

Emission of Dioxins in Biomass Using Furnaces

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INTRODUCTION

Several compounds of the dioxin-homologues are extremely toxic; therefore the decreasing of the dioxin emission has special importance in the environmental protection. The article gives a deeper review about the decrease of dioxins produced during the production of renewable energies, with special regard to the industrial wood firing systems. The latter is extremely important because - according to the Kyoto Protocol - the ratio of the wood firing will increase; and it should be considered that this fact should not increase the environmental pollution.

THE STRUCTURE OF THE DIOXINS

The collective name of the compounds having a polychlorinated-dibenzo-p-dioxin (PCDD) or polychlorinated-dibenzo-furan (PCDF) structure is dioxin; Fig. 1 shows the general formula [1].

The toxic effects of 17 dioxins have been unquestionably proven in. The most dangerous of these compounds is the 2,3,7,8-tetrachloro-dibenzo-p-dioxin (2,3,7,8-TCDD). This compound - taken orally, in a 0,6 µg/kg dose - killed half of the male guinea-pigs (o.v. LD 50). The other congeners have different, less toxic effect. Most commonly the compounds are characterized with their toxic equivalent factor (TEF). TEF expresses the toxicity of a compound relative to the most toxic one 2,3,7,8-TCDD [1]. The toxicity of dioxin mixtures are usually characterized by TEQ. TEQ is the quantity of dioxin and dioxin-like PCB congeners, weighed to their TEF values.

Dioxins cause skin defects (chloracne), diabetes and pulmonary oedema. They damage the immune system and the nervous system. Some of the compounds are carcinogenic (liver, thyroid gland, lung or ganglion) and defective effect. They disturb the enzyme and hormone functions.

The cancer caused by dioxins can originate from the disturbance of the aromatic hydrocarbon receptors [2, 3].

One of the infamous dioxin intoxication is the more than ten thousand natal defect induced by the "Agent Orange" - a compound used in the Vietnam war as a defoliating agent [4]. At Seveso in 1976 dioxins escaped into the air during an industrial acci-

dent as a by product of trochloro-phenol synthesis. Although there were no immediate human fatal victims of the accident, 3300 animals died and 80 000 had to be killed to avoid the compound to get into the food chain. It had been observed that after the accident the number of newborn girls had increased two times to the boys in the neighborhood and the number of cancer disease had increased [4].

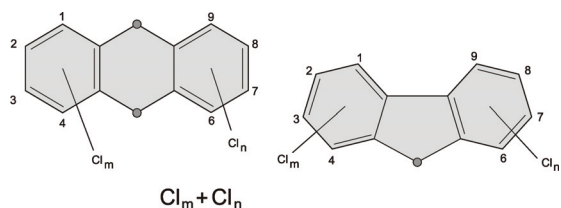


Fig. 1 General formula of polychlorinated-dibenzo-*p*-dioxins and polychlorinated-dibenzo-furans

HOW DIOXINS GET INTO HUMAN BODY

Although dioxins reach the environment through air, they enter the human body through the food-chain. The human intake of dioxins is mainly connected to fatty food (fish, dairy products etc.) because the dioxins are slightly soluble in water. Because of their low watersolubility dioxins accumulate in fat tissue and liver – they bio-accumulate. The case is worsened by the dioxin accumulation during the nutrition chain (biomagnification) and at the end they are taken into the human body. Dioxins are persistent organic compounds (POP) [5].

FORMATION OF DIOXINS

Dioxins are not produced on purpose, they form as by-products of industrial syntheses or during insufficient combustion [6]. The main structure elements (precursors) of the dioxin molecules are present during production process either as intermediates or byproducts of these compounds.

The dioxin syntheses starting from inorganic or smaller organic compounds have greater importance than the one through precursors. The main sources of dioxin formation are incomplete oxidation, combustion. These are metallurgy (iron, aluminum, copper), charred coal production, waste combustion, thermal power plants and household heating.

These reactions have different path. Most of the dioxins are formed according to the de Novo reaction [6, 7, 8, 9], where inorganic chlorine, carbon, water, oxy-

gen are the starting components.

A carbon having structure similar to graphite is formed during insufficient combustion; this is the carbon source of the reaction and the catalyst of the heterogeneous phase reaction. The ash settled in the chimney in the heat exchanger, carbon black, soot settled on the improperly adjusted sieves and the flying ash or carbon black can be the carbon source necessary for the reaction.

The coal particles that were formed in the above mentioned process form layers in a cycle of six. In this structure the layers are not parallel, but they are twisted relative to each other. The distance of the layers is larger than in natural graphite, this enables hydrogen chloride, oxygen and water molecules to penetrate in between the layers and to get into reaction with the coal.

The temperature range of the de Novo synthesis is between 200°C - 450°C and the maximum of the speed of reaction is at 325°C. Quite often the dioxins are not formed during combustion, but where the temperature is optimal, in the heat exchanger or filter. It was found, that the ashes in the combustion chamber contain less dioxin than the soot in the heat exchanger or the sieve. According to a study in case of wood firing the combustion chamber showed 1 pg/g TEQ value, while the soot found in the filter showed two magnitudes bigger values [8]. A misplaced ceramic filter can increase the dioxin emissions to 30 times as much. To prevent the unwanted synthesis either the time spent in this temperature range be decreased, or the turbulence should be increased. If the exhaust gases spend 1,6 seconds in a space where the temperature is between 200°C - 450°C, then the amount of dioxin formed is significant. If the time spent in the given temperature range is only 30 milliseconds, then the amount of dioxin formed decreases by 90%.

Chlorine reacts mostly in the form of HCl or other metallic chloride (e.g. copper). Its effect can be decreased by placing a charcoal or lime filter in the way of the exhaust. The formation of dioxin is significant if the source material contains over 1500 mg/kg of Cl. From other aspects above certain chlorine level is not coherent with the amount of dioxin formed [8]. The environment that lacks oxygen helps the decomposition, the dechlorinating of dioxin from the exhaust gases. From other aspects the lack of oxygen helps the formation of dioxin due to coal deposition and the lower temperature.

Certain metals (e.g. Cu, Fe, Zn, Al, Cr) catalyze the de Novo synthesis, copper is the one that does this most intensively. The oxygen molecules react to the copper at the surface of coal forming copper oxide. The copper oxide easily transfers its oxygen into carbon skeleton. The copper ions also help the chlorine to be built into the coal skeleton through copper chloride. However sulphur and nitrogen hinder the formation of dioxin.

In general it can be said, that the amount of dioxin formed primarily depends on the conditions of the combustion and only secondarily on the materials combusted. In other words if the appropriate technology is used, even if the material combusted contains significant amount of chlorine, still the formation of dioxin can be avoided, since on high temperatures dioxin decomposes. The catalytic oxidative filter can also decompose dioxin.

To avoid the dioxin formation, the combustion machinery has to be designed according to new design principles. The soot deposition has to be decreased, the time the exhaust gases spend in the critical temperature range has to be shortened and appropriate exhaust filters are to be used.

DIOXIN EMISSION

The analytical processes of dioxins needs sophisticated measuring devices, time consuming sample pretreatments, and in many cases it is impossible to take samples (e.g. illegal burning of garbage, forest fires, household heating devices, etc.). Due to the above mentioned difficulties a calculation chart has been made which gives an estimate on domestic and international level based on [10].

Unambiguously that the dioxin emission fell to the tenth in the USA. The decrease is due mainly to the development of technology in the industry (industrial garbage combustion, metallurgy, paper industry) and the use of appropriate environmental protection appliances. The emissions of industrial garbage combustion plants vanished, from 82% to 2%. The domestic garbage burning is responsible for more than the half (56%) of the dioxin emissions and it even increased. There was no success cutting the pollution caused by the power plants and the plants treating mud remaining from sewage water. The emission caused by wood combusting power plants even increased. It is remarkable, that significant dioxin level can be measured at the old garbage combustion plants.

The dioxin pollution coming from the industry gradually decreased due to the fact, that many factories closed or decreased its production in Eastern Europe.

The emissions is around 3g/year from power plants, including biomass burning, which is 3% of the total emission [11]. The reason for the good results from the environmental aspect is that in power plants to reduce the regular pollutants (SO_2 , NO_x , HCl, dust, etc.) investments were made and this had a positive effect on POP pollutants including dioxin emission. Since biomass burning is increasing this will mean the ratio will increase as well. For these methods it is an absolute necessity to have alongside the best available exhaust gas/end gas separation method (BAT), the filters and electrostatic exhaust, the use of semidry or moist exhaust gas cleaners [6].

Further decrease can be achieved using the following methods [12]:

- **Limiting household, illegal garbage burning. The polluted waste wood should only be combusted in furnaces with proper gas cleaners.**

- **Further improvement of furnace technology.**

DIOXIN EMISSION OF RENEWABLE POWER SOURCES

The Kyoto Protocol recommends the use of renewable fuels to reduce the greenhouse effect. However the use of these power sources cause significant dioxin emission if necessary precautions are not made. It was discussed in the previous chapter that the dioxin emission of treated wood is significant, because the wood proofing chemicals are a source of chlorine and precursors [6].

However the untreated plants are also significant sources which were examined in case of forest fires, wasteland burning and household heating [13, 14]. In case of household wood burning 0,35-2,4 $\mu\text{gTEQ/ton}$ is the rate of emission. Data from Germany show (15g/TEQ/year) that it is bigger than the one of the coal and oil furnaces (5g/TEQ/year) [14]. Examining smaller furnaces the emission rate is 0,0020 ng I-TEQ/ m^3 for oil and gas furnaces while it is 0,014-0,076 ng I-TEQ/ m^3 for furnaces burning wood [14, 15].

If non-arboreal plants are burnt (e.g. grass, hay) more dioxin is formed, because its salt and ash content is larger than of wood, as it can be seen on Fig. 6 [16,17].

If untreated biomass is burnt, the following causes the

formation of dioxin [13]:

- The lignin content of the plants is a precursor.
- The de Novo synthesis is helped by the soot that forms due to the insufficient burning.
- The salt content of the plants (0,001-0,01% chloride) is a chloride source.
- The moist content of wood decreases the efficiency of burning, its cooling effect decreases the temperature of the process.
- The basicity has catalytic effect.
- The traces of metal in the plants can also act as a catalyst in the de Novo synthesis.
- The insufficient filter is a good place for coal deposit and it acts as a catalyst.

To avoid the above mentioned, biography recommends the following:

- The wood is to be dried before burning, because the initial 60% moist content decreases to 20-25% by the next year.
- Soot deposition is to be avoided at such places, where the temperature is suitable for the de Novo synthesis.
- Appropriate flow profiles are to be created for turbulent flow.
- The time spent in the temperature range ideal for de Novo synthesis should be decreased.
- The treated and untreated wood should be separated and burnt under optimized circumstances.

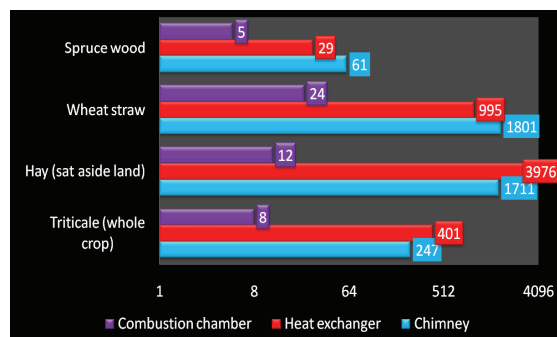


Fig. 2 Dioxin concentration in ash and chimney soot, combusting different kind of plants [16]

In the future, dioxin emissions can be effectively reduced by using appropriately designed furnaces as it was started in the USA in 1990 [18].

The high oxygen ratio decreases the amount of dioxin formed although it is not ideal from the aspect of energetic. The dioxin emission can be radically reduced by optimizing the input of fuel and oxygen. The wood burning power plants also have a signifi-

cant dioxin emission [11, 15].

These power plants have an emission rate of 1020 ng/kg, which is equal to 17,1 ng/kg wood value. According to experiments this can be decreased by 90% using a fabric filter.

DIOXIN EMISSION OF INDUSTRIAL WOOD BURNING

The source of fuel can be one of the following:

- Primary wood industry (Forest services).
- Secondary wood industry (Wood processing).
- Household source.

According to its form it can be:

- Lumpy (branch, lopping, bigger pieces).
- Wood chips.
- Bicket.
- Pellet.
- Dust (sawdust, chiseldust).
- Chipping.

The fuel coming from the primary wood industry has high water content (40-60%). Since the woods in Hungary are not treated with pesticides, this means the origin of the dioxin precursors are only coming from the air. Therefore this fuel can be treated as clean fuel. The fuel coming from the secondary wood industry are polluted, e.g. fungicide, paint, glue. Their moist content is small (<10%).

In Hungary the wood come from household is out of our scope, because their supervised collections, neither their industrial burnt are not solved.

According to what has been written in the previous chapters and we accept the following, that in case of wood burning the dioxin is formed according to

De Novo synthesis

- Sulphur (S) and (N_2) decreases the amount of dioxin formed
- pH < 7 (acid) ash is a catalyst for dioxin forming then we can create a (theoretically) optimally operating furnace system, that emits optimal amount of dioxin.

Choosing fuel

The water in moist fuel cools the combustion area, it draws the heat necessary to evaporate from the combustion area and the water vapor gets in the exhaust gases. The water content of the exhaust gases condense in the chimney and the condensate is polluted with dioxin [1, 6]. The size and shape of fuel material affect the burning efficiency of carbon content of fuel, i.e. the amount of ashes and soot formed. The burning of rate of carbon is the best if

the ratio of surface and volume (S/V) of the fuel is the biggest. This ratio can be increased by decreasing the size of the fuel.

FURNACE, FURNACE TECHNOLOGY

The size of the combustion area has to be such, that at all points of furnace are above the upper limit temperature (800°C) of the De Novo synthesis, avoiding formation of dioxin. There has to be excess oxygen so during the combustion the maximal combustion temperature is reached (800°C-1000°C). It must be guaranteed that the fuel spends maximal time in the combustion area. This ensures the best burning of carbon and due to this, the least amount of ash, soot and dust are formed.

Under industrial conditions the best available furnace is the fluid bed furnace; this is used internationally as well in Hungary.

EXHAUST GAS TECHNOLOGY

During combustion the exhaust gases leave the furnace at furnace temperature. At the exit point of the chimney the temperature of exhaust gases has to be higher than 100°C, otherwise the water that came from the fuel and the air used for combustion condenses in the chimney. The temperature of the exhaust gases can be utilized with a heat exchanger. After the heat exchanger the temperature of the exhaust gases drops under 200°C and no dioxin is formed during the remaining flow of gases in the system. According to researches and measurements the de Novo synthesis play important role in the processes of the heat exchangers. To prevent the de Novo synthesis, a prefilter has to be built in before the exhaust gas reach places (e.g. heat exchanger) having temperature range of de Novo synthesis (600-200°C). The prefilter removes the flying ash and the larger sized (>100µm) soot content of the exhaust gases. The prefilters have to be compatible with exhaust gases with a temperature $T > 600^{\circ}\text{C}$. For this purpose a cyclon, ceramic or an electric filter is suitable. After the heat exchanger before the exit point a fine filter (fabric filter) can be placed. With this method the formation of dioxin is not ceased, but their amount is decreased significantly. According to our concept the formation of dioxin can be further decreased if sulphur (S) or nitrogen (N_2) is introduced in some way to the area belonging to the De Novo synthesis.

METHOD FOR MEASURING DIOXIN

The measurement of dioxin requires dedicated sampling, complicated multi level cleaning process and the use of high resolution GC/MS instrument [19]. Due to the high cost and complexity of measurement it is common that the values of the industrial process is multiplied by factors -based on international practice- and this estimated result is accepted instead of measurement [20].

In case of sampling dioxin, the sampling is difficult. It is important to avoid the exhaust gas sampler to become a catalyst to the formation of dioxin with its metal parts and surface, which can lead to soot deposition. Due to the small concentration of materials multi level sample preparation processes are necessary. These steps can produce artifacts or severe loss of searched compounds. To avoid the contamination of other sources and to avoid poisoning of technical staff sample treatment of dioxin has to be done in a suitable laminar box. The separation of all compounds can not be achieved on one chromatographic column due to the large number of congeners. Furthermore to determine undoubtedly the exact structure of a congener, high resolution mass spectrometer has to be used. Due to the difficulties discussed above, the measurement of dioxin is not possible even in a well equipped routine environmental laboratory, In Hungary 7 laboratories claims they can measure dioxin, but only 3 has the required high resolution GC/MS device to provide uncountable analysis results.

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