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Reduction of Air Pollution by Combustion Processes

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1. Introduction

Among human activities, those in which fuel combustion processes intervene are those who contaminate the atmosphere greatly.

The combustion process is a process of rapid oxidation, followed by light phenomena and the release of large amounts of energy, able to maintain it at high temperatures. Compared with slow oxidation processes, it is characteristic to the combustion process sudden acceleration of the reaction rate to achieve theoretically infinite values. This applies, for example, to the stoichiometric mixture of methane - oxygen heated to a temperature of 560°C in a sealed container. Heating the same mixture to a temperature of only 200°C, result in a slow oxidation process, which produces methanol, formic acid, formaldehyde, carbon monoxide and carbon dioxide gas, with an overall response rate with an evolution with measured values up to a maximum, after which rate value decreases with the depletion of reagents. In everyday life we encounter slow oxidation processes at every step. Thus, minerals are subject to slow oxidation process which occurs at ambient temperature by consumption of oxygen from atmospheric air, with production of oxides in a state of maximum stability. Such a process is carbon steel corrosion under the action of atmospheric oxygen at ambient temperatures, which is transformed first into ferrous oxide (FeO) and then in a more stable substance, ferric oxide (Fe_2O_3). Also, living organisms consume oxygen in the atmosphere, at room temperature to oxidize nutrients over a slow but very complex process. In both examples above, as in any oxidation process, there are necessary two substances: the oxidant, which has the ability to quickly combine with the substance subject to oxidation, respectively, the substance that is oxidized, called fuel.

The transformation of chemical energy of fossil fuels in forms of energy directly useable, primarily mechanical energy, electrical energy and heat energy, is practically done only by means of combustion. In the production of electrical and heat energy, are consumed by burning, at present, 87% fossil fuels, the remainder being nuclear energy and regenerative energy (hydraulic, wind energy, solar, geothermal and marine) 6%, respectively 7%. At this consumption of the fossil fuels the consumption to produce mechanical energy in transports and the technological consumption, e.g. consumption of coal to produce metallurgical coke and for injection in blast furnaces, is added.

In 2008, according to the World Energy Outlook (2010), world consumption of fuels was 12 300 million toe (tons oil equivalent), of which 30 660 million barrels of oil and 3100 billion cubic meters of natural gas. For the year 2035, according to the script "new scenario" of the

World Energy Outlook (2010), total consumption will be increased up to16 700 million toe, of which 36 135 million barrels of oil and 4500 billion cubic meters of natural gas. These significant increases in world consumption of fuels results in conditions that anticipate an increase in the share of nuclear energy to 8% and regenerative energy to 14% in electrical and heat energy production. As a result, World Energy Outlook (2010), consider that the regulations of Copenhagen Accord (The United Nations Climate Change Conference in Copenhagen, 7-19 December 2009) to reduce CO2 emissions are not sufficient to halt the temperature increase with up to 2°C, worldwide.

In the fuel combustion processes the maximum release of energy is obtained with the complete combustion with, minimum excess of air, closer to stoichiometric combustion, which generally leads to the exclusive formation of CO_2, H_2O, SO_2 and N_2 gases, respectively O_2 and N_2 of the air excess. In practice, combustion processes slide away more or less from this ideal, both due to the complex structure of used fuels, such as coals and inferior oils, also due to imperfection of the combustion installations. Thus are formed unburned substances as solid particles, rich in carbon, which in most cases are accompanied by unburned gases. Unburned substances discharged into the atmosphere with the combustion gases, lead to heat energy loss, which leads to a decrease of the thermal efficiency of the process but at the same time, they have polluting action (Ghia & Gaba, 2000).

Sources of air pollution from burning fuels are classified as follows: stationary sources, mainly consisting of boilers, furnaces and gas turbines and mobile sources consisting of transport means, whose internal combustion engines are diesel (diesel-consuming, also called compression-ignition engines) and spark ignition engines, consuming gasoline. Lately there are used as stationary sources in heat energy and electricity production in cogeneration and internal combustion engines. Classification of stationary sources is done by industry type:

- Energy Industry (heat energy and electricity production, petroleum refining, manufacture of solid fuel and other industries);
- Manufacturing Industry and construction (iron and steel, chemicals, pulp, paper and printing, food processing, beverage and tobacco), called the EEA Industry (energy) sector. Also in EEA (European Environment Agency) publications mobile sources are classified in road transport and other transport.

Wastes scattered in the atmosphere by fuel combustion processes are called emissions (some are returning back on the ground forming immissions) and form two major categories: gases and solid particles.

Gases released into the atmosphere by fuel combustion process are: CO_2, SO_2, H_2O, N_2, O_2, CO, NO_x, PAHs (polycyclic aromatic hydrocarbons), VOCs (volatile organic compounds), dioxins, furans. Lately it was started the separate monitoring of CH_4 methane from volatile organic compounds, these remaining without CH_4 becoming NMVOCs (non-methane volatile organic compounds). With the exception of H_2O, N_2 and O_2, all other elements pollute the atmosphere directly and some by induced forms (usually synergistic, their effect being amplified, more than their cumulative effect) such as the greenhouse effect, smog and acid rain (acid deposition more accurately).

The greenhouse effect is due to more than 50% to CO_2 and in very small proportion to nitrous oxide N_2O, mainly as gases from combustion processes. 65% of CO_2 in the atmosphere comes from burning fuels. Carbon dioxide recently considered as pollutant, prevents the heat energy discharge from the surface of the Earth which is received by

radiation from the sun. With the passage of time, even a few degrees increase in the Earth temperature could lead to reduction of the ice cap, the spread of deserts, rising the levels of oceans and sea, as important changes of the climate. In consequence, inside United Nations it was negotiated a convention on climate change which was signed at the Rio Conference in 1992, with the objective of stabilizing greenhouse effect concentrations.

Smog is a synergy, which may be:

- Reducing, also called sulfur dioxide, wet or London type;
- Photochemical, also called an oxidizer or Californian type.

Reducing smog is formed due to the presence, in high concentrations, of SO_2 and soft particles in suspension (smoke) in a calm atmosphere with high humidity, at relatively low temperatures. Component substances that contribute to forming reducing smog are solid particles of soot, cenospheres, sulfur oxides and carbon oxide, derived from incomplete combustion of coals or oils. Cold water vapors condense around the solid particles of smoke, which have a large surface and can act as catalysts to form soft particles of fog. Sometimes reducing smog also contains soft particles of silicon, aluminum as metal oxides.

Photochemical smog is formed due to the presence, in high concentrations, of NO_x and VOCs, in a calm atmosphere, with temperatures over 18°C, in the absence of rain and wind. By the action of solar radiation on primary pollutants, NO_x and VOCs, mainly derived from heavy road traffic, secondary pollutants are formed as NO_2, which decompose under the action of solar radiation in highly toxic compounds, such as peroxiacetil nitrate (PAN).

Acid rain is also a form of pollution induced by pollutants emitted by combustion processes of fuels, SO_x and NO_x. Arrived in the atmosphere, sulphur and nitrogen oxides react with oxygen, water vapors and other substances forming acid compounds, such as dilute solutions of H_2SO_4, HNO_3 and their salts, sulfates and nitrates. These acid compounds reaching the Earth by rain, snow and fog, forming wet acidic depositions, respectively by particles, wind and stormwater forming dry acidic depositions. Acidic depositions have a negative impact on population health status and adverse effects on aquatic ecosystems, on forests and crops. Also, acidic depositions attack buildings and works of art.

Another form of pollution induced by pollutants emitted by fuel combustion processes, is the formation of tropospheric (high altitude) ozone (O_3). Precursors of tropospheric ozone O_3 formation are: nitrogen oxides (NO_x), non-methane volatile organic compounds (NMVOC), carbon monoxide (CO) and methane (CH_4). Because of the ozone in the atmosphere vegetation growth is reduced and aging occurs on the crops and forests. Solid particles in the air are classified by their size, their capacity of sedimentation and the possibility to penetrate the organisms, as following:

- Particles larger than 10 μm are deposited after the law of gravity with an uniform accelerated motion, also known as dust;
- Particles between 10 μm and 0.1 μm that are deposited after Stokes law, consisting mainly of ash and black smoke from burning fuel results;
- Particles smaller than 0.1 μm that are deposited and move after Brownian movement law.

Especially in large steam boilers, through the burning of coals and oils, solid particles driven by exhaust gases may contain non-ferrous metals (Pb, Zn, Ni, Cd, Sn etc.) and metalloids (F and As).

In diesel engines, through incomplete combustion the fumes can appear white, blue respectively, which consist of a suspension in gases of liquid particles of unburned fuel or

partially oxidized. Particles with diameter over 1 µm are found in the white smoke and particles with a diameter of about 0.5 µm appear in the blue smoke.

Black smoke from diesel engines contains solid carbonaceous particles, with average diameters of 1 µm.

Some experts consider that solid primary particles ranging in size from 0.01 to 0.05 µm, during the expansion and exhaustion of burning gases, find suited conditions to aggregate in soot particles with dimensions up to 0.6 µm occupying a specific surface of about 200 m^2/g. Experimentally it was found that these particles are formed under certain specific conditions, of: 20-90% amorphous carbon, 2-5% ash and 10-80% carcinogenic hydrocarbons.

In order to diminish air pollution by combustion processes, the following solutions are recommended (Baukal, 2001, Ghia & Gaba,2000):

- reducing the pollutant emission at origin, at the producing sources (primary procedures) by changing-replacing the combustion processes (use of renewable energy, production reducing, increase of production/technological lines efficiency, replace of production technologies), by using pretreatment procedures of fuels and oxidizer substances (changing fuels and oxidizers, improving the fuels characteristics by processing, preparation and use of additives) and by using improvement – changing procedures of combustion processes, both in case of combustion installations - especially the burners and burning chambers with reference to their construction (mixed stages, flue gases recirculation, auto-carburizing, steam or water spraying) and in case of combustion adjustment (control of excess air, burners out of service, adjustment of combustion air temperature);

- collecting and /or reducing the pollutants resulted from flue gasses before their suppression into the air by using the so-called secondary pollution reducing techniques or flue gases treatment (catalytic and non catalytic reactors, active carbon processes, SNOX and DESONOX processes, electrostatic precipitators, bag filters, scrubbers etc).

2. Formation and reduction pollutants in combustion processes

2.1 Carbon monoxide

The emission of carbon monoxide (CO) pollutant in combustion processes is produced when some conditions occur which lead to incomplete burning of fuels that contain carbon. Among heavy users of the most polluting fossil fuels, through emission of CO, are the means of transportation driven by spark ignition engines and compression ignition engines, and the lesser CO polluting are power plants.

If oxygen is missing during the combustion, compared to stoichiometric requirements, in an area of a fuel-air mixture, it will result CO even at a sufficiently high temperature. The possibility of CO subsequent oxidation, when the contribution of necessary oxygen to a lower temperature appears, is slower than forming CO.

In boilers and in furnaces, the presence of CO in the exhausted flue gases highlight essentially a disorder of the combustion equipment: burner, sprayer, combustion air blow installation, etc. Carbon oxide appears usually in the flue gases discharged from old, rudimentary combustion plants and is almost absent in the exhaust gases from modern industrial combustion plants of high-capacity. Also, at these facilities is taken into account that reducing the excess of air, which reduces the emissions of NO_x, can increase CO emission. As a result an optimal value for the air excess coefficient is established (Gaba, 2005).

Ensuring complete combustion is a measure considered to be BAT (best available techniques), which ensure the maintenance of the CO emission levels below 100 mg/Nm³, for 15% O_2 (for internal combustion stationary engines and gas turbines) and in boilers and furnaces, for 3% O_2, to run on liquid and gaseous fuels and 6% O_2 to run on solid fuels (Directive 2008/1/EC, 2008).

For mobile sources, which are the biggest pollutants with CO, as reduction techniques were developed, among others, multi-point injection engines that work at high pressures and oxidation catalysts (Duca et al., 2002).

The amount of CO emitted by transportation in European Union countries (EU-27) represents 89% of the total CO emissions at their level. Due to equipping vehicles with better catalysts and application in EU-27 of new regulations that produced engines up to Euro-6, CO emissions diminished, in 2008, compared to 1990, with 71% (EEA-TERM 003, 2011).

2.2 Sulfur oxides

Beside some gaseous fuels, the other industrial fossil fuels generally contain sulfur S. For engines, diesel has a low sulfur content, which is null to petrol diesel prompts. Sulfur content in diesel determines SO_2 polluting emissions, which on diesel engines represent about 10% of the polluting emissions of these engines, but are being endangered as a result of production, lately, of sulfur-free diesel fuels.

Maximum sulfur content from main fossil fuels is regulated, e.g. France, S ≤ 4% for industrial liquid fuels and S ≤ 1% for solid fuels.

Primarily coals and oils, which are used in industrial plants to produce electricity and heat, are responsible for environmental pollution by sulfur oxides, strong acidity of air and acid rains. Sulfur dioxide tendency is to reduce the "greenhouse effect" by "albedo" effect.

Crude oils contain variable quantities of sulfur depending on their origin. During refining operations, sulfur tends to gather in waste fractions which can be an important element to the industrial liquid fuels. The difficulty to reduce the sulfur content in crude oils and petroleum residues consist especially in their content of asfaltene and metals which lead to deactivation of catalysts. Researches are made in this respect. At a large scale of solid fuels the sulfur content is close to the values for heavy liquid fuels. Also, desulphurization of solid fuels with high content of sulfur is a major activity, that develops both through practical achievements and through researches.

Discharged in the atmosphere, SO_2 react in proportion of 1-2 ‰/h with oxygen under the action of solar ultraviolet radiation resulting SO_3 which combines with water vapor in the atmosphere to form sulfuric acid. In very wet days, with fog, the degree of conversion to sulfuric acid is up to 15.7%.

Also, starting from SO_2 gas, sulfate aerosols forms but they can be washed by the rain which becomes acid. To ensure a satisfactory dilution and dispersion of the SO_2 gas in the atmosphere, the combustion gases must be evacuated from the funnel with an adequate speed and to a convenient height from the ground. Thus the large thermoelectric oil plants funnels exceed 200m height frequently. Because of this the pollution due to pollutants produced by sulfur in the fuel may occur at great distances from where they were generated.

Generally, the growth of sulfur dioxide quantity in the atmosphere has the effect of increasing the overall morbidity rate of the population. At concentrations of sulfur dioxide in the cities air over 0.046 ppm (annual average) lead to an increasing frequency of

respiratory diseases, at concentrations of 0.52 ppm in the presence of other solid particles, overall mortality is increased. Sulfur dioxide and sulfuric acid aggravate the respiratory system of animals, but this is much more toxic than SO_2, its action being dependent on the size of aerosols. In a series of countries, particularly those located in northern area, the specific flora is affected even by the traces of sulfur dioxide, moss and lichens around large cities from Europe and America, disappear. Sulfur dioxide absorbed by plants leads to acute and chronic effects. Acute effects, that follow high concentrations and the relatively short exposures, manifest by changing the color (to yellow-ivory or red-brown) of damaged tissues. Chronic effects, results of prolonged exposure to low concentrations, manifest by perpetual yellowing of the plant foliage following the alteration of the chlorophyll production mechanism. It seems that, to the acute effects, the plant defend itself transforming sulfur dioxide into sulfuric acid and then in sulfates that are deposited in certain portions of tissues, but soon the balance of sulfates is disturbed and sulfuric acid appears in the plant cellular system which attacks its cells. Chronic effects are due to sulfate aggregations. Sulfur dioxide in small concentration (on the order of the size of 100 - 500 $\mu g/m^3$) react synergistically with both ozone and nitrogen dioxide, which affects the plants tissue, especially as these are more sensitive.

Sulfur dioxide and sulfuric acid formed have very corrosive action on metals, constructions, leather, paper and textiles, especially if relative humidity of air exceeds 70%. Attack of construction materials by SO_2 is due to next mechanism: SO_2 in the atmosphere prompts a condensation of water vapors as fog even when their partial pressure is lower than the saturation pressure at that temperature, due to the fact that SO_2 form with water a solution which a lower vapor pressure than pure water, slip by easily as fog state; the phenomenon can be facilitated by existing aerosols as particles in the smoke, which forms condensation nuclei. In soft drops of fog with SO_2 is obtained sulfurous acid and its oxidation to sulfuric acid. Reducing character of SO_2 manifests also by changing the color of some paint pigments. As such it is affected lead white. Calcium carbonate, a constituent of many construction materials, some of which serve to works of arts, is transformed into calcium sulfate. Destructive effect is accelerated by the acid rains.

In 1983 the first symptoms of forests etching have appeared in Western Europe, due to acid rains which gather both acid pollution and photooxidant pollution. It has been established that acidity in the atmosphere, most often originates in a ratio of 2/3 due to emissions of sulfur oxides, less than 1/3 because of NO_x, and the rest due to pollutants as fluorine or chlorine. Photooxidant pollution is due transforming NO_x in the presence of hydrocarbons and solar radiation.

Beside the negative effects outlined above, the presence of sulfur oxides in the air space reduces the visibility when the fog photochemical processes occurring and determines the appearance of an unpleasant smell.

In the atmosphere, oxidation of SO_2 to SO_3 takes place mainly through a photochemical process, although there are some opinions that it could take place catalytic processes also. During these reactions the presence of other pollutants such as nitrogen oxides or metal oxides may play an important role to accelerate the reactions. But there are occuring other factors such as concentration, residence time in the atmosphere, temperature, humidity, intensity and spectral distribution of radiations. In boilers furnaces sulfur trioxide, or sulfuric anhydride SO_3, derives from the oxidation sulfur dioxide. Actually, in the combustion gases is found 3-5% of the initial sulfur contained in the fuel, as SO_3.

Under certain circumstances SO_2 combines with water vapors, giving sulfurous acid gas H_2SO_3 and SO_3 combines still with water vapors, giving gaseous sulfuric acid H_2SO_4. Acid

vapors condensation on cold walls attack metals. Beside corrosion, due to SO_4H_2 vapors condensation, especially in thermal uninsulated funnels, it is favored the agglomeration of solid particles of soot and flying coke, who create acid rain too.

The fight against acid corrosion and pollution is done in three ways:

• Preventing the forming of anhydrides, especially SO_3;
• Neutralizing the formation of acids;
• Preventing the condensation of formed acid vapors.

Avoiding actual forming of anhydrides, means burning fuels with a low sulfur content. Heavy petroleum desulphurization is not generalized to an industrial scale today because of the high prices required. Fuels with low sulfur content can be subjected to industrial operations only when sulfur compounds are extremely harmful. Sometimes it is possible to have them burned out at low excesses of air, thus forming reduced SO_2 and SO_3 quantities. Limiting the excess of air at maximum 3% is difficult to do because:

• the burner must ensure the right mix between combustion air and fuel over the whole tuning;
• industrial boilers being equipped with numerous burners, each burner must have its own system of adjustment and control, which raise the cost of the related equipment. So the solution is applied only to very large boilers from thermoelectric power plants, which have numerous personnel for maintenance and exploitation.

Spraying silica allows to stop the catalytic action of deposits that form on the heating and overheating pipes, which reduces the amount of formed SO_3. Frequent cleaning of depositions of solid particles completes the action mentioned before, but does not reduce the formation of SO_3 from the flame. SO_3 action may be partially neutralized by injection into the combustion products of calcium carbonate, zinc oxide, dolomite and of ammonia, which allows some boilers to reduce significantly the corrosion of air preheaters. Injection technique is sensible and it must be assured a good distribution of the substances mentioned above, avoiding obstruction of the flue gas flow and solid particle entrainment in atmosphere. When using ammonia, neutralization does not stop at the stage of acid sulfate of ammonia, but it reaches the stage of neutral sulfate.

Primary procedures for reduction of SO_2 pollutant emissions make the desulphurization, reducing the content of SO_2 in the flue gas by injecting absorbent substances sprayed into the furnace, such as limestone, lime or dolomite. Desulphurization combustion can be seen as a primary technique for major reduction of SO_2, applied to certain types of boilers. For the first achieved version, when the flame is obtained from a conventional burner, the U.S. has developed an extensive research program LIMB (Limestone Injection in Multistage Burners) with several forms of application.

Desulphurization efficiency depends particularly on the magnitude of the temperatures in the furnace, but meritorious performances are obtained using high consumption of absorbent.

For the second achieved version, the combustion is developing in dense or circulating fluidized bed. Such techniques can achieve efficiencies of combustion and desulphurization with high values having a consumption of absorbent lower than the first version. It should be noted that circulating bed technique is superior as efficiency than the dense bed technique.

Dense fluidized bed is characterized by the flow speed, generally reduced, where the solid particles move relatively slow and require a moderate recirculation. Increasing the speed of flow, the volume occupied by the layer will increase, as the movement speed of solid

particles, which will require an intense recirculation of particles realizing the circulating fluidized bed. These particles are of two types:

- a kind of incompletely burned fuel, because the coal particles introduced into the furnace having a high temperature generate gaseous volatile mater and carbon tailing which require a much longer combustion time than the combustion gases;
- absorbent material, which is mostly limestone, which has three forms: $CaCO_3$, CaO and $CaSO_4$.

Because the system operates in stationary state, the continuously exhausted gases will have to contain very small quantities of combustible substances to obtain the highest possible energy efficiency. Also, the exhaust gases will contain $CaCO_3$ and CaO as well as a very high content of $CaSO_4$ for a good desulphurization. Conventional circulating fluidized bed boilers realize the burning and desulphurization in the same furnace known as reactor that is fed simultaneously with fuel and absorbent material. The differences between these boilers refer to the ways of extracting produced energy and the means of control operation of variation with load. IFP, Lardet-Babcock and Cecar made a boiler called self desulphurization to which combustion and desulphurization are produced in different rooms. This boiler has a circulating fluidized bed furnace which is fed with combustion gases, having the temperature of 500-850°C, instead of air, as conventional boilers are operating. Hot combustion gases, rich in SO_2, from the furnace, are routed through the loop of circulation of solid particles in suspension, where is added limestone. This loop does not have exchange surfaces for useful transfer of heat, so it is protected from the effects of the sulfuric corrosion. The combustion gases thus sweetened are directed to the heat exchange surfaces of a exhaust-heat boiler. Whatever the system, in principle, all types of boilers with circulating layer are operating with relatively soft particles of limestone, of a few hundred microns, rather than a few millimeters bed as the dense bed boilers user. We mention that circulating bed systems allow a better use of calcium than dense systems.

Although there are few studies of the kinetics for desulphurization in circulating bed, there are global and fragmentary results often achieved on industrial boilers where the degree of desulphurization was measured in given operational conditions, knowing the nature of absorbent and the fuel burned and the Ca/C ratio, respectively.

Secondary procedures for reducing pollutant emissions of SO_2 use desulphurization plants of exhaust gases. The most used are dry FGD (flue gas desulphurization) plants or wet FGD plants and to a lesser extent plants combined, for desulphurization and NOx reduction of exhaust gases, as DESONOX, which are regarded as techniques associated with BAT. FGD plants with lime or limestone wet scrubber have a rate of SO_2 reduction by 92-98%, those who dry scrubbers, with spray, by 85-92%.

Depending on the type of installation of boilers, old or (new), as its power, by applying the BAT techniques, the emission levels of SO_2, in mg/Nm^3, are limited, e.g. for liquid fuel (calculated at 3% O_2) to 350 (350) for powers under 100MWt, to 250 (200) for powers under 300MWt and to 200 (150) for powers over 300MWt (Directive 2008/1/EC, 2008).

The amount of SO_2 emitted in producing electricity and heat sector in European Union countries (EU-27) represents 69% of the total SO_2 emissions at their level (energy using industry sector is 10.2% and transportation 3.8%). Due to replacing solid and liquid fuels with high sulfur content with natural gases, the use of technologies of flue gas desulphurization and application in EU-27 of the new regulations which limited the sulfur content of some liquid fuels, the emissions of SO_2 have decreased from approx. 26000 kt, in 1990, by 71%, to approx. 7500 kt in 2007 (EEA -APE 001, 2010).
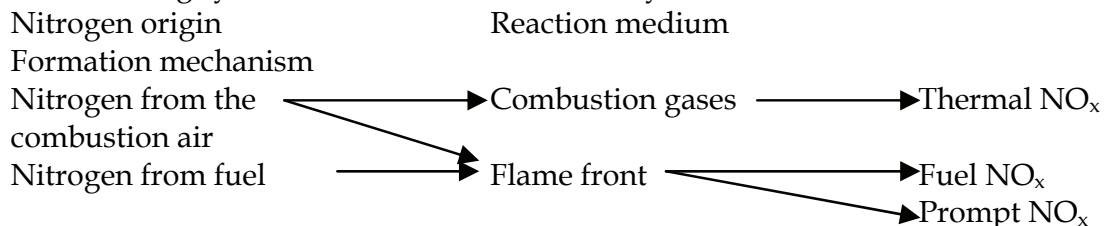
2.3 Nitrogen oxides

Among heavy users of the most polluting fossil fuels, through the NO_x emissions, are the means of transportation driven by spark ignition engines and compression ignition engines, followed by thermoelectric power plants and then by boilers and furnaces in the sector of energy use in Industry (EEA -APE 002, 2010).

NOx emission depends on the residence time of the molecules in the flame, most of NOx is formed in the second part of flame development, where the temperature is sufficiently high. Usage of the excess air raise the NOx equilibrium value, and the time needed to achieve balance is net superior to the stationary time of the molecules in the furnace, which explains the experimental values of NOx lower than the theoretical front.

There are three possible mechanisms of formation the NOx (De Soete,1982, Kramer, 1986, Skunca, 1981):

- thermal NOx from using the nitrogen from the combustion air;
- fuel NOx, by conversion of chemically bound nitrogen in the fuel;
- prompt NOx.

NOx forming synthesis is detailed schematically as follows:

Nitrogen origin   Reaction medium

Formation mechanism

Nitrogen from the ⟶ Combustion gases ⟶ Thermal NO_x
combustion air

Nitrogen from fuel ⟶ Flame front ⟶ Fuel NO_x
⟶ Prompt NO_x

The Zeldovich chain reaction pattern shows the exponential dependence for temperature of the emission of NO_x, until the temperature threshold is reached. The emission is directly proportional with the residence time in the furnace of the molecules and with the oxygen square concentration (Zeldovich, 1980).

The temperature is the strongest factor to influence the NO_x emission, exceeding significantly the influence of the oxygen concentration and the stationary time of the molecules. Stepped combustion is mainly intended to avoid forming high temperatures for reactants before reaching equilibrium, thus nitrogen oxides overall emission to be lower.

The wrong placement of the burners may determine through the jets interaction phenomenon local increases in temperature, which can lead to increased emissions of nitrogen oxides. Fuel nitrogen is present as organic compounds in the amines (NH and NC) and cyanides (CN) family.

These compounds react in two directions by:

- Reaction with substances that contain oxygen, forming NO and
- Reaction with substances containing nitrogen, forming molecular nitrogen.

Therefore not all the fuel nitrogen from combustion passes in NO_x.

Thermal NO formation occurs in the flame in the post-reaction area, according to distinct mechanisms corresponding to mixture of fuel with poor or rich air.

The main factors that influence the development of thermal NO production reactions are: the atomic oxygen concentration, the residence time of molecules and the temperature of the furnace, with higher values at 1300ºC, exert the strongest influence.

The reaction of molecular nitrogen with atomic oxygen is the slowest. Dissociation of molecular oxygen at normal combustion temperatures is insignificant. Thus, for example at 2000 K, atomic oxygen is formed having a concentration below 10 ppm.

NO formation from fuel nitrogen occurs in the flame after a complex mechanism, partially unknown. It is known that first CN radicals are formed, whose evolution in the presence of oxygen leads to the formation of NO. The main factors that influence the forming of NO in this case are the nitrogen content of the fuel, oxygen concentration in the fuel, residence time and the flame temperature.

NO formation from the nitrogen contained in the fuel flows a little faster than the formation of thermal NO, but is considerably slower than the prompt NO formation.

NO_2 formation occurs in the exhaust ducts of combustion gases, funnel and free atmosphere at temperatures below 650ºC, the main factors being: the temperature value, molecular oxygen O_2 concentration, residence time, air pollution and solar radiation.

Primary procedures for reducing pollutant emissions of NO_x have known three generations in development (ECE NOx Task Force, 1992)

- First generation consisting in reducing the temperature of the combustion air preheating (RAP), flue gas recirculation application in the furnace (FGR), use of low excess of combustion air (LEA) and burners-out-of-service (BOOS);
- The second generation consisting in production of low NO_x burners 1 (LNB) or air staging at burner, flue gas recirculation at burner (FGR) and over fire air (OFA);
- Third generation consisting in production of low NO_x burners 2 (LNB) or air and fuel - staging at burner and in furnace NOx reduction (IFNR) as well as burners improvement for NO_x decreased by increasing the internal flue gas recirculation.

In addition to these techniques there can be mentioned:

- Emulsification of oil with water;
- Injection of aerosols;
- Water-steam injection;
- Addition of fuel, combustion air, or spraying additives in flame (Ghia & Gaba, 2000).

NO_x emission depends on the size of volume of the furnace in which take place the development of flames produced by burners. Large furnaces allow the existence of higher temperatures in and after the area occupied by the flame, so the NO_x emission will increase, and the phenomenon is amplified by increasing the residence time. As a result, thermal charges of the volume and the cross section of the furnace represent important criteria for assessing the emissions of NO_x.

In large furnaces, which burn gaseous fuels, the NO_x emission is reduced by lowering the preheating temperature of the combustion air. Using this technique to oil burning is not recommended because it increases the percentage of unburned, especially soot production, as a result of lowering the burning temperature.

The amount of preheating temperature of the combustion air must have an optimum determined by the combustion to be more completely, NO_x emission below the normalized limit and high thermal efficiency for the heat production plant (Ghia & Gaba, 2000).

For industrial furnaces, where high temperatures in the furnace are required by the technological process, the amount of preheated temperature of the combustion air is dependent on this need taking into account, firstly, the type of the fuel used. Primary reduction of NO_x emission is done especially by removing the temperature peaks that are achieved mainly by the combustion gases recirculation.

Flue gases recirculation in the combustion air represent an efficient method of reduction of NO_x emissions for fuels and furnaces that allow development of high temperatures in the flame. The researches have shown that the most effective method of decreasing the levels of

NO_x is the recirculation gases mixture with the primary air or gaseous fuel, because in this case it acts on the maximum of temperature of the flame core. Thus the burning rate is reduced, which increase the length of the flame and reduces the NO_x content. As result there are necessary constructive changes to the burners and limiting the quantity of recirculation gases, so the complete combustion to be assured.

But it is noticed that by increasing the recirculation degree, the flue gas CO content is increasing, while the NO_x content is decreasing. Reducing the temperature of the flame decrease the useful transfer of the heat by convection, because of the increase of the gases flow from the combustion of fuel with recirculation flue gas flow.

To the Hrenox process, recirculation gases mixture with some cold combustion air is introduced into the burner separately from the rest of the combustion air that is preheated. For a high degree of flue gas recirculation of 15% and a proportion of cold air up to maximum 10%, the NO_x emission was below 200 mg/m³N for the combustion of gaseous fuels and below 250 mg/m³N for the combustion of high quality liquid industrial fuels.

Another way to reduce NO_x emissions is in using tertiary air injected through special slits, located above or below them.

The burners will work with decreased excess of air, the combustion being done by tertiary air which represent 15-30% of total combustion air. Often the application of this combustion technique is related to the existence of large furnaces, equipped with several rows of burners located at different heights, where only to the upper burners it may be introduced by blowing tertiary air.

Also, to the individual burners of natural gas, or oil, the burning in steps is a safe technique reduce the NO_x emissions. Combustion by-steps can be obtained by introducing fuel gradually by FS (air- fuel staged) process. The fuel added outside the primary burner forms a more under-stoichiometric flame after which, in the second stage NO_x is reduced by NH_3, HCN and CO radicals in N_2. Optimal proportion of the secondary fuel from total fuel consumption is 20-30%. The third stage follows when the process completes when the final combustion with reduced NO_x is done.

Insertion by-steps of the combustion air or fuel, reduces the NO_x emissions, but this process must be implemented by optimal constructive solutions, whereas the NO_x reduction processes are contrary to those of decreasing the CO and partially oxidized hydrocarbons.

The time required for combustion and reduction being relatively high, the FS process is recommended to apply to large furnaces. At the oil combustion, the FS process application may produce significant soot quantities in the primary flame, so it must be applied judiciously in case of combined oil-gas burners.

INFR combustion by-steps process implies the fuel injection in the furnace above the main combustion zone thereby causing a secondary under-stoichiometric area, after which it is added downstream the secondary air which completes the combustion. As a result, the combustion is divided into three zones. Hydro-carbonate radicals, formed in the second zone, occur to a temperature of over 1200ºC in the reduction atmosphere, reacting with nitrogen oxides produced in the main combustion zone so the N_2 and other components to be formed. In practice, reducing NO_x emissions by spraying water is rarely used, in large furnaces and only with superior fuels that form relatively high combustion temperatures and who have virtually no sulfur in the composition.

In the case of heat engines, primary measurements to reduce NO_x emissions refer to optimizing the combustion chamber, the injection or carburetion systems, engine operation with an appropriate adjustment, using recirculation of exhaust gases, to which it is added

the use of fuels treated by different methods (desulphurization, emulsifying with water, ultrasonic treatment).

Most of the researches conducted at the boilers to reduce the emissions of NO_x produced by burners referred to the oil - natural gas mixed burners to which the constructive solutions adopted are independent of fuel that they use. Primarily it is used the combustion by-steps and the combustion gases internal recirculation, as the ASR (Axial Stage Return Flow) burner is done. Part of the combustion air flow passes through the central tubing of the burner as primary air. The secondary air is repressed from the burner box through pipes equidistant distributed on a peripheric circumference, each pipe having two outputs for secondary air I and secondary air II, the supply being performed by a separate cold air fan. To delay the combustion with primary air, due to the ejection caused by axial repression with higher speed of secondary air, flue gases are absorbed from the furnace through a annular transversal section, forming a separating layer between the primary step and the secondary step. In this burner there were integrated essential components of techniques to reduce NO_x emissions:

- Supply with combustion air in three stages;
- Aspiration of the flue gas from the furnace ensuring internal recirculation;
- Separation of primary air from secondary air through a stream of combustion inert gases that reduces the burning rate;
- Liquid and gaseous fuels flows are adjustable allowing the control of the combustion processes to conditions of reduced NO_x.

Very low NO_x emissions were obtained by using the ASR burner alone and by applying additional techniques such as the addition of tertiary air, external flue gas recirculation and special spray nozzles for liquid fuel. To the combustion of oils with high sulfur content, according to the quality of these fuels, for entry into the solid particles and sulfur oxides emissions standards it is required the application of post-combustion control techniques that reside in the use of desulphurization systems, filters and cyclones.

For the furnaces of boilers burning solid fuel with low volatile content and a lot of bituminous ash having the liquid discharge of ash, NOx emissions level is relatively high. Since it is necessary to maintain a minimum value of the combustion gases temperature required for the liquids discharge of ash, NO_x emission control techniques are restricted in operation. Cyclone furnaces with second chamber downstream offer very good conditions for combustion by-steps. When inserted into the cyclone furnace the required air for combustion there are obtained high temperatures for oxygen excess, so the NOx emissions have high values to 1500-1800 mg/Nm^3. To the combustion by-steps the procedure is as follows:

- in the cyclone furnace is inserted about 80% of stoichiometric air;
- it is injected in the secondary chamber, as secondary and tertiary air, the remaining air required for fuel combustion. The optimal conditions for injection with tertiary air are met when the injection nozzles are designed and located so to provide the intimate mixture of the flue gas from the cyclone furnace and air. Respecting the above conditions, it was obtained a reduction in NO_x emissions of 30-40% depending on the operating mode. Further reduction in NO_x emissions was achieved by applying the external flue gas recirculation.

For mixed gas-oil burners the reduction of NO_x emissions is done by the swirling the combustion air to a turbulence degree of n<3 to prevent high temperature peaks as a result of excessive shortening of the flame.

Intensifying the internal recirculation of combustion gases is done with repressed secondary air with great speed through nozzles located at the end of the entry into splay, creating an important vacuum that absorb primary combustion products. Combustion air admission is done best in three steps to avoid local temperature increase to high values. It is recommended that the primary air to represent 55-60% of the total combustion air. Oil spraying is done especially with slightly overheated steam using Y-type injectors.

To reduce NO_x emissions and pollutants in general, it can be used the self-carburizing process for both boilers and furnaces (Gaba, 2010).

A low burner of original conception, with solid carbon particles formation in flame, is fitted on three condensation boilers for steam and hot water. The main burner elements provide the formation of annular jet of combustion air mixed with natural gas and of central fuel jet, which, by thermal cracking, forms subsequently particles of solid carbon. These particles lead to increase of flame emissivity. Having in view the NOx emission, the characteristics of this burner are the following:

- use of natural gas as fuel;
- the solid carbon particles formation in flame;
- three stages mixing of the fuel in the combustion air;
- the swirling motion of the ventilated combustion air.

The low NOx burner for boilers demonstrated excellent NOx and CO performance, producing emission levels below 60 ppm for CO(1.05 air ratio at nominal power and 1.09 air ratio at minimum power) and below 50 ppm for NOx (1.03 air ratio at nominal power and 1.09 air ratio at minimum power), operating with natural gas (Gaba, 2010).

Another low NOx burner of original conception, with solid carbon particles formation in flame, is fitted on forge and treatment furnaces (Gaba, 2009). The main constructive elements of this low NOx recuperative burner are: a ceramic quarl, a zone for the natural gas-ventilated air mixture, a zone for fuel atomization by collision with the compressed air, an air preheater and an ejector for exhaust gases. The ceramic quarl burner has a cylindrical combustion chamber and in the peripherical zone a few cylindrical channels for exhaust gases entrances. Between combustion chamber and cylindrical channels are another channels for exhaust gases recirculation. The zone for the natural gas-ventilated combustion air includes three concentric pipes: the central pipe with different orifices and nozzles for natural gas and two pipes for divided combustion air in primary, secondary and tertiary air. The air preheater ensures the heat exchange from exhaust gases to combustion air. Having in view the NO_x emission, the characteristics of this burner are the following:

- use of natural gas or heavy fuel;
- three stages mixing of the fuel with the combustion air;
- the solid carbon particles formation in flame;
- the exhaust gases recirculation.

The low NO_x recuperative burner demonstrated excellent NO_x and CO performance, producing emission levels below 30[50] ppm for CO(1.03 [1.08]air ratio, and 700⁰C furnace temperature) and below 120 [160] ppm for NO_x (1.30 [1.35] air ratio, and 1200⁰C furnace temperature), operating with natural gas[heavy fuel] (Gaba, 2009).

In conclusion, the solutions for upgrading the combustion plants for fossil fuels for boilers and furnaces can be grouped into:

- the completion of the measurement, control and automation equipment and establishing optimal operating parameters;

- the development of new types of burners;
- the development of new combustion installations with high complexity.

The following can be a part of the first type of solutions:

- operation with optimal values of the coefficient of combustion excess;
- operation with optimal values of the preheating temperature of the combustion air and the gaseous fuel, like BFG (blast furnace gas) that is used;
- operation with an optimal number of burners with a given unitary capacity.

The second group refers to making of:

- burners with the insertion by-steps of combustion air or fuel;
- burners with internal recirculation of flue gas;
- burners having gradual combustion.

In the last group of solutions there are:

- making of combustion plants with external recirculation;
- making of combustion plants with water-fuel liquid emulsions or additived aerosols for fluid ionization in the furnace;
- replacing of the solid fuels with liquid or gaseous fuels that are less pollutant. By applying primary techniques, the rate of reduction of NO_x emissions is 10-44% for operating with reduced air excess, 10-70% at the insertion by-steps of the fuel or oxidizer, 20-50% at flue gas recirculation, 20-30% at low preheating of the combustion air and 25-60% to use low NO_x burners.

Secondary procedures for reducing NO_x pollutant emissions use flue gases treatment plants. The most commonly used installations are SNCR (selective non-catalytic reduction) and SCR (selective catalytic reduction). In a less extent combined plants are used for desulphurization and NO_x reduction of exhaust gases, DESONOX and active carbon plants (ECE NO_x Task Force, 1992). Selective Catalytic Reduction occurs at temperatures of 300-400°C in the presence of catalysts, by injecting ammonia (NH_3). Catalysts used: TiO_2, WO_3, V_2O_5.

The rate of reduction of nitrogen oxides is 80-95% for SCR installations. Selective non-catalytic reduction occurs at temperatures of 900-1000°C in the absence of catalysts, by ammonia injection. The rate of reduction of nitrogen oxides is 30-50% (ECE NO_x Task Force, 1992).

The reactions presented in the literature are selective, indicating oxidation of ammonia and sulfur dioxide (SO_2) may not occur, the presence of oxygen being essential in the development of some reactions.

Treatment of exhaust gases by passing them in the activated carbon reactor is done at temperatures of 100-150°C.

Depending on the type of installation, old or (new), by applying BAT (best available techniques), the emission levels of NO_x, calculated as NO_2, in mg/Nm³, are limited to 100 (100) for boilers, operating on gaseous fuels (calculated at 3% O_2), to 90 (50) for gas turbines (calculated at 15% O_2) and to 100 (75) for internal combustion engines, stationary, for gaseous fuel, calculated at 15% O_2. In case of using liquid fuels on boiler installations, depending on the type of installation, old or (new), and its power by applying the BAT techniques, emission levels of SO_2, in mg/Nm³, calculated at 3% O_2, are limited to 350 (350) for power below 100MWt, 250 (200) for power below 300MWt and 200 (150) for power over 300MWt (Directive 2008/1/EC, 2008).

The amount of NO_x emitted in the means of transport sector in European Union countries (EU-27) represent 46.3% of the total of NO_x emissions at their level (electricity and heat

generation sector represent 20.5% and energy using industry represents 13.9%). Due mainly to use low NO_x combustion technology, to the replacement of solid fuels to natural gases, to the use flue gases treatment (selective non-catalytic and selective catalytic) emissions of SO_2 decreased from approx. 16900 kt, in 1990, with 31% to about 10300 kt in 2007 (EEA – APE 002, 2010).

2.4 Solid particles

Particles released into the atmosphere come both from combustion processes and the entrainment by the combustion gases from the raw material, e.g. rotary drum furnaces for clinker, limestone, dolomite, etc.

Result of the combustion processes, the black smoke is a heterogeneous mixture and variable in structure, between soft solid particulates, water vapors and gases that result from the incomplete combustion of fuels. As a result of the reduced size of suspended solid particles, the smoke refract light and color depending on the concentration and color of substances component in it. That is why the smoke comes in large range of dark colors from the weak gray to black, depending especially by the degree of perfection of the combustion and the quality of burned fuels. The determination of the index that characterizes smoke color is used for technical control of combustion quality, in combating environmental pollution, resulted in particular from burning of solid fuels and lower oils (Bacharach no.). Generally, the formation of unburned solid materials in fossil fuels flames is pointing out especially the wrong mixing between fuel with air that is insufficient to achieve combustion even before carbon oxide is obtained. To liquid fuels without mineral content these solid particles can virtually disappear by burning that if the oxygen is in adequate proportions, in warm enough areas of the furnaces and for a sufficient residence time. In black smoke it is noticed the emergence of two categories of unburned solid: very soft particles of soot and particles much larger than the first, sometimes called cenospheres from intermediate and heavy fuel combustion, or especially flying coke by combustion of solid fuels.

The mechanism of the formation process of soot particles in gaseous fuels flames is explained by theories that belong to three main groups. Thus, the first group includes theories that explain formation by thermal decomposition of hydrocarbons in fuel in carbon and hydrogen, with subsequent polymerization of the carbon. The second group of theories explains soot formation by oxidation of hydrocarbons until peroxides are formed and then by decomposition of peroxides free radicals are divided, which favors higher hydrocarbon formation, which under the high temperatures in the flame, are decomposing to form solid carbon particles. The third group of theories involves the formation of soot particles in flame by polymerization of the C_2 radical.

All these theories have a qualitative character, experiments verifying only certain assumptions that are made. The main factors that prompt the formation, quantity, quality and size of soot particles are as following (De Soete & Feugier, 1974):

- the degree of fuel enrichment (dosage), or lack of required air for stoichiometric combustion;
- physico-chemical properties of fuels, determined by the gravimetrically report C/H of carbon and hydrogen from fuels and by the molecular mass;
- the conditions of mixing fuel with combustion air which may be sufficient but unevenly distributed in relation to fuel gas;
- the temperature level in the combustion chamber, as the temperature rises the polymerization and hydrocarbon cracking processes intensify;

- the pressure in the combustion chamber which, by increasing, it intensifies the formation of soot process in flame.

The burner of industrial liquid fuels create the fuels spraying as drops, firstly, to increase their surface in contact with the oxidizer. Spraying of liquid fuels in the form of drops jets that ignite in a gaseous environment that lacks the oxygen required for complete combustion, can generate soft soot particles and relatively large solid particles with average diameter up to 100 µm.These last ones having a spongy aspect and spherical form, thus called cenospheres, are more numerous as the liquid fuel is more heavy, meaning that it contains molecules with more carbon atoms.

The cenospheres result from cracking hydrocarbons in liquid phase as soft drops, through decomposition reactions that lead to release of gaseous products and building of solid residue rich in carbon, but which also contains minerals from the original fuel. Similarly, the flying coke is made from soft coal particles, sprayed with air blast at coal dust operating burners. The heavy liquid fuels, in particular, build solid tailings from sediments and organ-metallic compounds that associate with carbon cracking residues. Overall mass of solid particles thus formed for heavy fuels may be in the order of a few decigrams per kilogram of fuel.

Cenospheres are in smaller numbers than particles of soot, but their overall mass is generally much bigger. Essentially, the presence of these relatively large solid particles, sometimes make the regulations compliance on pollution from the combustion of heavy liquid fuels difficult (Ghia & Gaba, 2000).

Given the size of cenospheres, their combustion is slower than the combustion of soot particles. This combustion is essentially controlled by the diffusion phenomena. Thus, its influence is decisive on: diffusion rate of oxygen to particle, diffusion rate of gases resulted from combustion by the ambient gaseous environment, the particle temperature and the activation energy of substances at work. It should not be missed the fact that the hydrocarbon skeleton of cenospheres contains mineral elements originally present in the fuel. These elements may be particularly harmful in contact with the heating furnaces charge, with the elaboration furnaces bath, refraction bricks from the furnace's walls, boilers or chemical industry ovens pipes. A negative example is the harmful action of vanadium salts on steel at temperatures above 600ºC. In flame, the vanadium is present mainly as V_2O_5 because V_2O_4, V_2O_3 and V_3O_5 oxides can be considered as intermediate steps to V_2O_5. When using a good quality combustion plant and properly exploited, the solid particles mostly disappear by burning, leaving behind ashes of the initial mineral mass of fuel. To the heat generators operating on industrial liquid fuels is imposed that solid suspensions should not exceed 100-200 mg/kg of fuel. This prevents the excessive pollution of the environment and the excessive increase of maintenance costs associated with deposition cleaning on the heat change pipes. Oil use with high sulfur content, requires operation at low excess of air close to the stoichiometric value, to reduce corrosion at low temperature. It is favored this way the increase of losses by unburned particles related to the soot and cenospheres and flying coke respectively. Reducing these polluting emissions is directly influenced by the ratio between carbon C and hydrogen H of the initial fuel and the presence of asfaltenes in oil.

Gaseous fuels with a high ratio C/H produce soot easier than those with the lower C/H ratio. Soot production in the flame makes this to be brighter and to transfer more useable heat by radiation. As a result of this advantage, there was developed a process (called self - carburizing) by which carbon particles produced in the initial zone of the flame are completely

oxidized to the top of the flame. This procedure has been used on some burners of boilers and furnaces, proving at the same time with the increasing efficiency very effective to reduce the emissions of CO, NO_x and partially oxidized hydrocarbons (Gaba, 2010).

Primary procedures for reducing particles emissions, are to replace the solid and heavy liquid fuels (oil) with light liquid fuel combustions and to use complete combustion methods.

Primary processes that reduce particle emissions resulting from incomplete combustion of liquid fuel are:

- prior physical treatment of liquid fuel consisting in preheating, filtration, centrifugation to remove the largest part of sediments, water, soft particles of minerals;
- high quality spraying of which are essential choosing of optimal spraying system, well adjusted preheat temperature of the fuel. After spraying by mechanical injection under pressure of heavy liquid fuels, a variation of the viscosity of dozen centistokes modify essentially the spraying features, with great repercussions on the process of combustion;
- fuel combustion with preheated air with a moderated air excess (below 30%), using especially overheated steam spraying;
- Improvement, by addition, of the combustion characteristics of industrial fuels used;
- Use of modern combustion techniques such as aerosols combustion, or water - liquid fuels emulsions combustion (with 3% - 5% water).

Secondary procedures for reducing particles emissions, most used by boilers and furnaces are:

- dry mechanical refinement, by which the particles settling is done under the action of gravity and/or centrifugal force;
- Wet refinement by passing the gases under a liquid mist;
- Refinement by filtration, by passing gases through porous materials;
- Electrical refinement by gas ionization and dispersed particles sedimentation in a high-voltage electrical field. There are considered BAT techniques the use of electrical filters (ESP), textile fabric filters (FF), the wet scrubbers and cyclones, when the latter are used together with ESP or FF. The retention efficiency of ESP for particles larger than 1μm, is 96.5%, the FF is 99.95%, the wet scrubber is 98.5%, and the cyclone is over 85% for particles larger than 5μm (Directive 2008/1/EC, 2008).

Depending on the type of installation of boilers, old or (new), also on its power, by applying the BAT techniques, the levels of particles emission, in mg/Nm³, are limited to 30 (20) for powers below 100MWt, 25 (20) for powers below 300MWt and 20 (10) for powers over 300MWt, for liquid fuel (calculated at 3% O_2) and for solid fuels (coal and lignite), calculated at 6% O2. For internal combustion engines, stationary, liquid fuel, BAT associated filtering techniques can lead to a maximum value of 30 mg/ Nm³, gas oil and 50 mg / Nm³, heavy liquid fuel (Directive 2008/1/EC, 2008).

The amount of PM 10 particles, with diameters less than 10μm, in European Union countries (EU-27), as primary products (directly discharged into the atmosphere) and secondary (derived from the precursors NO_x, SO_2 and NH_3, transformed by photochemical reactions into particles) were reduced by 53% between 1990-2005. The direct amount of PM10 were reduced from 4779 kt in 1990 to 2491 kt in 2005, and the secondary from 33588 kt to 19629 kt. The sector of combustion processes represents 70% of the overall direct emissions of particulates and 90% of the total secondary products. The sector of energy using industry

represented 39% of the overall direct emissions of PM10 particulates in 1990 and reached at 13% in 2005, the industry of power generating represented 14% of the overall emissions of PM10 particles in 1990 and reached 10% in 2005, and the means of transport reached from 13% to 21%. The sector of energy using industry represented 39% of the total secondary emission of PM10 particles in 1990 and reached 26% in 2005, the industry of power generation represented 15% of the total secondary emissions of PM 10 particles in 1990 and reached 11% in 2005, and the means of transport reached from 26% to 29%. These substantial reductions were done, due to the dusting techniques of the exhaust gases, the replacement of solid and liquid fuels with high content in sulfur with natural gases, the introduction of the primary techniques for achieving combustion with reduced NO_x emissions, the use of flue gases treatment and the application in EU-27 of new regulations which limited the content of sulfur from some liquid fuels and which used advanced catalysts in internal combustion engines for transportation (EEA– EN 07,2010).

2.5 Volatile organic compounds (VOCs) and persistent organic pollutants (POPs)

Volatile organic compounds are aliphatic and aromatic hydrocarbons, alcohols, ketones, esters, aldehydes, benzene, toluene, acetones, methanol and formaldehydes.

POPs are mainly composed of polycyclic aromatic hydrocarbons (PAHs), resulted in combustion processes of fuels in a smaller extent, but with particularly harmful effects, from dioxins and furans, resulted from the incineration of waste, pesticides and products of chemical industry.

Partially oxidized hydrocarbons are generated by the lack of oxygen (combustion air) in combustion process, or from slow oxidation.

Lack of oxygen in the combustion process can be explained locally or temporarily, because combustion installation from industry are supplied with excess of combustion air. Due to poor mixing of fuel-combustion air, in the flame can occur rich zones in fuels which are formed unsaturated hydrocarbons, aldehydes and acids and, in some cases, the process can continue until the formation of soot. These unburned elements may evolve, behind the flame front, depending on thermodynamic parameters and the interaction of oxidants.

To achieve sufficiently high oxidation rates the following are necessary:

- to set the mixture of fuel gas - combustion air between flammability limits;
- achieving a level of temperature high enough ahead of the flame front;
- creating a bigger turbulence;
- ensuring that the various intermediate elements stay a sufficient period of time in the flame (Gaba, 2005).

In combustion processes, the objective of reducing VOCs is their volatilization and oxidation to CO_2 and H_2O, by thermal oxidation, catalytic or bio-oxidation. In the case of incinerators, especially, is practiced burning in secondary outbreaks, in which the catalysts can be introduced, after the primary focus.

Among the sectors of fuel combustion processes that produce VOCs, transport is the most significant with 18,6% of total EU emissions, the rest being insignificant. Between 1990 and 2007, road transport has reduced VOCs by 60%, as a result of using the three-way catalytic converter and the improvement of diesel quality (EEA – APE 004, 2010).

Among the sectors of fuel combustion processes that produce PAHs, residential heating sector is the most significant with 41% of total EU emissions, and transport represents 15%. Between 1990 and 2007, residential heating sector reduced the production of PAHs by 14% and road transport by 47%, mainly due to the advanced catalyst (EEA – APE 006, 2010).

2.6 Atmospheric greenhouse gas concentrations

Among the gases that produce greenhouse effect, the carbon dioxide has the most important contribution, its percentage being 65%. It appears in an overwhelmingly proportion after fuel combustion processes. In the year 2009 the concentration of CO_2 in the atmosphere was 387ppm. Carbon dioxide recently considered as pollutant, prevents the discharge of heat energy from the surface of the Earth which is acquired by radiation from the sun. As the time passes, even the increase with a few degrees of the temperature could lead to reduction of the land ice cap, the spread of deserts, raising sea and oceans levels, as well as important climate changes. The concentration of CO_2 in the atmosphere has increased by 38% compared to the pre-industrial age, when it was 280 ppm (EEA – CSI 013, 2010).

In 1990, a report of a United Nations committee has confirmed the tendency of heating of the globe and considered that, if the world will not take measures to stabilize the gas flow released in the atmosphere (carbon dioxide, methanol, gases from chemical fertilizers, various hydrocarbons), the temperature will rise by three degrees until 2000. A United Nations Framework Convention on Climate Changes was negotiated between 1991 - 1992 and signed at Rio Conference in 1992. The Convention entered into force in 1995. The main objective of the Convention was to stabilize the greenhouse gas concentrations from atmosphere, especially carbon dioxide, at a level that will not endanger climate system.

Kyoto Protocol, signed in 1997, with the exception of USA, is an extension of the UNFCCC (United Nations Framework Convention on Climate Change) from 1993 and is the first step in an effort to reduce the long-term changes in emissions to prevent climate changes. Both at the global (UNFCCC, 2009) and the EU level (October 2008 Environment Council conclusions) this "dangerous anthropogenic interference" has been recognized by formulating the objective of keeping the long-term global average temperature rise below 2°C compared to pre-industrial times.

There is a consensus in EU-27 countries for collective action to reduce greenhouse effect gas emanations by: improving techniques for burning fossil fuels, the use of renewable sources for energy production (water, sun, wind, geothermal energy), improving industrial technologies, decreasing the consumption of fuels for road transport, increasing the share of public transport, reduce emanation of animal manure, reduce the fertilizers based on nitrogen, stopping the clearance of forest and accelerated action of forestation, reducing waste and gases from municipal waste dumps, etc. The commitment taken by the EU-27 for 2008-2012 compared to 1997, is a reduction of 8% versus 5%, as was stipulated in the Kyoto Protocol (EEA- EN 07, 2010).

3. Determination of pollutant emissions in combustion processes

Quantitative determination of pollutant emissions refers to:

- The determination of pollutant concentration, c_i [mg/Nm^3], representing the concentration of pollutant i in the gases released in atmosphere, required to screening verification in the emission limits stipulated by the regulations;
- Determination of pollutant quantity emission, which represents the amount of pollutants released into the atmosphere over a specified period, usually one year, E_i [t], required to establish the activities contribution from combustion processes at general air pollution.

Determination of pollutant concentration, c_i [mg/Nm^3] and the amount of pollutants E_i [t] produced by a combustion plants requires knowledge of the effluent gaseous composition

in point of measurement. In addition, at determination of pollutant quantity emission, it is necessary to know the amount of fuel consumed during the period, in m^3N, for gaseous fuels, or kg for liquid or solid fuels [1].

The measurements are based on national norms, which are prescribed the measuring and calculation methodologies, type of measurement devices that are accepted, as well as the execution range for measurements. For large combustion plants requires continuous monitoring. The automatic devices that are used:

- gas analyzer to determine the volumetric concentrations, from the flue gas mixture, O_2 [% volumetric], CO_2 [% volumetric], CO [ppm], NO_x [ppm], NO_2 [ppm], and SO_2 [ppm];
- automatic device to determine the volatile organic compounds;
- automatic instrument, with isokinetic probe for determining particulate matter (Gaba, 2005).

Gaseous effluent concentrations measured values are required, on the one hand to determine the quantity of emissions of pollutants and on the other hand directly to determine the concentration (in mg/Nm^3) of the emission of pollutants. Calculation of concentrations of different pollutants emissions i, c_i [mg/Nm^3], related to reference conditions, it is required to be done to compare it with the limit values set by national regulations, for periods of time, depending on the type, age and power plant and fuel type consumed.

E.g. if the analyzer indicates a concentration of 60 ppm SO_2, 80 ppm NO_x and 10.5% O_2, to measurement of gaseous effluents produced by burning a liquid fuel, it can be calculated the concentration of pollutant emission of SO_2, C_{SO_2}, NO_x, C_{Nox}, respectively, related to reference conditions, as [1.10]:

$$c_{SO_x}\left(mg/Nm^3\right) = c_{SO_xmas}(ppm) \cdot k1 \cdot \frac{21 - c_{O_{2ref}}}{21 - c_{O_{2mas}}} \tag{1}$$

$$c_{NO_x}\left(mg/Nm^3\right) = c_{NO_xmas}(ppm) \cdot k2 \cdot \frac{21 - c_{O_{2ref}}}{21 - c_{O_{2mas}}}$$

where:

$c_{SO2\ mas}$ - SO_2 emission concentration measured in ppm;

$c_{Nox\ mas}$ - NO_x emission concentration measured in ppm;

k1 – 2.85 – ppm conversion factor → mg/Nm^3 for SO_2;

k2 – 2.05 – ppm conversion factor → mg/Nm^3 for NO_2;

$C_{O2\ ref}$ – 3% volumetric - reference oxygen concentration for a gaseous fuel according to EU norms;

$C_{O2\ mas}$ – measured oxygen concentration in the gaseous effluent, in volumetric %.

Replacing in (1) with numeric values it is obtained:

$$C_{SO_x} = 60 \cdot 2{,}85 \cdot \frac{21-3}{21-10{,}5} = 293{,}1\ mg/Nm^3 \tag{2}$$

$$C_{NO_x} = 80 \cdot 2{,}05 \cdot \frac{21-3}{21-10{,}5} = 281{,}1\ mg/Nm^3$$

The amount thus calculated is compared with the emission limit for SO_2 and NO_x respectively, according to national norms, which are usually set for some period of time, depending on the type, age and power of the plant and fuel type consumed.

In the case of large combustion plants, which consume liquid fuels, in Table 1 are presented associated BAT limit values, for NO_x emissions calculated as NO_2 and SO_2, in mg/Nm^3, for 3% O_2, depending on the type and power of the plant (Directive 2001/80/EC, 2001).

Crt. No.	Plant type	Pollutant	Measure unit	Thermal power, MWt		
				<100	100-300	>300
1	Old	SO_2	mg/Nm^3	350	250	200
2	Old	NO_x	mg/Nm^3	450	200	150
3	New	SO_2	mg/Nm^3	350	200	150
4	New	NO_x	mg/Nm^3	300	150	100

Table 1. Limit values of SO_2 and NO_x emissions for electricity and heating generation.

It is found that the values calculated for the exemplified installation would not exceed the limits unless it would have a thermal power less than 100 MW.

To determine the exact amount of a pollutant i, Ei, in t for a certain period, the general relation can be used:

$$E_i = ki \cdot V_{gu} \cdot B \cdot c_i \cdot 10^9 [t] \tag{3}$$

where:

ki – conversion factor for the i pollutant, ppm $\rightarrow$ mg/Nm^3;

V_{gu} – volume of dry burned gases produced by burning the fuel, in m^3N/m^3N or m^3N/kg;

B – fuel consumption, in Nm^3 of consumed gas in the respective period, or kg of liquid or solid fuel;

c_i – measured concentration of i pollutant, in ppm

The specialty papers shows calculating relations for the volume of dry flue gases resulting from combustion of various fuels [10]. For example, for combustion of gaseous fuels to find the volume of dry flue gases produced from burning a Nm^3 of fuel, use the following formula:

$$V_{gu} = \frac{CO_2^{(c)} + CO^{(c)} + \Sigma m C_m H_n^{(c)}}{CO_2^{(g.a)} + CO^{(g.a)} + \Sigma m C_m H_n^{(g.a)}} \tag{4}$$

Values in the numerator results from the initial analysis of fuel gas composition and the denominator values are measured at the exhaust of plant flue gases, for example with a flue gas analyzer.

For less accurate calculations, but faster, it is used the relationship:

$$E_i = fi \cdot B \cdot PCI \cdot 10^6 [t] \tag{5}$$

where:

fi – emission factor, in g/GJ;

B – fuel consumption, in Nm^3 of consumed gas in the in the respective period, or kg of liquid or solid fuel;

PCI – low calorific power of the fuel, in GJ/Nm^3, GJ/kg respectively.

The factors *fi* (in g/GJ, respectively $lb/10^6$ Btu), are used in the EU and U.S. respectively, to calculate the amount of pollutants emitted into the atmosphere over a period of time and are tabled according to the many types of fuels, installation, etc. (US EPA- AP 42, 1995). In Table 2 are summarized the approximate amounts of various pollutants to be emitted into the atmosphere worldwide, calculated with the emission factors *fi* (taking the values for coals, oils and natural gas) for fuel consumption in 2030 provided by the World Energy Outlook -2008.

crt. no.	Fuel type		Pollutant				
			SO_2	NO_x	CO	PM10	VOC_S
1	Coals	Emission factor [g/GJ]	10746.5	4083.67	1308.49	3094.99	21.49
		Pollutant quantity [kt]	2207331	838786	268766	635713	4414
2	Oils	Emission factor [g/GJ]	7307.62	1590.48	143.57	343.89	38.68
		Pollutant quantity [kt]	1562457	340064	30697	73528	8270
3	Natural gas	Emission factor [g/GJ]	0.0	601.80	150.88	12.89	25.79
		Pollutant quantity [kt]	0.0	92430	23173	1979	3961

Table 2. Approximate amounts of various pollutants to be emitted into the atmosphere worldwide, calculated with emission factors fi, for fuel consumption in 2030.

To these annual amounts of pollutants emission the amount of CO_2 is added, approximate for the year 2030, to approx. 30 million kt, which would lead to a planetary temperature exceeding by more than 2°C.To reduce the quantity of air pollutants emissions it is necessary that reduction measures and techniques to be generalized on a planetary scale Also there should be mentioned the EU-27 achievements in the period 1990-2007, that have significantly reduced emissions of pollutants into the atmosphere: CO by 63%, NO_x by 31%, SO_2 by 69%, VOCs by 41%, PAHs by 63% and PM10 by 53%. For the future, the key to success in reducing the air pollution is increasing energy efficiency and using regenerative resources. In 2009, the EU agrees a Climate and Energy Package to:

- reduce greenhouse gas emission by 20% by 2020;
- increase the share of renewable energy by 20% by 2020;
- improve energy efficiency by 20% by 2020 (EEA – EN 07, 2010).

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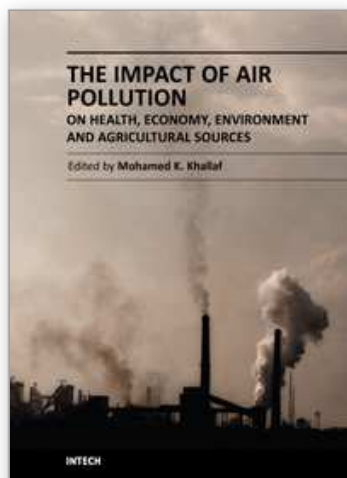
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The Impact of Air Pollution on Health, Economy, Environment and Agricultural Sources
Edited by Dr. Mohamed Khallaf

This book aims to strengthen the knowledge base dealing with Air Pollution. The book consists of 21 chapters dealing with Air Pollution and its effects in the fields of Health, Environment, Economy and Agricultural Sources. It is divided into four sections. The first one deals with effect of air pollution on health and human body organs. The second section includes the Impact of air pollution on plants and agricultural sources and methods of resistance. The third section includes environmental changes, geographic and climatic conditions due to air pollution. The fourth section includes case studies concerning of the impact of air pollution in the economy and development goals, such as, indoor air pollution in México, indoor air pollution and millennium development goals in Bangladesh, epidemiologic and economic impact of natural gas on indoor air pollution in Colombia and economic growth and air pollution in Iran during development programs. In this book the authors explain the definition of air pollution, the most important pollutants and their different sources and effects on humans and various fields of life. The authors offer different solutions to the problems resulting from air pollution.

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