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**Early evolution of coal nitrogen in opposed flow combustion
configurations**

Ghani, Muhammad Usman, Ph.D.

The University of Arizona, 1990

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EARLY EVOLUTION OF COAL NITROGEN
IN
OPPOSED FLOW COMBUSTION CONFIGURATIONS

by
Muhammad Usman Ghani

A Dissertation Submitted to the Faculty of the
DEPARTMENT OF CHEMICAL ENGINEERING
In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
In the Graduate College
THE UNIVERSITY OF ARIZONA

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As members of the Final Examination Committee, we certify that we have read
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CONFIGURATIONS

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Dedicated to
the *fish* in the *streams*
and
the *trees* in the *forests*

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ABSTRACT

A laminar opposed flow, pulverized coal combustion configuration was used to explore the early evolution of light gaseous nitrogenous and hydrocarbon species into the bulk gas phase. Two coals of different ranks were considered. Effects of pyrolysis environment, particle size and heating rates were investigated. Concentration profiles of HCN, NH_3 , NO, CH_4 , C_2H_2 , C_2H_4 and C_2H_6 were measured, under both oxidizing and reducing environments, for three particle sizes, and at high heating rates provided by the hot flue gases of a $\text{CO}/\text{O}_2/\text{Ar}$ flame. Net rates of formation into the bulk gas phase were calculated from the experimental data after correcting for diffusion and convection effects, and were then related to particle time-temperature histories.

Experimental data show that HCN precedes NH_3 and NO for both coals. It is the first light gaseous product of coal nitrogen evolution entering into the bulk gas phase. For low rank coals, either only a small amount of tar nitrogen is released or its subsequent oxidation to light gaseous products is slow. For high rank coals secondary reactions of tars are rapid and lead to substantial levels of nitrogenous species. Nature of nitrogenous species evolving into the bulk gas phase was found to be independent of particle size. Lower heating rates favor increased yields of ammonia.

Evolution of hydrocarbon species from high rank coals occurs via low molecular weight species, whereas low rank coals yield high molecular weight species. Evolution of hydrocarbon species was found to be independent of particle size and heating rates. Evolution of hydrogen occurs during late stages of devolatilization indicating that it is a product of secondary pyrolysis reactions.

A simple kinetic model is proposed to relate rates of formation of nitrogenous species to coal devolatilization kinetics. The latter are similar for three experiments, with fine particles, involving two coals and can be described by a single rate constant

given by $63.8 \exp(-5220/RT)$. Bituminous coal (fines), under oxidizing conditions, shows substantially higher rates, possibly due to energy feedback mechanisms in the vicinity of the particles. Literature values, which originated from solid phase measurements, underpredict the quantities of total XN entering the post flame zone by substantial amounts. Our value, which was derived from gas phase species measurements, yields a better prediction of total nitrogenous species entering the post flame zone, and can be incorporated in engineering models aiming at optimizing of pollutant emissions.

CHAPTER 1

INTRODUCTION

Coal has been a major source of energy for centuries, but lately the availability of cleaner fuels i.e., oil and gas have replaced its dominance. The energy crisis of the seventies brought the availability of large reserves of coal into prime focus. Coal has, since then, been considered a serious contender to cleaner fuels to meet the energy requirements of mankind. Use of coal as a primary source of energy, however, poses serious problems to the environment. Emissions of oxides of sulfur and nitrogen, both of which act as precursors to acid rain, constitute a major threat to marine and plant life. Although oil and gas were once plentiful, the limited supplies of cleaner fuels are, at current consumption rates, destined to be depleted quite rapidly. Therefore, research to understand the principles and mechanisms of coal combustion must continue. The situation is like the story of an old peasant who when asked by a young man "why was he planting new trees when he would not live to eat the fruit?", replied that he had consumed fruit from the trees he never himself planted. It is believed that continuation of work in the area of coal combustion, in the present era of oil glut, will ultimately result in a harvest of information to be reaped later, when cleaner fuels will be scarcer and when very stringent emission regulations will be applied. The wealth of information obtained now will, hopefully, result in improved technology to burn coal a bit cleaner and a bit more efficiently. Hence the work continues and what follows is a tiny part of it.

This chapter presents a summary of the current "state of the science" regarding the understanding of the coal combustion processes. Discussion is limited to very early stages of coal combustion with emphasis on the evolution of nitrogen species. The premise underlying the present research is presented in the next section which is followed by a brief description of the principles of coal pyrolysis and

devolatilization. Finally, the salient features of the experimental configuration are presented and the objectives and tasks of present research are outlined.

SCOPE OF PRESENT RESEARCH

Coal is described as “a chemically and physically heterogeneous mineral or rock consisting principally of carbon, hydrogen and oxygen, with lesser amounts of sulfur and nitrogen. Other constituents are the ash-forming inorganic compounds distributed, in part, as discrete particles of mineral matter throughout the coal substance”. The major use of coal had been and continues to be as an energy source and, as such, the electric utilities are its major consumers. Coal may also be hydrogenated to produce liquid fuels or hydrogasified to produce methane. Present estimates indicate that the existing reserves of coal can meet the energy requirements of mankind for over one hundred years, and thus warrants full exploration of its use as a primary energy source, in an optimal manner. In comparison to oil and gas, coal possesses larger quantities of nitrogen and sulfur which can not be easily removed from coal by pretreatment. Upon combustion, these nitrogen and sulfur compounds are ultimately converted into large quantities of nitrogen oxides (NO_x) and sulfur oxides (SO_x). Sulfur oxides can be removed from the flue gases by using the existing technology e.g., scrubbing. Removal of the oxides of nitrogen, on the other hand, can be more effectively achieved by in-furnace modifications of the combustion configuration, or through the design of new burners. An examples of such a modified combustion configuration is staged combustion (Wendt *et al.*, 1973), where combustion is completed in two stages, the first being fuel rich, followed by a second stage which is fuel lean. The staged combustion configuration, at present, is widely employed and results in lesser NO_x emissions. It has been established that the physical and the chemical processes occurring during very early stages of combustion processes can greatly influence the amounts of pollutants formed. Therefore, an understanding of the physical and chemical mechanisms which lead to the formation of these pollutants and translation of the knowledge, thus gained, into improved techniques of coal combustion provides the driving force behind this

investigation. The focus of this work is, therefore, restricted to the evolution and formation of nitrogenous (XN) species, in the *bulk* gas phase, during early stages of coal combustion.

REGIMES OF COAL COMBUSTION

Combustion of coal is a complex physicochemical process and has been the focus of extensive research over the past few decades. A major problem towards the formulation of a unified theory describing the behavior of coal during combustion is that coals vary greatly in their composition. Composition characteristics of coal can have significant effects on the physical behavior of coal upon combustion. In practice, coal combustion involves overlapping physical and chemical processes including changes in particle morphology, devolatilization, ignition of volatiles, reactions in the gas phase, and char burnout. These processes are too complex to be modeled as a whole and therefore simplified models had been proposed. One of these models is the classic model of coal combustion which assumes the following sequence of events (Smoot, 1984):

1. devolatilization: on entering the furnace the coal particles are heated rapidly and drive off the volatiles;
2. volatile oxidation during which the volatiles react (burn) either independently of the coal particle, or in its immediate neighborhood; and
3. char (defined as the residue after devolatilization) burnout.

Figure 1.1 shows the regimes involved in the combustion of a coal particle. Although, these regimes overlap and can not really be sequentially separated, this model does provide an engineering framework to allow understanding of the conversion processes involved in coal combustion. The time scales associated with the sequence of events proposed by the classic model are taken to be as follows:

1. devolatilization: up to 150 milliseconds;
2. volatile oxidation: up to 500 milliseconds; and
3. char burnout: up to two seconds.

Figure 1.1 Life Cycle of Coal Particles in a Pulverized Coal Flame.

Studies have shown that the processes which occur during the first few milliseconds of pulverized coal combustion are very complex and can be best understood if decoupled from the rate limiting char burnout process (Bose, 1989; Smoot, 1984).

DEVOLATILIZATION AND NITROGEN EVOLUTION

In practical combustion systems, coal particles are subjected to thermal decomposition under high heating rates which are known to be of the order of 10^4 to 10^6 K/s. During the initial stages, coal particles undergo devolatilization i.e., drive off volatiles, which is the most significant step in all coal utilization processes. This is due to the fact that the products of rapid devolatilization, and not the parent coal itself, react in the conversion device. The understanding of the thermal decomposition behavior of coal during rapid devolatilization is essentially important as it may control:

- the rate at which combustion proceeds;
- the rate at which oxygen is consumed; and
- the rate and form of nitrogen, sulfur and other trace species and the mechanisms governing the fate of these species.

The quantities of tars and light gases (which are the products of devolatilization) evolved depend upon the coal rank, maceral composition, ultimate temperature attained by the coal particle and the system pressure (Bengtsson, 1986). The composition of species evolved depends upon the final temperature, system pressure and time-temperature history of the stock. Smoot (1985) listed the critical issues which must be addressed to fully understand the devolatilization process and are given below:

- what are the physical processes by which volatiles are evolved and what influences these processes?
- what is the mass of volatiles evolved and what fraction of coal nitrogen is devolatilized?
- what is the composition of volatiles, particularly of the nitrogenous species?
- what are the rates of hydrocarbon, carbon monoxide and nitrogen evolution?

- how do the volatiles react and what is their role in ignition?

The next sections briefly address the issues more relevant to the present work.

Physical Behavior

The physical behavior of coal during early stages of devolatilization is critical in determining the species evolved, the form of char produced and the rate of devolatilization (Wendt, 1980). These mechanisms are governed by the pyrolysis conditions and, in particular, by coal structure. Bituminous and sub-bituminous coals exhibit plasticity as they heatup. These coals first become soft and then almost liquid as volatiles or gases produced within the particle escape from the surface as bubbles or jets. These coals do not maintain shape and show considerable swelling (Solomon *et al.*, 1982; Seeker *et al.*, 1981). For lower rank coals, mainly lignites, volatiles and gases escape through fissures, particle shape is maintained and swelling does not occur (Wendt, 1980). Plasticity behavior of coals depend upon the maceral composition and heating rate. The mechanisms by which plasticity occurs are, as yet, not well understood and this remains an active area in pulverized coal combustion research.

Mass Loss

The mass of volatiles evolved from coal, under practical combustion conditions, depends strongly upon particle size, coal rank (Annamalai and Gannon, 1981, see Morrison, 1986) and on final temperature (Wendt, 1980). Higher temperatures and lower rank coals yield larger quantities of volatiles. The heating rate may also influence the amounts of volatiles evolved but its effect, as yet, has not been fully quantified. Annamalai and Gannon (1981, see Morrison, 1986) observed the volatile yield to be independent of heating rate. Niksa *et al.* (1985) observed higher yields with increased heating rates up to 10,000 K/s with no effect above heating rates of 10,000 K/s. Particle size governs the transport limitations within the particles and, thus, increased particle size reduces the yield of volatiles (Suuberg *et al.*, 1979).

Pyrolysis conditions also influence the asymptotic volatile yields and the mass of volatiles evolved. Due to condensation and repolymerization of volatiles within the particle pores, the mass of volatiles evolved can be higher than the volatile matter contents of the coal. Essenhight (1981) measured the ' Q ' factor, defined as the ratio of actual to apparent (ASTM volatile contents) weight loss, to be within the range of 1.5 to 2.0. The ' Q ' factor is a variable quantity used to obtain an estimate of the true volatile matter from the ASTM measurements. The capture factor, which is the reciprocal of the ' Q ' factor is considered to account for the following three processes:

1. internal pore capture;
2. external surface capture; and
3. internal capture at such slow heating rates that it allows fundamental re-ordering of recrystallization of coal structure that binds material which would otherwise be lost at faster heating rates.

Major Species

A knowledge of the individual volatile species evolved can greatly enhance the understanding of the fundamental processes involved in combustion and has been the focus of numerous experimental studies. Suuberg *et al.* (1979) conducted experiments on a Montana lignite and a Pittsburgh bituminous coal under inert atmosphere. Their observations showed:

- Oxygenated species (CO , CO_2 , and H_2O) dominate the devolatilization products for lignites.
- Pyrolysis behavior of bituminous coal is dominated by hydrocarbon species. Heavy tars, having an empirical formula of $\text{CH}_{1.1}\text{O}_{0.08}\text{N}_{0.01}$ and a molecular weight of more than 300 are the major product.
- For lignite, several products showed a stepwise behavior with peak particle temperature, which indicates that some species may be evolved from more than one structure or chemical environment within the coal or via different mechanistic pathways.

- Bituminous coal did not show any stepwise behavior but four phases were distinguished as follows:

1. Low temperature removal of surface moisture.
2. Evolution of pyrolytically formed water (300 to 400 °C).
3. A broad phase involving softening of coal during which evolution of tars and hydrogen occurs (400 to 900 °C).
4. Evolution of Carbon monoxide and hydrogen (above 900 °C).

As weaker bonds are cleaved at lower temperatures resulting in light permanent gases, Wendt (1980) took the view that major portion of early volatiles is comprised of light permanent gases whereas the heavier components constitute the late volatiles. Findings of Suuberg *et al.* (1979) showed that the reverse trend is true and tar and hydrocarbons are evolved at temperatures lower than those at which light gases are observed. These trends were supported by the work of Freihaut *et al.* (1982) who determined that:

- For bituminous coals, formation and evolution of primary and secondary light gases is preceded by the formation and evolution of tars.
- In the case of lignites and sub-bituminous coals, evolution of light gases and formation and evolution of tars overlap and are not sequentially separable.

Work of other researchers (Solomon *et al.*, 1982; Solomon and Hamblen, 1983, 1985) showed similar trends, with the only exception being that stepwise behavior of pyrolysis products for lignite coals was not observed.

For bituminous coals, tars are the major volatile species which play a critical role in ignition, volatile burning and soot formation. Freihaut and coworkers (1982) conducted a parametric investigation of tar release during devolatilization and found that:

- Tar yield is greatly influenced by the coal rank and more correctly depends on the aromaticity of the parent coal.
- The aromaticity of parent coal dictates the thermal stability of the tars produced with tars from more aromatic coals being more stable.

- Tar formation also depends on heating rate and decreases with higher heating rates.

Solomon and Colket (1979), and Solomon and Hamblen (1985) observed the similarity, in elemental composition, of the organic structure of tars to that of parent coal. They suggested that tar is a primary decomposition product which undergoes little secondary reactions and postulated that the rates of evolution of volatiles and the nature of species evolved can be predicted from a detailed knowledge of the chemistry (functional groups) of coal.

Recently, Seery and coworkers (1989) conducted a detailed experimental study of tar evolution during devolatilization and proposed a kinetic model to predict the evolution of tar based upon the structure of the parent coal. The significant findings of their work are as follows:

1. For a specific set of heating conditions and the extent of tar evolution, the similarity of the “primary”, immediately quenched tars relative to the “average” parent coal depend on the coal rank. The lower rank coals yield tars which are more dissimilar to the parent coal.
2. For a given set of heating conditions and a particular coal type, the evolution of primary tars follow a definite sequence. More hydrogen rich tars, which are lower in molecular weights, are produced earlier in tar evolution process.
3. For a particular coal type, the yield, physical and chemical characteristics, and rate of particle mass loss as primary tars significantly varies with heating rate and final particle temperature attained.
4. The transient heat flux to the particle plays an important role in determining the molecular weight characteristics of the integrated tar mass.
5. Particle size and ambient pressure have second order effects on the yields or chemical characteristics of tars, provided their effect on heating rate is taken into account.
6. Different heating conditions lead to very different intraparticle chemistry and tar desorption processes and have an appreciable effect on the nature and yields of tars.

7. Secondary pyrolysis reactions of the primary tars, occurring in the gas phase, initiate around 600 °C. Between 600 and 800 °C mainly methane, carbon monoxide, carbon dioxide, water and ethylene are formed. At temperatures above 700 °C, secondary "gas phase" pyrolysis reactions result in the formation of acetylene, carbon monoxide, ethylene, benzene and hydrogen cyanide.

Nitrogenous Species

In pulverized coal flames, fuel nitrogen is distributed between the volatile and char fractions. A major portion of chemically bound nitrogen is evolved during devolatilization, approximately within the first 150 milliseconds, as nitrogen volatiles (tars and light gases) and, cocurrently, undergoes secondary decomposition in gas phase to form HCN, NH_3 , NO and N_2 . For some coals, early evolution of fuel nitrogen may be primarily as light gases (HCN and NH_3). Char nitrogen is the portion associated with the solid residue, either as a pyrolysis product of the tars or as the original coal char, which continues to react, heterogeneously, yielding HCN and NO.

Presently, there is no general agreement regarding the nature of nitrogenous species as they evolve into the *bulk* gas phase, thereby inhibiting a better understanding of formation of nitrogen oxides, from pulverized coal combustion. Wendt (1980) stated that most of nitrogen is evolved as tars. Freihaut *et al.* (1982) presented data showing that distribution of nitrogen in the tar, char and light gases depend upon the chemical characteristics of coal. Their research concluded that the primary nitrogen species are evolved as tar products from bituminous coal and as HCN from lignite. Chen and coworkers (1982), under the reducing conditions of staged combustion, found HCN and NH_3 to dominate the nitrogenous products from bituminous and lignites respectively. Peck *et al.* (1984) studied the conversion kinetics of fuel nitrogen to NO_x , for bituminous coal particles, in a flat flame burner. Their results indicated HCN as the primary volatile nitrogenous species accompanied by small quantities of NH_3 produced in fuel rich, high temperature flames. It is pointed out that all their data was above temperatures of 1500 K, well

beyond the mass loss conditions, and hence the products observed might be the outcome of secondary pyrolysis. Bose *et al.* (1988) reported that, in the bulk gas phase, HCN precedes NH_3 even for lignite coals.

The mechanisms involved in the formation of fuel NO are quite complex as the forms of chemically bound nitrogen may vary among coal stocks. Singer (1983) cited that pyridine, pyrrole and primary aromatic amine ($\text{C}_6\text{H}_5\text{NH}_2$) as the major structures of coal nitrogen. A complex chemical reaction network involving all the evolved species leads to the formation of NO. The processes involved in the formation of NO from chemically bound nitrogen are depicted in Figure 1.2.

The relative contribution of these two sources i.e., volatile and char nitrogen, towards NO_x emissions has been addressed by a number of researchers. Pershing and Wendt (1979) showed that about fifty percent of coal nitrogen is devolatilized and readily converted to NO_x , whereas conversion of char nitrogen to NO_x proceeds quite slowly and continues over much longer residence times. They observed that conversion of volatile nitrogen to NO_x could be readily controlled by changing the mixing characteristics of the system, while conversion of char nitrogen to NO_x was independent of mixing effects. Pohl and Sarofim (1977) reported that under fuel-lean conditions, at a furnace temperature of 1500 K, up to eighty percent of NO_x was formed by oxidation of volatile nitrogen. They observed that increasing equivalence ratio (defined as $(\text{fuel/oxidant})_{\text{actual}}/(\text{fuel/oxidant})_{\text{theoretical}}$) reduces the conversion efficiency of volatile nitrogen to NO_x . Therefore, understanding of the factors which influence the evolution and subsequent reactions of volatile nitrogen is essential to predict the fate of nitrogenous species in pulverized coal combustion. Studies have shown that fuel NO is insensitive to temperature but is greatly influenced by the petrographical characteristics of the coal.

SO_2 , which is also a pollutant product resulting from coal combustion, may also influence the emissions of NO_x . Wendt and others (1979) investigated the effect of fuel sulfur on fuel NO in fuel rich flames and found both enhancement and inhibition. Presently a mechanism accounting for these opposing effects on the NO_x yield does not exist.

Figure 1.2 Processes Leading to Formation of NO from Chemically Bound Nitrogen in Coal. (From Kennedy *et al*).

Recently several researchers (Bose, 1989; Dannecker, 1985) studied the fate of nitrogenous species in the post flame zone, after substantial devolatilization has occurred. Their data showed large quantities of XN species entering the post flame zone and led to models describing the fate of nitrogenous species in the post flame regime. These models could be further exploited if the distribution of nitrogenous species entering the post flame zone could be predicted. The devolatilization phase, therefore, is of critical significance for understanding of the formation of NO_x in coal combustion process, and is the subject of this work. Findings are expected to resolve the discrepancies regarding the nature of XN species, and lead to the development of integrated engineering models describing the overall process of pulverized coal combustion.

DEVOLATILIZATION KINETICS

As discussed in the previous section, heating rate plays a very significant role during coal devolatilization. Heat transfer effects within the particle associated with devolatilization are:

1. Devolatilization is an endothermic process and consume part of the energy available to the particle.
2. As devolatilization proceeds, thermal inertia of particle changes and heating rate also change.
3. Physical characteristics of the particle (particle density, particle size) change, which result in modified particle dynamics and ultimately effects the heating rate.

Above considerations make incorporation of mass loss behavior an integral part of coal combustion modeling. The simplest method of predicting the devolatilization rate and quantity of volatiles evolved is by a single reaction process postulated by Badzioch and Hawksley (1970). According to this model the devolatilization rate is proportional to the amount of volatile matter still remaining in the coal:

$$\frac{dV}{dt} = k(V^* - V)$$

the rate coefficient is given by

$$k = k_0 \exp(-E/RT)$$

V^* is the ultimate volatile matter yield obtained by the correlation

$$V^* = Q(1 - v_c)v_p$$

Q is the ‘ Q ’ factor discussed in the previous section, v_p is the ASTM volatile matter content of coal and v_c is a coal specific empirical constant. The single reaction model satisfactorily describes the pyrolysis trends, but the effect of heating rate is not adequately predicted. It requires estimation of four coal specific parameters and hence does not provide universal applicability.

Kobayashi *et al.* (1977) and Ubhayakar *et al.* (1977) proposed that devolatilization could be described by two, competing, first order irreversible reactions:

with the rate equations

$$\begin{aligned} \frac{dC}{dt} &= -(k_1 + k_2) C \\ \frac{dV}{dt} &= \frac{dV_1 + dV_2}{dt} = (\alpha_1 k_1 + \alpha_2 k_2) C. \end{aligned}$$

k_1 and k_2 are Arrhenius type rate coefficients given by $k_i = A_i \exp(-E_i/RT)$ with $E_1 < E_2$. This model adequately accounts for the heating rate and final temperature on the extent and rate of devolatilization. The second reaction describes the variation in volatile yield with temperature. α_i are the stoichiometric parameters, α_1 is estimated as the fraction of coal devolatilized during proximate analysis, and α_2 being the fraction that can be devolatilized at high temperatures, which is often

near unity. This model remarkably well predicted the mass loss behavior of a lignite and a bituminous coal studied by Kobayashi *et al.* and satisfactorily correlated the data of Badzioch and Hawksley (1970), and Kimber and Gray (1976). However, this model, too, is not of universal utility as it requires estimation of five coal specific parameters ($\alpha_2, E_1, E_2, A_1, A_2$).

A more elaborate model, proposed by Anthony *et al.* (1975), postulates that pyrolysis occurs through an infinite number of parallel reactions and assumes a continuous Gaussian distribution of activation energies along with a common value of frequency factor, such that

$$\frac{V^* - V}{V^*} = \int_0^\infty \exp\left[-\left(\int_0^t k dt\right)\right] f(E) dE$$

with

$$f(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(\frac{-(E - E_0)^2}{2\sigma^2}\right).$$

This model, like the previous two models, suffers from the drawback that four coal specific parameters (σ, k, E_0 , and V^*) must be estimated. The two reaction model is superior to the other ones as it also predicts the composition of volatile gaseous products (by mass balance of known functional group composition of coal) and the residue chars along with the rate of volatile evolution.

Evolution of Coal Nitrogen

Although, formation of fuel NO is insensitive to the temperatures encountered in practical situations, the amount of fuel nitrogen which is driven off during devolatilization strongly depends upon the pyrolysis temperature. Wendt (1980) presented data showing that all chemically bound nitrogen in the coal may devolatilize at pyrolysis temperatures higher than 1800 K. Therefore, at sufficiently high pyrolysis temperatures char may not contribute to the formation of NO. Harding *et al.* (1982) correlated the data for ten coals from different studies and determined that rate of evolution of nitrogen and rate of conversion of coal were approximately the same. Pohl and Sarofim (1977) showed that nitrogen evolution

paralleled the evolution of total volatiles. However, they did not observe the release of any nitrogen until about fifteen percent of devolatilization had taken place. Their pyrolysis data for lignites and bituminous yielded a nitrogen evolution rate constant of $9.3 \times 10^3 \exp(-22,700/RT) \text{ sec}^{-1}$, assuming a pseudo-first order Arrhenius expression. Wendt (1980) used the data on nineteen coals and two coal chars and proposed the following correlation:

$$L(T) = \frac{0.4861 \times VM + 3545.0 \exp(-20,460/RT)}{1 + 3545.0 \exp(-20,460/RT)}$$

where $L(T)$ is the mass fraction of nitrogen evolved at temperature T , VM is the proximate volatile matter, and R is the universal gas constant.

The author reported that for a Pittsburgh coal, nitrogen loss rate was greater than the rate of total mass loss, which indicated increased nitrogen contents of the volatiles at higher pyrolysis temperature. The author suggested that conversion of nitrogenous compounds to NO decreases with increasing nitrogen contents in the gas phase and may explain why fuel NO, from pulverized coal flames, exhibits such a weak temperature dependence. It was further noted that the evolution of nitrogen continues when the char is exposed to temperatures greater than the one at which it was formed, suggesting that nitrogen remaining in the char is not a product of pyrolysis but is the undevolatilized portion of the original coal nitrogen.

REACTIONS OF VOLATILES

The devolatilization of coal results in a variety of products which include tars, hydrocarbon liquids, hydrocarbon gases, CO_2 , CO , H_2 , H_2O , HCN etc. Several hundred hydrocarbon compounds, mostly aromatic, have been identified in the tars produced during devolatilization (McNeil, 1981). These products react in the vicinity of the particle, with oxygen or oxygenated species resulting in higher temperatures and oxygen depletion. The overall reaction network is very complex and is important towards the control of nitrogen oxides, formation of soot, stability of coal flames and ignition of char. An outline of important steps influencing the

subsequent conversion of volatiles is given below, which is followed by a discussion of volatile NO reaction pathways.

Smoot and Smith (1985) identified the major aspects of this process which are reproduced below:

1. release of volatile from coal;
2. condensation and repolymerization of tars in char pores;
3. evolution of hydrocarbon cloud through small pores from the moving particle;
4. cracking of hydrocarbon to lower molecular weight hydrocarbons with local production of soot;
5. condensation of gaseous hydrocarbons and agglomeration of soot particles;
6. macromixing of devolatilizing coal particles with air;
7. micromixing of volatiles cloud and oxygen;
8. oxidation of gaseous species to combustion products;
9. production of nitrogen oxides and sulfur oxides by reactions of devolatilized products and oxygen; and
10. heat transfer from the reacting fluid to the char particles.

Nitrogen containing tar compounds are a major portion of volatile products which ultimately lead to the formation of nitric oxide and hence above listed aspects are also important to understand pollutant formation from coal nitrogen. In practical flames, where temperatures are very high, seventy percent or more of reactive coal mass may burn by these processes. Several authors (Singer, 1983; Thurgood and Smoot, 1979; Engleman, 1976) have proposed gas phase reaction mechanisms involving individual species such as CO, H₂, CH₄, H₂C₂, HCN etc. but they also pointed out that the mixture of species formed under combustion conditions may burn differently than the individual species. In addition, char particles may exhibit catalytic activity in transformation of the volatiles.

At high temperature volatiles reaction process is very rapid and may be neglected in overall char burnout rates. However, Smoot and Smith (1985) reported that oxidation rates of chain hydrocarbons and particularly of HCN are low at

temperatures of practical flames, which may have significant implications for NO emissions.

In summary, very little is known about the kinetic mechanisms involving pyrolysis and reactions of volatile products and considerable work needs to be done before this facet of pulverized coal combustion could be adequately modeled.

Reaction Pathways to Volatile NO Formation

Volatile NO i.e., nitric oxide resulting from the reactions of volatile nitrogen, is the major source of NO_x emissions from the combustion of coal. A detailed kinetic mechanism for the reactions of gas phase volatile nitrogen, presently, is lacking as the exact composition of the volatile nitrogen is not well established. However development is underway in resolving the uncertainties associated with this critical stage of coal combustion. Existing knowledge regarding the interconversion reactions involving gas phase nitrogenous species, stems from the contributions of many investigators (Fenimore, 1976, 1979; Haynes, 1977; Haynes *et al.*, 1975; Axworthy, 1975; Fenimore *et al.*, 1961, 1981; and Miller *et al.*, 1983, 1984, 1987). A global model for the formation of volatile NO has been proposed and is reproduced (from Kennedy *et al.*, 1982) in Figure 1.3.

According to this global model, HCN is the dominant product of primary pyrolysis i.e., conversion of fuel nitrogen to HCN is extremely rapid and occurs within the flame zone. A portion of HCN undergoes oxidation reactions to form a CN pool. Three additional nitrogenous reactant system follow the formation of HCN: viz, NH pool, NO, and N₂. It should be noted that the formation of N₂ requires the existence of NO. In the CN pool, HCN tends to equilibrate with CN via the reaction

Possible reaction leading to the depletion of CN pool and the formation of NH pool, which also tends towards internal equilibration specially towards the higher order species, may include the following:

Figure 1.3 A Global Reaction Model for Formation of Volatile NO.
(From Kennedy *et al*).

Depletion of NH pool and formation of NO and N₂ may occur via the following probable reactions:

N₂ reacts with the hydrocarbon species by prompt NO reaction pathways. Hydrocarbon species may also react with NO to form HCN by the following route:

In summary, during very early stages of coal combustion, evolution of coal nitrogen occurs as a multitude of organic compounds, which undergo simultaneous conversion in the gas phase leading to various nitrogen pollutants. The coupling of nitrogen evolution and the interconversion reactions controlling the fate of these species is very complex and can be viewed as a sequence of elementary reactions. Present-day knowledge of this complex chemical network is not adequate and an improved understanding of this phenomena may greatly enhance the efficient utilization of large coal reserves. This work, hence, attempts to address the unresolved discrepancies regarding the nature and rates of evolution of various nitrogen species which enter the post flame zones. The resulting information, it is hoped, will be useful for integration with the existing knowledge-base and could be incorporated in engineering models aiming at combustion modifications for minimal pollutant emissions.

EXPERIMENTAL CONFIGURATIONS

Coal pyrolysis has been studied in various experimental configuration which fall under two categories:

1. Captive sample technique.
2. Entrained flow technique.

Both the techniques provide reasonable control over the variables of critical importance to the experimentalist but do suffer from few drawbacks.

Captive Sample Technique

In the captive sample configuration, a fixed amount of sample is placed in a chamber and heated either directly or indirectly e.g., electrically or by a laser beam. Details of this system are discussed in the monogram by Gavalas (1982). Heat flux to the particles and chamber environment can be precisely controlled and monitored and thus is amenable to extensive kinetic analysis under conditions of practical interest. The disadvantages of the system are, i) solid-sample interactions may not be easily accounted for; and ii) at high heating rates the so called "wall effects" (i.e., additional thermal cracking of the volatiles products when they come in contact with the chamber walls) may make the final product composition doubtful. In addition, captive sample technique does not replicate the conditions in industrial boilers and furnaces.

Entrained Flow Technique

The entrained flow technique more closely simulates the conditions encountered in industrial processes. In this setup, the coal particles are injected into a heated zone where they are subjected to pyrolysis. The temperature variation in the heated zone, usually a drop tube, is designed to achieve a desired heating rate, although partly influenced by the aerodynamics of the system. Another variation is that the particles are injected in the center of a flowing mass of plasma heated gas. Sampling is accomplished by placing a moveable probe along the flow axis and

collecting the particle-laden gas. Samples are usually quenched, either with water or helium, to prevent any subsequent reactions from occurring. In this configuration, sampling is done away from the solid boundaries which minimizes the wall effects. Disadvantages of this system are that probe may change the flow field and may act as a heat sink, therefore, these effects must be properly accounted for in determination of particles time-temperature histories. Furthermore, pyrolysis products may condense on the probe wall making exact weight loss measurements difficult.

A modification of entrained flow reactor is the "opposed flow configuration". This configuration was originally designed to investigate the chemistry and dynamics of gaseous flames. Experiments for the present work are conducted in this configuration and its salient features are discussed in the next section.

Opposed Flow Combustion Configurations

In the opposed flow configuration, two counter flowing streams impinge upon each other and provide a reaction space free of any physical boundary, thus eliminating any wall effects. Gaseous flames have been extensively studied in this configuration to either determine the chemistry involved or to validate the values of kinetic parameters. Hahn (1979) used this configuration to calculate the net rates of formation of species present in a diffusion flame. More recently Corley (1990) studied the behavior of nitrogenous species in a $\text{CO}/\text{H}_2/\text{N}_2$ and O_2/N_2 diffusion flame which could be of utility to understand the gas phase kinetics of nitrogenous species involved in coal flames. Wendt *et al.* (1990) studied the effect of superequilibrium concentration of radicals on NO destruction in a $\text{CH}_4/\text{O}_2/\text{N}_2$ diffusion flame.

Applicability of the opposed flow configuration to two phase system was first demonstrated by Graves (1981), who investigated the flammability characteristics of a coal diffusion flame. Graves and Wendt (1982) theoretically showed that the opposed flow configuration is one dimensional in species concentrations, temperature and particle number density whereas gas and particle phase velocities and pressure distribution are two dimensional. One dimensionality of temperature and species concentration was confirmed by their experiments.

Kram (1984) studied the physical and chemical behavior of coal particles during pyrolysis in flue gases from a $\text{CH}_4/\text{O}_2/\text{N}_2$ premixed flame. Focus of his work was on morphological changes in coal particle under high heating rates. Sampling was done with a 1/4 inch O.D. probe and the species concentration data provided only a qualitative picture of early coal pyrolysis. Only major species were measured in his experiments and, due to the use of CH_4 as fuel, precise contribution from coal could not be ascertained. McCaslin (1985) used a hydrogen flame instead, and focused on the evolution of carbonaceous species as a function of both pyrolysis environment and coal rank. Kram (1984) and McCaslin (1985) reported poor spatial resolution of species concentrations, which could be attributed to high flame velocity fuels used in their experiments leading to compressed devolatilization space and causing steep concentration gradients. Wendt and coworkers (1986) attempted to evaluate the kinetic parameters for the evolution of carbonaceous species but their values were much lower than those reported in the literature.

In summary, the opposed flow system may be a useful experimental configuration provided the difficulties reported above could be reasonably dealt with. This constitute one of the task of present work. Finally the pluses and minuses of opposed flow combustion configuration are listed below:

- + Opposed flow configuration is mathematically elegant and is amenable to detailed modeling.
- + Temperature, species concentration and particle number density are one dimensional making data analysis straight forward.
- + Pyrolysis environment can be easily changed by selection of appropriate fuels and stoichiometric ratio.
- + Various flame configurations (premixed, diffusion and hybrid) can be easily attained and their specific attributes may be fully exploited.
- + Wall effects are practically nonexistent.
- The biggest disadvantage of opposed flow configuration is that the operating conditions can not be independently controlled and are governed by the flame

velocity of the fuel/oxidant mixture. This may critically affect the heating rate and residence time of coal particles.

- Intrusive probe sampling effects the aerodynamics of the system and may act as a heat sink, thus introducing little uncertainty in the data.

FOCUS OF THIS WORK

The overall objectives of this work are to understand the physical and chemical mechanisms which influence the evolution of fuel nitrogen during early stages of coal combustion. In addition, to determine the rates of formation of nitrogenous species in the *bulk* gas phase and estimate the values of kinetic parameters for coal nitrogen evolution. These parameters can be incorporated in engineering models aiming at modifications of combustion configurations for lower pollutant emissions.

The picture which emerges from the state-of-the-art review, clearly shows that there is a general consensus regarding the complexity of processes which occur during very short time scales of coal conversion processes. The variables which influence these processes have been identified but their individual and combined effects have not, yet, been fully quantified. Present day knowledge of coal devolatilization is only phenomenological with little understanding of coal nitrogen speciation mechanisms. However, recent modeling efforts to predict the fate of nitrogenous species in the post flame zone are quite promising and have led to the modifications of combustion configurations which have resulted in reduced NO_x emissions. The nature and quantities of the species which enter the post flame zone, if adequately predicted, could enhance the effectiveness of existing models or may result in improved models leading to more efficient burning of coals.

The focus of this work is, therefore, on both speciation and the rates of evolution of nitrogenous species into the *bulk* gas phase. The following issues are specifically addressed:

1. Upon devolatilization of coal, what are the primary and secondary nitrogenous species appearing in the bulk gas phase?
2. How does this depend on the coal rank and devolatilization environment?

3. What are the effects of particle size and heating rate?
4. What are the effects of coal rank and pyrolysis environment on the absolute and relative rates of evolution of nitrogenous species?
5. Can rate coefficient for coal nitrogen evolution be determined from the measurements of nitrogen species in the bulk gas phase.
6. What are the important kinetic pathways effecting the composition of resulting nitrogenous species during short time scales?

Approach to this Work

The approach taken to address the issues outlined in the previous section is both experimental and theoretical, encompassing development of an experimental plan, data acquisition, data reduction and analysis, and finally the formulation of kinetic mechanisms to determine the rate coefficient(s) for early evolution of coal nitrogen. The specific tasks to be undertaken for this work are as follows:

- Task 1. To reconfigure the opposed flow combustion facility, and design and setup of a sampling system for study of early evolution of coal nitrogen.
- Task 2. To identify a gaseous mixture for the premixed flame, which has a low flame velocity and yields high temperatures. A low flame velocity fuel is required to resolve the spatial resolution problem and to provide a particle time-temperature history more conducive to nitrogen evolution. Additionally, the mixture should not pose any safety problems and be economical to use.
- Task 3. To obtain gas flame temperature measurements, in the opposed flow system, with the selected fuel/oxidant mixture to validate the achievement of high temperatures adequate for nitrogen evolution.
- Task 4. To study the coal pyrolysis behavior under different flame configurations i.e., premixed, diffusion and hybrid, and to determine the optimal configuration.
- Task 5. To investigate the effects of operating variables on nitrogen devolatilization and obtain a mix of optimal operating conditions for the quantitative runs.

- Task 6. To conduct quantitative runs with coals of different ranks under both oxidizing and reducing environments and to characterize the nitrogenous species evolved.
- Task 7. To study the effects of particle size and heating rate on the evolution of nitrogenous species.
- Task 8. To develop a model to calculate the rates of formation of chemical species into the *bulk* gas phase, and relate those to particle time-temperature histories.
- Task 9. To propose elaborate kinetic mechanism(s) and evaluate the rate coefficient(s) for the early evolution of coal nitrogen.

The strategy outlined above is aimed at obtaining information on the nature and rates of evolution of nitrogen species during short time scales. A unique approach taken in this work is that the evaluation of rate coefficients for nitrogen evolution is based upon the experimental measurements of nitrogenous species in the *bulk* gas phase, as opposed to the previous approaches where nitrogen evolution was studied in conjunction with mass loss behavior of coal particles. It is hoped that the kinetic parameters evaluated using this new approach will be more useful and could be incorporated in engineering models.

CHAPTER 2

EXPERIMENTAL FACILITIES AND DATA ACQUISITION PROCEDURES

This chapter describes the experimental apparatus and the data acquisition procedures employed in this study. The main part of the experimental facilities is the opposed flow combustor where coal particles pyrolyze under the conditions of practical interest i.e., high temperatures and rapid heating. The supporting systems consist of sample analysis train and tar extraction setup. Details of these facilities are given in the following sections.

OPPOSED FLOW COMBUSTOR

The opposed flow combustor consists of two co-axial cylindrical burners enclosed in a chamber (See Fig. 2.1). The enclosing chamber provides access to the flame through a sampling slot and is equipped with a glass window to determine the probe position and to monitor the flame. The chamber is connected to the exhaust system by a pipe through which the flue gases flow out of the enclosure. The chamber is operated under slight vacuum (about 6-12 mm of water) which can be controlled by the flappers in the exhaust pipe such that no visual disturbance to the flame is observed. A small window in the rear side of the enclosure is sealed with multiple layers of heavy duty aluminum foil to safeguard against excessive pressure build up.

Coal is fed to the upper burner, which practically serves as an injection tube, from a screw feeder driven by a 1/8 HP induction motor. The transport gas entrains the coal particles and injects them into an expanding cylindrical cone to ensure uniform distribution of particles in the gas. At the end of the aluminum

Figure 2.1 Experimental Setup

cone the gas-particle stream passes through a 7.5 cm aluminum honeycomb matrix with 3 mm holes. The honeycomb matrix serves as a crude flow laminarizer and feeds the suspension to the pyrolysis space.

The lower burner serves as a true flat-flame burner. The gaseous mixture is discharged into the lower portion of the burner through a perforated gas injection port and passes through two porous stainless steel plates ensuring extremely well mixed stream. A thermocouple, placed between the two sintered disks, is wired into a Chromalox temperature controller which operates a solenoid valve. The solenoid valve shuts-off the supply of the fuel stream to the burner, if the temperature between the sintered disks exceeds a preset value (around 300 °C). This safety mechanism protects the system from flashback through the feed lines.

Gases to the system are metered by appropriately sized Matheson 600 series rotameters. Plumbing was done in a way that various flame configurations are easily attainable. Mixing takes place within the lines as well as in the burners. Emergency cut-off valves are provided to interrupt the gas supply to the system, if such a need arises. Both the burners are water cooled to protect them from high temperatures. Cooling coils for the upper burner extend to 50 cm to make sure that the coal particles do not undergo any pyrolysis within the burner. Figure 2.1 shows the experimental setup of the opposed flow combustion system. Detailed specifications of the system are provided by Graves (1981) and McCaslin (1985).

FLAME CONFIGURATIONS

The pyrolysis of coal particles occurs in the space between the two burners. Various flame configurations can be realized in this system by appropriately directing the gas streams to either upper or the lower burner. In the first configuration, the coal particles, entrained into the carrier gas, are injected into this space where they impinge upon the hot rising flue gases from the premixed flame stabilized at the lower burner (Fig. 2.2). Heat transfer effects between the two streams and the coal particles cause the coal particles to pyrolyze. This flow arrangement will be

Figure 2.2 Schematic of Opposed Flow Combustion Configuration.

called the “**opposed flow premixed flame configuration**”. Figure 2.3 shows a typical coal flame in the opposed flow premixed flame configuration.

In the second configuration, the coal particles are transported with the fuel and inert gas mixture through the upper burner. The diluted oxidant stream enters the system through the lower burner. A diffusion flame is realized between the two burners where the oxidant and coal laden fuel streams meet. The possible advantage of this setup is that the plane of peak temperature moves closer to the upper burner and the coal particles are exposed to higher temperatures. However, a major drawback of this configuration is that this setup poses some stability problems at flame interface. This flow arrangement will be called the “**opposed flow diffusion flame configuration**”. A picture of a typical coal diffusion flame, without any fuel in the carrier stream, in this system is shown in Fig. 2.4.

The final flow arrangement, hereafter to be known as the “**opposed flow hybrid flame configuration**” combines the features of the two configurations described above. A secondary diffusion flame is stabilized against the oxygen containing flue gas from a primary premixed flame at the lower burner. By controlling the concentration of oxygen in the flue gas pyrolysis under reducing environment is possible, while at the same time shifting the high temperature plateau, resulting from the modified configuration, closer to the upper burner. This configuration does not pose any stability problems. The picture of a gaseous opposed flow hybrid flame is shown in Figure 2.5.

SAMPLING AND ANALYSIS SYSTEM

The sampling and analysis system consists of the following apparatus and instruments:

1. A water-quenched probe for extracting in-situ samples of pyrolysis products.
2. On-line instruments for continuous monitoring of O_2 , CO, CO_2 and NO as follows:
 - O_2 : Beckman Paramagnetic Analyzer, Model F3
 - CO and CO_2 : Beckman Infrared Analyzers, Model 864

Figure 2.3 A Coal Flame in the Opposed Flow Premixed Flame Configuration.

Figure 2.4 A Gaseous Diffusion Flame in the Opposed Flow Combustion Configuration.

Figure 2.5 A Gaseous Hybrid Flame in the Opposed Flow Combustion Configuration.

- NO: Thermo Electron Model 10 AR Chemiluminescence NO/NO_x analyzer with stainless steel convertor.
- 3. An off-line gas chromatograph equipped with seven molecular sieve columns, and two (a thermal conductivity and a flame ionization) detectors.
- 4. Orion gas and ion specific electrodes and 901 ion analyzer for NH₃ and HCN analysis.
- 5. A Soxhlet extraction apparatus to separate the tars and char.
- 6. A type R platinum and platinum-rhodium thermocouple for temperature measurements.

An approximate sampling rate of 4 liter/min was required for the continuous analyzers and as a result isokinetic sampling could not be done. Bose (1989) and Glass (1981) both used the same sampling train and did not report any adverse effects resulting from non-isokinetic sampling.

Sampling Probe

The size (O.D.) of the sampling probe may effect the spatial resolution as well as aerodynamics of the flame. A smaller size sampling probe is therefore recommended, but this causes the probe to clog with partially devolatilized coal particles very rapidly. Therefore, to obtain samples for reasonable duration of time* for the on-line continuous instruments leading to stable readings, some of the spatial resolution has to be sacrificed. In addition, nitrogenous species have been observed to be absorbed on stainless steel surfaces and its use is therefore not recommended. In view of these constraints, a 2mm O.D. water quenched quartz probe was used. The operational constraints i.e., removal and cleaning of probe after each sample and fragility of the quartz probes, practically required one probe per sampling location and it was, therefore, decided to use a 1/8 inch O.D. stainless probe. An experiment was conducted to see if stainless steel probe has any effect on

*O₂ analyzer has the longest time constant, ~ 5 mins, requiring sampling for at least 15 mins at each axial position.

measured concentrations of nitrogenous species. No significant effect was detected for the water quenched stainless steel probe and it was used in majority of the experiments. Details of both the quartz and the stainless steel probe are shown in Fig. 2.6.

ANALYSIS PROCEDURES

In situ samples were collected at various axial positions by using either a water quenched quartz or stainless steel probe. Sampling was done in two passes. In the first pass, on line measurements of O_2 , CO, CO_2 and NO were taken and samples for the off-line gas chromatograph were collected in 125 ml gas bulbs. In the second pass, NH_3 and HCN samples absorbed in water, as well as particle sample were collected. Two particle samples were collected at each axial position. A schematic of sampling and analysis system is shown in Figure 2.7.

On Line Measurements of Major Species

The coal-gas-water mixture from the probe was directed, through a three way valve, to a large knock-out pot where the solid particles and water were removed from the gas stream. The gas stream was then pulled through a glasswool filter to remove any remaining small particles and passed through a condenser and knockout pot to remove entrained moisture. The moisture and solid free gas was then fed to the on-line instruments and O_2 , CO, CO_2 , and NO concentrations were recorded. A 125 ml sample of the particle and moisture free gas was also collected for the GC analysis.

Wet Chemistry Analysis of Nitrogenous Species

In this pass, the coal-gas-water mixture from the probe was directed, through the three way valve, to a small knockout pot to rid the gas stream of water and solid particles. The gas stream then passed through a $2\ \mu m$ filter and through two bubblers in series. The first bubbler contained 120 ml water, whereas the second bubbler contained 100 ml of 0.1M NaOH solution. All the NH_3 and a major portion

Figure 2.7 Sampling and Analysis System.

of HCN, not absorbed in the quench water, were captured in the first bubbler. Any quantities of HCN which escaped the first bubbler were finally absorbed in the basic solution of second bubbler. The gas stream then passed through another knockout pot and metered through a precision Wet Test Meter. The sampling time for each sample was also recorded. Quench water was filtered and the amount of quench water collected was recorded. The quench water and the water from bubbler 1 were thoroughly mixed and split into two parts. One part was analyzed for N^+ using an Orion Ammonia Electrode and Orion 901 ion-analyzer. The second portion as well as the sample from bubbler 2 were individually treated with cadmium sulphate, thoroughly stirred and then were allowed to precipitate out any sulfur species which may interfere with CN^- measurements. The samples were filtered and analyzed for CN^- concentrations using an Orion HCN electrode. The aqueous phase concentrations of N^+ and CN^- were then converted to gas phase concentrations using the expression derived in Appendix B. (See Eq. 5). Manufacturer's recommendations were followed throughout the calibration and analysis steps.

The recovery of the trace species in this system was checked by using Matheson certified NH_3/N_2 calibration gas and was found to be in excess of 95% at all dilutions. Threshold detection limits for both the ammonia and cyanide electrodes were determined to 1 ppmv in the gas phase. Details of this analysis are given in Appendix B.

Gas Chromatograph Measurements

A Hach ACG-311 gas chromatograph was used to measure H_2 , and hydrocarbon species. Second readings of CO and CO_2 measurements were also obtained and checked against the on-line measurements. The chromatograph had seven molecular sieve columns and a thermal conductivity (TCD) and a flame ionization detector (FID). The thermal conductivity detector measured CO, CO_2 , H_2 , and N_2 . O_2 measurements were not possible for the samples with argon. Flame ionization detector measured the hydrocarbons. Detection limits for the TCD and FID were 200 ppmv and 1 ppmv respectively. Both the detectors were operated simultaneously

with a single sample injection. Samples were injected from the gas bulbs by water displacement. Calibration was also done, before analyzing each sample set, by the same procedure to ensure identical conditions. The chromatograph was connected to a Spectra-Physics SP4400 integrator which eliminated the need of manual calculations.

Extraction of Tar and Char Samples

Tars, light gases and char, which are the products of rapid coal pyrolysis, were extracted using a water quenched probe. Quenching of the sample permitted the measurement of true composition of the pyrolysis products by preventing the secondary pyrolysis reactions. One task of this work was to determine the distribution of coal nitrogen in tars, light gases and char. The extraction of tars from the particle samples and the filtered quench water was performed by following the procedure recommended by EPA and is outlined below.

A pre-weighed thimble was filled with the particle sample (char and tars) and reweighed to determine the weight of the sample and placed into a Soxhlet extraction apparatus (Fig 2.8). 175 ml of methylene chloride was placed in the round-bottomed flask of the apparatus. The condenser water turned on, and methylene chloride was brought to reflux. A piece of aluminum was placed around the top of the round-bottomed flask to maintain even heating. The solvent turned yellowish, and extraction was continued for twenty four hours. The thimble, which now contained char, was removed and weighed. The solvent, which contained the tars, was evaporated under argon environment. Both the char and the extracted tar samples were analyzed for their nitrogen contents.

A few selected samples of quench water were also extracted for their tar contents. The pH of the quenched water sample was raised to 12 with NaOH and extracted twice with 15 ml of CH_2Cl_2 . The aqueous phase was separated using a separatory funnel and its pH was lowered to 2 with H_2SO_4 and then, again, extracted twice with 15 ml of CH_2Cl_2 . The two extracts were combined and evaporated under nitrogen and weighed. The extracted tar samples were analyzed for

Figure 2.8 Soxhlet Extraction Apparatus.

their nitrogen contents. The amount of the tar extract for these selected samples was very small which led to the conclusion that all the tars are condensed and are retained on the filter. In view of this conclusion, the extraction of quench water samples was not performed for the remaining samples.

SUMMARY

Task 1 of the present work as outlined in Chapter 1 i.e., the setup of experimental facilities including reconfiguration of the opposed flow combustor to allow realization of different flame configurations and the design and construction of the analysis train was presented. The data acquisition procedures to be employed to obtain composition and temperature data were discussed. The recovery efficiency of the wet chemistry analysis system for nitrogenous species was thoroughly tested. Recovery of minor nitrogenous species was found to be in excess of 95% at all concentrations ranges.

CHAPTER 3

EXPERIMENTAL RESULTS – PRELIMINARY RUNS

This chapter covers the preliminary (Qualitative) runs, which were made in order to determine the optimal operating conditions for the final (Quantitative) runs, which are to be used for extraction of devolatilization kinetics. In the next section, the criteria used to select the premixed gas flame (Task 2) is presented. The experimental results for the runs made with the selected system are then presented and briefly discussed (Task 3). This is followed by the configuration experiments to determine the best flame configuration (Task 4) to be used for the quantitative runs. The results of a parametric investigation to determine the effects of various operating variables are, then, presented. The operating conditions for the final runs (Task 5) were based on the results of this parametric study. The final section presents the radial profiles in the opposed flow configuration.

SELECTION OF THE PREMIXED GASEOUS SYSTEM

The opposed flow combustion configuration was previously employed by Kram (1984) and McCaslin (1985). The premixed gaseous mixtures used by them were $\text{CH}_4/\text{O}_2/\text{N}_2$ and $\text{H}_2/\text{O}_2/\text{N}_2$ respectively. Both of them reported poor spatial resolution due to high flame velocities of the premixed flame system. The first task of the present work, therefore, was to identify a suitable premixed gaseous mixture, for which flame velocity was sufficiently low to allow improved spatial resolution. In addition, the focus of present work is on the evolution of nitrogenous species and hence it was necessary to identify a system which will not obscure the concentrations of nitrogenous species evolving from the coal. The following factors were, therefore, considered important in the selection of a suitable premixed gaseous flame mixture.

1. The premixed gaseous system should yield high temperature as amounts of the devolatilized coal nitrogen strongly depend upon temperature.
2. The premixed gaseous system should have low flame velocity to give better spatial resolution.
3. The products of combustion of the premixed gaseous flame should not interfere with the products of coal pyrolysis.
4. The mixture should be safe to operate as well as economical to run.

Two possible fuels, Acetylene (C_2H_2) and Carbon Monoxide (CO), were considered. Even though, combustion of hydrocarbon fuels results in undesirable species which interact with the pyrolysis products, C_2H_2 was considered because of its low hydrogen to carbon ratio. Detailed calculations were performed for adiabatic flame temperatures and equilibrium composition matrix for both the fuels with nitrogen as well as argon as a diluent species. The calculations were performed for stoichiometric ratios of 0.8 to 1.2 with increments of 0.1 and 50 to 90% dilution with increments of 10%. NASA's equilibrium code was used for these calculations.

Tables 3.1 to 3.3 show the results for the two fuels at stoichiometric ratio of 0.9. The results indicate that both mixtures would yield high temperatures. The adiabatic flame temperatures are slightly higher with argon as a diluent. A stable acetylene flame, which has a higher flame velocity, would require higher throughput for both the streams (premixed mixture to the lower burner and transport stream to the upper burner). This would further require higher coal feed rate to achieve reasonable concentrations of the nitrogenous species resulting from the pyrolysis of coal. The operating costs per hour of the two mixtures were found to be comparable. It was, therefore, decided to use a $CO/O_2/N_2$ mixture as the premixed flame because the selection criteria was met i.e.,:

1. The calculated adiabatic flame temperatures for $CO/O_2/N_2$ system were high enough to cause considerable devolatilization of coal nitrogen.
2. The hydrocarbon species which may obscure the species resulting from the coal were non existent.

TABLE 3.1
ACETYLENE FLAME – EQUILIBRIUM COMPOSITION MATRIX AT STOICHIOMETRIC RATIO = 0.9
DILUENT – NITROGEN

		Equilibrium Mole Fraction							
y_{N_2}	T_{AD}, K	CO	CO ₂	H ₂	H ₂ O	O ₂	H	OH	NO
0.50	2823	1.47E-1	1.53E-1	1.61E-2	1.61E-1	2.98E-2	1.12E-2	2.38E-2	1.17E-2
0.60	2667	9.79E-2	1.48E-1	1.05E-2	1.04E-1	1.58E-2	5.08E-3	1.28E-2	7.54E-3
0.70	2409	5.20E-2	1.36E-1	5.60E-3	8.58E-2	3.29E-3	1.23E-3	3.58E-3	2.43E-3
0.75	2184	3.63E-2	1.20E-1	4.27E-3	7.35E-2	3.12E-4	3.34E-4	7.99E-4	4.87E-4
0.80	1873	2.73E-2	9.77E-2	3.99E-3	5.85E-2	2.27E-6	4.06E-5	4.72E-5	1.88E-5
0.85	1529	1.93E-2	7.44E-2	4.10E-3	4.26E-2	–	1.58E-6	–	–
0.90	1160	1.09E-2	5.11E-2	4.61E-3	2.64E-2	–	–	–	–

TABLE 3.2
CARBON MONOXIDE FLAME – EQUILIBRIUM COMPOSITION MATRIX AT STOICHIOMETRIC RATIO = 0.9
DILUENT – NITROGEN

		Equilibrium Mole Fraction							
y_{N_2}	T_{AD} , K	CO	CO ₂	H ₂	H ₂ O	O ₂	H	OH	NO
0.50	2815	1.47E-1	2.21E-1	3.91E-6	4.06E-5	5.77E-2	1.70E-4	5.13E-4	1.71E-2
0.60	2634	8.27E-2	2.11E-1	4.39E-6	7.27E-5	3.32E-2	9.16E-5	3.72E-4	1.09E-2
0.70	2356	2.86E-2	1.90E-1	3.50E-6	1.34E-4	1.16E-2	2.39E-5	1.62E-4	4.25E-3
0.75	2145	1.05E-2	1.70E-1	1.90E-6	1.55E-4	4.25E-3	5.60E-6	6.00E-5	1.70E-3
0.80	1860	1.93E-3	1.41E-1	–	1.45E-4	7.23E-4	–	9.20E-6	3.30E-4
0.85	1514	1.56E-4	1.05E-1	–	1.10E-4	1.62E-5	–	–	1.33E-5
0.90	1140	7.24E-5	6.88E-2	–	7.24E-5	–	–	–	–

TABLE 3.3
CARBON MONOXIDE FLAME - EQUILIBRIUM COMPOSITION MATRIX AT STOICHIOMETRIC RATIO = 0.9
DILUENT - ARGON

		Equilibrium Mole Fraction						
y_{Ar}	T_{AD}, K	CO	CO ₂	H ₂	H ₂ O	O ₂	H	OH
0.50	2967	1.83E-1	1.75E-1	2.35E-6	1.63E-5	7.18E-2	2.17E-4	4.97E-4
0.60	2840	1.24E-1	1.63E-1	2.49E-6	2.28E-5	5.42E-2	1.48E-4	4.03E-4
0.70	2652	6.60E-2	1.48E-1	2.77E-6	4.05E-5	3.03E-2	7.81E-5	2.85E-4
0.75	2511	3.93E-2	1.39E-1	2.78E-6	6.05E-5	1.85E-2	4.37E-5	2.04E-4
0.80	2305	1.66E-2	1.25E-1	2.13E-6	8.93E-5	7.70E-3	1.44E-5	1.00E-4
0.85	1974	2.88E-3	1.02E-1	-	1.01E-4	1.37E-3	1.08E-6	1.65E-5
0.90	1483	8.91E-5	6.88E-2	-	7.23E-5	8.33E-6	-	-

3. The low flame velocity $\text{CO}/\text{O}_2/\text{N}_2$ system would yield improved spatial resolution.

An experiment was performed with $\text{CO}/\text{O}_2/\text{N}_2$ as the premixed flame fuel to determine if a stable flame with high peak temperature could be realized in the opposed flow combustion configuration. Figure 3.1 shows the experimental temperature profiles at three stoichiometric ratios. The temperatures obtained in the experimental setup (which is a non-adiabatic system) were considered to be high enough for the nitrogen evolution experiments.

The initial runs made with coal did not yield detectable amounts of ammonia and hydrogen cyanide. Furthermore, coal injection caused some problems with regard to the stability of the flame. The recovery system for these nitrogen species was tested for leaks and a detailed investigation of the recovery efficiency for the analysis system was conducted. The results of these experiments are presented in Appendix B. The recovery of ammonia, based on the results of the recovery analysis, was found to be in excess of 95% at all concentrations. The threshold detection limits for both the ammonia and cyanide electrodes were determined to be 1 ppmv in the gas phase.

The screening runs without coal, however, did yield small quantities of NO (of the order of 20 ppmv). In view of these observations, it was decided to use argon as the diluent and the carrier streams and to conduct a few runs in the “opposed flow diffusion” and “opposed flow hybrid” flame configurations with an objective to obtain higher temperatures and longer residence times.

EXPERIMENTAL RESULTS – MODIFIED CONFIGURATIONS

In this section, the results from preliminary runs made in the opposed flow diffusion flame configuration and opposed flow hybrid flame configuration are presented.

Figure 3.2 presents the major species and temperature profiles for the coal flame in the opposed flow diffusion flame configuration. Figure 3.3 shows the concentrations of nitrogenous species as measured in the coal flame. This configuration

Figure 3.1 Temperature Profiles of CO/O₂/N₂ Flame in Opposed Flow Premixed Flame Configuration.

Figure 3.2 Major Species and Temperature Profiles for Utah Bituminous #2 in Opposed Flow Diffusion Flame Configuration.
 Symbols: Experimental Curves: Smoothed
 ■ Temperature □ CO_2 ○ CO • O_2

Figure 3.3 Nitrogenous Species Profiles for Utah Bituminous #2 in Opposed Flow Diffusion Flame Configuration.
 Symbols: Experimental Curves: Smoothed
 ■ HCN • NO ○ NH₃ — Total XN

improved the flame stability and higher peak particle temperatures were attained. Appreciable amounts of ammonia and hydrogen cyanide were detected. Flame stability considerations in this configuration, however, required an oxygen rich stream from the lower burner. Pyrolysis under reducing conditions was not readily possible, as shown by Fig. 3.2, and, therefore, this configuration was not further pursued.

Figure 3.4 shows the nitrogenous species profiles for Utah bituminous #2 and Beulah lignite under reducing and oxidizing environments, in the opposed flow hybrid flame configuration. Flame stability, in this configuration, was vastly improved and high peak particle temperatures were obtained. Appreciable amounts of NH_3 and HCN were detected. The major observations and conclusions drawn from these results are as follows:

1. NH_3 concentrations were much lower than HCN concentrations, for all the reported runs, suggesting that HCN is the primary product of pyrolysis entering the gas phase for both bituminous and lignite coals.
2. HCN and NO concentrations were of the same order for the reducing flames. Under oxidizing conditions large quantities of NO were observed, as expected, in comparison with the other two nitrogenous species. However, considerable amounts of NO were detected even under reducing pyrolysis.
3. Both the high rank (bituminous) and low rank (lignite) coals gave similar distribution of nitrogenous species.

The scatter in the data for the nitrogenous species led to the conclusion that improved spatial resolution and precision were required to obtain meaningful kinetic parameters. Use of helium as inert and transport streams to attain higher particle temperatures and higher heating rates was also attempted but not further pursued due to flame stability problems.

In order to improve the spatial resolution and precision of the experimental data, a series of parametric runs were conducted which are presented and discussed in the next section.

Figure 3.4 Nitrogenous Species Profiles for Utah Bituminous #2 and Beulah Lignite in Opposed Flow Hybrid Flame Configuration.
 ■ HCN • NO ○ NH3 — Total XN

PARAMETRIC RUNS

The objective of the parametric runs was to obtain a mix of optimal operating conditions to study early evolution of coal nitrogen in the opposed flow combustion configuration. In these runs, measurements of nitrogenous species and temperature were taken at a fixed axial position while the *throughput* and *composition* of premixed flame mixture as well as *coal feed rate* and *transport argon flow rate* were varied. These parametric runs were made in the “opposed flow premixed flame configurations” as the temperature profiles obtained for the two (opposed flow hybrid and opposed flow premixed) configurations did not show any significant difference especially near the upper burner where devolatilization takes place (Fig. 3.5). In addition, based on the results of an exhaustive leak test of the system, the feed lines to the upper burner were blanketed and argon was bled in the blanket when the runs were made. This eliminated the large quantities of NO observed under reducing conditions as shown on Figure 3.4.

Figure 3.6 shows the effect of energy release (fuel consumption) as a function of stoichiometric ratio on temperature at a fixed axial location. Figure 3.7 presents the variation in measured NO concentration at a fixed axial position with energy release and stoichiometric ratio. Figure 3.8 shows the measured NO concentration at a fixed sampling position as a function of coal feed rate. In these experiments, the amount of NO was assumed to be an indication of the extent of coal nitrogen devolatilization. The energy release was varied by changing the throughput of CO in the premixed mixture. Stoichiometric ratios were varied by adjusting the fraction of oxygen stream in the premixed mixture. Both temperature and NO concentration show rapid increase till about stoichiometric ratio of 1.2. Beyond a stoichiometric ratio of 1.2 both temperature and NO concentration level off. Furthermore, higher throughput flame (18 liters of CO/min) yielded much higher temperatures and increased levels of NO. Further increase in CO throughput resulted in still higher temperatures causing the lower burner’s porous plate to become red hot and causing flash back of flame. The final operating conditions were, therefore, decided to be

Figure 3.5 Effect of Secondary Diffusion Flame on Temperature Field.

Figure 3.6 Effect of Fuel Consumption on Temperature at a Fixed Axial Location.

Figure 3.7 Effect of Fuel Consumption on NO Concentrations at a Fixed Axial Location.

Figure 3.8 Effect of Coal Feed Rate on NO Concentrations at a Fixed Axial Location.

about 18 liters of CO/min at stoichiometric ratios of 0.7 (reducing environment) and 1.2 (oxidizing environment).

RADIAL PROFILES

The opposed flow combustion configuration can theoretically be shown (See Chapter 5) to be one dimensional in species concentration, particle number density, temperature and axial velocities. However, it must be noted that the theoretical considerations require an infinitely wide configuration which is not practical. The diameters of the upper and lower burners in the system employed for the present work were 10 cm. Radial profiles for temperature and species concentrations were obtained to determine the range of one-dimensionality in the system. Figure 3.9 shows selected radial profiles for temperature in a coal flame and CO concentration data in a gas flame. Data clearly show that one-dimensionality holds extremely well for 80% of radius and then shows a decrease in temperature and concentration values. The drop in values is extremely sharp near the burner edge. Hence, all temperature and gas samples must be extracted from the one-dimensional region. The results of radial profiles, also, aid in determining the radial distance where the coal particles are considered to be swept out of the flame.

SUMMARY

Experiments to accomplish tasks 2-5, as outlined in chapter 1, i.e., a) to identify a low velocity high temperature premixed flame mixture; b) to determine the best opposed flow combustion configuration for nitrogen evolution; and c) to establish the optimal mix of the operating conditions for the quantitative runs, were presented in this chapter. A CO/O₂/Ar flame was identified as low velocity premixed gaseous mixture. The "opposed flow premixed flame configuration" was determined to be the most conducive configuration. A set of preliminary runs in this configuration were made and the optimal operating conditions for the quantitative runs were determined. Furthermore, one-dimensionality of opposed flow combustion configuration was experimentally verified.

Figure 3.9 Radial Profiles in Opposed Flow Premixed Flame Configuration.

CHAPTER 4

EXPERIMENTAL RESULTS — QUANTITATIVE RUNS

This chapter addresses the specific issues regarding the speciation of nitrogenous compounds as they evolve into the bulk gas phase. Experimental results for two coals of different ranks, namely, Illinois bituminous and Texas lignite are presented under both reducing and oxidizing environments. Furthermore, the effect of particle size on the speciation and evolution of nitrogenous species is investigated, and results are presented for both the coals for three particle size cuts; fines (smaller than $38\ \mu\text{m}$ particles), coarse (larger than $88\ \mu\text{m}$ and smaller than $125\ \mu\text{m}$ particles), and unclassified (as received). All experiments reported in this chapter were performed in the *opposed flow premixed flame configuration*.

EXPERIMENTAL CONDITIONS

The experimental conditions for the premixed flame, both for the reducing and oxidizing conditions, are shown in Table 4.1. All flow rates were kept constant with the only exception of O_2 flow rate which was varied to provide the reducing or oxidizing devolatilization environment. Particle size distributions for both coals (unclassified) are reported in Appendix A. Fines and coarse fractions were obtained by sifting the unclassified coal in two passes using a Tyler Ro-Tap Sieve Shaker and an Alpine Air-Jet Sieve System (Model AJS-200). The calculated mass mean diameters for the three size fractions used in this study are reported in Table 4.2. Nominal coal feed rate for these runs was 3 gm/min with the exception of Texas lignite (unclassified) runs where the nominal rate was 5 gm/min, leading to particle loadings of 59 mg/liter and 98 mg/liter respectively. The distribution of coal in the transport gas was reasonably uniform. Part of the coal feed, however, fell along the rim of the lower burner and, therefore, did not see the flame. In-situ coal feed rate

TABLE 4.1
EXPERIMENTAL CONDITIONS

	Reducing	Oxidizing
Lower Burner		
CO, (sl/min)	17.9	17.9
O ₂ , (sl/min)	6.5	10.9
Ar, (sl/min)	16.4	16.4
Velocity (at STP), (cm/s)	8.4	8.4
Upper Burner		
Ar, (sl/min)	50.1	50.1
Velocity (at STP), (cm/s)	10.3	10.3

TABLE 4.2
MASS MEAN DIAMETERS FOR THE COAL SIZE FRACTIONS

	Texas Lignite (μm)	Illinois Bituminous (μm)
Fines	32	31
Unclassified	55	55
Coarse	104	98

measurements were, therefore, made by collecting a coal sample close to the upper burner and metering the corresponding transport gas stream. In-situ coal feed rate, thus obtained, are reported in Appendix A, and were used in all subsequent calculations.

GAS RUNS

In this section, the baseline concentrations and temperature profiles for the reducing and the oxidizing premixed gas flames in the opposed flow configuration, without the presence of coal, are presented. Profiles of major species (O_2 , CO , CO_2) and temperature are shown on Fig. 4.1. The premixed flame was stabilized at the lower porous plate, as shown on Fig. 2.2, and the flame sheet was taken to be the lower boundary. In the reducing flame, CO concentration range from 11.7 %vol at the lower boundary to zero at the upper burner. The oxygen rich flame shows 2.5% CO in the post flame flue gas, which indicates that CO oxidation is kinetically controlled. Due to slow CO consumption, the O_2 contents in the premixed gas mixture for reducing flame was lowered till no oxygen was detected in the post flame flue gas. In the oxidizing run, O_2 concentration range from 6.6%vol at lower boundary to zero at the upper burner. As expected, the oxygen rich flame yielded slightly higher carbon dioxide concentrations as compared to the reducing flame. It must be noted, that for the oxidizing runs there is an additional dilution effect due to the larger quantities of oxygen in the premixed gas mixture.

The concentrations of NH_3 and HCN are always less than 1 ppmv under both oxidizing as well as reducing conditions (Fig. 4.2). NO concentration are around 1 ppmv for the reducing flame and around 2 ppmv in the oxidizing flame. These values, therefore, represent the background levels for the nitrogenous species. The detection limits of these species are 1 ppmv in the gas phase.

The temperature profiles show similar trends for the two flames. Peak temperature occurs at the lower burner and decays to 400 K at the upper burner. Temperatures were measured using a type R platinum and platinum-rhodium thermocouple and were corrected for the radiation losses assuming a Nusselt number

Figure 4.1 Major Species and Temperature Profiles for Baseline Gas Runs.

Symbols: Experimental Curves: Smoothed

■ Temperature □ CO₂ ○ CO • O₂

Figure 4.2 Nitrogenous Species Profiles for Baseline Gas Runs.

of 2.0. Computer code Temp-Corr, which implements the radiation correction, is listed in Appendix C. Peak temperature for the oxidizing flame is about 100 K higher as compared to the reducing flame. The adiabatic flame temperatures, as reported in Chapter 3, were much higher than the peak temperatures obtained in this configuration. This shows that considerable heat losses to the lower burner and the ambient occur in this system. McCaslin (1985), reported temperature profiles for $\text{H}_2/\text{O}_2/\text{N}_2$ flame both under oxidizing and reducing conditions in the same configuration. His profiles showed a peak temperature above the lower burner and a zone of almost constant temperature over large (up to 66%) portion of burner spacing. This is attributed to the high post flame velocities of $\text{H}_2/\text{O}_2/\text{N}_2$ mixture, causing the flame to stabilize slightly above the lower burner, which results in less heat losses. High post flame velocities (133 cm/s) also lead to extremely dominant convective heat transfer effects. For this reason, McCaslin assumed that his flames approached adiabatic conditions. For the present $\text{CO}/\text{O}_2/\text{Ar}$ flame the post flame velocities range from 42–45 cm/s under reducing conditions, and 51–52 cm/s under oxidizing conditions. The lower post flame velocities realized for the present set of experiments cause considerably more heat losses to the lower burner, and the convective heat transfer effects are not as dominant. This explains much lower peak temperatures for the present flames as compared to the corresponding adiabatic flame temperatures.

COAL RUNS

In this section, results for the runs, in the opposed flow premixed flame configuration, with the presence of coal are presented. First, the runs with fines are discussed, followed by coarse size fraction runs, and finally the runs for the unclassified size are presented.

Addition of coal caused an increase in the steady state temperature of the unburned premixed gaseous mixture. The increase in the steady state temperature was found to be a function of pyrolysis environment and the coal feed rate, and ranged from 70 K for the reducing cases to 110 K for the oxidizing environments.

A stable temperature reading indicated a constant coal feed rate, and therefore was monitored throughout the experiment.

In the following sections, experimental data are shown by various symbols. Measurements closest to the two boundaries could be made at one probe diameter away from the burners. The experimental data points for O_2 , CO , CO_2 and temperature at the lower boundary were, therefore, extrapolated. The values for H_2 , nitrogenous species and hydrocarbon species were taken to be zero. At the upper boundary, only argon is present and hence the concentrations for all other species were taken to be zero. The temperature of the transport stream was taken to be 400 K except for the unclassified Texas lignite runs where the temperature was taken to be 500 K. The reason for assuming higher temperature for these two runs was that the burners and the cooling system was reassembled before additional runs with narrower size cuts and with Illinois bituminous coal were made. The reassembled system exhibited slightly different heat loss behavior. It was further assumed that the coal particles leaving the drop tube were in thermal equilibrium with the carrier gas.

The curves represent the smoothed data obtained by using IMSL routines based on cubic spline algorithms. IMSL routine CSSED, which smooths the data with error detection, was used. In the absence of a large number of data points, especially in the vicinity of peak, the routine tended to consider the peak point in error and smoothed it down. Secondly, some agglomerate particles managed to fall all the way down to the lower burner and produced spurious readings, particularly for NO . These problems were circumvented by using the IMSL routine BSLSQ, which yields a least square, B-spline approximation of data. By the selection of appropriate weights, the smoothed curve was forced to pass through the maximum and the two boundaries. The points close to the lower burner were assigned less weight and hence the contribution of spurious values was minimized. The resulting curve was then used in combination with an interpolation routine to produce final input to the routine CSSED. The curves shown here are the output from this three step smoothing procedure.

Coal composition varied with coal rank and particle size cuts used. The ultimate analysis of the coals used for the present study is shown in Table 4.3. In all the runs, coal particles enter the devolatilization space from the upper burner which is 3.2 cm from the lower burner. The order of evolution of species discussed in the next sections is, therefore, with respect to **coal injection plane** i.e., the upper burner.

Fine Particles

Experimental data for these runs consist of temperature, major species, nitrogenous species, and hydrocarbon species profiles. For these runs, selected solid samples were extracted with methylene chloride and the resulting char and tar samples were sent to a local laboratory (Desert Analytics) to determine their nitrogen contents.

The profiles of temperature and major species are shown on Fig. 4.3. The profiles for O_2 , CO, CO_2 and temperature show expected trends and are similar to those of the baseline gas flame runs. The lower porous plate at which premixed flame was stabilized had a very short life due to large heat losses and had to be replaced a few times between the runs. Therefore, slightly different heat transfer characteristics of the system were encountered which account for different temperature profiles measured for the runs under similar conditions. The trajectories of the glowing particles could be visually observed in the flame. The luminous zone for the oxidizing runs was larger and more intense, this may effect the radiation heat transfer between the glowing particle, surrounding gas and the ambient. This also explains the increase in steady state temperature of the unburned premixed mixture.

Evolution of H_2 is slow for all the four runs. Peak levels of hydrogen always occurs close to the lower burner. Under reducing conditions the quantities of H_2 detected are five times more than the quantities measured under oxidative pyrolysis. This is expected, as the presence of oxygen in the post flame gases leads to rapid oxidation of H_2 . It is observed, that at all the sampling locations, where

TABLE 4.3
ULTIMATE ANALYSIS OF THE COALS

	Texas Lignite			Illinois Bituminous		
	Fines	Unclassified	Coarse	Fines	Unclassified	Coarse
C	33.47	38.37	44.45	56.88	58.64	61.25
H	3.22	3.60	3.95	3.53	3.99	4.14
N	0.56	0.62	0.71	1.01	1.24	1.21
S*	5.33	4.41	6.45	2.94	3.90	2.21
Ash	38.92	33.04	23.70	23.21	21.55	17.99

* By difference.

All values in weight%.

Figure 4.3 Major Species and Temperature Profiles – Fine Particles.
 Symbols: Experimental Curves: Smoothed
 ■ Temperature □ CO₂ ○ CO ● O₂ ◇ H₂ × 20 (Normalized)

H₂ measurements were made, evolution of H₂ continues for all the four cases which indicates that H₂ is formed as a result of secondary pyrolysis of hydrocarbon species.

Figure 4.4 shows the measured profiles of nitrogenous species. Since, in-situ coal feed rate for these runs varied, hence to facilitate the comparison all values are normalized by in-situ coal feed rate and plotted on one gram of coal/min basis (Fig. 4.5). The subsequent results (for all the runs) will be on this normalized basis.

For Texas lignite under reducing condition, quantities of HCN are always much higher than the other two nitrogenous species. Under oxidizing conditions NO is the dominant species with HCN initially present in substantial quantities, which decay rapidly. For Illinois bituminous under reducing conditions, HCN is the dominant light gaseous species. NO concentrations follow closely and peak concentrations for both species are similar. Under oxidizing conditions, initial HCN levels closely follow NO concentrations and then decay extremely rapidly to background levels. Large quantities of NO are observed, thereby making the yield of total nitrogenous species much higher for Illinois bituminous under oxidizing conditions.

Ammonia concentrations are always much smaller than the other two XN species for both coals under reducing as well as oxidizing conditions. The yield of total (light gaseous) XN species, as shown by the solid curve, for the Illinois bituminous increases in the presence of oxygen. In contrast to this, Texas lignite does not yield more XN species under oxidizing conditions. For both the high and the low rank coals, data for the reducing runs clearly show that HCN precedes other XN species.

Tables 4.4 and 4.5 show the fraction of initial coal nitrogen present in gaseous species (NO, NH₃, HCN), tars and char particle as a function of axial position. Nitrogen balance is closed within 20% for the samples obtained close to the upper burner. Away from the upper burner, however, nitrogen balance could not be closed within reasonable limits and shows a large discrepancy. It is due to the fact that these calculations were very sensitive to mass of the solids (char + tar) sample. The amounts of solids collected decrease as the sampling location moves closer to the lower burner. Furthermore, theoretically no coal particles should cross

Figure 4.4 Nitrogenous Species Profiles (as Measured) – Fine Particles.
 Symbols: Experimental Curves: Smoothed
 $\blacksquare$ HCN $\bullet$ NO $\circ$ NH₃ — Total XN

Figure 4.5 Normalized Profiles of Nitrogenous Species – Fine Particles.
 Symbols: Experimental Curves: Smoothed
 ■ HCN • NO ○ NH₃ — Total XN

TABLE 4.4
FRACTIONAL DISTRIBUTION OF INITIAL COAL NITROGEN IN PYROLYSIS PRODUCTS
Texas Lignite – Fines

Axial Position (cm)	NO	NH ₃	HCN	Char	Tar	Total Gaseous	Total
Under Reducing Environment							
3.200	0.00E+00	0.00E+00	0.00E+00	1.00E+00	0.00E+00	0.00E+00	1.00E+00
2.885	7.73E-04	8.66E-04	9.89E-04	8.84E-01	1.12E-02	2.63E-03	8.98E-01
2.560	3.09E-03	3.06E-03	6.80E-03	1.01E+00	9.80E-03	1.30E-02	1.03E+00
2.150	1.17E-02	8.84E-03	2.17E-02	8.73E-01	2.48E-03	4.22E-02	9.18E-01
1.870	1.86E-02	1.33E-02	3.88E-02	1.08E+00	1.69E-02	7.06E-02	1.16E+00
1.365	3.25E-02	1.95E-02	7.87E-02	4.26E-01	8.27E-04	1.31E-01	5.57E-01
Under Oxidizing Environment							
3.200	0.00E+00	0.00E+00	0.00E+00	1.00E+00	0.00E+00	0.00E+00	1.00E+00
2.890	2.52E-03	1.45E-03	4.72E-03	9.36E-01	0.00E+00	8.68E-03	9.44E-01
2.770	7.23E-03	2.17E-03	6.78E-03	9.41E-01	4.78E-04	1.62E-02	9.57E-01
2.410	2.76E-02	4.56E-03	1.62E-02	9.05E-01	7.73E-03	4.84E-02	9.61E-01
2.045	5.03E-02	1.01E-02	3.62E-02	8.99E-01	7.26E-03	9.66E-02	1.00E+00
1.785	6.76E-02	1.13E-02	4.87E-02	4.91E-01	3.35E-03	1.28E-01	6.22E-01
1.410	1.01E-01	6.45E-03	9.43E-03	1.64E-02	3.23E-03	1.17E-01	1.36E-01

TABLE 4.5
FRACTIONAL DISTRIBUTION OF INITIAL COAL NITROGEN IN PYROLYSIS PRODUCTS
 Illinois Bituminous – Fines

Axial Position (cm)	NO	NH ₃	HCN	Char	Tar	Total Gaseous	Total
Under Reducing Environment							
3.200	0.00E+00	0.00E+00	0.00E+00	1.00E+00	0.00E+00	0.00E+00	1.00E+00
2.840	2.43E-03	1.99E-03	3.62E-03	1.08E+00	4.02E-03	8.03E-03	1.09E+00
2.530	5.66E-03	4.41E-03	1.18E-02	9.96E-01	1.89E-02	2.19E-02	1.04E+00
2.310	1.07E-02	7.23E-03	2.43E-02	1.06E+00	5.41E-03	4.23E-02	1.11E+00
1.980	2.60E-02	1.27E-02	5.17E-02	9.36E-01	2.92E-02	9.05E-02	1.06E+00
1.750	4.12E-02	1.66E-02	7.11E-02	1.09E+00	3.37E-02	1.29E-01	1.25E+00
1.535	5.44E-02	1.76E-02	7.06E-02	2.16E-01	1.93E-02	1.43E-01	3.78E-01
1.265	6.01E-02	1.33E-02	3.41E-02	6.38E-02	4.26E-02	1.07E-01	2.14E-01
Under Oxidizing Environment							
3.200	0.00E+00	0.00E+00	0.00E+00	1.00E+00	0.00E+00	0.00E+00	1.00E+00
2.975	9.70E-03	2.17E-03	2.26E-03	1.26E+00	1.30E-02	1.41E-02	1.28E+00
2.800	2.59E-02	4.40E-03	9.54E-03	7.04E-01	3.19E-03	3.98E-02	7.47E-01
2.670	3.92E-02	5.82E-03	1.93E-02	1.07E+00	1.60E-02	6.44E-02	1.15E+00
2.370	7.27E-02	8.73E-03	4.91E-02	2.72E-01	1.97E-03	1.31E-01	4.04E-01
1.880	1.55E-01	1.12E-02	2.06E-02	7.17E-02	1.44E-03	1.87E-01	2.60E-01
1.685	1.83E-01	9.71E-03	8.92E-03	1.12E-01	4.19E-03	2.02E-01	3.18E-01

the coal stagnation plane. The location of the stagnation plane depends upon the relative momentum of the two opposed jets and on the physical properties, i.e., density and diameter, of the particle. However, some particles may form agglomerates and hence due to their larger mass may penetrate to a lower location. The mass of solid samples obtained below the theoretically calculated stagnation plane is significantly smaller and, therefore, introduces large error in nitrogen balance. The values reported in these Tables for axial locations below the stagnation plane, therefore, should not be given much weight unless an improved model is developed to account for polydispersed nature of the coal feed and the agglomerations effects. The data below the particle stagnation planes, however, does point out to important observations that the nitrogen loss from the particles increases considerably at higher temperatures. Secondly, up to 30% of initial coal nitrogen is evolved in these experiments.

The normalized values for the total gaseous-N and tar-N are plotted as equivalent ppmv N (Fig. 4.6). Data show some scatter for all the runs, however, trends can be clearly seen. Under reducing conditions, both coals show larger quantities of tar-N. Texas lignite yields much smaller quantities of tar-N as compared to Illinois bituminous, which may be attributed to the lower nitrogen contents of the lignite. Secondly, for Texas lignite, tar-N shows a peak and then decays. On the other hand, Illinois bituminous shows continued evolution of tar-N. Under oxidizing conditions, the quantities of tar-N for Texas lignite are slightly lower than those under reducing conditions. In contrast to this, Illinois bituminous yields much smaller quantities of tar-N under oxidizing conditions, which show very rapid decay to negligible quantities. It is, therefore, inferred that for Texas lignite evolution of tar-N is slow. In addition, subsequent oxidation of tar-N, in the presence of oxygen, is slow for the lignites. For Illinois bituminous, subsequent oxidation, especially, in the presence of oxygen, of tar-N is extremely rapid. This explains the presence of much higher quantities of gaseous XN species for the bituminous coal under oxidizing conditions, and the similar quantities of gaseous XN species for the lignite under both reducing and oxidizing conditions.

Figure 4.6 Total Gaseous and Tar Nitrogen (Normalized) as Equivalent ppmv N.
 o Total Gaseous Nitrogen • Tar Nitrogen

In summary, the quantities of the tar samples obtained for the fine particles show that tar yields for the low rank coals are low whereas high rank coals yield large quantities of tars. This agrees with the results of Freihaut and Seery (1985) who determined that distribution of nitrogen in devolatilization products is a strong function of chemical characteristics of coal, and reported that primary nitrogen species evolve as tar products from bituminous coal and HCN for the lignites. It is, furthermore, noted that the tar products undergo secondary pyrolysis reactions which are rapid for the bituminous and slow for the lignites. Data for the bituminous coal under oxidizing conditions clearly show that secondary pyrolysis is extremely rapid for smaller particle and lead to large quantities of NO_x . Present results fully complement the work of Pohl and Sarofim (1977) and Song et al. (1982) who reported that lower rank coals yield less volatile nitrogen than bituminous coals during the initial transients of rapid heating conditions. This phenomena, hence, leads to larger quantities of nitrogenous species, especially NO, for fine bituminous particles.

The normalized profiles of hydrocarbon species (CH_4 , C_2H_2 , C_2H_4 , C_2H_6) are shown on Fig. 4.7. As expected, both coals yield much larger quantities of gaseous hydrocarbons under reducing environment. Texas Lignite, under reducing conditions, yields largest quantities of C_2H_4 which are followed in decreasing order of magnitude by C_2H_2 , CH_4 and C_2H_6 . Under oxidizing conditions, composition matrix for hydrocarbon species, for Texas Lignite, shows similar trends with all peak values occurring simultaneously. Initial evolution of C_2H_4 , C_2H_2 and CH_4 occur at similar rates during very early stage of devolatilization process. C_2H_6 evolves much slowly during later stages of coal pyrolysis.

Illinois bituminous, shows similar behavior for the hydrocarbon species. A notable difference is that CH_4 is the dominant species, as compared to C_2H_4 for Texas Lignite, under both reducing as well as oxidizing conditions. All these species decay very rapidly and only negligible quantities are present below the coal stagnation plane. Under oxidizing conditions, like the reducing environment case, these species show extremely rapid decay with only negligible quantities present below

Figure 4.7 Normalized Profiles of Hydrocarbon Species - Fine Particles.
 Symbols: Experimental Curves: Smoothed
 • CH₄ ○ C₂H₂ □ C₂H₄ ◇ C₂H₆

the coal stagnation plane. C_2H_4 , shows much faster decay and drops down to trace levels very rapidly. The maximum levels of C_2H_4 , C_2H_2 , CH_4 , under oxidizing conditions, are less than half the maximum values observed under reducing conditions. C_2H_6 peak quantities, under oxidizing conditions, however, do not show such a significant reduction, which indicates that C_2H_6 evolves during later stages of coal devolatilization. Data for the bituminous coal clearly show that CH_4 precedes other hydrocarbon species and evolves during earlier stages of coal pyrolysis. A reverse trend is observed under oxidative pyrolysis and the evolution behavior of these two species is very similar.

The presence of oxygen, therefore, does not effect the evolution behavior of hydrocarbon species from either coal. From the relative magnitudes of hydrocarbon species, it can be further concluded that combustion of volatiles is rapid for higher rank coals, especially in the presence of oxygen. Finally, pyrolysis of a high rank coal results in more light weight hydrocarbons as compared to a low rank coal.

Coarse Particles

In this section, experimental data for the runs with 'coarse fraction', which represent an extreme with respect to particle size, are presented. Two experiments were conducted both under reducing environment, using Texas Lignite and Illinois Bituminous coals. These runs, therefore, shed some light on the effect of particle size on its devolatilization behavior. Experimental data consist of temperature, major species, nitrogenous species, and hydrocarbon species profiles. Solid samples were collected but were not extracted or analyzed for tar and char nitrogen.

The temperature and major species profiles are shown on Fig. 4.8. Trends for these variables are as expected and do not show any abnormal behavior. Both coals yield large quantities of H_2 , which initially evolves very slowly followed by a sharp increase during later stages. This indicates that H_2 is a product of secondary pyrolysis reactions.

The normalized profiles of nitrogenous species are shown on Figs. 4.9. HCN is the dominant species for both the coals. Illinois bituminous yields much larger

Figure 4.8 Major Species and Temperature Profiles – Coarse Particles.
 Symbols: Experimental Curves: Smoothed
 ■ Temperature □ CO₂ ○ CO ● O₂ ◇ H₂ x 20 (Normalized)

Figure 4.9 Normalized Profiles of Nitrogenous Species – Coarse Particles.
 Symbols: Experimental Curves: Smoothed
 ■ HCN ● NO ○ NH₃ — Total XN

quantities of HCN, this is due to the higher nitrogen contents. Initial levels of NH_3 are slightly higher than NO for both the coals. This is in contrast to the runs with fine particles, which yielded least quantities of NH_3 among the three XN species. HCN, similar to the runs with 'fine fraction', precedes the other two nitrogenous species and is the first nitrogenous light gas species evolving into the bulk gas phase.

Ammonia levels for the coarse particles are much higher than the quantities observed for the fine particles, for both the coals. This shows that ammonia formation may be effected by the particle size. Since larger particles heat up slowly, leading to lower heating rates, therefore, it can be concluded that low heating rates favor conversion of fuel nitrogen to ammonia. NO levels show a gradual increase but do not surpass NH_3 levels before ammonia starts to decay at which point HCN has already peaked out. This shows that both HCN and NH_3 are involved in the gas phase reactions leading to the formation of NO. Total XN is higher for the bituminous coal, due to its higher nitrogen contents.

The normalized profiles of hydrocarbon species are shown on Figs. 4.10. Texas lignite yields maximum quantities of C_2H_2 , followed by CH_4 , C_2H_4 and C_2H_6 . CH_4 evolves as the first hydrocarbon species, but during later stages of devolatilization the quantities of C_2H_2 surpass methane. For Illinois bituminous, CH_4 is the dominant species with similar concentrations of C_2H_2 . Other hydrocarbon species, C_2H_4 and C_2H_6 are present in smaller quantities. Illinois bituminous clearly shows the order of evolution for the hydrocarbon species. CH_4 precedes C_2H_2 , which in turn precedes C_2H_4 . C_2H_6 is the last species to be evolved. This shows that pyrolysis of higher rank coals favors lower molecular weight hydrocarbons and complements the observation made for the run with fine size cut. Due to scatter in the data for the Texas lignite run, definite conclusions for the precedence order of hydrocarbon species can not be made.

Unclassified Particles

This section describes the experimental data for the runs with unclassified (as received) size cut, which include both the extreme cases with respect to particle

Figure 4.10 Normalized Profiles of Hydrocarbon Species – Coarse Particles.
 Symbols: Experimental Curves: Smoothed
 ● CH₄ ○ C₂H₂ □ C₂H₄ ◇ C₂H₆

size i.e, fines and coarse. Results for both Texas lignite and Illinois bituminous coals, under both reducing and oxidizing environments, are presented. Concentration data for the hydrocarbon species for the Texas lignite runs were not taken. Solid samples were collected but were not analyzed for their tar and char nitrogen contents.

The temperature and major species profiles are shown on Fig. 4.11, and follow the usual trends. Under oxidizing conditions, for Illinois bituminous, larger quantities of H_2 , which is not as expected, are observed. Experimental data for H_2 show continued evolution as was observed for the runs with fine and coarse size cuts, which leads to the conclusion that H_2 is not a primary product of coal pyrolysis.

The normalized profiles of nitrogenous species are shown on Fig. 4.12. HCN and NO are the dominant species, under reducing and the oxidizing environments respectively, for both the coals as was the case for the runs with narrow size cuts. Under reducing conditions, both coals show rapid initial evolution of HCN with similar quantities of NO present at all times. Illinois Bituminous, however, show a little lag before appreciable quantities of NO are detected. As expected, under oxidizing conditions, NO quantities are considerably larger than the other two XN species. Bituminous coal, however, initially yields more HCN than NO whereas Lignite does not exhibit this behavior. Total XN species do not show an increase for oxidative run with bituminous coal as they did for the fine particles. Ammonia is present in least quantities for both the coals under both environments which complements the observation made for the fine size cut experiments and contrasts that of the coarse size cut runs.

The yields of total XN species are similar for both coals under either pyrolysis environments. This is due to the relative concentrations of NO and HCN. Under oxidizing conditions, large quantities of NO are present and they make the bulk of total XN species. For the reducing conditions, even though HCN is the dominant species, the quantities of NO are very similar with a significant contribution towards total XN values. The behavior of Texas lignite complements the observations made for the fines experiments. Absence of much higher quantities of total XN for Illinois

Figure 4.11 Major Species and Temperature Profiles – Unclassified Particles.
 Symbols: Experimental Curves: Smoothed
 ■ Temperature □ CO_2 ○ CO • O_2 ◇ $\text{H}_2 \times 20$ (Normalized)

Figure 4.12 Normalized Profiles of Nitrogenous Species – Unclassified Particles.
 Symbols: Experimental Curves: Smoothed
 ■ HCN • NO ○ NH₃ — Total XN

bituminous, under oxidizing conditions, is attributed to fact the energy feed back mechanisms become less pronounced for larger particles.

The normalized profiles of hydrocarbon species, for Illinois bituminous, are shown on Figs. 4.13. In both the cases, CH_4 is the dominant species. Other hydrocarbon species in decreasing order are C_2H_2 , C_2H_4 and C_2H_6 under both environments. The experimental data under oxidizing conditions show some scatter as does the data for methane under reducing conditions. Therefore, the data are inconclusive regarding the order of evolution under oxidizing conditions. The order of evolution of hydrocarbon species under reducing conditions is clearly noted and is same as that observed for the runs with fines and coarse particles.

SUMMARY

Higher initial nitrogen contents of the parent coal, in general, produce larger quantities of nitrogenous species. For the reducing runs, irrespective of the particle size and the coal rank, HCN is the dominant species. For small particle runs (fines and unclassified) NH_3 is present in the smallest quantities. For the coarse particles, the initial quantities of NH_3 obtained are of the same order as that of NO. It is, further, noted that the relative magnitude of NH_3 to that of NO increases with the particle size. This indicates that larger particles yield more ammonia. Since the temperatures attained by the large particles are lower, it can, therefore, be inferred that low temperatures favor the formation of NH_3 .

For both the high and low rank coals, data for the reducing runs clearly show that HCN precedes other XN species. This indicates that HCN, rather than NH_3 , is the first nitrogenous light gas product of pyrolysis evolving into the bulk gas phase. This complements the findings of Peck *et al.* (1984) and Freihaut and Seery (1985). Peck and coworkers studied the kinetics of fuel nitrogen conversion to NO_x for bituminous coal particles in a flat flame burner. Their results, for high temperature fuel rich flames, indicated HCN to be the primary volatile nitrogenous species with very small quantities of ammonia observed. It must be pointed out that their samples were extracted at locations where coal particles have already reached

Figure 4.13 Normalized Profiles of Hydrocarbon Species - Unclassified Particles.
 Symbols: Experimental Curves: Smoothed
 • CH₄ ○ C₂H₂ □ C₂H₄ ◇ C₂H₆

1500–1700 K, which is well beyond the initial mass loss regime and well into the secondary pyrolysis envelope. Findings of present study show no rank dependence for the nitrogenous species evolving into the bulk gas phase. This contradicts the results reported by Chen *et al.* (1982) who found that under the reducing conditions of staged combustion, HCN and NH_3 dominate the bituminous and lignite coals respectively. The results of this study are in agreement with the data reported by Bose *et al.* (1988) which showed that in the bulk gas phase HCN precedes NH_3 , even for lignite coals.

The hydrocarbon species evolution shows rank dependency and low rank coals tend to favor higher molecular weight species. This contradicts the results reported by McCaslin (1985), who observed that pyrolysis of lignites produces more light hydrocarbons. Furthermore, in the presence of oxygen, the higher molecular weight hydrocarbon species from the lignites undergo oxidation and produce more CO. For the high rank coal, the order in which the hydrocarbon species are evolved is clearly observed from the results of the experiments under reducing conditions. CH_4 is the first and the dominant species to be evolved followed by C_2H_2 , C_2H_4 and C_2H_6 . The same order is maintained for high rank coals under oxidizing conditions and, in addition, does not show any dependency on particle size. Low rank coals, on the other hand, show dependency on the particle size. Larger particles yield C_2H_2 as the dominant species which is followed by C_2H_4 , CH_4 and C_2H_6 . Fine particles yield maximum quantities of C_2H_4 which are followed by C_2H_2 , CH_4 and C_2H_6 . For bituminous coals, the relative quantities of heavy hydrocarbons are much smaller as compared to the concentrations of CH_4 indicating that oxidation of these compounds is very rapid.

The evolution of hydrogen is always very slow and shows a dependence on the particle size. Large particle size yield much higher quantities of H_2 . Significant production of hydrogen occurs at elevated temperatures which leads to the conclusion that it is a product of gas phase secondary pyrolysis reactions.

The following conclusions are, therefore, drawn:

1. High rank coals yield larger quantities of tars which very rapidly undergo secondary pyrolysis. Tar yields from the low rank coals are small and subsequent oxidation of the tars, even in the presence of oxygen, is slow.
2. HCN is the first light gaseous nitrogenous species to appear in the bulk gas phase for both high and low rank coals, under reducing as well as oxidizing environments.
3. Under oxidizing conditions, HCN decays very rapidly and is converted to NO which is the dominant nitrogenous species.
4. Results from the reducing runs clearly show that HCN precedes the other two XN species. It is further concluded that NH_3 precedes NO but conversion of ammonia to NO through the gas phase reactions is very rapid.
5. For bituminous coals in the presence of oxygen, secondary pyrolysis reactions of the tars, in the vicinity of the particles, lead to energy feedback mechanisms which result in extremely rapid oxidation of tar nitrogen and yield much larger quantities of NO. These energy feedback mechanisms are especially important for the small particles.
6. NH_3 to NO ratio increases with the particle size as large particle yield more ammonia. Thus formation of ammonia is favored at lower temperatures.
7. Gas phase reactions are extremely important even at moderate temperatures (above 900 K) and evolution of nitrogenous species in the opposed flow configuration must be studied in conjunction with gas phase chemistry.

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UMI

4. Species Conservation

$$\nabla \cdot N_i = R_i + \frac{\Omega_i S_e}{M_i} \quad (i = 1, \dots, N_S) \quad (4)$$

where S_v , S_m and S_e are the mass, momentum and energy source terms. Ω_i is the surface averaged mass flux fraction of chemical species i , flowing to the gas (Williams, 1985). N_R and N_S are the number of reactions and the number of chemical species involved in the system. Heat losses to the ambient and thermal diffusion have been neglected following Field *et al.* (1967). The mixture is considered to be an ideal gas, compressible newtonian fluid. Fourier's and Ficks's Laws are assumed to be applicable. Invoking the cylindrical symmetry of the opposed flow configuration, and neglecting the reversible and irreversible work terms in the energy equation, because of low mach number of the laminar flow and low density of fluid, the governing equations may be written as:

1. Continuity:

$$\frac{1}{r} \frac{\partial}{\partial r}(\rho r v_{g,r}) + \frac{\partial}{\partial z}(\rho v_{g,z}) = S_v \quad (5)$$

2. r -momentum:

$$\rho v_{g,r} \frac{\partial v_{g,r}}{\partial r} + \rho v_{g,z} \frac{\partial v_{g,r}}{\partial z} = -\frac{\partial p}{\partial r} - \left[\frac{1}{r} \frac{\partial}{\partial r}(r \tau_{rr}) - \frac{\tau_{\theta\theta}}{r} + \frac{\partial \tau_{rz}}{\partial z} \right] + S_{m,r} \quad (6)$$

3. z -momentum:

$$\rho v_{g,r} \frac{\partial v_{g,z}}{\partial r} + \rho v_{g,z} \frac{\partial v_{g,z}}{\partial z} = -\frac{\partial p}{\partial z} - \left[\frac{1}{r} \frac{\partial}{\partial r}(r \tau_{rz}) + \frac{\partial \tau_{zz}}{\partial z} \right] + \rho g_z + S_{m,z} \quad (7)$$

4. Energy:

$$\begin{aligned} -\frac{1}{r} \frac{\partial}{\partial r}(r c C_p T_g v_{g,r}) - \frac{\partial}{\partial z}(c C_p T_g v_{g,z}) + \frac{1}{r} \frac{\partial}{\partial r}(r k_g \frac{\partial T_g}{\partial r}) \\ + \frac{\partial}{\partial z}(k_g \frac{\partial T_g}{\partial z}) = -\sum_{j=1}^{N_R} R_j \Delta H_j + S_e \end{aligned} \quad (8)$$

5. Species:

$$\begin{aligned} \frac{1}{r} \frac{\partial}{\partial r} (rcD_i \frac{\partial x_i}{\partial r}) + \frac{\partial}{\partial z} (cD_i \frac{\partial x_i}{\partial z}) - \frac{1}{r} \frac{\partial}{\partial r} (cx_i v_{g,r}) - \frac{\partial}{\partial z} (cx_i v_{g,z}) \\ = -R_i + \frac{\Omega_i S_v}{M_i} \end{aligned} \quad (9)$$

The corresponding boundary conditions are:

$$\begin{aligned} v_g = v_g(0); \quad T_g = T_g(0); \quad x_i = x_i(0) \quad \text{at } z = 0 \\ v_g = v_g(z_0); \quad T_g = T_g(z_0); \quad x_i = x_i(z_0) \quad \text{at } z = z_0. \end{aligned} \quad (10)$$

All these conditions refer to the coordinate system as defined in Fig. 5.1.

Particle Phase Equations

The particle phase equations, in the Lagrangian frame of reference, are given by:

1. Particle motion in vector form:

$$m_p \frac{d\mathbf{v}_p}{dt} = m_p \mathbf{g} - \rho_p V_p \mathbf{g} + \frac{1}{2} C_D A_{pr} \rho_g (\mathbf{v}_g - \mathbf{v}_p) |(\mathbf{v}_g - \mathbf{v}_p)| \quad (11)$$

where C_D is the drag coefficient and m_p , A_{pr} and V_p are the particle mass, projected area and volume, respectively, given by:

$$m_p(t) = \frac{4}{3} \pi R_p^3(t) \rho_p(t) \quad (12)$$

$$A_{pr}(t) = \pi R_p^2(t) \quad (13)$$

$$V_p(t) = \frac{m_p(t)}{\rho_p(t)} \quad (14)$$

Introducing above expressions into Eq. 11 and rearranging, yields:

$$\frac{d\mathbf{v}_p}{dt} = (1 - \frac{\rho_g}{\rho_p}) \mathbf{g} + \frac{3}{4} \frac{C_D \rho_g}{\rho_p d_p} (\mathbf{v}_g - \mathbf{v}_p) |(\mathbf{v}_g - \mathbf{v}_p)| \quad (15)$$

The initial conditions are:

$$\begin{aligned} \mathbf{x}_p(0) &= \mathbf{x}_{p0} \\ \mathbf{v}_p(0) &= \mathbf{v}_{p0} \end{aligned} \quad (16)$$

Figure 5.1 Coordinate System for Opposed Flow Combustion Configuration.

Stokes law is assumed for the drag coefficient but correction is made for the mass transfer effects following Smoot and Smith (1979):

$$C_D = \frac{24}{\text{Re}} \exp(-B_m) \quad (17)$$

Reynold number, Re , is defined as:

$$\text{Re} = \frac{|\mathbf{v}_g - \mathbf{v}_p| d_p}{\nu} \quad (18)$$

and the blowing parameter B_m is given by the expression (Spalding, 1955):

$$B_m = \frac{C_{p_g}(-dm_p/dt)}{2\pi d_p k_g} \quad (19)$$

Mass loss behavior of the particle can be incorporated using one of the devolatilization models discussed in Chapter 1. A first order rate expression is used in the present work, as the emphasis is not on the prediction of mass loss behavior, but on proper modeling of the source terms and its effects on the mass transfer, heat transfer and drag coefficients. These factors, in turn, may effect the particle time-temperature history and hence must be properly accounted for. The model employed in the present work is described by:

$$-\frac{dm}{dt} = \frac{dV}{dt} = k(V^* - V) \quad (20)$$

with

$$k = k_0 \exp(-E/RT) \quad (21)$$

2. Particle Energy Balance

Particle energy balance is solved in spherical coordinates assuming a conduction limiting model and negligible heat of devolatilization (Fletcher, 1989), thereby:

$$\rho_p c_p(T_p) \frac{\partial T_p}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[k_p(T_p) r^2 \frac{\partial T_p}{\partial r} \right] \quad (22)$$

with the initial and boundary conditions:

$$T_p(0, r) = T_g(z_0) \quad (23)$$

$$\frac{\partial T_p(t, 0)}{\partial r} = 0 \quad (24)$$

$$k_p(T_p) \frac{\partial T_p(t, R_p(t))}{\partial r} = h(T_g(t)) [T_g(t) - T_p(t, R_p(t))] - \epsilon \sigma (T_p^4(t, R_p(t)) - T_\infty^4) \quad (25)$$

where the heat transfer coefficient is calculated using the following expression for the Nusselt Number:

$$\text{Nu} = (2.0 + 0.654 \text{Re}^{1/2} \text{Pr}^{1/3}) \left(\frac{B_m}{\exp(B_m) - 1} \right). \quad (26)$$

The change in particle size, for the swelling coal, is assumed to be a linear function of the extent of volatile release (Smoot and Pratt, 1979). The particle size can then be calculated as:

$$d_p = d_p^0 [1 + (1 - \gamma)(V/V^*)] \quad (27)$$

where swelling coefficient, γ , is the ratio of the initial particle diameter to the final diameter.

3. Particle Number Density

Assuming that particle-particle interaction and the processes contributing towards the destruction and formation of particles are negligible, then at steady state and for a given particle velocity field $\mathbf{v}_p$, the particle number balance is given by the expression:

$$\nabla \cdot (n \mathbf{v}_p) = 0 \quad (28)$$

Equation (28) simply states that at steady state the number of particles crossing any plane remains constant.

The Source Terms

In view of our assumption that all the particles are spherical and are represented by a single group i.e., all particles are identical in composition and size, the source terms are then expressed as:

$$S_v = n\dot{m} \quad (29)$$

$$S_{m_r} = -n \left[m_p \frac{dv_{pr}}{dt} + \dot{m}(v_r - v_{pr}) \right] \quad (30)$$

$$S_{m_z} = -n \left[m_p \frac{dv_{pz}}{dt} + \dot{m}(v_z - v_{pz}) \right] \quad (31)$$

$$S_e = -n \left[\dot{q} + \dot{m} \{ c_{p_s}(T_g - T_{p_s}) + \Delta H_{dev} \} \right] \quad (32)$$

where

$\dot{m}$ = rate of change of mass of a single particle

n = particle number density

m_p = mass of a single particle

SIMILARITY ANALYSIS

Equations (5)–(32) provide the framework to model the coal pyrolysis or combustion problem in the opposed flow combustion configuration. These equations and their solution may greatly be simplified if these could be transformed into ordinary differential equations. Such a transformation is possible, provided a suitable similarity transform exists. It is assumed that such a similarity transform exists, and then the conditions required for the existence of similarity are determined. Hence, one-dimensionality attributes of the system are first assumed and later proved by means of the similarity analysis.

Gas Phase Equations

For the gas phase, the following form of the solution is assumed:

$$\begin{aligned}
v_{g_r} &= r\psi(z) \\
v_{g_z} &= v_{g_z}(z) \\
T_g &= T_g(z) \\
x_i &= x_i(z) \\
c &= c(z)
\end{aligned} \tag{33}$$

where ψ is the proposed similarity variable, originally proposed by Seshadri and Williams (1978). All the transport properties for the gaseous mixture are assumed to be a function of temperature alone and thus, in turn, are function of axial coordinate, z , only. The equations take the following form:

Continuity:

$$\psi(z) = -\frac{1}{2\rho} \frac{d}{dz}(\rho v_{g_z}) + \frac{S_v}{2\rho} \tag{34}$$

r -momentum:

$$\psi^2 + v_{g_z} \frac{d\psi}{dz} = -\frac{1}{\rho r} \frac{\partial p}{\partial r} + \frac{1}{\rho} \frac{d}{dz}(\mu \frac{d\psi}{dz}) + \frac{S_{m_r}}{\rho r} \tag{35}$$

z -momentum:

$$\rho v_{g_z} \frac{dv_{g_z}}{dz} = -\frac{\partial p}{\partial z} + 2\mu \frac{d\psi}{dz} - \frac{4}{3}\mu \frac{d}{dz}(\psi + \frac{dv_{g_z}}{dz}) + \rho g_z + S_{m_z} \tag{36}$$

Energy:

$$-2cC_p T_g \psi - \frac{d}{dz}(cC_p T_g v_{g_z}) + \frac{d}{dz}(k \frac{dt}{dz}) = -\sum_{j=1}^{N_R} R_j \Delta H_j + S_e \tag{37}$$

Species:

$$-2cx_i \psi + \frac{d}{dz}(cD_i \frac{dx_i}{dz}) - \frac{d}{dz}(cx_i v_{g_z}) = -R_i + \frac{\Omega_i S_v}{M_i}. \tag{38}$$

Similarity will hold provided the first and last terms on the right hand side of equation (35) and the terms involving the mass, momentum or energy source are all independent of r . Now, in order to maintain similarity, $\partial p / \partial r$ must be proportional

to r , but at the same time, it must not introduce any r -dependency in equation (36). It is, therefore, proposed that:

$$\frac{\partial p}{\partial r} = rf(z) \quad (39)$$

Substituting the above expression into equation (35), differentiating with respect to r , and further noting that v_{g_z} , μ , ρ , ψ , etc. are all functions of z only, the expression reduces to:

$$-\frac{1}{\rho} \frac{\partial}{\partial r} \left(\frac{\partial p}{\partial z} \right) + \frac{1}{\rho} \frac{\partial}{\partial r} (S_{m_z}) = 0. \quad (40)$$

Further assuming that S_{m_z} is independent of r , yields:

$$\frac{\partial^2 p}{\partial r \partial z} = 0.$$

Interchanging the order of differentiation, and introducing the proposed expression for $\partial p / \partial r$, leads to:

$$r \frac{\partial f(z)}{\partial z} = 0.$$

The above expression requires that $f(z)$ must be a constant to be valid for all r . Hence:

$$f(z) = Q.$$

Solving for p and $\partial p / \partial z$ yields:

$$p = \frac{1}{2} r^2 Q - f_1(z) \quad (41)$$

and

$$\frac{\partial p}{\partial z} = -f_1(z). \quad (42)$$

The governing equations finally become:

$$\psi(z) = -\frac{1}{2\rho} \frac{d}{dz} (\rho v_{g_z}) + \frac{S_v}{2\rho} \quad (43)$$

$$\psi^2 + v_{g_z} \frac{d\psi}{dz} = -\frac{Q}{\rho} + \frac{1}{\rho} \frac{d}{dz} \left(\mu \frac{d\psi}{dz} \right) + \frac{S_{m_r}}{\rho r} \quad (44)$$

$$\rho v_{g_z} \frac{dv_{g_z}}{dz} = f_1(z) + 2\mu \frac{d\psi}{dz} - \frac{4}{3}\mu \frac{d}{dz} \left(\psi + \frac{dv_{g_z}}{dz} \right) + \rho g_z + S_{m_z} \quad (45)$$

$$-2cC_p T_g \psi - \frac{d}{dz} (cC_p T_g v_{g_z}) + \frac{d}{dz} \left(k \frac{dt}{dz} \right) = - \sum_{j=1}^{N_R} R_j \Delta h_j + S_e \quad (46)$$

$$-2cx_i \psi + \frac{d}{dz} (cD_i \frac{dx_i}{dz}) - \frac{d}{dz} (cx_i v_{g_z}) = -R_i + \frac{\Omega_i S_v}{M_i}. \quad (47)$$

Thus, it is shown that a similarity solution will exist, provided S_v , S_{m_r}/r , S_{m_z} , S_e and Ω_i are all independent of r . To show that this indeed is the case, the particle phase equations must be solved and the expressions for the source terms be determined. This is the focus of next two sections.

Particle Phase Equations

For the particle phase, we assume that the following form of solution exists:

$$\begin{aligned} v_{p_z} &= v_{p_z}(z) \\ v_{p_r} &= r\phi(z) \\ T_p &= T_p(z) \\ n &= n(z) \end{aligned} \quad (48)$$

where $\phi(z)$ is a similarity transform analogous to $\psi(z)$ in the gas phase. Introducing the expression for the drag coefficient into the particle motion equation (15), noting that $\rho_g \ll \rho_p$, simplifying and rewriting in the component form, gives:

$$\frac{dv_{p_z}(z)}{dt} = \frac{18\mu}{\rho_p d_p^2} (v_{g_z} - v_{p_z}) \exp(-B_m) + g_z \quad (49)$$

$$\frac{d\phi(z)}{dt} = \frac{18\mu}{\rho_p d_p^2} (\psi(z) - \phi(z)) \exp(-B_m) \quad (50)$$

with the initial conditions:

$$\begin{aligned} v_{p_z}(0) &= v_{p_z0} & \text{for all } r \\ \phi(0) &= 0 & \text{for all } r \end{aligned} \quad (51)$$

Now, all the gas properties are function of z only, and d_p depends upon the solutions of particle energy, mass loss and size change equations. All the terms appearing in these equations are functions of z alone, thereby rendering d_p a function of z only. The blowing parameter B_m also remains a sole function of z . Since the initial conditions (Eq. 51) are independent of r , it is, therefore, shown that similarity exist for the particle phase. All the particles will have the same trajectory and the same free stream (local gas phase conditions surrounding the particle) history. For the same initial temperature and initial diameter, all the particles will have same devolatilization history. A single particle, therefore, represents all particles crossing a specific plane, perpendicular to the axial coordinate.

Particle Number Balance

Expanding the particle number balance equation (28), gives

$$\nabla \cdot (n\mathbf{v}_p) = \mathbf{v}_p \cdot \nabla n + n \nabla \cdot \mathbf{v}_p = 0. \quad (52)$$

Further expanding the individual terms, and introducing relationships from equation set (48), yields:

$$\nabla \cdot (n\mathbf{v}_p) = \frac{1}{n} \frac{dn}{dz} + 2 \frac{\phi(z)}{v_{pz}} + \frac{1}{v_{pz}} \frac{dv_{pz}}{dz} = 0 \quad (53)$$

or

$$\frac{dn}{n} + \frac{dv_{pz}}{v_{pz}} = -2 \frac{\phi(z)}{v_{pz}} dz$$

integrating the above expression

$$\int_{n_0}^n \frac{dn}{n} + \int_{v_{pz0}}^{v_{pz}} \frac{dv_{pz}}{v_{pz}} = -2 \int_0^z \frac{\phi(z)}{v_{pz}(z)} dz$$

and finally

$$n(z) = \frac{n_0 v_{pz0}}{v_{pz}} \exp(-2\Phi(z)) \quad (54)$$

where $\Phi(z)$ is defined as:

$$\Phi(z) = \int_0^z \frac{\phi(z)}{v_{pz}(z)} dz. \quad (55)$$

The Source Terms

In this section, it is shown that terms involving mass, momentum or energy sources are independent of r . The mass loss behavior of the particles depend upon $T_p(z)$ and therefore does not introduce any r -dependency. Similarly, Ω_i is also a function of particle temperature and coal devolatilization or combustion kinetics, therefore any r -dependency does not arise. The source terms, finally, take the following forms:

$$S_v = n(z)\dot{m}(z) \quad (56)$$

$$\frac{S_{m_r}}{r} = -n(z) \left[m_p(z) \frac{d\psi(z)}{dt} + \dot{m}(z) \{ \psi(z) - \phi(z) \} \right] \quad (57)$$

$$S_{m_x} = -n(z) \left[m_p(z) \frac{dv_{p_x}(z)}{dt} + \dot{m}(z) \{ v_{g_x}(z) - v_{p_x}(z) \} \right] \quad (58)$$

$$S_e = -n(z) \left[\dot{q}(z) + \dot{m}(z) \{ c_{p_g}(z) (T_g(z) - T_{p_s}(z)) + \Delta H_{dev} \} \right]. \quad (59)$$

Now, since all the terms in the gas phase equations (43)–(47) are functions of z alone, hence it is proved that similarity exists for both the gas as well as particle phases. All the equations, except particle energy balance equation (which is a partial differential equation), result in a set of coupled, non-linear ordinary differential equations and can be solved numerically using the procedure developed by Hahn and Wendt (1981, 1982, 1985).

SUMMARY AND APPLICATIONS

It is shown in the previous sections, that a suitable similarity variable exists which transform the original system of partial differential equations to a system of coupled ordinary differential equations. It is further concluded that the opposed flow combustion configuration is:

- one dimensional in
 - gas and particle phase axial velocities,
 - gas and particle phase temperatures,
 - gas phase concentrations,

- particle number density, and
- two dimensional in
 - gas phase pressure distribution, and
 - gas and particle phase radial velocities.

The mathematical model described above has the following applications:

Prediction of Coal Flame Structure — “The Forward Problem”

In the forward problem, an adequate set of chemical reactions along with all the pertinent kinetic information must be known. Secondly, radiation heat transfer effects due to burning and glowing of coal particles must be incorporated in the model. The predicted flame structure can then be compared with the experimental results and validity of coal conversion kinetics can be tested. Additional relationships describing the char burnout will be needed.

Estimation of Kinetics Parameters — “The Inverse Problem”

Another important use of the opposed flow combustion model is to determine the pertinent kinetic parameters governing the evolution and subsequent reactions of pollutants and other species of interest. This is defined as the inverse problem and utilizes the measured experimental concentration data and temperature profile in the gas phase. An ideal experiment should aim at obtaining the gas phase composition, temperature and velocity fields as well as particle trajectories, measurements of the particle temperature, mass and size. In our experiments all these measurements were not possible, hence we resort to the model for evaluation of the missing information. A major portion of the present work deals with the estimation of rate coefficients for the evolution of early coal nitrogen and the governing equations and the solution procedure employed to solve the “inverse problem” are discussed in the next chapter.

CHAPTER 6

DATA REDUCTION

This chapter builds on the model developed in Chapter 5, which describes the devolatilization behavior of coal in opposed flow combustion configurations. The emphasis, here, is on the “inverse problem”. The equations used to solve the inverse problem are summarized in the next section. This is followed by finite difference formulation of the equations and a discussion of solution algorithm. The calculated rates of formation of nitrogenous species as they evolve into the *bulk* gas phase and are then presented and related to the calculated particle time-temperature histories. The calculated particle-time temperature histories and time resolved rates of formation for the quantitative runs are finally presented and discussed.

THE INVERSE PROBLEM

To determine the kinetic parameters for the early evolution of coal nitrogen, the rates of nitrogenous species as they appear in the *bulk* gas phase must be determined and related to particle time-temperature history. The data obtained from the experiments conducted for this work consisted of gas phase composition and temperature profiles as reported in Chapter 4. Velocity fields for both the gas and particle phases and measurements of particle temperatures, size, and mass were not made. Therefore experimental data must be used in conjunction with the model to calculate particle time-temperature histories.

The Transformed Gas Phase Equations

The particle loadings in the two phase (gas – particle) system encountered in the experiments conducted for the present work were very low. Therefore, the

system is further classified as a very dilute system and the source terms due to devolatilization of coal particles are neglected. The transformed governing equations for the gas phase, then become:

$$\psi(z) = -\frac{1}{2\rho} \frac{d}{dz}(\rho v_{g,z}) \quad (60)$$

$$\psi^2 + v_{g,z} \frac{d\psi}{dz} = -\frac{Q}{\rho} + \frac{1}{\rho} \frac{d}{dz}(\mu \frac{d\psi}{dz}) \quad (61)$$

$$2cx_i\psi - \frac{d}{dz}(cD_i \frac{dx_i}{dz}) + \frac{d}{dz}(cx_i v_{g,z}) = R_i.$$

Substitution of Eq. (60) in the above expression yields:

$$D_{im} \frac{d^2 x_i}{dz^2} + \left[\frac{1}{c} \frac{d(cD_{im})}{dz} - v_{g,z} \right] \frac{dx_i}{dz} + \left(\frac{v_{g,z}}{M} \frac{dM}{dz} \right) x_i = -\frac{R_i}{c}. \quad (62)$$

The z -momentum equation yields a solution of axial pressure distribution, which is not of interest and therefore is not solved.

The Auxiliary Equations – Particle Phase

The auxiliary equations describing the changes in particle properties, as discussed in Chapter 5, are reproduced below:

Mass Loss Behavior:

$$-\frac{dm_p}{dt} = \frac{dV}{dt} = k(V^* - V) \quad (63)$$

$$k = k_0 \exp(-E/RT).$$

The values of the pre-exponential factors and activation energies used for the Texas lignite and Illinois bituminous are given in Table 6.1.

Drag Coefficient:

$$C_D = \frac{24}{\text{Re}} \exp(-B_m). \quad (64)$$

Blowing Parameter:

$$B_m = \frac{C_{p_g}(-dm_p/dt)}{2\pi d_p(t)k_g}. \quad (65)$$

TABLE 6.1
COAL DENSITIES AND PARAMETER VALUES

	Texas Lignite	Illinois Bituminous
Pre-exponential Factor, s^{-1}	6.6E+6	2.3E+13
Activation Energy, kcal/mol	25.0	55.0
Swelling Coefficient, γ	1.0	0.9
Coal Density, gm/cm ³		
Fines	1.60	1.41
Unclassified	1.54	1.35
Coarse	1.41	1.32

Heat Transfer Coefficient:

$$\text{Nu} = (2.0 + 0.654 \text{Re}^{1/2} \text{Pr}^{1/3}) \left(\frac{B_m}{\exp(B_m) - 1} \right). \quad (66)$$

Particle Size Change:

$$d_p = d_p^0 \left[1 + (1 - \gamma)(V/V^*) \right]. \quad (67)$$

The values used for swelling coefficient γ , are, also, reported in Table 6.1.

Specific Heat of Coal:

Specific heat of coal can be calculated either by using the expression proposed by Merrick (1983) or Berkowitz (1985). The computer code listed in Appendix C incorporates both the procedures and the choice of the method is upon the discretion of the user. It is, however, noted that the specific heat calculated by the two methods differs by up to 30%, but the calculated particle time-temperature histories were within 5 K at all times. It is pointed out that the Merrick's model requires the average atomic weight of the coal particle which is a function of the ultimate composition of the coal and its ash contents. The difference between the values calculated by the two models is attributed to the use of initial average atomic weight of coal throughout the calculations. The average atomic weight of coal, for this work, could not be updated as composition of coal particles were not determined as pyrolysis progressed. The present work, therefore, employs the procedure proposed by Berkowitz which is outlined below.

The specific heat of coal is given by the weighted average of the specific heats of its constituents, i.e.,

$$s_{coal} = x_c s_c + x_{v_1} s_{v_1} + x_{v_2} s_{v_2} + x_a s_a \quad (68)$$

where x and s stand for mass fraction and specific heat respectively and subscripts c , v_1 , v_2 and a represent the constituents carbon, volatiles 1, volatiles 2 and ash.

The specific heats of these constituents are given by:

$$\begin{aligned}
 s_c &= 0.165 + 6.8 \times 10^{-4}T - 4.2 \times 10^{-7}T^2 \\
 s_{v_1} &= 0.395 + 8.1 \times 10^{-4}T \\
 s_{v_2} &= 0.710 + 6.1 \times 10^{-4}T \\
 s_a &= 0.18 + 1.4 \times 10^{-4}T.
 \end{aligned} \tag{69}$$

The mass fractions of carbon, volatiles and ash contents are updated as pyrolysis progresses.

Thermal Conductivity of Coal:

In the present work, the thermal conductivity of coal was taken to be constant at $6.64 \times 10^{-4} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$. This value was arrived at by taking an average of the range reported by Berkowitz (1985).

Density of Coal Particles:

Density of coal particles is calculated following the procedure outlined in Coal Conversion Systems Technical Data Book. Table 6.1 also lists the computed densities.

The Transformed Particle Phase Equations

The transformed governing equations for the particle phase are:

Particle Motion

Particle motion equations are solved in original variables i.e., v_{p_z} and v_{p_r} for the particle phase, along with the similarity variable ψ , which is solved in place of the gas phase radial velocity, and v_{g_z} . This leads to the following equations:

$$\frac{dv_{p_z}(z)}{dt} = \frac{18\mu}{\rho_p d_p^2} (v_{g_z} - v_{p_z}) \exp(-B_m) + g_z \tag{70}$$

$$\frac{dv_{p_r}}{dt} = \frac{18\mu}{\rho_p d_p^2} (r\psi - v_{p_r}) \exp(-B_m) \tag{71}$$

with the initial conditions:

$$\begin{aligned} v_{p_z}(0) &= v_{p_{z0}} & \text{for all } r \\ v_{p_r}(0) &= 0 & \text{for all } r. \end{aligned} \quad (72)$$

Particle Energy Balance

Particle energy balance constitute a moving boundary value problem, as the particle size may change with time. The problem is converted to a stationary boundary problem by the following transformation.

$$\begin{aligned} \eta &= \frac{r}{R_p(t)} \\ \eta_s &= \frac{R_p(t)}{R_p(0)}. \end{aligned} \quad (73)$$

The governing equations and the corresponding initial and boundary conditions, then become:

$$\begin{aligned} \frac{\partial T_p}{\partial t} &= \left[\frac{\eta}{\eta_s} \left(\frac{d\eta_s}{dt} \right) + \frac{2k_p + (\partial k_p / \partial \eta)}{\rho_p C_{p_p} R_{p0}^2 \eta_s^2 \eta} \right] \left(\frac{\partial T_p}{\partial \eta} \right) \\ &+ \left[\frac{k_p}{\rho_p C_{p_p} R_{p0}^2 \eta_s^2} \right] \left(\frac{\partial^2 T_p}{\partial \eta^2} \right) \quad \text{for } \eta \neq 0. \end{aligned} \quad (74)$$

The above equation has a singularity at $\eta = 0$, and by applying the L'Hopital's rule it takes the form:

$$\frac{\partial T_p}{\partial t} = \left[\frac{3k_p}{\rho_p C_{p_p} R_{p0}^2 \eta_s^2} \right] \left(\frac{\partial^2 T_p}{\partial \eta^2} \right) \quad \text{for } \eta = 0 \quad (75)$$

with initial and boundary conditions:

$$T_p(0, \eta) = T_{p0} \quad (76)$$

$$\frac{\partial T_p(t, 0)}{\partial \eta} = 0 \quad (77)$$

$$\frac{k_p(T_p)}{R_{p0} \eta_s} \frac{\partial T_p(t, 1)}{\partial \eta} = h(t) [T_g(t) - T_p(t, 1)] - \epsilon \sigma (T_p^4(t, 1) - T_\infty^4). \quad (78)$$

The equations presented in this section completely describe the coal devolatilization behavior during early stages in the opposed flow combustion configurations. In the next section, the finite difference formulation of these equations is presented and the outline of the solution algorithm is discussed.

FINITE DIFFERENCE FORMULATION

The differential equations describing the combustion phenomena in the opposed flow configuration, especially for the forward problem, are ill-conditioned because of the reaction rate terms, very steep spatial gradients due to diffusion, and a velocity which changes sign in the domain of interest. The equations for the inverse problem retain these characteristics except that the equation involving the reaction rate terms is not solved. Hahn and Wendt (1981, 1982, 1985) showed that the equations for the forward problem can be best solved numerically in a fully coupled, fully implicit manner, utilizing a modified discretization in the spatial domain. In the present work, the modified discretization scheme, proposed by the above mentioned authors, is employed to numerically solve the differential equations for the inverse problem.

The general form of the partial differential equation is:

$$\frac{\partial y}{\partial t} = A(z) \frac{\partial^2 y}{\partial z^2} + B(z) \frac{\partial y}{\partial z} + D(z)y + F(z) \quad (79)$$

where $F(z)$ is the forcing function. Discretization is performed around the point $(i, k+1)$, where i and k refer to spatial grid point and temporal step (iteration index in case of steady-state equation) respectively, according to the following scheme:

$$\left. \frac{\partial y}{\partial t} \right|_i^{k+1} = A(z) \left| \frac{\partial^2 y}{\partial z^2} \right|_i^k + B(z) \left| \frac{\partial y}{\partial z} \right|_i^k + D(z) \left| y \right|_i^k + F(z) \left| \right|_i^{k+1}. \quad (80)$$

In the above representation explicit coefficients are used. The finite difference formulations for the first and the second derivatives, utilizing the modified discretization, for a uniform mesh of grid spacing Δz , are given by:

$$\left. \frac{\partial y}{\partial z} \right|_i^k = \frac{W_{1,i+1}^k y_{i+1}^k - W_{1,i-1}^k y_{i-1}^k}{2\Delta z} + W_{1,0}^k \quad (81)$$

$$\left. \frac{\partial^2 y}{\partial z^2} \right|_i^k = \frac{W_{2,i+1}^k y_{i+1}^k - 2y_i^k + W_{2,i-1}^k y_{i-1}^k}{(\Delta z)^2} + W_{2,0}^k \quad (82)$$

where, $W_{1,0}^k$ and $W_{2,0}^k$ account for the contribution of the complimentary solution. The forcing function is quasi-linearized, by expanding $F(z)$ about the backward iteration, as:

$$F(z) \Big|_i^{k+1} = F(z) \Big|_i^k + \sum_{j=1}^N \left. \frac{\partial F}{\partial y_j} \right|_i^k (y_i^{k+1} - y_i^k) \quad (83)$$

At length discussion of the details of discretization procedure is given by Corley (1990).

The Discretized Gas Phase Equations

The transformed equations for the gas phase, which now involve variables ψ and $v(z)$, after discretization take the following form:

Axial Velocity:

$$\begin{aligned} v(2) &= v(1) \frac{\rho(1)}{\rho(2)} - \Delta z (\psi(2) + \psi(1) \frac{\rho(1)}{\rho(2)}) \\ v(i+1) &= v(i-1) \frac{\rho(i-1)}{\rho(i+1)} - 4\Delta z \psi(i) \frac{\rho(i)}{\rho(i+1)} \quad \text{for } i = 3, \dots, NGP - 1. \end{aligned} \quad (84)$$

$v(1)$ and $v(NGP)$ are the known boundary conditions.

Similarity Transform, ψ :

$$\begin{aligned} &\left[\frac{A_i^k}{(\Delta z)^2} W_{2,i-1}^k - \frac{B_i^k}{2\Delta z} W_{1,i-1}^k \right] \psi_{i-1}^{k+1} + \left[-\frac{2A_i^k}{(\Delta z)^2} - 2\psi_i^k \right] \psi_i^{k+1} \\ &+ \left[\frac{A_i^k}{(\Delta z)^2} W_{2,i+1}^k + \frac{B_i^k}{2\Delta z} W_{1,i+1}^k \right] \psi_{i+1}^{k+1} = (\psi_i^k)^2 - \frac{Q}{\rho_i^k} - A_i^k W_{2,0}^k - B_i^k W_{1,0}^k \end{aligned} \quad (85)$$

where

$$\begin{aligned} A_i^k &= \left(\frac{\mu}{\rho} \right) \Big|_i^k \\ B_i^k &= \left[\frac{1}{\rho_i^k} \left(\frac{\mu_{i+1}^k - \mu_{i-1}^k}{2\Delta z} \right) \right] - v_{gz} \Big|_i^k. \end{aligned} \quad (86)$$

Species:

The discretized form of the transformed species conservation equation, written for a specific species A , becomes:

$$\begin{aligned} (cD_{Am}) \Big|_i^k \frac{d^2 x_A}{dz^2} \Big|_i^{k+1} + \left[\frac{(cD_{Am}) \Big|_{i+1}^k - (cD_{Am}) \Big|_{i-1}^k}{2\Delta z} - (cv_{gz}) \Big|_i^k \right] \frac{dx_A}{dz} \Big|_i^{k+1} \\ \left(\frac{cv_{gz}}{M} \right) \Big|_i^k \frac{M_{i+1}^k - M_{i-1}^k}{2\Delta z} x_A \Big|_i^{k+1} = R_A \Big|_i^{k+1}. \end{aligned} \quad (87)$$

The Discretized Particle Phase Auxiliary Equations:

The auxiliary equations describing the physical properties of the particle, after discretization, take the following form:

$$\dot{m}(n) = k_0 \exp(-E/RT_{p_{\text{surface}}}(n-1)) \times (V^* - V(n-1)). \quad (89)$$

In the above equation, n is used to denote temporal step to avoid confusion with pre-exponential factor k .

$$m_p(k) = m_{p_0}(1.0 - V(k-1)) \quad (90)$$

$$\eta_s(k) = \eta_s(k-1) + (1.0 - \gamma)\dot{m}(k)\frac{\Delta t}{V^*} \quad (91)$$

$$d_p(k) = d_{p_0}\eta_s(k) \quad (92)$$

$$\rho_p(k) = \frac{m_p(k)}{V_p(k)} \quad (93)$$

$$B_m(k) = \frac{\dot{m}c_{gfs}m_{p_0}}{2\pi k_{gfs}d_p(k)M_{fs}} \quad (94)$$

where subscript, fs , refers to the free stream values.

$$\text{Nu}(k) = \frac{(2.0 + 0.654(\text{Re}(k))^{1/2}(\text{Pr}(k))^{1/3})B_m(k)}{(B_m(k) - 1)} \quad (95)$$

$$h(k) = \frac{\text{Nu}(k)k_{gfs}}{d_p(k)} \quad (96)$$

The Discretized Particle Phase Equations

Particle Motion:

The particle motion equations (70–72) are converted to a set of first order ordinary differential equations. A new set of variables is defined as follows:

$$\begin{aligned} y_1 &= t \\ y_2 &= z \\ y_3 &= v_{pz} \\ y_4 &= r \\ y_5 &= v_{pr}. \end{aligned} \quad (97)$$

The resulting system of ordinary differential equations becomes:

$$\begin{aligned} \dot{y}_1 &= 1.0 \\ \dot{y}_2 &= y_3 \\ \dot{y}_3 &= \alpha(-\dot{y}_2 + v_{gz}) - g \\ \dot{y}_4 &= y_5 \\ \dot{y}_5 &= -\alpha(\dot{y}_4 - y_4\psi_{fs}) \end{aligned} \quad (98)$$

where

$$\alpha = \frac{18\mu \exp(-B_m)}{\rho_p d_p^2}. \quad (99)$$

Viscosity and blowing coefficient are evaluated at the free stream conditions. Finally, the initial conditions are:

$$\begin{aligned}
 y_1(0) &= 0.0 \\
 y_2(0) &= z_0 \\
 y_3(0) &= v_{g_z}(z_0) \\
 y_4(0) &= r_0 \\
 y_5(0) &= 0.0.
 \end{aligned} \tag{100}$$

Particle Energy Equation:

The discretized form of the particle energy balance, with a uniform grid spacing within the particle of $\Delta\eta$ and a time step of Δt , after dropping the subscript p , becomes:

1. At the particle center:

$$\left(\frac{6A_1^k}{(\Delta\eta)^2} + \frac{1}{\Delta t} \right) T_1^{k+1} - \left(\frac{3(W_{2,i+1}^k + W_{2,i-1}^k)A_1^k}{(\Delta\eta)^2} \right) T_2^{k+1} = \frac{T_1^k}{\Delta t} \tag{101}$$

where

$$A_1^k = \left[\frac{k_p}{\rho_p C_{p_p} R_{p_0}^2 \eta_s^2} \right] \Big|_1^k \tag{102}$$

2. For the internal grid points ($i = 2, \dots, NGP - 1$):

$$\alpha_i^k T_{i-1}^{k+1} + \beta_i^k T_i^{k+1} + \gamma_i^k T_{i+1}^{k+1} = \frac{T_i^k}{\Delta t} \tag{103}$$

where

$$\begin{aligned}
 \alpha_i^k &= \left[-\frac{W_{2,i-1}^k A_i^k}{(\Delta\eta)^2} + \frac{W_{1,i-1}^k B_i^k}{2\Delta\eta} \right] \\
 \beta_i^k &= \left[\frac{1}{\Delta t} + \frac{2A_i^k}{(\Delta\eta)^2} \right] \\
 \gamma_i^k &= -\left[\frac{W_{2,i+1}^k A_i^k}{(\Delta\eta)^2} + \frac{W_{1,i+1}^k B_i^k}{2\Delta\eta} \right]
 \end{aligned}$$

$$\begin{aligned}
A_i^k &= \left[\frac{k_p}{\rho_p C_{p_p} R_{p_0}^2 \eta_s^2} \right] \Big|_i^k \\
B_i^k &= (B1)_i^k + \frac{2A_i^k + (B2)_i^k}{\eta_i} \\
(B1)_i^k &= \left(\frac{\eta}{\eta_s} \frac{d\eta_s}{dt} \right) \Big|_i^k \\
(B2)_i^k &= \left(\frac{\partial k_p / \partial T}{2\Delta\eta\rho_p C_{p_p} R_{p_0}^2 \eta_s^2} \right) \Big|_i^k \left(T_{i+1}^k - T_{i-1}^k \right)
\end{aligned} \tag{104}$$

3. At the particle surface, $i = NGP$:

$$\begin{aligned}
& \left(\alpha_{NGP}^k + \gamma_{NGP}^k \right) T_{NGP-1}^{k+1} + \left(\beta_{NGP}^k - \hat{D} \gamma_{NGP}^k \left\{ h^{k+1} + \epsilon\sigma(T^k - NGP)^3 \right\} \right) T_{NGP}^{k+1} \\
&= \frac{T_{NGP}^k}{\Delta t} - \hat{D} \gamma_{NGP}^k \left[h^{k+1} T_g^{k+1} + \epsilon\sigma T_\infty^4 \right]
\end{aligned} \tag{105}$$

where

$$\hat{D} = \frac{2R_{p_0} \Delta\eta \eta_s^k}{k_{p_{NGP}}^k} \tag{106}$$

$$B2 \Big|_{NGP}^k = \left(\frac{\hat{D}(\partial k_p / \partial T)}{2\Delta\eta\rho_p C_{p_p} R_{p_0}^2 \eta_s^2} \right) \Big|_{NGP}^k \left[h^k T_g^k + \epsilon\sigma T_\infty^4 + \left\{ h^k + \epsilon\sigma(T_{NGP}^k)^3 \right\} T_{NGP}^k \right] \tag{107}$$

α, β , and γ are given by the above expressions (100) with i replaced by NGP .

SOLUTION ALGORITHM

The logic of the solution algorithm to calculate the particle time-temperature histories and to determine the time-resolved rate of formation of species i is shown in Figure 6.1. A computer program titled `Inverse_Problem` implements the algorithm and is listed in Appendix C. A general description of the solution algorithm is given in the following paragraphs.

The smoothed temperature and concentrations, reported in Chapter 4, are used to obtain the transport and thermodynamic properties of the gaseous mixture.

Figure 6.1 Logic Flow Diagram Implementing the Solution of Inverse Problem.

Details of the equations employed are discussed by Hahn (1979). These properties are then used in equations (84–86) to evaluate the ψ and velocity fields for the gas phase. The solution of ψ and velocity fields also involves the eigenvalue Q , which is not known *a priori*. A value of Q is assumed as an initial guess and the bounds on Q are determined as a first step. Equations (84–86) are, then, solved iteratively using a regula falsi method. Once the converged ψ and velocity fields have been determined, they are subsequently substituted along with the computed transport and physical properties of the gaseous mixture and smoothed concentration data of species i in Eq. (87) to calculate the rate of formation of species i , in the bulk gas phase, after correcting for the diffusive and convective effects, as a function of axial position.

In the case of a premixed gaseous mixture, where all the products of combustion can not be experimentally measured, the unmeasured species are theoretically calculated. An example of such a system is $\text{CH}_4/\text{O}_2/\text{Ar}$, which gives H_2O as a product of combustion. Since the sampled gases are immediately quenched, determination of H_2O contents of the sampled gases is not possible. In such cases, the rates of formation calculated in the previous step are used and the concentration profile of the unmeasured species is calculated by an element balance. The transport and physical properties are then evaluated using the new composition matrix and new velocity, ψ and axial rates of formation are calculated. This procedure is repeated until the converged mixture composition is obtained. Figure 6.2 shows ψ and velocity field, typical to the opposed flow configuration and Figure 6.3 shows the axial rate of formation profiles for the nitrogenous species for Texas Lignite (Fines) under reducing conditions.

The next step is the calculation of particle time-temperature histories. The system of first order ordinary differential equations (98–100), which yields the particle position and velocities, is solved by employing an adaptive fifth-sixth order Runge-Kutta-Fehlberg algorithm. The particle motion equations are coupled to the particle physical properties which depend upon the particle temperature. These

Figure 6.2 Typical Velocity and ψ Profiles in Opposed Flow Premixed Flame Configuration.

Figure 6.3 Calculated Axial Rates of Formation of Nitrogenous Species for Texas Lignite (Fines) under Reducing Conditions.

equations are, therefore, solved in fully coupled form as described in the following paragraph.

The initial temperature of the particle is assumed to be same as the temperature of the carrier gas and particle system leaving the upper burner. The physical properties of the particle i.e., size, density, mass, mass fraction of the volatiles left in the particle and mass loss rate are calculated at that temperature. These calculated values along with the pre-calculated gas phase properties are used to calculate the blowing parameter and drag coefficient and the particle position and velocities are determined. The gas phase properties are known throughout the domain and once the new axial position of particle is determined, the gas phase properties corresponding to this position are used to determine particle temperature at the new location. The particle physical properties are, then, updated and this procedure is repeated until the particle is swept out of the pyrolysis space. At this stage, the particle time-temperature histories and the particle trajectories have been evaluated. Figure 6.4 shows calculated trajectory for a Texas lignite, 32 μm particle. The axial rates of formation are, then, related to the Lagrangian time and particle temperature. These time-resolved rates are amenable to further exploration in terms of mechanisms.

TIME-TEMPERATURE HISTORIES

The pyrolysis of coal strongly depends on the particle temperature and greatly influence the early rates. In the present work, this variable was calculated following the procedure outlined in the previous sections. It is, however, pointed out that even though time resolved measurements of particle temperature would be more accurate, these could not be easily performed in the opposed flow combustion configuration. The calculated time resolved temperatures are presented in this section.

Figure 6.4 Calculated Trajectory for a 32 μm Particle.
(Texas Lignite, under Reducing Conditions).

Fine Particles

The calculated time-temperature histories for the fines are shown on Fig. 6.5. For the fine particles, the intraparticle temperature gradients were negligible with a maximum difference between the temperatures at the particle surface and center to be 5 K. Figure 6.5 therefore, shows the free stream (the temperature particle is exposed to at any time) and particle surface temperatures. The peak particle temperatures for bituminous under oxidizing and reducing conditions and lignite under oxidizing and reducing conditions are 1234, 1149, 1196 and 1108 K respectively. The corresponding residence times and average heating rates are 76, 87, 75 and 85 ms and 11000, 8600, 10600 and 8300 K/s. At high temperatures, Illinois bituminous, show accelerated increase in particle temperatures. Texas lignite does not show such behavior. Furthermore, peak particle temperature for Texas lignite show slight lag from the free stream temperature where as temperature for the Illinois bituminous particles does attain the free stream temperature. This behavior is attributed to both the composition effects as well as to the particle physical properties especially swelling. The increased particle size for bituminous coal yields higher Reynolds number and thereby higher heat transfer coefficient.

Unclassified Particles

Figure 6.6 shows the calculated time-temperature histories for the unclassified runs. During these runs, the lower burner had to be rebuilt frequently as the burner's sintered disk warped upward. This accounts for the different temperature profiles. The maximum temperature difference between the particle surface and center for these runs, like the runs with fines, was small and hence only the particle surface temperatures are shown along with the free stream temperatures. The peak particle temperatures for bituminous under oxidizing and reducing conditions and lignite under oxidizing and reducing conditions are 1344, 1263, 1181 and 1132 K respectively. The corresponding residence times and average heating rates are 66, 77, 70 and 79 ms and 14300, 11200, 9700 and 8000 K/s.

Figure 6.5 Calculated Time-Temperature Histories - Fine Particles.

Figure 6.6 Calculated Time-Temperature Histories - Coarse Particles.

Coarse Particles

For the coarse particles, the intraparticle temperature difference become significant and Fig. 6.7 shows both the particle surface and center temperatures along with the free stream temperatures. Large lag between the particle temperatures and the free stream conditions clearly shows that the resistance to heat transfer mainly lies in the gas film. The peak particle temperatures for bituminous and lignite coals under reducing conditions are 1037 and 987 K respectively. The corresponding residence times and average heating rates are 89 and 94 ms and 11100 and 8200 K/s. Since the particles do not attain high enough temperatures, no accelerated increase in particle temperatures is observed for the bituminous coal.

TIME RESOLVED RATES OF FORMATION

In this section, the time resolved rates of formation of nitrogenous species, calculated following the procedure described in the previous sections, are presented.

Fine Particles

The calculated rates of formation of the nitrogenous species for the fines are shown on Fig. 6.8. Under oxidizing conditions both coals yield high initial rates of formation within 10 ms. Under reducing conditions, however, the initial rates of formation are insignificant below 20 ms. For the time scales involved in this study (up to 90 ms) no net destruction of total nitrogenous species is observed for either coal under both oxidizing and reducing conditions. Rates of formation of total XN start to decay after approximately 40–60 ms suggesting that although coal nitrogen continues to evolve, gas phase reactions leading to N_2 formation then become significant. Rates of formation of HCN for Illinois bituminous under oxidizing conditions show destruction of that species after 60 ms. For all other cases, destruction of any species is not observed.

Figure 6.7 Calculated Time-Temperature Histories – Unclassified Particles.

Figure 6.8 Time Resolved Rates of Formation (Normalized) for Nitrogenous Species - Fine Particles.
 Illinois Bituminous - Oxidizing: Plotted Values are 50% of Actual.

Unclassified Particles

Figure 6.9 shows the calculated rates of formation of nitrogenous species for the unclassified runs. The behavior of unclassified particles is similar to that of the fines, with insignificant initial rates of formation below 20 ms for both the coals under reducing conditions and high initial rates of formation within 10 ms under oxidizing conditions. The peak value for the total nitrogenous species occurs at 45 ms. The rates of formation of NO and HCN are very similar through out the pyrolysis period. Under oxidizing conditions, Texas lignite shows a significantly higher rate of formation for NO. The rates of formation for NH_3 does not show much change during the pyrolysis period. This may be because of the fact that due to different particle temperatures, a continuous supply of NH_3 is available.

Illinois bituminous, under reducing conditions, does show destruction of HCN after 55 ms and net destruction of total nitrogenous species after 60 ms. The peak rate of formation for the total nitrogenous species occurs at 48 ms and shows a very rapid decay afterwards. Under oxidizing conditions, however, Illinois bituminous does not show destruction of any species. This, reinforces our hypothesis that for higher rank coals larger quantities of tar nitrogen are evolved. Since particle temperatures vary with particle size, evolution of tar nitrogen and its conversion to gaseous species occurs continuously over longer time period. Net destruction of nitrogenous species is, therefore, not observed.

Coarse Particles

The rates of formation for the runs with coarse particles are shown on Fig. 6.10. Under reducing conditions, both coals show destruction of NO. Illinois bituminous, additionally, show destruction of NH_3 as well as HCN and hence the net destruction of total nitrogenous species. The destruction of all these species is observed to occur after 50 ms. Illinois bituminous, after 50 ms, shows very rapid destruction of all three nitrogenous species. This may be because of lower peak temperatures attained by the particles due to larger thermal inertia. This results in

Figure 6.9 Time Resolved Rates of Formation (Normalized) for Nitrogenous Species - Unclassified Particles.
 ■ HCN ● NO ○ NH₃ □ Total XN

Figure 6.10 Time Resolved Rates of Formation (Normalized) for Nitrogenous Species - Coarse Particles.

lower tar nitrogen evolution from the parent coal which rapidly undergoes conversion to gaseous nitrogenous species. At higher gas temperatures these species are further converted to N_2 .

Lower rates of formation of nitrogenous species for Illinois bituminous, in comparison with Texas lignite, complement our previous observation that secondary gas phase reactions of tar nitrogen are rapid for higher rank coals.

DISCUSSION AND SUMMARY

The calculated time-temperature histories for all the reported runs clearly show that the resistance to heat transfer mainly lies in the film. Larger the particle diameter, longer it takes for the particle to equilibrate with the free stream temperature, as evident by the temperature profiles for the coarse particles. Tables 6.2 and 6.3 summarize the peak temperatures, residence times and average heating rates for all the cases. Both coals, under reducing conditions for the three particle sizes considered yield significant rates of formation only after 20 ms. Under oxidizing conditions, however, initial rates of formation are high after only 10 ms. This is due to the higher temperatures obtained under oxidizing conditions.

The results for the coarse particles show evolution of nitrogen species at temperatures lower than 700 K. These temperatures are too low to observe significant devolatilization of nitrogen species. It is, therefore, a possibility that the calculated particle temperatures in the present work may be slightly lower and direct measurements of particles temperatures would yield better results. The lower calculated temperatures, especially for the larger particles, may be due to under correction of measured gas phase temperature which assumed a Nusselt number of 2. A more elaborate model e.g., Kaskan (1956) should yield better results. The rates of formation of the nitrogen species for the coarse particles, nonetheless, follow some expected trends. For the Illinois bituminous, destruction of all the nitrogen species indicate rapid gas phase reactions for higher rank coals. For the lignite after 60 ms where particle temperature do attain high values, rate of formation of HCN and total XN species shows some increase. This reinforces our hypothesis that HCN

TABLE 6.2
AVERAGE HEATING RATES – TEXAS LIGNITE

Size Fraction	Pyrolysis Conditions	Particle Residence Time (ms)	Particle Peak Temperature (K)	Average Heating Rate (K/s)
Fines	Reducing	85	1108	8,300
Fines	Oxidizing	75	1196	10,600
Unclassified	Reducing	79	1132	8,000
Unclassified	Oxidizing	70	1181	9,700
Coarse	Reducing	94	969	6,050

TABLE 6.3
AVERAGE HEATING RATES – ILLINOIS BITUMINOUS

Size Fraction	Pyrolysis Conditions	Particle Residence Time (ms)	Particle Peak Temperature (K)	Average Heating Rate (K/s)
Fines	Reducing	87	1149	8,600
Fines	Oxidizing	76	1234	11,000
Unclassified	Reducing	77	1263	11,200
Unclassified	Oxidizing	66	1344	14,300
Coarse	Reducing	86	1014	7,100

is the primary nitrogenous light gaseous species of coal devolatilization. The free stream temperatures in this regime are above 1100 K leading to formation of N_2 as evident from the destruction of NO.

The runs for the unclassified size particles also lead to an important conclusion. Since 60% of the particles were smaller than $38\text{ }\mu\text{m}$, which formed the fine size cut, the results for the unclassified and fine size cuts show similar trends. However, for the unclassified runs a full spectrum of particle size exists which in reality lead to a full spectrum of particle time-temperature histories and thereby yields higher rates of formation due to a continuous source of nitrogen. These trends are shown by the results for the unclassified runs where rates of formation do increase after showing some decay.

Fine particles more closely follow the gas streamlines due to smaller inertia and also the effects of the assumptions made in our model, e.g., sphericity of particles, heat exchange between the two phases etc., is not very pronounced. In the present work, fines have the narrowest particle size range and, therefore, the calculated rates of formation for the fine particles should be considered more accurate.

Results for all the reported runs show that rates of formation start to decay after approximately 40–60 ms, which indicate that even though coal nitrogen continues to evolve, gas phase reactions leading to N_2 formation become significant. This fact is later used in analysis of our data. Average heating rates and peak particle temperatures are comparable for both the coal under identical conditions (pyrolysis environment and particle size). This suggests that coal nitrogen evolution depends more strongly on composition than on heating rates. The rates of formation and the time-temperature histories can now be used in conjunctions with kinetics models to determine the rates of coal nitrogen evolution which is the topic of next chapter.

CHAPTER 7

NITROGEN EVOLUTION KINETICS

This chapter focuses on the determination of rate constants for early evolution of coal nitrogen. The time resolved rates of formation of nitrogenous species and the particle time– temperature histories, as reported in the previous chapter are used in conjunction with a simple kinetic mechanism. The calculated rate constants are then reported and compared with the literature values.

Proposed Mechanism

To calculate kinetic parameters for evolution of coal nitrogen into the bulk gas phase, the following simple mechanism is proposed:

where CN and TN represent coal nitrogen and tar nitrogen respectively and ν is the fraction of coal nitrogen evolved as tar nitrogen. The rate expressions for the proposed mechanism are:

$$\begin{aligned}
 \frac{d[\text{CN}]}{dt} &= -k_1[\text{CN}] = -k_1[\text{CN}]^0[\text{VM}] \\
 \frac{d[\text{TN}]}{dt} &= \nu k_1[\text{CN}]^0[\text{VM}] - k_2[\text{TN}] \\
 \frac{d[\text{HCN}]}{dt} &= (1 - \nu)k_1[\text{CN}]^0[\text{VM}] + k_2[\text{TN}] - k_3[\text{HCN}][\text{OH}] \\
 \frac{d[\text{NH}_3]}{dt} &= k_3[\text{HCN}][\text{OH}] - k_4[\text{NH}_3][\text{O}_2] - k_5[\text{NH}_3][\text{NO}]
 \end{aligned}$$

$$\begin{aligned}\frac{d[\text{NO}]}{dt} &= k_4[\text{NH}_3][\text{O}_2] - k_5[\text{NH}_3][\text{NO}] \\ \frac{d[\text{N}_2]}{dt} &= k_5[\text{NH}_3][\text{NO}].\end{aligned}$$

These expressions are combined to yield the following expression:

$$(1 - \nu)k_1[\text{CN}]^0\text{VM} + k_2[\text{TN}] = \frac{d\{[\text{HCN}] + [\text{NH}_3] + [\text{NO}]\}}{dt} + 2\frac{d[\text{N}_2]}{dt}.$$

The measured concentrations of N_2 showed too much scatter to be useful, therefore, the last term is replaced by a function f which depends upon gas temperature and concentrations of NH_3 , NO and radical OH (Bose and Wendt, 1989). The equation finally takes the form:

$$(1 - \nu)k_1[\text{CN}]^0\text{VM} + k_2[\text{TN}] = \frac{d\{[\text{HCN}] + [\text{NH}_3] + [\text{NO}]\}}{dt} + 2f(T_g, [\text{OH}], [\text{NH}_3], [\text{NO}]).$$

As a first approximation we assume $f \approx 0$, thus limiting our discussion to the first 50 ms of the devolatilization process. Furthermore, in view of the fact that only little devolatilization has taken place we set $\text{VM} \approx \text{VM}^*$ and propose that secondary tar pyrolysis is rapid compared to primary loss of N from coal, i.e., $d[\text{TN}]/dt \approx 0$, yielding the simplified expression:

$$k_1[\text{CN}]^0\text{VM}^* = \frac{d\{[\text{HCN}] + [\text{NH}_3] + [\text{NO}]\}}{dt}.$$

This allows k_1 to be evaluated as a function of particle temperature. The rates of formation of nitrogenous species into the *bulk* gas phase are per unit volume basis. These rates are converted to per gram of coal nitrogen basis, and then used in the expression for k_1 . The first order rate constants for the runs made with fines are plotted on Fig. 7.1. Literature values are also shown on the same figure. Chemically bound nitrogen in coals is classified into loosely bound nitrogen and tightly bound nitrogen. The loosely bound nitrogen evolves at low temperatures and during early stages of coal pyrolysis. Tightly bound nitrogen, on the other hand, evolves very slowly during later stages of the pyrolysis process. The ratio of these two forms of chemically bound nitrogen depends upon the chemical structure of coal. The

Figure 7.1 First Order Rate Constants for Coal Nitrogen Evolution.

- Texas Lignite (Fines) Under Reducing Conditions
- Texas Lignite (Fines) Under Oxidizing Conditions
- Illinois Bituminous (Fines) Under Reducing Conditions
- Illinois Bituminous (Fines) Under Oxidizing Conditions

literature values shown on Figure 7.1 are for both loosely-bound and tightly-bound nitrogen.

For the particle time-temperature envelope encountered, in our experiments only loosely-bound nitrogen evolves into the bulk gas phase. Computed rate constants for Texas lignite, under both reducing and oxidizing environments, and Illinois bituminous under reducing conditions fall on a single line given by $k_1 = 63.8 \exp(-5220/RT)$. The higher apparent rate constant for the bituminous coal, under oxidizing conditions, may be due to the additional heat gain caused by the oxidation of tars in the vicinity of coal particles.

The apparent activation energy obtained from this work is low, but similar to the values reported by Solomon and Colket (1977) for loosely bound nitrogen. Absolute values for our rate constants appear to be higher than literature values derived from mass loss measurements from captive particles. A low activation energy suggests that coal devolatilization is better described by several parallel reactions rather than by a single step first order reaction. Therefore, little physical significance should be attached to the first order rate constant reported here.

Rate Constants for Tar Nitrogen Conversion (k_2)

First order rate coefficient(s), k_2 , for tar nitrogen conversion reaction can be computed from the values of k_1 , as discussed below.

The pseudo steady state assumption for tar nitrogen leads to the following expression:

$$\nu k_1 [\text{CN}]^0 \text{VM} - k_2 [\text{TN}] = 0$$

Therefore,

$$k_2 [\text{TN}] = \nu k_1 [\text{CN}]^0 \text{VM}.$$

Further, assuming that during early stages, of coal pyrolysis, nitrogen evolution occurs mainly through tars, the stoichiometric coefficient ν can be taken as unity.

This leads to the following expressions:

$$k_2[\text{TN}] = \nu k_1[\text{CN}]^0 \text{VM} \\ = \frac{d\{[\text{HCN}] + [\text{NH}_3] + [\text{NO}]\}}{dt} + 2f(T_g, [\text{OH}], [\text{NH}_3], [\text{NO}]).$$

Noting that for the first 50 ms, function f is considered to be negligible, the final expression becomes:

$$k_2 = \frac{1}{[\text{TN}]} \frac{d\{[\text{HCN}] + [\text{NH}_3] + [\text{NO}]\}}{dt}.$$

Experimental data for tar nitrogen reported in Appendix A is used, after conversion to molar units, in the above expression. Figure 7.2 shows the values of rate constant, k_2 , for the four runs with fine particles. The loss of nitrogen from coal depends on the particle temperature, but secondary pyrolysis of tars occur in the gas phase and, hence, is a function of gas temperature. The values of rate constant for primary loss of nitrogen from coal i.e., k_1 , computed, therefore, at similar temperatures, are also shown for comparison on Fig. 7.2 by the solid line.

The values of k_2 show a lot of scatter as these are very sensitive to the concentration of tar nitrogen. Since, the quantities of tars extracted for these samples were very small, therefore, the reported values may not be accurate and hence are not of any physical significance. It is noted, that the final expression for k_2 , even though derived based on the assumption that k_1 is much smaller than k_2 , only involves experimental values of NO, NH₃, HCN and tar nitrogen and does not specifically include k_1 . The computed values of k_2 are always much larger than k_1 , which confirms that primary loss of nitrogen from coal is much slower than secondary pyrolysis reactions of tars thereby justifying our assumption.

COMPARISON OF RATE CONSTANTS

One of the objectives of this study is to determine a rate constant for coal nitrogen evolution which could be incorporated in a comprehensive engineering model describing the fate of nitrogen species over the complete combustion process.

Figure 7.2 Calculated First Order Rate Constants (k_2) for Tar Nitrogen Conversion.

- Texas Lignite (Fines) Under Reducing Conditions
- Texas Lignite (Fines) Under Oxidizing Conditions
- Illinois Bituminous (Fines) Under Reducing Conditions
- Illinois Bituminous (Fines) Under Oxidizing Conditions

The rate constants resulting from this study and those reported in literature differ significantly. A comparison of these rate constants is in order and can be made by looking at the predicted quantities of total nitrogenous species entering the post flame zone and comparing them with the experimental concentrations. This section presents the comparison by formulating a simplified forward problem.

Formulation of Simplified Forward Problem

In the present study, the rates of formation of species, i , are calculated by substituting its experimental concentrations in the transformed species equation (Eq. (62) Chapter 6) which also corrects for the convective and diffusives effects. If an expression is available to calculate the rate term, the same equation can be used to predict the concentration field of a specific species. This equation, therefore, forms the basis for the simplified Forward Problem.

$$D_{im} \frac{d^2 x_i}{dz^2} + \left[\frac{1}{c} \frac{d(cD_{im})}{dz} - v_{gz} \right] \frac{dx_i}{dz} + \left(\frac{v_{gz}}{M} \frac{dM}{dz} \right) x_i = -\frac{R_i}{c}. \quad (108)$$

The relative contributions of the convective and diffusive terms can be determined by calculating the Peclet number. Computed Peclet numbers, throughout the devolatilization region, were found to be quite large with a lower bound of about four close to the stagnation plane. Contribution of the last term on the left hand side of Eq. (108) was also found to be negligible. In view of these results, above equation can be reduced to:

$$v_{gz} \frac{dx_i}{dz} = \frac{R_i}{c}. \quad (109)$$

Now, defining a new variable t^* as:

$$t^* = \frac{z}{v_{gz}}$$

The above expression becomes:

$$c \frac{dx_i}{dt^*} = R_i.$$

Finally,

$$\frac{dc_i}{dt^*} = R_i. \quad (110)$$

The above expression, now, can be integrated to predict the concentration of species i . Since, the axial velocity of particles is coupled to gas phase axial velocity, the above expression can be considered to yield the concentration profile of species i along the particle trajectory. Writing the above expression for total gaseous nitrogenous species (XN) gives:

$$\begin{aligned}\frac{d[\text{XN}]}{dt^*} &= R_i \\ \frac{d[\text{XN}]}{dt^*} &= k_0 \exp(-E/RT_p).\end{aligned}\tag{111}$$

Application of Simplified Forward Problem

This section presents the application of the simplified forward problem first to “Opposed Flow Combustor” experiments and then to a “Down Fired Plug Flow Pulverized Coal Combustor” experiment.

Opposed Flow Combustor Experiments

The experimental concentrations of Total XN species and the corresponding values predicted using the rate constants from the present study, Pohl and Sarofim (1977) and Solomon and Colket (1978) are shown on Figures 7.3 and 7.4. Results based on the rate coefficients reported previously by above mentioned researchers underpredict total nitrogenous species by considerable amounts. The quantities of total XN species computed using the rate expression derived for present study reasonably well predict the total nitrogenous species during very early stages (before 50 ms), where Peclet Number is very large, but overpredict total XN quantities beyond 50 ms. This is also due, in part, to the fact that the rate coefficient derived, here, utilized experimental values upto 50 ms, as mechanisms leading to formation of N_2 become significant during later stages. In the next section, same rate expressions are applied to an experiment conducted in a Down Fired Plug Flow Pulverized Coal Combustor. The results of next section should provide an independent check for various rate coefficients.

Figure 7.3 Comparison of First Order Rate Constants for Coal Nitrogen Evolution – Texas Lignite (Fines), Reducing Run.
 o Experimental Curves: Predicted

Figure 7.4 Comparison of First Order Rate Constants for Coal Nitrogen Evolution - Illinois Bituminous (Fines), Reducing Run.
 o Experimental Curves: Predicted

Down Fired Plug Flow Combustor Experiment

Mereb (1990) studied the fate of nitrogenous species in a laboratory size down fired plug flow pulverized coal combustor. Details of furnace are described elsewhere (Bose, Dannecker and Wendt, 1988; Mereb, 1990). Bose (1989) showed that diffusive effects in that configuration were negligible and Eq. (111) is, therefore, applicable to this system. The first sampling port, in experiments conducted by Mereb, is in the post flame zone and corresponds to time well beyond the time scales associated with coal devolatilization.

Figure 7.5 shows the predicted profiles of total XN species for a typical experiment in the down fired furnace. The only experimental point shown on the figure represent total nitrogenous species at the first port. The experimental value, however, is a lower bound as Mereb did not report the quantity of N_2 , which may be present in significant quantities, at the first port. As pointed out previously, evolution of coal nitrogen depends on the particle temperature. In absence of measured particle temperatures, the following two scenarios are considered:

1. Coal particle temperatures are considered to be same as free stream temperatures.
2. Coal particle temperatures are calculated using the conduction limiting model as described in Chapter 5.

The predicted quantities of XN entering the post flame zone employing literature rate coefficients under scenario #1, are much lower than measured experimental value. The quantities of total nitrogenous species entering the post flame zone, computed using our rate coefficient, under scenario #1, are higher than the experimentally observed values. Whereas, our rate coefficient under scenario #2 yields a value very close to the experimental measurement. It is, therefore, concluded that the rate expression derived in the present work more realistically describes the early coal nitrogen evolution behavior. It is, however, pointed out that in a real combustion environment, coal particle temperature may lag the gas temperature

Figure 7.5 Prediction of Total Nitrogenous Species in a Down Fired Plug Flow Combustor.

for some time and then overshoot before equilibrating with the free stream temperature. Furthermore, our simplified forward problem does not take into account any destruction mechanisms and, hence, will overpredict the quantities of nitrogenous species during later stages of devolatilization process.

SUMMARY

The time resolved net rates of formation of nitrogenous species into the bulk gas phase and particle time-temperature histories were successfully used to determine the parameters for coal nitrogen devolatilization. This accomplished the final task of this work. Although, the coal nitrogen devolatilization rate constant from this study is higher than those reported in the literature, its activation energy is similar to that reported for loosely bound nitrogen. Indeed, since this rate constant was derived from measurements of gaseous species in the bulk gas phase and more reasonably predict the quantities of total nitrogenous species entering the post flame zone, it should have direct applicability to models describing NO formation and destruction in combustors. It is noted, however, that an improved model incorporating a more elaborate gas phase chemistry may yield more accurate estimates for kinetic parameters describing the evolution of coal nitrogen, as would direct measurements of the particle temperatures.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

An opposed flow combustion configuration was successfully used to study early evolution of coal nitrogen with emphasis on the speciation of nitrogenous species as they evolve into the bulk gas phase. The problems with the spatial resolution were solved by selecting a low-velocity high-temperature fuel. Two coals of different rank were studied under both reducing and oxidizing conditions. The effects of particle size on nitrogen evolution were investigated. Experimental measurements of the nitrogenous species were used in conjunction with a model to calculate the time-temperature histories of coal particles and to calculate the time-resolved rates of formation in the bulk gas phase. These rates were, then, employed along with a simple kinetic model to estimate the rate constant for early coal nitrogen evolution.

Although, opposed flow combustion configuration is a useful experimental tool, studies in this system are limited to moderate heating rates (up to 10,000 K/s) due to experimental constraints as discussed in the following section.

CRITICAL APPRAISAL OF OPPOSED FLOW CONFIGURATION

Opposed flow configuration offers some advantages over captive sampling techniques since it more closely simulates the combustion process in an actual industrial environment. It is also superior to entrained flow configuration in the respect that there are no so called "wall effects". These features of opposed flow configuration have successfully been utilized in gaseous diffusion flames and detailed kinetics of various systems have extensively been studied. This configuration has also been utilized to study turbulent diffusion flames and to understand the effect of stretch rate on flame extinction. Kram (1984) and McCaslin (1985) were

successful to investigate the changes in coal properties and the evolution of carbonaceous species into the bulk gas phase. Carbonaceous species generally evolve in the time-temperature envelope easily achievable in opposed flow configuration. Evolution of nitrogenous species, however, is a strong function of the final (peak) temperature attained by coal particles. In our initial experiments, peak particle temperatures achieved were not high enough to cause considerable coal nitrogen evolution. Attempts to attain a time-temperature history more conducive for coal nitrogen evolution were successful and higher peak temperatures were obtained. Increased flow rates which led to higher temperatures, however, resulted in shorter particle residence times, thereby limiting the studies to moderate heating rates. This was, partly, due to the inherent characteristics of opposed flow configuration which do not provide independent control over all operating variables.

Particle time-temperature histories are, essentially, dictated by the relative momentum of the two opposed jets. Higher temperatures can be obtained by allowing larger energy release (i.e., burning more fuel) in the lower burner's premixed flame, but the increased momentum of the rising jet pushes the particle stagnation plane closer to the upper burner resulting in decreased residence times. This effect can be counteracted by increasing the transport gas from the upper burner, which has a cooling effect on the temperature field. Therefore, one has to compromise for an optimal combination of these variables. Parametric runs performed to achieve an optimal mix of operating conditions led to acceptable time-temperatures histories and evolution of nitrogen species could be successfully studied.

The major problem, however, was with coal injection. The distribution of particles falling into the flames was very uniform. Part of the coal fell along the rim of the burner and did not see the flame. This introduces some uncertainty in the data. This problem was remedied by taking in-situ coal feed measurements for later use in calculations.

Entrained flow configuration may be superior to opposed flow system as it may yield higher heating rates by injecting the coal particles directly in a high

temperature stream. Furthermore, a precise control over coal feed may be possible. Both systems provide excellent control over pyrolysis environment.

In summary, opposed flow configuration is a useful experimental tool to study coal pyrolysis and short time scales processes. An improved coal injection system and use of a high temperature material to construct the burners may allow investigation of coal devolatilization/pyrolysis under even higher heating rates.

SPECIATION AND RATES OF FORMATION

The major conclusions drawn from this work are as follows:

1. The opposed flow combustion configuration is a useful tool which can yield interpretable pyrolysis data.
2. Studies in opposed flow configuration are limited to moderate heating rates (up to 10,000 K/s).
3. Evolution of coal nitrogen occurs through tars and HCN, irrespective of the coal rank and pyrolysis environment. However, higher rank coals yield much larger quantities of tars.
4. Evolution and subsequent oxidation of tars is slow for low rank coals. For higher rank coals, secondary pyrolysis reactions of tars are very rapid especially in the presence of oxygen.
5. HCN is the first light gaseous product of pyrolysis entering the bulk gas phase. It precedes ammonia for both low and high rank coals under reducing and oxidizing conditions.
6. Energy feed back mechanisms are important for high rank coals and lead to larger yields of nitrogenous species.
7. Data for the 'coarse fraction' runs indicate that yield of ammonia increases with particle size.
8. Effect of heating rate on the early evolution of coal nitrogen is not significant.
9. Net rates of formation of nitrogenous compounds in the bulk gas phase are not affected by particle size.

10. Experimental measurements of nitrogenous species can be used to determine kinetic parameters for coal nitrogen evolution. First order rate constant for early evolution of coal nitrogen is found to be independent of particle size and coal rank and is given by:

$$k_1 = 63.8 \exp(-5220/RT)$$

The low activation energy in the above expression stems from the first order reaction employed in our simple kinetic model. In reality, nitrogen evolution is described by a series of parallel reactions, therefore, no physical significance should be attached to the kinetic parameters reported here.

The rate constant for coal nitrogen evolution reported in this work more closely predict the total gaseous nitrogenous species entering the post flame zone. This can be incorporated in comprehensive engineering models describing the formation and fate of XN species over complete combustion process. However, this rate constant must be used in conjunction with an elaborate kinetic mechanism involving formation and destruction of XN species.

FUTURE WORK

The results obtained from this work point out to some improvements which should be incorporated in the theoretical model as well as experimental techniques for better results.

1. One dimensionality aspects of the opposed flow combustion configurations, so far, have been shown for monosized particles only. The model should be extended to account for a polydispersed feed. This will aid in interpreting the data for the 'unclassified fraction' runs.
2. Direct measurements of particle temperatures should be attempted to avoid any uncertainty in calculated particle temperature, which is the single most important variable for determining nitrogen evolution kinetics.
3. Kinetic mechanisms involving more elaborate gas phase chemistry should be explored to determine more accurate estimates of rate constants.

4. The nitrogen evolution kinetics reported here should be incorporated in the existing models describing the fate of nitrogenous species in the post flame zone.

Future work may also extend this work to more fundamental level, whereby, to investigate the nature of tars evolved as a function of structure of the parent coal. Other applications of opposed flow configuration should also be explored. An emerging application of this configuration may be formation of ceramics in this system. Screening runs were performed to study the formation of ceramics in this configuration by doping the two opposing streams with ammonia and injecting bauxite particles in this configuration. Due to low temperatures attained, the screening runs were not very promising. Use of smaller particles and higher temperature fuels may yield better results and should be attempted.

NOMENCLATURE

A_{pr}	Projected area of particle (cm^2).
B_m	Blowing parameter (see Eq. 19).
c	Molar density (gmol/cm^3).
C_D	Drag Coefficient.
C_p	Heat Capacity ($\text{cal}/\text{gmol K}$).
D_{im}	Pseudobinary diffusion coefficient of species i in gas mixture (cm^2/sec).
d_p	Particle diameter (cm).
E	Activation Energy (cal/mole).
k	Thermal conductivity of gaseous mixture ($\text{cal}/\text{cm-sec K}$).
M_i	Molecular weight of species i .
m_p	Particle mass (gm).
n	Particle number density ($\#/\text{cm}^3$).
N_R	Number of reactions.
N_S	Number of species.
P	Pressure (atm).
$\mathbf{q}$	Heat flux vector ($\text{cal}/\text{cm}^2\text{-sec}$).
Q	Eigenvalue for gas phase momentum equation ($\text{gm}/\text{cm}^3 \text{ sec}^2$).
R	Universal gas constant.
r	Radial distance (cm).
s	Specific heat ($\text{cal}/\text{gm K}$).
S_e	Source term for energy (see Eq. 3).
S_m	Source term for momentum (see Eq. 2).

S_v	Source term for mass (see Eq. 1).
t	Time (sec).
T	Temperature (K).
$\mathbf{v}_g$	Gas phase velocity vector (cm/sec).
v_{gr}	Radial component of gas velocity (cm/sec).
v_{gz}	Axial component of gas velocity (cm/sec).
$\mathbf{v}_p$	Particle phase velocity vector (cm/sec).
v_{pr}	Radial component of particle velocity (cm/sec).
v_{pz}	Axial component of particle velocity (cm/sec).
V	Molar volume (cm ³ /gmol).
V^*	Ultimate volatile matter yield.
x_i	Mole fraction of species i .
z	Axial distance (cm).

Greek Letters

α	Coefficient as defined in Eq. (99).
γ	Swelling coefficient (see Eq. 27).
Ω_i	Surface averaged mass flux fraction of species i .
η	Dimensionless radial coordinate within particle.
η_s	Instantaneous dimensionless particle radius.
μ	Viscosity of gas mixture (gm/cm-sec).
ρ	Mass density (gm/cm ³).
ψ	Gas phase similarity transform (sec ⁻¹).
ϕ	Particle phase similarity transform (sec ⁻¹).
τ	Shear stress tensor.

Subscripts

0	Refers to initial conditions.
fs	Refers to free stream conditions.
g	Refers to gas phase variables.
i	Refers to axial grid point.
p	Refers to particle properties.

Superscripts

0	Refers to initial conditions.
n	Refers to temporal step or iteration number.
k	Refers to temporal step or iteration number.

APPENDIX A
EXPERIMENTAL
AND
REDUCED DATA

TABLE A-1**EXPERIMENTAL COMPOSITION MATRIX – UTAH BITUMINOUS, UNCLASSIFIED****Combustion Configuration:** Opposed Flow Diffusion Flame**Lower Burner Flow Rates:**O₂: 13.3 lpm

Ar: 14.5 lpm

Stoichiometric Ratio: 2.2

Upper Burner Flow Rates:

CO: 12.1 lpm

Transport Argon: 16.5 lpm

In-situ Coal Feed Rate: 5.0 gm/min

Particle Loading: 175 mg/l

z^a (cm)	O ₂ (% vol)	CO (% vol)	CO ₂ (% vol)	NO (ppmv)	NH ₃ (ppmv)	HCN (ppmv)
2.750	0.63	35.60	6.88	150.0	3.0	9.0
2.580	2.40	20.76	11.03	185.0	12.1	52.8
2.210	9.38	2.65	8.91	71.3	4.4	26.5
1.985	11.12	1.45	4.68	98.5	1.3	0.7
1.525	13.75	0.99	4.24	65.0	1.8	1.2
1.225	18.50	0.27	0.37	20.0	1.5	1.5

 a : Axial distance, measured from the lower burner.

Data plotted on Figures 3.2 and 3.3.

TABLE A-2
Temperature Data – Utah Bituminous, Unclassified

Axial Position (cm)	Measured Temperature (K)	Corrected Temperature (K)
2.795	848	871
2.450	886	913
2.300	900	928
2.110	983	1024
1.934	988	1029
1.905	1034	1083
1.845	1047	1099
1.825	1043	1094
1.700	1067	1123
1.655	1112	1178
1.555	1077	1135
1.405	1140	1212
1.180	1125	1193
1.030	1090	1151
1.000	1102	1165
0.775	1024	1072
0.540	913	943
0.325	852	875
0.090	804	822

Data Plotted on Figure 3.2.

TABLE A-3

EXPERIMENTAL COMPOSITION MATRIX – BEULAH LIGNITE, UNCLASSIFIED, REDUCING CONDITIONS

Combustion Configuration: Opposed Flow Hybrid Flame

Lower Burner Flow Rates:

CO: 7.7 lpm

O₂: 3.3 lpm

Ar: 17.4 lpm

Premixed Flame SR: 0.86

Diffusion Flame SR: 0.0

Upper Burner Flow Rates:

CO: 7.6 lpm

Transport Argon: 20.1 lpm

In-situ Coal Feed Rate: 5.0 gm/min

Particle Loading: 181 mg/l

z^a (cm)	O ₂ (% vol)	CO (% vol)	CO ₂ (% vol)	NO (ppmv)	NH ₃ (ppmv)	HCN (ppmv)
2.665	0.02	13.02	13.81	43.5	8.7	20.7
2.470	0.00	11.15	14.26	35.5	9.5	44.4
2.215	0.00	12.47	15.04	46.0	9.0	26.2
1.865	0.05	8.88	13.09	24.0	8.7	41.2
1.530	0.05	9.46	17.13	47.0	4.7	18.8
1.150	0.20	8.66	18.89	43.0	3.6	11.0
0.760	0.20	7.80	19.53	39.0	3.0	6.7
0.410	0.35	8.10	19.10	30.0	3.8	1.8

a : Axial distance, measured from the lower burner.

Nitrogenous Species Data plotted on Figure 3.4.

TABLE A-4

Temperature Data – Beulah Lignite, Unclassified, Reducing Conditions

Axial Position (cm)	Measured Temperature (K)	Corrected Temperature (K)
2.990	736	749
2.845	749	762
2.745	783	799
2.645	828	848
2.635	843	864
2.405	878	903
2.195	958	994
1.960	1043	1094
1.816	1082	1141
1.815	1078	1136
1.610	1133	1203
1.360	1168	1247
1.190	1207	1297
0.950	1243	1344
0.765	1258	1363
0.560	1273	1383
0.415	1275	1386
0.355	1278	1390
0.345	1269	1378

TABLE A-5

EXPERIMENTAL COMPOSITION MATRIX – BEULAH LIGNITE, UNCLASSIFIED, OXIDIZING CONDITIONS

Combustion Configuration: Opposed Flow Hybrid Flame

Lower Burner Flow Rates:

CO: 7.6 lpm

O₂: 8.3 lpm

Ar: 19.7 lpm

Premixed Flame SR: 2.17

Diffusion Flame SR: 1.92

Upper Burner Flow Rates:

CO: 4.7 lpm

Transport Argon: 20.0 lpm

In-situ Coal Feed Rate: 5.0 gm/min

Particle Loading: 203 mg/l

z^a (cm)	O ₂ (% vol)	CO (% vol)	CO ₂ (% vol)	NO (ppmv)	NH ₃ (ppmv)	HCN (ppmv)
2.805	4.65	3.74	17.49	129.0	4.9	46.3
2.505	4.90	2.85	18.48	142.0	3.3	12.0
2.265	6.40	2.39	19.10	125.0	2.7	25.9
2.025	8.75	1.30	20.80	110.0	1.1	3.0
1.975	8.45	1.39	20.00	115.0	1.0	0.3
1.745	11.50	1.00	20.50	80.0	0.5	0.1
1.330	12.80	0.74	20.20	41.2	0.4	0.0
0.860	13.50	0.95	20.44	92.5	0.2	0.0
0.425	14.60	0.65	22.20	57.5	0.1	0.0

a : Axial distance, measured from the lower burner.

Nitrogenous Species Data plotted on Figure 3.4.

TABLE A-6

Temperature Data – Beulah Lignite, Oxidizing Conditions

Axial Position (cm)	Measured Temperature (K)	Corrected Temperature (K)
2.915	1021	1067
2.745	1050	1102
2.705	1057	1110
2.620	1071	1127
2.485	1089	1149
2.450	1091	1151
2.405	1100	1162
2.290	1113	1178
2.230	1117	1183
2.180	1091	1151
2.135	1129	1198
2.090	1100	1162
1.950	1113	1178
1.760	1131	1201
1.575	1148	1222
1.420	1163	1241
1.275	1177	1258
1.135	1190	1275
0.990	1198	1285
0.865	1205	1294
0.670	1213	1305
0.560	1222	1316
0.455	1166	1245
0.420	1129	1198
0.350	1129	1198
0.255	1113	1178
0.160	1067	1122
0.125	1033	1082

TABLE A-7

EXPERIMENTAL COMPOSITION MATRIX – UTAH BITUMINOUS, UNCLASSIFIED, REDUCING CONDITIONS

Combustion Configuration: Opposed Flow Hybrid Flame

Lower Burner Flow Rates:

CO: 7.7 lpm
O₂: 3.32 lpm
Ar: 17.4 lpm
Premixed Flame SR: 0.86
Diffusion Flame SR: 0.0

Upper Burner Flow Rates:

CO: 7.6 lpm
Transport Argon: 20.1 lpm
In-situ Coal Feed Rate: 5.0 gm/min
Particle Loading: 181 mg/l

z^a (cm)	O ₂ (% vol)	CO (% vol)	CO ₂ (% vol)	NO (ppmv)	NH ₃ (ppmv)	HCN (ppmv)
2.595	0.00	11.61	8.05	36.0	4.4	17.1
2.145	0.00	12.81	10.65	55.0	5.2	16.8
1.945	0.00	9.85	14.34	56.0	3.3	16.2
1.495	0.00	11.14	16.18	55.0	4.1	21.3
1.440	0.00	9.34	17.86	58.0	3.4	14.5
1.280	0.20	9.97	18.36	53.0	5.6	21.1
0.885	0.33	8.36	19.89	47.5	3.3	30.4
0.310	0.52	8.41	13.56	49.0	3.3	16.2

a : Axial distance, measured from the lower burner.

Nitrogenous Species Data plotted on Figure 3.4.

TABLE A-8

Temperature Data – Utah Bituminous, Reducing Conditions

Axial Position (cm)	Measured Temperature (K)	Corrected Temperature (K)
2.900	667	676
2.555	694	705
2.410	728	740
2.325	745	758
2.100	784	801
2.000	902	930
1.805	974	1013
1.585	1019	1065
1.440	1043	1094
1.330	1071	1127
1.175	1104	1167
1.010	1118	1185
0.875	1141	1213
0.775	1157	1233
0.619	1165	1243
0.510	1184	1267
0.345	1213	1305
0.065	1233	1331

TABLE A-9

EXPERIMENTAL COMPOSITION MATRIX - UTAH BITUMINOUS, UNCLASSIFIED, OXIDIZING CONDITIONS

Combustion Configuration: Opposed Flow Hybrid Flame

Lower Burner Flow Rates:

CO: 7.6 lpm

O₂: 8.3 lpm

Ar: 19.7 lpm

Premixed Flame SR: 2.17

Diffusion Flame SR: 1.92

Upper Burner Flow Rates:

CO: 4.7 lpm

Transport Argon: 20.0 lpm

In-situ Coal Feed Rate: 5.0 gm/min

Particle Loading: 203 mg/l

z^a (cm)	O ₂ (% vol)	CO (% vol)	CO ₂ (% vol)	NO (ppmv)	NH ₃ (ppmv)	HCN (ppmv)
2.095	4.63	5.56	16.75	107.5	4.5	17.4
2.800	1.88	4.50	17.88	225.0	5.9	16.7
1.570	9.00	1.28	20.50	88.0	2.8	2.2
1.170	11.25	0.51	22.00	58.0	2.0	2.0
0.880	10.00	1.15	24.00	77.5	0.3	2.4
0.405	9.25	1.65	22.50	97.5	5.9	0.0

a : Axial distance, measured from the lower burner.

Nitrogenous Species Data plotted on Figure 3.4.

TABLE A-10

Temperature Data – Utah Bituminous, Oxidizing Conditions

Axial Position (cm)	Measured Temperature (K)	Corrected Temperature (K)
2.420	910	940
2.410	988	1029
2.195	997	1039
2.135	1020	1066
1.925	1053	1106
1.800	1055	1108
1.515	1071	1127
1.410	1061	1115
1.290	1077	1134
1.095	1100	1162
1.075	1120	1187
1.035	1111	1176
0.905	1123	1191
0.820	1135	1206
0.760	1128	1197
0.450	1143	1216
0.260	1129	1198

TABLE A-11

COMPOSITION MATRIX – GAS FLAME, REDUCING CONDITIONS

Combustion Configuration: Opposed Flow Premixed Flame

Lower Burner Flow Rates:

CO: 17.9 lpm

O₂: 6.5 lpm

Ar: 16.4 lpm

Stoichiometric Ratio: 0.73

Upper Burner Flow Rates:

Transport Argon: 50.1 lpm

z^a (cm)	O ₂ (% vol)	CO (% vol)	CO ₂ (% vol)	NO (ppmv)	NH ₃ (ppmv)	HCN (ppmv)
3.100	0.05	0.21	0.29	0.2	–	–
3.025	0.05	0.41	0.44	0.1	–	–
2.965	0.05	0.63	1.05	0.2	–	–
2.575	0.05	0.93	1.35	0.2	0.36	0.20
2.410	0.10	1.38	2.32	0.2	–	–
2.180	0.05	2.17	4.32	0.5	0.42	0.26
1.930	0.05	4.21	10.17	0.5	–	–
1.550	0.10	5.97	16.57	1.0	0.38	0.36
1.345	0.10	7.48	21.06	0.7	–	–
0.940	0.10	9.80	29.50	1.0	0.44	0.34
0.680	0.05	9.56	28.14	0.3	–	–
0.450	0.10	11.26	35.32	0.6	–	–
0.125	0.05	11.67	37.39	0.7	–	–

a : Axial distance, measured from the lower burner.

Data plotted on Figures 4.1 and 4.2.

TABLE A-12
Temperature Data – Gas Flame, Reducing Conditions

Axial Position (cm)	Measured Temperature (K)	Corrected Temperature (K)
2.790	603	609
2.525	765	780
2.365	841	863
2.175	907	937
1.880	993	1036
1.640	017	1064
1.445	1147	1221
1.245	1185	1269
1.130	1201	1290
0.975	1233	1331
0.785	1273	1384
0.730	1282	1397
0.560	1315	1441
0.235	1353	1493
0.100	1368	1515
0.035	1383	1535

Data Plotted on Figure 4.1.

TABLE A-13

COMPOSITION MATRIX – GAS FLAME, OXIDIZING CONDITIONS

Combustion Configuration: Opposed Flow Premixed Flame

Lower Burner Flow Rates:

CO: 17.9 lpm

O₂: 10.9 lpm

Ar: 16.4 lpm

Stoichiometric Ratio: 1.21

Upper Burner Flow Rates:

Transport Argon: 50.1 lpm

In-situ Coal Feed Rate: 2.93 gm/min

Particle Loading: 57 mg/l

z^a (cm)	O ₂ (% vol)	CO (% vol)	CO ₂ (% vol)	NO (ppmv)	NH ₃ (ppmv)	HCN (ppmv)
3.130	0.10	0.03	0.15	0.2	–	–
2.820	0.25	0.07	0.58	0.4	0.3	0.51
2.725	0.50	0.17	1.92	0.8	–	–
2.330	0.90	0.31	3.73	1.5	0.4	0.51
2.050	1.50	0.47	7.42	1.5	–	–
1.760	2.50	0.73	14.41	2.0	0.4	0.57
1.590	3.10	0.73	19.10	1.5	–	–
1.360	3.50	0.99	20.39	2.0	–	–
1.120	4.50	1.42	27.72	2.0	0.4	0.66
0.925	5.10	1.79	31.20	1.5	–	–
0.720	5.45	1.96	33.41	1.2	–	–
0.585	5.70	1.99	35.69	1.5	0.4	0.68
0.260	6.20	2.28	38.55	1.0	–	–
0.050	6.50	2.47	40.50	1.0	0.5	0.92

^a z : Axial distance, measured from the lower burner.

Data plotted on Figure 4.1 and 4.2.

TABLE A-14
 Temperature Data – Gas Flame, Oxidizing Conditions

Axial Position (cm)	Measured Temperature (K)	Corrected Temperature (K)
2.735	696	707
2.590	774	790
2.370	862	887
2.235	932	965
2.120	974	1014
2.015	1018	1065
1.845	1073	1131
1.780	1118	1185
1.715	1147	1222
1.555	1181	1265
1.395	1233	1332
1.180	1282	1397
1.005	1318	1445
0.870	1352	1492
0.780	1378	1528
0.620	1396	1554
0.440	1429	1601
0.300	1429	1601
0.145	1442	1620
0.075	1458	1644

Data Plotted on Figure 4.1.

TABLE A-15

EXPERIMENTAL COMPOSITION MATRIX – TEXAS LIGNITE, FINES, REDUCING CONDITIONS

Combustion Configuration: Opposed Flow Premixed Flame

Lower Burner Flow Rates:

CO: 17.9 lpm

O₂: 6.5 lpm

Ar: 16.4 lpm

Stoichiometric Ratio: 0.73

Upper Burner Flow Rates:

Transport Argon: 50.1 lpm

In-situ Coal Feed Rate: 2.98 gm/min

Particle Loading: 58 mg/l

z^a (cm)	O ₂ (% vol)	CO (% vol)	CO ₂ (% vol)	NO (ppmv)	NH ₃ (ppmv)	HCN (ppmv)	H ₂ (ppmv)	C ₂ H ₄ (ppmv)	C ₂ H ₆ (ppmv)	C ₂ H ₂ (ppmv)	CH ₄ (ppmv)
2.885	0.05	0.14	0.10	0.5	1.8	4.3	0.01	9	0	6	13
2.560	0.05	0.77	0.96	2.0	3.4	4.4	–	–	–	–	–
2.150	0.10	1.38	3.92	5.0	4.9	8.9	0.03	76	9	75	83
1.870	0.10	3.92	7.81	12.0	8.6	25.1	0.08	104	15	122	103
1.625	0.10	5.45	12.27	17.0	11.0	44.5	–	–	–	–	–
1.365	0.10	6.86	16.75	21.0	12.6	50.9	0.46	234	40	205	194
0.980	0.10	10.00	27.84	22.0	8.2	21.5	–	–	–	–	–
0.580	0.10	11.45	32.97	14.0	5.5	16.6	–	–	–	–	–
0.260	0.10	12.03	39.23	9.0	2.2	5.0	–	–	–	–	–

a : Axial distance, measured from the lower burner.

Data plotted on Figure 4.3, 4.4, 4.5, and 4.7.

TABLE A-16

Temperature Data – Texas Lignite, Fines, Reducing Conditions

Axial Position (cm)	Measured Temperature (K)	Corrected Temperature (K)
2.975	586	591
2.840	671	680
2.730	736	749
2.575	811	830
2.375	923	955
2.095	1031	1080
1.935	1087	1148
1.760	1152	1227
1.520	1233	1331
1.350	1277	1390
1.135	1322	1450
0.930	1351	1490
0.760	1363	1506
0.715	1379	1530
0.640	1379	1530
0.475	1397	1555
0.290	1413	1579
0.105	1413	1577

Data Plotted on Figure 4.3.

TABLE A-17
TAR AND CHAR NITROGEN CONTENTS
Texas Lignite, Fines, Reducing Conditions

Axial Position (cm)	Char+Tar (gms)	Tar (gms)	Tar N (% wt)	Char N (% wt)
2.885	0.2710	0.0079	0.250	0.590
2.560	0.2587	0.0063	0.250	0.640
2.150	0.2280	0.0065	0.060	0.620
1.870	0.2222	0.0082	0.270	0.660
1.365	0.0751	0.0042	0.020	0.610

TABLE A-18
NORMALIZED EQUIVALENT N AND PARTICLE TIME-TEMPERATURE
Texas Lignite, Fines, Reducing Conditions

Axial Position (cm)	Eq. Tar N (ppmv)	Eq. Gaseous N (ppmv)	Particle Time (ms)	Particle T (K)
2.885	2.44	0.57	21	558
2.560	2.13	2.81	39	744
2.150	0.54	9.15	63	968
1.870	3.66	15.34	—	—
1.365	0.18	28.35	—	—

Equivalent N Data Plotted on Figure 4.6.

TABLE A-19

WATER ANALYSIS DATA - TEXAS LIGNITE, FINES, REDUCING CONDITIONS

Axial Position (cm)	Sampling Time (min)	Quench H ₂ O Collected (ml)	Gas Flow Rate (cm ³ /min)	QW+Bub 1 ^a N ⁺ (ppmm)	QW+Bub 1 ^a CN ⁻ (ppmm)	Bub 2 ^b CN ⁻ (ppmm)
2.885	8	165	659	0.018	0.063	0.044
2.560	8	191	603	0.023	0.055	0.036
2.150	8	180	590	0.041	0.110	0.081
1.870	8	173	493	0.061	0.282	0.142
1.625	10	379	429	0.050	0.326	0.245
1.365	8	204	381	0.063	0.402	0.216
0.980	10	225	398	0.050	0.206	0.126
0.580	10	385	308	0.018	0.091	0.043
0.260	10	340	389	0.010	0.038	0.017

a: Quench water and bubbler 1 (containing 120 ml water) combined.

b: Bubbler 2 (containing 100 ml 0.1M NaOH solution) analyzed for CN⁻ only.

Converted gas phase concentrations are reported in Table A-15.

TABLE A-20

EXPERIMENTAL COMPOSITION MATRIX - TEXAS LIGNITE, FINES, OXIDIZING CONDITIONS

Combustion Configuration: Opposed Flow Premixed Flame

Lower Burner Flow Rates:

CO: 17.9 lpm

O₂: 10.9 lpm

Ar: 16.4 lpm

Stoichiometric Ratio: 1.21

Upper Burner Flow Rates:

Transport Argon: 50.1 lpm

In-situ Coal Feed Rate: 2.93 gm/min

Particle Loading: 57 mg/l

z^a (cm)	O ₂ (% vol)	CO (% vol)	CO ₂ (% vol)	NO (ppmv)	NH ₃ (ppmv)	HCN (ppmv)	H ₂ (ppmv)	C ₂ H ₄ (ppmv)	C ₂ H ₆ (ppmv)	C ₂ H ₂ (ppmv)	CH ₄ (ppmv)
2.890	0.20	0.07	0.47	5.0	1.7	3.0	—	—	—	—	—
2.770	0.30	0.15	2.54	4.6	3.0	10.0	—	—	—	—	—
2.410	0.40	0.34	3.86	24.0	2.9	10.3	—	—	—	—	—
2.045	0.60	0.47	6.72	32.0	3.9	23.0	—	—	—	—	—
1.785	1.05	0.86	14.63	43.0	7.2	31.0	0.08	105	20	90	73
1.410	2.30	1.42	19.72	64.0	4.1	6.0	0.10	59	11	58	49
1.050	4.60	1.65	24.00	29.0	1.0	2.0	—	—	—	—	—
0.935	5.00	1.32	29.39	16.0	0.5	0.5	0.13	2	0	0	3
0.110	5.75	2.32	35.30	5.0	0.0	0.0	—	—	—	—	—

a : Axial distance, measured from the lower burner.

Data plotted on Figure 4.3, 4.4, 4.5, and 4.7.

TABLE A-21

Temperature Data – Texas Lignite, Fines, Oxidizing Conditions

Axial Position (cm)	Measured Temperature (K)	Corrected Temperature (K)
3.050	602	608
2.935	688	697
2.720	838	860
2.610	910	940
2.555	932	965
2.445	980	1020
2.245	1096	1159
2.055	1131	1202
1.775	1236	1335
1.495	1291	1408
1.305	1349	1488
1.170	1365	1510
0.920	1386	1540
0.740	1404	1565
0.575	1422	1590
0.315	1428	1599
0.110	1433	1606
0.010	1448	1628

Data Plotted on Figure 4.3.

TABLE A-22
TAR AND CHAR NITROGEN CONTENTS
Texas Lignite, Fines, Oxidizing Conditions

Axial Position (cm)	Char+Tar (gms)	Tar (gms)	Tar N (% wt)	Char N (% wt)
2.890	0.9256	0.0106	0.000	0.600
2.770	0.8442	0.0092	0.030	0.650
2.410	0.5591	0.0091	0.320	0.620
2.045	0.6251	0.0086	0.330	0.570
1.785	0.3006	0.0056	0.180	0.500
1.41C	0.0255	0.0039	0.240	0.220

TABLE A-23
NORMALIZED EQUIVALENT N AND PARTICLE TIME-TEMPERATURE
Texas Lignite, Fines, Oxidizing Conditions

Axial Position (cm)	Eq. Tar N (ppmv)	Eq. Gaseous N (ppmv)	Particle Time (ms)	Particle T (K)
2.890	0.00	1.88	19	614
2.770	0.10	3.51	25	701
2.410	1.68	10.51	43	921
2.045	1.58	20.97	74	1182
1.785	0.73	27.70	—	—
1.410	0.70	25.29	—	—

Equivalent N Data Plotted on Figure 4.6.

TABLE A-24

WATER ANALYSIS DATA – TEXAS LIGNITE, FINES, OXIDIZING CONDITIONS

Axial Position (cm)	Sampling Time (min)	Quench H ₂ O Collected (ml)	Gas Flow Rate (cm ³ /min)	QW+Bub 1 ^a N ⁺ (ppmm)	QW+Bub 1 ^a CN ⁻ (ppmm)	Bub 2 ^b CN ⁻ (ppmm)
2.890	8	215	2239	0.048	0.130	0.091
2.770	8	210	2202	0.084	0.438	0.280
2.410	8	215	2410	0.088	0.480	0.338
2.045	10	320	1193	0.056	0.518	0.408
1.785	10	380	918	0.070	0.485	0.361
1.410	10	422	886	0.035	0.093	0.017
1.050	10	392	843	0.009	0.030	0.012
0.935	10	388	819	0.004	0.007	0.006
0.110	10	385	798	0.000	0.000	0.000

a: Quecnh water and bubbler 1 (containing 120 ml water) combined.

b: Bubbler 2 (containing 100 ml 0.1M NaOH solution) analyzed for CN⁻ only.

Converted gas phase concentrations are reported in Table A-20.

TABLE A-25**EXPERIMENTAL COMPOSITION MATRIX – TEXAS LIGNITE, UNCLASSIFIED, REDUCING CONDITIONS****Combustion Configuration:** Opposed Flow Premixed Flame**Lower Burner Flow Rates:**

CO: 17.9 lpm

O₂: 6.5 lpm

Ar: 16.4 lpm

Stoichiometric Ratio: 0.73

Upper Burner Flow Rates:

Transport Argon: 50.1 lpm

In-situ Coal Feed Rate: 3.20 gm/min

Particle Loading: 63 mg/l

z^a (cm)	O ₂ (% vol)	CO (% vol)	CO ₂ (% vol)	NO (ppmv)	NH ₃ (ppmv)	HCN (ppmv)
2.720	0.10	1.65	3.73	7	1.9	7.1
2.630	0.10	2.85	7.03	17	3.5	13.5
2.390	0.10	3.70	9.94	23	5.0	23.0
2.035	0.10	6.86	16.75	30	4.8	42.3
1.665	0.10	9.67	21.81	38	8.0	46.2
1.225	0.20	7.72	16.65	31	6.6	30.7
0.980	0.20	13.12	28.14	18	4.4	17.5
0.395	0.10	11.91	34.75	22	1.3	22.1
0.170	0.20	11.62	39.75	8	1.0	4.0

 a : Axial distance, measured from the lower burner.

Data plotted on Figure 4.11, and 4.12.

TABLE A-26

Temperature Data – Texas Lignite, Unclassified, Reducing Conditions

Axial Position (cm)	Measured Temperature (K)	Corrected Temperature (K)
3.000	697	707
2.850	797	815
2.620	932	965
2.390	1037	1086
2.325	1072	1129
2.190	1118	1185
2.025	1179	1262
1.810	1225	1321
1.600	1266	1375
1.530	1275	1387
1.230	1314	1439
1.075	1331	1463
0.895	1349	1488
0.640	1373	1522
0.465	1376	1526
0.330	1383	1535
0.285	1404	1565
0.100	1386	1539

Data Plotted on Figure 4.11.

TABLE A-27

WATER ANALYSIS DATA – TEXAS LIGNITE, UNCLASSIFIED, REDUCING CONDITIONS

Axial Position (cm)	Sampling Time (min)	Quench H ₂ O Collected (ml)	Gas Flow Rate (cm ³ /min)	QW+Bub 1 ^a N ⁺ (ppmm)	QW+Bub 1 ^a CN ⁻ (ppmm)	Bub 2 ^b CN ⁻ (ppmm)
2.720	8.17	188	2353	0.063	0.406	0.087
2.630	8.00	167	2676	0.138	0.828	0.454
2.390	8.00	178	2549	0.180	1.234	0.917
2.035	8.00	158	2438	0.178	2.252	1.819
1.665	8.50	170	2319	0.287	2.452	1.808
1.225	8.00	198	2288	0.200	1.419	0.992
0.980	8.67	188	2311	0.151	0.957	0.488
0.395	8.00	158	2275	0.045	1.212	0.569
0.170	8.00	162	2181	0.033	0.207	0.099

a: Quench water and bubbler 1 (containing 120 ml water) combined.

b: Bubbler 2 (containing 100 ml 0.1M NaOH solution) analyzed for CN⁻ only.

Converted gas phase concentrations are reported in Table A-25.

TABLE A-28

EXPERIMENTAL COMPOSITION MATRIX – TEXAS LIGNITE, UNCLASSIFIED, OXIDIZING CONDITIONS

Combustion Configuration: Opposed Flow Premixed Flame

Lower Burner Flow Rates:

CO: 17.9 lpm

O₂: 10.9 lpm

Ar: 16.4 lpm

Stoichiometric Ratio: 1.21

Upper Burner Flow Rates:

Transport Argon: 50.1 lpm

In-situ Coal Feed Rate: 3.16 gm/min

Particle Loading: 62 mg/l

z^a (cm)	O ₂ (% vol)	CO (% vol)	CO ₂ (% vol)	NO (ppmv)	NH ₃ (ppmv)	HCN (ppmv)
2.970	0.20	0.10	0.34	9	1.7	5.3
2.865	0.05	0.17	0.96	18	1.6	7.4
2.595	0.10	0.47	3.59	50	1.7	14.6
2.345	0.50	0.44	5.10	53	4.9	25.3
1.915	0.20	0.61	11.12	70	5.0	21.3
1.725	1.90	0.83	22.00	85	3.7	5.2
1.425	3.60	1.25	32.77	89	2.2	1.6
0.905	4.00	1.42	27.12	63	2.1	3.3
0.675	4.80	1.09	35.26	63	0.7	0.6
0.285	5.20	1.68	36.45	25	0.6	2.0

a : Axial distance, measured from the lower burner.

Data plotted on Figure 4.11 and 4.12.

TABLE A-29

Temperature Data – Texas Lignite, Unclassified, Oxidizing Conditions

Axial Position (cm)	Measured Temperature (K)	Corrected Temperature (K)
3.000	760	774
2.925	829	850
2.750	953	988
2.570	1052	1105
2.390	1121	1189
2.290	1223	1319
2.020	1247	1350
1.870	1271	1381
1.675	1325	1455
1.525	1356	1497
1.330	1375	1525
1.150	1400	1559
1.010	1408	1571
0.850	1420	1588
0.615	1434	1609
0.475	1443	1622
0.340	1449	1631
0.105	1453	1636

Data Plotted on Figure 4.11.

TABLE A-30

WATER ANALYSIS DATA - TEXAS LIGNITE, UNCLASSIFIED, OXIDIZING CONDITIONS

Axial Position (cm)	Sampling Time (min)	Quench H ₂ O Collected (ml)	Gas Flow Rate (cm ³ /min)	QW+Bub 1 ^a N ⁺ (ppmm)	QW+Bub 1 ^a CN ⁻ (ppmm)	Bub 2 ^b CN ⁻ (ppmm)
2.970	8.0	220	2388	0.050	0.250	0.140
2.865	10.5	195	1911	0.054	0.370	0.288
2.595	8.0	116	1883	0.057	0.745	0.397
2.345	8.0	238	1642	0.095	0.763	0.523
1.915	8.0	185	1575	0.109	0.688	0.530
1.725	10.0	258	1672	0.086	0.206	0.073
1.425	10.0	280	1670	0.048	0.060	0.020
0.905	6.0	157	1115	0.027	0.071	0.018
0.675	10.0	295	1564	0.014	0.020	0.007
0.285	10.0	300	1564	0.012	0.069	0.018

a: Quench water and bubbler 1 (containing 120 ml water) combined.

b: Bubbler 2 (containing 100 ml 0.1M NaOH solution) analyzed for CN⁻ only.

Converted gas phase concentrations are reported in Table A-28.

TABLE A-31

EXPERIMENTAL COMPOSITION MATRIX – TEXAS LIGNITE, COARSE, REDUCING CONDITIONS

Combustion Configuration: Opposed Flow Premixed Flame

Lower Burner Flow Rates:

CO: 17.9 lpm

O₂: 6.5 lpm

Ar: 16.4 lpm

Stoichiometric Ratio: 0.73

Upper Burner Flow Rates:

Transport Argon: 50.1 lpm

In-situ Coal Feed Rate: 2.0 gm/min

Particle Loading: 39 mg/l

z^a (cm)	O ₂ (% vol)	CO (% vol)	CO ₂ (% vol)	NO (ppmv)	NH ₃ (ppmv)	HCN (ppmv)	H ₂ (ppmv)	C ₂ H ₄ (ppmv)	C ₂ H ₆ (ppmv)	C ₂ H ₂ (ppmv)	CH ₄ (ppmv)
2.970	0.05	0.21	0.20	0.5	1.6	2.4	0	6	6	0	11
2.590	0.05	1.35	1.71	2.5	3.2	7.0	0.023	61	7	71	78
2.290	0.05	2.03	3.19	3.0	3.4	11.0	0.022	55	7	67	64
2.165	0.05	3.18	5.77	5.3	8.4	17.3	0.041	72	9	123	86
1.955	0.10	4.65	10.64	7.8	10.1	20.6	0.046	78	11	140	90
1.730	0.10	5.62	12.25	9.5	10.3	27.5	0.047	80	11	129	79
1.370	0.15	8.49	19.72	13.0	9.8	22.9	0.120	90	14	173	109
1.210	0.10	10.34	24.39	15.0	6.7	21.3	–	–	–	–	–
0.985	0.10	11.74	28.98	14.0	4.2	20.6	0.580	42	7	118	66
0.320	0.10	10.34	34.10	7.0	0.5	6.0	–	–	–	–	–
0.075	0.10	11.50	39.58	4.0	3.5	3.1	–	–	–	–	–

a : Axial distance, measured from the lower burner.

Data plotted on Figure 4.8, 4.9, and 4.10.

TABLE A-32

Temperature Data – Texas Lignite, Coarse, Reducing Conditions

Axial Position (cm)	Measured Temperature (K)	Corrected Temperature (K)
2.880	757	771
2.705	874	900
2.525	946	981
2.315	1004	1048
2.090	1089	1149
2.020	1107	1171
1.880	1150	1225
1.755	1182	1265
1.405	1259	1365
1.140	1307	1430
0.980	1330	1462
0.800	1349	1488
0.615	1358	1500
0.495	1375	1524
0.315	1380	1531
0.245	1382	1533
0.115	1375	1525

Data Plotted on Figure 4.8.

TABLE A-33

WATER ANALYSIS DATA - TEXAS LIGNITE, COARSE, REDUCING CONDITIONS

Axial Position (cm)	Sampling Time (min)	Quench H ₂ O Collected (ml)	Gas Flow Rate (cm ³ /min)	QW+Bub 1 ^a N ⁺ (ppmm)	QW+Bub 1 ^a CN ⁻ (ppmm)	Bub 2 ^b CN ⁻ (ppmm)
2.970	8.00	192	2323	0.050	0.117	0.071
2.590	8.25	218	2907	0.120	0.425	0.207
2.290	8.00	194	2338	0.107	0.554	0.276
2.165	8.00	191	2673	0.305	0.947	0.679
1.955	8.00	194	2225	0.302	0.938	0.645
1.730	8.00	190	2674	0.375	1.508	1.087
1.370	8.00	186	2802	0.379	1.373	0.825
1.210	8.00	228	2696	0.219	1.091	0.703
0.985	8.00	245	2776	0.135	1.012	0.785
0.320	8.00	243	2649	0.015	0.301	0.154
0.075	8.00	225	2517	0.108	0.146	0.107

a: Quecnh water and bubbler 1 (containing 120 ml water) combined.

b: Bubbler 2 (containing 100 ml 0.1M NaOH solution) analyzed for CN⁻ only.

Converted gas phase concentrations are reported in Table A-31.

TABLE A-34

EXPERIMENTAL COMPOSITION MATRIX – ILLINOIS BITUMINOUS, FINES, REDUCING CONDITIONS

Combustion Configuration: Opposed Flow Premixed Flame

Lower Burner Flow Rates:

CO: 17.9 lpm

O₂: 6.5 lpm

Ar: 16.4 lpm

Stoichiometric Ratio: 0.73

Upper Burner Flow Rates:

Transport Argon: 50.1 lpm

In-situ Coal Feed Rate: 1.58 gm/min

Particle Loading: 31 mg/l

z^a (cm)	O ₂ (% vol)	CO (% vol)	CO ₂ (% vol)	NO (ppmv)	NH ₃ (ppmv)	HCN (ppmv)	H ₂ (ppmv)	C ₂ H ₄ (ppmv)	C ₂ H ₆ (ppmv)	C ₂ H ₂ (ppmv)	CH ₄ (ppmv)
2.840	0.05	0.14	0.15	1.5	1.9	2.9	0	3	2	5	10
2.530	0.10	1.02	1.35	3.5	4.1	7.3	0.01	24	8	30	66
2.310	0.10	1.45	2.20	5.2	5.0	4.6	0.01	34	11	44	83
1.980	0.15	4.40	10.88	15.0	7.5	32.0	0.06	58	19	80	122
1.750	0.15	3.31	6.48	10.0	8.1	44.0	0.04	53	16	77	137
1.535	0.15	9.08	20.50	30.0	10.9	44.8	0.07	88	26	228	242
1.265	0.20	11.46	26.96	38.0	8.2	16.7	0.08	68	17	118	177
0.865	0.20	12.14	33.51	24.0	7.1	5.7	1.07	11	0	15	20
0.495	0.20	11.91	29.39	21.0	6.3	5.8	–	–	–	–	–
0.155	0.25	12.14	33.51	20.0	2.0	1.0	–	–	–	–	–

a : Axial distance, measured from the lower burner.

Data plotted on Figure 4.3, 4.4, 4.5, and 4.7.

TABLE A-35

Temperature Data -- Illinois Bituminous, Fines, Reducing Conditions

Axial Position (cm)	Measured Temperature (K)	Corrected Temperature (K)
2.975	556	560
2.690	770	786
2.535	802	820
2.505	878	904
2.280	980	1020
2.105	1048	1100
1.930	1109	1175
1.710	1149	1223
1.550	1207	1298
1.375	1236	1335
1.220	1253	1357
1.090	1287	1403
0.925	1303	1425
0.760	1322	1450
0.575	1323	1451
0.275	1353	1492
0.145	1366	1512
0.045	1363	1506

Data Plotted on Figure 4.3.

TABLE A-36
TAR AND CHAR NITROGEN CONTENTS
 Illinois Bituminous, Fines, Reducing Conditions

Axial Position (cm)	Char+Tar (gms)	Tar (gms)	Tar N (% wt)	Char N (% wt)
2.840	0.7082	0.0090	0.340	1.170
2.530	0.2958	0.0107	0.620	1.230
2.310	0.3639	0.0080	0.270	1.190
1.980	0.1997	0.0106	0.680	1.220
1.750	0.1777	0.0089	0.770	1.310
1.535	0.0281	0.0049	0.440	1.040
1.265	0.0120	0.0048	0.870	0.870

TABLE A-37
NORMALIZED EQUIVALENT N AND PARTICLE TIME-TEMPERATURE
 Illinois Bituminous, Fines, Reducing Conditions

Axial Position (cm)	Eq. Tar N (ppmv)	Eq. Gaseous N (ppmv)	Particle Time (ms)	Particle T (K)
2.840	1.58	3.15	25	579
2.530	7.38	8.46	42	787
2.310	2.12	16.55	54	926
1.980	11.45	35.42	85	1144
1.750	13.18	50.47	—	—
1.535	7.56	55.84	—	—
1.265	16.66	42.05	—	—

Equivalent N Data Plotted on Figure 4.6.

TABLE A-38

WATER ANALYSIS DATA – ILLINOIS BITUMINOUS, FINES, REDUCING CONDITIONS

Axial Position (cm)	Sampling Time (min)	Quench H ₂ O Collected (ml)	Gas Flow Rate (cm ³ /min)	QW+Bub 1 ^a N ⁺ (ppmm)	QW+Bub 1 ^a CN ⁻ (ppmm)	Bub 2 ^b CN ⁻ (ppmm)
2.840	8	240	2984	0.066	0.171	0.062
2.530	8	225	1581	0.079	0.217	0.156
2.310	8	240	1566	0.092	0.129	0.099
1.980	8	250	967	0.080	0.568	0.322
1.750	8	290	799	0.067	0.580	0.377
1.535	8	260	438	0.053	0.351	0.204
1.265	8	270	385	0.034	0.120	0.035
0.865	8	245	341	0.028	0.038	0.015
0.495	8	260	357	0.025	0.038	0.017
0.155	8	235	335	0.008	0.006	0.003

a: Quecnh water and bubbler 1 (containing 120 ml water) combined.

b: Bubbler 2 (containing 100 ml 0.1M NaOH solution) analyzed for CN⁻ only.

Converted gas phase concentrations are reported in Table A-34.

TABLE A-39

EXPERIMENTAL COMPOSITION MATRIX - ILLINOIS BITUMINOUS, FINES, OXIDIZING CONDITIONS

Combustion Configuration: Opposed Flow Premixed Flame**Lower Burner Flow Rates:**

CO: 17.9 lpm

O₂: 10.9 lpm

Ar: 16.4 lpm

Stoichiometric Ratio: 1.21

Upper Burner Flow Rates:

Transport Argon: 50.1 lpm

In-situ Coal Feed Rate: 1.58 gm/min

Particle Loading: 31 mg/l

z^a (cm)	O ₂ (% vol)	CO (% vol)	CO ₂ (% vol)	NO (ppmv)	NH ₃ (ppmv)	HCN (ppmv)	H ₂ (ppmv)	C ₂ H ₄ (ppmv)	C ₂ H ₆ (ppmv)	C ₂ H ₂ (ppmv)	CH ₄ (ppmv)
2.975	0.20	0.07	0.25	6	2.5	1.4	0.01	10	6	8	39
2.800	0.40	0.27	1.00	16	3.0	5.9	0.01	38	20	25	104
2.670	0.70	0.83	7.03	47	3.7	6.9	0.03	43	16	40	69
2.370	1.20	0.86	11.00	45	4.7	30.9	0.04	26	11	30	48
1.880	6.50	3.10	37.26	97	6.9	3.9	—	—	—	—	—
1.685	3.70	1.82	26.39	114	3.5	4.4	0.23	0	2	6	12
1.525	2.80	2.07	21.64	120	5.8	3.0	—	—	—	—	—
1.095	4.70	2.10	34.08	95	2.5	2.0	0.27	0	0	0	0
0.805	6.10	3.16	38.39	74	5.5	2.5	0.31	0	0	0	0
0.385	6.30	2.97	41.11	52	1.9	2.1	—	—	—	—	—
0.185	6.40	3.06	39.79	44	2.3	2.1	—	—	—	—	—

 a : Axial distance, measured from the lower burner.

Data plotted on Figure 4.3, 4.4, 4.5, and 4.7.

TABLE A-40

Temperature Data – Illinois Bituminous, Fines, Oxidizing Conditions

Axial Position (cm)	Measured Temperature (K)	Corrected Temperature (K)
2.990	618	625
2.700	838	860
2.625	873	898
2.510	933	966
2.295	1049	1101
2.120	1138	1210
1.900	1201	1290
1.710	1292	1409
1.540	1310	1434
1.395	1336	1470
1.210	1377	1527
1.160	1399	1559
0.980	1424	1595
0.755	1430	1603
0.615	1461	1649
0.425	1465	1655
0.235	1449	1631

Data Plotted on Figure 4.3.

TABLE A-41
TAR AND CHAR NITROGEN CONTENTS
 Illinois Bituminous, Fines, Oxidizing Conditions

Axial Position (cm)	Char+Tar (gms)	Tar (gms)	Tar N (% wt)	Char N (% wt)
2.975	0.3411	0.0074	0.630	1.350
2.800	0.2037	0.0038	0.310	1.300
2.670	0.3420	0.0091	0.680	1.240
2.370	0.0900	0.0030	0.250	1.190
1.880	0.0286	0.0009	0.630	1.020
1.685	0.0493	0.0030	0.560	0.970

TABLE A-42
NORMALIZED EQUIVALENT N AND PARTICLE TIME-TEMPERATURE
 Illinois Bituminous, Fines, Oxidizing Conditions

Axial Position (cm)	Eq. Tar N (ppmv)	Eq. Gaseous N (ppmv)	Particle Time (ms)	Particle T (K)
2.975	5.09	5.53	16	547
2.800	1.25	15.58	25	685
2.670	6.27	25.20	32	783
2.370	0.77	51.14	48	988
1.880	0.56	73.03	—	—
1.685	1.64	79.06	—	—

Equivalent N Data Plotted on Figure 4.6.

TABLE A-43

WATER ANALYSIS DATA – ILLINOIS BITUMINOUS, FINES, OXIDIZING CONDITIONS

Axial Position (cm)	Sampling Time (min)	Quench H ₂ O Collected (ml)	Gas Flow Rate (cm ³ /min)	QW+Bub 1 ^a N ⁺ (ppmm)	QW+Bub 1 ^a CN ⁻ (ppmm)	Bub 2 ^b CN ⁻ (ppmm)
2.975	8	215	1408	0.044	0.039	0.023
2.800	8	210	1448	0.056	0.168	0.116
2.670	8	215	1516	0.071	0.201	0.145
2.370	8	200	1494	0.093	0.942	0.601
1.880	8	205	1546	0.138	0.127	0.058
1.685	8	255	1575	0.062	0.125	0.075
1.525	5	157	1783	0.098	0.083	0.031
1.095	8	260	1600	0.044	0.059	0.025
0.805	8	355	1487	0.073	0.055	0.030
0.385	8	420	1464	0.022	0.042	0.017
0.185	8	420	1467	0.026	0.041	0.018

a: Quench water and bubbler 1 (containing 120 ml water) combined.

b: Bubbler 2 (containing 100 ml 0.1M NaOH solution) analyzed for CN⁻ only.

Converted gas phase concentrations are reported in Table A-39.

TABLE A-44

EXPERIMENTAL COMPOSITION MATRIX – ILLINOIS BITUMINOUS, UNCLASSIFIED, REDUCING CONDITIONS

Combustion Configuration: Opposed Flow Premixed Flame

Lower Burner Flow Rates:

CO: 17.9 lpm

O₂: 6.5 lpm

Ar: 16.4 lpm

Stoichiometric Ratio: 0.73

Upper Burner Flow Rates:

Transport Argon: 50.1 lpm

In-situ Coal Feed Rate: 1.78 gm/min

Particle Loading: 35 mg/l

z^a (cm)	O ₂ (% vol)	CO (% vol)	CO ₂ (% vol)	NO (ppmv)	NH ₃ (ppmv)	HCN (ppmv)	H ₂ (ppmv)	C ₂ H ₄ (ppmv)	C ₂ H ₆ (ppmv)	C ₂ H ₂ (ppmv)	CH ₄ (ppmv)
2.800	0.05	0.07	0.05	0.3	2.3	1.9	0	0	0	0	0
2.435	0.05	0.21	0.28	2.5	3.8	12.3	0.01	7	4	7	27
2.245	0.05	0.14	0.10	1.0	1.8	18.9	–	–	–	–	–
2.090	0.05	2.14	3.19	12.0	7.5	27.6	0.04	36	11	57	102
2.010	0.05	2.43	4.24	19.0	10.5	39.6	–	–	–	–	–
1.820	0.05	4.45	8.63	30.0	12.3	68.8	0.06	49	16	86	143
1.735	0.05	11.89	30.02	55.0	11.0	68.1	0.08	52	17	105	137
1.485	0.05	11.36	27.71	60.0	8.2	49.6	0.08	57	17	124	135
1.190	0.05	11.96	30.58	42.0	3.8	42.4	0.11	39	9	115	259
0.825	0.05	11.83	30.19	26.0	7.6	22.8	0.18	12	3	60	40
0.435	0.05	13.81	33.92	12.0	1.0	30.1	–	–	–	–	–

a : Axial distance, measured from the lower burner.

Data plotted on Figure 4.11, 4.12, and 4.13.

TABLE A-45

Temperature Data – Illinois Bituminous, Unclassified, Reducing Conditions

Axial Position (cm)	Measured Temperature (K)	Corrected Temperature (K)
3.070	575	580
2.935	718	730
2.705	896	925
2.525	1014	1060
2.310	1092	1153
2.050	1177	1260
1.955	1196	1283
1.720	1245	1347
1.545	1277	1390
1.390	1295	1414
1.125	1329	1459
1.005	1340	1476
0.875	1343	1480
0.735	1356	1497
0.595	1354	1495
0.315	1368	1514
0.135	1368	1515

Data Plotted on Figure 4.11.

TABLE A-46

WATER ANALYSIS DATA – ILLINOIS BITUMINOUS, UNCLASSIFIED, REDUCING, CONDITIONS

Axial Position (cm)	Sampling Time (min)	Quench H ₂ O Collected (ml)	Gas Flow Rate (cm ³ /min)	QW+Bub 1 ^a N ⁺ (ppmm)	QW+Bub 1 ^a CN ⁻ (ppmm)	Bub 2 ^b CN ⁻ (ppmm)
2.800	8	237	2635	0.072	0.093	0.059
2.435	8	215	1687	0.081	0.408	0.258
2.245	8	245	2896	0.060	1.019	0.569
2.090	8	208	1154	0.111	0.659	0.333
2.010	4	120	1135	0.105	0.620	0.273
1.820	8	195	1173	0.193	1.631	1.187
1.735	8	192	1685	0.251	2.288	1.852
1.485	8	182	1454	0.167	1.533	1.021
1.190	9	200	1593	0.090	1.518	1.097
0.825	8	222	1655	0.155	0.743	0.416
0.435	8	206	1445	0.019	0.892	0.501

a: Quench water and bubbler 1 (containing 120 ml water) combined.

b: Bubbler 2 (containing 100 ml 0.1M NaOH solution) analyzed for CN⁻ only.

Converted gas phase concentrations are reported in Table A-44.

TABLE A-47

EXPERIMENTAL COMPOSITION MATRIX – ILLINOIS BITUMINOUS, UNCLASSIFIED, OXIDIZING CONDITIONS

Combustion Configuration: Opposed Flow Premixed Flame

Lower Burner Flow Rates:

CO: 17.9 lpm

O₂: 10.9 lpm

Ar: 16.4 lpm

Stoichiometric Ratio: 1.21

Upper Burner Flow Rates:

Transport Argon: 50.1 lpm

In-situ Coal Feed Rate: 1.40 gm/min

Particle Loading: 27 mg/l

z^a (cm)	O ₂ (% vol)	CO (% vol)	CO ₂ (% vol)	NO (ppmv)	NH ₃ (ppmv)	HCN (ppmv)	H ₂ (ppmv)	C ₂ H ₄ (ppmv)	C ₂ H ₆ (ppmv)	C ₂ H ₂ (ppmv)	CH ₄ (ppmv)
3.035	0.10	0.03	0.05	2	0.8	1.8	0	0	0	0	2
2.790	0.25	0.07	0.15	4	1.2	4.5	–	–	–	–	–
2.480	0.50	0.17	0.67	12	2.5	12.3	0.02	38	3	21	176
1.990	1.00	0.77	8.63	60	4.3	20.5	0.05	27	8	33	60
1.730	1.50	1.32	16.75	80	6.0	14.6	0.13	41	12	68	69
1.490	2.00	1.32	17.88	70	5.5	15.1	0.11	24	8	34	86
1.295	3.50	2.07	30.46	48	2.3	5.2	0.22	2	0	4	5
0.925	4.50	2.45	34.82	38	1.0	0.4	0.20	0	0	0	0
0.650	5.70	2.62	38.06	31	0.8	0.8	0.27	0	0	0	0
0.090	6.00	2.89	40.88	16	0.5	0.6	–	–	–	–	–

a : Axial distance, measured from the lower burner.

Data plotted on Figure 4.11, 4.12, and 4.13.

TABLE A-48

Temperature Data – Illinois Bituminous, Unclassified, Oxidizing Conditions

Axial Position (cm)	Measured Temperature (K)	Corrected Temperature (K)
3.095	609	615
2.935	842	863
2.795	770	786
2.680	1015	1061
2.525	1083	1142
2.150	1233	1332
1.980	1277	1390
1.845	1311	1435
1.670	1323	1452
1.665	1336	1470
1.550	1349	1487
1.460	1367	1513
1.350	1379	1530
1.300	1387	1541
1.215	1400	1559
0.980	1427	1599
0.965	1435	1610
0.960	1431	1604
0.650	1455	1639
0.470	1448	1630
0.255	1462	1650

Data Plotted on Figure 4.11.

TABLE A-49

WATER ANALYSIS DATA – ILLINOIS BITUMINOUS, UNCLASSIFIED, OXIDIZING CONDITIONS

Axial Position (cm)	Sampling Time (min)	Quench H ₂ O Collected (ml)	Gas Flow Rate (cm ³ /min)	QW+Bub 1 ^a N ⁺ (ppmm)	QW+Bub 1 ^a CN ⁻ (ppmm)	Bub 2 ^b CN ⁻ (ppmm)
3.035	8	110	3071	0.045	0.166	0.051
2.790	8	255	1367	0.018	0.108	0.078
2.480	8	280	1380	0.036	0.293	0.158
1.990	8	266	1429	0.067	0.506	0.343
1.730	8	260	2157	0.144	0.557	0.350
1.490	8	265	1591	0.096	0.408	0.311
1.295	8	260	1802	0.046	0.170	0.086
0.925	8	250	2157	0.025	0.016	0.008
0.650	8	240	2258	0.021	0.035	0.017
0.090	8	250	1809	0.010	0.020	0.010

a: Quench water and bubbler 1 (containing 120 ml water) combined.

b: Bubbler 2 (containing 100 ml 0.1M NaOH solution) analyzed for CN⁻ only.

Converted gas phase concentrations are reported in Table A-47.

TABLE A-50

EXPERIMENTAL COMPOSITION MATRIX – TEXAS LIGNITE, COARSE, REDUCING CONDITIONS

Combustion Configuration: Opposed Flow Premixed Flame

Lower Burner Flow Rates:

CO: 17.9 lpm

O₂: 6.5 lpm

Ar: 16.4 lpm

Stoichiometric Ratio: 0.73

Upper Burner Flow Rates:

Transport Argon: 50.1 lpm

In-situ Coal Feed Rate: 1.52 gm/min

Particle Loading: 30 mg/l

z^a (cm)	O ₂ (% vol)	CO (% vol)	CO ₂ (% vol)	NO (ppmv)	NH ₃ (ppmv)	HCN (ppmv)	H ₂ (ppmv)	C ₂ H ₄ (ppmv)	C ₂ H ₆ (ppmv)	C ₂ H ₂ (ppmv)	CH ₄ (ppmv)
2.975	0.05	0.07	0.05	0.5	3.3	2.1	0	0	0	1	3
2.495	0.05	0.21	0.20	4.5	5.4	4.6	0	3	2	5	11
2.070	0.05	0.67	0.67	10.0	5.7	10.5	0.01	15	4	20	43
1.815	0.05	1.52	1.92	10.0	7.6	8.8	0.02	27	9	44	73
1.660	0.05	7.63	15.70	37.0	12.7	33.3	0.08	65	23	136	192
1.580	0.05	2.66	4.17	15.0	9.5	16.0	0.03	38	9	64	98
1.385	0.05	4.60	8.63	20.0	24.2	55.7	–	–	–	–	–
1.150	0.05	8.09	17.11	33.0	16.6	50.2	–	–	–	–	–
0.950	0.05	11.68	26.96	38.0	11.7	39.9	0.31	26	7	87	74
0.375	0.10	12.88	35.09	33.0	8.8	7.0	1.57	2	1	7	21
0.155	0.10	12.52	35.66	27.0	6.9	1.9	–	–	–	–	–

a : Axial distance, measured from the lower burner.

Data plotted on Figure 4.8, 4.9, and 4.10.

TABLE A-51

Temperature Data – Illinois Bituminous, Coarse, Reducing Conditions

Axial Position (cm)	Measured Temperature (K)	Corrected Temperature (K)
3.040	637	645
2.985	696	707
2.925	742	756
2.765	865	890
2.550	980	1020
2.385	1034	1084
2.225	1083	1143
2.010	1146	1220
1.820	1189	1275
1.680	1225	1321
1.575	1239	1340
1.425	1270	1381
1.305	1291	1408
1.115	1322	1450
0.970	1330	1461
0.700	1356	1497
0.590	1368	1515
0.430	1372	1520
0.215	1378	1528
0.020	1388	1542

Data Plotted on Figure 4.8.

TABLE A-52

WATER ANALYSIS DATA – ILLINOIS BITUMINOUS, COARSE, REDUCING CONDITIONS

Axial Position (cm)	Sampling Time (min)	Quench H ₂ O Collected (ml)	Gas Flow Rate (cm ³ /min)	QW+Bub 1 ^a N ⁺ (ppmm)	QW+Bub 1 ^a CN ⁻ (ppmm)	Bub 2 ^b CN ⁻ (ppmm)
2.975	8.00	275	1348	0.048	0.050	0.025
2.495	8.00	273	1348	0.078	0.108	0.060
2.070	8.25	272	1372	0.087	0.245	0.205
1.815	8.00	265	1333	0.111	0.205	0.131
1.660	8.00	235	1618	0.244	0.998	0.678
1.580	8.00	260	1247	0.132	0.356	0.210
1.385	9.00	295	1201	0.332	1.212	0.869
1.150	8.00	252	1168	0.220	1.055	0.670
0.950	8.00	275	1440	0.180	0.960	0.708
0.375	8.00	275	1395	0.131	0.176	0.071
0.155	8.00	280	1394	0.101	0.045	0.028

a: Quench water and bubbler 1 (containing 120 ml water) combined.

b: Bubbler 2 (containing 100 ml 0.1M NaOH solution) analyzed for CN⁻ only.

Converted gas phase concentrations are reported in Table A-50.

TABLE A-53
CUMULATIVE PARTICLE SIZE DISTRIBUTION

Size Range (μm)	Illinois Bituminous	Texas Lignite
10 ⁺ – 25 ^{-*}	0.034	0.034
25 ⁺ – 32 ⁻	0.044	0.052
32 ⁺ – 38 ⁻	0.442	0.523
38 ⁺ – 53 ⁻	0.585	0.621
53 ⁺ – 63 ⁻	0.721	0.745
63 ⁺ – 90 ⁻	0.777	0.791
90 ⁺ – 106 ⁻	0.901	0.903
106 ⁺ – 124 ⁻	0.913	0.919
124 ⁺ – 150 ⁻	0.952	0.943
150 ⁺ – 180 ⁻	0.976	0.964
180 ⁺ – 212 ⁻	0.984	0.974
212 ⁺ – 250 ⁻	0.994	0.984

* Based on net loss from cyclone.

APPENDIX B

NITROGENOUS SPECIES RECOVERY ANALYSIS

Ammonia (NH_3) and Hydrogen Cyanide (HCN) concentrations, in the sampled gas, are measured by capturing these species in water and subsequently analyzing the water by ion and gas specific electrodes. This Appendix describes the experiments performed to test the operation of water quench probe and nitrogenous species trapping system as a function of operating parameters and quantifies the efficiency i.e., recovery of minor species, of the system. NH_3 was used as the trace species in these experiments.

TEST PROCEDURE

A calibration gas (1058 ppmv NH_3 in N_2 , Matheson Certified) and a diluent N_2 stream, to vary NH_3 concentration in the mixture, were metered through Matheson 604 and 605 rotameters. The gases were well mixed using a magnetic stirrer and fed to a 250 ml flask, placed in the opposed flow combustor's chamber (Fig. 2.1). Samples were pulled from the flask with a quartz probe at various ammonia concentrations in the feed gas. The flow rate of feed gas was kept considerably higher than the sampling rate to ensure a positive flow out of the flask in order to eliminate any possibility of sample dilution by ambient air. Quench water was sprayed at the probe tip to strip the NH_3 and was separated in a knock out pot. Gas was then bubbled through 120 ml of water to capture any remaining NH_3 . The flow rate of sampled gas was measured using a wet test meter. To obtain extremely low levels of ammonia in the sample gas, ambient air was passed through the recovery system and extremely small quantities of anhydrous ammonia were injected, using a, micro syringe.

The quench and bubbler water were thoroughly mixed and concentrations of resulting solution was measured with an Orion 95-12 Ammonia electrode and an Orion 901 Ion Analyzer. Water phase concentration was, then, converted to gas phase concentration and compared to the theoretical concentration of ammonia in feed gas.

RESULTS

Initial data for the recovered concentrations of NH_3 , over the entire possible range of theoretical concentrations showed some scatter and more than 100% recovery at few points. In order to reconcile this discrepancy, the effects of solution temperature and standard value used during the setup procedure were studied. Results did show effect of temperature and standard value on recovery of ammonia. It was determined that a sample temperature different from the temperature of calibration solution may lead to more than 100% recovery, as slope of the electrode changes with temperature. Gas phase concentrations leading to much different concentrations in the water phase as compared with the concentration of the calibration solution also showed deviation, in recovered ammonia, at levels away from that of the standard solution. Therefore, it was established that sample and calibration solution must be analyzed at identical temperatures and the standard value used must be in close proximity of the expected measurement levels.

The effect of quench water rate on NH_3 recovery for a fixed feed concentration was also investigated. It was found that recovery of ammonia was not affected by quench water rate. For few samples, quench and bubbler water were analyzed separately. Very little quantities of ammonia were captured in the bubbler water. However percent recovery by bubbler increases as the concentration of trace species in gas phase goes up. Use of a stainless steel probe in place of a quartz probe did not show any adverse effects on the measurements.

Figure B-1 shows the results after the setup procedure had been optimized. From this figure, we conclude that more than 95% NH_3 can be recovered, at all concentration ranges, in the existing setup. Additionally, sampling with ambient

Figure B-1 Ammonia Recovery in Sampling System.

- Feed Concentration Below 20 ppmv
- Feed Concentration above 20 ppmv

air, after converting the data back to gas phase, yielded values much less than 1 ppmv. Recovery with sample concentrations with less than 1 ppmv NH_3 in the gas phase were also successful. The threshold detection limit (conservative) of the ammonia electrode, therefore, was taken to be 1 ppmv.

Bose (1989), in a similar setup (i.e., without a bubbler), reported that part of HCN was not being captured by the quench water. A second bubbler, containing 100 ml of 0.1M NaOH solution, was, therefore, added to the sampling system, since HCN is more readily absorbed in basic solution. Few samples taken with a very dilute HCN stream confirmed above 95% recovery.

CONCLUSIONS

The pertinent conclusions from these experiments are as follows:

1. Minor species can be adequately captured in the existing system.
2. Capturing efficiency of the system is above 95%.
3. Lower detection limit of ammonia electrode is 1.0 ppmv in the gas phase.
4. Minor species recovery is independent of quench water rate.
5. Use of concentration option on Orion 901 Ion Analyzer is not recommended for low level measurements. Instead a calibration curve be made and use for each run using the millivolt option.
6. Extreme care must be taken to ensure that calibration and sampled solutions are at the same temperatures.
7. Procedure during calibration step and sample analysis step must be consistent with regard to stirring. Samples without stirring will take longer to equilibrate and give slightly higher reading. It is recommended that calibration and sample solutions be stirred moderately throughout the process.
8. Use of stainless steel probe in a water quenched sampling system does not pose any adverse effects on measurements of NH_3 and HCN.

CONVERSION FROM WATER TO GAS PHASE

The expression used to convert the measured water phase concentrations to corresponding gas phase concentrations is derived below:

Let the gas phase molar concentration of species i be c_i , measured mass concentration of species j in the water phase be c_j , and molar concentration of species i in the gas stream leaving the bubbler be c_{i_e} . Examples of species i and j are NH_3 and N^+ as well as HCN and CN^- , which respectively are measured in the gas and water phases. Then the expression for c_i , becomes:

$$c_i \text{ (ppmv)} = c_{i_e} \text{ (ppmv)} + c_j \text{ (ppmm)} \times CF, \quad (1)$$

where CF is the conversion factor to convert from water to gas phase values, given by:

$$CF = (CF)_{sp} \times (CF)_{ph}, \quad (2)$$

where $(CF)_{sp}$ and $(CF)_{ph}$ account for different species being measured in the two phases and conversion from one to the other phase. Now,

$$(CF)_{sp} = \frac{M_i}{M_j},$$

and

$$\begin{aligned} (CF)_{ph} &= \frac{\text{Amount of water (gms)}}{\text{Amount of gas bubbled (moles)}} \\ &= \frac{Q_{water} RT}{\dot{q}_{gas} t_{sampling} M_i P}, \end{aligned} \quad (3)$$

where

P = Pressure, *atm*

T = Temperature, *K*

Q = Amount of water, *gm*

R = Universal Gas Constant, $\frac{(\text{atm})(\text{cm}^3)}{(\text{gmol})(\text{K})}$

$\dot{q}$ = Gas flow rate, cm^3/min

$t_{sampling}$ = Sampling time, *min*

The expression, then, becomes:

$$c_i \text{ (ppmv)} = c_{i_e} \text{ (ppmv)} + \frac{c_j \text{ (ppmm)} Q_{water} RT}{\dot{q}_{gas} t_{sampling} M_j P}. \quad (4)$$

For our experiments, where recovery was always above 95%, therefore, $c_{i_e} \approx 0$, the expression finally takes the form:

$$c_i \text{ (ppmv)} = \frac{c_j \text{ (ppmm)} Q_{water} RT}{\dot{q}_{gas} t_{sampling} M_j P}. \quad (5)$$

APPENDIX C
PROGRAM LISTINGS
AND
RESULTS

APPENDIX C-1

```

PROGRAM TEMP_CORR
C   program to correct temperature measured by a thermocouple
C   (tbead) for radiation effects
C   corrected temperature is the true temperature of gas
C   heat transfer coefficient is calculated using a Nusselt
C   number of 2.0

DIMENSION NDATA(12)
REAL LOCATN,A,B,LAMBDA
CHARACTER SQUOTE*1,RUNID(12)*4,ID*6
PARAMETER (SIGMA=5.67E-8,A=0.0256,B=9.478E-5)
PARAMETER (TOL=0.1)

OPEN (10,FILE='TEPCOR.DAT',ACCESS='SEQUENTIAL',STATUS='OLD')
OPEN(11,FILE='TEPCOR.RES',STATUS='NEW',carriagecontrol='list')
SQUOTE='''

C   READ THE BEAD DIAMETER IN METERS AND BOTTOM BURNER LOCATION
READ (10,*) DIA,BOTLOC

C   READ THE AMBIANT TEMPERATURE
READ (10,*) TAMB
TAMP4=TAMB**4

DO LOOP=1,12
READ (10,*) RUNID(LOOP),NDATA(LOOP)
ID=SQUOTE//RUNID(LOOP)//SQUOTE
WRITE (11,*) ID,NDATA(LOOP)
DO 100 I=1,NDATA(loop)
NITER=1

C   READ THE TERMOCOUPLE LOCATION AND BEAD TEMPERATURE
READ (10,*) LOCATN,TBEAD
TBEAD=TBEAD+273.16
EMISS=A+B*TBEAD
TGOLD=TBEAD
IF (NITER.EQ.1) TGAS=TBEAD
10  LAMBDA=0.024057+7.27E-5*TGAS
    TGAS=TBEAD+(SIGMA*DIA*EMISS/(2.0*LAMBDA))*(TBEAD**4-TAMP4)
    IF (ABS(TGAS-TGOLD).LE.TOL) GO TO 50
    NITER=NITER+1
    TGOLD=TGAS
    GO TO 10
50  WRITE (11,201) LOCATN-BOTLOC,Tgas,Tbead,NITER
100 CONTINUE
END DO

```

```
201 FORMAT (5X,F7.3,2(3X,F8.1),3X,I2)
```

```
STOP
```

```
END
```


APPENDIX C-2

PROGRAM Inverse_Problem

```

PARAMETER (MTDP=25,MSDP=30,MGP=65,MGPM1=MGP-1)
PARAMETER (MSPNGC=6,MSPGC=5,MINERT=1,MDRIVD=0)
PARAMETER (MSPCIE=MSPNGC+MSPGC+MINERT+MDRIVD)
PARAMETER (GASCON=82.05,PATM=1.0,DELTAT=0.001,NEQN=5)
PARAMETER (NTMAX=201,NPICK=11,NPICM1=NPICK-1,MTEST=10)
PARAMETER (NGPP=21,PI=3.141592653589793)
PARAMETER (IN=8,IR=10,II=20,ID=30,IP=40)

CHARACTER LSTSPC(MSPCIE)*6,HEADER*130,CTITLE(13)*10,ERRMES*130
CHARACTER RUNID*80,HEAD*72,MESSAG*80
CHARACTER*11 DATFILE,RESFILE,INTFILE,DBGFILE,PLTFILE
INTEGER ERRCOD,MAXIT(MSPCIE),MIT,MITRT

LOGICAL LDEBUG,DRIVED,ECHO,INTRES,NEWPAG,PLOT,FORCE,intres1

REAL XTEP(MTDP),TEP(MTDP),DTD(MGP),D2TDX2(MGP)
REAL XCENG(MSDP),CEXNGC(MSPNGC,MSDP),XCEXGC(MSDP)
REAL CEXPGC(MSPGC,MSDP),CSMOTH(MSPCIE,MGP),STAT(12)
REAL DCDX(MSPCIE,MGP),D2CDX2(MSPCIE,MGP),TREG(NTMAX)
REAL TEXMOD(MTDP),CMODGC(MSPCIE,MSDP),CMDNGC(MSPCIE,MSDP)
REAL CHOLD1(MSDP),CHOLD2(MGP),CHOLD3(MGP),CHOLD4(MGP)
REAL AVGMW(MGP),PRESUR(MGP),THCOND(MGP),RHOMAS(MGP),RHOMOL(MGP)
REAL DIFFUS(MSPCIE,MGP),CPAVG(MGP),MCCOEF(4,MGP),MXCONC(NTMAX)
REAL TCOND(NPICK),GCOND(NPICK),CCOND(NPICM1,3),SPMOLF(NTMAX)
REAL RATES(MSPCIE,MGP),DUMMY(MGP),DUMMI(NTMAX),SPCOEF(4,MGP)
REAL XL(20),FL(20),XR(20),FR(20),TCOAL(NGPP),SPCONC(NTMAX)
REAL TIME(NTMAX),GASTEM(NTMAX),ZPOSIT(NTMAX),RPOSIT(NTMAX)
REAL TCENTR(NTMAX),TSRFAC(NTMAX),XTEMP(MSDP),CMAX(MSPCIE)
REAL YV(NEQN),YPRIME(NEQN),WORK(3+6*NEQN),IWORK(5)
REAL RFTNO(NTMAX),RFTNH3(NTMAX),RFTHCN(NTMAX)
REAL RNO(MGP),RNH3(MGP),RHCN(MGP),BREAK(MGP)
REAL RH2(MGP),RCH4(MGP),RC2H2(MGP),RC2H4(MGP),RC2H6(MGP)
REAL CNO(4,MGP),CNH3(4,MGP),CHCN(4,MGP),CC2H6(4,MGP)
REAL CH2(4,MGP),CCH4(4,MGP),CC2H2(4,MGP),CC2H4(4,MGP)
REAL RFTH2(NTMAX),RFTCH4(NTMAX),RFTC2H2(NTMAX),RFTC2H4(NTMAX)
REAL RFTC2H6(NTMAX),MDOT(NTMAX),PDENST(NTMAX),PDIAM(NTMAX)
REAL RHODOT(NTMAX),RDOT(NTMAX),PRNDTL(NTMAX),RENOLD(NTMAX)
REAL HTCDEF(NTMAX),BLOCOF(NTMAX),NU,PR,RE,HTCOF,BLOFAC
REAL CPACOF(MGPM1,3),GASVEL(NTMAX),PARVEL(NTMAX)
REAL RHOCOF(MGPM1,3),NUSELT(NTMAX),VOLATL(NTMAX),ETASVC(NTMAX)
REAL MWCOEF(MGPM1,3),MWLOC,XREG(NTMAX),YREG(NTMAX),TRATES(NTMAX)
REAL RCNO(NTMAX),RCNH3(NTMAX),RHCN(NTMAX),RTH2(NTMAX)
REAL RCCH4(NTMAX),RCC2H2(NTMAX),RCC2H4(NTMAX),RCC2H6(NTMAX)
REAL PREXFC(MSPCIE),ENGACT(MSPCIE),NRCNO(4,NTMAX)
REAL NRCNH3(4,NTMAX),NRHCN(4,NTMAX),BREAKT(NTMAX)

```

```

REAL NRNO(NTMAX),NRNH3(NTMAX),NRHCN(NTMAX),CONNO(NTMAX)
REAL CONNH3(NTMAX),CONHCN(NTMAX),CONSUM(NTMAX),NRTOTXN(NTMAX)
REAL XOBS(MTEST,NTMAX),YOBS(MTEST,NTMAX),XTMOD(MTDP)
REAL CNOZ(MGP),CNH3Z(MGP),CHCNZ(MGP),TOTXNZ(MGP),COFTXN(4,MGP)
REAL CNOT(NTMAX),CNH3T(NTMAX),CHCNT(NTMAX),TOTXNT(NTMAX)
REAL GAWR(NTMAX),GAWXN(NTMAX),PASR(NTMAX),PASXN(NTMAX)
REAL SACR(NTMAX),SACXN(NTMAX),DIFFNO(MGP),DIFNOC(MGPM1,3)
REAL PECLET(NTMAX)

INTEGER NOBSR(MTEST)

COMMON /PARAS/ XGRID(MGP),PSI(MGP),PSICOF(MGPM1,3),TSMOTH(MGP),
1      TEMCOF(MGPM1,3),VLOCTY(MGP),VELCOF(MGPM1,3),
2      VSCOCF(MGP),VISCOF(MGPM1,3),NGP
COMMON /CPARAS/ PDENZ,PDIAZ,XCRBNZ,XVOL1Z,XVOL2Z,XASHZ,EMMISS
1      VSTAR,PREEXF,ACTENG,PDIA,PDEN,VLTLFT,BLOWCF,ATOMWT

WRITE (*,*) 'ENTER NAME OF DATA INPUT FILE'
READ (*,*) DATFILE
OPEN ( 8,FILE=DATFILE,STATUS='OLD')
READ (8,*) RESFILE,INTFILE,DBGFILE,PLTFILE
OPEN (10,FILE=RESFILE,STATUS='NEW',CARRIAGECONTROL='LIST')
OPEN (20,FILE=INTFILE,STATUS='NEW')
OPEN (30,FILE=DBGFILE,STATUS='NEW')
OPEN (40,FILE=PLTFILE,STATUS='NEW',CARRIAGECONTROL='LIST')
OPEN (50,FILE='XNPRED1.PLT',STATUS='NEW',CARRIAGECONTROL='LIST')

LEVEL = 0

C      read in logical variable echo, intres and ldebug,plot,force
C      if echo is true then input will be echoed
C      if intres is true then intermediate results will be printed
C      if ldebug is true detailed results will be printed
C      if plot is true then results needed for plotting will be
C      printed for later use
C      if force is true then partially pre-smoothed experimental data
C      will be used for smoothing purposes

READ (IN,*) ECHO,INTRES,LDEBUG,PLOT,FORCE
IF (ECHO) WRITE (IR,*) ECHO,INTRES,LDEBUG,PLOT,FORCE

C      read in the run identification
READ (IN,1013) RUNID
IF (ECHO) WRITE (IR,1014) RUNID

C      read in burner spacing, lower burner velocity, upper
C      burner velocity initial radial position of particle

READ (IN,*) SPCING,VLOWER,VUPPER,RINITL

```

```

      IF (ECHO) WRITE (IR,*) SPCING,VLOWER,VUPPER,RINITL

C      read in the number of grid points in axial coordinate and
C      also read maximum number of iterations allowed for
C      smoothing routine

      READ (IN,*) NGP,MITRT
      IF (ECHO) WRITE (IR,*) NGP,MITRT
      IF (MGP.LT.NGP) STOP          ' MGP < NGP '

C      initialize all concentration data (experimental and grid)
C      points to 1.0e-30

      DO 5 ISP=1,MSPCIE
      DO 5 IGP=1,MGP
5     CSMOTH(ISP,IGP)=1.0E-30

      DO 10 IDP=1,MSDP
      DO 6 ISP=1,MSPNGC
6     CEXNGC(ISP,IDP)=1.0E-30
      DO 7 ISP=1,MSPGC
7     CEXPGC(ISP,IDP)=1.0E-30
10    CONTINUE

C      read in the actual number of data pairs for temperature, non-gc
C      species and gc species

      READ (IN,*) NTDP,NDPNGC,NDPGC
      IF (ECHO) WRITE (IR,*) NTDP,NDPNGC,NDPGC
      IF (MTDP.LT.NTDP) STOP        'MTDP < NTDP'
      IF (MSDP.LT.NDPNGC) STOP      'MSDP < NDPNGC'
      IF (MSDP.LT.NDPGC) STOP       'MSDP < NDPGC'

C      read in measured temperature data

      DO 20 IDP=1,NTDP
      READ (IN,*) XTEXP(IDP),TEXP(IDP)
      IF(ECHO) WRITE (IR,1003) IDP,XTEXP(IDP),TEXP(IDP)
20    CONTINUE

C      if smoothing is to be forced then read the partially pre-smoothed
C      values of experimental data for temperature to be used in imsl
C      smoothing routine

      IF (FORCE) THEN
      WRITE (IR,*) ' PARTIALLY PRE-SMOOTHED DATA FOR TEMPERATURE'
      READ (IN,*) NTDPF
      IF (ECHO) WRITE (IR,*) NTDPF
      IF (NTDPF.GT.MTDP) STOP 'NTDPF > MTDP'

```

```

DO 25 IDP=1,NTDPF
READ (IN,*) XTMOD(IDP),TEXMOD(IDP)
IF (ECHO) WRITE (IR,1003) IDP,XTMOD(IDP),TEXMOD(IDP)
25 CONTINUE
END IF

C      read in number of species for which experimental data was taken
C      (non-gc and gc species respectively) and number of species
C      whose concentrations will be derived and number of inert species

READ (IN,*) NSPNGC,NSPGC,NDRIVD,NINERT
IF (ECHO) WRITE (IR,*) NSPNGC,NSPGC,NDRIVD,NINERT

      NSPCIE=NSPNGC+NSPGC+NDRIVD+NINERT
      IF (NSPCIE.GT.MSPCIE) THEN
        STOP 'SPECIES TOTAL EXCEEDS DECLARED DIMENSION'
      ELSE IF (NINERT.NE.1) THEN
        WRITE (IR,*) ' PROGRAM CAN HANDLE ONLY ONE INERT SPECIE '
        STOP ' MORE THAN ONE INERT SPECIES '
      END IF

      IF (NDRIVD.EQ.0) THEN
        DRIVED=.FALSE.
      ELSE
        DRIVED=.TRUE.
      END IF

C      read in the names of measured non-gc species and gc species

      NMESRD=NSPNGC+NSPGC
      DO 30 ISP=1,NMESRD
      READ (IN,1001) LSTSPC(ISP),MAXIT(ISP)
30    IF (ECHO) WRITE (IR,1006) ISP,LSTSPC(ISP),MAXIT(ISP)

      IF (DRIVED) THEN
C        read in the names of derived species
        DO 35 ISP=NMESRD+1,NMESRD+NDRIVD
        READ (IN,1001) LSTSPC(ISP),MAXIT(ISP)
35    IF (ECHO) WRITE (IR,1006) ISP,LSTSPC(ISP),MAXIT(ISP)
        END IF

C      read in the name(s) of inert specie(s)
        DO 36 ISP=NMESRD+NDRIVD+1,NSPCIE
        READ (IN,1001) LSTSPC(ISP),MAXIT(ISP)
36    IF (ECHO) WRITE (IR,1006) ISP,LSTSPC(ISP),MAXIT(ISP)

C      read in the experimental data for measured non-gc species
        IF (ECHO) WRITE (IR,*)
1          ' MEASEARED CONCENTRATION DATA FOR NON-GC SPECIES'

```

```

DO 40 IDP=1,NDPNGC
  READ (IN,*) XCENG(CIDP),(CEXNGC(ISP,IDP),ISP=1,NSPNGC)
  IF (ECHO)
1    WRITE(IR,1005)IDP,XCENG(CIDP),(CEXNGC(ISP,IDP),ISP=1,NSPNGC)
40  CONTINUE

C    read in the experimental data for measured gc species
  IF (ECHO) WRITE (IR,*)
1    ' MEASURED CONCENTRATION DATA FOR GC SPECIES'
  DO 45 IDP=1,NDPGC
  READ (IN,*) XCEXGC(IDP),(CEXPGC(ISP,IDP),ISP=1,NSPGC)
  IF (ECHO)
1    WRITE(IR,1005) IDP,XCEXGC(IDP),(CEXPGC(ISP,IDP),ISP=1,NSPGC)
45  CONTINUE

  IF (DRIVED) THEN
C    read in the boundary concentration of derived species
    DO 48 ISP=NMESRD+1,NMESRD+NDRIVD
    READ (IN,*) CSMOTH(ISP,1)
48    IF (ECHO) WRITE (IR,1005) ISP,CSMOTH(ISP,1)
  END IF

C    read in the coal parameters
  READ (IN,*) PDENZ,PDIAZ,XCRBNZ,XVOL1Z,XVOL2Z,XASHZ,EMMISS,VSTAR,
1    PREEXF,ACTENG,SWELCF,ATOMWT
  IF (ECHO) WRITE(IR,1011)PDENZ,PDIAZ,XCRBNZ,XVOL1Z,XVOL2Z,XASHZ,
1    EMISS,VSTAR,PREEXF,ACTENG,SWELCF,ATOMWT

  READ (IN,*) CFRATE,WPNT
  IF (ECHO) WRITE (IR,1011) CFRATE,WPNT

C    set up the grid points and initialize the pressure at grid points
  DELTAX=SPCING/REAL(NGP-1)
  DO 50 I=1,NGP
  XGRID(I)=(I-1)*DELTAX
50  PRESUR(I)=PATM

C    smooth all the experimental data
C    smoothing the temperature data
  intres1=.true.
  IF (FORCE) THEN
1    CALL SMOOTH (INTRES1,MITRT,NTDPF,XMOD,TEXMOD,NGP,XGRID,TSMOTH,
      DTDX,D2TDX2,ERRCOD,'TEMP ')
  ELSE
1    CALL SMOOTH (INTRES1,MITRT,NTDP,XTEP,TEP,NGP,XGRID,TSMOTH,
      DTDX,D2TDX2,ERRCOD,'TEMP ')
  END IF
  IF (ERRCOD.NE.0) THEN
    WRITE (IR,101) ERRCOD

```

```

        STOP 'TEMPERATURE SMOOTHING UNSUCCESSFUL'
    ELSE
        WRITE (IR,1002)
        DO 60 IGP=1,NGP
60      WRITE (IR,1003) IGP,XGRID(IGP),TSMOTH(IGP),DTDX(IGP),
1          D2TDX2(IGP)
        END IF

C      smoothing the non-gc concentration data

        DO 70 ISP=1,NSPNGC
        MIT=MAXIT(ISP)
        IF (FORCE) THEN
            READ (IN,*) NTEMP
            IF (NTEMP.GT.MSDP) STOP 'NTEMP > MSDP '
            DO 62 IDP=1,NTEMP
62      READ (IN,*) XTEMP(IDP),CHOLD1(IDP)

            IF (ECHO) THEN
                HEAD=' PARTIALLY PRE-SMOOTHED DATA FOR SPECIES '//LSTSPC(ISP)
                WRITE (IR,*) HEAD
                DO IDP=1,NTEMP
                WRITE (IR,1005) IDP,XTEMP(IDP),CHOLD1(IDP)
                END DO
            END IF

            CALL SMOOTH (INTRES1,MIT,NTEMP,XTEMP,CHOLD1,NGP,XGRID,CHOLD2,
1          CHOLD3,CHOLD4,ERRCOD,LSTSPC(ISP))

        ELSE
            DO 65 IDP=1,NDPNGC
65      CHOLD1(IDP)=CEXNGC(ISP,IDP)
            CALL SMOOTH (INTRES1,MIT,NDPNGC,XCENG,CHOLD1,NGP,XGRID,CHOLD2,
1          CHOLD3,CHOLD4,ERRCOD,LSTSPC(ISP))
            END IF

        IF (ERRCOD.NE.0) THEN
            WRITE (IR,101) ERRCOD
            STOP 'CONCENTRATION SMOOTHING UNSUCCESSFUL'
        ELSE
            WRITE (IR,1004) LSTSPC(ISP)
            DO 66 IGP=1,NGP
            CSMOTH(ISP,IGP)=CHOLD2(IGP)
            IF (LSTSPC(ISP).EQ.'NO ') then
                CNOZ(IGP)=CHOLD2(IGP)
                ino=isp
            end if
            IF (LSTSPC(ISP).EQ.'NH3 ') CNH3Z(IGP)=CHOLD2(IGP)
            IF (LSTSPC(ISP).EQ.'HCN ') CHCNZ(IGP)=CHOLD2(IGP)

```

```

        DCDX(ISP,IGP)=CHOLD3(IGP)
        D2CDX2(ISP,IGP)=CHOLD4(IGP)
66      WRITE (IR,1003) IGP,XGRID(IGP),CSMOTH(ISP,IGP),
1        DCDX(ISP,IGP),D2CDX2(ISP,IGP)
      END IF

70    CONTINUE

C      smoothing the gc concentration data

      DO 80 ISP=NSPNGC+1,NSPNGC+NSPGC
      MIT=MAXIT(ISP)
      IF (FORCE) THEN
        READ (IN,*) NTEMP
        IF (NTEMP.GT.MSDP) STOP ' NTEMP > MSDP '
        DO 72 IDP=1,NTEMP
72      READ (IN,*) XTEMP(IDP),CHOLD1(IDP)

        IF (ECHO) THEN
          HEAD=' PARTIALLY PRE-SMOOTHED DATA FOR SPECIES '//LSTSPC(ISP)
          WRITE (IR,*) HEAD
          DO IDP=1,NTEMP
          WRITE (IR,1005) IDP,XTEMP(IDP),CHOLD1(IDP)
          END DO
        END IF

        CALL SMOOTH (INTRES1,MIT,NTEMP,XTEMP,CHOLD1,NGP,XGRID,CHOLD2,
1          CHOLD3,CHOLD4,ERRCOD,LSTSPC(ISP))

      ELSE
        DO 75 IDP=1,NDPGC
75      CHOLD1(IDP)=CEXPGC(ISP-NSPNGC,IDP)
        CALL SMOOTH (INTRES1,MIT,NDPGC,XCEXGC,CHOLD1,NGP,XGRID,CHOLD2,
1          CHOLD3,CHOLD4,ERRCOD,LSTSPC(ISP))
      END IF

      IF (ERRCOD.NE.0) THEN
        WRITE (IR,101) ERRCOD
        STOP 'CONCENTRATION SMOOTHING UNSUCCESSFUL'
      ELSE
        WRITE (IR,1004) LSTSPC(ISP)
        DO 76 IGP=1,NGP
        CSMOTH(ISP,IGP)=CHOLD2(IGP)
        DCDX(ISP,IGP)=CHOLD3(IGP)
        D2CDX2(ISP,IGP)=CHOLD4(IGP)
76      WRITE (IR,1003) IGP,XGRID(IGP),CSMOTH(ISP,IGP),
1        DCDX(ISP,IGP),D2CDX2(ISP,IGP)
      END IF
80    CONTINUE

```

```

C      all experimental data has been successfully smoothed
      LEVEL = 20

C      start the loop to evaluate the concentrations of derived species
C      three iterations will be performed

      DO 500 IDRIVD=1,3
      IF (INTRES.OR.LDEBUG) WRITE (II,1012) IDRIVD

C      remove the negative and tiny concentrations

      DO 110 ISP=1,NSPCIE
      DO 110 IGP=1,NGP
      CHOLD2(IGP)=CSMOTH(ISP,IGP)
      CSMOTH(ISP,IGP)=AMAX1(CSMOTH(ISP,IGP),0.0)

C      convert all concentration values to mole fractions

      CONFAC=1.0E6
      IF (LSTSPC(ISP).EQ.'O2   ') CONFAC=100.0
      IF (LSTSPC(ISP).EQ.'CO   ') CONFAC=100.0
      IF (LSTSPC(ISP).EQ.'CO2  ') CONFAC=100.0
      IF (LSTSPC(ISP).EQ.'H2   ') CONFAC=100.0
      CSMOTH(ISP,IGP)=CSMOTH(ISP,IGP)/CONFAC

      IF(LDEBUG) THEN
        WRITE (ID,1005) IGP,XGRID(IGP),CHOLD2(IGP),CSMOTH(ISP,IGP)
      END IF
110    CONTINUE

C      add the diluent specie
      DO 120 IGP=1,NGP
      CSUM=0.0
      DO 115 ISP=1,NMESRD+NDRIVD
115    CSUM=CSUM+CSMOTH(ISP,IGP)
120    CSMOTH(NSPCIE,IGP)=1.0-CSUM

      IF (INTRES.OR.LDEBUG) THEN
      DO 121 IGP=1,NGP
121    WRITE (II,1005),IGP,XGRID(IGP),(CSMOTH(ISP,IGP),ISP=1,NSPCIE)
      END IF

      IF (IDRIVD.EQ.1) THEN
        CALL TRSP1 (INTRES,MSPCIE,NGP,NSPCIE,LSTSPC,TSMOTH,CSMOTH,
1          PRESUR,AVGMW,THCOND,VSCOCT,DIFFUS)
        CALL THERMO (NSPCIE,NGP,LSTSPC,CSMOTH,MSPCIE,TSMOTH,CPAVG)
      END IF

```



```

      CALL TRSPO (INTRES,MSPCIE,NGP,NSPCIE,LSTSPC,TSMOTH,CSMOTH,
1          PRESUR,AVGMW,THCOND,VSCOCT,DIFFUS)
      CALL THERMO1 (NSPCIE,NGP,LSTSPC,CSMOTH,MSPCIE,TSMOTH,CPAVG)

C      calculate the mass and molar densities of the gas mixture
C      also put diffusivity of NO in a one dimensional array

      DO 130 IGP=1,NGP
      DIFFNO(IGP)=DIFFUS(INO,IGP)
      RHOMAS(IGP)=PRESUR(IGP)*AVGMW(IGP)/(TSMOTH(IGP)*GASCON)
130  RHOMOL(IGP)=RHOMAS(IGP)/AVGMW(IGP)

C      all physical and thermodynamic properties have been successfully
C      evaluated set level to 20+IDRIVD*1
      LEVEL = 20+IDRIVD*1

      IF (INTRES.OR.LDEDUB.OR.IDRIVD.EQ.3.OR.NDRIVD.EQ.0) THEN
      HEADER=' EVALUATION OF PHYSICAL PROPRERTIES AT EACH GRID POINT '
      CTITLE(1)='      XGRID'
      CTITLE(2)='SMTHD TEMP'
      CTITLE(3)=' VISCOCITY'
      CTITLE(4)='AVG MOL WT'
      CTITLE(5)='THRML COND'
      CTITLE(6)='MASS DENST'
      CTITLE(7)='MOLR DENST'
      CTITLE(8)='AV_MOLR_CP'

      IF (INTRES.OR.LDEBUG) THEN
      CALL OUTPUT (II,.TRUE.,8,NGP,HEADER,CTITLE,XGRID,TSMOTH,VSCOCT,
1          AVGMW,THCOND,RHOMAS,RHOMOL,CPAVG,DUMMY,DUMMY)
      END IF

      IF (NDRIVD.EQ.0.OR.IDRIVD.EQ.3) THEN
      CALL OUTPUT (IR,.TRUE.,8,NGP,HEADER,CTITLE,XGRID,TSMOTH,VSCOCT,
1          AVGMW,THCOND,RHOMAS,RHOMOL,CPAVG,DUMMY,DUMMY)
      END IF

      END IF

      HEADER=' COMPOSITION MATRIX FOR THE SYSTEM '
      CTITLE(1)='      GRID_#'
      CTITLE(2)=' MF_ '//LSTSPC(1)
      CTITLE(3)=' MF_ '//LSTSPC(2)
      CTITLE(4)=' MF_ '//LSTSPC(3)
      CTITLE(5)=' MF_ '//LSTSPC(4)
      CTITLE(6)=' MF_ '//LSTSPC(5)
      CTITLE(7)=' MF_ '//LSTSPC(6)
      CTITLE(8)=' MF_ '//LSTSPC(7)
      CTITLE(9)=' MF_ '//LSTSPC(8)
      CTITLE(10)=' MF_ '//LSTSPC(9)

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CTITLE(11)=' MF_'//LSTSPC(10)
CTITLE(12)=' MF_'//LSTSPC(11)
CTITLE(13)='MF_OF_'//LSTSPC(12)

IF (INTRES.OR.LDEBUG) THEN
CALL OUTPUT2(II,NEWPAG,12,MSPCIE,NGP,HEADER,CTITLE,CSMOTH)
END IF
IF (NDRIVD.EQ.0.OR.IDRIVD.EQ.3) THEN
CALL OUTPUT2(IR,.TRUE.,12,MSPCIE,NGP,HEADER,CTITLE,CSMOTH)
END IF

C      setup the boundary velocities and q for evaluating psi profile
C      after correcting the cold velocities for expansion

VLOCTY(1)=VLOWER*TSMOTH(1)/298.16
VLOCTY(NGP)=-VUPPER*TSMOTH(NGP)/298.16

C      establish the lower and upper bounds for q
Q=(SQRT(RHOMAS(NGP))*ABS(VLOCTY(NGP))+SQRT(RHOMAS(1)))*
1      ABS(VLOCTY(1))**2/(SPCING*SPCING)
140  CALL PSIV (NGP,SPCING,Q,.FALSE.,XGRID,RHOMAS,VSCOCT,VLOCTY,PSI)
VNEW=ABS(VLOCTY(NGP))
FV=VNEW-VUPPER
IF (FV.GT.0.0) THEN
XR(1)=Q
FR(1)=FV
ELSE
Q=10.0*Q
GO TO 140
END IF
150  Q=0.1*Q
CALL PSIV1 (NGP,SPCING,Q,.FALSE.,XGRID,RHOMAS,VSCOCT,VLOCTY,PSI)
VNEW=ABS(VLOCTY(NGP))
FV=VNEW-VUPPER
IF (FV.LT.0.0) THEN
XL(1)=Q
FL(1)=FV
ELSE
GO TO 150
END IF

C      bounds on q have been established, iterate using regular falsi
C      till velocity on the boundary match the experimental value

DO 160 K=1,20
Q=(XL(K)*FR(K)-XR(K)*FL(K))/(FR(K)-FL(K))
CALL PSIV1 (NGP,SPCING,Q,.FALSE.,XGRID,RHOMAS,VSCOCT,VLOCTY,PSI)
VNEW=ABS(VLOCTY(NGP))
FV=VNEW-VUPPER

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FVRATO=FV/VUPPER
IF (INTRES) WRITE (II,1008) K,Q,FL(K),FR(K)
IF (ABS(FVRATO).LT.1.0E-5) GO TO 170
  IF (FV*FL(K).LT.0.0) THEN
    XR(K+1)=Q
    FR(K+1)=FV
    XL(K+1)=XL(K)
    FL(K+1)=FL(K)
  ELSE
    XL(K+1)=Q
    FL(K+1)=FV
    XR(K+1)=XR(K)
    FR(K+1)=FR(K)
  END IF
160 CONTINUE

C   calculate convective and diffusive fluxes for NO
DO IGP=1,NGP
  CONFLUX=CSMOTH(INO,IGP)*RHOMOL(IGP)*VLOCTY(IGP)
  DIFFLUX=-DIFFNO(IGP)*DCDX(INO,IGP)*RHOMOL(IGP)*1.0e-6
  fluxratio=abs(conflux/difflux)
  peclet1=abs(vlocty(igp))*spcing/diffno(igp)
  WRITE (99,*) IGP,XGRID(IGP),CONFLUX,DIFFLUX,fluxratio,peclet1,
1    diffno(igp)
END DO

170 IF (INTRES.OR.IDRIVD.EQ.3.OR.DRIVED.EQ..FALSE.) THEN
  HEADER=' CONVERGED VELOCITY AND PSI PROFILES '
  CTITLE(1)='      XGRID'
  CTITLE(2)='VGZ PROFIL'
  CTITLE(3)='PSI PROFIL'
  IF (INTRES) THEN
    CALL OUTPUT (II,.TRUE.,3,NGP,HEADER,CTITLE,XGRID,VLOCTY,PSI,
1    DUMMY,DUMMY,DUMMY,DUMMY,DUMMY,DUMMY,DUMMY)
  END IF
  IF ((DRIVED.EQ..FALSE.).OR.(IDRIVD.EQ.3)) THEN
    CALL OUTPUT (IR,.TRUE.,3,NGP,HEADER,CTITLE,XGRID,VLOCTY,PSI,
1    DUMMY,DUMMY,DUMMY,DUMMY,DUMMY,DUMMY,DUMMY)
  END IF
END IF

C   converged velocity and psi profiles have been obtained
C   set level to 30+idrivid*2
LEVEL = 30 + IDRIVD*2

CALL ELEBAL (NGP,NSPCIE,XGRID,CSMOTH,DELTAX,LSTSPC,DIFFUS,
1    RHOMOL,AVGMW,VLOCTY,PSI,RATES,INTRES,DRIVED)

IF (INTRES.OR.IDRIVD.EQ.3.OR.DRIVED.EQ..FALSE.) THEN

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      HEADER=' RATES OF FORMATION MATRIX FOR THE SYSTEM '
      CTITLE(2)='RFZ_'//LSTSPC(1)
      CTITLE(3)='RFZ_'//LSTSPC(2)
      CTITLE(4)='RFZ_'//LSTSPC(3)
      CTITLE(5)='RFZ_'//LSTSPC(4)
      CTITLE(6)='RFZ_'//LSTSPC(5)
      CTITLE(7)='RFZ_'//LSTSPC(6)
      CTITLE(8)='RFZ_'//LSTSPC(7)
      CTITLE(9)='RFZ_'//LSTSPC(8)
      CTITLE(10)='RFZ_'//LSTSPC(9)
      CTITLE(11)='RFZ_'//LSTSPC(10)
      CTITLE(12)='RFZ_'//LSTSPC(11)

      IF (INTRES) THEN
        CALL OUTPUT1(II,.TRUE.,12,MSPCIE,NGP,HEADER,CTITLE,XGRID,RATES)
      END IF
      IF ((DRIVED.EQ..FALSE.).OR.(IDRIVD.EQ.3)) THEN
        CALL OUTPUT1(IR,.TRUE.,12,MSPCIE,NGP,HEADER,CTITLE,XGRID,RATES)
      END IF
    END IF

C      element balance has been computed with success
C      set level to 40+idrivd*3
      LEVEL = 40+IDRIVD*3

      IF (DRIVED.EQ..FALSE.) GO TO 600

500    CONTINUE
600    LEVEL = 50

C      gas phase equations have been solved , now particle phase
C      equations will be solved
C      evaluate the spline coefficients to interpolate viscosity,
C      velocity, psi and temperature profiles.

      CALL CUBSPL (XGRID,  PSI,NGP,10,1,MGPM1,PSICOF,IER)
      LEVEL = 51
      CALL CUBSPL (XGRID,VSCOCT,NGP,10,1,MGPM1,VISCOF,IER)
      LEVEL = 52
      CALL CUBSPL (XGRID,VLOCTY,NGP,10,1,MGPM1,VELCOF,IER)
      LEVEL = 53
      CALL CUBSPL (XGRID,TSMOTH,NGP,10,1,MGPM1,TEMCOF,IER)
      LEVEL = 54
      CALL CUBSPL (XGRID,CPAVG,NGP,10,1,MGPM1,CPACOF,IER)
      LEVEL = 55
      CALL CUBSPL (XGRID,RHOMAS,NGP,10,1,MGPM1,RHOCOF,IER)
      LEVEL = 56
      CALL CUBSPL (XGRID,AVGMW,NGP,10,1,MGPM1,MWCOEF,IER)
      CALL CUBSPL (XGRID,DIFFNO,NGP,10,1,MGPM1,DIFNOC,IER)

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LEVEL = 57
JUMP=NGP/10
DO 625 I=1,NPICK
  IF (I.EQ.1) THEN
    TCOND(I)=TSMOTH(I)
    GCOND(I)=THCOND(I)
  ELSE IF (I.EQ.NPICK) THEN
    TCOND(I)=TSMOTH(NGP)
    GCOND(I)=THCOND(NGP)
  ELSE
    TCOND(I)=TSMOTH(JUMP*I)
    GCOND(I)=THCOND(JUMP*I)
  END IF
625  CONTINUE

ERRCOD=0
CALL SORTA (NPICK,TCOND,GCOND,ERRCOD,ERRMES)
IF (ERRCOD.NE.0) THEN
  WRITE (ID,1009) ERRCOD,LEVEL,ERRMES
END IF

IF (ERRCOD.EQ.2) THEN
DO 650 I=1,NPICK-1
650  IF (TCOND(I).EQ.TCOND(I+1)) TCOND(I)=TCOND(I)-1.0
    ERRMES=' ABSCISSA HAVE BEEN MODIFIED, CONTINUING '
    WRITE (ID,1007) ERRMES
END IF

CALL CUBSPL (TCOND,GCOND,NPICK,10,1,NPICM1,CCOND,IER)

LEVEL=55

IF (LDEBUG) THEN
  WRITE (ID,1007) ' TEST FOR INTERPOLATION BY CUBIC SPLINE '
  DO 675 MUG=1,129
    XINT=SPCING*(MUG-1)/128
    VELINT= CSINTP (XINT,XGRID,VLOCTY,NGP,VELCOF,MGPM1,.FALSE.)
    PSIINT= CSINTP (XINT,XGRID, PSI,NGP,PSICOF,MGPM1,.FALSE.)
    TEMINT= CSINTP (XINT,XGRID,TSMOTH,NGP,TEMCOF,MGPM1,.FALSE.)
    VISINT= CSINTP (XINT,XGRID,VSCOCT,NGP,VISCOF,MGPM1,.FALSE.)
    WRITE (ID,1005) MUG,XINT,VELINT,PSIINT,TEMINT,VISINT
675  CONTINUE
  END IF

C    set up the parameters required for rkf45
H=0.0001
RELERR=1.0E-3
ABSERR=1.0E-5

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LEVEL=60

DO 700 ITAU=1,NTMAX
  TIME(ITAU)=FLOAT(ITAU-1)*DELTAT
  TOUT=TIME(ITAU)

  IF (ITAU.EQ.1) THEN
C    initial conditions for the variables' vector for particle velocity
      YV(1)=0.0
      YV(2)=SPCING
      YV(3)=VLOCTY(NGP)
      YV(4)=RINITL
      YV(5)=0.0

C    set up the initial temperature in the coal particle
C    initial particle temperature is taken same as gas temperature
C    leaving the upper burner

      DO IGPP=1,NGPP
        TCOAL(IGPP)=TSMOTH(NGP)
      END DO

      TSRFAC(ITAU)=TCOAL(NGPP)
      TCENTR(ITAU)=TCOAL(1)
      PDIA(ITAU)=PDIAZ
      PDENST(ITAU)=PDENZ
      PDIA=PDIA(ITAU)
      PDEN=PDENST(ITAU)
      RENOLD(ITAU)=0.0
      PRNDTL(ITAU)=CPAVG(NGP)*VSCOCT(NGP)/THCOND(NGP)/AVGMW(NGP)
      NUSELT(ITAU)=2.0
      PECLET(ITAU)=ABS(VLOCTY(NGP))*SPCING/DIFFNO(NGP)
      VOLATL(ITAU)=0.0
      MDOT(ITAU)=0.0
      RDOT(ITAU)=0.0
      BLOCOF(ITAU)=0.0
      GASVEL(ITAU)=VLOCTY(NGP)
      PARVEL(ITAU)=VLOCTY(NGP)
      ZPOSIT(ITAU)=YV(2)
      RPOSIT(ITAU)=YV(4)
      GASTEM(ITAU)=TSMOTH(NGP)
      PVOLUM=PI*PDIA*PDIA*PDIA/6.0
      PMASSZ=PDEN*PVOLUM
      ETAS=1.0
      GO TO 700

  END IF

CALL RKF56 (NEQN,YV,H,1,TOUT,RELERR,ABSERR,0.0005,3,KHIT,1,1)

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C      call funtmp to determine gas temperature surrounding
C      the coal particle at specific z-positions.

      ZPOSIT(ITAUI)=YV(2)
      RPOSIT(ITAUI)=YV(4)
      GASTEM(ITAUI)=CSINTP(YV(2),XGRID,TSMOTH,NGP,TEMCOF,MGPM1,.FALSE.)
      TGAS=GASTEM(ITAUI)
      CONLOC=SLINTP(TGAS,TCOND,GCOND,NPICK)
      VGZLOC=CSINTP(YV(2),XGRID,VLOCTY,NGP,VELCOF,MGPM1,.FALSE.)
      PSILOC=CSINTP(YV(2),XGRID,PSI,NGP,PSICOF,MGPM1,.FALSE.)
      GASVEL(ITAUI)=SQRT(PSILOC*PSILOC*YV(4)*YV(4)+VGZLOC*VGZLOC)
      PARVEL(ITAUI)=SQRT(YV(3)*YV(3)+YV(5)*YV(5))
      CPALOC=CSINTP(YV(2),XGRID,CPAVG,NGP,CPACOF,MGPM1,.FALSE.)
      VISLOC=CSINTP(YV(2),XGRID,VSCOCT,NGP,VISCOF,MGPM1,.FALSE.)
      RHOLOC=CSINTP(YV(2),XGRID,RHOMAS,NGP,RHOCOF,MGPM1,.FALSE.)
      RENOLD(ITAUI)=ABS(GASVEL(ITAUI)-PARVEL(ITAUI))*PDIA*RHOLOC
      RENOLD(ITAUI)=RENOLD(ITAUI)/VISLOC
      MWLOC=CSINTP(YV(2),XGRID,AVGMW,NGP,MWCOEF,MGPM1,.FALSE.)
      PRNDTL(ITAUI)=CPALOC*VISLOC/CONLOC/MWLOC
      DIVISR=SQRT(RHOLOC*ABS(VGZLOC))
      DIFNOL=CSINTP(YV(2),XGRID,DIFNO,NGP,DICNOC,MGPM1,.FALSE.)
      PECLET(ITAUI)=ABS(VGZLOC)*SPCING/DIFNOL
      WRITE (99,*) ITAUI,zposit(itaui),PECLET(ITAUI)
      TS=TSRFAC(ITAUI-1)
      IF (VOLATL(ITAUI-1).GT.VSTAR) VOLATL(ITAUI-1)=VSTAR

C      mdot is actually vdot (volatiles dot) which is -ve mdot
C      which has been normalized . multiply by pmassz to get
C      absolute mass transfer rate which is to be used to
C      calculate the blowing coefficient

      MDOT(ITAUI)=PREEXF*EXP(-ACTENG/(1.9872*TS))
C      next two lines use Kobayashi's two reaction model for
C      devolatilization behavior; not used here
C      MDOT(ITAUI)=0.3*2.0e5*exp(-25000.0/(1.987*ts))
C      MDOT(ITAUI)=mdot(itaui)+1.3e7*exp(-40000.0/(1.987*ts))
      MDOT(ITAUI)=MDOT(ITAUI)*(VSTAR-VOLATL(ITAUI-1))
      VOLATL(ITAUI)=VOLATL(ITAUI-1)+MDOT(ITAUI)*DELTAT
      VLTFLT=VSTAR-VOLATL(ITAUI)
      PMASS=PMASSZ*(1.0-VOLATL(ITAUI))
      RDOT(ITAUI)=(1.0-SWELCF)*MDOT(ITAUI)/VSTAR
      ETASPR=RDOT(ITAUI)
      ETAS=ETAS+ETASPR*DELTAT
      PDIAZ=PDIAZ*ETAS
      PDIA=PDIAZ*ETAS
      PVOLUM=PI*PDIA*PDIA*PDIA/6.0
      PDENST(ITAUI)=PMASS/PVOLUM
      PDEN=PDENST(ITAUI)
      BLOCOF(ITAUI)=MDOT(ITAUI)*CPALOC*PMASSZ/(2.0*PI*CONLOC*PDIA*MWLOC)

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      BLOWCF=BLOCOF(ITAU)
      DENOM=EXP(BLOCOF(ITAU))-1.0

C      following if block is added so that erroneous results are
C      not obtained when two numbers of same magnitude are subtracted

      IF (DENOM.LT.BLOWCF.OR.DENOM.LT.1.0E-6) THEN
      CORFAC=1.0
      ELSE
      CORFAC=BLOCOF(ITAU)/DENOM
      END IF
      NUSELT(ITAU)=2.0+0.654*SQRT(RENOLD(ITAU))*PRNDTL(ITAU)**(1./3)
      NUSELT(ITAU)=NUSELT(ITAU)*CORFAC
      HTCDEF(ITAU)=NUSELT(ITAU)*CONLOC/PDIA
      HTCDEF=HTCDEF(ITAU)

1      CALL PTEMP (ITAU,NGPP,TGAS,DELTAT,TCOAL,HTCOF,ETAS,ETASPR,
               ERRCOD,ERRMES)

      TCENR(ITAU)=TCOAL(1)
      TSRFAC(ITAU)=TCOAL(NGPP)

      IF ( (YV(2).LT.0.0) .OR. (YV(4).GT.5.0) ) THEN
      NTIME=ITAU-1
      GO TO 710
      END IF
      NTIME=NTMAX
700      CONTINUE

710      CALL SMOTH (INTRES,10,NTIME,TIME,GASTEM,GASTEM,'GASTEM')

      HEADER='PARTICLE TRAJECTORY AND SURROUNDING GAS TEMPERATURE'
      CTITLE(1)='TIME (sec)'
      CTITLE(2)=' GAS_TEMP'
      CTITLE(3)='P_Z_POSITN'
      CTITLE(4)='P_R_POSITN'
      CALL OUTPUT (IR,.TRUE.,4,NTIME,HEADER,CTITLE,TIME,GASTEM,ZPOSIT,
1              RPOSIT,DUMMI,DUMMI,DUMMI,DUMMI,DUMMI,DUMMI)

      HEADER='DIMENSIONLESS PARAMETERS AND PARTICLE PROPERTIES'
      CTITLE(1)='TIME (sec)'
      CTITLE(2)='P_Z_POSITN'
      CTITLE(3)=' GAS_TEMP'
      CTITLE(4)=' REYNOLD #'
      CTITLE(5)=' PRANDTL #'
      CTITLE(6)=' NUSULT #'
      CTITLE(7)=' M_DOT'
      CTITLE(8)=' H.T.-COEFF'
      CTITLE(9)='BLOW_COEFF'

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CTITLE(10)='VOLATILES'

CALL OUTPUT (IR,.TRUE.,10,NTIME,HEADER,CTITLE,TIME,ZPOSIT,GASTEM,
1          RENOLD,PRNDTL,NUSELT,MDOT,HTCOEF,BLOCOF,VOLATL)
C particle trajectory and gas and particle temperature evaluated
C LEVEL = 70

C set limit on time for which particle actually remains in the
C opposed flow environment without any edge effects

DO 750 ITAU=1,NTIME
IF (RPOSIT(ITAU).GT.(4.80)) THEN
    ITIME=ITAU-1
    GO TO 800
END IF
750 CONTINUE

C if particle is not swept out of the burner area then set the
C index to the maximum value i.e., ntime
ITIME=NTIME

800 WRITE (IR,1010) PDENZ,PDIAZ,GASTEM(1),EMMISS
LEVEL = 80

HEADER=' COAL PARTICLE AND SURROUNDING GAS PHASE TEMPERATURES, A
1ND PARTICLE DIAMETER AND DENSITY '
CTITLE(1)='TIME (sec)'
CTITLE(2)=' GAS_TEMP'
CTITLE(3)=' P_S_TEMP'
CTITLE(4)=' P_C_TEMP'
CTITLE(5)='P_DIAMETER'
CTITLE(6)=' P_DENSITY'

CALL OUTPUT (IR,.FALSE.,6,ITIME,HEADER,CTITLE,TIME,GASTEM,
1          TSRFAC,TCENTR,PDIAZ,PDENST,DUMMI,DUMMI,DUMMI,DUMMI)

KOUNT=0
DO 810 ISP=1,NSPCIE
    IF (LSTSPC(ISP).EQ.'NO    ') THEN
        KOUNT=KOUNT+1
        DO IGP=1,NGP
            RNO(IGP)=RATES(ISP,IGP)
        END DO
    ELSE IF (LSTSPC(ISP).EQ.'NH3  ') THEN
        KOUNT=KOUNT+1
        DO IGP=1,NGP
            RNH3(IGP)=RATES(ISP,IGP)
        END DO
    ELSE IF (LSTSPC(ISP).EQ.'HCN   ') THEN

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      KOUNT=KOUNT+1
      DO IGP=1,NGP
        RHCN(IGP)=RATES(ISP,IGP)
      END DO
    ELSE IF (LSTSPC(ISP).EQ.'H2  ') THEN
      KOUNT=KOUNT+1
      DO IGP=1,NGP
        RH2(IGP)=RATES(ISP,IGP)
      END DO
    ELSE IF (LSTSPC(ISP).EQ.'CH4  ') THEN
      KOUNT=KOUNT+1
      DO IGP=1,NGP
        RCH4(IGP)=RATES(ISP,IGP)
      END DO
    ELSE IF (LSTSPC(ISP).EQ.'C2H2  ') THEN
      KOUNT=KOUNT+1
      DO IGP=1,NGP
        RC2H2(IGP)=RATES(ISP,IGP)
      END DO
    ELSE IF (LSTSPC(ISP).EQ.'C2H4  ') THEN
      KOUNT=KOUNT+1
      DO IGP=1,NGP
        RC2H4(IGP)=RATES(ISP,IGP)
      END DO
    ELSE IF (LSTSPC(ISP).EQ.'C2H6  ') THEN
      KOUNT=KOUNT+1
      DO IGP=1,NGP
        RC2H6(IGP)=RATES(ISP,IGP)
      END DO
    END IF
    IF (KOUNT.EQ.8) GO TO 820
810  CONTINUE

820  CALL CSAKM (NGP,XGRID, RNO,BREAK, CNO)
      CALL CSAKM (NGP,XGRID, RNH3,BREAK, CNH3)
      CALL CSAKM (NGP,XGRID, RHCN,BREAK, CHCN)
      CALL CSAKM (NGP,XGRID, RH2,BREAK, CH2)
      CALL CSAKM (NGP,XGRID, RCH4,BREAK, CCH4)
      CALL CSAKM (NGP,XGRID,RC2H2,BREAK,CC2H2)
      CALL CSAKM (NGP,XGRID,RC2H4,BREAK,CC2H4)
      CALL CSAKM (NGP,XGRID,RC2H6,BREAK,CC2H6)

      DO 825 IGP=1,NGP
825  TOTXNZ(IGP)=CNOZ(IGP)+CNH3Z(IGP)+CHCNZ(IGP)
      CALL CSAKM (NGP,XGRID,TOTXNZ,BREAK,COFTXN)

      WFNIT=WPNIT/100.0
      TGFRATE=VUPPER*81.1*60.0
      FACNOR=14.0*TGFRATE/(CFRATE*298.16*WFNIT*VSTAR)

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NGPM1=NGP-1
DO 850 ITAU = 1,ITIME
  ZT=ZPOSIT(ITAU)
  TOTXNT(ITAU)=CSVAL(ZT,NGPM1,BREAK,COFTXN)
  RFTNO(ITAU) = CSVAL (ZT,NGPM1,BREAK,CNO)
  RFTNH3(ITAU) = CSVAL (ZT,NGPM1,BREAK,CNH3)
  RFTHCN(ITAU) = CSVAL (ZT,NGPM1,BREAK,CHCN)
  RFTH2(ITAU) = CSVAL (ZT,NGPM1,BREAK,CH2)
  RFTCH4(ITAU) = CSVAL (ZT,NGPM1,BREAK,CCH4)
  RFTC2H2(ITAU)=CSVAL (ZT,NGPM1,BREAK,CC2H2)
  RFTC2H4(ITAU)=CSVAL (ZT,NGPM1,BREAK,CC2H4)
850 RFTC2H6(ITAU)=CSVAL (ZT,NGPM1,BREAK,CC2H6)

ITS=1
CALL SMOTH (INTRES,ITS,ITIME,TIME,RFTNO,RFTNO,'RFTNO ')
CALL SMOTH (INTRES,ITS,ITIME,TIME,RFTNH3,RFTNH3,'RFTNH3')
CALL SMOTH (INTRES,ITS,ITIME,TIME,RFTHCN,RFTHCN,'RFTHCN')
CALL SMOTH (INTRES,ITS,ITIME,TIME,RFTH2,RFTH2,'RFTH2 ')
CALL SMOTH (INTRES,ITS,ITIME,TIME,RFTCH4,RFTCH4,'RFTCH4')
CALL SMOTH (INTRES,ITS,ITIME,TIME,RFTC2H2,RFTC2H2,'RFTC2H2')
CALL SMOTH (INTRES,ITS,ITIME,TIME,RFTC2H4,RFTC2H4,'RFTC2H4')
CALL SMOTH (INTRES,ITS,ITIME,TIME,RFTC2H6,RFTC2H6,'RFTC2H6')
CALL SMOTH (INTRES,ITS,ITIME,TIME,TOTXNT,TOTXNT,'TOTXNT')

HEADER=' RATES OF FORMATION OF NITROGENOUS SPECIES AS A FUNCTION
1 OF TIME AND AXIAL POSITION OF PARTICLE'
CTITLE(1)='TIME (sec)'
CTITLE(2)='P_Z_POSITN'
CTITLE(3)=' RFT_NO'
CTITLE(4)=' RFT_NH3'
CTITLE(5)=' RFT_HCN'
CTITLE(6)=' RFT_H2'
CTITLE(7)=' RFT_CH4'
CTITLE(8)=' RFT_C2H2'
CTITLE(9)=' RFT_C2H4'
CTITLE(10)=' RFT_C2H6'
CALL OUTPUT (IR,.TRUE.,10,ITIME,HEADER,CTITLE,TIME,ZPOSIT,
1 RFTNO,RFTNH3,RFTHCN,RFTH2,RFTCH4,RFTC2H2,RFTC2H4,
2 RFTC2H6)

DO ITAU=1,ITIME
  NRNO(ITAU) = RFTNO(ITAU)*GASTEM(ITAU)*FACNOR
  NRNH3(ITAU) = RFTNH3(ITAU)*GASTEM(ITAU)*FACNOR
  NRHCN(ITAU) = RFTHCN(ITAU)*GASTEM(ITAU)*FACNOR
  NRTOTXN(ITAU)=NRNO(ITAU)+NRNH3(ITAU)+NRHCN(ITAU)
END DO

HEADER=' NORMALIZED RATES OF FORMATION OF NITROGENOUS SPECIES AS
1 A FUNCTION TIME (G_ATOM N/G_ATOM INITIAL_VOLATILE_N *SEC))'

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```

CTITLE(1)='TIME (sec)'
CTITLE(2)='P_Z_POSITN'
CTITLE(3)='GAS_TMPRTR'
CTITLE(4)='P_S_TMPRTR'
CTITLE(5)=' NRFT_NO'
CTITLE(6)=' NRFT_NH3'
CTITLE(7)=' NRFT_HCN'
CTITLE(8)='NRFT_TO_XN'
CALL OUTPUT (IR,.TRUE.,8,ITIME,HEADER,CTITLE,TIME,ZPOSIT,
1          GASTEM,TSRFAC,NRNO,NRNH3,NRHCN,NRTOTXN,DUMMI,DUMMI)

IF (PLOT) THEN
WRITE (IP,1014) RUNID
WRITE (IP,1020) NTD,NSPNGC,NSPGC,NDPNGC,NDPGC,NGP,NSPCIE
DO 910 IDP=1,NTD
910 WRITE (IP,1005) IDP,XTEXP(IDP),TEXP(IDP)
DO 920 IGP=1,NGP
920 WRITE (IP,1005) IGP,XGRID(IGP),TSMOTH(IGP)
DO 930 IDP=1,NDPNGC
930 WRITE (IP,1005) IDP,XCENG(CIDP),(CEXNGC(ISP,IDP),ISP=1,NSPNGC)
DO 935 IDP=1,NDPGC
935 WRITE (IP,1005) IDP,XCEXGC(IDP),(CEXP(CIDP),ISP=1,NSPGC)
DO 940 IGP=1,NGP
940 WRITE (IP,1005) IGP,XGRID(IGP),(CSMOTH(ISP,IGP),ISP=1,NMESRD)
DO 950 IGP=1,NGP
950 WRITE (IP,1005) IGP,XGRID(IGP),VLOCTY(IGP),PSI(IGP)
DO 960 IGP=1,NGP
960 WRITE (IP,1005) IGP,XGRID(IGP),(RATES(ISP,IGP),ISP=1,NSPCIE)
WRITE (IP,*) NTIME,ITIME
DO 970 ITAU=1,NTIME
970 WRITE (IP,1005) ITAU,ZPOSIT(ITAU),RPOSIT(ITAU)
DO 980 ITAU=1,ITIME
980 WRITE (IP,1005) ITAU,TIME(ITAU),GASTEM(ITAU),TSRFAC(ITAU),
1          TCENTR(ITAU)
DO 990 ITAU=1,ITIME
990 WRITE (IP,1005) ITAU,RFTNO(ITAU),RFTNH3(ITAU),RFTHCN(ITAU),
1          RFTH2(ITAU),RFTCH4(ITAU),RFTC2H2(ITAU),
2          RFTC2H4(ITAU),RFTC2H6(ITAU)
DO 991 ITAU=1,ITIME
991 WRITE (IP,1005) ITAU,NRNO(ITAU),NRNH3(ITAU),NRHCN(ITAU)

DO 992 ITEST=1,1
WRITE (IP,1005) NOBSR(ITEST)
DO 992 IOBS=1,NOBSR(ITEST)
992 WRITE (IP,1005) IOBS,XOBS(ITEST,IOBS),YOBS(ITEST,IOBS)
END IF

LEVEL = 100

```

```

101  FORMAT (1X,'SMOOTHING UNSUCCESSFUL, ERROR CODE = ',I3)
1001 FORMAT (A6,I2)
1002 FORMAT ('1',1X,'SMOOTHED DATA FOR TEMPERATURE',/)
1003 FORMAT (1X,I4,6(2X,1PE14.5))
1004 FORMAT ('1',1X,'SMOOTHED DATA FOR SPECIE ',A6,/)
1005 FORMAT (1X,I4,9(1PE14.5))
1006 FORMAT (1X,I4,2X,A6,2X,I3)
1007 FORMAT (1X,T2,A130)
1008 FORMAT (1X,'AT REGULAR FALSI ITERATION # ',I3,' Q = ',1PE14.5,
1      ' FL = ',1PE14.5,' FR = ',1PE14.5)
1009 FORMAT (1X,'ERRCOD = ',I4,'LEVEL = ',I5,/,1X,T2,A130)
1010 FORMAT ('1',/,5X,' COAL PARTICLE HEAT UP ',/,
1      5X,' INITIAL COAL PARTICLE DENSITY (gm/cc) = ',F23.2,/,
2      5X,' INITIAL COAL PARTICLE DIAMETER (centimeter) = ',E17.2,/,
3      5X,' INITIAL COAL PARTICLE TEMPERATURE (deg K) = ',F19.2,/,
4      5X,' EMMISIVITY OF COAL = ',F42.2,///)
1011 FORMAT (1X,11(1X,1PE10.3))
1012 FORMAT ('1',/1X,'TRRESULTS FOR IDRIVED LOOP # ',I3)
1013 FORMAT (A80)
1014 FORMAT (1X,T2,A80)
1015 FORMAT (1X,'INTEGRATION CAN NOT BE PROCEEDED ANY FURTHER THAN ',
1      /,1X,' PARTICLE AXIAL POSITION ',1PE14.5,
2      /,1X,' PARTICLE RADIAL POSITION ',1PE14.5,
3      /,1X,' IFLAG = ',I2)
1020 FORMAT (1X,7I3)
1032 FORMAT (1X,A14,2(1PE14.5))

```

```

STOP 'ALL DONE, HAPPY CAMPER '
END

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SUBROUTINE RKF56 (N,Y,H,IEND,ENDPNT,MAXTOL,MINTOL,HMAX,IPRINT,
+ KHIT,IDIREC,HSIGN)

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C      SUBROUTINE RKF56 SOLVES A SYSTEM OF ORDINARY DIFFERENTIAL
C      EQUATIONS. THIS IS SET UP TO SOLVE UPTO TWENTY EQUATIONS.
C      TO SOLVE MORE THAN TWENTY EQUATIONS CHANGE THE VALUE OF
C      MAX IN THE PARAMETER STATMENT.

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C      SOLUTION IS BASED ON 5TH AND 6TH ORDER RUNGE KUTTA FEHLBERG
C      ALGORITHM. STEP SIZE IS ADJUSTED ACCORDING TO MAGNITUDE OF
C      ERROR BETWEEN THE 6TH ORDER (BETTER) AND 5TH ORDER (GOOD)
C      SOLUTION. ADJUSTMENT CRITERIA IS DESCRIBED LATER IN THE
C      ROUTINE.

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C      USER PROVIDES THE INITIAL CONDITIONS OF ALL THE VARIABLES
C      AND A VALUE OF END POINT FOR A SPECIFIC VARIABLE (INDEPENDENT
C      OR DEPENDENT). CONTROL IS TRANSFERED TO THE CALLING PROGRAM
C      ONCE THAT END POINT IS HIT. IN CASE THE CLCULATED VALUE
C      OF THAT SPECIFIC VARIABLE, NAMED TERMINATING VARIABLE IN THIS

```

C ROUTINE, IS JUMPED A LINEAR INTERPOLATION IS PERFORMED TO GET
 C AN ESTIMATE OF STEP SIZE. A NEW STEP IS TAKEN FROM THE LAST
 C POINT BELOW THE END POINT WITH THE NEW APPROXIMATED STEP SIZE.

C DESCRIPTION OF ARGUMENTS IS AS FOLLOWS:

C *****

C N = NUMBER OF EQUATIONS (INPUT)

C Y = VECTOR OF INITIAL VALUES OF VARIABLES (INPUT)

C = VECTOR OF FINAL VALUES OF VARIABLES (OUTPUT)

C H = INITIAL STEP SIZE (INPUT)

C = OPTIMAL STEP SIZE (OUTPUT)

C IEND = INDEX OF TERMINATING VARIABLE (INPUT)

C ENDPNT = FINAL VALUE OF TERMINATING VARIABLE (INPUT)

C MAXTOL = MAXIMUM ACCEPTABLE TOLERANCE (INPUT)

C MINTOL = MINIMUM ACCEPTABLE TOLERANCE (INPUT)

C HMAX = UPPER BOUND FOR THE STEP SIZE

C IPRINT = INTERMEDIATE OUTPUT CONTROL PARAMETE (INPUT)

C = 1 ALL GOOD INTERMEDIATE RESULTS ARE PRINTED

C = 2 ALL THE INTERMEDIATE RESULTS ARE PRINTED

C = 3 RESULTS AT THE END POINT IS PRINTED

C KHIT = CONVERGENCE STATUS FLAG

C = 0 SOLUTION HAS HIT THE END POINT

C = 1 SOLUTION IS STILL MARCHING TOWARDS THE END POINT

C = 2 SOLUTION HAS JUMPED OVER THE END POINT

C = 3 FUNCTION IS NONMONOTONIC, FOLLOW THE DIRECTIONS

C IDIREC = DIRECTION CONTROL PARAMETER

C = 1 IF MOVING IN INCREASING DIRECTION

C = -1 IF MOVING IN DECREASING DIRECTION

C HSIGN = STEP SIGN PARAMETER

C = 1 IF STEP SIZE IS POSITIVE

C = -1 IF STEP SIZE IS NEGATIVE

C *****

C DESCRIPTION OF OTHER IMPORTANT VARIABLES

C *****

C MAX = MAX NUMBER OF EQUATIONS TO BE HANDLED

C YOLD = VECTOR WHICH HOLDS THE OLD VALUES OF VECTOR V

C YSEND = VECTOR WHICH IS UPDATED FOR DERIVATIVES EVALUATIONS

C FIRST CALL TO DIFEQS IS WITH YOLD

C YTEMP = VECTOR WHICH HOLDS THE LATEST VECTOR Y BELOW THE ENDPNT

C YRK5 = VECTOR OF 5TH ORDER R-K SOLUTIONS

C YRK6 = VECTOR OF 6TH ORDER R-K SOLUTIONS

C WE CAN GET AROUND WITHOUT YSEND AND YRK6 BUT THESE ARE

C INTRODUCED SO THAT STUDENTS ARE NOT CONFUSED

C HOPTML = VALUE OF H SAVED JUST BEFORE INTERPOLATION STARTS

C LIMIT = A MACHINE DEPENDENT VALUE TO AVOID DIVISION BY ZERO

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C      COMON1 = A CONSTANT = H/8448
C      COMON2 = VECTOR OF COMMON PART FOR 5TH AND 6TH ORDER SOLUTIONS
C      OUT1 = UNIT NUMBER FOR OUTPUT FILE. IT IS SUGGESTED THAT IT
C             SHOULD BE SET DIFFERENT FROM THE ONE IN CALLING PROGRAM
C      K1 - K8 = VECTORS FOR RKF ALGORITHM
C      IERROR = FLAG TO DETERMINE TYPE OF ERROR TO BE COMPUTED
C                = 0 RELATIVE ERROR IS USED
C                = 1 ABSOLUTE ERROR IS USED
C      ERROR = ERROR VECTOR DEPENDING ON FLAG IERROR
C      INTER = FLAG TO KEEP THE OPTIMAL STEP SIZE
C                = 0 UPDATE THE OPTIMAL STEP SIZE AS SOLUTION IS STILL
C                   MARCHING TOWARDS THE END POINT
C                = 1 DO NOT CHANGE THE VALUE OF OPTIMAL H AS INTERPOLATION
C                   PROCESS HAS BEEN INITIATED
C                = 2 DO NOT CHANGE THE VALUE OF OPTIMAL H AS INTERPOLATION
C                   PROCESS TO ACCOUNT FOR NON-MONOTONIC BEHAVIOR IS IN
C                   PROGRESS
C      KOUNT = NUMBER OF ITERATIONS REQUIRED TO CONVERGE ON END POINT
C                ONCE INTERPOLATION PROCESS IS INITIATED.
C                = 0 BEFORE INTERPOLATION IS STARTED.
C      MKOUNT= MAXIMUM NUMBER OF ITERATIONS ALLOWED FOR INTERPOLATION
C      MTONIC= NUMBER OF ITERATIONS REQUIRED TO HIT THE END POINT FOR
C                THE CASE OF NON-MONOTONIC FUNCTION
C                IT IS RESET TO ZERO EVERY TIME THE NEW VALUE OF THE
C                TERMINATING VARIABLE IS BELOW THE END POINT
C      NREJEC= COUNTER FOR UNSUCCESSFUL STEP
C                = 0 STEP IS SUCCESSFUL
C      TREJEC= TOTAL UNSUCCESSFUL ITERATIONS BEFORE A SUCCESSFUL STEP
C                IS TAKEN
C      CUT   = FACTOR BY WHICH STEP SIZE IS CUT IF ITERATION IS SUCH
C                THAT AT LEAST ONE ERROR ELEMENT IS GREATER THAN
C                MAXTOL
C      INCRES= FACTOR BY WHICH STEP SIZE IS INCREASED IF ITERATION IS
C                SUCH THAT ALL THE ERRORS ARE LESS THAN MINTOL
C      NOTE:
C                IF CUT AND INCRES ARE SET TO 1.0 IN THE PARAMETER
C                STATEMENT THEN THIS BECOMES A CONSTANT STEP SIZE
C                5-6TH ORDER RUNGE-KUTTA-FEHLBERG ALGORITHM.

C      SUBROUTINE RKF56 CALLS SUBROUTINE DIFEQS WHICH CONTAINS
C      THE DERIVATIVES (DIFFERENTIAL EQUATIONS) FOR ALL THE VARIABLES.
C      THE CALLING STATEMENT IS
C      CALL (N,Y,F)
C      WHERE N = NUMBER OF EQUATIONS
C            Y = VECTOR OF VARIABLES
C            F = VECTOR OF DERIVATIVE EVALUATIONS
C      *****
C      I M P O R T A N T   N O T E :
C      *****

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C      VECTOR Y IS SET UP SUCH THAT Y(1) IS THE INDEPENDENT VARIABLE
C      SET THE THE SUBROUTINE DIFEQS ACCORDINGLY.
C      *****

      INTEGER N,IERROR,IEND,IPRINT,KHIT,KOUNT,OUT1,HSIGN,TREJEC

      REAL LIMIT,COMON1,MAXTOL,MINTOL,HMAX,H,HOPTML,INCRES
      PARAMETER (CUT=0.5,INCRES=2.0)
      PARAMETER (LIMIT=1.0E-30,MAX=20,OUT1=30,MKOUNT=20)
      REAL Y(N),YRK5(MAX),YRK6(MAX),YOLD(MAX),YSEND(MAX),YTEMP(MAX)
      REAL K1(MAX),K2(MAX),K3(MAX),K4(MAX),K5(MAX),K6(MAX)
      REAL K7(MAX),K8(MAX),ERROR(MAX),COMON2(MAX)

C      INITIAL TESTS

      IF ((IDIREC.EQ.-1.AND.Y(IEND).LT.ENDPNT) .OR.
+       (IDIREC.EQ.1.AND.Y(IEND).GT.ENDPNT)) THEN
          WRITE (OUT1,*) ' VALUE OF TERMINATING VARIABLE IS BEYOND ',
+           'THE END POINT, RETURNING TO MAIN '
          RETURN

      ELSE IF (Y(IEND).EQ.ENDPNT) THEN
          WRITE (OUT1,*) ' VALUE OF TERMINATING PARAMETER IS SAME ',
+           ' AS END POINT, RETURNING TO MAIN'
          RETURN

      END IF

C      TEST THE STEP SIZE FOR UPPER BOUND

      IF (ABS(H).GT.ABS(HMAX)) H=HMAX

C      IF END POINT IS FOR INDEPENDENT VARIABLE THEN CHECK IF THE
C      PRESENT VALUE OF H JUMPS OVER THE END POINT. IF YES THEN
C      RESET THE STEP SIZE.

      IF (IEND.EQ.1) THEN
          IF (IDIREC.EQ.-1) THEN
              IF ((H+Y(1)).LT.ENDPNT) H=Y(1)-ENDPNT
              ELSE IF ((H+Y(1)).GT.ENDPNT) THEN
                  H=ENDPNT-Y(1)
              END IF
          END IF

C      INITIALIZE THE PARAMETERS
      KOUNT=0
      INTER=0
      KHIT=1
      NREJEC=0

```



```

      DO 5 I=1,N
5      YTEMP(I)=Y(I)

10     DO 20 I=1,N
20     YOLD(I)=Y(I)

15     IERROR=0

C      EVALUATE VECTOR K1
      CALL DIFEQS (N,YOLD,K1)

      DO 30 I=1,N
30     YSEND(I)=YOLD(I)+H*K1(I)/6.0

C      EVALUATE VECTOR K2
      CALL DIFEQS (N,YSEND,K2)

      DO 40 I=1,N
40     YSEND(I)=YOLD(I)+H*(4.0*K1(I)/75.0+16.0*K2(I)/75.0)

C      EVALUATE VECTOR K3
      CALL DIFEQS (N,YSEND,K3)

      DO 50 I=1,N
50     YSEND(I)=YOLD(I)+H*(5.0*K1(I)/6.0-8.0*K2(I)/3.0+5.0*K3(I)/2.0)

C      EVALUATE VECTOR K4
      CALL DIFEQS (N,YSEND,K4)

      DO 60 I=1,N
60     YSEND(I)=YOLD(I)+H*(-8.0*K1(I)/5.0+144.0*K2(I)/25.0-
+       4.0*K3(I)+16.0*K4(I)/25.0)

C      EVALUATE VECTOR K5
      CALL DIFEQS (N,YSEND,K5)

      DO 70 I=1,N
70     YSEND(I)=YOLD(I)+H*(361.0*K1(I)/320.0-18.0*K2(I)/5.0+
+       407.0*K3(I)/128.0-11.0*K4(I)/80.0+55.0*K5(I)/128.0)

C      EVALUATE VECTOR K6
      CALL DIFEQS (N,YSEND,K6)

      DO 80 I=1,N
80     YSEND(I)=YOLD(I)+H*(-11.0*K1(I)/640.0+11.0*K3(I)/256.0-
+       11.0*K4(I)/160.0+11.0*K5(I)/256.0)

C      EVALUATE VECTOR K7

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      CALL DIFEQS (N,YSEND,K7)

      DO 90 I=1,N
90     YSEND(I)=YOLD(I)+H*(93.0*K1(I)/640.0-18.0*K2(I)/5.0
      +      +803.*K3(I)/256.0-11.0*K4(I)/160.0+99.0*K5(I)/256.0+K7(I))

C     EVALUATE VECTOR K8
      CALL DIFEQS (N,YSEND,K8)

C     CALCULATE R-K 5TH AND 6TH ORDER VALUES
      COMON1=H/8448.0
      DO 100 I=1,N
      COMON2(I)=3375.0*K3(I)+2376.0*K4(I)+1375.0*K5(I)
      YRK5(I)=YOLD(I)+COMON1*(682.0*K1(I)+COMON2(I)+640.0*K6(I))
      YRK6(I)=YOLD(I)+COMON1*(42.0*K1(I)+COMON2(I)+640.0*K7(I)+
      +      640.0*K8(I))

C     IF ANY ELEMENT OF VECTOR Y EXCEEDS THE UPPER OR LOWER LIMITS
C     THEN SET ERROR FLAG EQUAL TO 1.

      IF (ABS(YRK6(I)).LT.LIMIT) IERROR=1

100    CONTINUE

C     IF IERROR EQUALS 1 CONVERGENCE IS BASED ON ABSOLUTE ERROR
C     IF IERROR EQUALS 0 CONVERGENCE IS BASED ON RELATIVE ERROR

      DO 105 I=1,N
      ERROR(I)=ABS(YRK6(I)-YRK5(I))
      IF (IERROR.NE.1) ERROR(I)=ERROR(I)/YRK6(I)
105    CONTINUE

C     CHECK FOR ADJUSTMENT OF STEP SIZE

C     IF ANY ELEMENT OF THE ERROR VECTOR IS LARGER THAN THE MAXIMUM
C     ALLOWABLE TOLERANCE, THEN THE RESULTS ARE NOT ACCEPTABLE.
C     DISREGARD THE SOLUTION, CUT THE STEP SIZE AND REPEAT THE
C     CALCULATIONS.
      DO 110 I=1,N
      IF (ERROR(I).GT.MAXTOL) THEN
      H=H*CUT
      NREJEC=NREJEC+1
      GO TO 111
      END IF
110    CONTINUE
      TREJEC=NREJEC
      NREJEC=0

C     IF IPRINT EQUALS 2 THEN ALL THE INTERMEDIATE RESULTS ARE

```

```

C      PRINTED. IRRESPECTIVE OF WHETHER SOLUTION IS GOOD OR NOT.

111  IF (IPRINT.EQ.2) THEN
      WRITE (OUT1,201) (Y(I),I=1,N),H,NREJEC,IERROR,KOUNT,KHIT
      END IF

      IF (NREJEC.NE.0) GO TO 15

C      SINCE ALL THE ELEMENTS OF THE ERROR VECTOR ARE SMALLER THAN
C      MAXIMUM ALLOWABLE TOLERANCE, HENCE THE RESULTS ARE ACCEPTABLE.

      DO 115 I=1,N
115  Y(I)=YRK6(I)

C      IF IPRINT EQUALS 1 THEN THE INTERMEDIATE RESULTS ARE PRINTED
C      ONLY IF SOLUTION IS GOOD AND ACCEPTABLE.

      IF (IPRINT.EQ.1) THEN
          WRITE (OUT1,201) (Y(I),I=1,N),H,TREJEC,IERROR,KOUNT,KHIT
      END IF

C      TEST TO SEE IF STEP SIZE CAN BE INCREASED.

C      IF ANY ELEMENT OF ERROR VECTOR IS LARGER THAN THE MINIMUM
C      ALLOWABLE TOLERANCE. THEN KEEP THE SAME STEP SIZE ELSE INCREASE
C      THE STEP SIZE I.E., STEP SIZE IS INCREASED ONLY IF ALL THE
C      ELEMENTS OF ERROR VECTOR ARE SMALLER THAN THE MINIMUM ALLOWABLE
C      TOLERANCE.

      DO 120 I=1,N
      IF (ERROR(I).GT.MINTOL) GO TO 130
120  CONTINUE

C      ONCE THE END POINT IS OVERSHOOT. DO NOT INCREASE THE STEP SIZE.

      IF (INTER.EQ.0) H=INCRES*H

C      TEST TO TERMINATE THE PROGRAM
C      PROGRAM WILL BE TERMINATED WHEN THE END POINT IS HIT WITHIN
C      SOME ALLOWABLE REGION.

      IF (KOUNT.GT.MKOUNT) THEN
          WRITE (OUT1,*) 'MAXIMUM # OF ITERATIONS EXCEEDED'
          RETURN
      END IF

130  IF (ABS(Y(IEND)-ENDPNT).LE.1.0E-6) THEN
C      END POINT HAS BEEN HIT
      KHIT=0

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```

      IF (INTER.EQ.1) KOUNT=KOUNT+1
      H=HOPTML
      WRITE (OUT1,201) (Y(I),I=1,N),H,TREJEC,IERROR,KOUNT,KHIT
      RETURN
      END IF

      IF ((IDIREC.EQ.1.AND.ENDPNT.GT.Y(IEND))      .AND.
+        Y(IEND).GT.YTEMP(IEND))                .OR.
+        (IDIREC.EQ.-1.AND.ENDPNT.LT.Y(IEND))    .AND.
+        Y(IEND).LT.YTEMP(IEND)))                THEN

C      STILL MARCHING TOWARDS END POINT
C      SAVE THE RESULTS IN SOME TEMPORARY ARRAY.

      DO 135 I=1,N
135    YTEMP(I)=Y(I)
      KHIT=1

C      LATEST STEP SIZE BECOMES THE OPTIMAL STEP AS FAR AS WE HAVE NOT
C      JUMPED THE END POINT

      IF (INTER.EQ.0) HOPTML = H
      IF (INTER.EQ.1) KOUNT=KOUNT+1
      IF (INTER.EQ.2) MTONIC=0

C      TAKE ANOTHER STEP

      GO TO 10

      ELSE IF ((IDIREC.EQ.-1.AND.ENDPNT.GT.Y(IEND)) .AND.
+        ENDPNT.LT.YTEMP(IEND))                .OR.
+        (IDIREC.EQ.1.AND.ENDPNT.LT.Y(IEND))    .AND.
+        ENDPNT.GT.YTEMP(IEND)))                THEN

C      END POINT HAS BEEN JUMPED
C      INTERPOLATE TO GET AN ESTIMATE OF STEP SIZE WHICH WILL HIT THE
C      END POINT AND TAKE ANOTHER STEP FROM THE POINT NEXT BELOW THE
C      END POINT WITH NEW ESTIMATED H.

      KHIT=2
      INTER=1
      FACTOR=(ENDPNT-YTEMP(IEND))/(Y(IEND)-YTEMP(IEND))
      H=ABS(FACTOR*(Y(1)-YTEMP(1)))
      IF (HSIGN.EQ.-1) H=-H
C      RESET VALUES TO THE POINTS IMMEDIATELY BELOW THE END POINT

      DO 145 I=1,N
145    Y(I)=YTEMP(I)
      KOUNT=KOUNT+1

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```

      GO TO 10

      ELSE
C      FUNCTION IS NOT MONOTONIC. AN EXTREMUM IS ENCOUNTERED
C      CUT THE STEP SIZE AND ATTEMPT TO HIT THE END POINT
      KHIT=3
      INTER=2
      MTONIC=MTONIC+1
      H=CUT*H
C      RESET VALUES TO THE POINT IMMEDIATELY BELOW THE END POINT
      DO 155 I=1,N
155    Y(I)=YTEMP(I)
      IF (MTONIC.LT.MKOUNT) GO TO 10
      WRITE (OUT1,202)
      WRITE (6,202)
      WRITE (OUT1,201) (Y(I),I=1,N),H,NREJEC,IERROR,MTONIC,KHIT
      RETURN
      END IF

201    FORMAT (5X,1P6E16.8,2X,4I5)
202    FORMAT (5X,
+    'THE TERMINATING VARIABLE IS ONE OF THE DEPENDENT VARIABLE',/,
+    5X,'THE FUNCTIONAL BEHAVIOUR OF THIS DEPENDENT VARIABLE IS NOT'
+    ', ' MONOTONIC ',//,5X,'USE INDEPENDENT VARIABLE AS THE ',/,
+    5X,'TERMINATING VARIABLE ')

      END

      SUBROUTINE DIFEQS (N,Y,YPRIME)
      PARAMETER (MGP=65,MGPM1=MGP-1)
      COMMON /PARAS/ XGRID(MGP),PSI(MGP),PSICOF(MGPM1,3),TSMOTH(MGP),
1          TEMCOF(MGPM1,3),VLOCTY(MGP),VELCOF(MGPM1,3),
2          VSCOCT(MGP),VISCOF(MGPM1,3),NGP
      REAL Y(N),YPRIME(N)

C      COMPUTES DERIVATIVES OF Z AND R-PARTICLE MOMENTUM BALANCES

      GRAVITY=980.0
      Z=Y(2)
      ALPHA=ALP(Z)
      VELLOCO=CSINTP(Z,XGRID,VLOCTY,NGP,VELCOF,.FALSE.)
      PSILOC=CSINTP(Z,XGRID,PSI,NGP,PSICOF,.FALSE.)
      YPRIME(1)=1.0
      YPRIME(2)=Y(3)
      YPRIME(3)=ALPHA*(-YPRIME(2)+VELLOCO)-GRAVITY
      YPRIME(4)=Y(5)
      YPRIME(5)=-ALPHA*(YPRIME(4)-Y(4)*PSILOC)
      RETURN
      END

```

```

FUNCTION CSINTP (Z,X,Y,N,C,LDEBUG)
PARAMETER (IR=10,II=20,ID=30)
REAL X(N),Y(N),C(N-1,3)
LOGICAL LDEBUG
IF (Z.LT.X(1).OR.Z.GT.X(N)) THEN
    WRITE (IR,100) Z,X(1),X(N)
    RETURN
END IF

DO 10 I=1,N
    IF (Z.EQ.X(I)) THEN
        CSINTP=Y(I)
        RETURN
    END IF
10  CONTINUE

DO 20 I=1,N-1
    IF ((X(I).LT.Z).AND.(Z.LT.X(I+1))) THEN
        DIF=Z-X(I)
        CSINTP=((C(I,3)*DIF+C(I,2))*DIF+C(I,1))*DIF+Y(I)
        RETURN
    END IF
20  CONTINUE
100 FORMAT (1X,' Z IS OUT OF RANGE IN CSINTP ',3(1PE14.5))
END

FUNCTION SLINTP (Z,X,Y,N)
PARAMETER (IR=10,II=20,ID=30)
REAL X(N),Y(N)
IF (Z.LT.X(1).OR.Z.GT.X(N)) THEN
    WRITE (IR,100) Z
    RETURN
END IF

DO 10 I=1,N
    IF (Z.EQ.X(I)) THEN
        SLINTP=Y(I)
        RETURN
    END IF
10  CONTINUE

DO 20 I=1,N-1
    IF ((X(I).LT.Z).AND.(Z.LT.X(I+1))) THEN
        DIF=Z-X(I)
        SLINTP=Y(I)+DIF*(Y(I+1)-Y(I))/(X(I+1)-X(I))
        DUMMY=SLINTP
        RETURN
    END IF

```

```

20      CONTINUE
100     FORMAT (1X,' Z IS OUT OF RANGE IN SLINTP ',1PE14.5)
101     FORMAT (1X, I4,2(1PE14.5))
      END

      FUNCTION ALP(ZBAR)
C      DETERMINES THE VALUE OF VISCOCITY AND SUBSEQUENTLY THE COEFFICIENT
C      ALPHA BY USING THE EARLIER COMPUTED SPLINE COEFFICIENTS
C      CORRECTION IS ALSO MADE TO ACCOUNT FOR THE DEVOLATILZTION I.E.,
C      FOR THE THE MASS TRANSFER EFFECT

      PARAMETER (MGP=65,MGPM1=MGP-1)

      COMMON /PARAS/ XGRID(MGP),PSI(MGP),PSICOF(MGPM1,3),TSMOTH(MGP),
1          TEMCOF(MGPM1,3),VLOCTY(MGP),VELCOF(MGPM1,3),
2          VSCOCT(MGP),VISCOF(MGPM1,3),NGP
      COMMON / CPARAS / PDENZ,PDIAZ,XCRBNZ,XVOL1Z,XVOL2Z,XASHZ,EMMISS
1          VSTAR,PREEXF,ACTENG,PDIA,PDEN,VLTLFT,BLOWCF,ATOMWT

      VISCOS=CSINTP(ZBAR,XGRID,VSCOCT,NGP,VISCOF,MGPM1,.FALSE.)
      ALP=18.0*VISCOS/(PDEN*PDIA**2)*EXP(-BLOWCF)

      RETURN
      END

      SUBROUTINE SMOOTH (INTRES,MAXIT,NDATA,XDATA,YDATA,NOUT,XOUT,
1          YOUT,YPRIME,YDPRIM,ERRCOD,NAME)

      INTEGER ERRCOD,MAX,MAXM1,IBREAK

      PARAMETER (MAX=101,MAXM1=MAX-1)
      PARAMETER (IR=10,II=20,ID=30)
      PARAMETER (DIS=1.0,SC=0.0)
      LOGICAL INTRES
      REAL XDATA(NDATA),YDATA(NDATA),XOUT(NOUT),YOUT(NOUT)
      REAL YPRIME(NOUT),YDPRIM(NOUT),YSMTH1(MAX)
      REAL BREAK(2*MAX),CSCOE(4,MAX)
      CHARACTER*6 NAME
      EXTERNAL CSSED,CSAKM,CSVAL

      IF (NDATA.GT.MAX) THEN
          ERRCOD = 1
          RETURN
      END IF

C      call imsl subroutine cssed for cubic spline smoothing
C      with error detection

      CALL CSSED (NDATA,XDATA,YDATA,DIS,SC,MAXIT,YSMTH1)

```

```

C      CALL IMSL SUBROUTINE CSAKM TO GET THE COEFFICIENTS FOR
C      THE SMOOTHED DATA FOR LATER USE IN INTERPOLATION

      CALL CSAKM (NDATA,XDATA,YSMTH1,BREAK,CSCOEf)

C      now perform the interpolation, imsl function csval will be used

      DO 30 IOUT=1,NOUT
      T=XOUT(IOUT)
      YOUT(IOUT)= CSVAL(T,NDATA-1,BREAK,CSCOEf)
      YPRIME(IOUT)=CSDER(1,T,NDATA-1,BREAK,CSCOEf)
30     YDPRIM(IOUT)=CSDER(2,T,NDATA-1,BREAK,CSCOEf)

      IF (INTRES) THEN
      WRITE (II,100) NAME,MAXIT
      DO 20 I=1,NDATA
      T=XDATA(I)
      YINT=CSVAL(T,NDATA-1,BREAK,CSCOEf)
20     WRITE (II,101) XDATA(I),YDATA(I),YSMTH1(I),YINT
      END IF
      ERRCOD=0

100    FORMAT (//,1X,'INPUT AND SMOOTHED DATA FOR ',A6,' AFTER ',I3,
1       ' ITERATIONS')

101    FORMAT (1X,4(2X,1PE14.4))
      RETURN
      END

      SUBROUTINE SMOTH (INTRES,MAXIT,NDATA,XDATA,YDATA,YOUT,NAME)

      INTEGER ERRCOD,MAX,MAXM1,IBREAK
      PARAMETER (MAX=101,MAXM1=MAX-1)
      PARAMETER (IR=10,II=20,ID=30)
      PARAMETER (DIS=1.0,SC=0.0)
      LOGICAL INTRES
      REAL XDATA(NDATA),YDATA(NDATA),YOUT(NDATA),YSMTH1(MAX)
      REAL xs(max),ys(max),BREAK(2*MAX),CSCOEf(4,MAX)
      CHARACTER*6 NAME
      EXTERNAL CSSED,CSAKM,CSVAL

      IF (NDATA.GT.MAX) THEN
      ERRCOD = 1
      RETURN
      END IF

      NS=1
      DO I=1,NDATA,5

```



```

      IF ((5*NS+1).GT.NDATA) THEN
      XS(NS)=XDATA(NDATA)
      YS(NS)=YDATA(NDATA)
      ELSE
      XS(NS)=XDATA(I)
      YS(NS)=YDATA(I)
      NS=NS+1
      END IF
      END DO

C      call imsl subroutine cssed for cubic spline smoothing
C      with error detection
      CALL CSSED (NS,XS,YS,DIS,SC,MAXIT,YSMTH1)

C      CALL IMSL SUBROUTINE CSAKM TO GET THE COEFFICIENTS FOR
C      THE SMOOTHED DATA FOR LATER USE IN INTERPOLATION

      CALL CSAKM (NS,XS,YSMTH1,BREAK,CSCOE)

C      now perform the interpolation, imsl function csval will be used

      IF (INTRES) WRITE (II,100) NAME,MAXIT
      DO 30 IOUT=1,NDATA
      YOUT(IOUT)= CSVAL(XDATA(IOUT),NS-1,BREAK,CSCOE)
      IF (INTRES) WRITE (II,101) XDATA(IOUT),YDATA(IOUT),YOUT(IOUT)
30      CONTINUE

      IND = -1
      DO I=1,NDATA
      IF (IND.NE.1) THEN
          IF (YOUT(I).LE.1.OE-12) THEN
              YOUT(I)=0.0
          ELSE
              IND = 1
          END IF
      END IF
      END DO

      IF (INTRES) THEN
          DO I=1,NS
              WRITE (II,101) XS(I),YS(I),YSMTH1(I)
          END DO
      END IF
      ERRCOD=0

100  FORMAT (//,1X,'INPUT AND SMOOTHED DATA FOR ',A6,' AFTER ',I3,
1      ' ITERATIONS')
101  FORMAT (1X,4(2X,1PE14.4))
      RETURN

```

END

```

1  SUBROUTINE TRSP1(DEB,NRO,M,N,LSTSPE,TEMP,C,PRESS,AVWT,THK,
      AMU,DIFFU)

```

```

C  SUBROUTINE THAT CALCULATES BINARY DIFFUSION COEFFICIENTS,
C  THERMAL CONDUCTIVITY OF EACH SPECIE,VISCOSITY OF EACH
C  SPECIE AND FINALLY CALCULATES THE PROPERTIES OF THE MIXTURE,
C  USING MIXING RULES SUGGESTED BY REID AND SHERWOOD.

```

```

C  THIS IS A MODIFIED VERSION OF ROUTINE WRITTEN BY: WERNER HAHN

```

```

C  ARGUMENTS:      AMU      VISCOSITY OF THE MIXTURE AT EACH
C                   GRID POINT.
C                   AVWT    AVERAGE MOLECULAR WEIGHT AT EACH
C                   GRID POINT.
C                   C       CURRENT VALUES OF THE DEPENDENT
C                   VARIABLES.
C                   DEB     LOGICAL VARIABLE THAT CONTROLS
C                   DEBUGGING WRITE STATEMENTS.
C                   DIFFU   PSEUDOBINARY DIFFUSIVITY OF SPECIE
C                   I IN MIXTURE AT EACH GRID POINT.
C                   DIL     NAME OF THE DILUENT.
C                   LSTSPE  LIST OF SPECIES PARTICIPATING IN
C                   THE REACTIONS.
C                   M       TOTAL NUMBER OF GRID POINTS.
C                   N       NUMBER OF SPECIES.
C                   NN      NUMBER OF DEPENDENT VARIABLES.
C                   PRESS   PRESSURE AT EACH GRID POINT.
C                   THK     THERMAL CONDUCTIVITY AT EACH
C                   GRID POINT.

```

```

      PARAMETER (NSDS=34,IR=10,II=20,ID=30)
      LOGICAL DEB
      DIMENSION AKI(NSDS),AMUI(NSDS),AUX2(NSDS),AUX3(NSDS),
1  AUX4(NSDS),INDEX(NSDS),TRSPIN(NSDS,2:4)
      DIMENSION AMU(M),AVWT(M),C(NRO,M),DIFFU(NRO,M),
1  PRESS(M),THK(M),TEMP(M)
      CHARACTER LSTSPE(N)*6,NAME(NSDS)*6

```

```

C  TRSPIN IS A LIST CONTAINING BASIC TRANSPORT IFORMATION ABOUT
C  EACH SPECIE.

```

```

C  NAME=NAME OF THE SPECIE.
C  TRSPIN(I,2)=MOLECULAR WEIGHT.
C  TRSPIN(I,3)=EPSILON(I)/K
C  TRSPIN(I,4)=SIGMA(I)
C

```

```

C  IF SPECIES ARE ADDED TO THIS LIST, NSDS HAS TO BE RESET TO      C

```

C NEW Number of Species in Data Set IN PARAMETER STATEMENT C

```
DATA NAME( 1),(TRSPIN( 1,K),K=2,4)/'CH4      ',16.043,148.600, 3.8/
DATA NAME( 2),(TRSPIN( 2,K),K=2,4)/'O2       ',32.000,106.700, 3.5/
DATA NAME( 3),(TRSPIN( 3,K),K=2,4)/'N2       ',28.016, 71.400, 3.8/
DATA NAME( 4),(TRSPIN( 4,K),K=2,4)/'CO       ',28.011, 91.700, 3.7/
DATA NAME( 5),(TRSPIN( 5,K),K=2,4)/'H2       ', 2.016, 59.700, 2.8/
DATA NAME( 6),(TRSPIN( 6,K),K=2,4)/'NH3      ',17.032,558.300, 2.9/
DATA NAME( 7),(TRSPIN( 7,K),K=2,4)/'HCN      ',27.027,569.100, 3.6/
DATA NAME( 8),(TRSPIN( 8,K),K=2,4)/'NO       ',30.008,116.700, 3.5/
DATA NAME( 9),(TRSPIN( 9,K),K=2,4)/'CO2      ',44.011,195.200, 3.9/
DATA NAME(10),(TRSPIN(10,K),K=2,4)/'CH       ',13.019,148.000, 3.8/
DATA NAME(11),(TRSPIN(11,K),K=2,4)/'CH2      ',14.027,148.000, 3.8/
DATA NAME(12),(TRSPIN(12,K),K=2,4)/'CH3      ',15.035,148.600, 3.8/
DATA NAME(13),(TRSPIN(13,K),K=2,4)/'CHO      ',29.019, 91.700, 3.7/
DATA NAME(14),(TRSPIN(14,K),K=2,4)/'CH2O     ',30.027, 91.700, 3.7/
DATA NAME(15),(TRSPIN(15,K),K=2,4)/'CH3O     ',31.035, 91.700, 3.7/
DATA NAME(16),(TRSPIN(16,K),K=2,4)/'CN       ',26.019,106.700, 3.5/
DATA NAME(17),(TRSPIN(17,K),K=2,4)/'H2O      ',18.016,506.000, 2.7/
DATA NAME(18),(TRSPIN(18,K),K=2,4)/'H        ', 1.008, 18.350, 3.0/
DATA NAME(19),(TRSPIN(19,K),K=2,4)/'OH       ',17.008,506.000, 2.7/
DATA NAME(20),(TRSPIN(20,K),K=2,4)/'O        ',16.000,218.900, 2.5/
DATA NAME(21),(TRSPIN(21,K),K=2,4)/'HO2      ',33.008,106.700, 3.5/
DATA NAME(22),(TRSPIN(22,K),K=2,4)/'N        ',14.008,218.900, 2.5/
DATA NAME(23),(TRSPIN(23,K),K=2,4)/'HNO      ',31.016,106.700, 3.5/
DATA NAME(24),(TRSPIN(24,K),K=2,4)/'NH       ',15.016,106.700, 3.5/
DATA NAME(25),(TRSPIN(25,K),K=2,4)/'NH2      ',16.024,106.700, 3.5/
DATA NAME(26),(TRSPIN(26,K),K=2,4)/'N2O      ',44.016,232.400, 3.8/
DATA NAME(27),(TRSPIN(27,K),K=2,4)/'NO2      ',46.008,232.400, 3.8/
DATA NAME(28),(TRSPIN(28,K),K=2,4)/'NCO      ',42.019,106.700, 3.5/
DATA NAME(29),(TRSPIN(29,K),K=2,4)/'H2O2     ',34.016,600.000, 4.0/
DATA NAME(30),(TRSPIN(30,K),K=2,4)/'HE       ', 4.000, 10.220,2.576/
DATA NAME(31),(TRSPIN(31,K),K=2,4)/'AR       ',39.994,113.500,3.465/
DATA NAME(32),(TRSPIN(32,K),K=2,4)/'C2H2     ',26.038,209.000,4.100/
DATA NAME(33),(TRSPIN(33,K),K=2,4)/'C2H4     ',28.054,280.800,3.971/
DATA NAME(34),(TRSPIN(34,K),K=2,4)/'C2H6     ',30.070,252.300,4.302/
```

FKTR=2.*SQRT(2.)

C IDENTIFY EACH SPECIE AND PULL INFORMATION FROM TRSPIN,
C STORE IN AUXILIARY LIST,WHICH WILL BE EMPLOYED LATERON.

```
DO 100 I=1,N
DO 101 J=1,NSDS
K=J
IF(LSTSPE(I).EQ.NAME(J))GO TO 1
101 CONTINUE
WRITE(6,90)LSTSPE(I)
90 FORMAT('1SPECIES ',A6,'NOT IN TRANSPORT LIBRARY')
```

```

        STOP ' ENCOUNTERES A NON LIBRARY SPECIE '
1      CONTINUE
        AUX2(I)=TRSPIN(K,2)
        AUX3(I)=TRSPIN(K,3)
        AUX4(I)=TRSPIN(K,4)
100    CONTINUE
        RETURN

ENTRY TRSPO(DEB,NRO,M,N,LSTSPE,TEMP,C,PRESS,AVWT,THK,AMU,DIFFU)

C      CALCULATE TRANSPORT COEFFICIENTS.

      DO 103 L=1,M
      T=TEMP(L)
      T1=SQRT(T)
      T2=T*T1

C      CALCULATE DIFFUSION COEFFICIENT.

      PREF=0.001858*T2/PRESS(L)
      DO 105 I=1,N
      S=0.
      DO 106 J=1,N

C      CALCULATE BINARY DIFFUSIVITY.

      IF(I.EQ.J)GO TO 106
      SIGIJ=0.5*(AUX4(I)+AUX4(J))
      AKOEIJ=T/(SQRT(AUX3(I)*AUX3(J)))
      OMEGAD=1.06036/AKOEIJ**0.15610
      IF(AKOEIJ.LT.24.)OMEGAD=OMEGAD+0.193/EXP(0.47635*AKOEIJ)+
1 1.03587/EXP(1.52996*AKOEIJ)+1.76474/EXP(3.89411*AKOEIJ)
      DIJ=PREF*SQRT(1./AUX2(I)+1./AUX2(J))/
1 (SIGIJ*SIGIJ*OMEGAD)

C      ADD FOR MIXING RULE.

      S=S+C(J,L)/DIJ
106    CONTINUE
105    DIFFU(I,L)=(1.-C(I,L))/S

C      CALCULATE VISCOSITY AND CONDUCTIVITY OF SPECIE I.

      DO 107 I=1,N
      SIGSQ=AUX4(I)**2
      AKOEI=T/AUX3(I)
      OMEGAM=1.16145/AKOEI**0.14874
      IF(AKOEI.LT.15.)OMEGAM=OMEGAM+0.52487/EXP(0.7732*AKOEI)+
1 2.16178/EXP(2.43787*AKOEI)

```

```

      AMUI(I)=2.6693E-5*SQRT(AUX2(I)*T)/(SIGSQ*OMEGAM)
      AKI(I)=1.9891E-4*SQRT(T/AUX2(I))/(SIGSQ*OMEGAM)
107  CONTINUE

C      CALCULATE VISCOSITY AND CONDUCTIVITY OF MIXTURE.

      S1=0.
      S2=0.
      DO 108 I=1,N
      IF(LSTSPE(I) .EQ. 'H2    ')GOTO 108
      AMI=AUX2(I)
      SS1=0.
      SS2=0.

C      in case the concentration of specie i is less than 1.0e-9
C      there is no contribution to viscosity or thermal conductivity
C      hence skip the entire loop and jump to 108 for next specie at
C      the same grid point

      IF (C(I,L).LE.1.0E-9) GO TO 108
      DO 109 J=1,N
      IF(I.EQ.J)GO TO 109
      AMJ=AUX2(J)
      F1=(AMJ/AMI)**0.25
      F2=1./F1
      F3=SQRT(1.+AMI/AMJ)
      FIIJ=(1.+SQRT(AMUI(I)/AMUI(J))*F1)**2/(FKTR*F3)
      GIJ=1.065*(1.+SQRT(AKI(I)/AKI(J))*F2)**2/(FKTR*F3)
      SS1=SS1+C(J,L)/C(I,L)*FIIJ
      SS2=SS2+C(J,L)/C(I,L)*GIJ
109  CONTINUE
      S1=S1+AMUI(I)/(1.+SS1)
      S2=S2+AKI(I)/(1.+SS2)
108  CONTINUE
      AMU(L)=S1
      THK(L)=S2
103  CONTINUE

C      CALCULATE AVERAGE MOLECULAR WEIGHT

      DO 110 I=1,M
      S=0.
      DO 111 J=1,N
111  S=S+C(J,I)*AUX2(J)
110  AVWT(I)=S
      RETURN
      END

SUBROUTINE OUTPUT (IOUT,NEWPAG,NC,NR,HEADER,CTITLS,C1,C2,C3,C4,

```

```

1          C5,C6,C7,C8,C9,C10)

LOGICAL NEWPAG
CHARACTER HEADER*130,CTITLS(NC)*10
REAL C1(NR),C2(NR),C3(NR),C4(NR),C5(NR),C6(NR),C7(NR),C8(NR)
REAL C9(NR),C10(NR)
IF (NEWPAG) WRITE (IOUT,101)
IF (HEADER.NE.'NONE') WRITE (IOUT,102) HEADER
IF (CTITLS(1).NE.'NONE') THEN
    WRITE (IOUT,104) '  I',(CTITLS(J),J=1,NC)
END IF
DO 50 J=1,NR
    IF (NC.EQ.1) THEN
        WRITE (IOUT,103) J,C1(J)
    ELSE IF (NC.EQ.2) THEN
        WRITE (IOUT,103) J,C1(J),C2(J)
    ELSE IF (NC.EQ.3) THEN
        WRITE (IOUT,103) J,C1(J),C2(J),C3(J)
    ELSE IF (NC.EQ.4) THEN
        WRITE (IOUT,103) J,C1(J),C2(J),C3(J),C4(J)
    ELSE IF (NC.EQ.5) THEN
        WRITE (IOUT,103) J,C1(J),C2(J),C3(J),C4(J),C5(J)
    ELSE IF (NC.EQ.6) THEN
        WRITE (IOUT,103) J,C1(J),C2(J),C3(J),C4(J),C5(J),C6(J)
    ELSE IF (NC.EQ.7) THEN
        WRITE (IOUT,103) J,C1(J),C2(J),C3(J),C4(J),C5(J),C6(J),
1          C7(J)
    ELSE IF (NC.EQ.8) THEN
        WRITE (IOUT,103) J,C1(J),C2(J),C3(J),C4(J),C5(J),C6(J),
1          C7(J),C8(J)
    ELSE IF (NC.EQ.9) THEN
        WRITE (IOUT,103) J,C1(J),C2(J),C3(J),C4(J),C5(J),C6(J),
1          C7(J),C8(J),C9(J)
    ELSE IF (NC.EQ.10) THEN
        WRITE (IOUT,103) J,C1(J),C2(J),C3(J),C4(J),C5(J),C6(J),
1          C7(J),C8(J),C9(J),C10(J)
    ELSE
        WRITE (IOUT,102) ' NUMBER OF COLUMNS EXCEED TEN'
        RETURN
    END IF
50  CONTINUE

101  FORMAT ('1',/)
102  FORMAT (1X,A130,/)
103  FORMAT (1X,I4,10(1PE12.4))
104  FORMAT (1X,A4,10(2X,A10))
RETURN
END

```

```

SUBROUTINE OUTPUT1 (IOUT,NEWPAG,NC,NRD,NR,HEADER,CTITLS,X,DATA)

LOGICAL NEWPAG
CHARACTER HEADER*130,CTITLS(NC)*10
REAL DATA(NRD,NR),X(NR)

IF (NC.GT.12) THEN
    WRITE (IOUT,102) ' NUMBER OF COLUMNS EXCEED TWELVE'
    RETURN
END IF

IF (NEWPAG) WRITE (IOUT,101)
IF (HEADER.NE.'NONE') WRITE (IOUT,102) HEADER
IF (CTITLS(1).NE.'NONE') THEN
    WRITE (IOUT,104) ' I',(CTITLS(J),J=1,NC)
END IF
DO 50 J=1,NR
    WRITE (IOUT,103) J,X(J),(DATA(I,J),I=1,NC-1)
50 CONTINUE

101 FORMAT ('1',/)
102 FORMAT (1X,A130,/)
103 FORMAT (1X,I4,12(1PE10.2))
104 FORMAT (1X,A4,A10,2X,11A10)
RETURN
END

SUBROUTINE OUTPUT2 (IOUT,NEWPAG,NC,NRD,NR,HEADER,CTITLS,DATA)

LOGICAL NEWPAG
CHARACTER HEADER*130,CTITLS(NC+1)*10
REAL DATA(NRD,NR)

IF (NC.GT.12) THEN
    WRITE (IOUT,102) ' NUMBER OF COLUMNS EXCEED TWELVE'
    RETURN
END IF

IF (NEWPAG) WRITE (IOUT,101)
IF (HEADER.NE.'NONE') WRITE (IOUT,102) HEADER
IF (CTITLS(1).NE.'NONE') THEN
    WRITE (IOUT,104) (CTITLS(J),J=1,NC+1)
END IF
DO 50 J=1,NR
    WRITE (IOUT,103) J,(DATA(I,J),I=1,NC)
50 CONTINUE

101 FORMAT ('1',/)
102 FORMAT (1X,A130,/)

```

```

103  FORMAT (1X,I10,12(1PE10.2))
104  FORMAT (1X,A10,2X,12A10)
      RETURN
      END

      SUBROUTINE SORTA (N,X,Y,IFLAG,ERRMES)
      PARAMETER (MAX=100,IR=10,II=20,ID=30)
      CHARACTER ERRMES*130
      LOGICAL LDEBUG
      REAL X(N),Y(N),TEMP1(MAX),TEMP2(MAX)
      LDEBUG=.FALSE.
      IF (N.GT.MAX) THEN
          IFLAG=1
          ERRMES='DATA PAIRS MORE THAN DIMENSIONED LOCALLY'
          RETURN
      END IF

      DO 10 I=1,N
          TEMP1(I)=X(I)
10    TEMP2(I)=Y(I)

      DO 20 I=1,N-1
      DO 20 J=I+1,N
          IF (TEMP1(I).GT.TEMP1(J)) THEN
              HOLD1=X(I)
              HOLD2=Y(I)
              X(I)=TEMP1(J)
              Y(I)=TEMP2(J)
              X(J)=HOLD1
              Y(J)=HOLD2
              TEMP1(I)=X(I)
              TEMP2(I)=Y(I)
              TEMP1(J)=HOLD1
              TEMP2(J)=HOLD2
          END IF
20    CONTINUE
      IF (LDEBUG) THEN
          WRITE (ID,40) ' DATA PAIRS TO BE SORTED IN ASCENDING ORDER '
          DO 25 I=1,N
25    WRITE (ID,50) I,X(I),Y(I)
          END IF
          DO 30 I=2,N-1
              IF (NOT(X(I-1).LT.X(I).AND.X(I).LT.X(I+1))) IFLAG=2
              ERRMES=' HAVE SOME REPEATED PAIRS '
              RETURN
30    CONTINUE

          IFLAG=0
40    FORMAT (1X,A130)

```



```

50  FORMAT (1X,I4,2(1PE14.5))

      RETURN
      END

      SUBROUTINE PSIV (M,DIST,Q,LDEBUG,XOUT,RHO,AMU,V,PSI)

C     WRITTEN 12/10/83 JOLW
C     TO CALCULATE PSI AND VEL PROFILE FOR
C     FLAT PLATE FLAME GIVEN DENSITY,VISCOSITY FIELDS
C     AND INITIAL VELOCITY
C     USES GAS PHASE CONTINUITY AND R-MOMENTUM, EQNS (43) AND (46)
C     TO ARRIVE AT PSI AND VEL PROFILES.
C     INTERNAL DIMENSIONS ARE SET TO 101
      DIMENSION RHO(M),XOUT(M),V(M),AMU(M),PSI(M)
      DIMENSION PSII(101),A(101),B(101),D(101),F(101),DMUDX(101)
      DIMENSION W1P1(101),W1M1(101),W1O(101),W2P1(101),W2M1(101),
1    W2O(101)
      DIMENSION ALPHA(101),BETA(101),GAMMA(101),DELTA(101)
      DIMENSION IL(101)
      LOGICAL LCONV,LDEBUG

C     SET UP INITIAL PSI,STAG PLANE ETC

      RD=RHO(M)/RHO(1)
      XSTAG=DIST/(1.-SQRT(RD))*V(M)/V(1))
      MM1=M-1
      MM2=M-2
      DX=DIST/MM1
      DO 102 I=1,M
      IF(XOUT(I).LE.XSTAG) THEN
          PSI(I)=V(1)*XOUT(I)/XSTAG**2
      ELSE
          PSI(I)=-V(M)*(DIST-XOUT(I))/(DIST-XSTAG)**2
      ENDIF
102  CONTINUE

      ENTRY PSIV1 (M,DIST,Q,LDEBUG,XOUT,RHO,AMU,V,PSI)
      IF(LDEBUG)WRITE(6,1000)Q,DIST,XSTAG
1000  FORMAT(1H1,3X,'FW  Q=      ',E10.3,' DIST =  ',E10.3,
1     'STAGNATION PLANE (COLD) IS AT',E10.3)

C     BEGINNING OF BIG ITERATION LOOP
      DO 500 IDUM=1,25
C     CALCULATE VELOCITY PROFILE FROM PSI

      V(2)=V(1)*RHO(1)/RHO(2)-DX*(PSI(2)+
1    PSI(1)*RHO(1)/RHO(2))
      DO 104 I=2,MM1

```

```

V(I+1)=V(I-1)*RHO(I-1)/RHO(I+1)-2.*DX*2.*RHO(I)*PSI(I)/RHO(I+1)
104  CONTINUE

C      PRINT OUT RESULTS AT IT NO 1,24,25

      IF(LDEBUG.AND.(IDUM.EQ.1.OR.IDUM.EQ.24.OR.IDUM.EQ.25)) THEN
          WRITE(6,1002)IDUM
1002  FORMAT(1H,'AT ITERATION',I3/1X,' I',' XOUT ',' VZ ',
1      ' PSI ',' RHO ')
          DO 300 KR=1,M
300      WRITE(6,1003)KR,XOUT(KR),V(KR),PSI(KR),RHO(KR)
1003  FORMAT(1X,I3,4E10.3)
          ENDIF
C      SET UP INTERIOR POINTS ONLY

      DO 150 I=1,MM2
      K=I+1
      PSII(I)=PSI(K)
      DMUDX(I)=(AMU(K+1)-AMU(K-1))/(2.*DX)
      A(I)=AMU(K)/RHO(K)
      B(I)=(1./RHO(K))*DMUDX(I)-V(K)
      D(I)=0.
      F(I)=-2.*Q/RHO(K)-PSII(I)**2
150  CONTINUE

C      SET UP FINITE DIFFERENCE COEFFICIENTS

      CALL W(A,B,D,F,MM2,DX,W1P1,W1M1,W10,W2P1,W2M1,W20,0,0,IL)

C      CAUTION::: IWO SET EQ 1 TO COMPARE WITH HAHN'S CODE
C      SHOULD BE 0 FOR NORMAL USE

      DO 200 I=1,MM2
      ALPHA(I)=A(I)*W2M1(I)/(DX**2)-B(I)*W1M1(I)/(2.*DX)
      BETA(I)=-2.*A(I)/(DX**2)-2.*PSII(I)
      GAMMA(I)=A(I)*W2P1(I)/(DX**2)+B(I)*W1P1(I)/(2.*DX)
      DELTA(I)=F(I)-A(I)*W20(I)-B(I)*W10(I)
200  CONTINUE
      CALL TRIDAG(1,MM2,ALPHA,BETA,GAMMA,DELTA,PSII)

C      CHECK TOLERANCE
      LCONV=.FALSE.
      DIF=0.

      DO 210 I=1,MM2
      K=I+1
      DIFFER=(PSII(I)-PSI(K))/PSI(K)
      DIFFER=ABS(DIFFER)
      PSI(K)=PSII(I)

```

```

      DIF=AMAX1(DIFFER,DIF)
210  CONTINUE
      IF(DIF.LT.1.0E-3)LCONV=.TRUE.
      IF(LCONV.AND.LDEBUG) THEN
          WRITE(6,1002)IDUM
          DO 310 KR=1,M
310      WRITE(6,1003)KR,XOUT(KR),V(KR),PSI(KR),RHO(KR)
      ENDIF
      IF(LCONV) RETURN
500  CONTINUE
      END

      SUBROUTINE W(A,B,D,F,MP1,H,W1P1,W1M1,W10,W2P1,W2M1,
1      W20,IWO,IW,IL)

      DIMENSION A(101),B(101),D(101),F(101),W1P1(101)
      DIMENSION W1M1(101),W10(101),W2P1(101),W2M1(101)
      DIMENSION W20(101),IL(101)

      DO 100 I=1,MP1
      DISCR=B(I)**2 - 4.*A(I)*D(I)
      IF(DISCR)50,30,10

C      REAL,DISTINCT ROOTS.  D(I) IS NON-ZERO

10    IF(D(I).EQ.0.)GOTO15

      P1=0.5*(-B(I) + SQRT(DISCR))/A(I)
      P2=0.5*(-B(I) - SQRT(DISCR))/A(I)
      FD=F(I)/D(I)
      L=1
      IL(I)=1
      GOTO60

C      REAL,DISTINCT ROOTS.  D(I) IS ZERO

15    IF(A(I).EQ.0.)GOTO20

      P1=-B(I)/A(I)
      P2=0.
      FB=F(I)/B(I)
      L=2
      IL(I)=2
      GOTO60

C      REAL ROOTS.  A(I) AND D(I) ZERO
C      FOR THIS SPECIAL CASE STANDARD CENTRAL DIFFERENCE
C      FORMULAS RESULT

```

```

20  IF(D(I).NE.0.)GOTO25

    P1=0.
    P2=0.
    FB=0.
    L=3
    IL(I)=3
    GOTO60

C    REAL ROOTS.  A(I) IS ZERO BUT D(I) IS NON-ZERO
C    THE DIFFERENCE FORMULAS ARE SPECIAL CASES OF
C    THOSE OBTAINED FOR REAL, EQUAL ROOTS.

25  P1=-D(I)/B(I)
    P2=0.
    FB=0.
    L=4
    IL(I)=4
    GOTO60

C    REAL,  EQUAL ROOTS.  B(I) AND D(I) NON-ZERO

30  IF(B(I).EQ.0..AND.D(I).EQ.0.)GOTO35

    P1=-0.5*B(I)/A(I)
    P2=P1
    FD=F(I)/D(I)
    L=5
    IL(I)=5
    GOTO60

C    REAL, EQUAL ROOTS.  B(I) AND D(I) ZERO
C    FOR THIS SPECIAL CASE THE FORMULAS REDUCE TO
C    STANDARD CENTRAL DIFFERENCE APPROXIMATIONS.

35  P1=0.
    P2=0.
    FD=0.
    L=6
    IL(I)=6
    GOTO60

C    COMPLEX ROOTS.  P1 IS THE REAL PART OF THE ROOT AND
C    P2 IS THE COMPLEX COEFFICIENT:
C
C          
$$P = P1 \ (+/-) \ (P2 * I)$$

C

50  P1=-0.5*B(I)/A(I)
    P2=0.5*SQRT(-DISCR)/A(I)

```

```

        FD=F(I)/D(I)
        L=7
        IL(I)=7

60      IF(IW.EQ.0)GOTO65

C        USE STANDARD CENTRAL DIFFERENCE FORMULAS

        W1P1(I)=1.
        W1M1(I)=1.
        W10(I)=0.
        W2P1(I)=1.
        W2M1(I)=1.
        W20(I)=0.
        GOTO100

C        DETERMINE WEIGHTING FUNCTIONS

65      CALL COEF(P1,P2,H,W1,W2,W3,W4,W1Z,W2Z,FD,FB,L)

        W1P1(I)=W1
        W1M1(I)=W2
        W10(I)=W1Z
        W2P1(I)=W3
        W2M1(I)=W4
        W20(I)=W2Z

C        IF IWO = 1, THEN USE FORMULAS DERIVED WITHOUT
C        FORCING FUNCTION.

        IF(IWO.NE.0)W10(I)=0.
        IF(IWO.NE.0)W20(I)=0.

100     CONTINUE

        RETURN
        END

        SUBROUTINE COEF(P1,P2,H,W1,W2,W3,W4,W1Z,W2Z,FD,FB,L)

        GOTO(10,20,50,20,30,50,40)L

C        REAL, DISTINCT ROOTS.  D(I) NON-ZERO

10      A=P1*H
        B=P2*H
        C=A-B
        DEN=1./SINH(C)
        D=0.5*A*A

```

```

E=0.5*B*B
W1=(P1*EXP(-B) - P2*EXP(-A))*DEN*H
W2=(P1*EXP(B) - P2*EXP(A))*DEN*H
W1Z=0.5*FD/H*(-W1+W2)
W3=((1.+D)*EXP(-B) - (1.+E)*EXP(-A))*DEN
W4=((1.+E)*EXP(A) - (1.+D)*EXP(B))*DEN
W2Z=-FD/H**2*(W3+W4-2.)

```

```

C      NOTE: MANIPULATED FORMULAS SO THAT UNDERFLOW DOES NOT OCCUR.
C      THIS WAS DONE BY MOVING '/H' CLOSER TO THE SMALL NUMBER.
C      EX. -FD*(W3+W4-2.)/H**2 CHANGED TO -FD/H**2*(W3+W4-2.)

```

```

RETURN

```

```

C      REAL, DISTINCT ROOTS WITH D(I) ZERO, OR
C      SOLUTION FOR A(I) ZERO

```

```

20  A=P1*H
    B=0.5*A*A
    DEN=1./SINH(A)
    W1=A*DEN
    W2=W1
    W1Z=FB*(1.-W1)
    IF(L.EQ.4)W1Z=0.
    W3=1. - (COSH(A) -1. - B)*DEN
    W4=2. - W3
    W2Z=2.*FB/H*(1.-W3)
    IF(L.EQ.4)W2Z=0.
    RETURN

```

```

C      REAL, EQUAL ROOTS.

```

```

30  A=P1*H
    B=0.5*A*A
    C=EXP(-A)
    D=EXP(A)
    W1=C*(1.+A)
    W2=D*(1.-A)
    W1Z=0.5*FD/H*(W2-W1)
    W3=W1 + C*B
    W4=W2 + D*B
    W2Z=FD/H**2*(2. - W3 - W4)
    RETURN

```

```

C      COMPLEX ROOTS

```

```

40  A=P1*H
    B=P2*H
    DEN=1./SIN(2.*B)

```

```

      AM1=(2. + A*A - B*B)*SIN(B)
      AM2=2.*A*B*COS(B)
      D=EXP(-A)
      E=EXP(A)
      W1=2.*H*D*(P2*COS(B)+P1*SIN(B))*DEN
      W2=2.*H*E*(P2*COS(B)-P1*SIN(B))*DEN
      W1Z=0.5*FD/H*(-W1+W2)
      W3=D*(AM1+AM2)*DEN
      W4=E*(AM1-AM2)*DEN
C      W2Z=FD/H**2*(2.+2.*COSH(A)/COS(B)-W1-W2)
C      TIM MODIFIED COEF WITH THIS NEW FORMULA
      W2Z=FD/H**2*(2.-W3-W4)
      RETURN

C      LIMITING CASES WHICH REDUCE TO STANDARD CENTRAL
C      DIFFERENCE FORMULAS

50    W1=1.
      W2=1.
      W1Z=0.
      W3=1.
      W4=1.
      W2Z=0.

      RETURN
      END

      SUBROUTINE ELEBAL(M,NSP,XOUT,CMS,DX,LSTSPE,DIFFU,CONC,
1     AVWT,V,PSI,R,INTRES,DRIVED)

C      CALCULATES ELEMENT BALANCE
C      JOLW 12/23/83
C      MODIFIED TO CALCULATE INITIAL FLUXES TO CHECK ELEMENT BALANCE
C      JOLW 1/3/84

      PARAMETER (II=20)
      REAL XOUT(M),CMS(NSP,M),DIFFU(NSP,M),CONC(M),V(M),AVWT(M)
      REAL PSI(M),RZ1(101),RZ2(101),XZ(101)
      REAL Y(101),A(101),B(101),D(101),F(101),DCDX(101)
      REAL D2CDX(101),ALPHA(101),BETA(101),GAMMA(101),DELTA(101)
      REAL W1P1(101),W1M1(101),W1O(101),W2P1(101),W2M1(101),W2O(101)
      REAL IL(101),R(NSP,M)
      REAL FLUX1(101),FLUX2(101),FLUX3(101),RCBN(101),ROXN(101)
      REAL YH2O(101)
      REAL AXDFL(101),AXCFL(101),ARG(101),FLUXO(20,101)
      REAL FLUXL(20,101),DUM1(101),DUM2(101)
      REAL CBNFL(101),OXNFL(101),HYDFL(101),HELFL0(101),HELFL1(101)
      REAL ARG1(101),FLXB(20,101),FLXT(20,101),DUM3(101),DUM4(101)
      CHARACTER*6 LSTSPE(NSP)

```

```

LOGICAL INTRES,DRIVED

C IDENTIFY SPECIES INDEX

DO 100 I=1,NSP
  IF(LSTSPE(I).EQ.'H2')KH2=I
  IF(LSTSPE(I).EQ.'H2O')KH2O=I
  IF(LSTSPE(I).EQ.'CO')KCO=I
  IF(LSTSPE(I).EQ.'CO2')KCO2=I
  IF(LSTSPE(I).EQ.'O2')KO2=I
  IF(LSTSPE(I).EQ.'HCN')KHCN=I
  IF(LSTSPE(I).EQ.'NH3')KNH3=I
  IF(LSTSPE(I).EQ.'NO')KNO=I
  IF(LSTSPE(I).EQ.'N2')KINERT=I
  IF(LSTSPE(I).EQ.'HE')KINERT=I
  IF(LSTSPE(I).EQ.'AR')KINERT=I
100 CONTINUE

MM1=M-1
MM2=M-2

DO I=1,MM2
  XZ(I)=XOUT(I)
END DO

DO 110 NS=1,NSP
C HANDLE EACH SPECIES ONE AT A TIME
C BE CERTAIN NS=H2 COMES BEFORE NS=H2O

DO 105 I=1,M
105 Y(I)=CMS(NS,I)

C LOOP OVER INTERIOR GRID POINTS
DO 120 I=1,MM2
  K=I+1
  A(I)=CONC(K)*DIFFU(NS,K)
  B(I)=(CONC(K+1)*DIFFU(NS,K+1)-CONC(K-1)*DIFFU(NS,K-1))/
1 (2.*DX)-CONC(K)*V(K)
  D(I)=(CONC(K)*V(K)/AVWT(K))*(AVWT(K+1)-AVWT(K-1))/(2.*DX)
  F(I)=0.
120 CONTINUE

CALL W(A,B,D,F,MM2,DX,W1P1,W1M1,W1O,W2P1,W2M1,W2O,1,0,IL)

DO 135 I=1,MM2
  K=I+1
  DCDX(I)=(W1P1(I)*Y(K+1)-W1M1(I)*Y(K-1))/(2.*DX)
  D2CDX(I)=(W2P1(I)*Y(K+1)-2.*Y(K)+W2M1(I)*Y(K-1))/(DX**2)
  FLUX1(I)=A(I)*D2CDX(I)

```



```

      FLUX2(I)=B(I)*DCDX(I)
      FLUX3(I)=D(I)*Y(K)
      RZ1(I)=-(FLUX1(I)+FLUX2(I)+FLUX3(I))
      IF (INTRES) THEN
        WRITE(II,1003)K,XOUT(K),CMS(NS,K),DCDX(I),D2CDX(I),RZ1(I),
1          FLUX1(I),FLUX2(I),FLUX3(I)
      END IF
135  CONTINUE
C    Smooth Large noise in the calculated rates, if any
      ITS=1
      CALL CSSED (MM2,XZ,RZ1,1.0,0.0,ITS,RZ2)
      DO I=1,MM2
        R(NS,I)=RZ2(I)
      END DO
      DO 140 I=1,MM2
        IF (DRIVED.EQ..FALSE.) GO TO 140
        AXDFL(K)=-A(I)*DCDX(I)
        AXCFI(K)=CONC(K)*V(K)*Y(K)
        ARG(K)=R(NS,I)-2.*PSI(K)*CONC(K)*Y(K)
        ARG1(K)=ARG(K)-R(NS,I)
140  CONTINUE
        IF (DRIVED.EQ..FALSE.) GO TO 110
        AXDFL(1)=AXDFL(2)
        AXCFI(1)=CONC(1)*V(1)*Y(1)
        ARG(1)=0.
        AXDFL(M)=AXDFL(M-1)
        AXCFI(M)=CONC(M)*V(M)*Y(M)
        ARG(M)=0.
        ARG1(1)=0.
        ARG1(M)=0.
        IF(NS.NE.KH20) GO TO 130
        DO 220 I=1,MM2
          K=I+1
          A(I)=CONC(K)*DIFFU(KH20,K)
          B(I)=(CONC(K+1)*DIFFU(KH20,K+1)-CONC(K-1)*DIFFU(KH20,K-1))/
1          (2.*DX)-CONC(K)*V(K)
          D(I)=(CONC(K)*V(K)/AVWT(K))*(AVWT(K+1)-AVWT(K-1))/(2.*DX)
          F(I)=0.
220  CONTINUE
          CALL W(A,B,D,F,MM2,DX,W1P1,W1M1,W10,W2P1,W2M1,W20,1,0,IL)
          DO 200 I=1,MM2
            ALPHA(I)=A(I)*W2M1(I)/DX**2-B(I)*W1M1(I)/(2.*DX)
            BETA(I)=-2.*A(I)/(DX**2)+D(I)
            GAMMA(I)=A(I)*W2P1(I)/DX**2+B(I)*W1P1(I)/(2.*DX)
            DELTA(I)=R(KH2,I)
200  CONTINUE
            DELTA(1)=DELTA(1)-ALPHA(1)*CMS(NS,1)
            CALL TRIDAG(1,MM2,ALPHA,BETA,GAMMA,DELTA,YH20)
            DO 201 I=1,MM2

```

```

      K=I+1
      CMS(KH2O,K)=YH2O(I)
201  CONTINUE
      CMS(KH2O,M)=1.0E-30
130  CONTINUE
      DO 132 I=1,M
      DUM1(I)=FINTFL(1,I,ARG,DX)
      DUM3(I)=FINTFL(1,I,ARG1,DX)
      FLUXO(NS,I)=AXDFL(I)+AXCFL(I)-DUM1(I)
      FLXB(NS,I)=AXDFL(I)+AXCFL(I)-DUM3(I)
      DUM2(I)=FINTFL(M,I,ARG,DX)
      DUM4(I)=FINTFL(M,I,ARG1,DX)
      FLUXL(NS,I)=AXDFL(I)+AXCFL(I)-DUM2(I)
      FLXT(NS,I)=AXDFL(I)+AXCFL(I)-DUM4(I)
      WRITE(6,1013)I,XOUT(I),FLUXO(NS,I),FLUXL(NS,I),AXDFL(I),
1    AXCFL(I),DUM1(I),DUM2(I),ARG(I),ARG1(I)
1013  FORMAT(1X,I3,9E10.3)
      132  CONTINUE
      110  CONTINUE
      IF (IDRIVD.EQ..FALSE.) GO TO 3000
2500  WRITE(6,1005)
1003  FORMAT(1X,I3,8(1PE12.4))
1005  FORMAT(1H1,'! TOTAL RATES FOR ELEMENTS'/4X,' R CARBON ',
1    ' R(CO) ', ' R(CO2) ', 'R OXYGEN ', ' R(O2) ',
1    ' R(H2O) ', ' R(H2) ', 'CARBON FLX',
1    ' OXYGEN FLX', 'HYDGEN FLX', 'HELIUM BOT', 'HELIUM TOP')
      DO 300 I=1,MM2
      RCBN(I)=R(KCO,I)+R(KCO2,I)
      ROXN(I)=R(KO2,I)+R(KCO2,I)+0.5*R(KCO,I)+0.5*R(KH2O,I)

C      ELEMENT FLUX BALANCE WITHOUT ANY RATES OF FORMATION
C      USES FLXB,FLXT INSTEAD OF FLUXO,FLUXL

      CBNFL(I)=(FLXT(KCO,I)+FLXT(KCO2,I))/FLXT(KCO,M)
      OXNFL(I)=(FLXB(KO2,I)+FLXB(KCO2,I)+0.5*FLXB(KCO,I)+
1    0.5*FLXB(KH2O,I))/FLXB(KO2,I)
C      HYDFL(I)=(FLXT(KH2,I)+FLXT(KH2O,I))/FLXT(KH2,M)
      HELFLO(I)=FLXB(KINERT,I)/FLXB(KINERT,1)
      HELFLL(I)=FLXT(KINERT,I)/FLXT(KINERT,M)
      K=I+1
300  WRITE(6,1007)K,RCBN(I),R(KCO,I),R(KCO2,I),ROXN(I),R(KO2,I),
1    R(KH2O,I),R(KH2,I)
1    ,CBNFL(I),OXNFL(I),HYDFL(I),HELFLO(I),HELFLL(I)
1007  FORMAT(1X,I3,12E10.3)
3000  RETURN
      END

      FUNCTION FINTFL(IS,IE,ARG,DX)

```

```

C      WRITTEN 3/1/84   JOLW
C      INTEGRATES ARGUMENT FROM IS TO IE WITH EQUALLY SPACED
C      INTERVALS SEPARATED BY DX
      DIMENSION ARG(101),FCT(101)
      DO 30 K=1,101
30     FCT(K)=0.
      IF(IE-IS) 1,2,3
      2     FINTFL=0.
          RETURN
      3     FCT(IS+1)=(DX/2.)*(ARG(IS+1)+ARG(IS))
          FINTFL=FCT(IS+1)
          IF((IS+1).EQ.IE) RETURN
          DO 10 K=IS+1,IE-1
          FCT(K+1)=FCT(K-1)+2.*DX*ARG(K)
10     CONTINUE
          FINTFL=FCT(IE)
          RETURN
      1     FCT(IE+1)=(DX/2.)*(ARG(IE+1)+ARG(IE))
          FINTFL=-FCT(IE+1)
          IF((IE+1).EQ.IS) RETURN
          DO 20 K=IE+1,IS-1
          FCT(K+1)=FCT(K-1)+2.*DX*ARG(K)
20     CONTINUE
          FINTFL=-FCT(IS)

      RETURN
      END

```

SUBROUTINE CUBSPL (X,Y,N,IOUT,IEND,NCROW,C,IER)

```

*****
C      SUBROUTINE CUBSPL:
C
C          THIS SUBROUTINE COMPUTES THE COEFFICIENTS
C          OF A CUBIC SPLINE THROUGH A SET OF DATA. THE COEFFICIENTS
C          RETURNED ARE TO BE USED IN NESTED MULTIPLICATION FORM, GIVEN
C          AS:
C          YINT=Y(I)+DIF*(C(I,1)+DIF*(C(I,2)+C(I,3)*DIF))
C          WHERE YINT IS THE INTERPOLATED VALUE AT XINT
C          AND      X(I) <= XINT <= X(I+1)
C          AND      DIF = XINT - X(I)
*****
C          X = ARRAY OF X VALUES TO BE FITTED, MUST BE IN ACSENDING
C          ORDER
C          Y = ARRAY OF CORRESPONDING Y VALUES TO BE FITTED
C          N = NUMBER OF DATA PAIRS
C          IOUT = UNIT NUMBER FOR OUTPUT FILE
C          IEND - TYPE OF END CONDITIONS
C          IEND = 1, LINEAR ENDS (NATURAL CUBIC SPLINE)
C          SD(1) = 0.0, SD(N) = 0.0, SD = SECOND DERIVATIVE
C          IEND = 2, PARABOLIC ENDS, SD(1)=SD(2), SD(N)=SD(N-1)
C          IEND = 3, CUBIC ENDS, SD(1) AND SD(N) ARE EXTRAPOLATED

```

```

C      NCROW = ROW DIMENSION OF COEFFICIENT MATRIX C EXACTLY AS
C      SPECIFIED IN CORRESPONDING MATRIX IN CALLING PROGRAM
C      A = WORKING MATRIX, LOCAL TO THE SUBROUTINE. HOLDS INTERMEDIATE
C      VALUES.
C      A(I,1) - A(I,4) MATRIX OF AUGMENTED COEFFICIENTS TO EVALUATE
C      SECOND DERIVATIVES.
C      A(I,5) = THIS COLUMN CONTAINS THE SECOND DERIVATIVES.
C      C = COEFFICIENT MATRIX CONTAINING SPLINE COEFFICIENTS FOR
C      NESTED MULTIPLICATION FORM.
C      IER - ERROR FLAG
C      IER = 0 NO ERROR, NORMAL RETURN TO CALLING PROGRAM
C      IER = 1 NON-ORDERED ABCSSICA
C      IER = 2 INSUFFICIENT DATA PAIRS FOR LINEAR END CONDITIONS
C      IER = 3 INSUFFICIENT DATA PAIRS FOR PARABOLIC END CONDITIONS
C      IER = 4 INSUFFICIENT DATA PAIRS FOR CUBIC END CONDITIONS
C      IER = 5 TYPE OF END CONDITIONS NOT SPECIFIED
C      IER = 6 NUMBER OF DATA PAIRS EXCEED PARAMETER MAX
C      ADJUST THE VALUE OF MAX AND RUN AGAIN
C      IER = 7 ROW DIMENSION OF COEFFICIENT MUST AT LEAST BE N-1
*****
      PARAMETER (MAX=100,ID=30)
      LOGICAL LDEBUG
      REAL X(N),Y(N),A(MAX,5),C(NCROW,3)
      LDEBUG=.FALSE.
C      CHECK THAT ARGUMENTS VALUES ARE CONSISTENT WITH THE SUBPROGRAM
C      SETUP. PROPER SETUP WILL RETURN A VALUE OF IER=0
C      INCONSISTENT SETUP WILL PRINT AN ERROR MESSAGE AND RETURN TO
C      CALLING PROGRAM.
      DO 5 I=1,N-1
        IF (X(I).GT.X(I+1)) THEN
          IER=1
          WRITE (IOUT,151)
          RETURN
        END IF
5     CONTINUE

      IF (IEND.EQ.1.AND.N.LT.2) THEN
        IER=2
        WRITE (IOUT,152) IER
        RETURN
      ELSE IF (IEND.EQ.2.AND.N.LT.3) THEN
        IER=3
        WRITE (IOUT,153) IER
        RETURN
      ELSE IF (IEND.EQ.3.AND.N.LT.4) THEN
        IER=4
        WRITE (IOUT,154) IER
        RETURN
      ELSE IF (IEND.LT.1.OR.IEND.GT.3) THEN

```

```

        IER=5
        WRITE (IOUT,155)
        RETURN
    ELSE IF (N.GT.MAX) THEN
        IER=6
        WRITE (IOUT,157)
        RETURN
    END IF

    IF (NCROW.LT.(N-1)) THEN
        IER=7
        WRITE (IOUT,156) N-1
        RETURN
    END IF

    NM2=N-2
    NM1=N-1

    DX1=X(2)-X(1)
    DY1=(Y(2)-Y(1))/DX1*6.0

    DO 10 I=1,NM2
        DX2=X(I+2)-X(I+1)
        DY2=(Y(I+2)-Y(I+1))/DX2*6.0
        A(I,1)=DX1
        A(I,2)=2.0*(DX1+DX2)
        A(I,3)=DX2
        A(I,4)=DY2-DY1
        DX1=DX2
10      DY1=DY2

    IF (IEND.EQ.2) THEN
        A(1,2)=A(1,2)+X(2)-X(1)
        A(NM2,2)=A(NM2,2)+X(N)-X(NM1)
    ELSE IF (IEND.EQ.3) THEN
        DX1=X(2)-X(1)
        DX2=X(3)-X(2)
        A(1,2)=(DX1+DX2)*(DX1+2.0*DX2)/DX2
        A(1,3)=(DX2*DX2-DX1*DX1)/DX2
        DXN2=X(NM1)-X(NM2)
        DXN1=X(N)-X(NM1)
        A(NM2,1)=(DXN2*DXN2-DXN1*DXN1)/DXN2
        A(NM2,2)=(DXN1+DXN2)*(DXN1+2.0*DXN2)/DXN2
    END IF

C      SOLVE THE TRIDIAGONAL SYSTEM, FIRST REDUCE

    DO 100 I=2,NM2
        A(I,2)=A(I,2)-A(I,1)/A(I-1,2)*A(I-1,3)

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100  A(I,4)=A(I,4)-A(I,1)/A(I-1,2)*A(I-1,4)
C    NOW BACK SUBSTITUTE

      A(NM2,4)=A(NM2,4)/A(NM2,2)
      DO 120 I=2,NM2
        J=NM1-I
120   A(J,4)=(A(J,4)-A(J,3)*A(J+1,4))/A(J,2)
C    NOW LOAD THE SECOND DERIVATIVE VECTOR

      DO 130 I=1,NM2
130   A(I+1,5)=A(I,4)
C    LOAD SECOND DERIVATIVE AT END POINTS ACCORDING TO END CONDITIONS

      IF (IEND.EQ.1) THEN
        A(1,5)=0.0
        A(N,5)=0.0
      ELSE IF (IEND.EQ.2) THEN
        A(1,5)=A(2,5)
        A(N,5)=A(NM1,5)
      ELSE IF (IEND.EQ.3) THEN
        A(1,5)=((DX1+DX2)*A(2,5)-DX1*A(3,5))/DX2
        A(N,5)=((DXN2+DXN1)*A(NM1,5)-DXN1*A(NM2,5))/DXN2
      END IF
C    EVALUATE COEFFICIENTS FOR NESTED MULTIPLICATION

      DO 200 I=1,NM1
        DELTAX=X(I+1)-X(I)
        DELTAY=Y(I+1)-Y(I)
        DELTAS=A(I+1,5)-A(I,5)
        C(I,1)=-DELTAX*(A(I+1,5)/6.0+A(I,5)/3.0)+DELTAY/DELTAX
        C(I,2)=0.5*A(I,5)
200   C(I,3)=DELTAS/(6.0*DELTAX)
C    SET ERROR FLAG IER EQUAL TO ZERO FOR RETURN WITHOUT ANY ERROR
      IER=0
      IF (LDEBUG) THEN
        DO 300 I=1,N-1
300   WRITE (ID,160) I,X(I),Y(I),C(I,1),C(I,2),C(I,3)
        WRITE (ID,160) I,X(I),Y(I)
      END IF

151  FORMAT (5X,'ABSCISSA OF DATA PAIRS IS NOT IN ACSENDING ORDER',/)
152  FORMAT (5X,'MINIMUM OF ',I1,' DATA PAIRS NEEDED FOR LINEAR',
1    ' ENDS ',/)
153  FORMAT (5X,'MINIMUM OF ',I1,' DATA PAIRS NEEDED FOR PARABOLIC',

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1          ' ENDS ',/)
154  FORMAT (5X,'MINIMUM OF ',I1,' DATA PAIRS NEEDED FOR CUBIC',
1          ' ENDS ',/)
155  FORMAT (5X,'TYPE OF END CONDITIONS NOT SPECIFIED',/)
156  FORMAT (5X,'MINIMUM ROW DIMENSION OF MATIRX C MUST BE ',I3,/)
157  FORMAT (5X,'NUMBER OF DATA PAIRS EXCEED PARAMETER MAX ',/)
160  FORMAT (1X,I4,5(1PE14.5))
      RETURN
      END

      SUBROUTINE TRIDAG(START,NOSE,SUBDAG,DIAG,SUPDAG,RHS,SOLNS)

C      START = INDEX FOR THE FIRST UNKNOWN
C      NOSE  = NUMBER OF SIMULTANEOUS EQUATIONS
C      SUBDAG = SUBDIAGONAL VECTOR
C      DIAG  = DIAGONAL VECTOR
C      SUPDAG = SUPERDIAGONAL VECTOR
C      RHS   = RIGHT HAND SIDE VECTOR
C      SOLNS = SOLUTION VECTOR

      INTEGER START
      REAL SUBDAG(NOSE-1),DIAG(NOSE),SUPDAG(NOSE-1),RHS(NOSE)
      REAL SOLNS(NOSE),BETA(101),GAMMA(101)

      BETA(START)=DIAG(START)
      GAMMA(START)=RHS(START)/BETA(START)

      DO 1 I=START+1,NOSE
          IM1=I-1
          BETA(I)=DIAG(I)-SUBDAG(IM1)*SUPDAG(IM1)/BETA(IM1)
          GAMMA(I)= (RHS(I)-SUBDAG(IM1)*GAMMA(I-1))/BETA(I)
1      CONTINUE

      SOLNS(NOSE)=GAMMA(NOSE)
      NM1=NOSE-1

      DO 2 I=NM1,START,-1
          SOLNS(I)=GAMMA(I)-SUPDAG(I)*SOLNS(I+1)/BETA(I)
2      CONTINUE

      RETURN
      END

      SUBROUTINE COALPR (N,TEMP,CP,KOND,DKOND)

      REAL TEMP(N),CP(N),KOND(N),DKOND(N)
      COMMON / CPARAS / PDENZ,PDIAZ,XCRBNZ,XVOL1Z,XVOL2Z,XASHZ,EMMISS
1      VSTAR,PREEXF,ACTENG,PDIA,PDEN,VLTLEFT,BLOWCF,ATOMWT

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TOTAL=XCRBNZ+VLTFLT+XASHZ
XCARNB=XCRBNZ/TOTAL
XVOL=VLTFLT/TOTAL
XASH=XASHZ/TOTAL
DO 1 I=1,N
TK=TEMP(I)
TC=TK-273.16
! CP(I)=CPMERIK(ATOMWT,XASH,TK)
CP(I)=CPBERKO(TC,XCARNB,XVOL,XASH)
! IF (I.EQ.1) WRITE (77,*) XASH,TEMP(I),CP(I)
KOND(I)=6.64E-4
1 DKOND(I)=0.0
RETURN
END

REAL FUNCTION CPBERKO (T,XCARNB,XVOL,XASH)
CPBERKO=XCARNB*(0.165+6.8E-4*T-4.2E-7*T*T)
CPBERKO=CPBERKO+0.5*XVOL*(0.395+8.1E-4*T)
CPBERKO=CPBERKO+0.5*XVOL*(0.710+6.1E-4*T)
CPBERKO=CPBERKO+XASH*(0.18+1.4E-4*T)
RETURN
END

REAL FUNCTION CPMERIK (ATOMWT,XASH,TK)
G=0.0
DO J=1,2
IF (J.EQ.1) TCHAR=380.0
IF (J.EQ.2) TCHAR=1800.0
Z=TCHAR/TK
EXPZ=EXP(Z)
DENOM=(EXPZ-1.0)/Z
DENOM=DENOM*DENOM
G1=EXPZ/DENOM
G=G+G1
IF (J.EQ.2) G=G+G1
END DO
CPDAF=1.987*G/ATOMWT
CPMERIK=XASH*(0.18+1.4E-4*(TK-273.16))+(1.0-XASH)*CPDAF

RETURN
END

SUBROUTINE THERMO (NSP,NGP,LSTSPE,MFRCTN,NROW,TEMP,CPAVG)

PARAMETER (NSDB=15,GASCON=1.9872)
CHARACTER*6 NAME(NSDB),LSTSPE(NSP)
REAL CPCOEF(NSDB,12),MFRCTN(NROW,NGP),TEMP(NGP),CPAVG(NGP)
REAL ACP(NSDB,2),BCP(NSDB,2),CCP(NSDB,2),DCP(NSDB,2)
REAL ECP(NSDB,2),FCP(NSDB,2)

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DATA NAME(1),(CPCOEF(1,J),J=1,12)/'H2      ',0.30558123E1,
1 0.597404E-3,0.16747471E-8,-0.21247544E-10,0.25195487E-14,
2 -0.86168476E3,0.29432327E1,0.34815509E-2,-0.77713819E-5,
3 0.74997496E-8,-0.25203379E-11,-0.97695413E3/

DATA NAME(2),(CPCOEF(2,J),J=1,12)/'H2O      ',0.26110472E1,
1 0.3156313E-2,-0.92985438E-6,0.13331538E-9,-0.74689351E-14,
2 -0.29868167E5,0.41677234E1,-0.1811497E-2,0.59471288E-5,
3 -0.48692021E-8,0.15291991E-11,-0.30289969E5/

DATA NAME(3),(CPCOEF(3,J),J=1,12)/'N2      ',0.28532899E1,
1 0.16022128E-2,-0.62936893E-6,0.11441022E-9,-0.78057465E-14,
2 -0.89008093E3,0.37044177E1,-0.14218753E-2,0.28670392E-5,
3 -0.12028885E-8,-0.13954677E-13,-0.10640795E4/

DATA NAME(4),(CPCOEF(4,J),J=1,12)/'CO      ',0.29840696E1,
1 0.1489138E-2,-0.57899684E-6,0.10364577E-9,-0.6935355E-14,
2 -0.14245228E5,0.37100928E1,-0.16190964E-2,0.36923594E-5,
3 -0.20319674E-8,0.23953344E-12,-0.1435631E5/

DATA NAME(5),(CPCOEF(5,J),J=1,12)/'CO2      ',0.44608041E1,
1 0.30981719E-2,-0.12392571E-5,0.22741325E-9,-0.15525954E-13,
2 -0.48961442E5,0.24007797E1,0.87350957E-2,-0.66070878E-5,
3 0.20021861E-8,0.63274039E-15,-0.48377527E5/

DATA NAME(6),(CPCOEF(6,J),J=1,12)/'CH4      ',0.15027072E1,
1 0.10416798E-1,-0.39181522E-5,0.67777899E-9,-0.44283706E-13,
2 -0.99787078E+4,0.38261932E1,-0.39794581E-2,0.2455834E-4,
3 -0.22732926E-7,0.69626957E-11,-0.1014495E5/

DATA NAME(7),(CPCOEF(7,J),J=1,12)/'HE      ',2.5,4*0.0,
1 -0.74537498E3,2.5,4*0.0,-0.74537498E3/

DATA NAME(8),(CPCOEF(8,J),J=1,12)/'AR      ',2.5,4*0.0,
1 -0.74537502E3,2.5,4*0.0,-0.74537498E3/

DATA NAME(9),(CPCOEF(9,J),J=1,12)/'HCN      ',0.37068121E1,
1 0.33382803E2,-0.1191332E-5,0.19992917E-9,-0.12826452E-13,
2 0.14962636E5,0.24513556E1,0.87208371E-2,-0.10094203E-4,
3 0.67255698E-8,-0.17626959E-11,0.15213002E5/

DATA NAME(10),(CPCOEF(10,J),J=1,12)/'NH3     ',0.23168577E1,
1 0.6284146E-2,-0.21251163E-5,0.3401869E-9,-0.21470026E-13,
2 -0.64265487E4,0.37729747E1,-0.82975716E-3,0.11801882E-4,
3 -0.12126874E-7,0.4167379E-11,-0.66908514E4/

DATA NAME(11),(CPCOEF(11,J),J=1,12)/'NO      ',3.189,
1 0.13382281E-2,-0.52899318E-6,0.95919332E-10,-0.64847932E-14,

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2  0.9828329E4,0.40459521E1,-0.34181783E-2,0.7981919E-5,
3  -0.61139316E-8,0.15919076E-11,0.97453934E4/

  DATA NAME(12),(CPCOEF(12,J),J=1,12)/'C2H2 ',4.2415665,
1  5.5764832E-3,-2.1333704E-6,4.0861171E-10,-3.0528932E-14,
2  2.5738219E4,0.61421707,2.4428965E-2,-3.8282464E-5,
3  3.0843189E-8,-9.541144E-12,2.6282505E4/

  DATA NAME(13),(CPCOEF(13,J),J=1,12)/'C2H4 ',1.4123688,
1  1.6011999E-2,-7.8197196E-6,1.8585104E-9,-1.7429644E-13,
2  5.1630811E3,1.3411045,1.18860336E-2,6.798035E-6,
3  -1.503917E-8,6.302856E-12,5.3537314E3/

  DATA NAME(14),(CPCOEF(14,J),J=1,12)/'C2H6 ',0.2417817,
1  2.3588549E-2,-1.1602678E-5,2.7703074E-9,-2.6055703E-13,
2  -1.11143591E4,2.0500574,1.114617E-2,1.7029881E-5,
3  -2.4776356E-8,9.2876513E-12,-1.1297839E4/

  DATA NAME(15),(CPCOEF(15,J),J=1,12)/'O2 ',3.6122139,
1  7.4853166E-4,-1.9820647E-7,3.3749008E-11,-2.3907374E-15,
2  -1.1978151E3,3.7837135,-3.0233634E-3,9.9492751E-6,
3  -9.8189101E-9,3.3031825E-12,-1.0638107E3/

DO 100 ISP=1,NSP
DO 20 IDB=1,NSDB
IF (NAME(IDB).EQ.LSTSPE(ISP)) THEN
  DO 10 I=1,2
    IF (I.EQ.1) NADD=0
    IF (I.EQ.2) NADD=6
    ACP(ISP,I)= CPCOEF(IDB,NADD+1)
    BCP(ISP,I)= CPCOEF(IDB,NADD+2)
    CCP(ISP,I)= CPCOEF(IDB,NADD+3)
    DCP(ISP,I)= CPCOEF(IDB,NADD+4)
    ECP(ISP,I)= CPCOEF(IDB,NADD+5)
10   FCP(ISP,I)= CPCOEF(IDB,NADD+6)
    GO TO 100
  END IF
20  CONTINUE
STOP ' SPECIE IS NOT IN DATA BANK FOR THERMODYNAMIC PROPERTIES'
100 CONTINUE
RETURN

ENTRY THERMO1 (NSP,NGP,LSTSPE,MFRCTN,NROW,TEMP,CPAVG)

DO 200 IGP=1,NGP
CPAVG(IGP)=0.0
T=TEMP(IGP)
DO 150 ISP=1,NSP
IF (T.GT.1000.0) I=1

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      IF (T.LE.1000.0) I=2
      CPI=ACP(ISP,I)+T*(BCP(ISP,I)+T*(CCP(ISP,I)+T*(DCP(ISP,I)
1      +T*(ECP(ISP,I))))
      CPAVG(IGP)=CPAVG(IGP)+MFRCTN(ISP,IGP)*CPI
150  CONTINUE
200  CPAVG(IGP)=CPAVG(IGP)*GASCON

      RETURN
      END

      SUBROUTINE PTEMP (ITAU,NOGP,TGAS,DTIME,TCOAL,HTCOEF,ETAS,ETASPR,
1      ERRCOD,ERRMES)

C      subprogram to calculate coal particle temperature given the
C      particle temperature at previous time step and surrounding gas
C      temperature
C      written: November 1989, M. Usman ghani

      PARAMETER (IR=10,II=20,ID=30,MNGP=21,MNGPM1=MNGP-1)
      PARAMETER (SIGMA=1.356E-12,TAMB=300.0,PI=3.1415926535898)
      PARAMETER (TAMB4=TAMB**4)

      INTEGER IL(MNGP),ERRCOD
      CHARACTER*130 ERRMES
      LOGICAL INTRES
      REAL W2P1(MNGP),W2M1(MNGP),W20(MNGP),W1P1(MNGP),W1M1(MNGP)
      REAL W10(MNGP),A(MNGP),B1(MNGP),B2(MNGP),B(MNGP),D(MNGP)
      REAL RI(MNGP),SUBDAG(MNGPM1),DIAG(MNGP),SUPDAG(MNGPM1),RHS(MNGP)
      REAL SOLNS(MNGP),KCOAL(MNGP),DKCOAL(MNGP),CPCOAL(MNGP)
      REAL TCOAL(MNGP),T(MNGP),ETAS,ETASPR,RHOCOAL

      COMMON / CPARAS / PDENZ,PDIAZ,XCRBNZ,XVOL1Z,XVOL2Z,XASHZ,EMMISS
1      VSTAR,PREEFX,ACTENG,PDIA,PDEN,VLTLFT,BLOWCF,ATOMWT
C      evaluate the constant factors
      IF (NOGP.GT.MNGP) THEN
          ERRCOD=1
          ERRMES='NUMBER OF ACTUAL GRID POINTS EXCEED MAXIMUM ALLOWED
1INTERNALLY'
          RETURN
          END IF
          RHOCOAL=PDEN
          NOGPM1=NOGP-1
          DETA=1.0/NOGPM1
          DETP2I=1.0/(DETA*DETA)
          DETT2I=1.0/(2.0*DETA)
          RZERO=0.5*PDIAZ
          FA=1.0/(RZERO*RZERO)
          DTIMEI=1.0/DTIME
          RADFAC=EMMISS*SIGMA

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C      call subroutine coalpr to evaluate the heat capacity
C      and thermal conductivity vectors

      CALL COALPR (NOGP,TCOAL,CPCOAL,KCOAL,DKCOAL)

      FB=FA/(RHOCOAL*ETAS*ETAS)
      DO 300 I=1,NOGP
      A(I)=FB*KCOAL(I)/CPCOAL(I)

      IF (I.EQ.1) THEN
         B1(I)=0.0
         B2(I)=0.0
         B(I)=0.0
      ELSE
         ETA=DETA*(I-1)
         B1(I)=ETA*ETASPR/ETAS
         FC=FB/(2.0*DETA*CPCOAL(I))

         IF (I.EQ.NOGP) THEN
            DHAT=2.0*RZERO*DETA*ETAS/KCOAL(I)
            B2(I)=DKCOAL(I)*DHAT*FC
         ELSE
            B2(I)=DKCOAL(I)*FC*(TCOAL(I+1)-TCOAL(I-1))
         END IF

         B(I)=B1(I)+(2.0*A(I)+B2(I))/ETA
      END IF

      D(I)=0.0
      RI(I)=0.0
300    CONTINUE

C      call the subroutine W to determine the weighting factors

      CALL W(A,B,D,RI,NOGP,DETA,W1P1,W1M1,W1O,W2P1,W2M1,W2O,1,0,IL)

      DO 400 I=1,NOGP
      IF (I.EQ.1) THEN
         DIAG(I)=6.0*A(I)*DETP2I+DTIMEI
         SUPDAG(I)=-3.0*(W2P1(I)+W2M1(I))*A(I)*DETP2I
         RHS(I)=DTIMEI*TCOAL(I)
C      WRITE (6,*) i,DIAG(i),SUPDAG(i),RHS(i)
         GO TO 400
      END IF

      ALPHA=-A(I)*W2M1(I)*DETP2I+B(I)*W1M1(I)*DETT2I
      BETA=DTIMEI+2.0*A(I)*DETP2I
      GAMMA=-A(I)*W2P1(I)*DETP2I-B(I)*W1P1(I)*DETT2I

```

```

C      WRITE (6,*) I,ALPHA,BETA,GAMMA

      IF (I.EQ.NOGP) THEN
          SUBDAG(I-1)=ALPHA+GAMMA
          DIAG(I)=BETA-DHAT*GAMMA*(RADFAC*TCOAL(I)**3+HTCOEF)
          RHS(I)=TCOAL(I)*DTIMEI
          RHS(I)=RHS(I)-DHAT*GAMMA*(RADFAC*TAMB4+HTCOEF*TGAS)
C      WRITE (6,*) I,SUBDAG(I-1),DIAG(I),RHS(I)

      ELSE
          SUBDAG(I-1)=ALPHA
          DIAG(I)=BETA
          SUPDAG(I)=GAMMA
          RHS(I)=DTIMEI*TCOAL(I)
C      WRITE (6,*) I,SUBDAG(I-1),DIAG(I),SUPDAG(I),RHS(I)

      END IF

400  CONTINUE

C      CALL THE SUBROUTINE TRIDAG TO SOLVE THE RESULTING
C      TRIDIAGONAL MATRIX

      CALL TRIDAG(1,NOGP,SUBDAG,DIAG,SUPDAG,RHS,SOLNS)
      DO 500 I=1,NOGP
500   TCOAL(I)=SOLNS(I)
1000  CONTINUE

      TIME=REAL(ITAU+1)*DTIME
C      WRITE (*,990) TIME,(TCOAL(N),N=1,NOGP,2)
C      write (*,*) i,time,tcoal(1),tcoal(nogp)
      IF (INTRES) THEN
          WRITE (II,990) TIME,(TCOAL(N),N=1,NOGP,2)
      END IF

990  FORMAT (5X,'TIME= ',F9.6,11(1X,F9.2))
991  FORMAT (//,'EVALUATION OF SPLINE COEFFICIENTS TO INTERPOLATE',
1    ' TEMPERATURE DATA UNSUCCESSFUL',//)
992  FORMAT (//,'EVALUATION OF SPLINE COEFFICIENTS TO INTERPOLATE',
1    ' GAS CONDUCTIVITY DATA UNSUCCESSFUL',//)
993  FORMAT (5X,F10.5,10F10.1)

      RETURN
      END

      SUBROUTINE DPINTG (N,X,Y,IL,IU,VINT)
      REAL X(N),Y(N),VINT

      VINT=0.0
      IF (IL.EQ.IU) RETURN

```

```
IF (IL.LT.IU) THEN
  ISTART=IL
  IFINISH=IU
ELSEIF (IL.GT.IU) THEN
  ISTART=IU
  IFINISH=IL
END IF

DO I=ISTART+1,IFINISH
  VINT=VINT+0.5*(X(I)-X(I-1))*(Y(I)+Y(I-1))
END DO
IF (IU.LT.IL) VINT=-VINT
RETURN
END
```

APPENDIX C-3: RESULTS – TEXAS LIGNITE, FINES (38 MINUS MICRON), REDUCING RUN

SMOOTHED DATA FOR TEMPERATURE

Grid.#	XGRID	TEMPERATURE
1	0.00000E+00	1.54930E+03
3	2.00000E-01	1.57572E+03
5	4.00000E-01	1.56428E+03
7	6.00000E-01	1.54147E+03
9	8.00000E-01	1.50642E+03
11	1.00000E+00	1.46868E+03
13	1.20000E+00	1.42980E+03
15	1.40000E+00	1.37941E+03
17	1.60000E+00	1.29500E+03
19	1.80000E+00	1.20500E+03
21	2.00000E+00	1.11425E+03
23	2.20000E+00	1.01800E+03
25	2.40000E+00	9.15001E+02
27	2.60000E+00	8.11000E+02
29	2.80000E+00	7.04460E+02
31	3.00000E+00	5.74000E+02
33	3.20000E+00	4.00000E+02

COMPOSITION MATRIX FOR THE SYSTEM

GRID.#	MF_O2	MF_CO	MF_CO2	MF_NO	MF_NH3	MF_HCN	MF_H2	MF_C2H4	MF_C2H6	MF_C2H2	MF_CH4	MF_OF_AR
1	1.00E-03	1.23E-01	3.50E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.26E-01
3	1.00E-03	1.21E-01	3.54E-01	6.57E-06	1.64E-06	3.27E-06	1.67E-03	7.08E-05	1.30E-05	6.41E-05	6.01E-05	5.22E-01
5	1.00E-03	1.18E-01	3.46E-01	1.08E-05	3.65E-06	9.82E-06	3.03E-03	1.30E-04	2.44E-05	1.18E-04	1.11E-04	5.31E-01
7	1.00E-03	1.14E-01	3.32E-01	1.44E-05	5.69E-06	1.74E-05	4.09E-03	1.80E-04	3.36E-05	1.65E-04	1.53E-04	5.49E-01
9	1.00E-03	1.08E-01	3.08E-01	1.84E-05	7.54E-06	2.59E-05	4.80E-03	2.19E-04	3.97E-05	2.01E-04	1.87E-04	5.77E-01
11	1.00E-03	9.81E-02	2.74E-01	2.18E-05	9.45E-06	3.50E-05	5.20E-03	2.41E-04	4.26E-05	2.22E-04	2.03E-04	6.21E-01
13	1.00E-03	8.50E-02	2.18E-01	2.28E-05	1.17E-05	4.40E-05	5.25E-03	2.44E-04	4.27E-05	2.23E-04	2.01E-04	6.90E-01
15	1.00E-03	7.05E-02	1.66E-01	2.02E-05	1.25E-05	5.14E-05	4.33E-03	2.28E-04	3.86E-05	1.99E-04	1.90E-04	7.58E-01

17	1.00E-03	5.61E-02	1.27E-01	1.69E-05	1.11E-05	4.63E-05	2.77E-03	1.87E-04	2.83E-05	1.68E-04	1.51E-04	8.13E-01
19	9.69E-04	4.36E-02	9.34E-02	1.33E-05	9.28E-06	3.07E-05	1.22E-03	1.44E-04	1.73E-05	1.37E-04	1.13E-04	8.60E-01
21	8.73E-04	3.17E-02	6.22E-02	9.66E-06	7.28E-06	1.78E-05	4.64E-04	1.01E-04	1.19E-05	1.07E-04	8.99E-05	9.04E-01
23	7.51E-04	2.14E-02	3.72E-02	6.35E-06	5.20E-06	1.23E-05	3.13E-04	6.93E-05	8.14E-06	7.98E-05	7.00E-05	9.40E-01
25	6.10E-04	1.30E-02	1.88E-02	3.55E-06	3.20E-06	7.58E-06	1.94E-04	4.86E-05	4.95E-06	5.50E-05	5.11E-05	9.67E-01
27	4.82E-04	6.58E-03	7.98E-03	1.72E-06	1.75E-06	3.61E-06	9.52E-05	2.99E-05	2.09E-06	3.31E-05	3.31E-05	9.85E-01
29	5.12E-04	2.49E-03	2.23E-03	7.46E-07	8.35E-07	1.17E-06	3.10E-05	1.39E-05	1.87E-07	1.36E-05	1.82E-05	9.95E-01
31	3.90E-04	3.94E-04	2.99E-06	2.36E-07	2.73E-07	1.17E-07	0.00E+00	3.83E-06	0.00E+00	0.00E+00	6.87E-06	9.99E-01
33	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.43E-12	9.31E-13	0.00E+00	9.78E-16	0.00E+00	0.00E+00	1.00E+00

EVALUATION OF PHYSICAL PROPERTIES AT EACH GRID POINT

I	XGRID	SMTHD TEMP	VISCOCITY	AVG MOL WT	THRML COND	MASS DENST	MOLR DENST	AV_MOLR_CP
1	0.0000E+00	1.5493E+03	6.1779E-04	3.9924E+01	1.1199E-04	3.1407E-04	7.8666E-06	8.5564E+00
3	2.0000E-01	1.5757E+03	6.2375E-04	3.9891E+01	1.1297E-04	3.0855E-04	7.7347E-06	8.9505E+00
5	4.0000E-01	1.5643E+03	6.2220E-04	3.9840E+01	1.1270E-04	3.1040E-04	7.7912E-06	9.5493E+00
7	6.0000E-01	1.5415E+03	6.1910E-04	3.9788E+01	1.1220E-04	3.1458E-04	7.9065E-06	1.0157E+01
9	8.0000E-01	1.5064E+03	6.1463E-04	3.9738E+01	1.1152E-04	3.2150E-04	8.0905E-06	1.0716E+01
11	1.0000E+00	1.4687E+03	6.1173E-04	3.9702E+01	1.1119E-04	3.2946E-04	8.2984E-06	1.1190E+01
13	1.2000E+00	1.4298E+03	6.1275E-04	3.9632E+01	1.1187E-04	3.3782E-04	8.5240E-06	1.1388E+01
15	1.4000E+00	1.3794E+03	6.0998E-04	3.9631E+01	1.1187E-04	3.5015E-04	8.8354E-06	1.1384E+01
17	1.6000E+00	1.2950E+03	5.9432E-04	3.9709E+01	1.0934E-04	3.7371E-04	9.4113E-06	1.0241E+01
19	1.8000E+00	1.2050E+03	5.7462E-04	3.9785E+01	1.0606E-04	4.0240E-04	1.0114E-05	8.3645E+00
21	2.0000E+00	1.1142E+03	5.5273E-04	3.9834E+01	1.0236E-04	4.3571E-04	1.0938E-05	6.9074E+00
23	2.2000E+00	1.0180E+03	5.2625E-04	3.9865E+01	9.7722E-05	4.7727E-04	1.1972E-05	6.1688E+00
25	2.4000E+00	9.1500E+02	4.9445E-04	3.9899E+01	9.2003E-05	5.3145E-04	1.3320E-05	5.1554E+00
27	2.6000E+00	8.1100E+02	4.5887E-04	3.9938E+01	8.5468E-05	6.0019E-04	1.5028E-05	5.0473E+00
29	2.8000E+00	7.0446E+02	4.1893E-04	3.9967E+01	7.8060E-05	6.9146E-04	1.7301E-05	4.9917E+00
31	3.0000E+00	5.7400E+02	3.6484E-04	3.9986E+01	6.7986E-05	8.4902E-04	2.1233E-05	4.9700E+00
33	3.2000E+00	4.0000E+02	2.8182E-04	3.9994E+01	5.2509E-05	1.2186E-03	3.0469E-05	4.9680E+00

CONVERGED VELOCITY AND PSI PROFILES

I	XGRID	VGZ PROFIL	PSI PROFIL
1	0.0000E+00	4.3518E+01	0.0000E+00
3	2.0000E-01	4.3959E+01	1.6853E+00

5	4.0000E-01	4.2689E+01	3.3768E+00
7	6.0000E-01	4.0440E+01	5.1108E+00
9	8.0000E-01	3.7194E+01	6.9294E+00
11	1.0000E+00	3.3188E+01	8.8230E+00
13	1.2000E+00	2.8498E+01	1.0845E+01
15	1.4000E+00	2.2780E+01	1.3482E+01
17	1.6000E+00	1.5405E+01	1.7829E+01
19	1.8000E+00	6.2856E+00	2.4027E+01
21	2.0000E+00	-4.2528E+00	2.5475E+01
23	2.2000E+00	-1.2092E+01	1.6406E+01
25	2.4000E+00	-1.5502E+01	9.5137E+00
27	2.6000E+00	-1.6601E+01	6.2408E+00
29	2.8000E+00	-1.6283E+01	3.9774E+00
31	3.0000E+00	-1.4320E+01	1.9655E+00
33	3.2000E+00	-1.0292E+01	0.0000E+00

RATES OF FORMATION MATRIX FOR THE SYSTEM

I	IGRID	RFZ_O2	RFZ_CO	RFZ_CO2	RFZ_NO	RFZ_NH3	RFZ_HCN	RFZ_H2	RFZ_C2H4	RFZ_C2H6	RFZ_C2H2	RFZ_CH4
1	0.00E+00	1.21E-09	-1.53E-06	1.20E-05	1.07E-08	2.30E-09	3.09E-09	3.55E-06	1.04E-07	1.82E-08	9.45E-08	9.70E-08
3	2.00E-01	1.86E-09	-2.75E-06	-6.57E-06	6.82E-09	2.79E-09	8.28E-09	2.97E-06	8.70E-08	1.60E-08	7.94E-08	8.11E-08
5	4.00E-01	1.85E-09	-4.90E-06	-1.50E-05	5.38E-09	3.29E-09	9.94E-09	2.48E-06	7.19E-08	1.31E-08	6.70E-08	6.60E-08
7	6.00E-01	1.68E-09	-6.46E-06	-2.56E-05	5.52E-09	2.66E-09	1.04E-08	1.88E-06	5.74E-08	9.04E-09	5.40E-08	5.61E-08
9	8.00E-01	1.18E-09	-9.97E-06	-3.54E-05	4.91E-09	2.48E-09	1.13E-08	1.24E-06	3.68E-08	4.95E-09	3.48E-08	3.60E-08
11	1.00E+00	2.07E-09	-1.39E-05	-6.11E-05	3.68E-09	3.03E-09	1.07E-08	1.29E-06	1.23E-08	1.41E-09	1.22E-08	4.58E-09
13	1.20E+00	3.05E-11	-1.46E-05	-5.50E-05	-7.19E-10	1.93E-09	9.57E-09	2.11E-06	-3.57E-09	-1.29E-09	-1.27E-08	-2.35E-09
15	1.40E+00	-1.63E-09	-1.28E-05	-3.94E-05	-2.60E-09	-2.91E-10	1.53E-09	-1.49E-06	-2.28E-08	-5.64E-09	-2.69E-08	-3.28E-08
17	1.60E+00	2.23E-08	-7.17E-06	-1.86E-05	-1.83E-09	-9.92E-10	-3.67E-09	-9.76E-07	-2.38E-08	-7.48E-09	-1.71E-08	-2.32E-08
19	1.80E+00	1.65E-08	-1.72E-06	-4.93E-06	-3.93E-10	-5.17E-11	-5.84E-09	-1.50E-06	-4.92E-09	-1.74E-09	-3.57E-09	-8.29E-09
21	2.00E+00	6.12E-08	4.25E-06	9.63E-06	1.34E-09	9.45E-10	1.85E-09	-1.44E-07	4.98E-09	1.45E-09	1.22E-08	8.94E-09
23	2.20E+00	1.19E-07	5.81E-06	1.16E-05	1.88E-09	1.59E-09	3.58E-09	7.93E-08	1.54E-08	2.35E-09	1.84E-08	1.49E-08
25	2.40E+00	1.03E-07	5.45E-06	7.46E-06	1.34E-09	1.03E-09	3.30E-09	3.89E-08	1.69E-08	2.40E-09	1.96E-08	1.72E-08
27	2.60E+00	-6.03E-08	3.43E-06	4.31E-06	7.76E-10	8.41E-10	1.90E-09	3.74E-08	1.41E-08	1.36E-09	1.86E-08	1.45E-08
29	2.80E+00	2.43E-07	1.68E-06	1.50E-06	4.69E-10	5.09E-10	6.94E-10	-2.10E-08	8.27E-09	-5.28E-12	8.57E-09	1.14E-08
31	3.00E+00	4.42E-07	-6.33E-08	-1.72E-10	1.20E-10	2.05E-10	-8.72E-12	-5.43E-15	1.40E-09	-1.61E-18	0.00E+00	5.22E-09
33	3.20E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

PARTICLE TRAJECTORY AND SURROUNDING GAS TEMPERATURE

I	TIME (sec)	GAS_TEMP	P.Z_POSITN	P.R_POSITN
1	0.0000E+00	4.0000E+02	3.2000E+00	2.0000E+00
6	5.0000E-03	4.6502E+02	3.1389E+00	2.0011E+00
11	1.0000E-02	5.2815E+02	3.0665E+00	2.0071E+00
16	1.5000E-02	5.8426E+02	2.9871E+00	2.0202E+00
21	2.0000E-02	6.4033E+02	2.9024E+00	2.0415E+00
26	2.5000E-02	6.9615E+02	2.8134E+00	2.0720E+00
31	3.0000E-02	7.4818E+02	2.7214E+00	2.1124E+00
36	3.5000E-02	7.9648E+02	2.6281E+00	2.1643E+00
41	4.0000E-02	8.4472E+02	2.5351E+00	2.2293E+00
46	4.5000E-02	8.9228E+02	2.4437E+00	2.3102E+00
51	5.0000E-02	9.3792E+02	2.3553E+00	2.4120E+00
56	5.5000E-02	9.8107E+02	2.2719E+00	2.5438E+00
61	6.0000E-02	1.0196E+03	2.1955E+00	2.7196E+00
66	6.5000E-02	1.0527E+03	2.1280E+00	2.9589E+00
71	7.0000E-02	1.0799E+03	2.0721E+00	3.2750E+00
76	7.5000E-02	1.1014E+03	2.0277E+00	3.6739E+00
81	8.0000E-02	1.1173E+03	1.9944E+00	4.1474E+00
86	8.5000E-02	1.1285E+03	1.9698E+00	4.7209E+00
88	8.7000E-02	1.1320E+03	1.9620E+00	4.9731E+00

DIMENSIONLESS PARAMETERS AND PARTICLE PROPERTIES

I	TIME (sec)	P.Z_POSITN	GAS_TEMP	REYNOLD #	PRANDTL #	MUSULT #	M_DOT	H.T.COEFF	BLOW.COEFF	VOLATILES
1	0.0000E+00	3.2000E+00	4.0000E+02	0.0000E+00	6.6669E-01	2.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
6	5.0000E-03	3.1389E+00	4.6502E+02	1.7232E-02	6.7238E-01	2.0752E+00	1.8646E-07	3.7688E-02	5.4423E-10	5.8569E-10
11	1.0000E-02	3.0665E+00	5.2815E+02	1.4581E-02	6.7403E-01	2.0692E+00	1.7141E-06	4.1099E-02	4.5735E-09	4.6265E-09
16	1.5000E-02	2.9871E+00	5.8426E+02	1.1464E-02	6.7184E-01	2.0613E+00	2.0817E-05	4.4058E-02	5.1638E-08	5.3441E-08
21	2.0000E-02	2.9024E+00	6.4033E+02	9.4537E-03	6.6835E-01	2.0556E+00	2.2152E-04	4.7041E-02	5.1428E-07	5.9416E-07
26	2.5000E-02	2.8134E+00	6.9615E+02	7.5312E-03	6.7172E-01	2.0262E+00	1.8167E-03	4.8934E-02	4.0066E-06	5.3404E-06
31	3.0000E-02	2.7214E+00	7.4818E+02	6.0149E-03	6.7453E-01	2.0394E+00	1.0578E-02	5.1604E-02	2.2355E-05	3.5490E-05
36	3.5000E-02	2.6281E+00	7.9648E+02	4.4504E-03	6.7791E-01	2.0371E+00	4.4965E-02	5.3748E-02	9.1737E-05	1.7480E-04
41	4.0000E-02	2.5351E+00	8.4472E+02	2.6713E-03	6.8199E-01	2.0296E+00	1.5153E-01	5.5514E-02	2.9968E-04	6.7561E-04

46	4.5000E-02	2.4437E+00	8.9228E+02	4.9281E-04	6.9916E-01	2.0121E+00	4.2894E-01	5.6858E-02	8.4068E-04	2.1687E-03
51	5.0000E-02	2.3553E+00	9.3792E+02	2.3127E-03	6.6499E-01	2.0255E+00	1.0523E+00	5.9018E-02	1.9029E-03	5.9958E-03
56	5.5000E-02	2.2719E+00	9.8107E+02	5.4466E-03	7.5745E-01	2.0393E+00	2.2969E+00	6.1010E-02	4.6059E-03	1.4682E-02
61	6.0000E-02	2.1955E+00	1.0196E+03	1.0655E-02	8.5249E-01	2.0539E+00	4.4322E+00	6.2703E-02	9.7809E-03	3.2184E-02
65	6.4000E-02	2.1406E+00	1.0465E+03	1.1205E-02	8.6865E-01	2.0504E+00	6.8387E+00	6.3445E-02	1.5168E-02	5.5764E-02
70	6.9000E-02	2.0824E+00	1.0749E+03	1.4137E-02	8.8123E-01	2.0508E+00	1.0376E+01	6.4368E-02	2.3000E-02	1.0043E-01
75	7.4000E-02	2.0356E+00	1.0976E+03	1.0153E-02	9.1249E-01	2.0322E+00	1.3610E+01	6.4476E-02	3.0915E-02	1.6239E-01
80	7.9000E-02	2.0003E+00	1.1145E+03	1.0133E-02	9.3618E-01	2.0281E+00	1.5287E+01	6.4867E-02	3.5354E-02	2.3632E-01
85	8.4000E-02	1.9741E+00	1.1266E+03	9.1081E-03	9.4502E-01	2.0264E+00	1.4665E+01	6.5123E-02	3.4027E-02	3.1187E-01
88	8.7000E-02	1.9620E+00	1.1320E+03	8.9121E-03	9.5707E-01	2.0291E+00	1.3230E+01	6.5347E-02	3.1015E-02	3.5313E-01

COAL PARTICLE HEAT UP

INITIAL COAL PARTICLE DENSITY (gm/cc) =	1.60
INITIAL COAL PARTICLE DIAMETER (centimeter) =	0.32E-02
INITIAL COAL PARTICLE TEMPERATURE (deg K) =	400.00
EMMISSIVITY OF COAL =	0.70

COAL PARTICLE AND SURROUNDING GAS PHASE TEMPERATURES, AND PARTICLE DIAMETER AND DENSITY

I	TIME (sec)	GAS_TEMP	P_S_TEMP	P_C_TEMP	P_DIAMETER	P_DENSITY
1	0.0000E+00	4.0000E+02	4.0000E+02	4.0000E+02	3.2000E-03	1.6000E+00
6	5.0000E-03	4.6502E+02	4.1723E+02	4.1510E+02	3.2000E-03	1.6000E+00
11	1.0000E-02	5.2815E+02	4.5267E+02	4.4893E+02	3.2000E-03	1.6000E+00
16	1.5000E-02	5.8426E+02	4.9716E+02	4.9254E+02	3.2000E-03	1.6000E+00
21	2.0000E-02	6.4033E+02	5.4715E+02	5.4186E+02	3.2000E-03	1.6000E+00
26	2.5000E-02	6.9615E+02	6.0029E+02	5.9459E+02	3.2000E-03	1.6000E+00
31	3.0000E-02	7.4818E+02	6.5330E+02	6.4737E+02	3.2000E-03	1.5999E+00
36	3.5000E-02	7.9648E+02	7.0433E+02	6.9833E+02	3.2000E-03	1.5997E+00
41	4.0000E-02	8.4472E+02	7.5404E+02	7.4794E+02	3.2000E-03	1.5989E+00
46	4.5000E-02	8.9228E+02	8.0274E+02	7.9657E+02	3.2000E-03	1.5965E+00
51	5.0000E-02	9.3792E+02	8.5057E+02	8.4430E+02	3.2000E-03	1.5904E+00
56	5.5000E-02	9.8107E+02	8.9755E+02	8.9131E+02	3.2000E-03	1.5765E+00
61	6.0000E-02	1.0196E+03	9.4254E+02	9.3657E+02	3.2000E-03	1.5485E+00
66	6.5000E-02	1.0527E+03	9.8440E+02	9.7904E+02	3.2000E-03	1.4988E+00
71	7.0000E-02	1.0799E+03	1.0225E+03	1.0179E+03	3.2000E-03	1.4216E+00

76	7.5000E-02	1.1014E+03	1.0560E+03	1.0524E+03	3.2000E-03	1.3176E+00
81	8.0000E-02	1.1173E+03	1.0846E+03	1.0820E+03	3.2000E-03	1.1973E+00
86	8.5000E-02	1.1285E+03	1.1076E+03	1.1059E+03	3.2000E-03	1.0782E+00

RATES OF FORMATION OF NITROGENOUS SPECIES AS A FUNCTION OF TIME AND AXIAL POSITION OF PARTICLE

I	TIME (sec)	P_Z_POSIT#	RFT_NO	RFT_NH3	RFT_HCN	RFT_H2	RFT_CH4	RFT_C2H2	RFT_C2H4	RFT_C2H6
1	0.0000E+00	3.2000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
6	5.0000E-03	3.1389E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
11	1.0000E-02	3.0665E+00	2.8248E-11	6.5868E-11	0.0000E+00	0.0000E+00	1.6644E-09	0.0000E+00	2.2026E-10	0.0000E+00
16	1.5000E-02	2.9871E+00	1.4514E-10	2.2373E-10	0.0000E+00	0.0000E+00	5.3102E-09	0.0000E+00	2.4489E-09	0.0000E+00
21	2.0000E-02	2.9024E+00	3.3062E-10	3.4597E-10	1.7539E-10	0.0000E+00	8.7594E-09	2.1853E-09	5.1577E-09	0.0000E+00
26	2.5000E-02	2.8134E+00	4.5322E-10	4.8685E-10	6.2103E-10	0.0000E+00	1.1154E-08	7.3087E-09	7.8929E-09	0.0000E+00
31	3.0000E-02	2.7214E+00	5.3370E-10	6.4009E-10	1.1279E-09	8.2360E-09	1.2777E-08	1.5942E-08	1.0227E-08	3.5582E-10
36	3.5000E-02	2.6281E+00	7.0654E-10	7.9464E-10	1.7064E-09	3.3598E-08	1.4117E-08	1.8566E-08	1.3203E-08	1.0573E-09
41	4.0000E-02	2.5351E+00	9.4390E-10	9.3676E-10	2.3472E-09	3.0872E-08	1.5569E-08	1.9031E-08	1.5802E-08	1.8439E-09
46	4.5000E-02	2.4437E+00	1.2083E-09	9.9608E-10	2.9940E-09	3.1848E-08	1.6846E-08	1.9468E-08	1.6921E-08	2.2776E-09
51	5.0000E-02	2.3553E+00	1.5022E-09	1.1551E-09	3.5151E-09	5.2863E-08	1.7303E-08	1.9548E-08	1.6644E-08	2.4837E-09
56	5.5000E-02	2.2719E+00	1.7278E-09	1.4355E-09	3.6536E-09	7.5558E-08	1.6375E-08	1.9179E-08	1.6070E-08	2.4889E-09
61	6.0000E-02	2.1955E+00	1.8819E-09	1.5068E-09	3.4798E-09	7.9500E-08	1.4805E-08	1.8295E-08	1.5369E-08	2.3421E-09
66	6.5000E-02	2.1280E+00	1.9225E-09	1.4096E-09	3.2143E-09	6.8582E-08	1.3125E-08	1.6881E-08	1.3232E-08	2.1262E-09
71	7.0000E-02	2.0721E+00	1.7903E-09	1.2131E-09	2.8779E-09	3.9169E-08	1.1509E-08	1.5344E-08	1.0332E-08	1.8862E-09
76	7.5000E-02	2.0277E+00	1.5349E-09	1.0589E-09	2.4811E-09	-4.9276E-08	9.9476E-09	1.3655E-08	6.8039E-09	1.6257E-09
81	8.0000E-02	1.9944E+00	1.2980E-09	9.1941E-10	1.6754E-09	-1.6672E-07	8.7360E-09	1.1834E-08	4.7590E-09	1.4134E-09
86	8.5000E-02	1.9698E+00	1.1171E-09	8.0480E-10	8.2158E-10	-2.8358E-07	7.7646E-09	1.0192E-08	4.9450E-09	1.2194E-09

NORMALIZED RATES OF FORMATION OF NITROGENOUS SPECIES AS A FUNCTION TIME (G_ATOM N/G_ATOM INITIAL_VOLATILE_N *SEC))

I	TIME (sec)	P_Z_POSIT#	GAS_TMPRTR	P_S_TMPRTR	NRFT_NO	NRFT_NH3	NRFT_HCN	NRFT_TO_XN
1	0.0000E+00	3.2000E+00	4.0000E+02	4.0000E+02	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
6	5.0000E-03	3.1389E+00	4.6502E+02	4.1723E+02	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
11	1.0000E-02	3.0665E+00	5.2815E+02	4.5267E+02	4.1633E-03	9.7080E-03	0.0000E+00	1.3871E-02
16	1.5000E-02	2.9871E+00	5.8426E+02	4.9716E+02	2.3664E-02	3.6478E-02	0.0000E+00	6.0141E-02
21	2.0000E-02	2.9024E+00	6.4033E+02	5.4715E+02	5.9078E-02	6.1821E-02	3.1341E-02	1.5224E-01
26	2.5000E-02	2.8134E+00	6.9615E+02	6.0029E+02	8.8045E-02	9.4580E-02	1.2065E-01	3.0327E-01

31	3.0000E-02	2.7214E+00	7.4818E+02	6.5330E+02	1.1143E-01	1.3364E-01	2.3550E-01	4.8057E-01
36	3.5000E-02	2.6281E+00	7.9648E+02	7.0433E+02	1.5704E-01	1.7662E-01	3.7928E-01	7.1294E-01
41	4.0000E-02	2.5351E+00	8.4472E+02	7.5404E+02	2.2250E-01	2.2082E-01	5.5329E-01	9.9662E-01
46	4.5000E-02	2.4437E+00	8.9228E+02	8.0274E+02	3.0086E-01	2.4802E-01	7.4551E-01	1.2944E+00
51	5.0000E-02	2.3553E+00	9.3792E+02	8.5057E+02	3.9317E-01	3.0233E-01	9.2002E-01	1.6155E+00
56	5.5000E-02	2.2719E+00	9.8107E+02	8.9755E+02	4.7302E-01	3.9302E-01	1.0003E+00	1.8663E+00
61	6.0000E-02	2.1955E+00	1.0196E+03	9.4254E+02	5.3547E-01	4.2876E-01	9.9014E-01	1.9544E+00
66	6.5000E-02	2.1280E+00	1.0527E+03	9.8440E+02	5.6476E-01	4.1409E-01	9.4422E-01	1.9231E+00
71	7.0000E-02	2.0721E+00	1.0799E+03	1.0225E+03	5.3952E-01	3.6556E-01	8.6729E-01	1.7724E+00
76	7.5000E-02	2.0277E+00	1.1014E+03	1.0560E+03	4.7176E-01	3.2546E-01	7.6260E-01	1.5598E+00
81	8.0000E-02	1.9944E+00	1.1173E+03	1.0846E+03	4.0471E-01	2.8666E-01	5.2235E-01	1.2137E+00
86	8.5000E-02	1.9698E+00	1.1285E+03	1.1076E+03	3.5179E-01	2.5345E-01	2.5874E-01	8.6398E-01

APPENDIX C-4: RESULTS – TEXAS LIGNITE, FINES (38 MINUS MICRON), OXIDIZING RUN

SMOOTHED DATA FOR TEMPERATURE

Grid.#	XGRID	TEMPERATURE
1	0.00000E+00	1.64360E+03
3	2.00000E-01	1.60392E+03
5	4.00000E-01	1.59495E+03
7	6.00000E-01	1.58125E+03
9	8.00000E-01	1.56433E+03
11	1.00000E+00	1.53658E+03
13	1.20000E+00	1.49609E+03
15	1.40000E+00	1.44400E+03
17	1.60000E+00	1.38008E+03
19	1.80000E+00	1.30470E+03
21	2.00000E+00	1.22161E+03
23	2.20000E+00	1.13200E+03
25	2.40000E+00	1.03686E+03
27	2.60000E+00	9.31588E+02
29	2.80000E+00	8.10199E+02
31	3.00000E+00	6.52000E+02
33	3.20000E+00	4.00000E+02

COMPOSITION MATRIX FOR THE SYSTEM

GRID.#	MF_O2	MF_CO	MF_CO2	MF_NO	MF_NH3	MF_HCN	MF_H2	MF_C2H4	MF_C2H6	MF_C2H2	MF_CH4	MF_OF_AR
1	5.80E-02	2.50E-02	3.90E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.27E-01
3	5.70E-02	2.49E-02	3.87E-01	1.47E-06	9.69E-09	9.08E-10	4.67E-04	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.30E-01
5	5.56E-02	2.45E-02	3.69E-01	3.83E-06	6.26E-08	1.06E-08	8.55E-04	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.50E-01
7	5.38E-02	2.35E-02	3.48E-01	7.18E-06	1.69E-07	8.67E-08	1.16E-03	0.00E+00	0.00E+00	2.37E-07	0.00E+00	5.74E-01
9	5.16E-02	2.18E-02	3.19E-01	1.13E-05	3.41E-07	2.97E-07	1.29E-03	0.00E+00	0.00E+00	1.75E-06	0.00E+00	6.06E-01
11	4.83E-02	1.96E-02	2.81E-01	2.14E-05	7.70E-07	1.37E-06	1.27E-03	4.53E-06	7.54E-07	5.21E-06	8.34E-06	6.50E-01
13	3.60E-02	1.71E-02	2.40E-01	4.05E-05	2.49E-06	3.22E-06	1.18E-03	2.85E-05	4.72E-06	2.37E-05	2.93E-05	7.06E-01
15	2.47E-02	1.43E-02	1.99E-01	6.27E-05	4.38E-06	6.62E-06	1.07E-03	5.75E-05	1.07E-05	5.01E-05	4.83E-05	7.60E-01

17	1.56E-02	1.14E-02	1.58E-01	6.16E-05	6.17E-06	2.02E-05	9.35E-04	8.67E-05	1.57E-05	7.55E-05	6.15E-05	8.13E-01
19	1.02E-02	8.38E-03	1.17E-01	4.91E-05	7.15E-06	3.19E-05	7.89E-04	1.05E-04	1.95E-05	9.07E-05	7.39E-05	8.63E-01
21	6.42E-03	5.47E-03	7.73E-02	3.80E-05	6.10E-06	2.57E-05	6.10E-04	1.04E-04	2.06E-05	9.19E-05	8.00E-05	9.10E-01
23	5.10E-03	3.02E-03	4.29E-02	2.66E-05	4.48E-06	1.77E-05	4.50E-04	7.68E-05	1.60E-05	7.76E-05	6.60E-05	9.48E-01
25	4.05E-03	1.87E-03	2.39E-02	1.53E-05	3.04E-06	1.06E-05	3.23E-04	4.84E-05	8.73E-06	4.77E-05	4.55E-05	9.70E-01
27	3.10E-03	1.30E-03	1.39E-02	8.63E-06	1.77E-06	6.04E-06	2.15E-04	2.47E-05	4.22E-06	2.09E-05	2.96E-05	9.81E-01
29	2.00E-03	9.00E-04	7.30E-03	4.25E-06	7.74E-07	3.37E-06	1.30E-04	8.11E-06	1.55E-06	7.37E-06	1.48E-05	9.90E-01
31	9.64E-04	4.01E-04	1.71E-03	2.09E-06	2.68E-07	1.55E-06	6.28E-05	6.30E-07	2.98E-07	1.77E-06	3.74E-06	9.97E-01
33	0.00E+00	0.00E+00	1.49E-10	0.00E+00	0.00E+00	2.38E-13	0.00E+00	0.00E+00	0.00E+00	4.77E-13	0.00E+00	1.00E+00

EVALUATION OF PHYSICAL PROPERTIES AT EACH GRID POINT

I	XGRID	SMTD TEMP	VISCOCITY	AVG MOL WT	THRL COND	MASS DENST	MOLR DENST	AV_MOLR_CP
1	0.0000E+00	1.6436E+03	6.4545E-04	4.0797E+01	1.1444E-04	3.0252E-04	7.4152E-06	8.8461E+00
3	2.0000E-01	1.6039E+03	6.3570E-04	4.0778E+01	1.1272E-04	3.0986E-04	7.5987E-06	8.7986E+00
5	4.0000E-01	1.5950E+03	6.3663E-04	4.0707E+01	1.1307E-04	3.1106E-04	7.6414E-06	8.6255E+00
7	6.0000E-01	1.5812E+03	6.3713E-04	4.0634E+01	1.1339E-04	3.1319E-04	7.7076E-06	8.4189E+00
9	8.0000E-01	1.5643E+03	6.3813E-04	4.0552E+01	1.1387E-04	3.1594E-04	7.7910E-06	8.1607E+00
11	1.0000E+00	1.5366E+03	6.3813E-04	4.0451E+01	1.1433E-04	3.2085E-04	7.9317E-06	7.8912E+00
13	1.2000E+00	1.4961E+03	6.3564E-04	4.0419E+01	1.1428E-04	3.2927E-04	8.1464E-06	7.6352E+00
15	1.4000E+00	1.4440E+03	6.2958E-04	4.0381E+01	1.1367E-04	3.4083E-04	8.4402E-06	7.5178E+00
17	1.6000E+00	1.3801E+03	6.1956E-04	4.0328E+01	1.1243E-04	3.5615E-04	8.8312E-06	8.3061E+00
19	1.8000E+00	1.3047E+03	6.0526E-04	4.0247E+01	1.1050E-04	3.7597E-04	9.3413E-06	8.8127E+00
21	2.0000E+00	1.2216E+03	5.8736E-04	4.0159E+01	1.0793E-04	4.0065E-04	9.9767E-06	7.7511E+00
23	2.2000E+00	1.1320E+03	5.6508E-04	4.0068E+01	1.0447E-04	4.3139E-04	1.0767E-05	6.6860E+00
25	2.4000E+00	1.0369E+03	5.3692E-04	4.0020E+01	9.9616E-05	4.7042E-04	1.1754E-05	5.9115E+00
27	2.6000E+00	9.3159E+02	5.0226E-04	4.0000E+01	9.3359E-05	5.2331E-04	1.3083E-05	5.0922E+00
29	2.8000E+00	8.1020E+02	4.5919E-04	3.9991E+01	8.5455E-05	6.0158E-04	1.5043E-05	5.0311E+00
31	3.0000E+00	6.5200E+02	3.9785E-04	3.9986E+01	7.4113E-05	7.4745E-04	1.8693E-05	4.9833E+00
33	3.2000E+00	4.0000E+02	2.8182E-04	3.9994E+01	5.2509E-05	1.2186E-03	3.0469E-05	4.9680E+00

CONVERGED VELOCITY AND PSI PROFILES

I	XGRID	VGZ PROFIL	PSI PROFIL
1	0.0000E+00	5.1178E+01	0.0000E+00
3	2.0000E-01	4.9596E+01	1.8499E+00

5	4.0000E-01	4.8300E+01	3.6898E+00
7	6.0000E-01	4.6134E+01	5.5259E+00
9	8.0000E-01	4.3168E+01	7.3675E+00
11	1.0000E+00	3.9211E+01	9.3004E+00
13	1.2000E+00	3.4129E+01	1.1465E+01
15	1.4000E+00	2.7990E+01	1.4057E+01
17	1.6000E+00	2.0668E+01	1.7610E+01
19	1.8000E+00	1.1759E+01	2.3251E+01
21	2.0000E+00	7.2365E-01	2.8833E+01
23	2.2000E+00	-1.0039E+01	2.3375E+01
25	2.4000E+00	-1.6032E+01	1.3426E+01
27	2.6000E+00	-1.8352E+01	8.3088E+00
29	2.8000E+00	-1.8427E+01	5.1851E+00
31	3.0000E+00	-1.6190E+01	2.5359E+00
33	3.2000E+00	-1.0292E+01	0.0000E+00

RATES OF FORMATION MATRIX FOR THE SYSTEM

I	XGRID	RFZ_D2	RFZ_CO	RFZ_CO2	RFZ_NO	RFZ_NH3	RFZ_HCN	RFZ_H2	RFZ_C2H4	RFZ_C2H6	RFZ_C2H2	RFZ_CH4
1	0.00E+00	-1.28E-06	4.43E-08	1.55E-05	1.77E-09	-1.25E-11	-5.26E-13	1.08E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00
3	2.00E-01	-1.76E-06	-3.49E-07	-2.29E-05	3.19E-09	5.26E-11	-2.31E-12	8.97E-07	0.00E+00	0.00E+00	0.00E+00	0.00E+00
5	4.00E-01	-2.34E-06	-9.61E-07	-2.85E-05	4.52E-09	1.28E-10	5.91E-11	7.77E-07	0.00E+00	0.00E+00	-1.36E-10	0.00E+00
7	6.00E-01	-2.96E-06	-2.15E-06	-3.40E-05	5.86E-09	2.16E-10	2.12E-10	7.94E-07	0.00E+00	0.00E+00	1.60E-09	0.00E+00
9	8.00E-01	-2.37E-06	-2.68E-06	-4.62E-05	4.17E-09	4.36E-11	-3.12E-11	2.39E-07	1.80E-09	-3.83E-10	1.83E-09	7.55E-09
11	1.00E+00	-1.27E-05	-3.21E-06	-5.06E-05	2.90E-08	2.01E-09	1.96E-09	-8.15E-08	2.06E-08	3.34E-09	1.38E-08	2.58E-08
13	1.20E+00	-1.47E-05	-3.07E-06	-4.58E-05	2.63E-08	2.41E-09	1.23E-09	-9.44E-08	3.29E-08	6.55E-09	2.90E-08	2.78E-08
15	1.40E+00	-1.07E-05	-2.84E-06	-3.91E-05	1.31E-08	1.90E-09	6.89E-09	-1.13E-07	2.83E-08	5.58E-09	2.79E-08	1.39E-08
17	1.60E+00	-5.66E-06	-2.21E-06	-2.93E-05	-8.99E-09	1.92E-09	1.31E-08	-1.06E-07	2.97E-08	2.95E-09	1.67E-08	9.92E-09
19	1.80E+00	-2.27E-06	-1.04E-06	-1.45E-05	-3.33E-09	1.27E-09	3.24E-09	-8.07E-08	6.43E-09	2.42E-09	4.99E-09	1.24E-08
21	2.00E+00	-9.28E-08	1.28E-08	2.97E-06	2.74E-09	2.80E-10	-8.99E-10	-9.01E-08	8.58E-09	4.03E-09	1.08E-08	1.29E-08
23	2.20E+00	7.18E-07	2.53E-07	7.09E-06	7.83E-09	9.47E-10	3.82E-09	2.55E-08	1.97E-08	3.47E-09	2.08E-08	8.61E-09
25	2.40E+00	9.00E-07	4.38E-07	7.27E-06	3.12E-09	1.08E-09	3.43E-09	8.12E-08	1.84E-08	3.43E-09	2.20E-08	1.48E-08
27	2.60E+00	1.18E-06	4.39E-07	6.19E-06	3.47E-09	9.60E-10	2.20E-09	4.38E-08	1.39E-08	1.98E-09	8.32E-09	1.54E-08
29	2.80E+00	1.20E-06	6.08E-07	5.22E-06	2.38E-09	4.29E-10	1.73E-09	8.91E-08	4.93E-09	9.28E-10	5.00E-09	9.69E-09
31	3.00E+00	9.16E-07	3.14E-07	-1.48E-07	2.12E-09	2.12E-10	1.33E-09	5.64E-08	-6.84E-11	3.51E-11	2.04E-10	2.18E-09
33	3.20E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

PARTICLE TRAJECTORY AND SURROUNDING GAS TEMPERATURE

I	TIME (sec)	GAS_TEMP	P_Z_POSITN	P_R_POSITN
1	0.0000E+00	4.0000E+02	3.2000E+00	2.0000E+00
6	5.0000E-03	5.1373E+02	3.1370E+00	2.0015E+00
11	1.0000E-02	6.0469E+02	3.0589E+00	2.0097E+00
16	1.5000E-02	6.8251E+02	2.9711E+00	2.0281E+00
21	2.0000E-02	7.5564E+02	2.8764E+00	2.0585E+00
26	2.5000E-02	8.2557E+02	2.7765E+00	2.1026E+00
31	3.0000E-02	8.8946E+02	2.6740E+00	2.1624E+00
36	3.5000E-02	9.4785E+02	2.5719E+00	2.2411E+00
41	4.0000E-02	1.0008E+03	2.4726E+00	2.3434E+00
46	4.5000E-02	1.0477E+03	2.3790E+00	2.4790E+00
51	5.0000E-02	1.0886E+03	2.2940E+00	2.6646E+00
56	5.5000E-02	1.1227E+03	2.2202E+00	2.9235E+00
61	6.0000E-02	1.1494E+03	2.1607E+00	3.2752E+00
66	6.5000E-02	1.1704E+03	2.1156E+00	3.7206E+00
71	7.0000E-02	1.1856E+03	2.0830E+00	4.2659E+00
76	7.5000E-02	1.1957E+03	2.0597E+00	4.9215E+00

DIMENSIONLESS PARAMETERS AND PARTICLE PROPERTIES

I	TIME (sec)	P_Z_POSITN	GAS_TEMP	REYNOLD #	PRANDTL #	NUSULT #	M_DOT	H.T_COEFF	BLOW_COEFF	VOLATILES
1	0.0000E+00	3.2000E+00	4.0000E+02	0.0000E+00	6.6669E-01	2.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
6	5.0000E-03	3.1370E+00	5.1373E+02	9.9987E-03	6.7675E-01	2.0574E+00	4.3452E-07	3.9806E-02	1.1902E-09	1.0207E-09
11	1.0000E-02	3.0589E+00	6.0469E+02	8.3941E-03	6.7871E-01	2.0527E+00	1.2746E-05	4.4539E-02	3.1167E-08	2.5279E-08
16	1.5000E-02	2.9711E+00	6.8251E+02	6.6987E-03	6.7503E-01	2.0470E+00	2.9308E-04	4.8286E-02	6.6114E-07	6.4314E-07
21	2.0000E-02	2.8764E+00	7.5564E+02	4.5589E-03	6.7507E-01	2.0250E+00	4.1835E-03	5.1746E-02	8.7621E-06	1.0214E-05
26	2.5000E-02	2.7765E+00	8.2557E+02	3.5421E-03	6.7601E-01	2.0342E+00	3.6580E-02	5.4936E-02	7.2485E-05	1.0501E-04
31	3.0000E-02	2.6740E+00	8.8946E+02	2.3923E-03	6.9279E-01	2.0280E+00	1.9757E-01	5.7419E-02	3.8285E-04	6.8226E-04
36	3.5000E-02	2.5719E+00	9.4785E+02	8.4330E-04	6.4906E-01	2.0152E+00	7.3968E-01	5.9384E-02	1.2905E-03	3.0668E-03
41	4.0000E-02	2.4726E+00	1.0008E+03	1.4213E-03	7.3186E-01	2.0182E+00	2.1044E+00	6.1399E-02	4.0013E-03	1.0414E-02
46	4.5000E-02	2.3790E+00	1.0477E+03	4.5719E-03	8.1224E-01	2.0311E+00	4.8599E+00	6.3511E-02	9.9694E-03	2.8554E-02
51	5.0000E-02	2.2940E+00	1.0886E+03	9.9973E-03	8.4348E-01	2.0419E+00	9.2902E+00	6.5321E-02	1.9339E-02	6.5517E-02
56	5.5000E-02	2.2202E+00	1.1227E+03	1.1153E-02	8.9203E-01	2.0337E+00	1.4742E+01	6.5963E-02	3.1916E-02	1.2825E-01

61	6.0000E-02	2.1607E+00	1.1494E+03	1.0359E-02	9.2436E-01	2.0215E+00	1.9106E+01	6.6294E-02	4.2294E-02	2.1606E-01
66	6.5000E-02	2.1156E+00	1.1704E+03	9.2141E-03	9.5581E-01	2.0165E+00	1.9532E+01	6.6664E-02	4.4319E-02	3.1487E-01
71	7.0000E-02	2.0830E+00	1.1856E+03	8.7720E-03	9.7646E-01	2.0249E+00	1.5197E+01	6.7344E-02	3.4986E-02	4.0108E-01
76	7.5000E-02	2.0597E+00	1.1957E+03	7.7782E-03	9.9727E-01	2.0365E+00	8.8153E+00	6.7997E-02	2.0644E-02	4.5788E-01

COAL PARTICLE HEAT UP

INITIAL COAL PARTICLE DENSITY (gm/cc) =	1.60
INITIAL COAL PARTICLE DIAMETER (centimeter) =	0.32E-02
INITIAL COAL PARTICLE TEMPERATURE (deg K) =	400.00
EMISSIVITY OF COAL =	0.70

COAL PARTICLE AND SURROUNDING GAS PHASE TEMPERATURES, AND PARTICLE DIAMETER AND DENSITY

I	TIME (sec)	GAS_TEMP	P_S_TEMP	P_C_TEMP	P_DIAMETER	P_DENSITY
1	0.0000E+00	4.0000E+02	4.0000E+02	4.0000E+02	3.2000E-03	1.6000E+00
6	5.0000E-03	5.1373E+02	4.3275E+02	4.2892E+02	3.2000E-03	1.6000E+00
11	1.0000E-02	6.0469E+02	4.9115E+02	4.8505E+02	3.2000E-03	1.6000E+00
16	1.5000E-02	6.8251E+02	5.5699E+02	5.4996E+02	3.2000E-03	1.6000E+00
21	2.0000E-02	7.5564E+02	6.2843E+02	6.2031E+02	3.2000E-03	1.6000E+00
26	2.5000E-02	8.2557E+02	7.0071E+02	6.9226E+02	3.2000E-03	1.5998E+00
31	3.0000E-02	8.8946E+02	7.6948E+02	7.6108E+02	3.2000E-03	1.5989E+00
36	3.5000E-02	9.4785E+02	8.3391E+02	8.2571E+02	3.2000E-03	1.5951E+00
41	4.0000E-02	1.0008E+03	8.9408E+02	8.8614E+02	3.2000E-03	1.5833E+00
46	4.5000E-02	1.0477E+03	9.5051E+02	9.4301E+02	3.2000E-03	1.5543E+00
51	5.0000E-02	1.0886E+03	1.0030E+03	9.9617E+02	3.2000E-03	1.4952E+00
56	5.5000E-02	1.1227E+03	1.0512E+03	1.0455E+03	3.2000E-03	1.3948E+00
61	6.0000E-02	1.1494E+03	1.0952E+03	1.0908E+03	3.2000E-03	1.2543E+00
66	6.5000E-02	1.1704E+03	1.1336E+03	1.1306E+03	3.2000E-03	1.0962E+00
71	7.0000E-02	1.1856E+03	1.1645E+03	1.1628E+03	3.2000E-03	9.5827E-01
75	7.4000E-02	1.1941E+03	1.1821E+03	1.1811E+03	3.2000E-03	8.8150E-01

RATES OF FORMATION OF NITROGENOUS SPECIES AS A FUNCTION OF TIME AND AXIAL POSITION OF PARTICLE

I	TIME (sec)	P_Z_POSITN	RFT_NO	RFT_NH3	RFT_HCN	RFT_H2	RFT_CH4	RFT_C2H2	RFT_C2H4	RFT_C2H6
1	0.0000E+00	3.2000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00

6	5.0000E-03	3.1370E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	3.5750E-12	0.0000E+00
11	1.0000E-02	3.0589E+00	9.0806E-10	8.4784E-11	5.5613E-10	2.3200E-08	8.1523E-10	0.0000E+00	-2.1178E-11	0.0000E+00	0.0000E+00
16	1.5000E-02	2.9711E+00	2.1885E-09	2.5639E-10	1.1844E-09	6.3024E-08	2.8676E-09	7.3847E-10	-1.1520E-10	1.2746E-10	0.0000E+00
21	2.0000E-02	2.8764E+00	2.3252E-09	3.7186E-10	1.6369E-09	8.0487E-08	5.8451E-09	3.4727E-09	1.8306E-09	5.7293E-10	0.0000E+00
26	2.5000E-02	2.7765E+00	2.3023E-09	4.5117E-10	1.7711E-09	6.3268E-08	1.0758E-08	5.2885E-09	5.8856E-09	1.0347E-09	0.0000E+00
31	3.0000E-02	2.6740E+00	2.2516E-09	6.3362E-10	1.9745E-09	4.4745E-08	1.4559E-08	6.0592E-09	1.0183E-08	1.5060E-09	0.0000E+00
36	3.5000E-02	2.5719E+00	3.9594E-09	8.7824E-10	2.3133E-09	4.9645E-08	1.5659E-08	1.0071E-08	1.4358E-08	2.1953E-09	0.0000E+00
41	4.0000E-02	2.4726E+00	4.9883E-09	1.0606E-09	2.8879E-09	7.2075E-08	1.5715E-08	1.6901E-08	1.7615E-08	2.9779E-09	0.0000E+00
46	4.5000E-02	2.3790E+00	5.4168E-09	1.0849E-09	3.4882E-09	7.9364E-08	1.4472E-08	2.1490E-08	1.8738E-08	3.5122E-09	0.0000E+00
51	5.0000E-02	2.2940E+00	5.8073E-09	1.0996E-09	3.5520E-09	5.6737E-08	1.2453E-08	2.2821E-08	2.0439E-08	3.5878E-09	0.0000E+00
56	5.5000E-02	2.2202E+00	7.5767E-09	1.0030E-09	3.7594E-09	3.2023E-08	1.1114E-08	2.1205E-08	2.0511E-08	3.5621E-09	0.0000E+00
61	6.0000E-02	2.1607E+00	7.4677E-09	8.2374E-10	4.1592E-09	2.2580E-08	1.0842E-08	2.0015E-08	1.7680E-08	3.5710E-09	0.0000E+00
66	6.5000E-02	2.1156E+00	6.1482E-09	6.7584E-10	4.6806E-09	2.3998E-08	1.5502E-08	1.9011E-08	1.5165E-08	3.6966E-09	0.0000E+00
71	7.0000E-02	2.0830E+00	5.2205E-09	5.6603E-10	4.2676E-09	9.5086E-09	1.6297E-08	1.7627E-08	1.3288E-08	3.7864E-09	0.0000E+00
75	7.4000E-02	2.0637E+00	4.6324E-09	5.0048E-10	3.2004E-09	-1.1850E-08	1.4939E-08	1.6268E-08	1.2209E-08	3.8444E-09	0.0000E+00

NORMALIZED RATES OF FORMATION OF NITROGENOUS SPECIES AS A FUNCTION TIME
(G_ATOM N/G_ATOM INITIAL-VOLATILE_N *SEC))

I	TIME (sec)	P_Z_POSITN	GAS_TMPRTR	P_S_TMPRTR	NRFT_NO	NRFT_NH3	NRFT_HCN	NRFT_TO_XN
1	0.0000E+00	3.2000E+00	4.0000E+02	4.0000E+02	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
6	5.0000E-03	3.1370E+00	5.1373E+02	4.3275E+02	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
11	1.0000E-02	3.0589E+00	6.0469E+02	4.9115E+02	1.5585E-01	1.4551E-02	9.5446E-02	2.6584E-01
16	1.5000E-02	2.9711E+00	6.8251E+02	5.5699E+02	4.2395E-01	4.9666E-02	2.2943E-01	7.0304E-01
21	2.0000E-02	2.8764E+00	7.5564E+02	6.2843E+02	4.9867E-01	7.9752E-02	3.5105E-01	9.2947E-01
26	2.5000E-02	2.7765E+00	8.2557E+02	7.0071E+02	5.3945E-01	1.0571E-01	4.1500E-01	1.0602E+00
31	3.0000E-02	2.6740E+00	8.8946E+02	7.6948E+02	5.6842E-01	1.5996E-01	4.9845E-01	1.2268E+00
36	3.5000E-02	2.5719E+00	9.4785E+02	8.3391E+02	1.0652E+00	2.3626E-01	6.2232E-01	1.9237E+00
41	4.0000E-02	2.4726E+00	1.0008E+03	8.9408E+02	1.4169E+00	3.0126E-01	8.2032E-01	2.5385E+00
46	4.5000E-02	2.3790E+00	1.0477E+03	9.5051E+02	1.6107E+00	3.2258E-01	1.0372E+00	2.9705E+00
51	5.0000E-02	2.2940E+00	1.0886E+03	1.0030E+03	1.7943E+00	3.3973E-01	1.0974E+00	3.2314E+00
56	5.5000E-02	2.2202E+00	1.1227E+03	1.0512E+03	2.4142E+00	3.1958E-01	1.1979E+00	3.9317E+00
61	6.0000E-02	2.1607E+00	1.1494E+03	1.0952E+03	2.4362E+00	2.6873E-01	1.3569E+00	4.0618E+00
66	6.5000E-02	2.1156E+00	1.1704E+03	1.1336E+03	2.0424E+00	2.2451E-01	1.5549E+00	3.8218E+00
71	7.0000E-02	2.0830E+00	1.1856E+03	1.1645E+03	1.7567E+00	1.9047E-01	1.4360E+00	3.3832E+00
75	7.4000E-02	2.0637E+00	1.1941E+03	1.1821E+03	1.5700E+00	1.6962E-01	1.0847E+00	2.8242E+00

APPENDIX C-5: RESULTS – ILLINOIS BITUMINOUS, FINES (38 MINUS MICRON), REDUCING RUN

SMOOTHED DATA FOR TEMPERATURE

Grid.#	XGRID	TEMPERATURE
1	0.00000E+00	1.50690E+03
3	2.00000E-01	1.49653E+03
5	4.00000E-01	1.48164E+03
7	6.00000E-01	1.46241E+03
9	8.00000E-01	1.43900E+03
11	1.00000E+00	1.40990E+03
13	1.20000E+00	1.37326E+03
15	1.40000E+00	1.32894E+03
17	1.60000E+00	1.27715E+03
19	1.80000E+00	1.21576E+03
21	2.00000E+00	1.14296E+03
23	2.20000E+00	1.05844E+03
25	2.40000E+00	9.58000E+02
27	2.60000E+00	8.31712E+02
29	2.80000E+00	6.85020E+02
31	3.00000E+00	5.42000E+02
33	3.20000E+00	4.00000E+02

COMPOSITION MATRIX FOR THE SYSTEM

GRID.#	MF_O2	MF_CO	MF_CO2	MF_NO	MF_NH3	MF_HCN	MF_H2	MF_C2H4	MF_C2H6	MF_C2H2	MF_CH4	MF_DF_AR
1	5.00E-03	1.25E-01	3.25E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.45E-01
3	2.40E-03	1.27E-01	3.36E-01	7.70E-06	8.30E-07	6.71E-07	5.47E-03	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.29E-01
5	2.08E-03	1.27E-01	3.38E-01	1.54E-05	1.87E-06	1.73E-06	9.34E-03	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.23E-01
7	1.94E-03	1.26E-01	3.37E-01	2.24E-05	3.08E-06	3.34E-06	1.13E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.24E-01
9	1.82E-03	1.23E-01	3.29E-01	2.88E-05	4.46E-06	5.88E-06	1.12E-02	5.15E-06	0.00E+00	5.11E-06	3.11E-06	5.35E-01
11	1.72E-03	1.18E-01	3.11E-01	3.42E-05	5.83E-06	9.19E-06	7.50E-03	2.89E-05	5.02E-06	4.32E-05	7.15E-05	5.61E-01
13	1.62E-03	1.12E-01	2.79E-01	3.72E-05	7.49E-06	1.38E-05	1.45E-03	5.97E-05	1.43E-05	9.88E-05	1.53E-04	6.06E-01
15	1.53E-03	1.01E-01	2.37E-01	3.65E-05	9.64E-06	3.14E-05	6.74E-04	7.96E-05	2.23E-05	1.79E-04	2.21E-04	6.59E-01

17	1.50E-03	8.37E-02	1.90E-01	3.15E-05	1.12E-05	4.72E-05	5.26E-04	9.08E-05	2.62E-05	2.26E-04	2.34E-04	7.24E-01
19	1.50E-03	6.37E-02	1.44E-01	2.33E-05	9.74E-06	4.16E-05	4.01E-04	8.28E-05	2.33E-05	1.48E-04	1.73E-04	7.90E-01
21	1.50E-03	4.39E-02	9.72E-02	1.54E-05	7.61E-06	3.14E-05	3.02E-04	5.64E-05	1.85E-05	7.75E-05	1.19E-04	8.57E-01
23	1.40E-03	2.59E-02	4.80E-02	9.15E-06	5.83E-06	2.06E-05	2.15E-04	4.14E-05	1.36E-05	5.32E-05	8.80E-05	9.24E-01
25	1.18E-03	1.15E-02	8.18E-03	5.00E-06	4.17E-06	1.17E-05	1.43E-04	2.83E-05	9.24E-06	3.84E-05	5.84E-05	9.79E-01
27	8.88E-04	4.74E-03	3.31E-03	2.98E-06	2.54E-06	6.55E-06	7.69E-05	1.60E-05	5.56E-06	2.61E-05	3.28E-05	9.91E-01
29	5.61E-04	1.81E-03	1.67E-03	1.70E-06	1.42E-06	2.84E-06	1.25E-05	4.66E-06	2.49E-06	1.49E-05	1.33E-05	9.96E-01
31	2.68E-04	4.06E-04	8.31E-04	7.62E-07	8.70E-07	7.70E-07	0.00E+00	2.12E-07	5.40E-07	5.86E-06	1.39E-06	9.98E-01
33	0.00E+00	1.49E-11	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.38E-13	1.00E+00

EVALUATION OF PHYSICAL PROPERTIES AT EACH GRID POINT

I	XGRID	SMTHD TEMP	VISCOCITY	AVG MOL WT	THRLM COND	MASS DENST	MOLR DENST	AV_MOLR_CP
1	0.0000E+00	1.5069E+03	6.1033E-04	3.9762E+01	1.1109E-04	3.2159E-04	8.0879E-06	8.3321E+00
3	2.0000E-01	1.4985E+03	6.0441E-04	3.9594E+01	1.0989E-04	3.2245E-04	8.1440E-06	8.5044E+00
5	4.0000E-01	1.4816E+03	5.9929E-04	3.9452E+01	1.0894E-04	3.2452E-04	8.2258E-06	8.6263E+00
7	6.0000E-01	1.4624E+03	5.9421E-04	3.9392E+01	1.0798E-04	3.2830E-04	8.3340E-06	8.7586E+00
9	8.0000E-01	1.4390E+03	5.8976E-04	3.9403E+01	1.0717E-04	3.3372E-04	8.4696E-06	8.9005E+00
11	1.0000E+00	1.4099E+03	5.8623E-04	3.9527E+01	1.0662E-04	3.4168E-04	8.6444E-06	9.0030E+00
13	1.2000E+00	1.3733E+03	5.8367E-04	3.9699E+01	1.0641E-04	3.5233E-04	8.8750E-06	9.0539E+00
15	1.4000E+00	1.3289E+03	5.7975E-04	3.9681E+01	1.0602E-04	3.6392E-04	9.1710E-06	1.0138E+01
17	1.6000E+00	1.2772E+03	5.7488E-04	3.9711E+01	1.0538E-04	3.7896E-04	9.5429E-06	1.0889E+01
19	1.8000E+00	1.2158E+03	5.6686E-04	3.9774E+01	1.0418E-04	3.9873E-04	1.0025E-05	9.7640E+00
21	2.0000E+00	1.1430E+03	5.5462E-04	3.9830E+01	1.0231E-04	4.2471E-04	1.0663E-05	8.3076E+00
23	2.2000E+00	1.0584E+03	5.3750E-04	3.9853E+01	9.9697E-05	4.5889E-04	1.1515E-05	6.8897E+00
25	2.4000E+00	9.5800E+02	5.1140E-04	3.9871E+01	9.5345E-05	5.0724E-04	1.2722E-05	5.0722E+00
27	2.6000E+00	8.3171E+02	4.6746E-04	3.9939E+01	8.7124E-05	5.8525E-04	1.4654E-05	5.0095E+00
29	2.8000E+00	6.8502E+02	4.1125E-04	3.9973E+01	7.6630E-05	7.1119E-04	1.7792E-05	4.9858E+00
31	3.0000E+00	5.4200E+02	3.5048E-04	3.9990E+01	6.5298E-05	8.9924E-04	2.2487E-05	4.9746E+00
33	3.2000E+00	4.0000E+02	2.8182E-04	3.9994E+01	5.2509E-05	1.2186E-03	3.0469E-05	4.9680E+00

CONVERGED VELOCITY AND PSI PROFILES

I	XGRID	VGZ PROFIL	PSI PROFIL
1	0.0000E+00	4.2327E+01	0.0000E+00
3	2.0000E-01	4.1872E+01	1.7159E+00

5	4.0000E-01	4.0577E+01	3.4450E+00
7	6.0000E-01	3.8394E+01	5.2026E+00
9	8.0000E-01	3.5352E+01	7.0092E+00
11	1.0000E+00	3.1391E+01	8.9288E+00
13	1.2000E+00	2.6520E+01	1.1062E+01
15	1.4000E+00	2.0851E+01	1.3663E+01
17	1.6000E+00	1.4007E+01	1.7544E+01
19	1.8000E+00	5.4224E+00	2.3143E+01
21	2.0000E+00	-4.5784E+00	2.4273E+01
23	2.2000E+00	-1.2235E+01	1.6381E+01
25	2.4000E+00	-1.5865E+01	1.0061E+01
27	2.6000E+00	-1.6770E+01	6.6248E+00
29	2.8000E+00	-1.5713E+01	4.1068E+00
31	3.0000E+00	-1.3491E+01	1.9842E+00
33	3.2000E+00	-1.0292E+01	0.0000E+00

RA1ES OF FORMATION MATRIX FOR THE SYSTEM

I	XGRID	RFZ_O2	RFZ_CO	RFZ_CO2	RFZ_NO	RFZ_NH3	RFZ_HCN	RFZ_H2	RFZ_C2H4	RFZ_C2H6	RFZ_C2H2	RFZ_CH4
1	0.00E+00	-7.07E-06	5.38E-06	2.70E-05	1.12E-08	1.12E-09	7.04E-10	1.26E-05	0.00E+00	0.00E+00	0.00E+00	0.00E+00
3	2.00E-01	-5.65E-07	2.24E-06	5.24E-06	1.12E-08	1.45E-09	1.27E-09	1.04E-05	0.00E+00	0.00E+00	0.00E+00	0.00E+00
5	4.00E-01	-2.49E-07	-1.44E-06	1.84E-06	1.05E-08	1.63E-09	1.85E-09	7.70E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00
7	6.00E-01	-1.64E-07	-3.18E-06	-7.20E-06	8.89E-09	1.95E-09	2.81E-09	4.73E-06	2.61E-09	0.00E+00	-3.26E-09	-3.51E-09
9	8.00E-01	-1.41E-07	-5.53E-06	-1.41E-05	7.87E-09	1.79E-09	3.54E-09	8.81E-06	2.03E-08	4.51E-09	3.50E-08	5.62E-08
11	1.00E+00	-1.26E-07	-6.09E-06	-3.29E-05	4.82E-09	1.45E-09	3.58E-09	-1.41E-05	3.40E-08	1.08E-08	5.81E-08	9.74E-08
13	1.20E+00	-9.71E-08	-7.54E-06	-3.87E-05	1.67E-09	2.27E-09	1.38E-08	-5.89E-06	2.56E-08	7.83E-09	7.48E-08	7.70E-08
15	1.40E+00	-7.42E-08	-1.02E-05	-3.65E-05	-1.36E-09	2.11E-09	1.82E-08	-2.23E-07	1.19E-08	7.20E-09	9.44E-08	7.32E-08
17	1.60E+00	-1.14E-09	-9.93E-06	-2.22E-05	-3.11E-09	9.73E-10	1.82E-09	-1.50E-07	1.19E-08	1.10E-10	-1.19E-08	-2.22E-08
19	1.80E+00	1.78E-09	-8.05E-07	-6.77E-07	-7.43E-10	-1.21E-10	6.51E-10	-4.89E-08	-4.91E-09	-2.31E-10	-3.60E-08	-2.74E-08
21	2.00E+00	1.19E-07	6.65E-06	2.27E-05	1.79E-09	5.75E-10	4.68E-09	1.94E-08	6.37E-09	2.28E-09	9.46E-09	1.44E-08
23	2.20E+00	2.13E-07	9.02E-06	1.67E-05	2.35E-09	1.34E-09	5.21E-09	2.54E-08	9.62E-09	2.75E-09	7.85E-09	2.15E-08
25	2.40E+00	3.18E-07	3.05E-06	2.38E-06	1.12E-09	1.53E-09	3.67E-09	6.32E-08	1.11E-08	3.17E-09	1.12E-08	2.31E-08
27	2.60E+00	3.37E-07	2.31E-06	6.19E-07	1.19E-09	7.50E-10	3.29E-09	6.72E-08	1.07E-08	2.53E-09	1.04E-08	1.82E-08
29	2.80E+00	2.98E-07	1.32E-06	7.59E-07	9.51E-10	7.05E-10	1.48E-09	-5.07E-08	1.88E-09	1.38E-09	7.89E-09	8.55E-09
31	3.00E+00	2.52E-07	-5.52E-08	6.59E-07	6.62E-10	9.55E-10	4.45E-10	0.00E+00	5.92E-11	1.74E-10	4.30E-09	-2.68E-10
33	3.20E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

PARTICLE TRAJECTORY AND SURROUNDING GAS TEMPERATURE

I	TIME (sec)	GAS_TEMP	P_Z_POSITN	P_R_POSITN
1	0.0000E+00	4.0000E+02	3.2000E+00	2.0000E+00
6	5.0000E-03	4.4131E+02	3.1403E+00	2.0012E+00
11	1.0000E-02	4.9009E+02	3.0720E+00	2.0074E+00
16	1.5000E-02	5.4353E+02	2.9983E+00	2.0205E+00
21	2.0000E-02	6.0034E+02	2.9197E+00	2.0413E+00
26	2.5000E-02	6.6068E+02	2.8368E+00	2.0709E+00
31	3.0000E-02	7.2448E+02	2.7501E+00	2.1105E+00
36	3.5000E-02	7.8926E+02	2.6603E+00	2.1618E+00
41	4.0000E-02	8.5237E+02	2.5686E+00	2.2270E+00
46	4.5000E-02	9.1192E+02	2.4769E+00	2.3089E+00
51	5.0000E-02	9.6589E+02	2.3874E+00	2.4118E+00
56	5.5000E-02	1.0106E+03	2.3023E+00	2.5418E+00
61	6.0000E-02	1.0479E+03	2.2237E+00	2.7101E+00
66	6.5000E-02	1.0791E+03	2.1541E+00	2.9327E+00
71	7.0000E-02	1.1051E+03	2.0954E+00	3.2202E+00
76	7.5000E-02	1.1240E+03	2.0479E+00	3.5884E+00
81	8.0000E-02	1.1381E+03	2.0122E+00	4.0259E+00
86	8.5000E-02	1.1492E+03	1.9851E+00	4.5466E+00
89	8.8000E-02	1.1548E+03	1.9718E+00	4.9019E+00

DIMENSIONLESS PARAMETERS AND PARTICLE PROPERTIES

I	TIME (sec)	P_Z_POSITN	GAS_TEMP	REYNOLD #	PRANDTL #	NUSULT #	M_DOT	H_T_COEFF	BLOW_COEFF	VOLATILES
1	0.0000E+00	3.2000E+00	4.0000E+02	0.0000E+00	6.6669E-01	2.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
6	5.0000E-03	3.1403E+00	4.4131E+02	1.8571E-02	6.7090E-01	2.0780E+00	3.3517E-17	3.7613E-02	8.3806E-20	8.5317E-20
11	1.0000E-02	3.0720E+00	4.9009E+02	1.5267E-02	6.7354E-01	2.0708E+00	1.7350E-15	4.0323E-02	4.0341E-18	2.9925E-18
16	1.5000E-02	2.9983E+00	5.4353E+02	1.0744E-02	6.7336E-01	2.0594E+00	2.8489E-13	4.3196E-02	6.1549E-16	4.3894E-16
21	2.0000E-02	2.9197E+00	6.0034E+02	8.7719E-03	6.6941E-01	2.0536E+00	5.3959E-11	4.6299E-02	1.0855E-13	8.3712E-14
26	2.5000E-02	2.8368E+00	6.6068E+02	6.4594E-03	6.7083E-01	2.0460E+00	6.9328E-09	4.9104E-02	1.3113E-11	1.1346E-11
31	3.0000E-02	2.7501E+00	7.2448E+02	4.5485E-03	6.7334E-01	2.0387E+00	5.5776E-07	5.1995E-02	9.9537E-10	9.7177E-10
36	3.5000E-02	2.6603E+00	7.8926E+02	3.0541E-03	6.6963E-01	2.0316E+00	2.8924E-05	5.5057E-02	4.8390E-08	5.3831E-08
41	4.0000E-02	2.5686E+00	8.5237E+02	1.7987E-03	6.8936E-01	2.0245E+00	8.9370E-04	5.7822E-02	1.4612E-06	1.8320E-06

46	4.5000E-02	2.4769E+00	9.1192E+02	6.9682E-04	6.2111E-01	2.0147E+00	1.5481E-02	5.9871E-02	2.1822E-05	3.6238E-05
51	5.0000E-02	2.3874E+00	9.6589E+02	1.5674E-04	7.1725E-01	2.0066E+00	1.5565E-01	6.1720E-02	2.4453E-04	4.2692E-04
56	5.5000E-02	2.3023E+00	1.0106E+03	3.5451E-03	8.4138E-01	2.0348E+00	1.0179E+00	6.4249E-02	1.8356E-03	3.2645E-03
61	6.0000E-02	2.2237E+00	1.0479E+03	6.1325E-03	9.1563E-01	2.0410E+00	4.4079E+00	6.5058E-02	8.4814E-03	1.6965E-02
66	6.5000E-02	2.1541E+00	1.0791E+03	7.5711E-03	9.7315E-01	2.0294E+00	1.3220E+01	6.4659E-02	2.6411E-02	6.2737E-02
71	7.0000E-02	2.0954E+00	1.1051E+03	1.3381E-02	1.0341E+00	2.0197E+00	2.6932E+01	6.3335E-02	5.5234E-02	1.6953E-01
76	7.5000E-02	2.0479E+00	1.1240E+03	6.2144E-03	1.0821E+00	1.9893E+00	3.0402E+01	6.0641E-02	6.2637E-02	3.2494E-01
81	8.0000E-02	2.0122E+00	1.1381E+03	5.4185E-03	1.1183E+00	2.0311E+00	8.8826E+00	6.0983E-02	1.8457E-02	4.1637E-01
86	8.5000E-02	1.9851E+00	1.1492E+03	5.2118E-03	1.1478E+00	2.0487E+00	2.4262E-01	6.1571E-02	5.1410E-04	4.2688E-01
89	8.8000E-02	1.9718E+00	1.1548E+03	5.3258E-03	1.1617E+00	2.0502E+00	6.2958E-03	6.1683E-02	1.3481E-05	4.2700E-01

COAL PARTICLE HEAT UP

INITIAL COAL PARTICLE DENSITY (gm/cc) =	1.41
INITIAL COAL PARTICLE DIAMETER (centimeter) =	0.31E-02
INITIAL COAL PARTICLE TEMPERATURE (deg K) =	400.00
EMISSIVITY OF COAL =	0.70

COAL PARTICLE AND SURROUNDING GAS PHASE TEMPERATURES, AND PARTICLE DIAMETER AND DENSITY

I	TIME (sec)	GAS_TEMP	P_S_TEMP	P_C_TEMP	P_DIAMETER	P_DENSITY
1	0.0000E+00	4.0000E+02	4.0000E+02	4.0000E+02	3.1000E-03	1.4100E+00
6	5.0000E-03	4.4131E+02	4.1174E+02	4.1046E+02	3.1000E-03	1.4100E+00
11	1.0000E-02	4.9009E+02	4.3977E+02	4.3742E+02	3.1000E-03	1.4100E+00
16	1.5000E-02	5.4353E+02	4.7935E+02	4.7611E+02	3.1000E-03	1.4100E+00
21	2.0000E-02	6.0034E+02	5.2673E+02	5.2280E+02	3.1000E-03	1.4100E+00
26	2.5000E-02	6.6068E+02	5.7918E+02	5.7464E+02	3.1000E-03	1.4100E+00
31	3.0000E-02	7.2448E+02	6.3637E+02	6.3117E+02	3.1000E-03	1.4100E+00
36	3.5000E-02	7.8926E+02	6.9825E+02	6.9238E+02	3.1000E-03	1.4100E+00
41	4.0000E-02	8.5237E+02	7.6215E+02	7.5584E+02	3.1000E-03	1.4100E+00
46	4.5000E-02	9.1192E+02	8.2429E+02	8.1796E+02	3.1000E-03	1.4099E+00
51	5.0000E-02	9.6589E+02	8.8259E+02	8.7643E+02	3.1003E-03	1.4090E+00
56	5.5000E-02	1.0106E+03	9.3606E+02	9.3042E+02	3.1024E-03	1.4022E+00
61	6.0000E-02	1.0479E+03	9.8337E+02	9.7839E+02	3.1123E-03	1.3697E+00
66	6.5000E-02	1.0791E+03	1.0251E+03	1.0209E+03	3.1455E-03	1.2650E+00
71	7.0000E-02	1.1051E+03	1.0634E+03	1.0602E+03	3.2231E-03	1.0419E+00

76	7.5000E-02	1.1240E+03	1.0995E+03	1.0976E+03	3.3359E-03	7.6384E-01
81	8.0000E-02	1.1381E+03	1.1275E+03	1.1266E+03	3.4023E-03	6.2249E-01
86	8.5000E-02	1.1492E+03	1.1441E+03	1.1437E+03	3.4099E-03	6.0718E-01
88	8.7000E-02	1.1530E+03	1.1486E+03	1.1482E+03	3.4100E-03	6.0702E-01

RATES OF FORMATION OF NITROGENOUS SPECIES AS A FUNCTION OF TIME AND AXIAL POSITION OF PARTICLE

I	TIME (sec)	P_Z_POSITN	RFT_NO	RFT_NH3	RFT_HCN	RFT_H2	RFT_CH4	RFT_C2H2	RFT_C2H4	RFT_C2H6
1	0.0000E+00	3.2000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
6	5.0000E-03	3.1403E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	1.6569E-11	0.0000E+00	0.0000E+00	0.0000E+00
11	1.0000E-02	3.0720E+00	1.6915E-10	2.4077E-10	1.2079E-10	0.0000E+00	-4.8918E-11	1.0997E-09	1.1159E-11	2.3375E-11
16	1.5000E-02	2.9983E+00	6.6551E-10	6.5144E-10	4.5230E-10	0.0000E+00	-2.6966E-10	4.3259E-09	6.0261E-11	1.7912E-10
21	2.0000E-02	2.9197E+00	8.1349E-10	9.8663E-10	7.6826E-10	0.0000E+00	1.1408E-09	5.5518E-09	1.6926E-10	5.4775E-10
26	2.5000E-02	2.8368E+00	9.1438E-10	7.9671E-10	1.2111E-09	0.0000E+00	6.0863E-09	7.1927E-09	9.3312E-10	1.1218E-09
31	3.0000E-02	2.7501E+00	9.5632E-10	5.6318E-10	1.8915E-09	0.0000E+00	1.2366E-08	8.6904E-09	3.7038E-09	1.7307E-09
36	3.5000E-02	2.6603E+00	1.0516E-09	4.6442E-10	2.7070E-09	0.0000E+00	1.6244E-08	9.8163E-09	8.0875E-09	2.2838E-09
41	4.0000E-02	2.5686E+00	1.2499E-09	9.3455E-10	3.5121E-09	3.4740E-08	1.8914E-08	1.0698E-08	1.0081E-08	2.6984E-09
46	4.5000E-02	2.4769E+00	1.3198E-09	1.4123E-09	3.7659E-09	6.4435E-08	2.1101E-08	1.1207E-08	1.0929E-08	3.1237E-09
51	5.0000E-02	2.3874E+00	1.4571E-09	1.5375E-09	4.0019E-09	6.2784E-08	2.3352E-08	1.1154E-08	1.1123E-08	3.1750E-09
56	5.5000E-02	2.3023E+00	1.6893E-09	1.5282E-09	4.3652E-09	5.3992E-08	2.3220E-08	1.0762E-08	1.0891E-08	3.1465E-09
61	6.0000E-02	2.2237E+00	2.2039E-09	1.3870E-09	5.0105E-09	3.0997E-08	2.1897E-08	8.3143E-09	9.9278E-09	2.9966E-09
66	6.5000E-02	2.1541E+00	2.4806E-09	1.2453E-09	5.6348E-09	1.9745E-08	2.0762E-08	7.8441E-09	8.9532E-09	2.8318E-09
71	7.0000E-02	2.0954E+00	2.3742E-09	1.0780E-09	6.1159E-09	1.6470E-08	1.9829E-08	9.3435E-09	8.0510E-09	2.9059E-09
76	7.5000E-02	2.0479E+00	2.1653E-09	8.3782E-10	5.6663E-09	1.8238E-08	1.8412E-08	1.1044E-08	7.2706E-09	2.6555E-09
81	8.0000E-02	2.0122E+00	1.9033E-09	6.3707E-10	4.9247E-09	1.9669E-08	1.5758E-08	1.0966E-08	6.6124E-09	2.3848E-09
86	8.5000E-02	1.9851E+00	1.6414E-09	4.9954E-10	4.3882E-09	1.8598E-08	1.2285E-08	7.3010E-09	5.5735E-09	2.1488E-09
88	8.7000E-02	1.9760E+00	1.5366E-09	4.6083E-10	4.2198E-09	1.7424E-08	1.0714E-08	4.8809E-09	5.0515E-09	2.0635E-09

NORMALIZED RATES OF FORMATION OF NITROGENOUS SPECIES AS A FUNCTION TIME (G_ATOM N/G_ATOM INITIAL_VOLATILE_N *SEC))

I	TIME (sec)	P_Z_POSITN	GAS_TMPRTR	P_S_TMPRTR	NRFT_NO	NRFT_NH3	NRFT_HCN	NRFT_TO_XN
1	0.0000E+00	3.2000E+00	4.0000E+02	4.0000E+02	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
6	5.0000E-03	3.1403E+00	4.4131E+02	4.1174E+02	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
11	1.0000E-02	3.0720E+00	4.9009E+02	4.3977E+02	2.8611E-02	4.0726E-02	2.0431E-02	8.9768E-02
16	1.5000E-02	2.9983E+00	5.4353E+02	4.7935E+02	1.2484E-01	1.2220E-01	8.4848E-02	3.3190E-01

21	2.9000E-02	2.9197E+00	6.0034E+02	5.2673E+02	1.6855E-01	2.0443E-01	1.5918E-01	5.3216E-01
26	2.5000E-02	2.8368E+00	6.6068E+02	5.7918E+02	2.0850E-01	1.8167E-01	2.7616E-01	6.6633E-01
31	3.0000E-02	2.7501E+00	7.2448E+02	6.3637E+02	2.3912E-01	1.4082E-01	4.7294E-01	8.5288E-01
36	3.5000E-02	2.6603E+00	7.8926E+02	6.9825E+02	2.8646E-01	1.2651E-01	7.3739E-01	1.1504E+00
41	4.0000E-02	2.5686E+00	8.5237E+02	7.6215E+02	3.6769E-01	2.7493E-01	1.0332E+00	1.6758E+00
46	4.5000E-02	2.4769E+00	9.1192E+02	8.2429E+02	4.1539E-01	4.4449E-01	1.1853E+00	2.0452E+00
51	5.0000E-02	2.3874E+00	9.6589E+02	8.8259E+02	4.8573E-01	5.1255E-01	1.3341E+00	2.3324E+00
56	5.5000E-02	2.3023E+00	1.0106E+03	9.3606E+02	5.8922E-01	5.3302E-01	1.5225E+00	2.6448E+00
61	6.0000E-02	2.2237E+00	1.0479E+03	9.8337E+02	7.9704E-01	5.0161E-01	1.8120E+00	3.1107E+00
66	6.5000E-02	2.1541E+00	1.0791E+03	1.0251E+03	9.2385E-01	4.6377E-01	2.0986E+00	3.4862E+00
71	7.0000E-02	2.0954E+00	1.1051E+03	1.0634E+03	9.0554E-01	4.1118E-01	2.3327E+00	3.6494E+00
76	7.5000E-02	2.0479E+00	1.1240E+03	1.0995E+03	8.4000E-01	3.2502E-01	2.1981E+00	3.3631E+00
81	8.0000E-02	2.0122E+00	1.1381E+03	1.1275E+03	7.4764E-01	2.5025E-01	1.9345E+00	2.9324E+00
86	8.5000E-02	1.9851E+00	1.1492E+03	1.1441E+03	6.5103E-01	1.9813E-01	1.7405E+00	2.5897E+00
88	8.7000E-02	1.9760E+00	1.1530E+03	1.1486E+03	6.1150E-01	1.8339E-01	1.6793E+00	2.4742E+00

APPENDIX C-6: RESULTS – ILLINOIS BITUMINOUS, FINES (38 MINUS MICRON), OXIDIZING RUN

SMOOTHED DATA FOR TEMPERATURE

Grid_#	XGRID	TEMPERATURE
1	0.00000E+00	1.66580E+03
3	2.00000E-01	1.66471E+03
5	4.00000E-01	1.65638E+03
7	6.00000E-01	1.64100E+03
9	8.00000E-01	1.61795E+03
11	1.00000E+00	1.58100E+03
13	1.20000E+00	1.52808E+03
15	1.40000E+00	1.46778E+03
17	1.60000E+00	1.40391E+03
19	1.80000E+00	1.33693E+03
21	2.00000E+00	1.26400E+03
23	2.20000E+00	1.16900E+03
25	2.40000E+00	1.05280E+03
27	2.60000E+00	9.25000E+02
29	2.80000E+00	7.95000E+02
31	3.00000E+00	6.17000E+02
33	3.20000E+00	4.00000E+02

COMPOSITION MATRIX FOR THE SYSTEM

GRID_#	MF_O2	MF_CO	MF_CO2	MF_H2O	MF_NH3	MF_HCN	MF_H2	MF_C2H4	MF_C2H6	MF_C2H2	MF_CH4	MF_DF_AR
1	6.50E-02	3.20E-02	3.89E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.14E-01
3	6.39E-02	3.21E-02	3.97E-01	2.02E-05	0.00E+00	2.11E-06	1.00E-03	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.06E-01
5	6.29E-02	3.16E-02	3.99E-01	3.78E-05	0.00E+00	2.11E-06	1.80E-03	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.05E-01
7	6.03E-02	3.08E-02	3.95E-01	5.55E-05	9.19E-08	2.36E-06	2.37E-03	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.12E-01
9	5.54E-02	2.96E-02	3.84E-01	7.28E-05	7.00E-07	2.50E-06	2.78E-03	3.79E-08	0.00E+00	0.00E+00	0.00E+00	5.28E-01
11	4.88E-02	2.80E-02	3.68E-01	8.82E-05	1.91E-06	2.19E-06	3.00E-03	1.66E-07	0.00E+00	0.00E+00	0.00E+00	5.52E-01
13	4.12E-02	2.57E-02	3.45E-01	1.02E-04	3.16E-06	1.84E-06	3.02E-03	3.17E-07	6.31E-08	1.21E-07	4.52E-07	5.85E-01
15	3.31E-02	2.24E-02	3.16E-01	1.14E-04	4.40E-06	1.66E-06	2.85E-03	4.78E-07	5.18E-07	1.04E-06	3.51E-06	6.26E-01

17	2.57E-02	1.86E-02	2.81E-01	1.18E-04	5.56E-06	2.78E-06	2.49E-03	6.35E-07	1.38E-06	3.70E-06	8.98E-06	6.72E-01
19	1.99E-02	1.48E-02	2.40E-01	1.04E-04	6.57E-06	9.80E-06	1.93E-03	7.78E-07	3.09E-06	9.75E-06	1.68E-05	7.24E-01
21	1.50E-02	1.12E-02	1.93E-01	8.27E-05	6.93E-06	1.71E-05	1.29E-03	2.71E-06	5.57E-06	1.67E-05	2.72E-05	7.79E-01
23	1.08E-02	8.20E-03	1.43E-01	6.14E-05	6.20E-06	2.43E-05	6.90E-04	1.48E-05	8.47E-06	2.40E-05	3.64E-05	8.37E-01
25	7.30E-03	5.80E-03	9.26E-02	4.26E-05	5.24E-06	2.95E-05	4.20E-04	2.76E-05	1.15E-05	3.11E-05	5.00E-05	8.94E-01
27	4.50E-03	3.70E-03	4.53E-02	2.88E-05	4.05E-06	1.61E-05	2.70E-04	3.91E-05	1.48E-05	3.82E-05	6.37E-05	9.46E-01
29	2.40E-03	1.90E-03	1.00E-02	1.60E-05	2.72E-06	5.90E-06	1.50E-04	3.80E-05	2.00E-05	2.61E-05	1.04E-04	9.85E-01
31	9.00E-04	5.00E-04	2.03E-03	4.80E-06	1.17E-06	1.02E-06	6.00E-05	8.21E-06	4.28E-06	6.10E-06	3.59E-05	9.96E-01
33	0.00E+00	7.45E-11	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.19E-13	0.00E+00	1.00E+00

EVALUATION OF PHYSICAL PROPERTIES AT EACH GRID POINT

I	XGRID	SMTHD TEMP	VISCOCITY	AVG MOL WT	THRML COND	MASS DENST	MOLR DENST	AV.MOLR_CP
1	0.0000E+00	1.6658E+03	6.4971E-04	4.0654E+01	1.1556E-04	2.9744E-04	7.3164E-06	8.9001E+00
3	2.0000E-01	1.6647E+03	6.4782E-04	4.0655E+01	1.1510E-04	2.9765E-04	7.3212E-06	9.2059E+00
5	4.0000E-01	1.6564E+03	6.4533E-04	4.0647E+01	1.1460E-04	2.9908E-04	7.3580E-06	9.2148E+00
7	6.0000E-01	1.6410E+03	6.4237E-04	4.0638E+01	1.1405E-04	3.0182E-04	7.4270E-06	9.1815E+00
9	8.0000E-01	1.6179E+03	6.3878E-04	4.0634E+01	1.1341E-04	3.0609E-04	7.5328E-06	9.0628E+00
11	1.0000E+00	1.5810E+03	6.3279E-04	4.0631E+01	1.1239E-04	3.1321E-04	7.7088E-06	8.8242E+00
13	1.2000E+00	1.5281E+03	6.2374E-04	4.0626E+01	1.1088E-04	3.2403E-04	7.9758E-06	8.5096E+00
15	1.4000E+00	1.4678E+03	6.1355E-04	4.0620E+01	1.0924E-04	3.3729E-04	8.3035E-06	8.1543E+00
17	1.6000E+00	1.4039E+03	6.0307E-04	4.0597E+01	1.0768E-04	3.5243E-04	8.6813E-06	7.8655E+00
19	1.8000E+00	1.3369E+03	5.9197E-04	4.0545E+01	1.0615E-04	3.6961E-04	9.1162E-06	8.0511E+00
21	2.0000E+00	1.2640E+03	5.7919E-04	4.0465E+01	1.0447E-04	3.9017E-04	9.6422E-06	8.1563E+00
23	2.2000E+00	1.1690E+03	5.5919E-04	4.0355E+01	1.0161E-04	4.2073E-04	1.0426E-05	8.1228E+00
25	2.4000E+00	1.0528E+03	5.3051E-04	4.0219E+01	9.7211E-05	4.6559E-04	1.1576E-05	7.8301E+00
27	2.6000E+00	9.2500E+02	4.9474E-04	4.0082E+01	9.1431E-05	5.2812E-04	1.3176E-05	5.3485E+00
29	2.8000E+00	7.9500E+02	4.5291E-04	3.9983E+01	8.4264E-05	6.1295E-04	1.5330E-05	5.0562E+00
31	3.0000E+00	6.1700E+02	3.8312E-04	3.9986E+01	7.1367E-05	7.8984E-04	1.9753E-05	4.9854E+00
33	3.2000E+00	4.0000E+02	2.8182E-04	3.9994E+01	5.2509E-05	1.2186E-03	3.0469E-05	4.9680E+00

CONVERGED VELOCITY AND PSI PROFILES

I	XGRID	VGZ PROFIL	PSI PROFIL
1	0.0000E+00	5.1869E+01	0.0000E+00
3	2.0000E-01	5.1463E+01	1.8514E+00

5	4.0000E-01	5.0109E+01	3.7041E+00
7	6.0000E-01	4.7810E+01	5.5717E+00
9	8.0000E-01	4.4556E+01	7.4824E+00
11	1.0000E+00	4.0194E+01	9.5286E+00
13	1.2000E+00	3.4672E+01	1.1828E+01
15	1.4000E+00	2.8174E+01	1.4490E+01
17	1.6000E+00	2.0680E+01	1.7961E+01
19	1.8000E+00	1.1776E+01	2.3321E+01
21	2.0000E+00	8.3208E-01	2.8692E+01
23	2.2000E+00	-9.9238E+00	2.3726E+01
25	2.4000E+00	-1.5899E+01	1.3747E+01
27	2.6000E+00	-1.7985E+01	8.3872E+00
29	2.8000E+00	-1.7965E+01	5.1988E+00
31	3.0000E+00	-1.5275E+01	2.5500E+00
33	3.2000E+00	-1.0294E+01	0.0000E+00

RATES OF FORMATION MATRIX FOR THE SYSTEM

I	XGRID	RFZ_O2	RFZ_CO	RFZ_CO2	RFZ_NO	RFZ_NH3	RFZ_HCN	RFZ_H2	RFZ_C2H4	RFZ_C2H6	RFZ_C2H2	RFZ_CH4
1	0.00E+00	-1.78E-06	5.76E-07	1.53E-05	3.44E-08	0.00E+00	5.17E-09	2.22E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00
3	2.00E-01	-1.56E-06	-5.44E-07	6.14E-06	2.78E-08	0.00E+00	-5.98E-11	2.11E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00
5	4.00E-01	-2.36E-06	-1.04E-06	-2.81E-06	2.72E-08	-1.29E-10	3.26E-10	1.44E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00
7	6.00E-01	-5.90E-06	-1.55E-06	-1.18E-05	2.67E-08	2.53E-10	3.61E-10	1.18E-06	-2.33E-11	0.00E+00	0.00E+00	0.00E+00
9	8.00E-01	-8.50E-06	-1.97E-06	-1.90E-05	2.27E-08	1.73E-09	-2.19E-10	7.30E-07	1.58E-10	0.00E+00	0.00E+00	0.00E+00
11	1.00E+00	-9.68E-06	-2.44E-06	-2.56E-05	1.94E-08	1.70E-09	-5.33E-10	3.96E-07	1.81E-10	-3.56E-11	-8.82E-11	-5.67E-10
13	1.20E+00	-9.42E-06	-3.28E-06	-2.97E-05	1.49E-08	1.56E-09	-3.27E-10	2.25E-07	1.80E-10	3.14E-10	5.93E-10	1.99E-09
15	1.40E+00	-7.92E-06	-3.73E-06	-3.06E-05	1.33E-08	1.25E-09	-1.00E-09	2.06E-07	1.55E-10	6.42E-10	5.92E-10	3.84E-09
17	1.60E+00	-4.98E-06	-2.71E-06	-2.68E-05	2.27E-10	8.72E-10	4.15E-09	-3.90E-08	1.11E-10	8.51E-10	3.34E-09	4.10E-09
19	1.80E+00	-1.91E-06	-1.34E-06	-1.22E-05	-4.79E-09	7.32E-10	2.44E-09	-2.19E-07	-2.61E-09	5.25E-10	2.10E-09	1.98E-09
21	2.00E+00	5.95E-07	2.68E-07	1.25E-05	4.11E-09	3.04E-10	-1.62E-09	-1.28E-07	-5.21E-09	-7.62E-10	-1.68E-09	-1.41E-09
23	2.20E+00	2.03E-08	1.42E-06	3.22E-05	9.83E-09	7.92E-10	-1.65E-10	-5.24E-07	-7.01E-09	-1.99E-09	-4.77E-09	-9.43E-09
25	2.40E+00	2.26E-08	1.84E-06	3.98E-05	1.16E-08	1.20E-09	1.15E-08	7.61E-08	-1.05E-08	-3.12E-09	-6.06E-09	-1.48E-08
27	2.60E+00	1.94E-06	1.78E-06	2.53E-05	1.33E-08	1.56E-09	8.18E-09	9.95E-08	1.55E-08	4.89E-09	1.36E-08	4.97E-08
29	2.80E+00	1.41E-06	1.30E-06	4.43E-06	1.12E-08	1.72E-09	3.48E-09	6.31E-08	2.64E-08	1.61E-08	1.69E-08	7.35E-08
31	3.00E+00	7.18E-07	1.82E-07	6.45E-07	2.83E-09	1.12E-09	5.03E-11	3.57E-08	1.74E-09	2.21E-09	2.24E-09	2.43E-08
33	3.20E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

PARTICLE TRAJECTORY AND SURROUNDING GAS TEMPERATURE

I	TIME (sec)	GAS_TEMP	P_Z_POSITW	P_R_POSITW
1	0.0000E+00	4.0000E+02	3.2000E+00	2.0000E+00
6	5.0000E-03	4.7023E+02	3.1394E+00	2.0015E+00
11	1.0000E-02	5.4875E+02	3.0676E+00	2.0098E+00
16	1.5000E-02	6.3163E+02	2.9871E+00	2.0276E+00
21	2.0000E-02	7.1326E+02	2.8988E+00	2.0567E+00
26	2.5000E-02	7.8950E+02	2.8039E+00	2.0985E+00
31	3.0000E-02	8.5614E+02	2.7056E+00	2.1552E+00
36	3.5000E-02	9.2053E+02	2.6068E+00	2.2294E+00
41	4.0000E-02	9.8371E+02	2.5095E+00	2.3257E+00
46	4.5000E-02	1.0429E+03	2.4160E+00	2.4521E+00
51	5.0000E-02	1.0959E+03	2.3292E+00	2.6234E+00
56	5.5000E-02	1.1406E+03	2.2524E+00	2.8621E+00
61	6.0000E-02	1.1755E+03	2.1894E+00	3.1868E+00
66	6.5000E-02	1.2007E+03	2.1412E+00	3.6164E+00
71	7.0000E-02	1.2177E+03	2.1055E+00	4.1318E+00
76	7.5000E-02	1.2317E+03	2.0786E+00	4.7598E+00
77	7.6000E-02	1.2341E+03	2.0741E+00	4.8987E+00

DIMENSIONLESS PARAMETERS AND PARTICLE PROPERTIES

I	TIME (sec)	P_Z_POSITW	GAS_TEMP	REYNOLD #	PRANDTL #	MUSULT #	M_DOT	H.T.COEFF	BLOW.COEFF	VOLATILES
1	0.0000E+00	3.2000E+00	4.0000E+02	0.0000E+00	6.6669E-01	2.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
6	5.0000E-03	3.1394E+00	4.7023E+02	1.3185E-02	6.7527E-01	2.0659E+00	1.0025E-16	3.8892E-02	2.4099E-19	1.8284E-19
11	1.0000E-02	3.0676E+00	5.4875E+02	8.9869E-03	6.7941E-01	2.0545E+00	5.0896E-14	4.3012E-02	1.1015E-16	6.7871E-17
16	1.5000E-02	2.9871E+00	6.3163E+02	5.1602E-03	6.7622E-01	2.0412E+00	6.2383E-11	4.7443E-02	1.2174E-13	8.2592E-14
21	2.0000E-02	2.8988E+00	7.1326E+02	2.7003E-03	6.7516E-01	2.0298E+00	4.8560E-08	5.1914E-02	8.6600E-11	6.8182E-11
26	2.5000E-02	2.8039E+00	7.8950E+02	3.2907E-03	6.8498E-01	2.0331E+00	1.1664E-05	5.4698E-02	1.9963E-08	1.8627E-08
31	3.0000E-02	2.7056E+00	8.5614E+02	2.2049E-03	6.9951E-01	2.0029E+00	6.3552E-04	5.6383E-02	1.0600E-06	1.2097E-06
36	3.5000E-02	2.6068E+00	9.2053E+02	6.6950E-04	7.2375E-01	2.0152E+00	1.3992E-02	5.9260E-02	2.3176E-05	3.1069E-05
41	4.0000E-02	2.5095E+00	9.8371E+02	1.3538E-03	7.3326E-01	2.0217E+00	1.8045E-01	6.1286E-02	2.9194E-04	4.5815E-04
46	4.5000E-02	2.4160E+00	1.0429E+03	4.2414E-03	1.0307E+00	2.0396E+00	1.5241E+00	6.3465E-02	3.3565E-03	4.4162E-03
51	5.0000E-02	2.3292E+00	1.0959E+03	7.4209E-03	1.1045E+00	2.0376E+00	8.8144E+00	6.4534E-02	2.0155E-02	2.9676E-02

56	5.5000E-02	2.2524E+00	1.1406E+03	9.0184E-03	1.0986E+00	1.9919E+00	3.2560E+01	6.2569E-02	7.0811E-02	1.3683E-01
61	6.0000E-02	2.1894E+00	1.1755E+03	1.0893E-02	1.1165E+00	1.9746E+00	4.5654E+01	5.9655E-02	9.4426E-02	3.6588E-01
66	6.5000E-02	2.1412E+00	1.2007E+03	5.4659E-03	1.1170E+00	2.0502E+00	0.0000E+00	6.1583E-02	0.0000E+00	4.2700E-01
71	7.0000E-02	2.1055E+00	1.2177E+03	6.0663E-03	1.1174E+00	2.0529E+00	0.0000E+00	6.1995E-02	0.0000E+00	4.2700E-01
76	7.5000E-02	2.0786E+00	1.2317E+03	6.1786E-03	1.1193E+00	2.0534E+00	0.0000E+00	6.2294E-02	0.0000E+00	4.2700E-01
77	7.6000E-02	2.0741E+00	1.2341E+03	6.3068E-03	1.1192E+00	2.0539E+00	0.0000E+00	6.2346E-02	0.0000E+00	4.2700E-01

COAL PARTICLE HEAT UP

INITIAL COAL PARTICLE DENSITY (gm/cc) =	1.41
INITIAL COAL PARTICLE DIAMETER (centimeter) =	0.31E-02
INITIAL COAL PARTICLE TEMPERATURE (deg K) =	400.00
EMMISSIVITY OF COAL =	0.70

COAL PARTICLE AND SURROUNDING GAS PHASE TEMPERATURES, AND PARTICLE DIAMETER AND DENSITY

I	TIME (sec)	GAS_TEMP	P_S_TEMP	P_C_TEMP	P_DIAMETER	P_DENSITY
1	0.0000E+00	4.0000E+02	4.0000E+02	4.0000E+02	3.1000E-03	1.4100E+00
6	5.0000E-03	4.7023E+02	4.2112E+02	4.1892E+02	3.1000E-03	1.4100E+00
11	1.0000E-02	5.4875E+02	4.6832E+02	4.6429E+02	3.1000E-03	1.4100E+00
16	1.5000E-02	6.3163E+02	5.3261E+02	5.2699E+02	3.1000E-03	1.4100E+00
21	2.0000E-02	7.1326E+02	6.0858E+02	6.0162E+02	3.1000E-03	1.4100E+00
26	2.5000E-02	7.8950E+02	6.8542E+02	6.7856E+02	3.1000E-03	1.4100E+00
31	3.0000E-02	8.5614E+02	7.5598E+02	7.4935E+02	3.1000E-03	1.4100E+00
36	3.5000E-02	9.2053E+02	8.2287E+02	8.1609E+02	3.1000E-03	1.4099E+00
41	4.0000E-02	9.8371E+02	8.8795E+02	8.8107E+02	3.1003E-03	1.4089E+00
46	4.5000E-02	1.0429E+03	9.5098E+02	9.4412E+02	3.1032E-03	1.3994E+00
51	5.0000E-02	1.0959E+03	1.0113E+03	1.0049E+03	3.1215E-03	1.3400E+00
56	5.5000E-02	1.1406E+03	1.0701E+03	1.0647E+03	3.1993E-03	1.1072E+00
61	6.0000E-02	1.1755E+03	1.1342E+03	1.1309E+03	3.3656E-03	6.9868E-01
66	6.5000E-02	1.2007E+03	1.1851E+03	1.1838E+03	3.4100E-03	6.0700E-01
71	7.0000E-02	1.2177E+03	1.2093E+03	1.2086E+03	3.4100E-03	6.0700E-01
76	7.5000E-02	1.2317E+03	1.2266E+03	1.2262E+03	3.4100E-03	6.0700E-01

RATES OF FORMATION OF NITROGENOUS SPECIES AS A FUNCTION OF TIME AND AXIAL POSITION OF PARTICLE

I	TIME (sec)	P_Z_POSITN	RFT_NO	RFT_NH3	RFT_HCN	RFT_H2	RFT_CH4	RFT_C2H2	RFT_C2H4	RFT_C2H6
1	0.0000E+00	3.2000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
6	5.0000E-03	3.1394E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
11	1.0000E-02	3.0676E+00	8.1777E-10	3.4698E-10	0.0000E+00	1.1100E-08	7.7559E-09	3.8633E-10	1.5317E-10	6.9587E-10
16	1.5000E-02	2.9871E+00	3.2469E-09	8.5724E-10	1.3450E-10	3.7589E-08	2.7209E-08	2.8001E-09	2.4860E-09	2.4971E-09
21	2.0000E-02	2.8988E+00	6.2968E-09	1.3608E-09	1.6913E-09	4.9941E-08	4.7390E-08	8.4269E-09	1.2332E-08	4.5807E-09
26	2.5000E-02	2.8039E+00	9.5673E-09	1.7045E-09	3.4089E-09	6.2591E-08	7.2473E-08	1.6629E-08	2.5909E-08	1.5858E-08
31	3.0000E-02	2.7056E+00	1.2698E-08	1.9048E-09	5.5473E-09	6.9964E-08	7.6536E-08	1.9295E-08	2.7483E-08	1.2666E-08
36	3.5000E-02	2.6068E+00	1.3276E-08	1.5756E-09	8.0048E-09	9.9180E-08	5.4856E-08	1.4406E-08	1.6549E-08	5.5932E-09
41	4.0000E-02	2.5095E+00	1.3015E-08	1.3713E-09	1.0610E-08	8.1609E-08	-2.4138E-08	2.3600E-09	2.9120E-10	-3.7306E-09
46	4.5000E-02	2.4160E+00	1.1840E-08	1.2289E-09	1.0934E-08	7.6779E-08	-1.6930E-08	-5.5456E-09	-1.0628E-08	-3.2292E-09
51	5.0000E-02	2.3292E+00	1.0644E-08	1.0939E-09	7.9504E-09	6.4016E-08	-1.1382E-08	-6.5830E-09	-9.6318E-09	-2.8290E-09
56	5.5000E-02	2.2524E+00	9.9751E-09	9.2331E-10	3.1453E-09	-1.7753E-07	-9.8580E-09	-5.5550E-09	-8.0916E-09	-2.3478E-09
61	6.0000E-02	2.1894E+00	9.7870E-09	7.6567E-10	-7.7843E-10	-4.2163E-07	-9.4435E-09	-4.6332E-09	-6.8899E-09	-1.9276E-09
66	6.5000E-02	2.1412E+00	9.6162E-09	6.4500E-10	-3.0737E-09	-6.6378E-07	-1.0447E-08	-4.0295E-09	-6.8864E-09	-1.7020E-09
71	7.0000E-02	2.1055E+00	9.2225E-09	5.5565E-10	-3.5633E-09	-6.5583E-07	-1.0790E-08	-3.5401E-09	-6.8857E-09	-1.5122E-09
76	7.5000E-02	2.0786E+00	8.4611E-09	4.8860E-10	-3.1428E-09	-5.6505E-07	-9.5548E-09	-3.1074E-09	-6.5728E-09	-1.3287E-09

NORMALIZED RATES OF FORMATION OF NITROGENOUS SPECIES AS A FUNCTION TIME (G_ATOM N/G_ATOM INITIAL-VOLATILE-N *SEC))

I	TIME (sec)	P_Z_POSITN	GAS_TMPRTR	P_S_TMPRTR	NRFT_NO	NRFT_NH3	NRFT_HCN	NRFT_TO_XN
1	0.0000E+00	3.2000E+00	4.0000E+02	4.0000E+02	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
6	5.0000E-03	3.1394E+00	4.7023E+02	4.2112E+02	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
11	1.0000E-02	3.0676E+00	5.4875E+02	4.6832E+02	1.5488E-01	6.5715E-02	0.0000E+00	2.2059E-01
16	1.5000E-02	2.9871E+00	6.3163E+02	5.3261E+02	7.0781E-01	1.8687E-01	2.9320E-02	9.2401E-01
21	2.0000E-02	2.8988E+00	7.1326E+02	6.0858E+02	1.5501E+00	3.3498E-01	4.1633E-01	2.3014E+00
26	2.5000E-02	2.8039E+00	7.8950E+02	6.8542E+02	2.6069E+00	4.6446E-01	9.2886E-01	4.0002E+00
31	3.0000E-02	2.7056E+00	8.5614E+02	7.5598E+02	3.7521E+00	5.6284E-01	1.6391E+00	5.9541E+00
36	3.5000E-02	2.6068E+00	9.2053E+02	8.2287E+02	4.2177E+00	5.0058E-01	2.5432E+00	7.2614E+00
41	4.0000E-02	2.5095E+00	9.8371E+02	8.8795E+02	4.4187E+00	4.6557E-01	3.6021E+00	8.4864E+00
46	4.5000E-02	2.4160E+00	1.0429E+03	9.5098E+02	4.2615E+00	4.4233E-01	3.9353E+00	8.6391E+00
51	5.0000E-02	2.3292E+00	1.0959E+03	1.0113E+03	4.0261E+00	4.1377E-01	3.0072E+00	7.4471E+00
56	5.5000E-02	2.2524E+00	1.1406E+03	1.0701E+03	3.9269E+00	3.6349E-01	1.2382E+00	5.5287E+00

61	6.0000E-02	2.1894E+00	1.1755E+03	1.1342E+03	3.9707E+00	3.1064E-01	-3.1582E-01	3.9655E+00
66	6.5000E-02	2.1412E+00	1.2007E+03	1.1851E+03	3.9848E+00	2.6728E-01	-1.2737E+00	2.9784E+00
71	7.0000E-02	2.1055E+00	1.2177E+03	1.2093E+03	3.8759E+00	2.3352E-01	-1.4976E+00	2.6119E+00
76	7.5000E-02	2.0786E+00	1.2317E+03	1.2266E+03	3.5967E+00	2.0770E-01	-1.3360E+00	2.4684E+00

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