

GHGT-11

Performance and NO_x Emissions of Refinery Fired Heaters Retrofitted to Hydrogen Combustion

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Abstract

Pre-combustion CO₂ Capture applied to industrial sources is an alternative for achieving low CO₂ emissions at a moderate cost. The potential of the technology to be used as retrofit would further expand its possibilities and could be a real benefit to the industry in terms of achieving CO₂ emission reduction at relatively low cost. The retrofitting of a boiler to hydrogen fuel bears some difficulties due the significant differences in gas and combustion properties between hydrogen and gaseous hydrocarbon fuels. The present investigations by CFD simulations revealed that the effect on the overall performance of the fired heater when the fuel is switched to hydrogen is likely to be minimal. The simulations also showed that the NO_x-emissions with pure hydrogen fuel is in fact lower than with the refinery fuel gas on mass basis, or similar on ppm basis. This is due to the rather large contribution from the prompt-NO mechanism that obviously is absent in the hydrogen case. Similarly, the effect of switching fuel from methane to hydrogen was investigated experimentally on a lab scale model low NO_x burner. The burner, first characterized for methane in terms of emissions and stability, was operated with hydrogen without modification and then by applying a first development modification. The later version of the burner allowed first to solve an overheating issue recognized when in the direct switch configuration. Furthermore, the NO_x performance revealed to be even better than with methane as fuel, which contradicts most of the previous studies found on this topic, but confirms the CFD analysis of the full refinery heater simulation. Energetic requirements for post-combustion capture using MEA as solvent, an auto-thermal reformal based pre-combustion scheme with aMDEA as solvent and steam methane reformer with pre- and post-combustion capture using MEA and aMDEA were evaluated. Post-combustion capture has the least energy requirements followed by auto-thermal reformer based pre-combustion route. It is expected that the pre-combustion route will be competitive when rather than stand-alone H₂ fuel production for fired heaters power production in an integrated reforming combined cycle is also included in the scheme

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Selection and/or peer-review under responsibility of GHGT

Hydrogen combustion; NO_x emissions; pre-combustion capture from refinery heaters.

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1. Introduction

Carbon Capture and Storage (CCS) is an important part of a carbon-constrained energy scenario to reduce global emissions. Although the power (and heat) sector has been the focus of much research related to CO₂ capture, industries account for one third of world energy use and 40% of worldwide CO₂ emissions [1]. CO₂ capture in large point sources of the most energy (and CO₂ emission) intensive industries could potentially result in considerable CO₂ emission reductions. The IEA CCS Roadmap [2] envisages 5.5 Gt CO₂ captured from the power sector and 4.5 Gt CO₂ captured from industries in 2050. Two significant sources in refineries with a high potential for CO₂ capture are fired heaters and fluidized catalytic cracker regenerators.

Fired heaters contribute typically around 30-60% of the emissions in a refinery. Post-combustion capture for fired heaters has been widely discussed but van Straelen et al. [3] point to the potential problems with post-combustion capture. One of the main issues is that fired heaters are spread out in the refinery and large ducts would be required to collect the exhaust. Additionally, refineries are constrained with respect to steam availability, a utility in significant demand for post-combustion capture.

Earlier work [4, 5] has shown that pre-combustion route to capture in refineries is feasible and competitive. Moreover the requirement of hydrogen is expected to grow in refineries [5]. A pre-combustion route for fired heaters in conjunction with power generation and hydrogen production for refinery hydrogen network can be envisaged in the future as shown in Figure 1.

In this paper the pre-combustion route for CO₂ capture from fired heaters is studied to explore if a low-cost retrofit is possible rather than a complete rebuild of the fired heater. In particular, a multi-faceted approach to the effect of replacing the refinery fuel gas in the burners of the radiant section of fired heater with hydrogen is undertaken.

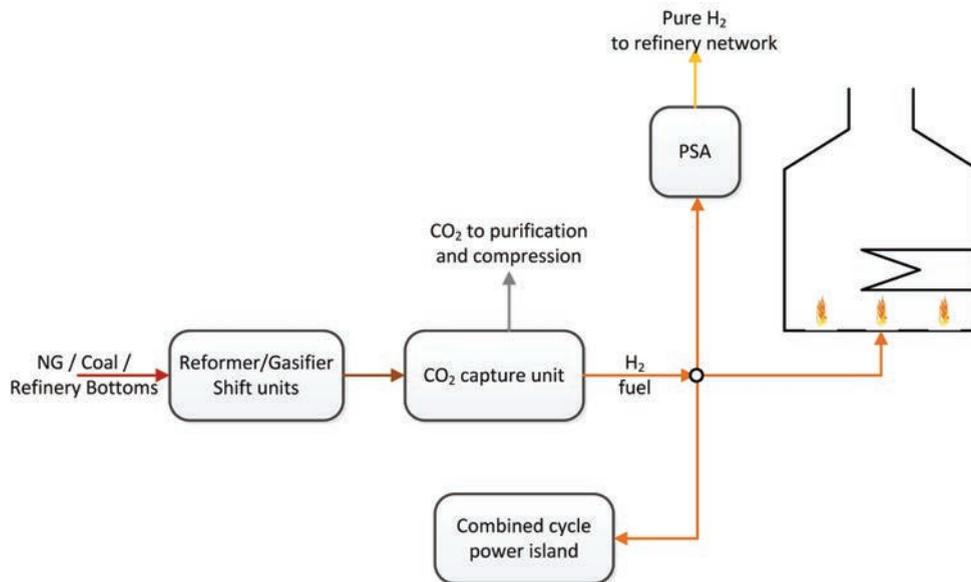


Figure 1: Potential pre-combustion route for power generation and hydrogen production in refinery.

2. Investigations of hydrogen retrofitted boiler by CFD simulations

The first step in this process is to check the effect of switching the fuel to hydrogen on the radiative heat load distribution on the boiler heat transfer surfaces, the heat transported to the convective section and the emissions. Large scale Computational Fluid Dynamics (CFD) simulations with detailed combustion chemistry were performed [7] revealing that when switching from a typical refinery fuel to hydrogen, the impact on the overall performance of the heater is likely to be minimal. Indeed, the heat distribution did change, but not to an extent where a rebuild of the heater would be expected. The maximum heat flux with hydrogen as fuel was found to be slightly lower than that when refinery fuel gas is used, and the average heat flux also showed the same trend.

Despite the higher flame temperature with the pure hydrogen case, the NO_x levels were comparable to the case with conventional refinery fuel. As Figure 2 shows, the computed integrated mass flow of NO_x is higher for the base case with refinery fuel gas than with pure hydrogen. On ppm dry basis the NO_x emissions are estimated to approximately the same level for these two cases. This is due to the significant contribution from the less temperature dependent prompt-NO mechanism in the base case which contains hydrocarbon fuel, while absent in the pure hydrogen case. Prompt-NO is formed through the CH-radical and the rate limiting reaction is the CH+N₂=HCN+N. The importance of the prompt-NO mechanism was further confirmed by simulating one case with refinery fuel gas where all NO_x-chemistry but the thermal contribution was switched off. This is shown as the "base, only thermal NO_x" curve in Figure 2. For this case, the NO_x-emissions were reduced to 12% of the regular base case simulations, meaning that only 12% of the NO_x-emissions in the base case are from thermal NO_x. The major contribution to the NO_x emissions for the hydrogen fired heaters is from thermal NO_x produced in the hottest region of the furnace. To reduce these hotspots, a conventional reduction strategy is to dilute the fuel with steam or another inert gas. Applying this strategy in our large scale CFD calculations by diluting hydrogen with steam, the peak temperature was reduced by approximately 140 K and the NO_x emissions reduced accordingly by close to 50% as shown in Figure 2.

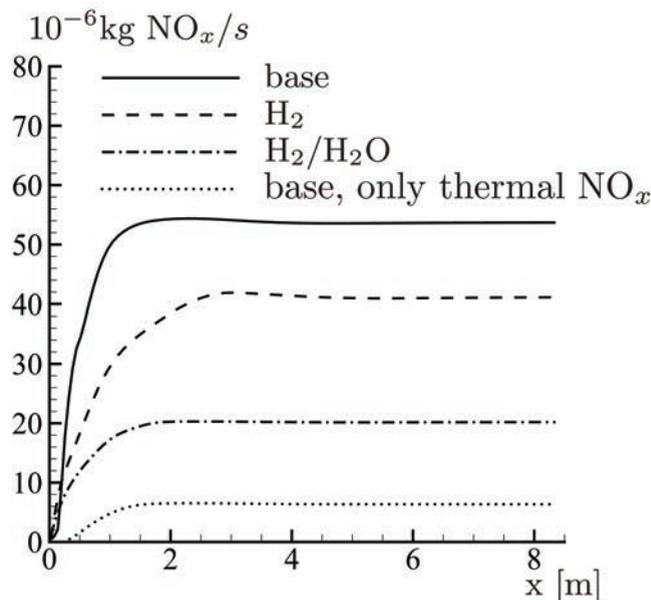


Figure 2: Calculated NO_x emissions along the streamwise direction of the fired heater radiant section in three firing conditions: refinery fuel gas ("base"), hydrogen ("H₂"), and hydrogen diluted with steam ("H₂/H₂O") [7].

3. Experimental retrofit of a lab scale model burner to hydrogen fuel.

To further study the findings from CFD simulation showing that the refinery gas fired boiler has higher NO_x emissions than when hydrogen fired, a lab scale low NO_x burner initially optimized for hydrocarbon fuels has been switched to hydrogen. The low NO_x burner is a 20 kW class burner based on bluff body stabilization mechanism. The combustion chamber is water cooled and instrumented with gas temperature, heat flux probe, and emission probe for flue gas analysis. Since the burner is a research model, several geometrical parameters can be varied and is therefore well suited for straightforward optimization. A full matrix of experimental conditions were run at varying air excess ratio, power, and two burner variables affecting the flow pattern: a fuel distribution ratio between two injection ports, termed *RP*, and a geometrical distance, termed *L2*.

The burner was successively fired with methane and with hydrogen. Ideally retrofitting a burner to another fuel would be to simply switch fuel distribution lines and no modification on the burner. Attempting to do so, showed limits of operation clearly related to the differences in reactivity between the two fuels. Indeed, the first observation indicates that the stability is good. This is as expected since flame speed and flame temperature are both higher with hydrogen than with methane. Even though the burner is not of a premix type, an overheating problem of the bluff body was present in the hydrogen case. In addition, the NO_x emission values obtained exhibited higher values, as commonly accepted. However, because the burner is overheating these values are little relevant as the burner does not qualify for normal operation. The identified overheating problem is due to too low velocity of the hydrogen jets compared to the laminar flame speed, which stabilizes the flame to close to the bluff body. It must be stressed that although this result cannot be generalized (burner design dependent), most burners would experience this phenomenon due to the density difference and higher flame speed with hydrogen as fuel.

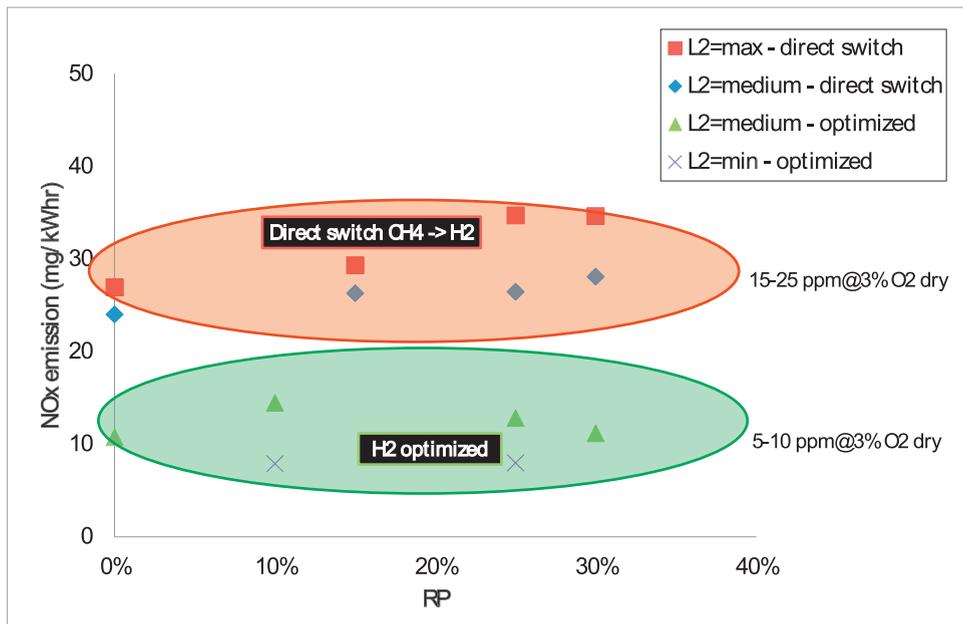


Figure 3: NO_x emissions H₂ fired burner in direct switch and first development mode.

One concludes from the direct retrofit operation that with the given burner, switching from methane to hydrogen is not possible due to burner damage and higher NOx levels. The first modification that comes to mind is to adapt the fuel port size in order to push the flame anchoring further downstream. The implementation of this first development, made the burner to operate satisfactorily, without any overheating and with good stability performance. The NOx emissions are shown in Figure 3 with different sets of burner parameters. It appears that the performance have been greatly improved, where in terms of flue gas concentration the NOx emissions experience a 10 ppm drop down to below 10 ppm@ 3% O₂ dry. Reported per input fuel energy it is a three times reduction. Another encouraging point is that the emissions are lower than with methane as a fuel, despite a higher flame temperature. The conclusion of this experimental analysis on a laboratory scale burner confirms the behavior of the CFD simulation revealing that there is more in NOx emissions from hydrogen combustion than a simple temperature dependent Arrhenius law.

4. Overall process design

Earlier work [4] has evaluated the process for the pre-combustion route for refineries. However, they limited the option of reformer to steam methane reformer (SMR). SMR burns fuel (natural gas or refinery fuel gas) to generate heat for the endothermic reforming reaction. While SMR is one of the most efficient technologies for hydrogen production, a limitation with CO₂ capture in this case is that both pre-combustion and post-combustion capture will need to be applied to ensure 90% capture.

In this work auto-thermal reforming (ATR) is considered for hydrogen production. ATRs are not common in refining applications, it is expected that with CO₂ capture, ATR or partial oxidation will be the more appropriate reforming technology. This is compared with SMR with pre- and post-combustion capture.

Reformer fired heaters (one charge and 3 inter-heaters) are considered to perform preliminary process design and comparisons. The duties of the reformers are 24.3 MW, 28.1 MW, 13.5 MW and 6.5 MW respectively. The efficiency of the fired heaters is taken to be 90% [4]. CO₂ capture rate is fixed 90%. The specification of the refinery fuel gas is taken from [4] to be:

Table 1: Composition of refinery fuel gas

Component	Mol%
H ₂	20
CH ₄	45
C ₂ H ₆	10
C ₃ H ₈	10
C ₄ +	15

An oxygen fired ATR and SMR processes are designed using an optimization procedure [8]. The reforming processes design is challenging where many different parameters require to be fixed for performing process calculations. To ensure consistent comparison between the different processes, an optimization procedure is used. The procedure uses meta-models developed from detailed steady state simulations performed in HYSYS and is optimized in General Algebraic Modelling Software (GAMS)

using BARON as the solver. The pre-combustion capture unit uses activated MDEA as solvent while post-combustion uses MEA as solvent.

Energetic requirements for the post-combustion capture, pre-combustion using ATR and pre-combustion using SMR were evaluated. Post-combustion capture required the least energy followed by ATR and SMR. ATR requires significant energy for preheating feed streams. This would require a large heat source, which is not included in this work. In a future refinery scenario with an Integrated Reforming Combined Cycle (IRCC) power plant and/or hydrogen production for refinery network (Figure 1), the ATR could be attractive. The combined cycle will provide the required heat for preheating the ATR feed streams.

5. Conclusions

Pre-combustion CO₂ Capture applied to industrial sources is an alternative for achieving low CO₂ emissions at a moderate cost. The potential of the technology to be used as retrofit would further expand its possibilities and could be a real benefit to the industry in terms of achieving CO₂ emission reduction at relatively low cost. The retrofitting of a boiler to hydrogen fuel bears some difficulties due the significant differences in gas and combustion properties between hydrogen and gaseous hydrocarbon fuels.

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Acknowledgements

This publication has been produced with support from the BIGCCS Centre, performed under the Norwegian research program Centres for Environment-friendly Energy Research (FME). The authors acknowledge the following partners for their contributions: Aker Solutions, ConocoPhillips, Det Norske

Veritas, Gassco, Hydro, Shell, Statoil, TOTAL, GDF SUEZ and the Research Council of Norway (193816/S60).

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