

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY

LUT School of Engineering Science

Master of Science (Technology) in Chemical and Process Engineering

Techno-economic analysis (TEA) tool for NO_x mitigation solutions

Examiners: Prof. Tuomas Koiranen

Prof. Esa Vakkilainen

Supervisors: M.Sc. Satu Simila

M.Sc. Joonas Arola

Saqlain Zafar

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ABSTRACT

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Tight NO_x limits set by the regulatory authorities have necessitated the suppliers of NO_x removal technologies to consider the cost-effective alternatives for their industrial customers. The objective of the master thesis is to develop a techno-economic analysis (TEA) tool for industrial NO_x mitigation technologies. The techno-economic comparison facilitates in the preliminary selection of the most feasible NO_x abatement concept among various alternatives. Currently, the typical NO_x control systems that prevail in the industrial market are selective non-catalytic reduction (SNCR), selective catalytic reduction (SCR) and NO_x scrubbers. NO_x scrubbers are categorized according to the oxidant type such as ozone (O₃) scrubber and chlorine dioxide (ClO₂) scrubber in this study. The number of choices for these concepts are further increased by combining these technologies to form a hybrid system such as SNCR + SCR and SNCR + NO_x scrubber.

In the TEA tool, technology selection and economic evaluation tasks are executed for the above-mentioned concepts. Technology selection procedure depicts the functioning of NO_x removal technologies according to the set criteria by an investor. The critical demands from an investor are typically the NO_x out contents and ammonia slip in the exhaust flue gas after the treatment system. The economic evaluation of NO_x control methods is assessed by taking into account the capital expenses (CAPEX) and operating expenses (OPEX) for lifetime.

Feasibility analysis is comprised of negative cash flows (costs) without any profit because there is no revenue generation in NO_x abatement technologies.

The SCR and NO_x scrubber technologies have a greater potential of NO_x reduction efficiency up to 95% as compare to SNCR (25-50%). Similarly, more strict NO_x out and ammonia slip limits in the exhaust flue gas are accomplishable through SCR and NO_x scrubbers as compare to SNCR method. Economic outcomes clearly show that SNCR is the least expensive NO_x reduction technique from both CAPEX and OPEX viewpoint, only in circumstances where its applicable in the combustion device and it meets the investor demands criteria. Tool findings of CAPEX in the SCR and NO_x scrubbers are not explicit because it depends upon the scope of investment and varies from case to case. OPEX results are more clear because the ozone scrubber system proves to be the most expensive than all other alternatives mainly due to electricity and oxygen gas consumption in the ozone generator. Ozone consumption trend for the target NO_x removal is analyzed through the simulation work in Aspen plus 9.0 software. Simulation results show that the optimal molar ratio of O₃/NO_x is between 1-2 for the oxidation and absorption of NO_x in the scrubber. The ClO₂ scrubber system can also turn out to be a costly option if the investment is requisite for the ClO₂ plant. Auxiliary effects of the technology are considered too for economic comparison such as effluent wastewater treatment in NO_x scrubbers. SCR method typically costs less than ClO₂/O₃ scrubber system in terms of OPEX according to the tool findings.

These economic findings differ in the scenarios where scrubber system removes the other pollutants simultaneously with NO_x contents such as acid gases, dust and ammonia whilst this principle also applies to the SCR method for removing altogether the ammonia slip, dioxins and furans with NO_x from the flue gas. In conclusion, there is no one rule of thumb for selecting the most feasible NO_x mitigation concept in the flue gas cleaning because investment prospect, suitability and scope differ especially in the retrofit cases.

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Lappeenranta, 3rd September 2018

Nomenclature

Symbols

C_i	- Concentration of component (i) / kmole m ⁻³
C_l	- Concentration of pollutant in liquid / kmole m ⁻³
C_g	- Concentration of pollutant in gas / kmole m ⁻³
$C_{g/l}$	- Equilibrium concentration of pollutant in gas / kmole m ⁻³
$C_{l/g}$	- Equilibrium concentration of pollutant in liquid / kmole m ⁻³
D_l	- Diffusivity of pollutant in liquid / m ² s ⁻¹
D_g	- Diffusivity of pollutant in gas / m ² s ⁻¹
E	- Activation energy / J mole ⁻¹
F	- Mass flux / kmole m ⁻² s ⁻¹
k	- Pre-exponential factor / m ³ kmole ⁻¹ s ⁻¹
K_H	- Henry's volatility constant / -
N	- Number of components / -
n	- Temperature exponent / -
T	- Absolute temperature / K
T_o	- Reference temperature / K
r	- Rate of reaction / kmole m ⁻³ s ⁻¹
R	- Gas law constant / J K ⁻¹ mole ⁻¹
v_{tot}	- Total velocity / m s ⁻¹
z_g	- Thickness of gas layer /mm
z_l	- Thickness of liquid layer / mm
α_i	- Exponent of component (i) / -
Π	- Product operator / -
\sim	- Approximately / -

Abbreviations

BAT	-	Best available techniques
BAT-AELs	-	Best available techniques associated emission levels
BFB	-	Bubbling fluidized bed
BHF	-	Baghouse filter
BOOS	-	Burners out of service
CFB	-	Circulating fluidized bed
Char-N	-	Char-nitrogen
DeNO _x %	-	NO _x reduction/removal efficiency, %
EU	-	European Union
ESP	-	Electrostatic precipitator
EPA	-	Environmental protection agency
Fuel-N	-	Fuel-nitrogen
FGR	-	Flue gas recirculation
LEA	-	Low excess air
LNB	-	Low NO _x burner
MR	-	Molar ratio
MW _{th}	-	Megawatt thermal
NSR	-	Normalized stoichiometric ratio
OFA	-	Overfire air
SNCR	-	Selective non-catalytic reduction
SCR	-	Selective catalytic reduction
TEA	-	Techno-economic analysis
volatile-N	-	volatile-nitrogen
WACC		Weighted average cost of capital

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1 Introduction

The combustion process in the power plant or chemical incinerator emits the gaseous side-product (flue gas) that is useless and dispersed into the atmosphere by means of a stack. The reasons for transporting the flue gas away from combustion facilities are the temperature and composition of the flue gas which is different from the ambient air at ground-level. Flue gas composition is significantly different from the ambient air because of combustion products water (H_2O), carbon dioxide (CO_2) and beside of these bulk species more concern is towards the other pollutants such as carbon monoxide (CO), unburnt hydrocarbons, oxides of nitrogen and sulfur, acidic compounds, trace elements such as mercury (Hg), nickel (Ni) and some super-hazardous compounds furan and dioxins. All these side products are undesired and produced from the combustion reaction of fuel or waste material with an excess supply of air.

Air pollution results from the harmful substances being emitted into the atmosphere and can cause adverse effects to living organisms and environment. Air pollution makes up one of the important issues in urban areas, where various air born pollutants are being concentrated by many sources (Chaloulakou, Mavroidis and Gavriil, 2008). The numerous sources of air pollution are automobiles, heat & power plants, chemical or waste incinerators and several industrial processes. Key combustion generated air-contaminants are oxides of sulfur and nitrogen, carbon monoxide, particulate matter and unburnt hydrocarbons. Among nitrogen oxides, most hazardous oxides as a consequence of the combustion process are nitric oxide (NO) and nitrogen dioxide (NO_2). NO_x notation typically refers to the sum of NO and NO_2 molecules and expressed as NO_2 . NO_x are considered primary pollutants for atmosphere since they cause environmental alarming issues such as photochemical smog, acid rain, tropospheric ozone formation and stratospheric ozone layer depletion. In addition, humans exposed to the high concentration of these gases may cause health problems.

Emissions of toxic pollutants in the ambient air are monitored by regulatory authorities such as Gothenburg and Kyoto Protocols and European Union (EU) directives. Ever-tightening environmental regulations are being imposed by the concerned authorities to cut down the NO_x emissions in the environment. Social dissatisfaction in urban areas and awareness among the political decision-makers with current state of the environment are some causes behind such stringent laws.

In the literature, three main approaches for NO_x emission control are noticed, pre-combustion, combustion modifications and post-combustion techniques. Chapter 4 elaborates these NO_x control strategies and a key focus in this study is only post-combustion methods.

1.1 Objective

The main aim of this work is to formulate a techno-economic analysis (TEA) tool for the cost comparison of NO_x emission control technologies. Various post-combustion NO_x control methods currently prevail in the commercial market such as selective non-catalytic reduction (SNCR), selective catalytic reduction (SCR) and oxidation-scrubber systems using oxidants such as ozone (O₃) and chlorine dioxide (ClO₂). Furthermore, these NO_x control treatments can be combined in order to achieve higher NO_x reduction efficiency (DeNO_x%) for example SNCR + SCR hybrid system. Hence, It's important to have such TEA tool for NO_x control technologies which exhibits the technical possibility from an investor viewpoint and present the economic comparison based on the capital and annual operating expenses. The TEA tool is developed in the Microsoft Excel and suggests about the selection of most feasible concept based on the certain input parameters set by the user. Overall TEA tool facilitates in the preliminary selection of technically-suitable and economically-feasible NO_x control technique during the sale phase of an investment.

Apart from this economic evaluation, process simulation of ozone scrubber system is performed in order to find the optimum O₃/NO_x molar ratio for the target DeNO_x%. The optimal molar ratio is a critical parameter in O₃ scrubber system and the required ozone generator capacity affects significantly the capital and operating cost. Aspen Plus 9.0 is used in this simulation work to generate the sensitivity analysis of ozone consumption vs nitric oxide (NO) removal. Ozone consumption trend is used for cost estimation purpose in O₃ scrubber system. Finally, economic indicators such as annual accumulative cash flows and Net present value (NPV) exhibit the investment feasibility among the various alternatives.

2 Nitrogen oxides

NO_x are also called the fresh nitrogen oxides as they reach the atmosphere in NO and NO₂ forms (Skalska, Miller and Ledakowicz, 2010). Other types of nitrogen oxides exist too in the environment such as nitrous oxide (N₂O), dinitrogen trioxide (N₂O₃), dinitrogen tetraoxide (N₂O₄) and dinitrogen pentoxide (N₂O₅). NO and NO₂ are produced simultaneously during the high-temperature combustion process. NO is oxidized rapidly in the atmosphere into NO₂ and thus, NO₂ formation in the air contributes as a secondary pollutant as a consequence of NO photochemical oxidation. NO₂ reactions continue to yield the different smog-related compounds having particulate and gas phases. Some important properties of nitrogen oxides are summarized in Table 1.

Table 1. Properties of Nitrogen oxides (Skalska, Miller and Ledakowicz, 2010)

Properties	N ₂ O	NO	N ₂ O ₃	NO ₂	N ₂ O ₄	N ₂ O ₅
Colour (EPA, 1999)	Colourless	Colourless	Black	Red-brown	Transparent	White
Solubility in water (g/dm ³) (Dora et al., 2009)	0.111	0.032	500	213	213	500
State of matter (ambient temperature)	Gas	Gas	Liquid	Gas	Liquid	Solid
Density (g/dm ³) (Edwards, Kuznetsov and Slocombe, 2013)	1.8	134 (293 K)	1447 (275 K)	3.4	1492.7 (273 K)	2050 (288 K)

Dinitrogen tetraoxide (N₂O₄) exist in equilibrium with NO₂ as pointed in reaction equation (1). At ambient temperature, NO₂ exist in dimer form (N₂O₄) while at high-temperature NO₂ is highly favoured. Both these nitrogen oxides absorb UV light readily and hence contribute to the photochemical reaction that eventually yields ozone and miscellaneous compounds in the atmosphere (Richards, 2000).



N₂O is stable at ambient condition and doesn't absorb UV light. So it doesn't participate in a photochemical reaction that outcomes ozone formation in the troposphere (Richards, 2000). In the combustion process, N₂O is destroyed rapidly at high-temperature flame zone and its

emission to the atmosphere is in trace quantity. Unlike NO and NO₂, the half-life of N₂O is more than 100 years because of its stable nature, and once it enters the atmosphere it remains there until it is dissociated in stratosphere zone (EPA, 1999). N₂O depletes the ozone layer in the stratosphere by breaking the chemical bonds of O₃ and therefore, it is classified as a greenhouse gas (Aneja et al., 2001). Other oxidized nitrogen compounds such as a nitrous acid (HNO₂) and nitric acid (HNO₃) are also formed in the atmosphere as result of photochemical reactions. These chemicals are typically emitted from the chemical and fertilizer industries in substantial quantities instead of combustion power plants (Richards, 2000).

2.1 Origins of NO_x

Key sources of NO_x emission are the automobiles and stationary combustion units. NO_x emission from the combustion process constitutes 95% NO and 5% NO₂ (Gómez-García, Pitchon and Kiennemann, 2005) (Van Durme et al., 2008)(Wang et al., 2007) ('Formation and control of nitrogen oxides', 1988). Nitrous oxide (N₂O) is although a greenhouse gas but not included in NO_x, and besides of being released from the combustion power plants, also discharged from the industrial chemical activities such as adipic acid and nitric acid production. Furthermore, human (anthropogenic) activities and natural sources of N₂O emissions are also worth listing such as agricultural activities (fertilizers usage in fields, burning residues for clearing land), lightning and sewers. Emissions of hazardous nitrogen oxides with a source of origin are shown in Table 2.

Table 2. Sources of Nitrogen oxides emission (Zevenhoven and Kilpinen, 2001)

Nitrogen oxides	Source	Contribution (%)
NO _x	Traffic	~60
	Fossil fuel-fired heat and power	~30
	Industry	~10
N ₂ O	Fossil fuel-fired heat and power	~30
	Forest fires, landgain, and oceans	~60
	Industry (e.g. adipic acid production)	~10

2.2 NO_x regulation

The environmental regulatory bodies such as EU Legislation set the emissions limit which ensures that under normal operating conditions emissions don't exceed the levels associated with the best available techniques (BAT). All fuels are considered for emissions limit under EU directives such as gaseous, liquid and solid combustible material. For instance, BAT listed for solid fuels (biomass, peat, coal and lignite) are combustion optimization, primary techniques (air staging, fuel staging, flue gas recirculation and low NO_x burner), SNCR, SCR and combined techniques for the NO_x and SO_x reduction. Best available techniques associated emission levels (BAT-AELs) of NO_x from the combustion of solid biomass or peat are classified in Table 3 under EU implementing decision 2017/1442. BAT-AELs of NO_x from the combustion of other fuels such as coal, lignite heavy fuel oil, natural gas, petroleum-derived fuels, iron and steel process gases, process fuels from the chemical industry and waste materials are also mentioned in EU directives (Commission Implementing Decision (EU) 2017/1442, 2017).

Table 3. EU regulations of NO_x emission from the combustion of solid biomass or peat at a reference oxygen content of 6 vol-% O₂

Combustion plant total rated thermal input (MW _{th})	BAT-AELs (mg/Nm ³)			
	Yearly average		Daily average or average over the sampling period	
	New plant	Existing plant	New plant	Existing plant
50-100	70-150	70-225	120-200	120-275
100-300	50-140	50-180	100-200	100-220
≥ 300	40-140	40-150	65-150	95-165

3 NO_x phenomenon in combustion process

The nitrogen content varies substantially in different types of fuels. For example, natural gas contains almost no nitrogen whilst, wood waste from the furniture production has contents of urea formaldehyde glue, which contains more than 30% nitrogen. In natural gas, nitrogen is usually found in molecular form as N₂ gas whereas, in other fuels, it exists in chemical bounded organic form. Fuel-nitrogen (fuel-N) in coal is mostly present in aromatic compounds such as pyrroles and pyridines while in the wood and peat amino type structures are more common. These nitrogen compounds are released in different forms during the pyrolysis or devolatilization stage, coal liberates mostly fuel-N in the form of hydrogen cyanide (HCN) while, peat and wood liberate fuel-N in the form of ammonia (NH₃). These intermediate compounds HCN and NH₃ may determine the final release form of nitrogen as either NO, NO₂, N₂O, or N₂ gas from the combustion process (Hämäläinen, Aho and Tummavuori, 1994). The typical nitrogen content in the fuels including fossil and biomass-derived fuels is summarized in Table 4.

Table 4. Nitrogen content in the fuels (dry %-wt) (Zevenhoven and Kilpinen, 2001)

Fossil fuels	(dry %-wt)	Biomasses & waste-derived fuels	(dry %-wt)
Coal	0.5 - 0.3	Wood	0.1-0.5
Oil	< 0.1	Bark	~ 0.5
Natural gas	0.5 - 20	Straw	0.5-1
Peat	1 - 2	Sewage sludge	~ 1
Petroleum coke	~ 3	Municipal solid waste	1-5
Light fuel oil	~ 0.2	Refuse derived fuels	~ 1
Heavy fuel oil	~ 0.5	Package derived fuels	~ 1
Leather waste	~ 12	Auto shredder residues	~ 0.5
Car tire scrap	~ 0.3	Black liquor solids	0.1 - 0.2

Waste-derived fuels contain polymer and plastic fractions and hence make the nitrogen reaction chemistry very complex in the combustion process. Nylon materials and end of life refrigerators have high nitrogen content in the order 10%-wt. During the combustion, some fuel-N is released in the form of volatile-nitrogen (volatile-N) whilst, rest remains in the char as a char-nitrogen (char-N). This division of fraction between volatile and char nitrogen has

an importance because NO_x reducing techniques such as combustion modifications have no significant effect on char-N as compare to volatile-N. Information of char-N is important for the estimation of NO_x emission, but at what point and in what form the fuel-N is released either in gasification or combustion stage is mostly unknown (Bockhorn et al., 1996)(Cullis, C.F., Hirschler, 1981).

To describe the NO_x emission, it necessitates the kinetics of formation and decomposition reactions of NO_x and N₂O components. NO_x emission comprises of NO and NO₂ gases from the combustion process. NO may form from the two sources of nitrogen, N₂ gas in the combustion air and fuel-N exist in the fuel. The phenomenon of NO formation from N₂ gas in combustion process can be categorized into three pathways; Thermal NO, Prompt NO and NO generation via N₂O intermediate (Table 5) (Zevenhoven and Kilpinen, 2001).

Table 5. NO formation from the molecular nitrogen (N₂) in burner combustion

No.	Reactions
1	Thermal NO $N_2 + O \rightarrow NO + N$ $N + O_2 \rightarrow NO + O$ $N + OH \rightarrow NO + H$
2	Prompt NO $N_2 + CH \rightarrow HCN + N$ $HCN \xrightarrow{+O} NCO \xrightarrow{+H} NH \xrightarrow{+H} N \xrightarrow{+O_2, +OH} NO$
3	Generation via N ₂ O intermediate $N_2 + O + M \rightarrow N_2O + M$ $N_2O + O \rightarrow 2NO$

3.1 Thermal NO

Molecular nitrogen (N₂) in the combustion air has a strong bond between two nitrogen atoms (bond energy approx. 950 kJ/mol). Hence the formation of NO from N₂ and O₂ demands the cleavage of a strong bond, and either an oxygen atom or molecule is not capable to break the bond under combustion conditions even at high temperature. So, the occurrence of reaction (2) is typically overly slow.



Rather, NO formation occurs in a chain reaction and initiated by an oxygen atom and nitrogen molecule.



The reaction mechanism (3) & (4) is referred to the Zeldovich mechanism. The nitrogen atom in reaction (4) may oxidize by hydroxyl radicals under less excess air and stoichiometric reducing conditions because O_2 is less oxidative in the less excess air (reaction 5). NO formation according to Zeldovich mechanism is generally named as thermal NO.



Combining the reactions (3), (4) & (5) is called the extended Zeldovich mechanism. In the Zeldovich mechanism, reaction (3) is a rate-limiting step due to higher activation energy ($E_a = 320 \text{ kJ/mol}$). The required oxygen atoms concentration for triggering the reaction (3) is directly proportional to temperature. Figure 1 shows the NO_x formation mechanism from methane combustion in a stirred reactor at 1 bar pressure (Zevenhoven and Kilpinen, 2001).

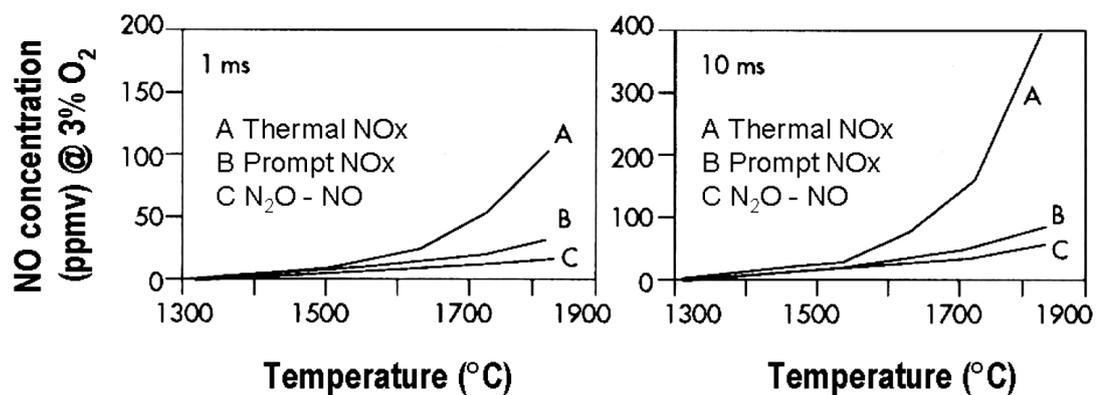
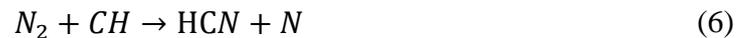


Figure 1. NO_x formation from methane as a function of temperature and residence time of 1 millisecond (left side diagram) & 10 milliseconds (right side diagram)

Figure 1 depicts that thermal NO formation is insignificant below the combustion temperature of 1400°C whilst, formation rate steadily increases over 1600°C. Therefore, by minimizing the temperature peaks and lowering the flue gas residence time at high-temperature combustion zones, thermal NO formation may cut downs. This can be exercised by either flue gas recirculation at a cooled temperature or lessen the preheating of combustion air or air staging to have a long flame with efficient radiation in the furnace. Low excess air also outcomes the reduction in NO formation due to a decrease in the concentration of oxygen atoms (Zevenhoven and Kilpinen, 2001).

3.2 Prompt NO

Fenimore in the 1970s suggested that all NO formation cannot be explained by Zeldovich mechanism, especially in under-stoichiometric hydrocarbon flames. He demonstrated another mechanism that initiates between a CH radical and N₂ to form NO in the under-stoichiometric conditions (6).



In the presence of oxygen atom, hydrogen cyanide (HCN) and nitrogen react further with a chain of reactions to form NO as follows:



Reaction (7) occurs only if hydrocarbon radicals are present in a flame zone of combustion, because of incomplete combustion. Formation of NO under reaction pathway (7) is typically very fast and is called prompt NO. It is less dependent on the temperature as compared to thermal NO. Prompt NO is more favourable under the shorter residence time, cooler and under-stoichiometric conditions. The fraction of prompt NO is typically low about 5% during actual burner operation (Zevenhoven and Kilpinen, 2001).

3.3 Formation via N₂O intermediate

Another mechanism of NO formation was proposed in the 1970s through nitrous oxide (N₂O) as an intermediate component. This route involves any gas or other third component represented by M in the reaction between the oxygen atom and nitrogen molecule (reaction 8).



The laughing gas (N_2O) react back to either N_2 or NO depending upon the combustion conditions. However, by increasing the temperature and air ratio, NO formation increases and competes for N_2 formation (9).



Importance of reactions (8) & (9) in NO formation is not clarified in actual combustion operation. However, it is most probably that NO formation via N_2O intermediate is rather small and likely bit larger than prompt NO . Figure 2 demonstrates the significance of N_2O intermediate pathway and NO formation increases with the excess air.

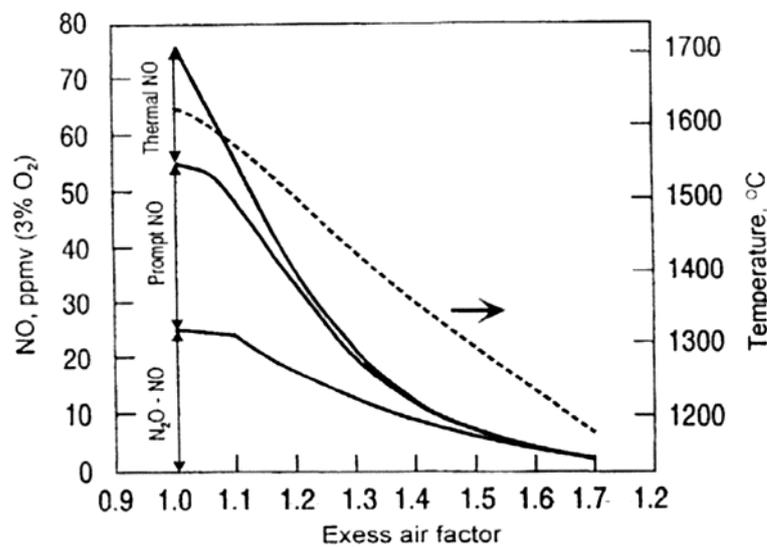


Figure 2. NO formation vs excess air factor (Zevenhoven and Kilpinen, 2001)

3.4 Fuel NO

Although the fuel-N is much less in proportion than N_2 in the combustion air nevertheless, it is considered more reactive than N_2 in the air. Fuel-N exist in a variety of compounds depend upon the type of fuel. The bond energy of nitrogen-containing compounds varies between 150 and 750 kJ/mol. Moreover, the fuels rich in nitrogen content have higher NO emissions than fuels containing no nitrogen. For example, NO emission from the pulverized coal-fired unit is ~80% from the fuel-N. When coal is pyrolyzed during combustion, partly nitrogen in fuel is released into the smaller gaseous molecules cyanide, cyano and amino groups (HCN and NH_3). If oxygen-containing compounds exist there, HCN and NH_3 are further oxidized to nitric oxide which is known as fuel NO . If the combustion zone conditions

are under-stoichiometric and reducing, HCN and NH_3 react further and form N_2 rather than NO. Fuel NO is produced at rather a low temperature and therefore weakly dependent on the temperature. In coal firing, the temperature can determine the type of nitrogen-containing species released during the pyrolysis.

Fuel NO is generally more sensitive to stoichiometry than combustion air and fuel type. HCN and NH_3 are transformed to NO or N_2 through many intermediate pathways. Only significant chain reactions under typical conditions are shown in Figure 3. HCN can react to form N_2O under below 900°C temperature. Reducing atmosphere can be arranged in the furnace during the devolatilization stage to avoid NO formation from the fuel-N such as rearranging the distribution of combustion air in furnace also called as the air staging. In case of less volatile fuel, a considerable part of fuel-N is retained in char residues. Char nitrogen (Char-N) is hardly affected by reducing conditions to form molecular nitrogen but under excess air supply, char nitrogen oxidizes to NO. Several researches at laboratory scale have shown the insight of fuel-N release during the combustion and Figure 3 highlights the reaction pathways of NO_x formation from biomass and black liquor in kraft pulp mill (Di Nola, de Jong and Spliethoff, 2010)(Konttinen *et al.*, 2005)(Winter, Wartha and Hofbauer, 1999).

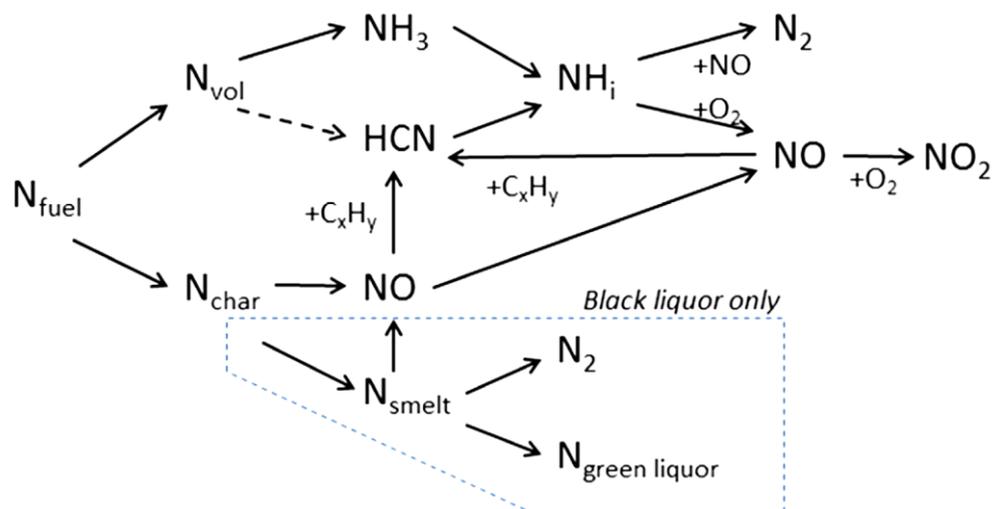


Figure 3. NO_x formation from fuel-N of biomass and black liquor (Abelha, Gulyurtlu and Cabrita, 2008)

Conversion of char-N to NO varies between 20-80% in pulverized coal combustion and it's more dependent on the coal type rather than temperature and stoichiometric ratio. Therefore, NO formation from char-N cannot be governed straightaway by air staging in the furnace rather, the contrary effect has been observed of higher NO formation with air staging from char-N. There are some fuels which do not contain organic nitrogen, especially hydrocarbon gases such as natural gas and it forms easily hydrocarbon radicals which reduce the NO molecule to N₂ gas. Utilization of fuel to reduce NO can be carried out with fuel staging, also named as reburning or three-stage combustion (Zevenhoven and Kilpinen, 2001).

3.5 NO₂ formation and decomposition

NO₂ forms from the NO during combustion by hydrogen peroxide radical (HO₂). The reaction equation (10) follows as:



HO₂ radical is produced when hydrogen atom and oxygen molecule react in the presence of a third gaseous component (M). Hydrogen atom and oxygen molecule can react directly to result in oxygen atom and hydroxyl radical in the absence of third component.



In the combustion process, the latter reaction (12) usually rules, however, the significance of reaction (11) rises when the temperature falls. Thus, in the cooler zones, if significant NO is present, HO₂ radical may react with NO to form NO₂ according to reaction equation (10).

NO₂ decomposes very rapidly to NO at hotter parts of flame by reacting with either oxygen or hydrogen atom according to reactions (13) & (14).



NO₂ decomposition reactions may be stopped due to the greatly lowered concentration of H and O atoms in the flue gas and results in a higher NO₂ fraction. This situation may arise when cold and hot streams are mixed rapidly in combustion equipment.

3.6 NO_x emission in Recovery boiler

NO_x emission in recovery boiler mostly originates from the small amount of nitrogen 0.1-0.2 %wt-dry solids in the black liquor as shown in Table 4. NO_x emission from the recovery boiler typically varies between 30-120 ppm (8% O₂, dry). As more than 95% of NO_x is NO, and it has been indicated in previous researches that fuel-NO is a major part of NO emission due to fuel-bound nitrogen in the black liquor. Thermal NO seems to be a minor part of NO emission and its due to the comparatively low temperatures in recovery furnace (Forssen, Kilpinen and Hupa, 2000). The significant source of NO formation in recovery furnace was proposed to be the ammonia oxidation that is formed during the liquor droplets devolatilization. Forssén et, al. demonstrated that an important part of liquor nitrogen may exit the furnace in smelt as an inorganic compound (Forssén, Mikael, Hupa and Peter, 1997). A few studies have been accounted concerning the effect of combustion modifications on NO formation in recovery furnace (Engblom *et al.*, 2016). Staged air supply, liquor dry solids content and liquor droplet size have been reported to affect NO emission both positively and negatively. Figure 3 also explains the fuel-N release from the black liquor into smelt, N₂ and NO_x.

3.7 NO_x emission in Lime kiln

Lime kiln is an integral part of recovery cycle in kraft pulp mill. NO_x emission in the lime kiln is relatively low and depend upon the several factors such as choice of fuel, materials composition fed to the kiln, lime mud calcination reactions and emissions control approaches for particulate matter. Combustion operation modifications are typically useful for controlling the NO_x emission but are restricted by site-specific conditions and impact on product quality (calcium oxide). Although cement kilns contain some similarities with lime kilns in respect to equipment configuration, however, they differ principally on the basis of fuel input, end product quality demands and emission regulations. Most ordinarily fuels utilized for lime kilns include natural gas, oil and petroleum coke. Cement kiln is generally fired with hazardous waste unlike with lime kiln, therefore are subject to strict regulation and emission control.

NO_x formation in the lime kiln is the end result of combustion of fossil fuels such as fuel oil and natural gas. The emission range is wide and data is ambiguous, whether oil or gas is associated with higher NO_x levels. Introducing reduced sulfur compound (RSC) streams and

other fuels such as stripper off-gases (SOG_s) which are comparatively rich in nitrogen, increase the NO_x emission potential. The best prospect for reducing the NO_x emission is combustion modification, apart from the fact these opportunities are greatly limited due to the combustion conditions that are crucial to sustain the end product quality. Hence NO_x control schemes for lime kilns need to be evaluated by each specific case since formation mechanism and control strategies are not well understood (NESCAUM, 2005).

Reducing air supply in the combustion zone may be helpful for NO_x reduction in oil-fired kilns, however carbon monoxide and TRS emissions would be considered as well. Moreover, combustion modification will be dependent on the kiln geometry and configuration, impact on process performance, process control and stability. The NO_x formation in lime kiln relates to the fuel-N content and includes other substances combusted in it. Flame temperature and burner design are significant factors in order to attain good heat of radiation for the bed of lime (NCASI, 2008). In the new lime kiln, NO_x control may be achieved by decreasing hot-end temperature (gas-fired kiln) and minimizing the oxygen supply in the combustion zone (oil-fired kiln). In addition, these operation modifications are difficult to set up in existing lime kilns due to their inherent design and product quality implications (IPPC, 2001). Other kiln emissions also need to be considered with their implications. NO_x emission was tested in both oil and gas fired lime kilns along with operating data, it was found that inter and intra-kiln variability was higher in gas-fired kiln relatively to the oil-fired kiln, therefore, it attributes to the higher sensitivity of NO_x emission in gas-fired kiln due to fluctuations in dry-end temperature. The results also depicted that in oil-fired kiln all NO_x formation was mainly derived from the fuel NO_x mechanism. This study also suggested that lime dust does not capture the NO_x generated in the kiln to a significant extent (R. Crawford, 2003).

4 NO_x control strategies

Main sources of NO_x emission are combustion power plants, motor vehicles and chemical incinerators as shown in Table 2. Each of these sources has their preferred control strategies to mitigate the NO_x emission. NO_x emission limit is set and monitored by respective regional environmental authorities and it depends upon the several factors such as combustion fuel type, the capacity of a combustion device (MW_{th}) and unit type either it's a new or retrofit. Example of NO_x regulation under EU directive is briefed in the previous discussion Table 3. This chapter aims to explore the NO_x reduction technologies in combustion power plants and chemical industries. Typically, three approaches for NO_x abatement are recognized: pre-combustion methods, combustion modifications and post-combustion treatments.

Pre-combustion methods are based on the phenomenon of either fuel purification to get rid of nitrogen content or selecting those fuels which contain no or traces of nitrogen, for example choosing natural gas as a fuel instead of diesel oil. It is well proved that fuel type is directly linked with NO_x formation through the fuel bound nitrogen (Friebel and Köpsel, 1999). NO_x formation for fuels increases in the given order as methanol, ethanol, natural gas, butane, fuel oil and coal (Latta and Weston, 1998). Moreover, the replacement of combustion air with pure oxygen can reduce the NO_x formation and hence, none of thermal NO_x, prompt NO_x and NO_x via N₂O intermediate can be formed (Sterner and Turnheim, 2009). The main setback for such approach is a high cost involved due to the installation of both air separation unit and fuel purification process.

The second solution to lower the NO_x emission is an adjustment of design and operating parameters often known as combustion modifications. These alterations are the primary measures and considered as a priority step for any possible NO_x reduction. However, these optimization outcomes are not sufficient to meet the stringent NO_x emission limits. More common modifications are Low excess air (LEA), Burners out of service (BOOS), Overfire air (OFA), Low NO_x burner (LNB) with air staging or fuel staging, Flue gas recirculation (FGR), Water/Stream injection and Fuel reburning. These techniques are not explained here but a short summary of their advantages, disadvantages and NO_x reduction efficiency (DeNO_x%) is gathered in Table 6 (EPA, 1999) (European Commission, 2006) (Graus and Worrell, 2007).

Table 6. Summary of combustion modification techniques

Technique	Description	Pros	Cons	DeNO _x %
Low Excess Air	Less oxygen available	Ease of modification and suitable for rebuild cases	Low NO _x reduction and incomplete combustion	10-44%
Burners Out of Service	Staged combustion	No capital cost and suitable for retrofit	Restricted to oil or gas-fired processes and higher air flow to account CO	10-70%
Over Fire Air	-	All Fuels	The possibility of high levels of CO	-
Low NO _x Burner air staged	Internal staged combustion	Low operating cost	Fairly high capital costs	25-35%
Low NO _x Burner fuel staged	-	All fuels	-	Up to 20%
Low NO _x Burner flue gas recirculation	-	Useful for retrofit cases	-	50-60%
Flue Gas Recirculation	Up to 30% of flue gas recirculated to a lower temperature	High NO _x reduction for low nitrogen fuels	Moderately high capital and operating cost, high energy consumption and flame instability	20-50%
Water/Stream Injection	Decrease flame temperature	Moderate capital cost and NO _x reduction like FGR	Fan power higher and penalty in efficiency	70-80%
Fuel Reburning	Injection of fuel to react with NO _x	Moderate cost and moderate NO _x removal	Incomplete combustion, increase in residence time, not appropriate for retrofit	50-60%

DeNO_x% is defined by equation (15).

$$\text{DeNO}_x\% = \frac{\text{NO}_{x\text{in}} - \text{NO}_{x\text{out}}}{\text{NO}_{x\text{in}}} * 100 \quad (15)$$

NO_{xin}: Primary NO_x content in the flue gas stream leaving from the combustion unit

NO_{xout}: NO_x content in the exhaust flue gas stream after the NO_x abatement method

4.1 Post-combustion methods

Post-combustion techniques are employed to mitigate the NO_x content in the exhaust flue gas stream leaving from the incineration process. These techniques may be utilized in coupling with combustion modifications to enhance the overall $\text{DeNO}_x\%$ because combustion operation adjustments are not solely enough to meet the rigorous emission limits. Post-combustion methods have gained a lot of attention now a day's due to the capability of achieving higher $\text{DeNO}_x\%$ either using one method or combination of different technologies. Those combination schemes will be discussed later in this study after reviewing each technology.

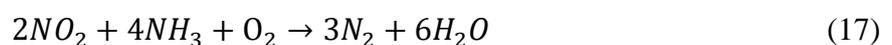
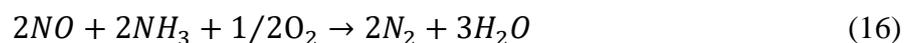
Typically, two approaches can be noticed while considering the abatement of NO_x , the first one is NO_x destruction and the second is the removal of NO_x to another medium. The first strategy involves the reduction reaction of the chemical additive with NO_x to result in the benign product at the outlet such as N_2 gas, which is not an environmental hazard. The destruction process of NO_x can be accompanied with the catalyst in addition of a chemical additive to achieve higher $\text{DeNO}_x\%$ at lower process temperature, and therefore it is generally distinguished from the non-catalytic process. The non-catalytic method is commonly known as a selective non-catalytic reduction (SNCR) and the following process with the addition of catalyst is generally referred to as selective catalytic reduction (SCR).

The second approach is the removal of NO_x from flue gas to another medium such as water usually by absorption or adsorption process. The major drawback of such an approach is only transferring of NO_x to another medium thus, it generates the waste stream which requires again treatment before its disposal to the environment. While the first methodology doesn't pose such threats as NO_x are reduced to a benign product such as N_2 gas and only deactivated catalyst after its lifetime is a hazardous waste. Wet scrubbers remove the pollutants from flue gas by absorption (utilizing the liquid stream for removal of gaseous pollutants). For this reason, wet scrubbers are also identified as absorbers, employ for the gaseous pollutant removal from the flue gas. Currently, both strategies are being employed on an industrial scale depending upon suitability, $\text{DeNO}_x\%$ and other investor requirements. In the following part, NO_x control methods which exist currently on a commercial scale are discussed.

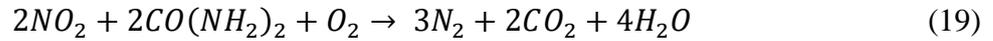
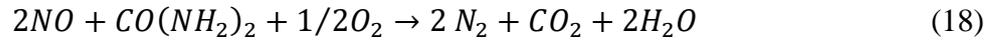
5 SNCR

Selective non-catalytic reduction (SNCR) is conceptually a simple post-combustion method for NO_x reduction. It involves the injection of any amine-based reagent or reducing reagent, for example, ammonia (NH₃), urea CO(NH₂)₂ and cyanuric acid within the combustion unit at the properly determined location. It is also referred to thermal DeNO_x process and it involves the reduction of NO_x to N₂, as a consequence of chemical reaction with amine-based reagents in the presence of O₂. The point of reagent injection in the combustion equipment is determined on the basis of specific temperature window 870°C to 1090°C (Ishak and Jaafar, 2011). Adequate residence time enables the thoroughly mixing of flue gas stream containing NO_x with a particular reagent and it yields a rapid gas phase homogeneous reaction.

The reducing reagent can react with miscellaneous components other than NO_x in the flue gas however, NO_x reduction reaction is favoured among the other reactions due to the selective temperature range and the presence of oxygen, thereby it is named as selective reduction method (Sorrels, Randall, Fry, *et al.*, 2016a). Combustion unit acts itself as a reaction chamber for the SNCR process and the reagent injection occurs with nozzles, which are mounted through the wall and penetrate in the combustion equipment. The boiler heat provides the energy for reduction reaction between NO_x and reducing reagent. After the reduction reaction, NO_x reduces to N₂ gas and leaves out of the combustion unit. Multilevel injection configuration can be effective for NO_x reduction, as it provides the optimum point of injection for increasing the reduction efficiency. The reagent can be vaporized by a separate vaporizer or by the heat of boiler after injection. Vaporized ammonia or urea decomposes to free radicals NH₃ and NH₂, and finally the amine radicals come into contact with NO_x molecules and reduce it to N₂ gas. As NO_x consist of both NO and NO₂ oxides, so net reduction reactions for both components are written individually with both reagents ammonia and urea:



Net reaction equations for the urea reagent are:



Reactions (16) & (18) mostly prevail due to a significant part of NO (95%) contribution to overall NO_x. The reduction process happens as a result of two-step chain reaction, in which ammonia first reacts with hydroxyl radical to form amine radical and water. The amine radical comes in contact with nitric oxide to produce N₂ and H₂O in 2nd step (ERG, 2006).

The net reaction equations are:



Nitrous oxide (N₂O) as a side product is also formed in the SNCR process from both reagents urea or ammonia, however, in the urea-based system more N₂O is generated. N₂O formation depends upon the temperature and reagent feed rate, higher N₂O emission correlates with greater NO_x reduction (Wójtowicz, Pels and Moulijn, 1993)(Grosso and Rigamonti, 2009).

The selection of reagent is based on the cost, physical properties and several operational considerations. Clearly, the reagent cost accounts for a significant portion of operating expenses. Ammonia can be provided either in anhydrous form as a gas or aqueous solution. Anhydrous ammonia exists in the gas phase at normal temperature and hence, must be supplied and stored under pressure, which raises safety concerns and an increase in transportation cost (EPRI, 2004). Aqueous ammonia is typically stored and transported at 29.4% ammonia concentration in water. Injection of ammonia in a combustion unit is executed either in aqueous solution or in the vapor phase. For injection in the vapor phase, it necessitates a vaporizer despite of 29.4% ammonia solution has a significant vapor pressure at normal temperature. Urea is typically stored in a strength of 50% aqueous solution and at this concentration, its freezing point (atmospheric pressure) is quite low 18°C hence, in the presence of cold atmosphere it must be heated and circulated during the storage (ICAC, 2008). Urea can be transported either in pellet form or in high concentration solution,

however, it must be diluted to 50% aqueous solution at the facility for utilizing in SNCR system (EPRI, 2004). Urea solution is less volatile and non-toxic hence, it makes easier and safer to handle. one another advantage in the urea-based system is better mixing of urea solution droplets with flue gas and it's because of greater penetration of urea droplets in the flue gas.

Performance parameters of the SNCR system are important due to their effect on the NO_x reduction. Major design and operational factors are; reaction temperature (furnace temperature), reaction time (injection location of reagent), degree of mixing, primary/uncontrolled NO_x , reagent feed consumption and the ammonia slip. The optimum temperature window for ammonia is 870°C to 1100°C (1600°F to 2000°F) and for urea reagent, the temperature ranger is typically higher as shown in Figure 4. The reaction rate is too slow below 800°C and ammonia slip is higher due to unreacted ammonia.

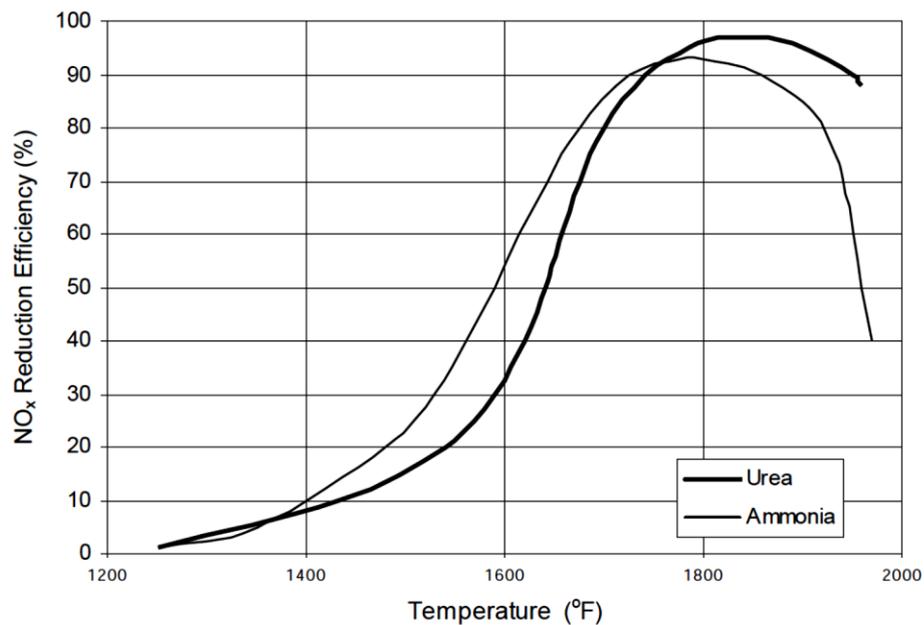


Figure 4. Temperature window for SNCR system with ammonia and urea (Sorrels, Randall, Fry, et al., 2016b)

The residence time for the SNCR process may range from 0.001 to 10 seconds (Lyon, R.K., 1975). It is reported in one investigation that reaction completes within 200 milliseconds from the point of ammonia injection (Muzio, L.J., Arand, J.K., Teixeira, D.P., 1976). The NO reduction ceases at the point, where no ammonia is present for the reaction. Typically, the higher residence time available, the greater conversion is achieved and in result increase

in $\text{DeNO}_x\%$. The reagent needs to get properly mixed with flue gas for optimal reaction rates and minimizing the reagent consumption. The multi-point injection system is generally installed in a combustion unit. Injector atomizes the reagent solution and handles precisely the spray angle, direction of spray and velocity. Usually, this distribution system is reagent and boiler specific. The NO reduction is observed to be less at lower initial NO level. It was determined in one combustion experiment that NH_3 proves to be less effective with initial NO level below than 400 ppm whereas, a little effect was observed on NO_x reduction when initial NO level was greater than 400 ppm (Muzio, L.J., Arand, J.K., Teixeira, D.P., 1976). The reason is due to slow reaction kinetics and thermodynamic considerations as initial NO concentration decreases.

The notation normalized stoichiometric ratio (NSR) defines the amount of reagent required to achieve the target $\text{DeNO}_x\%$. Based on reactions (16) & (18), theoretically, 2 moles of NO can be reduced with 2 moles of ammonia or 1 mole of urea, whereas for reduction of 1 mole of NO_2 (reactions 17 & 19), 2 moles of ammonia or 1 mole of urea is needed. In practice, more reagent than theoretical molar ratio is needed to achieve desired NO_x reduction and its due to the fact of complexities involved in the actual chemical reaction and mixing limitations. Typically, NSR values are between 0.5 to 3 moles of ammonia per mole of NO_x and Figure 5 shows the that NSR values over 2.0 don't increase the NO_x reduction significantly.

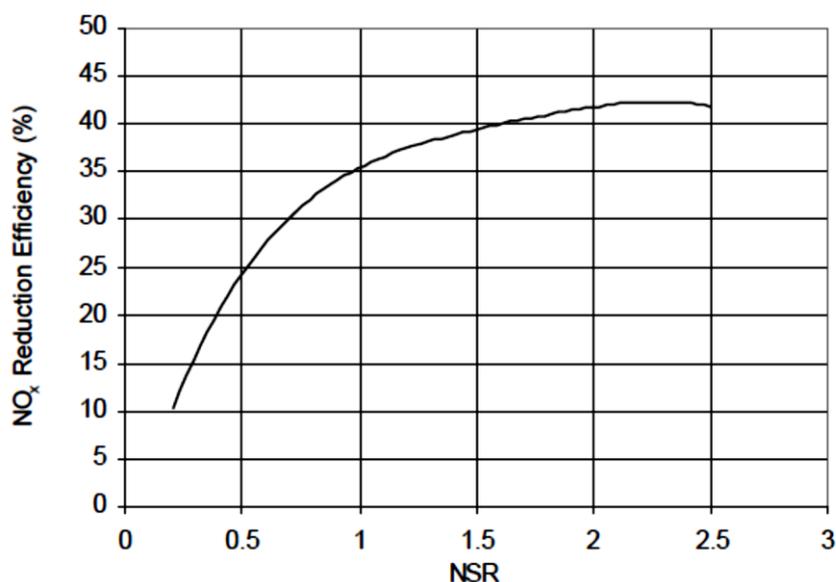


Figure 5. NSR effect on $\text{DeNO}_x\%$ (Sorrels, Randall, Fry, et al., 2016b)

Ammonia slip refers to the unreacted ammonia content in the exhaust flue gas stream due to excess reagent injection in the combustion equipment. Ammonia slip is more significant in the reagent of ammonia injection but can happen with urea reagent. NH_3 slip can be reduced by injecting the reagent in appropriate dosage and in the desired temperature window zone of the furnace. In urea injection system mixing, vaporization and decomposition of urea play an important role to determine the NH_3 slip. Minimum slip is always desirable due to the environmental regulations and wastage cost of unreacted reagent. Ammonia has a detectable level of 5 ppm and poses health concern at the degree of 25ppm or more. NH_3 can cause to react with chlorine compounds and form ammonium chloride, which creates the issue of stack plume visibility. When burning excess sulfur-containing fuels, ammonium sulfate and ammonium bisulfate can form, and these side products can corrode, foul and plug the downstream equipments such as flue gas ducts, air preheaters and flue gas fan.

Among the technologies prevailing for combustion of biomass and waste-derived fuels, bubbling fluidized bed boiler (BFB) and circulating fluidized bed boiler (CFB) are considered to be most suitable, due to their high mass & heat transfer, enough efficiency and flexibility with the versatility of biomass. Although nitrogen content in various types of biomass is low but apart from the fact, post-combustion NO_x control techniques are inescapable due to tight environmental legislation. Despite of significant NO_x reduction is accomplishable through combustion modification, but to comply with the emission standards additional post-combustion abatements are essential. SNCR system can be employed in fluidized bed boilers by injecting urea or ammonia at different levels of the furnace. SNCR system relies on the performance factors, which are briefly discussed in the previous section. SNCR application in BFB and CFB boilers is well known and commercialized from the decades, however, SNCR employment in the recovery boiler and lime kiln is complicated due to the absence of appropriate temperature window. In the lime kiln required elevated temperature regime is unavailable for SNCR application (IPPC, 2001). NO_x emission limits are getting more stringent for these chemical incinerators and in future, there would be a requirement of additional NO_x abatement technology.

6 SCR

Currently, the most prevailing method for NO_x control is a selective catalytic reduction (SCR) and it can facilitate the $\text{DeNO}_x\%$ up to 95%. Similar to SNCR method, SCR process relies on the chemical reduction of NO_x molecules by injection of an amine-based reducing reagent such as ammonia or urea derived ammonia. Principally the difference between SNCR and SCR method is that the SCR system employs the metal-based catalyst having activated sites to enhance the rate of NO_x reduction. The basic components of the SCR system are the reagent delivery and storage system, reagent injection grid and the catalytic reactor (Foerter, D., 2006).

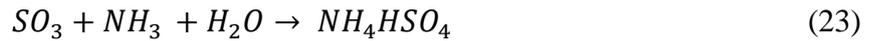
Catalyst has primarily two advantages, one is greater $\text{DeNO}_x\%$ and secondly, the reduction reaction occurs within lower and broader temperature window. However, both benefits are accompanied by much increase in capital cost and operating cost. Capital cost raise up happens due to the catalytic reactor required for reduction reaction whilst, operating cost increment is mostly a result of catalyst replacement after its deactivation (Cichanowicz, 2013).

Generally, the SCR method is executed with the ammonia reagent in the presence of oxygen. The ammonia is supplied either in anhydrous gas phase or aqueous form, in the latter case, it is vaporized before contact to a catalyst with vaporizer or boiler heat. Gas-phase ammonia then decomposes to free radicals including NH_3 and NH_2 within an appropriate temperature window and reacts with NO_x molecule, reduce it into the N_2 gas. The reduction reactions are similar to SNCR reaction equations (16) & (17) with ammonia reagent. The reaction (16) dominates apparently in reduction mechanism because of 95% NO_x in the flue gas is NO gas. The presence of a catalyst increases the reaction rate and lowers the activation energy for reduction reaction. Activated sites of catalyst surface readily absorb the ammonia and NO_x molecules to form the activated complex, which produces N_2 gas and water as a result of the reduction reaction. N_2 and water are then desorbed to flue gas and catalyst sites are reactivated by oxidation.

SCR catalyst also causes to occur some undesirable side reactions, such as oxidation of SO_2 to SO_3 , which can lead to the sulfuric acid formation and it can corrode the downstream equipments at a lower temperature (reaction 22).



SO₃ from above reaction can react with ammonia too and form ammonium bisulfate (NH₄HSO₄) and ammonium sulfate ([NH₄]₂SO₄) consequently, as shown in reactions (23) & (24). Both these side products form sticky and corrosive deposits, which lead to catalyst deactivation and further restrict the gas flows in downstream equipment's (Richards, 2000).



Some combustion units use the urea derived ammonia system and aqueous ammonia is produced from urea on the site. Anhydrous ammonia is gas at normal temperature and it is classified as a hazardous compound, so safety precautions are recommended before transportation, handling and storage. Utilization of aqueous ammonia reduces the storage and transport concerns related to safety. However, in practice aqueous ammonia is commonly utilized and reagent selection affects the capital and annual operating cost.

The catalyst is composed of active metals with greatly porous structure. Activated sites exist within pores and are reactivated via oxidation or dehydration. Over time under operation, catalyst activity decreases and after a certain period it requires either replacement or cleaning/washing or regeneration depending upon the catalyst management plan (Sorrels, Randall, Schaffner, et al., 2016).

In the 1980s, typical catalyst material was composed of metal oxides such as vanadium pentoxide (V₂O₅) and zirconium oxide (ZrO₂) on a support of titanium oxide (TiO₂) and they were specifically employed to widen the temperature range. Zeolites and crystalline alumina silicates were also applied mainly for high-temperature applications, however, zeolites proved to be cost prohibitive. However, vanadium catalysts have some cons such as lack of thermal durability and high potential of oxidizing SO₂ to SO₃. To tackle those shortcomings, addition of Molybdenum trioxide (MoO₃) or Tungsten trioxide (WO₃) supported on TiO₂ was used to improve the thermal stability and hindering the SO₂ oxidation to SO₃. At present V₂O₅–WO₃(MoO₃)/TiO₂ catalyst has been widely applied on an industrial scale due to greater DeNO_x% at high temperature (300–400°C)(Shang *et al.*, 2012)(Qi *et al.*, 2017). A review of catalysts in the NH₃-SCR system is shown in Table 7.

Table 7. Review of catalysts and their performance in $\text{NH}_3\text{-SCR}$ (Gao et al., 2017)

Catalysts	Preparation Method (Cal. Tem./°C)	Reaction Conditions	NO_x Conversion/% (Tem./°C)
MnO_x	Precipitation (350 °C)	[NO] = [NH ₃] = 500 ppm, [O ₂] = 5 vol %, N ₂ balance, GHSV = 25,000 h ⁻¹	100% (75–175 °C)
MnO_x	Rheological phase (350 °C); Solid phase (60 °C); co-precipitation (100 °C)	[NO] = [NH ₃] = 500 ppm, [O ₂] = 3 vol %, N ₂ balance, GHSV = 47,000 h ⁻¹	~100% (80–150 °C)
Mn-Ce-O_x	Citric acid method (650 °C)	[NO] = [NH ₃] = 1000 ppm, [O ₂] = 2 vol %, He balance, GHSV = 42,000 h ⁻¹	~100% (120–150 °C)
Mn-FeO_x	Co-precipitation (500 °C)	[NO] = [NH ₃] = 800 ppm, [O ₂] = 5 vol %, N ₂ balance, GHSV = 24,000 h ⁻¹	~100% (120–300 °C)
$\text{MnO}_2/\text{TiO}_2$	Impregnating (400 °C)	[NO] = [NH ₃] = 500 ppm, [O ₂] = 3 vol %, N ₂ balance, GHSV = 24,000 h ⁻¹	~100% (150–200 °C)
Mn/ZSM-5	Ion-exchange (300 °C)	[NO] = [NH ₃] = 600 ppm, [O ₂] = 4.5 vol %, N ₂ balanced, GHSV = 36,000 h ⁻¹	~100% (150–390 °C)
VO_x/CeO_2	Hydrothermal (400 °C)	[NO] = [NH ₃] = 500 ppm, [O ₂] = 5 vol %, N ₂ balance, GHSV = 120,000 h ⁻¹	95–100% (250–350 °C)
$\text{Ce}_{10}\text{Mo}_5/\text{TiO}_2$	Impregnating (500 °C)	[NO] = [NH ₃] = 500 ppm, [O ₂] = 5 vol %, He balance, GHSV = 128,000 h ⁻¹	~90% (275–400 °C)
Ce-Sn-O_x	Co-precipitation (400 °C)	[NO] = [NH ₃] = 500 ppm, [O ₂] = 5 vol %, N ₂ balance, GHSV = 20,000 h ⁻¹	90–100% (200–400 °C)
CuCe-ZSM-5	Ion-exchange (600 °C)	[NO] = [NH ₃] = 1000 ppm, [O ₂] = 10 vol %, He balance, GHSV = 15,000 h ⁻¹	~90% (148–427 °C)
$\text{Fe}_{0.95}\text{Ce}_{0.05}\text{O}_x$	Co-precipitation (400 °C)	[NO] = [NH ₃] = 1000 ppm, [O ₂] = 3 vol %, N ₂ balanced, GHSV = 30,000 h ⁻¹	79–100% (175–300 °C)
$\text{Fe}_{0.5}\text{WCeO}_x$	Sol-gel method	[NO] = [NH ₃] = 450 ppm, [O ₂] = 2.5 vol %, N ₂ balanced, GHSV = 20,000 h ⁻¹	80% at 160 °C; 95–100% (250–500 °C)

Choice of catalyst mainly relies on the performance parameters including flue gas flow rate, temperature window, fuel type, catalyst poisons impurities in the flue gas, SO_2 oxidation, catalyst selectivity & activity and its operating life. Disposal cost after catalyst lifetime is also considered in total cost estimation.

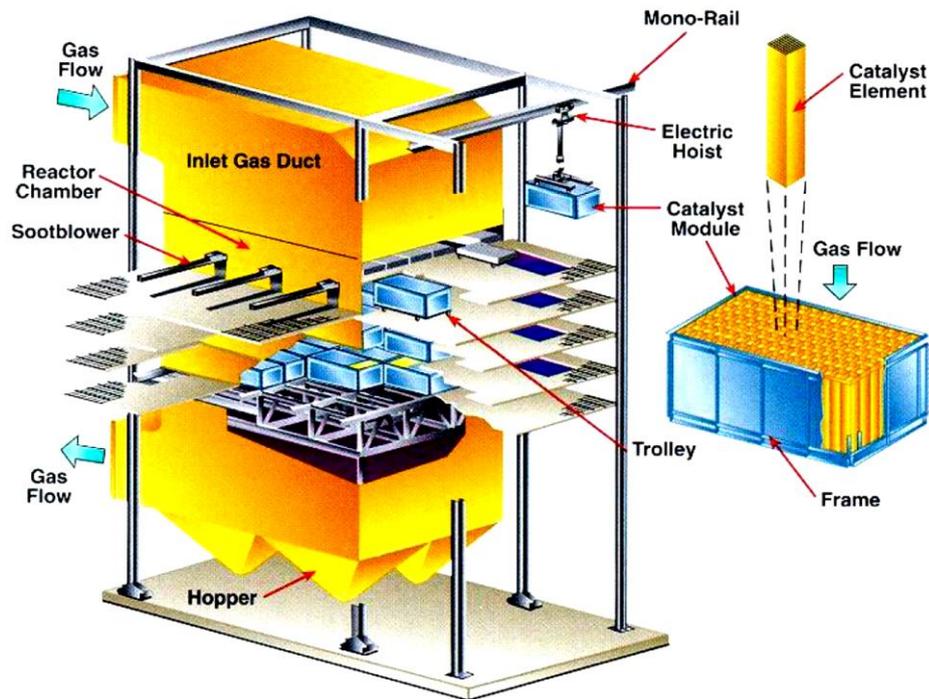


Figure 6. Layout of vertical flow SCR reactor (US DOE, 1997)

Most catalyst formulations include the additional compounds or support to increase the surface area or maintaining the structural and thermal stability. Catalyst configurations are either pleated metal plate or ceramic honeycomb in a fixed bed reactor, which allows for the high surface area to volume ratio (Figure 7). Pellet form of the catalyst also available in fluidized bed but are susceptible to plugging issues (ICAC, 1997). Catalyst elements are placed in a frame and its forms a catalyst module. These modules are stack together in multiple layers to make a reactor bed of required catalyst volume Figure 6. The catalyst layers may be washed/cleaned or regenerated in order to extend the life as catalyst activity falls with the increase in operating hour's.

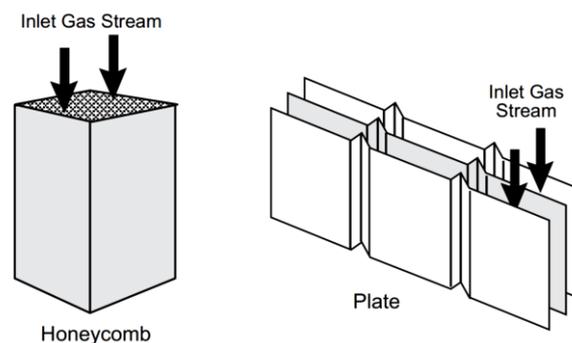


Figure 7. Types of catalyst (Richards, 2000)

The major operational factors of SCR that affect the DeNO_x% are similar to SNCR performance parameters such as reaction temperature, residence time, the degree of mixing, the molar ratio of reagent to primary NO_x, primary NO_x level and ammonia slip. Moreover, additional operational and design parameters which are specific to SCR process include the following: catalyst activity and selectivity, the pressure drop across the catalyst bed, dust loading and ash management, catalyst pitch, SO₂ & SO₃ concentration in the flue gas, and catalyst management plan. Majority of commercial (metal oxide) catalysts have operating temperature window from 250-430°C. DeNO_x% as a function of temperature using a typical metal oxide catalyst is shown in Figure 8 (Rosenberg, H.S., 1993).

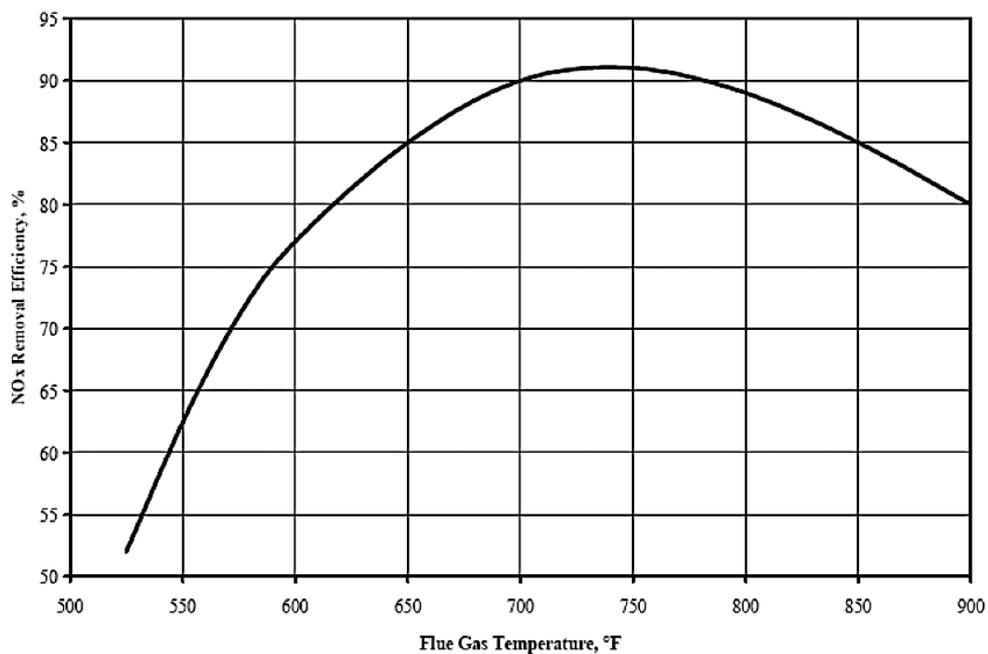


Figure 8. DeNO_x% as a function of temperature (Rosenberg, H.S., 1993)

SCR system configuration is based on the placement of catalyst in the flue gas stream and it depends upon the temperature requirements, catalyst performance and catalyst lifetime. High-dust SCR configuration is shown in Figure 9. In high-dust SCR, catalytic reactor position is located downstream of economizer, and upstream of air preheater and particulate control device. Flue gas temperature is ideal for NO_x reduction at this location. The catalyst is primarily susceptible to the fly ash buildup because it is positioned before the dust and other impurities separation.

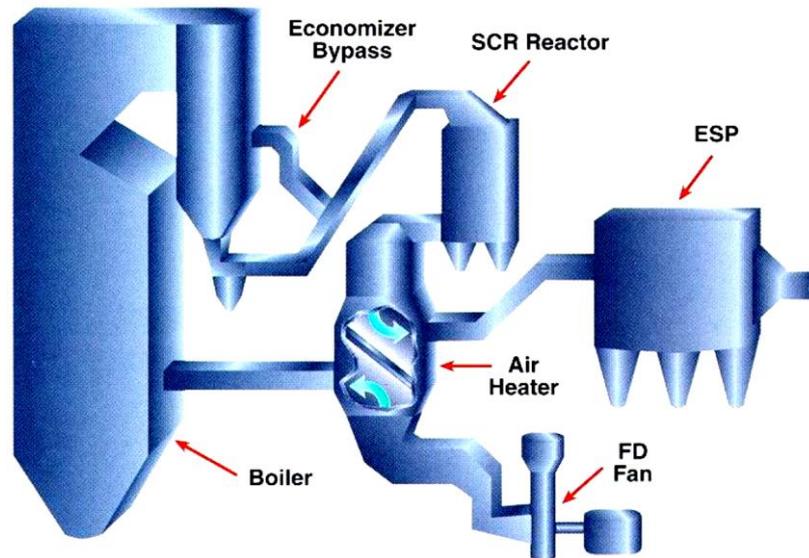


Figure 9. High-dust SCR configuration (US DOE, 1997)

The other two configurations of the SCR system are Low-dust and Tail-End. In Low dust SCR, reactor chamber is placed downstream of particulate removal devices such as electrostatic precipitator (ESP) or baghouse filter (BHF). In this position, the flue gas is usually dust free and ash is removed by ESP or BHF, which contains alkali metals, arsenic and other elements that can be threatening to catalyst life. Low-dust SCR has more lifetime due to mitigation of catalyst poison constituents.

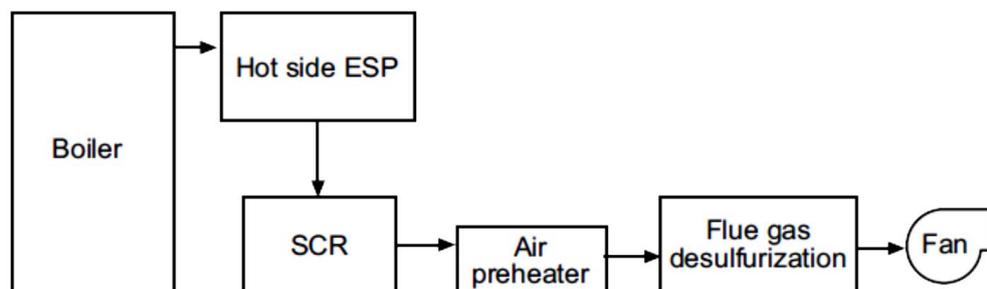


Figure 10. Low-dust SCR system (Richards, 2000)

A low-dust SCR requires low catalyst volume due to honeycomb structure and hence less catalyst layers relatively to high-dust SCR. Flue gas temperature commonly does not decrease to the level where reheating is required, which cause extra capital and operating cost. Tail-End SCR configuration positions the catalytic reactor in the downstream after all contaminant removal devices as shown in Figure 10.

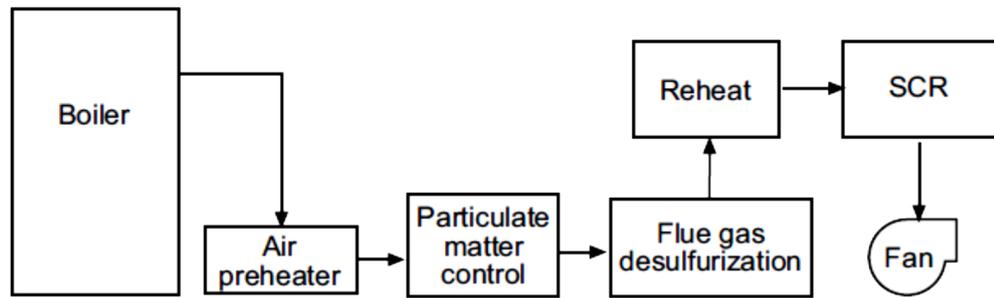


Figure 11. Tail-End SCR arrangement (Richards, 2000)

SCR reactor is located downstream of wet flue gas desulfurization (FGD) and upstream of the stack, since flue gas constituents are detrimental to catalyst activity. Flue gas temperature is usually below from required temperature window for NO_x reduction reaction hence, flue gas may require reheating by using oil or natural gas burner. That's why tail-end configuration results in additional capital and operational cost.

7 Oxidation-absorption processes

SCR has got a status of best available technology (BAT) because of efficient NO_x emission control. Despite of BAT status, the high capital cost is a weak point of this technology and lifetime of the catalyst is also limited due to fly ash erosion. Moreover, the temperature requirements for catalyst functioning are strict in the SCR system. Oxidation-absorption processes are promising alternatives to the SCR for simultaneously getting rid of NO_x and mercury (Hg) from the flue gas, which could be combined with flue gas desulfurization (FGD)(Ellison, 2003). Wet processes utilize the chemical absorbents and serve the advantage of low investment cost and removal of other pollutants from flue gas such as dust, NH₃ and acid gases. Mercury typically exists in the flue gas in elemental form (Hg⁰) and oxidized form (Hg⁺²). 90% of Hg⁺² is removable by wet flue gas desulfurization (WFGD) technology but none of Hg⁰. Therefore, conversion of NO and Hg⁰ to Hg⁺² and NO₂ through oxidation can control the mercury emission in the flue gas (Xu *et al.*, 2009).

Oxidation-absorption processes are based on the low-temperature oxidation of weakly soluble NO and followed by the absorption of high-order nitrogen oxides in alkaline solution. NO occupies a major portion of NO_x and since its less soluble in water than NO₂, therefore its oxidation to NO₂ enhance the NO_x removal efficiency. Several oxidizers have been investigated regarding the oxidizing capability, economic and safety issues during the last decades. NO_x scrubbing concept with oxidants: O₂, O₃, ClO₂ and NaOCl, NaClO₂, KMnO₄ and H₂O₂ has been reported in the literature. In this work, ClO₂ and O₃ oxidants are reviewed for NO oxidation purpose.

7.1 Chlorine dioxide Scrubber

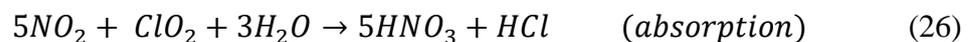
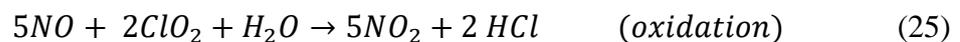
Chlorine dioxide (ClO₂) is a neutral oxy-chlorine molecule and it is a strong oxidant and disinfectant. ClO₂ has gained a significant commercial attention due to the wide application in the areas of bleaching, oxidation and disinfection. It is commercially utilized in pulp and paper bleaching, textile, wastewater treatment, food processing and medical treatments. ClO₂ is a powerful oxidant for oxidizing the NO into NO₂ in order to get high solubility in the water. Thereby treatment of waste industrial gases by aqueous ClO₂ solution has got the attraction in industrial application.

ClO_2 exist in three different types with distinct chemical characteristics. Table 8 identifies the types of ClO_2 and in literature and patents, it is occasionally not a clear which form of ClO_2 is used in a specific application. $(\text{ClO}_2)^0$ is dramatically more efficient at removing NO_x than $(\text{ClO}_2)^-$ and the reason is that $(\text{ClO}_2)^0$ is a gas and reacts with NO_x in gas phase but $(\text{ClO}_2)^-$ is ionic and only exist in water, hence treats the NO_x in water (liquid phase). This understanding is important in NO_x scrubbing because NO_x is composed of NO and NO_2 , and NO is very weakly soluble in water. Therefore, it's difficult for $(\text{ClO}_2)^-$ to get react with NO in water. The $(\text{ClO}_2)^0$ exist in the gas phase, so it reacts with NO effortlessly in the gaseous environment and destructs NO_x rapidly.

Table 8. ClO_2 types (Richardson, 2014)

IUPAC Name	Ionic charge	Conventional formula	Formula used in this study
Chlorine dioxide	0	ClO_2	$(\text{ClO}_2)^0$
Chlorite	-1	ClO_2^-	$(\text{ClO}_2)^-$
Chloryl	+1	ClO_2^+	$(\text{ClO}_2)^+$

The standard oxidation potential of ClO_2 in the solution and gas phase is -1.27 V and -0.95 V respectively. With this viewpoint, the aqueous ClO_2 solution is more effective for oxidation of NO to NO_2 . It was observed that ClO_2 can oxidize NO into NO_2 completely (reaction 25) and a consistent NO_x absorption efficiency of about 60% is achievable (reaction 26) (Deshwal et al., 2008).



The overall reaction for NO_x removal can be written as equation (27):



In the acidic medium, SO_2 reaction with ClO_2 takes place with the following mechanism:



A schematic process flowsheet of lab scale ClO_2 reactor and scrubber is shown in Figure 12 (Hultén et al., 2017). Flue gas composition is obtained by mixing the proportion of different gases, N_2 , CO_2 , O_2 , NO , SO_2 , and H_2O . Humidifier produces the water vapour to add in the

flue gas and flue gas is preheated to avoid condensation. Pre-heater and reactor system consist of the pipe where ClO_2 gas is added. The ClO_2 gas is produced from an aqueous solution of ClO_2 by stripping. After the reactor, the flue gas is cooled in condenser trap before it enters to scrubber column (packed with rasching rings). The scrubber operates with a countercurrent liquid stream of Na_2SO_3 and Na_2CO_3 as an absorption solvent. The scrubber liquid effluent at bottom of the scrubber is recycled by circulating pump and pH of scrubbing liquid is maintained by NaOH solution. Analyzers are located at different points in process flow scheme for analysis of flue gas samples.

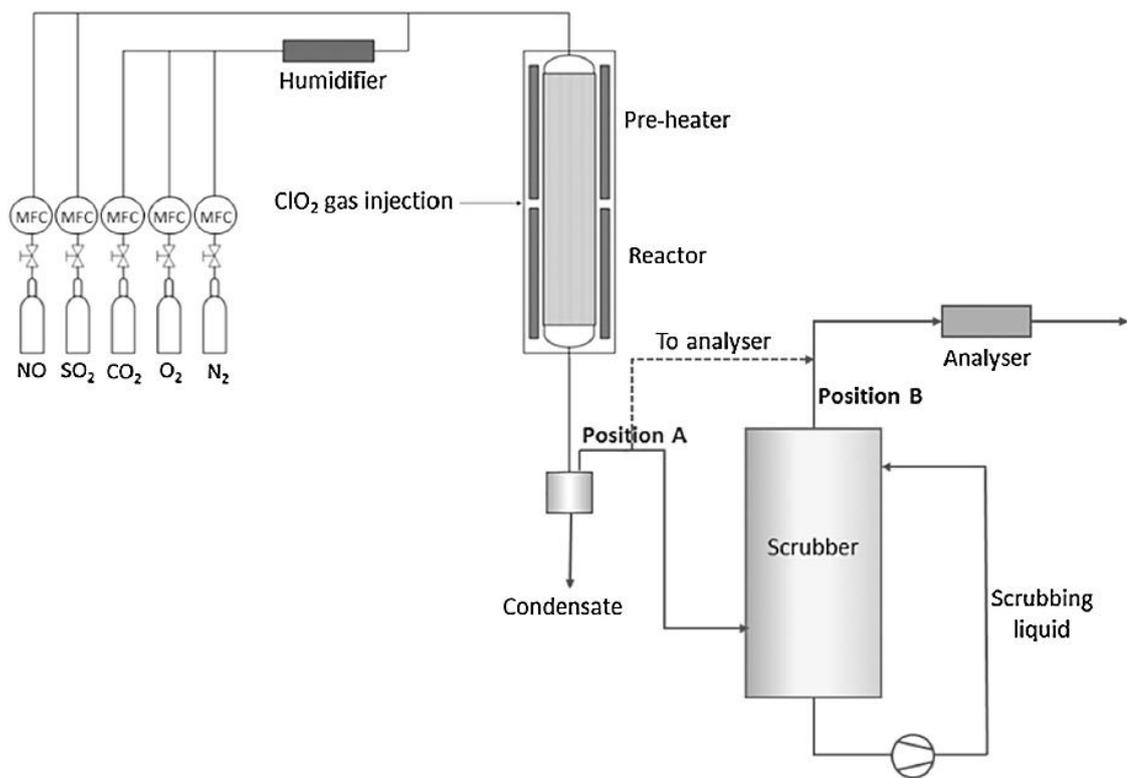


Figure 12. Lab scale process outline of ClO_2 scrubber (Hultén et al., 2017)

Deshwal and Lee studied the simultaneous removal of NO (350 ppm) and SO_2 (500 ppm) at the conditions of $T=45^\circ\text{C}$ and $\text{pH}=3.5$. SO_2 was found more reactive so it was oxidized first and then surplus oxidant converted the NO into NO_2 . The effect of increasing the oxidant feed resulted in greater NO_x absorption efficiency. NO_x and SO_2 absorption efficiency of around 72% and 100% respectively were achieved at an oxidant (euchlorine) feed rate of 3.045 mmole/min (Deshwal and Lee, 2009). A mixture of ClO_2 and Cl_2 with a molar ratio of 2:1 is known as euchlorine. Figure 13 depicts the NO_x reduction efficiency in the flue gas with and without the SO_2 presence at 65°C and 160°C . The NO_x input is 200 ppm in all cases

and the flue gas is humidified in these experiments. Almost a linear correlation exists between NO_x removal efficiency and ClO_2/NO molar ratio. Somewhat a higher NO_x removal is achieved when ClO_2 is added at 160°C and water vapour 8 vol% as compare to 60°C and 80% relative humidity.

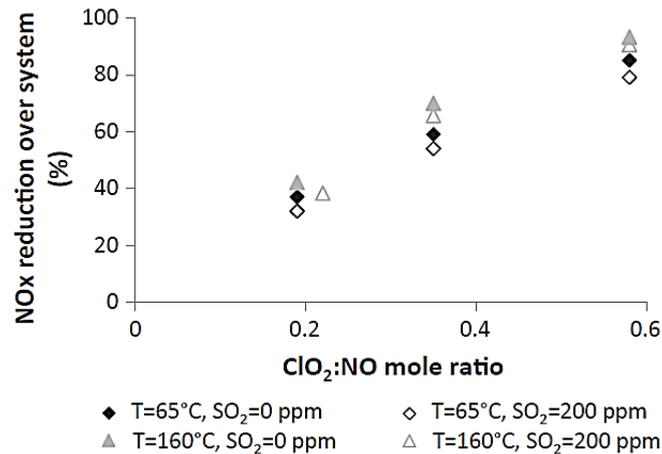


Figure 13. Effect of ClO_2/NO molar ratio on NO_x reduction over scrubber system (Hultén et al., 2017)

Figure 14 shows the SO_2 conversion as a function of ClO_2/NO molar ratio at different temperature and humidified conditions. Without water contents in the flue gas, SO_2 conversion is nearly 10% and independent of ClO_2 gas addition. However, in the presence of water vapour conversion is greater and it is believed that liquid phase nitrogen-sulfur reactions are the main reason for SO_2 conversion.

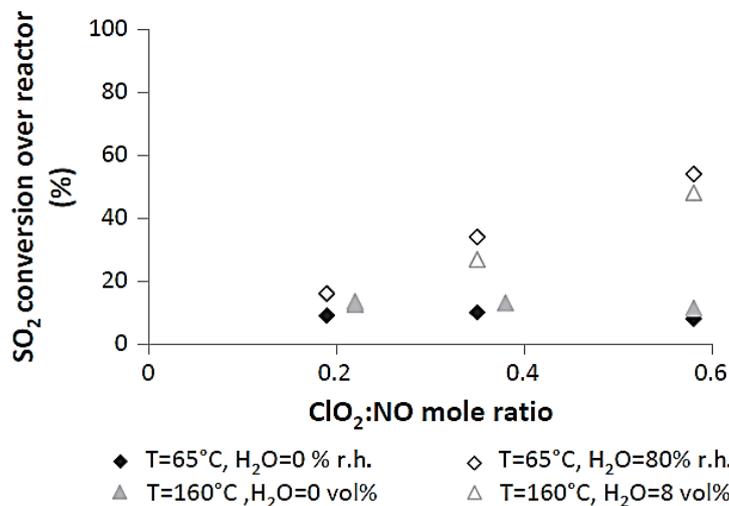


Figure 14. SO_2 conversion over the reactor with ClO_2/NO variation (Hultén et al., 2017)

Figure 15 presents the effect of SO_2 input on NO_x removal efficiency over the bubbling reactor and absorber at conditions of 45°C and input NO concentration 350 ppm. It shows that NO_x removal efficient increases from 66% to 70% as SO_2 input concentration increases from 0 to 500 ppm. This enhancement is believed due to the reaction of sulphur species with NO_2 molecules and in consequence increase the NO_2 absorption.

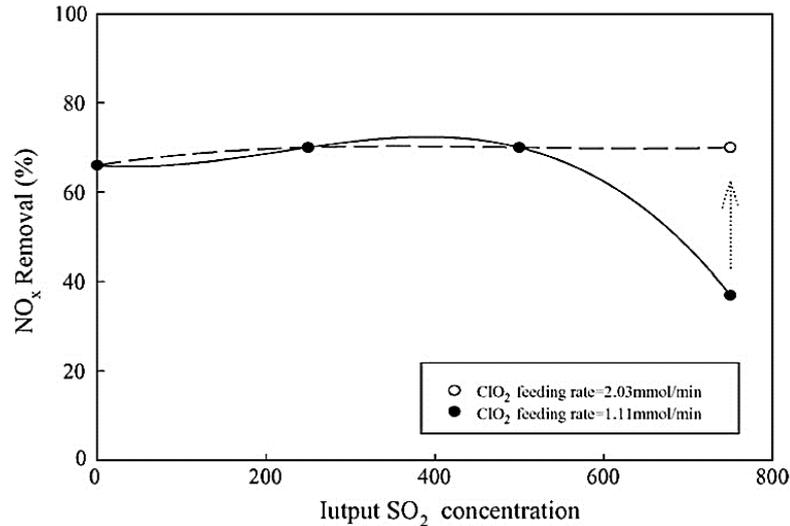


Figure 15. Effect of input SO_2 concentration (ppm) on NO_x removal (Jin et al., 2006)

Various effects of pH on NO_x out concentration and removal efficiency are shown in Figure 16. Conditions of the test are ClO_2 feed rate 1.11 mmole/min and input concentrations of NO and SO_2 are 350 ppm and 250 ppm respectively. There is a slight decrease in NO_x removal effect can be seen by increasing the pH and it may be due to disproportionation of ClO_2 at higher pH. Disproportionation of ClO_2 means it oxidizes and reduces simultaneously to two different products.

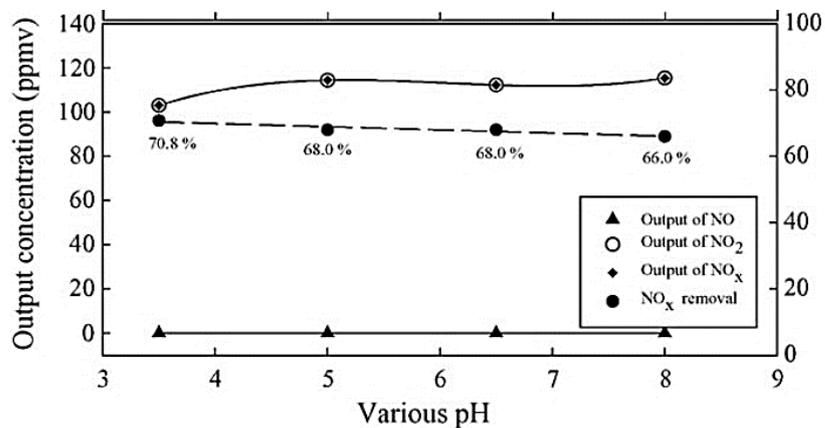


Figure 16. pH effect on NO_x removal over ClO_2 scrubber system (Jin et al., 2006)

8 Ozone Scrubber

Ozone (O_3) is a gas phase oxidizer with high oxidation efficiency. It is a promising oxidizer due to lack of reaction with SO_2 , a longer lifetime to sustain in traditional flue gas conditions and results in nonpolluting absorption solution (Sun et al., 2011).

Several features of ozone injection in the flue gas have been reported in the literature. Oxidation effect of ozone on NO was investigated in the presence of SO_2 and Hg and the findings suggested that SO_2 has a little effect on NO oxidation by O_3 (Wang et al., 2007). It was determined that with an O_3/NO_x molar ratio of slightly below than 2, more than 95% of the NO_x removal can be achieved and an ideal temperature for maximum NO_x removal efficiency was found to be $100^\circ C$ (Stamate, Irimiea and Salewski, 2013).

Laboratory scale experiments were performed to analyze simultaneous removal of NO_x and SO_2 from flue gas. In these experiments, NO first oxidizes to NO_2 and then NO_2 and SO_2 were reduced to nitrogen and sodium sulfate (Na_2SO_4) by using Na_2S as reducing agent. Results pointed out that 95% NO_x removal efficiency and 100% SO_2 removal efficiency can be accomplished, although consumption rate of reducing agent Na_2S was found to be four times higher than NO_x and SO_2 removed (Mok, 2006). Puri (1995) simulation results indicated that oxidation of NO to NO_2 is ideal at low temperature, and high residence time doesn't favour the larger NO_x removal efficiency (Puri, 1995). Nelo et al. (1997) proved that ozone is a selective oxidant and it oxidizes the only NO_x in presence of SO_2 and it was suggested from experimental results that NO_2 is desired product when ozone is below stoichiometric level, while N_2O_5 is dominant product in case of excess amount of ozone injection (Nelo, Leskelä and Sohlo, 1997).

In addition to the study of ozone reaction behaviour with NO_x , absorption of nitrogen oxides in chemical solvents have also been investigated by many researchers. NO_x absorption in water and sodium hydroxide was anticipated at various operating parameters (Thomas and Vanderschuren, 1999). Simulation models of rate-based absorption in water were presented by (Hupen and Kenig, 2005) and (Loutet et al., 2011). Skalska et al. (2011) performed the direct measurements of NO ozonation products and proposed a kinetic model with rate constants on lab experiment scale (Skalska, Miller and Ledakowicz)(Skalska, Miller and Ledakowicz, 2011).

8.1 Process description

Process flow diagram of the ozone scrubber system is shown in Figure 17 (Asif and Kim, 2014). NO_x and ozone are feed streams which are injected into a reactor in which oxidation reaction occurs. NO_x stream in the flow diagram is a mixture of NO and NO_2 with other flue gas contents, while ozone stream comes from ozone generator and generally it is diluted in oxygen gas.

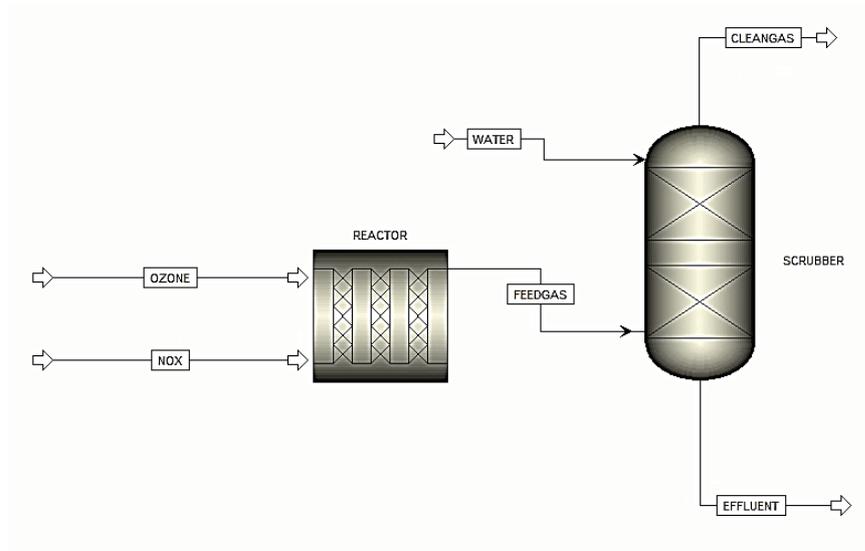


Figure 17. Process flow diagram of Ozone Scrubber (Asif and Kim, 2014)

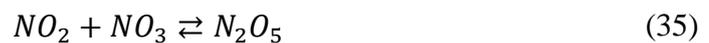
After a suitable residence time (approx. 2 seconds) in the reactor, NO is converted to high-order nitrogen oxides such as NO_2 , NO_3 , N_2O_3 , N_2O_4 and N_2O_5 (Jakubiak and Kordylewski, 2012). These reaction products (FEEDGAS) are fed to the bottom of scrubber column. Chemical solvent or water enters from the top of column in the countercurrent direction of flue gas. The nitrogen oxides are absorbed in water and clean gas from NO_x content is taken at top of the column, while nitrogen oxides react with water and form nitrous acid (HNO_2) and nitric acid (HNO_3) which are drawn from the bottom of column as an effluent stream. As nitrogen oxides react with water through multiple reactions in the liquid phase, for this reason, it's called as reactive absorption. If the alkaline solution (NaOH) is fed as a chemical solvent in scrubber then in bottom effluent sodium nitrite (NaNO_2) and sodium nitrate (NaNO_3) will be produced as a result of the reaction between acids and NaOH. (Sun *et al.*, 2017).

8.2 Reactions

NO is relatively a non-reactive and it is oxidized by ozone to more reactive oxide NO₂ or even more water-soluble oxide N₂O₅ by supplying excess ozone in the reactor. The reaction of ozone with NO_x is homogenous gas phase reaction and highly selective by manipulating the O₃/NO_x molar ratio. The oxidation reactions occurring in ozone reactor has been named as gas phase reactions according to the Figure 17.

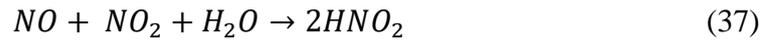
8.2.1 Gas phase reactions

The reaction between NO and O₃ has a high selectivity and when O₃ is mixed with NO in flue gas stream the following reactions occur (Thomas and Vanderschuren, 1999)(Sun et al., 2014):



When the O₃/NO_x molar ratio (MR) is less than 1, reaction (29) is a dominant reaction and NO is mainly oxidized to NO₂. When $1 > MR > 1.5$ the major oxidation products are NO₂ and N₂O₅ through reactions (29), (31), (34) and (35). Other oxidant product N₂O₃ and N₂O₄ are also formed according to reactions (32) and (33) due to the higher oxidizing power of O₃. N₂O₃ and N₂O₄ are rapidly converted to N₂O₅ via reactions (33) and (34) due to the shorter lifetimes of 0.0009 second and 0.0025 second respectively as compared to 300 second for N₂O₅ (Janssen, Simone and Guinet, 2011). Equilibrium constants are also small

for N_2O_3 and N_2O_4 in the gas phase, therefore major reaction products are NO_2 and N_2O_5 under the $MR > 1$. In the presence of water vapor in the gas phase, HNO_2 and HNO_3 are produced according to the following reactions:



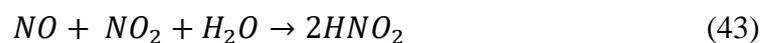
O_3 also oxidizes the HNO_2 to HNO_3 with the following reaction:

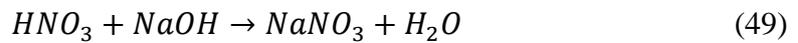
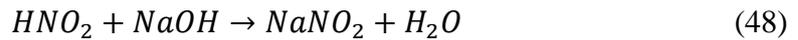
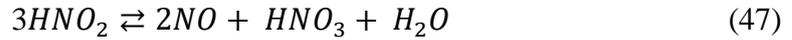
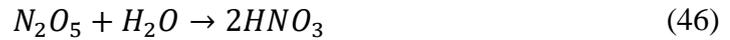


The equilibrium concentration of HNO_3 is much lower than HNO_2 and it was found that no HNO_3 exist if $MR < 1$. Therefore, in existence of water vapor NO_2 and HNO_2 are major products under the condition of $MR < 1$ and conversely NO_2 , N_2O_5 , HNO_2 and HNO_3 are result products when $MR > 1$. Since N_2O_5 , HNO_2 and HNO_3 are easily soluble in water than NO thus oxidation of NO is beneficial for the NO_x removal.

8.2.2 Liquid phase reactions

When gas phase stream contacts with $NaOH$ aqueous solution in the scrubber column, first NO_x reacts with water to form HNO_2 and HNO_3 and thereafter neutralized with $NaOH$ to form $NaNO_2$ and $NaNO_3$ respectively. Primarily following reactions may take place:





Despite of NO_2 solubility is more than NO but it's still relatively low ($HNO_2 = (7.0 \pm 0.5) \times 10^{-3} \text{ Lmol}^{-1}\text{atm}^{-1}$ at 22°C). At low partial pressure reaction (42) is slow, irreversible and a 2nd order reaction. While reactions (44) and (45) are fast and irreversible but they can be neglected since the main oxidation species in the gas stream is NO_2 . Reaction (46) is a reversible reaction and it emits again NO in scrubber gas outlet but, NO formation from the reaction (47) can be prevented by instantaneous reaction (48) with an alkaline solution ($NaOH$). Instantaneous reaction of HNO_2 with $NaOH$ solution (reaction 48) converts it to $NaNO_2$ salt and prevents the NO formation in flue gas. Considering very short lifetime of N_2O_3 and N_2O_4 in the gas and having low MR, main reactions in liquid phase are assumed to be (42), (43), (48) and (49), whilst reactions (42) and (43) are the rate controlling steps (Sun et al., 2017).

8.3 Mass transfer

In the scrubber column, liquid phase reactions and transport mechanisms are involved. The two-film theory is typically applied to the description of mass and heat transfer between gas and liquid phases (Figure 18). In this film theory, it is assumed that bulk liquid and gas phases are perfectly mixed with uniform temperature and concentration. The mass transfer resistances are assumed to lie in the two film layers near the interface. At the interface, vapor and liquid are in equilibrium so concentrations can be derived from Henry law. Both liquid and vapor films are stagnant with a certain thickness, so only diffusive mass transfer occurs without any convective mass transfer. Thereby all transport resistance happens when the

component is diffusing through both gas and liquid films, i.e. one-dimensional diffusion transport takes place normal to the interface. The flux through both layers will be the same because of mass balance and resulting equation of mass flux is given by equation (50). Wet processes also require the intensification of mass transfer from the gas phase to liquid in order to increase the removal efficiency.

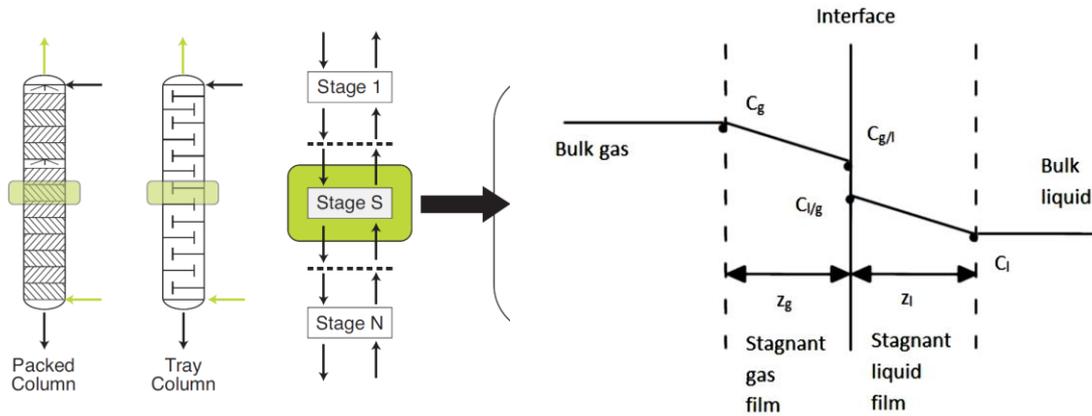


Figure 18. schematic of two film model (Michael K. Stenstrom, 2015)

$$F = v_{tot} \left(C_l - \frac{C_g}{K_H} \right) \quad (50)$$

$$K_H = \frac{C_g}{C_l} \quad (51)$$

$$v_{tot} = \frac{1}{z_l/D_l + z_g/(D_g * K_H)} \quad (52)$$

- F - Mass flux / kmole $m^{-2} s^{-1}$
- v_{tot} - Total velocity / $m s^{-1}$
- C_l - Concentration of pollutant in liquid / kmole m^{-3}
- C_g - Concentration of pollutant in gas / kmole m^{-3}
- K_H - Henry's volatility constant / -
- $C_{g/l}$ - Equilibrium concentration of pollutant in gas / kmole m^{-3}
- $C_{l/g}$ - Equilibrium concentration of pollutant in liquid / kmole m^{-3}
- z_l - Thickness of liquid layer /mm

- D_l - Diffusivity of pollutant in liquid / $\text{m}^2 \text{s}^{-1}$
- z_g - Thickness of gas layer /mm
- D_g - Diffusivity of pollutant in gas / $\text{m}^2 \text{s}^{-1}$

8.4 Simulation model

Unlike Physical absorption (without chemical reactions), reactive absorption provides high throughput at moderate partial pressure accompanied by chemical reaction. Reactive absorption occurs far from thermodynamic equilibrium and it is a complex rate controlled process. Therefore accurate and reliable rate based models are required and equilibrium models are insufficient to describe process kinetics. Equilibrium model assumes that each gas stream leaving a particular tray or packing segment is in equilibrium with the corresponding liquid stream exiting the same tray or packing segment.

In reality, thermodynamic equilibrium is rarely reached in reactive absorption. Thereby, correlation parameters such as Height equivalent to theoretical stage (HETS) or tray efficiencies are introduced to adjust conditions from equilibrium based theoretical concept to real column, however, these simplified concepts fail for multicomponent mixtures. Hence a rate based approach is a more consistent way to describe the multicomponent reactions including with mass and heat transfer. Mass transfer at the gas-liquid interface is generally described by two-film theory due to a broad spectrum of correlations are available in the literature for different column internals.

8.5 Process simulation

The main objective of the simulation model is to evaluate the ozone consumption in the scrubber for NO_x removal. Therefore, a sensitivity analysis of NO_x removal vs ozone consumption is targeted in order to find the optimum O_3/NO_x molar ratio (MR). Optimum MR is crucial for overall process economics because ozone consumption is directly linked to investment cost and annual operating cost of ozone generator in a scrubber system.

For this purpose, process simulation is performed on a steady state simulation software Aspen Plus 9.0. Aspen Plus simulator is typically used for process synthesis, design and optimization for academic and commercial purposes. Open loop process flowsheet has mainly two units, ozone reactor and absorber column (scrubber) as presented in Figure 19.

Recycling concept of effluent stream (WOUT) as a liquid inlet (WIN) of scrubber (closed-loop process) is not investigated in this simulation work.

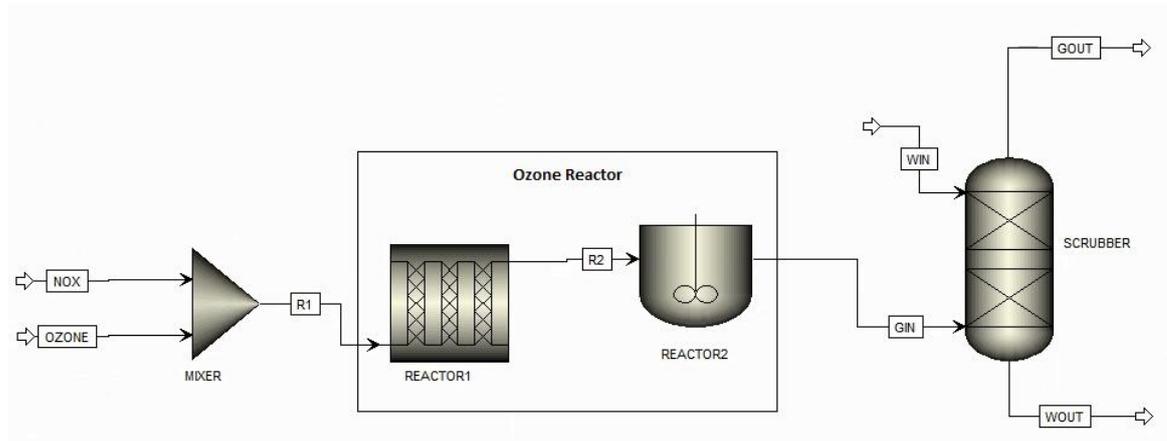


Figure 19. Aspen Plus Ozone Scrubber process flowsheet

To get the better understanding of flowsheet, description of unit's mixer, ozone reactor and scrubber are summarized below.

8.5.1 Mixer

NO_x stream in the flowsheet (Figure 19) is a gas phase stream consist of nitrogen oxides, NO (95%) and NO_2 (5%) on a molar basis. Ozone stream represents the only ozone component and its feed rate is set according to specific O_3/NO_x molar ratio. Mixer purpose is to combine the input streams and results one feed stream for the ozone reactor.

8.5.2 Ozone reactor

Chemical reactions for oxidation of NO_x with ozone are already mentioned in the previous section. To avoid the complexity of multiple reactions involve in the oxidation process, a reduced set of rate-controlling reactions are considered in this simulation work. Oxidation products such as NO_2 and NO_3 further react through multiple series and parallel reactions and form high-order nitrogen oxides such as N_2O_3 , N_2O_4 , N_2O_5 . For this reason, reactions are dived in two reactors in series, Reactor 1 and Reactor 2 (Figure 19).

Reactor 1 is chosen as a plug flow reactor (PFR) and it assumes the perfect mixing between and within the phases. PFR can handle kinetic reactions (irreversible) with a description of the power law. Reactor conditions such as temperature, pressure and dimension (length and

diameter) are mentioned as input in the PFR model. The component concentration of reactants are known and products concentration are determined by specified kinetics and stoichiometry. Table 9 describes the rate controlled reactions involve in Reactor 1 and their kinetic data is specified by built-in power law expression for specified reference temperature (T_o) given in equation (53) and for unspecified reference temperature equation (54). The kinetic parameters (k , n and E) are obtained from the NIST data bank (Manion *et al.*, 2015).

Table 9. Reactor 1 reaction kinetics

ID	Gas phase reactions	n	k	E	Order of reaction
1	$NO + O_3 \rightarrow NO_2 + O_2$	2.2	1.49E+08	6360	2
2	$NO_2 + O_3 \rightarrow NO_3 + O_2$	0	7.23E+07	20370	2

$$r = k \left(\frac{T}{T_o} \right)^n e^{-\left(\frac{E}{R}\right) \left[\frac{1}{T} - \frac{1}{T_o} \right]} \prod_{i=1}^N C_i^{\alpha_i} \quad (53)$$

$$r = kT e^{-\left(\frac{E}{R}\right) \frac{1}{T}} \prod_{i=1}^N C_i^{\alpha_i} \quad (54)$$

- r - Rate of reaction / kmole m⁻³ s⁻¹
- k - Pre-exponential factor / m³ kmole⁻¹ s⁻¹
- T - Absolute temperature / K
- T_o - Reference temperature / K
- n - Temperature exponent / -
- E - Activation energy / J mole⁻¹
- R - Gas law constant / J K⁻¹ mole⁻¹
- Π - Product operator / -
- N - Number of components / -
- C_i - Concentration of component (i) / kmole m⁻³
- α_i - Exponent of component (i)

Reactor 2 is a rigorous continuous stirred tank reactor (RCSTR). RCSTR can handle simultaneously both kinetic (irreversible) and equilibrium (reversible) reactions, however,

in this work, only equilibrium reactions (31), (32) and (35) are defined in Reactor 2. Moreover, assumed conditions in RCSTR are isothermal, phase equilibrium, isobaric and ideal mixing within and between phases. Reactor holdup is defined in this work by specifying the volume of the reactor. Equilibrium constants of reactions are determined from Gibbs free energy calculations built in Aspen Plus.

8.5.3 Scrubber

NO_x scrubber is based on a rate-based model in Aspen Plus (RadFrac column). The rate-based approach utilizes the Maxwell-Stefan model to calculate the mass transfer between gas and liquid phases and it relies on two film theory in which mass transfer resistances occur only in a thin layer adjacent to the bulk phases. Radfrac model requires column dimension, packing specification and selection of various correlation methods for rate-based calculations.

Water as a liquid solvent is sprayed from top of the packed column and it reacts with nitrogen oxides to form nitrous acid (HNO₂) and nitric acid (HNO₃) as end product which is collected from the bottom of column. Packing material increases the surface area to enable the greater mass transfer between the gas and liquid phases. Liquid phase reactions in scrubber column are briefed in Table 10 and it includes the both kinetic (irreversible) and equilibrium (reversible) reactions. The power law kinetic parameters are obtained from the NIST kinetic database (Manion *et al.*, 2015).

Table 10. Liquid phase scrubber reactions

ID	Liquid phase reactions	n	k	E	Order of reaction
1	$NO_2 + H_2O \rightarrow HNO_2 + HNO_3$	0	46999.15	0	2
2	$NO + NO_2 + H_2O \rightarrow 2HNO_2$	0	3.79E+10	8.88	3
3	$N_2O_3 + H_2O \rightarrow 2HNO_2$	0	2.52E+11	11.59	2
4	$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$	0	0.15	0	2
5	$N_2O_5 + H_2O \rightarrow 2HNO_3$	0	2.2E+07	0	2
6	$3HNO_2 \rightleftharpoons 2NO + HNO_3 + H_2O$	Equilibrium reaction			

The electrolyte NRTL (ELECNRTL) model is taken as property methods for determining the thermophysical properties of components in gas and liquid phases. ELECNRTL is basically an extension of NRTL (non-random two-liquid) model that includes the electrolytes and it is suitable for a multi-solvent system where electrolytes are present in aqueous solution. ELECNRTL model calculates the liquid phase thermodynamic properties such as enthalpy, activity coefficient and Gibbs free energy. Vapor phase fugacity coefficients are determined by the Redlich-Kwong (RK) equation of state. NRTL binary interaction parameters b_{ij} and b_{ji} for each pair are adopted from literature (Asif and Kim, 2014). The component properties are taken from built-in Aspen plus data banks and missing parameters are estimated by Aspen plus property estimation.

8.5.4 Results

Sensitivity analysis is generated in Aspen Plus to visualize the trend of NO_x removal vs ozone feed variation. Figure 20 shows the ozone consumption relationship with NO_x oxidation products in the ozone reactor. NO and NO_2 contents in the flue gas are specified in molar flows 0.46 mol/sec and 0.02 mol/sec respectively, with zero ozone feed supply. To remember, NO_x is comprised of 95% NO and 5% NO_2 contents in this simulation. O_3/NO_x molar ratio (MR) is indicated at points MR=1 and MR=2 in Figure 20 and NO and NO_2 concentrations can be spotted at these molar ratios. MR=1 means that molar flows of reduced NO_x contents and O_3 are equal ($\text{O}_3/\text{NO}_x=1$) and it is indicated approximately at ozone feed rate of 0.21 mol/sec. To reduce the further NO_x contents in flue gas, molar ratio is increased to MR=2 and nearly zero NO concentration in flue gas can be accomplished. The target NO_x levels vary in each case and typically defined by the investor as per emission limits. An optimal MR is ultimately selected according to set desired NO_x levels in the exhaust flue gas.

The trend of NO curve shows that NO concentration decreases linearly by increasing the ozone molar feed while on the contrary NO₂ concentration increases and it always exists even if MR=2.5 (Sun *et al.*, 2017). High-order nitrogen oxides N₂O₃, N₂O₄ and N₂O₅ concentration appears to be extremely low even at MR=2. The reason behind that can be the equilibrium concentrations of N₂O₃ and N₂O₄ are very low according to equilibrium constants and their shorter lifetimes.

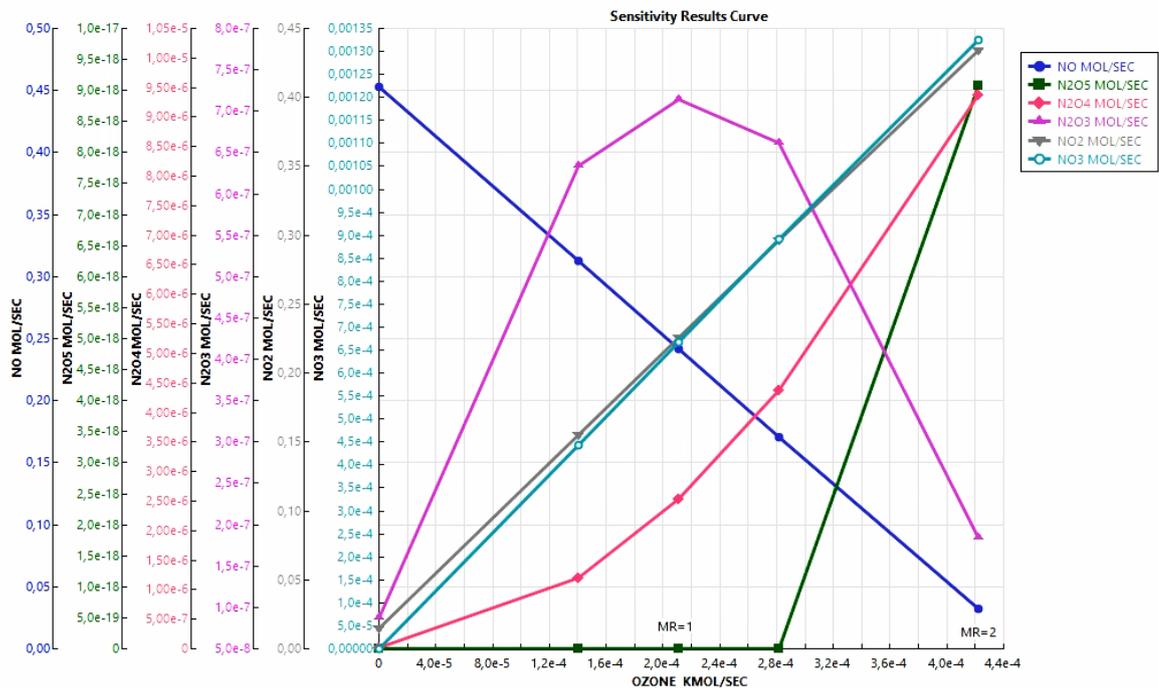


Figure 20. Ozone reactor sensitivity analysis

Figure 21 shows the variation of NO_x concentration at the scrubber outlet (GOUT) with ozone feed. NO₂ concentration in GOUT appears to very low and it is mainly due to the absorption in water to form nitrous acid and nitric acid. when MR < 1, NO contents decrease almost linearly and under the condition of MR > 1, NO reduction happens at a slower rate and the reason is the reversible reaction of nitrous acid (reaction 46) that emits again NO to scrubber outlet gas stream(Thomas and Vanderschuren, 1999).

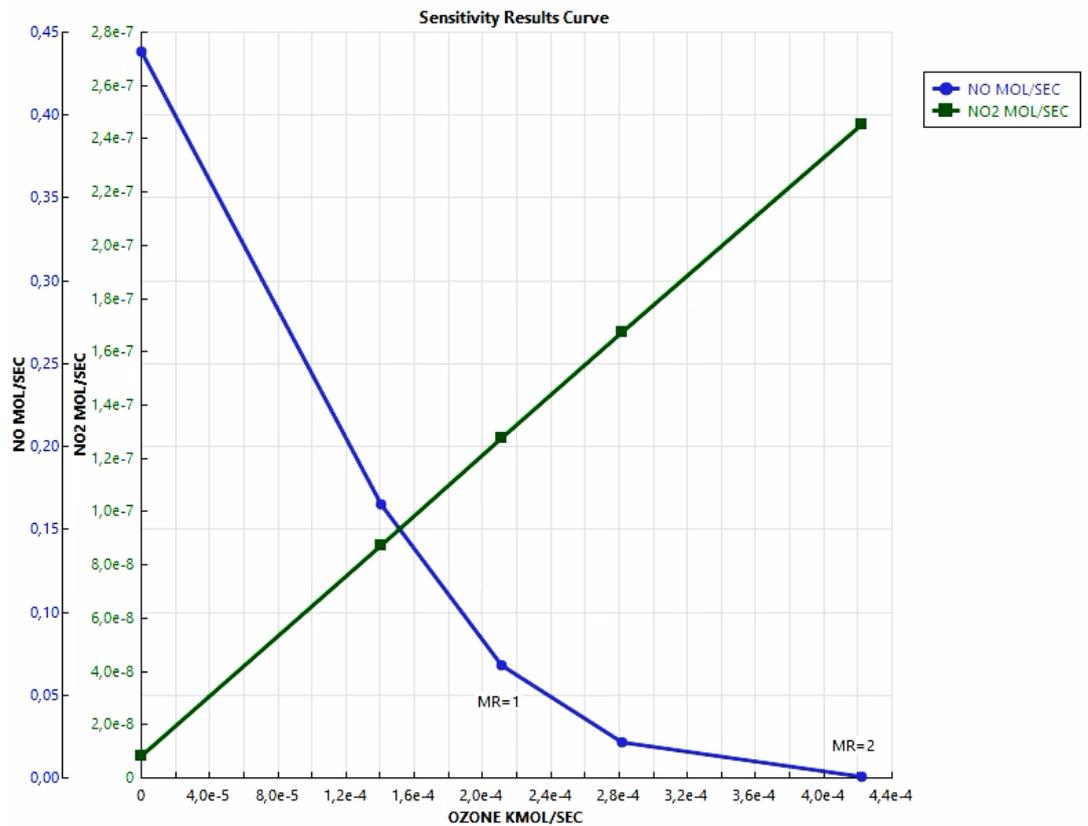


Figure 21. NO_x removal in ozone scrubber as a function ozone consumption

For this reason, Nitrous acid formation starts decreasing when $MR > 1$ as a result of reversible reaction which produces NO and nitric acid (Sun *et al.*, 2017). Nitric acid formation increases steeply under $MR > 1$ and it's because of more NO is converted to high-order nitrogen oxides and they ultimately solubilize in water to generate acid at the bottom of scrubber (Figure 22).

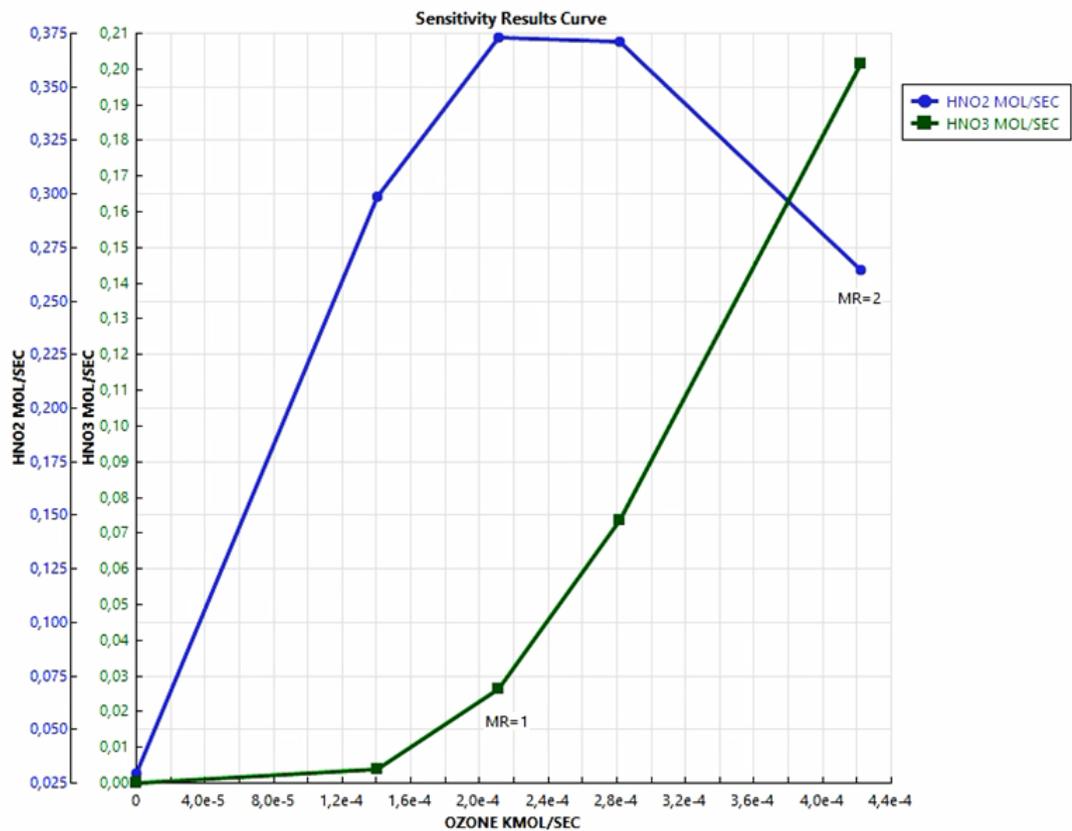


Figure 22. Acid formation vs ozone consumption

Simulation findings are applied in selecting the optimal O_3/NO_x molar ratio for achieving the target $DeNO_x\%$ and furthermore, design calculation for ozone generator capacity and consumables are performed. Moreover, these findings are utilized for the cost estimation of ozone scrubber system in the techno-economic analysis.

9 Techno-economic analysis

NO_x abatement methods which currently prevail in the industrial market are described in this section including with their potential combinations. The technologies that are considered in this scope of the study are SNCR, SCR, ClO₂ Scrubber and O₃ Scrubber. Introduction of these NO_x removal methods with their application in combustion units has been explained in the previous chapters. Each diminution method has its own advantages and limitations for application in different combustion equipment's. For instance, SNCR application is highly dependent on the availability of appropriate temperature window for effective reduction reaction in the combustion device. SNCR is applicable for achieving DeNO_x% between 25-50% in different types of boilers. More stringent regulations demand greater DeNO_x% in stationary fired equipments and SNCR application is not enough to meet higher DeNO_x% >50% requirements.

SCR method has the capability of reaching greater DeNO_x% up to 95% because of the catalyst presence, which enhances the reduction reaction and results in lower NO_x content in the exhaust flue gas. SCR system is subjected to high capital investment due to the necessity of catalyst volume and reactor assembly for meeting greater DeNO_x%. High capital cost creates the barrier for investor especially in the cases where combustion unit operates seasonally and flexibility of operation is demanded. However, oxidation-absorption processes involve the injection of oxidizing agents O₃ or ClO₂ and then followed by absorption in water for NO_x removal from the flue gas. One particular advantage scrubber serves at the downstream of flue gas cleaning is that ammonia slip, dust, ash and acid gases (HCl, HF, SO₂) are also washed by scrubbing liquid simultaneously. Scrubber bottom effluent stream contains nitrates (NaNO₃) and nitrites (NaNO₂) in case of injecting alkaline (NaOH) scrubbing liquid, which poses environmental concerns and necessitate further wastewater treatment.

Therefore, in the scrubber operation DeNO_x% is mainly dependent upon the oxidant supply and nearly all NO_x contents are obliterated from the flue gas undersupplying excess chemical oxidants. Oxidant consumption is associated with the operating cost, thereby NO_x scrubbers are suitable for flexible operating combustion systems for instance, lowering NO_x peak values in high load operation and circumstances in which the slight DeNO_x% is requisite for fulfilling the environmental regulation. For combustion units which operate continuously

for a whole year and require greater DeNO_x%, then annual operating charges can be significantly higher for scrubber system thereby, SCR can be a promising solution in such scenarios as it doesn't cost very high in terms of operating charges. Thus, investor financial attractiveness varies in favouring either investment cost or operating cost.

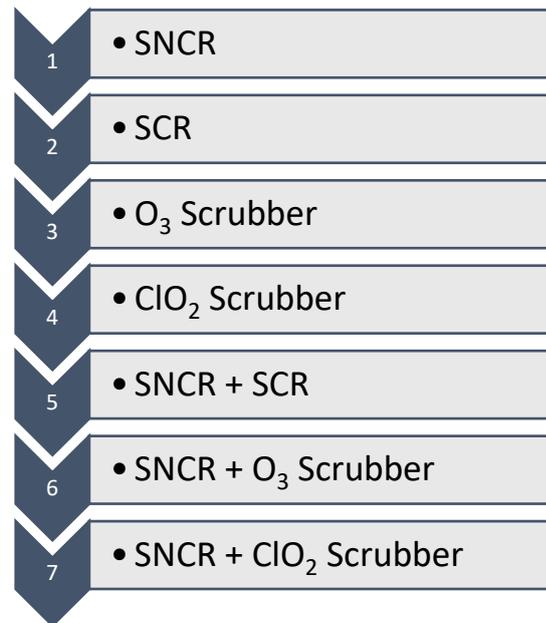


Figure 23. NO_x mitigation methods and combinations in TEA tool

Combinations of NO_x abatement methods are alternative choices for reducing the greater DeNO_x% and simultaneously considering the economic picture in terms of capital and operating cost. NO_x regulations set by concerned authorities vary with respect to location, combustion unit type, fuel type and either retrofit or new case, therefore DeNO_x% demands fluctuate from case to case. Hence all these factors necessitate to consider the coupling of NO_x reducing methods as alternative choices to the investor. Figure 23 shows the selected NO_x mitigation methods and their hybrid systems in TEA tool development.

The hybrid system of SNCR + SCR is already applied on an industrial scale and it reduces the NO_x level in two stages, first employing the SNCR method in the combustion unit and then followed by SCR implementation in the second stage. Such a joint system is also referred as slip catalyst because of unreacted ammonia from SNCR step is consumed as a reducing reagent in the SCR system and as a result, there is no ammonia emission in the exhaust flue gas. Such a hybrid system provides the flexibility of functioning in situations where a significant reduction of NO_x is expected. Tight ammonia slip demands between 2-5

ppm are achievable with slip catalyst configuration. A drawing of the SNCR + SCR hybrid system is shown in Figure 24.

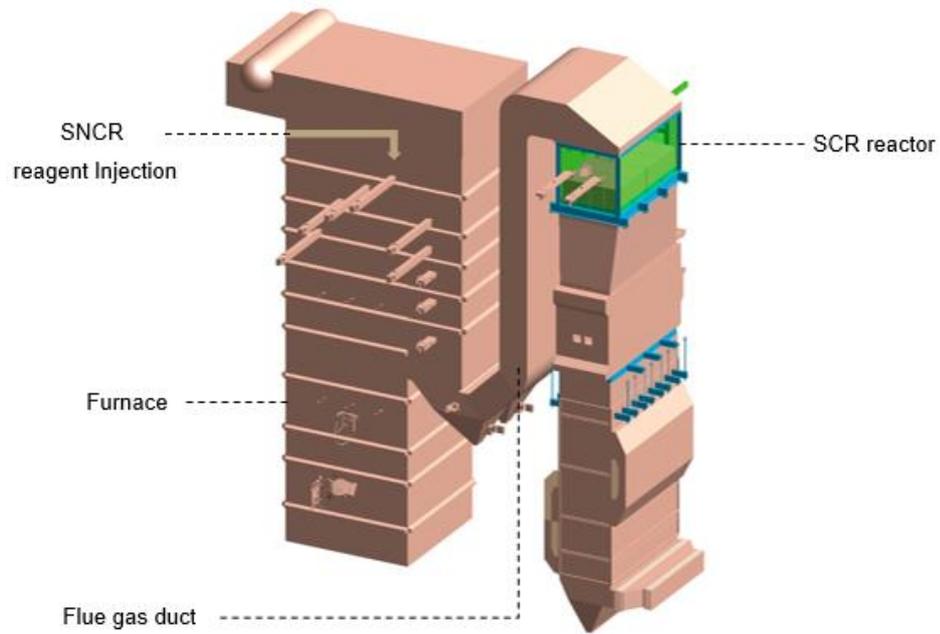


Figure 24. Hybrid SNCR + SCR system for NO_x reduction

SNCR integration with NO_x scrubbers also offers the higher DeNO_x% attainment in scenarios where alone SNCR is not sufficient. The NO_x mitigation takes place with SNCR method in the first stage and then followed by NO_x scrubber in 2nd stage. The flexibility of operation with scrubber system aids in the elimination of NO_x peak values during overload run of combustion unit and switch off facility by no injection of oxidative reagent when no further DeNO_x% is required. In practice, the injection quantity of oxidizing reagent controls the DeNO_x% and therefore process economics is more affiliated with operating cost. A drawing of SNCR and NO_x scrubber hybrid system is presented in Figure 25.

Similarly, the conjunction of SCR system with NO_x scrubber can be one possible combination for situations where excessive DeNO_x% is required with the strict demand of ammonia slip and acid gases in the flue gas, especially in the variable load operation.

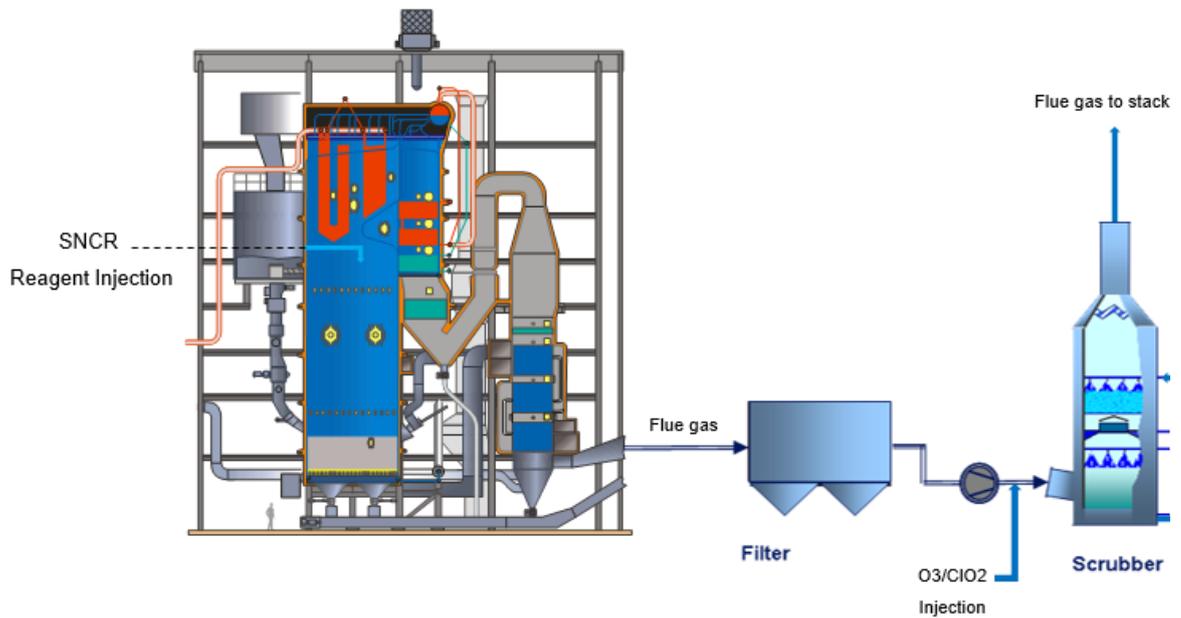


Figure 25. The hybrid system of SNCR + Oxidizing Scrubber

9.1 Technology selection procedure

The NO_x abatement methods and their combinations provide the several choices for selection of most feasible technology in the flue gas cleaning system. The selection is first subjected to meet the technical demands of NO_x reduction system set by the investor such as NH_3 slip and NO_x content in the exhaust flue gas stream (NO_x out). After fulfilling the above-mentioned requirements choice is made between most economically feasible technology among the other alternatives. The considered NO_x removal technologies in this selection concept study are summarized in Figure 23. The decision matrix is constructed for each NO_x removal technology to highlight the most significant parameters involved in it. Generally, most relevant decision-making parameters in developing the technology selection procedure are $\text{DeNO}_x\%$, NH_3 slip and NO_x out. In the technology evaluation procedure, investor demanded values for these parameters are assessed according to design specifications and then the preliminary decision is made for its possibility of functioning in such scenario. Selection criteria for all individual technologies is further elaborated in below section.

The chosen parameters in the SNCR system are $\text{DeNO}_x\%$, NO_x out and NH_3 slip. Primary NO_x contents in the flue gas vary with a load of operation in combustion unit. Variation in a load of operation affects the reagent injection level and dosing amount due to a fluctuation

in the appropriate temperature window inside the unit. Therefore, in SNCR application, DeNO_x% and NH₃ slip are dependent on a load of operation. NO_x out is defined as NO_x contents in the exhaust flue gas stream leaving from the treatment method. NH₃ slip is unreacted ammonia detected at the exit of NO_x treatment method.

Two evaluations are performed in SCR technology selection, first to determine the technology functioning according to constraints set by the investor and secondly the position of catalyst in the downstream flue gas stream. Parameters such as DeNO_x%, NO_x out and NH₃ slip are taken into account, in order to assess the possibility of technology functioning. Catalyst position is determined based on fuel type and impurities in the flue gas such as dust contents, alkaline metals (Na, K), heavy metals and acid gases. According to the impurities level in the flue gas, catalyst location is determined as either High dust, Low dust or Tail end.

Selection criteria for NO_x scrubbers is analogous to SNCR and SCR methods and the crucial parameters for technology evaluation are DeNO_x%, NO_x out and NH₃ slip. Hybrid systems of SNCR with SCR and NO_x scrubbers have also the same selection methodology as for individual technologies. The SNCR system reduces primary NO_x contents in the first stage and rest is mitigated by introducing either SCR or O₃/ClO₂ scrubber as a second stage. Thus, NO_x out from SNCR step is considered as the NO_x inlet for the second NO_x reducing method. Catalyst type and position for hybrid SNCR + SCR system is the same as SCR system. Whilst in conjunction system of SNCR and NO_x scrubbers, consumption of oxidizing agents O₃/ClO₂ is less as compare to solely scrubber system and it is due to part of primary NO_x is reduced from SNCR in the first stage.

9.2 Economic evaluation

Economic assessment has a vital role before investing in any NO_x removal technology for the flue gas cleaning. The analysis determines the financial aspects of the treatment method in the long run and its profitability with competing alternatives. The procedure of technology selection in the previous section outcomes the technical possibility of NO_x removal technologies and their combinations. Technology functioning is not the only rule of thumb for the final selection, cost evaluation and economic picture has a significant importance before an investment decision making.

NO_x removal technologies don't generate any revenue and its whole package of only costs that investor has to pay off for operating the system until its lifetime. However, any revenue generation possibility is subjected to the country regulations that support investor and exempt the NO_x fees. One cash inflow option is heat recovery from NO_x scrubbers, but it's also a matter of need and economic benefits from the heat recovery in that location. Apart from those scenarios, there is no probability of cash inflow by investing in NO_x abatement technologies and sole purpose is to comply with emission limits posed by regulatory authorities. This discussion leads to inquire about the economic evaluation of NO_x removal technologies to demonstrate the picture of cost differences among different alternatives. The feasibility analysis in TEA tool exhibits the economic view of NO_x mitigation technologies and results in the ease of preliminary selection.

9.2.1 CAPEX estimation

Costs involved in the NO_x abatement technologies are distributed in capital expenditures (CAPEX) and annual operating expenses (OPEX). A large sum of one-time expenses incurs on the purchase of necessary equipment's, machinery and land to construct a plant for producing the goods or rendering of service. In addition to the equipment's purchase cost, mechanical erection, electrification, instrumentation & control, installation & commissioning and other service facilities must be obtained. Fixed capital cost is breakdown into the direct cost and indirect cost. Direct cost typically comprises of purchased equipment, installation, piping, building and utility facilities whilst, indirect cost generally includes engineering design, supervision, construction expenses, contractors fee and contingency charges. In this study, only major direct and indirect costs are taken into account in CAPEX estimation because of their impact on the overall economic summary. Description of costs incorporated in CAPEX of NO_x abatement methods is presented below.

End design features of SNCR system such as level of injections, the number of nozzles/injection lances, reagent chemical selection (ammonia or urea) are determined. Other direct costs in the CAPEX of SNCR system are piping, reagent storage handling, pumps, platform & support structure, mechanical erection, electrification, instrumentation & control and installation. Indirect costs such as supervision, administration and engineering and project management are minor costs.

SCR cost estimation is based on the design specifications of the catalyst and reactor assembly. Catalyst design is a volatile function of various inputs, especially fuel impurities such as dust, alkaline metals, acid gases and heavy metals. These contaminants in the flue gas are responsible for the deactivation of catalyst and affect its lifetime. Other factors involved in the design of catalyst are DeNO_x%, NH₃ slip, temperature and moisture content in the flue gas. These input specifications determine the position, type of catalyst, catalyst volume and reactor dimension. Typically, two catalyst types exist in the market for NO_x reduction, plate and honeycomb. The catalyst reactor is basically the inner steel support structure of beams for carrying catalyst blocks in the designed dimension. Inner steel support structure is also needed for steam-sootblowers and rectification grid in the reactor. There are external steel supports required for holding the complete assembly of reactor between the flue gas ducts. Dimensioning of flue gas ducts before and after the reactor is based on the flue gas parameters. Inlet duct to the reactor contains guide vanes and static mixer which direct the flow channel and mixing of reagent chemical with flue gas constituents.

Pressure drop in the SCR reactor is a notable measure and it affects the electricity consumption of the flue gas fan. Minimum temperature required for catalyst functioning is a significant cost affecting design feature. In circumstances where the temperature of the flue gas is lower than the minimum required temperature, side reactions happen and especially the formation of ammonium bisulfate (NH₄HSO₄) and ammonium sulfate ((NH₄)₂SO₄). These side products are corrosive and sticky in nature and can deactivate the catalyst. The temperature of the flue gas is increased through steam preheater or flue gas heat exchanger before the catalytic reactor. However, it raises the extra capital and operating cost for SCR system. Insulation of reactor and flue gas ducts avoids the heat losses and maintain the necessary minimum temperature for NO_x reduction reaction. Ammonia or Urea injection system comprises of similar components involve in the SNCR system whereas vaporizer or hydrolyzer system is typically required for ammonia or urea injection respectively. Mechanical erection, electrification and instrumentation & control are a significant proportion of CAPEX while engineering, project management and completion are minor cost items.

CAPEX of NO_x scrubbers is estimated by correlation curves which are generated as a function of the flue gas flow. ClO₂ scrubber requires the corrosion resistant material such as titanium oxide, thus it raises the extra capital cost than ordinary steel manufactured column.

Heat exchanger recovers the possible heat from the flue gas by condensing and heated water is used as a utility stream. This is one likelihood of revenue generation from NO_x removal system. Ozone generator cost is a significant part of O₃ scrubber system and the generator capacity is designed on the basis of ozone flow required for specific DeNO_x%. For greater DeNO_x% the larger capacity of the ozone generator is needed and the end result is the extensive capital cost. Utilities for the ozone generator are O₂ gas, electricity and cooling water, their consumption is also dependent upon the capacity of the ozone generator. On the other side, the ClO₂ scrubber is less cost-effective, when ClO₂ supply is already available at the site, for example in pulp mills, ClO₂ takes part in the bleaching process. On the contrary scenario of ClO₂ unavailability, the ClO₂ plant requires the extra capital investment and it will be taken account in the total CAPEX.

CAPEX estimation of hybrid systems SNCR + SCR, SNCR + O₃ scrubber, SNCR + ClO₂ scrubber is also approximated in this work for economic comparison. In the hybrid system of SNCR + SCR, after SNCR application in the first stage, catalyst design calculations are performed for remaining DeNO_x%. In the combination system of SNCR with NO_x scrubbers, cost calculations are based on the correlation curves as explained earlier, whilst chemical consumptions and utilities are calculated based on the remaining DeNO_x% requirement after the 1st stage of SNCR application.

9.2.2 OPEX estimation

CAPEX is combined with the process operating cost (OPEX) to determine the economic evaluation of NO_x mitigation methods. The costs associated with the day-to-day operation of NO_x removal technologies are estimated for the assessment of economic feasibility. In order to estimate the OPEX, process consumables are important to know in all NO_x removal methods such as raw materials, catalyst, chemical solvents and utilities. Other OPEX items are depreciation, property taxes, insurances, rent, administration, marketing and research & development work. In this work, only selective OPEX are chosen in each NO_x removal technology due to their significant impact on overall economics.

The OPEX are minor in SNCR technology and chemical reagent for reduction reaction (ammonia/urea) is an only considered consumption. Reagent consumption is estimated at a particular molar ratio of reagent to NO_x in the flue gas. Dilution water or electricity

consumption for pumps is neglected in this scope of study due to their insignificant effect on economics.

OPEX in the SCR system are mainly the catalyst replacement after its deactivation, electricity consumption for flue gas fan to accommodate the pressure drop in reactor, and consumption of reducing reagent (ammonia/urea). The pressure drop across the reactor is noticeable due to the narrowly spaced catalyst units in a certain dimension. Inlet flue gas duct to the reactor contains the static mixer for better mixing of the reagent with flue gas constituents and it also causes the pressure drop of the flue gas. Therefore, electricity consumption in the flue gas fan is accounted to accommodate this pressure drop. Catalyst deactivation is fastest at the beginning of catalyst lifetime and then slows down but generally, the lifetime varies between 1-5 years and replacement cost is considered on annual basis in the OPEX estimation.

OPEX are more significant in NO_x scrubbers as compared to the SNCR and SCR methods. Electricity consumption for ozone generator is an enormous part of overall OPEX in the ozone scrubber. Chemical consumptions in the ozone scrubber are NaOH solution to maintain the pH of scrubbing liquid and pure O_2 gas as a feed stream for the ozone generator. Cooling water circulation is also necessary for ozone generator to maintain its necessary temperature. ClO_2 replaces the ozone as an oxidant in the ClO_2 scrubber and for this reason, there is neither extra electricity consumption nor O_2 gas needed. While in case of investing in the new ClO_2 plant, then along with its capital cost, operating cost will also be considered in total OPEX.

Similarly, OPEX estimation of the hybrid systems SNCR + SCR, SNCR + O_3 scrubber and SNCR + ClO_2 scrubber is performed using the same methodology as for individual NO_x removal methods. Process consumables are calculated in two stages, first by applying SNCR methods and then remaining $\text{DeNO}_x\%$ is achieved by either induction of SCR or one of the NO_x scrubber.

9.2.3 Feasibility analysis

Feasibility analysis is important to know about an investment to be worthwhile in building a new plant or revamping the existing facility. Economic indicators such as accumulated cash flow, discounted accumulative cash flow and Net present value (NPV) is calculated and these are based on the CAPEX and OPEX of NO_x abatement methods. In this TEA analysis,

there is no revenue or cash inflows, so there is a continuous consumption of operating utilities in terms of costs.

Discounted cash flows and NPV take into account the time value of money due to the inflation and cost of borrowed money as an interest rate. Non-discounted cash flows give a snapshot view of the future cash flows without considering the inflation and compounding effect of interest. Hence, it is important to estimate the time value of money at a specific interest/discount rate. An amount of money at the current time is referred as present value (P) or present worth and may not be the same at future date. If an amount is invested with an interest rate over a certain period of time, the interest is added to the initial invested amount, and value of money at future date is the future amount (F). The interest which is the compensation for use of money over the duration of time is the difference between the future and the present value of money. Compound interest is calculated at each period on the principal amount plus the accumulated interest and after compound interest period (n), the principal increases according to the equation (55);

$$F = P(1 + i)^n \quad (55)$$

The equation obtained is used for calculating the present value (P) of future amount (F) with interest rate (i) after (n) years. The term weight average cost of capital (WACC) is synonymously used with interest rate.

Cash flow is defined as the net balance of money into or out of a company due to an investment and it can be positive or negative. Cash flows are computed for each year to the projected life of the plant. In the evaluation of any investment, CAPEX is always a negative cash flow and annual profit after the tax and depreciation charges is a positive cash flow. In NO_x removal methods as there are no cash inflows, thus there is no profit and all annual cash flows are negative. The salvage value of an investment after the plant lifetime is considered zero. In present worth technique, all costs and revenues in future are discounted to present worth with interest rate (i) and these are called the discounted cash flows. The sum of all discounted cash flows is NPV. NPV is a quantitative measure of comparing the competing investments and an investment to be profitable, it has to be positive. Another rigorous profitability measure is the internal rate of return (IRR) and it is the interest rate at which NPV becomes equal to zero. As in this study, no profit is expected, so IRR calculations are neglected.

10 Conclusions & Summary

The development of TEA tool is based on the NO_x mitigation solutions for industrial applications. Technology selection procedure in the TEA tool demonstrates the technical functioning of NO_x control methods according to the investor demanded criteria. Hybrid systems such as SNCR+SCR, SNCR + O₃ scrubber and SNCR + ClO₂ scrubber generate the alternative choices for new investment. A brief summary of this selection procedure is that a greater DeNO_x% upto 95% is achievable through SCR and NO_x scrubbers (O₃ & ClO₂) technologies, while SNCR can reach DeNO_x% only between 25-50% depending upon the type of combustion unit. SNCR application is also constrained to the availability of appropriate temperature window inside the combustion device. Tight ammonia slip demand in the exhaust flue gas (less than 5 ppm) is accomplishable in SCR and NO_x scrubber methods whereas such tight slip demand is undoable through SNCR application. Similarly, with SCR and NO_x scrubber solutions, NO_x out contents in the exhaust flue gas can be reduced to a much lower limit than SNCR technology.

Economic evaluation is the second part of TEA tool in which cost comparison is performed by taking into account the CAPEX and OPEX of NO_x mitigation solutions. Consideration of only significant cost items in the feasibility analysis makes it a preliminary selection tool for a new investment. Economic findings are not clearly explicit in terms of which mitigation concept is most feasible one because it varies from case to case and depends a lot on the scope of investment and customer suitability for different auxiliary effects such as wastewater treatment in NO_x scrubbers. One clear outcome is that SNCR is a least expensive concept for NO_x mitigation unless it is unqualified to meet the investment criteria. Economic illustration of SCR and NO_x scrubbers vary according to the investment scope and suitability particularly the CAPEX. Generally, OPEX of the ozone scrubber system are higher than other concepts because of electricity and O₂ gas consumption in an ozone generator. Upon the availability of ClO₂ oxidant at the site (for example in pulp mills), then OPEX are CAPEX of ClO₂ scrubber are significantly less than ozone scrubber, on the contrary investment on the new ClO₂ plant will make it most expensive choice. OPEX of SCR system are less than any NO_x scrubber according to the tool findings.

Cost estimation of ozone scrubber shows that CAPEX and OPEX are a volatile function of ozone consumption, hence the selection of optimum O₃/NO_x molar ratio (MR) play an

important role in economic evaluation. Ozone scrubber process simulation in Aspen Plus shows that up to the $MR = 1$, NO removes from the flue gas linearly with ozone consumption. when $MR > 1.5$ then the NO removal efficiency slows down and one reason is the reversible reaction of HNO_2 in the scrubber column to form again NO in the exhaust flue gas.

As scrubber system removes NO_x simultaneously with the dust, acid gases and ammonia slip from the flue gas, then extra advantages will be taken into account for the economic comparison. Also, there are retrofit scenarios in which scrubber column is already existing for removing other pollutants from the flue gas, then only the ozone generator will be an additional cost for the NO_x solution investment. Similarly, extra gains in SCR technology are removing the ammonia slip, furan and dioxins from the flue gas, hence these advantages will be considered too in economic evaluation.

More strict regulations are resulting in the novel NO_x mitigation solutions through R&D work. Other post-combustion methods are also found in the literature such as the application of non-thermal plasma, electron beam, photocatalytic oxidation and adsorption on the activated carbon. Most of these emerging methods still exist either on lab or pilot scale and their demonstration to commercial scale can result in the more economical NO_x mitigation solutions in future.

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