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CONVERSION OF DIETHYLAMINE INTO NITROGEN OXIDES DURING COMBUSTION IN CHEMICALLY ACTIVE FLUIDIZED BED

KONWERSJA DIETYLOAMINY DO TLENKÓW AZOTU PODCZAS SPALANIA W AKTYWNYM CHEMICZNIE ZŁOŻU FLUIDALNYM

Abstract: Combustion processes of gaseous fuel (propane) without and with addition of various amounts of diethylamine in fluidized bed, made of chemically active calcium oxide, were run and studied. On the basis of registered temperature, dynamic pressure in reaction zone and composition of exhaust fumes, analysis of diethylamine conversion into nitrogen oxides and its influence on kinetics of propane combustion process was carried out. The complexity of solid fuels (alternative or biomass which can contain large amount of nitrogen compounds in a form of amines, heterocyclic compounds, amino acids etc.) combustion caused that at this phase of researches, incineration of gaseous fuel was run. Amine was dosed into the reaction zone in such amounts, which could give similar nitrogen oxides concentration in exhaust fumes, to those registered from combustion of alternative fuels with high nitrogen content (circa: 900, 1800, 3250 ppm). Results of experimental works revealed that up to 78% of nitrogen compound was converted to N_xO_y. The conversion rate was higher when greater amounts of $(C_2H_5)_2NH$ were dosed into reaction zone. The main nitrogen oxide created within combustion was nitric oxide, which constituted more than 95% of total N_xO_y. The remaining amount of amine was converted into nitrogen. $(C_2H_5)_2NH$ influenced on kinetics of the propane combustion process in noticeable way, but this impact was also limited. Diethylamine and products of its conversion, such as radicals present in the combustion zone, influenced on oxidization reactions of carbon monoxide and volatile organic compounds.

Keywords: nitrogen oxides emission, fluidised bed combustion, alternative fuels combustion, biomass combustion

Increasing energy demand causes, that fuels alternative to conventional *ie* biomass or wastes, are more often applied as a sources of energy in combustion processes next to fossil fuels (coal, gas, oil) which are still main energy sources. Combustion processes must be carried out in the most effective way from economical and what is very important environmental point of view. Combustion of materials such as biomass and wastes entails various types of complications. Often they contain large amount of nitrogen compounds in their composition in the form of amines, amides, heterocyclic compounds etc. The main products of their combustion are nitrogen oxides which emission can reach up to 2500 mg/m^3 [1]. Those oxides can be created during incineration from atmospheric and fuel-nitrogen via thermal, *prompt* or/and fuel nitrogen mechanisms [2-11]. In combustion zone, nitrogen is present transiently in the radicals HCN, CN, HNO and NH_i which transformations in this area lead to nitrogen oxides creation [4]. The fact is, that maintaining temperature above 900ºC in the freeboard zone of fluidized bed reactor, causes that NO emission is significantly higher than emission of N_2O and NO_2 [12].

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Reactions of nitrogen oxidation, especially fuel-nitrogen, are complex homogeneous, heterogeneous or catalytic processes, what causes that researches on them are carried on all over the world [13-20]. In the initial stage of nitrogen oxides creation from fuel nitrogen, during coal combustion HCN is produced. This particle is one of the main intermediate products of nitrogen oxidation, no matter how complex the conversion process occurs. It is also a product of decomposition of the amines in the initial phase of the process and its further reactions lead to the formation of nitrogen oxides N_xO_y. However, complex composition and structure of solid fuels (biomass, wastes) and specific hydrodynamic and temperature conditions in a fluidized bed cause that a detailed course of their combustion is not fully known. The goal of presented researches is to get knowledge about issue of conversion of fuel nitrogen into nitrogen oxides. Complexity of solid fuels combustion process caused, that as the first phase of researches combustion of propane with the addition of controlled amounts of diethylamine was carried out. Amine (N-compound) was dosed into the reaction zone in such amounts, which can be indicated in solid fuels.

Material and methods

Experimental researches were run in the laboratory scale, atmospheric fluidized bed reactor, which was applied during previous experiments of combustion processes [3]. The reactor was equipped with a system for supplying fuel, gaseous and liquid mixtures such as diethylamine.

The material of the bed, within all experiments, was chemically active calcium oxide which particles size was from the range 0.5-0.6 mm, its weight was about 350 g and its static height in reactor was approximately 41 mm but in dynamic conditions (temperature ~1000°C) height was increasing to approx. 100 mm.

The fluidized bed had a temperature control system consisting of a movable radiation shield and blower of a cold air.

In aim of control of combustion processes and its further detailed analysis temperature, exhaust fumes composition and dynamic phenomena were registered during whole experiments. The temperature in the fluidized bed was measured by a set of eight uncovered thermocouples mounted in the reactor axis, at distances from 5 to 70 mm above the distributor in parallel with measurements run by two sheathed thermocouples which joints were permanently mounted 20 and 50 mm above gas distributor. Dynamic phenomena occurred during combustion were analyzed on the basis of the registered dynamic pressure changes. Registration was carried out using a difference pressure sensor mounted under gas distributor and by the microphone which was located about 550 mm above the surface of the bed. Measurements and recordings of exhaust fumes composition were carried out using analytical equipment: total organic compounds analyzer equipped with flame ionization detector (JUM® Model 3-200); O_2, CO, NO, NO_2, SO_2 analyzer equipped with electrochemical detectors (ECOM® SG Plus); O_2, CO, CO_2, SO_2 NO_x, N_2O analyzer equipped with electrochemical, nondispersive IR and chemiluminescence detectors (Horiba® PG250); FTIR analyzer equipped with Fourier transform IR detectors (Gasmet® DX-4000); O_2, CO, NO, NO_2, SO_2, CH_4, CO_2 analyzer equipped with electrochemical, nondispersive IR detectors (MRU® Vario Plus).

In the series of combustion experiments, propane was incinerated in fluidized bed reactor with as well as without addition of diethylamine. The series when only propane was present in reaction zone were carried out to get comparative data to the main part of the process. Diethylamine conversion and influence of amine compound presence in the reaction zone, as well as application of its different quantities to the reactor, on the conditions of fluidized bed combustion were analyzed. All experiments were carried out similar way. First stage was fluidization of the bed by air (rate of flow 1.66 dm^3/s) at ambient temperature. Next step was starting up of diethylamine dosage to the reactor, rate of flow was maintained constant during one single experiment, whereas in subsequent experiments different amounts of $(C_2H_5)_2NH$ were dosed (chosen rate of flows ensured respectively concentrations of amine approx. 900, 1800 and 3250 ppm in fuel-air mixture). Third stage was initiation of propane dosing into the reactor (rate of flow ~0.043 dm^3/s), which resulted in the creation of such fuel-air mixture composition, that the air-fuel ratio - λ_{bed} - was about 1.4. Start of propane addition was equivalent with ignition and beginning of combustion process. In a subsequent step incineration was carried out in a manner to obtain a gradual increase in bed temperature from ambient temperature to about 1000ºC and after receiving it, cooling of the reactor with outside air stream, to lower the temperature of the bed, was run. In experiments without addition of diethylamine to propane, only the step with dosage of this compound to the reactor was omitted.

Results and discussion

Changes of location of reaction zone in a fluidized bed as well as dynamic pressure and associated with those changes of chemical reactions mechanisms, depended strongly on temperature in combustion area. Additionally composition of flue gases depended strongly on temperature and whether diethylamine was or was not added to the reaction zone. To get knowledge about presented combustion processes, analysis of those parameters, as a function of the average bed temperature (mean arithmetic of four temperature measured by the thermocouples located from 10 to 30 mm above the distributor) was done.

Incineration under low bed temperature ~400ºC, was carried on above the bed (higher than 60 mm above the gas distributor) (Fig. 1a). Further increasing of the average bed temperature caused increase of the volume of gas flowing through the bed, what resulted in increase of the bed height. After exceeding the temperature above about 500ºC, the highest temperature measured in bed was located at surface of the bed (combustion was taking place at this location). Under average temperature above 600ºC combustion process runs mainly in the bed (Fig. 1a). In parallel to changes of bed height, changes of location of combustion zone with average temperature in fluidized bed were observed (Fig. 1a). Combustion of only gaseous fuels with air, as well as with addition to this mixture of diethylamine, led to movement of the maximum temperature location in the bed (zone of the most intense exothermic reaction) downwards, toward the gas distributor with increasing of average temperature (Fig. 1a). When average temperature in the bed was above 840ºC, combustion took place mainly in the area from 12 to 29 mm above the distributor (Fig. 1a), because autoignition in bubbles occurred during the shorter time that was necessary to pass their way through the bed. It was conclude that during combustion of propane with addition of diethylamine (1800 or 3250 ppm), area of the most intense reactions was moving faster towards distributor (Fig. 1a).

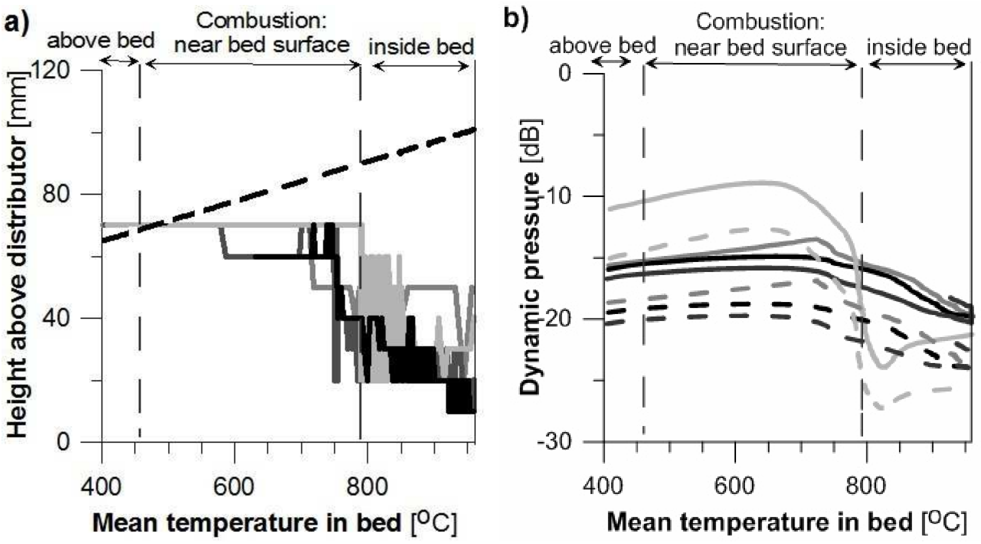

Fig. 1. Changes of chosen parameters of propane combustion processes with and without addition of diethylamine: a) height of the fluidized bed (▬ ▬) and the maximum temperature location during process (amount of diethylamine addition to propane: ▬ - 0 ppm; ▬ - 900 ppm; ▬ - 1800 ppm; ▬ - 3250 ppm); b) dynamic pressure registered by microphone (amount of diethylamine addition to propane: ▬ - 0 ppm; ▬ - 900 ppm; ▬ - 1800 ppm; ▬ - 3250 ppm) and pressure difference sensor (amount of diethylamine addition to propane: ▬ ▬ - 0 ppm; ▬ ▬ - 900 ppm; ▬ ▬ - 1800 ppm; ▬ ▬ - 3250 ppm)

Registered dynamism pressure provided information about changes of the process dynamics related with increase of the temperature [21, 22]. When the temperature in the fluidized bed was relatively low (lower than 500ºC), signal amplitude in all analyzed experiments was low, what was result of continuous manner of combustion in flame (Fig. 1b). With the temperature increase, combustion on the bed surface was initiated. That was related with the change of the combustion mechanism into periodic, explosive combustion in large bubbles, what resulted in an increase of registered acoustic pressure. Within the temperature of about 700ºC dynamics of acoustic signals reached the maximum level. Further increasing of temperature resulted in the movement of process deeper into the bed. Bubbles with gases exploding inside them became less noisy and the energy released during the explosions was smaller what caused together, with occurrence of high bed layer located over the area of reaction, that registered acoustic effects were lower (Fig. 1b). Changes in the dynamic pressure recorded by microphone and by difference pressure sensor were similar in all experiments where diethylamine was added to the propane (Fig. 1b). Different situation took place when only propane was incinerated. In this case dynamic pressure (under the temperature lower than 800ºC) was noticeably higher than in the case of propane combustion with diethylamine. On the other hand, within combustion in the bed (temperature higher than 800ºC) acoustic signal amplitude in this case was lower (Fig. 1b). This can suggests that the kinetics of propane combustion without and with diethylamine addition is not completely similar. These phenomena could be a result of amine influence on the rate of combustion reactions (change of activation energy of particular reactions) which occurred in bubbles. Radicals which were products of amine conversion in reaction zone, caused that reaction with propane took place faster and bubbles during explosion contained smaller amount of fuel than in the case where only propane was incinerated. That could be a cause of registration of higher dynamic pressure when only propane was combusted, because explosions were more violent.

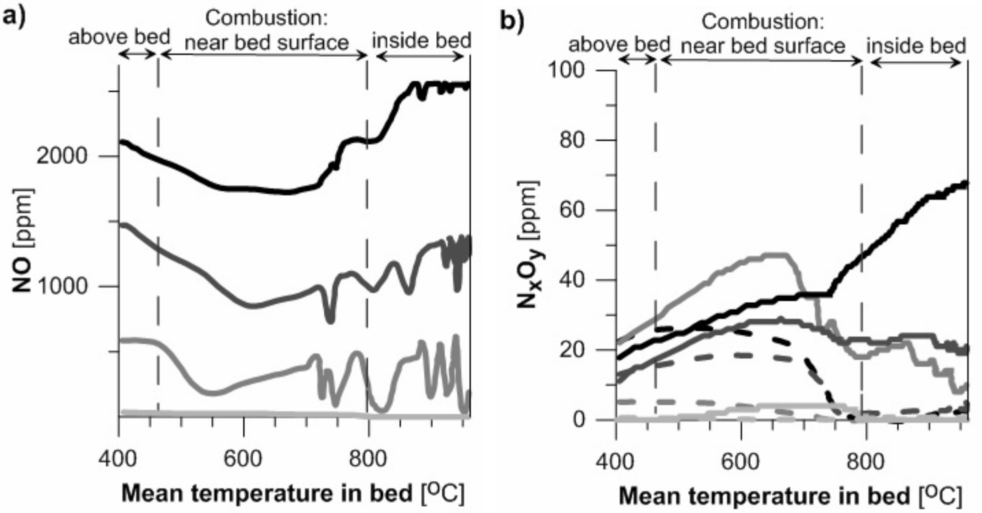

Fig. 2. Changes of nitrogen oxides concentration in flue gases as a function of mean bed temperature: a) nitric oxide (amount of diethylamine addition to propane: ▬ - 0 ppm; ▬ - 900 ppm; ▬ - 1800 ppm; ▬ - 3250 ppm); b) nitrous oxide (amount of diethylamine addition to propane: ▬ ▬ - 0 ppm; ▬ ▬ - 900 ppm; ▬ ▬ - 1800 ppm; ▬ ▬ - 3250 ppm) and nitrogen dioxide (amount of diethylamine addition to propane: ▬ - 0 ppm; ▬ - 900 ppm; ▬ - 1800 ppm; ▬ - 3250 ppm)

The main products of diethylamine conversion, during combustion process, were nitrogen oxides. When amine was not dosed into the reaction zone, concentration of nitric oxide (the major oxide formed mostly by the *prompt* mechanism during combustion of hydrocarbon fuels in fluidized bed [2]) in the exhaust fumes did not exceed 30 ppm. Nitrogen dioxide concentration was 3-4 ppm and nitrous oxide concentration was lower than the gas detector sensivity (Fig. 2b). In the series of experiments where diethylamine was dosed into reaction zone, concentration of N_xO_y in exhaust fumes was relatively higher. The efficiency of amine conversion into N_xO_y during combustion was up to 78% and was higher when greater amounts of $(C_2H_5)_2NH$ were dosed into reaction zone. The main product of these reactions was, as mentioned before, nitric oxide which constituted more than 95% of the total created nitrogen oxides (Fig. 2a, b). Except N_xO_y no other compounds containing nitrogen in their structure were detected, therefore it was assumed that nitrogen is the only other product of diethylamine conversion. Initiation of amine oxidation process caused that concentration of NO in flue gases reached maximum value 2530, 1350, 580 ppm, when amine was dosed to the bed in respective amounts of 3250, 1800 and 900 ppm, under temperature higher than 900ºC (Fig. 2a). Concentrations of NO_2 and N_2O did not exceed respectively 70 and 30 ppm, when the highest amount of diethylamine was added to the reaction zone (Fig. 2b).

Analysis of efficiency of NO formation from diethylamine as a function of temperature revealed, that its maximum concentration occurred within the highest temperature. When only propane was incinerated, concentration of NO decreased with increase of temperature. Observed, different changes of nitric oxides concentrations with temperature in case of propane combustion with and without amine, cause necessity of further detailed analysis of these phenomena, because formation of NO in these both cases run under different kinetics.

In all experiments the amount of carbon monoxide in the exhaust fumes was increasing sharply with temperature increase and reached the maximum value at about 750ºC (Fig. 3a). This was a result of the inhibitory effect of bed, not hot enough, on the oxidation of CO to CO_2. Further increase of temperature caused a rapid decrease of CO concentration in the exhaust fumes (Fig. 3a). Addition of amine into reaction zone caused, that the highest CO concentration in flue gases was about half lower in comparison to experiment when no $(C_2H_5)_2NH$ was added to the propane (Fig. 3a).

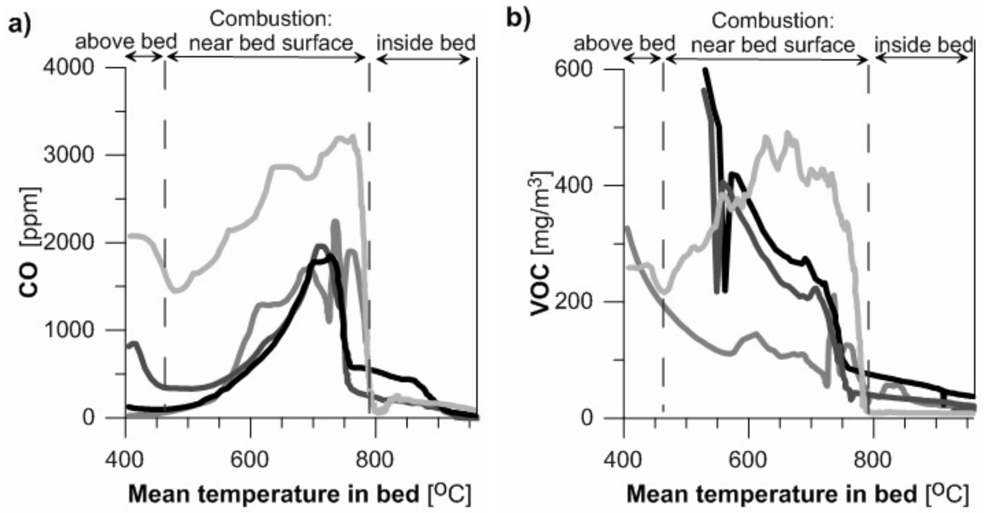

Fig. 3. Changes of chosen compounds concentration in flue gases as a function of mean bed temperature: a) carbon monoxide (amount of diethylamine addition to propane: ▬ - 0 ppm; ▬ - 900 ppm; ▬ - 1800 ppm; ▬ - 3250 ppm); b) volatile organic compounds (amount of diethylamine addition to propane as in Figure a)

The highest concentration of volatile organic compounds in the exhaust fumes was about 480 mg/m^3, in the case when propane was incinerated alone within the bed temperature 650ºC. In all experiments, obtainment of temperature higher than 800ºC caused rapid decrease of VOC concentration in exhaust fumes (Fig. 3b). In experiments with the application of diethylamine, the maximum VOC concentration was significantly lower within temperature range 620-750°C, than for experiment where only propane was incinerated. Similarly to the case of carbon monoxide reactions, addition of diethylamine to reaction zone influenced on VOC oxidization reactions.

On the basis of observed phenomena, it can be surmised that radicals, which were the intermediate products of diethylamine conversion, were involved in the reactions of CO and VOC oxidation.

Conclusions

Diethylamine, added to the propane during combustion in fluidized bed, was converted into N_xO_y up to 78% and residual amine was converted into nitrogen. The degree of conversion into N_xO_y was higher when greater amount of amine was dosed into reaction zone. The main formed nitrogen oxide was nitric oxide (more than 95%).

Radicals which were products of diethylamine conversion, present in the reaction zone, influenced on reactions involving CO and VOCs. They affected the acceleration of oxidization processes. The degree of CO and VOCs conversion was at high level even by temperature lower than 800°C, when the combustion took place yet near bed surface.

During combustion, N_2O was detected in flue gases at a level not exceeding 30 ppm.

Effect of diethylamine on the kinetics of propane combustion process is noticeable but limited. It can therefore be assumed that amine impact will also be noticeable during the combustion of alternative fuels with high fuel-nitrogen content. Amines are in fact one of the major compounds which are source of bounded nitrogen in fuels. Their further reactions lead to the formation of nitrogen oxides.

Acknowledgments

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KONWERSJA DIETYLOAMINY DO TLENKÓW AZOTU PODCZAS SPALANIA W AKTYWNYM CHEMICZNIE ZŁOŻU FLUIDALNYM

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Abstrakt: Przeprowadzono i przeanalizowano procesy spalania paliwa gazowego (propanu) bez oraz z dodatkiem różnych ilości dietyloaminy, w złożu fluidalnym zbudowanym z chemicznie aktywnego tlenku wapnia. Na podstawie temperatury, ciśnienia dynamicznego w strefie reakcji oraz składu spalin dokonano analizy procesów konwersji dietyloaminy do tlenków azotu i jej wpływu na kinetykę procesu spalania propanu. Złożoność procesu spalania paliw stałych (alternatywnych lub biomasy, które mogą zawierać wysoką ilość związków azotu w postaci amin, związków heterocyklicznych, aminokwasów itp.) spowodowała, że na tym etapie badań zdecydowano się na przeprowadzenie spalania paliwa gazowego. Aminę dozowano do strefy reakcyjnej w takich ilościach (około: 900, 1800, 3250 ppm), które mogłyby dawać stężenia tlenków azotu w spalinach podobne do rejestrowanych podczas spalania paliw alternatywnych o dużej zawartości azotu. Wyniki badań wykazały, że do 78% związku azotowego ulegało konwersji do N_xO_y. Stopień konwersji był większy, gdy większe ilości $(C_2H_5)_2NH$ dozowano do strefy reakcji. Głównym tlenkiem azotu utworzonym podczas spalania był tlenek azotu(II), który stanowił ponad 95% całkowitej ilości N_xO_y. Pozostała amina była przekształcana do azotu. Stwierdzono zauważalny, ale ograniczony wpływ $(C_2H_5)_2NH$ na kinetykę procesu spalania propanu. Dietyloamina i produkty jej konwersji, takie jak rodniki obecne w strefie spalania, wpływały na reakcje utleniania tlenku węgla i lotnych związków organicznych.

Słowa kluczowe: emisja tlenków azotu, spalenie w złożu fluidalnym, spalanie paliw alternatywnych, spalanie biomasy