POTENTIAL NO_x REDUCTION TECHNOLOGY FOR AN OLEFIN PLANT

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A SPECIAL RESEARCH PROJECT SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF ENGINEERING (CHEMICAL ENGINEERING)
FACULTY OF ENGINEERING
KING MONGKUT'S UNIVERSITY OF TECHNOLOGY THONBURI
2011

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Special Research Project Title	Potential NO_x Reduction Technology for an Olefin plant
Special Research Project Credits	6
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Program	Master of Engineering
Field of Study	Chemical Engineering
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Abstract

Nitrogen oxides (NO_x) belong to one of the pollutant families about which many industries are concerned in the past decades, as they have a harmful effect on creatures and the ecosystem. A lot of research exist that study NO_x reduction and some are practically adopted by industrial plants. The Siam Cement Group (SCG), like many other chemical plants, is also concerned about NO_x emission although SCG has already applied ultra low NO_x burners to some of its ethylene crackers which results in a significant reduction of NO_x level. However, the current NO_x level emitted by one of the olefin plants nearly exceeds the allowable limit. Moreover, SCG has planned to expand olefin production in the future by increasing the number of ethylene crackers which are the main NO_x producers. Therefore, NO_x level must be further reduced in order to support the NO_x credit required for the increasing NOx emitted from the incoming crackers. Currently, SCG has attempted to find alternative NO_x reduction technologies that benefit the plant operationally and economically. In this study, we aim to study some of the NO_x reduction technologies that are being used in olefin industries. Selective Catalytic Reduction (SCR) process is focused in this work because it requires least modification to the existing process and gives high removal efficiency. We use COMSOL Reaction Engineering Lab to model this process to determine thermodynamics and mass transport parameters. Moreover, we employ COMSOL Multiphysics to develop a 2-dimensional model of the catalyst to predict the required minimum catalyst area. The simulation results suggest that 3 catalyst layers are required to achieve a NO_x conversion of 85%. Each layer is equivalent to about 28 standard catalyst modules with the dimension of 0.9m x 0.9m x 1m each.

Keywords : NO_x Reduction technology/ Selective Catalytic Reduction (SCR)

หัวข้อโครงการศึกษาวิจัย	เทคโนโลยีการลดปริมาณไนโตรเจนออกไซด์ในโรงงานผลิตโอเลฟินส์
หน่วยกิต	6
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บทคัดย่อ

ไนโตรเจนออกไซด์คือสารเคมีตระกูลหนึ่งในสารมลพิษ ซึ่งเป็นปัญหาสำคัญอย่างหนึ่งของอุตสาหกรรมหลายแห่งมาเป็นเวลานาน เนื่องจากไนโตรเจนออกไซด์ส่งผลกระทบร้ายแรงต่อสิ่งมีชีวิตและระบบนิเวศน์ การศึกษาเรื่องการลดปริมาณไนโตรเจนออกไซด์นั้นมีงานวิจัยอยู่มาก แต่มีเพียงบางเทคโนโลยีเท่านั้นที่อุตสาหกรรมนำไปใช้จริง เช่นเดียวกับโรงงานอุตสาหกรรมเคมีอื่นๆ บริษัทสยามซีเมนต์กรุ๊ปมีความเป็นห่วงเรื่องปริมาณการปลดปล่อยไนโตรเจนออกไซด์ออกสู่บรรยากาศ แม้ว่าทางบริษัทจะมีการปรับเปลี่ยนมาใช้ Ultra low NO_x burner กับเตาปฏิกรณ์บางตัวแล้วก็ตาม ซึ่งผลที่ได้คือสามารถลดปริมาณไนโตรเจนออกไซด์ได้ส่วนหนึ่ง อย่างไรก็ตาม ปริมาณไนโตรเจนออกไซด์ที่ปล่อยออกจากโรงงานผลิตโอเลฟินส์ในขณะนี้เกือบจะเกินมาตรฐานการปลดปล่อยที่กำหนดแล้ว และทางสยามซีเมนต์กรุ๊ปยังวางแผนที่ขยายกำลังการผลิต และจะต้องมีการตั้งเตาปฏิกรณ์ซึ่งเป็นหน่วยหลักที่ผลิตไนโตรเจนออกไซด์เพิ่มขึ้นอีก ดังนั้น ปริมาณการปลดปล่อยไนโตรเจนออกไซด์จะต้องลดลงเพื่อรองรับปริมาณที่เพิ่มขึ้นจากการขยายกำลังการผลิต บริษัทกำลังมองหาเทคโนโลยีอื่นที่มีประสิทธิภาพใกล้เคียงกับ Ultra low NO_x burner ที่ใช้อยู่ เพื่อประเมินความเป็นไปได้ในการใช้ และความคุ้มค่าทางด้านเศรษฐศาสตร์ เมื่อพิจารณาแต่ละเทคโนโลยีแล้ว เทคโนโลยีที่เหมาะสมกับโรงงานที่สุดจะถูกนำมาสร้างแบบจำลองเพื่อคาดคะเนประสิทธิภาพ โครงสร้าง เงื่อนไขการผลิตของระบบ เทคโนโลยีที่เลือกคือกระบวนการบำบัดด้วยปฏิกิริยาเคมีโดยใช้ตัวเร่งปฏิกิริยาแบบจำเพาะ โปรแกรมที่นำมาสร้างโมเดลคือคอมโซล (COMSOL) ซึ่งใช้พิจารณาทั้งเทอร์โมไดนามิค ทรานสปอร์ต และพฤติกรรมของก๊าซภายในแบบจำลองตัวเร่งปฏิกิริยา จุดประสงค์ของแบบจำลองนี้คือ หาพื้นที่ตัวเร่งปฏิกิริยาที่ต้องใช้ในการลดปริมาณไนโตรเจนออกไซด์ได้ 85% ผลที่ได้คืออุปกรณ์นี้ต้องมีตัวเร่งปฏิกิริยา 3 ชั้น ชั้นละประมาณ 23 ตามรางเมตร หรือเท่ากับประมาณ 29 มอดูลของโมโนลิทขนาดมาตรฐาน

คำสำคัญ : เทคโนโลยีการลดปริมาณไนโตรเจนออกไซด์/ ปฏิกิริยาเคมีโดยใช้ตัวเร่งปฏิกิริยาแบบจำเพาะ

ACKNOWLEDGEMENTS

I would like to show my gratitude to those who made this thesis possible. Firstly, it is a pleasure to thank my thesis advisor, Dr. Hong-ming Ku whose suggestions and guidance from the initial to the final level enabled me to develop an understanding of this subject. I also thank the committee, both from KMUTT; Dr. Kwanchanok Viravaidya; and from SCG; Dr. Pimporn Lek-Utaiwan; who thoroughly offered helpful suggestions.

In addition, my appreciation also goes to my ChEPS-14 friends who gave me the support and some useful suggestions. Moreover, I cannot forget to mention the Chemical Engineering Practice School (ChEPS) and The Siam Cement Group (SCG) which gave me a great experience.

Last but not least, I wish to sincerely thank my family for their support and encouragement that has enabled me to come this far.

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CHAPTER 1 INTRODUCTION

1.1 Background

Nitrogen oxides (NO_x) are an important family of air pollution compounds consisting of seven compounds, i.e. nitrous oxide (N_2O), nitric oxide (NO), dinitrogen dioxide (N_2O_2), dinitrogen dioxide (N_2O_3), nitrogen dioxide (NO_2), dinitrogen tetroxide (N_2O_4) and dinitrogen pentoxide (N_2O_5). The formation of each is based on various ionization levels of the nitrogen atom which results in different numbers of oxygen as partners. The representative of this family is nitrogen dioxide (NO_2) regulated by EPA as it is the most prevailing form of NO_x existing in the air that is produced by human activities.

NO_x can be emitted whenever there is fuel combustion especially at high temperature. About half of NO_x is generated from mobile sources such as vehicles. The rest comes from stationary sources especially from industrial boilers, incinerators, gas turbines, or even from households.

It is a well known fact that NO_x affect the environment significantly as they are pollutants which irritate the respiratory system when they dissolve in water and decompose to form nitric acid (HNO_3) and nitrate salts. It can be said that NO_x and their derivatives can be harmful in any forms i.e. gases, dissolved acid gases or salts, which eventually contribute to acid rain. Moreover, NO_x can also react in the presence of air and ultraviolet light (UV) to cause a chain reaction producing ozone (O_3). The amount of tropospheric ozone is what the world is most concerned about because it is in the ambient air which humans breathe.

Due to the continuous growth of national concern about environmental quality, many countries including Thailand have consequently established the allowable NO_x emission levels to control industrial enterprise. As a result of more stringent government regulations, NO_x concentration released has noticeably diminished in proceeding decades. A number of science and engineering institutes have had the challenge of developing a range of control technologies which have their own strengths and weaknesses. First of all, one should comprehend that control of NO_x for nitric acid manufacturing and pickling baths differs from control at combustion sources. NO_x in acid plants can be captured using wet scrubbers and suitable absorbents, an issue not covered in this research. For combustion sources, basically, NO_x abatement principles involve the alteration of the valence level of nitrogen and can be categorized into two main strategies:

1) Pollution prevention methods which aim to minimize NO_x generation.
2) Add-on technologies that attempt to reduce NO_x emission.

Many factors e.g. NO_x concentration produced, removal efficiency, capital costs and also operating costs, should be considered thoroughly before the decision of which technology to apply is made. Sometimes, only one NO_x removal unit cannot achieve the desired emission level; thus a combination of techniques may be required.

This thesis is sponsored by one of the major Olefin manufacturers in Thailand. Like many petrochemical plants, the key equipment including cracking furnaces and utility boilers cause substantial amounts of NO_x to be released into the atmosphere. As with the environmental issue in Maptapud Industrial Estate at this moment, this is a crisis being addressed by every industry. If one of the pollutant compounds, namely NO_x, CO_x or SO_x, reaches the maximum release quota, a capacity expansion of the existing plant would not be possible. Although the plant has already adopted ultra-low NO_x burners in two of the cracking furnaces and they have performed well, the company is still looking for other potential technologies that give the plant long-term benefits. Therefore, the company intends to develop a practical reduction unit of NO_x which is currently the most critical emission problem.

1.2 Objectives

a) To explore technologies for NO_x reduction and removal.

b) To develop and simulate a process model that can be practically applied for the reduction of NO_x produced from flue gas at an Olefin plant

1.3 Scope of work

a) Explore the available technologies for NO_x reduction from various sources of information

b) Benchmark each technology in various aspects including economics and select the best option for process design

c) Develop a process model of the selected option and simulate it in order to determine the operating and investment costs

d) Evaluate the economical and operational feasibility of the proposed process design

e) Propose recommendations for installation of the unit into the plant

CHAPTER 2 LITERATURE REVIEWS AND THEORIES

Diatomic molecule nitrogen (N_2) is mostly an inert gas that exists in about 80% of the atmosphere, while the element nitrogen (N) is reactive and possesses ionization levels or valence states from plus one to plus five. This results in the formations of several different oxides as shown in Table 2.1. Nitrogen varies its number of partners, oxygen, with its valence state (Clean Air Technology Center, 1999).

Table 2.1 Family of nitrogen oxides (NO_x)

Formula	Name	Nitrogen Valence	Properties
N_2O	Nitrous oxide	1	Colorless gas Water soluble
NO N_2O_2	Nitric oxide Dinitrogen dioxide	2	Colorless gas Slight water soluble
N_2O_3	Dinitrogen trioxide	3	Black solid Water soluble, decomposes in water
NO_2 N_2O_4	Nitrogen dioxide Dinitrogen tetroxide	4	Red-brown gas Very water soluble, decomposes in water
N_2O_5	Dinitrogen pentoxide	5	White solid Very water soluble, decomposes in water

The change in the ionization level occurs due to the following situations:

1) NO_x is hit with a photon of UV or a shorter wavelength light
2) NO_x is hit with enough protons until they can transfer enough energy to change its ionization level
3) NO_x is catalyzed
4) NO_x is stimulated by thermal energy (IR)
5) NO_x reacts with a reducing or oxidizing radical
6) NO_x reacts with a reducing or oxidizing ion

Although nitrogen forms seven different oxides, the two most common oxides, nitric oxide (NO) and nitrogen dioxide (NO_2) are what cause most of the air pollution. In addition, nitrous oxide (N_2O) has become more of a concern as it is an important contributor to global warming and can devastate the ozone layer.

The liquid forms of these oxides come from dissolution in water and decomposition in which they form nitric acid (HNO_3) or nitrous acid (HNO_2). When they are neutralized, nitric acids forms nitrate salts, while nitrous acid forms nitrite salts. Therefore, it can be said that NO_x exists in the environment in the forms of either gas in the air, as acids dissolved in water, or as salts. Any forms can contribute to air pollution problems and are attributed to acid rain.

Nitrous oxide (N_2O), or more commonly known as laughing gas, is generated plentifully by biogenic sources e.g. yeasts and plants. Despite its mildly reactive and analgesic properties, N_2O can cause ozone depletion by reacting with O_3 in both the troposphere and in the stratosphere, and it also possesses a long half-life i.e., about 100 to 150 years. The oxidation of N_2O with O_3 happens at any temperature and yields oxygen, either NO or dimer of NO and dinitrogen dioxide (N_2O_2). NO or N_2O_2 is very oxidative to form NO_2. After NO_2 is hit by a photon of ionizing radiation or UV in sunlight, it will create an ozone molecule. That is why N_2O is one of 'greenhouse gases' like carbon dioxide, because it absorbs long wavelength infrared radiation to keep heat from emitting from earth, thus leading to global warming.

The fuel combustions mainly emit NO_x in the form of NO. The rate of NO_x formation principally depends on combustion temperature and oxygen availability. In moderate-temperature processes e.g. below 760 ^{o}C, NO is produced in very low concentrations or even not produced at all. The concentration of NO generated will be more violent when the mixture is on the fuel-lean side of the stoichiometric ratio or operate with high excess air, according to the Zeldovich Equations:

$$N_2 + O \rightarrow NO + N \tag{2.1}$$
$$N + O_2 \rightarrow NO + O \tag{2.2}$$
$$N + OH \rightarrow NO + H \tag{2.3}$$

Apart from soils, lightning and natural fires, NO is generally produced by human activities. NO affects the blood circulatory system as carbon monoxide (CO) does, and causes the malfunction of oxygen absorption into blood. Actually, NO poses little harm except to infants and low immune individuals.

NO_2 is present in the air and in acid rain as nitric acid dissolved in water droplets. When NO_2 reacts with a proton, O_2 is changed into O_3 and NO_2 becomes NO. NO is consequently oxidized to NO_2 within hours by radicals from the photo reaction of volatile organic compounds (VOC). Thus, VOC and NO_x together result in the chain reactions producing ozone layers in the atmosphere.

The minority concentrations in flue gas are dinitogen trioxide (N_2O_3) and dinitrogen tetroxide (N_2O_4). N_2O_4 is another dimer of two molecules of NO joined together and has the same reactivity as NO_2; therefore its presence may be covered up by the more prevalent NO_2.

Another form of NO_x that is present in a small concentration is dinitrogen pentoxide (N_2O_5) unless it is released from some specific processes such as nitric acid production plants. The compound is the most highly ionized compounds in NO_x family and has high reactivity. When N_2O_5 decomposes in water, it forms nitric acid (HNO_3).

Nevertheless, there have been some disagreements about the surrogate of NO_x family. Some experts suggest that NO_2 is the best representative because NO can be rapidly converted into NO_2, while N_2O has such a long half-life as it is not that reactive. However, others feel that the roles of both NO and NO_2 in producing ozone should be considered as the criterion, then NO and NO_2 are categorized as NO_x. Both NO and NO_2 are the most plentiful compounds and they are largely generated by anthropogenic sources. For environmental regulations, NO_2 concentration is sufficiently high enough as the surrogate of NO_x due to its precursor for ozone.

NO_x is generated through the combustion processes within both mobile sources and stationary sources. Automobiles and other mobile sources contribute almost half of the total NO_x emission. The stationary sources like electric power plants produce about a third, which comes from fuel combustion in boilers. Additionally, the substantial contributors are from anthropogenic sources as industrial boilers and incinerators, gas turbines and diesel engines in stationary sources, petroleum refineries, and nitric acid manufacture. The various sources produce different amounts of each oxide whose percentages are shown in Table 2.2.

Table 2.2 Nataional emissions for nitrogen oxides in 2008

Source Category	Total NO_x (million short tons)	Percent of total
Highway vehicles	5.21	31.9%
Other off-highway	4.26	26.0%
Transportation total	9.46	57.9%
Stationary fuel combustion total	5.57	34.1%
Industrial processes total	0.93	5.7%
Waste disposal and recycling total	0.12	0.7%
Miscellaneous total	0.26	1.6%

Scientists classify the nitrogen oxides found in combustion gases as thermal, prompt, and fuel NO_x (Joseph Colannino, 2004).

i) Thermal NO_x – is generally the most significant and formed NO_x during combustion processes by the oxidation of the atmospheric nitrogen, either in a flame or by some other external heating, e.g., a lightning bolt, at very high temperature. It is controlled by the molar concentration of O_2 and N_2 and the temperature of combustion. Thermal NO_x mechanism comprises several steps; reactions (2.1) and (2.2) are the reduced form of the elemental steps, representing atomic and molecule entities involved in product forming. Nitrogen and oxygen atoms require high temperature to form, a level most industrial flame can achieve. Reaction (2.4) is the net result of nitric oxide formation.

$$N_2 + O_2 \rightarrow 2NO \tag{2.4}$$

At the temperature below 1,300 ^{o}C, thermal NO_x is produced in much smaller concentrations. As oxygen atom is easier to rupture than nitrogen atom, the rate limiting step is reaction (2.2). The rate law governing NO production can be written as in Eq. (2.5)

$$[\mathrm{NO}] = A[N_2] \int e^{-\frac{b}{T}} \sqrt{[O_2]}\, d\theta \tag{2.5}$$

Where [ ] represents species' volume concentration
T represents absolute temperature
θ represents time under those condition
and A, b are constants

Eq. (2.5) is used to indicate the variables affecting NO_x formation; thus NO_x reduction can be achieved using the following strategies:

- Reduce the peak flame temperature
- Reduce the oxygen concentration
- Reduce the residence time at peak temperature

ii) Fuel NO_x – is formed by conversion of organic nitrogen originally present in the fuel to NO_x. Coal and some high-boiling petroleum fuels contain a large amount of organic nitrogen while low-boiling petroleum fuels and natural gas contain practically none. The mechanism of fuel NO_x formation starts with a rapid pyrolysis of fuel molecules into cyano intermidiates as shown in reaction (2.6) :

$$C_xH_yN \rightarrow HCN + CN + \ldots \tag{2.6}$$

These intermediates are later oxidized to nitric oxide as in Eq. (2.7)

$$HCN + CN + O_2 \rightarrow NO + \ldots \tag{2.7}$$

The rate law describing fuel NO_x formation is shown below in Eq.(2.8), which was derived under assumptions that cyano oxidation in reaction (2.7) is the rate-limiting step and cyano intermediates are proportional to nitrogen concentration in parent fuel.

$$[\mathrm{NO}] = k \int [N_2]^{\alpha}[O_2]^{\beta}\, d\theta \tag{2.8}$$

Where k, α and β are experimental constant
The rate law suggests that the reduction of nitrogen content in fuel and the deficiency of oxygen can limit the fuel NO_x formation.

iii) Prompt NO_x – refers to the nitrogen oxides that form very quickly as a result of the interaction of nitrogen molecules with some of the active hydrocarbon species derived from the fuel in the fuel-rich parts of flames, which exist to some extent in all combustion. They are not observed in flames of fuels with no carbon, e.g., H_2. Cyano intermediates are also formed as reaction (2.9).

$$CH_x + N_2 \rightarrow HCN + CN + \ldots \tag{2.9}$$

The cyano intermediates go through the same path as fuel NO_x mechanism in reaction (2.7). By assuming that reaction (2.9) is the rate-limiting step, a rate law is proposed as Eq. (2.10)

$$[\mathrm{NO}] = \mathrm{k}[\mathrm{N_2}] \int [\mathrm{CH_x}]\, d\theta \tag{2.10}$$

It is not practical to limit nitrogen in the air feed, except for glass melting furnaces. Thus the only method that can reduce prompt NO_x is diluting the fuel before combustion. This can be executed within a burner by allowing the fuel jet to entrain combustion products in the furnace before reaching an ignition zone.

The nitrogen oxides play an important role in the photochemistry of the troposphere and stratosphere. NO_x catalyzed ozone destruction occurs via the following reactions (Sounak Roy, 2009):

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{2.11}$$
$$NO_2 + O \rightarrow NO + O_2 \tag{2.12}$$

These reactions are largely responsible for the ozone decline. NO_x have a lifetime of several days as they are transparent to most wavelengths of light and allow a large amount of protons to pass through. NO_2 is a compound that have even longer lifetime because it can be recycled from NO by the reaction of VOC with a proton that makes more ozone. NO_2 is capable of traveling significant distances before ozone is created. EPA's findings reported that ozone plume extends more than a hundred miles out to the sea of the east coast before the concentrations drop to 100 ppb. This was not a problem only on the sea coast. The distance of the emission of NO_x and the generation of ozone differ depending on plume or wind transport speeds as well as meteorological factors. Under some conditions, power plant plumes may travel such long distances without much loss of VOC and NO_x concentrations. These pollutants then participate in photochemical reactions to produce ozone smog in the atmosphere layers that costs society billions of dollars annually from illnesses and deaths.

NO_x can also cause acid rain which impacts the ecosystems and leads to biological death of lakes and rivers. Another adverse compound that can be formed from nitric oxide is peroxyacetylene nitrates (PAN) which contributes considerably to global photo-oxidation pollution.

From some biological studies, NO functions as an messenger that transmits the necessary information to the white blood cells and to the neurotransmitters which can benefit the body system, as it can destroy tumor cells and dilate the blood vessels, respectively. However, the biologically active NO is a poisonous product of the in vivo enzyme-catalyzed transformation of the amino acid, arginine. NO diffuses through the alveolar-cells and capillary vessels of the lungs and damages the alveolar structures and their functions throughout the lungs provoking both lung infections and respiratory allergies like bronchitis, pneumonia, etc.

Effective techniques for the control of NO_x emissions from furnaces or boilers can be subdivided into three categories based on which stage of combustion process NO_x is emitted. These techniques include pre-combustion, combustion and post-combustion control. The widely used techniques are described in the following section.

2.1 Pre-combustion Controls

Fuel selection is one of the simplest methods in minimizing NO_x emissions, since a part of NO_x is produced from the oxidation of nitrogen content in fuels called fuel NO_x, and a removal of nitrogen prior to a combustion process is not practical. Natural gas is considered a very clean burning fuel in which the nitrogen level in generally low, and is also free from sulfur, non-combustible gases and solid residue. While distillate and residue oils produce some NO_x, its level is still lower than that is produced from coals. There will be some circumstances in which fuel switching is not a feasible options, they are when the supply of such fuel is not readily available or the fuel choice affects boiler operations and efficiency.

2.2 Combustion Controls

2.2.1 Operational modifications

The operational modifications are based on the knowledge of NO_x formation chemistry as described above. NO_x is controlled by kinetics, not equilibrium or the total formation. Thus, by knowing that the rate of NO_x formation is strongly influenced by the flame temperature and the residence time at elevated temperatures, such critical factors are minimized to reduce NO_x formation. The availability of oxygen at peak temperature also needs to be minimized to suppress the production of NO_x during combustion processes. However, such changes can affect boiler performances such as flame stability, radiant heat release, increased CO etc. Therefore, the most effective principle of NO_x reduction by operational modifications is to reduce NOx formation as much as possible while boiler or furnace performances are affected as little as possible. One or more of the following techniques are now being used in combination with other add-on control system and low NO_x burner to attain less NO_x emission level.

i) Water/Steam injection

An injection of water or steam into flame or directly into combustion air reduces flame temperatures and thermal NO_x formation. When using natural gas as fuels, this technique can reduce NO_x up to 80% (Nexus, 2002); meanwhile the efficiency is lower in case of oil-fired and coal-fired boiler. Heat from the flame is removed as heat of vaporization in case of using water injection, and fuel has to increase as much as 5% (Ron D. Bell) in order to make up for such heat. If steam is used, 50% more mass rate than that of water is required to achieve the same quenching effect. There is a limitation of the amount of water or steam injected as condensation problems and 3-

10% loss to thermal efficiency may be experienced, yet some advance designs do not have significant impact on boiler efficiency. Steam/water injection is usually used in conjunction with other NO_x control methods such as low NO_x burner or FGR.

Water/steam injection is more suitable for small single burners operated infrequently. The amount of water injected varies between 25-75 wt% of the natural gas feedrate. However, the important impacts are energy and CO emission problems especially at lower loads.

One vendor offers an advanced design base on hypermixing. Instead of injecting steam into air or fuel stream, high pressure steam is directly injected at the burner head and acts as a source of mixing power. The temperature uniformity within the furnace, and also excess air requirement, are improved by the better mixing, resulting in lower NO_x formation.

ii) Low Excess Air (LEA)

Stoichiometry is the measure of the minimum amount of oxygen required to completely burn out fuels. By minimizing the amount of surplus air at peak temperatures, the peak temperature and also the availability oxygen are reduced. In addition, the fan power and nitrogen introduced in the unit are reduced, which means NO_x is also reduced. As the result of decreasing air, the boiler efficiency is improved; yet an increasing CO and unburned hydrocarbon due to incomplete combustion also lower the efficiency. The percentage of excess air represents an additional percent of air over the theoretical air calculated for complete combustion.

LEA is an easy technique to adopt as it requires only physical modifications. The excess air rates are fine-tuned by altering the control system. Despite the promising efficiency of LEA, the level of excess air is limited by the increased volatile organic compounds and CO emissions as shown in Figure 2.1.

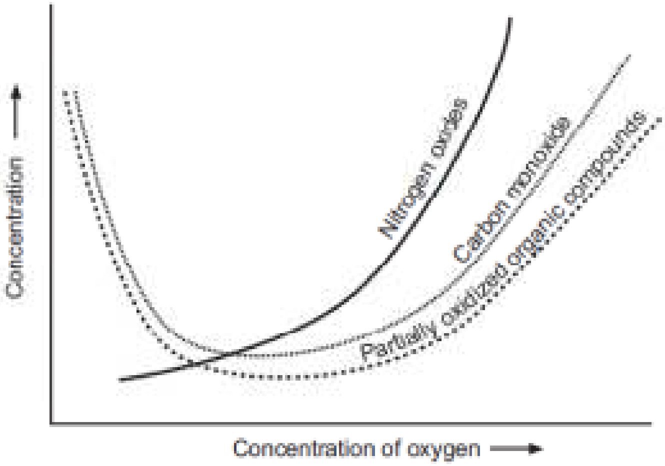

Figure 2.1 Relationship between CO emissions, NO_x formation and oxygen concentrations at low and high oxygen levels

At very low excess air, not only smoke, CO, and volatile organic compounds increase, but the cooling in the combustion chamber due to the use of excessive air also causes an increase in such compounds. The optimum point for LEA is different for each type of boiler and it is reached when a rise of excess air reduction is equal to the loss from the increase in ppm of CO (Richards, 2000).

iii) Staged Combustion

Staged combustion involves a variation of fuel and air injection patterns in order to minimize the flame temperature and the oxygen concentration in the primary combustion zone. Staging can be either performed within the burner body, which the designs are cooperated into low NO_x burners, or done externally through the separated ports within a furnace. Staged combustion can be classified as either staged air burners or staged fuel burners:

Staged air combustion

The combustion air is divided to reduce the oxygen concentration in the primary combustion zone, leading to a lower amount of NO_x formed and probable increasing NO_x reducing agents. After that, a smaller amount of secondary air (and/or tertiary air) is introduced to complete combustion. A less than total air required in primary and the lower temperature in secondary zone contribute to the reduction of NO_x formation in range of 35-50% (Marc Cremer, 2003) reduction for natural gas.

The potential impacts to furnace efficiency are the longer flame length than that of conventional burners which causes flame impingement on furnace wall, resulting in tube failure and corrosion. Besides, staged air burners are usually wider and longer, thereby the existing windbox may be modified.

Staged air combustion can also be accomplished by external air injection which is usually used in larger boilers. The techniques include:

- Burners-out-of-service (BOOS)

BOOS is described by an introduction of an additional gas through operational burners at a lower furnace zone to create fuel-rich condition. The secondary air is supplied through non-operating burners above the lower zone to complete combustion. This technique gives the benefit of unit capacity reduction.

- Over-Fire-Air (OFA)

OFA involves the reduction of primary airflow, coupled with the injection of secondary air through OFA ports above top burner level. This division creates a fuel-rich zone which gives lower NO_x generation.

Staged fuel combustion

The fuel is divided into primary and secondary streams when combustion air is directly injected. Despite high oxygen concentration in the primary zone, fuel-lean condition limits the production of NO_x. Moreover, excess air quenches flame to limit flame temperature and also provides active NO_x reducing agents. Inert from the primary zone functions as dilution for oxygen concentration in the secondary combustion zone and also remove a portion of heat to limit flame peak temperature.

An advantage of staged fuel burners over staged air burners is the former produce short flame length and consequently decrease flame impingement.

2.2.2 Flue Gas Recirculation (FGR)

FGR involves the recirculation of a portion of cool exhaust gases back into furnace or burner to absorb heat generation during combustion process and lower flame temperature. This technique can be executed in two ways (Charles E. Baukal, 2004);

- External flue gas recirculation: external fan and piping routes flue gas from stacks back to burners.
- Induced flue gas recirculation: flue gas is routed by duct work or internally to the combustion air fan and premixed with the combustion air before being introduced to flame through the burner. This induced FGR is becoming popular due to its uncomplicated design and reliability.

The testing of FGR rated effect on NO_x emission in a 4 MMBtu/hr firetube boiler with different preheat air temperature was developed (Timothy, 2001). The results showed that in the absence of FGR, NO_x emission was a function of preheat level. However, when FGR is introduced, even with high air preheat level, NO_x can be reduced to single digit levels with only 25% FGR with the help of a staging burner while the CO emission does not exceed 5 ppm.

FGR has no impact on heat transfer efficiency of units. However, as the recycle flue gas increases the total mass through the unit, the pressure drop is increased resulting in higher heat duty and operation costs of air fans. The operation is forced to be closer to the flammability limits so that an air-fuel ratio control needs to be controlled precisely.

The improved technology of FGR is called ‘Gas Conditioning’ which has proven to lessen the amount of diluents required and the impact on system performances. Instead of recirculating flue gas to the combustion air, gas conditioning introduces flue gas to fuel supplied to burners by the driving force of additional steam. The diluted fuel generates lower NO_x emission with 30-50% more effectiveness at reducing NO_x. This technique requires no more additional fans to move the flue gas as added steam not only serves as NO_x reduction tool but also as a motive force for inducing flue gas.

The above operational modifications can reduce NOx emission into the 30 ppm range. The most widely used techniques are water/steam injection and flue gas recirculation, of which both are adopted in conventional burners.

2.2.3 Burner Designs

The above operational modifications, especially water/steam injection and flue gas recirculation which are the most widely-used techniques, are adopted in the existing conventional burner. Many designs can reduce NO_x to the 30 ppm range. In order to further decrease this NO_x level, the critical parameter that needs to be concerned when boilers or furnaces are retrofitted is the ability to maintain a stable combustion at lower flame temperatures. Burner designs have been developed based on the principle of lowering peak flame temperature and oxygen concentration during the combustion process to control the amount of NO_x produced, while the combustion units are not impacted by abnormal flame behaviors.

i) Low NO_x Burner (LNB)

In an attempt to decrease NO_x emission to the sub-30 ppm range, low NO_x burner designs incorporate staged combustion to delay the mixing of fuel and air. This approach creates a fuel-rich zone in the primary combustion zone to limit the oxygen level and lower the peak flame temperature. Then air is added downstream to burn out fuels. Some designs create a fuel-lean in the primary combustion zone that lowers the flame temperature and also thermal NO_x formation, and then inject the remaining fuel to consume the excess air. For NO_x level in sub-30 ppm range, such staging designs can be complex and may cause long flame length and flame stability problems that are restricted by burner turndown[1]. The staged low NO_x burners are therefore used together with water/steam injection and flue gas recirculation techniques. The Venturi low NO_x burner such as the TODD Variflame^{TM} or Dynaswirl^{TM} (Timothy, 2001) have been developed to handle high burner turndown and allow the flexibility of combustion staging and flame shaping capability.

ii) Ultra Low NO_x Burner (ULNB)

Ultra low NOx burners apply stoichiometry of air and fuel as the basis beyond the low flame temperature and excess air principles to design the sub-9 ppm NO_x burner or TODD Rapid Mix Burner (RMB^{TM}) (Timothy, 2001). The avoidance of fuel-rich conditions can eliminate a part of prompt NO_x generated. In addition, recirculated flue gas mixed with combustion air upstream of burners or high excess air to control flame temperature and thermal NO_x formation. Fuel-rich region can be evaded by creating a rapid fuel-air mixing near the burner exit resulting in a nearly uniform fuel/air mixture at the ignition point. The operational benefit of this type of burner is that it can eliminate the possibility of flashback as the fuel is added inside the burner, upstream of the refractory throat. Moreover, the rapid mix design also provides an exceptionally stable flame and a shorter flame length eliminating the possibility of flame impingement that is the common problems of conventional low NO_x burner. In some combustion applications where FGR is impractical such as dryer, the high excess air

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[1] Turndown ratio is a ratio of full fire capacity to its lowest firing point before shutdown

condition is preferred as it provides the same cooling effect as FGR. The rapid-mix burners result in the reverse NO_x level trend as increasing excess air reduces NO_x formation contrary to the low NO_x burner.

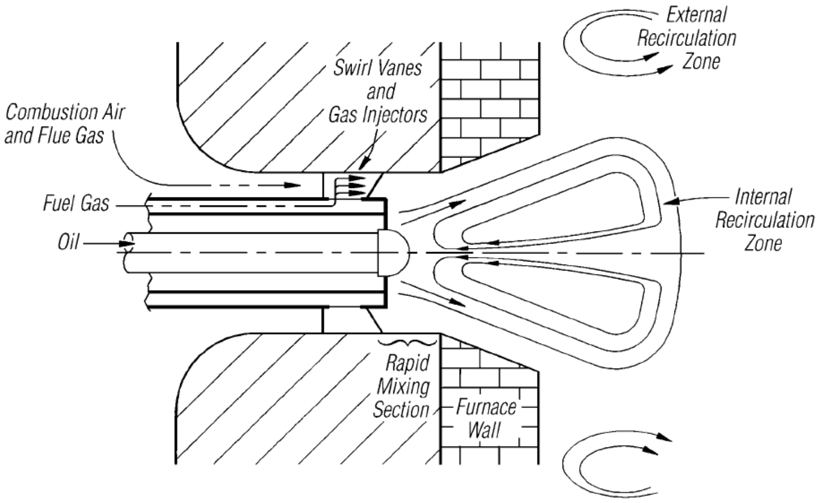

Figure 2.2 The rapid mix ultra low-NO_x burner

The swirly geometry as shown in Figure 2.2 supports an internal recirculation of a large amount of hot combustion gases which allow the burner to operate at lower flame temperatures. The flame is stable at as high as 60% FGR which extends the 25-30% limit range of typical FGR. The burner structure is a parallel-flow air register with no moving parts. Combustion air and flue gas are pre-mixed before passing through the swirl vanes attached with the hollow bases. Thus, these vanes act as the gas injector and provide the nearly perfect fuel/gas mixing condition.

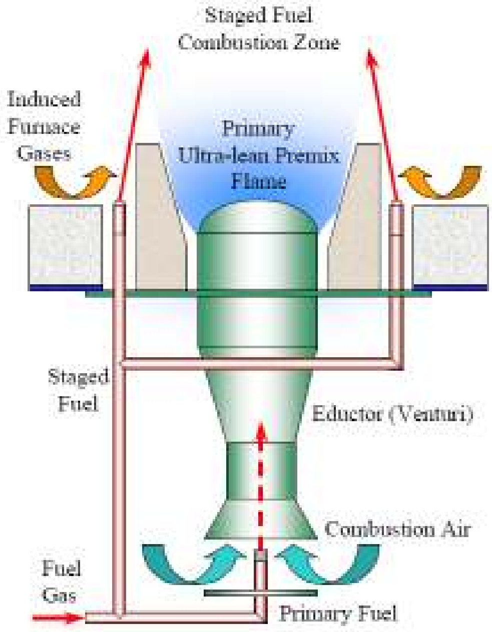

Figure 2.3 Schematic of Ultra-Lean Premix Burner

Another example of new burner design technologies also adapting the fuel-lean combustion is called Ultra-lean Premix Burner (Jason McAdams, 2002) in which part of fuel is injected through a venturi eductor and is then premixed with the entire combustion air to create a fuel-lean condition as illustrated in Figure 2.3. The remaining fuel is injected and mixed with induced furnace gases before being ignited by the remaining oxygen from the primary combustion zone. One advantage of this technology is that it does not affect the furnace efficiency. Furthermore, the technology can yield NO_x emission at less than 10 ppm in a single burner test and 10-20 ppm in actual ethylene furnaces

2.2.4 Oxy-Fuel Burner

Oxy-fuel burners are specific burner designs in which high-purity oxygen (90-99.9% O_2) and recycled flue gas serve as the oxidizer. Eliminating N_2 content in air can substantially reduce the formation of thermal NO_x. As the air separation processes have been improved providing low cost oxygen supply, oxy-burner application becomes more attractive to high-temperature industrial processes. Like air burner, oxy-fuel burner offers different designs that result in various flame shapes and low NO_x production. Although the use of oxygen as an oxidant over air substantially increases operating costs, it benefits the operation in many ways other than decreasing NO_x emission as listed below (Hisashi Kobayashi, 2004);

- Fuel which is saved as the energy needed to heat nitrogen contained in air is eliminated. The amount of fuel saved needs to be known for the proper size of the burner to be designed. Figure 2.4 shows the fuel saving percentage versus flue gas temperature with varied air preheat temperature in a natural gas-fired furnace for different industrial applications represented by shade areas.

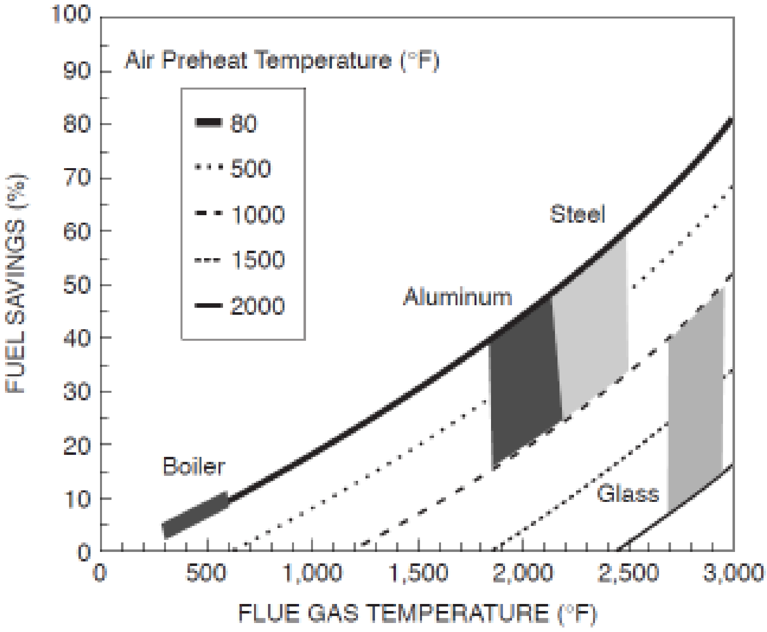

Figure 2.4 Fuel saving with oxy-fuel combustion

- An increase of production is possible because oxy-fuel flames are denser than air flames, giving a higher energy release in a certain furnace space. However, the improvement of product yield needs more study in the furnace limitation such as the effect on furnace wall temperature which may diminish the life of refractory wall
- The reduction of NOx by 80-95% is achieved. Moreover, particulates are often reduced due to reduced carryover or volatilization.
- Capital costs are partly reduced as the size of flue gas handling is decreased
- Maintenance costs are reduced due to reduced flue gas volume.
- The flexibility of operating conditions is achieved because of better flame stability. The flame is very stable as a result of high flame velocity and wider flammability limits.

Traditional oxy-fuel burners usually provide high-temperature flames. For example, adiabatic flame temperature in methane-oxygen combustion is around 5000 ^{o}F compared to 3520^{o}C in methane-air combustion. However, the absence of N_2 content in air enables the Zeldovich mechanism (Eq.(2.1)-(2.3)) to reduce NO at high temperature.

Oxy-fuel burners are notably different from air burner in dissociation behavior, radiant heat transfer and formation of NO_x. New types of oxy-fuel burners provide more uniform heating around furnace, eliminating the concern of high temperature flames which cause high thermal NO_x formation. The operation that can execute the problem was studied by Fredrik et al (Fredrik Normann, 2008). The NO_x formation in high-temperature combustions is limited by equilibrium which can be lower at negligible air ingress, high-purity oxygen, sub-stoichiometric combustion zones, and long residence time in a furnace. The most important consideration of oxy-fuel burners is safety due to combustion with oxygen. In the enrich-oxygen environment, many materials or chemical compounds can be ignited easily and blaze robustly because of oxygen's high reactivity. The procedures of oxygen storage and distribution must be carefully followed. The oxy-fuel burner safety design is basically the same as that of an air burner, but a proper purging system prior to an ignition initiation sequence should be installed as well.

2.2.5 Fuel Reburning (FR)

Fuel reburning involves an injection of hydrocarbon fuel immediately after the primary combustion zone. The reburning fuel can be gaseous (e.g natural gas), solid (e.g. coal char or wood) or liquid (e.g. residual oil). It is based on fuel staging of the three zones (L. D. Smoot, 1998) as shown in Figure 2.5.

i) Primary zone is operated under fuel-lean conditions where the main fuel is burnt in a slightly oxidizing medium using excess air of about 5%. This zone is where NO_x is formed.

ii) Reburning zone is where the reburning fuel is injected into to create a chemically reducing zone. This zone generates CH_y hydrocarbonated radicals that can decompose NO_x into other nitrogen compounds such as HCN or NH_i; then they are finally converted to N_2.

iii) Burnout zone is where tertiary air is slowly blended to complete the combustion process and convert the remaining nitrogen types into N_2 (with a small part into NO).

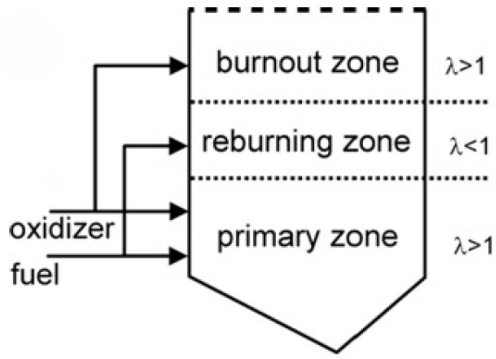

Figure 2.5 Schematic of the reburning process (**λ** is the stoichiometric ratio)

Oliver S. et al. (Olivier Sorriau), studied NO_x reduction performance by natural gas reburning on a 4 MWth furnace by varying the four parameters that have an impact on NO_x reduction rate; stoichiometry (ratio of primary air to flow of natural gas), residence time of the reburning zone, temperature and initial NO_x concentration at the entrance to the reburning zone. The results gave a global efficiency of a NO_x reduction rate at 20-65% in relation to standard combustion, depending on the value of the mentioned parameters. The experiment showed that an increase in the residence time from 200 to 900 ms and a reduction of the reburning stoichiometry from 0.94 to 0.88 can reduce the NO_x emission by a significant percentage from 20% to 60%. However, this favourable NO_x reduction rate also led to a considerable increase in the CO content in the flue gas and in the unburned solid residue content in the fly ash. At the temperature of 1100 ^{o}C, the injection of the reburning fuel was too late, leading to a too low temperature at the entrance of the burnout zone which was not enough to allow the combustion of the unburned gas residues. On the other hand, at 1300 ^{o}C, the reburning fuel was injected too soon, thus the combustion in the primary zone was not complete, also leading to an increase of unburned solid residues. Thus, to obtain the optimal conditions of the reburning process, all four parameters should be well investigated to effectively reduce the nitrogen oxides, while a low CO content and solid unburned residues are maintained. Current research suggests several advanced reburning concepts, for example, SNCR process after reburning fuel injection. One promising concept for NO_x reduction combines aspects of reburning with selective non-catalytic reduction (SNCR) (L. D. Smoot, 1998), through the combination use of a hydrocarbon (e.g. CH_4) and ammonia or urea. In this scheme, urea or ammonia is injected into the flue gas stream downstream of the hydrocarbon fuel injection point to further reduce NO_x. This approach is labeled advanced reburning. It is an attractive method as it has been reported that up to 85% of NO_x is reduced, while carbon loss problems, slagging and tube wastage may be avoided. The scheme of using ammonia of urea in advanced reburning differs from that of in SNCR. In the advanced reburning, ammonia is injected into the burnout zone, after hydrocarbon fuel injection, to create a slightly fuel-rich zone, combined with more air. With reburning fuel injection, CO increases, leading to;

$$CO + OH \rightarrow CO_2 + H \qquad (2.13)$$
$$H + O_2 \rightarrow OH + O \qquad (2.14)$$
$$O + H_2O \rightarrow OH + OH \qquad (2.15)$$

The chain branching sequence provides additional OH radicals to initiate the ammonia oxidation sequence.

2.3 Post-combustion Controls

2.3.1 Selective Non-Catalytic Reduction (SNCR)

SNCR involves an injection of a particular reagent such as ammonia, urea or cyanuric acid which is then thoroughly mixed in a flue gas stream containing NO_x under high temperature of 850-1175 ^oC. "Selective" means an injected reagent selectively reduces NO leaving oxygen untouched (when ammonia or urea reacts with oxygen, it leads to the formation of nitrous oxide). A schematic of SNCR concept is elaborated in Figure 2.6. SNCR is attractive due to its lower capital and operating costs as it is a catalyst-free system. It is also applicable to all types of stationary-fired equipment and is only slightly affected by fly ash. In most full-scale applications, the choice of ammonia or urea is utilized, while cyanuric acid has been investigated as a potential reagent in laboratory and pilot scale.

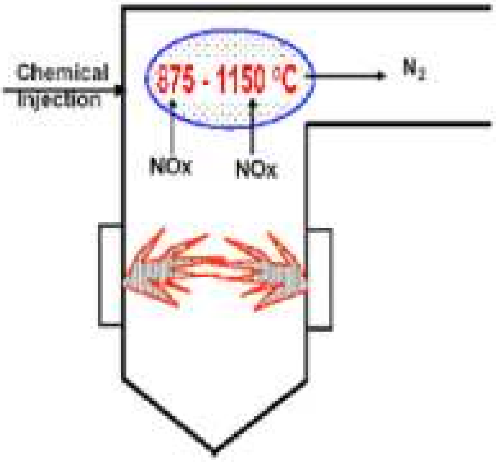

Figure 2.6 Schematic of SNCR concepts

In case of ammonia, the range of temperature in which the reaction takes place is defined as the temperature window. This window is quite narrow, as below 800 ^oC the reaction is too slow and most of ammonia remains unreacted (or so-called ammonia-slip). At temperature beyond the temperature window, says 1200 °C, ammonia tends to oxidize to form NO rather than reduce it. The range varies with system parameters such as flue gas constituents, flue gas velocity gradient and geometry which impact the mixing between the reagent and flue gas.

The NO reduction is initiated by the reaction of ammonia with hydroxyl radicals or with oxygen atom in the absence of water vapor to give amidogen ($-NH_2$) via reaction (2.16) and (2.17).

$$NH_3 + OH \leftrightarrow NH_2 + H_2O \qquad (2.16)$$

$$NH_3 + O \leftrightarrow NH_2 + OH \qquad (2.17)$$

The amidogen radical is highly selective towards NO, and its mechanism can be explained by chain branching sequence. NH_2 primarily removes NO by the reactions (2.18) and (2.19)

$$NH_2 + NO \leftrightarrow N_2 + H_2O \qquad (2.18)$$

$$NH_2 + NO \leftrightarrow NNH + OH \qquad (2.19)$$

The SNCR process is self-sustaining as chain branching component obtained from the reactions (2.18) and (2.19) regenerate OH and O via the following reactions to continue the NH_3 to NH_2 conversion.

$$NNH + NO \leftrightarrow N_2 + HNO \qquad (2.20)$$

$$HNO + M \leftrightarrow H + NO + M \qquad (2.21)$$

$$H + O_2 \leftrightarrow OH + O \qquad (2.22)$$

$$O + H_2O \leftrightarrow OH + OH \qquad (2.23)$$

Below optimum temperatures (i.e. less than 730 °C), reactions (2.22) and (2.23) which are strongly temperature dependent, have a low rate, thus OH is not refilled fast enough to convert NH_3 into NH_2; thereby the chain reactions are terminated. On the contrary, an excessive increase in OH radical concentrations leads to a formation of NH radicals via the reaction (2.24) at above the optimum temperature (beyond 1000 °C). This radical initiates the formation of NO competing with the NO reduction sequence.

$$NH + OH \leftrightarrow NH + H_2O \qquad (2.24)$$

The most investigated parameter affecting SNCR performance is NH_3/NO molar ratio. It is clear that higher ratio gives higher NO reduction percentage; yet unreacted ammonia or ammonia-slip becomes an issue. There was a research (M. Tayyeb Javeda, 2007) showing that at ratio greater than 1.3, detectable ammonia-slip occurred. The ammonia-slip depends on the interaction of numerous factors with the major factors being the flue gas concentration including NO_x, water vapor, O_2, SO_2, particulate etc., reaction time-temperature relationship, mixing efficiency of flue gas and ammonia. Due to this complexity, ammonia-slip must be evaluated for a particular fired equipment. Some investigators suggested that as the temperature increased beyond 1030 ^{o}C and the excess O_2 increased from 2% to 4%, a decrease in ammonia emission occurred.

When using urea as a reducing agent, Saliman and Hanson (M. Tayyeb Javeda, 2007) proposed that urea could directly decompose into amidogen radicals, but under lower temperature window. The advantage of using urea in place of ammonia is its non-corrosive properties. Urea is easily handled and can be readily introduced into a combustion gas stream either as a solid or in solution. However, there are only a few studies of various parameters involving urea, unlike ammonia; still, it is claimed that urea injection has been successfully applied to a wide variety of fuels.

2.3.2 Selective Catalytic Reduction (SCR)

Catalytic technologies are relatively more attractive because they give high removal efficiency with low cost operation. The effective process, so-called SCR process can effectively de-NO_x flue gases from stationary sources. This technology was first developed in the 1970s and is widely used worldwide today.

Nitrogen oxides are mostly generated as thermal NO_x during the combustion processes. The following chemical reactions are the oxidation of the atmospheric nitrogen that occurs at very high temperatures:

$$N_2 + O_2 \rightarrow 2NO \tag{2.4}$$
$$NO + ½\, O_2 \rightarrow NO_2 \tag{2.25}$$

Typically, NO_x consist of 95% NO and 5% NO_2, while the others are fuel NO_x and prompt NO_x. From the previous studies, it can be concluded that the reaction (2.25) occurs negligibly under the diluted gas conditions. Therefore, it is reasonable to assume NO as the actual reactant in SCR process. In the typical SCR conditions, the reaction stoichiometry follows these reactions (Guido Buscaa, 1998):

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \tag{2.26}$$
$$4NH_3 + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O \tag{2.27}$$
$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \tag{2.28}$$
$$4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O \tag{2.29}$$

Eq. (2.26) represents the catalytic reduction of the main reactant, NO, in the presence of oxygen. When NO is converted in the absence of oxygen, it follows Eq. (2.28) which is considered as a combination of the reverse of reaction (2.4) plus reaction (2.26). NO_2 is also involved in the process as shown in Eq. (2.27) in which it is oxidized. Besides, the undesired reactions can also occur to form N_2O as shown in Eq. (2.29). Under typical SCR conditions, with NH_3/NO near 1, a few percents of oxygen, and a temperature above 400 ^{o}C, reaction (2.26) accounts for the overall stoichiometry and the ratio of converted moles of NO and NH_3 is 1.

When the ratio of converted NO and NH_3 is less than 1, it can be implied that ammonia is converted by ways other than reaction (2.26) , i.e. ammonia is oxidized by oxygen instead of NO:

$$2NH_3 + 3/2O_2 \rightarrow N_2 + 3H_2O \qquad (2.30)$$
$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \qquad (2.31)$$
$$2NH_3 + 5/2O_2 \rightarrow 2NO + 3H_2O \qquad (2.32)$$

Although reaction (2.30), in principle, can allow the reduction of the ammonia slip if SCR is worked with excess of ammonia, an investigation is now in progress.

The kinetic models that have been proposed were mostly based on the reaction stoichiometry in Eq. (2.26) because of a little impact of CO and SO_2. It was confirmed from all experiments that the selectivity of N_2 and H_2O was higher than 99%. Therefore, no side reaction had to be taken into account.

For the temperatures above 200 °C which are typical operating conditions for the SCR process, the catalytic behavior can be described by the first order for nitric oxide and zeroth order for ammonia. The oxygen concentration also affects the kinetics in which low oxygen contents were sufficient to maintain the catalyst activity. However, there was only a slight effect when oxygen concentration exceeded 4% as the experiment of R. Willi et al (R. Willi, 1996) demonstrated.

The effluence of oxygen was accounted in Lungmuir adsorption isotherm expression, at which it is normalized to 10% oxygen in exhaust gas as indicated in Eq. (2.33).

$$r = k\, p_{NO_x} \frac{\dfrac{K_{O2} p_{O2}}{1 + K_{O2} p_{O2}}}{\dfrac{K_{O2}\, p_{O2}\big|_{10\%}}{1 + K_{O2}\, p_{O2}\big|_{10\%}}} \qquad (2.33)$$

$$k(T) = k^o(T_{Ref})\exp\left(\frac{-E_A}{R}\left(\frac{1}{T} - \frac{1}{T_{Ref}}\right)\right) \qquad (2.34)$$

$$K_A(T) = K_A^0(T_{Ref})\exp\left(\frac{-\Delta H_A}{R}\left(\frac{1}{T} - \frac{1}{T_{Ref}}\right)\right) \qquad T_{Ref} = 500\,K \qquad (2.35)$$

Eq. (2.34) and (2.35) provide the correlation between the reaction rate constant (k) and the equilibrium constant of adsorption (K_A) with respect to pre-exponential factors (k^0, $K_A{}^0$).

The industrial catalysts for the SCR process are based on TiO_2-supported V_2O_5-WO_3 and/or V_2O_5-MoO_3 oxides (Guido Buscaa, 1998). Among metal oxides, pure vanadia and vanadia supported on oxides carriers such as alumina, silica, zirconia and titania (which is the choice support nowadays) have been extensively investigated. Catalyst components which give rise to high selectivity in partial oxidation (V_2O_5, WO_3 and MoO_3) when supported on TiO_2 also gives rise to high selectivity in the SCR reaction.

CHAPTER 3 METHODOLOGY

This chapter discusses the procedures on how to complete this thesis. Since the problem is fairly wide-open (there are many NO_x reduction technologies), the approach the author focuses on may not cover all the technologies mentioned in Chapter 2. Instead, the zero-NO_x approach in which the Olefin plant takes an interest will be investigated. The methodology consists of 5 steps as illustrated in Figure 3.1 below.

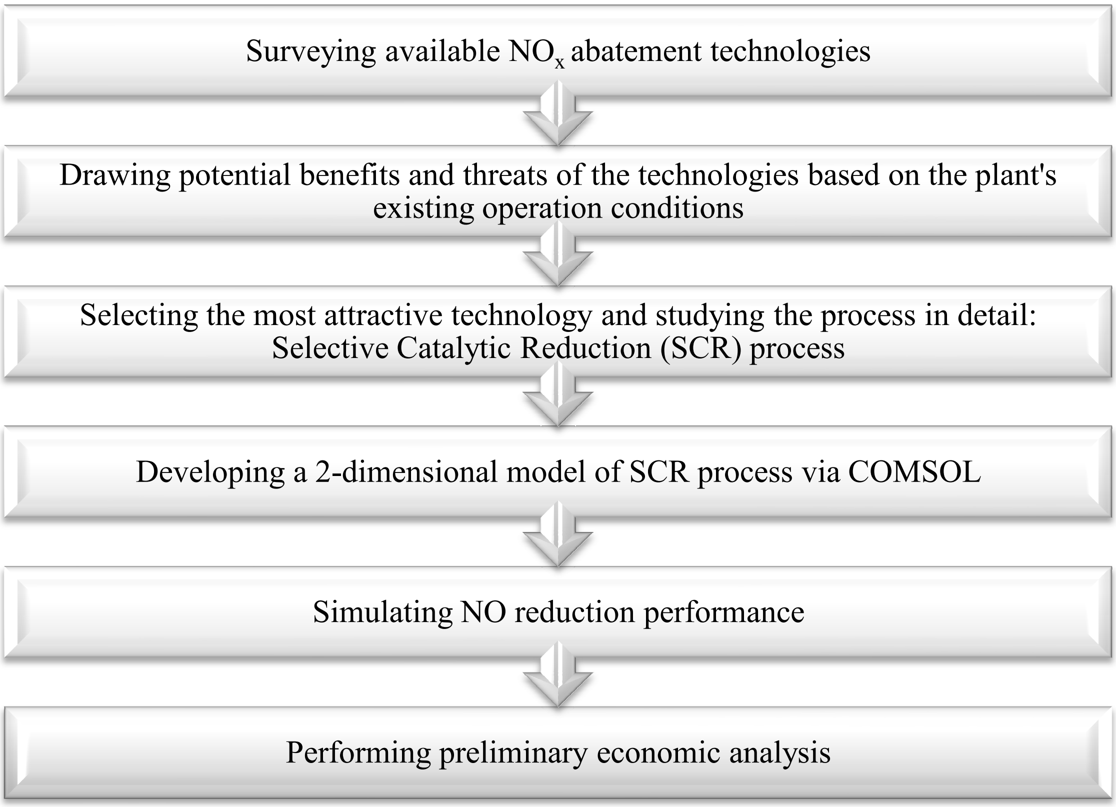

Figure 3.1 The methodology of development of an NO_x reduction unit for ethylene cracking furnaces in ROC

3.1 Surveying the available NO_x abatement technologies

Firstly, the detail of any currently available NO_x abatement technology is gathered to provide the author an understanding of the development of the technology over the past few decades. This kind of information is mostly found in science or engineering research materials - the operation of the actual industrial plants are usually concealed. It is found that there are many NO_x abatement methods; however, some of them did not provide sufficient data that warranted further study, while some had only little success in either technical or economic aspects so that they were not practical in the actual industry.

3.2 Drawing potential benefits and threats of the technologies based on ROC's existing operating conditions

After information on existing NO_x control technology is prepared, the infeasible ones should be disregarded first. The primary criteria for deciding which methods to apply to the ROC process is the extent of potential benefits and threats, the intensity of the re-construction of the existing units, and the cost required for construction and annual operation. Table 3.1 below shows summaries of each technique which helps decide which technique is most suitable for the existing ROC plant.

Table 3.1 Comparisons of NO_x technologies in performances and economic aspects

NO_x control technique	% NO_x reduction (2005)	[2]Cost effectiveness ,$/ton NO_x removed (2006)	Potential impacts	Application
Ultra low NO_x burner	Up to 50% depending on burner design	3200 or more	- Long flame length results in impingement and corrosion at walls - May increase furnace fouling - Require precise control of fuel and air flows, and rate of mixing Longer and wider configurations	- All fuels - Capable for large furnaces Lean premix is usually used for single boiler up to 250 MMBtu/h
Oxy/fuel burner	80-95%	Burner replacement and oxygen supply costs	- Refractory damage due to improper burner position and firing rate - Hot spots due to increased flame temperature	- Cement/glass/iron-steel/pulp-paper industries - Chemical/petroleum industries

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[2] Cost effectiveness = owning cost of NOx technology/tons of NOx removed

Owning cost = capital, operating and maintenance costs

Tons of NO_x removed based on the same inlet and outlet NO_x concentration

NO$_x$ control technique	% NO$_x$ reduction (2005)	[2]Cost effectiveness ,$/ton NO$_x$ removed (2006)	Potential impacts	Application
Steam/water injection	10-30 ppm	680	- CO emission because of the quenching effect on combustion - Thermal efficiency loss because of an increase in moisture content in flue gas Require strictly control (avoid undesired side effect such as PM formation → corrosion)	For small single burner e.g. marine engines
Over fire air	Additional 10-25% beyond LNB		- May reduce boiler efficiency - May affect fly ash quality	May be used in conjunction with LNB
SNCR	30-66%	2800	- May need multiple injection zones - Efficiency higher for smaller boilers	- Majority of industrial boilers achieve over 50% reduction - Applied to coal, oil, gas, biomass, municipal waste
SCR	80-90+%	12000	- Catalyst deactivation requires implementation of catalyst (Good distribution of ammonia critical)	Applied from automotive to high temperature furnaces
Fuel reburning	39-67%	Depending on the intensity of duct work	- Flame stability - May increase CO emissions - Choice of reburning fuel affects plant design	Typically used with large boilers firing coal or residual oil

Among the technologies mentioned above, the Selective Catalytic Reduction (SCR) process has always been kept under observation and continuously developed in both operation and choice of catalyst aspects. This method attracts ROC most as it is considered as zero-NOx approach despite its high investment cost.

3.3 Selecting the most attractive technology and studying the process in detail: Selective Catalytic Reduction (SCR) process

More kinetic and transport parameters must be collected in order to use COMSOL. As mentioned in Chapter 2, the key step involves the reaction of gas-phase NO with surface-adsorbed NH_3 according to Eq. (2.26), while the other side reactions are digested into an oxidation of ammonia with oxygen [ref].

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \tag{2.24}$$
$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \tag{3.1}$$

The following rate equation (Eq. (3.2) to (3.5)) taken from the early studies regarding intrinsic SCR kinetic (G. Schaub, 2003) is used in the simulation model.

$$r_1 = k_1 c_{NO} \frac{a c_{NH_3}}{1 + a c_{NH_3}} \tag{3.2}$$

$$r_2 = k_2 c_{NH_3} \tag{3.3}$$

$$k_j = k_{j0} \exp\left(-\frac{E_j}{RT}\right) \tag{3.4}$$

$$a = a_0 \exp\left(-\frac{A}{RT}\right) \tag{3.5}$$

Each parameter value is shown in Table 3.2. The activation energy values (E_1, E_2) are taken from the published information of G. Schaub. The pre- exponential factor (k_{10}) is estimated from NO conversion, assuming that below 593 K, the oxidation of ammonia (Eq.(3.1)) is negligible. The other parameters are estimated by minimizing the sum of the squares of the calculated and experimental data.

Table 3.2 Parameter description and values in rate equations

Parameter	Symbol	Value	Unit
Reaction rate	r_i		mol/(m^3.s))
Chemical reaction rate	k_j		
Pre-exponential factor of Arrhenius equation	k_{10} k_{20}	1×10^6 6.8×10^7	s-^{1}
Activation energy	E_1 E_2	60 85	kJ/mol
Adsorption constant	a		m^3/mol
Pre-exponential factor of adsorption equation	a_0	2.68×10^{-17}	m^3/mol
Heat of adsorption	A	-243	kJ/mol

In addition, the catalyst structure that is commonly used in industrial plants should be understood so that a suitable 2-D model is set up. An SCR reactor consists of layers of catalyst elements which are assembled into standard steel-cased modules as represented in Figure 3.2.

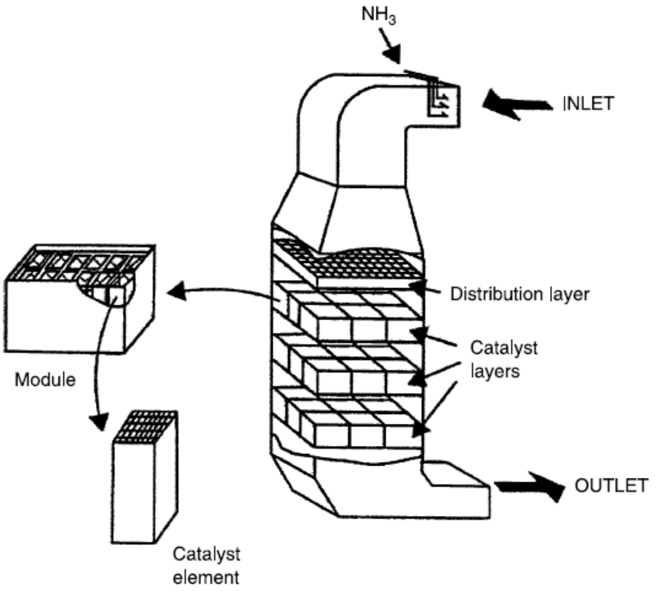

Figure 3.2 Structure of SCR monolith reactor

Among the 3 types of catalyst element shown in Figure 3.3 i.e. honeycomb, plate and corrugated catalyst, honeycomb monolith is the most widely used as it provides higher active surface area.

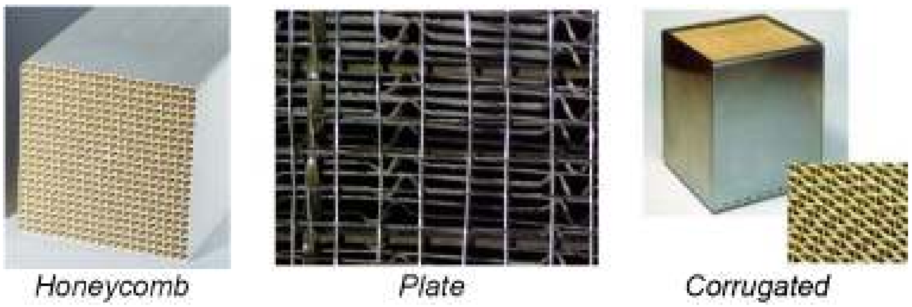
Honeycomb *Plate* *Corrugated*

Figure 3.3 Honeycomb, Plate and Corrugated SCR catalysts

3.4 Developing a two-dimensional model of the SCR process via COMSOL

When the basic theories are well understood and the important parameters are all collected, the model is ready to be generated. To get started with COMSOL, the simplest way is learning how to use COMSOL from a tutorial available in the program. The tutorial includes an example of NO$_x$ reduction simulation; thus it can be followed easily. In order to develop a model of the SCR process, two main programs are required, namely COMSOL Reaction Engineering Lab and COMSOL Multiphysics. The COMSOL Reaction Engineering Lab is used for creating models of reacting systems by inputting related reaction formulas such as kinetic and transport parameters, and flowrates. These models are then exported to COMSOL Multiphysics to develop a two-dimensonal model of the SCR catalyst vessel. Important missing information that may be initially guessed based on the literature is the geometry of the catalyst. The obligation of the COMSOL Multiphysics is to perform mass and momentum balances (since the operation is isothermal, no energy balance is required.) The input approach is provided in Appendix B .

3.4.1 2-D model creation

To predict how many elements are sufficient for achieving the NOx reduction target of 6.5 g/s or 85% (See Appendix A), COMSOL Reaction Engineering Lab is used first under the following assumptions:

a) A channel dimension is 5.9 mm x 5.9 mm x 1000 mm [Isabella Nova,]
b) A catalyst channel behaves as a plug-flow reactor
c) A system is operated isothermally.
d) NO is assumed to be the only compound representing NO_x
e) NH_3/NO feed rate is assumed to be 1

The inlet molar flowrates calculated from Appendix A are input along with reaction kinetic rates and their parameters as represented in Eq. (3.2)-(3.5) and Table 3.2. This program creates models of reacting systems including the material, energy and momentum balance (as mentioned before, energy balance will not be considered as the system is assumed to be isothermal). Moreover, the sensitivity of initial reaction rates to temperatures can also be predicted. After exporting these models to COMSOL Multiphysics, a two-dimensional model is then created under the assumption that a catalyst channel is divided into two subdomains i.e., the gas-phase subdomain and porous-medium (catalyst wall) subdomain with dimensions of;

- Gas-phase : cross-sectional area of 5.9 mm x 5.9 mm, the length depends on the varied catalyst layers.
- Porous-medium : 1.2 mm x 1.2 mm x 1000 mm per catalyst layer

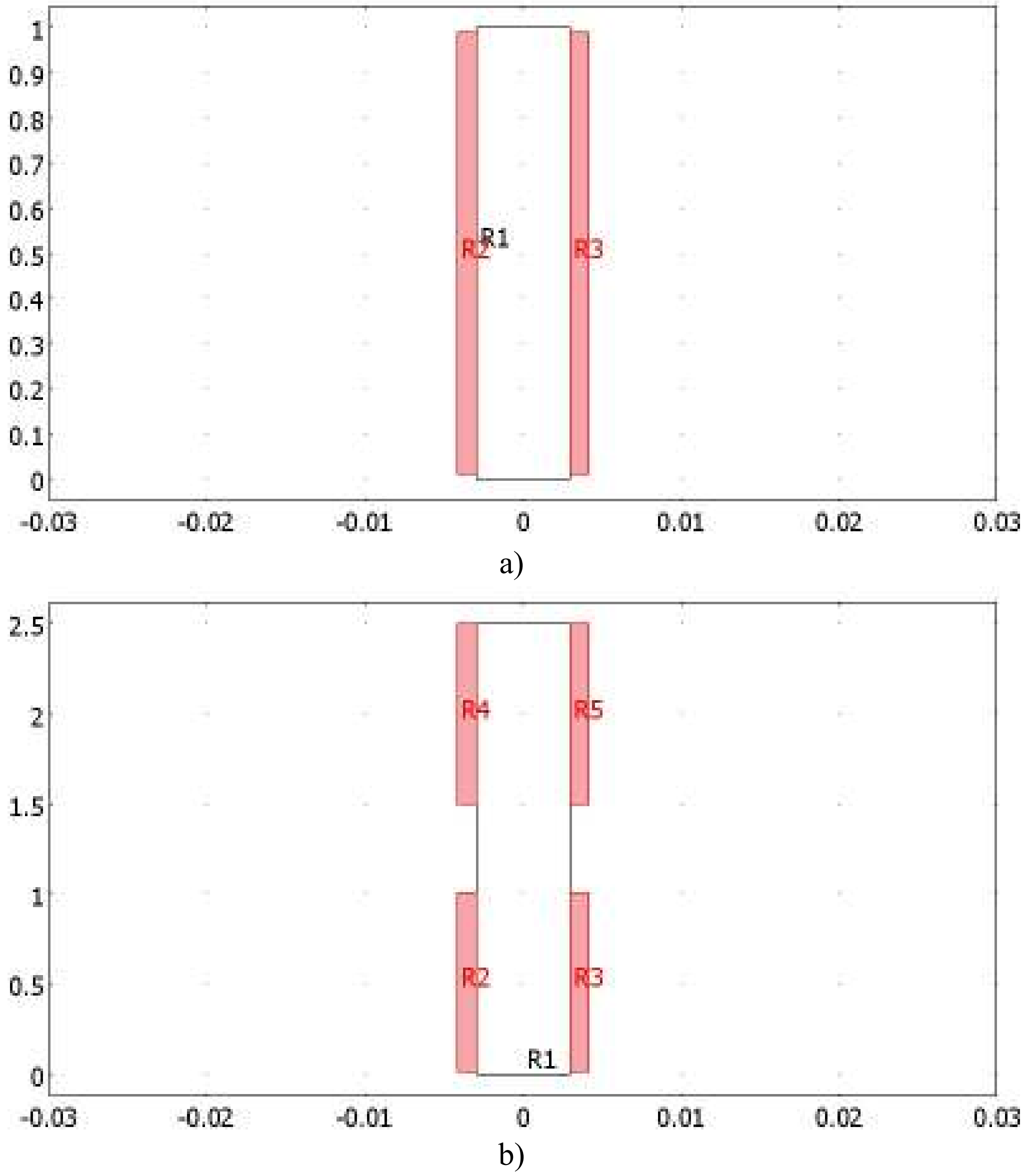

Figure 3.4 2-D models of a catalyst channel

a) assumed 1 catalyst layer b) assumed 2 catalyst layers

3.4.2 Mesh generation

For a 2D geometry, the mesh generator usually partitions the subdomain into triangular or quadrilateral mesh elements. In this case, a triangular mesh provides a more simplex mesh element. To fully resolve this model requires a very dense mesh, thus, the setting of *Extremely fine* on the *Free Mesh Parameters* results in a model size of roughly over than 300,000 degrees of freedom. This high DOF requires large memory consumption and solution time; however, a higher accuracy is obtained. As the porous-medium subdomains need more refined meshing to manage with the sensibility of the reactions occurred, the advanced mesh parameter i.e., maximum element size is additionally defined to all porous-medium subdomains. The example of outcome mesh is shown in Figure 3.5. One parameter that should be concerned after meshing is the minimum element quality; it is not supposed to be lower than 0.2. This parameter can ensure that the selected mesh method is suitable.

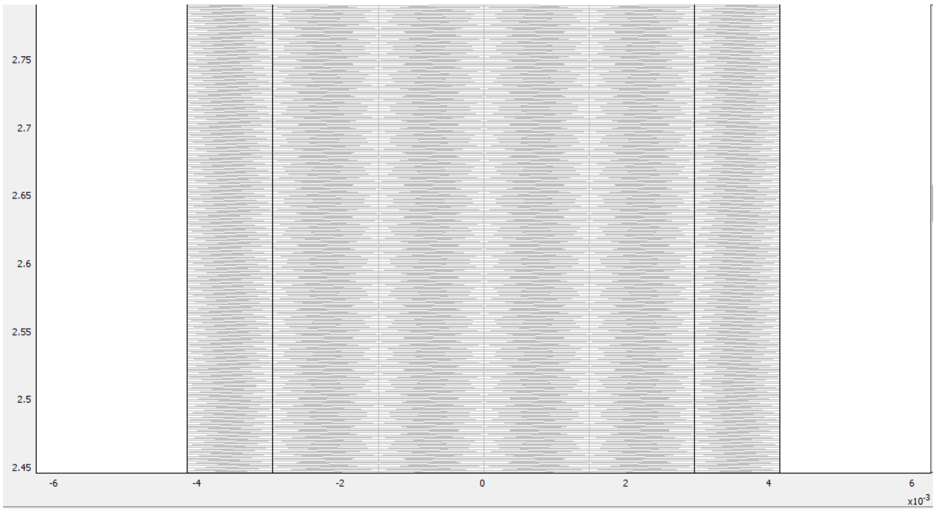

Figure 3.5 Mesh of a catalyst channel

3.5 Simulating NO reduction performance

In this work, the model of a single channel with a symmetrical peripheral wall is used for simulating the SCR reaction performance. The inlet fluid is a mixture of NO, NH_3, H_2O and air, which reacts on the inner walls. The flow is laminar when it enters the monolith channels. The governing equations solved by the program in this specific application are summarized as below;

3.5.1 Mass transport equations

The mass-balance equations for the model are the diffusion-convection equations at steady-state.

$$-\nabla \cdot (-D_i \nabla c_i + c_i \mathbf{u}) = R_i \tag{3.6}$$

Here D_i denotes the diffusion coefficient (m^2/s), c_i is the species concentration, and **u** is the velocity vector (m/s). The term R_i corresponds to the species' net reaction rate which is a function of the reaction rates, Eq. (2.26) and Eq. (3.1) and the reaction stoichiometry.

The gas-phase diffusivities (D_i) exported from the Reaction Engineering Lab are modified by

$$D_i, \mathrm{eff} = \frac{\emptyset \sigma D_i}{\tau} \tag{3.7}$$

Where $\emptyset$ is the porosity, σ is the constriction factor, and τ is the tortuosity. Typical values of the constriction factor and the tortuosity are, respectively, $\sigma = 0.8$, $\tau = 3.0$ [Szent-Gyorgyi A.]. In addition, the material porosity is 0.5 [G.Shaub, 2003]

Here, the material properties are grouped into the effectiveness factor;

$$k_{eff} = \frac{\emptyset\sigma}{\tau} \tag{3.8}$$

with the typical values stated above, k_{eff} is then equal to 0.133.

In the free channel, the inlet conditions are equal to the inlet concentrations.

$$c = c_{in} \tag{3.9}$$

at the outlet, use the convective flux condition

$$\mathbf{n} \cdot (-D_i \nabla c + c\mathbf{u}) = 0 \tag{3.10}$$

All other boundaries use the insulating or symmetry condition.

3.5.2 Momentum transport equations

The flow in the free channel is described by the Navier-Strokes equations

$$\begin{gathered} \nabla \cdot \big(-\eta_i(\nabla\mathbf{u} + (\nabla\mathbf{u})^T + p\mathbf{I}\big) = -\rho(\mathbf{u}\cdot\nabla)\mathbf{u} \\ \nabla\cdot\mathbf{u} = \mathbf{0} \end{gathered} \tag{3.11}$$

Where ρ denotes density (kg/m^3), **u** represents the velocity (m/s), η denotes viscosity (kg/(m.s)), and p is pressure (Pa). In the porous domain, the Brinkman equations describe the flow:

$$\begin{gathered} \nabla \cdot \left(-\frac{\eta}{\varepsilon_p}(\nabla\mathbf{u} + (\nabla\mathbf{u})^T + p\mathbf{I}\right) = -\frac{\eta}{\kappa}\mathbf{u} \\ \nabla\cdot\mathbf{u} = \mathbf{0} \end{gathered} \tag{3.12}$$

Here ε_p denotes the porosity (dimensionless) and κ refers to the permeability (m^2) of the porous medium. The term on the right-hand side of the Navier-Strokes formulation corresponds to momentum transported by convection in free flow. In the Brinkman formulation, this term is replaced by a contribution associated with the drag force experienced by the fluid as it flows through a porous medium. COMSOL Multiphysics effortlessly combines free flow and porous-media flow.

Here, the porosity (ε_p) and permeability (κ) defined in Brinkman equation are assumed to be 0.64 and $1\text{x}10^{-8}$ m^2, respectively (G. Schaub, 2003).

The boundary conditions are

$$\begin{array}{ll} \text{Inlet} & \mathbf{u}\cdot\mathbf{n} = v_0 \\ \text{Walls} & \mathbf{u} = 0 \\ \text{Outlet} & p = p_{ref} \end{array} \tag{3.13}$$

At the outlet, viscous stresses are ignored and the pressure is set to 1 atmosphere.

Thus, the following constants shown in Table 3.3 are entered in COMSOL Multiphysics;

Table 3.3 Constant values and descriptions entered in COMSOL Multiphysics

Name	Expression	Description
v_av	*Trial and error* [m/s]	Average inlet velocity
p_ref	101325 [Pa]	Pressure
eps_p	0.64	Porosity
Kappa	1e-8 [m^2]	Permeability
k_eff	0.133	Effectiveness factor
c_NO_in	4.289e-3 [mol/m^3]	Inlet concentration
c_NH3_in	6.434e-3 [mol/m^3]	Inlet concentration
c_O2_in	3.837 [mol/m^3]	Inlet concentration
c_H2O_in	13.025 [mol/m^3]	Inlet concentration

All subdomains and boundaries are set according to mass (Convection and Diffusion) and momentum (Incompressible Navier-Strokes) balances described above.

3.6 Performing preliminary economic analysis

By knowing the number of catalyst elements and ammonia consumption from the simulation model, the investment and operating costs can be evaluated. Figure 3.6 illustrates the optimizing SCR project costs stated by one of the SCR construction companies. The catalyst cost is estimated and then is used as a base case for other costs referred in the figure. For the operating cost, only ammonia assumption can be predicted as the other units such as flue gas preheater or pre-treatrment units are not modeled. The ammonia price can be found from chemicals suppliers providing a roughly annual ammonia cost; yet this ammonia amount is under the assumption that NH_3/NO ratio is 1 as mentioned before

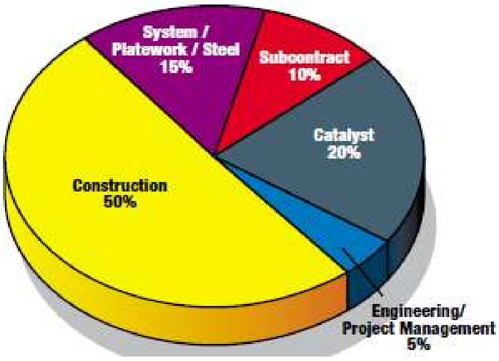

Figure 3.6 Overall SCR project costs
(The clear choice for turnkey SCR experience, 2000)

CHAPTER 4 RESULTS AND DISCUSSION

Selective Catalytic Reduction or SCR is one of the zero-NO_x approaches which guarantees over 85% of NOx reduction. The ROC's average NO_x emission per stack is around 3.26 g/s (See Appendix A). If the efficiency of SCR is treated at 85% and usable NOx credit is at 80% of the total reduction, the treatment of at least 3 stacks is sufficient for NOx credit of 6.5 g/s required to place another two baby crackers as demonstrated in Table 4.1.

Table 4.1 NO_x flowrate before and after SCR treatment

No. of stacks	NO_x emission (g/s)	Amount of NO_x reduced (g/s)	NO_x credit (g/s)
1	3.26	2.77	2.22
2	6.52	5.55	4.44
3	9.79	8.32	6.66

Hereafter, any figures and the model are based on one stack simulation, and other stacks are assumed to have identical behaviors as such model. The assumptions used in COMSOL Reaction Engineering Lab are as follows;

a) The model behaves as a plug-flow reactor
b) The operating conditions are 573 K and 1.01324×10^5 Pa
c) Ignore the energy balance as the system is operated isothermally

From COMSOL Reaction Engineering Lab, NO, NH_3, O_2 and H_2O initial concentrations are also provided to be used as input in COMSOL Multiphysics as shown in Table 4.2. N_2 is set as the solvent in TYPE list; in other words, N_2 mass balance is removed or the concentration is assumed to be constant. Furthermore, the thermodynamic and transport properties of the reacting mixture are based on the properties of the solvent species.

Table 4.2 Components' initial concentrations obtained from COMSOL Reaction Engineering Lab

Component	Initial concentration (mol/m^3)
NO	0.004289
NH_3	0.004289
O_2	3.8371
H_2O	13.0254

4.1 Simulation results of a catalyst channel

The objective of the simulation is to determine the maximum average velocity of flue gas entering a catalyst channel that gives a minimum NO conversion of 85%. This maximum velocity can then be used to calculate the minimum cross-sectional area of a catalyst layer and the number of monoliths required per layer. This minimum area can be calculated under the following assumptions:

a) A catalyst element size is 150 mm x 150 mm [Isabella Nova]. One element contains a 25x25 channel with a channel size of 5.9 mm x 5.9 mm
b) One monolith contains 6x6 elements which results in 0.81 m^2 (0.15x0.15x36) cross-sectional area of a monolith.

Initially, a single-channel model is developed and is firstly assumed to have one catalyst layer. The average velocity (denoted as v_av in COMSOL Multiphysics) is varied until the concentration of NO is reduced by 85% (NO conversion is 85%). The honeycomb monolith is assumed that the inside multi-channel is neglected and only the four-side walls are covered with catalyst materials. The dimension of the model is 150mm x 150mm x 1000mm with 10mm catalyst thickness. The result of varying the inlet flue gas velocity is shown in Figure 4.1. The velocity has to be set to be as low as 10^{-3} m/s which is not quite practical to make gas flows that slowly. The reason why the outcome was unrealistic is that 4-wall catalyst monolith cannot explain the real behavior of NO_x concentration and the assumption is not suitable. Thus, the smaller scale of the model is required i.e, from monolith scale (150mm x 150mm x 1000mm) to channel scale (5.9mm x 5.9mm x 1000mm).

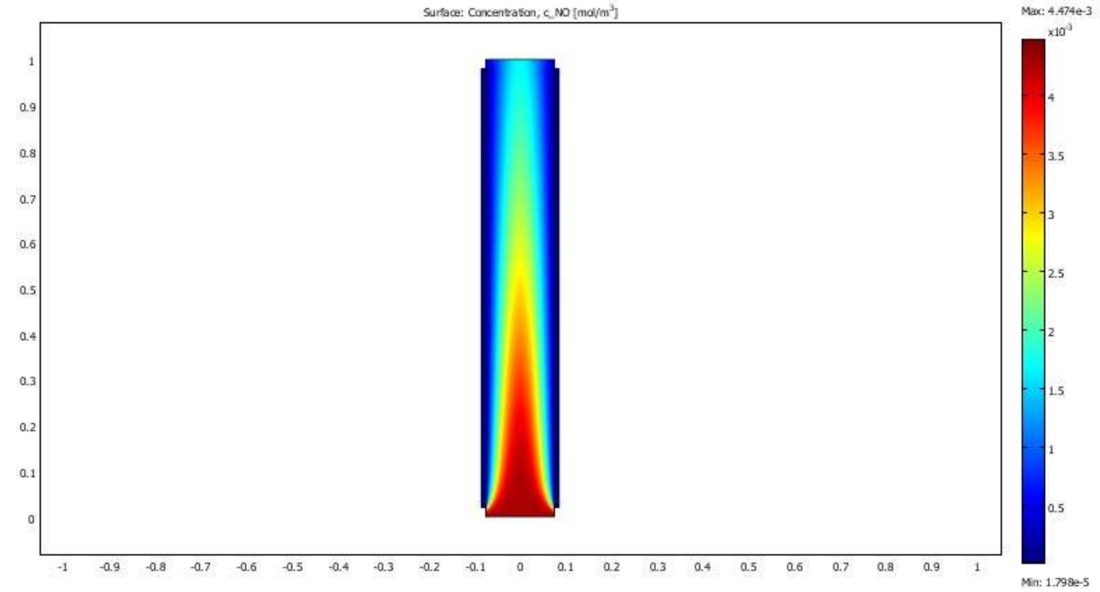

Figure 4.1 The 150 mm x 150 mm x 1000 mm monolith model with the inlet gas velocity of 0.0018 m/s

After adjusting the model to the channel size, the proposed model described in Chapter 3 needs to be demonstrated that it can represent the complexity of multi-channel of the honeycomb monolith. Thus, the model of two identical channels is set up as shown in Figure 4.2. The result shows that these 2 channels have the same profile, thus it can be assumed that the wall effects are negligible and one channel can also explain the flow behavior of the whole monolith.

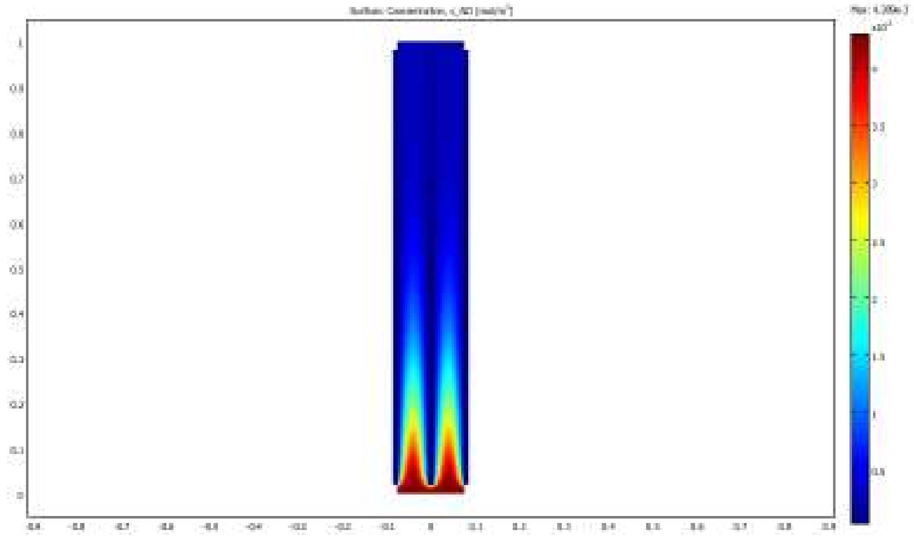

Figure 4.2 NO_x concentration profile of a 2-channel model of honeycomb monolith

Figure 4.3 shows the concentration profile of the model with 5.9mm x 5.9mm x 1000mm in size. The result shows that the maximum velocity of 0.34 m/s can achieve the NO reduction target. However, this velocity value is quite low, resulting in the minimum area being significantly large.

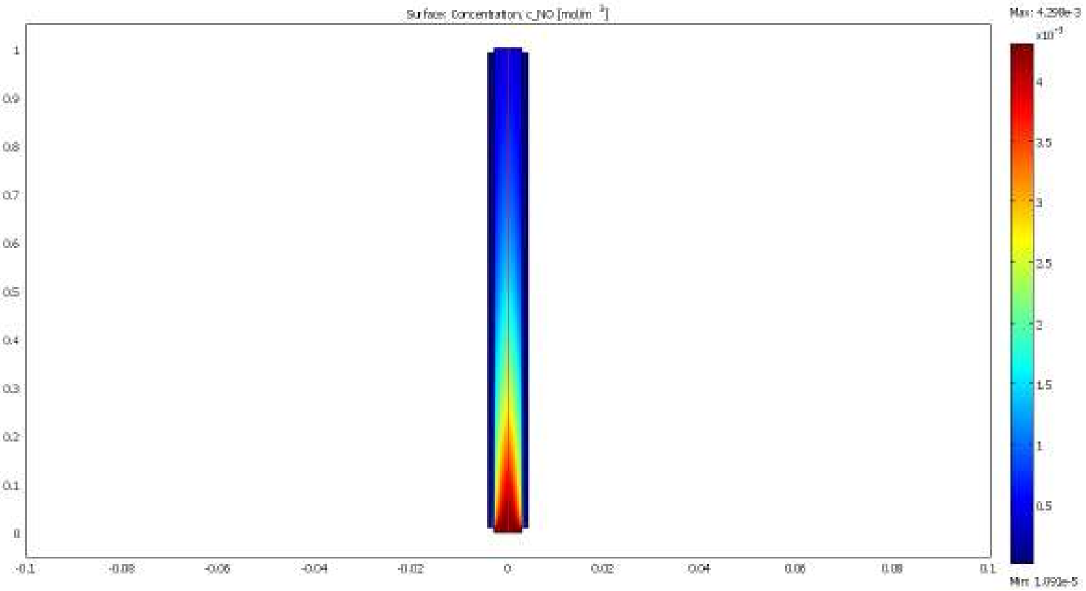

Figure 4.3 NO_x concentration profile of a single-channel, one catalyst layer model velocity = 0.34 m/s

With the total volumetric flowrate of 91,290 m^3/h or 25.36 m^3/s, the total required area is about 75 m^3. From the above assumptions, the total number of monolith required is about 92 monoliths per layer. It results in a very large SCR unit, and consequently, high investment cost and operating cost. Thus, it is clear that 1 catalyst layer is not economically suitable. To roughly predict the number of catalyst layers, the 92 monoliths are divided by 2 and 3 (indicating the number of catalyst layers) which give about 45 and 30 monoliths, respectively. A total of 30 monoliths per layer is more acceptable; therefore, a model of a catalyst channel of 3 catalyst layers is then generated. The simulation steps are the same, and the average velocity is varied. It can be noticed that the target NO reduction can be reached even though the velocity is increased by almost 5 times. In the 3-catalyst-layer case, the result is displayed as a 2-D surface plot of NO as shown in Figure 4.4. The flue gas containing NO flows through the catalyst channel from the bottom and is gradually treated by the porous medium on both sides of the wall. The maximum velocity is 1.1 m/s.

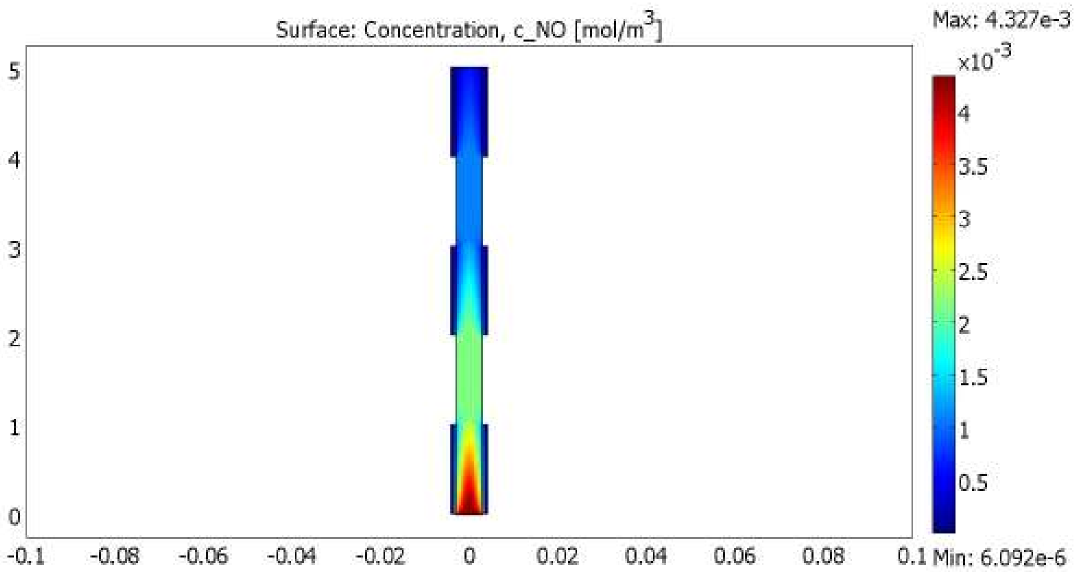

Figure 4.4 A 2-dimensional surface plot of NO concentration; 3 catalyst layers, velocity = 1.1 m/s

To further find the number of monolith required, the volumetric flowrate of 25.36 m^3/s is divided by the obtained velocity to get the total catalyst area per layer. Then this area is divided by the based module size of 0.81 m^2 per piece. It results in about 28 modules per layer. Table 4.3 includes the final concentration of NO, the total area, and the number of monoliths required at various velocities.

Table 4.3 The calculations of the number of monolith required

Data	Value		
Volumetric flowrate (m^3/s)	25.36		
Average velocity (m/s)	1.2	1.1	1
Total area required (m^2)	21.13	23.05	25.36
Catalyst volume required (m^3)	63.40	69.16	76.08
Initial NO concentration (mol/m^3)	4.289×10^{-3}		
Final concentration (mol/m^3)	7.50×10^{-4}	6.32×10^{-4}	5.19×10^{-4}
NO conversion (%)	82.51	85.26	87.90
Element dimension	25x25 channels		
Element size (m^2)	0.0225		
Module dimension	6x6 elements		
Module size (m^2)	0.81		
No. of modules required	26	28	31

The mesh statistics are the confirmation that the model is detailed enough. As Table 4.4 shows, the minimum element quality is 0.7968 which is significantly higher than the minimum acceptable mesh quality of 0.2.

Table 4.4 Mesh statistics

Extended mesh	
Number of degrees of freedom	305704
Base mesh	
Number of mesh points	13222
Number of elements	22304
Triangular	22304
Quadrilateral	0
Number of boundary elements	7720
Number of vertex elements	26
Minimum element quality	0.7968
Element area ratio	0.0152

4.2 Temperature sensitivity of the reactions involved

The reactions involved in the model consist of 2 reactions i.e., the oxidation of NO and the oxidation of NH_3. The first reaction is clearly preferred; the temperature is one of the control variables that contribute to the higher selectivity. Figure 4.5 shows that at temperatures between 550 K and 640 K, the oxidation of NO performs better than the consumption of NH_3 by O_2.

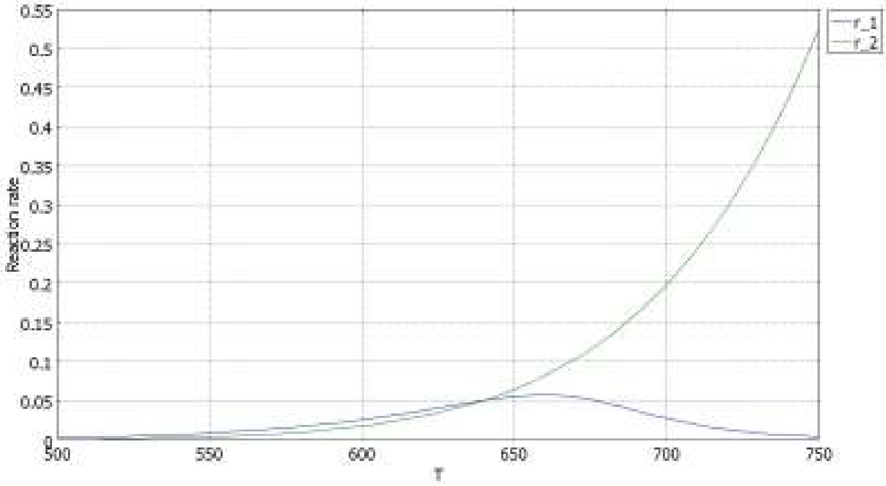

Figure 4.5 Temperature sensitivity of the reactions involved

4.3 Preliminary economic analysis

As only the catalyst volume is modeled, the catalyst cost at start-up period is used as a base to other relative costs according to the following cost portions [Babcock&Wilcox yearly report, 2000];

Catalyst	20%
Construction	50%
System/Platework/Steel	15%
Subcontract	10%
Engineering project management	5%

This set of cost portions is referred from one of the experienced SCR vendors. The construction portion of most SCR projects approaches or exceeds 50% of the total cost, while the other steel work and control systems take about 15%. In addition, the management of contract and engineering cost about 15% overall.

One of the Chinese chemical suppliers offers the SCR catalyst at around 10,000$ per volume; thus, the catalyst in the construction period costs about 700,000$. From the catalyst cost, the other costs can be predicted as shown in Figure 4.6

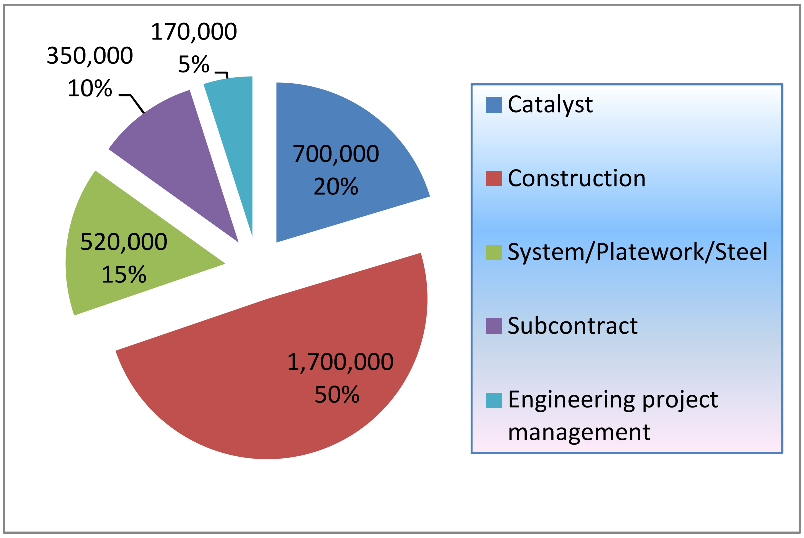

Figure 4.6 Overall SCR project costs

The above are the investment costs. For the operating costs, the main cost comes from ammonia consumption which is assumed to be equal to the NO_x emitted, or about 53 tons/yr. The price of ammonia is about 565 $/ton; thus the ammonia costs about 30,000 $/yr/stack.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

As the olefin plant at ROC faces the NOx emission problem but still wants to increase the production capacity, the plant needs to install more NO_x reduction units. Other than the replacement of burners that produce lower NOx than the existing ones, the chemical reduction in the presence of catalyst or so called Selective Catalytic Reduction (SCR) process is one of the attractive options, as it can achieve higher than 90% NO_x reduction. The model of the SCR catalyst was generated via COMSOL Reaction Engineering Lab and COMSOL Multiphysics. The input data including kinetic rates and operating condition ranges are referenced from the literature. The model gives NO_x concentration profile along the length of a catalyst channel which is used to determine a suitable velocity, the catalyst area and so on.

The initial suggestions for SCR reactor configuration and operating condition are as follows;

- The operating temperature ranges from 550 – 640 K, and the pressure is 1 atm
- The variation of NH3 to NO feed ratio gives very small alteration in NO conversion. However, if this ratio exceeds 1, the ammonia slip can be a problem.
- The SCR unit area is approximately 23 m^2
- The SCR reactor contains 3 catalyst layers. Each layer structure has 28 catalyst monoliths with 6x6 elements inside. The element size is 150x150x1000 mm each. An element has 25x25 channels with 5.9 mm pitch and 1.2 mm catalyst wall.
- The maximum inlet gas velocity is 1.1 m/s.
- The overall SCR reactor costs is about 3,440,000 $/stack treated and the ammonia assumption is around 30,000 $/yr

5.2 Recommendations

The size of the SCR reactor can be smaller by installing a gas deceleration unit ahead of the reactor. This technique also diminishes the amount of catalyst; thus the investment and operating costs are lower. The SCR system is sensitive to the number of operating conditions or factors such as the optimal NH_3 to NO ratio, the catalyst type, and the optimal operating temperature, that need to be estimated first. A pilot plant of SCR is recommended so that the effect of each parameter can be investigated. Note that this model is based on a flue gas profile emitted from one stack which was calculated by averaging the emission data. Therefore, this model may not be compatible for some stacks whose profiles deviate significantly from the average number.

Catalysts need to be analyzed in order to determine the exact catalyst performance. The process used to regenerate the catalyst is called ‘deionized (DI) water-based process’ (LLC, 2006), which can remove the physical materials plugged on the catalyst layers. This process should be performed regularly in order to decrease the chance of having to replace the whole catalyst, which can result in a significant operating cost. To conveniently operate the regeneration process, the space between catalyst layers should be at least 6 ft and manholes should be provided.

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APPENDIX A

NO$_x$ EMISSION DATA FROM THE OLEFIN PLANT AND PRELIMINARY CALCULATIONS

A.1 NO_x emission data from the olefin plant

displays the NO_x emission data obtained from the olefin plant. The numbers of emission rate of furnaces using low NO_x burner are averaged. The result is 3.26 g/s, this number is assumed to be the predicted NO_x emission rate of the two baby crackers each. Thus, the NO_x required credit is about 6.5 g/s.

Table A.1 NO_x emission data from the olefin plant

	NOx EMISSION				O_2 content (%)	H_2O content (%)	Volumetric flowrate (m^3/h)
Equip.	LOW NO_x BURNER		ULTRA LOW NO_x BURNER				
	RATE (g/s)	CONC (ppmv)	RATE (g/s)	CONC (ppm)			
H-100A	3.13	47.3			3.2	14.82	92754
H-100B	3.01	55.8			5.4	14.95	89268
H-100C	3.56	54.6			12.2	16.02	94096
H-100D	3.09	48.4			4.4	16.13	89770
H-100E	3.25	49.4			4.8	14.89	81318
H-100F	3.41	fix				15.82	100056
H-100G			2.54	30.2	7.1	14	99176
H-100H	3.35	41.4			4.9	16.94	97810
H-100I	3.45	56.5			4	14.42	92955
H-100J			2.04	37.6	4.2	15.83	92153
H-100K	2.96	49			4.1	17.75	84983
H-100Q	3.19	0				17.79	89777
H-120R	2.79	62.2			4.9	16.59	82657
H-840	0.14	58.1			14.1	9.88	6772
Avg	3.26	50.48			4.52	15.33	91290

A.2 Inlet molar flowrate calculations

COMSOL Reaction Engineering Lab requires inlet molar flowrates of all species in **Mass balance** tab.

- The average NO_x emission rate is 3.26 g/s
  by assuming NO is the only compound representing NO_x.
  Molecular weight of NO is 30 g/mol
  Thus, NO inlet molar flowrate is $3.26\ \frac{\text{g}}{\text{s}} \times 30 \frac{\text{g}}{\text{mol}} = 0.1087\ \frac{\text{mol}}{\text{s}}$
- Assume NH_3/NO mole ratio is 1
  Thus, NH_3 inlet molar flowrate is 0.1087 $\frac{mol}{s}$
- From Table A.1 NOx emission data from the olefin plant
  The average O_2 content is 4.52 %vol.,
  and NO average concentration is 50.48 ppmv
  Thus, O_2 inlet molar flowrate is
  $$0.1087\ \frac{\text{mol NO}}{\text{s}} \times \frac{4.51\ \text{O}_2}{100\ \text{flue gas}} \times \frac{10^6\ \text{flue gas}}{50.48\ \text{NO}} = 97.39\ \frac{\text{mol}}{\text{s}}$$
- N_2/O_2 ratio in air is $\frac{0.79\ \text{N}_2}{0.21\ \text{O}_2}$
  Thus, N_2 inlet molar flowrate is $97.39\ \frac{\text{mol O}_2}{\text{s}} \times \frac{0.79\ \text{N}_2}{0.21\,\text{O}_2} = 366.04\ \frac{\text{mol}}{\text{s}}$
- From Table A.1 NOx emission data from the olefin plant
  The average H_2O content is 15.33 %vol.,
  Thus, H_2O inlet molar flowrate is
  $$0.1087\ \frac{\text{mol NO}}{\text{s}} \times \frac{15.33\ \text{H}_2\text{O}}{100\ \text{flue gas}} \times \frac{10^6\ \text{flue gas}}{50.48\ \text{NO}} = 330.30\ \frac{\text{mol}}{\text{s}}$$

Table A.2 Inlet molar flowrates input in COMSOL Reaction Engineering Lab

Component	Inlet molar flowrate (mol/s)
NO	0.1087
NH_3	0.1087
O_2	97.39
N_2	366.04
H_2O	330.30

APPENDIX B
MODEL APPROACH

B.1 Model navigator for COMSOL Reaction Engineering Lab

Table B.1 Information input in COMSOL Reaction Engineering Lab

Model settings		
General		
Reactor type	Plug flow	
Reacting fluid	Gas	Calculate thermodynamic properties
		Calculate species transport properties
Temperature	573 K	
Pressure	$1.01325\text{x}10^5$ Pa	
Mass Balance		
Volumetric flowrate	v_av*A	v_av = inlet gas velocity (m/s)
		A = gas phase area
Reaction settings		
$4NO+4NH_3+O_2 \rightarrow 4N_2 + 6H_2O$		
Arrhenius parameters		
Frequency factor, A	$1\text{x}10^6$	s^{-1}
Activation energy, E	$60\text{x}10^3$	J/mol
Reaction rate	kf_1*c_NO*a*c_NH3/(1+a*c_NH3)	$mol/(m^3.s)$
Adsorption constant	a = a0*exp(-A/(Rg*T))	
Pre-exponential factor	a0 = $2.68\text{x}10^{-17}$	m^3/mol
Heat of adsorption	A = -243	kJ/mol
4NH3 + 3O2 → 2N2 + 6 H2O		
Arrhenius parameters		
Frequency factor, A	$6.8\text{x}10^7$	s^{-1}
Activation energy, E	$85\text{x}10^3$	J/mol
Reaction rate	kf_2*c_NH3	

B.2 Model navigator for COMSOL Multiphysics

Table B.2 Information input in COMSOL Multiphysics

Constant settings		
General		
Average inlet velocity	v_av	Guess value
Pressure	P_ref	101325 Pa
Permeability	kappa	1x10^{-8} m^2
[3]Effectiveness factor	k_eff	0.133

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[3] Effectiveness factor is used as the correction factor of diffusion coefficient by multiplying kappa with diffusion coefficient obtained from COMSOL Reaction Engineering Lab

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