ABSTRACT
Flameless oxidation (FLOX®) technology has already demonstrated great potential in reducing thermal NOx while burning natural gas [1-3]. However, the tests with biogenous fuels have shown a limited ability to reduce NOx, where most of the NOx emissions are related to the fuel-bond nitrogen [4,5].

During the gasification process, the nitrogen contained in the solid fuel is partly released to the product gases as ammonia (NH3) or hydrogen cyanide (HCN). These compounds are partly converted to NOx in the combustion processes. In this paper, the influence of the gas composition on the fuel nitrogen conversion (simulated by ammonia addition) to nitric oxide was investigated. Synthetic gases with different methane concentrations and CO/H2 concentration ratios were doped with ammonia and burned in flameless mode. The concentration of ammonia, related to the total pre-combustion mixture (fuel gas and air), was the same for all experiments.

The NOx emissions were measured and conversion ratios of ammonia to NOx were determined. The results showed that the gas composition has a significant influence on the conversion of ammonia to NOx. In particular, the methane content influences the ammonia-to-NOx conversion. The lowest NOx emissions and therefore the lowest conversion ratios were measured while burning methane-free gas. An increase of methane concentration in the gas corresponded to a rapid increase in the conversion ratios. The CO/H2 content ratio had a minor influence on the conversion of ammonia to NOx.

1 INTRODUCTION
Flameless oxidation (FLOX®) is one of the most rapidly developing technologies in the last twenty years. This technology is based on the strong flue gas recirculation in the combustion zone created by the high momentum of the injected air. The stability of the combustion process without any flame stabilisation and the very good mixing conditions are big advantages of this technology. Flameless oxidation technology has already demonstrated great potential in reducing thermal nitrogen oxides (NOx) while burning natural gas. The high internal recirculation of the hot flue gases dilutes the pre-combustion mixture and therefore reduces the high temperature peaks in combustion zone. This fact leads to significant reduction of thermal NOx. Therefore, this technology can also be easily combined with the heat recovery (air preheating) which leads to significant reduction of fuel consumption and thus CO2 emissions with very low thermal NOx emission.

FLOX® technology has also been adapted to burn Low Calorific Value gases (LCV) generated by the biomass gasification [4,5]. Due to the high stability of the combustion process, LCV gaseous fuel even with a varying composition can be burned without adjustments of the burner and problems related to the flame instabilities. However, the tests
with different syngases generated by the biomass gasification, shows a limited ability to reduce NO\textsubscript{x} emissions [4] while burning nitrogen-rich biofuels in FLOX\textsuperscript{®} mode. During gasification of biomass, the nitrogen contained in the solid fuel is partly released to the product gases as ammonia (NH\textsubscript{3}) or hydrogen cyanide (HCN) [6,7]. During combustion of such gases, the nitrogen containing species may be oxidized to NO\textsubscript{x} or reduced to N\textsubscript{2}. The selectivity of this process depends on the gas composition, temperature and mixing of the reactants. Therefore, the final fuel NO\textsubscript{x} emission depends on the nitrogen content in the biogenous fuel, gasification process and finally on the subsequent combustion process parameters.

Schuster et al. [8] investigated the formation of fuel nitrogen oxides during flameless combustion. The tested synthetic gas mixtures were supplied by mixing station that allows mixing CO, CO\textsubscript{2}, CH\textsubscript{4}, H\textsubscript{2} and N\textsubscript{2}. In order to investigate the fuel nitrogen conversion, ammonia at different concentrations were added to the fuel stream. The compositions of the selected fuels are presented in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>NG</th>
<th>MFG</th>
<th>MCG</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{4} vol-%</td>
<td>95.6</td>
<td>-</td>
<td>6.5</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{6} vol-%</td>
<td>-</td>
<td>2.4</td>
<td>-</td>
</tr>
<tr>
<td>H\textsubscript{2} vol-%</td>
<td>25.0</td>
<td>8.6</td>
<td>-</td>
</tr>
<tr>
<td>CO vol-%</td>
<td>-</td>
<td>18.0</td>
<td>8.8</td>
</tr>
<tr>
<td>CO\textsubscript{2} vol-%</td>
<td>15.0</td>
<td>15.6</td>
<td>-</td>
</tr>
<tr>
<td>N\textsubscript{2} vol-%</td>
<td>42.0</td>
<td>60.5</td>
<td>-</td>
</tr>
<tr>
<td>LCV MJ/m\textsuperscript{3 stp}</td>
<td>36.1</td>
<td>5.0</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Table 1 Composition of the selected gases

A compilation of the results are shown in Figure 1. The results of Schuster et al. showed that for all tests an increase of nitrogen oxides emissions were observed with increasing content of ammonia. Moreover, in the cases of natural gas (NG) and methane-containing syngas (MCG) the conversion of NH\textsubscript{3} to NO\textsubscript{x} was found to be similar and relatively high. In contrast, the NO\textsubscript{x} emission while burning methane-free gas (MFG) was significantly lower. It is an indication that the ammonia chemistry in flameless combustion is strongly influenced by the composition of the fuel gas, particularly with respect to the hydrocarbon content in the fuel.

Figure 1 NO\textsubscript{x} concentration in the flue gas for three different gases as a function of ammonia concentration in the pre-combustion mixture (fuel and combustion air)

Therefore, the main goal of this paper is the detailed investigation of the influence of gas composition (CO, H\textsubscript{2} and CH\textsubscript{4}) and combustion process parameters on ammonia-to-NO\textsubscript{x} conversion.
2 EXPERIMENTAL FACILITY AND TEST CONDITIONS

In the following chapter the burner test rig for the experimental investigations, the methodology of the investigation including the characterization of the tested fuels as well as the applied analysis methods are described.

2.1 Experimental facility – 20 kW FLOX®- burner

The experiments were performed using a 20 kW FLOX®- burner. The burner had been originally developed for natural gas and was subsequently modified to combust low calorific value gases. The test rig is shown in Figure 2.

![Figure 2 Scheme of FLOX®-burner test rig (1 - LCV gas with ammonia, 2 – natural gas, 3 – combustion air, 4 – flue gas, 5 – cooling, 6 – recuperator pipe, 7 – thermocouples)](image)

The combustion chamber is heated up in flame mode up to 850°C using natural gas (2). Above this temperature the burner can be switched to flameless mode and fired with ammonia doped LCV gas (1). The combustion air is preheated while flowing through the ceramic recuperator pipe (6). The temperature of the combustion chamber can be controlled using the air-cooled pipe (5). The low calorific value fuels used in these experiments were prepared using a mixing station which allows mixing of CH₄, CO₂, CO, H₂ and N₂. Each component of the reactant gases was controlled by digital mass flow controllers, mixed evenly by a mixer and supplied to the reactor at room temperature. Additionally ammonia/argon mixture was introduced to the fuel stream to simulate the fuel related nitrogen oxides precursors. The amount of the NH₃/Ar mixture was controlled by a digital mass flow controller as well.

2.2 Fuel characterisation

As indicated by the fuel compositions summarized in Table 2 [9-12], CO and H₂ are the main combustible components in the biomass-gasified fuels produced in air blown and oxygen-blow gasifiers. The amount of CH₄ was relatively small. The lower heating values varied from 4 MJ/m³ stp by the air-blown gasifiers, up to ca 9 MJ/m³ stp by the oxygen-blow gasifiers.

<table>
<thead>
<tr>
<th>Gasifier type</th>
<th>2-stage gasifier (Viking)</th>
<th>Fluidised bed (Umsicht)</th>
<th>Circulating fluidised bed (Termiska)</th>
<th>Fluidised-bed (CFB-ECN)</th>
<th>Oxygen blown gasifier (Entrained flow (Carbo-V))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>H₂ vol-%</td>
<td>CO vol-%</td>
<td>CH₄ vol-%</td>
<td>CO₂ vol-%</td>
<td>LHV MJ/m³ stp</td>
</tr>
<tr>
<td></td>
<td>30.5</td>
<td>19.6</td>
<td>1.2</td>
<td>15.4</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>15.5</td>
<td>20.0</td>
<td>3.3</td>
<td>17.8</td>
<td>4.0 – 4.5</td>
</tr>
<tr>
<td></td>
<td>7.0 – 9.0</td>
<td>9.0 – 13.0</td>
<td>6.0 – 9.0</td>
<td>12.0 – 14.0</td>
<td>4.0 – 7.0</td>
</tr>
<tr>
<td></td>
<td>7.0</td>
<td>12.0</td>
<td>3.2</td>
<td>15.5</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.3</td>
</tr>
</tbody>
</table>

Table 2 Typical gas composition produced from biomass gasification
In the present studies CO and H₂ were also the main combustible components in the tested synthetic fuels. To cover the whole range of different gas compositions presented in Table 2, three synthetic gases with CO/H₂ ratios of 0.5, 0.7 and 1.5 were investigated. For each of the CO/H₂ ratio, methane content was varied between 0 and 10 vol-% to examine the effect of CH₄ in low concentration on the ammonia-to-NOx conversion during flameless combustion. The CO₂ concentration was assumed to be 15 vol-% for all experiments. The ammonia was introduced to the fuel using 9.15 vol-% NH₃/Ar gaseous mixture. All the experiments input data are presented in Table 3.

<table>
<thead>
<tr>
<th>CO/H₂ Ratio</th>
<th>CO</th>
<th>H₂</th>
<th>CO₂</th>
<th>CH₄</th>
<th>LHV</th>
<th>NH₃ in fuel</th>
<th>NH₃ in pre-combustion mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas 1</td>
<td>0.5</td>
<td>18</td>
<td>36</td>
<td>15</td>
<td>0-10</td>
<td>6.16-9.74</td>
<td>2020-2974</td>
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<tr>
<td>Gas 2</td>
<td>0.7</td>
<td>18</td>
<td>25</td>
<td>15</td>
<td>0-10</td>
<td>4.97-8.55</td>
<td>1754-2713</td>
</tr>
<tr>
<td>Gas 3</td>
<td>1.5</td>
<td>27</td>
<td>18</td>
<td>15</td>
<td>0-10</td>
<td>5.35-8.93</td>
<td>1803-2761</td>
</tr>
</tbody>
</table>

Table 3 Composition of the synthetic gas mixtures used in the experiments

The experiments were carried out at the same power input of 18 kW. The CO and H₂ concentration was kept constant. Therefore, increasing the methane content, the lower heating value of the gas was also increasing. The concentration of ammonia was assumed to be 700 ppmv for all tested gases. The concentration of ammonia was related to the pre-combustion mixture of the fuel and the combustion air to ensure the same partial pressure of ammonia for every CO/H₂ ratio and methane concentration.

2.3 Analysis methods
Each flue gas component, such as NO, NO₂, NOₓ, O₂, CO, CO₂ was continuously measured by the gas analyzer at the reactor exit. The ammonia-to-NOx conversion ratio was calculated according to the following equation:

\[ CR_{NH3-NOx} = \frac{[NO_x]_{fluegas} \cdot \frac{V_{N,fluegas}}{V_M}}{[NH_3]_{fuel} \cdot \frac{V_{N,fuel}}{V_M}} \]

where \([NO_x]_{fluegas}\) is the concentration of the total NOx measured in flue gas, \([NH_3]_{fuel}\) is the calculated concentration of ammonia in the fuel, \(V_{N,fluegas}\) is the calculated amount of the flue gas, \(V_M\) is the molar volume of the substance at normal conditions.

It has to be mentioned that the total NOₓ measured in the flue gas originates not only from the ammonia added to the fuel stream. A part of the total NOₓ in the flue gas can be formed from atmospheric nitrogen. However, by flameless combustion of low calorific value gases the part of the NOₓ coming from other sources then ammonia is relatively small and therefore, neglected in this paper.

3 RESULTS AND DISCUSSION
The development and adaptation of the FLOX® technology for low calorific value gases allow ammonia behaviour comparison in gases varied significantly in the composition. The lower heating value of the fuels varies from 5 to 10 MJ/m³ stp in this studies. Due to the burner flexibility and combustion stability, the comparison of ammonia conversion can be done under very similar conditions for all tested fuels. The high dilution of the reaction zone caused by the recirculation of hot flue gases significantly decreases the temperature peaks in the combustion chamber. Therefore, the combustion for all fuels used in these studies occurs at
very similar intermediate temperature conditions. Moreover, the hot recirculated gases include
nitrogen oxides that influence the nitrogen chemistry in the flameless jet.
In the following chapter the influences of methane in low concentrations, CO/H₂ ratio, excess
oxygen and process temperature on ammonia-to-NOₓ conversion are presented. Moreover, the
results were discussed in order to indicate the possible explanations for the observed
phenomena.

3.1 Influence of methane content on NH₃-to-NOₓ conversion by different CO/H₂ ratios
In order to examine the influence of CH₄ content in the fuel on the ammonia-to-NOₓ
conversion, experiments with varying methane content were conducted. All experiments were
carried out at power input of 18 kW. The air ratio (λ) was assumed to be 1.5. Therefore, the
amount of combustion air was adjusted for every tested CO/H₂ ratio and methane
concentration. The temperature of the combustion chamber was approximately the same for
all experiments. However, when increasing the methane content the temperature was slightly
changing in the range of 960 °C to 980 °C.
Figure 3 shows the NOₓ concentration in the flue gas for three different CO/H₂ ratios as a
function of methane concentration in the fuel.

Figure 3 NOₓ concentration in the flue gas for three different CO/H₂ as a function of
methane concentration in the fuel; (T=970 °C, λ=1.5, P=18 kW)
For all tested CO/H₂ ratios the NOₓ emissions were about 150 ppmv (dry) when no methane was
added to the fuel. Increasing the methane content from 0 to ca. 6 vol-%, the concentration of
NOₓ in the flue gas was rising rapidly. Further increase above 6 vol-% of methane content had
only minor influence on the NOₓ emissions. At concentration of 10 vol-% the emissions
reached the maximum observed values. Moreover, the emission of NOₓ was increasing with
decreasing CO/H₂ ratio. However, this effect was observed rather due to changing content of
water vapour when varying CO/H₂ ratio. The dry flue gas volume gets lower due to increasing
H₂ content in the fuel.

Figure 4 Ammonia-to-NOₓ conversion ratio for three ratios as a function of methane
concentration in the fuel; (T=970 °C, λ=1.5, P=18 kW)
Figure 4 shows the ammonia-to-NOx conversion ratio as a function of methane concentration in the fuel. The conversion ratio was similar in all cases. The investigated CO/H2 ratios had no significant influence on ammonia-to-NOx conversion ratio. Varying the methane concentration, the conversion ratios were increasing from ca. 0.16 for methane-free mixtures to above 0.6, when 10 vol-% of methane was present in the fuel.

There are a few possible explanations reported in the literature for the observed phenomena. Choudhuri et al. [13] have studied the combustion characteristics of hydrogen-hydrocarbon hybrid fuels. They reported that the presence of hydrocarbons in the fuel causes significant decrease of the mixture reactivity, which ultimately increases the ignition time. Since the ignition delay depends on the fuel composition, the high velocity of the jet and the strong recirculation, characteristic for flameless combustion, can lead to crucial change of local air ratio at which the mixture ignites and the ammonia decompose. The longer ignition delay the higher amount of air and recirculated gases are mixed with the fuel in the jet when igniting. Since the ignition zone is not stabilized in the flameless combustor, it can significantly influence the ammonia-to-NOx conversion. Moreover, the recirculated flue gas contains a significant amount of nitrogen oxides. Frassoldati et al. [14] have studied the combustion of carbon monoxide/hydrogen mixtures. They reported that the addition of NO can inhibit the reactivity of the system under stoichiometric and particular under fuel rich conditions, as a consequence of the growing importance of chain-termination reactions involving NO.

In the case of methane-free gas, due to the high reactivity of the fuel, the ammonia can decompose directly after the burner nozzle under fuel reach conditions. The hydrogen present in the fuel in high concentration oxidizes releasing high amounts of radicals such as H, OH and O. A part of these radicals reacts with the CO. Skreiberg et al. [15] investigated the ammonia chemistry below 1400 K under fuel-rich conditions in a flow reactor. They reported that the ammonia can decompose even at very high CO concentration. They observed that the carbon monoxide is oxidized almost exclusively through the reaction with OH radicals. The hydrogen and oxygen radicals, formed during the H2 and CO oxidation reactions, are then available for oxidation of ammonia. In the same work [15] it was observed that methane in relatively low concentrations, comparing to ammonia, can strongly inhibit the ammonia conversion under fuel-rich conditions.

Increasing the methane content in the fuel, ammonia and methane can start to compete for the same radicals occurring in the flameless jet. Therefore, the decomposition of ammonia can be delayed and shifted toward the fuel lean-side of the jet, thus increasing the conversion of ammonia to NOx.

### 3.2 Influence of the air ratio and temperature on NH3-to-NOx conversion by varying methane content

In order to investigate the influence of the air ratio on the NOx emissions, ammonia doped fuel with CO/H2 ratio of 0.7 and varying methane concentration was burned with two different air ratios (λ) of 1.3 and 1.6. The methane content was varied between 0 and 4.5 vol-%. Figure 5 shows the NOx emissions obtained in these experiments. The tests were carried out at 970 °C and the power input of 18 kW. Similar to the previous experiments the NOx emissions were increasing with methane content in the fuel for both investigated air ratios. However, for methane-free mixtures the air ratio had a minor influence on the NOx emissions. The ammonia-to-NOx conversion ratio, presented in Figure 6, was similar for both air ratios for methane-free gas. Increasing the methane content in the fuel, the influence of air ratio was slightly growing.

The same experiments were additionally carried out at 900 °C to investigate the influence of the operating temperature on the NOx emissions. The results are shown in Figure 7. Both of the measurements for λ=1.3 and 1.6 shows similar results for the tested temperatures. The temperature difference was too small to observe any major differences in ammonia-to-NOx conversion. However, the investigation under higher operating temperature was limited by the low calorific values of the tested fuels. The lower operating temperature was limited by the minimal required temperature of the combustion chamber for flameless combustion.
Figure 5 NO\textsubscript{x} concentration in the flue gas for CO/H\textsubscript{2}=0.7 and $\lambda=1.3$ and 1.6 as a function of methane concentration in the fuel; (T=970 °C, P=18 kW)

Figure 6 Ammonia-to-NO\textsubscript{x} conversion ratio for CO/H\textsubscript{2}=0.7 and $\lambda=1.3$ and 1.6 as a function of methane concentration in the fuel; (T=970 °C, P=18 kW)

Figure 7 NO\textsubscript{x} concentration in the flue gas for CO/H\textsubscript{2}=0.7 and $\lambda=1.3$ and 1.6 as a function of methane concentration in the fuel; (T=970 °C and 900 °C, P=18 kW)

4 CONCLUSIONS
The present studies show the influence of the fuel composition on ammonia-to-NO\textsubscript{x} conversion during flameless combustion of low calorific value gases. Depending on the gas composition, there can be a large difference in the conversion of NH\textsubscript{3} to NO\textsubscript{x}. In particular, the methane content influences the ammonia-to-NO\textsubscript{x} conversion. The lowest NO\textsubscript{x} emissions and therefore the lowest conversion ratios were measured while burning methane-free gas. Increasing the methane content from 0 to ca. 6 vol-%, the concentration of NO\textsubscript{x} in the flue gas was rising rapidly. Further increase above 6 vol-% of methane content had smaller influence
on the NO$_x$ emissions. The tested CO/H$_2$ ratios in fuel had a minor influence on the conversion of ammonia to NO$_x$. Higher air ratio enhanced the emission of NO$_x$. The influence of the stoichiometry was growing with the methane content in the fuel.

5 REFERENCES
[12] www.bgg.mek.dtu.dk