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TECHNOLOGY, COMMUNICATION AND TRANSPORT

ESTIMATION OF SCR SYSTEM PERFORMANCE

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Tiivistelmä

Typen oksidien prosessiperäisten päästöjen on havaittu pysyneen suhteessa samalla tasolla paperiteollisuuden tuotannon kanssa Suomessa. Typen oksidien vähenemät on suurimmalta osaltaan seurausta energiateollisuuden päästövähennyksien kautta.

Opinnäytetyössä selvitettiin, voidaanko soodakattilassa muodostuvia typen oksidien päästöjä vähentää lisäämällä ammoniakkia savukaasuihin osana prosessia. Työssä tutkittiin kuinka SCR-katalyytin ja ammoniakin mahdollinen yhteisvaikutus pienentää typpipäästöjä ammoniakkivirtausta ja lämpötilaa säätämällä. Työ toteutettiin yhteistyönä Savonia-ammattikorkeakoulun ja Andritz Oy:n kanssa kesän 2022 aikana. Opinnäytetyöhön sisältyi kaikkiaan kolmen kuukauden mittainen testausjakso eräällä soodakattilalla. Testaus sisälsi testilaitoksen operointia sekä päästömittausaineiston koostamista FTIR-laitteiston avulla. Operointijakso kattoi myös muita testausyhdistelmiä, joita työssä ei niiden laaja-alaisuuden vuoksi ole mahdollista esittää.

Tuloksissa on esitetty savukaasujen lämpötiloja suhteuttamalla prosessilämpötilat kalibroituihin tarkastusmittauksiin. Lisäksi työssä vertailtiin FTIR-mittalaitteiston tuloksien avulla saman aikaisesti mitattuja savukaasun arvoja ennen ammoniakin lisäämistä savukaasuihin ja niiden ohjausta SCR-katalyytille sekä näiden jälkeen. Näiden lisäksi tuloksissa on esitetty pölyn erotuksen ja SCR-katalyytin paine-erojen vaikutuksia pölymääriin nähden. Tuloksista voidaan huomata, että typen oksideja on mahdollista vähentää ilman, että jäännösammoniakkia syntyy.

Avainsanat		
nox, päästöt, scr, katalyytti, soodakattila		

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Abstract

The emissions of nitrogen oxides have been observed to stay in line with pulp, paper, and cardboard industry production in Finland. The reduction of nitrogen oxides seems to be mostly a consequence of the reduction of energy industry emissions.

The aim of the thesis was to answer the question whether it is possible to reduce the nitrogen oxides of recovery boiler by adding ammonia to flue gases. The project was about researching the synergy possibilities of SCR catalyst and ammonia by adjusting the ammonia flow and the temperature of flue gases. The thesis was implemented in co-operation with Savonia University of Applied Sciences and Andritz Oy.

The thesis included a testing period in a recovery boiler that took three months. The testing period contained operating of the test plant and measuring emissions with a FTIR. The test period included other test combinations, but all the results are not covered in this thesis.

In the results the temperatures of flue gases are shown as original and calibrated values. The FTIR measurements were made before and after feeding ammonia to the flue gases. Therefore, the results cover comparison of FTIR measurements. The results show that it is possible to reduce NO_x emissions without ammonia slip.

CONTENTS

LIST OF FIGURES

TERMINOLOGY AND EXPLANATIONS

BAT	Best Available Techniques
BBF	Biased burner firing
BOFA	Boosted overfire air
BOOS	Burners out of service
DLN	Dry Low NO_x
EGR	Exhaust gas recirculation
ELPI	Electrical low-pressure impactor
ESP	Electrostatic precipitator
FTIR	Fourier transform infrared
g	Grams
g/mol	Molar mass
kPa	Kilopascals
LNB	Low NO_x burners
mg/Nm^3	Milligrams per normal cubic meter
Nl/min	Normal liters per minute
NTP	Normal temperature and pressure
OFA	Overfire air
PPC	Pulp, paper, and cardboard
ppm	Parts per million
SCR	Selective catalytic NOx reduction
SNCR/SNR	Selective non-catalytic NOx reduction

CHEMICALS

CH	Methylidyne radical
ClO_2	Chlorine dioxide
H	Hydrogen
H_2O	Water
HCl	Hydrochloric acid
HCN	Hydrogen cyanide
Hf	Hafnium
HO_2	Hydroperoxyl radical
M	Gas component x
MoO_3	Molybdenum trioxide
N	Atomic nitrogen
N_2	Molecular nitrogen
N_2O	Nitrous oxide
NCO	Cobalt hexamine
NH_3	Ammonia
NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
NO_x	Nitrogen Oxides
O	Oxygen
O_2	Molecular oxygen
OH^-	Hydroxide
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
TiO_2	Titanium trioxide
V_2O_5	Vanadium pentoxide
WO_3	Tungsten trioxide
HCl	Hydrochloric Acid
HF	Hydrogen fluoride

CH_4 Methane

C_2H_6 Ethane

C_3H_8 Propane

C_2H_4 Ethylene

C_6H_{14} Hexane

$CHOH$ Ethenyl

1   INTRODUCTION

In the past, it has been discovered that recovery boilers all form particles like dust and the formation of sodium which can be called as a poison for SCR systems. (Vakkilainen 2005, 11-5.) As the recovery boiler systems have developed the way of NO_x developing reduction methods have stalled. Dust or small particles of emissions suspend still in the air. As figure 1 below shows there has been plenty of development work to minimize the particles to air and there is no correlation between pulp, paper, and cardboard production. Most of the particles seem to come into existence from process emissions. The relation between dust emissions seems to depend highly on the boiler's load and nowadays electrostatic precipitators have a solution for filtering the particles and reducing emissions. (Vakkilainen 2005, 11-1-2.)

FIGURE 1. Dust emissions of mass and paper industry to air in Finland (adapted from Finnish Forest Industry Ry 2021).

It is good to notice that the decrease of nitrogen oxides (NO_x) could also be a consequence from limiting of gases in vehicles. Annual limits are still exceeded in some specific areas. Nitrogen dioxide percentages in the air are higher whereas the NO_x emissions have come down. (Ministry of the Environment 2017.) A generally known fact is that the two largest sources of nitrogen oxides are traffic and fuel combustion. Other biological processes in water and soils, and forest fires produce NO_x emissions as well. (Vakkilainen 2005, 11-3.) The NO_x emissions have decreased after the 1990s in every measured area (see figure 2). The parts of the emissions of process have stayed similar whereas the emissions from pure energy production seem to have decreased. This seems to follow the pattern of pulp, paper, and cardboard production. (Finnish Forest Industry Ry, 2021.)

The relationship between emissions and production is notable. However, in the last ten years, NO_x emissions have been in line with PPC production. The timeline of Finnish Forest Industry for emissions starts from the year 1992 when there was one of the biggest recessions in Finland. Years after that the economy started to recover as the emission increased. The next remarkable decreases were in the years 2005, 2009, and 2020. In the spring of 2005, the Finnish Paper Union declared the first short strike to which the Finnish Forest Industry responded by a lockout. This industrial conflict lasted altogether one and a half months. At the same time all pulp and paper plants in Finland were

shut down. (Heima 2018, YLE.) By looking back to those events, it explains lower emissions for multiple factories in some years.

In 2009 the world started to recover from Wall Street big stock market crash or better-known economic crisis that impacted the global economy in all industries. Meanwhile in Finland, according to Salo (2015) all three biggest pulp and paper companies; Stora Enso Oyj, UPM Kymmene Oyj, and Metsä Group restructured and shut plants in the years 2008 and 2009 (Salo 2015, 26-31). This caused lower production in all pulp, paper, and cardboard industries. After this peak nitrogen oxides have been stable and in line with PPC production until 2020 COVID-19 spread and caused a total lockdown all over the world. This lockdown decreased the demand of the printing and writing paper demand. Companies turned more to remote mode and working culture which caused a giant leap in digitalization and online culture. (Fisher International 2020.)
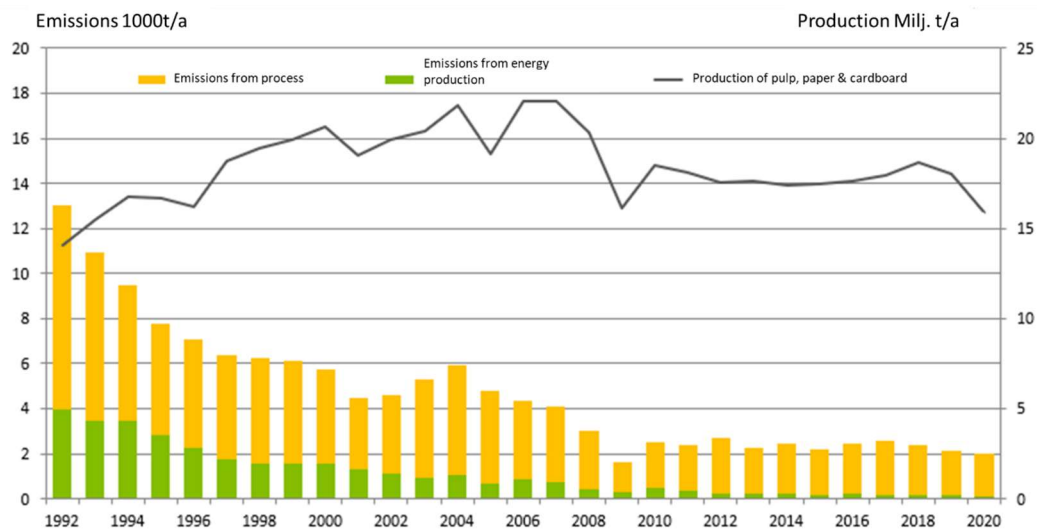

FIGURE 2. NOₓ emissions of mass and paper industry in Finland (adapted from Finnish Forest Industry Ry 2021),

It is proved that nitrogen oxide emission percentages are under appointed limit values from both health and environmental point of view (Ministry of the Environment 2017). The NO_2 emissions limit values are 40 mg/m^3 to protect health and 30 mg/m^3 to save the ecosystem and flora (Ministry of the Environment 2013).

The aim of the thesis was to find out if there is a possibility to reduce pollution caused by NOₓ emissions and dust particles at the same time. Therefore, Andritz is searching for a way to separate dust and NOₓ from flue gases with integrated solution. This thesis will present the results of the measurement period. The measurement period was implemented in one of the recovery boilers. This research follows the published thesis where Kettunen (2022) prepared for the testing period and made a maintenance plan for FTIR measurement equipment. The thesis aimed to clarify what possibilities there are to minimize NOₓ emissions in energy production by analyzing the efficiency of used catalyst. History can provide explanations for changes in NOₓ emissions, but the actual challenge is how to separate the link between NOₓ emissions and energy industries. Even more must be done to cut NOₓ emissions that are generated in power plants and other industries that produce energy.

2   FUNCTION OF RECOVERY BOILER

The recovery boiler is used mainly in the pulp and paper industry. The recovery boiler has two roles which make the usage of the boiler more challenging than that of other power plant boilers. The recovery boiler enables a closed chemical cycle. Separated chemicals from the furnace run through a causticizing plant where treated chemicals are fed back to cooking after the causticizing process. The main function of the recovery boiler is to regenerate and recycle chemicals from cooking and burn the organic material in an environmentally friendly way and recover the heat. All these processes are separated from each other. Circulation of chemicals improves the environmentally friendly pulping process because in the early stages recovery boiler scrubber water was drained to waterways. Steam production focuses on efficient recycle of the water and the steam functions that are fed all over to process. (Knowpulp 2022.)

The purpose of pulp cooking is to separate wood fibres from each other by dissolving wood binder, and lignin. As the product of pulp bleaching is a pulped mass that conducts further to the process. Besides the pulp mass, raw water and chemicals are used in the bleaching of pulp as the proportion of mixtures is different for each scrubber. From the last scrubbers runs the clearest water meanwhile at the first scrubber the water is most soiled. This soiled water is mostly black liquor and cooking chemicals that can be burnt in the recovery boiler to produce energy. Before the black liquor is delivered to the boiler it runs through evaporation where additional water is dried out and this rises the part of dry solids. (Knowpulp 2002.) Black liquor includes different inorganic chemicals from the cooking process, lignin which is a binder of wood, and other organic raw materials. Before weak black liquor is fed to the recovery boiler the unnecessary water from scrubbers needs to evaporate. The dry solids of weak black liquor depend on scrubbers in the cooking area, but mainly dry solids are around 15-18 %. At evaporation, the dry solid percentage rises step by step and in the last stage, the dry solid content of black liquor is around 60-80 %. This is how the black liquor turns into strong liquor and is ready for the recovery boiler. (Huhtinen 2003, 69.)

As previously mentioned, the black liquor is burnt for energy in the recovery boiler. Energy is produced by steam that is released from the recovery boiler. The steam is fed first to a turbine and then the steam expands to lower pressure to produce heat for the process. (Huhtinen 2003, 69.) Black liquor burns in the furnace and during the combustion all liquid which includes black liquor evaporates. All organic materials will burn while inorganic solids melt at high temperatures. The smelts are delivered to the dissolving tank. (Knowpulp 2022.) Liquor guns are used to deliver black liquor to the furnace of recovery boilers. The component which sprays black liquor liquid into the furnace is called nozzle. It is also the end part of the liquor gun. (Vakkilainen 2005, 9-1.) When black liquor is delivered to the nozzle and crashes its headboard the liquor bursts into droplets and spouts all over the furnace. It is possible to adjust the size of drops by changing the temperature of black liquor. Temperature equals viscosity. Nozzles are located all over the furnace walls a few meters below the bed. (Huhtinen 1999, 69-72.)

Flue gas as a part of the recovery boiler process

Combusted material from the furnace proceeds to the flue gas system. The flue gases run through heat transfer surfaces and flow from there to flue gas ducts and fans. Typically, the flue gas runs from fans to electrostatic precipitator and in some processes to scrubber and stack as well. Whereas the recovery boilers are natural circulation boilers and therefore it appeared a challenge for density that the stack is long enough from the furnace. This is sufficient so that the flue gases can be pulled out without induced drafts as known as ID fan. The ID fan of flue gas also controls the draft of the furnace. This requires that the pressure level of the liquor gun stays below the pressure of the whole boiler house. From air systems, flue gas fans direct the air from the furnace to the stack. (Vakkilainen 2005, 7-7–7-8)

Fly ash which is mostly sodium and sodium sulphate, proceeds with flue gas flow, and it is removed from gasses by a precipitator. In the course of time the design of the recovery boilers has changed. Nowadays superheaters are protected from the radiation of the furnace. Another part of evaporation piping is curtain pipes that could also be seen as a way of turning the temperature of flue gases to a lower level. The evaporators are located after superheaters so that the flue gas with the highest temperature meets the ascending water first on the pipes. Figure 3. presents how the combustion air is brought in three stages to the recovery boiler. (Huhtinen 2013, 72-74.)
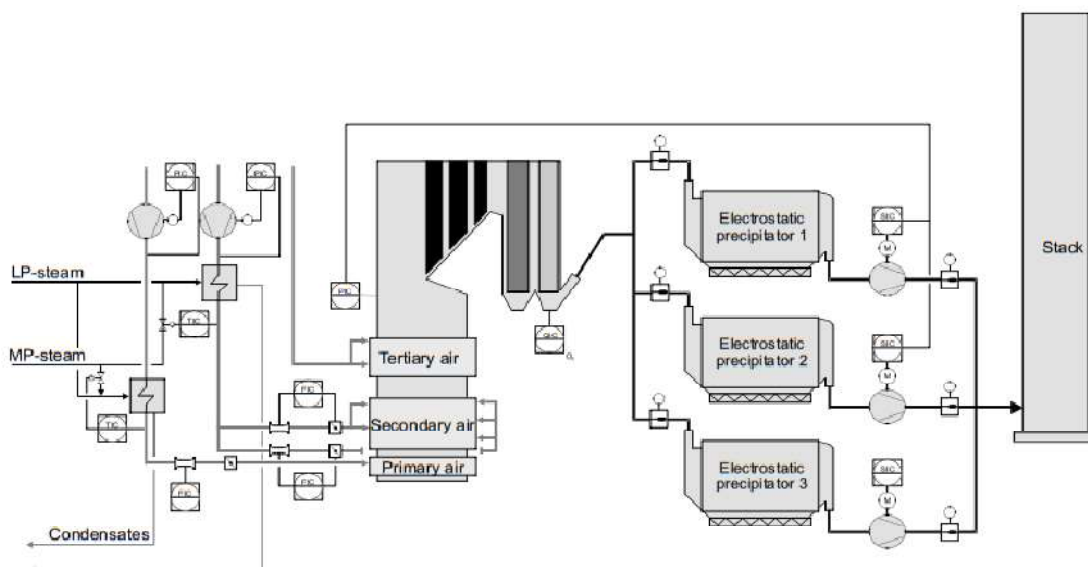
FIGURE 3. The air and flue gas system of the Recovery Boiler (adapted from Huhtinen 2013, 73,).

The way to control the airflow from furnace openings, is through dampers. The dampers are designed to control the air blowers in the duct. These blowers could have rotative speed changes, and the vanes of the inlet. Controlling of the airflow by dampers turns duct air pressures higher and by that, each opening ensures even flow through the furnace openings. (Vakkilainen 2005, 7-2)

3   NOₓ REACTIONS

Thermal NO

Thermal NO is formed during combustion. Generally, the source for nitrogen is the air that comes into boiler as molecular. Thermal NO is typically formed in higher temperatures (1400 °C) in furnace but it increases in lower temperatures as well depending on combustion. The formation of thermal NO is reduced by keeping the boiler temperatures stable. (Vakkilainen 2005, 9-13-14, 9-18.)

The definition of thermal NO is known as Zeldovich's mechanism. NO can form from the combustion air by reaction molecular nitrogen (N_2) and organic nitrogen (O). Organic nitrogen is typically a part of few precise fuels. The forming of NO basically needs that the N_2 gets a force to break a chemical bond. This binding energy is around 950 kJ/mol. During the combustion in high temperatures there is not enough time to have a complete reaction with O_2, so it can be said that the reaction is too slow to happen. However, there is time to N_2 to start the forming to NO when the nitrogen and oxygen start to react to each other. This is called the Zeldovich's mechanism from the 1940s when it was found. (Kilpinen 2002, 304-305.)

$$N_2 + O \rightarrow NO + N, \quad\quad\quad (1)$$

$$N + O_2 \rightarrow NO + O, \quad\quad\quad (2)$$

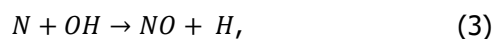It was discovered that the meaning of oxygen in N oxidizer decreases (2). This is caused by lower air residue as well as reductive circumstances of sub-air. This affects that N oxidizes to NO with hydroxyl radical as:

$$N + OH \rightarrow NO + H, \quad\quad\quad (3)$$

When all three formulas are considered, it can be said that this extends to extend Zeldovich's mechanism. There are two things that affect to get NO extremely sensitive to temperatures with combustion air. Firstly, during the combustion, the $N_2 + O$ constrains the speed of the reaction as well there is high activation energy (320 kJ/mol). Secondly, O-atoms depend on the combustion temperature. (Kilpinen 2002, 305.)

Prompt NOx

The Zeldovich's mechanism is not a complete explanation for nitrogen monoxide that has formed under air and carbon hydroxide flames. In the 1970s Fenimore presented that the nitrogen in combustion air starts a reaction with N_2 and CH. The mechanism has been confirmed, and the reaction goes like this:

$$N_2 + CH \rightarrow HCN + N, \quad\quad\quad (4)$$
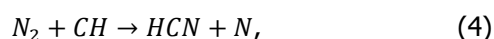
When there is oxygen HCN available, and N continues reacting to NO it is called reaction path:

$$HCN \rightarrow NCO \rightarrow NH \rightarrow N \rightarrow NO, \quad\quad\quad (5)$$
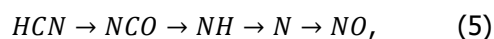
NO forms extremely fast and it is slightly related to the temperatures of combustion. Typical to prompt NO is that it appears greater under pressure and cold circumstances as shorter lags of time. (Kilpinen 2002, 306-307.)

NO formation by N$_2$O

The third mechanism from molecular nitrogen transformation to nitrogen monoxide was found in the 1970s. In this mechanism nitrous oxide emerges from oxygen and N$_2$ combines with any gas component (X).

$$O + N_2 + X \rightarrow N_2O + X, \qquad (6)$$
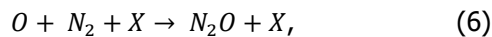
Depending on the circumstances nitrous oxide reacts with N2 or NO. Whereas molecular nitrogen is dominant as a reaction product, there is a way to the formation of nitrogen monoxide as well from nitrous oxide. This happens when the lambda and temperature both rise.

$$N_2O + O \rightarrow 2NO_2, \qquad (7)$$

There is no clarified way to explain these reactions as a part of NO emissions. However, the higher lambdas are combined to be a remarkable part of calculations of the NO emissions. It is also shown that the meaning of mechanism is remarkable when pressure rises. (Kilpinen 2002, 307.)

4 NO$_X$ REDUCTION METHODS

The designation of nitrogen oxides (NO$_x$) is used when speaking of nitric oxide (NO) and nitrogen dioxide (NO$_2$). The most of NO$_x$ emissions of recovery boiler consists of NO compounds <95 % and NO$_2$ compounds >5 %. (Kilpinen 2002, 33; Vakkilainen 2005, 11-3–4.) Differences between nitric oxides and nitrogen dioxides are in color and odor. As much as nitric oxide is a colorless and odorless gas, nitrogen dioxide is more like a red-brown and pungent gas. (Vakkilainen 2005, 11-3.)

Traditional ways to control NO$_x$ emissions are by changing the combustion or by purifying flue gasses. (Energia Suomessa 2004.) The most common side effects of NO$_x$ emissions are discovered in the environment on waters and soil acidifications. The discovered health effects are lung diseases like asthma. Roughly it can be said that the higher the percentages of NO$_x$ are, the more it consist to health and the environment. (Vakkilainen 2005, 11-3). The nitrogen emissions of the recovery boiler are caused by black liquor which contains organic nitrogen. Hardwoods (birch and aspen) seem to bind more nitrogen than softwoods (pine and spruce). Nitrogen appears on wood mainly as a protein in pine and softwoods. (Knowpulp 2022; KCL Reports 2672 2003, 162)

4.1 Primary control methods

The aim of primary emission control methods is to make an impact on combustion plants. In practice by reducing nitrogen oxides in both cases before and after the formation. However, in the case of introduced combustion modifications, it has to be made sure that the chosen method will not be harmful to plant operations or accelerate the formation other pollutants. On Best Available Techniques (BAT) for large combustion, the plant has listed criteria that need to be considered in, for example, the impact on basic operating parameters that need to be minimize as well as pollutant emissions that could be formed. (Industrial Emissions Directive 2010/75/EU, 109-110.)

4.1.1 Air staging

Air staging is the creation of at least two combustion zones in each the combustion chamber. These chambers include departed oxygen content that reduce NO_x emissions and optimize complete combustion. The general NO_x reduction rate by air staging is 10-70 %. Typically, primary combustion is lacking oxygen, and a secondary excesses oxygen to ensure burnout is complete. The combustion air is supplied only to the primary combustion zone because available oxygen is reduced to there or to primary air. Total primary airflow is 40-60 % on biomass boilers. The airflow is the same in the secondary zone where the air of combustion is sprayed on the furnace. The completed combustion happens in this last zone, and it increase the volume of the flame. From a sub-stoichiometric perspective, air staging offers to the primary zone a way to suppress the conversion of nitrogen from the fuel into NO_x. There is a possibility to limit temperature peak and that way reduce the formation of thermal NO_x. (Industrial Emissions Directive 2010/75/EU, 191-192)

The air staging in boilers and furnaces can be divided into four options: BBF, BOOS, OFA, and BOFA. However, it seems that only OFA and BOFA are efficient enough to reduce the formation of NO_x. The NO_x reduction rate of OFA is 10-40 % and the boosted OFA when fully loaded is over 60 % and with lower loads 50 %. Air staging is a way to improve the energy efficiency of the industry. Generally, air is added to combustion to achieve stoichiometric conditions and to complete the combustion process. 900 °C temperature prevents the formation of thermal NOx in circulating bed. Meanwhile the lower temperatures made the formation of N_2O further and step-up unburnt carbon. (Industrial Emissions Directive 2010/75/EU, 191-194)

4.1.2 Low excess air firing

Low excess air firing is developed to minimize the air leakages from the furnace. To minimize NO_x generation there is need to reduce available oxygen in the combustion zone. This causes complete combustion by limiting the oxygen. For using this method there need to be some modifications to the design of the combustion chamber. Low excess air is simple to implement for operational measures to reduce NO_x emissions and those reductions have been significant. BAT (2010) mentions that this method is quite general in many pending large combustion plants. The general NO_x reduction rate is from 10 % to 44 %. As a side effect, there may be perceptible unburnt materials like carbon-in-ash. (Industrial Emissions Directive 2010/75/EU, 189-191)

4.1.3 Reduction of combustion air temperature

For limiting the generation of thermal NO_x there is a way to lower the flame temperature in the combustion by preheating the used air. It is shown that there is a significant impact on NO_x formation in gas- and oil-firing systems. The reduction rate of this method is between 20-30 %. (Industrial Emissions Directive 2010/75/EU 198-199)

4.1.4 Fuel gas recirculation

It is possible to cut the generation of NO_x by recirculating a part of the flue gas. Replacement can be done by adding fresh air to the combustion chamber. This cools flame temperatures and limits O_2 on nitrogen oxidation. The roots of the flame cool down and the oxygen reduce the higher flame

temperatures. The thermal NO_x is reduced when the oxygen cools the flame directly and therefore decreases the temperature of the flame. The idea of the flue gas recirculation is to lead 20-30 % of the flue gas back through the air preheater as downstream air to the boiler. In this method the separated flue gas flow is blended with the combustion air of burner from upstream. There it is possible increase the general NO_x reduction rate from 20 % to 60 %. For two-stroke engines, a similar technique called EGR has been designed. However, it demands development of plant cooling and cleaning systems that to recirculation of the gas to engines is possible. (Industrial Emissions Directive 2010/75/EU, 195-197)

4.1.5 Fuel staging

The aim of fuel staging – as known as reburning, is the flame temperature reduction or to point the so said "hot spot" from combustion zones. The description of fuel staging is about the different zones of the furnace that are staged for the injection of fuel and air. By obtaining successful staging it is possible to convert the already formed nitrogen oxides back to nitrogen. The combustion itself can be seen in three zones. The fuel (80-85 %) is burnt by oxidizing or reducing the atmosphere in the primary combustion zone. This is called primary burnout and it is an important part of blocking the excess oxygen to transfer into the secondary – reburning zone. The reburning zone obtains the injection of fuel to reduce the air of furnace for producing hydrocarbon radicals to react with the nitrogen oxides and ammonia that have been formed in the primary zone. The last zone is about finalizing the combustion and spreading the final air to the burnout zone. This method reduce both NO_x and CO emissions into the air as well. The NO_x reduction rate is 50-60 % and 70-80 % when the formation of NO_x happens in the primary combustion zone. (Industrial Emissions Directive 2010/75/EU 205-206.)

4.1.6 Dry Low NO_x

The dry low NO_x (DLN) burner combines air and fuel before the combustion. As a result, for lower NO_x emissions and to achieve a lower flame temperature, homogenous temperature needs to be distributed. DLN burners combine the injection system of fuel/air and zones for premixing and flame stabilization. The primary zone of DNL has multiple fuel injections that use the air to achieve rapid fuel distribution. The design of the mixing zone is made to unite the mixing and flames aerodynamic features. The focus on flame stabilization is to prevent the spreading of the flame inside the mixing zone because of possible hazards to the combustor. The General NO_x reduction rate is 90 % by this method. (Industrial Emissions Directive 2010/75/EU 208-209)

4.1.7 Low NO_x burners

Low NO_x burners shortened as LNB are designed to both delay and improve combustion at the same time and by that grow the length of the flame. In bigger images, heat radiates and reduces peaks in flame temperature during combustion by staging the used air of fuel. To get higher combustion efficiencies mixtures from air or fuel are needed. In the same way the oxygen content is reduced and peaks in flame temperatures are achieved. This delays the conversion with fuel bounded nitrogen to the formation of NO_x and thermal NO_x. (Industrial Emissions Directive 2010/75/EU, 199, 203-204.)

Modifying has affected the development of low NO_x burners. There are four different LNB stages that are focused on reducing the NO_x formations; air staged, flue gas recirculation, fuel staged, and new generation burners. Air-staged LNB is when the fuel is mixed with the primary air which produces a flame that is "fuel-rich". This causes the flame to be basically cool and oxygen deficiency at the same time, and the nitrogen oxides will not form under these conditions. Primary flame is formed from the fuel-air mixture and the secondary air is blown to the flame. The inner recirculation zone creates a swirl between secondary air and the conical opening of the burns. This affects the rapid warming of fuel and keeps the flame steady. In this way, NO_x can be reduced by 25-35 %. (Industrial Emissions Directive 2010/75/EU 199-200.)

Nitrogen content can be that much higher than the fuel NO dominating over thermal NO. In this case, the oxygen level needs a coil, so the unburnt carbon won't form. On flue gas recirculation LNB the aim is to separate flames by spraying recirculated flue gases internally. The flue gas can be injected into the combustion zone or its air supply. Meanwhile, the flame temperature and concentration of oxygen get lower by preventing the reduction of NO_x formation. There are similarities with air staged LNB, however, the main difference is the distance between the primary and secondary nozzles, that is wider by creating a layer of flue gases. By this method is possible to recirculate around one-fourth of flue gases internally with the combustion air – the NO_x formation delays by reducing the flame temperature and oxygens partial pressure. The NO_x reduction rate is more than 20 %. (Industrial Emissions Directive 2010/75/EU 200-201.)

The NO_x reduction can be tackled after the NO_x has already formed. The most familiar and used gas application is fuel staged LNB. It is based on the combustion of fuel portions with high excess air. This enables lower flame temperatures and offers the NO_x formation an inhibition. To keep flame stable it needs the internal recirculation zone and nearly stoichiometric combustion. The fuel is injected downstream for a primary flame to boost a secondary flame. On third stage forms the burn-out zone. By flue staged LNB is possible to achieve a 50-60 % reduction rate. Flames that are produced by fuel staged LNB are 50 % longer than the other burners. (Industrial Emissions Directive 2010/75/EU 201.)

There are designed hybrid and ultra LNBs that combine air and fuel staging, and flue gas recirculation. These new generations of LNBs called functions can enable ultra-low NO_x emissions. The new generation LNBs achieve similar results to reduce NO_x emissions by a smaller impact on the shape of the flame and even more reductions by offering decent firebox volume. The presented burner generation NO_x reduction rate is 50-70 %. (Industrial Emissions Directive 2010/75/EU 202.)

4.2   Secondary control methods

Secondary techniques are based on reduction where nitrogen oxides (NO_x) have already formed in the boiler. The typically used technique is located at the end of the pipe in the fuel gas duct. It is common that methods are either independent or in combination with other primary techniques such as low-NO_x burners. Reducing NO_x emissions depends on the used chemicals, ammonia, urea, or other compounds. By the reaction of chosen chemical, the flue gas reduces it to molecular nitrogen. (Industrial Emissions Directive 2010/75/EU, 110-111.)

4.2.1 Selective catalytic NO$_x$ reduction

Selective catalytic NO$_x$ reduction known as SCR has been presented to be one of the most efficient techniques to purify fuel gasses from nitrogen oxidizes (NO$_x$). The method bases on added ammonia (NH$_3$) what is fed to the flue gasses are around 250-500 °C. With ammonia, nitrogen oxides reduce to molecular nitrogen, there reforms also water (H$_2$O) (see formula 8). There is a possibility to reach over nitrogen 90 % efficiency of reduction with molar ratio NH$_3$ to NO without elevated (<5 ppm) ammonia emissions. (Kilpinen 2002, 332-333.)

Kilpinen (2002) mentions that the reliability of two-year period for catalysts is required. It is also required that the catalyst will not deactivate consequently for example corrosion or contamination. The factor of corrosion in the fuel gas duct is seen as a consequence of catalysing sulphur dioxides (SO$_2$) that are burning to sulphur trioxides (SO$_3$). When these sulphur trioxides react with previously presented ammonia and water, ammonia sulphate compounds (NH$_4$HSO$_4$) emerge. These compounds can be found melted in low temperatures (<280 °C). Melt is a challenge in fuel gas ducts, and it functions because it complicates the fouling process by catching other solids with itself. It is shown that precise biomasses can cause deactivations. The SCR method is not recommended to use if process is releasing carbons, or the percentage of sulphur is over 0,75 p- %. (Kilpinen 2002, 332-333.)

When the reduction of NO$_x$ to nitrogen happens in a catalytic bed the reaction optimum temperature is 300-450 °C but sometimes the temperature range can be wider from 170 °C to 510 °C. The SCR system is designed to be more modular as low loads or wide flue-gas temperatures are both possible to use with special catalysts or preheaters.

Typically used catalysts can be both vanadium pentoxide (V$_2$O$_5$) and tungsten trioxide (WO$_3$) It is general that the mass of the catalyst is bounded by titanium dioxide (Kilpinen 2002, 332). The reactor of the SCR can happen in three catalysts. These catalyst types (see figure 4.) are honeycomb, plate, and corrugates. Honeycombs' design seems to be like the original comb structures. The catalyst mass is a homogenous titanium dioxide (TiO$_2$) ceramic that is extruded to contain catalytically active V$_2$O$_5$ with WO$_3$. Plate catalyst's mass is like honeycombs' however catalytically active containers can be V$_2$O$_5$ with molybdenum trioxide (MoO$_3$) or V$_2$O$_5$ with WO$_3$ that's rolled onto supportive stainless-steel wire mesh. The third type of catalyst is corrugated whose mass is ceramic TiO$_2$. The mass of V$_2$O$_5$ and WO$_3$ is impregnated onto the surface of the fiberglass catalyst and the design looks like a corrugated box. (Industrial Emissions Directive 2010/75/EU, 220)
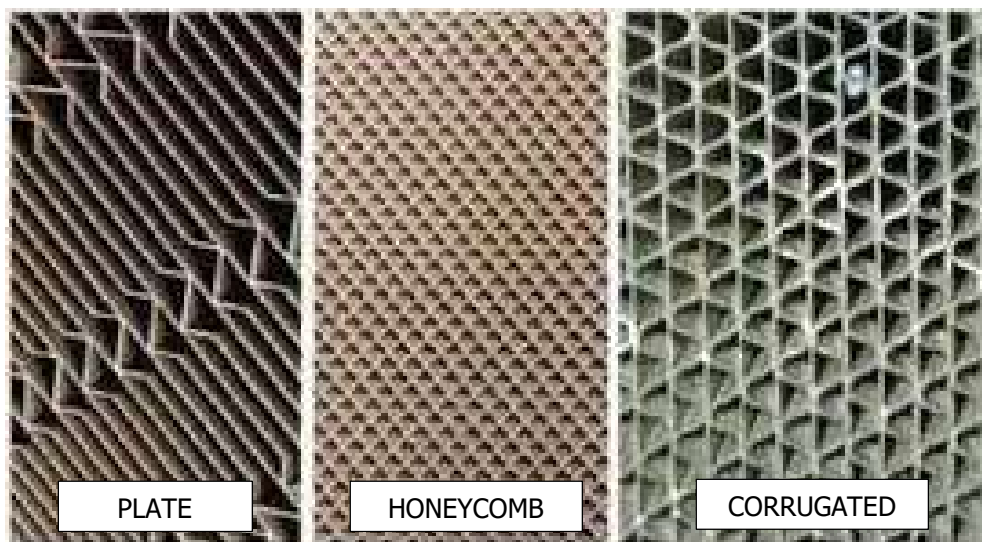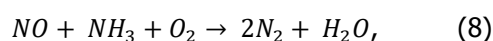
FIGURE 4. Catalyst types (adapted from Gretta 2018).

Muzio, Bogseth and Vitse (s.a.) highlight in an article the challenge with SCR catalysts operating in simply-cycle and 420-450 °C temperatures. Typically, on selective catalytic reaction NO and NH_3 reacts with O_2 and releases N_2 and H_2O:

$$NO + NH_3 + O_2 \rightarrow 2N_2 + H_2O, \qquad (8)$$

Oxidation of ammonia can happen at the surface of SCR catalyst on direct (9) and indirect (10):

$$NH_3 + O_2 \rightarrow N_2 + H_2O, \qquad (9)$$

$$NH_3 + O_2 \rightarrow NO + H_2O, \qquad (10)$$
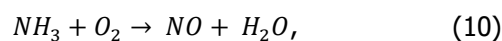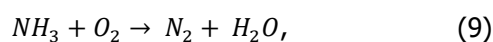
The inlet's NH_3/NO_x ratio should be 1,2, which points to the activity of used measuring. When the reaction happens in its authentic way there is less ammonia. However, this depends on available molecules as well as the combustion conditions. Below (see figure 5) is an illustrated example of relation between NO_x reduction and NH_3 slip. By injected ratio it is possible to see how the reduction of NO_x increases and what kind of NH_3/NO_x ratio there is. This can be noticed when the top reduction seems to be established and the curve starts to flatten. In this figure it is possible to see NH_3 slip as well and how that increases in specific circumstances. (Muzio, Bogseth & Vitse, s.a.)
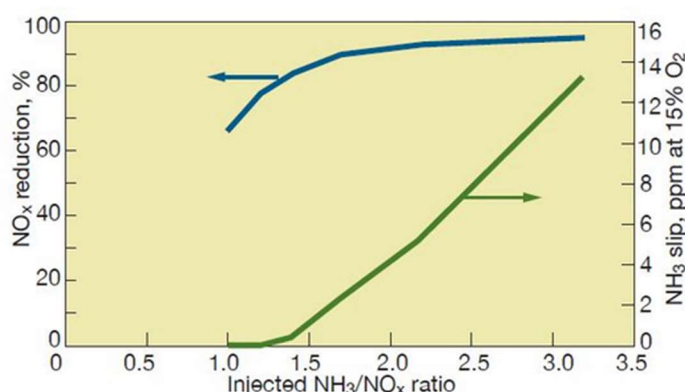

FIGURE 5. Example of showing the ratio between injected NH_3 and NO_x (adapted from Muzio, Bogseth & Vitse, s.a.)

4.2.2 Selective non-catalytic NO_x reduction

Selective non-catalytic NO_x reduction known as SNR or SNCR happens when ammonia is added to nitrogen monoxides and that reaction reduces molecular nitrogen. This can be done in flue gasses between 800 °C to 1 100 °C to have an optimal reaction. Variation in the temperature range is caused by the used reagent. When the temperature is lower, there is observed formed ammonia that makes the conversion rate low as well. From other extreme ends of higher temperatures, ammonia can be oxidized. (Kilpinen 2002, 314-315; Industrial Emissions Directive 2010/75/EU, 230-231.)

4.2.3 NO_x scrubber

Valmet has invented a solution for challenging process conditions and that is called the NO_x scrubber. Scrubbers have been used as a technology where the NO of flue gases is oxidized by a chosen oxidant (e.g., O_3 or ClO_2) to form nitrogen oxides. These NO_x flue gas runs to a scrubber where they are washed by an alkaline liquid as a regular flue gas scrubber. The NO_x scrubber of Valmet is possible to integrate heat and water recoveries as well. Valmet says that the NO_x reduction by scrubber is over 70 % and offers to minimize O_3 and ClO_2 consumptions with reduction. (Valmet 2022.)

5 INTRODUCTION OF TEST EQUIPMENT

5.1 Plant introduction

5.2 FTIR as measuring device

6   ESTIMATED PERFORMANCE OF THE TEST EQUIPMENT

6.1   Temperatures

6.2   Average flue gas components

6.3   Performance of dust filtration

6.4   Performance of SCR honeycomb catalyst

7   CONCLUSION

As a conclusion of the thesis, the results show that the combination of added ammonia and SCR honeycomb catalyst system can reduce majority of NO_x in test environment. The plant seemed to be the most efficient when the ammonia flow was 20 % and 25 % from maximum flow. Injected NH_3/NO_x ratio from measurements are presented in chapter 5.4. It is notable that both NH_3 slip, and NO_x reduction happen in the same relation to SCR systems as in the example (see chapter 4.2.1). The pressure differences were enough to keep the dust filtration clean. However, the cleaning processes started every time when the equipment was shutting down which was each day. Equipment maintenance must be planned considering all day usage.

Process temperatures were neatly under design values. Mostly temperatures were between 177-202 °C when the design values were 210-230 °C. However, the effects of temperature were not that significant on test results in a test plant of this size. The need of temperature calibration was realized at an early stage. The operating values were lower than expected and that could have caused operation failure with the ammonia and the SCR catalyst.

To support the quality of the thesis the most significant recommendations from the measuring with FTIR were brought up. The recommended layout of the measuring ports was difficult to execute because test equipment plans were made to fit just in the assigned area. This assigned area was the only possibility for the tests at the mill. The flue gas components were measured on behalf of Savonia, as the circumstances enabled the use of standardized methods. The maintenance of both FTIR devices was made when it was possible or needed by checking conditions of the devices on daily level. During the test period, there was no confirmed information about the circumstances of combustion or operation. This gives a challenge to give the concrete estimation of results. As pointed out the O_2-values were higher on first emission measuring day as there was fluctuation in the CO-values on other days. On the basis of that it cannot be said for certain what the quality of combustion was. The mill was having challenges during summer and there were maintenance shutdowns during the test period. Seems like the measuring values stabilized after the first shutdown. This means that the flue gas components were more stabilized in both ports and the greater part of measuring peaks per day were observed less frequently.

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APPENDIX 1: MEASUREMENT DATA FROM FTIRS

APPENDIX 2: MEASUREMENT AVERAGES ON DAILY

APPENDIX 3: TEMPERATURE ANALYZER'S CALIBRATION CERTIFICATE

APPENDIX 4: TEMPERATURE CORRELATION

APPENDIX 5: TRENDLINES FROM OTHER DISTRUPTIVE GAS COMPONENTS