

# Nox Formation During Combustion Process and in-Furnace Control Technologies

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## Abstract

*Coal has been and will remain a major source of energy and power for mankind. Unfortunately, the demerit associated with coal-fired energy generation systems is the pollutant gaseous emissions like NO<sub>x</sub>, SO<sub>2</sub>, CO<sub>2</sub> and CO. There is increasing concern for regulating air quality and off setting the emissions from coal-fired power plants due to more stringent limits on these emissions. There are many in-furnace NO<sub>x</sub> control techniques. All these techniques are based on two staged or three staged combustion by controlling air and fuel flow rates to create fuel lean or fuel rich zones to suppress the NO<sub>x</sub> formation during devolatilization and then its destruction by utilising the reductive power of the hydrocarbons from fuel. NO<sub>x</sub> formation mechanisms in combustion systems and two staged combustion/air staging and three staged combustion/reburning control techniques have been discussed which are important to understand while applying any combustion modification scheme. The proximate and ultimate analysis of two cross continental biomass fuels have been presented to explore their potential as substitute fuel and agent to control gaseous pollutants from coal fired power stations.*

*Keywords: Devolatilization, Combustion, Air-staging, Reburning*

## Introduction

Coal is the largest source of electricity generation in the world today. Total global share of the electricity generated by coal is 40.3% (IEA, 2007). In future, fossil fuels will remain the dominant source of energy worldwide, meeting 83% of the increase in energy demand. Emissions from power generation will account for 44% of global energy-related emissions by 2030, as demand for electricity rises, Coal will provide the largest incremental source of power generation. Over 70% of the increase in global primary energy

demand will come from developing countries (DTI, 2007).

Most of the UK's power stations closures over the next decade are being driven by EU environmental legislation aimed at reducing SO<sub>2</sub> and NO<sub>x</sub> emissions. The Large Combustion Plant Directive (LCPD) imposes two separate constraints on coal and oil stations. One requires that about 11GW of "opted-out" coal and oil stations close by 2015 and the second restricts the operation post -2016 of around 20 GW of coal stations that "opted in" to meet the requirements of the LCPD. The extent to which the operation of

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power stations is affected by this second constraint depends on how much further investment firms decide to make in their power stations between now and 2016 to comply with reduced limits for NO<sub>x</sub> emissions (DTI, 2007).

Directive of the European parliament for emission have tighten the limits for NO<sub>x</sub> as follows;

**Table 1. Limits for NO<sub>x</sub>**

NO <sub>x</sub> (for O <sub>2</sub> content 6%)	
50 to 500 MWth	600 mg/ Nm <sup>3</sup>
>500 MWth:	200 mg/ Nm <sup>3</sup>

The term NO<sub>x</sub> refers to the sum of nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>). Among these oxides of nitrogen which are referred as NO<sub>x</sub> as a result of coal combustion NO constitute 90-95% of total amount of Nox produced (Cances et al. 2008).

Coal combustion generates significant quantities of nitrogen oxides (NO<sub>x</sub>), which contribute to photochemical smog and acid rain. The emission of nitrogen oxides from combustion of coal remains a problem of considerable interest, whether the concern is with acid rain, stratospheric ozone chemistry, 'greenhouse' gases or the more stringent NO<sub>x</sub> control conditions. This interest has led to a large amount of work on the kinetics and mechanism of reduction of NO by various means Combustion modification techniques reducing NO<sub>x</sub> emissions, such as staged combustion and reburning or post-combustion treatment by injection of selective reducing agents reaction (Kambara et al., 1995; Aarna and Suuberg 1997).

This paper summarizes NO<sub>x</sub> formation mechanisms during combustion process and in-furnace staged technologies to reduce NO<sub>x</sub> by utilising the kinetics of the formation mechanisms. Moreover, the potential of Co-firing of biomass with coal to control NO<sub>x</sub> and generate green power is indicated.

## Pathways of NO<sub>x</sub> formation in combustion systems

There are three identified homogeneous gas phase reaction pathways for the formation of NO<sub>x</sub> according to the source of nitrogen and chemical kinetics of this nitrogen oxidation known as thermal, prompt, and fuel NO<sub>x</sub> mechanisms (Hill and Smoot 2000; Williams et al. 1997).

### Thermal NO<sub>x</sub> formation

Thermal NO<sub>x</sub> is formed by the oxidation of the nitrogen present in the air supplied for combustion under fuel-lean conditions. The formation of thermal NO has a strong dependence on temperature, residence time, and a linear dependence on the concentration of oxygen atoms. In other words, formation of thermal NO is usually associated with high temperature and fuel lean environments. During the combustion process, at high temperatures free oxygen atoms, produced in flames by dissociation of O<sub>2</sub>, attack nitrogen molecules which can be described by the widely accepted two-step Zeldovich mechanism given below.



In the case of fuel-rich flames where the OH radicals are present in higher concentrations than atomic hydrogen or oxygen, the two-step mechanism under-predicts NO generated, so a third elementary step that considers the effect of OH radicals is used as given by the extended Zeldovich mechanism.



The kinetics of these reactions is slow and generally in pulverised coal combustion, there is a sufficient amount of excess oxygen present. Thus by invoking "quasi steady state" approximation that the rate of consumption of nitrogen atoms equals its rate of formation due to thermal mechanism may be expressed (Bowman 1991):

$$\frac{d[NO]}{dt} = 2k_1 [N_2] \frac{1 - \frac{[NO]^2}{K [O_2] [N_2]}}{1 + \frac{k_{-1} [NO]}{k_2 [O_2]} + \frac{k_3 [H]}{k_2 [O_2]}} \quad (4)$$

Where  $K = (k_1/k_{-1}) (k_2/k_{-2})$  is the equilibrium constant for the reaction between  $N_2$  and  $O_2$  the maximum NO formation rate can be written as (Bowman 1991):

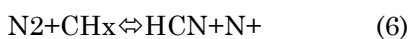
$$\frac{d[NO]}{dt} = 1.45 \times 10^{20} T^{-1/2} \exp\left(-\frac{6940}{T}\right) [O_2]^{1/2} [N_2] \quad (5)$$

This is quite evident from the above equation that the rate of thermal NO formation is strongly dependent on the temperature and relatively weaker dependent on the oxygen concentration. Hence, thermal NO reduction can be achieved either by opting temperature reduction techniques like flue gas recirculation (RFG) low excess air (LEA),  $CO_2$  injection in the combustion air, water or steam injection etc.

Thermal NO formation occurred less in fuel rich conditions due to low concentration of oxygen atoms and in low temperature flames (<1800K) but thermal NOx mechanism is prevalent during the combustion of clean fuels i.e. fuels which do not contain inherent nitrogenous compounds like natural gas.

**Prompt NOx formation**

Prompt NO is formed in fuel-rich environments with short flame-residence times; formation being initiated through various hydrocarbon fuel fragments like CH and  $CH_2$  produced as a result of devolatilisation process. These hydrocarbon fragments attack molecular nitrogen near the reaction zone of the flame. This phenomenon occurred very rapidly. The prompt NO formation is described by the Fennimore reaction given below:



The cyano species reacts further to form NO through the following reaction

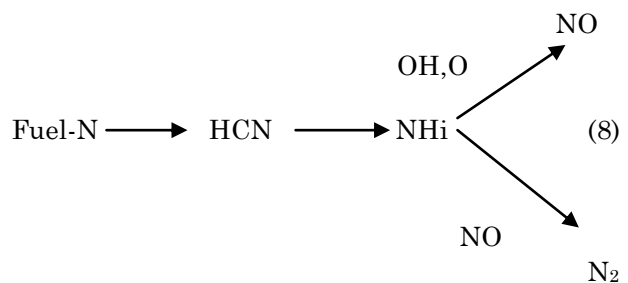


NO formation through this path increases as the hydrocarbon concentration increases.

**Fuel Nox formation**

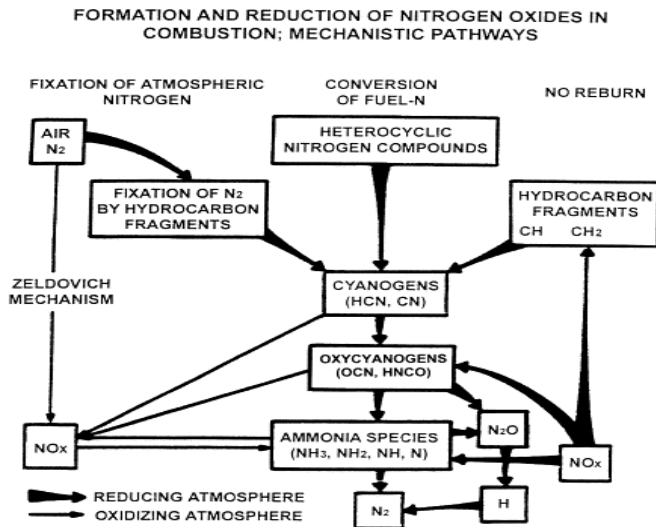
The principal source of  $NO_x$  emission in combustion systems is the nitrogen that is chemically bound in the fuel (Ikeda et al., 2003). Fuel NO can be formed from the homogeneous oxidation of nitrogen constituents released during the devolatilisation process or from heterogeneous oxidation of nitrogen compounds remaining in the char following devolatilisation.

Therefore fuel  $NO_x$  can be reduced by measures which affect both homogeneous and heterogeneous reactions. (Pershing and Wendt 1979). The yield of the devolatilized nitrogen contains 90-95wt% of HCN and  $NH_3$  (Kambara et al. 1995). The conversion of fuel nitrogen to HCN is not rate limiting (Miller et al., 1984). HCN is then slowly converted to amine species ( $NH_i; i=0,1,2,3$ ) which then has two competing routes to form NO or  $N_2$ . (Haynes 1977a, 1977b)



(Kambara et al., 1995) developed an index for estimating fuel nitrogen conversion ratio.

$\frac{[\text{VolatileN}] * [NH_3]}{[HCN]}$ . Fig1. illustrates chemical pathways of nitrogen compound interconversions in fuel lean and fuel rich flames.



Fig;1. Chemical pathways of NO<sub>x</sub> formation and destruction.

Source: Beer.J.M., (2000)

### Control of NO<sub>x</sub> emissions

The various techniques for the control of NO<sub>x</sub> emissions can be classified into two broad categories:

- Combustion control/In furnace NO<sub>x</sub> formation control/Combustion modification technologies
- Post combustion control/Flue gas treatment

Traditional combustion control systems include:

- Flue- gas Recirculation (FGR)
- Burners-Out-of-Service (BOOS)
- Low Excess Air (LEA)
- Low NO<sub>x</sub> Burner (LNB)
- Air Staging/Over Fire Air (OFA)
- Fuel Staging/Reburning
- Water steam injection

Combustion control refers to techniques which aim to minimise the NO<sub>x</sub> emissions during

the formation stages of combustion by creating the conditions necessary for the generation of NO<sub>x</sub> through the various mechanisms discussed above. Combustion control techniques achieve reduction of NO<sub>x</sub> by lowering either flame temperature, creating fuel-rich regions at the maximum flame temperature to suppress volatilisation process by reducing the availability of the oxygen in the flame, lowering the residence time under oxidizing conditions or the combination of this. This approach can reduce both fuel and thermal NO<sub>x</sub>. Basically, this technology is based on air or fuel staging techniques to take advantage of the NO<sub>x</sub> formation kinetics.

The post-combustion control methods reduce NO<sub>x</sub> emissions after the NO<sub>x</sub> is formed by converting them into N<sub>2</sub> with reagents. Two important post-combustion treatments are Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR). These are usually very costly due to catalyst, reagents costs and frequent maintenance costs.

### Air Staging

The general principal of air staging is to create a condition in which the burner operates under fuel rich conditions, producing relatively low-temperature and oxygen deficient primary zone and then a fuel lean secondary combustion zone is created by the injection of a portion of combustion air later in the furnace for complete combustion. (Clarke and Williams 1991). This is also referred as Two Stage Combustion (TSC). The conversion of primary zone to sub-stoichiometric region encourages fuel nitrogen conversion to molecular nitrogen rather than NO<sub>x</sub>. Creation of fuel rich zone and fuel lean zone delays the combustion process, imparts less mixing of air with fuel resulting lower flame temperature and suppression of NO<sub>x</sub> formation due to Oxygen deficiency in the designated region (Liu 1995) Thermal NO<sub>x</sub> is also reduced since the peak temperature occurs where the oxygen concentration is low.

Generally there are two ways of injecting remaining necessary air for complete combustion:

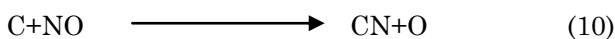
- (1) by adding through openings located high up in the furnace called Over Fire Air (OFA) ports whereby the all the burners are run under fuel rich conditions.
- (2) by operating selected burners fuel rich whereas the remaining burners operate under air –rich or air alone conditions

This kind of staging is termed as burners out of service (BOOS).

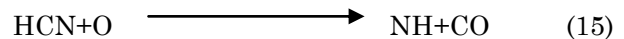
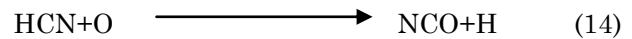
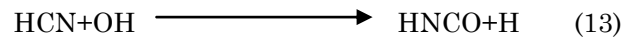
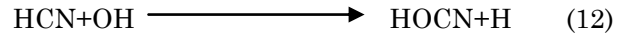
Furnace air staging alone as a NO<sub>x</sub> control technique is used in over 116 coal-fired units world wide, with a total generation capacity of 50GW. Air staging in combination with low-NO<sub>x</sub> burners/FGR has also been in operation in 175 coal-fired units with a total capacity of 53GW ( Coal Research and Development 1997). About 20-30%NO<sub>x</sub> reduction can be achieved with air staging (Boardman et al. 1993).

### Fuel Staging/Reburning

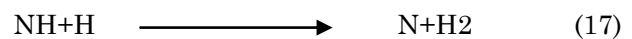
Reburning or fuel staged combustion technique utilises reductive power of hydrocarbons (Burch et al. 1994). Based on the staged fuel supply and combustion air, combustion scheme in “Reburning” can be divided into three combustion zones operating under fuel lean, fuel rich and fuel lean conditions. In the primary zone, the primary /main fuel is burnt under fuel lean condition. In the next zone which is termed as “Reburn Zone” secondary fuel which is referred as the reburn fuel is injected to create fuel rich reducing atmosphere producing hydrocarbon radicals. The reburn fuel can also be different from the primary fuel. These radicals react with the NO formed in the primary zone to produce molecular nitrogen (N<sub>2</sub>) (Harding and Adams. 2000).



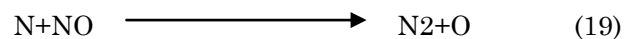
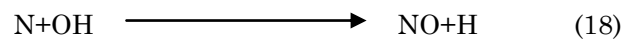
The HCN is then converted to other nitrogenous species via the following reactions (Thorne et. al., 1986):



The subsequent conversion of N atoms is very fast and occurs through the rapid decay of NCO (Chen et al., 1986)



These N atoms are either recycled to form NO or converted to N<sub>2</sub> via the reverse Zeldovich reaction:



The last zone is called burnout zone in which the additional or final air is introduced to create overall lean environment to complete the combustion process. More than 188GW of electric power generating capacity currently in operation internationally has been fitted by these staging measures (Beer, 2000)

### Co-Combustion

Another option to reduce in furnace NO<sub>x</sub> formation is replacement of fossil fuel by co-firing with a fuel containing lower nitrogen content and high volatile content. Co combustion refers to simultaneous combustion of supplementary fuel (i.e.biomass) with a base fuel (i.e.coal).Co-firing biomass with coal is seen as cheapest way of green power generation in utility plants(Sami etal,2001,Baxter,2005;Demirbas,2005).A

combination of co-firing with air and fuel staging could improve the combustion modification technology significantly.

The term “biomass” refers to forestry, purpose grown agricultural crops, trees, plants, organic wastes, agricultural, agro-industrial and municipal waste (Garg and Datta 1998) Co-firing of Biomass and coal is an effective method of control NO<sub>x</sub> and SO<sub>2</sub> (Broek et al., 1996; Bainetal., 1998; Hein and Bemtgen., 1998; Spliethoff and Hein., 1998; Tillman 2000; Demirbas, 2003a; Demirbas, 2005; Hartmann and Kaltschmit., 1999).

Two different kind of agricultural residues (1) Cotton Stalk (2) Sheameal along with Russian coal RC2 were evaluated. Cotton stalk is the stem of cotton plant (*Gossypium*) without branches and leaves which is a leftover waste of the cotton crop. Cotton stalk (CS) samples were obtained from southern agricultural fields of the Punjab in Pakistan. Shea meal (SM) is the residue from the nut of the shea tree (*Vitellaria paradoxa*) after the removal of fatty ‘butter’ for cooking and contains the fleshy mesocarp, shell and husk. This biomass material is currently used as fuel in the UK power generating industry (Munir S et al., 2009). Shea meal sample and coal (Russian coal) RC2 for this study was provided by (RWE npower) UK. The proximate and ultimate analysis along with bulk densities of the samples are given in Table 2. Proximate analysis and ultimate analysis measurements were conducted using a thermogravimetric analyser (Shimadzu TGA-50) and CE Instruments Flash EA1112 series, respectively. The proximate TG method involves heating the sample (under N<sub>2</sub>) at a rate of 10 oC/min to 110 oC then holding for 10 min to obtain the weight loss associated with moisture. The temperature is then ramped from 110 oC at a rate of 25 oC/min to 910 oC (under N<sub>2</sub>) and held for 10 min to obtain the weight loss associated with volatiles release. Air is then introduced into the furnace chamber to oxidise the carbon in the char and the weight loss associated with this is the

fixed carbon. The remaining material after combustion is the ash. The calorific values were determined by using Parr 6200 oxygen bomb calorimeter. Ultimate and proximate analysis and HHV of the coal used RC2, and SM and CS, are given in table 2. This is evident from table 2 that CS and SM contain a higher proportion of oxygen, hydrogen and less carbon, which reduces the heating value because the energy contained in carbon–oxygen and carbon–hydrogen bonds is less than carbon–carbon bonds.

The H/C ratio of SM=0.12 and O/C=0.77 falls in the overlapping region attributed to biomass and RDFs on a Van Kerevelin type diagram whereas CS (H/C=0.09; O/C=0.89) is located in the region that is typically attributed to biomass. VM/FC of the CS=4 and SM=2.3 as compared to RC2=0.66 (Table 2) which is the measure of the ease with which a fuel can be ignited or oxidised. This is quite evident from the proximate and ultimate analysis given in table 2 and the placement of biomasses in the van kerevelin type diagram figure 2 that Biomass as a class seems very much different from coals. They have high volatile matter, higher hydrogen content, generally low nitrogen content and little or zero sulphur (Sami et al., 2001; Demibas 2003) therefore net SO<sub>2</sub> emissions can also be reduced by co-firing coal and biomass.

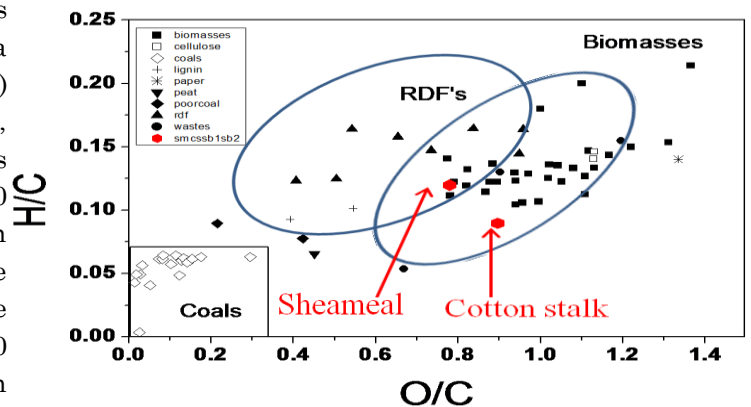


Figure 2. Van Kerevelin type diagram

**Table2. Ultimate and Proximate analysis of the fuels**

Fuel	Ultimate Analysis <sup>a</sup>					Proximate Analysis <sup>a</sup>			Bulk <sup>c</sup> density (kg/m <sup>3</sup> )	HHV (MJ/kg)
	C (%)	H (%)	O <sup>b</sup> (%)	N (%)	S (%)	Ash (%)	FC (%)	VM (%)		
CS	47.07	4.58	42.10	1.1	--	5.1	18.8	76.1	310	17.7
SM	48.56	5.86	37.60	2.88	0.1	5.0	28.7	66.3	490	17.70
RC2	70.69	4.68	9.57	2.23	0.37	12.46	52.42	35.12	623	27.39

As volatile matter content in the biomasses is much higher than the coals this would reduce the ignition temperature in the case of co-combustion resulting reduction in Thermal NO<sub>x</sub> formation. Biomasses have more hydrogen than coals so greater concentration of CH<sub>i</sub> radicals from biomass devolatilization process utilises reductive power of the hydrocarbons, under low O<sub>2</sub> conditions, as HC are known to react with NO<sub>x</sub> to produce molecular N<sub>2</sub>. This process is called 'Nox reburning'.

Another anticipated advantage of this combination is the catalytic reduction of NO<sub>x</sub> because the volatile biomass fuel nitrogen preferably forms NH<sub>3</sub> in contrast to HCN formed by coal nitrogen (Splietoff and Hein1998; Werther et al., 2000; Baxter, 2005) and the biomass with slightly higher nitrogen content during reburning could achieve NO<sub>x</sub> reductions equivalent to those obtained by the addition of ammonia which is termed 'advance reburning'. As the majority of fuel nitrogen released during biomass combustion ends up as NH<sub>3</sub> rather than HCN, N<sub>2</sub>O formation is not a problem because the only latter is the principal source of N<sub>2</sub>O emissions (Werther et al., 2000). It is expected that because of the high content of volatiles, biomasses (agricultural residues) are ideally suited for the application of NO<sub>x</sub> reducing processes, such as air staging and reburning. Biomasses are believed as CO<sub>2</sub> neutral fuels as they emit the same amount of CO<sub>2</sub> during combustion as they had absorbed during their life cycle More over they are renewable as well. . It is

expected to utilize biomass as a low-cost, substitute fuel and an agent to control emission.

## Conclusion

Thermal NO<sub>x</sub> is formed by the oxidation of the nitrogen present in the air supplied for combustion under fuel-lean conditions. The formation of thermal NO has a strong dependence on temperature, residence time, and a linear dependence on the concentration of oxygen atoms. Fuel NO can be formed from the homogeneous oxidation of nitrogen constituents released during the devolatilisation process or from heterogeneous oxidation of nitrogen compounds remaining in the char following devolatilisation.

In-furnace NO<sub>x</sub> control techniques achieve reduction of NO<sub>x</sub> by lowering either flame temperature, creating fuel-rich regions at the maximum flame temperature to suppress volatilisation process by reducing the availability of the oxygen in the flame, lowering the residence time under oxidizing conditions or the combination of this. This approach can reduce both fuel and thermal NO<sub>x</sub>. Basically, this technology is based on air or fuel staging techniques to take advantage of the NO<sub>x</sub> formation kinetics. Co-firing of biomasses with coal could also be an attractive in-furnace option to control Nox because of because of higher volatiles release from biomass devolatilization to produce larger fuel rich zones

for the destruction of NO<sub>x</sub>. The energy potential, proximate and ultimate analysis of two potential cross continental biomasses have also been presented. This was found that SM and CS have much higher VM than RC2. Similarly SM and CS are highly oxygenated with less sulphur and higher VM/FC. Therefore, co-combustion of biomass with coal not only control gaseous pollutants due to their share as cleaner substitute but also due to the release of lighter hydrocarbons due to the higher volatiles in the biomasses.

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