N$_2$O CONVERSION IN ACTIVE AND CHEMICALLY INERT FLUIDIZED BED

The subject of the research was the influence of N$_2$O on propane combustion in a fluidized bed reactor with active and chemically inert beds. It was determined that CaO has a significant influence on shifting the area in which the reaction is most intensive deeper into the bed and on the combustion result. It was also observed that adding nitrous oxide causes a decrease in VOC and CO concentration in exhaust gas. It was established that N$_2$O, when added, is the determining factor of NO$_x$ creation, which takes place in a similar manner as via the prompt mechanism.

1. INTRODUCTION

Nitrous oxide is a non-combustible, colourless gas, which has oxidizing properties. Its global warming potential (GWP) is approx. 310 times higher than that of carbon dioxide and approx. 15 times higher than that of methane [1]. Oceans and soil in tropical and temperate regions are the main natural sources of N$_2$O, they account for 80% of the total N$_2$O emission into the atmosphere. The remaining 20% is anthropogenic, i.e. related to agriculture (use of fertilizers, animal husbandry), industry (nitric acid and adipic acid) and fuel used in energy industry and transport. It is estimated that approx. 8% of man-made contribution to global warming is the result of nitrous oxide emission. While the natural N$_2$O emission is constant, the anthropogenic emission has a rising tendency and causes an increase in nitrous oxide concentration in the atmosphere by approx. 0.25% p.a. [2]. Nitrous oxide, considering its natural lifetime (approx. 110–150 years), easily reaches the stratosphere where it is subject to photodecomposition resulting in the creation of nitric oxide, which devastates the ozone layer.

The anthropogenic emission of nitrous oxide in Poland is estimated at approx. 95000 tons [3], where fuel combustion, industry and agriculture generate respectively

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8.7, 15 and 68.9 thousand tons. The European strategy of increasing the use of biofuels and the estimated growth in electrical energy demand can result in an increase in the amount of nitrous oxide released into the atmosphere.

During combustion, nitrous oxides can be formed as a result of the oxidation of nitrogen in the air or char nitrogen found in fuels. The first process can be observed in high-temperature combustion. ZELDOVICH describes the process of high-temperature combustion [4] through the following reactions:

\[
N_2 + O \leftrightarrow NO + N, \quad (1) \\
N + O_2 \leftrightarrow NO + O. \quad (2)
\]

This mechanism was, of course, further developed in order to capture more aspects of this complex process [5]–[8].

The combustion of nitrogen-free fuels in an FBR (Fluidized Bed Reactor) is conducted at a temperature of approx. 850 °C, it cannot be a source of thermal nitrogen oxides as they are created according to the Fenimore (prompt) mechanism and include CH radicals [9]. According to this mechanism, the reaction, which limits NO resulting from N₂, is as follows:

\[
CH + N_2 \leftrightarrow HCN + N. \quad (3)
\]

The resulting HCN is the main source of nitrogen in nitrogen oxides which are formed in homogeneous reactions. When O or OH radicals are applied, it yields NCO or CN and NO in the next step:

\[
HCN + O \leftrightarrow NCO + H, \quad (4) \\
HCN + OH \leftrightarrow CN + H_2O, \quad (5) \\
CN + O_2 \leftrightarrow NCO + O, \quad (6) \\
NCO + O \leftrightarrow NO + CO, \quad (7) \\
NCO + OH \leftrightarrow NO + CO + H. \quad (8)
\]

Lower combustion temperature yields more N₂O. Regardless of different views on the kinetics of the subsequent base reactions (e.g. [10]) the most important reactions, which proceed with N₂O, are:

\[
N_2 + O + M \leftrightarrow N_2O + M, \quad (9) \\
NH + NO \leftrightarrow N_2O + H, \quad (10) \\
NCO + NO \leftrightarrow N_2O + CO, \quad (11) \\
N_2O + H \leftrightarrow N_2 + OH. \quad (12)
\]
N\textsubscript{2}O conversion in fluidized bed

\begin{align*}
\text{N}_2\text{O} + \text{H} \leftrightarrow \text{NO} + \text{NH} , \\
\text{N}_2\text{O} + \text{O} \leftrightarrow \text{NO} + \text{NO} , \\
\text{N}_2\text{O} + \text{O} \leftrightarrow \text{N}_2 + \text{O}_2 .
\end{align*}

Nitrous oxide concentration inside conventional furnaces does not exceed 10 ppm, however, the concentration of nitrous oxide in fluidizing furnaces is in the range of 20–300 ppm [11]. Studies on nitrous oxide emission during the combustion of fuels containing nitrogen have established that reducing this oxide emission is possible if the process is conducted at high temperature and when the freeboard area has a temperature of at least 920 °C [13]. Adding lime stone as an SO\textsubscript{2} sorbent to the fuel resulted in a significant decrease of SO\textsubscript{2} concentration in the exhaust gases and a decrease of N\textsubscript{2}O and NO\textsubscript{x} emission [12]. This effect is credited to the catalytic properties of CaO, which catalyses the conversion of nitrogen in the fuel into NO\textsubscript{x} and the decomposition of N\textsubscript{2}O to N\textsubscript{2} [14].

2. EXPERIMENTAL PART

The combustion was conducted in a fluidizing reactor, the side surface of which is a quartz tube (96 mm inner diameter; 400 mm tall). The tube is fixed on a flat distributor made of 1mm thick chrome-nickel steel. The distributor has evenly distributed holes (0.6 mm in diameter) through which both air and fuel pass. The reactor is equipped with a moving insulating layer (covering the sidewall) and a cold air intake system, which enables quick temperature decrease of the bed during the experiment. In fact it is the basic means of temperature control. Chemically inert quartz sand (300 g; granulation of 0.384–0.43 mm) and calcium oxide, which has catalyst properties (159 g; granulation of 0.5–0.6 mm) were used for the bed. The characteristics of the combustion process have been established by analyzing exhaust-gases and measuring the temperature inside the fluidizing layer. The exhaust-gases were collected from the freeboard with a heated probe and directed to a system of analyzers. The reactor’s diagram, along with the analyzing system and the data recording system, is shown in figure 1. Seven thermocouples, fixed on top of each other on the reactor’s axis, 12–70 mm above the distributor, were used for measuring the temperature. In this paper, the thermocouples are listed 2–8 consistent with the previous research [15]–[17]. Their location is shown in figure 2. The reactor was used to combust propane (at technical purity) at excess air coefficient 40%. During one part of the experiments N\textsubscript{2}O was added to achieve the intake amount of 1000 ppm. Figures 3–6 illustrate the experiments. Each experiment consisted of two stages: 1) heating the reactor to a temperature above 950 °C and 2) controlled decreasing and increasing the temperature.
Fig. 1. Diagrammatic representation of the fluidised bed reactor used:

1 – computer storing the acoustic and pressure data, 2 – A/D convertor for acoustic signals, 3 – heated probe for sampling the flue gases, 4 – microphone, 5 – exhaust fan, 6 – pilot flame, 7 – cyclone, 8 – ash trap for coarser particles, 9 – freeboard space, 10 – moveable radiation shield, 11 – set of 7 thin thermocouples vertically mounted, 12 – bubbling bed, 13 – rotameters (from left: N₂O, air and fuel), 14 – fuel supply valve, 15 – blower, for fluidizing air, 16 – N₂O supply valve, 17 – pressure difference sensor, 18 – flat perforated metal plat distributor, 19 – A/D convertor for thermocouple signal; 20 – computer storing chemical analyses quantities and temperature.

Analytical block: A – O₂, CO, NO, NO₂, SO₂, CH₄, CO₂ analyser (MRU Vario Plus), B – total hydrocarbon analyser (JUM Model 3-200), C – O₂, CO, NO, NO₂, SO₂ analyser (ECOM SG Plus), D – CO₂ analyser (Madur), E – N₂O analyser (Horiba VA3000), F – O₂, CO, CO₂, SO₂, NOₓ, N₂O analyser (Horiba PG250), P – Peltier’s cooler
2.1. COMBUSTION OF PROPANE IN THE SAND BED

Temperature changes over the course of the experiment are shown in figure 3a. In the initial combustion phase, the combustion was performed in a bed which was 40 mm tall. Thermocouples placed above the bed recorded the highest temperature as they had direct contact with the flame. Thermocouples placed lower were immersed in the fluidized bed and the temperature increase was significantly slower. Three minutes after ignition, the dynamic height of the bed was approx. 60 mm and all thermocouples had contact with it. From that moment an increase of temperature was recorded by all thermocouples until the process ended. A detailed analysis of temperature variations inside the bed shows that there is a vertical profile with a visible maximum. The location of the thermocouple, which recorded the maximum temperature at a given moment, and the location of the bed are shown in figure 3b. An increase in the average temperature is accompanied by the maximum temperature zone movement deeper into the bed. When the average temperature is at its highest, the maximum temperature zone is located 12 mm above the distributor. In the second stage, lowering the tem-
perature results in shifting the maximum temperature zone higher. Valuable information on the combustion is the recorded fluctuation of the temperature measured at various heights inside the reactor (figure 3c). The recurrent (explosive) manner of the combustion inside the bubbles or on the bed surface causes both pressure and temperature changes [18]–[20]. The area which fluctuates the most is always the place where the highest temperature is recorded (see figure 3b and c). The lack of temperature fluctuation 12 mm above the distributor, recorded by the tc-2 thermocouple (see figure 3c: 4140–4200 s), indicates that the highest temperature zone and the most fluctuating zone are closer to the distributor at that time [21].

The exhaust gases composition changes in accordance with temperature fluctuations and the changing location of the zone in which the reaction is most intense (figure 3d and e). When the bed heats up and expands, a periodic increase of carbon oxide and VOC concentration occurs. As the highest temperature zone shifts deeper into the bed, the combustion takes place in a different manner: from continuous combustion in the flame located on the fluctuating bed surface into periodic combustion inside the bubbles. This is manifested by a decrease of VOC concentration in the fumes (which means that the fuel is combusted more efficiently) and an increase of CO concentration. The latter is linked with the relatively low temperature of the bed which results in lower oxidization efficiency of CO to CO₂. When the temperature exceeds 690 °C, CO concentration begins to reduce and reaches values near zero when the temperature exceeds 880 °C. After exceeding the initially assumed temperature, the temperature is lowered to approx. 780 °C and CO and VOC concentration rises to 2600 ppm and 230 mg/m³, respectively. Changes of NO, NO₂ and NOₓ concentrations were measured by autonomous devices shown in figure 3e. The total concentration of nitric oxide and nitrogen dioxide fluctuated within the range of 10 to 18 ppm depending on the phase of the experiment and nitric oxide concentration constituted for 70–95% of that amount. No N₂O in the exhaust-gases was picked up by the measuring devices.

Adding N₂O to the air – fuel mixture combusted in the FBR – does not influence the way the process shifts into the bed, nor does it influence the temperature fluctuation in the areas of maximum local temperature (figure 4a, b and c), although the amplitudes of these fluctuations are smaller during the second stage of the experiment. The comparison of the lower CO and VOC concentration measured in the second stage, after lowering the temperature, may indicate that N₂O influences the combustion (compare figure 3c, d: 4200–4800 s with figure 4c, d: 2100–2600 s). As a result of the combustion inside the fluidizing bed, nitrous oxide decreases from an initial 1000 ppm, at the reactor’s intake, to 40 – 95 ppm in the exhaust gases, depending on the phase of the experiment (figure 4e). This means that more than 90% of that gas is converted. N₂O added to the fuel is a significant source of nitrogen oxides (NOₓ) when the fuel is combusted over a sand bed. At temperatures below 1000 °C, the thermal mechanism of nitric oxide formation in air (the Zeldowich mechanism) is not very
Fig. 3. Combustion over the sand bed without additional N₂O – time series:
a) temperature recorded by selected thermocouples, b) changes in the bed’s surface location and the maximum temperature inside the bed, c) temperature fluctuations at different depths inside and above the bed, d) CO₂, CO and VOC concentration converted to 6% O₂ in the flue gases, e) nitrogen oxides concentration converted to 6% O₂ in the flue gases
Fig. 4. Combustion over the sand bed with additional N$_2$O – time series:
   a) temperature recorded by selected thermocouples, b) changes in the bed’s surface location
   and the maximum temperature inside the bed, c) temperature fluctuations at different depths inside
   and above the bed, d) CO$_2$, CO and VOC concentration converted to 6% O$_2$ in the flue gases,
   e) nitrogen oxides concentration converted to 6% O$_2$ in the flue gases

significant. NO$_x$ concentration during combustion is 6–8 times higher when N$_2$O is
added than during combustion without additional N$_2$O. Such a big change does not
result from the reaction proceeding according to the “prompt” mechanism, but it is mostly the result of N₂O conversion.

2.2. COMBUSTION OF PROPANE IN THE BED OF CALCIUM OXIDE

The combustion of fuel containing carbon in the FBR with a calcium oxide bed has a number of characteristic features. In the solid phase, at temperatures below 700 °C CaO can adsorb CO₂. At temperatures higher than 700 °C calcium carbonate decomposes (calcination, calcining). Carbonisation and calcination inside the FBR containing CaO have already been quantitatively described [22], [23]. Figure 5a and 5d shows the bed temperature as well as VOC and carbon oxide concentration changes over the course of the experiment. Similarly to the experiments with a sand bed, after the initial combustion of the mixture, a sharp CO₂ concentration rise in the exhaust gases is observed. The temperature increase makes the bed adsorb carbon dioxide from the fumes, which causes a decrease in CO₂ (figure 5d: 4200–4260 s). When CO₂ sorption is complete, the temperature increase is not as rapid as before because above 700 °C the endothermic process of calcination of the previously formed carbon dioxide occurs (see figure 5a and 5d: 4260–4310 s). N₂O presence in the air – fuel mixture does not influence this process significantly (see figure 6a and 6d: 2020–2170 s). Relocating the zone, in which the reaction is most intensive, towards the distributor is not accompanied by intense fluctuation of the local maximum temperatures as it was the case with a sand bed reactor (figure 5c). Only thermocouples tc-8 and tc-7 (70 and 60 mm above the distributor) recorded similar amplitudes. One has to be advised that these thermocouples were placed above the bed and were contacted only by the bed material bursting upwards. The other thermocouples show far fewer fluctuations of the temperature regardless of their location. This suggests a different combustion mechanism than in the case of rapid and periodical combustion inside the bubbles. Another feature of the calcium bed is a small quantity of nitrogen oxides formed during the combustion of nitrogen-free fuels containing carbon. Shortly after the initial combustion NOₓ is present in the exhaust gases as a result of burning fuel above the bed (figure 5e). When the reaction zone is shifted closer to the distributor, NOₓ concentration stabilizes in the range of 4–6 ppm.

Adding nitrous oxide to the mixture combusted in a CaO bed does not change the spatiotemporal behaviour of the combustion process (figure 6a, b, c and figure 5a, b, c). Just like in the previous experiment, one can observe the increase in average temperature and shifting the maximum temperature zone towards the distributor. Similarly to the combustion inside a calcium oxide bed without N₂O, no increased amplitude of the maximum temperature fluctuation can be observed. This suggests that there are two autonomous combustion mechanisms in a calcium oxide bed. Carbon dioxide concentration decreases during bed carbonization and increases during calcination –
Fig. 5. Combustion over the CaO bed without additional N₂O – time series:
a) temperature recorded by selected thermocouples,
b) changes in the bed’s surface location and the maximum temperature inside the bed,
c) temperature fluctuations at different depths inside and above the bed,
d) CO₂, CO and VOC concentration converted to 6% O₂ in the flue gases,
e) nitrogen oxides concentration converted to 6% O₂ in the flue gases
Fig. 6. Combustion over the CaO bed with additional N₂O – time series:
   a) temperature recorded by selected thermocouples,
   b) changes in the bed’s surface location and the maximum temperature inside the bed,
   c) temperature fluctuations at different depths inside and above the bed,
   d) CO₂, CO and VOC concentration converted to 6% O₂ in the flue gases,
   e) nitrogen oxides concentration converted to 6% O₂ in the flue gases
similarly to combustion without N\textsubscript{2}O. The concentration of N\textsubscript{2}O in the exhaust gases (figure 6e) varied from 0 to 60 ppm in the initial phase of the experiment and was in the range from 0 to 35 ppm at the later stage. These values were lower than during the combustion in a sand bed. This means that there was a higher level of nitrous oxide conversion. Adding N\textsubscript{2}O influenced also NO and NO\textsubscript{2} concentration in the exhaust gases, their concentration was higher than during the experiment in which N\textsubscript{2}O was not added. However, in comparison with sand bed combustion it was lower and fell in the range of 5–50 and 1–22 ppm, respectively. NO\textsubscript{x} concentration was 7–50 ppm and its lowest values were recorded when the reaction shifted toward the perforated bottom.

2.3. ANALYSIS OF THE IMPACT OF TEMPERATURE ON THE COURSE OF THE PROCESS

The above described experiments suggest that the process management and its location in a defined area inside the reactor, as well as its dynamics and effects (flue gases composition) depend mostly on the fluidized layer temperature. Therefore, the dependence of all examined parameters on the average temperature, measured by the thermocouples which always remained inside the bed (the average values recorded by thermocouples tc-2–tc-5), is described below. The results obtained in the initial phase of the experiment were analysed in more detail since the dependencies making up this complex combustion process are more explicit.

![Graph showing temperature dependence of CO, VOC, and nitrous oxides concentration](image_url)

**Fig. 7.** CO, VOC and nitrous oxides concentration converted to 6% O\textsubscript{2} in the flue gases depending on the average temperature of the bed; sand bed without additional N\textsubscript{2}O in the fuel

These dependencies for propane combustion in a sand (inert) bed without the addition of 1000 ppm of nitrous oxide and with this addition are shown in figures 7 and
The stepped line shows the location of the temperature maximum in the vertical profile which is linked to the location of the area where the most heat is released (the location of combustion).

Shifting the process from the area above the bed (regime A) into the sand bed (regime B) occurs at a relatively low temperature of 630 °C. A similar effect can be observed in the case of methane or ethane combusted in similar conditions [15], [16]. Further temperature increase causes a slight change in the location of intense reaction area. Only when the temperature exceeds 820 °C the process shifts further from 50 mm above the bed towards the perforated bottom. The temperature increase above the auto-combustion point of the bubbles, before they reach the bed surface, causes a change of the reaction zone movement dynamics. The changes in the zone location and the related acoustic and thermal effects [18]–[21] allow us to distinguish the third regime of the combustion process which depends on the bed temperature (regime C). However, N₂O presence in the fuel does not affect the location of the boundaries of regimes A, B and C. Its contribution to the main process of oxidizing hydrocarbons is negligible. Considering the fact that the combustion zone is the sum of the processes happening inside each bubble floating through the bed, its location is subject to some fluctuation. This is illustrated by vertical line segments coming upwards or downwards from the stepped line representing the average location.

An important chemical effect of the combustion is the increase of CO concentration according to the temperature increase in regimes A and B. Regime C shows a very low concentration of this gas in flue gases. The highest CO concentration (4650 ppm) occurs at approx. 690 °C. After adding N₂O to the fuel, the maximum CO concentration was only 4300 ppm and the corresponding temperature decreased to 8, respectively.
630 °C. The relation between VOC concentration in the exhaust gases and the temperature is similar to that of CO; however, when N$_2$O was not added the highest VOC concentration was 1220 mg/m$^3$ at 650 °C. When N$_2$O was added, the highest VOC concentration reached 510 mg/m$^3$ and it occurred when the average bed temperature was 580 °C. The changes of CO and VOC concentration indicate that there is a high probability of the reaction of N$_2$O, or substances resulting from its conversion, with particles (radicals) determining CO oxidation and hydrocarbons decomposition. A significant decrease in VOC and CO emission can be obtained by increasing the average temperature of the bed above 700 and 800 °C, respectively. The near zero level of VOC and CO emission is reached when the bed temperature exceeds 750 and 900 °C, regardless of the presence or absence of N$_2$O in the fuel.

Both nitric oxide and nitrogen dioxide are in the flue gases but in order to assess the combustion, it’s more important to analyze the total concentration of these two substances in relation to the temperature. This comes from the fact that according to the Zeldowich mechanism [4] and the prompt mechanism [9], NO is formed as a result of combustion and it can be further oxidized to NO$_2$. In regime A, the NO$_3$ concentration is initially low, for example: 10 ppm at 500 °C, however, it grows according to the temperature increase throughout regimes A and B and peaks at 18 ppm on the boundary of the combustion regimes B and C at 820 °C. Further temperature increase results in lowering NO$_3$ concentration to approx. 15 ppm at 1000 °C. These changes result from the fact that nitric oxide concentration increases according to the temperature increase, whereas NO$_2$ concentration reaches a maximum of 6 ppm at 800 °C – also on the boundary between regimes B and C. Given the fact that lowering NO$_3$ concentration is a priority, the above changes form a clear suggestion that the combustion should be conducted at the temperature higher than 850 °C – then the process will occur according to the kinetic mechanism of combustion inside the bubbles.

There is a striking resemblance between the dependence of NO$_x$ concentration in the exhaust gases on the temperature of the fluidized layer during the combustion of propane in the fluidized bed when N$_2$O is added and the propane combustion without the addition of nitrous oxide. The key difference is only the concentration value. The NO$_x$ concentration in regime A does not change significantly and fluctuates around approx. 90 ppm. After moving to regime B there is an increase of NO$_x$ concentration to a maximum value of 155 ppm (the boundary between regimes B and C). Afterwards it falls to 130 ppm at 1000 °C. The recorded concentrations of NO$_x$ are 9–10 times higher when N$_2$O was not added. Changes of NO concentration determine the NO$_x$ changes, especially in regime B, during which NO makes up 60–70% of NO$_x$, and in regime C, during which NO is more than 90% of NO$_x$ (above 900 °C). The proportionality of NO$_x$ concentration with or without the additional N$_2$O and regardless of the temperature suggests that there is a reaction, whose activation energy and the temperature exponent in the Arrhenius equation are the same as in the reaction in which NO is formed according to the prompt mechanism.
Changing the bed material from sand to calcium oxide, without adding nitrous oxide into the bed (figure 9), caused a shift in the process boundaries towards lower temperatures. Shifting the combustion from above the bed towards the interior takes place at 550 °C, and from regime B to C at 720 °C. This means that calcium oxide significantly influences the combustion. It is suggested to use a mechanism [24], according to which a part of the process happens as a heterogenic reaction, in which an O radical (from CaO) separates hydrogen radicals from hydrocarbons. VOC concentration in the flue gas created in the CaO bed is lower than in the case of a sand bed. It reaches a maximum of 650–660 mg/m³ in the range of 540–640 °C, which is the boundary between regimes A and B. In regime C, VOC concentration in the exhaust gases is almost zero. Adding N₂O significantly decreases the maximum emission of VOC (90 mg/m³) and shifts it towards a lower temperature range of 450–520 °C, i.e. to the flame combustion area above the bed (figure 10). The presence of CaO, which acts as a catalyst, does not conceal the influence of N₂O on the effective fuel combustion.

![Diagram](image)

Fig. 9. CO, VOC and nitrous oxides concentration converted to 6% O₂ in the flue gases depending on the average temperature of the bed; CaO bed without additional N₂O in the fuel

The concentration of carbon oxide is much the same as in the experiment with the sand bed, although the maximum concentration of 2500 ppm occurs during the process as a wide plateau in the range of 540–640 °C (figure 9). Further temperature increase causes a rapid decrease in CO concentration. When the temperature exceeds 900 °C, there is a decrease of CO concentration to near-zero values. Adding N₂O to the fuel causes a significant decrease of maximum CO concentration to 2050 mg/m³ at 540–580 °C (figure 10). Switching from a sand to a CaO bed allowed a significant reduction of CO and VOC emission.
The dependencies of nitrogen oxides concentration upon the bed temperature underwent significant changes in comparison with those in the experiment using the sand bed. It is a well-known phenomenon which has already been observed [14], [17], [25]. The highest NO\textsubscript{x} concentration (approx. 5 ppm; figure 9) was observed in regimes A and B with a slightly downward trend after exceeding 700 °C. In regime C, a minimum of 2 ppm at 850 °C was observed. Above 900 °C, the NO\textsubscript{x} concentration in the flue gases stabilized at 6 ppm. NO and NO\textsubscript{x} contribution was 50% in regimes A and B, while in regime C it increased to approx. 95%. From the technological point of view, taking into account the emission values, the most efficient combustion takes place in the range of 850–900 °C.

Adding 1000 ppm of N\textsubscript{2}O to the fuel results in NO\textsubscript{x} concentration at approx. 50 ppm (incl. NO – approx. 30 ppm) inside the flame combustion area, which is more than 10 times higher than in the case when no N\textsubscript{2}O was added. As the temperature rises, NO\textsubscript{x} concentration decreases reaching a minimum of 7 ppm at 880 °C. In the range of 890–920 °C there is a sharp increase of NO\textsubscript{x} concentration to approx. 35 ppm and at 1000 °C, NO\textsubscript{x} concentration stabilizes at approx. 45 ppm. This low concentration of NO\textsubscript{x} can be reduced by different methods, e.g. ozonation [26].

The concentration of the added N\textsubscript{2}O, after a rapid decline during the initial combustion, reaches a maximum of 55 ppm at 580–670 °C, which is close to the activation temperature for calcination, and afterwards it decreases. At 735 °C, i.e. the temperature at which calcination ceases (figure 6a, e: 2140 s), the N\textsubscript{2}O concentration reaches a minimum. After reaching the global maximum (60 ppm) in regime C at 820 °C, there is a sharp decrease in N\textsubscript{2}O concentration to 15 ppm at 900 °C. Further temperature increase causes a decrease in N\textsubscript{2}O concentration in the exhaust-gases to near-zero values at 1000 °C.
3. SUMMARY

Adding N₂O to the air-fuel mixture caused significant changes in the flue gases composition. CO and VOC concentration decreased (regardless of the bed material), however, NOₓ concentration increased. Increasing the level of fuel conversion indicates that N₂O can be used in reactions assisting fuel conversion (as a source of O radicals). The increase of N₂O concentration in the flue gases results from the increase of CaCO₃ inside the bed, and its decrease is related to a smaller amount of CaCO₃. This indicates the significant role of heterogenic mechanisms involving nitrous oxide at low temperatures. The NO concentration increase in the flue gases, regardless of the bed type, is important in the homogenous process involving N₂O. Considering the similarities in NO changes recorded when adding N₂O to the changes of NO concentration without the additional N₂O, we obtain the following reaction:

\[ \text{N}_2\text{O} + \text{CH} \leftrightarrow \text{HCN} + \text{NO}. \] (16)

REFERENCES


