

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY

School of Energy Systems

Degree Program of Energy Technology

Master's thesis

Jaana Särkkä

NITROGEN OXIDE REDUCTION IN LIME KILN GAS BURNING

Examiners: Professor, D.Sc. (Tech) Esa Vakkilainen

D.Sc. (Tech) Jussi Saari

Supervisor: M.Sc. (Tech) Pekka Törmikoski

Savonlinna 4.11.2019

ABSTRACT

Lappeenranta University of Technology
School of Energy Systems
Degree Program of Energy Technology

Jaana Särkkä

Nitrogen oxide reduction in lime kiln gas burning

Master's thesis

2019

77 pages, 30 figures, 6 tables and 17 appendices.

Examiners: Professor, D.Sc. (Tech) Esa Vakkilainen
Postdoctoral researcher, D.Sc. (Tech) Jussi Saari

Supervisor: Service Engineer, M.Sc. (Tech) Pekka Törmikoski

Keywords: lime kiln, nitrogen oxide emission, best available technology, burner, natural gas, pitch oil

The aim of this Master of Science thesis was to investigate the use of combustion technology in the reduction of nitrogen oxide emissions in the combustion of gases. The lime kiln is one of the biggest sources of emissions at pulp mills. In Finland, natural gas and fuel oil are the typical lime kiln fuels. Constantly tightening environmental regulations for nitrogen oxide emissions are forcing the industry to develop new methods to achieve emission targets. There are various methods already available to reduce nitrogen oxides at pulp mills, but they are costly to use and require high investments.

The theoretical part of the research includes a description of a lime kiln in the pulp process and the theory of nitrogen oxide reduction methods.

In this Master of Science thesis, measurements were limited to the interaction of pitch oil and natural gas to nitrogen oxide emissions. The results of the measurements show the use of pitch oil can reduce nitrogen oxide emissions.

TIIVISTELMÄ

Lappeenranta teknillinen yliopisto
School of Energy Systems
Energiatekniikan koulutusohjelma

Jaana Särkkä

Typpioksidien vähennys meesauunin kaasun poltossa

Diplomityö

2019

77 sivua, 30 kuvaa, 6 taulukkoa ja 17 liitettä.

Työn tarkastajat: Professori, TkT Esa Vakkilainen
Tutkijatohtori, TkT Jussi Saari

Työn ohjaaja: Service insinööri, DI Pekka Törmikoski

Hakusanat: meesauuni, typenoksidien päästöt, paras käytettävissä oleva tekniikka, poltin, maakaasu, pikiöljy

Tämän diplomityön tavoitteena oli tutkia typpioksidipäästöjen vähentämistä polttoteknisin keinoin kaasun poltossa. Meesauuni kuuluu suurimpiin päästöjen aiheuttajiin sellutehtaalla. Suomessa meesauuneissa käytetään yleensä maakaasua ja polttoöljyä. Jatkuvasti kiristyvät viranomais määräykset typpioksidipäästörajoituksille pakottavat teollisuuden kehittämään uusia menetelmiä päästötavoitteiden saavuttamiseksi. Typpioksidien vähentämiseen sellutehtailla on saatavilla jo erilaisia menetelmiä, mutta ne ovat investointina ja käytössä kalliita menetelmiä.

Tutkimuksen teoriaosuus sisältää kuvauksen meesauunista selluprosessissa ja typpioksidin vähennysmenetelmistä kertovaa teoriaa.

Tässä diplomityössä rajattiin mittaukset pikiöljyn ja maakaasun yhteisvaikutukseen typpioksidipäästöihin. Mittaustulokset osoittavat, että pikiöljyn käytöllä voidaan vaikuttaa typpioksidipäästöihin alentavasti.

ACKNOWLEDGEMENTS

I would like to thank my employer Andritz Oy for its cooperation and providing me with the opportunity to do this Master's thesis along with my paid employment. Working and studying simultaneously has been difficult, but my perseverance has been rewarded and I am satisfied to have completed the studies.

I would like to thank you, my manager Pertti Kaikkonen, for the giving me the flexibility and opportunity to do this Master's thesis. Thank you very much to my colleague and supervisor Pekka Törmikoski for the thesis topic, for supervising and supporting.

Thanks also to Professor Esa Vakkilainen for guiding, reviewing and making comments, which helped me to move forward. Samuli Särkelä from UPM-Kymmene, I thank you for the necessary information and the opportunity to visit the mill.

Special thanks go to my friends, who joined in the spirit of my task and helped to motivate me throughout. And not forgetting my beloved pets who patiently waited for my attention when I was writing in the evenings and at weekends.

Savonlinna, 4 November, 2019

Jaana Särkkä

TABLE OF CONTENTS

SYMBOLS AND ABBREVIATIONS	7
1 INTRODUCTION.....	10
1.1 Background.....	10
1.2 Research problem	10
1.3 Objectives and scope	11
1.3.1 Research questions	11
1.4 Structure of the thesis	11
2 LIME KILN IN THE PULPING PROCESS	13
2.1 Rotary lime kiln	14
2.1.1 Conventional Lime kiln.....	17
2.1.2 Lime Mud Drying.....	18
2.2 Burners.....	20
2.2.1 Rotary kiln flames	21
2.3 Fuels.....	21
3 NO _x EMISSIONS IN A LIME KILN.....	24
3.1 Formation of nitrogen oxides in combustion and NO _x emissions.....	24
3.1.1 Thermal NO _x	26
3.1.2 Prompt NO _x	27
3.1.3 Formation of NO by N ₂ O intermediate	27
3.1.4 Fuel NO _x	28
3.2 Importance of NO _x reduction	29
3.3 Factors that influence kiln emissions of NO _x	30
4 NO _x EMISSION REGULATIONS	31
4.1 Regulations of the European Union.....	31
4.2 Regulations of the USA	33
4.3 NO _x emissions data according to the BAT enquiry	34
4.4 Sanctions and incentives relating to NO _x emissions	37
5 NO _x REDUCTION BY COMBUSTION CONTROL	38
5.1 Reducing temperature	40
5.1.1 Staging of combustion air.....	41

5.1.2	Flameless combustion	41
5.1.3	Steam or water injection	42
5.1.4	Flue gas recirculation.....	43
5.2	Reducing residence time	44
5.3	Fuel reburning	44
5.4	Low-NOx burner.....	45
5.5	Removal of nitrogen from combustion	46
5.5.1	Less Excess Air	46
5.5.2	Selection for fuels.....	47
6	NO _x REMOVAL BY POST-COMBUSTION METHODS	48
6.1	Chemical reduction of NO _x	49
6.2	Selective Non-Catalytic Reduction.....	49
6.3	Selective Catalytic Reduction	51
7	COMPARISON OF AVAILABLE TECHNOLOGIES IN PULP MILLS	52
7.1	Available technologies in pulp mills	52
7.2	Comparison of technologies	53
8	NO _x REDUCTION IN LIME KILN GAS BURNING	55
8.1	The challenges of NO _x emissions for the pulp mill	55
8.2	Research object and method	56
8.3	Pitch oil effects for NO _x reduction.....	59
8.3.1	Other measurement objects	64
9	RESULT.....	67
9.1	Further objects of research.....	67
10	SUMMARY AND CONCLUSION	69

REFERENCES

APPENDICES

Appendix I. Factors in Lime kiln Emissions of NO_x

Appendix II. External Combustion NO_x Limiting Technologies

SYMBOLS AND ABBREVIATIONS

ADt	Air dry ton
BAT	Best Available Technique
BOOS	Burner out of Services
BREF	Best Available Technology Reference Document
CaCO ₃	Calcium carbonate
CaO	Calcium oxide (lime)
ClO ₂	Chlorine dioxide
CH	Hydrocarbon
CNCG	Concentrated Non-Condensable Gases
CO ₂	Carbon dioxide
EU	European Union
EPA	Environmental Protection Agency
ESP	Electrostatic precipitator
FGD	Flue gas desulfurization
FGR	Flue gas recirculation
FR	Fuel Reburning
H	Hydrogen
HCl	Hydrogen chloride
HNO ₃	Nitric acid
HO ₂	Hydrogen peroxy
HiTAC	High temperature air combustion
LEA	Less Excess Air
LMD	Lime Mud Dryer
LNB	Low NO _x Burner

LRK	Long rotary kiln
N	Nitrogen
NAAQS	National Ambient Air Quality Standards
N_2O_5	Dinitrogen pentoxide
Na_2CO_3	Sodium carbonate
$NaNO_3$	Sodium nitrate
Na_2SO_4	Sodium sulphate
NaOH	Sodium hydroxide
NCG	Non-Condensable Gases
NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
NO_3	Nitrate
NO_x	Nitrogen oxides
N_2O	Nitrous oxide
N_2O_2	Dinitrogen dioxide
N_2O_3	Dinitrogen trioxide
N_2O_4	Dinitrogen tetroxide
N_2O_5	Dinitrogen pentoxide
O	Oxygen
O_3	Ozone
OH	Hydroxyl radical
OFA	Over Fire Air
PM	Particulate matter
ppm	Parts per million
PRK	Rotary kiln with preheater
rpm	Revolutions per minute

SCR	Selective Catalytic Reduction
SNCG	Strong gases
SNCR	Selective Non-Catalytic Reduction
TRS	Total reduced sulfur
UV	Ultraviolet light
VOC	Volatile organic compounds

1 INTRODUCTION

1.1 Background

The Master of Science thesis has been done for Andritz Oy and is part of the development work related to the emissions of lime kilns. The author of the thesis is employed by the company in the service team of the white liquor plant. The topic of the thesis was the issue of NO_x deductions, because this is very topical in relation to emissions from lime kilns and is an attempt to find a way to reduce nitrogen oxides by small investments or to utilize existing burners.

NO_x reduction at pulp mills has been investigated and will be further investigated. Andritz has supplied 154 lime kilns around the world, mostly with heavy oil and natural gas as their main fuels. Official regulations for NO_x emissions are putting pressure on the development of new methods to reduce NO_x emissions. For older lime kilns, there is a need to find a method for NO_x reductions that can also be used in new lime kilns. This thesis focuses on investigating the combustion of natural gas and the impact of pitch oil on NO_x emissions. In this case, an investigation was carried out with an existing burner and data was collected over a longer period of time.

1.2 Research problem

Nitrogen oxides are among the most significant pollutants in pulp mills and the lime kiln is the second largest source of emissions former at pulp mills after the recovery boiler. There are old technology kilns and new technology kilns whose burners mainly fired by fossil fuels. Flame and flame radiation raise or reduce the temperature in the kiln fire head and this affects the properties of the lime. Official regulations for NO_x emissions are tightening up all the time and there is a need to find a solution for deductions. The research goal of the thesis was to prove the effect of the test substance in the combustion of gas in reducing NO_x emissions and to justify the ongoing development work.

1.3 Objectives and scope

The aim of the company's development work is to obtain information on the effect of liquids and solids on combustion technology through NO_x emissions. The aim of the thesis was to research the effect of pitch oil in the combustion of natural gas on flame radiation and NO_x concentrations. Based on the results of the measurement curves obtained, the effect of pitch oil on emissions was analyzed visually.

The review focused on the effect of pitch oil in the combustion of natural gas on NO_x reduction. Other solids and liquids will be researched later in the development work. Other emissions were also omitted. No separate measurements were made in the review, but the mill's own continuous measurements of NO_x emissions and pitch oil and natural gas inputs were utilized, providing the necessary information.

1.3.1 Research questions

The research questions are follows:

Can NO_x emissions from lime kilns be influenced at the fire end?

How does pitch oil affect NO_x values?

1.4 Structure of the thesis

In the literature research, methods available to reduce NO_x emissions were explored. The mill control system was able to view the measurement curves for the selected time period. In the absence of accurate trend number data, the analysis was performed visually comparing the results of the measured curves and their effects.

The theoretical part of the thesis is reviewed in chapters 2 to 6. Chapter 2 generally tells about kilns, burners and fuels. Chapter 3 explains NO_x emissions in a lime kiln. Chapter 4 contains NO_x emission requirements and Chapters 5 and 6 describe NO_x reduction methods. Chapter 7 presents the availability of DeNO_x techniques for pulp mills and compares them.

Thesis processing is included in Chapter 8, which tells about natural gas and what it contains. Also discussed are the selection and method of the research subject and the effect of pitch oil on NO_x emissions in natural gas burning. The results are presented in Chapter 9. The chapter also contains research topics for further development. The concluding Chapter 10 analyzes the results.

2 LIME KILN IN THE PULPING PROCESS

Lime kilns produce burnt lime from lime mud and are part of the chemical pulping process in the chemical recovery cycle. After causticizing, lime is in the form of calcium carbonate. Lime reburning converts calcium carbonate back into calcium oxide. Lime regeneration is called reburning, since the lime mud changes at high temperature into burnt lime, calcium oxide, and carbon dioxide. Calcium oxide is needed in the causticizing reaction, in which white liquor is produced from green liquor coming from the recovery boiler. In practice, the causticizing reaction converts the sodium carbonate Na_2CO_3 of green liquor into sodium hydroxide NaOH for use in cooking. In the causticizing reaction, burnt lime reacts with calcium carbonate to form lime mud. In lime burning, lime mud is converted back into oxide. Figure 1 shows the chemical recovery cycle of the sulfate pulp process. (Engdahl et al. 2008, 161)

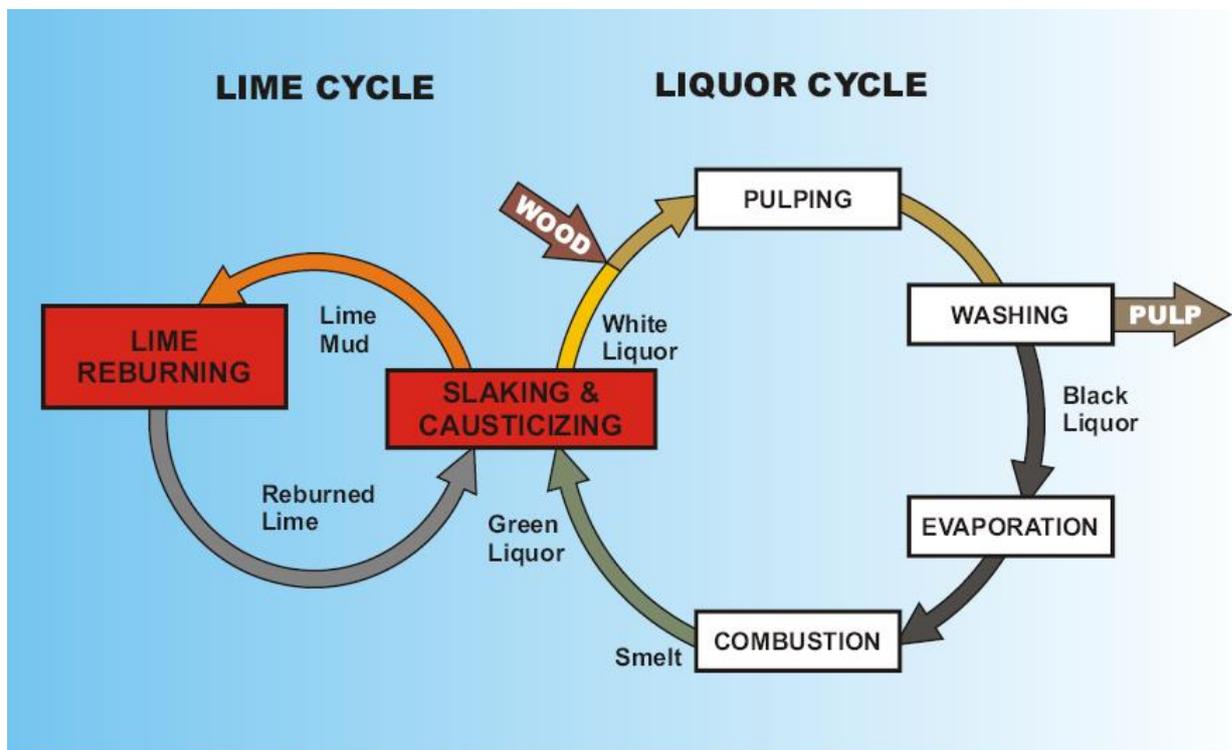


Figure 1. Chemical recovery cycle (Andritz Oy 2017, 4)

The operating principle of a lime kiln is countercurrent. Lime mud is fed into the kiln from the feed end. Due to gravity and kiln rotation, lime flows to the burner end which is on lower level. The flue gases formed leave the kiln from the feed end. Lime mud from causticizing is fed into the kiln, where CaCO_3 dissociation to CaO and CO_2 begins, When the temperature exceeds 800°C , the rising temperature accelerates the reaction. Sufficient reaction is achieved at about 1100°C . Calcium carbonate is thermally decomposed into calcium oxide and carbon dioxide. Equation 1 shows the reaction of lime mud into lime. (Engdahl et al. 2008, 131; Hakkarainen 2014, 16; Andritz Oy 2017, 78)



In addition to the main components of lime mud, CaCO_3 , the lime mud fed into the kiln also includes unreacted lime (CaO), water, small amounts of alkali and impurities. The amount of impurities in lime mud dry solids is typically 7 % - 10 %, depending on the amount of impurities involved in the process with green liquor and make-up lime. The lime mud decomposition temperature is a function of carbon dioxide partial pressure and also depends on the impurities content of the lime mud. The decomposition starting temperature varies from 800°C to 820°C and CO_2 concentration in the kiln gas between 12 % and 25 %. CO_2 concentration is lowest at the burner end and highest at the feed end. (Tran 2008, 1-2; Engdahl et al. 2008, 131)

2.1 Rotary lime kiln

The function of a lime kiln is to convert the lime mud into lime for the causticizing process. The lime kiln is part of a kraft pulp mill. The layout of a rotary lime kiln is shown in Figure 2.

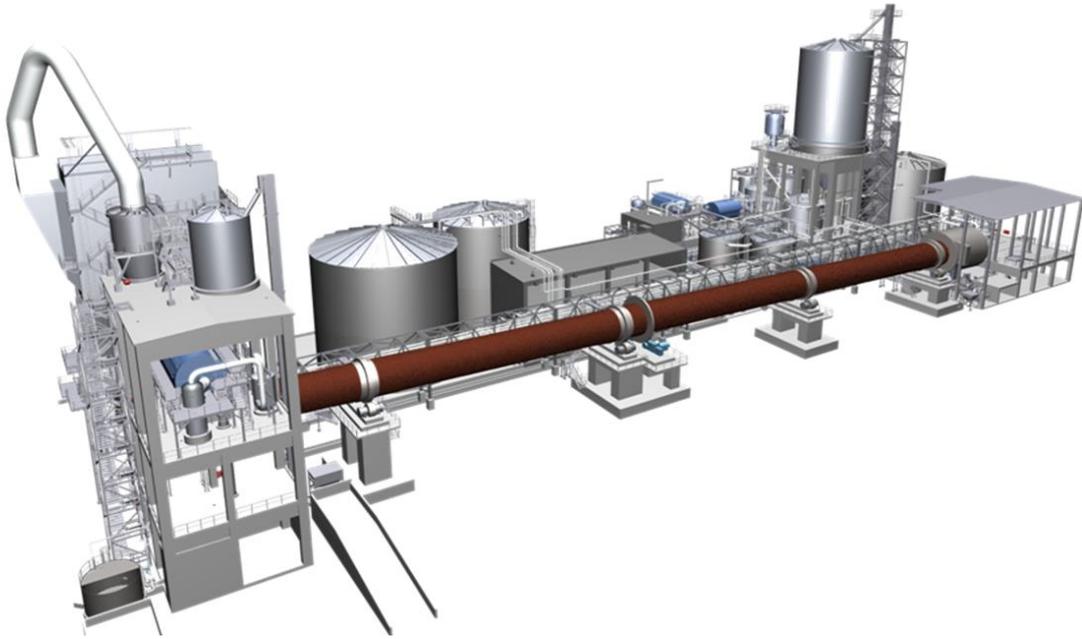


Figure 2. Lime kiln layout (Andritz Oy 2017, 10)

The lime kiln is divided into four process zones (KnowPulp 2016):

- Drying; the water coming with the lime mud evaporates
- Heating; lime mud is heated to the reaction temperature
- Calcination; calcium carbonate decomposes into calcium oxide and carbon dioxide
- Cooling; the lime is cooled before it is removed from the kiln

In the first stage, the dry solids concentration of the lime mud is increased by drying. In the second stage, the lime mud temperature is raised to the calcination point. In the third stage, calcium carbonate calcines or decomposes into calcium oxide and carbon dioxide. In the fourth stage, lime is cooled and the heat released during cooling is utilized to heat the combustion air of the lime kiln. (KnowPulp 2016)

The process stages of the first three zones require externally generated heat. For this reason, usually natural gas and/or oil is burned in the lime kiln. Heat transfer in the kiln is mostly based on radiation. There is valid contact heat transfer in the drying stage because the flue gas

temperature has decreased significantly. Heat from the burner moves directly by radiating into the lime mud or reflecting from the walls to the lime mud. Calcination reaction and radiation heat transfer require a high temperature to function, so the lime kiln has high combustion temperatures. (KnowPulp 2016)

The combustion aims to produce homogeneous porous lime from which the lime mud generated is easily separated from the lye and slaked well before causticizing. An excessive temperature causes changes in the crystal structure of the lime. Smooth operation of the kiln is an important prerequisite for successful lime burning. The residence time of the lime mud through the kiln is about 4 – 5 hours depending on the speed of rotation. (KnowPulp 2016)

A lime kiln is a long steel drum lined with inside bricks, slightly inclined horizontally and slowly rotating on riding rings. The inclination of the kiln is usually 1.5 – 2.5 % and rotation speed 0.5 – 1.5 revolutions per minute. The kiln is supported from 2 – 5 positions with riding rings for the support rollers. This number depends on the length of the kiln. The length of the shell varies according to the production and structure options from 50 to 200 meters and diameter 2.5 – 5.5 meters. Lime mud is fed in from the feeding end, and passes through the kiln towards the burner or firing end. At the firing end, there is also a cooler that cools the lime mud and recycles heat back to the kiln. Figure 3 shows a general view of a lime kiln. (KnowPulp 2016; Andritz 2017)

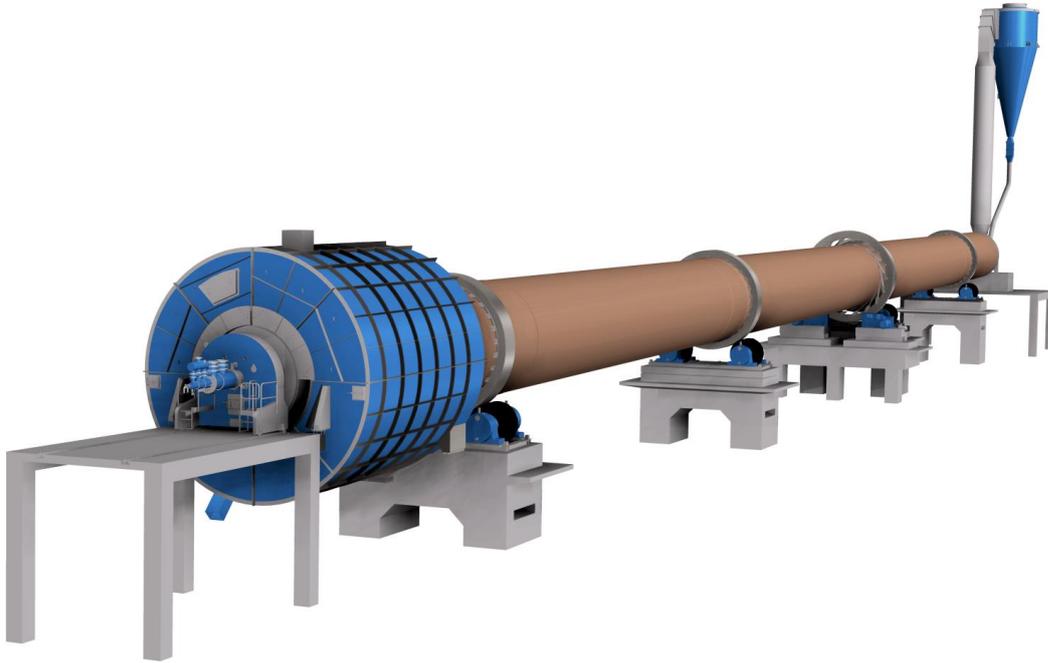


Figure 3. Rotary lime kiln (Andritz Oy 2017)

2.1.1 Conventional Lime kiln

In older kilns, lime mud drying occurs inside the kiln itself. The kiln has a chain zone where chains are attached to the inner surface of the shell to intensify heat transmission. The chains are attached from either one end or at both ends. When the chains hang only at one end, it is called a chain curtain, and when they are attached at both ends it is called a garland system. Figure 4 there are presented different chain systems of rotary kiln. The chains absorb the heat of the flue gases and transfer them to the lime mud. The function of the chain zone is to dry the lime mud, and its length is determined when the lime mud is completely dry after the zone. The length of the zone comprises the dry content of lime mud, the particle size of the lime mud and the heat transmission capacity of the flue gases. (Adams 2008, 2)

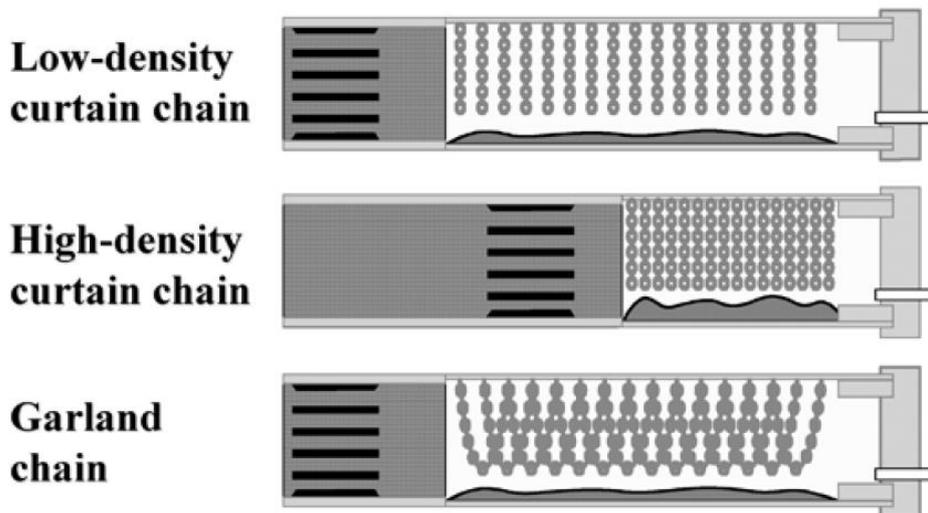


Figure 4. Rotary kiln chain system (Adams 2008, 2)

2.1.2 Lime Mud Drying

Andritz has different solutions for lime mud drying by flue gas. The older type is called a lime mud dryer (LMD) and the new type LimeFlash. Before feeding into the kiln, the lime mud is dried by flue gas in the LMD to almost 100 % dryness at the feeding end of the lime kiln. The LMD forms a duct about 15 meters high, which begins at the feeding end and is associated with the cyclone. The dried lime mud is fed to the flue gas stream at a temperature of about 500 °C. The flue gas temperature flowing to the electrostatic precipitator (ESP) is 200 °C. The large contact surface between the flue gases and lime mud allows quick drying. The development of LMD kilns has made it possible to shorten the kilns, because the length of a kiln can be reduced by the length of the former drying zone, about 30 %. Installing an LMD in an old kiln will increase the capacity by about 30 %. (Hart et al. 2012, 10; Andritz Oy 2017)

The separation of the dried lime mud from the flue gases occurs in a cyclone separator. From the cyclone, lime mud is dropped into a rotary feeder and from a chain conveyor to the feed end of the kiln. Flue gases are passed through the electrostatic precipitator (ESP), which purifies flue gases from the dust going to the drag conveyor. The drag conveyor feeds ash through the

rotary feeder to the chain conveyor from where it is dropped into the lime kiln. (Andritz Oy 2017)

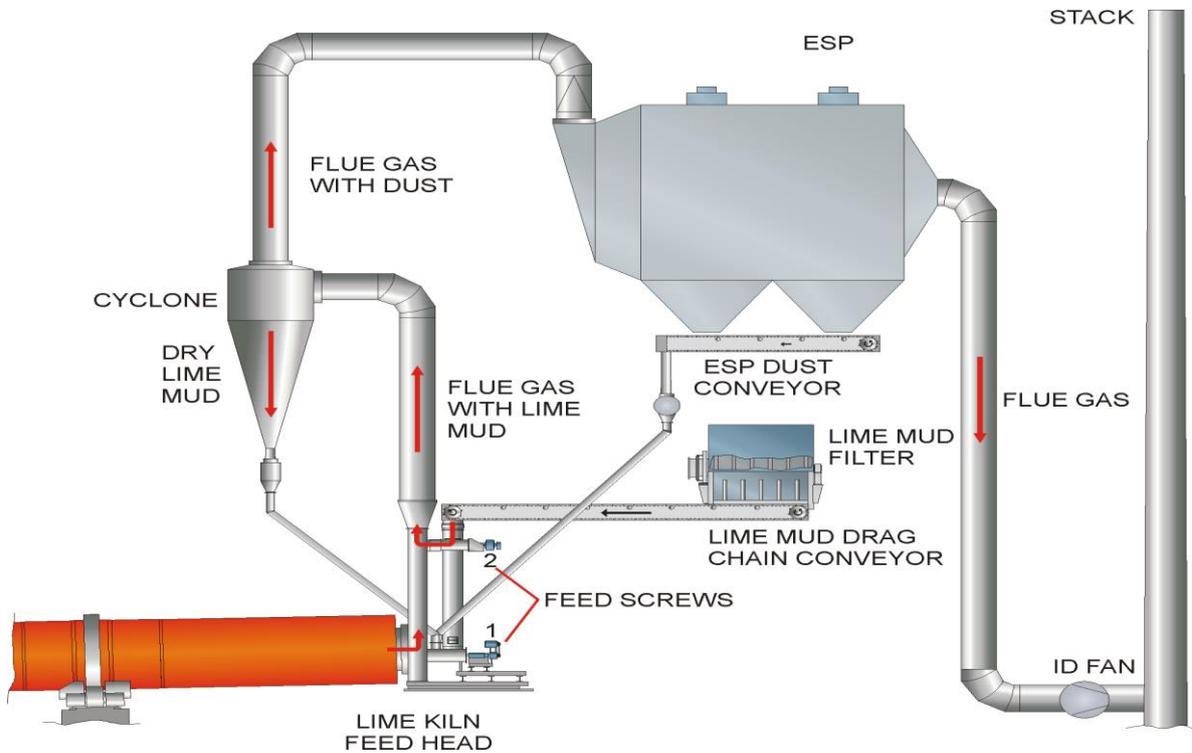


Figure 5. LMD kiln (Andritz Oy 2017, 62)

The lime mud drops down the chute into the LMD feed screw, then drops to the feed screw and flows into the LMD riser duct, where it dries and is fed to the cyclone. The cyclone separates the dry lime mud from the flue gas. From the cyclone, dried lime mud is returned and conveyed to the kiln. From the LMD feed screw, wet mud overflows to the lower feed screw and is conveyed directly to the kiln. The benefit of the LMD kiln compared to conventional kilns is that the whole of the kiln length is available for calcining and heating. (Adams 2008, 4; Hart et al. 2012, 11; Andritz Oy 2017)

In a later solution, LimeFlash dries and pre-heats the lime mud before it is fed to the lime kiln. The LimeFlash prevents hot flue gases from leaking into the atmosphere. Kiln capacity increases by drying the lime mud before the kiln. The entire length of the lime kiln is used for

pre-heating and calcination. The LimeFlash allows the feed end of the kiln to run at higher temperatures without plugging. Both are due to the exchange of heat at the feed head and the help of air blasters in the rising duct. (Andritz Oy 2016)

2.2 Burners

The burner of a lime kiln is located at the lower end of the drum, and the firing end is surrounded by a hood. The main lime kiln burner can be designed for burnt oil, natural gas and other fuels like wood gas, biogas and wood dust. The combustion of fuel occurs in the same space as where the lime mud is calcined. For this reason, fuel ash and flue gases affect the properties of the lime. The burner is installed at the end of the lime kiln so that its position in the kiln can be adjusted to suit the conditions. To prevent overheating the burner, it is positioned as far away from the lime deposit as possible. The burner is ignited by an ignition burner, which can be fueled with, for example, propane or natural gas. (Andritz Oy 2017; KnowPulp 2016)

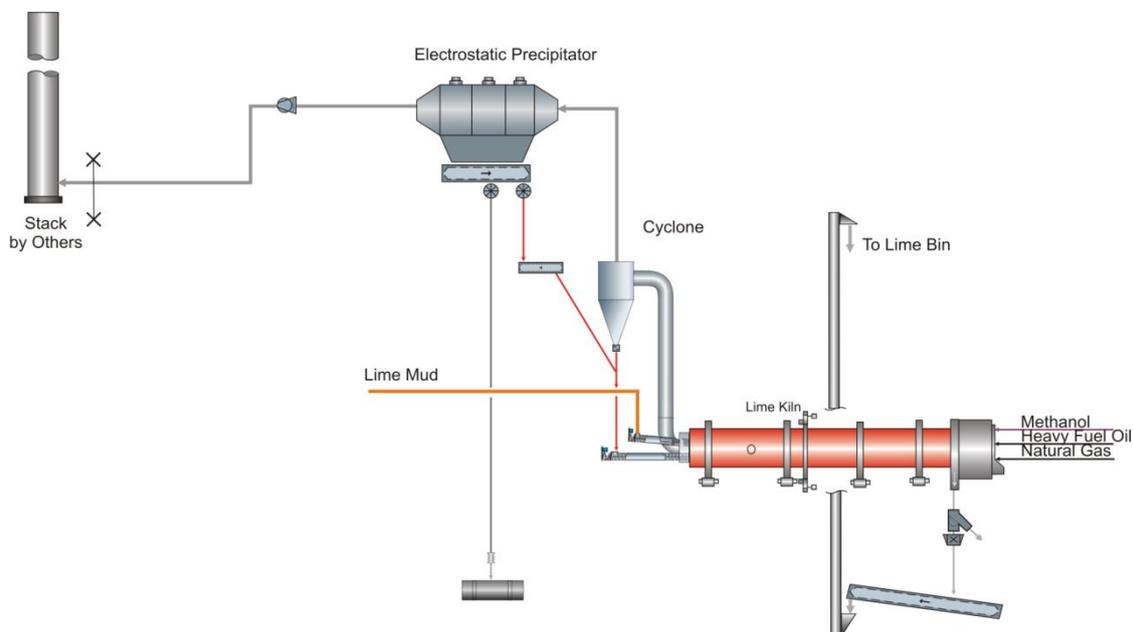


Figure 6. Burner and lime cooling (Andritz Oy 2017, 64)

2.2.1 Rotary kiln flames

The burner and flame play important roles in product quality. The primary air fan produces air flow for the burner to adjust the shape of the flame. Higher flame temperatures mean higher production capacity and efficiency. It should be noted that excessive temperatures can cause an over-burned, slow-reacting lime product, and refractory damage. This balance is found in a performance result that compromises in flame length. Excessively short flames are too hot and cause over-burned lime and brick failures, while excessively long flames cause loss in efficiency, production capacity and product quality. A medium-length flame approximately three times the kiln diameter in length is usually a good balance between efficiency and refractory service life. Figure 7 shows three types of rotary kiln flames. (Adams 2008, 2)

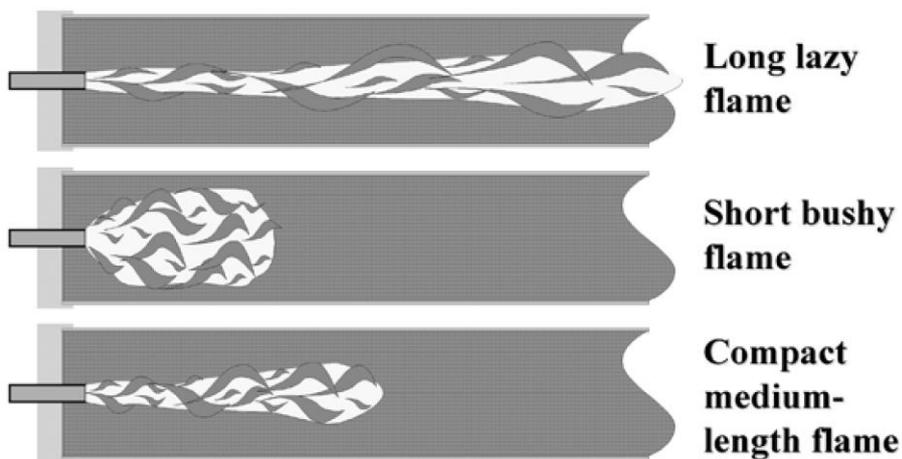


Figure 7. Rotary kiln flame shapes (Adams 2008, 2)

2.3 Fuels

In general, lime kiln fuel is either oil or natural gas, because they have a high combustion temperature. Other liquid fuels can also be used. Tall oil can replace oil in whole or in part, and up to 10 – 15 % of methanol can be used in kiln heat input. (Andritz Oy 2017)

A lime kiln can also be used as a combustion kiln for non-condensable gases from cooking and evaporation. The gases give combustion heat, which reduces the heat consumption of the kiln. Steam ejectors are used to forward the gases. The portion of NC gases from the heat requirement of a lime kiln must be less than 15 %, because they increase the flue gas flow and often vary greatly in flow and composition. Alternative fuels like petroleum coke, peat, bark and other wood waste have also been used, but may cause problems with the formation of inert material growth. (Adams 2008, 7; Andritz Oy 2017)

The following fuels can be used in addition to the main ones (Andritz Oy 2017, 70; Törmikoski 2018):

- Turpentine (very high heat value, requires good control)
- Hydrogen (max. 10 % of heat. If more, special bricks needed)
- Liquid methanol (max 10 – 15 %, low heat value, high moisture)
- Tall oil (acid pH)
- Glycerol
- SOG (stripper of gas) from evaporation plant (contains methanol, ammonia compounds)
- SNCG Strong gases from a pulp mill (flow and composition variations)
- Petroleum coke from an oil refinery (very high sulfur content)
- Gasification gas (from biofuel such as bark, wood, etc.) (high temperature, low heat value)
- Wood powder (must be dry and fine)
- Biogas (mainly methane and inert)
- Gasification gas from coal (low temperature, low heat value)
- LNG (liquid natural gas) (low pressure, burner design)

The use of biofuels is increasing due to rising fossil fuel prices and tighter environmental regulations. In a large number of kilns, it is possible to use various fuels in the burner. For this reason, it fuels already available at the factory can be used. There is great interest in biofuels

because they are available either as raw material or as a by-product. Tall oil and methanol produced as by-products are liquid fuels suitable for use due to their small process change needs. Solid fuels, such as lignin and bark, require preparation before they can be fed into the burner. (Lundqvist 2009, 7; Adams 2008, 7)

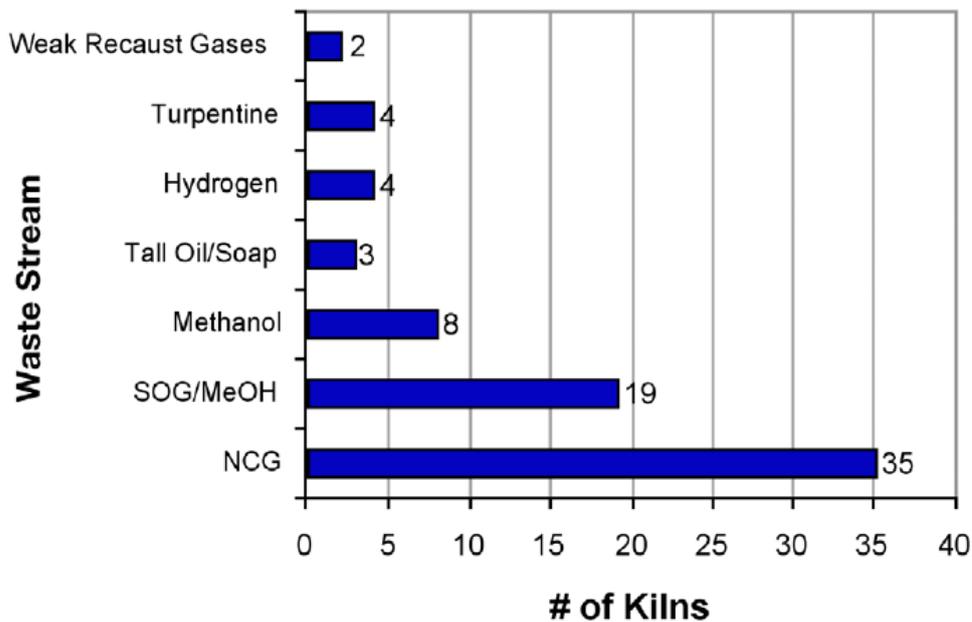


Figure 8. Waste stream presently burned in lime kilns (Francy et al. 2011, 22)

Figure 8 shows the variety of waste/by-product streams burned in lime kilns. Kilns burn by-product streams either constantly or occasionally. The distinction between by-product streams and alternative fuels is that by-product streams are by-products of the mill or a nearby industry such as petroleum coke (the carbonaceous by-product of the oil refining coking process). Alternative fuels can be purchased from an outside vendor or produced on site and require processing prior to being burned in the lime kiln. (Francy et al. 2011, 22; U.S. Environmental Protection Agency 2014, 2 – 37)

3 NO_x EMISSIONS IN A LIME KILN

Nitrogen oxides belong to the main emission components of a lime kiln and are a major concern when applying for official permits. Other flue gas emissions are sulfur dioxide, reduced sulfur compounds (TRS), carbon monoxide (CO) and particulate matter. Requirements for emissions of volatile organic compounds (VOC) exist in some places. Emissions are monitored during scheduled measurement periods or by continuous measurement. Currently NO_x emissions are largely dependent on kiln burner design, the nitrogen content of the fuel and the flame temperature. (European Commission 2013a, 241; Engdahl et al. 2008, 178)

Pernicious nitrogen compounds are formed in combustion and the most important of these are nitrogen monoxide (NO) and nitric oxide (NO₂), commonly referred to as NO_x. The majority of flue gas nitrogen oxide emissions consist of NO. In the atmosphere, NO reacts with oxygen, so the environmental impact of the atmospheric oxides of nitrogen are the same regardless of what nitrogen oxide is formed in the kiln. Usually 95 % or more of NO_x is in the form of NO, whereas the fraction of NO₂ is less than 5 %. The most significant factors in combustion for NO_x formation are oxygen availability, residence time in the combustion zone, combustion temperature, fuel nitrogen content and the conversion ratio of fuel-bound nitrogen. (Kilpinen & Zevenhoven 2004, 4-1)

3.1 Formation of nitrogen oxides in combustion and NO_x emissions

The chemical element nitrogen (N) can be reactive and have ionization levels from plus one to plus five. Nitrogen can form several different oxides and nitrogen oxides including seven different compounds. The family of NO_x compounds and their properties are shown in Table 1. (U.S. Environmental Protection Agency, 2)

Table 1. Different nitrogen oxide, NO_x, compounds (U.S. Environmental Protection Agency, 2)

Formula	Name	Nitrogen Valence	Properties
N ₂ O	nitrous oxide	1	colorless gas water soluble
NO N ₂ O ₂	nitric oxide dinitrogen dioxide	2	colorless gas slightly water soluble
N ₂ O ₃	dinitrogen trioxide	3	black solid water soluble, decomposes in water
NO ₂ N ₂ O ₄	nitrogen dioxide dinitrogen tetroxide	4	red-brown gas very water soluble, decomposes in water
N ₂ O ₅	dinitrogen pentoxide	5	white solid very water soluble, decomposes in water

Nitrous acid (HNO₂) or nitric acid (HNO₃) is formed when any of these oxides dissolve in water and decompose. Nitric acid forms nitrate salts when it is neutralized and nitrous acid also forms salts. NO_x and its derivatives therefore exist and react with gases in the air, acid in droplets of water and salt. Acid gases and salt together contribute to pollution. (U.S. Environmental Protection Agency 1999, 3)

The formation and decomposition of nitrogen oxides in combustion is a rather complex reaction. The most important reactions are currently well-known and can be observed when investigating the formation and reduction of nitrogen emissions. The formation of NO_x in gas, oil flames and coal has been studied. NO_x emissions formed from combustion are mostly in the form of NO.

In all combustion there are three opportunities for the formation of NO_x:

- thermal NO_x
- prompt NO_x
- fuel NO_x

Nitrogen oxide formation pathways in combustion are presented in Figure 9. The three reaction paths are responsible for the formation of NO_x during combustion processes with unique characteristics.

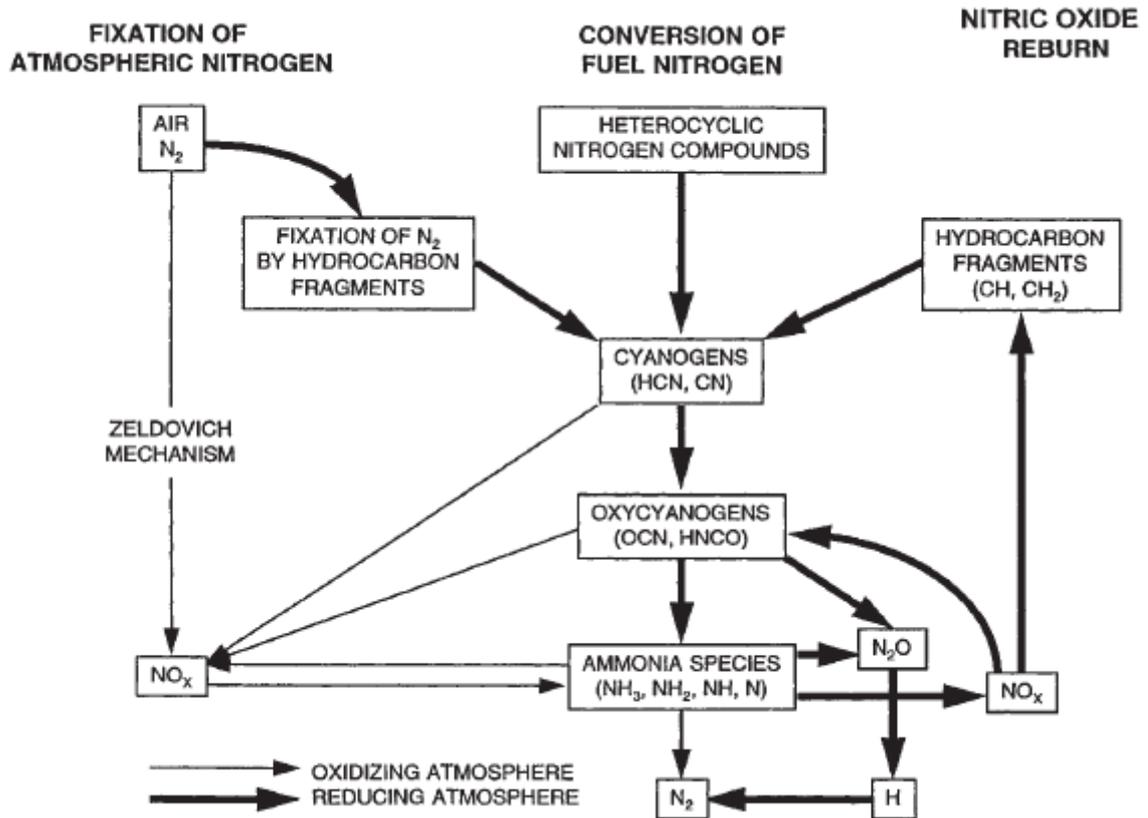
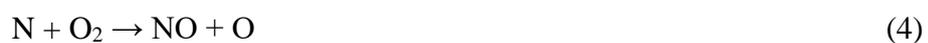
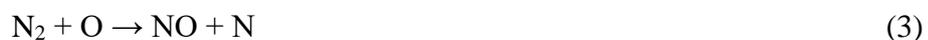


Figure 9. Nitrogen oxide formation pathways in combustion (Perry 1997, 27-27)

3.1.1 Thermal NO_x

Nitrogen monoxide is formed from nitrogen from fuel or organic nitrogen, and from nitrogen from combustion air or molecular nitrogen. The formation of nitrogen monoxide occurs through a chain reaction, which starts a reaction between the molecule nitrogen and the oxygen atom.



Under completely under-conditions or over-air reduction, the above-described reaction will not occur. In this case, the formation of nitrogen monoxide occurs mainly by the hydroxyl radical (OH). Under such conditions, the reaction takes place through the following reaction:



The formed nitrogen monoxide is called thermal nitrogen monoxide. Thermal NO_x forms in the burning zone where temperatures are sufficiently high. (Raiko et al. 2002, 304 – 305)

3.1.2 Prompt NO_x

Nitrogen monoxide can also be formed with the CH radical, whereby the formed nitrogen oxide is referred to as prompt NO. Prompt nitrogen oxide is formed only in the combustion zone of the flame. The formation of high NO occurs through the following two reactions if oxygenous components are present in the combustion:



The formation of nitrogen monoxide by the above mechanism occurs only in the combustion zone of the flame, where the hydrocarbon radicals required in reaction 6 are present and the combustion of fuel is incomplete. The formation of nitrogen monoxide is very prompt and the formed nitrogen monoxide is called prompt NO. (Raiko et al. 2002, 306 – 307)

3.1.3 Formation of NO by N₂O intermediate

Third in the mechanism of combustion air nitrogen, nitrogen monoxide is formed through an intermediate of N₂O, where M is any gas component.



It is likely that in normal burning combustion the mechanism of portions 8 and 9 from NO emission is slight, possibly a little higher than that of prompt NO. The importance of the mechanism increases as pressure increases.

Nitrogen oxide formation occurs when NO reacts with the hydrogen peroxy radical (HO_2) as follows:



The HO_2 required for the reaction is generated when the hydrogen atom and oxygen molecule react with a gas component (M).



When the nitrogen oxide enters the hotter areas of the flame, it decays back to nitrogen monoxide. For this reason, the amount of nitrogen monoxide in the flue gases is higher than the nitrogen oxide. (Raiko et al. 2002, 307)

3.1.4 Fuel NO_x

In addition to thermal NO and prompt NO, nitrogen monoxide is also formed from nitrogen from fuel, or from organic nitrogen. In the flue gases of nitrogenous fuels, the majority of NO formed is generated by the decomposition of the nitrogen compounds of the fuel and the

reaction with oxygen. The greatest influence is on the availability of oxygen from flames while the temperature has little effect on the reaction. (Kilpinen & Zevenhoven 2004, 4-17)

Compared to the amount of nitrogen in the combustion air nitrogen, the amount of fuel nitrogen is much smaller, but it is much more reactive. When fuel is pyrolyzed, some of the nitrogen is released and forms small molecule gaseous cyanogen and cyanide compounds such as hydrogen cyanide HCN, and amino compounds such as ammonia NH₃. When oxygenous components are present, HCN and NH₃ compounds continue to oxidize to the nitrogen monoxide called fuel NO. Fuel NO is slightly dependent on temperature, and nitrogen monoxide is easily formed from fuel nitrogen even at low temperatures. (Raiko et al. 2002, 308)

3.2 Importance of NO_x reduction

The formation and disintegration kinetics of nitrogen oxides in combustion are complex. Nitrogen oxide formation and decomposition mechanisms have been studied at elementary reaction levels over the last 50 years, as knowledge of nitrogen oxide formation and decomposition criteria is a precondition for reducing nitrogen oxide emissions. The formation of nitrogen oxides in combustion can largely be reduced and this has contributed to the development of new combustion methods. (Raiko et al. 2002, 302)

NO_x plays a major role in several important environmental effects. NO_x reacts with volatile organic compounds in the presence of sunlight to form ozone. In addition, NO_x and other impurities react in the air to form compounds that promote acidic depositions and thus damage forests and lakes causing soil acidification. NO_x has immediate adverse health effects on living organisms and can cause corrosion-related injuries. (U.S. Environmental Protection Agency 1999, 1)

By the effects of ultraviolet light (UV) and air, NO_2 reacts by forming ozone and nitric oxide (NO). After this, the NO reacts with free radicals in the atmosphere, and the operation of volatile organic compounds (VOC) also affects UV radiation.

3.3 Factors that influence kiln emissions of NO_x

The formation of NO_x is related to the nitrogen content of the fuel and other substances burned in a lime kiln. Flame temperature and burner design are significant factors due to the need to reach a high flame temperature for good radiation onto the surface of lime. The NO_x level in newer lime kilns may be reached by reducing the available oxygen in the combustion zone in oil-fired lime kilns and by minimizing the fire end temperatures in gas-fired lime kilns. These combustion modifications may be difficult to accomplish in certain existing lime kilns due to their design and influence on product quality. Appendix I presents lime kiln control technology options. (Environmental footprint comparison tool, 2013, 47)

4 NO_x EMISSION REGULATIONS

Nitrogen oxide emissions may be difficult to keep below regulatory levels if the nitrogen content is more than 1 % nitrogen in the fuel. Emission regulations refer to NO_x calculated as NO₂, because in the ambient atmosphere NO is oxidized within about one day to NO₂. Table 2 shows typical nitrogen oxide emissions from a lime kiln to air. (Kilpinen & Zevenhoven 2004, 2-10)

Table 2. Typical nitrogen oxide emissions to air from a lime kiln (Dahl 2008, 126)

Nitrogen oxides (as NO ₂)		
- oil firing	240 – 380	mg/m ³ n
	130 – 200	mg/MJ
	0.2 – 0.3	kg/Adt
- gas firing	380 – 600	mg/m ³ n
	200 – 320	mg/MJ
	0.3 – 0.4	kg/Adt

The higher combustion temperatures of gas firing can explain higher NO_x emissions appearing from a gas-firing kiln. NO_x emissions are given as kg per produced ton of CaO. For example, in the US the total NO_x emission from lime kilns was 9,000 tons of NO_x in 2005. NO_x emissions for gas-fired lime kilns were reported as 0.77 kg/t_{CaO} (1.69 lb/t_{CaO}) and for oil-fired lime kilns 0.54 kg/t_{CaO} (1.18 lb/t_{CaO}). (Pinkerton 2007, 3 – 4)

4.1 Regulations of the European Union

In November 2010, the requirement for controlling NO_x emissions was set down in directive 2010/75/EU of the European Parliament and of the Council on industrial emissions (integrated pollution prevention and control). The European IPPC Bureau of the Institute for Prospective Technology Studies at the EU Joint Research Centre stipulates that the permit conditions including emission limit values must be based on the Best Available Techniques (BAT). BAT

Conclusion 2014/687/EU is a legitimate document and results are processed in the BAT Reference document (BREFs). (European Commission 2014, 1)

The NO_x emissions levels are presented in Table 3 according to BAT Conclusion document for the Production of Pulp, Paper and Board. According to European Commission (2014), NO_x emission limits are given as both source-specific (mg/Nm³) and mill-specific (kg NO_x/ADt) for new pulp mills.

Table 3. BAT-associated emission levels for NO_x emissions from a lime kiln (European Commission 2014, 284/101)

Parameter		Long-term average mg/Nm ³ at 6 % O ₂	Yearly average kg NO _x /ADt
NO _x	Liquid fuels	100 – 200 ⁽¹⁾	0.1 – 0.2 ⁽¹⁾
	Gaseous fuels	100 – 350 ⁽²⁾	0.1 – 0.3 ⁽²⁾
<p>⁽¹⁾ When using liquid fuels originating from vegetable matter (e.g. turpentine, methanol, tall-oil), including those obtained as by-products of the pulping process, emission levels up to 350 mg/Nm³ (corresponding to 0,35 kg NO_x/ADt) may occur.</p> <p>⁽²⁾ When using gaseous fuels originating from vegetable matter (e.g. non-condensable gases), including those obtained as by-products of the pulping process, emission levels up to 450 mg/Nm³ (corresponding to 0,45 kg NO_x/ADt) may occur.</p>			

Specific emission levels for kilns in the cement industry have also been determined and they are significantly different from the lime kilns of the pulp and paper industry. (European Commission 2013b)

According to the European Commission (2014), the Best Available Technologies for reducing NO_x emissions from lime kiln are (1) Optimized combustion and combustion control, (2) Good mixing of fuel and air, (3) Low-NO_x burner and (4) Fuel selection/low-N fuel. The Best Available Techniques are described in Table 4 as given by the European Commission.

Table 4. Best Available Technologies to reduce NO_x emissions from lime kilns (European Commission 2014, 100, 119)

Technique	Description
Optimized combustion and combustion control	Based on permanent monitoring of appropriate combustion parameters (e.g. O ₂ , CO content, fuel/air ratio, unburnt components), this technique uses control technology to achieve the best combustion conditions. NO _x formation and emissions can be decreased by adjusting the running parameters, air distribution, excess oxygen, flame shaping and temperature profile.
Good mixing of fuel and air	
Low-NO _x burner	Low-NO _x burners are based on the principles of reducing peak flame temperatures, delaying but completing the combustion and increasing the heat transfer (increased emissivity of the flame). It may be associated with a modified design of the furnace combustion chamber.
Fuel selection/low-N fuel	The use of fuels with a low nitrogen content reduces the amount of NO _x emissions from the oxidation of nitrogen contained in the fuel during combustion. The combustion of CNCG or biomass-based fuels increases NO _x emissions compared to oil and natural gas, as CNCG and all wood-derived fuels contain more nitrogen than oil and natural gas. Due to higher combustion temperatures, gas firing leads to higher NO _x levels than oil firing.

As shown in Table 4 above, according to the European Commission (2014) the Best Available Technique in lime kiln is to use a combination of technologies. The BAT conclusion document did not give a description for “Good mixing of fuel and air”.

4.2 Regulations of the USA

The U.S. Environmental Protection Agency (EPA) has established National Ambient Air Quality Standards (NAAQS) for NO₂ and tropospheric ozone. The NAAQS define necessary levels of air quality to protect public health (primary standard) and public welfare (secondary standard) from any known or anticipated adverse effects of pollution. According to the standards, the primary and secondary levels for NO₂ are 0.053 parts per million (ppm) (100

micrograms per cubic meter). The level is given as annual arithmetic mean concentration, which describes the concentration in the ambient air. (U.S. Environmental Protection Agency 1999, 1)

In the USA, the levels for lime kilns are given regionally. For example, San Joaquin Valley Air Pollution District in California has established the following limits emissions for nitrogen oxide compounds for a lime kiln:

- 43 mg/MJ (0.10 pounds (lb) per million Btu) when burning gaseous fuel
- 51 mg/MJ (0.12 lb per million Btu) when burning distillate fuel oil
- 85 mg/MJ (0.20 lb per million Btu) when burning residual fuel oil

In the above limits, NO_x is given as NO₂. The Montana Department of Environmental Quality has also set the NO_x limit that applies to rotary kilns at 45 kg/h (100 lb/hr). Emission limits are very strict when compared to the common emission limits in Table 2, although there is no indication of where oxygen content values have been measured. (San Joaquin Valley Air Pollution Control District 2013, Montana Department of Environmental Quality 2013, 14)

4.3 NO_x emissions data according to the BAT enquiry

According to the European Commission 2013, NO_x emissions from rotary kilns range from between 300 and 2000 mg/Nm³ depending on the kiln type and dependent upon the content of nitrogen in the fuels, process temperatures, excess air and product being manufactured. The fuels used and the lime type produced are shown in Figure 10. 68 % of the NO_x emissions from rotary kilns are below 500 mg/Nm³. Specific flue gas flow is as follows:

- 5000 Nm³/t at 11 % for LRK (long rotary kiln)
- 4000 Nm³/t at 11 % for PRK (rotary kiln with preheater),

and the specific nitrogen oxide flow is the range between 1.5 - 10 kg/t lime for LRK and 1.2 - 8kg/t lime for PRK (European Commission 2013, 229).

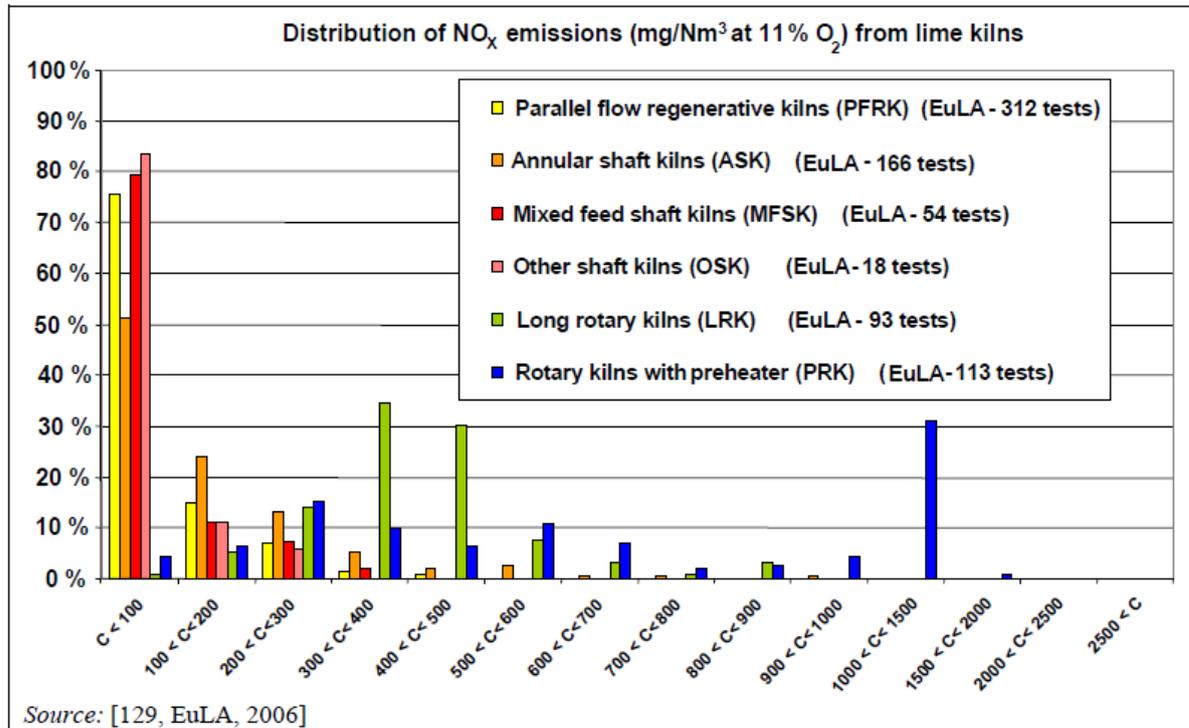


Figure 10. NO_x emissions measured from different types of lime kilns in the EU-27 (spot measurements as half-hourly values) (European Commission 2013, 229).

Data from an enquiry conducted by European Union on used fuel is presented in figures 11 and 12. The annual average NO_x emissions caused by lime kilns are only presented considering the fuels used. For example, LNO_x + CNCG means that kiln has a Low NO_x-burner and Concentrated Non-Condensable Gases are burned. NA means that the selected fuels are not indicated.

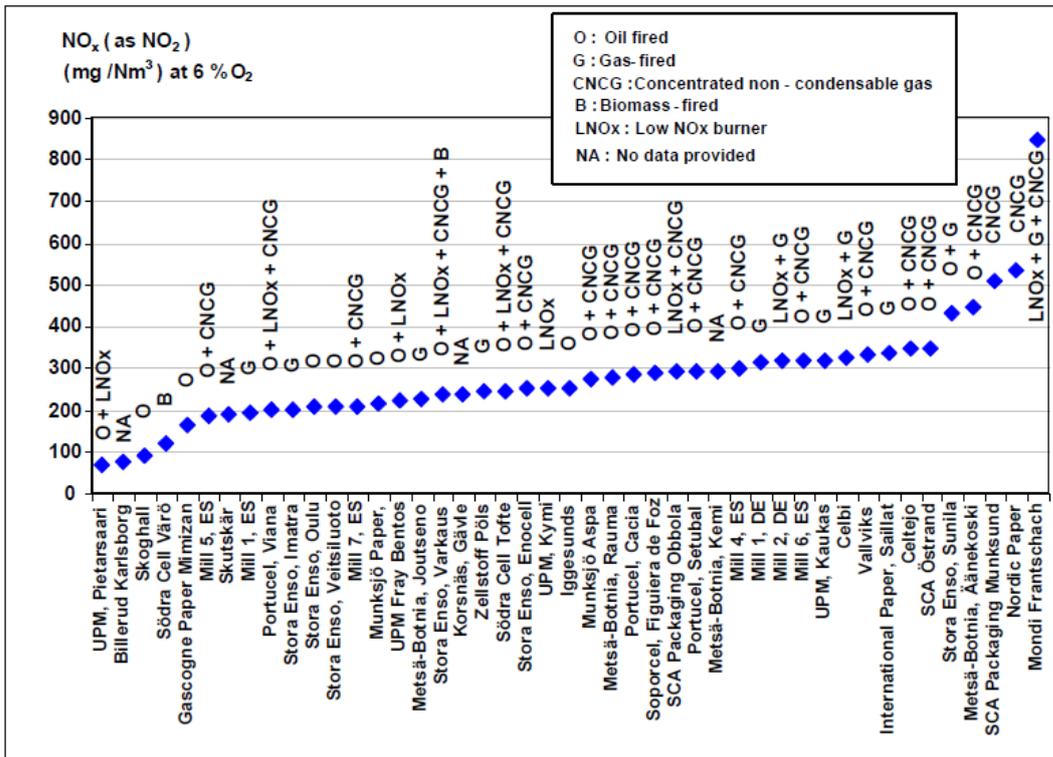


Figure 11. NOx emission concentrations from lime kilns for various fuels (European Commission 2015, 335)

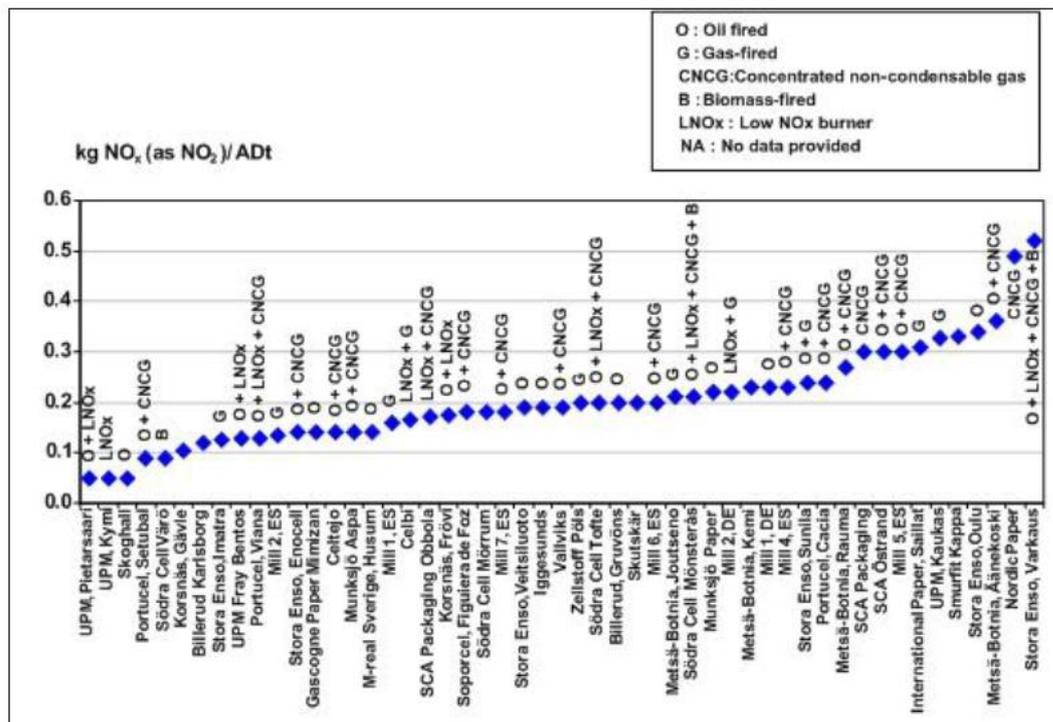


Figure 12. NOx emission loads from lime kilns for various fuels (European Commission 2015, 336)

4.4 Sanctions and incentives relating to NO_x emissions

The three terms 'charges', 'taxes' and 'environmental fees' are largely interchangeable in terms of their effects. They are part of different methods aimed at reducing emissions. Pollution fees, charges and taxes are collected at all levels of government and are among the most prevalent economic incentives in use today. (National Center for Environmental Economics 2004, 3)

Sweden has been imposing a nitrogen oxide emission charge of 4.43 € (40 SEK) per kg on energy producers since 1992. Revenues are rebated to the sources of the tax based on their energy generation. The imposed standard rates are 600 mgNO_x/MJ for gas turbines and 250 mgNO_x/MJ for other installations. These standards give polluters a strong incentive to install measuring equipment, because without measuring equipment the average emission level applied is 1.5 times greater. (National Center for Environmental Economics 2004, 17)

The Air Law regulates emissions in China. For emissions, pollution levies are applied to emissions in excess of the standard. For example, a fee of €0.01/kg (0.08 yuan/kg) applies to NO_x emissions in excess of the standards. China is fighting against emissions to air and is aiming to reduce its NO_x emissions. (National Center for Environmental Economics 2004, 18)

Sanctions and incentives encourage supplier and plant owners to develop and invest in NO_x removal equipment. The aim is to develop equipment for existing applications and completely new devices.

5 NO_x REDUCTION BY COMBUSTION CONTROL

NO_x abatement and control technologies are extensive and complex issues. NO_x reduction methods can be divided into primary and secondary methods. Primary methods affect the combustion process. In primary methods, the combustion process is modified so that less NO_x will exit the furnace. Secondary methods clean flue gas. NO_x is removed from flue gas without affecting the combustion process. Primary NO_x reduction methods are often cheaper and simpler than secondary methods. (U.S. Environmental Protection Agency 1999, 8)

When comparing the efficiency of the reduction or removal of NO_x, it is important to know the actual and reduced concentrations of NO_x in flue gas. Many new lime kilns embodying NO_x prevention methods in their design generate less NO_x than old lime kiln burner systems. That is why NO_x relative values are not comparable. Table 5 presents principles or methods used to reduce NO_x. (U.S. Environmental Protection Agency 1999, 8)

Table 5. NO_x Control Methods (U.S. Environmental Protection Agency 1999, 9)

Abatement or Emission Control Principle or Method	Successful Technologies	Pollution Prevention Method (P2) or Add-on Technology (A)
1. Reducing peak temperature	Flue Gas Recirculation (FGR) Natural Gas Reburning Low NO _x Burners (LNB) Combustion Optimization Burners out of Service (BOOS) Less Excess Air (LEA) Inject Water or Steam Over Fire Air (OFA) Air Staging Reduced Air Preheat Catalytic Combustion	P2 P2 P2 P2 P2 P2 P2 P2 P2 P2 P2
2. Reducing residence time at peak temperature	Inject Air Inject Fuel Inject Steam	P2 P2 P2
3. Chemical reduction of NO _x	Fuel Reburning (FR) Low NO _x Burners (LNB) Selective Catalytic Reduction (SCR) Selective Non-Catalytic Reduction (SNCR)	P2 P2 A A
4. Oxidation of NO _x with subsequent absorption	Non-Thermal Plasma Reactor Inject Oxidant	A A
5. Removal of nitrogen	Oxygen Instead of Air Ultra-Low Nitrogen Fuel	P2 P2
6. Using a sorbent	Sorbent in Combustion Chambers Sorbent in Ducts	A A
7. Combinations of these Methods	All Commercial Products	P2 and A

A combination of different NO_x removal methods can also be applied to reducing NO_x emissions. Combining various methods improves NO_x reduction. Nitrogen oxides are formed only under certain conditions. When these conditions are reduced or not realized, the formation of nitrogen oxides is reduced. NO_x reduction techniques for stationary applications are shown in Figure 13. (Hakkarainen 2014, 40)

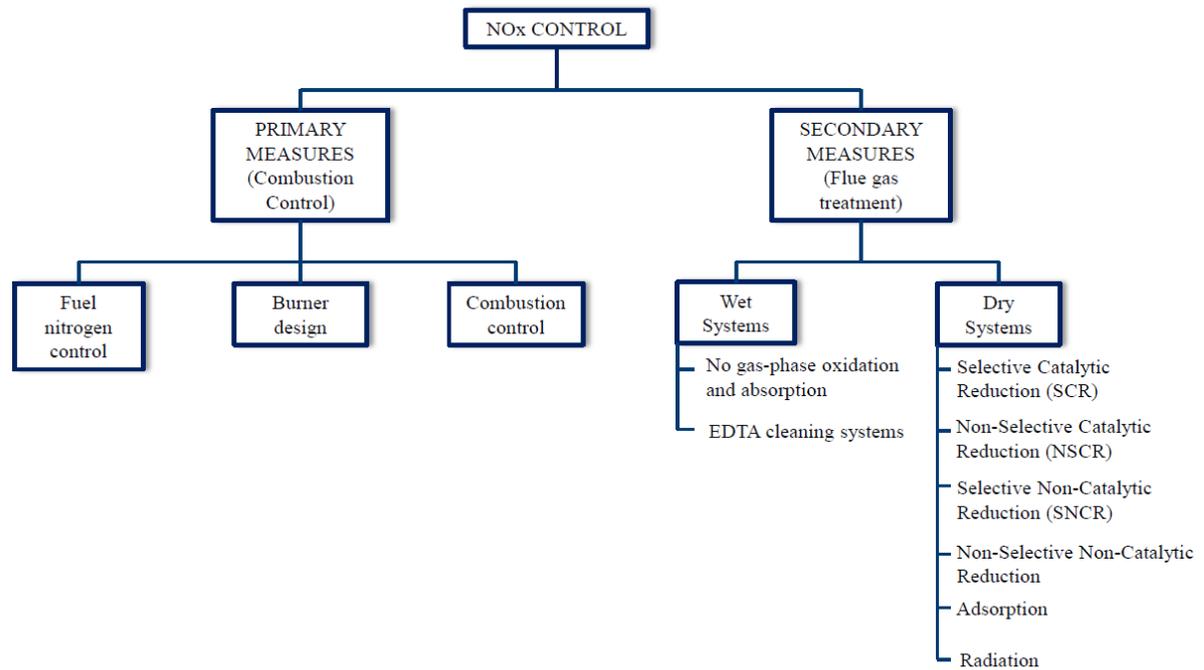


Figure 13. NO_x reduction techniques for stationary applications (Modified Hakkarainen 2014, 41)

A detailed list of external combustion NO_x limiting technologies according to the U.S. Environmental Protection Agency (1999) is presented in Appendix II.

5.1 Reducing temperature

This technique dilutes concentrations of NO_x with an excess of fuel, air, flue gas, or steam. Combustion controls use different forms of this technique and are different for fuels with high and low nitrogen content. Control of NO_x from the combustion of low-nitrogen fuels such as gas and oil can be seen as lean versus rich fuel and air ratios. This technique generates higher temperatures that in turn generate higher concentrations of thermal NO_x. (U.S. Environmental Protection Agency 1999, 10)

According to the U.S. Environmental Protection Agency (1999), combustion temperature may be reduced by:

1. using fuel-rich mixtures to limit the amount of oxygen available
2. using fuel-lean mixtures to limit temperature by diluting energy input
3. injecting cooled oxygen-depleted flue gas into the combustion air to dilute energy
4. injecting cooled flue gas with added fuel
5. injecting water or steam

Low-NO_x burners are based partially on this principle. The aim of this technique is to reduce the temperature of combustion products with excess fuel, air, flue gas or steam. This method keeps the great majority of nitrogen from becoming ionized. (U.S. Environmental Protection Agency 1999, 10)

5.1.1 Staging of combustion air

Combustion air is divided into two streams. The first stream is mixed with fuel in a ratio that generates a reducing flame, and the second stream is injected downstream of the flame and makes the net ratio slightly excess air. Nitrogen oxide emissions can be controlled by adjusting the primary air distribution and splitting burning air into primary, secondary and tertiary air. The kiln temperature profile, flame shaping and adjustment affect the combustion temperature and NO_x formation. (U.S. Environmental Protection Agency 1999, 16, European Commission 2015, 243)

5.1.2 Flameless combustion

The technology is called high temperature air combustion (HiTAC). It is an industry-proven combustion method allowing emissions reduction and combustion process improvement. The main feature of HiTAC combustion technology is propagation of the combustion process to almost total furnace volume and carrying out the combustion process at low oxygen concentration. In HiTAC technology, fuel and combustion air are injected directly into the combustion chamber by separate nozzles. (Szewczyk et al. 2010, 3)

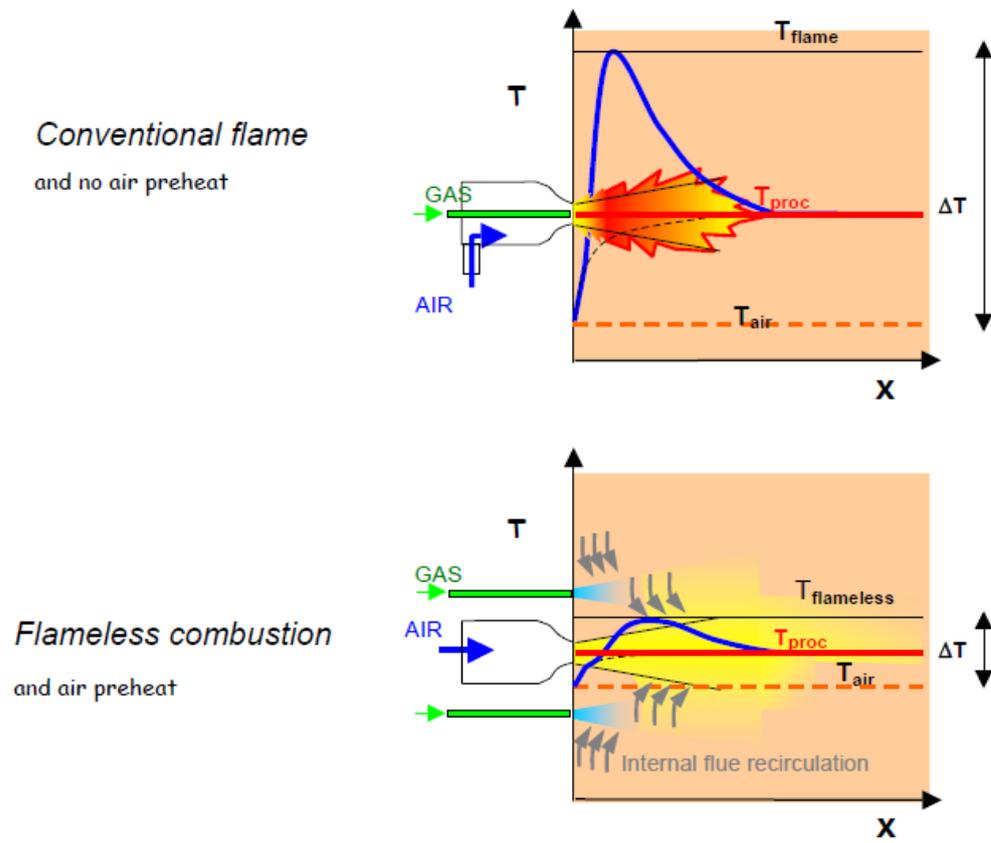


Figure 14. High velocity gas burner: flame and flames firing (Milani & Wüning 2012, 4)

The principle of flameless combustion is presented in Figure 14. Control of the temperature distribution and the composition of flue gas mean that there are no temperature peaks with a high fraction of radicals. Both temperature and the amount of radicals play an important role in all NO_x creation mechanisms. Using the HiTAC, and thus avoiding the peak temperature and high concentration of radicals typical of conventional combustion technology, makes NO_x creation very low. (Szewczyk et al. 2010, 4)

5.1.3 Steam or water injection

Steam/water injection is a common technique. The injection of water or steam changes the stoichiometry of the mixture and increase steam by burning calorie dilutions. Both these actions reduce the combustion temperature. Thermal NO_x is not formed in as great a concentration if temperature is sufficiently reduced. (U.S. Environmental Protection Agency 1999, 16)

Steam or water can be mixed to the air flow to reduce combustion temperature. In one case, the combustion temperature was decreased below 760 °C to limit NO_x generation to about 40 ppm. This can increase the CO emissions and unburned hydrocarbons due to incomplete burning. These can be burned by a catalyst, afterburner or another stage of combustion. Using water spray to reduced peak temperature will increase the heat combustion of a kiln. (U.S. Environmental Protection Agency 1999, 20)

5.1.4 Flue gas recirculation

The recirculation of combustion products is a technique to reduce flame temperature. The recirculation of cooled flue gas reduces the temperature by diluting the combustion air. The oxygen content is decreased causing heat reduction in the flame. The reduction of temperature decreases NO_x concentration. (U.S. Environmental Protection Agency 1999, 15)

Flue gas recirculation (FGR) is a good technique to reduce NO_x emissions in various types of combustion process. About 25 % of recirculated flue gases through the burner reduce NO_x emissions down to 25 % of normal levels. (Eclipse 1992, 1)

Flue gas recirculation decreases NO_x in two ways:

1. The cooled, mostly inert, recirculated flue gas serves to cool the incinerator, adsorbing heat and lowering peak flame temperatures.
2. When mixed with the combustion air, the oxygen content is reduced. The reduction in oxygen content has the effect of limiting NO_x production by reducing one of the ingredients needed for the reaction that produces NO_x. (Eclipse 1992, 1)

In a lime kiln, cooled flue gas should be channeled to the burner end. However, it should be noticed that calcination reactions require high temperature and a certain residence time in the lime kiln, then a significant reduction in temperature will affect the dimensioning of the kiln. The application of flue gas recirculation to a lime kiln is problematic, because the peak flame

reduction prevents proper lime generation, the long flame weakens the lime quality, and the stack at the burner end requires additional ducting. An FGR application has never been installed in lime kiln, and FGR is considered a technically infeasible control technology for lime kilns. (Hakkarainen 2014, 44)

5.2 Reducing residence time

Reducing residence time at high combustion temperatures can be done by ignition or injection timing with internal combustion engines. It can also be done by restricting the flame to a short region in which the combustion air becomes flue gas. The short residence time at peak temperature keeps the majority of nitrogen from becoming ionized. This bears no relationship to the total residence time of a flue gas. NO emission can be reduced when increasing the delay time of the combustion in NO reducing conditions. (U.S. Environmental Protection Agency 1999, 10)

5.3 Fuel reburning

Increase in fuels to the recirculation of cooled flue gas dilutes the combustion air, and primary combustion temperature can be reduced. Added fuel can be natural gas, oil spray or pulverized coal. For NO_x emission reductions, added fuel is consumed only partially and at a later stage combustion air nozzles or over-fire-air completion of burning are used. This is quite similar to flue gas recirculation. (U.S. Environmental Protection Agency 1999, 16)

Rotation of the rotary kiln causes fuel feeding to be possible only at the end of the burner. Avoiding some of the thermal NO_x compounds can be part of the fuel burn at a reduced temperature. This allows interaction between the local reduction conditions at the secondary firing point and with NO_x generated in the primary combustion zone. (Hansen 2002, 1)

Recirculation of flue gases is effective in the combustion of natural gas, cutting of temperature peaks to reduce thermal NO_x is essential. Staged feeding of fuel has similar effects. Overly intense burning may cause incomplete combustion, which in turn will cause other emissions and inefficiencies. (Jalovaara et al. 2003, 49, 72)

5.4 Low-NO_x burner

At the burner level, a controlled NO_x reduction produced by the combustion process is called a low-NO_x burner (LNB). The same low-NO_x burner technology is used in steam boilers and in power plants as in lime reburning. Low-NO_x burners are engineered so that flame temperature can be reduced, also reducing thermal and NO_x rooted in fuel. The primary air is divided into two streams, which are necessary to ensure flame stability and the correct shape of the flame. The low-NO_x burner construction is designed so that the primary air portion reduces NO_x formation in combustion air. (European Commission 2015, 338)

Generally in air staging, 75 – 85 % air is fed to the primary combustion zone with the needed fuel for the boiler. While in the lime kiln, the portion of primary air is only about 15-20 % of the total air. This enriches the fuel flame zone where the formation of NO_x is slowed down by the lack of oxygen to provide complete combustion of fuel under combustion conditions. In other words, residual air is fed outside the primary combustion zone for complete combustion of the fuel. According to Bell et al. (2015), low-NO_x burners achieve NO_x reductions of 40 – 50 % in gas-fired kilns and 30 – 40 % for oil-fired and coal-fired kilns. (Bell et al. 2015, 5)

In fuel staging, the low-NO_x burner works opposite air staging. The air is fed into about 60 – 70 % of the fuel in the primary zone. The low temperature means that NO_x formation is slowed down. Prompt NO_x is also reduced, because the burner is highly oxidized. According to Bell et al. (2015), staged fuel can reduce NO_x formation by up to 60 % for gas-fired kilns and, when applied to coal or oil-fired kilns, requires the use of reburning technology. (Bell et al. 2015, 5)



Figure 15. Modern Low NO_x Burner for Oil/Gas Fuels (Bell et al. 2015, 5)

Low-NO_x burner efficiency depends on fuel, particle size and air distribution between burners. The reduction stage in emissions depends on the fuel characteristics such as low fuel ration and nitrogen content. Low-NO_x burners using liquid fuels can reach nearly the same emission levels as solid fuels or reduction of about 300 – 500 mg/m³ occurs. The burner retrofits have caused problems with particulate emissions because particle precipitators are lacking from oil boilers and low oxygen content in gas burning. (Finnish Environment Institute 2001, 53)

5.5 Removal of nitrogen from combustion

There are two options to remove nitrogen from combustion: (1) using oxygen instead of air in the combustion process; or (2) using ultra-low nitrogen content fuel to form less fuel NO_x. Method 1 produces an intense flame and needs to be diluted. Method 2 reduces NO_x formation from fuel, but does not eliminate NO_x completely. (U.S. Environmental Protection Agency 1999, 10)

5.5.1 Less Excess Air

The excess air flow for combustion corresponds to the produced NO_x amount. Less excess air (LEA) is used to improve kiln combustion efficiency and reduce NO_x emissions. The objective

of LEA is for the kiln to be used at the lowest air level that produces efficient and complete combustion. The effectiveness of the heat transfer surfaces of the kiln also affects the amount of excess air, which again reduces the flue gas stream. (Bell et al. 2015, 11)

According to Bell et al. (2015), low excess air is essentially a burner optimization strategy that should be part of normal kiln operation. With current fuel features and kilns, it should be noticed that process control may be required to identify the optimum operating point for tuning and combustion testing (Bell et al. 2015, 11).

5.5.2 Selection for fuels

The selection of fuels has a major impact on emissions from lime kilns. The combustion of natural gas in lime kiln produces more NO_x emissions than oil, even though oil contains organic nitrogen. The high temperature of a natural gas flame causes thermal NO_x. The combustion of sawdust, pulverized wood or the gasification of biomass gases in the lime kiln also increases NO_x emissions. Similarly, the most common burning of malodorous gases increases NO_x emissions, as malodorous gases carry excess nitrogen into the kiln. (European Commission 2015, 334)

Heavy fuel oil has a nitrogen content of 0.3 - 0.4 % in dry solid. The nitrogen content of natural gas is lower (<1 %) than the nitrogen content of biogas, which is 0 – 25 %. The nitrogen content of wood powder is affected by the nitrogen content of woodchips, bark and sawdust from 0.1 - 0.8 % of the dry solid content. Avoiding the use of high nitrogen content fuels, leads to lower NO_x emissions. (Alakangas et al. 2016, 206; Alakangas 2000, 156)

6 NO_x REMOVAL BY POST-COMBUSTION METHODS

Post-combustion methods are also called secondary methods for NO_x removal. They are based on nitrogen oxide reduction after the burner. Figure 16 shows post-combustion methods.

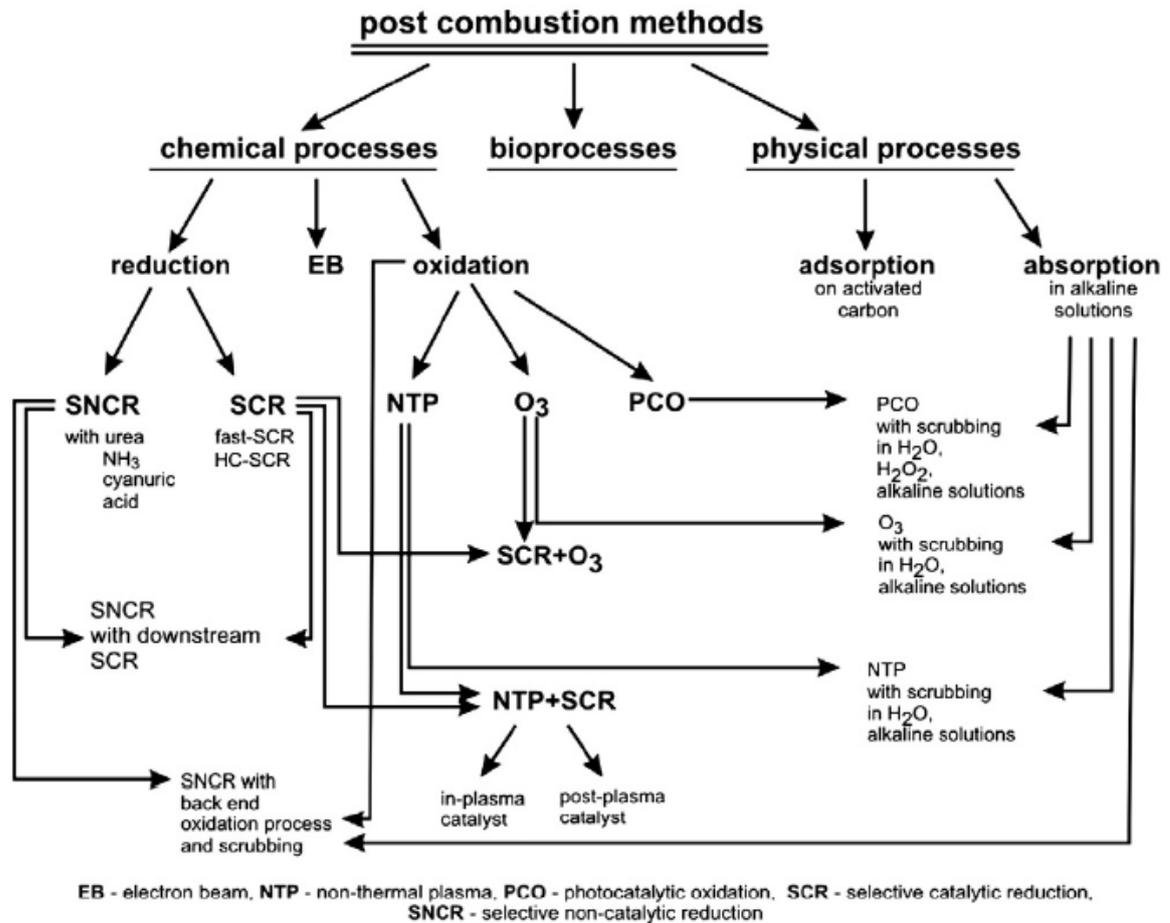
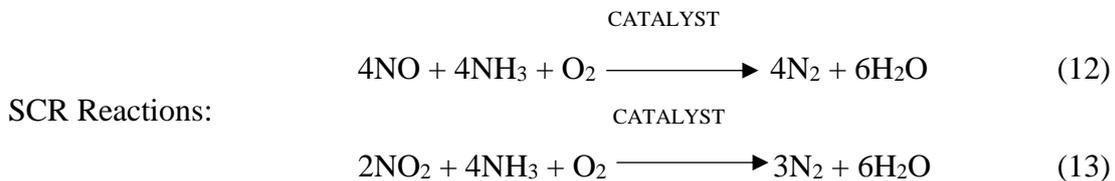


Figure 16. Schematic presentation of described NO_x abatement post-combustion methods (Ledakowicz et al. 2010, 7)

This chapter describes the chemical processes selective non-catalytic reduction SNCR and selective catalytic reduction SCR.

6.1 Chemical reduction of NO_x

This technique chemically removes oxygen from nitrogen oxides. SCR uses ammonia as an additive and SNCR uses ammonia or urea and fuel reburning (FR). Non-thermal plasma is used with a reducing agent, which chemically reduces the amount of NO_x. This principle is also used for low-NO_x burners. The following equations 12 - 14 show simplified reactions for both technologies. (U.S. Environmental Protection Agency 1999, 10)



Most kilns where post-combustion techniques are used to reduce NO_x emissions use urea or ammonia. If urea is used, it is decomposed as part of the flue gas reaction as the ammonia required for the reaction. (Bell et al. 2015, 13)

6.2 Selective Non-Catalytic Reduction

Selective non-catalytic reduction (SNCR) is a method for the chemical reduction of NO_x. The gas temperature of the injection region should be 815 – 1150 °C (1500 – 2100 °F). The reaction rate decreases with low flue gas temperatures and may cause an increase in NO_x content. While, in the highest flue gas temperatures, the NO_x content decreases, NO_x levels may increase due to oxidation. The operating range of SNCR is relatively narrow in the high temperature range, so it is not suitable for all applications. (Bell et al. 2015, 14)

Typical SNCR operating temperatures are presented in Figure 17.

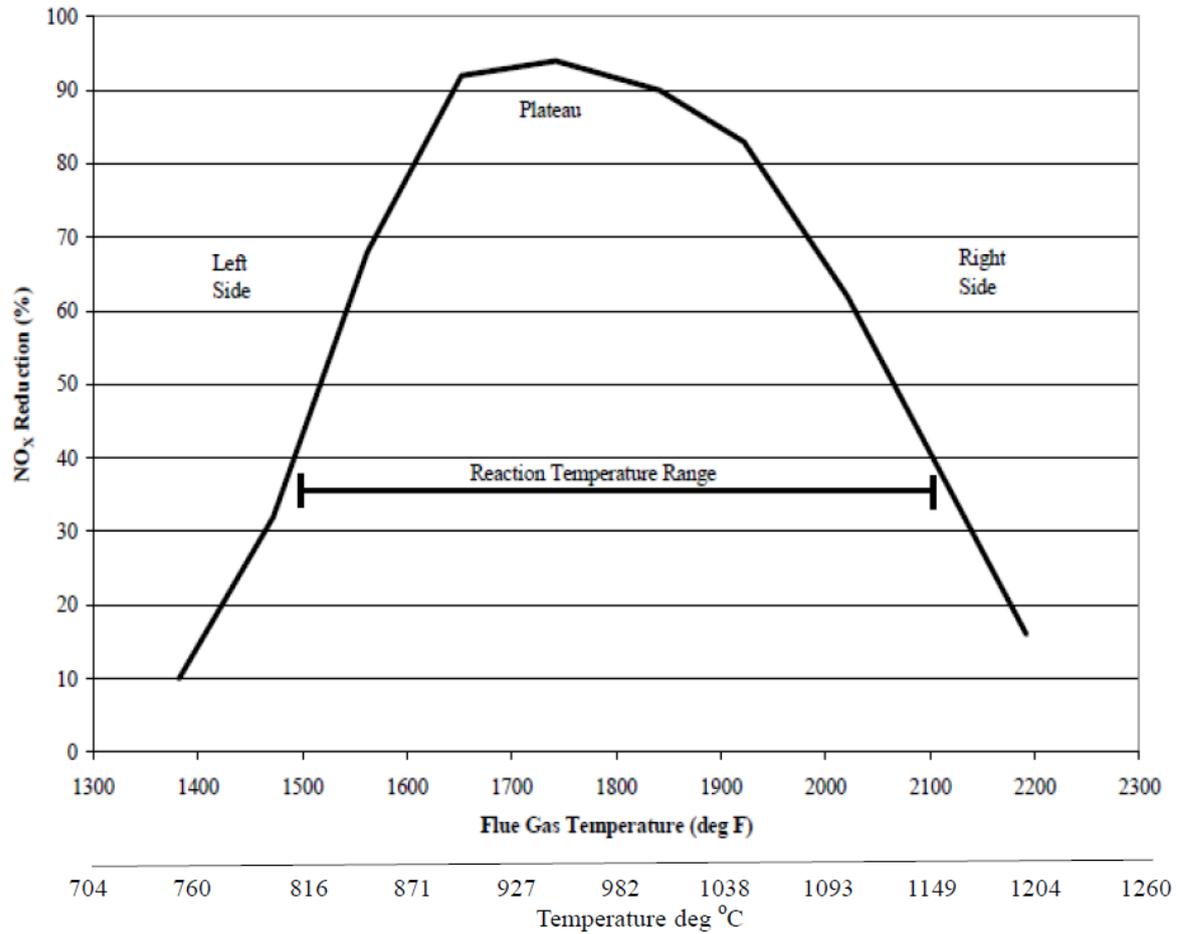


Figure 17. Typical SNCR Operating Curve (Bell et al. 2015, 14)

SNCR design should use multiple injection nozzles to achieve perfect coverage in the kiln. This is accomplished by installing multiple injectors or using retractable lances with multiple nozzles. (Bell et al. 2015, 14)

The SNCR method requires the presence of oxygen to function. In the reaction, the ammonia decomposes into amino radicals (NH_2), which react with nitrogen oxide:



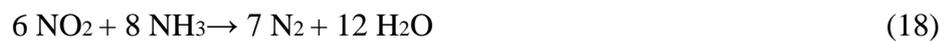
Temperature sensitivity is the main SNCR problem in practice. When the temperature is high, ammonia NH_3 reacts with nitrogen oxide, and when the temperature is lower the NH_3 decomposes slowly, causing significant NH_3 slip. (Kilpinen & Zevenhoven 2004, 4-32)

It is technically difficult to spray ammonia and urea into the rotary kiln through the shell. The technique developed for mid-kiln firing allows spraying once during rotation, but this has been considered impractical for SNCR. A rotating valve for piping can also be installed at the kiln feed end. (Sorrels et al. 2016, 8)

6.3 Selective Catalytic Reduction

The most efficient method for reducing NO_x from flue gases is selective catalytic reduction (SCR). In the process, ammonia is injected into the flue gas duct at a temperature of about 350 – 400 °C. The ammonia reacts with nitrogen oxide NO , producing water and nitrogen. SCR methods have achieved reductions of up to 90 – 95 %. (Kilpinen & Zevenhoven 2004, 4-30)

Chemical reactions are shown in equations 16 -18;



The disadvantage of the use of catalysts is possible corrosion in the flue gas duct causing oxidation of sulfur dioxide to sulfur trioxide, and ammonium sulfate compounds may be added (Raiko et al. 2002, 333).

7 COMPARISON OF AVAILABLE TECHNOLOGIES IN PULP MILLS

7.1 Available technologies in pulp mills

Available and applicable technologies are SNCR, SCR, NO_x-scrubbing and all primary measures in combustion. SNCR and Ozone/ClO₂ scrubbing are used in lime kilns. There are challenges in using these methods in terms of existing and new plants, the use of parameters for temperatures and available chemicals at the plants. (Andritz 2019)

Hydrous ammonia 25 % is injected into the kiln using SNCR technology. Feeding can occur via injection lances with pressurized air or steam. Usually many reagent injection levels are installed. Ammonia is added when the temperature of the flue gases is below 1050 °C. (Andritz 2019)



Figure 18. Injection lances in lime kiln (Andritz 2019)

In Ozone/ClO₂ scrubbing, NO_x is commonly 95 % NO and 5 % NO₂ with very low water solubility. The production and injection of Ozone occurs in the flue gas duct. NO_x is oxidized

by O_3 or ClO_2 to $NO_2/NO_3/N_2O_5$, which is highly soluble and nitrides dissolve to HNO_3 in the scrubber. Neutralization occurs with additives such as $NaOH$ to $NaNO_3$. The chemical reaction is shown in Figure 19. (Andritz 2019)

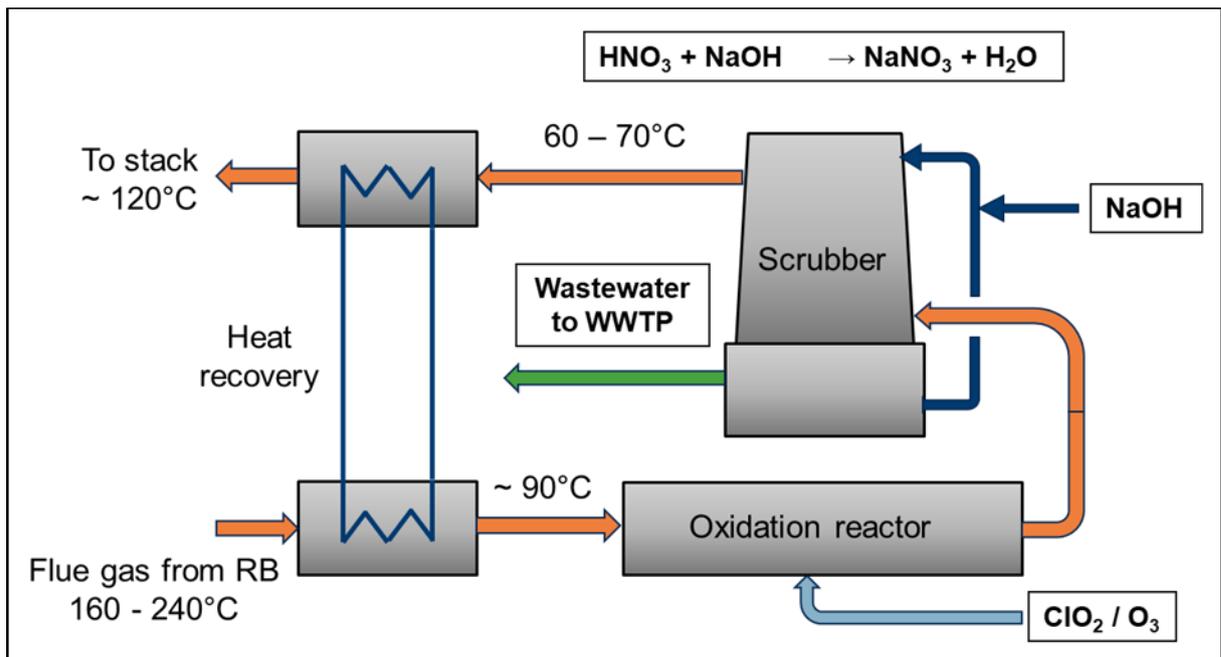


Figure 19. General features ozone/ ClO_2 scrubbing

An invention has been devised to recover ammonia from ammonia-containing material flows in a pulp mill to reduce nitrogen oxide emissions. In the process, the pH of the ammonia-containing material flow is adjusted to more than 10 with alkali and steam is introduced to separate the ammonia from the material flow. Ammonia is used as a chemical in pulp mill combustion plants to reduce harmful nitrogen oxide emissions. (Eneberg et al. 2004)

7.2 Comparison of technologies

When comparing technologies to each other, the effect of the SCR on NO_x reduction is 95 % and the effect of the SNCR is only 50 %. The effect of the NO_x scrubber with ClO_2 is 60–85 %, but operating costs are high for these methods. Table 6 shows a comparison of technologies.

Table 6. Comparison of technologies (Modified Andritz 2019)

	SNCR	SCR	NO _x – Scrubber with O ₃	NO _x – Scrubber with ClO ₂
NO _x removal efficiency	~50 %	> 95 %	> 85 % with single stage	< 60 % with single stage < 85 % with multi stage
Reaction product	N ₂ , H ₂ O	N ₂ , H ₂ O	N ₂ , HCl, HNO ₃ , NaNO ₃ , Na ₂ SO ₄	N ₂ , HCl, HNO ₃ , NaNO ₃ , Na ₂ SO ₄
Reaction temperature	> 850 – 950 °C	> 225 °C	No requirements. Possible to recover waste heat (low temperature)	
New pollutant	Higher NH ₃ , slip	Very little NH ₃	HCl, HNO ₃ , Na ₂ SO ₄	ClO ₂ , HCl, HNO ₃ , Na ₂ SO ₄
Material consumption	Electricity and ammonia water/urea	Electricity and ammonia water. Steam for startup preheating.	Water, electricity, chemicals NaOH, effluent treatment	Water, electricity, chemicals ClO ₂ and NaOH, effluent treatment
Investment	Lowest	Middle	High	Very high
Operation costs	Middle	Low	High	High

8 NO_x REDUCTION IN LIME KILN GAS BURNING

Natural gas is a rock gas, which is recovered as a finished product. The natural gas used in Finland is about 99 % methane and the rest is ethane, propane and nitrogen. Natural gas is often used as a substitute for oil. Its advantages are good combustion efficiency, easy combustion control and wide adjustment range. The ignition limit for natural gas is 650 °C and the effective calorific value is about 36 MJ/m³. Above this temperature, natural gas will burn regardless of the mixture ratio. The flame from natural gas is low-emitting. Significant flue gas emissions from natural gas combustion are nitrogen oxides formed by the nitrogen contained in the combustion air. (Jalovaara et al. 2003, 51 – 53)

The emission limit for nitrogen oxides in gas-fired combustion plants is fixed at NO_x 100mg/m³ by Directive 2010/75/EU of the European Parliament and of the Council. The amount of oxygen is not reported in the directive. (European Commission 2014)

In natural gas burners, combustion air and fuel mixing are essential. Burners are often also oil-fired composite burners and auxiliary fuels can be burned in the same burner. (Andritz 2019)

8.1 The challenges of NO_x emissions for the pulp mill

The challenge for pulp mills is to minimize NO_x emissions from lime kilns to meet future requirements. Increasing energy efficiency does not significantly reduce NO_x emissions in pulp production, but as production increases, NO_x emissions also rise. Mainly fossil fuels like natural gas are used in lime kilns. The use of alternative fuels requires new technology and new investments. Lime kiln disturbances and unplanned shutdowns are having an increasing impact on NO_x emissions.

8.2 Research object and method

The mill was selected as the object of investigation, when using natural gas and pitch oil in the burner of lime kiln, so it was possible to use the existing burner without modification. The mill has continuous measurement of emissions, which also allowed measurements without separate measuring devices. Pitch oil and natural gas are burned simultaneously when the former is available. The amount of pitch oil was normally about 40 % of the total amount of fuel. Its consumption is constant and the consumption of natural gas regulated.

Figure 20 shows fuel feeding and pitch oil termination.

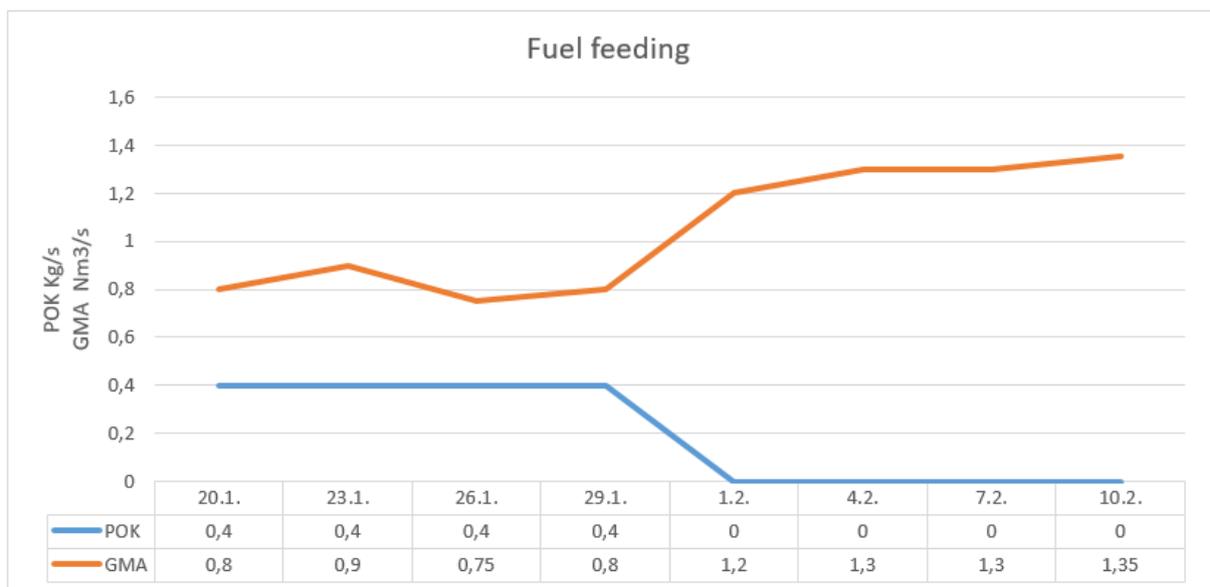


Figure 20. Fuel feeding

In Figure 20, POK is pitch oil and GMA natural gas.

Trend number data was collected from the following locations:

- Natural gas GMA, Appendix III
- Pitch oil POK, Appendix IV
- NO₂ from stack, Appendix V

- Primary air amount, Appendix VI
- Temperature of fire head, Appendix VII
- Temperature of pyrometer, Appendix VIII
- Carbon monoxide, Appendix IX
- Oxygen of feed head, Appendix X
- O₂ from stack, Appendix XI
- Flue gas temperature after cyclone, Appendix XII
- Lime mud feeding, Appendix XIII
- Lime mud flow, Appendix XIV
- Temperature of feed end, Figure 21
- Residual carbonate, Figure 21

Figure 21 shows the locations for causticization and the lime kiln. Only natural gas is in use, dated 14.2.2019.

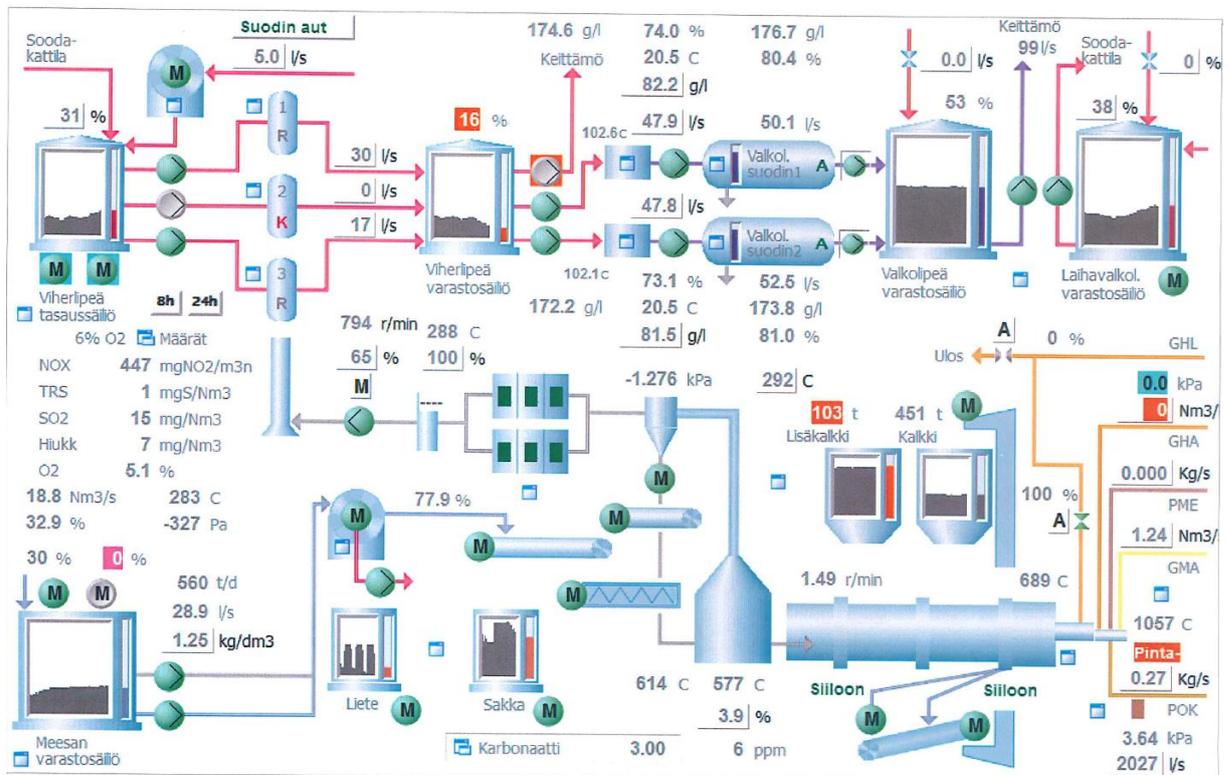


Figure 21. Recausticizing and lime kiln.

Figure 22 shows the fuel feed to the lime kiln, dated 14.2.2019. It also shows pitch oil flow to tank circulation even though feeding to the kiln has been terminated.

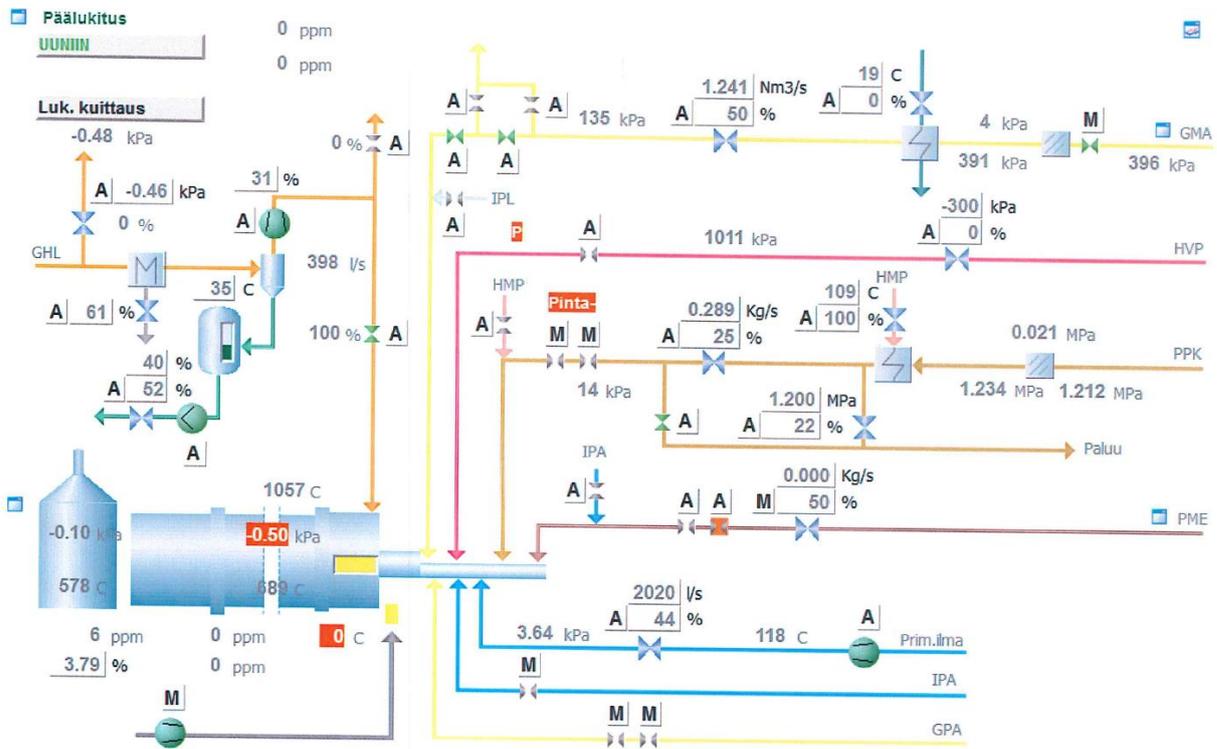


Figure 22. Lime kiln burning

The period during which the research was done was 17.1. – 14.2.2019. The use of pitch oil had been terminated at the end of January and the effect of this on NO_x emissions can be seen in the results. The mill alarm limit for NO_x emissions is 500 mgNO₂/m³n. The research also covered the period 17.12.2018 – 14.1.2019, which shows the effects of short shutdowns on natural gas, pitch oil and NO_x emissions. The research was based on visually obtained measurement curves.

8.3 Pitch oil effects for NOx reduction

Appendix XI and Figure 23 show the effect of pitch oil on NOx emissions. There is a very clear difference when pitch oil is used with natural gas and when pitch oil ends. Pitch oil was terminated at the end of January. The appendix shows the exceedance of the NOx alert limit on 23 January. This was investigated and it was found that the measuring device had encountered an error. No other clear explanation was observed and no deviation was recorded for the period.

Figure 23 shows information from the appendices V, XI and Figure 24.

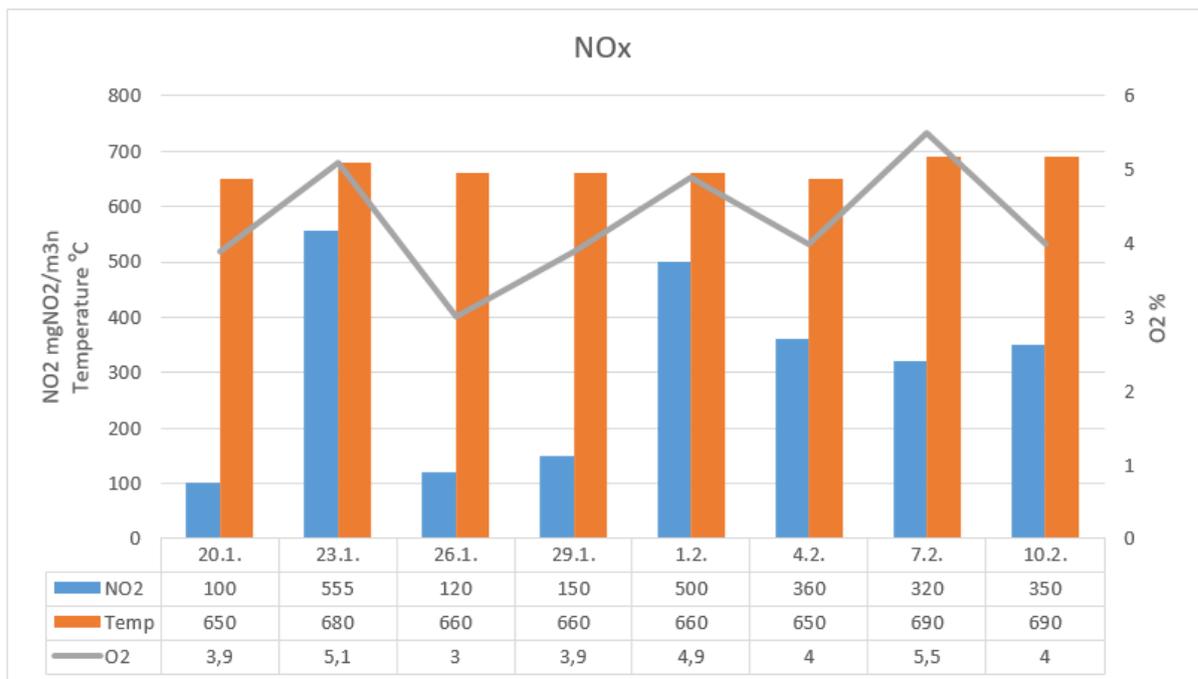


Figure 23. NOx emissions

In Figure 23, NO₂ is NO₂ from the stack, Temp. is the temperature of the fire head and O₂ is O₂ from the stack.

With pitch oil in use, NOx emissions are low at 100 mgNO₂/m³n, while natural gas alone has an NOx emissions level of about 450 mgNO₂/m³n or close to the alert limit. The fire head

temperature is approximately 700 °C and the feed head temperature approximately 580 °C, when using natural gas only. The pitch oil does not appear to have an effect on the temperature of the fire head. Figure 24 shows temperature of fire head.

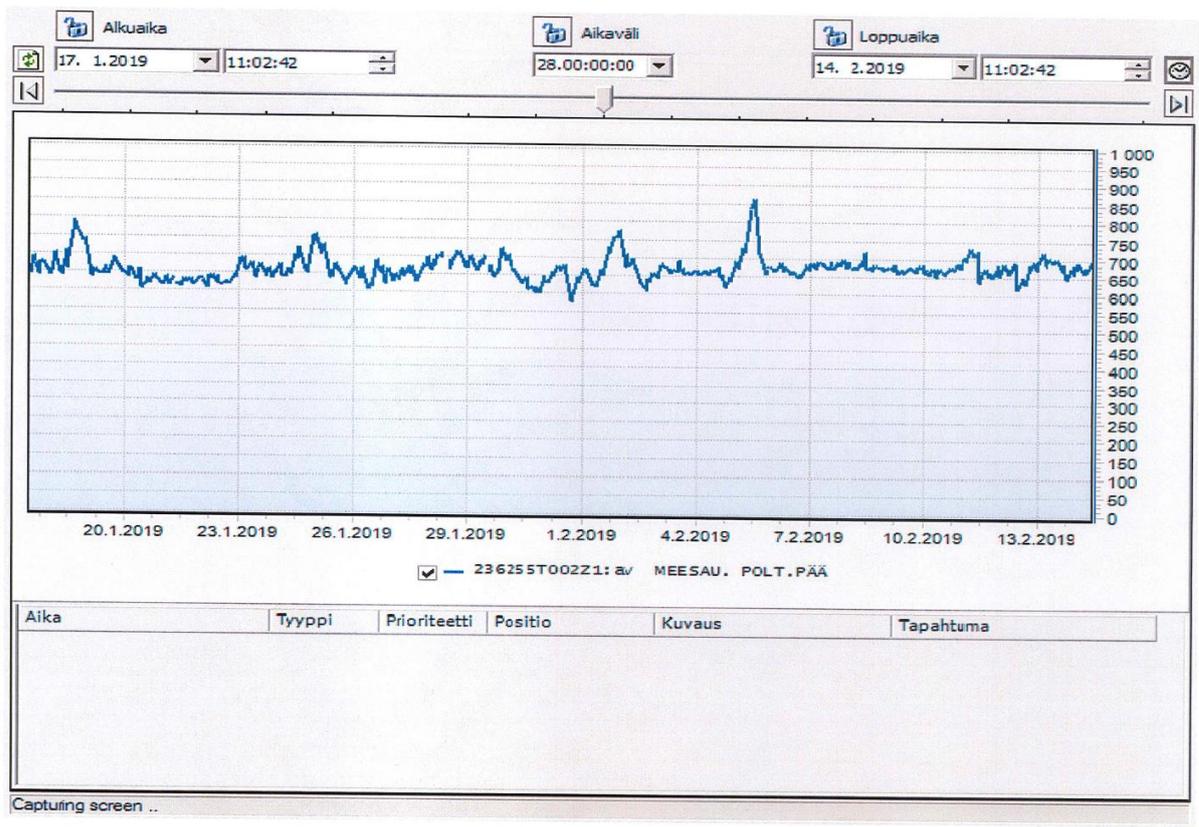


Figure 24. Temperature of the fire head

To compare the results, they are changed to normal conditions. The emission measurements are converted to a specific residual oxygen content, which depends on the main fuel used by the plant. Figure 25 shows the factor by which NO_x is reduced to an O₂ concentration of 10 %.

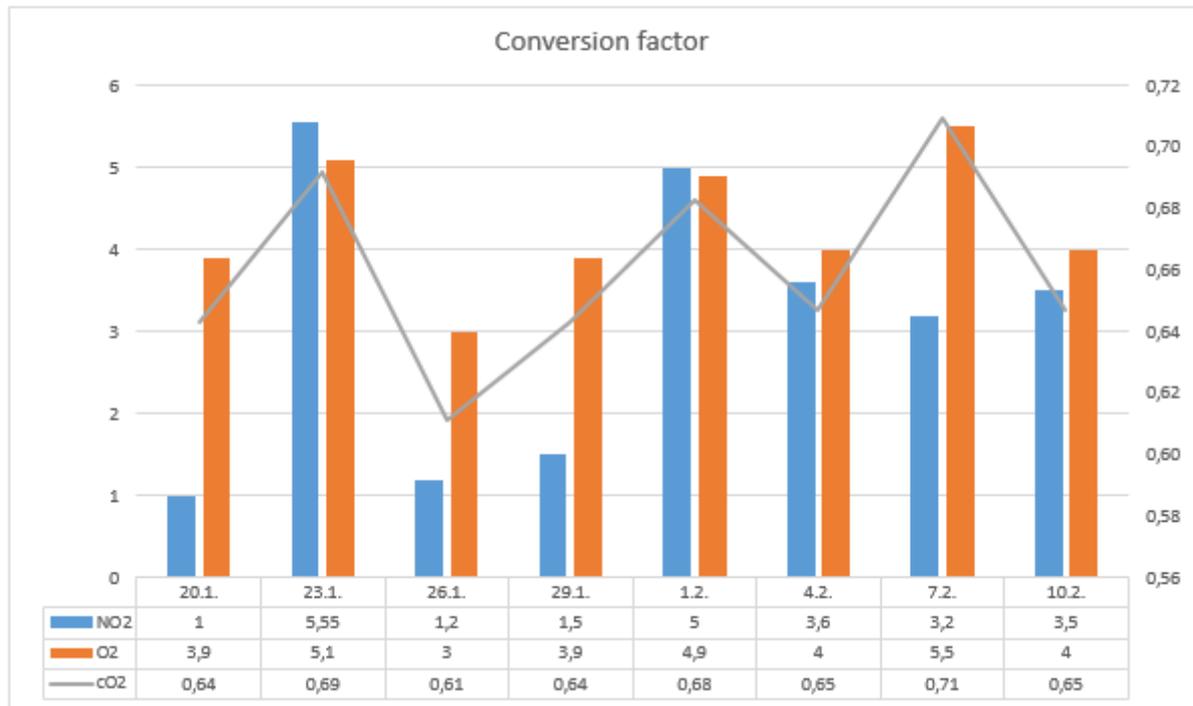


Figure 25. Conversion factor

In Figure 25, NO₂ is NO₂ from the stack, O₂ is O₂ from the stack and cO₂ is the conversion factor.

The measurement results are reduced to the desired oxygen concentration using Equation 19 as shown. Oxygen conversion is done on the basis of dry gases, because the limit values are defined as the concentrations of dry gases at a given dry gas oxygen concentration. (VTT 2007, 52)

$$C_{\text{red}} = C_{\text{mea}} \times ((21 - O_{2,\text{red}})/(21 - O_{2,\text{mea}})), \text{ where} \quad (19)$$

C_{mea} = measured concentration (ppm)

$O_{2,\text{red}}$ = reduction concentration used (e.g. 10 %)

$O_{2,\text{mea}}$ = measured oxygen content (%)

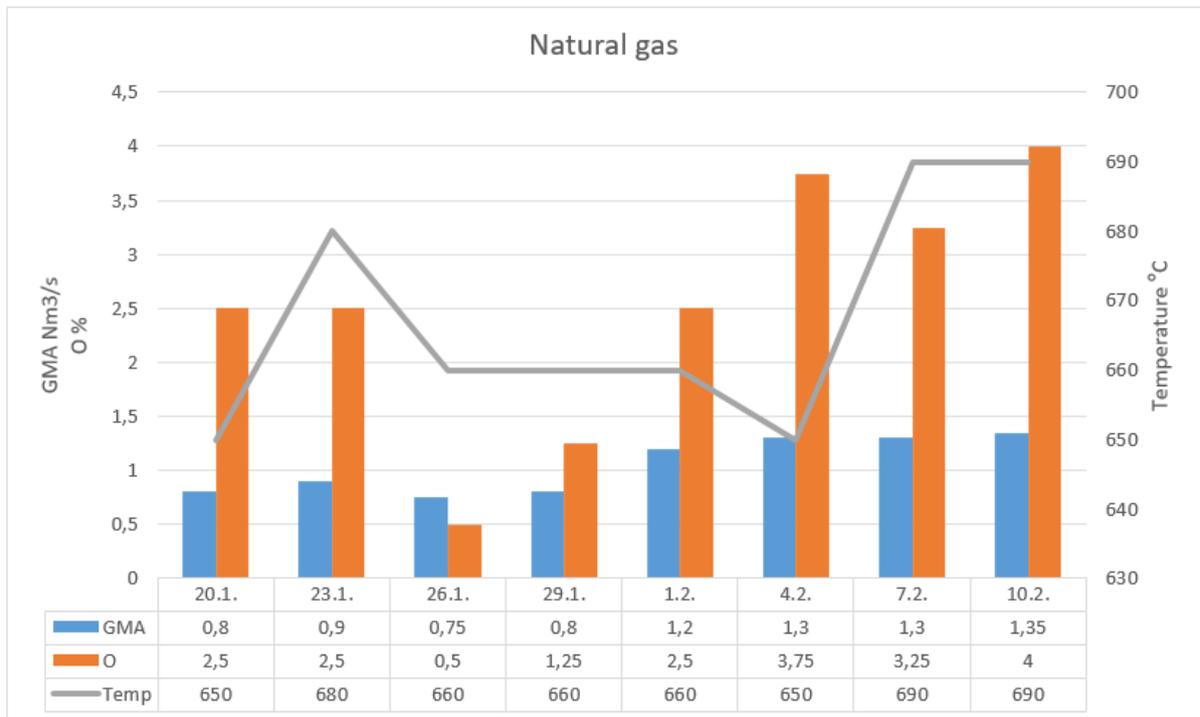


Figure 26. Natural gas feeding

In Figure 26, GMA is natural gas, O is the oxygen of the feed head and Temp. is the temperature of the fire head.

Natural gas feeding is regulated. The termination of pitch oil is reflected in the increase in natural gas and oxygen. In order to keep CO emissions low, more oxygen must be supplied.

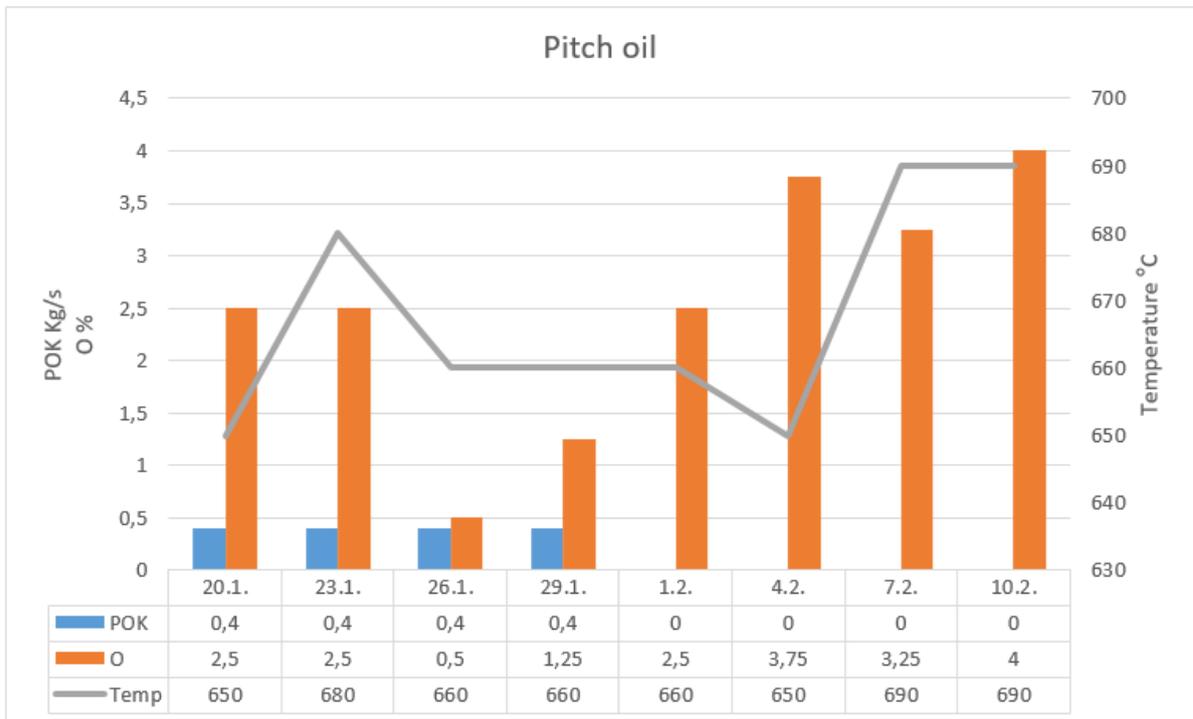


Figure 27. Pitch oil feeding

In Figure 27, POK is pitch oil, O is the oxygen of the feed head and Temp. is the temperature of the fire head.

Pitch oil feeding is uniform. Oxygen and temperature are increasingly affected by the termination of pitch oil. In appendices XV, XVI and Figure 28, it can be seen that the shutdown did not have a significant impact on NO_x emissions. Only when the burner is started has been clear increase in NO_x emissions after shutdown, but the increase has been momentary.

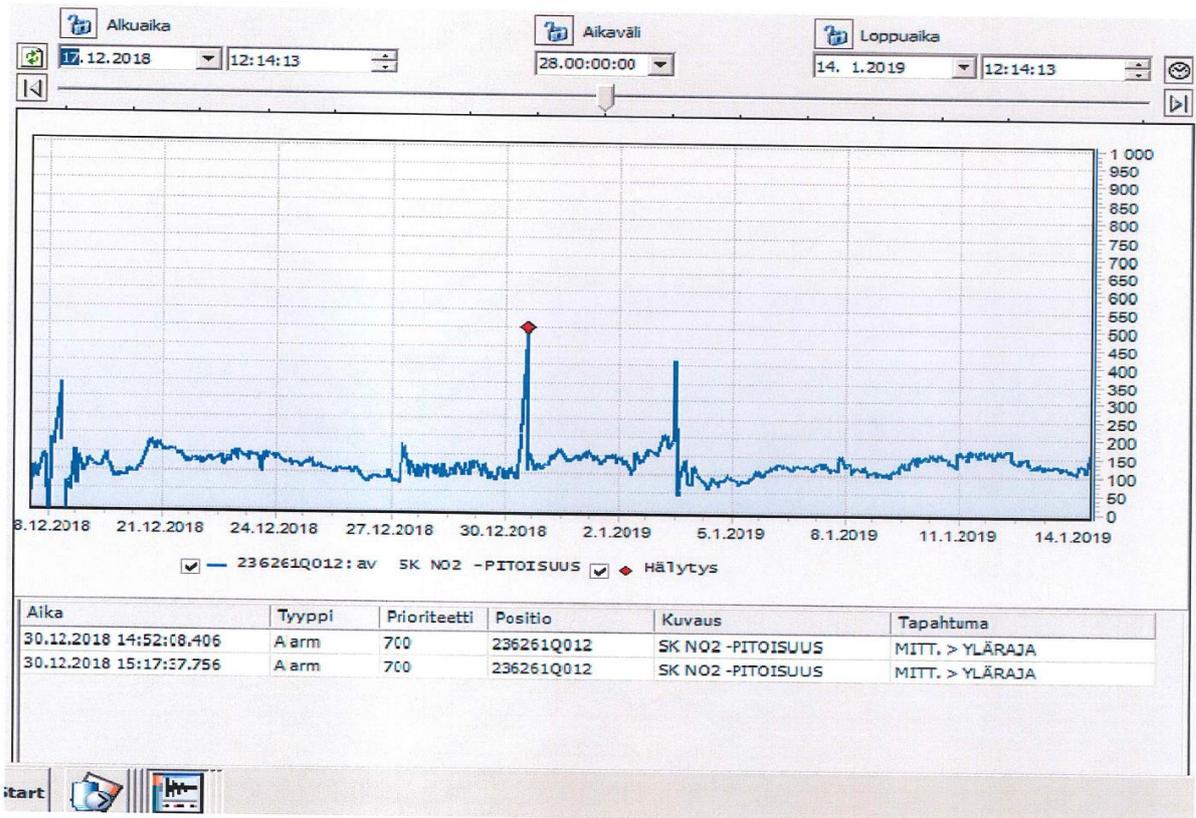


Figure 28. NO₂ from the stack 17.12.2018 – 14.1.2019

8.3.1 Other measurement objects

The effect of pitch oil on other locations where trend information was available was examined. Primary air has been kept constant during the period under review. Pitch oil termination has no effect and there is no need to add primary air (Appendix VI). The temperature of the pyrometer during pitch oil is slightly higher than that of natural gas alone, as shown in Figure 29.

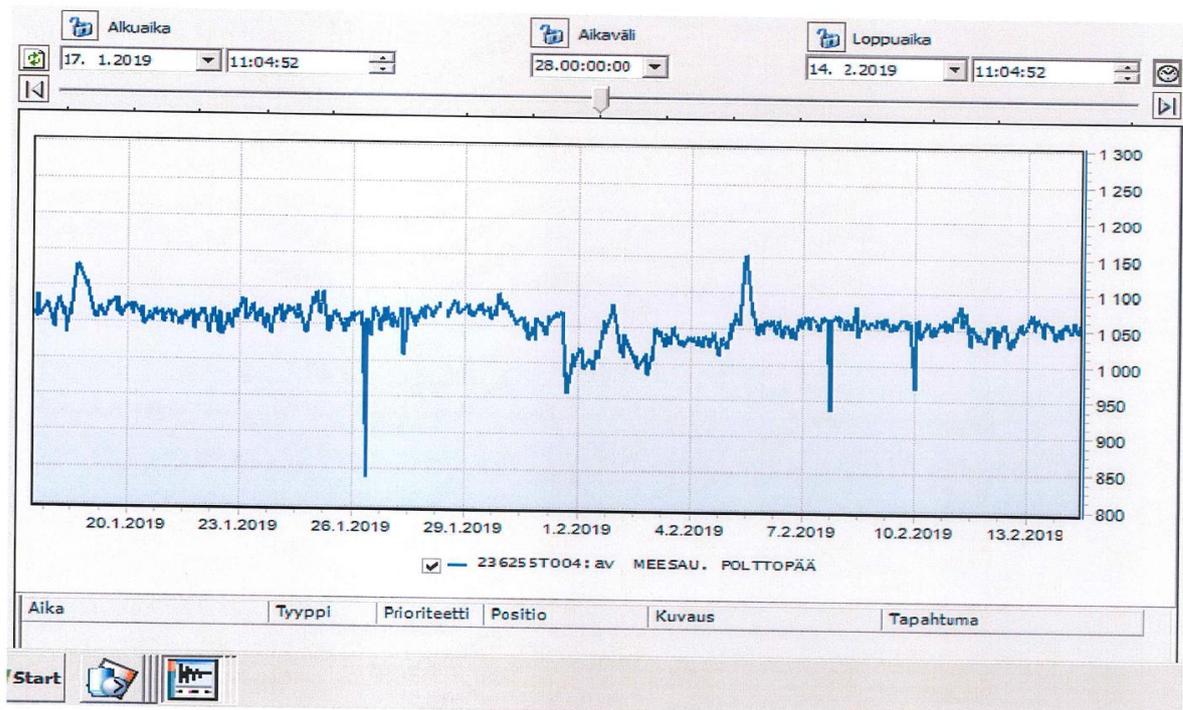


Figure 29. Temperature of the pyrometer

During the use of pitch oil, some carbon monoxide emissions are generated compared to the use of natural gas alone (Appendix IX). Oxygen remains relatively uniform with pitch oil. It rises somewhat during natural gas only (Appendix X). The O_2 content remains constant so has no effect on the termination of pitch oil, which can be seen in Figure 30. After the cyclone, the temperature of the flue gas remains the same throughout the period considered (Appendix XII). Lime mud supply and flow remain constant throughout the period under review (Appendices XIII and XIV). Pitch oil would not appear to have any effect on other measured trend number data.

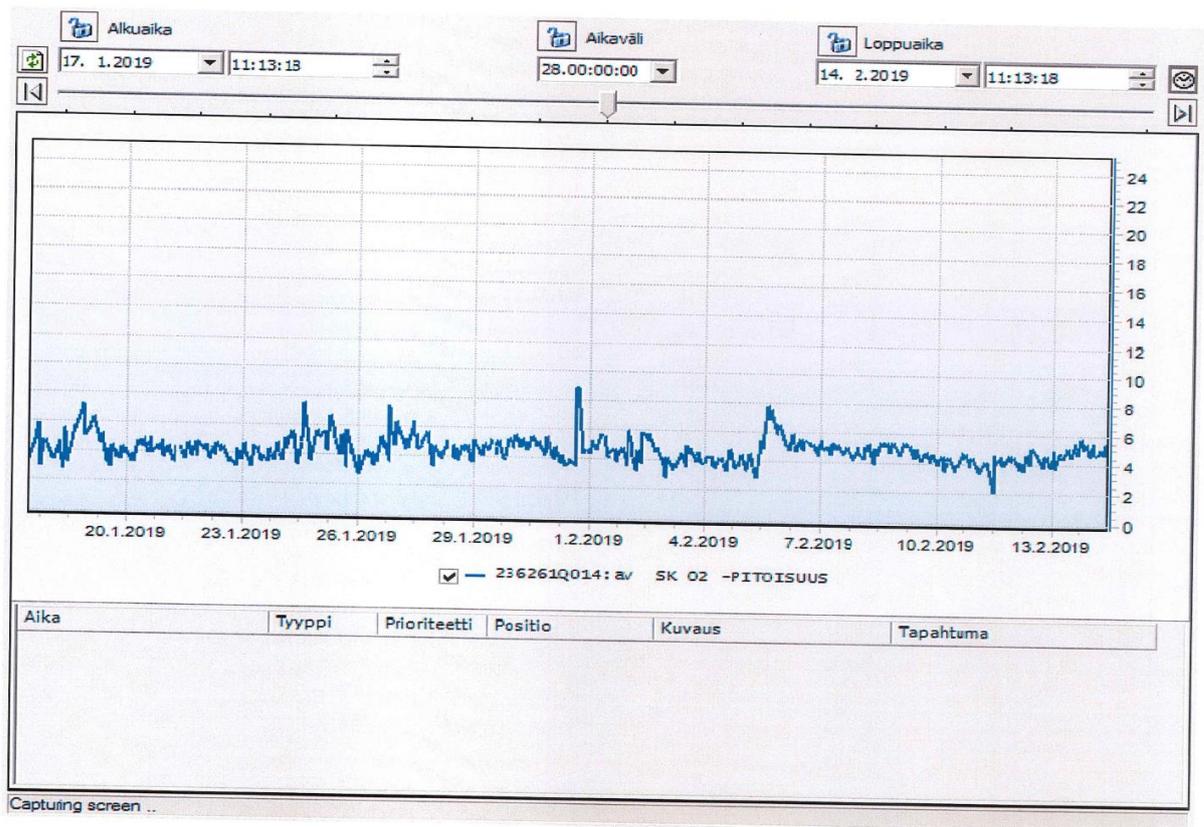


Figure 30. O₂ from the stack

9 RESULT

Interpretation of the measurements shows that pitch oil has a positive effect on NO_x reduction in natural gas burning. For the case investigated, NO_x reduction was about 80 %. Investment costs may not be incurred as natural gas burners are usually combined burners. Burning pitch oil at the same time as natural gas makes the flame radiate better.

When comparing the effects, investment and costs of pitch oil with other applicable technologies, the costs are virtually non-existent because of the use of existing technology and available pitch oil at the mill. The effect on NO_x emissions is excellent. Pitch oil can be replaced by regular oil because it works in the same way, but only generates operating costs depending on prices.

9.1 Further objects of research

Further research should investigate the effect of variations in oil content on NO_x reduction and flame radiation. Even a small amount can have a beneficial effect. It is recommended to determine the amount that is a potential alternative to NO_x reduction.

Water cools the flame and its effect on NO_x emissions is worth investigating. The technique of adding water to the flame should be researched. Water spraying is in use, but more detailed research is lacking.

The use of different solids to increase flame radiation for NO_x reduction is recommended because solids are readily available at the mill. Solids recommended for research are wood dust, dry lime and lime mud-lime dust. At the same time, the technique of feeding the solid into the flame must be researched. It should also be investigated whether solids affect the durability of materials and cause plugging in the burner.

It is worthwhile further investigating the effects of various liquids and solids on the radiation, shape and temperature of the flame and how they affect the combustion of the lime and the operation of the lime kiln.

10 SUMMARY AND CONCLUSION

The aim of this thesis was to investigate the effect of pitch oil on NO_x emissions from natural gas combustion and at the same time determine whether ongoing development work on the topic will be continued. The work focused on the interaction between pitch oil and natural gas.

At the beginning of the work, the lime kiln in the pulping process was introduced. Lime burning was introduced to the lime kiln as part of the chemical pulping process in the chemical recovery cycle, conventional lime kiln, lime mud drying, burners and fuels used in the lime kiln.

The work investigated the formation of nitrogen oxides in combustion and NO_x emissions and the current state of NO_x emissions regulations and sanctions in Europe and USA. The work also investigated various techniques for removing nitrogen oxide from a rotary kiln, NO_x reduction by combustion control and NO_x removal by post-combustion methods. The suitability of each technique must be considered on a case-by-case basis, because many of the methods adopted are used in applications other than lime kilns and may not be suitable for lime kilns or are difficult to implement or do not work in lime kilns.

A comparison of the methods used in the lime kiln and the available techniques for reducing NO_x emissions were considered. The lime kiln may not be able to use the best available technology to remove NO_x, but it can use the best applicable technology, which is currently SNCR and NO_x scrubbing. The effect of NO_x removal on SNCR is about 50 % and on NO_x scrubbing with ClO₂ 60 – 85 %. The costs for both methods are an investment and the methods are quite expensive to use.

When considering nitrogen oxide reduction, it is good to know and take into account the initial NO_x level, the concentration of nitrogen oxides after removal and the reduced oxygen content, then the results are comparable. Emissions of nitrogen oxides depend mainly on the nitrogen content of the lime kiln fuel, excess O₂ level and combustion temperature. Removal of nitrogen

oxides to fulfill current legislation can be achieved by currently available emission technologies. This may be required in the use of fuels that produce large amounts of nitrogen oxides, which may mean that these fuels may not be available everywhere due to tightening permit restrictions and the high cost of NO_x reduction.

It became clear that adding oil to the flame when burning natural gas has a positive effect on the reduction of NO_x emissions. The effect on NO_x reduction was about 80 %. Operating and investment costs remain low with the use of existing technology and available fuels from the mill. This supports the research of adding liquids and solids to the flame and its effect on flame radiation and NO_x emissions. Emissions legislation will tighten globally in the future, so it is necessary to research the efficiency and cost of combustion processes in the removal of nitrogen oxides. It must be taken into account that in the future natural gas and oil prices, emissions charges and taxes will probably increase. This research clearly supports the continuation of research to reduce NO_x emissions from the lime kiln burner and its related ongoing development work.

REFERENCES

Adams, T. N. 2008. Lime Kiln Principles and Operations. TAPPI Kraft Recovery Course, Manuscript. January 7-10, 2008. St. Petersburg, Florida, USA. 15 pages. [Online publication] [Reference 27.6.2018]. Available: <http://www.tappi.org/content/events/08kros/manuscripts/2-2.pdf>

Alakangas, E. 2000. Suomessa käytettävien polttoaineiden ominaisuuksia. Research Notes 2045. Technical Research Centre of Finland. 196 pages. ISBN 951-38-5740-9.

Alakangas, E., Hurskainen, M., Laatikainen-Luntama, J., Korhonen, J. 2016. Suomessa käytettävien polttoaineiden ominaisuuksia. VTT Technical Research Centre of Finland Ltd. VTT, Espoo. 263 pages. ISBN 978-951-38-8419-2. Available: <http://urn.fi/URN:ISBN:978-951-38-8419-2>

Andritz Group. 2019. Basic of lime burning. Internal training material.

Andritz Group. 2019. DeNOx for P&P. Internal training material.

Andritz Oy. 2017. Cross Tech Training, White Liquor Plant. Vierumäki 30.5. – 01.06.2017. Internal training material.

Andritz Oy. 2016. LimeFlash™. Internal training material.

Andritz Oy. 2016. Pulp Mill Processes in a Nutshell. Savonlinna 21.6.2016. Internal training material.

Bell, R.D., Buckingham, F.P. 2015. An overview of technologies for reduction of oxides of nitrogen from combustion furnaces. MPR Associates, Inc. [Online publication] [Reference 17.9.2018]. Available: <https://www.mpr.com/uploads/news/nox-reduction-coal-fired.pdf>

Dahl, O. 2008. Environmental Management and Control, Second Edition. Papermaking Science and Technology, Book 19. Jyväskylä: Gummerus Printing. 304 pages. ISBN 978- 952-5216-30-1.

Eclipse. 1992. Flue Gas Recirculation for NO_x Reduction. Eclipse Combustion. SP-417. 4 pages. [Online publication]. [Reference 15.8.2019]. Available: <http://www.genesyscombustion.com/whitepages-417.pdf>

Engdahl, H., Halinen, E., Jäntti, J., Kapanen, J., Kottila, M., Lankinen, M., Lintunen, T., Näsänen, H., Toropainen, T. & Parviainen, K. 2008. White Liquor preparation. Original text by Arpalahti, O., Engdahl, H., Jäntti, J., Kiiskilä, E., Liiri, O., Pekkinen, J., Puumalainen, R., Sankala, H. & Vehmaan-Kreula, J. In: Tikka, P. 2008. Chemical Pulping. Part 2: Recovery of Chemicals and Energy. Papermaking Science and Technology Book 6, Chemical Pulping, Jyväskylä: Gummerus Printing. 387 pages. ISBN 978-952-5216-26-4.

Eneberg, H., Honkanen, R., Jaakkola, H., Lammentausta, S., Mattelmäki, E., Saviharju, K., Schönberg, Å. 2002. Patent Publication FI120363B. Menetelmä sellutehtaan typpioksidien vähentämiseksi. 8 pages. [Online publication] [Reference 29.9.2019] Available: <https://patentimages.storage.googleapis.com/53/fc/7c/f7da285f2d0ee3/FI120363B.pdf>

Environmental footprint comparison tool. 2013. Trade-offs and co-benefits accompanying SO_x and NO_x control. National Council for Air and Stream Improvement. 52 pages. [Online publication] [Reference 6.8.2018]. Available: http://www.paperenvironment.org/PDF/SOxNOx/SOxNOx_Full_Text.pdf

European Commission. 2013. Best Available Techniques (BAT) Reference Document for the Production of Cement, Lime and Magnesium Oxide. Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control). Publications Office of the

European Union, 2013. pages 506. ISBN 978-92-79-32944-9 (pdf). [Online publication] [Reference 12.7.2018]. Available: http://eippcb.jrc.ec.europa.eu/reference/BREF/CLM_Published_def.pdf

European Commission. 2015. Best Available Techniques (BAT) Reference Document for the Production of Pulp, Paper and Board. Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control). Publications Office of the European Union, 2015. pages 906. ISBN 978-92-79-48167-3 (pdf). [Online publication]. [Reference 12.7.2018]. Available: http://eippcb.jrc.ec.europa.eu/reference/BREF/PP_revised_BREF_2015.pdf

European Commission. 2013b. Commission Implementing Decision of 26 March 2013 establishing the best available techniques (BAT) conclusions, under Directive 2010/75/EU of the European Parliament and of the Council, for the production of cement, lime and magnesium oxide. In: Official Journal of the European Union, L100. Volume 56, 9 April 2013. ISSN 1977-0677. [Online publication]. [Reference 12.7.2018]. Available: <https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=OJ:L:2013:100:FULL&from=EN>

European Commission. 2014. Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control). Official Journal of the European Union. 17.12.2010. [Online publication]. [Reference 12.7.2018]. Available: <https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32010L0075&from=EN>

European Commission. 2014. Commission Implementing Decision of 26 September 2014 establishing the best available techniques (BAT) conclusions, under Directive 2010/75/EU of the European Parliament and of the Council, for the production of pulp, paper and board. Official Journal of the European Union. 30.9.2014. [Online publication]. [Reference 12.7.2018]. Available: <https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32014D0687&from=EN>

Finnish Environment Institute. 2001. Finnish Expert Report on Best Available Techniques in Large Combustion Plants. Edita Oyj, Helsinki. ISBN 952-11-0861-4. [Online publication] [Reference 17.9.2018] Available: https://helda.helsinki.fi/bitstream/handle/10138/40632/FE_458.pdf?sequence=1

Francey S., Tran H. & Berglin N. 2011. Global survey on lime kiln operation, energy consumption, and alternative fuel usage. TAPPI Journal, August 2011. [Online publication]. [Reference 22.7.2018]. Available: https://www.researchgate.net/profile/Honghi_Tran/publication/291973034_Global_survey_on_lime_kiln_operation_energy_consumption_and_alternative_fuel_usage/links/56a8206908ae860e0255abf9/Global-survey-on-lime-kiln-operation-energy-consumption-and-alternative-fuel-usage.pdf

Hakkarainen, T. 2014. Reduction of nitrogen oxide emissions in lime kiln. Master's thesis. Lappeenranta University of Technology. 103 pages. [Online publication]. [Reference 28.7.2018]. Available: https://www.doria.fi/bitstream/handle/10024/102230/Reduction%20of%20nitrogen%20oxide%20emissions%20in%20lime%20kiln_doria.pdf?sequence=2

Hart P. W., Colson G. W., Clapper M. H., Pollet B. M. & Doughty W. K. 2012. Increasing lime production while decreasing kiln plug gage through installation of the first LimeFlash lime kiln feed system in North America, TAPPI Journal, Vol. 11 No. 8, August 2012. [Online publication]. [Reference 12.8.2018]. Available: https://www.researchgate.net/profile/Renata_Bura2/publication/288063671_The_sulfite_mill_as_a_sugar-flexible_future_biorefinery/links/572fa79308ae3736095c1d9c/The-sulfite-mill-as-a-sugar-flexible-future-biorefinery.pdf

Jalovaara, J., Aho, J., Hietamäki, E., Hyytiä, H. 2003. Paras käytettävissä oleva tekniikka (BAT) 5-50 MW polttolaitoksissa Suomessa. Suomen Ympäristökeskus. Vammalan Kirjapaino Oy. Vammala 2003. 129 pages. ISBN 952-11-1489-4 (PDF).

Kilpinen, P. & Zevenhoven R. 2004. Control of pollutants in flue gases and fuel gases. 3rd edition. Report TKK - ENY – 4. ISBN 951 - 22 - 5527 – 8. [Online publication]. [Reference 15.8.2018]. Available: <http://users.abo.fi/rzevenho/gasbook.html>

KnowPulp, 2017. KnowPulp-Learning environment 2017. Version 16.0. Internal material.

Ledakowicz S., Miller J. S. & Skalska K. 2010. Trends in NO(x) abatement: a review. Technical University of Lodz, Faculty of Process and Environmental Engineering, Wolczanska 213/215, 90-924, Lodz, Poland. Science of the Total Environment (Impact Factor: 3.26). 09/2010; 408(19):3976-89. DOI: 10.1016/j.scitotenv.2010.06.001

Milani, A. & Wüning, J. 2012. What is Flameless Combustion. A Combustion File downloaded from the IFRF Online Combustion Handbook. ISSN 1607-9116. [Online publication]. [Reference 16.7.2018]. Available: <http://www.handbook.ifrf.net/handbook/cf.html?id=171>

Montana Department of Environmental Quality. 2013. Operating Permit Technical Review document. Permitting and Compliance Division. Graymont Western U.S., Inc. [Online publication]. [Reference 25.8.2018] Available: <https://deq.mt.gov/Portals/112/Air/AirQuality/Documents/ARMpermits/TRD1554-05.pdf>

National Center for Environmental Economics. 2004. International Experiences with Economic Incentives for Protecting the Environment. U.S. Environmental Protection Agency. EPA-236-R-04-001. 77 pages. [Online publication]. [Reference 13.7.2018]. Available: <https://www.epa.gov/sites/production/files/2017-08/documents/ee-0487-01.pdf>

Perry, R. H. 1997. Perry's Chemical Engineers' Handbook 7th. Published by McGraw-Hill, printed in United States. 2640 pages. ISBN 0-07-049841-5. Available: <https://chembugs.files.wordpress.com/2015/12/perrys-chemical-engineering-handbook1.pdf>

Pinkerton, J. E. 2007. Sulfur dioxide and nitrogen oxides emissions from U.S. pulp and paper mills, 1980-2005. *Journal of the Air & Waste Management Association*, 57(8), 901- 906. Available: <https://www.tandfonline.com/doi/pdf/10.3155/1047-3289.57.8.901>

Raiko, R., Saastamoinen, J., Hupa, M., Kurki-Suonio, I. 2002. *Poltto ja palaminen*. International Flame Research Foundation – Suomen Kansallinen Osasto. Teknillistieteelliset akatemiati. Jyväskylä. Gummerus Kirjapaino Oy. Printing. 750 pages. ISBN 951-666-604-3

San Joaquin Valley Air Pollution Control District. SJVUAPCD. Rule 4313, Lime Kilns (adopted on March 27, 2003, submitted on June 5, 2003. [Online publication]. [Reference 27.8.2018]. Available: <https://www.arb.ca.gov/drdb/sju/curhtml/R4313.pdf>

Sorrels, J.L., Randall, D.D., Fray, C.R., Schaffner, K.S. 2016. *Selective Noncatalytic Reduction*. Research Triangle Park. [Online publication]. [Reference 24.09.2018]. Available: <https://www.epa.gov/sites/production/files/2017-12/documents/snrcostmanualchapter7thedition20162017revisions.pdf>

Szewczyk, D., Engdahl, J., Stachowski, A. 2010. High Temperature Burners (HTB) as the result of the connection of HiTAC combustion technology with central recuperative systems. ICS Industrial Combustion Systems Sp. z o.o. 10 pages. [Online publication]. [Reference 15.11.2018]. Available: http://www.icsco.eu/images/files/artykuly_pdf/publications/ics-8hitacg-2010-p02-final-2010.06.18.pdf

Szewczyk, D., Skotnicki, P., Stachowski, A. 2010. HiTAC - one combustion technology – a wide range of industrial applications. ICS Industrial Combustion Systems Sp. z o.o. 14 pages. [Online publication]. [Reference 30.11.2018]. Available: http://www.icsco.eu/images/files/artykuly_pdf/publications/ics-8hitacg-2010-p04-final-2010.06.22.pdf

Törmikoski P. 2018. Master's Thesis review. 27.09.2018. Savonlinna

U.S. Environmental Protection Agency. 1999. Technical bulletin, Nitrogen oxides (NO_x), Why and how they are controlled. EPA 456/F-99-006R. 48 pages. [Online publication]. [Reference 30.11.2018]. Available: <https://www3.epa.gov/ttnecatc1/dir1/fnoxdoc.pdf>

U.S. Environmental Protection Agency. 2014. Universal Industrial Sectors Integrated Solutions Model for the Pulp and Paper Manufacturing Industry – Universal ISIS – PNP. 144 pages. [Online publication]. [Reference 21.10.2019]. Available: https://cfpub.epa.gov/si/si_public_record_report.cfm?dirEntryId=311359&Lab=NRMRL

VTT Prosessit. 2007. Päästömittausten käsikirja osa 1. 110 pages [Online publication] [Reference 30.9.2019]. Available: <https://ilmansuojeluyhdistys.files.wordpress.com/2015/05/osa1.pdf>

Factors in Lime kiln Emissions of NO_x (Environmental footprint comparison tool, 2013) - Appendix I

	NO _x Impact	Other Aspects
Lime Kiln Control Technology Option		
Burner Design	Low NO _x burners are technically infeasible due to complex factors that result in poor efficiency, increased energy usage, and decreased calcining capacity of the lime kiln (NESCAUM 2005; IPPC 2001). Reduced flame temperature, however, could be conducive to iminished thermal NO _x formation, especially in gas-fired kilns.	
Combustion Air Control	Combustion zone availability of O ₂ is a key factor in NO _x formation; especially in oil-fired kilns (IPPC 2001). Primary air feed is driven by flame control requirements, limiting the opportunity for staging combustion air. Air supply must be sufficient to sustain oxidizing conditions throughout the kiln (NCASI 2008).	Detuning a burner from optimized combustion incurs an energy penalty by virtue of requiring greater heat input per ton of product. Inadequate air supply (IPPC 2001) contributes to excessively high emissions of TRS and CO (NCASI 2008), as well as excessive carbon deposits in the lime
Fuel Selection	Fuel nitrogen is the principal source of NO _x in oil-fired kilns, unlike gas-fired kilns where thermal NO _x formation is prevalent. There is typically little difference in reported emissions between oil and gas, though instances have been reported showing somewhat higher gas levels (NCASI 2008; Nichols 2004; IPPC 2001)	
Flue Gas Recirculation (FGR)	A possibly promising but untested approach (NCASI 2008).	Altering kiln temperature profiles with FGR would possibly adversely affect calcining efficiency (NCASI 2008).
SCR	Infeasible due to kraft lime kiln configuration (IPPC 2001). High particulate loadings preclude SCR prior to particulate control and temperature requirements are not met after particulate control.	Reheating the flue gas after the particulate control device and ahead of the SCR section would incur a substantial energy (IPPC 2001)
SNCR	Infeasible due to kraft lime kiln configuration. The necessary elevated temperature regime required for SNCR is unavailable in kilns (IPPC 2001).	
Scrubber	NO _x emissions are largely unaffected by wet scrubbing (NCASI 2008).	Particulate scrubbers are designed and optimized for particulates. Associated high velocities are not conducive to gas absorption (NCASI 2008); SO _x removal would not likely equal what might be achievable with a scrubber designed for that purpose.

External Combustion NOx Limiting Technologies(U.S. Environmental Protection Agency 1999) - Appendix II (1/3)

Technique	Description	Advantages	Disadvantages	Impacts	Applicability
Less Excess Air (LEA)	Reduces oxygen availability	Easy modification	Low NOx reduction	High CO Flame length Flame stability	All fuels
Off Stoichiometric a. Burners Out of Service (BOOS) b. Over Fire Air (OFA)	Staged combustion	Low cost No capital cost for BOOS	a. Higher air flow for CO b. High capital cost	Flame length Fan capacity Header pressure	All fuels Multiple burners for BOOS
Low NOx Burner (LNB)	Internal staged combustion	Low operating cost Compatible FGR	Moderately high capital cost	Flame length Fan capacity Turndown stability	All fuels
Flue Gas Recirculation (FGR)	<30 % flue gas recirculated with air, decreasing temperature	High NOx reduction potential for low nitrogen fuels	Moderately high capital cost and operating cost Affects heat transfer and system pressures	Fan capacity Furnace pressure Burner pressure drop Turndown stability	All fuels Low nitrogen fuels
Water/Steam Injection	Reduces flame temperature	Moderate capital cost NOx reduction similar to FGR	Efficiency penalty Fan power higher	Flame stability Efficiency penalty	All fuels as Low nitrogen fuels
Reduced Air Preheat	Air not preheated, reduces flame temperature	High NOx removal potential	Significant efficiency loss (1% per 40 °F)	Fan capacity Efficiency penalty	All fuels Low nitrogen fuels

External Combustion NOx Limiting Technologies(U.S. Environmental Protection Agency 1999) - Appendix II (2/3)

Technique	Description	Advantages	Disadvantages	Impacts	Applicability
Selective Catalytic reduction (SCR) (add-on technology)	Catalyst located in the air flow, promotes reaction between ammonia and NOx	High NOx removal	Very high capital cost High operating cost Catalyst siting Increased pressure drop Possible water wash required	Space requirements Ammonia slip Hazardous waste Disposal	All fuels
Selective Non-Catalytic Reduction (SNCR) (add-on technology) a. urea b. ammonia	Inject reagent to react with Nox	a. Low capital cost Moderate NOx removal Non-toxic chemical b. Low operating cost Moderate NOx removal	a. Temperature dependent NOx reduction less at lower loads b. Moderately high capital cost Ammonia storage, handling, injection system	a. Furnace geometry Temperature profile b. Furnace geometry Temperature profile	All fuels
Fuel Reburning	Inject fuel to react with Nox	Moderate cost Moderate NOx removal	Extends residence time	Furnace temperature profile	All fuels (pulverized solid)
Combustion Optimization	Change efficiency of primary combustion	Minimal cost	Extends residence time	Furnace temperature profile	Gas Liquid fuels
Catalytic Combustion	Catalyst causes combustion to be at low temperature	Lowest possible NOx	Very high capital cost High operating cost Catalyst siting	Space requirements Disposal	Gas Liquid fuels
Non-Thermal Plasma	Reducing agent ionized or oxidant created in flow	Moderate cost Easy siting High NOx removal	Fouling possible Ozone emission possible	Uses electrical power	All fuels

External Combustion NO_x Limiting Technologies(U.S. Environmental Protection Agency 1999) - Appendix II (3/3)

Technique	Description	Advantages	Disadvantages	Impacts	Applicability
Inject Oxidant	Chemical oxidant injected in flow	Moderate cost	Nitric acid removal	Add-on	All fuels
Oxygen instead of Air	Uses oxygen to oxidize fuel	Moderate to high cost Intense combustion	Eliminates prompt NO _x Furnace alteration	Equipment to handle oxygen	All fuels
Ultra-Low Nitrogen Fuel	Uses low -nitrogen fuel	Eliminates fuel NO _x No capital cost	Slight rise in operating cost	Minimal change	All ultra-low nitrogen fuels
Use Sorbents (add-on technology) in: a. Combustion b. Duct to Baghouse c. Duct to Electrostatic Precipitator	Use a chemical to absorb NO _x or an adsorber to hold it	Can control other pollutants as well as NO _x Moderate operating cost	Cost of handling sorbent Space for the sorbent storage and handling	Add-on	All fuels
Air Staging	Admit air in separated stages	Reduce peak combustion temperature	Extend combustion to a longer residence time at lower temperature	Adds ducts and dampers to control air Furnace modification	All fuels
Fuel Staging	Admit fuel in separated stages	Reduce peak combustion temperature	Extend combustion to a longer residence time at lower temperature	Adds ducts and dampers to control air Furnace modification	All fuels