

# Pollutant Formation in Combustion Processes

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## 1. Introduction

Each combustion process is a source of various emissions. During combustion, are formed not only carbon dioxide and water, but still a lot of other products of combustion and incomplete combustion. Knowledge of the mechanisms and the pathways of formation allow the use of so-called primary methods of reducing emissions and thereby reduce emissions to the atmosphere.

## 2. Various fuels composition

From the chemical point of view combustion is the oxidation reaction of organic compounds. Organic compounds - a variety of hydrocarbons which have in the molecule the atoms of carbon (C) and hydrogen (H). The oxidation reaction of hydrocarbons is accompanied by the emission of large amount of heat - that is why the reaction is exothermic. Hydrocarbons and their derivatives containing other atoms in the molecule, such as sulfur (S), nitrogen (N), oxygen (O), chlorine (Cl), etc. make a flammable substance which can be called fuel only when it meets certain qualitative conditions. Fuels can be divided according to several methods. One of them is the division according to the state of matter - into solid, liquid and gas fuels. Another method is the division according to the origin - natural fuels (e.g. fossil fuels) and synthetic fuels produced by processing natural fuels.

Natural solid fuels include mainly coal, lignite, peat, wood, etc. Natural liquid fuels include first of all oil from which numerous synthetic fuels such as petrol, kerosene, diesel, fuel oil, etc. are produced. In a group of natural gas fuels natural gas is crucial, while synthetic gas fuels include blast furnace gas, generator gas, water gas, city gas or extracted gas fractions such as methane, propane or butane as well as their mixtures.

Another type of fuel are wastes and produced from them the so-called alternative fuel which is known as refuse derived fuel (RDF) or secondary recovered fuel (SRF). Generally, fuel, in addition to the information about its form (physical state), is first of all characterized by elemental composition i.e. the contents of basic elements such as carbon (C), hydrogen (H), sulfur (S), nitrogen (N), oxygen (O), chlorine (Cl), etc. Apart from the contents of these elements, the content of water (W) and non-flammable substance (A), also known as ash, in the fuel are extremely important. Typical elemental composition of selected solid, liquid and gas fuels is shown in Table 1.

Fuel	C	H	O	N	S	Cl	W	A
hydrogen	-	100	-	-	-	-	-	-
acetylene	92,3	7,7	-	-	-	-	-	-
methane	75	25	-	-	-	-	-	-
propane	81,8	18,2	-	-	-	-	-	-
butane	83	17	-	-	-	-	-	-
natural gas	69,4	22,9	0,7	7,0	0,05	-	-	-
blast furnace gas	41,6	19,4	9,0	2,2	-	-	-	-
coke oven gas	15,0	50,0	23,0	12,0	-	-	8,5	-
petrol	85	15	-	-	0,05	-	-	-
diesel	87	13	-	-	0,05	-	-	-
heating oil	86	13	-	-	0,2	-	-	-
coal	72-83	3,4-5,3	1,8-12,5	1,0-1,2	0,1-6,5	0,1-1	3-20	3-30
lignite	25-77	2-6,5	1,5-20	0,1-0,5	0,2-6,5	0,1-1	10-60	3-30
peat	40	5	25	2	1	0,1	20	7
coke	80-90	0,3-1,5	1,0-2,0	1,2-2,2	0,5-1,0	0,5	1,5-8,5	2-17
wood	35-50	5-7	35-45	0,3-07	0,01-0,1	0,01	5-65	0,3-7

Table 1. Typical elemental composition of selected solid, liquid and gas fuels [in %]

### 3. Lower and upper heat value

The elemental composition determines another very important parameter which characterizes fuel i.e. heat of combustion so called upper heat value. Heat of combustion ( $H_o$ ) - is the amount of heat that is generated during complete and perfect burning of unit weight or unit volume of the analyzed substance in constant volume, wherein:

- temperature and pressure are constant,
- non-volume work is equal to zero,
- products of combustion are present at the initial temperature,
- water contained in exhaust gas is in liquid state,
- nitrogen in the products is in the form of molecules (as  $N_2$ ),
- sulfur contained in the fuel after combustion is in the form of  $SO_2$

The term complete combustion means the process in which all the fuel (organic matter) will be oxidized (burned) and perfect combustion occurs when all the combustion products are non-flammable. Data on typical values of combustion heat of the selected fuels are shown in Table 2.

Heat of combustion ( $H_o$ ) can be easily estimated on the basis of the elemental composition. The approximate value for the heat of combustion of solid and liquid fuels (upper heat value) can be calculated from the formula (Recknagel et al., 1994):

$$H_o = 34,8 \cdot C + 93,9 \cdot H + 10,5 \cdot S + 6,3 \cdot N - 10,8 \cdot O \quad (1)$$

where:

- $H_o$  - combustion heat [MJ/kg]  
 $C$  - carbon content in the fuel [kg/kg],  
 $H$  - hydrogen content in the fuel [kg/kg],  
 $S$  - sulfur content in the fuel [kg/kg],  
 $N$  - nitrogen content in the fuel [kg/kg],  
 $O$  - oxygen content in the fuel [kg/kg].

Fuel	Heat of combustion (upper heat value)	Heat value (lower heat value)
hydrogen	147,8	119,9
acetylene	49,9	48,2
methane	55,5	50,1
propane	50,3	46,4
butane	49,5	45,7
natural gas	41,1	37,5
blast furnace gas	4,1	4,0
coke oven gas	19,7	17,5
petrol	46,1	42,7
diesel	44,7	41,8
heating oil	44,8	42,7
coal		19-31
lignite		6-14
peat		12-16
coke		28-32
wood		10-18

Table 2. Combustion heat and calorific value of fuel (in MJ/kg)

Heat of combustion can be determined experimentally in an adiabatic calorimeter. However, fuel usually contains also water (moisture) whose presence and evaporation significantly reduces the amount of heat generated during the combustion of the fuel unit. In order to determine the amount of heat that can be effectively generated in the combustion process the concept of heat (calorific) value ( $H_u$ ), called the lower heat value, was introduced.

The calorific (heat) value is the amount of heat emitted during combustion of mass unit or volume unit of fuel at its complete and perfect combustion, assuming that the steam contained in the exhaust gas does not condense, even though the temperature of the exhaust gases reach the initial temperature of the fuel. Knowing the heat of combustion the calorific value can be calculated from the formula (Recknagel et al., 1994):

$$H_u = H_o - (9 \cdot H + W) \cdot r_w \quad (2)$$

where:

- $H_u$  - calorific value [MJ/kg]  
 $W$  - water content in the fuel [kg/kg],  
 $r_w$  - water evaporation heat [MJ/kg].

#### 4. Oxygen excess

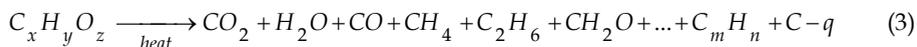
Every combustion process is conducted with an excess of oxygen relative to stoichiometric amount resulting from the oxidation reaction of individual components of the fuel. The measure of this excess is so called coefficient of excess air ( $\lambda$ ) defined as a ratio of the actual amount of air supplied to the combustion process to the theoretical amount of air required to carry out the complete and perfect combustion – the amount resulting from the stoichiometry of combustion (oxidation) reaction. If in the combustion process coefficient  $\lambda$  is equal to 1 then exactly the same amount of air that is required by the stoichiometry of the oxidation reaction is supplied to the process. If the coefficient  $\lambda$  amounts to less than 1 the combustion process is incomplete. As mentioned above, each actual combustion process is conducted with an excess of air, hence the coefficient  $\lambda$  is usually more than 1. Practically, its value depends on the type of fuel burned (gaseous and liquid fuels require less excess air than solid fuels) and design of the equipment in which combustion is carried out.

If the thermal process takes place without the presence of oxygen it is the process of pyrolysis. Pyrolysis – is the thermal decomposition of flammable substance without oxygen. This is an endothermic process that requires supplying heat from the outside. Pyrolysis process usually takes place at temperatures of 450-900°C in which the organic part of the fuel is converted into: the gas phase (pyrolysis gas), the liquid phase (pyrolysis oils) and solid phase (pyrolysis coke). Pyrolysis is sometimes also called degassing or carbonization. Depending on the temperature we distinguish: smouldering (below 600°C) and coking (above 600°C).

The composition and quantity of pyrolysis products depend on the type of fuel, their physicochemical properties and the temperature of the process. During the process of pyrolysis the mass of fuel is converted into (Thome-Kozmiensky, 1994):

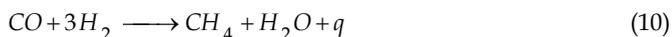
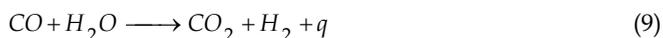
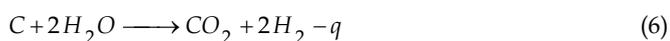
- pyrolysis gas containing mainly hydrogen, methane, ethane and their homologues, carbon monoxide and carbon dioxide as well as other compounds such as: hydrogen sulfide, ammonia, hydrogen chloride and hydrogen fluoride
- pyrolytic coke – a solid phase containing carbon and metals as well as other inert substances
- liquid phase containing a mixture of oils, tars and water as well as dissolved in it simple aldehydes, alcohols and organic acids.

The process of pyrolysis of hydrocarbons can be described by the following simplified chemical equation:

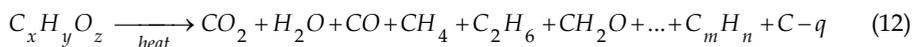


However, if the thermal process takes place with limited access of air (oxygen) – when the coefficient  $\lambda$  is less than 1, often fuel gasification process occurs. Gasification is a total

conversion of solid fuels into gas fuels under the influence of gasifying medium e.g. air or steam or both. During the flow through the glowing layers of solid fuel intended for the gasification a reaction of oxygen or water with carbon takes place in result of which carbon monoxide (CO) and hydrogen (H<sub>2</sub>) are formed as well as small amounts of methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), nitrogen (N<sub>2</sub>) and water steam (H<sub>2</sub>O). The process of gasification of solid hydrocarbons can be described by the following simplified chemical equations (Thome-Kozmiensky, 1994):



which are accompanied at the same time by thermal decomposition according to the simplified reaction equation:



Some of the mentioned above chemical reactions are exothermic (+q - proceeding with heat emission) and some endothermic (-q - requiring supplying heat from the outside).

## 5. Volume of flue gases from combustion processes

The stream of flue gases from the combustion process consists of a stream resulting from the oxidation reaction of flue gases and a stream of excess air supplied to the combustion process (with excess air coefficient  $\lambda$  greater than 1). Knowing the elemental composition of the fuel or only its calorific value it is possible to estimate both stoichiometric amount of air needed for combustion process and the amount of flue gases generated in the process.

For liquid and solid fuels, the amount of air needed for combustion reaction (stoichiometric) can be calculated from the formula (Recknagel et al., 1994):

$$V_T = 8,88 \cdot C + 26,44 \cdot H + 3,32 \cdot S - 3,33 \cdot O \quad (13)$$

where:

$V_T$  - minimal (stoichiometric) amount of air for combustion converted to standard conditions ( $T = 273K$ ,  $P = 1013hPa$ ) [ $m^3/kg$ ]

The volume of flue gases can be calculated on the basis of known elemental composition of the fuel from the formula (Recknagel et al., 1994):

$$V_S = 1,85 \cdot C + 11,11 \cdot H + 0,68 \cdot S + 0,8 \cdot N + 1,24 \cdot W \quad (14)$$

where:

$V_S$  - volume of flue gas from the combustion process converted to standard conditions [ $m^3/kg$ ]

$N$  - nitrogen content in the fuel [ $kg/kg$ ],

In case the elemental composition of fuel is not known the minimum amount of combustion air and exhaust gas volume can be calculated from approximate formulas taking into account only the calorific value of fuel (Recknagel et al., 1994):

- for solid fuel:

$$V_T = 0,241 \cdot H_u + 0,5 \quad (15)$$

$$V_S = 0,212 \cdot H_u + 1,65 \quad (16)$$

- for liquid fuel:

$$V_T = 0,203 \cdot H_u + 2,0 \quad (17)$$

$$V_S = 0,265 \cdot H_u \quad (18)$$

The total gas flow (after taking into account the excess air coefficient  $\lambda$ ) under normal conditions can be calculated from the formula:

$$V_C = (\lambda - 1) \cdot V_T + V_S \quad (19)$$

Multiplying the value of the total flue gas stream  $V_C$  by the amount of fuel burned per unit of time we can calculate the volumetric flow of flue gases from combustion process converted to standard conditions:

$$V_N = B \cdot V_C \quad (20)$$

where:

$V_N$  - volumetric flow of flue gases from the combustion process converted to standard conditions [ $m^3/h$ ]

$B$  - fuel consumption [ $kg/h$ ],

Taking into account the current temperature ( $T$ ) and flue gases pressure ( $P$ ) it is possible to estimate flue gas stream in the real conditions from the formula:

$$V = V_N \cdot \frac{T + 273}{273} \cdot \frac{1013}{P} \quad (21)$$

where:

$T$  – flue gas temperature [°C]

$P$  – flue gas pressure [hPa]

## 6. Combustion as an autothermal process

Heat emitted in a chemical reaction of oxidation in the combustion process is used for heating of flue gases from the process (combustion products and excess air supplied to the combustion process), solid secondary products of the combustion process (slag and ashes) and the equipment in which the combustion process is conducted (plus the obvious loss to the environment) up to the process temperature. This is illustrated in Figure 1.

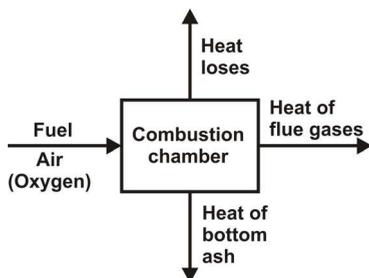


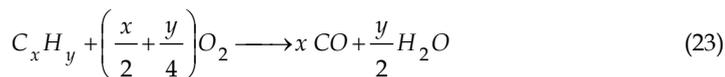
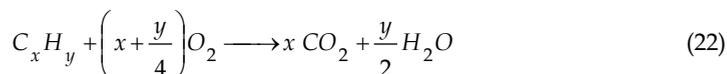
Fig. 1. Simplified heat balance in the combustion chamber

It is obvious that, if the generated amount of heat is too small, the combustion process does not run properly, its temperature is too low and the flue gases do not reach the required temperature. If, however, fuel of high calorific value is burned the amount of heat is sufficient to ensure proper combustion temperature and temperature of flue gases. This is particularly important in the case of waste incineration, where the law (Directive 2000/76/EC on the incineration of waste) requires that the exhaust gases have a minimum temperature of 850°C and remain in this temperature for at least 2 seconds when the waste fuel contains less than 1% chlorine. When the chlorine content in waste exceeds 1% it is required to achieve a minimum temperature of 1100°C. If the required temperature of flue gas (and the combustion process) is reached in the device, in which the combustion process is run, it is called autothermal combustion process, but when due to too low calorific value of fuel the required temperatures cannot be reached, combustion is not an autothermal process and requires additional fuel of higher calorific value.

## 7. Combustion as a set of chemical reactions

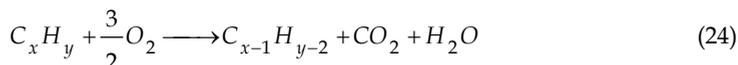
As mentioned at the beginning from the chemical point of view combustion is the reaction of oxidation of hydrocarbons. Combustion of gaseous fuel is the simplest combustion, in

which simple reaction of hydrocarbons oxidation takes place according to the simplified reaction scheme:



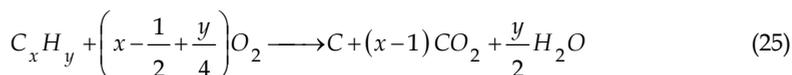
and the basic products of oxidation are carbon dioxide and water. In case of insufficient oxygenation of the combustion zone the additional reaction product is carbon monoxide. Flammable gas usually mixes well with air, causing a kinetic character of the combustion i.e. controlled by the rate of chemical oxidation reaction. In rare cases, when the flammable gas is mixed with air, the process can be controlled by diffusion of oxygen to the reaction zone. With inadequate oxygenation of the reaction zone the product of the combustion process is carbon monoxide, and elemental carbon (soot), because the reaction rate of water formation is higher than the rate of carbon oxidation.

Combustion of liquid fuels is a more complicated process, because to ensure the oxidation (combustion) it is necessary to evaporate the liquid, because its vapor is burned. Evaporation is promoted by the liquid spray, however, it is very difficult to obtain a homogeneous mixture of liquid vapor and air, hence the combustion of liquid fuels has rarely kinetic character, usually this is a diffusion combustion. Organic liquids generally have a more complex chemical structure than gases, and hence more often we are dealing with the formation of products of incomplete combustion, some of them being other organic compounds:



of course simpler than the compound that is subject to burning.

In extreme cases there can be a situation when due to shortage of air in result of the combustion process the decomposition of organic compounds contained in the fuel will be incomplete and not all carbon will be oxidized. Consequently, in addition to gaseous products from the combustion process a solid product will be also formed - elemental carbon (C) or soot:



The process of solid fuel combustion runs in even more complicated way. It is a multidirectional and multi-stage process, a combination of combustion (oxidation), gasification, thermal decomposition, including pyrolysis (lack of oxygen process). One should be aware that direct heterogeneous reaction between gaseous oxygen and solid hydrocarbon is problematic and because of the hetero phases it must be slow. Thus, direct combustion of solid phase fuel runs in a minimal degree. The real combustion process is

much more complicated. In the initial period, at sufficiently high temperatures degassing processes (pyrolysis) begin and flammable gases are emitted from the solid fuel. They are relatively easily oxidized (burned) in the gas phase generating heat flux heating the solid phase and accelerating the release of flammable gases. These processes run as long as fuel in a given element does not run out of hydrogen. The solid phase in result of degassing is enriched in the process of carbonization in carbon hence degassing process (the release of flammable gases) is accompanied by solid phase carbonization. At this point a change in the mechanism of the process takes place and the process of gasification of solid fuel begins (using air and/or steam), which results in carbonization phase being converted into flammable gases (carbon monoxide and hydrogen), which then in the gas phase are oxidized (burning). In the gas phase the oxidation reaction dominates, however, at the same time a number of other reactions take place - such as synthesis, cyclization, etc.

Apart from that we should not forget about other reactions running in parallel such as Boudouard reaction in which carbon dioxide, previously formed during the combustion, at the temperature in the range 400-950°C can be reduced with the participation of carbon to less oxidized form - a flammable carbon monoxide according to the equation:



which can participate in further reactions e.g. oxidation.

It is assumed that depending on the temperature in the combustion process of solid fuels several important steps can be defined (Thome-Kozmiensky, 1994):

- 100–200°C - thermal drying process, separation of water (physical process),
- 250°C - deoxidation reductive processes, reduction, decomposition of sulfuric acid esters, separation of bound moisture and carbon dioxide, depolymerization, the beginning of the release of hydrogen sulfide,
- 340°C - formation of aliphatic compounds, including unsaturated, the beginning of release of methane and other aliphatic compounds,
- 380°C - beginning of carbonization in the smouldering process,
- 400°C - beginning of the formation of the compounds of carbon with oxygen and nitrogen,
- 400–600°C - transformation of bituminous substances into smouldering oil or tar,
- 600°C - cracking of bituminous substances in the direction of thermally persistent substances (gases, hydrocarbons of short chain structure), formation of new compounds (benzene derivatives in result of cyclization of unsaturated aliphatic compounds),
- > 600°C - further course of the hypothetical reaction of dimerization of butylene formation, dehydration to butadiene, the formation of cyclohexane  $\text{C}_6\text{H}_{12}$ , thermal aromatization to benzene and other higher aromatic compounds.

## 8. Complete and uncompleted combustion

However, we should be aware that the actual combustion process is far from ideal - that is complete and perfect combustion. The combustion process (thermal decomposition and

oxidation) of many organic compounds (in particular those contained in the waste) is not a perfect process that produces only carbon dioxide, carbon monoxide and water. In this process usually a large number of intermediate products of decomposition and oxidation are formed which then are not further decomposed. It would seem that in the drastic combustion conditions, at about 1000°C any organic material must be burned. Unfortunately this is not true. Many chemical compounds, often flammable, are not subject to complete destruction during process of combustion. Some of the organic compounds are generated in result of many secondary reactions running in the combustion zone and outside it. Simplified diagram of the formation of pollutants in combustion processes is shown in Figure 2.

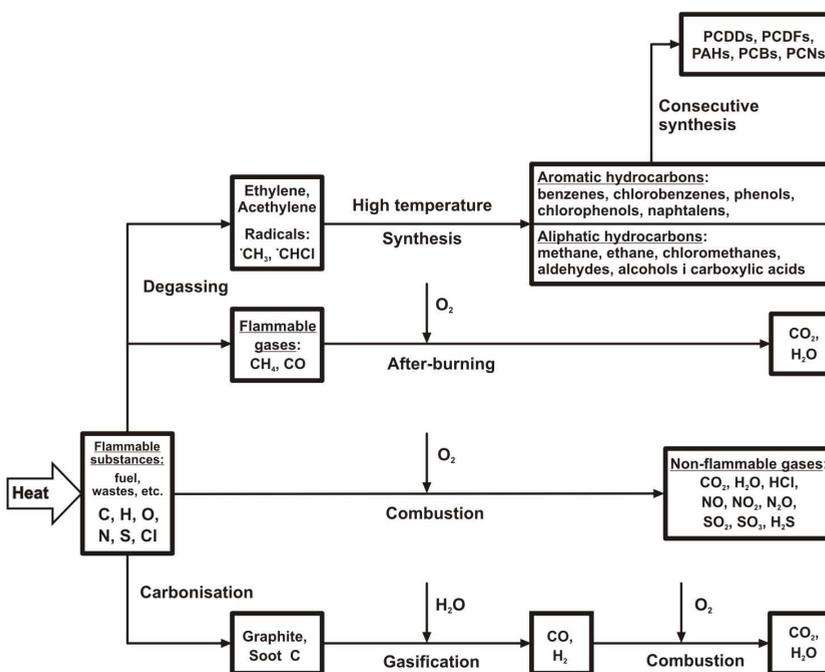


Fig. 2. Simplified diagram of the formation of pollutants in the combustion process of solid flammable substance (fuel, waste, etc.)

In the process of fuel combustion there are four main pathways. The first pathway - direct oxidation reactions. If we treat fuel as a collection of various chemicals consisting of carbon, hydrogen, oxygen, nitrogen, sulfur, chlorine, etc. so in result of direct oxidation typical flammable gases will appear such as carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O) in accordance with reaction equation (22) and also sulfur dioxide (SO<sub>2</sub>), nitrogen oxides (NO, NO<sub>2</sub>, N<sub>2</sub>O) or hydrogen chloride (HCl). At the same time the combustion process will be conducted according to other two pathways. In the process of thermal decomposition flammable gases will be emitted that contain for example carbon monoxide (CO), methane (CH<sub>4</sub>) and other simple hydrocarbons, which are relatively easily oxidized to carbon dioxide and water in the gas phase. Thermal decomposition process impoverishes the solid phase of fuel in hydrogen and other volatile substances, causing its carbonization.

On the third pathway carbonized solid phase is gasified with water and/or air to carbon monoxide and hydrogen which in the gas phase are easily oxidized to carbon dioxide and water. The last fourth pathway of the course of combustion processes is a secondary synthesis path. In result of decomposition and gasification processes in the gas phase simple hydrocarbons and hydrocarbon radicals are formed. Since virtually all fuels contain trace admixtures of chlorine (carbon even sometimes even about 1%!) in the gas phase there are also simple chlorinated hydrocarbons (including unsaturated - for example, acetylene  $C_2H_6$ ) and chlorinated hydrocarbon radicals. They are extremely reactive and in the gas phase appear a number of synthesis reactions, including cyclization. In this way chlorinated and non-chlorinated aliphatic hydrocarbons are formed (methane, ethane, chloromethanes, chloroethanes etc., aldehydes: e.g. formaldehyde and acetaldehyde, alcohols: e.g. methanol, simple carboxylic acids: e.g. formic acid and acetic acid) and aromatic hydrocarbons (benzenes, chlorobenzenes, phenols and chlorophenols, naphthalenes and many others). The latter take part in the synthesis of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs) and polycyclic aromatic hydrocarbons (PAHs) (Wielgościński, 2009).

## 9. Formation of sulphur oxides

Practically all fuels solid, liquid and gas contain some amounts of sulphur (Table 3).

Kind of fuel	Sulphur content
Gas fuels: LNG, CNG, LPG	below 0,01%
Diesel oil	below 0,10%
Petrol	below 0,05%
Heating oil	0,2 - 0,3%
Wood	0,02 - 0,04%
Coal (Poland)	0,5 - 2,5%
Coal (World)	0,1 - 4,5%
Lignite (Poland)	0,4 - 1,2%
Lignite (World)	0,4 - 6,5%
Coke	0,2 - 1,0%
Municipal waste	0,2 - 0,6%

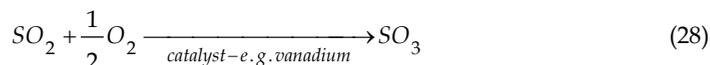
Table 3. Sulphur content in different fuels

Sulphur in the combustion process is relatively easily oxidized to sulphur dioxide ( $SO_2$ ) in accordance with the simplified reaction scheme.



The rate of this reaction at temperatures, under which the combustion process is run, is very high. On the basis of many research results it can be assumed that approximately 90-95% of the sulfur contained in fuel in the combustion process will be oxidized to  $SO_2$ . The presence

in the burned material of the non-combustible fraction containing some metals (e.g. vanadium - V) will result in partial catalytic oxidation of the formed sulfur dioxide to sulfur trioxide ( $SO_3$ ) in accordance with reaction equation:



Coal as a chemical element, like hydrogen, has reductive properties. In high temperature accompanying the combustion process, in the conditions of limited access of oxygen, in the presence of hydrogen in the gasification reaction, sulfur contained in the fuel can be reduced to hydrogen sulphide according to reaction equation:



Hydrogen sulphide formed during the reaction (30) is a flammable gas and at a later stage may be oxidized to sulphur dioxide and water according to reaction equation:



It should be clearly stated that in the flue gases from combustion process both  $SO_3$  and  $H_2S$  may be present in trace amounts (well below 1% of the total emissions of sulfur compounds) and sulphur dioxide -  $SO_2$  will be the main pollutant that is emitted. It is the so called raw material pollutant whose quantity in the exhaust almost in 100% corresponds to the amount of sulphur introduced to the combustion process. This allows relatively accurate calculation of sulphur emissions from combustion processes.

## 10. Formation of nitrogen oxides

The studies of the combustion processes lead to the conclusion that the formation of nitrogen oxides ( $NO_x$ ) is observed for many fuels. This applies primarily to nitric oxide ( $NO$ ), nitrogen dioxide ( $NO_2$ ) and nitrous oxide ( $N_2O$ ). Of course there are known many other chemical compounds which are a combination of oxygen and nitrogen, however, in the flue gas from combustion they are in fact absent. The basic nitrogen oxide formed in the combustion process is nitrogen monoxide -  $NO$ . The extensive literature on the subject gives the information about three mechanisms of the formation of this compound in thermal processes. They are:

- thermal mechanism of Zeldovich,
- fuel mechanism,
- Fenimore prompt mechanism (radical).

**Thermal mechanism** was discovered and described for the first time by Zeldovich in the forties of the last century (Zeldovich, 1946). It includes the direct synthesis of nitric oxide from oxygen and nitrogen contained in air at high temperature. In the first stage there is decomposition of molecular oxygen to two molecules of active atomic oxygen in result of contact with high-energy inert molecule  $M$ , acting as a catalyst (it may be e.g. a molecule of hot metallic wall of the combustion chamber, burner, etc.):



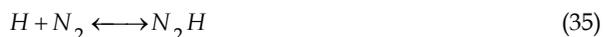
At high temperature molecular oxygen is decomposed into highly active form of atomic oxygen. Atomic oxygen molecules attack the nitrogen molecules and nitric oxide is formed, while formed in this reaction active nitrogen atoms, by attacking oxygen molecules, also form nitric oxide and active atomic oxygen. So it is a classic example of chain reaction, for which the first reaction (30) is the stage of initiation while the next two reactions (31) and (32) are the propagation stage:



in fuel-rich mixtures where the concentration of hydroxyl radicals is significant, greater than the concentration of hydrogen and oxygen atoms ( $OH \gg H > O$ ) the following reaction can be considered as the last stage of termination:



An additional source of nitric oxide formation may be the following reactions in accordance with the mechanism described by Bozzelli (Bozzelli et al., 1994):



The rates of formation of nitrogen oxides in the thermal mechanism are relatively high but only at high temperatures. This mechanism becomes negligible at temperatures above 1400°C.

**Fuel mechanism** is directly related to nitrogen content in fuels. As shown in Table 1 most solid and liquid fuels contain nitrogen. So the source of nitrogen in this mechanism is fuel while the source of oxygen is air introduced to the combustion process. The formation of nitric oxide in this mechanism is quite long and it goes through a number of succeeding-parallel reactions (Bowman et al., 1982, Miller & Bowman, 1989) shown in Figure 3.

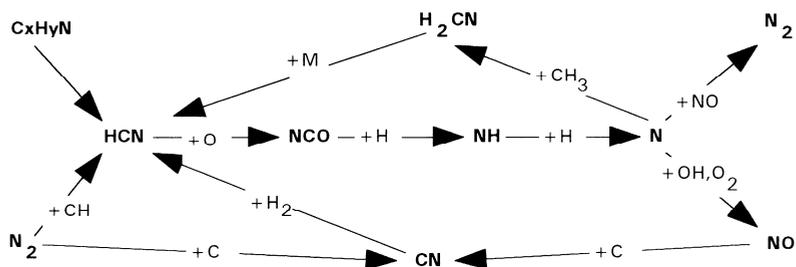


Fig. 3. Diagram of nitric acid formation according to fuel mechanism

In the first stage from organic matter, subject to combustion process (hydrocarbons containing nitrogen), hydrogen cyanide is released which by further oxidation and hydrogenation gives first radical  $NCO$ , next  $NH$  and then free atomic nitrogen ( $N$ ). At this point there are three possible further courses of reactions - oxidation reaction in which nitric oxide is formed, the reaction with previously formed nitric oxide in result of which neutral molecular nitrogen is formed and the reaction with hydrocarbon radical returning the reaction to the beginning. Thus, only one course leads to the formation of nitric oxide while the other two effectively reduce its quantity - hence you can see that there are technical possibilities of influencing on the amount of produced nitrogen oxides - through the organization of the combustion process.

**Prompt mechanism** was first described by Fenimore in 1971 (Fenimore, 1971). He noted that in the early stage of flame, in the presence of numerous hydrocarbon radicals, occurs a synthesis of nitric oxide from oxygen and nitrogen introduced into the combustion process. Since  $NO$  formation reactions occur in the early stage of flame this mechanism was called the prompt mechanism. The prompt mechanism is complementary to the fuel mechanism and some chemical reactions follow the same path. Generally it can be assumed that the following reactions proceed in this mechanism:



The rate of formation of nitric oxide in this mechanism is very high, but the amount of formed  $NO$  according to this mechanism is relatively small.

Generally, during combustion of fuels, especially solid fuels, the greatest amount of nitrogen oxide is produced by the fuel mechanism (sometimes even 80-90%). Thermal mechanism begins to play a role only after exceeding the temperature of  $1400^\circ\text{C}$ , so the contribution of this mechanism usually does not exceed 10-20%. The contribution of the prompt mechanism is usually at the level of 1-5%. Of course the contribution of thermal mechanism increases with the increase of temperature.

In recent years, it was noted that during low-temperature combustion of fuel-poor mixtures with low excess air there appears an additional mechanism of nitric oxide formation. It is connected with the described by Malte and co-workers (Steele et al., 1995) synthesis of nitrous oxide in the combustion conditions. Most likely, this reaction occurs with the participation of active atoms of hydrogen, oxygen or carbon monoxide - a product of incomplete combustion according to the following equations:





Reactions of nitric oxide formation from nitrous oxide proceed relatively quickly at temperatures below 1200°C in the area of good oxygenation of the combustion zone. The nitrous oxide synthesis itself proceeds according to several possible paths, one of them requires, just as in the thermal mechanism, the contact with the high-energy inert molecule *M*:



The reaction (45), (46) and (47) shows that the synthesis of  $N_2O$  can take place outside the combustion zone with the participation of nitric oxide previously formed in the presence of numerous radicals.

The studies of combustion products show above all the presence of nitric oxide (*NO*) and small quantities of nitrous oxide ( $N_2O$ ). Nitrogen dioxide ( $NO_2$ ), from the oxidation of *NO* formed during combustion, is a component of flue gas as well. The formation of  $NO_2$  has been described by Miller and Bowman in 1989 (Miller & Bowman, 1989). As a result of diffusion of hydrogen radicals beyond flame zone to the area of lower temperatures (below 750°C) in the presence of excess oxygen there are formed, involving high-energy inert particles of *M*,  $HO_2$  radicals which also in the same zone can react with nitric oxide according to the reaction:



In parallel to the synthesis reaction, nitrogen dioxide decomposition reactions take place:



Moreover, in the further zone of the installation, after heat recovery systems, at temperatures below 200°C occurs direct oxidation of *NO* to  $NO_2$  by oxygen present in the flue gas:



Under proper combustion conditions, the participation of  $NO_2$  in the whole stream of emitted nitrogen oxides does not exceed 5-10%.

Nitrogen oxides ( $NO_x$ ) understood as the sum of  $NO$ ,  $NO_2$  and  $N_2O$  are pollutants whose rate of emission is minimally dependent on nitrogen content in the fuel. Their emissions is a direct result of plant construction and organization of the combustion process.

## 11. Particulate matter emission

The problem of particulate matter emissions practically applies only to solid fuel combustion process. It occurs in a minimal degree during the combustion of liquid fuels and practically does not occur during the combustion of gaseous fuels. The presence in the burned material of inorganic solid substance - non-flammable, most often called ash makes that in the combustion process solid residue in the form of slag and ash is formed. The flow of air through the combustion zone results in entrainment of fine solid particles and thus dust emission from combustion processes is formed. This emission is the higher, the better is the oxygenation of the combustion zone and the higher are air velocities observed in this zone. Solid particles, lifted in the flue gas stream from the combustion zone, have usually very small diameter and their main component is silicon dioxide ( $SiO_2$  - silica). At the same time these particles are carriers of metals, elemental carbon (soot) as well as the adsorbed products of incomplete combustion and products of secondary synthesis outside the flame zone. In modern solid fuel combustion installations the release of solid particles is usually not more than 60% for the pulverized fuel and fluidal installations, and about 25-40% for the grate installations. The emission of solid particles, as dust from the combustion process is proportional to the content of non-flammable substances in the fuel and the factor of proportionality, the so called release factor, which is different for each installation and depends on its structure. So it depends partly on raw materials characteristics.

## 12. Metals emission

The emission of metals from the combustion process is very closely linked with the emission of solid particles (particulate matter) and therefore this problem does not exist during the combustion of gaseous fuels; it occurs to a small extent during combustion of liquid fuels and it applies fully to the combustion of solid fuels containing significant admixtures of non-flammable substance. Metals (mainly heavy metals), due to the speciation in the products of combustion, can be divided roughly into three groups:

- metals easily evaporated in the combustion zone and present mainly in emission to air,
- metals with high melting points and boiling points cumulative in solid combustion products (slag and grate ash)
- metals of intermediate properties for which there is division into gas and solid combustion products.

The first group includes above all mercury ( $Hg$ ) and cadmium ( $Cd$ ). Similar properties have selenium ( $Se$ ). Most metals belong to the second group - they are mainly iron ( $Fe$ ), magnesium ( $Mg$ ), cobalt ( $Co$ ), chromium ( $Cr$ ), copper ( $Cu$ ), manganese ( $Mn$ ), molybdenum ( $Mo$ ) and nickel ( $Ni$ ). Similar properties also have aluminum ( $Al$ ) and titanium ( $Ti$ ). The third intermediate group, includes mainly arsenic ( $As$ ), lead ( $Pb$ ), tin ( $Sn$ ) and zinc ( $Zn$ ) as well as antimony ( $Sb$ ). The detailed data on the speciation of the selected metals in the combustion process, based on the example of waste incineration plants (Belevi & Moench, 2000, Belevi & Langmaister 2000, Sukrut et al., 2002), are given in Table 4.

Metal	Solid phase [%]	Gas phase [%]
Antimony - Sb	25	75
Arsenic - As	68,6	31,4
Chromium - Cr	92	8
Tin - Sn	50,8	49,2
Zinc - Zn	52	48
Aluminium - Al	87,8	12,2
Cadmium - Cd	9,5	90,5
Cobalt - Co	90,1	9,9
Magnesium - Mg	91,9	8,1
Manganese - Mn	94	6
Copper - Cu	97,3	2,7
Molybdenum - Mo	91,7	8,3
Nickel - Ni	98,2	1,8
Lead - Pb	59	41
Mercury - Hg	0,7	99,3
Titanium - Ti	85,3	14,7
Iron - Fe	99,1	0,9

Table 4. Speciation of the selected metals in the combustion process

The situation is substantially changed, if in the burned area appear halides - especially chlorine and bromine. Melting point and boiling point of heavy metal salts (chlorides) is significantly lower than the melting point and boiling point of pure metal or its oxide.

According to Barton (Barton et al., 1991) and Niessen (Niessen, 2002) it is particularly evident in the case of nickel (*Ni*), thallium (*Tl*) and lead (*Pb*). This is illustrated by the data included in Table 5.

Metal	Volatility temperature [°C]	
	0% Cl	10% Cl
Antimony - Sb	660	660
Arsenic - As	32	32
Chromium - Cr	1613	1610
Cadmium - Cd	214	214
Nickel - Ni	1210	693
Lead - Pb	627	-15
Mercury - Hg	14	14
Selenium - Se	318	318
Thallium - Tl	721	138

Table 5. Volatility temperature (reaching resilience 0,1 Pa) for the selected metals in the absence and in 10% presence of chlorine.

So the emission of metals from combustion processes largely depends on the type of metal, temperature of the combustion process, but also on the presence of halides - chlorine and bromine which significantly increase the presence of some metals in flue gas.

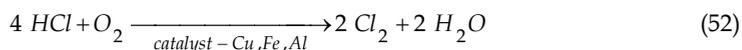
### 13. Hydrogen chloride emission

Chlorine (Cl) is an element that is widespread in the environment. Its small, sometimes even trace amounts are found in each fuel. Of course, the least amount of chlorine (almost immeasurable amount) is in fuel gas, slightly more in liquid fuels, while in solid fuels its content may be as high as 2%. In the process of combustion, chlorine - like metals is subject to speciation. The largest part of chlorine (50-60%) is bound in the form of chlorides in the fly ash, a part is also bound in a similar way in slag and grate ashes. The remaining part of chlorine is released into the environment as emissions of hydrogen chloride (HCl), while only a small amount is released in form of molecular chlorine (Cl<sub>2</sub>). With the increase of combustion temperature, the amount of chlorine released in the form of emissions increases and at the same time the amount of chlorine present in the slag and ashes decreases. Data on the speciation of chlorine in the combustion process at different temperatures according to the work of Liu (Liu et al., 2000) are shown in Table 6

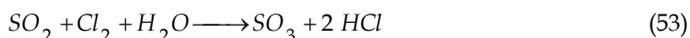
Presence of chlorine	Temperature (°C)					
	600	650	700	750	800	900
HCl	7,6	10,7	10,1	19,9	27,4	43,7
Cl <sub>2</sub>	0,5	0,2	0,4	0,6	0,8	1,3
Fly ash	50,9	47,5	56,3	53,2	62,4	51,9
Slag	40,5	41,3	32,8	25,6	8,5	1,2

Table 6. Speciation of chlorine in the combustion process depending on the temperature

The presence of chlorine in fly ash is of great importance in the formation of chloroorganic compounds outside the combustion zone. The presence of free chlorine which can participate in the chlorination and oxychlorination reactions outside the combustion zone is of similar importance. In the flue gas, outside the combustion zone, hydrogen chloride may undergo a catalytic decomposition (Deacon reaction) in accordance with the reaction equation (Griffin, 1986):



In the case of sulfur dioxide (SO<sub>2</sub>) present in flue gas, at the same time proceeds hydrogen chloride reproduction reaction (Lindbauer et al., 1994):



The balance in a chlorine - hydrogen chloride system is also affected by hydroxyl radicals and water present in the flue gas:

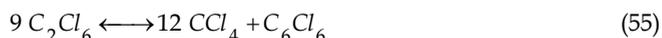


Thus the concentration of hydrogen chloride and free chlorine in the flue gas depends on many factors, including temperature and that is why their emission rates cannot be predicted on the basis of chlorine content in the fuel.

#### 14. Products of incomplete combustion

The term products of incomplete combustion (PICs) means organic compounds introduced to combustion and formed during combustion that were not oxidized in the combustion zone as well as products of secondary synthesis outside the combustion zone. As already mentioned when discussing the combustion process paths shown in Figure No. 2, in the combustion zone and directly next to it, in the gas phase there are many hydrocarbon and chlorinated hydrocarbons radicals as well as simple aliphatic hydrocarbons, often unsaturated, which may participate in secondary, high-temperature synthesis reactions. Among these radicals there is also acetylene, which plays a key role in the later stages of synthesis.

The key here is a reaction first described by Aubrey and van Wazer (Aubrey & van Wazer, 1964), in which in high temperature aromatic compounds are formed from aliphatic compounds (acetylene):



A special role is played by acetylene. It is always present in the flue gas from the combustion process and is a precursor of the formation of many chloro-aromatic compounds (Lenoir et al., 2001). It is subject in the first stage to chlorination to dichloroacetylene in result of ligand exchange reaction and then is subject either to cyclization to hexachlorobenzene or condensation to hexachlorobutadiene (Lenoir et al., 1998). Subsequent studies have shown that, for example from acetylene at high temperatures chlorobenzenes, chlorophenols and chloronaphthalenes can be formed.

In addition, the presence in the waste of organic substances of unsaturated character, that is containing in the molecule double or triple carbon-carbon bonds ( $C=C$  or  $C\equiv C$ ) causes that at a temperature of about 500-800°C, occurs the synthesis reaction of polycyclic aromatic hydrocarbons (Liow et al., 1997). Polycyclic aromatic hydrocarbons (PAHs) are among the most dangerous substances in the environment. Many of them, such as benzo(a)pyrene, benzo(a)anthracene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, indeno(1,2,3-c,d)pyrene are classified by the International Agency for Research on Cancer (IARC) as substances with proven carcinogenic effect. They are emitted to the atmosphere practically from all combustion processes, not only from the waste incineration plants (Mastral et al., 2000).

The result of these reactions, which proceed outside the combustion zone, is the presence of pollutants in the flue gas, among others such as (Eduljee, 1994):

- hydrocarbons  $C_1$  and  $C_2$ ,
- acrylonitrile, acetonitrile,
- benzene, toluene, ethylbenzene, xylene,
- 1,2-dichlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, hexachlorobenzene,
- phenol, 2,4-dinitrophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol, pentachlorophenol,

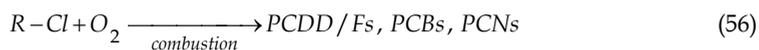
- chloromethane, chloroform, methylene chloride, carbon tetrachloride,
- 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane,
- 1,1-dichloroethylene, trichloroethylene, tetrachloroethylene,
- formaldehyde, acetaldehyde, acetone, methyl-ethyl-ketone,
- vinyl chloride, diethyl phthalate,
- formic acid, acetic acid and many others.

Subsequent studies conducted by other researchers (Wienecke et al., 1995, Jay & Stieglitz, 1995, Mascolo et al., 1997, Trenholm 1998) showed the presence of more than 350 different types of chemical compounds (organic) in the flue gases from the waste incineration plants in concentrations above 5  $\mu\text{g}/\text{m}^3$ . Similar results were obtained for burning of wood and other biomass. Unfortunately, there are no such test results for the combustion of coal, although it is expected that the situation is similar.

### 15. Formation of PCDD/Fs, PCBs, PCNs and PAHs

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs) and polycyclic aromatic hydrocarbons (PAHs) are also products of incomplete combustion formed outside the combustion zone. Their common feature is the negative biological impact - some of them have proven carcinogenic properties (PAHs), others are xantolestrogens (endocrine disrupters) that disrupt the hormonal balance of living organisms. In recent years many myths referring to them have appeared, however, most of them have nothing to do with reality.

According to the diagram in Figure 2 showing the combustion process of solid fuels, the crucial stage for the synthesis of PCDD/Fs, PCBs, PCNs and PAHs is the formation of hydrocarbon radicals, often including halogenated (mainly chlorinated) ones as well simple unsaturated hydrocarbons e.g. ethylene and acetylene. These reactions proceed at high temperatures and in the next stage their products undergo further reactions such as cyclization - the formation of aromatic often chlorinated compounds - including benzene, naphthalene, chlorobenzenes and chlorophenols. All these chemical compounds are formed in virtually any combustion process of solid and liquid fuels and also, although less frequently, gas fuels. If in the zone of respective temperatures appear chlorine, oxygen and organic matter chlorinated compounds are formed - such as PCDD / Fs, PCBs and PCNs. This phenomenon is observed not only for combustion process but also for most thermal processes running at temperatures of 200-700°C. The overall reaction is as follows:



On the basis of the critical analysis of numerous literature data, we can assume the following paths of appearance of dioxins (as well as PCBs and PCNs) in the flue gas stream from combustion:

- dioxins introduced to the system which did not participate in any chemical reactions or were subject to the reactions of partial chlorination and/or dechlorination of the molecule (Tosine et al., 1985),

- dioxins from the aromatic rings formation and rearrangement of substituents with the participation of chlorinated precursors such as PVC, PCBs, chlorinated benzenes, chlorinated phenols directly behind the combustion zone - this is a reaction that occurs in the gas phase at temperatures of 500-700°C (Ballschmiter et al., 1985),
- dioxins formed outside the combustion zone in result of the reaction of non-chlorinated organic compounds such as PAHs, lignin, lignite, etc. and then chlorination reaction as well as from various types of chlorinated organic precursors such as chlorophenols, chlorobenzenes, polychlorinated diphenyl ethers, polychlorinated biphenyls and other products, etc. as well as other products of incomplete combustion which may react with each other and on the surface of metals in the fly ash particles (Dickson & Karasek 1987), where they are subject to the reactions of chlorination and dechlorination of the molecule,
- dioxins formed outside the combustion zone of molecular carbon (carbonized residues of the combustion, unburned carbon in the particles of dust, soot and organic or inorganic chlorine in the presence of fly ash at a temperature of 200-400°C usually called *de novo* synthesis (Vogg & Stieglitz 1986).

The main difference in these mechanisms is the source of carbon and the temperature range in which the synthesis takes place. In the light of the research results it seems that the most important mechanism owing to which most dioxins are formed is the third mechanism (*de novo*), then the second and least dioxins are produced by the first mechanism (Huang & Buekens, 1995).

The analysis of the above mentioned paths of appearance of dioxins in the flue gas stream from thermal processes, including combustion of solid fuels shows that the first case is relatively unlikely. PCDD/Fs and PCBs are not chemicals of high thermal stability. In the combustion conditions (presence of oxygen, mixing, flow) practically most organic compounds, including dioxins, is decomposed at the temperature about 850°C. The temperature of 99.9% of the destruction of PCDD/Fs is around 700°C while the temperature of the destruction of other compounds that are precursors of the synthesis of dioxins can reach up to 950°C. However, in the case of lack of oxygen the limit of the decomposition of organic compounds may be increased to around 1000°C. It therefore seems unlikely that the dioxins contained in the material subject to combustion at temperatures reaching and exceeding 1000°C could not be subject to destruction, although in the case of poor construction of the combustion installation and the formation of cold zones in the combustion chamber this is not excluded.

The second path of the appearance of PCDD/Fs, PCBs, PCNs in flue gas is a high temperature synthesis which is a condensation of precursor molecules - benzene, naphthalene, phenanthrene, acetone, trichloroethanes, benzaldehyde, dibenzofuran, benzofuran, phenol, mono-, di-, trichlorophenoles, chlorobenzenes, tetrachlorethylene or polychlorinated diphenyl ethers. These precursors may react with each other both at 500-700°C in the gas phase and on the surface of fly ash at a temperature of 200-500°C. The key to the formation of dioxins in result of synthesis in the gas phase are the conditions for conducting the combustion process. Numerous studies have shown a very close relationship between the formation of chlorinated and non-chlorinated aromatic compounds in the combustion and afterburning chamber (at a temperature 650-900°C) and the parameters of combustion. It was also noted that by-products of gas fuel combustion - such as natural gas,

acetylene, ethane and ethylene may be a sufficient source of carbon for the synthesis of dioxins.

Outside the combustion zone at temperatures below 500°C dioxins are formed as a result of a series of catalytic reactions occurring on the surface of dust containing metals. Usually it is assumed that dioxins are formed there by two mechanisms - the catalytic synthesis of precursors such as chlorobenzenes, chlorophenols, polychlorinated naphthalenes and polychlorinated biphenyls (similarly as in the gas phase) and catalytic synthesis of elemental carbon (soot) contained in dust particles or polycyclic aromatic hydrocarbons as well as gaseous chlorine and oxygen.

The first of these two mechanisms was first described in 1987 by Dickson (Dickson & Karasek 1987). Numerous studies conducted in subsequent years have shown that this reaction proceeds in principle as a condensation reaction of chlorobenzenes or chlorophenols or as a reaction of selective oxychlorination of polychlorinated naphthalenes and polychlorinated biphenyls. This reaction can be catalyzed by many metals - e.g. copper, titanium, manganese, cobalt, zinc but definitely copper has by far the largest catalytic ability. The characteristic of the condensation mechanism (high temperature in gas phase or on the surface of dust particles) is the fact that in this way are formed low chlorinated dioxins, containing from one to maximum 3-4 atoms of chlorine. So the problem of the origins of high chlorinated dioxins, containing from 4 to 8 atoms of chlorine per molecule, in flue gas remained unresolved. The third mechanism of dioxin formation offers the solution to this problem - the *de novo* synthesis.

The second mechanism of the formation of dioxins in the zone after the combustion chamber, in the area of flue gas cooling, was discovered in the late eighties of the last century by Stieglitz and co-workers, the so called mechanism of *de novo* synthesis (Vogg & Stieglitz 1986). The *de novo* synthesis is a slow heterogenic catalytic reaction in which dioxins are formed without the formation of gaseous intermediate products. It occurs within the temperature range 200-500°C from carbon particles contained in fly ash, through the formation and closure of benzene rings, which then react with oxygen and chlorine on the catalyst surface (Stieglitz & Vogg, 1987). The source of carbon in *de novo* synthesis is usually so called elemental carbon contained in fly ash particles, as a carbonized residue of thermal decomposition and oxidation in the combustion process. In practice it is impossible to achieve complete burnout of carbon contained in the fuel and small amounts of unburned carbon are present in flue gas in form of soot which is made up of elemental carbon and the polycyclic aromatic hydrocarbons - PAHs. The emission of dioxins from the combustion of pure wood suggests that the carbon source can also be large, complex molecules of organic compounds such as lignin and lignite. The chlorinating agent in *de novo* synthesis can be free, molecular chlorine, chlorinated organic compounds as well as volatile inorganic chlorine salts - such as NaCl or FeCl<sub>3</sub>. However, the fundamental role in the formation of dioxins plays the concentration of chlorine free radicals in the zone of combustion reaction and cooling. Despite the obvious role of chlorine in *de novo* synthesis the data from over 1 900 research works on an industrial scale (Rigo & Handler, 1998) shows that there is no clear relationship between the amount of chlorine introduced in the fuel to the combustion process and the amount of dioxins emitted. There is, however, relationship between the amount of dioxins emitted and the concentration of chlorine or hydrogen chloride at the outlet of the combustion chamber.

The emission of dioxins depends primarily on the construction of the combustion unit and burning conditions. The concentration of chlorine in the flue gases significantly affects the profile of formed congeners PCDD and PCDF. The higher the concentration the greater the share of congeners with higher number of chlorine atoms. This suggests that *de novo* synthesis is the reaction of subsequent chlorination of individual congeners of dioxins and furans. Analyzing the above mechanism of *de novo* synthesis it can be stated that on the fly ash containing  $\text{CuCl}_2$  there can also run the follow-chlorination of lower substituted dioxins generated in the gas phase as well as dechlorination of higher chlorinated dioxins. The optimal temperature assumed for *de novo* synthesis is about  $350^\circ\text{C}$ . Oxygen concentration also influences the course of the *de novo* synthesis. This is obvious if we consider that oxygen is present in the molecule of both dibenzo-p-dioxin and dibenzofuran. Studies have confirmed that the increase in oxygen concentration outside the combustion zone significantly increases the amount of generated dioxins, the increase in the concentration of hydrogen chloride and gives the same effect.

The catalyst in the *de novo* synthesis is primarily copper chloride. Copper has a very strong effect in supporting the formation and closing the rings such as chlorophenols. Subsequent studies have shown that transition metals catalyze both ring closing and the process of chlorination and *de novo* synthesis may be treated as an electrophilic substitution reaction that runs in two stages - the first stage includes the chlorination of carbon surface while the second stage is oxidation and decomposition in which dioxins and furans are formed. Similar to the catalytic properties of copper, in the *de novo* synthesis similar properties also have aluminum, iron, magnesium, manganese, cobalt as well as sodium, potassium and zinc. Other metals - such as nickel does not exhibit catalytic activity or they decrease the amount of generated dioxins e.g. chromium, wolfram or vanadium. But there is no doubt that the best catalyst for *de novo* synthesis is copper. In reality, however, on the surface of fly ash there are many metals, whose influence on the synthesis of dioxins is different - some of them catalyze the *de novo* synthesis or the chlorination process of low chlorinated dioxins formed earlier (in the synthesis in gas phase) - for example, copper, zinc, iron or aluminum, while others catalyze the decomposition of generated dioxins or their dechlorination - e.g. chromium, vanadium, tungsten or nickel.

After analyzing the emissions of dioxins from combustion processes and all the described paths of the presence of dioxins in the flue gas, especially the paths of their synthesis it should be noted that probably most dioxins are formed outside the combustion zone. According to Goldfarb, who analyzed the problem of dioxin emissions from Canadian incineration plants, this is most probably the vast majority (Goldfarb, 1986).

Summing up the problem of paths of dioxins formation in combustion processes we should first mention the decisive influence of the combustion process conditions on the quantity of produced dioxins and furans. Combustion process conditions include first of all temperature, residence time of gases from the combustion in the zone of high temperatures, oxygen concentration in the combustion zone and directly connected with it concentrations of carbon monoxide in the flue gas. Poor combustion conditions i.e. too low temperature and high concentration of carbon monoxide contribute to the formation of incomplete combustion products such as chlorobenzenes and chlorophenols which are precursors of dioxins and can undergo condensation reactions in both high and low temperature zone in the presence of metals catalyzing condensation reactions. Poor combustion conditions also

favor the formation of polycyclic aromatic hydrocarbons (PAHs) and unburned coal residues in the dust entrained in the air which is an excellent raw material for *de novo* synthesis and this in turn means that you can prove the thesis that there is a direct impact of the combustion conditions on the amount of dioxins generated in all three known mechanisms described earlier.

When conducting combustion processes we are always dealing with two opposing reactions (reaction systems) - formation of dioxins as a result of various homo- and heterogenic reactions and decomposition of dioxins as a result of high temperature and catalytic reactions. Graphic illustration of this problem is shown in Figure 4. Most of the dioxins generated in waste incineration plants is formed in result of *de novo* synthesis in the temperature range 200-400°C with maximum temperatures around 300°C. This maximum is the result of synthesis and decomposition processes running in parallel.

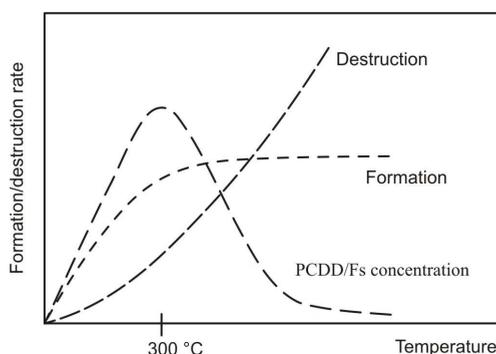


Fig. 4. Formation and decomposition of dioxins in a catalytic process on dust particles.

The process of formation of PCDD/Fs, PCBs, PCNS and PAHs during combustion depends on many factors and that is why it is very difficult to predict how much of these compounds will be formed in a specific process with fixed parameters. Momentary dioxin emissions results not only from the current combustion conditions. Due to the fact that probably most of the dioxins is produced by *de novo* synthesis, which is a very slow reaction, the formation of dioxins and their release continues long after the optimization of the parameters of the combustion process and minimizing the amount of generated dioxins. This is so called memory effect occurring in waste incineration plants. In the case of unstable operation of incinerators high concentrations of dioxins in the flue gas can be observed over long periods of time (Hunsinger et al., 2007).

## 16. Primary methods of emission reduction

Understanding the mechanisms of pollutants formation in the combustion process enables the development of such technologies and methods of combustion which ensure the smallest amount of generated pollutants. There are well known so called low emission combustion processes relating to carbon monoxide and nitrogen oxides - the use of the combustion zone, in stages, flue gas recirculation and the so-called reburning (introducing fuel to the periphery of flame zone) allows to reduce  $\text{NO}_x$  emissions by about 50-60% compared to the original process (Jarosiński, 1996, Hill & Smoot, 2000).

Such efforts to reduce emissions, which are an interference in the combustion process are called primary methods of reducing emissions. They become more and more important in recent years, because from the economic point of view, they are more cost effective (cheaper) than the secondary methods, called "end of pipe technologies". Their effectiveness is generally lower than that of flue gas cleaning methods, however, they significantly help to improve the work of the latter, allowing to obtain the total degree of purification of gases at a level above 99%.

In recent years the determination of the effect of parameters of the combustion process on the emission of metals, PAHs, dioxins and other organic substances from the combustion process became an important issue. Numerous literature reports clearly show that keeping good combustion process parameters significantly affects the reduction of emissions of organic substances (including PAHs and dioxins) to the atmosphere. A parameter which characterizes "good combustion conditions" very well is the concentration of carbon monoxide in the flue gas. Other parameters defining the "good combustion conditions" are above all so called "3T" - temperature, turbulence and time of flue gas residence in proper temperature. Detailed conditions are specified among others in the Directive on the incineration of waste (2000/76/EC) - they are as follows: flue gas residence time at 850°C should be not less than 2 seconds at high gas turbulence (for waste containing less than 1% of chlorine compounds, in the case of waste containing more than 1% of chlorine compounds the temperature should be higher than 1100°C).

It is essential, however, to ensure combustion conditions close to complete and perfect combustion, with minimized amount of formed carbon monoxide. Such conditions prevail in properly oxygenated combustion zone at an optimal concentration of oxygen (for coal combustion 6-8%, excess air coefficient about 1.4-1.8). In the case of waste incineration better oxygenation of the combustion zone and providing excess air coefficient of the order of 2,0-2,4 (oxygen concentration 10-13%) is required. The effect of oxygen concentration and combustion temperature on the concentration of carbon monoxide in the flue gas is illustrated in Figure 5 (Seeker, 2001).

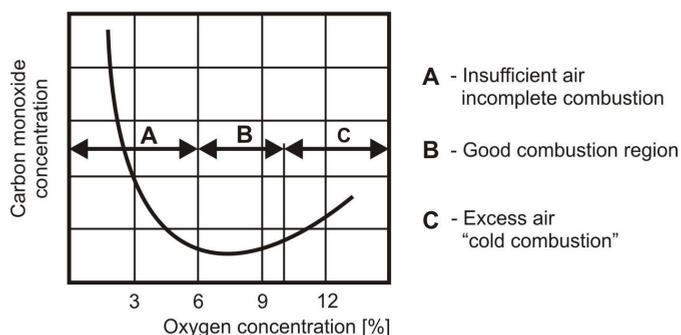


Fig. 5. The effect of oxygen concentration in the combustion zone on the carbon monoxide emission.

According to the research of Seeker (Seeker, 2001) the concentration of carbon monoxide, that is combustion conditions, has a great impact on the amount of dioxins produced in the combustion process and their emission. This is illustrated in Table 7.

Combustion parameters	Slag, bottom ash	Fly ash	Dust from electrostatic precipitator	Emission to atmosphere
T = 830 °C CO = 25 ppm	0,33 µg/Mg	0,14 µg/Mg	21,2 mg/Mg	11,2 µg/Mg
T = 850 °C CO = 1 ppm	0,35 µg/Mg	0,22 µg/Mg	21,2 mg/Mg	1,6 µg/Mg

Table 7. The effect of combustion conditions on the rate of PCDD/Fs emission to atmosphere and the concentration in secondary waste from the combustion process (per 1 Mg of incinerated waste).

The research conducted by Schmöckel (Schmöckel & Streit, 1994) of wood combustion process in plants with a capacity of 11 kW to 13.9 MW have shown a very close correlation between the concentration of some pollutants in the flue gas and the concentration of carbon monoxide, which clearly shows the impact of combustion conditions on the emission of organic pollutants. The results of these studies are shown in Figure 6.

Combustion parameters have also great impact on emissions of metals. This is due to the different volatility of metals and their speciation depending on the forms of occurrence. The presence of chlorine and hydrogen chloride in the combustion zone causes that different amounts of metals are in slag, fly ash, ash from de-dusting equipment or in gases emitted to the atmosphere (Chiang et al. 1997). There is also a clear effect of combustion temperature and oxygen concentration in different zones of combustion on the balance of metals in individual secondary products of the combustion process (Wunsh et al., 1995, Wey et al., 1998). For example, controlling the amount of primary air in the individual zones of the grate and the temperature can result in almost zero emission of some metals with almost 100% their content in the slag (Modigell & Liebig, 1999). The use of primary methods of reducing emissions makes that secondary purification of flue gas to the level required by law (e.g. Directive 2000/76/EC) is easier. The positive effect of the use of primary methods of reducing emissions on the concentration of pollutants in flue gas is shown in Table 8.

Pollution	Unit	Installation without the use of primary methods	Installation using the primary methods	Allowable concentration according to Directive 2000/76/EC
Dust	mg/m <sup>3</sup>	2 000 - 10 000	1 000 - 1 500	10
Carbon monoxide	mg/m <sup>3</sup>	50 - 80	10 - 15	50
Sum of organic compounds	mg/m <sup>3</sup>	10 - 100	0,5 - 1	10
PCDD/Fs	ng TEQ/m <sup>3</sup>	5 - 12	0,6 - 1,2	0,1

Table 8. The effect of the primary methods for reducing emissions of pollutants in waste incineration plants (Büttenberger & Hansen 1997).

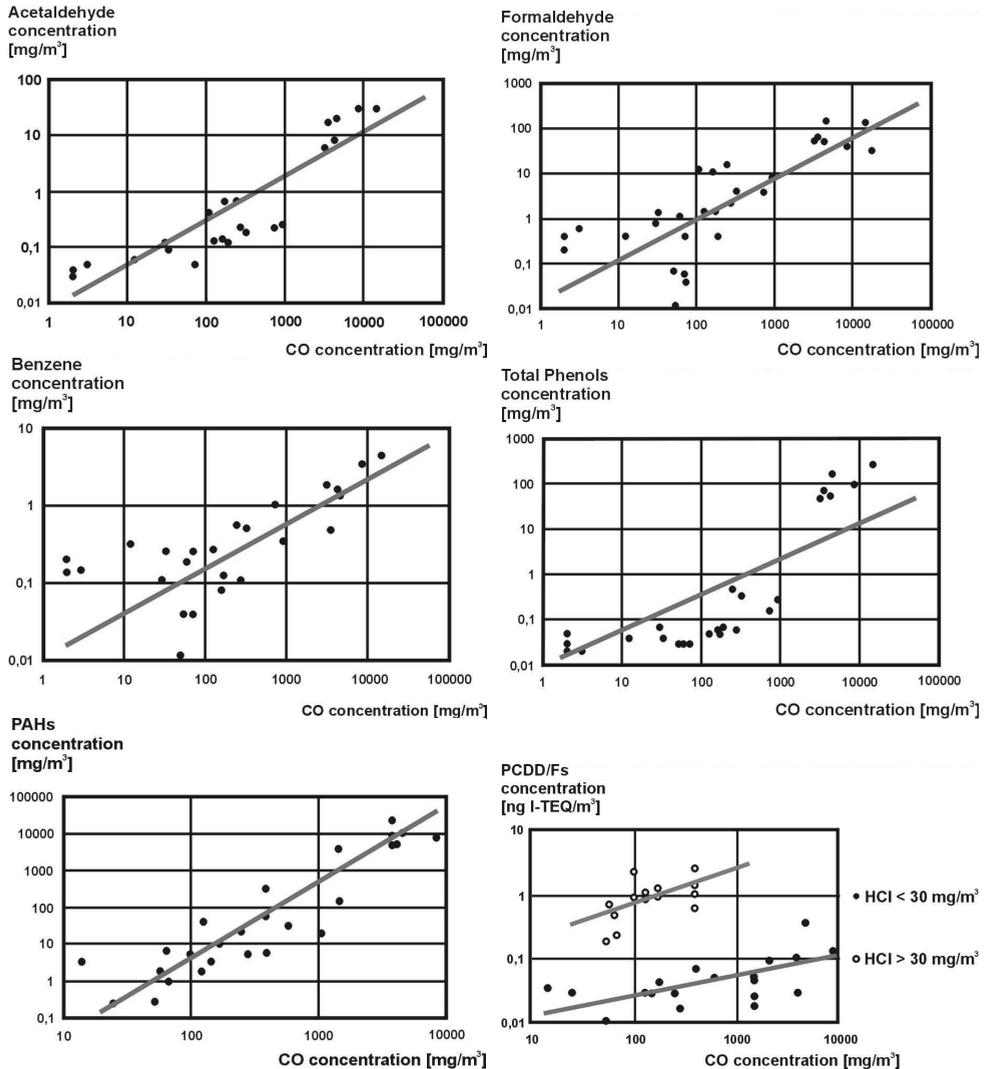


Fig. 6. The effect of combustion conditions (concentration of CO in flue gas) on the emission of some organic pollutants from combustion process (Schmöckel & Streit, 1994).

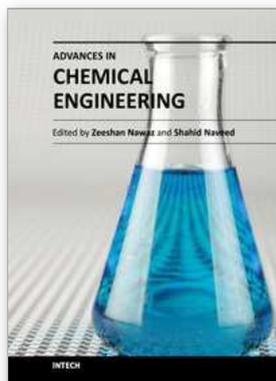
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## **Advances in Chemical Engineering**

Edited by Dr Zeeshan Nawaz

ISBN 978-953-51-0392-9

Hard cover, 584 pages

**Publisher** InTech

**Published online** 23, March, 2012

**Published in print edition** March, 2012

Chemical engineering applications have been a source of challenging optimization problems in terms of economics and technology. The goal of this book is to enable the reader to get instant information on fundamentals and advancements in chemical engineering. This book addresses ongoing evolutions of chemical engineering and provides overview to the state of the art advancements. Molecular perspective is increasingly important in the refinement of kinetic and thermodynamic modeling. As a result, much of the material was revised on industrial problems and their sophisticated solutions from known scientists around the world. These issues were divided into two sections, fundamental advances and catalysis and reaction engineering. A distinct feature of this text continues to be the emphasis on molecular chemistry, reaction engineering and modeling to achieve rational and robust industrial design. Our perspective is that this background must be made available to undergraduate, graduate and professionals in an integrated manner.

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Grzegorz Wielgosiński (2012). Pollutant Formation in Combustion Processes, *Advances in Chemical Engineering*, Dr Zeeshan Nawaz (Ed.), ISBN: 978-953-51-0392-9, InTech, Available from: <http://www.intechopen.com/books/advances-in-chemical-engineering/pollutants-formation-in-combustion-processes>

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