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Low-Emission Combustion of Alternative Solid Fuel in Fluidized Bed Reactor

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1. Introduction

Incineration of conventional fuels is hitherto the main method of worldwide energy obtainment. In view of this fact researches on finding alternative fuels, which may successfully replace fossil fuels, are carried out continually. Both environmental criteria and economic viability are taken into consideration. Materials which fulfill these criteria are different types of waste (industrial, municipal and agricultural) and biomass. These fuels can be significantly less expensive than conventional ones. Moreover, they sources seem to be unfailing at present considering their excessive production by human. Deposited, not processed wastes are even more serious threat to the environment. However, to have possibility of carrying out thermal utilization of this type of material, they must have adequately high calorific value. The material meets this and other above-mentioned criteria, selected to researches which are presented in this paper, is the sewage sludge. Its gross calorific value can exceed 20 MJ [1]. It can successfully be proecological alternative to fossil fuels. Depending on the material used and applied combustion technology, the process may entail various complications.

1.1. Fluidized bed reactors

In processes involving solid-phase fluidized beds show several valuable properties. In fluidization conditions mass and heat transfer is very good and mixing of the components of the reaction mixture is excellent. Therefore, fluidization of solid particles has a number of industrial applications such as combustion of coal and other combustible materials, fluid catalytic cracking (FCC) of heavy oil into gasoline, spray drying of aqueous solutions, drying of solids like cement and limestone, obtaining very pure silicon by decomposition of silane, separation of fine dust of solids and many others. The possibility of obtaining state of fluidization depends strongly on the particle size and density [2]. With the increase in the flow rate

of gas or liquid through the solid layer several operating regimes of bed are distinguished: packed bed, minimum fluidization, bubbling fluidization, turbulent fluidization and pneumatic transport (with lean phase fluidization). In industrial practice fluidized-bed processes are performed in each of these regimes.

Combustion of fuels in a fluidized bed has the advantage that during vigorous stirring oxygen is supplied to the particulate fuel. This virtually eliminates the occurrence of oxygen-poor zones in the reactor and this results in relatively even emission of heat from the combustion process. Processes of drying and degassing which always accompany the burning of solid fuels take place intensely in the whole volume of fluidized bed (on all the grains put into the fuel) and not, as in the case of a constant fuel layer only in a narrow zone of high temperature. In the power industry stationary fluidized bed boilers (usually bubbling), fluidized bed with a thermal capacity of less than 150-200 MW, often less than 15 MWe and fluidized bed boilers with circulating fluidized bed of high power - up to about 500 MWe are used. Currently units with a capacity of 600-800 MW, which will fulfil in the near future high requirements of municipal operators, are designed.

In the power plant Łagisza situated in Bedzin (Poland) in the year 2009, first Supercritical CFB (circulating fluidized bed) boiler also being the world's largest CFB unit with a capacity of 460 Mwe, started to work. Capital expenditures for the construction of the CFB boiler was more than 15% lower than expected expenditures for the construction of dust boiler of the same power along with the necessary installation of flue gases desulphurization. The boiler produces 361 kg/s steam at 560 °C and a pressure of 27.5 MPa. For heating the boiler maximum 187 t/h of coal is consumed in the presence of SO₂ and NO_x emissions less than 200 mg/Nm³, and dust emission below 30 mg/Nm³. An additional advantage of such boiler is its fuel flexibility. Circulating Fluidized Bed combustion has given boiler and power plant operators a greater flexibility in burning a wide range of coal and other fuels. All this without compromising efficiency and with reduced pollution.

The necessity of transformation of a large mass of particulate solid into a fluidized state causes that air have to be used to this aim, in an amount much greater than required for combustion of the fuel. That is the reason why gas production in fluidized bed boilers is on considerable amount. Since combustion takes place at a temperature of 750-900 °C, too low to be able to play an important role in the processes of synthesis of NO from nitrogen and oxygen contained in the air, the content of NO_x in the exhaust gases is significantly lower than during the combustion of fuel using other methods. Intense mixing of solid particles, however, causes that exhaust gases leaving the boiler contain more dust than those from other types of boilers. Installation for fluidized bed combustion requires much more efficient dust collection systems.

In the European Union obtains the directive [3] in which emission values limits for selected air pollutants are defined for power equipment of specified size. Crucial data for existing installations (i.e. combustion plants which have been granted a permit before 7 January 2013) are summarized in Table 1.

Total rated thermal input (MW)	Coal and lignite and other solid fuels	Biomass	Peat	Coal and lignite and other solid fuels	Biomass and peat	Coal and lignite and other solid fuels	Biomass and peat
	SO ₂ , mg/Nm ³			NO _x , mg/Nm ³		dust, mg/Nm ³	
50-100	400	200	300	300*)	300	30	30
100-300	250	200	300	200	250	25	22
>300	200	200	200	200	200	20	20

*) 450 in case of pulverized lignite combustion

Table 1. SO₂, NO_x and dust emission standards in UE

In the case of thermal utilization of sewage sludge, biomass, and other wastes, the problem is in very high emission of nitrogen oxides into the atmosphere. It is well known that nitrogen oxides creating and penetrating into the atmosphere from combustion processes carried out both in industrial processes, power industry and in households, pose a serious threat to the environment and health. Sludge contains nitrogen bound in organic and inorganic compounds. According to Petersen [4], the high nitrogen content in the sludge results in nitrogen oxides emission up to 2500 mg/m³, during its combustion. Reduction of nitrogen oxides concentration in flue gases, produced during thermal utilization of solid alternative fuel, is the main topic of this paper. A technique that has been used for this purpose is the reburning. The study was conducted in a laboratory scale fluidized bed reactor.

1.2. Nitrogen oxides formation

Due to the fact of availability, costs and the properties the most commonly used oxidizer in combustion processes is oxygen from the air. However, its use in the thermal utilization processes has also disadvantages. One of these is that under certain conditions, reacts with nitrogen leads to unavoidable formation of nitrogen oxides irrespectively of type of fuel which is used and combustion technology which is applied. Nitrogen oxides can be formed in the combustion processes by a number of mechanisms from atmospheric or fuel nitrogen. During the synthesis of NO, which consists of a number of complex processes, multiplicity of radicals are created, which quantity can be influenced depending on thermodynamic and stoichiometric conditions applied in the process.

Formation of nitrogen oxides from atmospheric nitrogen is explained by means of thermal mechanism (Zeldovich mechanism) [5]. The beginning of the processes leading to the formation of NO here is the thermal dissociation of oxygen and nitrogen molecules present in the air.



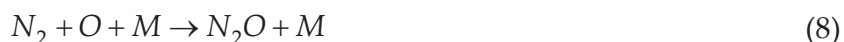


Dissociation processes of those molecules take place efficiently in a high temperature (over 1400 °C) which means that in practice, during the combustion processes in a fluidized bed reactor it can be omitted part NO formed in accordance with a thermal mechanism.

Formation of NO in the flue gases during the combustion of hydrocarbon fuels at a temperature lower than 1000 °C describes proposed by Fenimore „prompt” mechanism [6]. Crucial role plays in it CH radicals, which undergoes transformation in reactions with nitrogen and oxygen from the air, they are source of the NO formation at a high level [6-9].



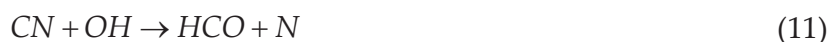
Under increased pressure significant path for NO formation is through N₂:



Such conditions are not met often in fluidized installations, usually working under atmospheric pressure.

The most important role in the creation of NO plays mechanism whereby to the formation of nitrogen oxides, nitrogen bound in fuel is used. Nitrogen - usually bounded in the organic matter in a form of cyclic compounds or amines - reacts easier at elevated temperatures. In the combustion processes nitrogen occurs in hydrogen cyanide and radicals CN, HNO and NH. As a result of transformation of these radicals in the reaction with oxygen and OH radicals NO is produced [10,11]. OH radical which plays a central role in the oxidation of carbon, associated in organic matter, to CO also plays an important role in the oxidation of nitrogen bounded in fuel to nitrogen oxide.





1.3. Reduction methods of nitrogen oxides

1.3.1. SNCR and SCR metod

Due to the requirements of environmental protection and associated regulations, NO_x produced during combustion processes must be removed from the flue gases which enter the atmosphere. In practice, the NO_x reduction processes are carried out directly in the boiler (primary methods – Selective Non-Catalytic Reduction (SNCR), reburning) or in separate installations (secondary methods – Selective Catalytic Reduction (SCR)).

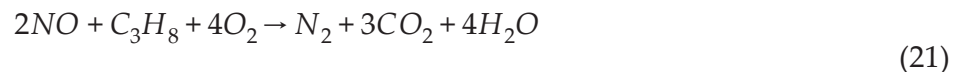
The essence of the SNCR method is addition to the combustion zone stoichiometrically selected amounts of ammonia or urea. These substances are transformed and as results NH_i radicals are created, which in turn react with NO reducing it to N_2 [12]. In case of use of ammonia process is carried out at a temperature of 770 - 1000 °C. In the case of urea, the first stage of the process (the decomposition of urea) it is carried out in the temperature range 300-620 °C. In

this method it is important to maintain a suitable temperature, because at temperatures above 1093 °C the process of ammonia oxidation, with oxygen from the air which results in considerable amounts of NO, becomes extremely important. Applying the SNCR method a 70% reduction of NO can be achieved [12,13] and in practice urea is used more often because of its safety.

In the SCR method [14] - NO_x reduction is carried out outside the combustion chamber after thorough dedusting of flue gases. Reactions are taking place there on properly selected catalyst and the most commonly reducing reagent used is ammonia. Application of catalyst in this case decreases the activation energy for the reduction reaction of nitrogen oxides leading to N₂. Catalysts, which are used in the SCR technology are: platinum, tungsten-vanadium supported on TiO₂, ZrO₂, SiO₂, Al₂O₃ and zeolite carriers [14,15].

1.3.2. Reburning method

Reburning is one of the primary methods of NO_x reduction. This technology involves the introduction of additional hydrocarbon fuel into the zone of flue gases, which means the creation in this area of the second combustion zone. The authors of this method - Wendt and collaborators [16] called it reburning. They proposed it in 1973 to reduction of SO₂ to SO₃ and NO_x to N₂. A sine qua non for the occurrence of the reduction process in this second combustion zone is creation of a reducing environment there. In such environment CH_x, OH, CN and other radicals are present, which are involved in the complex mechanism of NO reduction summary described by the equation:



Reburning method since the beginning of its implementation was and still is widely used in the technics [17-23]. Its main advantages are: the reduction of NO_x at a satisfactory level (up to 70% in industrial installations), the economic viability (it is cheaper method compared to SCR), technological simplicity and safety compared to the SCR and SNCR where ammonia is used. The reducing reagent in reburning method is a hydrocarbon fuel, often the same which is used in the first combustion zone. Broad applicability criterion of reburning process causes that continual research on its modification are carried on, the reason of that is obtaining the flue gases of the best composition. The practical significance of this method is evident when there is taken into consideration the power industry which is one of the main producers of NO_x. Reburning is used there as nitrogen oxides removal method from flue gases [20, 24-26]. NO_x concentration reduction degree achieved in industrial installations of this type exceeds 70% [26]. First who showed this technology on such large scale - the reactor MW-power coal-fired, at the end of 80's was The Babcock & Wilcox Company [20]. They obtained then the degree of nitrogen oxide concentration reduction of about 50%.

There are carried out researches to optimize the process of combustion in the second zone. They are usually focused on the selection and use of various reburning fuels. Initially coal was

used as a reburning fuel, what is practice until today. Combustion installations are one of the main sources of nitrogen oxides emissions. Many of them do not have technical solutions, which provide simultaneous combustion of two fuels - solid as a primary fuel and gas or liquid as reburning fuel. In connection with this fact continual researches of the two zone combustion process where coal is the reburning fuel are carried on [17]. Efficiency of those processes is at level about 60 - 70%, when air excess coefficient in the reburning area is 0.7 - 1.1.

Other commonly used reburning fuels are gaseous fuels [18,22-25,27-29]. Studies have shown that by using such reburning fuel, with a suitably selected residence time of the reactants in the combustion chamber in the installation of 350 MW power, it can be achieved the degree of NO conversion of more than 60% [18].

Increasingly, there are made attempts to use biomass and other wastes, such as meat or waste tires as reburning fuel [30-34]. The obtained results indicate that a reduction of the NO concentration which can be achieved here is about 70% [34] and even up to 80% [32,33].

1.4. Aim of the researches

In the simplest version of the process organization, in the reactor with stationary (bubbling) fluidized bed combustion is carrying on exclusively in one zone. However conducting processes this way causes that thermal utilization of the materials with a high fuel-nitrogen content, such as sewage sludge, becomes impossible due to the fact of the emission of nitrogen oxides. On the other hand the effective waste management taking into account i.a. costs of transport may suggest, application of a scattered spatially, small scale devices where a gaseous fuel is used as a reburning factor and location of NO_x reduction zone is in the rare zone of the fluidized bed. In the literature, there is a lack of reliable information about carrying on reburning processes using this configuration. Aim of this study is to examine the reburning process, achieved by introducing additional gaseous fuel - propane - to rare zone of the bed during combustion of alternative solid fuel.

2. Experimental

2.1. Experimental equipment

The results of the experimental works presented below have been obtained in laboratory scale installation up to 10 kW, which works under atmospheric pressure. In Figure 1 it is shown schematic representation of installation adapted to two-zone combustion of solid alternative fuel.

Fluidized bed reactor, which is the central part of the installation, consists of a quartz tube with an outside diameter 100 mm, height 500 mm and a wall thickness of 2 mm. It is placed on a perforated plate (distributor) made of chrome nickel steel having a thickness of 1 mm. Distributor has holes with a diameter of 0.6 mm which surface area is 1.8% of the total surface of the distributor. During cold fluidization of bed and autothermal combustion of alternative solid fuel fluidizing factor was air. Ignition and warming up the reactor was carried out by

combusting propane pre-mixed with air. Mixing chamber with a distributor, air blower, a set of pipes, valves and rotameters composed supply system of gaseous components and fuels to the reactor.

An open top design of the reactor results in the possibility of placing inside it, at different heights relatively to the distributor, measuring elements, gas sampling probes and the batcher which allows for dosing solid fuel into the reactor. In order to prevent of uncontrolled penetration of gases from the reactor to the environment, in its upper part underpressure is maintained. It is obtained by combination of the reactor hood with exhaust fan. In this part of installation – dedusting part - mixing the gas with the air, a substantial cooling and removing most of the dust in cyclone and ash trap for coarser particles takes place (Figure 1).

The reactor was equipped with a temperature control system consisting of a moveable radiation shield and cold air blower with adjustable airflow. This allows for conduction of autothermal combustion within the temperature 700 - 1000 °C, without changing the composition of the air-fuel mixture.

The course of combustion in a fluidized bed reactor depends on the way of providing the reactants and the temperature distribution within it. During one zone combustion the fuel and oxidant are introduced only into the fluidized bed. Through zone above the bed (rare zone) flow then gaseous products of reactions from the fluidized bed, and a considerable amount of air. This creates favorable conditions for the use of this space in reactor as an additional combustion zone.

1 - heated probe for sampling the flue gases, 2 - set of 8 thin thermocouples, 3 - reburning burner, 4 - batcher, 5 - pilot flame, 6 – exhaust fan, 7 – computer storing data from Gasmeter DX-4000, 8 - cyclone, 9 - ash trap for coarser particles, 10 – outlet of reburning fuel, 11 - movable radiation shield, 12 – fluidized bed, 13 - rotameters (from left: air and primary and secondary fuel), 14 – rotameter of CO₂, 15 - fuel supply valves (from left: fuel supplying the pilot flame, reburning fuel, total fuel, CO₂), 16 - blower, for fluidising air, 17 – two thermocouples, 18 - flat, perforated metal plate distributor, 19 - A/D convertor for thermocouple signals; 20 - computer storing chemical analyses quantities and temperature. Analytical block I: A - total organic compounds analyser (JUM Model 3-200), B - ECOM SG Plus, C - Horiba PG250, P – Peltier's cooler. Analytical block II: D – mobile conditioning system of Gasmeter DX-4000, E - analyzer FTIR (Gasmeter DX-4000), F - MRU Vario Plus.

To carry out the process of reduction of nitrogen oxides in the freeboard of the reactor, applying reburning method, burner comprising eight nozzles was installed. It is designed to distribute uniformly gaseous reburning fuel in the chosen height above the bed (Figure 1, item 3). In the exploded state and in the state of working outside the reactor it is shown in Figure 2. Slightly cross-sectional area of exhaust nozzles (Figure 2, item A) causes that the horizontal velocity of the gas reaches high value which provides high turbulence and rapid and uniform mixing of the reactants. During reactor operation, through the reburning burner small quantity of CO₂ was passed continuously in order to prevent the formation of char in the burner nozzles and to ensure better mixing in reburning zone. In this experiment, the reburning fuel nozzles distance from the distributor was 180 mm.

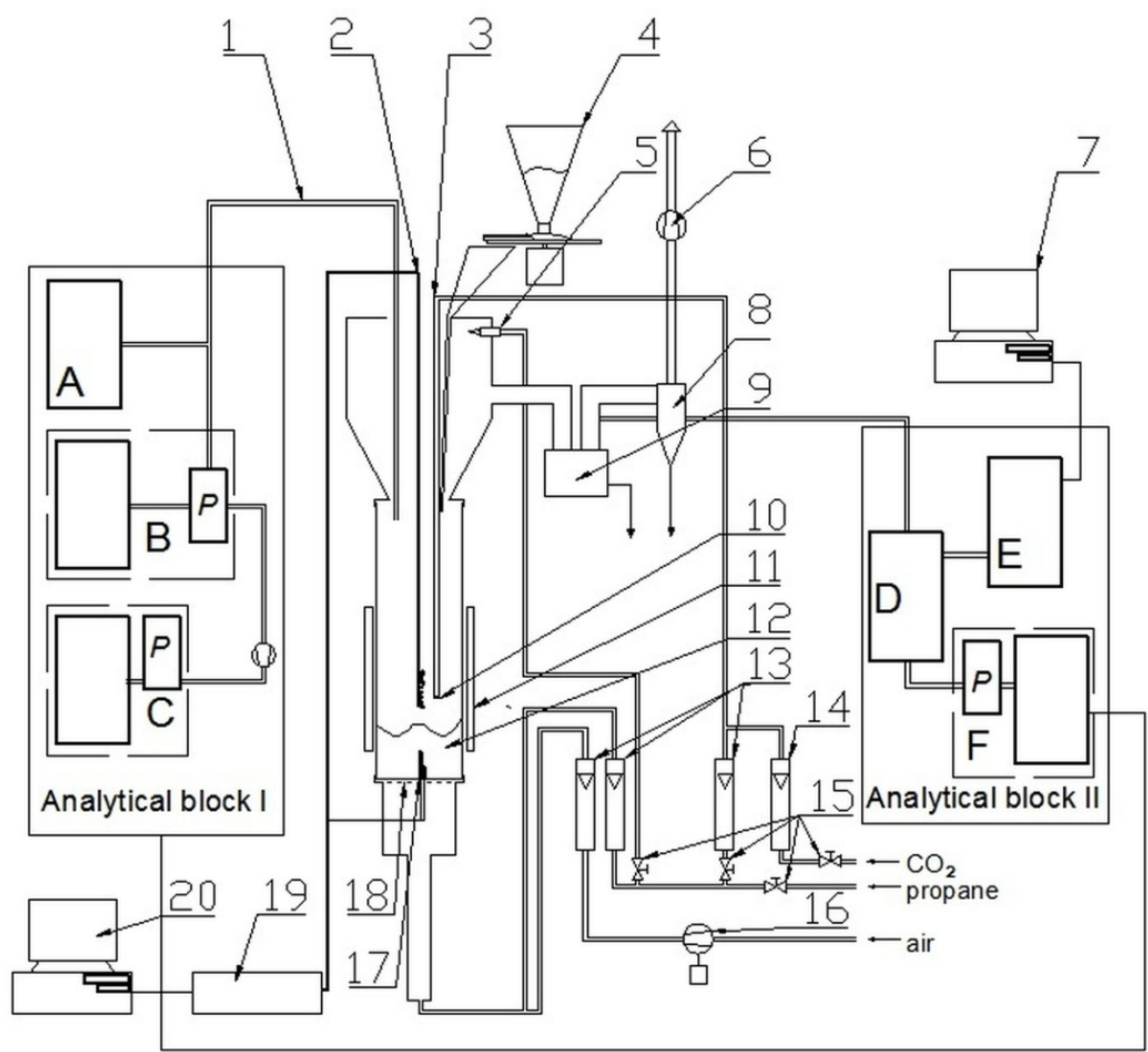


Figure 1. Schematic representation of the fluidized bed reactor:

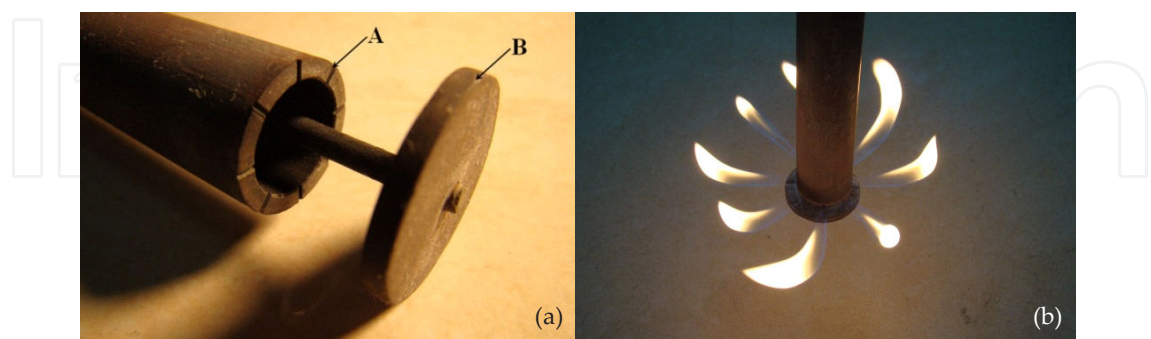


Figure 2. The reburning fuel nozzle views: exploded state (A – burning nozzle forming channel, B – plate sealing nozzles) and during working outside the reactor.

Alternative solid fuel was dosed into the reactor from its top through the batcher (Figure 1, item 4). It consists of a reservoir of material dispensed and beneath it a plate with an adjustable

rotating frequency. The amount of material dosed from the plate to the hopper and then to the reactor was regulated by scraper setting. It was verified that such a construction allows a batcher to dose a steady stream of fuel mass to the reactor.

As an inert fluidized bed, sand was used with a mass of 250 g and particle size of 0.375-0.430 mm. This material does not wear out during the process, has an adequate mechanical strength, has a high softening temperature (about 1050 °C) and does not react with the compounds present in the reaction environment during the process of combustion.

2.2. Analytical and measuring equipment and methodology

The temperature measurement system was organized in the way to be able to measuring temperature both in bed and in the area above the fluidized bed. The temperature in the bed was measured using two NiCr-Ni thermocouples which connectors were located at a height of 20 and 50 mm above the distributor (Figure 1, item 17). In the zone above the bed temperature measurements were made using a specially designed set of eight thermocouples (Figure 1, item 2). There are made of wires with a diameter of 1 mm. One part of each thermocouple consisted of nickel wire which was joint for every thermocouple, second part consisted of eight wires made of chrome-nickel alloy. Application of one joint wire gave opportunity of setting thermocouples connectors at a constant distance from each other and limiting number of additional elements that could influence the process through hydrodynamics or catalytic effects. This enabled also the exact determination of each measurement point relative to the distributor and reburning burner nozzles.

Analyzers applied to measure the concentration of individual chemical components in the flue gases were divided into two analytical blocks (Figure 1). For measuring the flue gases composition, the standard analytical methods were used. They allow for the direct processing of the measured physical quantities into electric signals, wherein with reference to some components the duplicate measurements, based on the different physical properties of the measured components, were done. This procedure helped to eliminate the cross-effects on obtained data and to verify them. On the base of those data values of air excess coefficient and the degree of reduction of nitrogen oxides concentration were calculated. Analyzers used in researches use the following methods for the detection of chemical compounds. MRU Vario Plus analyzer (Figure 1, item F) measures the concentration of O₂, CO, NO, NO₂, SO₂ using electrochemical sensors (EC), CO₂ and volatile organic compounds (marked in the case of the analyzer as C_xH_y) are measured using IR detection (non-dispersive infrared NDIR). The analyzer of volatile organic compounds VOCs JUM Model 3-200 (Figure 1, item A) makes measurements using flame ionization detector (FID). Analyzer ECOM Plus SG (Figure 1, item B) measures the concentration of O₂, CO, NO, NO₂, SO₂ using electrochemical sensors (EC). Analyzer Horiba PG250 (Figure 1, item C) consists of three kinds of sensors. O₂ concentration is measured by electrochemical sensor (EC), for determining the amount of gases such as CO, CO₂, SO₂ analyzer uses in the IR detectors (non-dispersive infrared NDIR), concentration of nitrogen oxides (II) and (IV) - NO_x is measured using a chemiluminescence technique (CLA). Analyzer Gasmeter DX-4000 (Figure 1, item E) measures the concentration of inorganic and

organic compounds based on the method of infrared spectroscopy with Fourier transform (FTIR).

Application of analyzer Gasmet DX-4000 in measurements, resulted in necessity to adjust the sensitivity of the analyzer to the expected range of concentrations of the components analyzed by it. Therefore, analyzers used for the determination of chemical compounds in the flue gases were divided into two separate blocks (Figure 1). Part of the exhaust fumes was taken from area above second combustion zone by heated probe, mounted 475 mm above the distributor (collection point I) and led to the analytical block I (Figure 1). The second part of the flue gases was directed to the analytical block II. It was taken from the reactor after passing through first cross-section measurement, quickly cooled and mixed with secondary air in 1:3 ratio. Then from flue gases stream, partially dedusted in ash trap for coarser particles, sample was collected (collection point II) and passed to analytical block II. The concentration values obtained by the FTIR analyzer should be verified, because in the case of the complex composition of the gas sample optimization method can also generate results contain errors. Therefore, in the analytical block II was mounted analyzer MRU Vario Plus, which allowed for doubling the measurements of CO₂, CO, NO_x, SO₂ and to measure O₂ in this measurement point. The flue gases to be analyzed first had to be diluted. Data obtained from those analyzers were calculated into values before dilution, the aim of this was having values of concentration as they were passing the first measuring point and in turns data from all the analyzers were studied. The dilution degree of flue gases between the first and the second measuring point, necessary for this calculation, was determined on the basis of the mass balance of the two components: CO₂ and CO, assuming that the diluting air is practically free from these components (in comparison to their concentrations in the exhaust fumes). This structure of measuring blocks allowed for execution of quantitative determinations of chosen organic substances in the flue gases, when the concentration of these compounds in reburning zone significantly exceeded the measuring range of the analyzer Gasmet DX-4000.

In the case of flue gases from the thermal utilization of alternative fuels, we have to deal with the presence of organic and inorganic compounds in it, derived from the first and second combustion zone. Their presence is the result of a complex chemical composition of solid fuel (e.g. presence of HCl and HF), the complexity of the combustion of solid alternative fuels and the interaction between the various components of the flue gases. It can be expected that, compared to the combustion of gaseous fuel, in the flue gases from this processes there will be more organic compounds. Analyzer, which makes possible measuring the composition of such a complex mixture is the Gasmet DX-4000 - FTIR. Applied detection method in this analyzer, utilizes the phenomenon of the absorption of infrared radiation by the analyzed components. An important modification of the method is to replace the spectrometer by interferometer. Unit of the equipment, on which method is basing, the does not generate an infrared absorption spectrum (as in the dispersive infra-red spectroscopy - DIR) does not generate directly the absorbance values for the selected wavelength (as in the non-dispersive infra-red spectroscopy - NDIR). In this method, the answer is obtained in the form of a complex relationship between the position of the interferometer mirrors and the size of the measured signal [35]. This relationship is interferogram. Interferogram has the form of implicit informa-

tion about the absorbance of the analyzed gases in the entire wavelength range of electromagnetic radiation from a source. This relationship is unraveling after a Fourier transform on the data forming the interferogram [35]. The advantage of FTIR over other methods based on absorption of infrared radiation by analyzed components is that as the measurement data absorbance spectrum in a wide wavelength range of infrared radiation is obtained, not for the narrow range or at a point. On the basis of a single measurement obtained with a single gas chamber, information on concentration of a number of components is gained. Amount and type of components need not be imposed in advance. The individual concentrations are matched by comparing the spectrum of the sample with the reference spectrums for typed, as present in the sample, components. In such a situation, significant becomes appropriate selection of the spectra library which is used by optimization method described above. If the list of the compounds is too short, in the residual spectrum remain the signals from components which are not included in the analysis, and the accuracy of the determination of concentrations of the analyzed compounds will be small. Too long list of compounds in turn leads to numerical errors that reduce the accuracy of the calculations. Changes to the list of compounds for analysis can be made based on the knowledge of the combustion processes occurring in certain conditions, resulting from the review of the literature data and own preliminary experiments. For the DX-4000 analyzer manufacturer has set the standard method of calculation takes into account the following compounds: H₂O, CO₂, CO, NO, NO₂, N₂O, SO₂, HCl, HF, NH₃, CH₄, C₂H₆, C₃H₈, C₂H₄, C₆H₁₄, HCHO, acetaldehyde, acrolein and HCN. As a result of tests this list was supplemented about ethin, propene, butane, isobutane, pentane, benzene, toluene, xylenes, styrene, ethyl benzene, ethanol, methanol, acetone, formic acid and acetic acid. Not all substances added to the database of compounds included in the analysis of FTIR were detected in the analyzed gases, but the extension of the standard library of compounds allowed for the determination in the flue gases components specific for the combustion process carrying on in lack of oxygen conditions. It has also increased the accuracy of the determinations of components which are relevant to the assessment of NxOy reduction process and residual IR absorbance spectrum decreased compared to the standard library.

2.3. Alternative solid fuel

In the fluidized bed reactor, that has been discussed above, thermal utilization of alternative solid fuel has been carried on. Fuel selected to researches consisted of municipal sewage sludge (30%mass) – SS, wasted bleaching earth (62%mass) – BE, and lime - consisting almost exclusively of CaCO₃ (8%mass). This last component allows usage of fluidized bed for the absorption of SO₂. This fuel composition was caused by the assumptions in the direction of researches lead to obtain a solid alternative fuel with a high, known and fixed nitrogen content bound in it. The base of the fuel was sludge with a high content of nitrogen and sulfur. By controlled addition of wasted bleaching earth it was yielded a fuel with a high nitrogen content, but less than in the case of sludge. This composition allowed for thermal utilization of two wasted materials deposited in landfills, and gave ability of controlling amount of nitrogen bounded in the fuel. Detailed elemental composition of the fuel, mineral content, and the heat of combustion are presented in Table 2. C, H and N content in the sample was determined using analyzer PerkinElmer 2400 Series II CHNS/O Elemental Analyzer based on Pregl-Dumas's

method. Mineral content was determined by incineration of the sample and then calcination of the residue to constant weight in a chamber furnace at a temperature of 815 oC. The heat of combustion was determined by calorimetric method.

This material was dosed into the reactor in the form of particles of suitable size and form. Essential shape of the material was obtained by realization of several operations. The first stage was crushing pieces of municipal sewage sludge into grains with a smaller diameter and separation from it fraction with a grain diameter of 0,3-4,0 mm. Then a measured amount of wasted bleaching earth, originating from the bleaching of paraffin waxes, was melted in a water bath. To liquefied bleaching earth was gradually added, prepared in advance, municipal sewage sludge and calcium carbonate. The prepared material after cooling down for the most part was in the form of granules, the rest of the material easily give up granulation. The resulting granulate was sieved to obtain grains agglomerates having a diameter 0.3-4.0 mm.

C, % _{mass} .	31.32
H, % _{mass} .	5.60
N, % _{mass} .	1.19
O + S, % _{mass} .	6.10
Mineral parts, % _{mass} .	52.46
Humidity, % _{mass} .	3.33
Heat of Combustion, MJ/kg	16.22

Table 2. Alternative solid fuel: SS (30%)+BE (62%)+CaCO₃ (8%) - composition and heat of combustion

2.4. Course of the combustion process

The combustion of alternative fuels in a fluidized bed reactor consisted of a series of stages. The first is the start of the fluidization process at ambient temperature – cold fluidization. When fluidization of the bed is reached, the ignition and warm up the bed by combustion a mixture of propane (0.056 ± 0.001 dm³/s) with air (1.66 ± 0.08 dm³/s) in it took place, it was the initial phase of the experiment. After the bed temperature reached approximately 900 °C dosage of alternative solid fuel was started, with simultaneously closing the flow of propane to the reactor - the only source of heat was now combustion of solid fuel. Alternative fuel was dosed into the fluidized bed reactor at a rate of approximately 17 g/min. The thermal utilization of the fuel was carried on at this stage only in one zone. The purpose of this was to obtain comparative data for the main study process. In the next stage, dosage of the reburning gas – propane to the rare zone of the reactor, zone above the bed, was initiated. Its flow during the entire two zone combustion was maintained at level 0.018-0.026 dm³/s. During this step combustion of solid fuel in the bed was carried out with simultaneous reduction of nitrogen oxides in the second combustion zone. In the final stage of experiment, the flow of reburning fuel was closed while combustion of solid fuel in a fluidized was continued, also for comparison purposes. Process parameters are summarized in Table 3.

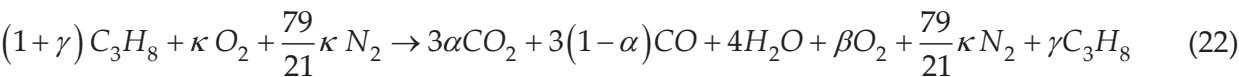
Material of the Bed	sand	mass	250.60 g
		fraction	0.375-0.430 mm
Reburning fuel	propan	flow	0.018-0.026 dm ³ /s
Solid fuel	alternative fuel	dosage	17 g/min
		fraction	0.3-4.0 mm
Fluidization	air	flow	1.66 dm ³ /s

Table 3. Parameters of solid alternative fuel combustion process

3. Discussion of two zone combustion results

The temperature and the concentrations of the individual compounds in the flue gases were recorded by the analytical and measuring equipment for the whole time of the process.

On the basis of the experimental data temporary and average values of air excess coefficient in reburning area - λ_r were calculated. Reduction degree of nitrogen oxides in reburning area depends on air excess coefficient in this zone. Air excess coefficient was calculated on base of stochiometric model of reburning fuel combustion, which is shown below. Presence in exhaust fumes of CO₂, CO, remaining O₂, and uncombusted fuel are taken into consideration in this model:



Air excess coefficient λ is defined as quotient of amount of oxygen delivered to reaction zone and amount of oxygen used in combustion processes. For combustion reaction [22] this dependence can be written as:

$$\lambda = \frac{\kappa}{5(1 + \gamma)} \quad (23)$$

where coefficient κ was calculated from stoichiometric equation [22]:

$$\kappa = 3\alpha + \frac{1}{2} \cdot 3(1 - \alpha) + 2 + \beta = \frac{3}{2}\alpha + \beta + \frac{7}{2} \quad (24)$$

and coefficients α , β , γ can be calculated from dependences:

$$\kappa = 3\alpha + \frac{1}{2} \cdot 3(1-\alpha) + 2 + \beta = \frac{3}{2}\alpha + \beta + \frac{7}{2}; \quad \frac{n_{\text{VOCs}}}{n_{\text{CO}_2}} = \frac{\gamma}{3\alpha};$$

$$\frac{n_{\text{CO}}}{n_{\text{CO}_2}} = \frac{3(1-\alpha)}{3\alpha} \quad (25)$$

those equations after modifications are in form which allows to use molar fractions in calculations:

$$\alpha = \left(\frac{n_{\text{CO}_2}}{n_{\text{CO}} + n_{\text{CO}_2}} \right) = \frac{\frac{n_{\text{CO}_2}}{n_{\text{ss}}}}{\frac{n_{\text{CO}}}{n_{\text{ss}}} + \frac{n_{\text{CO}_2}}{n_{\text{ss}}}} = \frac{y_{\text{CO}_2}}{y_{\text{CO}} + y_{\text{CO}_2}} \quad (26)$$

$$\beta = \frac{3n_{\text{O}_2}}{n_{\text{CO}} + n_{\text{CO}_2}} = \frac{3y_{\text{O}_2}}{y_{\text{CO}} + y_{\text{CO}_2}} \quad (27)$$

$$\gamma = \frac{3n_{\text{VOCs}}}{n_{\text{CO}} + n_{\text{CO}_2}} = \frac{3y_{\text{VOCs}}}{y_{\text{CO}} + y_{\text{CO}_2}} \quad (28)$$

were:

- n_{ss} is a sum o moles of all compounds in flue gases, dry conditions,
- n_{VOCs} is an amount of unburnt compounds

Equations [23-28] give possibility of calculate of air excess coefficient based on measured concentrations (y_{CO_2} , y_{CO} , y_{O_2} , y_{VOCs}):

$$\lambda_r = \frac{1}{5} \left(\frac{5y_{\text{CO}_2} + \frac{7}{2}y_{\text{CO}} + 3y_{\text{O}_2}}{y_{\text{CO}} + y_{\text{CO}_2} + 3y_{\text{VOCs}}} \right) \quad (29)$$

where: y – molar fractions of individual compounds present in flue gases (VOCs-volatile organic compounds)

Values of the air excess coefficient in the first combustion zone during the thermal utilization were maintained at level 1.3-1.6, as shown in Figure 3, while periods when the reburning was not carried out. Air excess coefficient in reburning area during two zone combustion was

maintained at a level similar to 1.0 or slightly lower. It is a sine qua non for carrying out the process of NOx reduction and obtaining the optimal effect.

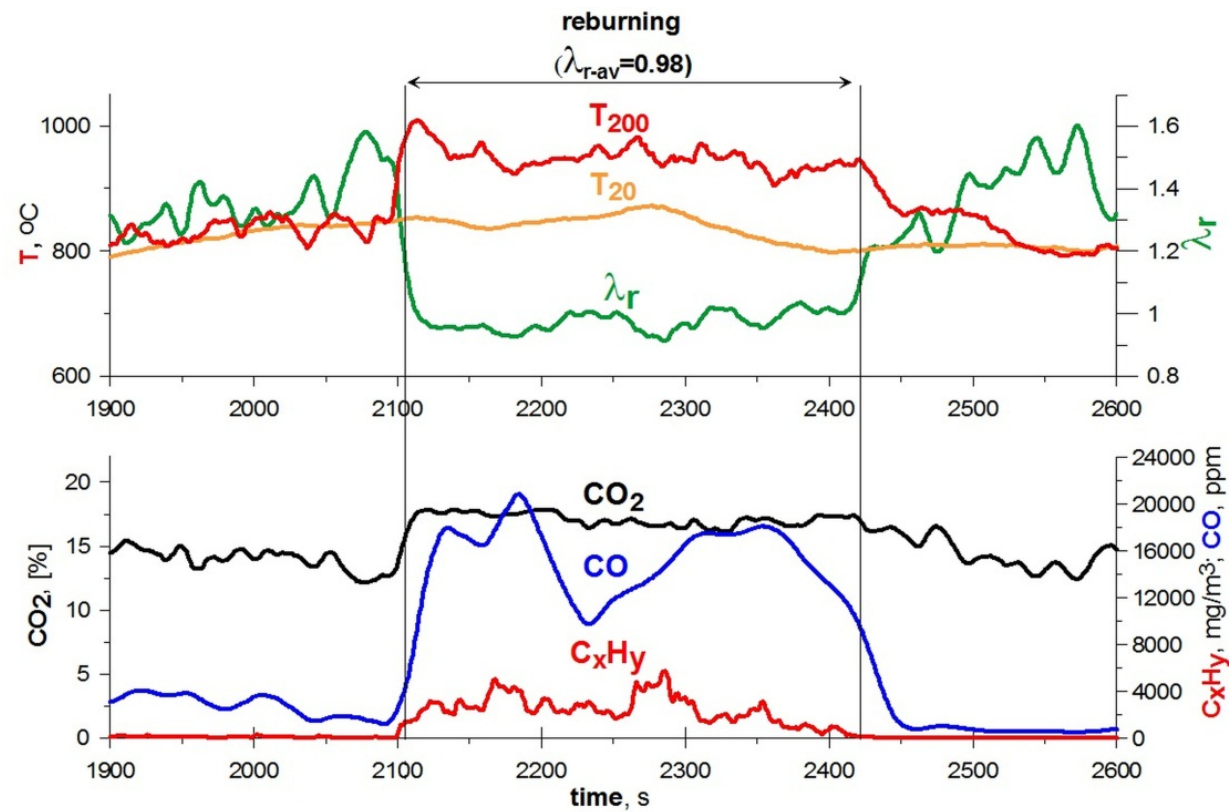


Figure 3. Temperature, air excess coefficient in reburning area and concentrations of chosen gaseous compounds, containing carbon in their structure, in exhaust fumes. (Indexes: digits - height (in mm) of thermocouple above distributor: 20-in fluidized bed, 200-in second combustion zone; index r – in reburning zone; index $r-av$ – average value in reburning zone)

Comparing the temperature changes occurring in the fluidized bed with those in the second combustion zone during the periods when only alternative fuel combustion in a fluidized bed was carried on, it can be seen that recorded values were similar in both cases (Figure 3). However, it notes fact that set of eight thermocouples located in the area above the bed recorded the larger fluctuations. The reasons for this can lay in the properties of the applied solid fuel. It contains in its composition readily volatile paraffins, behave good cohesiveness thanks to that and most of it burned in the bed. The intense mixing that occurs in the fluidized bed resulting in the intensification of heat transfer and hence a more uniform temperature distribution in the area. In the rare zone of the reactor periodically appeared uncombusted dust of sewage sludge dumped from the bed during the process. It underwent complete combustion in rare zone and this resulted in temporary increases in temperature increasing fluctuations in the area of carrying on the reburning process.

When such a comparison will be made for a period of time when reburning process in the reactor was carried on (Figure 3), it can be seen that with the beginning of reburning the

temperature in the second combustion zone is higher about 100 °C than in the bed. It is a natural phenomena because with starting the reburning additional combustion process appears and is source of heat. It is noteworthy that, during the combustion in the second zone the temperature in the bed increases about 20-30 oC. This is due to the transport of heat from reburning zone to the bed. This effect is desirable since it allows to maintain the proper temperature in the bed, and hence appropriate autothermic conditions of solid fuel combustion.

With the beginning of propane dosage to zone above the fluidized bed and the creation of the second combustion zone, an increase in the concentration of CO₂ in the flue gases from about 14% to over 17% was registered (Figure 3).

During the combustion of alternative solid fuel exclusively in the fluidized bed, the carbon monoxide concentration was about 3000 ppm (Figure 3). Along with the initiation of the process of nitrogen oxides reduction in the second combustion zone, the CO concentration increased, reaching a maximum value exceeding 20000 ppm. For most time of the reburning process CO concentration was maintained at a level higher than 14000 ppm. The reason for this is that in the second zone during the combustion process the oxygen concentration is stoichiometric and in certain periods there are even reductive conditions – for this reason part of the CO was not oxidized to CO₂.

A similar situation occurs in the case of volatile organic compounds - VOCs. When the combustion was carried on only in one zone – fluidized bed, VOCs level did not exceed 300 mg/m³. During conduction of the reburning process an increase in concentrations of these compounds up to a maximum value of 6000 mg/m³ was observed (Figure 3).

A detailed analysis of the composition of the hydrocarbons in the flue gases during two-zone combustion was done. As a result, it was found absence of propane in the flue gases. The analyzer indicated the presence of ethane in them. His concentration did not exceed 220 ppm (Figure 4). Compounds identified in larger quantities approximately up to 10-fold higher than the concentration of ethane were methane, ethene and ethine. Their concentration was in the range of about from 500 to 2000 ppm (Figure 4). Their quantities are similar, with the highest concentrations found in the case of ethine. The presence of those hydrocarbons in the flue gases is desired. These compounds are the products of propane structural transition in thermal processes. They are source of CH_x radicals and those radicals play a leading role in the reburning process [7].

Compounds, which may also be created as a result of thermal degradation of propane are organic compounds containing oxygen, such as formic acid, methanol and formaldehyde. The concentration of formic acid showed by the FTIR analyzer during the research is negligible (Figure 4). Methanol is present in the flue gases, but in small amounts, with a peak concentration of 48 ppm (Figure 4). The highest concentration in the flue gases during reburning process, received formaldehyde. Its maximum value was at a level slightly greater than 300 ppm (Figure 4).

The presence of the identified organic compounds in the exhaust fumes (containing or not oxygen in their structure) at high concentrations, in the absence of a propane which was reburning fuel, provides advance of the reburning process carrying on in the second zone. It

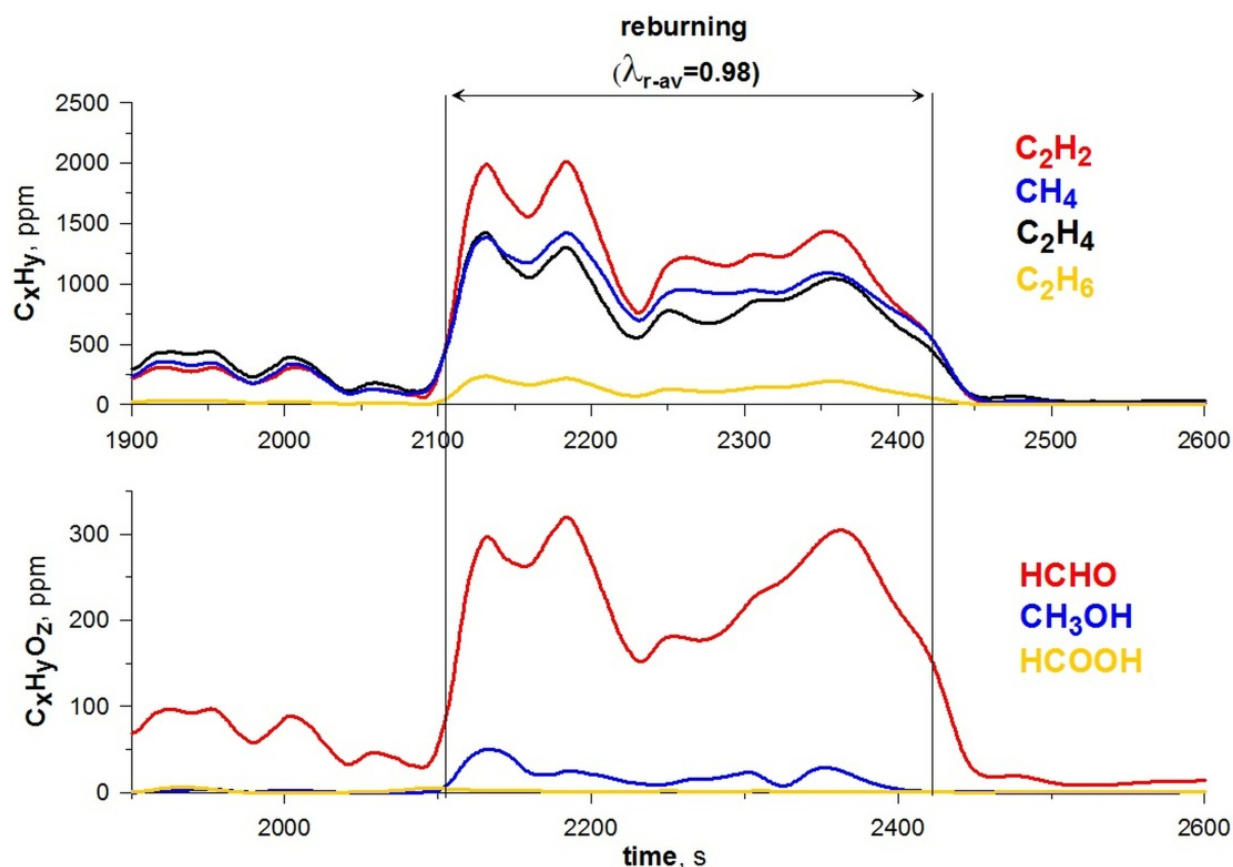


Figure 4. Concentrations of chosen organic compounds, registered by Gasmeter DX-4000 analyzer, in flue gases. (Index λ_{r-av} – average value in reburning zone).

should be remembered, however, that it is unacceptable that flue gases with such a high content of carbon compounds to get into atmosphere. These compounds must be combusted in the next - third combustion zone.

The fuel used in the tests characterizes a high sulfur content (Table 2). One of the products of thermal utilization of such alternative fuel is sulfur dioxide, which amount in the exhaust gases is strictly regulated by law. The problem that was encountered during the study was that at this stage it is not possible to correctly analyze the SO_2 concentration values in the flue gases, during the period when the reburning process was carried on. The reason for this is the application for the detection of this gas by electrochemical methods or IR radiation absorption. In devices where the SO_2 determination by electrochemical sensors is used, the results are questionable because these sensors have a cross-sensitivity to C_2H_4 and others [36]. During researches when the reburning process was conducted, conditions of oxygen insufficiency were present in the second combustion zone, resulting in that these compounds are present in significant quantities in the flue gases (Figure 3,4). Moreover, the products of propane combustion are unsaturated hydrocarbons and aldehydes. They characterize an intense absorption of IR radiation in the range $1000 - 1800 \text{ cm}^{-1}$, overlap the typical range for SO_2 absorption ($1150 - 1450 \text{ cm}^{-1}$). Their high concentration during carrying on combustion in the reburning zone also reduces

the IR method as a reliable for determining the SO₂ concentration values. The concentration of sulfur dioxide can be correctly determined in those phases of the experiment, in which the reburning fuel was not dosed to the reactor.

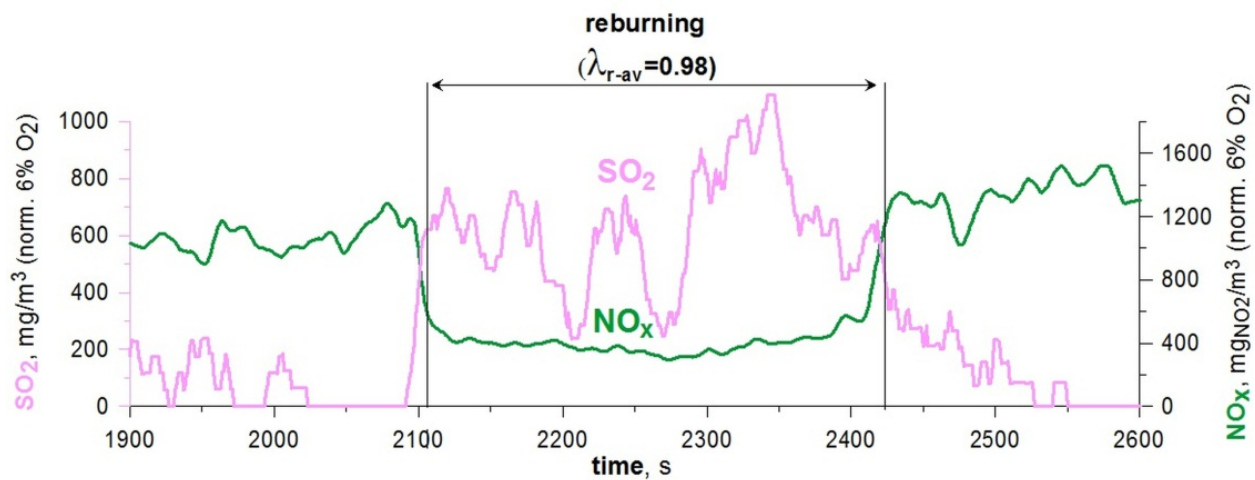


Figure 5. Concentrations of SO₂ and NO_x in exhaust fumes. (Index *r-av* – average value in reburning zone).

The composition of utilized fuel (Table 2) was selected in a manner to bound SO₂ present in the flue gases by CaO formed from the CaCO₃ contained in the fuel. Analysis of the concentration of sulfur dioxide was carried out only at a time of one-zone combustion. They showed that its concentration did not exceed 250 mg/m³ then (Figure 5). The obtained value is satisfactory, which means that this desulphurization method is fully sufficient during such processes.

During combustion of alternative fuels with high fuel-nitrogen content, as in the case of the researched material (Table 2) NO_x emission level is of about 1100-1400 mgNO₂/m³ (normalized at 6% of O₂ in the flue gases) with a highest value more than 1500 mgNO₂/m³ (Figure 5). These values are very high, often exceeding the emission standards in Europe [3]. With the beginning of reburning fuel dosage into the rare zone of the reactor and creation of the second combustion zone, NO_x concentration in the flue gases leaving this zone decreased to approximately 400 mgNO₂/m³. By more than half of time when reburning process was carried on the NO_x concentration was lower than 400 mgNO₂/m³. These results are entirely satisfactory, however, an important conclusion associated with the use in the process of the fuel which consisted of 8% of calcium oxide brings up. Hayhurst and Lawrence indicate [37] that even 2% addition of calcium oxide to the process environment may contribute up to twentyfold increase in the rate of NO_x formation. The reason of that, is catalytic activity of CaO in the oxidation reaction of CN radical to CNO and further oxidation of CNO to CO and NO. Therefore it can be concluded that decreasing the amount of CaO in the combustion environment will result in reduction in the concentration of nitrogen oxides after reduction in the second combustion zone.

Evaluation of effectiveness of nitrogen oxides reduction process was done by calculating of degree of reduction of NO_x concentration and presenting it as a function of air excess coefficient in reburning zone (Figure 6). The degree of reduction - k was determined from the relationship [30]:

$$k = \frac{c_0 - c_{reb}}{c_0} \tag{30}$$

where: C₀ - the concentration of NO_x in the flue gases normalized at 0% O₂, when the reburning process is not carried on,

C_{reb} - the concentration of NO_x in the flue gases normalized at 0% O₂, when the reburning process is carried on.

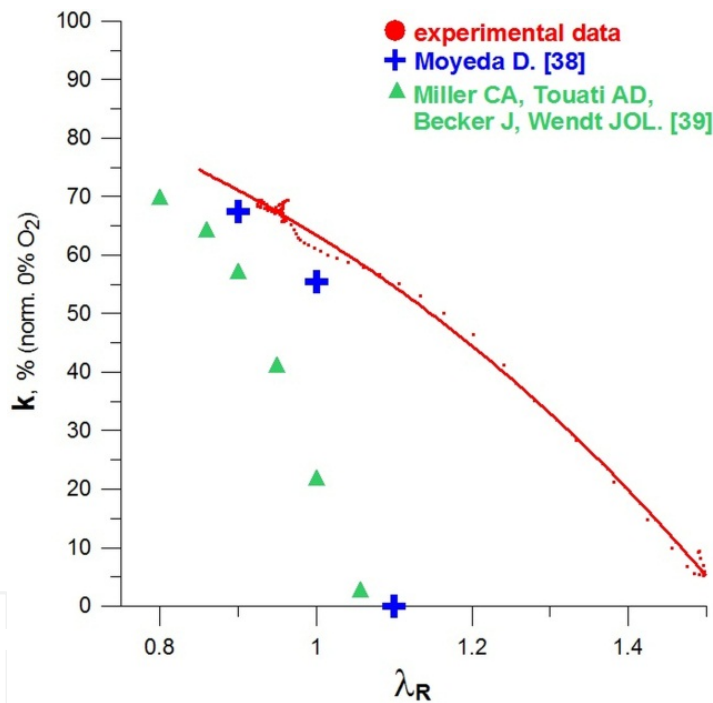


Figure 6. Degree of reduction of NO_x concentration – k, depending on air excess coefficient in reburning zone, related to comparable conditions – 0% O₂ in flue gases

The values obtained were normalized to the concentration of oxygen in the flue gases equal to 0%, in order to be able to compare them with the literature data. When the values of the air excess coefficient in the reburning zone were equal 1.1, the degree of reduction of nitrogen oxides concentration reached about 55% (Figure 6). Increasing the amount of propane dosed to the reburning zone causes a decrease in the amount of oxygen in this zone, so decrease of λ_r with increase of degree of NO_x reduction. For stoichiometric conditions $\lambda_r=1$, k value exceeded 60%. Reducing of air excess coefficient to the value of $\lambda_r < 1$ allows to obtain even

77% degree of reduction of NO_x concentration at $\lambda_r \approx 0.9$. Further increasing of the amount of dosed reburning fuel did not have an effect on increase of the reduction of NO_x.

The obtained values of degree of reduction of NO_x concentration were compared with literature data for industrial boiler [38] and the laboratory scale boiler [39]. None of them worked in the fluidized bed technology. In the case of industrial scale reactor [38], where residence times of the particles in the second combustion zone are larger (about 1 s) than in the reactor of about 10 kilowatts power used in the tests (residence times 0.2-0.3 s), the maximum degree of reduction achieved was about 69% with a air excess coefficient - $\lambda_r = 0.9$. It also may be noted that in the case of the literature data, despite longer residence times of compounds in reaction zone - air excess coefficient - λ_r have to be more reduced to achieve the same degree of reduction of nitrogen oxides concentration than in case of presented studies. The results submitted by Wendt et al. [39] for reactor of similar scale to that which was used in the presented study, the maximum degree of NO_x reduction that has been achieved was 70% for $\lambda_r = 0.8$. In presented in this paper experiment for $\lambda_r > 1.1$ and thus for much less amount of fuel added into the reburning zone, the degree of reduction of the nitrogen oxide concentration was over 50%, which for ecological and economic reasons is very important. Lowering of the air excess coefficient below 1.0 is associated with an increasing in dosage of fuel to second combustion zone, thus resulting in increase of the procesal cost. Simultaneously, the deficit of oxygen in the reburning zone increases the concentration of CO and hydrocarbons in the flue gases which for environmental reasons is unacceptable. In this case, flue gases from second combustion zone have to be combusted which increases the cost of the process. It could signify that obtained results presage well about legitimacy of using proposed method of nitrogen oxides reduction in small-scale systems, where installation costs play an important role. The achieved results from the reburning process are better than those obtained in industrial reactors and significantly better than those obtained in laboratory scale reactors operating in other than a fluidized bed technique.

4. Modeling of the third combustion zone

4.1. Introduction

High concentrations of carbon monoxide and volatile organic compounds in the flue gases from the reburning zone causes, from legal and ecological point of view, that they should not be emitted into the atmosphere. It is necessary that in the device, where the combustion using reburning to reduce NO_x concentration is carried out, it have to be prepared an extra space in which the carbon-containing compounds (other than CO₂) will be combusted. This can be achieved by introducing an additional air stream above the zone of nitrogen oxides reduction (Figure 7) [20]. The amount of additional air should be suitably selected in aim not to increase the losses at the outlet of the reactor and obtain gases of the proper quality. The flue gases leaving this zone are directed to the heat exchanger, purified from the ashes, and the cold, dry and clean flue gases reach the atmosphere.

In the designing process of the third combustion zone two main factors must be balanced. The first is residence time of combusting gases in this zone. It should ensure a significant reduction in the concentration of CO and VOCs, preferably to a value less than required by local emission standards. The second is the amount of air supplied to the zone. Further increasing the air flow supplied to this zone should reduce the concentration of CO and VOCs in the flue gases. In order to determine the optimal parameters for the task of effective lowering the concentration of main impurities of the flue gases, the simulation calculations were done.

The starting point of the calculations of flue gas composition leaving the third combustion zone was the composition of the exhaust fumes leaving the reburning zone. The measured composition was converted into wet gases composition, the amount of components present in flue gases was reduced because of requirements of used kinetic model. It was assumed that in the inlet stream there are presented O₂, H₂O, CO, CO₂, N₂, NO, CH₄, C₂H₂, C₂H₄, C₂H₆, HCHO and CH₃OH. The amount of water carried by the exhaust fumes was determined on the basis of the balance calculations. The share of remaining components, not taken into consideration was negligibly small.

Next, the temperature and composition of the inlet stream was corrected in accordance to addition of overflame air stream introduced into the third combustion zone. Addition of varying amounts of air (from 0 to 12%) results in changes in the temperature (from 930 °C to 820 °C) and content of O₂ (from 0.12 to 1.93%), N₂ (from 62.54 to 63.97%), H₂O (from 21.48 to 19.62%) and VOCs (from 0.42 to 0.40%) in diluted exhaust fumes. As the temperature of the gas entering the third zone it was assumed temperature calculated from the heat balance, taking into account the temperature of flue gases measured in the reburning zone and room temperature of added air. Overfire air stream was given as a volume fraction of the primary air introduced into the reactor. Simulation of the combustion process was carried out assuming plug flow, isothermal conditions and mass balance for any chosen component *i* of this system in the form of differential equation:

$$\frac{dm_i}{dt} = V \cdot M_i \cdot \dot{v}_i \quad (31)$$

where: *v_i* - the molar production rate of the *i*th species by all elementary reactions taking into account,

M_i - the molecular weight of the *i*th species,

V - the volume element of the plug flow system.

Specified species can participate in a variety of elementary reactions, and their set can describe even complex processes. Simulation of the combustion process was carried out by solving set of equations (10) using kinetic model of elementary reactions provided by Marinov [40]. Tests of different kinetic models, performed during the preparation of other work of authors [41], revealed that in the case of propane combustion application of a different model e.g. Konnov model [42] - did not give satisfactory results. Konnov model is not appropriate in this procesal

conditions, when in the reaction environment there are present higher (than methane) hydrocarbons and their derivatives. The Marinov model turned out to be an appropriate to apply in a case of propane combustion. The latter describes by 638 equations of chemical reaction together with their kinetic parameters, the combustion process which consists of reactions of 126 particles involved therein. Knowing the concentration of the components of the reaction mixture introduced into the third combustion zone and the temperature at the initial instant, the mixture composition after any time can be calculated numerically.

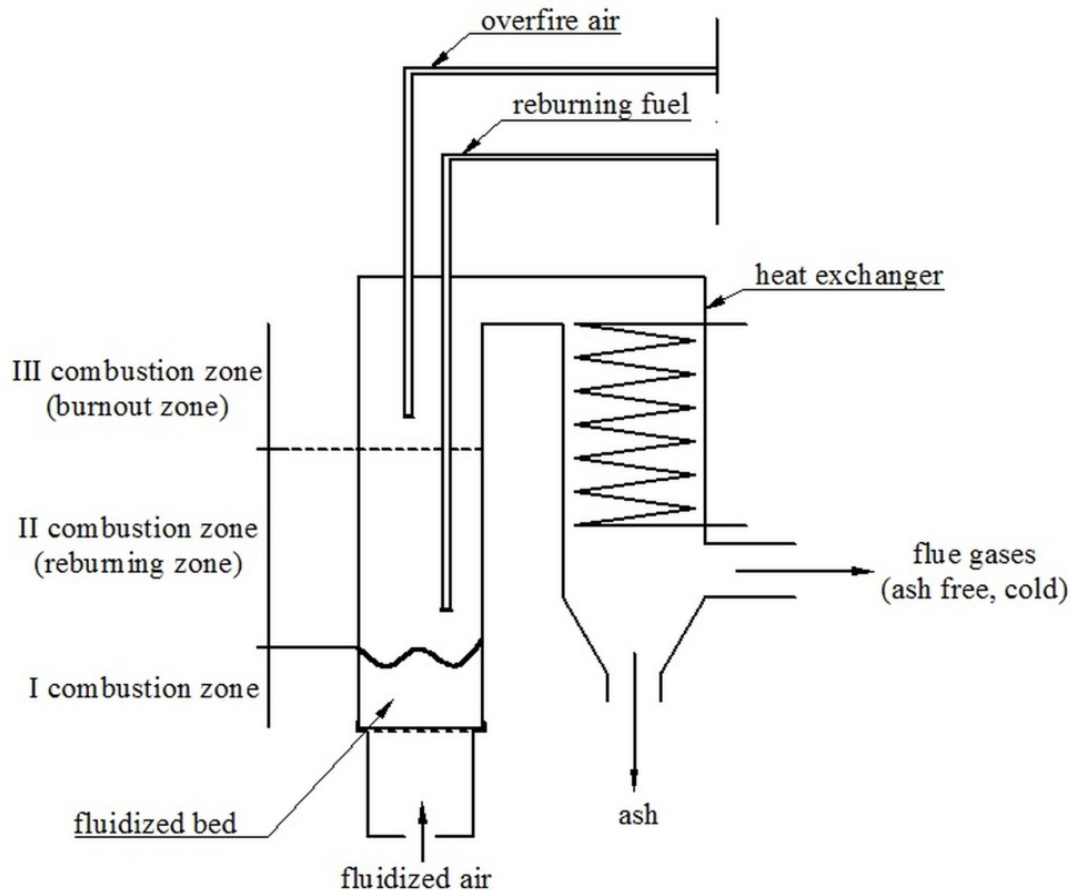


Figure 7. Schematic representation of combustion zones in reactor during conduction of the reburning process

4.2. Results of simulation

For purposes of modeling it was assumed that the residence time for the reactants in the model reactor, so in the third combustion zone, is equal to 2 seconds. From the combustion reaction kinetics point of view of, this time is sufficient for degradation of many complex hydrocarbons and their combustion to CO₂. Legal requirements in the European Union [3] provides that in the case of waste incineration, flue gases holding time at 850 °C cannot be less than 2 seconds. By a certain velocity of gas flow through the reactor, two-second time determines the reactor area that will have to be occupied by the third-combustion zone. Calculation results are

concentrations of individual compounds in selected cross-section of this zone. Calculations were performed for an additional air stream in the size of 1-12% of air used for combustion of fuel. In Figure 8a,b,c there are shown changes in concentrations of VOC, CO and O₂. With the increase in the amount of air supplied to the III combustion zone VOCs concentration in the flue gases leaving this zone decreased sharply in a short time. Only by addition of 1% of air VOC concentration changed mild. Where air stream of the size 4% or more (in relation to the air used for combustion of the fuel) is used the concentration of VOCs is reduced about 300 times in less than 0.1 s. The result is that speed of the process of hydrocarbons oxidation reaches almost zero value and model calculations indicate no changes in the concentration of VOCs.

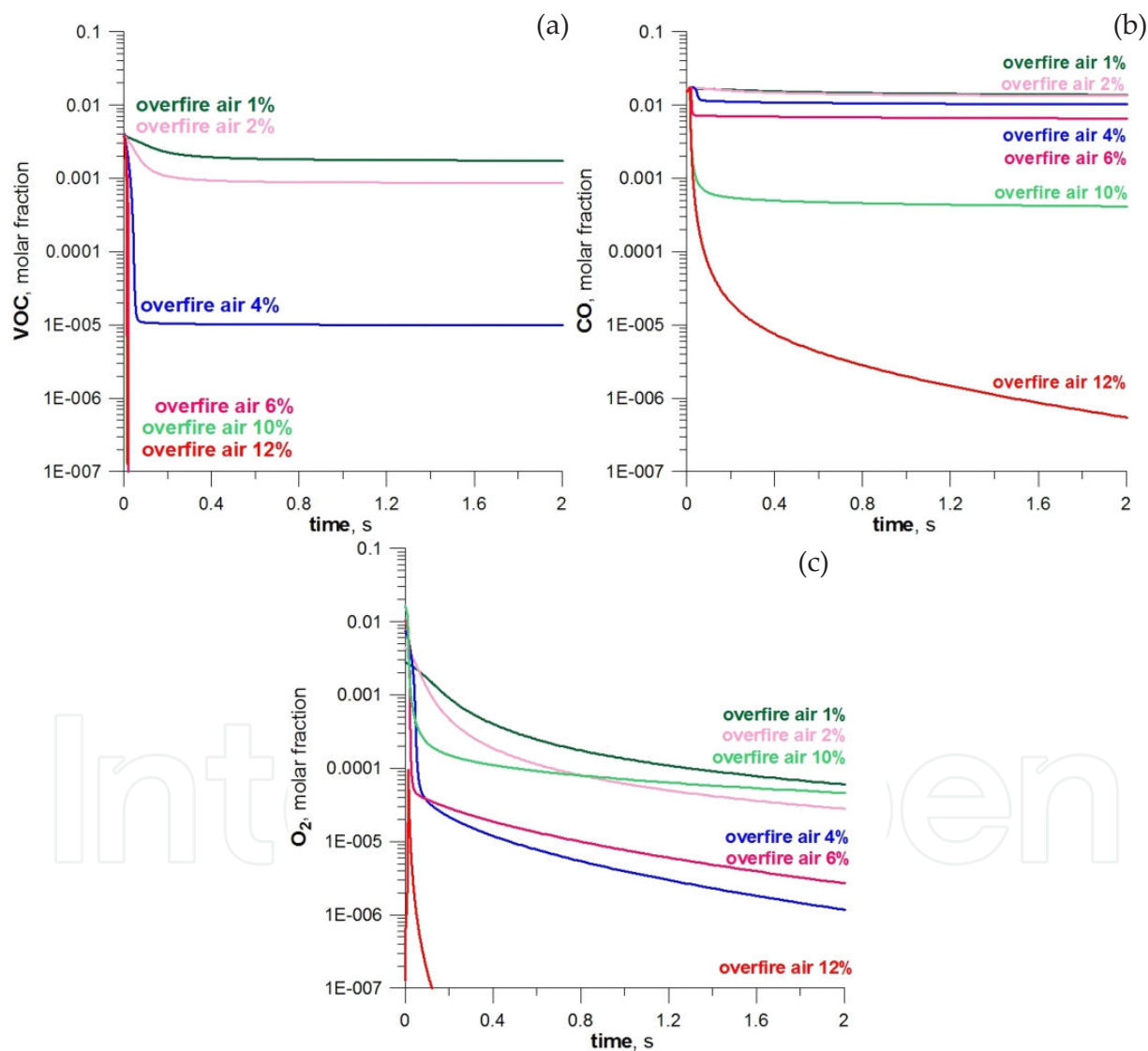


Figure 8. Time profiles of model of VOC, CO and O₂ in third combustion zone

Change in CO concentration in the flue gases occurs slightly different. After entering the air at first CO concentration increases slightly. This is due to taking place parallel hydrocarbon

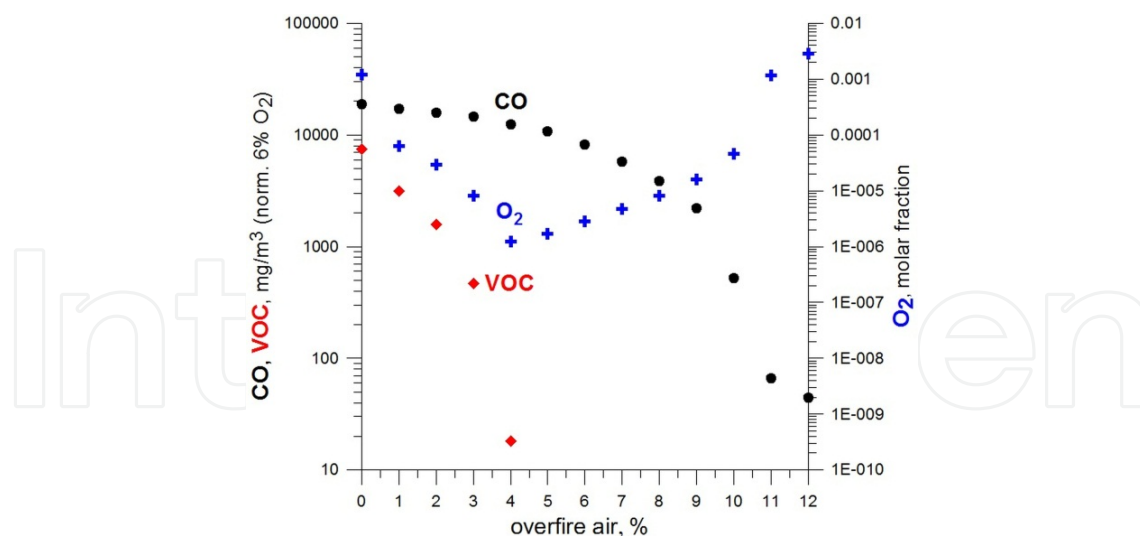


Figure 9. VOC, CO, and O₂ concentrations in flue gases from III combustion zone depending on amount of overfire air in this zone

combustion reactions, which main product is CO [43]. Complete oxidation of hydrocarbons is associated with a sizable decrease in the CO concentration, this phenomena is greater as larger is the stream of additional air. The calculations showed that at the output of the third combustion zone the concentration of CO is equal to 20 ppm after about 0.2 seconds with a stream of additional air constituting 12% of the air supplied the first zone.

Changes in the concentration of oxygen in the gases leaving the third combustion zone strongly depend on the size of the air stream introduced into this zone, which determines the quantity of available oxidant. The oxidation of VOCs and CO causes that at the beginning more or less dynamic decrease in the concentration of oxygen occurs. The fastest decrease in this concentration is observed when the amount of the additional air stream was 4-6% of the amount of primary air. For these values, the concentration of oxygen at the end of the zone is the smallest. This means that virtually all supplied oxygen is consumed in the process. When the size of stream added to the third combustion zone is 1-2% amount of the primary air, a low concentration of oxygen is a factor limiting the VOC and CO oxidation reaction speed and at the end of this zone its concentration is comparable to the concentration which is obtained by introducing into the third combustion zone stream of the size 10% of the primary air stream. Figure 8 a and 8b shows that for the smaller air streams introduced into the third zone changes in the concentration of VOCs and CO are small.

In Figure 9 there are summarized the results of calculations of concentrations of volatile organic compounds and carbon monoxide in the flue gases from the third combustion zone, converted to mg/m³ and standardized at 6% of oxygen in the flue gases and the molar fraction of oxygen in the flue gases, obtained for different amounts of air stream introduced into the third combustion zone. Amount of hydrocarbons in the flue gases decreases rapidly with increasing amount of additional air. These changes are followed by changes in oxygen concentration. The addition of air stream which constitutes 4% of the primary air caused decrease in the VOCs

concentration practically to 20 mg/m³. Under the same conditions, the concentration of CO in the third zone is reduced slightly. Only increase the amount of supplied air to this zone caused a significant decrease in the concentration of CO and the simultaneous increase in the concentration of O₂.

The simulation of the third combustion zone, as a necessary element in the combustion process, reveals that the adjustment of the composition of the flue gases in this way is possible and does not require building of special installations. Most of the oxidation reactions take place at high speed and the combustion process is almost completed in less than 0.5 seconds.

5. Conclusions

Results of presented researches showed that fluidized bed reactors can be applied as a part of the energy unit, where alternative solid fuels are combusted. The problem of high emission of nitrogen oxides, which occurs during thermal utilization of this kind of fuels, is under control through application of reburning process in the zone above the bed (rare zone). This technique of NO_x reduction gives a significant reduction of nitrogen oxides concentration, what has been achieved by dosing such amount of reburning fuel at which value of the air excess coefficient in reburning zone has been near, but not lower than 0.9. In course of researches it was proven the rare zone which is created from the sand presented above the fluidized bed shall not prevent the NO_x reduction process, but is an additional factor for ensuring transport of the heat from the space above the fluidized bed (reburning zone) in the direction of the fluidized bed. It helps maintain its proper bed temperature, even in conditions of irregular supply of solid fuel.

Despite the fact of satisfyingly low concentration of nitrogen oxides in flue gases from reburning process, CO and volatile organic compounds concentrations in them is at very high level (Figure 4, 5). Their concentration has to be reduced in the additional third combustion zone. The simulations of third combustion zone model revealed that air addition in the area above the reburning zone, which results in final air excess coefficient equal to aprox. 1.05, allows virtually for complete combustion of organic compounds and reduces the CO concentration to 70 ppm in the gases leaving the third combustion zone.

Nomenclature section

α - stoichiometric coefficient for CO₂

β - stoichiometric coefficient for O₂ in products

BE - wasted bleaching earth

C0 - the concentration of NO_x in the flue gases normalized at 0% O₂, when the reburning process is not carried on

CFB - circulating fluidized bed

CLA - chemiluminescence technique

Creb - the concentration of NO_x in the flue gases normalized at 0% O₂, when the reburning process is carried on

DIR - dispersive infrared spectroscopy

EC - electrochemical sensors

FCC - fluid catalytic cracking

FID - flame ionization detector

FTIR - infrared spectroscopy with Fourier transform

γ - stoichiometric coefficient for volatile organic compounds in products

IR - infra red detection

K - degree of reduction of NO_x concentration

κ - stoichiometric coefficient for oxygen delivered to the reaction zone as substrate

λ - air excess coefficient

λ_r - air excess coefficient in reburning area

m - mass of reacting gases mixture

M_i - the molecular weight of the *i*th species,

N - number of components present in the modeled reaction zone

v_i - the molar production rate of the *i*th species by elementary reaction,

n_{CO} , n_{CO_2} , n_{VOCs} , n_{O_2} - number of moles of carbon monoxide, carbon dioxide, volatile organic compounds, oxygen

NDIR - non dispersive infrared spectroscopy

NiCr-Ni - nickel chrome-nickel thermocouples

n_{ss} - sum o moles of all compounds in flue gases, dry conditions

SCR - Selective Catalytic Reduction

SNCR - Selective Non-Catalytic Reduction

SS - sewage sludge

t - time

V - the volume element of the plug flow system

VOCs - volatile organic compounds

y_{CO} , y_{CO_2} , y_{VOCs} , y_{O_2} - molar fractions of carbon monoxide, carbon dioxide, volatile organic compounds, oxygen

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