

## COMBUSTION OF LIQUID FUELS AND POLLUTANT FORMATION: A REVIEW PART II. POLLUTANT FORMATION

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*(Received 12 July 1984 • accepted 25 July 1984)*

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**Abstract** — In Part II of a two-part contribution, progress on understanding of pollutant formation from liquid fuel combustion process is reviewed. The review concentrates on soot and nitrogen oxides emissions. Future perspectives on the combustion and pollutant formation from alternative fuel sources, and air pollution as a global issue are briefly discussed.

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### **1. POLLUTANT EMISSIONS FROM LIQUID FUEL UTILIZATION**

#### **1.1. Micro Gaseous Combustion Products**

Combustion products appearing only in trace concentrations include nitrogen dioxide,  $\text{NO}_2$ , sulfur dioxide,  $\text{SO}_2$ , nitric oxide,  $\text{NO}$ , the unburnt or partially reacted hydrocarbons including polycyclic aromatics, and metallic compounds.

The nitrogen oxides are generally considered together as  $\text{NO}_x$ , and occur by either the high temperature oxidation of atmospheric nitrogen (thermal  $\text{NO}_x$ ), the oxidation of fuel-bound nitrogen compounds (fuel  $\text{NO}_x$ ), or the fixation by hydrocarbons and subsequent oxidation of atmospheric nitrogen (prompt  $\text{NO}_x$ ). Among these the fuel-bound nitrogen is the main source of nitrogen oxides emission from high nitrogen content fuel combustion process.  $\text{NO}_x$  emission and control problem has been an important subject of current research efforts and is surveyed in a separate section.

Sulfur dioxide does not appear to be a major pollutant from vehicles as the fuels are desulfurized at refineries in most countries, but it does result from combustion of the heavier high-sulfur residual fuels and coal.  $\text{SO}_2$  has an acrid odor and leads to acidic corrosion. It is also known to be the main cause of acid rain [NRC(1983a)]. Installation of  $\text{SO}_2$  scrubbing facilities at coal fired power plants is a common practice. The technology of  $\text{SO}_2$  scrubbing is well established [Singer(1981)], however, it cannot be always justified to be economical and has the problem of finding waste

disposal sites.

Unburnt or partially reacted hydrocarbons are produced by imperfect mixing of fuel and air by quenching of partially reacted fuel within the combustion chamber. Although the original reasons for concerns with these emissions have been the efficiency and clean operation of the combustion process, recent interest has been motivated by the concern with health effects of soot and polycyclic aromatic hydrocarbons, the latter of which may be a precursor to the former species [Bittner(1981), Haynes and Wagner(1981), NIEHS(1982), Longwell(1983)].

#### **1.2. Carbonaceous Particulates**

On the assumption that any air-borne dust is either consumed in the flame or filtered out beforehand, the main particulates present in combustion products are likely to be carbonaceous, which may either deposit on the walls of the combustion chamber or discharge as smoke. Carbonaceous particulates from liquid fuel combustion process can be classified into two kinds; soot which is believed to form from the gas phase reaction of fuel, and coke which is believed to form from the liquid phase reaction of fuel.

Soot formation is indicated by a yellow luminosity, and is clearly more likely in diffusion than in premixed flames. In non-sooting flames soot becomes oxidized completely in later stages of combustion. Luminous non-sooting flames are required for heat transfer, and non-luminous non-sooting flame for work transfer. Further discussions on the soot formation in conjunction with liquid fuel combustion process are developed later

in this review.

## 2. NO<sub>x</sub> EMISSIONS

Seven oxides of nitrogen are known to occur: NO, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O, N<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>4</sub> and N<sub>2</sub>O<sub>5</sub>. Of these, NO(nitric oxide) and NO<sub>2</sub>(nitrogen dioxide) are emitted in sufficient quantities from fuel combustion processes to be significant in atmospheric pollution. In this paper, "NO<sub>x</sub>" refers to either or both of these two oxides of nitrogen. NO<sub>2</sub> is deleterious to human respiratory function and is a key participant in the formation of photochemical smog. NO, taken alone, is relatively less harmful but is important as the main precursor to NO<sub>2</sub>.

formation in the atmosphere. Recently, growing concerns began to appear on the acid rain, of which NO<sub>x</sub> is one of the possible causes [NRC(1983a)].

Approximately 95% of oxides of nitrogen emanating from stationary combustion sources are emitted as NO. Three different mechanisms, thermal NO formation, prompt NO formation, and fuel NO formation have been identified as generating NO during fossil fuel combustion.

An overview of stationary sources of NO<sub>x</sub> is provided in Figure 1 [FPA(1978)]. The first division is by application and the second by use sector. The final description level is the important equipment type.

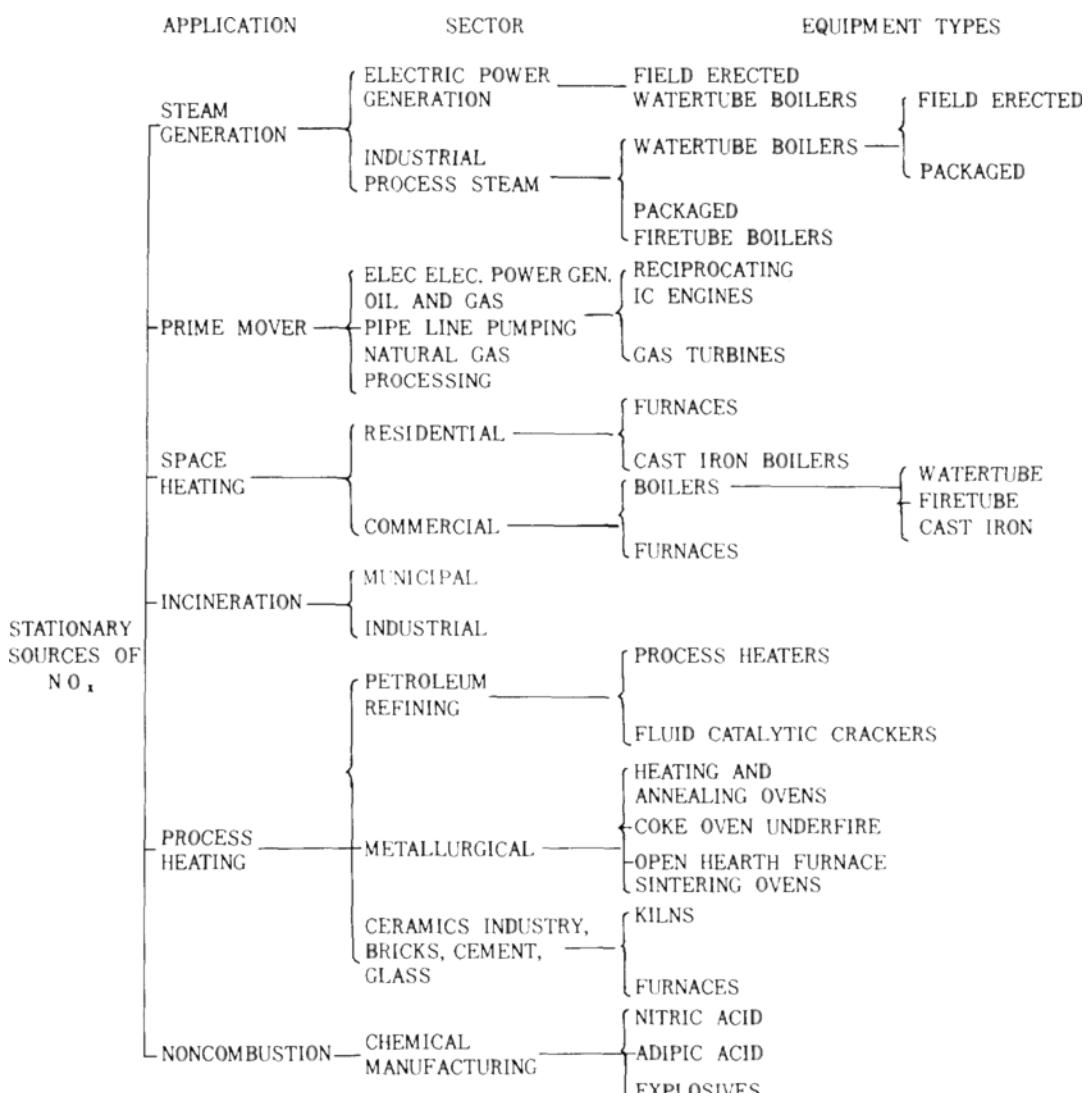


Fig. 1. Stationary sources of NO<sub>x</sub> emissions.

## 2.1. Thermal NO

The kinetics of the extended Zeldovich mechanism [Zeldovich(1946)]



has been studied widely and well reviewed [Bowman and Seery(1972), Bowman (1975)].

Reaction (1) is much slower than reactions (2) and (3). Therefore, it determines the rate of NO formation. The creation of an NO molecule from reaction (1) is accomplished by the release of an N atom, which rapidly forms another NO molecule from reactions (2) and (3). Reactions (1) and (3) are the chain-breaking and chain-making mechanisms, and the oxygen atom is the chain carrier. This mode of NO formation is basically a fuel-lean, high temperature phenomenon that has been relatively amenable to control techniques.

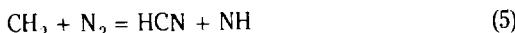
## 2.2. Prompt NO

The existence of non-Zeldovich pathway to the fixation of molecular nitrogen was first proposed by Fenimore(1971), and the NO generated in this fashion was called *prompt* NO. The prompt NO mechanism is believed to be initiated by hydrocarbon radicals attacking molecular nitrogen.

The nature of the hydrocarbon-nitrogen interaction is not yet definitely known, although the reaction



seems like a candidate [Fenimore(1971)]. Other reactions that have been considered include [Blauwens, et al. (1977)]:



It appears that prompt NO may occur in the flame zone by both the Zeldovich mechanism on the fuel-lean side of the flame and the CH-radical mechanism on the fuel-rich side of the flame [Blauwens, et al. (1977), Hayhurst and Vince(1980)].

## 2.3. Fuel NO

Fuel NO is derived from bound nitrogen introduced with the fuel. This mode of NO formation, which has proved difficult to control with existing techniques [Beér, et al. (1981, 1983)], predominates when the nitrogen content of the fuel exceeds a few tenth of a per cent, a condition very likely to occur in alternative fuels like coal-derived fuels or shale oils [Byrnes(1980)].

In the fuel-lean and stoichiometric flames, the conversion of fuel nitrogen to NO (and perhaps  $NO_2$ ) is practically complete and occurs on a time scale comparable to that of the combustion itself [Levy, et al.

(1978)]. In fuel-rich flames, fuel-bound nitrogen converts rapidly to HCN, which then subsequently converts to other nitrogen-bearing intermediates and products [Fenimore(1976), Haynes(1977)]. A schematic of the mechanistic pathways of fuel nitrogen conversion and its interaction with thermal NO is represented in Figure 2.

## 2.4. NO Formation from Burning Droplets

A few studies have considered NO production around individual quiescent droplets [Altenkirch, et al. (1972), Kestin(1972), Bracco(1973)]. The NO production mechanism for the thermal NO is superimposed on the basic droplet burning structure. The results suggest that the envelope flame surrounding the droplet could be a significant source of NO. Hart, et al.(1975) studied the formation of NO and  $NO_x$  in the forward stagnation region of flames surrounding burning fuel cylinders simulating the droplet combustion. They found that the maximum yields of NO and  $NO_x$  were situated towards the lean side of the maximum flame temperature. And also it has been shown that considerable NO is formed near the liquid surface by a prompt NO mechanism.

Hanson, et al. (1983) performed experiments on 150  $\mu m$  droplet array of fuel oils revealed non-equilibrium evolution of nitrogenous components. They have shown that the interplay between the volatility and mass transfer effects is directly responsible for the acceleration of the evolution of fuel-nitrogen, and because of these effects heavy petroleum fuels lend themselves favorably to application of staged combustion for the control of fuel  $NO_x$  emission.

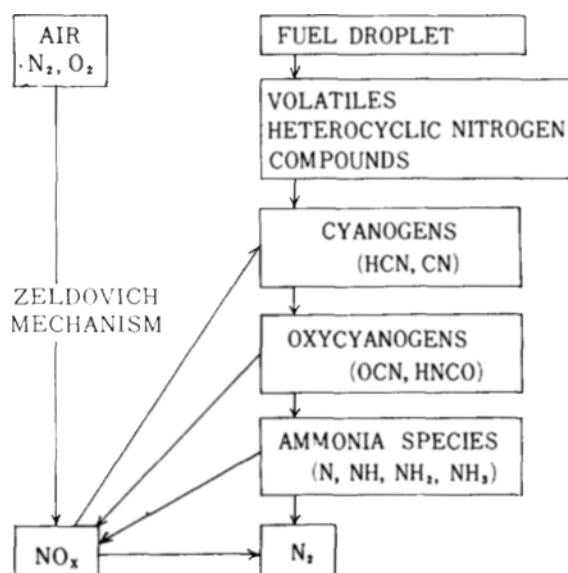


Fig. 2. Pathways of fuel nitrogen conversion.

Recently, Rah (1984) has shown from experimental studies on combustion of fuel oil droplet arrays that the overall equivalence ratio is important for the fuel-NO emission as long as there is an envelope flame around the droplets.

### 2.5. NO<sub>x</sub> Emission Control

Because of more stringent regulation of NO<sub>x</sub> emissions from combustion sources, combustor designs have been modified to reduce oxide formation through control of flame temperature—staged combustion, reduced excess air percentage, use of overfire air, tangential firing, and gas recirculation [Sarofim and Flagan(1976), Singer(1981)]. Although these steps have been effective, and have been found adequate in many countries, any further reduction in allowable NO<sub>x</sub> may require some form of post-combustor gas treatment. Many flue-gas treatment systems are in operation, principally in Japan [Rosenberg, *et al.*(1980), Singer(1981)].

By far the most attractive NO<sub>x</sub> control strategy involves modification of the combustion process by employing staged combustion technique. In this technique the major proportion of the fuel-bound nitrogen is converted in fuel-rich zone to relatively inactive molecular nitrogen. Complete combustion of the fuel is accomplished in a subsequent fuel-lean zone in which carefully controlled conditions minimize the formation of thermal NO. Studies at Massachusetts Institute of Technology 3 MW Combustion Research Facility [Beér, *et al.*(1981, 1983)] have demonstrated the potential applicability of the staged combustion technique. A summary of general stationary source NO<sub>x</sub> control technique is given on Table 1 [EPA(1978)].

## 3. SOOT FORMATION

The combustion of fuels with insufficient air produces a black smoke containing extremely small carbon particles which, when separated from combustion gases, comprise a fluffy powder of intense blackness. The term soot or carbon black refers to a wide range of such products made by partial combustion or thermal decomposition of hydrocarbons in the vapor phase, in contrast to cokes and chars which are formed by the pyrolysis of solids (or liquids).

The physical and chemical properties of soot and the process of soot formation have been studied intensively for the various following reasons:

- (i) soot emission reflects poor combustion conditions and a loss of efficiency;
- (ii) soot pollutes the environment;
- (iii) soot in a flame causes it to be highly luminous, an effect which is widely used as an important heat transfer mechanism in many furnaces;
- (iv) soot is widely employed in many branches of

technology, (e.g. as a pigment or reinforcing agent for rubber products, particularly tires) and is produced in vast quantities.

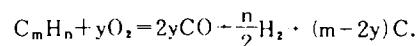
There are a number of comprehensive reviews on soot formation [Palmer and Cullis(1965), Lahaye and Prado(1978), Bittner and Howard(1978), Wagner(1979), Haynes and Wagner(1981), Smith(1981)]. The physical and chemical properties of soot and the methods of manufacturing carbon black have been treated by Schubert, *et al.*(1967) and Dannenberg(1978). Flame radiation involving soot particles is treated in several reviews and monographs [Hottel and Sarofim(1967), Beér(1974), Siegel and Howell(1981), Tien and Lee(1982)].

### 3.1. Fundamentals of Soot Formation

Soot is not a uniquely defined substance. It looks black and consists mainly of carbon, but it is quite different from graphite (Table 2). in addition to chemically combined surface oxygen, soot contains varying amounts of moisture, solvent-extractable hydrocarbons which are mostly condensed hydrogen, and inorganic salts. Extractable hydrocarbons result from the adsorption of small amount of incompletely burned hydrocarbons. The combined sulfur and inorganic salt contents have their origin in the feedstocks.

The basic units of soot are spherical or nearly spherical particles with diameters often in the range of 20-30 nm. These "elementary particles" aggregate together to produce straight or branched chains, which form the fluffy soot flocculates, sometimes visible in the atmosphere. It was pointed out by Palmer and Cullis(1965) that soot particles do not differ much in size whether derived from a furnace flame, a piston engine, a gas turbine or a premixed flame.

From a thermodynamic point of view [Wagner(1979)] soot emission should begin at a C/O ratio exceeding unity, corresponding to the condition  $m < 2y$ , in



Experimentally determined limits of soot formation do not occur at C/O = 1 but close to C/O ≈ 0.5 [Street and Thomas(1955), Wright(1969)]. This reveals that the carbon formation is not an equilibrium process.

The amount of soot generated is a function of both fuel composition and local environment in the combustor. Emission of soot increases with increasing C/H ratio and aromaticity of the fuel in the following order (in general):

paraffins, olefins, naphthenes, aromatics, polycyclic aromatics.

Since the C/O ratio will always exceed 0.5 in some region of a diffusion flame, clearly soot will always be emitted from that region. Whether or not soot will be

Technique	Principle of Operation	Status of Development	Limitations	Applications	
				Near-Term	Long-Term
Combustion Modification	Suppress thermal $\text{NO}_x$ through reduced flame temperature, reduced $\text{O}_2$ level; suppress fuel $\text{NO}_x$ through delaying fuel/air mixing or reduced $\text{O}_2$ level in primary flame zone	Operational for point sources; pilot-scale and full scale studies on combined modifications, operational problems and advanced design concepts for area sources	Degree of control limited by operational problems	Retrofit utility, industrial boilers; improved designs; new utility boilers	Optimized design area, point sources
Flue Gas/Noncombustion Tail Gas Treatment	Additional absorption of $\text{NO}_x$ to $\text{HNO}_3$ ; conversion of $\text{NO}_x$ to $\text{NH}_4\text{NO}_3$ ; reduction of $\text{NO}_x$ to $\text{N}_2$ by catalytic treatment	Operational for existing and new nitric acid plants meeting NSPS; pilot scale feasibility studies for conventional combustion systems	New wet processes developing experience in applications; old catalytic processes have high costs; interference by fuel sulfur or metallic compounds	Noncombustion sources (nitric acid plants)	Possible supplement to combustion modifications; simultaneous $\text{SO}_x/\text{NO}_x$ removal
Fuel Switching	Simultaneous $\text{SO}_x$ and $\text{NO}_x$ control by conversion to clean fuels; synthetic gas or oil from coal; SRC; methanol; hydrogen	Synthetic fuel plants in pilot-scale stage; commercial plants due by mid-1980's	Fuel cost differential may exceed $\text{NO}_x, \text{SO}_x$ , control costs with coal	Negligible use	New point sources, (combined cycle) Conventional area sources (residential)
Fuel Additives	Reduce or suppress $\text{NO}_x$ by catalytic action of fuel additives	Inactive; preliminary screening studies indicated poor effectiveness	Large make-up rate of additive for significant effect; presence of additive as pollutant	Negligible use	Not promising
Fuel Denitrification	Removal of fuel nitrogen compounds by pretreatment	Oil desulfurization yields partial denitrification	Effectiveness for coal doubtful; no effect on thermal $\text{NO}_x$	Negligible use	Supplement to combustion modification
Catalytic Combustion	Heterogeneously catalyzed reactions yield low combustion temperature, low thermal $\text{NO}_x$	pilot-scale test beds for catalyst screening, feasibility studies	Limited retrofit applications; requires clean fuels	Small space heaters	Possible use for residential heating, small boilers, gas turbines
Fluidized Bed Combustion	Coal combustion in solid bed yields low temperature, low $\text{NO}_x$	Pilot-scale study of atmospheric and pressurized systems; focus on sulfur retention devices	Fuel nitrogen conversion may require control (staging) may require large make-up of limestone sulfur absorbent	Negligible use	Utility, industrial boilers beginning 1980's; possible combined cycle, waste fuel application

**Table 2. Forms of carbon and characteristics.**

Form	Crystal System	Specific Gravity	C-C distance, nm	layer distance, nm
diamond	cubical	3.52	0.155	
graphite	hexagonal	2.27	0.142	0.335
carbon black	hexagonal turbostatic*	1.86-2.04	0.142	0.365
cokes (oven and calcined)	"	1.3-2.1		
chars and activated carbons	"	1.1-1.3		
fibrous carbons	"	1.65		
viterous carbon	"	1.47		
pyrolytic graphite	"	1.2-2.2		

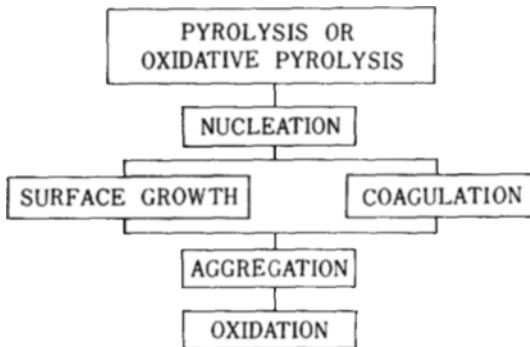
Source: Dannenberg (1978)

\* Turbostatic crystals have randomly oriented planes.

observed as a final combustion product depends on the rate of destruction in the flame region of  $C/O \leq 0.5$ . Soot oxidation in this region is favored by low emissions from the region of formation and growth, small particle diameter, large concentrations of the predominant species, and high temperatures.

Useful studies of soot formation fundamentals have been performed in relatively simple environments. Studies in premixed flames [Street and Thomas(1955), McFarlane, *et al.*(1964), Bonne, *et al.*(1965), Homann and Wagner(1967), Homann(1968), Wesborg, *et al.*(1973, 1975), Haynes, *et al.*(1980), Bittner and Howard(1981)], diffusion flames [Clarke, *et al.*(1946), Schalla and McDonald(1955), Chakraborty and Long(1968), Tesner, *et al.*(1971), Schug, *et al.*(1980), Glassman and Yaccarino(1980, 1981), Haynes and Wagner(1980), Nishida and Mukohara(1982)], and well-stirred reactors [Wright(1969), Blazowski, *et al.*(1978), Blazowski(1980)] have produced useful results. Experiments in such unsteady devices as shock tubes [Graham(1977), Wang, *et al.*(1981)] and constant volume bombs [Flower and Dyer(1980)] have also resulted in significant contributions.

The fundamental mechanism and kinetics of soot formation in flames have been of interest to combustion researchers for many years as represented by the large volume of literature on this subject [Haynes(1981)]. The mechanism by which soot is now believed to be formed from the vapor phase in flames is depicted schematically in Figure 3. Concurrent with the formation processes, the destructive process will also occur in flame regions where oxidizing species are present. Despite several suggested models on soot formation process in the light

**Fig. 3. The mechanism of soot particulate formation in combustion system.**

of kinetics [Tesner(1959), Khan and Greeves(1974), Jenson(1974), Edelman, *et al.*(1979), Wang, *et al.*(1981)] the comprehensive understanding and modeling of soot formation seem to be far from completion at present. Recent advances in modeling of soot formation are reviewed by Palmer and Cullis(1978), and Haynes(1981).

### 3.2. Soot Formation in Droplet Burning

As in a gaseous diffusion flame, formation of soot in burning droplet flame is determined by the local fuel and oxidizer concentrations. Good mixing of the fuel-vapor with air is therefore one of the necessary conditions to limit soot formation. However, in the burning of droplets, evaporation of the fuel by heat transfer plays a role. As the fuel spray approaches the flame, the smaller droplets may have time to evaporate completely before burning, while the larger ones may conceivably burn in an "envelope flame" mode. At low relative velocities between the droplet and the surrounding oxidizer, the droplet is completely surrounded by the envelope flame. While above a critical velocity, the envelope flame is established downstream of the droplet [Sjögren(1973), Gollahalli and Brzustowski(1973)]. The amount of soot in these two types of flames differ markedly. The total amount of soot present in the wake flame as a whole is less than 10% of that in the envelope flame [Gollahalli and Brzustowski(1973)].

Recently, Rah, *et al.*(1982), in a study on the combustion of fuel droplet array, found that the soot formation is strongly dependent upon the formation of an envelope flame about the droplets, increasing dramatically as the oxygen concentration was increased beyond the point of ignition. They pointed out the importance of ignition phenomena in relation to the formation of soot in liquid fuel combustion. It was shown that the suppression of soot formation could be achieved by choosing conditions that lead to the extinction of the envelope flame.

### 3.3. Staged Combustion and Soot Formation

As was discussed earlier in this review, the staged combustion technique is the most promising strategy for  $\text{NO}_x$  emission control. However, Beér, *et al.* (1983) pointed out that there is concern over soot emission from staged combustion of fuels of highly aromatic and high C/H ratio contents. The operating conditions in the fuel-rich first stage result in the formation of a significant amount of soot. Complete burn-out of this soot must be achieved in the fuel-lean second stage by ensuring good mixing and sufficient residence time at elevated temperatures.

Suppression of ignition or extinction of the envelope flame about the droplet may result in lower level of soot formation in the first stage. However, the premixed flame nature of the subsequent stage may provide better conditions for  $\text{NO}_x$  formation. There is a definite trade-off between  $\text{NO}_x$  control and soot formation in the staged combustion technique [Blazowski, *et al.* (1981)].

Rah (1984) has shown that the control of the emission of both soot and nitrogen oxides can be achieved by use of low oxygen concentration in the oxidation gas to delay ignition and suppress soot formation by using a high fuel/air ratio to reduce  $\text{NO}_x$ .

## 4. PERSPECTIVES

The above discussions on the combustion of liquid fuels only treated the use of conventional petroleum-based fuel oils. Recent increased interest on slurries of coals with either oil or water brings about the necessity of research on fundamental aspects of coal-slurry utilization. Physical property estimation, rheology of highly loaded suspensions, phase stability, atomization of slurry, ignition and combustion of coal-slurry, ash formation and deposition, and economics of coal-slurry process are several examples of disciplines related to the coal-slurry technology [ICE(1983)].

The discussions on the combustion-generated air pollutants were limited to the formation of soot and  $\text{NO}_x$ . And the control strategies were more or less on the local levels. There are growing concerns over the issues of acid rain due to increased levels of  $\text{SO}_x$  and  $\text{NO}_x$  concentrations in the atmosphere [NRC(1983a)] and of the greenhouse warming of the atmosphere caused by an increase of  $\text{CO}_2$  concentration in the atmosphere [NRC(1983b)]. Both the issues are of global concerns and should be considered very seriously for the generations to come. For the case of the acid rain, they agree on its devastating impacts on the environment and ecological systems, however, there are different opinions either passimistic or optimistic on the impact of increased  $\text{CO}_2$  concentration in the atmosphere [Idso(1983)]. The

whole situation provides a challenging opportunity of enhanced degrees of cooperations between experts on various subjects to find solutions to a problem facing the humankind on the earth, air pollution.

### Acknowledgements

I would like to acknowledge the scholarship from the Ministry of Education of the Republic of Korea, with which I could start my study at MIT. I thank Professor Adel F. Sarofim and Professor János M. Beér for their encouragements and supports.

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