CHAPTER II
LITERATURE SURVEY

Nitric oxide is a primary pollutant that causes acid rain and ozone depletion. Nitric oxide reacts with water and O_2 in the atmosphere to form nitric acid which is a contributor to acid rain. It also can contribute to ozone depletion by the reaction

$$NO + O_3 \longrightarrow NO_2 + O_2$$

which is swift and practically irreversible.

Nitric oxide is a colorless gas that has some harmful effects on health, but these effects are substantially less than those of an equivalent amount of NO_2. In the atmosphere and industrial devices NO reacts with O_2 to form NO_2, a brown-colored gas that is a serious respiratory irritant. It also can be oxidized by ozone, OH, or HO_2 radicals to form the higher oxides of nitrogen, such as NO_2, HNO_2 and HO_2NO_2. Thus if NO is prevented from entering the atmosphere, most of the downstream effects of NO_x pollution can be eliminated.

2.1 Source of Nitric Oxide

The main source of nitric oxide is the combustion of petroleum products by mobile sources and the combustion of fossil fuels from stationary sources,

especially when combustion takes place at high temperatures and pressures. The burning of fossil fuels for generation of steam heat, electricity, and for general industrial activity contributed about as much NO to the atmosphere as that from traffic. Other sources include kraft and paper mils, wood burning, waste incineration, oil refining and gas production, cement processing, steel and iron industries, and ethanol production.

NO from large furnaces is dissipated into the atmosphere by chimneys, but it is a source of photochemical smog, and contributes to acid rain. Starting in the early 1970s a policy has gradually evolved in various countries, notably Japan, the United States and Germany, to establish a program of reducing emission levels of NO in flue gases from fossil-fuel-fired power stations.

Table 2.1 National emissions estimates for 1991 (De Nevers, 1995)
(Values in millions of metric tons/yr)

Source category	**PM_{10}**	**SO_x**	**CO**	**NO_x**	**VOCs**	**Pb**
Transportation	1.51	0.99	43.49	7.26	5.08	0.00162
Fuel combustion	1.10	16.55	4.67	10.59	0.67	0.00045
Industrial processes	1.84	3.16	4.69	0.60	7.86	0.00221
Solid waste disposal	0.26	0.02	2.06	0.10	0.69	0.00069
Miscellaneous	0.73	0.01	7.18	0.21	2.59	0.00000
Total	5.44	20.73	62.09	18.76	16.89	0.00497
Percentage of 1982 total	97%	101%	69%	92%	87%	9.5%

PM_{10} = particulate matter, 10 μ or smaller SO_x = all sulfur oxides mostly SO_2 CO = carbon monoxide NO_x = all nitrogen oxides, mostly NO VOCs = volatile organic compounds Pb = lead

2.2 The Formation and Reduction of NO in FBC

Johnsson (1994) reported that because the final NO emission is a balance between the reactions which lead to its formation and those with promote its destruction. So these followings show how NO is formed and reduced simultaneously in fluidized-bed combustion (FBC).The emissions of NO are very dependent on a number of operating conditions, and many homogeneous and heterogeneous reactions are important for the formation and destruction of NO. During the combustion of fossil fuel, nitric oxide gas arises from nitrogen from the air (thermal-NO) and the oxidation of nitrogen compounds (fuel-NO). During devolatilization, fuel-nitrogen is divided between char-nitrogen and volatile nitrogen compounds, mainly in the tar and as NH_3 and HCN. When combustion occurs, the char-nitrogen is oxidized to NO and N_2O and simultaneously partly reduced to N_2, but small amounts of NH_3 and HCN may also be formed. The volatiles-N may be oxidized to NO, N_2O or N_2, or may take part in the reduction of NO and N_2O together with CO and H_2 homogeneously, or heterogeneously with char, limestone, ash and sand as catalysts. This reaction scheme is used as a framework for the discussion of the formation and reduction of NO and N_2O in FBC. There is no thermal NO formation in FBC because of the low combustion temperature, but a small amount of prompt NO may be formed.

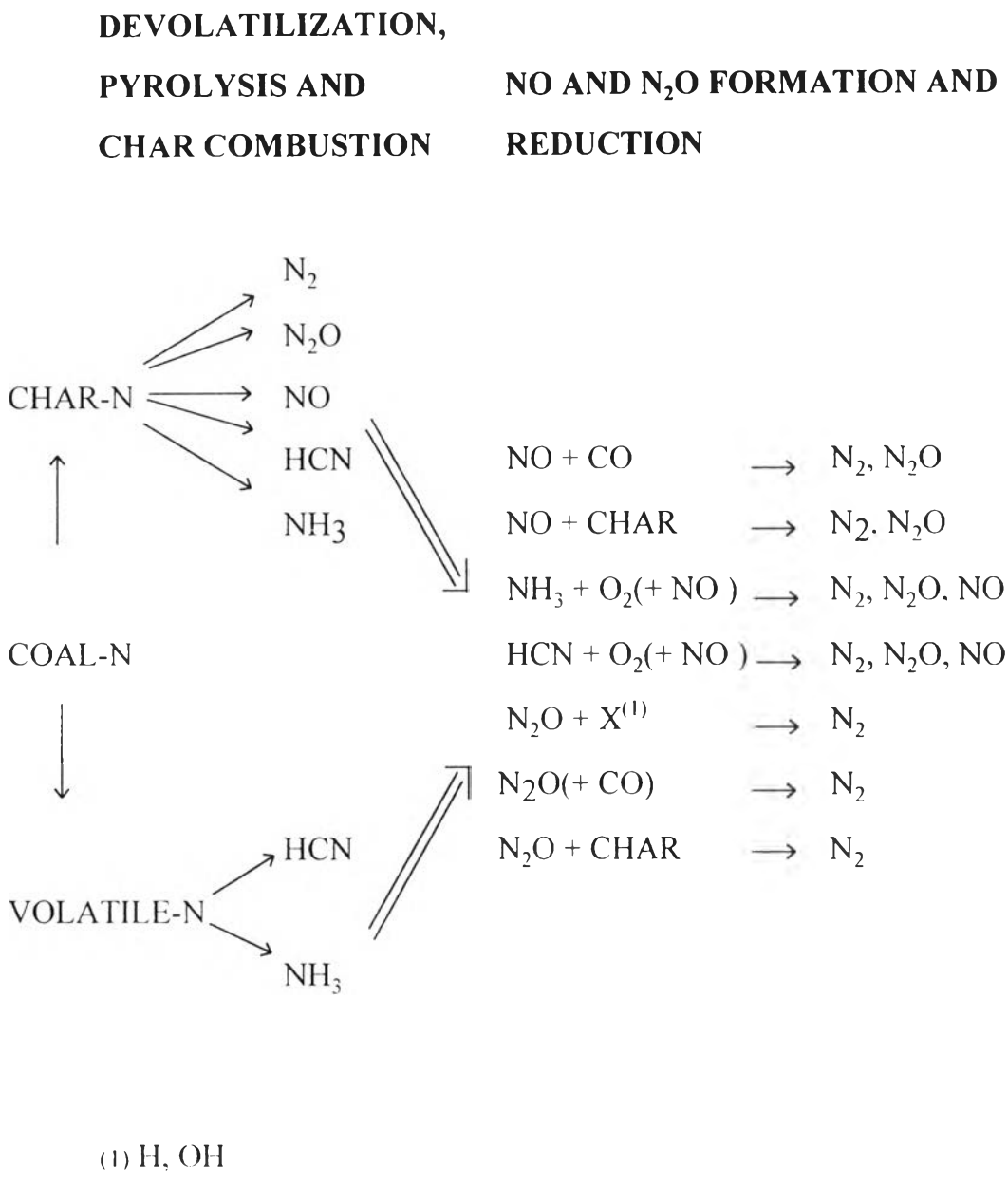


Figure 2.1 A simplified scheme for the conversion of fuel-nitrogen in fluidized-bed combustion (FBC) (Johnsson, 1994).

2.3 NO Emission Control

NO emission can be controlled by various methods of combustion control or by a variety of flue gas treatments. It can be reduced by the use of catalytic converters, activated carbon as an adsorbent, lowering combustion temperatures, careful air/fuel control during combustion, reducing the nitrogen content of fuels, and injection of either water or steam into the combustion chamber of boilers.

There are a number of commercial approaches to NO removal. A process for the cleanup flue gas using carbon for simultaneous removal of SO_2 and NO_x has been proposed by Knoblauch et al., 1981. In this process, activated carbon is used as an adsorbent for SO_2 removal and as a catalyst for NO_x reduction with NH_3. This technology is known as SCR (Selective catalytic reduction). However, the rate of denitrification with commercial activation carbons may not be high enough to match the rapid desulfurization rate. Therefore metals such as copper and nickel have been impregnated on the carbon (Illan-Gomez et al., 1996). Another approaches is carbon activated with sulfuric acid (Mochida et al., 1985). By these means, the catalytic activity for the reduction of NO with NH_3 is enhanced. However, these measures add to the cost of preparing the carbon.

It was recognized that NO produced during combustion can be heterogeneously reduced in-situ by the carbonaceous solid intermediates of combustion (Furusawa et al., 1985; Shimizu et al., 1992). Oxides of nitrogen formed during the combustion of coal can subsequently react with carbon to produce N_2, a highly desirable reaction. These reactions can be written as follows:

$$C + NO \longrightarrow CO + \tfrac{1}{2} N_2$$

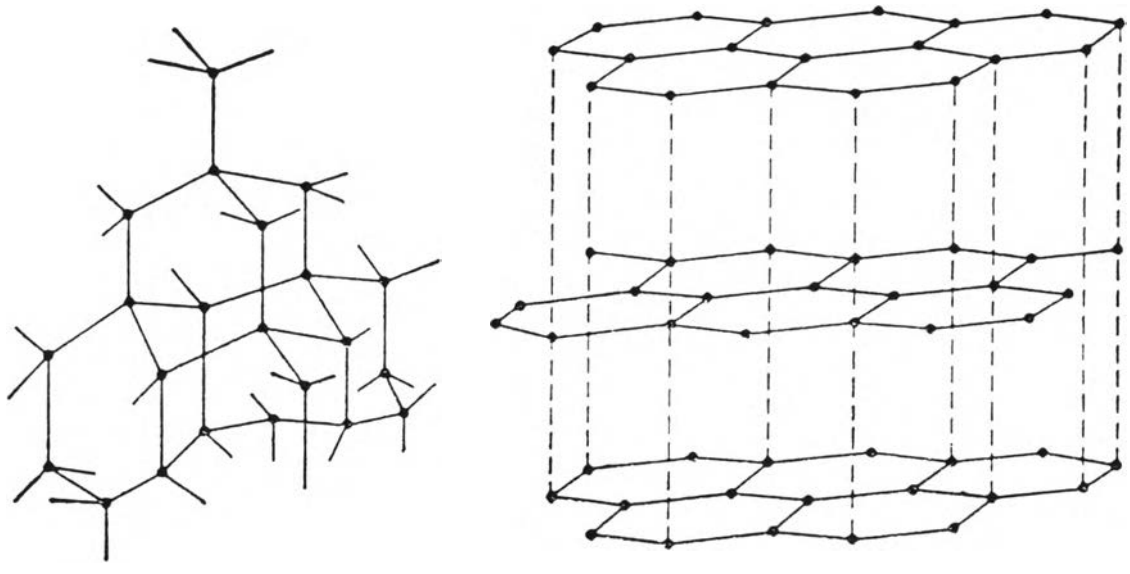
$$C + 2NO \longrightarrow CO_2 + N_2$$

Pereira et al. (1975) observed that nitric oxide formed in the lower part of the fluidized bed was significantly reduced in the upper part of the fluidized bed as well as in the free-board. Thus the overall emission level of nitric oxide is determined by the relative importance of the formation and in-situ destruction processes.

2.4 Carbon Gasification

The gasification of carbon is a most important process in our society. In some cases, it is a highly desirable reaction which we want to proceed at a maximum rate. In other cases, it is a highly undesirable reaction, which we want to proceed at a negligible rate. In both cases, understanding the fundamentals of carbon gasification is vital to our making the desired technological advances.

It is generally not recognized how important many types of carbon are to our society. Carbon comes in two main crystallographic forms : graphite and diamond as shown in Figure 2.2. Graphite has trigonal bonding of carbon atoms; diamond has tetrahedral bonding. The structure of the carbonaceous solid produced and the presence of heteroatoms and inorganic species will determine the ease with which the solid is gasified. In some processes and use of carbonaceous solids, it is desirable that gasification rates be rapid; in others, it is equally important that gasification rates be very slow.



Diamond arrangement Graphite arrangement

Figure 2.2 The arrangement of carbon atoms in the graphite and diamond - lattice (Walker et al., 1986).

The followings are the global chemistry of important gasification reactions (Walker et al.,1986).

2.4.1 C-O_2 Reaction

Arguably, the combustion of carbon to produce heat is the most important chemical reaction available to mankind. However, as we will see shortly, carbon gasification by O_2 is most undesirable when carbon is used as a material. It has been shown that upon the reaction of carbon with O_2 , two primary gasification products, CO and CO_2, are formed.

$$C + O_2 \longrightarrow CO_2$$

$$C + \tfrac{1}{2} O_2 \longrightarrow CO$$

Following these reactions, secondary reactions can occur, as follows

$$CO + \tfrac{1}{2}O_2 \longrightarrow CO_2$$

$$C + CO_2 \longrightarrow 2CO$$

2.4.2 <u>C-H_2O Reaction</u>

As we will see, carbon gasification by steam is most important reaction. Like the C-O_2 reaction, there are instances where the reaction is desirable: there are other instances where it is undesirable. Following the gasification of carbon by steam, other reactions can occur which can be of great importance. Some are listed.

$$C + H_2O \longrightarrow CO + H_2$$

$$CO + H_2O \longrightarrow CO_2 + H_2$$

$$C + CO_2 \longrightarrow 2CO$$

$$C + 2H_2 \longrightarrow CH_4$$

$$3H_2 + CO \longrightarrow CH_4 + H_2O$$

2.4.3 <u>C-NO Reaction</u>

In addition to O_2, H_2O, CO_2, and H_2 being important molecular reactants for the gasificatin of carbon, other reactants should be mentioned. Interaction of several of these reactants with carbon has considerable significance to the air pollution field. For example, oxides of nitrogen formed

during the combustion of coal can subsequently react with carbon to produce N_2, a highly desirable reaction.

$$C + NO \longrightarrow CO + \tfrac{1}{2} N_2$$

$$C + 2NO \longrightarrow CO_2 + N_2$$

2.5 Graphite

Graphite is a crystalline form of carbon. It melts at about 3,650 °C and vaporizes at about 4,500 °C. At 650-750 °C it slowly decomposes in the presence of oxygen to form carbon dioxide. Artificial graphite can be manufactured from petroleum coke.

The first structural analysis of graphite was proposed by Debye and Scherrer in 1917 but was incorrect as the stacking was described in A-B-C-A-B-C sequences. Five years later Hull re-examined the graphite lattice and stated that adjacent layers are translated by a bond length. but alternative layers have identical projections, these being A-B-A-B sequences with the unit cell of a hexagonal lattice. In 1924 Bernal published his careful analyses of single crystal graphite and confirmed the postulates of Hull. The unit cell was 0.682 nm high and 0.245 nm on each side. The interlayer spacing is assigned as 0.3354 nm, the density being 2.267 g cm^{-3}. The hexagonal structure of graphite is shown is Figure 2.3.

The surfaces of a graphitic carbon consist of two types; the basal plane surface and the edge plane surface. The surface areas of the graphites are quite low, and dominated by basal plane area. It is the edge sites and other imperfections in the planar aromatic structure that are commonly thought to be the main locus of the C-NO reactions.

It has been well demonstrated by the use of electron microscopy and optical microscopy that vacancies and the edge sites on carbon surfaces are active sites and that only these sites contribute to gasification reactions (Baker, 1986). The defect-free basal plane has only negligible reactivity that make no or little contribution to gasification reaction. Therefore, the edge surface area is responsible for gasification.

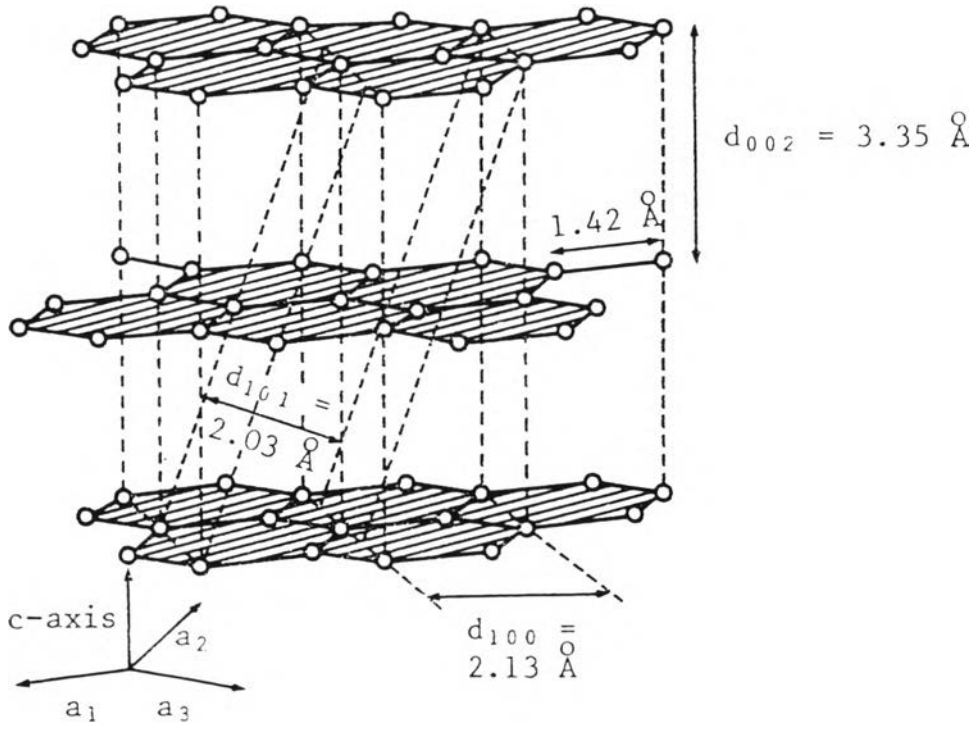


Figure 2.3 The hexagonal structure of graphite (Walker et al., 1986).

2.6 The Carbon-Nitric Oxide Reaction

Because the carbon-nitric oxide reaction is favorable thermodynamically and carbon is relatively inexpensive, therefore the use of carbon to convert NO to CO or CO_2 and N_2 is a possible way of reducing NO. By using carbon as a reducing agent, obvious potential advantages are offered. It eliminates the environmentally problematic "slip" of the gaseous reducing agent e.g., ammonia (Illan - Gumez et al., 1996).

The reaction of carbons with NO has been less studied and is so arguably even less well understood. The key variables affecting measured kinetics are temperature and nitric oxide partial pressure (Aarna and Suuberg, 1997).

In many of the kinetic investigations reported in the literature the reaction of pure nitric oxide with carbons is generally first order with respect to nitric oxide partial pressure (Furusawa et al., 1980). However reaction orders between 0.42 and 0.73 have also been found (Jonhsson et al., 1991 and Schuler J., 1987). This confusion in the literature regarding this issue may arise from experimental system artifacts.

Aarna and Suuberg (1997) observed the activation energy changes with temperature, indicating a complex reaction mechanism. There is substantial evidence of the often-reported "break" in the Arrhenius plot, whereas the activation energy of the reaction process increases as temperature being raised beyond a certain threshold. There is, however, no general agreement as to the temperature of the break point. It is seen to occur at temperature as high as around 1075 K and as low as 850 K. There are also several studies which gave no evidence of a break in these Arrhenius plots. There is no immediately apparent reason why this should be so.

The particular reactor system chosen to perform the study has a small influence on the results. Also the rates are not mass transport controlled in the range of temperature of 648-1250 K. It is consistent with the fact that there is no evidence of a second high temperature "break" in any of the Arrhenius plots, involving a transition to low apparent activation energies. Such behavior is often indicative of an onset of mass transport limitations.

The amount of the various reaction products formed is dependent on the gasification temperature. It was found that at low temperatures N_2 and CO_2 were formed, while at temperature above the temperature corresponding to the increase in the activation energy N_2, CO and CO_2 were formed (Furusawa et al.,1986).

2.7 Turnover Frequency

The *turnover number*, or *turnover frequency*, is the number of molecules that react per site per unit time. As a basic measure of true catalytic activity, this is a useful concept, but it is limited by the difficulty of determining the true number of active sites (Satterfield, 1991).