

Note                      Notes for the BREF LCP

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## 1. Introduction

This note has been written in support of the current revision of the Reference document for Best Available Technologies for Large Combustion Plants (abbreviated as BREF LCP). The Dutch government commissioned ECN to provide their insights on the following subjects:

- *The influence of hydrogen in process gases on emissions.*
- *The environmental performance of blast furnace gas combustion.*
- *The environmental performance of fuel gas combustion.*

The research conducted for this note has been registered at ECN under project number 5.1569.01.03

## 2. Influence of hydrogen in process gases on emissions

Under the current Dutch legislation, emissions resulting from the combustion of fuels in installations larger than 50 MW<sub>th</sub> are regulated by the BEES A legislation. The Dutch abbreviation BEES A can be translated as the Decree on Emission Requirements for Large Combustion Plants. In this decree, a correction for hydrogen in gas compositions is described, which effectively allows for higher NO<sub>x</sub> emissions as compared to the emission requirements for combustion of hydrogen-free gases. This correction is proportional to the relative amount of hydrogen in gases and is applied in a linear manner. If, for example, a gas composition contains 15 vol-% of hydrogen, the NO<sub>x</sub> requirement, as prescribed in BEES A, is multiplied with a factor of 1.15. This is particularly relevant for industrial sectors that produce process gases containing hydrogen, since several process gases are suitable for combustion in steam boilers or gas turbines. This correction factor may also be considered for the current review of the BREF LCP. This section describes a review of experimental combustion results from hydrogen containing gases.

### *Gas engines*

Although most stationary gas engines are smaller than 50 MW<sub>th</sub>, the last couple of years quite some research has been devoted to the application of hydrogen enriched gases in stationary gas engines. The main reason is to decrease the amount of unburned gases. Results of hydrogen enriched compressed natural gas have been described by (Deng et al, 2011). Volume percentages of hydrogen of 0%, 30%, 55% and 75% have been investigated in an idling, spark-ignited engine. Due to low load conditions during these experiments, NO<sub>x</sub> formation was very low. Adding of hydrogen did not lead to additional NO<sub>x</sub> formation, apart from the 75% hydrogen-enriched natural gas (Deng et al,

2011). Experiments performed in the USA by TIAX LLC on the lean operation of hydrogen enriched natural gas-fuelled reciprocating engines demonstrated that  $\text{NO}_x$  formation was substantially reduced when 8%  $\text{H}_2$  (LHV  $\text{H}_2$ /LHV  $\text{CH}_4$ ) was used. A reduction of 400 ppm to 10-15 ppm  $\text{NO}_x$  was realized through hydrogen addition and by operating the installation at a higher  $\text{O}_2$  percentage in the flue gas (10% instead of 7,5%), which is enabled by an enhanced combustion stability (Smutzer, 2005). The deployment of natural gas and hydrogen mixtures in engines using two different types of combustion chambers demonstrated that hydrogen addition increased the combustion rate, resulting in a more stable combustion close to the lean limit. Although  $\text{NO}_x$  formation was slightly increased at the same air-to-fuel ratio, a more stable combustion allows for burning at leaner limits and therefore lower  $\text{NO}_x$  emissions were obtained at higher air-to-fuel ratios (Tunestal et al, 2002).

### *Gas turbines*

Research performed by (Maughan et al, 1996) on gas turbine emissions through hydrogen-enhanced, steam-injected combustion showed that  $\text{NO}_x$  emissions from natural gas turbines can be reduced by steam injection, but results in increasing unburned components. This can be counterbalanced by hydrogen injection, which reduces the amount of unburned components, but increases the  $\text{NO}_x$  formation. In general, however, when sufficient steam was injected for significant  $\text{NO}_x$  suppression, CO emissions were lowered more than  $\text{NO}_x$  emissions were increased. Hydrogen/fuel molar ratios of approximately 15 to 20% were required for CO reductions of 50% (Maughan et al, 1996). Today, new gas turbines fuelled by gas with a stable composition are fitted with DLN (Dry Low  $\text{NO}_x$ ) burners and the hydrogen effect may be different. In gas turbines with a varying fuel gas composition, steam injection (or SCR) is an  $\text{NO}_x$  reduction option.

### *Boilers*

The combustion of hydrogen-natural gas mixtures in boilers has been investigated by (Hoelzner & Szyszka, 1993). The measurements has also been performed at a constant lambda (i.e. air-to-fuel ratio). Compared to large industrial boilers, the boilers used by (Hoelzner & Szyszka, 1993) were relatively small: 20 kW<sub>th</sub>. However, interesting observations were made about various gas mixtures and partial and full boiler loads. At partial load,  $\text{NO}_x$  emissions increased at higher hydrogen levels, while at full-load the  $\text{NO}_x$  emissions reached a maximum level at 50/50 vol-% for natural gas and hydrogen. In all cases, the  $\text{NO}_x$  emissions did not increase at the same rate as the hydrogen content. As the authors themselves also pointed out, it would have been interesting to vary the lambda and hence reduce the flame temperature, since lower  $\text{NO}_x$  emissions are expected then (Hoelzner & Szyszka, 1993). Early 2000, John Zink Company reported a >90%  $\text{NO}_x$  reduction for old refinery boilers fuelled with refinery gas. This gas consisted for about 25% of hydrogen. This was not realised by the implementation of SCR, but by burner adaptations and fuel dilution with flue gas (Webster et al, 2001). (Maurel et al, 2008) observed a linear  $\text{NO}_x$  increase when adding hydrogen to natural gas in a steam boiler. However, it was noted, that the flow rate of the fuel mixture was increased to maintain the same thermal input (Maurel et al, 2008). This seems to be one of the few adjusted parameters and therefore this result might approach situations in which boilers are operated with a limited number of operational parameters.

### *Low $\text{NO}_x$ burners*

More complex  $\text{NO}_x$  emissions behavior was observed when low  $\text{NO}_x$  burners were applied: the  $\text{NO}_x$  concentration in the flue gas remained more or less the same, regardless of the applied  $\text{H}_2$  concentration in the fuel (up to 20 vol-%) (Rortveit et al, 2002). Since the addition of hydrogen to natural gas results in a lower flue gas volume per unit of energy, the  $\text{NO}_x$  emissions in this study decreased per unit of fuel input upon hydrogen addition. Moreover, this study demonstrated that the addition of hydrogen results in stable combustion at high air-to-fuel ratios (Rortveit et al, 2002). The combustion of hydrogen enriched methane in swirl stabilized burners demonstrated that, due to the stable combustion at leaner limits,  $\text{NO}_x$  emissions did not increase in comparison to pure methane (Schefer et al, 2002).

One may conclude that the effect of hydrogen addition on the combustion performance and emissions of various installations may result in increasing NO<sub>x</sub> emissions, but also allows for leaner operation of an installation. In general, a leaner operation will mitigate the increased NO<sub>x</sub> emissions compared to the operation at the original lambda. The final NO<sub>x</sub> emission will depend on the lambda factor, but also depends on the gas composition and installation parameters, with the burner design being one of the most important factors. It is important to note that adjustment of the lambda factor or flue gas recirculation in boilers may have a negative impact on the efficiency. Therefore, lowering of the NO<sub>x</sub> emissions should preferably be realised through burner design and better control of burners, air and fuel.

Compared to the reference situation various NO<sub>x</sub> emissions may be realized, since both lower as well as higher emissions have been reported. A linear relation of NO<sub>x</sub> formation with the hydrogen content in gaseous fuels cannot be straightforwardly applied to various fuels and installations.

Apart from the gas composition, NO<sub>x</sub> emissions seem to be closely related to variation in gas quality and gas quantity. For example, it has been described by (Sticher et al, 2003) that the blast furnace gas-fuelled cogeneration plant in Hamborn normally remains far below the emission requirements at stable operation, but that NO<sub>x</sub> emissions mainly increase when blast furnace gas compositions start to vary. This indicates that hydrogen present in blast furnace gas (up to 6 vol-%) is not the major cause of NO<sub>x</sub> emissions, but that NO<sub>x</sub> formation is mainly induced by operating installations with variable fuel compositions and quantities, even when the installation was recently constructed (Sticher et al, 2003).

### 3. The environmental performance of blast furnace gas combustion

Blast furnace gas is the process gas resulting from pig iron production in a blast furnace (Hoppesteyn, 2008). At several steel mills, the process gases produced by various production steps for steel production are deployed for steam and/or power generation. It is possible to use either a boiler/steam turbine technique or a combined cycle power plant for the combustion of blast furnace gas. The advantages and disadvantages of both techniques have been described by (Stolbrink & Reyser, 2009). The boiler/steam turbine technique has the advantage of being more mature and the possibility to combust gases with a wide range of calorific values (Stolbrink & Reyser, 2009). In this section, the current status of applied technologies for the combustion of blast furnace gas in boilers is reviewed with respect to environmental performance.

In a brochure, the ANDRITZ Group describes the realisation of a DeNO<sub>x</sub> installation in the blast furnace gas-fired boiler/steam turbine plant of the Voest Alpine steel mill in Linz (Andritz company, 2012). This has been confirmed by Voest Alpine's environmental statement of 2007 (Voest Alpine, 2007). According to this environmental statement, the NO<sub>x</sub> requirements will be settled to 100 mg/m<sub>0</sub><sup>3</sup> for these combustion units, which is amply met as a yearly average in 2005, 2006 and 2008, 2009 for all power plant units (Voest Alpine, 2007; Voest Alpine, 2010). Information has been requested from the Umweltbundesamt of Austria and they confirmed that this requirement of 100 mg/m<sub>0</sub><sup>3</sup> is applicable at 3% O<sub>2</sub> and as a mean average of half an hour (30 minutes). The Umweltbundesamt also confirmed that the DeNO<sub>x</sub> installation at the Voest Alpine power plant units is applied as a retrofit technique for the unit 4, 5 and 6 in Linz.

An extensive article describes the construction of a cogeneration power plant in Hamborn by RWE (Sticher et al, 2003). This plant is designed as a conventional boiler/steam-turbine plant and is fuelled with blast furnace gas from Thyssen-Krupp-Stahl AG in Duisburg and cokes oven gas from a new cokes plant in Duisburg-Schweigern. The thermal power of this plant is 535 MW and the electrical power output is 225 MW. The process steam is exported to Thyssen-Krupp-Stahl. Exten-

sive experience with low NO<sub>x</sub> combustion of blast furnace gas has been gained by RWE at a blast furnace gas power plant in Huckingen. At this power plant in Huckingen, low NO<sub>x</sub> combustion is also applied and under stable conditions, NO<sub>x</sub> formation are kept well below the emission requirement of 100 mg/m<sub>0</sub><sup>3</sup> (dry, at 3 vol-% O<sub>2</sub>). It may therefore be concluded that low NO<sub>x</sub> combustion for blast furnace gas is a commercially available technology (Sticher et al, 2003). The availability of this technique is also confirmed by the SAACKE Group in a presentation on swirl burners. This type of low NO<sub>x</sub> burner has been used for relatively small boilers (2 x 11 MW) at a steel mill in Bremen and NO<sub>x</sub> emissions are kept below 30 mg/m<sup>3</sup>; further details on the measurement conditions were not described (Schopf, 2012).

(Sticher et al, 2003) explained that despite these technological developments, it was expected that fluctuations on blast furnace gas quantities and qualities would result in increased NO<sub>x</sub> emissions. It was also expected that combustion of cokes oven gas would result in enhanced NO<sub>x</sub> emissions. Therefore, a DeNO<sub>x</sub> system consisting of SCR was deployed as well at this power plant (Sticher et al, 2003). This way, fulfilment of the emission requirement of 100 mg/m<sub>0</sub><sup>3</sup> (dry, at 3 vol-% O<sub>2</sub>) can be guaranteed. Information on the measurement regime has been requested from RWE and they confirmed that this emission requirement is applied on a daily average basis.

The Dutch steel producer Corus in IJmuiden, nowadays called Tata Steel, has submitted an environmental impact statement for the construction of a 525 MW<sub>e</sub> cogeneration power plant, which will be fuelled by their process gases (Corus, 2012). This environmental impact statement is part of the license procedure for the construction of such an installation in the Netherlands. Corus described that application of low NO<sub>x</sub> burners and SCR is planned for this installation to keep NO<sub>x</sub> emissions well below 100 mg/m<sub>0</sub><sup>3</sup> (3 vol% O<sub>2</sub>; dry) on a yearly basis as well as on a daily basis (Corus, 2012).

The above described references demonstrate that application of low NO<sub>x</sub> burners and SCR is technical feasible and has been demonstrated for blast furnace gas combustion and will result in emissions below 100 mg/m<sub>0</sub><sup>3</sup> (3 vol% O<sub>2</sub>; dry).

#### 4. Environmental performance of fuel gas combustion

Ethylene, also called ethene, is one of the most important chemical building blocks and is produced in massive volumes as a petrochemical. The current production of ethylene is mainly based on oil products or natural or associated gas as feedstock. Steam cracking is the major technology for the production of ethylene. During this process, several by-products are produced. Some of these by-products are used as a fuel to serve several processes at an ethylene plant (Zimmerman & Walzi, 2012). The fuel gas composition from naphtha cracking typically consists mainly of methane, but hydrogen is also a substantial component of the fuel gas. Some percentages of higher hydrocarbons are often present as well (Ren, 2009; Zimmerman & Walzi, 2012).

The environmental performance of fuel gas combustion at ethylene plants can be adjusted with modern technologies. For commercially available ethylene cracking furnaces, several suppliers have low-NO<sub>x</sub> burners and SCR available that can be used for this type of combustion (Zimmerman & Walzi, 2012). For cracking furnaces, a chromium deposition at the SCR catalyst has been reported, due to the use of a chromium alloy in the furnace (Kunz & von Alten, 2002; O'Leary et al, 2004). One of the first SCR-equipped cracking furnaces was installed at the ethylene plant of the Maruzen Petrochemical Company. They reported the issue of chromium deposition as well (Funahashi et al, 2001). However, these issues seem to have been solved, resulting in commercially available SCR catalysts (Bowen, 2006; Jensen et al, 2009).

On their website, Selas-Linde provides feasible emission limits for ethylene cracking furnaces fuelled with fuel gas from the cracking process. Without a DeNO<sub>x</sub> catalyst, <100 mg NO<sub>x</sub>/m<sub>0</sub><sup>3</sup> is feasible, while with a DeNO<sub>x</sub> catalyst, <60 mg NO<sub>x</sub>/m<sub>0</sub><sup>3</sup> is feasible (Selas-Linde, 2012). Selas-Linde confirmed that these limits are true for 3% O<sub>2</sub>. Averaging in time does not seem to be an issue, since heavy fluctuations in gas compositions are not that much abundant for the ethylene cracking process. According to Selas-Linde, deployment of a DeNO<sub>x</sub> catalyst is possible for the combustion of fuel gas resulting from naphtha cracking, regardless of being burned in a cracking furnace or in a boiler. However, actual implementation is uncommon: it depends on the local requirements, but the majority of cracking furnaces are not equipped with a DeNO<sub>x</sub> catalyst, according to Selas-Linde.

According to (Kunz & von Alten, 2002), 14.9 ppmd NO<sub>x</sub> is realised at 4.1% O<sub>2</sub> at the ethylene plant of Maruzen with SCR. Recalculated, this results in 33 mg NO<sub>x</sub>/m<sub>0</sub><sup>3</sup> at 3% O<sub>2</sub>. Haldor Topsøe reported NO<sub>x</sub> emissions well below 10 ppm without a reference O<sub>2</sub> percentage. Recalculated, even with very high O<sub>2</sub> percentages, emissions remain below 60 mg NO<sub>x</sub>/m<sub>0</sub><sup>3</sup>. This suggests that the emission ranges of Selas-Linde are reasonable.

Combustion of fuel gases in boilers may result in comparable emissions as for cracking furnaces, when a comparable combustion regime is applied. If used for the combustion of fluctuating quantities and compositions of fuel gases, one may reasonably expect somewhat higher NO<sub>x</sub> emissions. Low-NO<sub>x</sub> burners remain the first choice reduction technology. The application of SCR is commercially available for ethylene cracking furnaces. These furnaces are often operated at a high load and a high number of operating hours per year. For the actual implementation of SCR at a fuel gas-fired boiler that is operated at partial load and fluctuating amounts and compositions of fuel gas, a balance between its actual emissions and load-duration seems to be relevant. Starting points may be the feasible emission limits as provided by Selas-Linde compared to the actual emissions of a boiler.

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