_h}{E_{Ar} + E_g} = \frac{E - E_g - E_h}{E_{Ar} + x1 * E} \quad (H.3)$$

where E_{Ar} is the input enthalpy of the argon; E_g is heat loss from the plasma gun; and E_h is energy contained in the heated gases which does not contribute to dissociation.

$x1$ is the ratio of the heat loss on the plasma gun to the total heat input to the plasma gun.

For the special consideration of dissociation without heat loss and argon as a carrier gas, a dissociation efficiency is defined as the efficiency of using energy for dissociation in relation to the total energy required, and depends strongly on the specific enthalpy of the gas. The calculation of the dependence of the dissociation efficiency on the specific enthalpy of the plasma gas can be used to establish the optimal efficiency of dissociation. Therefore, we can deduce the absolute minimum power requirements and to assess the specific enthalpy at which plasma jets should be operated in practice. The dissociation efficiency is defined as

$$\eta_d = \frac{E_d}{E_d + \text{The Enthalpy of Plasma Gas}} \quad (H.4)$$

H.2 Results and Discussion

The system efficiencies were calculated for the nitrogen and ammonia plasma. All the calculations are based on empirical data from power plant operation conditions, which are given in section H.4. Section H.4 also gives thermodynamic data used in the calculations.

Nitrogen Plasma

The following assumptions were made in the calculations:

1. Using argon as a carrier gas
2. No mixing loss ($x2\%=0$)
3. No other reactions ($x3\%=0$)

Figure H-2: Gun Efficiency vs. Mass Ratio of Argon to Nitrogen

4. All the reactions are under chemical equilibrium conditions

Figures H-2 and H-3 demonstrate the gun efficiency and the normalized energy requirement vs. mass ratio of argon to nitrogen and the temperature of argon. The calculations were based on the fixed mole number of nitrogen atom from section H.5. For a given temperature of argon, the mixture temperature, and the mole number of nitrogen and argon change with the mass ratio of argon to nitrogen according to the thermodynamic and chemical equilibrium calculations. The figures show a maximum for the gun efficiency and a minimum for the normalized energy requirement. The reason is that when the mass ratio of Ar/N₂ is too small, the mixture temperature is too low so that a large amount of nitrogen and argon are required to produce enough N atom. When the mass ratio of Ar/N₂ is too large, the input energy is too much to generate much additional N atom.

From Figure H-2 and H-3, we can also see that the effect of the argon temperature is

Figure H-3: Normalized Energy Requirement vs. Mass Ratio of Argon to Nitrogen

very strong. When Argon temperature is lower than 7000 K, the gun efficiency is very low and a great deal of energy, which is even more than the electric power, is required. Only when argon temperature is high enough (e.g. 10000 K), can a relatively high gun efficiency and a low energy requirement be obtained. This is because the difference between the specific heats of nitrogen and argon is not large enough so that a "high temperature bath" must be provided by argon for dissociating nitrogen.

Ammonia Plasma

The calculations for Ammonia plasma are based on the following assumptions:

1. Using argon as a carrier gas
2. No mixing loss ($x_2\%=0$)
3. No other reactions ($x_3\%=0$)
4. All the reactions are under locally chemical equilibrium conditions

The data about the mole number of ammonia plasma required for removing 600 ppm NO and the relevant energy requirement correspond to the conditions in the calculation of chemical mechanism [42] (see section H.6). The results of calculations are given in Figures H-4, H-5 and H-6. All the calculations are based on the fixed mole number of NO and NH_2 atoms, and given mixture temperatures (e.g. 6000 K or 8000 K) so that the temperature and the mass flux of argon change with the mass ratio of argon to ammonia.

Figure H-4 gives the relationship between the temperature of argon and the mass ratio Ar/NH_3 for a given mixture temperature. From the figure, we can see that the difference between the temperatures of the mixture and the argon is small when the mass ratio is larger than 7.

Figures H-5 and H-6 show that the gun efficiency and the normalized energy requirement change with the mass ratio Ar/NH_3 . For a given mixture temperature and a given mole number of NH_3 , when the mass ratio increases, the gun efficiency decreases and the normalized energy requirement increases. The reason is that the mass flux of argon is in

Figure H-4: Temperature of Argon vs. Mass Ratio Ar/NH_3

Figure H-5: Gun Efficiency vs. Mass Ratio of Ar/NH₃

proportion to the mass ratio, while the temperature of the argon changes slightly when the mass ratio is not small. Therefore, the total enthalpy of the argon increases with the mass ratio.

For all the calculations, the gun efficiency is higher and the energy requirement is lower when the mixture temperature equals 6000 K than that when the mixture temperature is equal to 8000 K. This is because the dissociation energy at temperature 8000K ($E_d=377.69$ kJ/mole) is lower than that ($E_d=417.77$ kJ/mole) at 6000K, but the total enthalpy of the argon is higher when the mixture temperature is 8000 K. This indicates that there is a maximum gun efficiency and a minimum energy requirement at a mixture temperature lower than 6000K, since too low mixture temperature will obviously decrease the gun efficiency and increase the energy requirement.

From the results of calculations, we can see that the dissociation energy and the energy requirement of the ammonia plasma is lower than that of the nitrogen plasma,

Figure H-6: Normalized Energy Requirement vs. Mass Ratio Ar/NH_3

which shows that the ammonia plasma has stronger potential than the nitrogen plasma for the use of the plasma inject from the viewpoint of the low energy requirement.

One thing should be noted is that the calculation for the nitrogen plasma is based on the reduction of NO from 600 ppm to 120 ppm while the calculation for the ammonia plasma is based on removing 600 ppm NO.

Another point which should also be mentioned again is that the data in the calculation for the ammonia plasma corresponds to the results of the chemical mechanism studies, which are not under the chemical equilibrium state.

H.3 The Data Used in the Calculations

(A). Power Plant Operation Conditions

- Coal Combustion
- Excess Air = 46%
- The Total Input Energy $W = (3700 \text{ kJ/kg steam}) \times (2 \times 10^6 \text{ kg/hr}) = 2.0 \times 10^6 \text{ kJ/s}$
- The Temperature of Fuel Gas = 560 K
- The Flowrate of Flue Gas = 215912.1836 kg/hr
- Average Molecular Weight of the Dry Flue Gases = 30.44 g
- The Concentration of NO in Flue Gases = 600 ppm
- The Concentration of NO after Reacting with N = 120 ppm
- The Mole Number of NO in Flue Gases = 7039 kmole/hr
- The Mole Number of NO in Flue Gases $Y1 = 1.18 \text{ mole/s}$
- The Mole Number of NO After Reacting with N $Y2 = 0.24 \text{ mole/s}$

(B). The Constant Pressure Specific Heat [49, 50]

$$C_{pAr} = 20.80 - 3.2 \times 10^{-5}T + 5.17 \times 10^{-8}T^2 \text{ j/(mole K)}$$

$$C_{pH} = 20.786 \text{ j/(mole K)}$$

$$C_{pN} = 20.74 + 4.0 \times 10^{-5}T \text{ j/(mole K)}$$

$$C_{pNH_2} = 41.3825 + 3.4 \times 10^{-3}T \text{ j/(mole K)}$$

$$C_{pNH_3} = 38.03 + 1.5 \times 10^{-2}T \text{ j/(mole K)}, \text{ When } T < 1000 \text{ K}$$

$$C_{pNH_3} = 50.363 + 7.95 \times 10^{-3}T \text{ j/(mole K)}, \text{ When } T > 1000 \text{ K}$$

Note: There are some approximations in the formulations.

(C). The Enthalpy of Formation $H^0(298K)$ [51]

$$H^0_H = 218,300 \text{ j/mole}$$

$$H^0_N = 473,326 \text{ j/mole}$$

$$H^0_{N_2} = 0 \text{ j/mole}$$

$$H^0_{NH_2} = 167,894 \text{ j/mole}$$

$$H^0_{NH_3} = -45,965 \text{ j/mole}$$

(D). The Entropy at Reference State $S^0(298K)$ [51]

$$S^0_H = 114.773 \text{ j/(mole K)}$$

$$S^0_N = 153.413 \text{ j/(mole K)}$$

$$S^0_{N_2} = 0 \text{ j/(mole K)}$$

$$S^0_{NH_2} = 194.785 \text{ j/(mole K)}$$

$$S^0_{NH_3} = 192.866 \text{ j/(mole K)}$$

H.4 The Efficiency Calculations for the Nitrogen Plasma

(A). The Mole Number of N Atom for Reducing NO

Assumption: NO is reduced by:

Under Chemical Equilibrium State:

$$(Y1)NO + (Y3)N \rightleftharpoons (Y2)NO + (Y3 + Y2 - Y1)N + (Y1 - Y2)N_2 + (Y1 - Y2)O \quad (H.6)$$

The Definition of equilibrium Constant:

$$K_p = \frac{P_{N_2} P_O}{P_N P_{NO}} = \frac{(Y1 - Y2)^2}{Y2(Y3 - Y1 + Y2)} \quad (H.7)$$

The Formulation of Equilibrium Constant:

$$K_p = \exp\left(\frac{-G^0}{RT}\right) \quad (H.8)$$

where, G^0 - The Standard Gibb's Free Energy Difference:

$$G^0 = 2\mu^0_{N_2} + \mu^0_O - \mu^0_{NO} - \mu^0_{N_2} \quad (H.9)$$

where, μ^0_i - The Chemical Potential:

$$\mu^0_i(T) = a_i[T - T_0 - T \ln\left(\frac{T}{T_0}\right)] - 0.5b_i(T - T_0)^2 + H^0_i - TS^0_i \quad (H.10)$$

Therefore, the mole number of N atom required for reducing NO from Y1 to Y2 mole is:

$$Y3 = (Y1 - Y2) + \frac{(Y1 - Y2)^2}{Y2K_p} \quad (H.11)$$

(A). The Mole Number of N Atom for Reducing NO

• The Degree of Dissociation

The Dissociation Reaction:

Under the chemical equilibrium condition, 1 mole of N_2 can produce Y mole of N :

$$N_2 \rightleftharpoons (Y)N + (1 - 0.5Y)N_2 \quad (H.13)$$

By definition, the equilibrium constant is :

$$K_p = \frac{P_N}{P_{N_2}^{1/2}} = \frac{Y P^{1/2}}{[(1 - 0.5Y)(1 + 0.5Y)]^{1/2}} \quad (H.14)$$

Therefore,

$$Y = \frac{K'p}{\frac{Kp^{1/2}}{4} - P^{1/2}} \quad (H.15)$$

• The Dissociation Energy

The Dissociation Energy for One Mole of N Atoms:

$$e_d = Cp_N(T_p - T_0) + H^0_N - 0.5[Cp_{N_2}(T_p - T_0) + H^0_{N_2}] \quad (H.16)$$

where, H^0_N and $H^0_{N_2}$ are standard heat of formation;

Cp_N and Cp_{N_2} are specific heat: $Cp_i = a_i + b_i T_{AV}$;

T_{AV} is average temperature: $T_{AV} = 0.5(T_p + T_0)$;

and T_p is plasma temperature.

Therefore, the dissociation energy for $Y3$ mole of N atoms is:

$$E_d = Y3e_d \quad (H.17)$$

• The Enthalpy of N_2 Plasma Gas

$$E_N = \frac{Y3}{Y} Cp_{N_2}(T_p - T_0) \quad (H.18)$$

- The Dissociation Efficiency

$$\eta_d = \frac{E_d}{E_d + E_N} \quad (\text{H.19})$$

(C). N₂ Gas Heated By Argon Plasma Gas

Assumption: The mixing of nitrogen and argon is completed.

- The Temperature of the Mixture

$$T_m = \frac{C_{pN_2}T_{N_2} + RC_{pAr}T_{Ar}}{C_{pN_2} + RC_{pAr}} \quad (\text{H.20})$$

Where, R is mass ratio of argon to nitrogen;

T_{N₂} is the temperature of nitrogen (300K);

T_{Ar} is the temperature of argon (7000K - 10000K).

- The Enthalpy of Argon Plasma Gas

$$E_A = Y_{Ar}C_{pAr}(T_{Ar} - T_0) \quad (\text{H.21})$$

- The Gun Efficiency

$$\eta_g = \frac{E_d}{E} \quad (\text{H.22})$$

where, E is the total energy of gun input:

$$E = \frac{E_A}{1 - x_1} \quad (\text{H.23})$$

x₁ is ratio of heat loss on the plasma gun to the total gun input.

- The Normalized Energy Requirement:

$$\eta = \frac{E}{W} \quad (\text{H.24})$$

where, W is the input power to the power plant.

H.5 The Efficiency Calculations for the Ammonia Plasma

(A). The Mole Number of N Atom for Reducing NO

Assumption: NO is reduced by:

From the calculation in the part of chemical mechanism studies of this research, at 500k of temperature, the concentration of NH_2 required to remove 600 ppm is 600 ppm. Therefore, the mole number of NH_2 atom required is :

$$Y_3 = Y_1 = 1.18 \text{ mole/} \quad (H.27)$$

(B). Energy for Producing required Amount of Plasma

• The degree of Dissociation

The dissociation reaction is :

From the calculation in the part of chemical mechanism studies of this research, the optimum conditions for the dissociation are as follows:

- When the temperature of plasma $T_m=6000K$, the concentration of NH_2 is 0.67 concentration of NH_3 , i.e. $Y=0.67$.

- When the temperature of plasma $T_m=8000K$, the concentration of NH_2 is 0.85 concentration of NH_3 , i.e. $Y=0.85$.

Therefore, $(1/Y)$ mole of NH_3 can produce 1 mole of NH_2 atoms; (Y3/Y)
 mole of NH_3 can produce $(Y3)$ mole of NH_2 atoms.

• The Dissociation Energy

The dissociation energy for one mole of NH_2 atoms is:

$$e_d = [C_{p_{NH_2}}(T_p - T_0) + H^0_{NH_2} + C_{p_H}(T_p - T_0) + H^0_H] - [C_{p_{NH_3}}(T_p - T_0) + H^0_{NH_3}] \quad (H.29)$$

where, $H^0_{NH_2}$, H^0_H and $H^0_{NH_3}$ are standard heat of formation;

$C_{p_{NH_2}}$, $C_{p_{NH_3}}$ and C_{p_H} are specific heat:

$$C_{p_i} = a_i + b_i T_{AV} \quad (H.30)$$

T_{AV} is average temperature: $T_{AV} = 0.5(T_p + T_0)$;

and T_p is plasma temperature.

Therefore, the dissociation energy for $Y3$ mole of NH_2 atoms is:

$$E_d = Y3e_d \quad (H.31)$$

(C). NH_3 Gas Heated by argon Plasma Gas

Assumption: The mixing of ammonia and argon is completed.

• The Temperature of the Mixture

$$T_m = \frac{C_{p_{NH_3}}T_{NH_3} + RC_{p_{Ar}}T_{Ar}}{C_{p_{NH_3}} + RC_{p_{Ar}}} \quad (H.32)$$

Where, R is mass ratio of argon to ammonia;

T_{NH_3} is the temperature of ammonia (300K);

T_{Ar} is the temperature of argon (6000K - 8000K);

Specific Heat:

$$Cp_{Ar} = a_{Ar} - b_{Ar}T + c_{Ar}T^2 \quad (H.33)$$

- **Temperature of Argon**

In the calculation, T_m , T_{NH_3} , Cp_{NH_3} and R are known. The temperature of argon T_{Ar} is solved from the following equation:

$$\begin{aligned} Rc_{Ar}T_{Ar}^3 - (Rb_{Ar} + Rc_{Ar}T_m)T_{Ar}^2 + (Ra_{Ar} + Rb_{Ar}T_m)T_{Ar} \\ - [(Cp_{NH_3}(T_m - T_{NH_3}) + Ra_{Ar}T_m)] = 0 \end{aligned} \quad (H.34)$$

- **The Enthalpy of Argon Plasma Gas**

$$E_A = Y_{Ar}Cp_{Ar}(T_{Ar} - T_0) \quad (H.35)$$

- **The Gun Efficiency (with Argon heating):**

$$\eta_g = \frac{E_d}{E} \quad (H.36)$$

where, E is the total energy of gun input:

$$E = \frac{E_A}{1 - x_1} \quad (H.37)$$

x_1 is ratio of heat loss on the plasma gun to the total gun input.

- **The Normalized Energy**

$$\eta = \frac{E}{W} \quad (H.38)$$

where, W is the input power to the power plant.

Appendix I

Radical Freezing Through a Supersonic Nozzle

In order to prolong the life of the radicals and to retain high concentrations during the mixing process, it is necessary to quench the radical reactions by rapid cooling. One possible method of quenching radical reactions is to use an expansion through a converging-diverging supersonic nozzle. Through the nozzle, the temperature and pressure of the plasma gas are rapidly reduced and the reaction chemistry is 'frozen'. The expansion process is studied to determine the effects of certain nozzle geometries and pressure drops on the cooling of gases.

Figure I-1 shows a converging-diverging nozzle. The flow pattern is dependent on the ratio of the back pressure P_b to the stagnation pressure P_0 . In the designed operation condition, the converging flow is subsonic, the diverging flow is entirely supersonic, and the pressure at the exit of the nozzle P_e equals P_b . Through the nozzle, when the plasma gas is expanded, the velocity increases continually. The velocity reaches sonic at the throat and goes supersonic in the diverging section. As the velocity increases, the temperature and the pressure decrease.

The flow through a nozzle can be assumed to be isentropic under design conditions. Therefore, the stagnation temperature and the stagnation pressure do not change during

Figure I-1: Nozzle Schematic

the process. Using this, idealized thermodynamic theory shows that the temperature, pressure and the area ratios at any location are given in terms of the local Mach number and the initial conditions by the following expressions[52]:

$$\frac{T_0}{T} = 1 + \frac{k-1}{2} Ma^2 \quad (I.1)$$

$$\frac{P_0}{P} = \left(\frac{T_0}{T} \right)^{\frac{k}{k-1}} \quad (I.2)$$

$$\frac{A_e}{A^*} = \frac{1}{Ma} \left[\frac{1 + 0.5(k-1)Ma^2}{0.5(k+1)} \right]^{\frac{1}{2} \frac{k+1}{k-1}} \quad (I.3)$$

where, $k = \frac{C_p}{C_v}$; C_p and C_v are the specific heats for constant pressure and volume conditions respectively. The superscript (*) refers to sonic conditions. At the exit of the

nozzle, P_e , T_e , A_e and Ma_e are reached.

Calculations were performed for argon and nitrogen plasma using Equations (I.1), I.2 and I.3, and the results are shown in Figures I-2 and I-3.

Figure I-2 gives the relationship between the pressure drop and the temperature drop at the exit of the nozzle. The temperature drop increases as the pressure drop increases. The desired temperature drop to quench the radicals is from 6000 K to 2000 K, which is a temperature drop ratio of 3:1. The corresponding pressure drop ratio is 50:1 for nitrogen, and 20:1 for argon. This technique can be used to generate high radical concentrations at high temperatures and then to increase radical lifetimes at the lower temperatures. Using argon as the carrier gas is more efficient because it requires a lower pressure drop ratio than nitrogen.

Fig I-3 shows the relationship between the ratio of area at the exit to area at the throat of the nozzle and the temperature drop for both argon and nitrogen plasma. When the temperature drop increases, the area ratio increases. If temperature drop ratio is 3:1 (e.g. from 6000K to 2000K), the A_e/A^* is about 2.0 for argon and 5.4 for nitrogen.

Therefore, according to Figures I-2 and I-3, pure nitrogen plasma is not a good choice, because it requires a larger pressure drop and area ratio for the same freezing effect due to the low k value.

Figure I-2: Pressure Drop vs. Temperature Drop at the Nozzle Exit

Figure I-3: Area Ratio vs. Temperature Drop at the Nozzle Exit

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