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Review

Trends in NO_x abatement: A review

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ABSTRACT

Implementation of stringent regulations of NO_x emission requires the development of new technologies for NO_x removal from exhaust gases. This article summarizes current state of NO_x abatement strategy. Firstly, the influence of NO_x on environment and human health is described. The main focus is put on NO_x control methods applied in combustion of fossil fuels in power stations and mobile vehicles, as well as methods used in chemical industry. Furthermore the implementation of ozone and other oxidizing agents in NO_x oxidation is emphasized.

Contents

1. Introduction

In recent years environmental awareness of political circles significantly grew. This can be attributed to social dissatisfaction with the state of the environment. As a result more rigorous environmental laws are introduced.

Air pollution constitutes one of the major problems in urban areas where many sources of air born pollutant are concentrated (Chaloulakou et al., 2008). The notion 'air pollutant' covers all substances which may harm humans, animals, vegetation and material. The main source of air pollution are the combustion processes of fossil fuels used in power plants, vehicles and other incineration processes. Key combustion-generated air contaminants are sulfur oxides (principally SO_2), particulate matter, carbon monoxide, unburned hydrocarbons and nitrogen oxides (NO_x). NO_x are considered the primary pollutants of the atmosphere, since they are responsible for such environmental problems like photochemical smog, acid rain, tropospheric ozone, ozone layer depletion and even global warming caused by N_2O. Further to the above they cause many health problems in humans exposed to high concentrations of these gases.

In the face of rising restrictions regarding NO_x emission, which are being imposed by the Gothenburg and Kyoto Protocols, development

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Table 1
Properties of selected nitrogen oxides.

Properties	N_2O	NO	N_2O_3	NO_2	N_2O_4	N_2O_5
Color	Colorless[a]	Colorless[a]	Black[a]	Red-brown[a]	Transparent[e]	White[a]
Solubility in water g/dm^3	0.111[e]	0.032[e]	500.0[e]	213.0[e]	213.0[e]	500.0[e]
State of matter (ambient temperature)	Gas	Gas	Liquid	Gas	Liquid	Solid
Density (g/dm^3)	1.8	1.3402 (293 K)[d]	1447 (275 K)[d]	3.4	1492.7 (273 K)[d]	2050 (288 K)[d]
IR absorbents peaks (cm^{-1})	1276.5[d] 2200–2300[g]	1876[d,f] 1908[g,i]	no data	749.7[d] 1322.5[d] 1600–1596[b] 1617.75[d] 1632–1629[b] 2891[g] 2917[g]	808[d] 1262[d] 1379.6[d] 1712[d] 1748[d]	722[d] 743[c] 824[d] 1050[d] 1247[c] 1400[d] 1413[d] 2375[d]

[a] Environmental Protection Agency (1999).
[b] Mentel et al. (1996).
[c] Mogili et al. (2006).
[d] Bailar et al. (1973).
[e] Dora et al. (2009).
[f] Hadjiivanov (2000).
[g] Mok and Yoon (2006).
[i] Smeets et al. (2007).

of new technologies and improvement of currently used methods are necessary. Nowadays, the most popular technology is selective catalytic reduction (SCR) with ammonia in the presence of oxygen, used mainly to reduce NO_x emission from combustion processes (Brüggemann and Keil, 2008). Of course other techniques like absorption, adsorption or electrical discharge are also widely used (Mok and Lee, 2006). Nevertheless, all these methods have their limitations and disadvantages. Furthermore, restrictions regarding NO_x emission, imposed on some developed countries, are extremely severe. Therefore, researches are being held throughout the world to obtain more efficient techniques or to find a better catalyst.

The objective of this paper is to summarize the current situation in the field of NO_x abatement. In contrast to a wide array of reviews already available on the subject of NO_x abatement (Javed et al., 2007; Liu and Woo, 2006; Muzio and Quartucy, 1997; Roy et al., 2009) this paper tries to present a more overall view. Therefore, we do not focus on one specific source of emission or method used to reduce the amount of emitted NO_x. Instead, this review gives an extensive survey of NO_x emission control technologies for three major anthropogenic sources of emission, i.e. power plants, vehicles and chemical industry. Further to the above, this paper presents new and alternative methods like hybrid system of SCR and O_3 injection, fast SCR, electron beam gas treatment, etc.

1.1. NO_x

Interest in NO_x emission has been steadily increasing since 1952, when the role of nitrogen oxides in the formation of photochemical smog was formulated (Muzio and Quartucy, 1997). Several types of nitrogen oxides exist in the environment: N_2O, NO, NO_2, N_2O_3, N_2O_4, NO_3, and N_2O_5 (Table 1). The abbreviation NO_x usually relates to nitrogen monoxide NO and nitrogen dioxide NO_2, which from photochemical point of view can be called 'fresh' nitrogen oxides since in these forms they reach atmosphere. Another important nitrogen oxide is N_2O and it may be also called 'fresh' for the same reasons.

1.2. Sources of NO_x

In 2007 total nitrogen oxides emission in Poland reached 890 Gg, in terms of NO_2 this was 50 Gg more than in 2000 (Central Statistical Office, 2009). This is principally a product of power plants and vehicles, Fig. 1. Following the accession to the EU, Poland agreed to reduce the emission limits of NO_x below 200 mg/m^3 after 2015 (Dora et al., 2009).

Global shares of NO_x anthropogenic sources are similar to those observed in Poland. Cited after Elzey et al. (2008) the primary sources of NO_x emission include motor vehicles (55%) and industrial, commercial combustion processes (45%). Increased combustion of fossil fuels since the last century has been a primary source of NO_x, leading to the increase of pollutants concentration in the atmosphere. However, other sources of NO_x such as the production and use of nitric acid should not be neglected. During nitric acid plant operation as well as nitrification and oxidation of organic compounds with the use of nitric acid, nitrous gases in varying concentrations are formed (Dyer-Smith and Jenny, 2005).

NO_x emitted from incineration processes consist in 95% of NO nitric oxide and 5% NO_2 nitrogen dioxide (Gomez-Garcia et al., 2005; Van Durme et al., 2008; Wang et al., 2007). Therefore, nitrogen dioxide formed in the atmosphere through the photochemical oxidation of nitric oxide is a secondary pollutant. However, it has been proved that for mobile sources of NO_x the share of NO_2 primary emission might be variable. Furthermore, it is dependent on the vehicle type, and conditions of operation (Carslaw and Beevers, 2004). Kartenbuch et al. (2001) performed experiments estimating the amount of primary NO_2 emitted from petrol, diesel vehicles and diesel trucks. They obtained NO_2/NO_x mix ratio of <0.2 vol.%, 5.9 vol.% and 11.0 vol.% for petrol, diesel vehicles and diesel trucks, respectively. Whereas, nitrous oxide N_2O besides being produced in combustion processes of fossil fuel and biomass is also emitted from chemical industry activities such as adipic acid production for Nylon 6.6 and nitric acid manufacture.

Natural sources of NO_x, in spite of not being as crucial as anthropogenic ones, are still worth listing: oxidation of NH_3, lightning, and volcano activities.

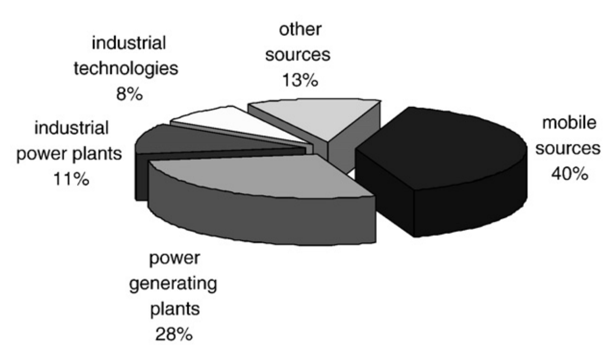

Fig. 1. Nitrogen oxides emission in Poland in 2007 (Central Statistical Office, 2009).

1.3. Environmental impact

Air pollution has not only acute but also chronic effect on human health. It has many pathways of entering human body. Primarily, humans get in contact with air pollutants via inhalation and ingestion, while dermal contact represents a minor route of exposure (Nakatsuji et al., 1999). Air pollution penetrates to water and soil therefore also to food which is consumed by humans. The impact of air pollution on humans can differ.

Taking NO_x into consideration, only nitric oxide and nitrogen dioxide are thought to be toxic. Regardless of being the major component of NO_x, nitric oxide is less toxic than nitrogen dioxide. It causes eye and throat irritation. As most radicals, NO is unstable and reacts readily with oxygen to form NO_2 which even at low doses can be a source of acute lung injury with pneumonitis and fulminant pulmonary edema (Woodrow, 1997). Studies focused on risk assessment have showed that high outdoor NO_2 concentration observed in residential areas contributes to increased respiratory and cardiovascular diseases and mortality (Chaloulakou et al., 2008). Furthermore, NO_x are precursors of tropospheric ozone which in fact is also toxic.

Taking into account the variety of contaminants emitted to the atmosphere, it is clear that humans are exposed to a mixture of pollutants, so it is difficult to precisely describe all health risks involved. Another important matter is the exposure time and dose of pollutants as well as individual features of a human being.

Further to the above, NO_x emission contributes to many environmental problems like acid rain, photochemical smog, greenhouse effect, etc. NO_x and many volatile organic compounds (VOC) are considered ground-level ozone precursors (Anon., 1995). Furthermore, the mixture of NO_x and VOC in the atmosphere exposed to sunlight can result in the formation of photochemical smog, whereas NO and NO_2 together with sulfur dioxide SO_2 are the major contributors to acid rain. Acid rain is likely to generate further environmental effects like deforestation and soil and water acidification. It also causes material losses, e.g. destruction of buildings and monuments, and crop damage (Devahasdin et al., 2003).

It is known that N_2O is one of the greenhouse gases, besides it takes part in complex reactions in the stratosphere which can lead to a depletion of ozone layer (Aneja et al., 2001). As a greenhouse gas it absorbs infrared radiation with 270-time higher intensity than carbon dioxide (CO_2) (Wright, 2003). Moreover, it indirectly affects the ozone layer through photochemical reactions (Ogawa and Yoshida, 2005). Unlike NO and NO_2, N_2O has a long half-life around 100 to 150 years (Environmental Protection Agency, 1999). However, it is not as reactive as NO and NO_2. As a result of these traits NO and NO_2 are mainly the problem in close range of its emission sources, whereas N_2O emission can be considered more as a global problem.

1.4. Complexity of NO_x reactions in the atmosphere

Majority of environmental problems and health hazards is a result of various processes occurring in the atmosphere. The array of potential NO_x reactions with different compounds present in the atmosphere (O_3, VOC, etc.) is quite complex. Furthermore, in the presence of sunlight various photochemical reactions are possible. Additionally, the type of reactions is dependent on the atmosphere layer that is considered, since different species are present at different heights with various concentrations. What is more, different ranges of solar radiation are observed in thermo-, meso-, strato- and troposphere as a result of the ability of different chemical molecules to absorb different wavelengths of radiation. In connection with these factors it is extremely important to have at least basic understanding of processes occurring in the atmosphere. It enables us to understand why NO_x abatement is such a complex and crucial matter. Furthermore, this knowledge could be a source of new ideas for development of NO_x control technologies.

Some reactions which NO_x can undergo in the atmosphere are presented here briefly (Fig. 2). In order to understand the chemistry of atmosphere, it is necessary to begin with the thermosphere and then move to consecutive parts of the atmosphere. In this zone atoms and molecules are exposed to solar radiation in entire range of radiation frequencies. For instance highly energetic ultraviolet radiation can cause dissociation of dinitrogen and dioxygen present in the thermosphere to their atoms according to:

$$N_2 + h\upsilon(\lambda \approx 126\text{nm}) \rightarrow 2N \tag{1}$$

$$O_2 + h\upsilon(\lambda \approx 240\text{nm}) \rightarrow 2O \tag{2}$$

In the mesosphere radiation is absorbed by ozone which causes its dissociation to excited states of molecular oxygen and atomic oxygen (marked with *) (Atkinson, 1995; Van Loon and Duffy; 2005):

$$O_3 + h\upsilon(\lambda \approx 325\text{nm}) \rightarrow O_2^* + O^* \tag{3}$$

In the stratosphere higher concentration of ozone can be observed, since it is generated via reactions of atomic oxygen generated in photolysis, with molecular oxygen. Nowadays we are exposed to the hazards connected with the problem of ozone layer depletion, as a result of various reactions in stratosphere which can be catalyzed by radicals included in three categories (Van Loon and Duffy; 2005):

- HO_x–$^{\bullet}H$, $^{\bullet}OH$ and $HOO^{\bullet}$

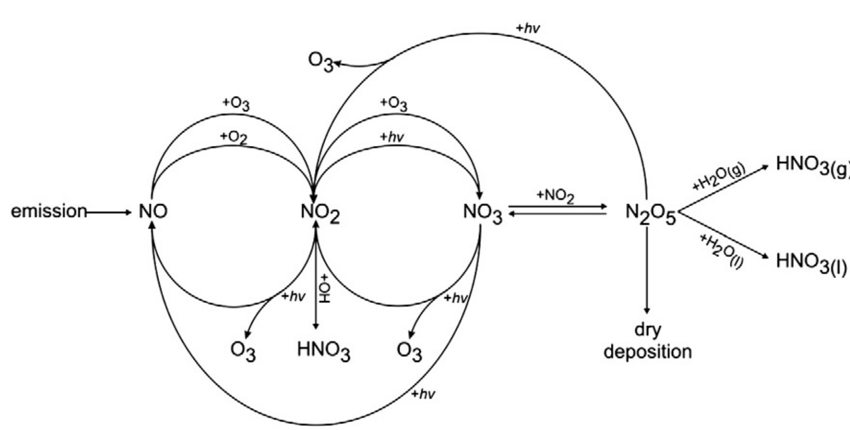

Fig. 2. Schematics of atmospheric NO_x reactions.

- NO_x–$^{\bullet}NO$ and $^{\bullet}NO_2$
- ClO_x–$^{\bullet}Cl$ and $ClO^{\bullet}$

Although NO and NO_2 are radicals, from now on they will be referred to as NO and NO_2 without indication.

In our deliberations we will consider barely NO_x which in lower stratosphere dominate in the catalytic decomposition of ozone (Atkinson, 1995):

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (4)$$

$$\underline{NO_2 + O \rightarrow NO + O_2} \quad (5)$$

$$O + O_3 \rightarrow 2O_2 \quad (6)$$

The UV radiation is absorbed in the stratosphere, where the ozone concentration is higher, as a result only some part of radiation reaches the troposphere. It is posited that around 50% of solar radiation reaches the earth surface.

NO and NO_2 have both short lifetimes (around 4 days) in the atmosphere, since they are removed from the troposphere after their transformation to HNO_3. Consequently, the amount of these gases reaching the stratosphere is small. However, some emission of NO_x is present in the stratosphere as a result of aircraft traffic and reactions of N_2O with exited state oxygen according to (Atkinson, 1995; Van Loon and Duffy; 2005):

$$N_2O + O(1D) \rightarrow 2NO(60\%) \quad (7)$$

$$N_2O + O(1D) \rightarrow N_2 + O_2(40\%) \quad (8)$$

Further to the above, N_2O undergoes photochemical reactions under solar UV radiation into N_2 (95%) and NO (5%) (Wright, 2003):

$$N_2O + h\upsilon \rightarrow NO + N \quad (9)$$

$$N_2O + h\upsilon \rightarrow N_2 + O \quad (10)$$

The nitrous oxide is stable in the troposphere, hence big amounts of this pollutant reach the stratosphere where after reaction (7) in the form of NO it can participate in a wide array of reactions with ozone, i.e. reaction (4) and following reactions (Atkinson, 1995; Van Loon and Duffy; 2005):

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (11)$$

$$NO_3 + NO_2 \rightarrow N_2O_5 \quad (12)$$

Reaction (11) is much slower than reaction (4). Reaction (11) determines the rate of N_2O_5 formation (Cox and Coker, 1983).

In the aspect of air pollution the most important part of the atmosphere is troposphere, since basically all the pollutants are emitted to the troposphere and not many of them reach higher layers of the atmosphere in unchanged state. NO_x with other pollutants contribute to the formation of photochemical smog, tropospheric ozone and acid rains. One of the most important photochemical reactions taking place in the troposphere is the decomposition of nitrogen dioxide (Van Loon and Duffy; 2005; Carslaw and Beevers, 2004):

$$NO_2 + h\upsilon(\lambda < 440\text{nm}) \rightarrow NO + O \quad (13)$$

Atomic oxygen formed in this reaction can react with oxygen molecule to form ozone, this is the main root of the tropospheric ozone formation (Van Loon and Duffy; 2005). Nitric oxide does not absorb radiation above 230 nm and it cannot be an initiator of photochemical reactions in the polluted lower atmosphere. However, NO_2 absorbs radiation from a wide range of frequencies, thus atomic oxygen can be formed (Bailey, 2002). Also in the troposphere reactions (11) and (12) are observed and play a significant role in the formation of photochemical smog (Wu et al., 1973). N_2O_5 can be removed from the atmosphere by reaction involving water (Matsumoto et al., 2006; Smith et al., 1995; Wu et al., 1973):

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad (14)$$

N_2O_5 is considered as a reservoir of NO_x and it is usually observed during nighttime.

In daytime NO_3 undergoes rapid photolysis to NO and O_2:

$$NO_3 + h\upsilon \rightarrow NO + O_2 \quad (15)$$

or to NO_2 and O

$$NO_3 + h\upsilon \rightarrow NO_2 + O \quad (16)$$

In daylight the lifetime of NO_3 with respect to photolysis is around 10 s and thus less N_2O_5 can be formed (Bailey, 2002; Cox and Coker, 1983). The NO_3 radical exists normally in the thermal equilibrium with NO_2 and N_2O_5 and it can be present in significant concentrations at night (Wängberg et al., 1992).

Furthermore, N_2O_5 itself also absorbs near-ultraviolet radiation and is decomposed according to the reaction (Swanson et al., 1984):

$$N_2O_5 + h\upsilon(\lambda < 401\text{nm}) \rightarrow 2NO_2 + O \quad (17)$$

Table 2 gives a wide range of reactions basically between NO_x, O_3 and H_2O and their standard reaction enthalpies calculated according to Hess's law and based on standard enthalpies of formation according to the National Institute of Standards and Technology (National Institute of Standards and Technology, 2009). Even in such a seemingly uncomplicated system the number of possible chemical reactions is significant and that is without taking into consideration photochemistry. Majority of the reactions shown in Table 2 are exothermic and thus thermodynamically favorable, however there are other factors like the coefficient of collision probability and activation energy that determine if the reaction takes place in the atmosphere.

It should not be forgotten that in the atmosphere more chemical substances are present, which can react with each other or catalyze formation or decomposition of other chemicals. Thereby chemistry of the atmosphere is still profoundly studied, especially as this knowledge turns out to be useful in the improvement of NO_x abatement methods. In Sections 2.1.2 and 2.3 a few examples of implementing this knowledge are described.

2. NO_x emission abatement

As it was shown in Fig. 1, nitrogen oxides are emitted from various sources. In this aspect there is a variety of NO_x control techniques. First of all, these methods can be categorized in three groups taking into account the type of NO_x emission source:

- control methods in power plants,
- car engines,
- chemical industry.

Each of these groups has its own preferred methods of NO_x emission control. However, some technologies can find application in NO_x emission abatement for all three types of sources of these pollutants.

2.1. NO_x abatement methods for industrial and general power plants

In the case of incineration processes occurring in power stations three approaches to abatement of NO_x emission are known: pre-combustion, combustion modification and post-combustion techniques which are further characterized in Sections 2.1.1–2.1.2.

Table 2
The possible reactions occurring in the NO_x, O_3 and H_2O system with the calculated standard reaction enthalpies.

Reactions	$\Delta H_{reaction}$(kJ/mol)	k_{298} (mol L s)	Reactions	$\Delta H_{reaction}$(kJ/mol)	k_{298} (mol L s)
$O_3 + H = O_2 + OH$	−321.68	4.408×10^{11}	$NO + O(+M) = NO_2(+M)$	−306.37	1.363×10^{10}
$O_3 + H = O + HO_2$	−109.4	4.520×10^{8}	$NO + OH = HNO_2$	−206.01	5.450×10^{14}
$O_3 + OH = O_2 + HO_2$	−179.57	3.991×10^{7}	$O + HNO_2 = NO_2 + OH$	−100.36	5.338×10^{5}
$O_3 + H_2O = O_2 + H_2O_2$	235.27	6.620×10^{-2}	$H + HNO_2 = HNO + OH$	−2.7	$3.175 \times 10^{+8}$
$O_3 + HO_2 = 2O_2 + OH$	−105.77	2.791×10^{15}	$H + HNO_2 = NO_2 + H_2$	−108.17	1.823×10^{8}
$O_3 + N = O_2 + NO$	−525.06	6.000×10^{4}	$H + HNO_2 = NO + H_2O$	−292.81	2.953×10^{10}
$O_3 + NO = NO_2 + O_2$	−199.86	1.080×10^{7}	$O_3 + HNO_2 = O_2 + HNO_3$	−200.25	3.010×10^{2}
$O_3 + NO_2 = O_2 + NO_3$	−104.64	2.103×10^{4}	$HNO_3 + O = NO_3 + OH$	−4.75	1.810×10^{4}
$O_3 = O_2 + O$	106.51	2.023×10^{-2}	$HNO_3 + H = NO_3 + H_2$	−12.56	1.836×10^{1}
$O_3 + O = 2O_2$	−391.85	6.361×10^{8}	$HNO_3 + H = NO_2 + H_2O$	−292.42	3.173×10^{10}
$H + O_2 + M = HO_2 + M$	−215.91	6.690×10^{9}	$HNO_3 + NO = NO_2 + HNO_2$	0.39	4.480×10^{0}
$H + H + M = H_2 + M$	−436	3.354×10^{9}	$HNO_3 + OH = NO_3 + H_2O$	−75.38	4.820×10^{5}
$H + H + H_2 = H_2 + H_2$	−436	3.014×10^{9}	$HNO_3 + OH = NO_2 + H_2O_2$	264.53	4.820×10^{5}
$H + H + H_2O = H_2 + H_2O$	−436	6.439×10^{10}	$HNO_3 = NO_2 + OH$	206.4	1.979×10^{-16}
$H + OH + M = H_2O + M$	−498.82	1.800×10^{11}	$HNO + O = NO + OH$	−219.48	2.290×10^{10}
$H + O + M = OH + M$	−428.19	2.031×10^{9}	$HNO + HNO = N_2O + H_2O$	−358.94	2.710×10^{13}
$O + O + M = O_2 + M$	−498.36	3.872×10^{8}	$HNO + H = NO + H_2$	−227.29	4.853×10^{11}
$H_2O_2 + M = OH + OH + M$	−58.13	5.499×10^{-20}	$HNO + NO_2 = NO + HNO_2$	−119.12	2.128×10^{7}
$H_2 + O_2 = 2OH$	77.98	1.529×10^{-25}	$HNO + OH = NO + H_2O$	−290.11	9.055×10^{9}
$OH + H_2 = H_2O + H$	−62.82	4.220×10^{6}	$H + HO_2 = OH + OH$	−142.11	7.842×10^{11}
$O + OH = O_2 + H$	−70.17	2.091×10^{10}	$NO_2 + HO_2 = HNO_2 + O_2$	−111.92	2.200×10^{-4}
$O + H_2 = OH + H$	7.81	5.909×10^{3}	$NO + HO_2 = HNO + O_2$	7.2	4.599×10^{-2}
$O + HO_2 = O_2 + OH$	−33.27	2.286×10^{9}	$NO + HO_2 = NO_2 + OH$	−20.29	1.724×10^{9}
$2OH = O + H_2O$	−70.63	9.884×10^{11}	$NO + HO_2 = HNO_3$	−226.69	5.443×10^{13}
$H + HO_2 = H_2 + O_2$	−220.09	1.250×10^{10}	$H_2O + HO_2 = H_2O_2 + O_2$	375.85	2.490×10^{-14}
$H_2O_2 + H = HO_2 + H_2$	−352.02	2.611×10^{6}	$HO_2 = H + O_2$	215.91	4.220×10^{-23}
$N + O_2 = NO + O_2$	−382.39	4.742×10^{4}	$N + NO_2 = O + O + N_2$	−7.42	1.300×10^{-4}
$N + OH = NO + H$	−203.38	3.800×10^{10}	$NO_2 + H = NO + OH$	−121.82	7.643×10^{10}
$NO + M = N + O + M$	631.57	0.000	$NO + NO = O_2 + N_2$	−180.58	1.388×10^{-36}
$N + HO_2 = NO + OH$	−345.49	7.015×10^{3}	$NO + N_2O = NO_2 + N_2$	−139.24	5.265×10^{-21}
$NO + N = N_2 + O$	−313.79	1.875×10^{10}	$NO + NO_3 = 2NO_2$ [a]	−95.22	1.566×10^{10}[c]
$NO_2 + NO_3 = NO_2 + NO + O_2$ [a]	19.16	2.211×10^{5}	$NO_2 + NO_3 = N_2O_5$ [a]	−92.93	8.431×10^{8}[c]
$NO_3 = NO + O_2$[a]	19.16	3.255×10^{-3}	$N_2O_5 = NO_2 + NO_3$ [a]	92.93	1.159×10^{17}[b]
$N_2O_5 + H_2O = 2HNO_3$	96.22	1.506×10^{-1}			

Reference: Wei et al. (2007); [a]—Wängberg et al. (1992); [b]—Mok and Nam (2004); [c]—Atkinson et al. (2004).

2.1.1. Pre-combustion and combustion modification

Pre-combustion basically means fuel purification in order to reduce the amount of nitrogen or choosing the fuel with low nitrogen content like natural gas instead of diesel oil etc. It is well known that fuel type affects the formation of NO_x through the amount of fuel bound nitrogen (Friebel and Köpsel, 1999). The amount of formed NO_x increases for such fuels as methanol, ethanol, natural gas, propane, butane, ultra-low nitrogen fuel oil, fuel oil and coal (Latta et al., 1998). Furthermore, replacement of air in the combustion process by pure oxygen can also significantly decrease the formation of NO_x. Therefore, neither thermal, nor prompt NO_x can be formed (Sterner and Turnheim, 2009). The main drawback of this solution is its high cost. Thanks to pre-combustion methods it is easier to reach the required levels of NO_x emission with the use of remaining two ways of NO_x emission control.

Combustion modification can be simply described as alteration of operational conditions in order to decrease the NO_x formation. These methods became quite common in Poland, since they enabled to fulfill domestic standards of NO_x emissions (500–600 mg/m^3) (Dora et al., 2009). However, they are not sufficient to meet new much more rigorous EU emission limits.

The first tests on reducing NO_x emission by means of combustion modification were performed in the late 1950s (Muzio and Quartucy, 1997). In 1959 the influence of O_2 level on nitrogen oxides emission as well as fuel type was assessed in Southern California Edison's El Segundo Generating Station (Muzio and Quartucy, 1997). It is well known that main factors influencing the formation of nitrogen oxides in combustion processes are combustion temperature (the higher the temperature the higher the NO_x formation), proportion between the amount of air and fuel, mixing degree of air, fuel and incineration products distribution. Hence, the main target of combustion modification techniques is to create oxygen deficient stoichiometric conditions, reduce flame temperature or to vary the residence time within different parts of the combustion zone (Gomez-Garcia et al., 2005; Javed et al., 2007). This can be achieved through the application of various technologies presented in Table 3.

To handle the NO_x emission problem low excess air (LEA) is used. This method can be explained as limiting the excess air flow under 2%, and has been proved to strongly lower the NO_x content in exhaust gases (Environmental Protection Agency, 1999). The ultimate level of excess air is limited by smoke and CO emission in the stack (Javed et al., 2007).

Low NO_x burners (LNBs) are designed to control air and fuel mixing to achieve staged combustion (Javed et al., 2007). Their special construction leads to air staging in the incineration process and enables reduction of fuel NO_x formation or decrease of temperature therefore reducing the thermal NO_x generation (Muzio and Quartucy, 1997). These burners provide stable flame with many zones, e.g. primary combustion zone, fuel reburning (FR) zone and final combustion zone (National Energy Technology Laboratory, 2008). The main advantage of LNBs is the reduction of NO_x generation as high as 30–50% and the easiness of their application in both existing and new furnaces (Ballester et al., 1997). However, this procedure causes an increase of carbon content in ashes and greater CO formation (Gomez-Garcia et al., 2005). Despite this, low NO_x burners are one of the most popular NO_x control technologies (Ballester et al., 1997).

Another popular air staging method in which the combustion air (10–25%) is injected into furnace above the normal combustion zone is Over Fire Air (OFA) (Javed et al., 2007; Muzio and Quartucy, 1997; Environmental Protection Agency, 1999). As a result a fuel-rich primary combustion zone and fuel-lean lower temperature secondary combustion zone are formed (Javed et al., 2007; Muzio and Quartucy, 1997). This method is frequently used in combination with LNBs (National Energy Technology Laboratory, 2008). The Advanced Over Fire Air technique, which was first employed in Hommond power

Table 3
The comparison of combustion modification techniques.

Technique	Description	Advantages	Disadvantages	General NO_x reduction
Low Excess Air (LEA)	Reduces oxygen availability	Easy modification Useful for retrofit of existing power plants[a]	Low NO_x reduction Incomplete burned out (can lead to high levels of CO)[a]	10–44%[a]
Burners Out of Service (BOOS)	Staged combustion	No capital cost Useful for retrofit of existing power plants[a]	Generally restricted to gas or oil-fired combustion processes[a] Higher air flow for CO	10–70%[a]
Over Fire Air (OFA)		All fuels[a]	Can lead to high levels of CO[a] High capacity cost	
Low NO_x Burner (LNB) air staged	Internal staged combustion	Low operating cost	Moderately high capacity costs	25–35%[a]
Low NO_x Burner (LNB) flue gas recirculation		All fuels[a]		up to 20%[a]
Low NO_x Burner (LNB) fuel staged		Useful for retrofit of existing power plants[a]		50–60%[a]
Flue Gas Recirculation (FGR)	<30% flue gas recirculated with air, decreasing temperature	High NO_x reduction potential for low nitrogen fuels	Moderately high capital cost and operating cost Affects heat transfer and system pressures High energy consumption[a] Flame instability[a]	20–50%[a]
Water/Steam Injection	Reduces flame temperature	Moderate capital cost NO_x reduction similar to FGR	Efficiency penalty Fan power higher	70–80%[b]
Fuel Reburning	Inject fuel to react with NO_x	Moderate cost Moderate NO_x removal	Extends residence time Incomplete combustion Less appropriate for retrofit of existing power plants[a]	50–60 %[a]

Reference: Environmental Protection Agency (1999), [a]—Integrated Pollution Prevention and Control (2006), [b]—Graus and Worrell (2007).

station, is altered OFA. The main difference is that this method includes greater percentage of air injected and new burner design (Javed et al., 2007).

Another way to limit the formation of NO_x is injection of diluents. For this purpose water, steam or flue gas can be used. The injection of water or steam should be placed in close range of the burner flame. In this way it lowers the flame temperature and decreases oxygen content, thus reducing the formation of thermal NO_x (Anon., 1995; Latta et al., 1998).

Flue Gas Recirculation (FGR) includes injection of small portion of flue gas back to the secondary air stream prior to entering the boiler (Javed et al., 2007; Muzio and Quartucy, 1997). It reduces NO_x generation by lowering flame temperature (below 1033 K thermal NO_x formation is negligible) and reducing oxygen concentration (Anon., 1995; Javed et al., 2007; National Energy Technology Laboratory, 2008, Environmental Protection Agency, 1999). It was reported that with the 20% flue gas recirculation the 30% reduction could be achieved for hard coal as fuel, whereas for gas and oil the reduction ranged from 65% to 80%, for about 25% flue gas recirculation (Javed et al., 2007). However, the amount of flue gas recirculated cannot be too high, otherwise it will destabilize the burner flame (Latta et al., 1998).

The principle of the fuel reburning (FR) technique is to inject part (typically 10–25%) of the incinerator fuel above the main burners in a separate reburn zone (National Energy Technology Laboratory, 2008; Javed et al., 2007). In this secondary combustion zone the NO_x formed in the primary combustion zone is decomposed as a result of reduction of NO_x by hydrocarbons (Javed et al., 2007). Since the amount of added fuel is only partially used in reducing NO_x the OFA is injected above the reburning zone in order to complete combustion (Environmental Protection Agency, 1999; National Energy Technology Laboratory, 2008). The reburning was first applied to a full scale coal-fired boiler in Japan by Mitsubishi in the 1980s, with a 50% reduction of NO_x.

Burners Out Of Service (BOOS) is one of fuel staging techniques which is conducted by fuel flow termination at selected burners, whereas the air flow is left unchanged, hence BOOS are flowing air only (Muzio and Quartucy, 1997; Latta et al., 1998). However, the amount of fuel sent to other burners is increased in order to keep the same total fuel flow (Muzio and Quartucy, 1997; Latta et al., 1998). As a result, flame temperature and O_2 content are reduced thereby NO_x formation is also decreased (Muzio and Quartucy, 1997). In studies performed in Southern California Edison in 1976, effectiveness of BOOS reached 30% (Muzio and Quartucy, 1997).

According to the Environmental Protection Agency, the effectiveness of combustion modification technologies depends on the type of the combustion system. In general, they can achieve 30–70% NO_x reduction, only for gas turbines higher efficiencies can be obtained (70–85%) (Environmental Protection Agency, 1999). More detailed information concerning this subject can be found in Environmental Protection Agency Technical Bulletin (1999).

2.1.2. Post-combustion methods

Post-combustion methods, as the term suggests, are dealing with nitrogen oxides in exhaust gases from incineration processes. They can be used as alternative or supplementary to combustion modification. In this chapter the abundance of post-combustion methods was presented. They have gained a lot of attention, since they can provide high NO_x emission reduction. However, nowadays it is difficult to fulfill the stringent emission requirements using just one strategy.

We prepared a scheme (Fig. 3) that summarizes all the post-combustion methods described in this chapter. First of all, two main approaches can be observed when NO_x abatement is considered; the first one is NO_x removal from flue gas and the second is NO_x destruction. In the case of the first approach, NO_x are usually removed in absorption or adsorption processes. The main drawback of these techniques is transferring the NO_x from flue gas to another medium and thus in many cases generating waste which has to be treated then. The second approach to the problem does not pose such a threat since NO_x are usually transformed to benign products. Currently, the most commonly used NO_x control method is selective catalytic reduction (SCR) by ammonia, which can provide up to 85% reduction of NO_x (Gomez-Garcia et al., 2005; Barman and Philip, 2006; Brüggemann and Keil, 2008). The first commercial SCR system began to appear in Japan around 1975 (Muzio and Quartucy, 1997). Then in 1985, the first pilot-scale SCR tests were performed on a coal-fired unit in the United States (Muzio and Quartucy, 1997). Generally, SCR is

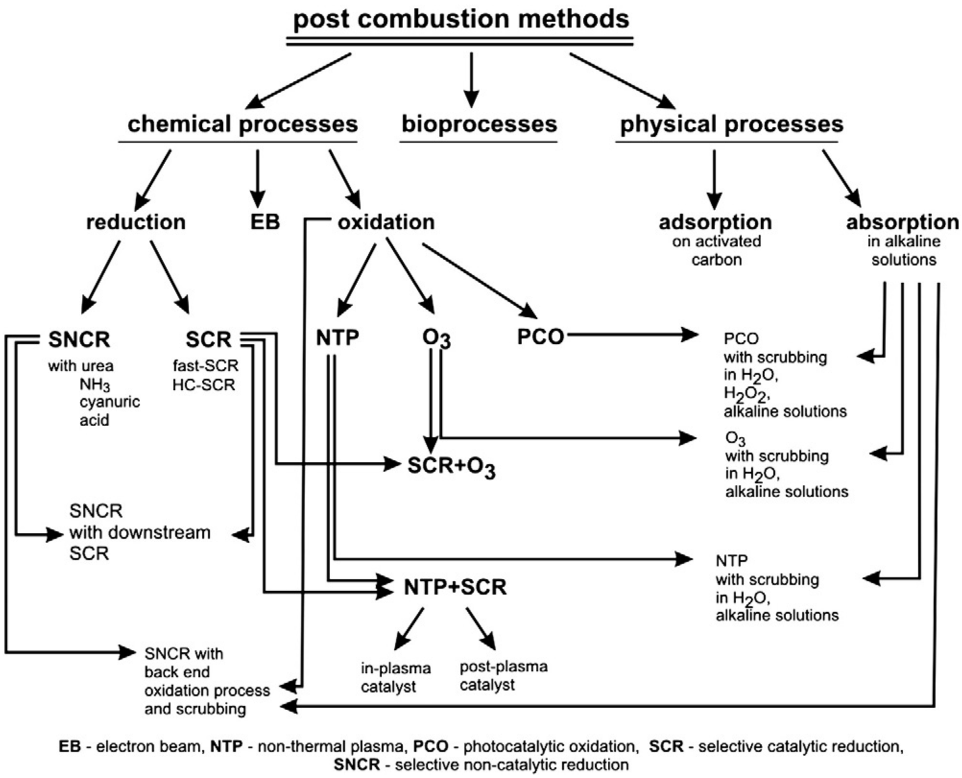

Fig. 3. Schematic presentation of described NO_x abatement post-combustion methods.

performed with ammonia in the presence of oxygen. The stoichiometry of this reaction is:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{18}$$

The reaction is promoted by a catalyst which enables the reaction to proceed at low temperatures. There are many types of catalysts used in SCR and many new ones are being developed. Basically three main groups of catalysts can be distinguished:

- Supported noble metal catalysts, e.g. Pt/Al_2O_3
- Base metal oxide catalysts, e.g. those containing vanadium
- Metal ion exchanged zeolites–crystalline silicate, consisting of regularly occurring internal pores of molecular dimensions and framework of linked cages and channels, e.g. Cu-ZSM-5 (Gomez-Garcia et al., 2005; Elzey et al., 2008).

Depending on the catalyst used the optimal temperature range for the reaction varies but usually fits 300–800 K (Muzio and Quartucy, 1997; Gomez-Garcia et al., 2005). Recently, metal oxides-based catalysts are being replaced by zeolites-based catalysts. Special attention is devoted to Fe-ZSM-5 catalyst used both in NH_3-SCR and HC-SCR. The reason for that is its high activity, high resistance to SO_2 and H_2O under SCR reaction conditions (Qi and Yang, 2005).

The effectiveness of the SCR is influenced by many factors like catalyst type, positioning of the catalyst, distribution of ammonia, etc. It is extremely important to get NH_3 perfectly distributed to ensure adequate value of NH_3/NO_x ratio and limiting NH_3 slip to the exhaust gas (Gomez-Garcia et al., 2005). At low temperatures (<500 K) the efficiency of SCR is strongly dependent on initial NO_2 concentration in exhaust gas stream (Van Durme et al., 2008), while in general NO_2 constitutes only 5% of NO_x present in exhaust gases (Gomez-Garcia et al., 2005; Van Durme et al., 2008). Gomez-Garcia et al. (2005) reported that SCR can remove 60% to 85% of NO_x when using 0.6 and 0.9 mol NH_3 for 1 mol of NO_x and leaves 1–5 ppm of unconverted NH_3. Not only NO_x emission but also the emission of ammonia is regulated by law, so NH_3 slip is an important issue. Although SCR is the most popular NO_x control method it is not demerit free. The use of a catalyst is also a source of other problems like limited catalyst life, catalyst poisoning by constituents present in flue gas, catalyst erosion by dust, etc. (Javed et al., 2007).

Elzey et al. (2008) investigated selective catalytic reduction of NO_2 with ammonia at 298 K on nanocrystalline sodium Y (NaY), Aldrich NaY and nanocrystalline copper Y (CuY) zeolites. Results of the studies demonstrated that the kinetics of SCR on nanocrystalline NaY zeolite was 30% faster than the one on Aldrich NaY. Nanocrystalline CuY zeolite turned out to be a potential catalyst for SCR with ammonia since it enhanced NO_x reduction.

Xu et al. (2008) studied Ce/TiO_2 catalyst for the process of NH_3-SCR in the temperature range 423–723 K. TiO_2 anatase has been the most widely used as the support material for the SCR catalyst since TiO_2 has excellent sulfur tolerance. In these studies it has been proved that Ce/TiO_2 catalyst is highly active and selective for the NO reduction in temperature range 548–673 K.

One of many SCR modifications is the fast SCR process, which makes available higher NO_x removal efficiency than the standard SCR by using an oxidation catalyst at upstream of the SCR unit (Irfan et al., 2008). About 50% of NO gets oxidized to NO_2 enabling the volume reduction of SCR catalyst (Irfan et al., 2008). A number of oxidation catalysts have been investigated: Pt-based catalyst, metal oxide catalyst without support (MnO_x, CuO_x, etc.), commercial catalyst like V_2O_5/TiO_2 promoted by WO_3 and/or MoO_3 catalyst (Irfan et al., 2008). Irfan et al. (2008) studied applicability of Co_3O_4 based catalyst for this process. Co_3O_4 turned out to be a very effective oxidation catalyst, up to 76% NO conversion was obtained at 573 K. Instead of oxidation catalyst ozone injection can be applied to SCR in order to increase NO_x removal efficiency. As it was reported by Mok and Yoon (2006) the injection of ozone increased NO_x removal efficiencies from 51, 67, 76, 93% at temperatures 423, 443, 473 and 503 K up to 80, 86, 90 and 97%, respectively.

As mentioned above, NH_3 usage causes the problem of slip but also difficulty of its transport and storage (Gomez-Garcia et al., 2005). These obstacles can be overcome by replacing NH_3 with hydrocarbons (HC-SCR). In 1992 Li and Armor proved that selective catalytic reduction can be performed by methane over Co-ZSM-5 as a catalyst (cited after Gomez-Garcia et al., 2005). Other hydrocarbons were also studied for HC-SCR, e.g. methane, ethylene, propane and higher hydrocarbons. Niu et al. (2006) compared CH_4 with C_2H_4 and C_2H_2 as reductants over Co-HZSM-5 catalyst in a non-thermal plasma reactor. The best NO_x conversion of 95% was obtained for addition of 500 ppm C_2H_2 at 573 K, whereas for 500 ppm of C_2H_4 and 1000 ppm of CH_4, 70% and 29% conversion was reached, respectively.

Another NO_x emission abatement method is selective noncatalytic reduction (SNCR) performed with the use of ammonia, aqueous urea (Eq. (19)) or cyanuric acid (Gomez-Garcia et al., 2005; Muzio and Quartucy, 1997).

$$CO(NH_2)_2 + 2NO + 1/2O_2 \leftrightarrow 2N_2 + CO_2 + 2H_2O \tag{19}$$

In contrast to SCR in the case of SNCR higher temperature (1149–1423 K) is required to enable NO_x reduction (Gomez-Garcia et al., 2005). The main drawback of SNCR is its low efficiency from 30% to 75% (Gomez-Garcia et al., 2005). This method appeared first in the mid 1970s. In 1974 Wendt and Sterling injected NH_3 into the post flame gas and observed a reduction of NO (Javed et al., 2007; Muzio and Quartucy, 1997). The SNCR is an attractive strategy to reduce NO_x emission due to its simplicity. Owing to a catalyst-free system all issues connected with the use of the catalyst present in SCR are absent in the SNCR. Thus, the capital and operation costs are lower. Further to the above, SNCR is easy to install in existing plants and can be applied in all types of stationary-fired equipments (Javed et al., 2007). However, with its low effectiveness it needs to be premised with the combustion modification techniques or combined with another post-combustion method. Apart from these difficulties the SNCR can be also a source of N_2O (up to 70–200 ppm) and CO emission (in the case of urea injection) (Javed et al., 2007).

One of the combined methods using SNCR can be a hybrid system utilizing a urea-based SNCR with downstream SCR which was investigated by Krigmont et al. in 1993 (cited after Muzio and Quartucy, 1997). The studies showed that 72 to 91% reduction of NO_x can be achieved, which proves that this hybrid system can be as effective as the single SCR. The advantage of the hybrid system over the conventional SCR is the reduction of operational costs, as a result of lower amount of catalyst needed comparing to the single SCR.

According to Javed et al. (2007) another SNCR coupling technology is combining selective noncatalytic reduction with back-end process in which the residual NO can be oxidized to NO_2 and removed by scrubbing (Javed et al., 2007). They discussed also combination of SNCR with reburning, electron beam or radiation, and plasma technology. Lazaroiu et al. (2007) presented an electron beam non-thermal plasma hybrid system for simultaneous removal of NO_x and SO_2. In series of experiments the removal up to 98% for SO_2 and 80% for NO_x was obtained.

Besides SCR and SNCR, various methods find application in NO_x emission reduction. One of them is non-thermal plasma (NTP) utilizing pulsed corona discharge or dielectric barrier discharge. Two kinds of reactions are possible in non-thermal plasma for NO_x reduction. NO_x can be converted into N_2 directly by N radicals or NO_x can be oxidized to higher nitrogen oxides by atomic oxygen and O_3 (Wang et al., 2007).

Non-thermal plasma alone cannot achieve enough high NO_x emission abatement, because it cannot reduce NO_x to N_2 when oxygen is present in the exhaust gas (Mok et al., 2003). By itself non-thermal plasma generates oxygen ions and ozone within the air flow and thus the principal action is the oxidation of NO to NO_2.

Non-thermal plasma, when combined with absorption process, can provide NO_x removal by absorbing NO_2 formed since it is better soluble than NO. Water, hydrogen peroxide or alkaline fluid can be used as sorbents (Environmental Protection Agency, 1999). Depending on the sorbent used different products are obtained. Yamamoto et al. used wet scrubbing technique with Na_2SO_3 solution to form N_2 from NO_x previously produced by non-thermal plasma (cited after Mok et al., 2003).

The second combination is the addition of a reducing agent to non-thermal plasma. This is usually performed with the use of a catalyst. Practically, this is a better idea since both methods are dry processes (Mok et al., 2003) and the presence of 30% to 50% of NO_2 in fuel gas stream greatly enhances the performance of selective catalytic reduction in NO_x removal processes (Van Durme et al., 2008). Furthermore, it is a good technology to reduce NO_x at low temperatures (Mok and Lee, 2006). Many researches concerning this subject are being conducted worldwide (Mok et al., 2003; Mok et al., 2004; Rajanikanth and Rout, 2001). The non-thermal plasma with a catalyst can be operated in two configurations: positioning the catalyst in the discharge zone (in-plasma catalysis) or downflow the discharge zone (post-plasma catalysis) (Van Durme et al., 2008).

Mok et al. (2003) studied the influence of non-thermal plasma addition to catalytic removal of nitrogen oxides over V_2O_5/TiO_2 and Cr_2O_3/TiO_2. The post-plasma catalysis enabled the removal of 80% and 40% of NO_x over V_2O_5/TiO_2 and Cr_2O_3/TiO_2, respectively, whereas without plasma generation only 50% and 10% reduction was achieved.

Rajanikanth and Rout (2001) studied the in-plasma catalysis process. The corona reactor was packed with dielectric pellets made of Al_2O_3, Al_2O_3 coated with palladium Pd and barium titanate $BaTiO_3$. With $BaTiO_3$ pellets, almost 99% removal of NO was achieved for an initial concentration of 265 ppm. According to Oda et al. (1997), not only catalysts can improve effectiveness of NTP but also injection of additives. The addition of hydrocarbons to the flue gas enhanced the oxidation of NO and thus improved NO_x removal efficiency. Although NTP is a highly effective technology with moderate operating and capital costs, the use of this method bears a risk of ozone emission and the formation of by-products like carbon oxide (Van Durme et al., 2008; Environmental Protection Agency, 1999). Another important issue is the influence of temperature on ozone formation in non-thermal plasma since generation of this oxidative agent decreases with the increase of temperature (Mok et al., 2003). Furthermore, it decomposes faster when temperature rises. Non-thermal plasma is a promising technology not only for NO_x control but also for SO_2 and volatile organic compounds (VOC) (Mok et al., 2003; Rajanikanth and Rout, 2001; Van Durme et al., 2008).

Another promising technology is electron beam flue gas treatment, mainly because it is one of multipollutants control technologies, capable of simultaneous removal of NO_x and SO_2. It is a fairly new approach to the problem of NO_x emission reduction, since it was developed in the early 1980s in Japan. From that time forth this technology has been widely studied all over the world, e.g. in USA, Germany, Japan, Poland, Bulgaria and China (Chmielewski, 2007). Soon after the laboratory scale studies conducted at the end of 1980s in the Institute of Nuclear Chemistry and Technology in Warsaw, the pilot plant has been constructed in Kawęczyn Power Station (Chmielewski et al., 1992). Thanks to these studies the first industrial installation located in Electric Power Station “Pomorzany” in Szczecin, north of Poland (Chmielewski et al., 2001) and two others in China were built.

In the electron beam process the irradiation of flue gas with fast (300–800 keV) electrons takes place (Basfar et al., 2008). This produces active radicals which react with SO_2 and NO_x to form nitric and sulfuric acids. In the presence of ammonia these acids are converted to ammonium sulfate $(NH_4)_2SO_4$ and ammonium sulfate nitrate $(NH_4)_2SO_4$–$2NH_4NO_3$ (Licki et al., 1998). These by-products can be filtered and used as an agricultural fertilizer (Licki et al., 1998, Chmielewski et al., 2004, Basfar et al., 2008). As Basfar et al. (2008) have informed recently, high removal efficiencies of SO_2 up to 95% and NO_x up to 85% were obtained. Apart from the lack of waste, the electron beam flue gas treatment has more advantages, first the simplification of installation construction and required space reduction. Furthermore, the total cost of simultaneous removal of NO_x and SO_2 does not exceed the cost of desulfurization in a conventional installation (Chmielewski et al., 2004).

Bioprocesses are a relatively new post-combustion control technology. Biological systems can be operated under ambient temperature (Yang et al., 2007). Biofiltration has been already successfully used for removal of odors and volatile organic compounds (VOC) (Wang et al., 2006; Yang et al., 2007). This method involves passing contaminated gases through biologically active material. Soil and compost can be used as active material (Barnes et al., 1995). Here, the purification process relies on the activity of denitrifying organisms. Barnes et al. (1995) investigated feasibility of biofiltration for NO_x removal by bacteria indigenous to wood compost. They obtained up to 90% NO removal. In 1997 Nagase et al. studied biological system exploiting unicellular microalga *Dunaliella tertiolecta* for NO_x removal. With NO_x concentration from 25 to 500 ppm in gas flow of 150 ml/min, about 65% of the NO_x was removed. Moreover, in 1998 Nagase et al. obtained a removal of 96% of NO_x with the use of *D. tertiolecta* in a counter-flow type airlift reactor. Yang et al. (2007) conducted research aimed at evaluation of the effect of various parameters on NO_x removal efficiency. A biofilter filled with medium containing wood chips and compost provided up to 99% NO_x removal. Results of these studies indicate that denitrification process is oxygen-inhibited, high concentrations of NO_x are better removed and that the addition of glucose to the biofilter would significantly enhance removal effectiveness.

A biotrickling filter is the effective method for the treatment of gas with relatively low concentration of pollutants at very large volumetric flux (Chen and Ma, 2006). A variety of microorganism and also higher plants are known to possess such ability (Barnes et al., 1995; Nagase et al., 1998). The abiotic and biological mechanism of NO_x removal was studied by Chen and Ma (2006) in the biotrickling filter. The results showed that both chemical oxidation and bionitrification were involved in NO_x removal. 64% NO_x removal was obtained but only 42 to 48% of NO_x removal can be assigned to biological processes. These results were obtained for empty bed residence time (EBRT) equal to 6 min. Even though biofiltration is a viable and cost-effective technology, it has two major drawbacks with existing biofilters and biotrickling filters, i.e. uneven distribution of ingredients and difficulty to control excess of biomass (Wang et al., 2006). Wang et al. (2006) applied a rotating drum filter to overcome these problems. Satisfactory 98% NO_x removal was obtained for empty bed residence time (EBRT) of 65 s, drum-rotating speed of 0.5 rpm and NO inlet concentration of 529 ppm.

As mentioned already, NO_2 can be effectively removed from the exhaust gas by wet techniques. However NO_2 constitutes only 5% of NO_x present in the exhaust gas this is why NO has to be first submitted to an oxidation to increase the share of NO_2 in the treated gas stream. This can be conducted in many different ways through non-thermal plasma, photocatalytic oxidation and ozone injection, etc. Non-thermal plasma has already been discussed in this paper. Photocatalytic oxidation (PCO) employs semiconductors such as $SrTiO_3$, TiO_2, ZnO, ZnS and CdS as photocatalysts, however, TiO_2 is the most widely used (Devahasdin et al., 2003). PCO dealing with NO_x removal from ambient environment has been widely investigated (Devahasdin et al., 2003; Ichiura et al., 2003; Maggos et al., 2007; Wang et al., 2008). Maggos et al. proposed the use of TiO_2-containing paint for photocatalytic degradation of NO_x gases in indoor car parks. TiO_2 is chemically activated by UV light (<387 nm) (Devahasdin et al., 2003). This can be considered as a limitation for its application. Introduction of TiO_2 catalyst modified in such a way that its activation under visible light would be possible can broaden the area for photocatalysis application. Various approaches have been studied already in order to extend the absorption wavelength range (Anpo, 2000; Ishibai et al., 2007). Ishibai et al. (2007) compared four Pt-modified TiO_2 photocatalysts with a standard version of TiO_2 under UV and visible light. The applied modification improved effectiveness under both UV and VIS range. In the case of UV the NO_x removal increased from 76% for standard TiO_2 up to 82% for Pt-modified. Furthermore, under VIS the increase was more significant from 9% up to 68%. Wang et al. (2008) studied photocatalytic oxidation over Zn–TiO_2. The oxidation of NO achieved for Degusa TiO_2 powder and Zn–TiO_2 were 50% and 70%, respectively.

Instead of photocatalytic oxidation ozone injection can be applied in order to convert NO to NO_2. Mok and Lee (2006) used ozone injection followed by absorption process with Na_2S as reducing agent for simultaneous removal of NO_x and SO_2. NO_x was first oxidized to NO_2, while SO_2 was hardly affected by ozone injection. Then in an absorber NO_2 was reduced to N_2 according to reaction (20):

$$2NO_2 + Na_2S \rightarrow N_2 + Na_2SO_4 \tag{20}$$

Whereas SO_2 can be removed by Na_2S as follows:

$$2SO_2 + Na_2S \rightarrow 2S + Na_2SO_4 \tag{21}$$

Through this process 95% removal of NO_x and 100% of SO_2 was obtained.

Wang et al. (2007) investigated also the process of simultaneous NO_x and SO_2 removal improved by the ability to remove elementary Hg. Mercury is one of the heavy metals emitted from coal-fired power plants, and like with other air pollutants its level of emission is regulated by law. The studies were performed in temperature range from 373 to 673 K, with the use of alkaline solution in a wet scrubber. The obtained removal efficiencies were similar to these achieved by Mok and Lee (2006), 97% for NO_x and 100% for SO_2 while 360 ppm ozone was added. More than 80% of atomic mercury can be oxidized to Hg^{2+} with 80 ppm ozone added. It is well known that Hg^{2+} can be easily trapped in the wet flue gas desulfurization (Wang et al., 2007).

Recently, Deshwal et al. (2008) proposed a method for nitric oxide removal from fuel gas in a lab-scale bubbling reactor by aqueous chlorine dioxide ClO_2 scrubbing solution. Here both oxidation and absorption processes are conducted in the wet bubbling reactor by means of ClO_2. Chlorine dioxide first oxidizes NO to NO_2 (Eq. (22)) which can be then removed by absorption according to Eq. (23):

$$5NO + 2ClO_2 + H_2O \rightarrow 5NO_2 + 2HCl \tag{22}$$

$$5NO_2 + ClO_2 + 3H_2O \rightarrow 5HNO_3 + HCl \tag{23}$$

ClO_2 seems to be a promising additive for NO_x removal since 100% NO oxidation and 60% NO_x removal efficiency were achieved. What is more, the products HNO_3 and HCl can be easily handled by adjusting pH. Other wet scrubbing methods for simultaneous removal of NO_x and SO_2 were presented by Long et al. (2008). The kinetics of the process with the use of a novel homogenous catalyst (cobalt ethylenediamine $Co(en)_3^{3+}$) was investigated.

Following the need for an effective, environment-friendly and cost-effective NO_x removal method, Barman and Philip (2006) proposed an integrated system for flue gas treatment. The system consisted of photocatalytic and ozone oxidation of NO followed by scrubbing and biological denitrification. The process making use of all of these methods proved to be highly effective, as well as the one without photocatalytic oxidation. Although ozone demand decreased with the use of photocatalysis, application of this method requires two additional units thus the capital and operational costs grow (Barman and Philip, 2006).

In this chapter, already applied and newly proposed solutions to NO_x abatement in power plants are described. SCR is a well established technology for this kind of NO_x sources, however in general it is capable of providing 80–90% NO_x removal. Even less effective is SNCR which enables a 30–75% NO_x reduction. Thus, studies are conducted around the world to redevelop these methods or find better solutions. In Table 4 we present a comparison of alternative methods. Several promising techniques have been proposed. Some, like SCR hybrid systems with NTP or O_3, turned out to be more effective than the single SCR. However, there are other important aspects of NO_x control techniques that have to be taken into consideration, mainly the investment and operational costs, generation of waste, etc. In the case of SCR, there are several problems with the application of catalysts and reducing agents. Therefore, the combination of NTP or O_3 with absorption seems to be a more interesting method. Especially, since it can additionally provide SO_2 and Hg emission reduction. So far most of post-combustion technologies have been performed individually. This approach generates more costs than the application of simultaneous removal technologies, therefore multiple pollutants removal methods are becoming more popular. Especially interesting is the electron beam flue gas treatment technology, which is very effective and, what is more, already applied in a few locations around the world.

2.2. NO_x abatement for car engines

In the case of mobile NO_x sources EU imposed emission regulation by the so-called Euro standards. Currently, NO_x emissions are limited to 150 and 80 mg km^{-1} for gasoline engines Euro-3- and Euro-4-passenger cars, respectively (Heeb et al., 2008). In the case of diesel vehicles this limits are about three times higher, 500 and 250 mg km^{-1} for Euro-3- and Euro-4-diesel passenger cars, respectively (Heeb et al., 2008). As a result of the above and different types of pollutants produced by gasoline and diesel engines, various NO_x control techniques are applied.

It appears that for gasoline vehicles a three-way-catalyst (TWC) is the state-of-the-art technology (Bröer and Hammer, 2000) as it is capable of simultaneous removal of NO_x, CO and C_xH_y. The development of TWC began in the 1980s. It appeared as an extension of "two-way catalysis", capable of removal of incomplete combustion products, CO and residual hydrocarbons (HC) to simultaneously abate the NO_x emission (Roy et al., 2009). The effectiveness of TWC can reach more than 95% (Heeb et al., 2008). The primary reaction in TWC is NO reduction by CO (Roy et al., 2009):

$$NO + CO \rightarrow 1/2N_2 + CO_2 \tag{24}$$

However, it does not remove NO_x in the case of diesel and lean-burn gasoline engines, because of high amounts of O_2 present in flue gases (Brandenberger et al., 2008; Bröer and Hammer, 2000; Liu and Woo, 2006; Nakatsuji et al., 1999; Takahashi et al., 2007). Recently diesel and lean-burn gasoline engines became more popular around the world, as a result of lower fuel consumption than in conventional gasoline engines. By applying excess air, the fuel consumption has been lowered up to 30% compared to the stoichiometric combustion with a simultaneous decrease of CO, HC and CO_2 emission (Fanson et al., 2003; Liu and Woo, 2006). In these types of vehicles traditional TWC is ineffective, since it requires fuel-rich conditions to effectively remove NO_x. In the last 20 years extensive researches were carried out in order to find three-way catalysts that would be active under lean-burn conditions, however without positive results (Fanson et al., 2003, Yamazaki et al., 2004). The way out turned out to be two technologies proposed in the 1990s, namely the NO_x storage reduction (NSR) and selective NO_x recirculation (SNR) (Roy et al., 2009). Proposed first by Toyota in the mid 1990s NO_x storage and reduction (NSR) is a promising technology for diesel vehicles (Fanson et al., 2003; Muncrief et al., 2004). This process consists of two stages: oxidative adsorption and reduction (Muncrief et al., 2004; Takahashi et al., 2007). During the former phase under an oxidative or lean-burn atmosphere, NO is oxidized over precious metals to NO_2, which combines as nitrates with NO_x storage compounds. In this phase hydrocarbons, nitrogen and carbon monoxide are oxidized into water and carbon dioxide (Roy et al., 2009). In the later stage under stoichiometric or reductive atmosphere (fuel-rich) the stored nitrates ions are released and reduced to nitrogen through reactions with hydrocarbons, hydrogen and carbon monoxide (Roy et al., 2009; Takahashi et al., 2007). Usually NO_x storage materials consist of alkaline–earth metals and alkaline and noble metals such as platinum and rhodium dispersed on the support, e.g. Pt–Ba/Al_2O_3 (Roy et al., 2009). This method is regarded as one of the leading technologies for NO_x control from lean-burn engines. It is worth noting that in this method no additional reducing agent is generally needed (Liu and Woo, 2006). Muncrief et al. (2004) studied NSR over Pt/BaO/alumina with the propylene injection. They obtained high NO_x conversions over wide temperature window (473–673 K). Studies conducted by Takahashi et al. (1996) on the Pt/Ba/Al_2O_3 catalyst proved that it could provide 90% NO_x conversion, whereas Castoldi et al. (2006) proved that the Pt–Ba/Al_2O_3 NSR catalyst was able to simultaneously remove both soot and NO_x. The NSR system with the Pt catalyst and hydrocarbons worked well for a long period in the absence of SO_x, however it deteriorated quickly in the presence of SO_x (Nakatsuji et al., 1999). Nakatsuji et al. (1999) managed to surmount this problem by applying catalytic reduction over Rh/alumina catalyst with periodic two steps, named dual-phase NO_x reduction. The operation in oxidizing conditions and relatively short operation in reducing conditions proved to be effective and resistant to SO_x present in the flue gas. This was proved by durability tests in the presence of 40 ppm SO_2 performed for more than 20 h, in which no deactivation of the Rh/alumina catalyst was observed. This method can be practically used in vehicles with diesel engines, lean gasoline engines and gasoline direct injection (GDI) engines (Nakatsuji et al., 1999). In order to solve the sulfur problem, wide array of studies were performed by Toyota researchers (Liu and Woo, 2006). According to Liu and Woo (2006) Toyota improved sulfur tolerance by adding TiO_2 or LiO_2 to the alumina support as well as by combining Rh and Pt. In general, the NSR still fails when fuel contains high levels of sulfur (Roy et al., 2009), thus other methods like selective catalytic reduction (SCR) gain interest. NSR faces also other problems like thermal deterioration of catalysts. Recently Fanson et al. (2003) and Yamazaki et al. (2004) proved that addition of iron to the NSR catalysts might improve thermal stability. According to Fanson et al. (2003) addition of iron also improves the long-term stability against sulfur.

Another, however not often applied method to reduce NO_x emission from fuel-lean or diesel engines is the selective NO_x recirculation (SNR) which was developed by Daimler-Chrysler in 1994 (Roy et al., 2009). The SNR involves concentration and recirculation of NO_x into combustion zone of the engine where they are thermally decomposed (Roy et al., 2009).

In addition to these two methods, namely NSR and SNR, in the 1990s also the use of selective catalytic reduction (SCR) for mobile sources of NO_x was proposed. However, as it was mentioned in Section 2.1.2, the SCR faces some serious difficulties like poisoning of catalysts, distribution of ammonia, ammonia slip, etc. For mobile sources there are even more problems. As Roy et al. (2009) report, the first generation of catalysts applied in vehicles were monoliths made of anatase crystalline form of TiO_2 supported on V_2O_5 or WO_3. This type of catalyst was popularized as an industrial catalyst in SCR from stationary sources. However, its application to mobile sources is connected with the problem of toxicity of vanadium (Roy et al., 2009). Furthermore, at high temperatures (>673 K) this type of catalyst tends to form nitrous oxide (Koebel et al., 2000). For mobile diesel engines Fe-ZSM-5 is one of the most suitable catalysts because of its

Table 4
The comparison of alternative NO_x control technologies.

Method	Conditions	Efficiencies (%)	Advantages	Disadvantages	Reference	Comments
O_3 + SCR (selective catalytic reduction)	T = 443 K T = 473 K T = 503 K C_{NOx} = 300 ppm Flow rate = 5 L/min	 55 64 68	Benign products More effective in lower temperatures than single SCR	Relatively high energy consumption	Mok and Nam (2004)	V_2O_5/TiO_2 NH_3 as a reducing agent
	503 K 473 K 443 K 423 K	97/93 (without O_3) 90/76 (without O_3) 86/67 (without O_3) 80/51 (without O_3)	Benign products Effective in lower temperatures than single SCR	Relatively high energy consumption	Mok and Yoon (2006)	
NTP (non-thermal plasma) + SCR	C_{O2} = 20% T upto 473 K C_{inNOx} = 200–400 ppm Flow rate: 5 l/min $C_{ethylene}$ = 750 ppm	80/50 (without NTP) 40/10 (without NTP)	Effective in lower temperatures than single SCR	Consumes more energy than O_3 injection Risk of CO, O_3 and formaldehyde emission	Mok et al. (2003)	V_2O_5/TiO_2 Cr_2O_3/TiO_2
HC-SCR + NTP (plasma over catalyst)	T = 573 K 500 ppm C_2H_2 500 ppm C_2H_4 1000 ppm CH_4	 95 80 30	More effective in lower temperatures than single SCR	Risk of CO and O_3 emission	Niu et al. (2006)	Co-HZSM-5
Electron beam flue gas treatment	Flow rate = 5 m^3/h T = 673–813 K C_{inNOx} ≈ 160 ppm C_{inSO2} > 1200 ppm	85 NO_x 95 SO_2	No wastes Useful by-products formation Easy to control and to operate	High energy consumption Exhaust gas should be cleaned off soot and other particulates	Basfar et al. (2008)	By-product—$(NH_4)_2SO_4$–$2NH_4NO_3$ can be used as a fertilizer
Electron-beam NTP	T = 338–343 K Flow rate = 1 m3/h C_{inSO2} = 2000 ppm C_{inNOx} = 750 ppm NH_3 in stoichiometric amounts	80 NO_x 98 SO_2	No wastes Generation of useful by-products	High energy consumption	Lazaroiu et al. (2007)	Authors used microwaves to reduced the consumption of energy By-product—$(NH_4)_2SO_4$–$2NH_4NO_3$ can be used as a fertilizer
Biofiltration	C_{inNOx} = 100–500μL/L Flow rate = 1 L/min	90	Low operating cost	Requires cooling system for exhaust gases	Barnes et al. (1995)	
	C_{NOx} = 25–500 ppm Flow rate = 150 mL/min	65		Sensible to pollutants load and temperature variations	Nagase et al. (1997)	*Dunaliella tertiolecta*
	C_{inNOx} = 100 ppm	96		Problem with excess biomass	Nagase et al. (1998)	*Dunaliella tertiolecta* Counter-flow type air-lift reactor
	C_{inNOx} = 200 ppm Flow rate = 30 L/min	99	Low operating cost	Applicable for low concentrations of NO_x and high volumetric flux	Yang et al. (2007)	Medium containing wood chips and compost/anaerobic conditions
Rotating drum filter	C_{inNOx} = 529 ppm Flow rate = 0.8 m^3/h Rotation speed = 0.5 rpm	98	Solves the problem with excess biomass		Wang et al. (2006)	
PCO (photocatalytic oxidation)	C_{inNOx} = 3 ppm Flow rate = 3 L/min	76 82 8 68	Pt-modified TiO_2 PCO can work under visible light irradiation	Tested on very small NO_x concentrations	Ishibai et al. (2007)	Standard TiO_2 (UV) Pt-modified TiO_2 (UV) Standard TiO_2 (VIS) Pt-modified TiO_2 (VIS)
PCO	C_{inNOx} = 90 ppm Flow rate = 2 L/min	70		Additional catalyst	Wang et al. (2008)	$ZnTiO_2$
O_3 injection with absorption–reduction	C_{inNOx} = 300 ppm C_{inSO2} = 300 ppm Flow rate: 5 L/min C_{Na2S} = 0.6%(w/w) T = 298–503 K	95 NO_x 100 SO_2	NO_x reducted to N_2 SO_2 is transformed to Na_2SO_4 non toxic product	H_2S might be emitted High energy consumption	Mok and Lee (2006)	Na_2S as reducing agent
O_3 injection with absorption	373–673 K Flow rate: 1 L/min C_{inNOx} = 215 ppm C_{inSO2} = 220 ppm C_{Hg} = 50 μg/m^3	 97 NO_x 100 SO_2 >80 Hg	Multi-pollutant controlling system	High energy consumption	Wang et al. (2007)	Alkaline solution
Absorption	C_{inNOx} = 150–1180 ppm C_{inSO2} = 0–1800 ppm Flow rate = 45 L/min T = 318 K	60	Easily handled products Multi-pollutant controlling system	Low effectiveness Application of chlorine compounds	Deshwal et al. (2008)	Aqueous ClO_2

high activity and durability (Iwasaki et al., 2008). Another serious contraindication for application of the standard SCR in vehicles is the employment of ammonia as a reducing agent linked with NH_3 slip, manipulation, storage and NH_3 corrosion (Liu and Woo, 2006). Thus, instead of using NH_3 in mobile SCR, the application of urea was proposed. This was published first by Held et al. in 1990 (Liu and Woo, 2006). The non-toxic urea can be used as a reducing agent, since it releases ammonia under thermal conditions according to:

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3 \tag{25}$$

Additionally, there are other reducing agents formed from urea like $^{\cdot}NH_2$ radicals or other intermediates (Liu and Woo, 2006).

This method is preferred for heavy-duty vehicles, however its application in diesel engines results in a complex exhaust after-treatment system consisting of a diesel oxidation catalyst, NH_3 dosing unit, SCR catalyst, and NH_3 oxidation catalyst (Roy and Baiker, 2009). According to Brosius et al. (2005), in 2005 DaimlerChrysler commercialized the urea-SCR based post-treatment system for heavy duty trucks under the name of BlueTec technology.

For lean gasoline engines and gasoline direct injection (GDI) engines the method of choice would be probably the selective catalytic reduction with hydrocarbons, which are easily available in fuel. An example of the reaction occurring in this process with methane is presented below (Nakatsuji et al., 1999):

$$NO + CH_4 + 3/2O_2 \rightarrow 1/2N_2 + CO_2 + 2H_2O \tag{26}$$

For HC-SCR NO_x technology various hydrocarbons such as methane, propane and ethane have been studied. Recently, studies have been carried out on the use of ethanol as a reducing agent in HC-SCR, which show that it is superior to other hydrocarbons enabling over 90% reduction of NO_x for temperature window 623–773 K (cited after Tham et al., 2009).

Cu-ZSM-5 was the first catalyst for HC-SCR that showed high NO_x reduction in oxygen-rich conditions (Nakatsuji et al., 1999; Roy et al., 2009). Since the development of HC-SCR various catalysts have been proposed. In general, for NO_x reduction from mobile sources, zeolite-based catalysts are more popular than the catalysts based on metal oxides. The activity of zeolite-based catalysts depends on the type of zeolite, its structure and type of metal ion (Brandenberger et al., 2008; Liu and Woo, 2006). These catalysts are not demerit-free, they have poor hydrothermal stability. Okada et al. (1997) compared Cu and Co exchanged zeolite ZSM-5 for propane-SCR. The Co-based catalyst turned out to be better in the presence of water vapor.

Next improvement to the SCR in mobile sources was introduced by Toyota Company. They have developed the diesel particulate–NO_x reduction system (DPNR) which enables simultaneous removal of soot particulate and NO_x (Liu and Woo, 2006).

Certain number of researches in the field of NO_x abatement from diesel engines was devoted to the application of plasma technologies: plasma–catalyst with hydrocarbon injection method, plasma–SCR with urea injection, oil droplet plasma injection system, silent discharge plasma system, corona radical shower system (Okubo et al., 2008). Tonkyn et al. (2003) achieved a significant reduction of NO_x over broad temperature window by combining atmospheric plasma with appropriate catalysts. Another approach with the same effect of NO oxidation to NO_2, that is more energy-efficient than employment of plasma and electron beam, is the ozone injection to the exhaust gas (Roy et al., 2009). In the case of plasma application, energy consumption is major demerit, since plasma must be always turned on during post-treatment (Okubo et al., 2008). Okubo et al. (2008) proposed a total diesel emission control system which can give plasma-assisted non-catalytic diesel particulate and NO_x simultaneous reduction using ozone injection and plasma desorption.

Recently Song et al. (2009) proposed application of dielectric barrier discharge (DBD) to simultaneously remove NO_x, particulate matter (PM) and hydrocarbons (HC). For the operating conditions they obtained the maximum PM, HC and NO_x removal effectiveness of more than 80%, 75% and 65%, respectively.

2.3. NO_x abatement in chemical industry

Approximately 6% of global NO_x emission comes from industrial sources, mainly chemical industry where HNO_3 is produced or used for nitrification or oxidation of organic compounds, e.g. monosaccharides to oxalic acid (Jethani et al., 1992) and for the production of metal nitrates (Dyer-Smith and Jenny, 2005). Opposite to exhaust gases coming from combustion processes, the composition of NO_x in chemical flue gases is variable. The mixture of NO and NO_2 depends on acid concentration, the higher the concentration the higher the percentage of NO_2. Moreover, the volumes of these gases are relatively low but concentration of NO_x very high (Dyer-Smith and Jenny, 2005). Usually absorption in alkali solutions or reduction with the use of hydrogen, methane or ammonia is applied for 'end of the pipe' NO_x emission control (Chacuk et al., 2007; Miller et al., 2005). The process of NO_x absorption is found to be extremely complex. It is mainly due to numerous species of nitrogen compounds which are involved in various reversible and irreversible reactions occurring in this process (Chacuk et al. 2007; Miller et al., 2005; Thomas and Vanderschuren, 1997). Further to the above various scrubbing solutions can be used thus different products are formed. The production of nitrites and nitrates is the effect of application of alkaline scrubbing solution, whereas in the case of water usage the mixture of nitric and nitrous oxides is formed (Dyer-Smith and Jenny, 2005). Moreover, the composition of products is also dependent on NO_x composition in flue gas (Dyer-Smith and Jenny, 2005). The main drawback of the traditional absorption is disability to obtain flue gas without NO_x. The reason for this is that HNO_2 formed during absorption, decomposes in the presence of strong acids to form nitric acid and nitric oxide according to Eq. (27) (Chacuk et al., 2007; Miller et al., 2005; Thomas and Vanderschuren, 1996, Thomas and Vanderschuren, 1997):

$$3HNO_3 \rightarrow HNO_3 + 2NO + H_2O \tag{27}$$

It appears reasonable to introduce an oxidizing agent into the absorption solution as nitrous and nitric acid can be transformed into compounds with higher level of nitrogen oxidation (Chacuk et al., 2007; Miller et al., 2005). Potassium permanganate, sodium chlorite, sodium hypochloride, hydrogen peroxide, chlorine dioxide and ozone can be used for this purpose (Thomas and Vanderschuren, 1996,). At the threshold of the 21st century, Thomas and Vanderschuren (1996) performed NO_x absorption in aqueous and nitric acid solutions containing H_2O_2. In the presence of H_2O_2 nitrous acid gets oxidized to nitric acid (Eq. (28)), therefore NO_x concentration in the outlet gas decreases (Thomas and Vanderschuren, 1996, 1997).

$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O \tag{28}$$

This method is valuable for nitric acid production plants, since the addition of H_2O_2 to scrubbing solution generates additional amounts of nitric acid without forming other by-products. In more recent works Miller et al. (2005) and Chacuk et al. (2007) investigated ozonation of nitrous acid in the nitric acid solution. They concluded that ozone usage made it possible to oxidize the whole amount of nitrous acid present in the solution. An oxidizing agent can also be applied directly to a manufacturing process as Dyer-Smith and Jenny (2005) reported. They compared effectiveness of ozone and hydrogen peroxide application during industrial nitrification and oxidation with nitric acid. Both oxidizing agents were used in the copper nitrate production process. In both cases nitrogen oxides are oxidized to dinitrogen pentoxide which forms nitric acid through reaction with water. Although both O_3 and H_2O_2 proved to be effective in NO_x emission abatement without generating by-products, the application of the former one appeared to be more cost-effective.

The homogenous process of oxidizing NO to NO_2 with ozone followed by SCR scrubbing etc. was widely studied (Jaroszyńska-Wolińska, 2002; Mok and Lee, 2006; Mok and Yoon, 2006; Wang et al., 2007). However, other researchers have proposed to extend the oxidation process up to the moment when N_2O_5 is formed which, as mentioned above, with water forms nitric acid (Mogili et al., 2006; Wei et al., 2007). In this application, however, bigger amounts of ozone are needed to obtain N_2O_5. Experimental results show that N_2O_5 starts to be generated when NO/O_3 ratio approaches the value of 1 (Mok and Lee, 2006, Skalska et al., 2009). In 2001 the process called low-temperature NO_x ($LoTO_x$) absorption won the Kirkpatrick Award. $LoTO_x$ can provide very high, over 90% NO_x removal efficiency. Other air pollutants can also be effectively removed in this process (Anon., 2001). Wei et al. (2007) proposed a kinetic model of homogeneous low-temperature multipollutant oxidation by ozone. The mixture of pollutants consisted of CO, CO_2, Hg, H_2O, NO, NO_2, O_2, H_2, SO_2, and H_2S as well as varying fractions of HCl, O_3 and SO, N_2 served as balance gas.

Air pollution control in chemical industry is extremely complex, since more chemical species have to be removed than in other NO_x anthropogenic sources of NO_x. As mentioned above, the composition of flue gases from chemical industry is different for each type of chemical plant and additionally it varies according to process parameters. This, along with other features of chemical industry in which NO_x might be emitted, makes the development of an universal technology very unlikely. However, it can be observed that many technologies already used in stationary and mobile combustion processes are applicable to chemical industry. Some can even generate higher effectiveness of production, like ozone injection followed with the absorption process. Nevertheless, on the basis of the literature survey one may conclude that the studies on the subject of NO_x abatement in chemical industry are not as extensive as the studies on power plants and vehicle NO_x emission control.

3. Summary

As it was presented in this review, many studies are conducted all over the world in order to improve already existing technologies or to develop new ways to handle the problem of NO_x emission. Some of these have been applied in industry, however did not go beyond laboratory scale. It can also be observed that the diversity of proposed NO_x control methods is extensive, starting with chemical processes focused on NO_x reduction, oxidation, photochemical processes to even biological processes. Additionally, the number of methods proposed for NO_x emission reduction is increased by development of hybrid technologies, like SCR/non-thermal plasma, absorption–oxidation with different oxidizing agent, etc., or technologies in which NO_x can be removed simultaneously with other pollutants, like SO_x, Hg and VOC. A relatively new and interesting method seems to be the use of ozone as an oxidizing agent either injected to exhaust gases or generated by non-thermal plasma or electron beam.

The choice of the method for specific source of NO_x depends on many factors, like the source itself, regulations concerning this type of source, amount of NO_x present in the flue gas, composition of NO_x, presence of other pollutants, temperature of the flue gas, etc. In the case of stationary combustion processes NO_x abatement can be performed by carefully thought out arrangement of pre-combustion, combustion modification and post-combustion technologies. This way the efficiency of the reduction of NO_x emission could be significantly improved. What is more, in the face of stringent regulations of NO_x emission, simultaneous application of the various NO_x abatement methods is a necessity. Additionally, this approach can significantly influence general costs of the NO_x emission control. Fewer options are available for mobile sources and chemical industry.

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