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Effect on NOx Emissions of Hydrogen Addition to Natural Gas in Industrial Boilers and Heaters

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EXECUTIVE SUMMARY

The hydrogen-enriched natural gas (HENG) could serve as a bridge between the fossil fuel used today and a hydrogen fuelled economy in the medium future. In the context of MSAPR (Multi-Sector Air Pollutants Regulations), the existing industrial boilers & heaters (with heat input greater than 10.5 GJ/h or 2.94 MW) will have to limit NO_x emissions to 26 g/GJ and to 16 g/GJ for the new equipment.

Unfortunately, there is limited data published for the industrial scale on the effects of HENG on NO_x emissions. Increasing the hydrogen content of HENG from 0% to 20% by volume would produce an increase in NO_x emissions between 12% and 17% compared to natural gas. In the Power-to-Gas scenario of fluctuating hydrogen content with no adjustment in burner control settings, an increase of 1% in the hydrogen content of HENG (e.g., from 7% to 8%) will produce an increase in NO_x emissions around 0.5%.

The availability of advanced burner technology, the sophistication of burner suppliers, the option of flue gas recirculation or post-combustion reduction, means that the operators of boilers and heaters in Canada should be able to meet the NO_x emission limit of 26 g/GJ, even with 20% HENG.

RECOMMENDATION: These conclusions are based on very limited experimental data on the effect of hydrogen enrichment at the industrial scale. Validation could be done on a full-scale boiler or heater, at least 10.5 GJ/h. The experimental campaign should look at different levels of hydrogen addition to natural gas (0%, 5%, 10%, 15%, and 20% hydrogen) controlling for heat input and stack oxygen concentration. The NO_x emissions and thermal performance of the unit should be reported.

Testing for a higher level of hydrogen (60% to 80%) as for a micro-grid scenario would require an engineering assessment of the host facility. This may be better performed at the test facility of a burner supplier.

CFD (Computational Fluid Dynamics) simulation of the tests should also be attempted. If the simulation reproduces the experimental results then this could be a lower-cost tool to answer future questions on the effects of hydrogen enrichment on the performance of combustion equipment.

A measurement campaign looking for nitrous oxide in the stack gas of industrial equipment firing HENG should be considered if there are any future papers in the scientific literature finding nitrous oxide in the combustion products of HENG combustion.

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INTRODUCTION

Natural gas is the lowest carbon intensity fossil fuel, giving 2.74 kg CO₂/kg NG or 49.5 kg CO₂/kJ fired. Hydrogen combustion produces H₂O only, with NO_x being the major pollutant of concern. The hydrogen-enriched natural gas (HENG) could serve as a bridge between the fossil fuel used today and a hydrogen fuelled economy in the medium future.

In the context of MSAPR (Multi-Sector Air Pollutants Regulations), the existing industrial boilers & heaters (with heat input greater than 10.5 GJ/h or 2.94 MW) will have to limit NO_x emissions to 26 g/GJ and to 16 g/GJ for the new equipment.

These limits should be attainable at 100% NG without equipment change. In fact, since these are hard limits with no allowance to exceed them, even lower NO_x emission rate would be the regular operation. However, the addition of hydrogen to the NG network may affect the ability to meet these limits.

The purpose of this report is to answer the following questions:

- Which types of burners could reach the above NO_x limits with:
 - 100% natural gas, and
 - 20% HENG;
- Whether the burners capable of complying with the 26 g/GJ NO_x limit with a 20% HENG could be retrofitted into an existing equipment; and
- What are the challenges or limitation in retrofitting those burners (with 20% HENG and limit of 26g/GJ) in existing equipment.
- If it were not possible to retrofit existing burners so they can comply with actual limits, what limits would be attainable considering 20% HENG.

COMBUSTION CHARACTERISTICS RELEVANT TO HENG IN BOILERS AND HEATERS

HENG has several significant changes in combustion properties compared to natural gas. The heating value on a volumetric basis (Figure 1) decreases with increasing hydrogen content as well as the air-to-fuel ratio (AFR) (Figure 3). These contribute to the increase in adiabatic flame temperature (AFT) (Figure 2). For the range of hydrogen content from 0% to 20% by volume the AFT is approximately linear in hydrogen content. This linear approximation will be used later to estimate the impact of the Power-to-Gas scenario for fluctuating hydrogen injection into the NG network.

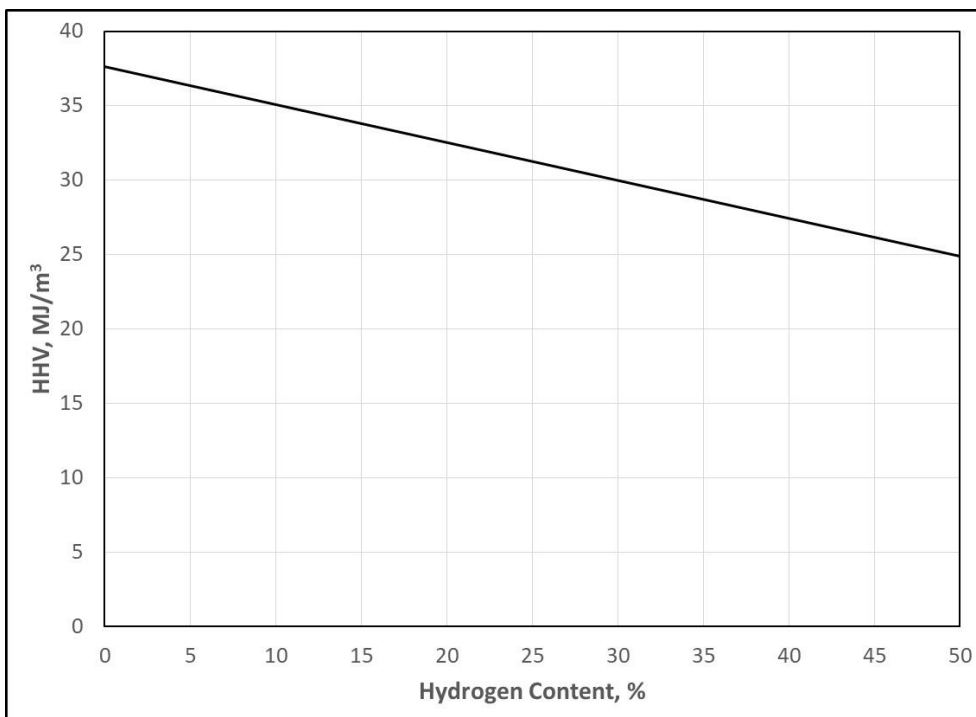


Figure 1 - Volumetric higher heating value HENG as hydrogen content increases.

Hydrogen content in HENG is presented in volume percent in this report unless explicitly stated otherwise. Some publications use energy percent, since fired equipment control for energy input, which is a much higher volume percent.

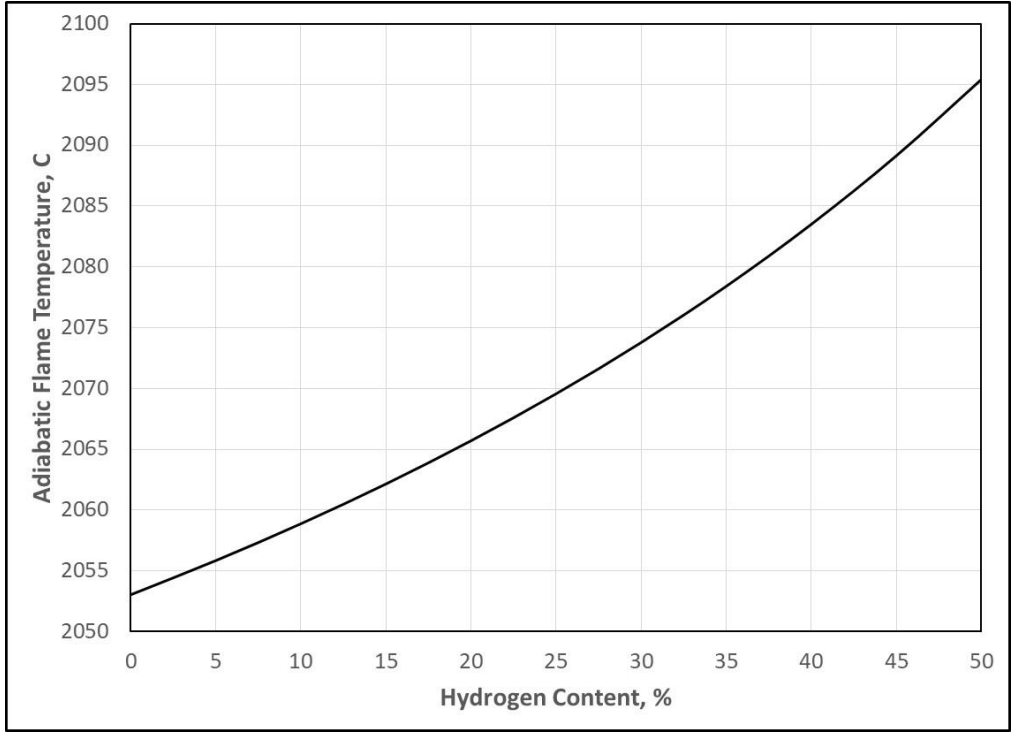


Figure 2 - Calculated adiabatic flame temperature for HENG with increasing hydrogen content.

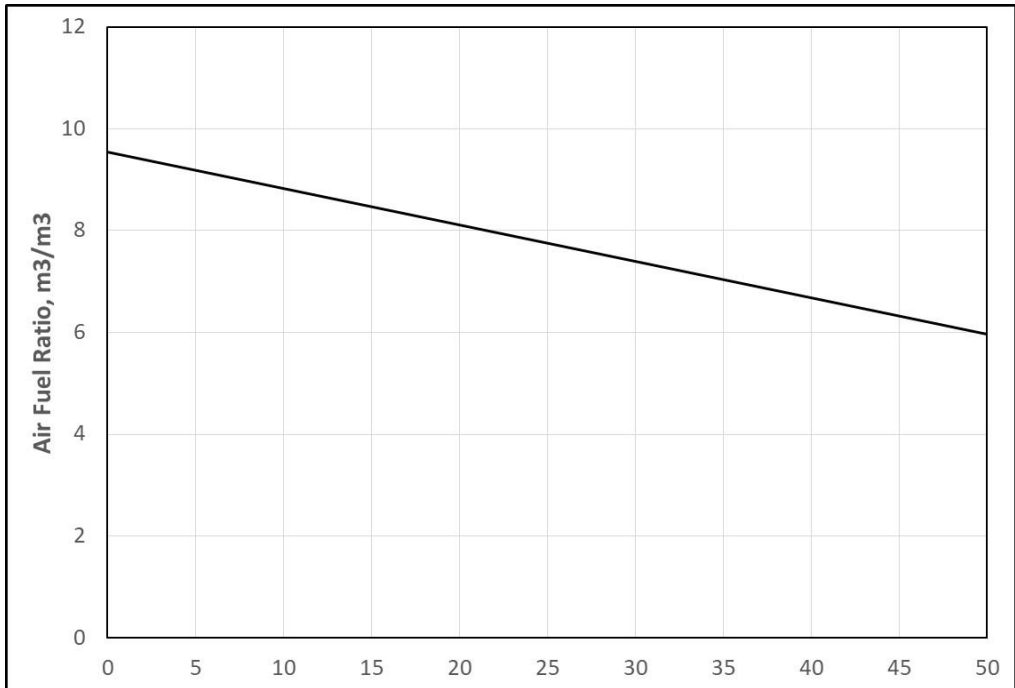


Figure 3 - Volumetric air-to-fuel ratio for stoichiometric combustion of HENG with increasing hydrogen content.

NO_x FORMATION IN COMBUSTION OF GASES

NO_x includes both NO and NO₂. Combustion of gases generally produces some amount of both of these species, though NO is usually the dominant one. Three mechanisms have been identified:

- **Fuel NO_x** – the oxidation of nitrogen containing species in the fuel.
- **Thermal NO_x** – oxidation of molecular nitrogen in the combustion air due to high flame temperature.
- **Prompt NO_x** – oxidation of molecular nitrogen via hydrocarbon radicals from the fuel.

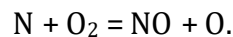
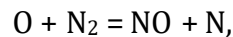
Fuel NO_x

Coal, biomass, and heavy fuel oil generally contain some amount of nitrogen that will be released by evaporation or pyrolysis into the gas phase. Biomass derived gases, such as producer gas, or by-product gases from pyrolysis or carbonization will also have some amount of nitrogen containing species. Fuel gases in refineries and chemical plants may have some amount of nitrogenous species. While there is a great variety of nitrogen containing compounds in practice, the basic chemical mechanisms are divided into those with carbon, represented by HCN, and those without carbon, represented by NH₃. The simple representative molecules are taken to be the ultimate result of thermal decomposition of the larger, more complex molecules like amines and ureas.

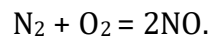
The ALTERNATIVE GAS fired in heaters and boilers of refineries and chemical plants may have fuel nitrogen as a source of NO_x emissions. HENG, however, does not and so the fuel NO_x mechanism will not be included in the discussion that follows.

Thermal NO_x

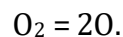
The high temperature in the vicinity of flame front produces radicals that are highly reactive. On the air side of the flame, the oxygen molecule decomposes to two oxygen atoms which can attack the molecular nitrogen that is also present. This is known as the Zeldovich mechanism and contains the pair of reactions:



These reaction combine to give the global reaction



The dissociation reaction is taken to be in thermal equilibrium



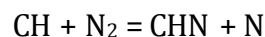
A global formation rate for thermal NO_x can be written as

$$[\text{NO}] = A e^{-T_{eq}/T} [\text{N}_2] \sqrt{[\text{O}_2]} \quad [\text{E1}]$$

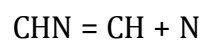
This form conveys the main dependencies of the thermal NO_x mechanism: temperature through the Arrhenius factor and a weaker dependence on the local oxygen concentration.

Prompt NO_x

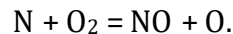
On the fuel-rich side of the flame front the hydrocarbon molecules break down and the resulting CH radical attacks molecular nitrogen as follows



The CHN molecule breaks down in the high temperature zone



The CHN, CH and N formed can move through the flame front to react with oxygen and produce NO as happens in the thermal NO_x mechanism



This reaction path is much less productive than the thermal NO_x route for conventional burners. Ultra-low NO_x burners are able to reduce the thermal NO_x sufficiently that prompt NO_x becomes a significant contribution to the total emissions. It is worth noting that ultra-low NO_x burners firing HENG experience a reduction of NO_x emissions as the hydrogen content approaches 100% because the prompt NO_x mechanism requires hydrocarbon radicals.

However, the scope of this report is to look at the effect of HENG on NO_x emissions from conventional burners in boilers and heaters and so prompt NO_x is not a significant contributor to those emissions. Thermal NO_x is the only significant mechanism in such circumstances and the equation E1 is used to guide the discussion.

Nitrous Oxide

Nitrous oxide, N₂O, can be formed from fuel nitrogen in solid fuel combustion, primarily coal. An active research area thirty years ago, it has mostly disappeared once the gas measurement artefacts were discovered and solved so that the significance of these emissions were negligible compared to the nitrous oxide produced from nitrogenous fertilizer use in the agricultural sector.

Colorado et al. (2017) found measurable nitrous oxide emissions at the lean limit for combustion of natural gas (previously thought only to come from fuel nitrogen) with the enrichment with hydrogen increasing the emissions of N₂O. They claim that some published reaction mechanisms can explain this. Nothing further was found in the literature. It is worth noting this paper as N₂O has GWP over 250 times greater than CO₂ so that if HENG produces N₂O in measureable quantities then the GHG reduction benefits of HENG may be reduced significantly. In the future, a measurement campaign looking for nitrous oxide in the stack gas of industrial equipment firing HENG should be considered.

Kinetic Modelling

The discussion above only covers the basics of the mechanisms involved in the calculation of the NO_x production in real burners. The full mechanisms used in sophisticated computational fluid dynamic (CFD) reacting flow models have hundreds of reactions and over fifty species. These are an area of active research. These kinetic models for general HENG combustion need validation with reliable data for conditions of use. Mével et al. (2012) shows different models perform differently for experimental validation with laboratory equipment including jet-stirred reactor, laminar flame speed, ignition delay time, detonation cell size. These are lab scale experiments with high precision measurements. Generally, only one or two of the bench-scale equipment are used for validation of computational mechanisms. Mével et al. (2012) and Zhang et al. (2017) showed the generally failed when applied to combustion situations different from those used to validate the model.

While the amount of work and the accomplishments of these kinetic models are scientifically impressive, there is still doubt about whether they are fully reliable for simulation of the NO_x emissions from industrial-scale fired equipment.

BURNERS

Conventional Burners

The conventional burners for boilers were designed to give reliable operation under variations of fuel and air supply. The flames are compact so the boiler would not take up space, meaning the fuel and air are mixed rapidly giving intense flames. The combustion air enters through a register that imparts swirl that shortens and widens the flame. Fuel gas enters through a header with uniformly spaced holes to distribute the fuel evenly into the air. A refractory quarl or tile with conical opening helps to shape the recirculating flow of hot combustion gases produced by the swirl. The quarl also provides thermal inertia to stabilize the flame when using low or variable heating value fuel. The intense combustion produces a hot flame that is good for heat transfer to the boiler. The high temperature also produces thermal NO_x.

Industrial size burners have two ways of introducing the combustion air. Forced draft has the air pushed into the burner using a fan. Burners may share a windbox for this air flow. Induced draft uses an induced draft fan in the ductwork to produce a negative pressure in the firebox that draws the air around the burner. The forced draft burner has greater control over the flow and mixing, therefore combustion. Forced draft burners generally have lower NO_x emissions.

More advanced burners have some division of the air between primary and secondary air. This allows staging of the air injection and control of the fuel/air mixing process. If the mixing with the secondary air is delayed, the peak temperature is reduced and thereby the formation of thermal NO_x. This delayed mixing, either by staging the fuel or staging the air or both, is the basic design principle for low-NO_x burners. One consequence is that the flame shape is changed, giving longer flames and more distributed heat release. The flow pattern around the flame is also changed, purposefully drawing furnace

gas that has lower concentration of oxygen into the flow to lower the flame temperature by diluting the fuel/air mixture.

Classifications

There are many variables that affect the NO_x emissions from fired equipment. Burner design is the main determinant but factors such as firebox operating temperature, number of burners, total heat release can have significant impact (Tsiralnikov et al. 2003). The classification of burners as 'low NO_x' and 'ultra-low NO_x' are generally based on the emissions from a single burner in a test furnace. When the burners are installed and tested for compliance, the rule of thumb is that the NO_x emissions should not exceed 80% of the permitted limit to provide a margin for any variability in operating conditions (Baukal 2001, Colannino 2006) .

Low NO_x burners are usually described in comparison to conventional burners, with phrases like "reduction in NO_x emissions of 50% to 75%" compared to conventional burners. The range of NO_x emissions from a conventional burner can be from 100 ppm to 125 ppm at 3% oxygen firing natural gas, which is from 50 g/GJ up to 65 g/GJ. Crudely, the range of emission factor could be from 13 g/GJ up to 33 g/GJ, though a more realistic upper bound would be 25 g/GJ. In a paper on retrofit case studies (Schalles and Valancius 2015), the NO_x emission factor was 0.044 lb/MMBTU or 21 g/GJ for the installed upper limit for several of the low NO_x burners installed.

Ultra-low NO_x burners are promoted as being capable of achieving 'single digit' ppm emissions. Taking these to be normalized to 3% oxygen in the stack gas, this translates to less than 5.1 g/GJ emission factor when firing natural gas. When including the additional effects in furnace operation, a heater or boiler equipped with ultra-low NO_x burners should have emissions below 10 g/GJ.

Scale Effects on NO_x Emission Studies

Weber and Mancini (2020) reviewed the experimental work on scaling of laboratory flames to industrial-scale burners, drawing implications for the utility of both small-scale burner work and computer simulation that are validated using small-scale data. Industrial burners have firing rates greater than 1 MW. Laboratory burners are in the range of 10 kW to 50 kW, and pilot-scale burners in the range 100 kW to 500 kW. There is significant experimental evidence that results from gas-fired burners at the laboratory and pilot-scale do not scale up to industrial burners. In particular, the Scaling 400 studies looked at NO_x emissions from geometrically scaled burners at 30 kW, 300 kW, 1.3 MW, 4 MW, and 12 MW (thermal scaling ratio of 400 from smallest to largest) (Bollettini et al. 2000). It was found that the NO_x emissions from 30 and 300 kW burners did not match those of the larger ones, which did line up. Hsieh et al. (1998), operators of the 30 kW and 300 kW burners, presents a sophisticated modelling approach to reconcile the Scaling 400 study results for smaller burner with the large industrial burner. This involved identifying the mixing and reaction zones for the burner and noting the differing contributions of the zones to the total NO_x emissions. This work provides interesting insight into how mixing and reaction contribute to NO_x emissions but reinforces the conclusion that a direct comparison of laboratory scale and pilot-scale burner results to full scale is not valid for NO_x emissions. Therefore, NO_x emission results for burners smaller than 0.5 MW have to be used with caution for making conclusions regarding emissions from industrial burners. Bollettini et al. (2000) makes the categorical statement that “The minimum thermal input, which can be considered large enough for scaling purposes, seems to be around 1.3 MW.” A recent study by Meraner et al. (2020) did a purely numerical study of scaling for a prototype hydrogen burner for firing rates from 10 kW to 500 kW. They did find that combustion regime changed above 250 kW and that there was a flow field change around 500 kW.

The lower limit for burner size to produce results directly transferrable to industrial burners is therefore between 300 kW and 1.3 MW. A burner of 500 kW is likely to be big enough, with 1 MW a much safer lower limit. The pilot-scale furnaces at CanmetENERGY in Ottawa have a maximum firing rate of 400 kW (1.6 GJ/h). This may not be large enough for reliable experiments on the effects of hydrogen enrichment on NO_x emissions.

BOILERS AND HEATERS

Boilers and process heaters are the fired equipment covered in this report. As a rule boilers operate at a lower temperature in the firebox than process heaters. Process heaters often fire alternative gases like refinery fuel gases, which are mixtures of off-gases from the process equipment in the plant. In such circumstances, the burners on process heaters have to be more robust, able to handle the variation in the fuel properties without significant impact on the productivity of the heater either through changes in heat release or by formation of hot spots on heat transfer surfaces. Process heaters are more likely to have induced draft air injection, while boilers have forced draft. There will be heat transfer surfaces in the firebox and in the exit duct work.

Large boilers and heaters will have multiple burners and perhaps multiple rows of burners. The firing rate of the burner will be controlled to avoid impingement of the flame on the opposite wall. Low NO_x burners typically have flames 25% to 50% longer than conventional burners of the same firing rate. The spacing between burners, both horizontal and vertical, is large enough that the burners do not interact significantly. Here too the low-NO_x burner can require greater spacing to avoid interaction. The configuration of burners, the shape of the firebox, and the placement of the heat transfer surfaces are not standardized so that the total heat rate of two units may be the same but have different number of burners. Different number of burners can produce different NO_x emissions, even with the same total firing rate (Tsiralnikov et al. 2003).

Burners can share a windbox so that the distribution of air among the burners is an important consideration for the optimal thermal performance of the heater, but also for the production of NO_x. It can happen that changes to burner configuration and operation will improve the thermal performance of the heater and reduce the NO_x emissions at the same time, such that the expenditure is recovered through productivity improvements.

A final consideration for boilers and heaters is that the relative spacing of the units can have impacts on operation of induced draft units and the prospects for retrofits or installation of post-combustion NO_x reduction equipment. A facility with a stand-alone boiler can have greater flexibility for retrofits than a process heater placed among other fired equipment.

EFFECT OF HYDROGEN ADDITION ON NO_x EMISSIONS

There is little data published on the effect of hydrogen addition on NO_x emissions with conventional industrial scale burners. Two papers cited in Gogolek (2019), Slim et al. (2006) and Leicher et al. (2017) tested performance of conventional burners with HENG used pilot-scale burners.

Slim et al. (2006) looked at HENG effects in various combustion equipment. Relevant here is the work done with a 150 kW commercial process burner fired in a kiln. NO_x emissions rates reported for HENG up to 50% H₂ at 4 different furnace temperatures. Results for the emission rates are presented in Figure 4. NO_x increases with increased furnace temperature. Hydrogen enrichment has greater effect with lower furnace temperature. There was little increase in NO_x emissions for HENG above 20% H₂ content when furnace temperature is above 500°C. The increase relative to natural gas firing is shown in Figure 5. The relative increase of NO_x emission factor due to hydrogen enrichment decreases with increasing furnace temperature.

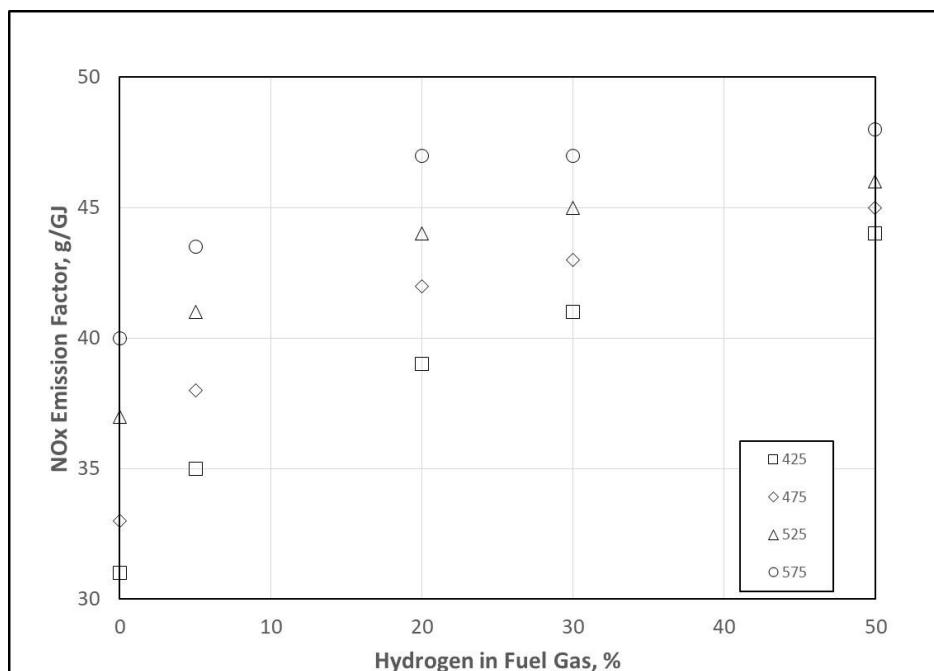


Figure 4 - NO_x emission factors for HENG at different furnace temperatures from Slim et al. (2006). Hydrogen content in volume percent.

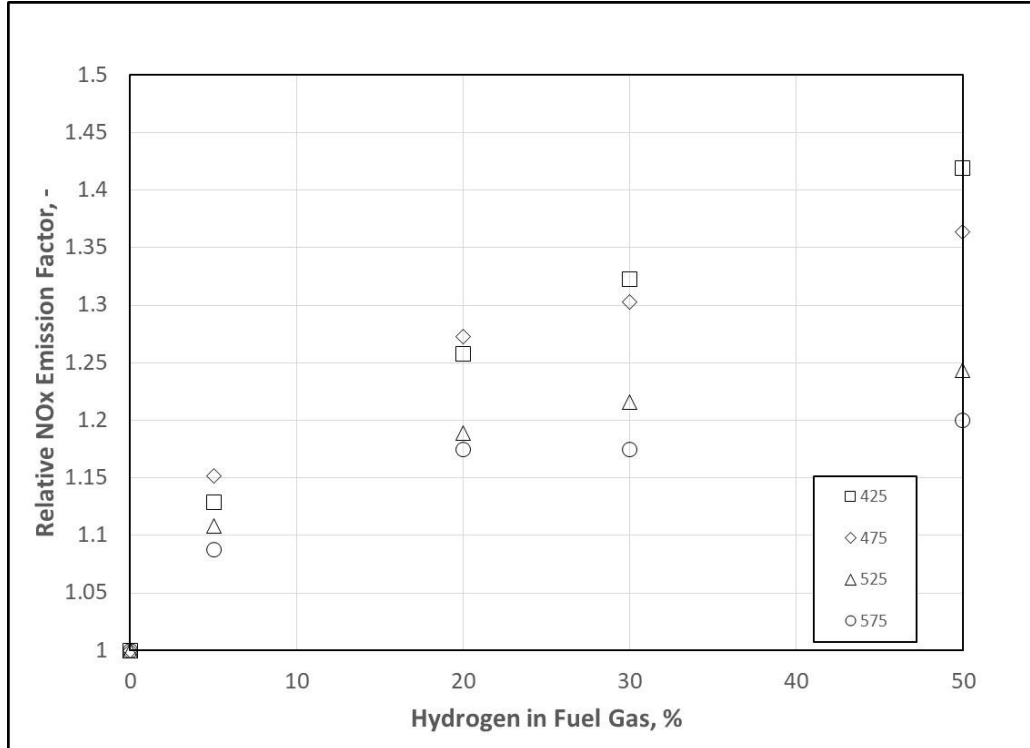


Figure 5 – Relative NO_x emission factors for HENG at different furnace temperatures from Slim et al. (2006). Hydrogen content in volume percent.

Schalles and Cochran (2020) give a curve for NO_x emissions (normalized to 3% oxygen) from a conventional burner firing HENG for the full range of hydrogen content, reproduced in Figure 6. The NO_x emission factor was calculated from these data by this author and is presented in Figure 7. There is a maximum around 88 g/GJ for hydrogen content between 70% and 80%, and a decrease to 80 g/GJ at 100% hydrogen.

The generalized curves for the increase in NO_x emission factor with hydrogen content in HENG relative to natural gas for industrial scale burners from Modi and Waibel (1995) (as found in Waibel et al. (1995)) is presented with that from Schalles and Cochran (2020) in Figure 8. It is likely that the furnace temperatures were much higher for the Modi and Waibel curve, since the publications of these authors generally address issues of the petrochemical heater industry. As well, the fuel was possibly a model refinery fuel gas rather

than HENG. The range of increase of NO_x at 20% hydrogen content from both sources is from 12% to 17% above that firing natural gas.

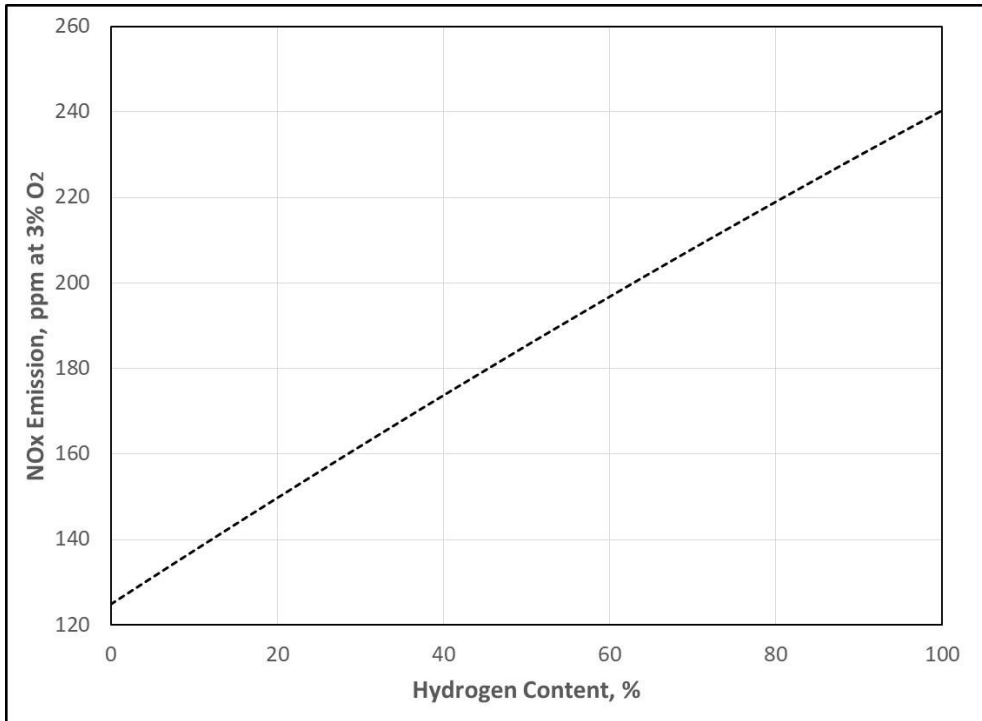


Figure 7 - Effect of hydrogen content on normalized NO_x emissions after the data in Schalles and Cochran (2020). Hydrogen content in volume percent.

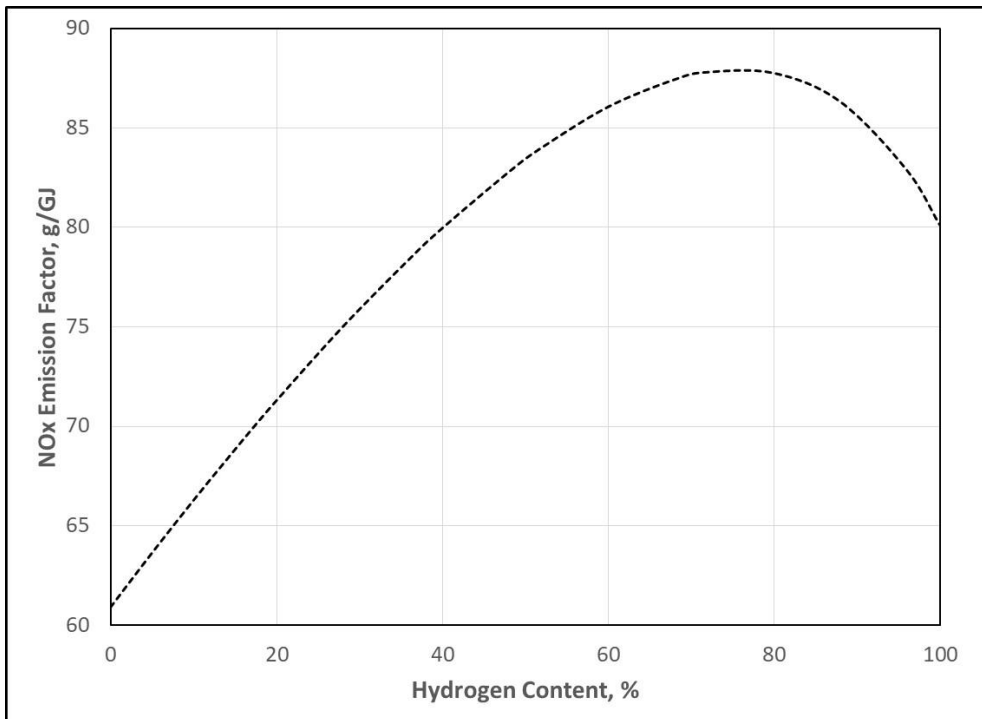


Figure 6 - Effect of hydrogen content on NO_x emission factor after the data in Schalles and Cochran (2020). Hydrogen content in volume percent.

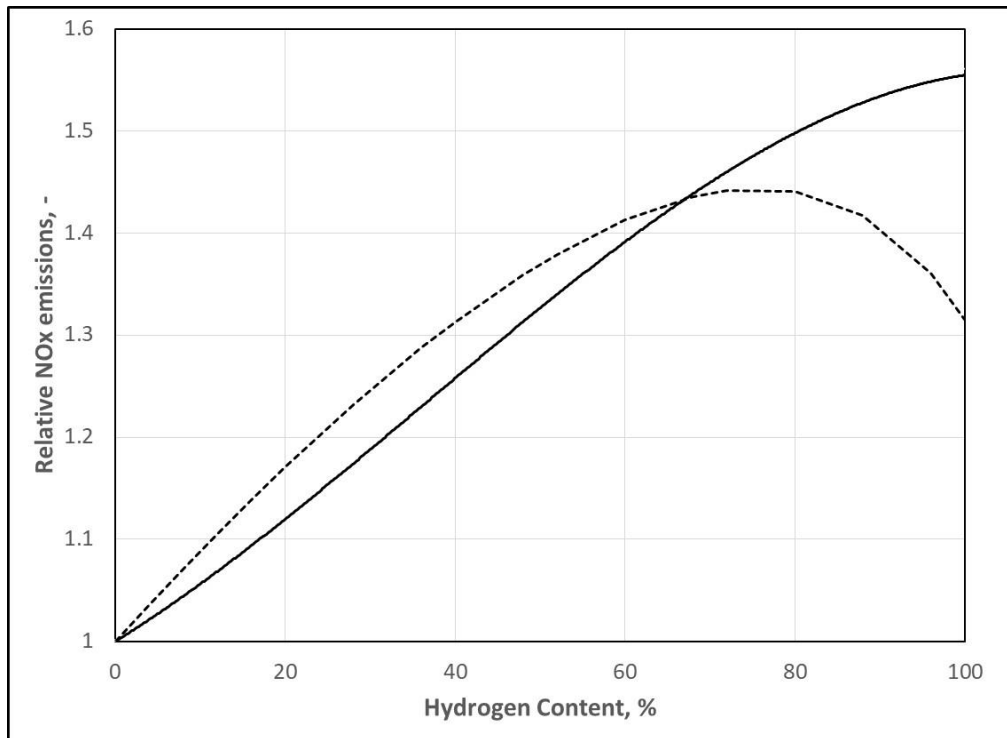


Figure 8 - NOx emission factor for HENG combustion relative to natural gas for Schalles and Cochran (2020) (dashed line) and Modi and Waibel (1995) (solid line). Hydrogen content in volume percent.

The question of the applicability of the Slim data points has to be addressed. The burner is only 150 kW. The lower limit for a burner to be scalable to industrial burners is at least 500 kW, perhaps as high as 1.3 MW, as noted in the section “Scaling Effects” above. Comparing these data from Slim et al. (2006) in Figure 5 to the generalized curves in Figure 8 it is clear that even the general shapes are different. The Slim values increase rapidly up to 20%-v hydrogen and then level off (Figure 5). The large-scale curves in Figure 8 more uniform over the range of 0 to 50 %-v. As well, the Slim data are for a kiln not a boiler or heater so that the geometry and heat transfer are completely different. In what follows only the industrial-scale information of Schalles and Cochran (2020) and Modi and Waibel (1995) will be used.

A higher furnace temperature displays a lower impact of the increase in hydrogen content. There is an empirical linear relation for the effect of furnace temperature used at John Zink for large burners and reported in Colannino (2006)

$$\frac{Y_{NO}}{Y_{NOref}} = \frac{T_f - 204}{T_{ref} - 204} \text{ with temperatures in } ^\circ\text{C}.$$

As the reference furnace temperature increases, the effect of changing the furnace temperature, as represented by the slope of the line, is reduced. This can help explain the difference between the two curves in Figure 8. Process heaters operate at a higher temperature than boilers. The flame temperature will increase with increased hydrogen content. The NOx formation zone will therefore increase more with a cooler firebox relative to the reference condition (no hydrogen addition) than for a hot firebox.

Using the data from Schalles and Cochran (2020) and Modi and Waibel (1995) for full-scale burners, the scenario of moving from natural gas to 20%-v hydrogen content HENG will give an increase of NOx emission between 12% and 17%. Thus, it can reasonably be expected that boilers and heaters with conventional burners firing HENG of 20%-v hydrogen will display a similar increase of NOx emissions of 10% to 20% compared to firing natural gas.

Variable Hydrogen Content

The discussion above deals with a steady hydrogen content for which the burners are controlled with specific fuel and air flow rates. However, a variable hydrogen content is another possibility, such as with the Power-to-Gas scenario where surplus renewable electricity is used to generate green hydrogen that is injected into the natural gas supply. This produces a time varying hydrogen content.

Let us consider a boiler or heater firing HENG at a fixed hydrogen content. The volumetric fuel and air supply are fixed to give the desired heat input into the firebox, with a fixed excess air. These conditions will generate thermal NOx according to the rate equation E1 from the section on Thermal NOx above and reproduced here.

$$[NO] = A e^{-T_{eq}/T} [N_2] \sqrt{[O_2]} \quad [E1]$$

If the hydrogen content increases but the fuel and air supply are not changed to accommodate the modified fuel, then several things happen at the burner. Gas supply is controlled to keep the volumetric flow constant, therefore the heat input decreases because the volumetric heating value decreases with increasing hydrogen content (see Figure 1). Since the air flow isn't adjusted, the amount of available air increases because the stoichiometric requirement decreases with increasing hydrogen content (see Figure 3). The flame temperature increases with increased hydrogen content (see Figure 2). Thermal NO_x will increase with increased flame temperature and increased oxygen concentration, according to equation E1. Looking at the sensitivity of the thermal NO_x rate to the changes in temperature and oxygen concentration gives

$$\frac{\Delta[NO]}{[NO]} = \frac{T_{eq}}{T} \frac{\Delta T}{T} + \frac{\Delta[O_2]}{2[O_2]} \quad [E2]$$

Here the relative change in the thermal NO_x formation rate is the sum of the sensitivity to the temperature change and the oxygen concentration change. Using a linear approximation of the AFT and AFR over the range of hydrogen content from 0% to 20%-v, the changes in temperature and oxygen concentration are proportional to the change in hydrogen content. An empirical value for T_{eq} used by Colannino (2003) is 1000K. Using that value and 10,000K to check the sensitivity gives increases of 0.4% and 0.5% for the NO_x emission using E2. The conclusion is that a varying hydrogen content, such as potentially produced under the Power-to-Gas scenario, will give a change of approximately 0.5% in NO_x formation for a change of 1%-v in the hydrogen content. The implication is that the variability in hydrogen content in the Power-to-Gas scenario will produce a small change in the formation of thermal NO_x. If a burner is operating with the 20% margin of safety for the regulated limit, then the relatively small uncontrolled fluctuation due to Power-to-Gas is unlikely push NO_x emissions over the limit.

Results for Ultra-low NOx Burners

Waibel et al. (1995) looked at the effect of fuel composition on ultra-low NOx burners for process heaters. The fuel components were natural gas, propane and hydrogen. The results for HENG firing for the standard flame shape is presented in Figure 9. For the range of primary interest, from 0%-v to 20%-v, the NOx emissions increase linearly to a maximum of 7% above the NOx emissions firing natural gas, well below the increases observed with conventional burners. Although data were not found for low NOx burners, it is a reasonable estimate that the increase in NOx emissions for a low NOx burner firing 20%-v hydrogen in HENG would be between 7% for ultra-low NOx burners and 12% for conventional burners.

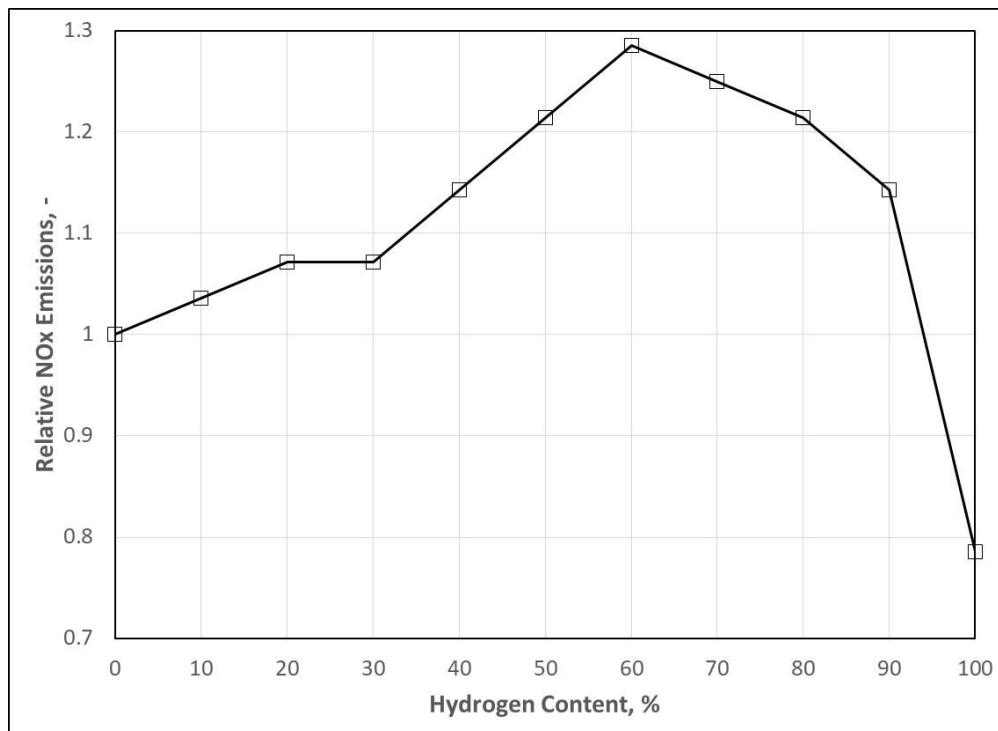


Figure 9 - NOx emission factors for HENG relative to NG after Waibel et al. (1995). Hydrogen content is in volume percent and the balance is natural gas.

High Hydrogen Content

Another possibility for the HENG is to have a very high hydrogen content in specific corridors or micro-grids. The hydrogen content could be from 70%-v to 100%-v. Whatever the merits of such an arrangement for GHG reductions or transitions to a hydrogen economy, it is not a good range for NO_x emissions from boilers and heaters. Consider Figures 8 and 9 that present the relative NO_x emissions for conventional and ultra-low NO_x burners. There is a maximum for the NO_x emissions in the range from 60%-v hydrogen to 80%-v hydrogen. Having pure hydrogen and not HENG would seem to be a better option for NO_x emissions.

NO_x REDUCTION STRATEGIES IN BOILERS AND HEATERS

There are strategies that can be implemented in boilers and heaters to provide significant reduction of NO_x emissions without the installation of low-NO_x burners or the installation of post-combustion NO_x reduction technologies. The basic idea is to reduce the peak flame temperature that is responsible for the formation of thermal NO_x.

The first strategy is to inject something into the reaction zone of the burner that lowers the temperature. Recirculating flue gas, steam and water have all been used. Flue gas recirculation (FGR) is usually accomplished by pumping gas from the stack after all the heat exchangers and injecting it into the windbox for the burners. This reduces the oxygen concentration, increases the nitrogen and carbon dioxide concentrations, and thereby reduces the flame temperature. This requires the installation of duct work and a fan to move the flue gas. The flue gas is usually warm, from 250°C to 400°C, with oxygen between 1% and 3%. The rate of FGR is reported as a fraction of the air supply rate. The typical range for optimal NO_x reduction is FGR to be 14% to 18% of the air supply. This can achieve from 50% to 70% NO_x reduction relative to no FGR.

Water injection is most effective technique for a small number of high firing rate burners in a confined firebox. The vaporization and dilution effects combined effectively lowers the maximum flame temperature and NO_x formation.

Steam injection, for the same water injection rate, produces a lower NO_x reduction because there is no heat sink for vaporization. A direct comparison of the two techniques was done on an industrial boiler (Tsiralnikov et al. 2003). At a equal mass flow rate of water (as liquid and as steam), steam injection reduced NO_x emissions by approximately 28% compared to 46% for

water injection. An increase of the injection rate gave a reduction of 41% with steam and 51% with water.

All three injection techniques have an effect on the thermal efficiency of the boiler. The order of magnitude ranking is that for a given level of NO_x reduction, water injection reduces boiler efficiency by a percent, steam injection by tenths of a percent, and FGR by hundredths of a percent. However, the simplicity, low cost, and effectiveness of steam and water injection makes these attractive options for meeting NO_x emissions targets.

The second strategy is to stage the air injection over the furnace, rather than in each burner. The basis of the strategy is to divide the firebox into two zones. The lower zone has the burners firing with a reduced air supply, which produces a low amount of NO_x and significant amounts of partially combusted fuel. The remainder of the air is injected in the second, upper zone to complete the combustion of the fuel but at a much lower temperature than would be produced if all the air was injected at the burners. Overfire air has special air injection ports in the upper section of the furnace. The key here is to have sufficient mixing to ensure complete combustion. However, the possible effects are longer flames and impingement and elevated CO emissions if the mixing is poor or the residence time in the firebox is too short. Where there are multiple levels of burners staging can be accomplished by taking the top row of burners out of service (BOOS). All the fuel is moved to the lower burners while the division of the air flow is maintained. This requires no new equipment. There is the possibility of longer flames and impingement.

In all these strategies, there will be a change to the heat release profiles, flame shapes, and heat transfer. Boilers are less sensitive to these changes (as long as flames do not impinge on walls or tubes). Process heaters are more sensitive to such changes because they are processing compounds that can decompose if overheated. Decomposition can produce deposits that impede flow and heat transfer, and will ultimately lead to premature shutdown for maintenance or even tube blockage and rupture during operation.

RETROFIT OF LOW NO_x BURNERS

There are many circumstances where the retrofit of low NO_x or ultra-low NO_x burners is the best choice for NO_x reduction to meet regulatory requirements. Whereas the techniques of FGR and water or steam injection impose an efficiency penalty on the operation of the unit, upgrading to a modern burner can improve thermal efficiency to give operational savings and reduced CO₂ emissions. However, there are constraints imposed by the existing firebox and duct work that have to be carefully considered.

Low NO_x burners produce flames that are 25% to 50% longer than those produced by the conventional high-intensity burners at the same firing rate (Tsiralnikov et al. 2003). Sometimes more burners are installed with a lower individual firing rate giving the same total heat input but keeping the individual flames within confines of the firebox. However, often this is not possible and the firebox size is an insurmountable barrier to a burner retrofit. However, if the existing burner has induced draft air supply, switching to forced draft air supply with the low NO_x burner can often meet the firebox size constraint because forced draft allows greater control on the combustion process.

Installing new burners to meet NO_x emission regulations can be an opportunity to improve the productivity and thermal efficiency of a furnace. Schalles and Valancius (2015) describes several case studies where the installation of ultra-low NO_x burners increase the thermal efficiency from 37% to 51% (HHV basis) while reducing the NO_x emission factor by two-thirds.

Gilmartin and Kraus (2013) describe the process for successful retrofit of burners to meet NO_x regulations while maintaining the firing rate, outlet temperature and productivity. The process starts with a review of the heater including the operating data. For each candidate burners, a CFD simulation is performed to check on the flame dimensions. The selected burner is put

through a burner test at the supplier's facility to confirm the NO_x emissions, and the CFD calculations are confirmed by this test. If the burner provides the required NO_x reductions and meets the geometric constraints on the flame shape, then these are installed and tested in the field. This process will take time but is required to ensure the NO_x emissions and flame shape meet the requirements of the owner/operator.

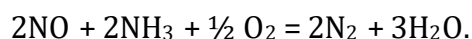
Chen et al. (2011) describes the role of CFD modeling in burner retrofits. Low NO_x and especially ultra-low NO_x burners are sensitive to large-scale flow patterns in the firebox. This is particularly true with multiple burners and involves more than ensuring a minimum spacing between burners. The large scale flows can produce burner-burner interactions that change heat release patterns, reduce thermal efficiency, reduce combustion efficiency and prevent the burners from achieving the necessary NO_x reductions. The flows are calculated with the CFD models to find a suitable arrangement, but the actual NO_x is determined by experiment.

In summary, retrofitting conventional burners with modern low NO_x burners is not a simple process. It requires collaboration between the owner/operator and the burner supplier. However, there can be performance improvements for the boiler or heater that will offset the cost of the new equipment and the downtime¹ required for the installation.

¹ The author has heard of retrofits being performed on a refinery heater while the heater continued operation.

POST COMBUSTION ALTERNATIVES

Post-combustion treatment of the flue gases can be an effective alternative to burner retrofit. Selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) involve injection of nitrogen containing chemical reductant such as ammonia or urea in flue gas to reduce the NO_x. The basic idea is illustrated by the following reaction



The reductant, in this case ammonia, reacts with the NO to produce molecular nitrogen and water. The oxygen is in the flue gas from 1%-v to 3%-v, which is well in excess of the NO present, so it will not be a limiting reactant. There is a temperature window for this reaction to be effective. A catalyst reactor can be used to promote the reaction at lower temperatures.

Mixing and residence time are important. The reductant has to be injected in a manner that mixes well with the flue gas. The reactor volume has to be large enough that the reaction can proceed to equilibrium. A catalyst reactor will be smaller and have better mixing than the non-catalytic reactor. Catalyst can be poisoned or contaminated and lose effectiveness with time.

Slippage can be an issue. This happens when the reductant ends up in the stack gas. This can happen because of poor mixing, gas temperature being too low in the reactor, poisoned or otherwise deactivated catalyst, or excessive injection.

Retrofit requires installation of reactor in the flue gas exit ductwork before the stack. The reactor is often installed at ground level next to the boiler or heater because of the structures that would be required to support the weight of the catalyst reactor. Capital and operating costs significant but can be competitive with retrofitting low NO_x burners or if firebox geometry does not allow low NO_x burners.

However, water is one of the products of the reaction. Elevated water in the flue gas reduces the effectiveness of SCR and SNRC since the equilibrium is shifted towards the NO_x and reductant. This means that HENG with increased hydrogen in the fuel giving increase water in the flue gas will decrease the effectiveness of this post combustion treatment.

CONCLUSION AND RECOMMENDATIONS

Hydrogen addition to natural gas does produce many benefits, especially that of reducing the emission of GHGs from industrial combustion processes. However, it can also produce an increase in NO_x emissions. Thermal NO_x is the primary formation mechanism for these NO_x emissions and the increase in flame temperature due to the presence of hydrogen is the primary driver.

The boilers and heaters under consideration have thermal rating greater than 10.5 GJ/h (2.94 MW). Studies on burners smaller than 0.5 MW are not directly scalable to the industrial scale. In addition, there are additional factors in the operation of a boiler or heater, such as firebox temperature, firebox geometry, and number of burners, that affect the NO_x emissions. Unfortunately, there are very limited data published for the industrial scale burners on the effects of HENG on NO_x emissions, but the following conclusions can be drawn:

- Increasing the hydrogen content of HENG from 0% to 20% would produce an increase in NO_x emissions between 12% and 17% compared to natural gas for conventional burners. The increase is less for low NO_x and ultra-low NO_x burners.
- In the Power-to-Gas scenario of fluctuating hydrogen content with no adjustment in burner control settings, an increase of 1% in the hydrogen content of HENG (e.g., from 7%-v to 8%-v hydrogen) will produce an increase in NO_x emissions around 0.5% for a conventional burner. Similarly, a decrease in HENG content of 1% produces a decrease in NO_x emissions of around 0.5%. Low NO_x and ultra-low NO_x burners that mitigate the effect of thermal NO_x should be even less sensitive to fluctuation in hydrogen content.
- Because there are multiple variables that affect the NO_x emissions in fired equipment, it isn't possible to set firm *a priori* boundaries for the NO_x emission factors achievable by a burner. The following are reasonable estimates for burners firing natural gas:

- Conventional burners have NO_x emission factors of 50 g/GJ to 65 g/GJ.
 - Low NO_x burners can operate in the range from 13 g/GJ to 33 g/GJ.
 - Ultra-low NO_x burners can achieve emission factors below 10 g/GJ.
- Fired equipment is generally operated with a margin of safety of 20% on emission limits (Baukal 2001, Colannino 2006). A boiler or heater currently operating to meet the limit of 26 g/GJ on natural gas should be operating around 20 g/GJ. Using HENG with 20%-v hydrogen content would bring the operating emissions up to 23.5 g/GJ, which is too close to the regulated limit even though it does not exceed it. Since the regulated limits cannot be exceeded without penalty, operators will want to retain the 20% margin of safety. However, since these numbers are based on very small amount of experimental data, more data should be collected before the limit could be increased.
- Changing air supply from induced draft to forced draft improves burner control and thermal efficiency and can reduce NO_x emissions.
- Flue gas recirculation (FGR), steam injection or water injection at the burner are effective and low cost methods of reducing NO_x emissions though with a thermal efficiency penalty. The order of magnitude of the efficiency loss is a percentage point for water injection, a tenth of a percent for steam injection and a hundredth of a percent for flue gas recirculation.
- Selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) use a nitrogen containing compound like ammonia or urea in a post-combustion reactor to reduce NO_x. This has an installation cost and an operating cost for the reductant. An additional risk is that the reductant can end up in the flue gas, known as slip, due to excessive injection, poor mixing, or catalyst contamination. Since water vapour reduces the efficiency of the reaction, increased hydrogen content in the HENG combustion products will have a negative impact on this method of NO_x reduction.

- Burner retrofit, done properly, is a process involving the collaboration of the boiler or heater operator and the burner supplier. Low NO_x burners have longer and wider flames with more diffuse heat release pattern. Impingement on tubes or walls is a possibility as is burner-burner interactions. The burner supplier should be able to ensure safe operation that meets the NO_x emission target, even with 20%-v hydrogen content HENG, through a combination of burners tests, CFD modelling and installation testing. This may produce improved thermal performance of the boiler or heater as well as NO_x emission reductions that mitigate the cost and downtime for the upgrade.
- Ultra-low NO_x burners should be able to meet the 16 g/GJ limit without problem, with the 20% margin of safety, even with 20% hydrogen content HENG. However, these burners produce longer and more diffuse flames than low NO_x burners and can be sensitive to the firebox geometry. There may also be control issues in the Power-to-Gas scenario of fluctuating hydrogen content.
- The scenario of a high hydrogen content HENG corridor or micro-grid is problematic for NO_x emissions. The relative NO_x emission factors for conventional burners and ultra-low NO_x burners appear to have a maximum in the range of 60%-v to 80%-v hydrogen in HENG. This is the range of hydrogen content being considered for the corridor. A pure hydrogen corridor would have lower NO_x emissions.

The availability of advanced burner technology, the sophistication of burner suppliers, the option of flue gas recirculation, steam or water injection means that the operators of boilers and heaters in Canada should be able to meet the NO_x emission limit of 26 g/GJ, even with 20% HENG. Post-combustion treatment of flue gas for NO_x reduction (SNCR and SCR), are also effective but the effectiveness with decrease with increased water content in the flue gas due to increased hydrogen in the fuel.

RECOMMENDATIONS: These conclusions are based on very limited experimental data on the effect of hydrogen enrichment at the industrial scale. Validation could be done on a full-scale boiler or heater, at least 10.5 GJ/h. The experimental campaign should look at different levels of hydrogen addition to natural gas (0%, 5%, 10%, 15%, and 20% hydrogen, for example) controlling for heat input and stack oxygen concentration. The NO_x emissions and thermal performance of the unit should be reported.

Testing for a higher level of hydrogen (60% to 80%) as for a micro-grid scenario would require an engineering assessment of the host facility. This may be better performed at the test facility of a burner supplier.

CFD simulation of the tests should also be attempted. If the simulation reproduces the experimental results then this could be a lower-cost tool to answer future questions on the effects of hydrogen enrichment on the performance of combustion equipment.

A measurement campaign looking for nitrous oxide in the stack gas of industrial equipment firing HENG should be considered if there are any future papers in the scientific literature supporting the findings of Colorado et al. (2017).

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APPENDIX

Table 1 - Variability of composition of natural gas delivered by Union Gas.²

Component	Range (mole %)
Methane	87.0 - 97.0
Ethane	1.5 - 9.0
Propane	0.1 - 1.5
Nitrogen	0.2 - 5.5
Carbon Dioxide	0.05 - 1.0
Hydrogen	trace - 0.02
Gross Heating Value (MJ/m ³)	36.0 - 40.2
Wobbe Number (MJ/m ³)	47.5 - 51.5

² As reported on the Union Gas website, <https://www.uniongas.com/about-us/about-natural-gas/chemical-composition-of-natural-gas>, accessed on 2020-01-28.

Table 2 - Basic properties relevant to combustion for methane and hydrogen.

		CH ₄	H ₂
Density	kg/m ³	0.679	0.085
LHV v	MJ/m ³	34.3	10.4
LHV m	MJ/kg	50.5	122.4
HHV v	MJ/m ³	37.6	12.1
HHV m	MJ/kg	55.4	142.0
LFL	%	5.0	4.0
UFL	%	15.0	74.2
SAF	kg/kg	17.20	34.29
Products/unit mass fuel			
CO ₂	kg/kg	2.74	0.00
H ₂ O	kg/kg	2.25	8.92
N ₂	kg/kg	13.21	26.22
Products/unit energy			
CO ₂	kg/kJ	49.5	0.0
H ₂ O	kg/kJ	40.5	62.8
N ₂	kg/kJ	238.4	184.7
Wobbe Number	MJ/m ³	50.5	45.9
Flame Speed ³	cm/s	40.5	210
Adiabatic Flame Temperature ⁴	°C	2053	2247

³ At stoichiometric conditions.

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