

## **Production of Dioxins with Special Regard to Furnaces Using Renewable Energy**

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### **1 Introduction**

Several compounds of the dioxin-homologues are extremely toxic; therefore the decreasing of the dioxin emission has special importance in the environmental protection. This article gives a brief overview of the structure of dioxins as well as the mechanisms of the production, describes their toxic effects, their appearances and their determination methods. 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.

### **2 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; Figure 1 shows the general formula [1, 2].

Different compositions of polychlorinated compounds –congeners – can be found in environmental and in biological samples. These materials have wide range of toxic effects. The substitution level and the location of substituents highly depend on the reaction conditions. There are usually more dibenzo-dioxins than dibenzo-furans in different origin mixtures.

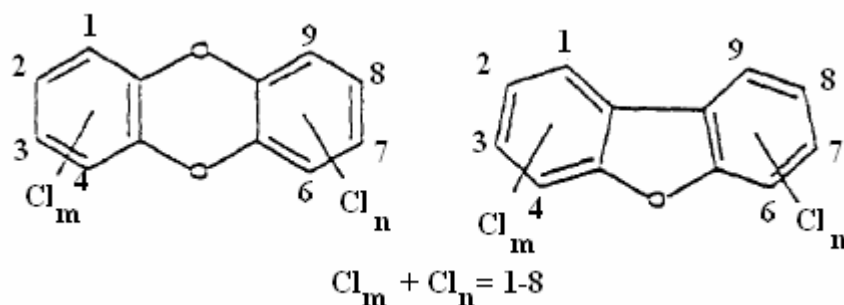


Figure 1  
 General formula of polychlorinated-dibenzo-p-dioxins and polychlorinated-dibenzo-furans

### 3 The Biological Effect of Dioxins

The extremely high toxic effect of 17 dioxins has been unquestionably proven (see Table 1).

The most dangerous of these compounds is the one shown on Figure 2; 2,3,7,8-tetrachloro-dibenzo-p-dioxin (2,3,7,8-TCDD)

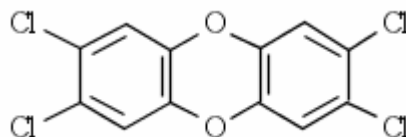


Figure 2  
 The structure of the most toxic compound, having the master unit of the toxic equivalent factor (TEF):  
 2,3,7,8-tetrachloro-dibenzo-p-dioxin (2,3,7,8-TCDD)

This compound – taken orally, in a 0,6 µg/kg dose - - killed half of the male guinea-pigs (o.v. LD<sub>50</sub>). The other congeners have different, less toxic effect. Most commonly the compounds are characterized with their toxic equivalent factor (TEF), but other kinds of units are also used in the literature (Eadon, Nordic, I-TEF) [1, 2, 3]. TEF expresses the toxicity of a compound relative to the most toxic one 2,3,7,8-TCDD) (see Table 1) [1, 2]. The toxicity of dioxin mixtures are usually characterized by TEQ – Toxic equivalent quotient, but some other expressions are used also (I-TEQ, WHO-PCDD/F-TEQ etc.) TEQ is the quantity of dioxin and dioxin-like PCB congeners, weighed to their TEF values. In this way.

Homologue group	Toxic isomer	Eadon	Nordic	TEF
<b>TCDD</b>	2,3,7,8	1	1	1
<b>PCDD</b>	1,2,3,7,8	1	0.5	0.5
<b>HxCDD</b>	1,2,3,4,7,8	0.03	0.1	0.1
	1,2,3,6,7,8	0.03	0.1	0.1
	1,2,3,7,8,9	0.03	0.1	0.1
<b>HpCDD</b>	1,2,3,4,6,7,8	—	0.01	0.01
<b>OCDD</b>	1,2,3,4,6,7,8,9	—	0.001	0.001
<b>TCDF</b>	2,3,7,8	0.33	0.1	0.1
<b>PCDF</b>	1,2,3,7,8	0.33	0.01	0.05
	2,3,4,7,8	0.33	0.5	0.5
<b>HxCDF</b>	1,2,3,4,7,8	0.01	0.1	0.1
	1,2,3,6,7,8	0.01	0.1	0.1
	1,2,3,7,8,9	0.01	0.1	0.1
	2,3,4,6,7,8	0.01	0.1	0.1
<b>HpCDF</b>	1,2,3,4,6,7,8		0.01	0.01
	1,2,3,4,7,8,9		0.01	0.01
<b>OCDF</b>	1,2,3,4,6,7,8,9		0.001	0.001

Table 1  
Various weighting factors of the toxicity of different dioxins

Dioxins chlorinated on 2, 3, 7, and 8 position have the worse toxicity. The toxic effect decreases from 4 substituent to 8.

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 [4, 5].

The toxicity factor is different for different test species. Human effect is related to mammal factors [6]. Fish are more sensitive to dioxin exposure than aquatic invertebrates or reptilians. It is an accepted opinion that 10pg/body mass /day TEQ is tolerable for human beings [7].

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. At the same time the number of cancer disease and diabetes had increased too. Dioxins were contaminants of the defoliating agent 2,4,5-trichlorophenoxy- acetic acid [8].

At Seveso in 1976 dioxins escaped into the air during an industrial accident as a by product of trichloro-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 [8].

In 1999 in Belgium 7 million of chicken and 60 thousand of pig had to be killed because of dioxin poisoning [8]. Victor Yuschenko, Ukrainian president had been poisoned with dioxin in 2004. He got cloracne on his face that deforms his face until today. Nowadays in Hungary – 2007 – the dioxin contaminated guargum makes difficulties.

#### 4 How Dioxins Get Into Human Body

Although dioxins reach the environment through air, they enter the human body through the food-chain (Figure 3).

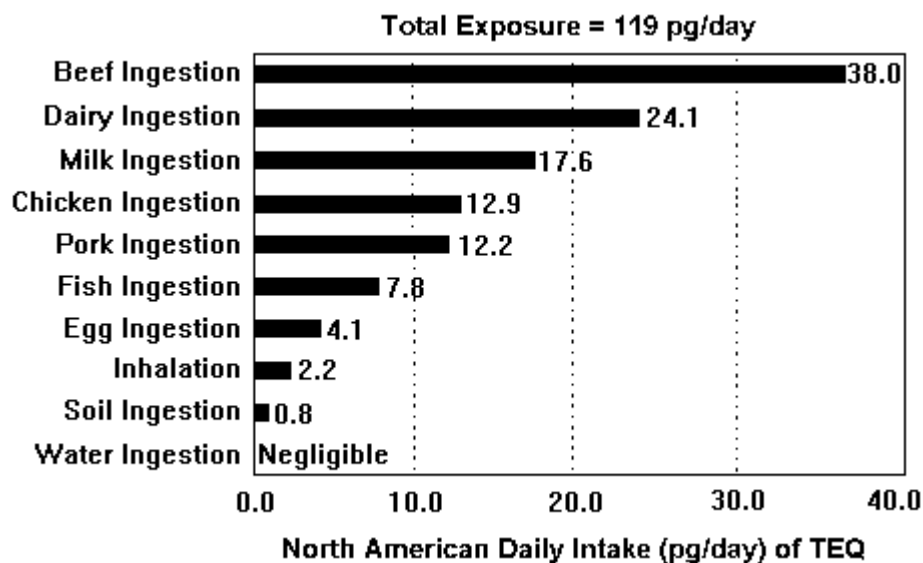


Figure 3  
Human dioxin intake from different sources in North America [7]

The human intake of dioxins is mainly connected to fatty food (fish, dairy products, etc.) because the dioxins are slightly soluble in water. There are exceptions: contamination at the workplace (black coal, aluminum industry, secondary copper metallurgy, etc.) or flats close to of huge environmental contaminants (waste combustion, coal power plants).

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) [9]. For example the human half-decay period of 2,3,7,8-TCDD is 7 years. Their persistent character causes their emission decrease and elimination are emphasized in Stockholm convention [9].

In EU, including Hungary, the limit values of dioxins are 1- 3 pg/g (depending on the species) for animal fats and 0.75 pg/g for vegetable fat in WHO-PCDD/F-TEQ/g units.

## 5 Formation of Dioxins

Carbon, oxygen, hydrogen, and chlorine are required to form dioxin. The components should be present as elements or as compounds. Dioxins are not produced on purpose, they form as by-products of industrial syntheses or during insufficient combustion.

Dioxins can form as by-products on industrial syntheses of fungicide Pentachlorophenol, herbicide chloroxy-acids, disinfectant trichlorozane, hydraulic liquid PCB-s (polychlorinated biphenyls) and paper bleaching [11]. The main structure elements (precursors) of the dioxin molecules are present during production process either as intermediates or byproducts of these compounds. The formation of these kind of dioxins is demonstrated by Figure 4 – showing how dioxin is formed during the syntheses of 2,4,5 –trichloro-phenoxy-acetyl acid. The following parameters help dioxins formation in these cases: high temperature (>150 °C), basic environment, catalytic effect of heavy metals, chemical entity forming factors (UV light) chlorine containing compounds. The susceptibility sequence of different chlorine containing compounds to form dioxin is as follows: chlorinated phenols > chlorinated benzenes > chlorinated aliphatic hydrocarbons > inorganic chlorine compounds.

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.

PCB-s, herbicides (2,4,5 trichloro-phenoxy-acidic, lindane), dyes, chlorine containing cyclic compounds of wood impregnating products, are precursors of dioxin formation if the materials are heated over 400°C and the combustion is incomplete [12-14]. Similarly to the formation of the production by-products, dioxins are formed from bigger structures, like it is demonstrated on Figure 5 [14].

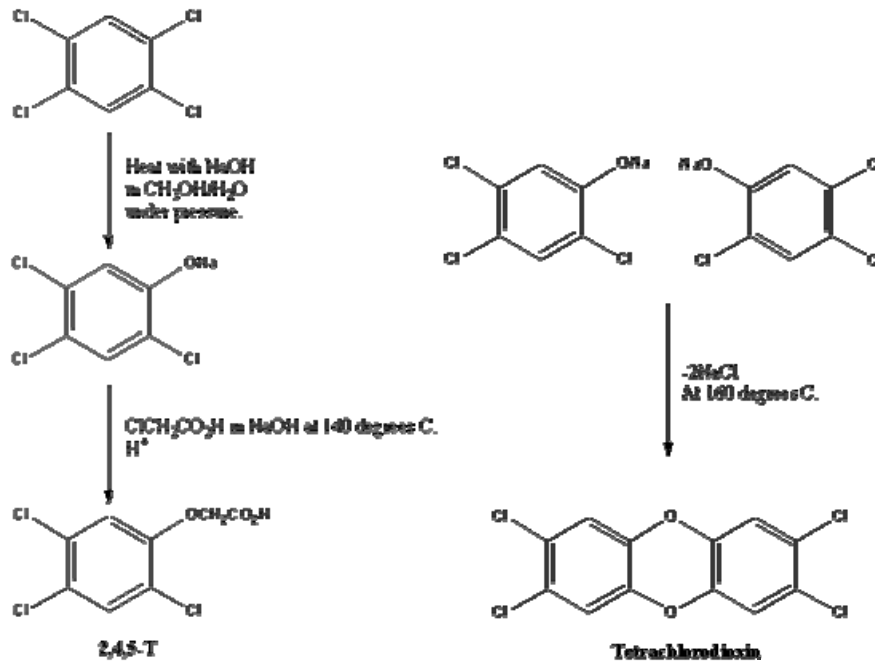


Figure 4  
 Synthesis of 2,4,5-trichloro-phenoxy-acetic acid (2,4,5-T) and the dioxin generated from the intermediate [11]

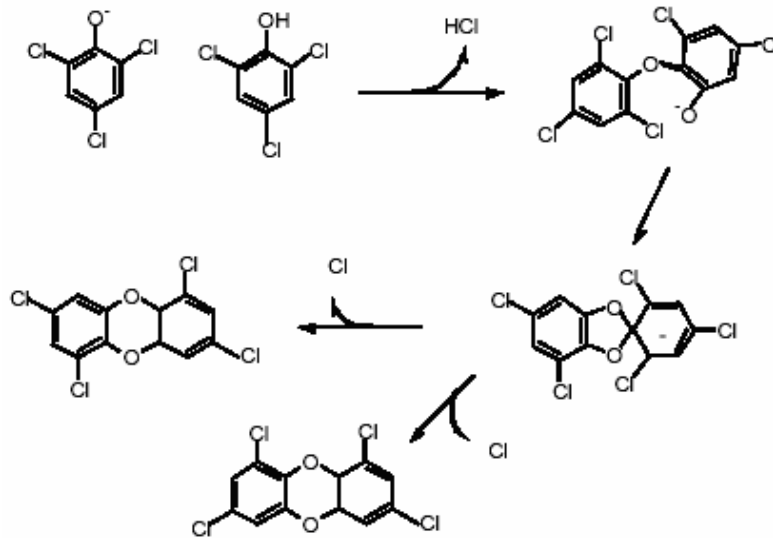


Figure 5  
 Dioxin formation from trichlorophenol precursor with carbon black catalysis [13]

The dioxin syntheses starting from inorganic or smaller organic compounds have greater importance than the one through precursors. These reactions have different paths.

The importance of the homogeneous gaseous phase reaction is negligible, because the reaction rate increases only over 600 °C [12, 13]. It has been stated that the rate of dioxin formation from PCB-s increases up to 700 °C, but over 800 °C the reaction rate is negligible [15].

Most of the dioxins are formed according to the de Novo reaction [11, 14, 16, 17], where inorganic chlorine, carbon, water, oxygen 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 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 ITEQ value, while the soot found in the filter showed two magnitudes bigger values [16].

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 [16].

The amount of CO and CO<sub>2</sub> does not influence the formation of dioxin in the de Novo synthesis, the oxygen necessary for the formation diffuses from air into the crystal structure of the coal. 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.

## 6 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 [18].

The emission of dioxin reached its maximum in the seventies but it decreases since then due to measures taken. This decrease varies country by country.

The sources of dioxin are divided into ten categories as it can be seen in Table 2.

Category	1987	% Total	1995	% Total	2002/4	% Total
<b>1 Combustion:</b>						
<i>Municipal waste</i>	8 877	77	1 250	71	12	32
<i>Medical waste</i>	2 590	22	488	27	7	18
<i>Sewage sludge</i>	6	0.05	14	0.84	14	39



Category	1987	% Total	1995	% Total	2002/4	% Total
<i>Hazardous waste</i>	5	0.04	5	0.33	3	9
<b>Combustion total</b>	11 478	82	1 758	54	37	3
<b>2 Backyard barrel burning</b>	604	4	628	19	628	56
<b>3 Metal smelting</b>	955	6	301	9	35	3
<b>4 Cement kilns</b>	131	0.94	173	5	25	2
<b>5 Land-applied sewage sludge</b>	76	0.55	76	2	76	6
<b>6 Pulp &amp; paper</b>	372	2.67	23	0.71	15	1
<b>7- Coal-fired utilities</b>	50	0.36	60	1	60	5
<b>8 Industrial wood burning</b>	26	0.19	27	0.85	27	2
<b>9 Residential wood burning</b>	89	0.64	62	1	62	5
<b>10 Diesel trucks</b>	27	0.20	35	1	35	3
<b>11 Other</b>	137	0.98	103	3	100	9
<b>TOTAL</b>	<b>13 949</b>	<b>100</b>	<b>3 252</b>	<b>100</b>	<b>1 106</b>	<b>100</b>

Table 2  
Decrease of the dioxin emissions due to the environmental measures in USA [8]

Table 2 shows unambiguously that the dioxin emission fell to the tenth in the USA during the examined period. 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.

To summarize, it can be said, that the dioxin emissions halved in 10 years due to the Stockholm act [19].

Table 3 is a summary based on Hungarian measurements and estimates made on dioxin emissions in 2004 [20].

Kat.	Source categories	PCDD/PCFD emission (g TEQ/year) 2004				
		Air	Water	soil	Product	Production by-product
1	Waste combustion	<b>0,890</b>	0,000	0,000	0,000	6,225
2	Iron and other metallurgy	<b>28,461</b>	0,000	0,000	0,000	30,652
3	Heat and energy production	<b>21,670</b>	0,000	0,000	0,000	2,015
4	Mineral production	<b>3,347</b>	0,000	0,000	0,000	0,000
5	Traffic	<b>0,685</b>	0,000	0,000	0,000	0,000
6	Uncontrolled combustion	<b>37,188</b>	0,000	54,375	0,000	0,000
7	Chemical and other goods production	<b>0,256</b>	0,269	0,000	0,058	0,000
8	Different other technologies	<b>0,350</b>	0,000	0,000	0,000	1,216
9	Waste deposition	<b>0,000</b>	0,000	0,000	0,000	0,000
10	Possible other emission	<b>10,000</b>				
<b>1-10</b>	<b>Total</b>	<b>102,847</b>	<b>0,269</b>	<b>54,375</b>	<b>0,058</b>	<b>40,108</b>

Table 3  
 Estimated dioxin emission values in Hungary, 2004 [20]

Table 3 shows significant values for metal manufacturing, power plants and not controlled burning (illegal garbage burning). According to the EU regulation the appropriate limit, 0,1 ngTEQ/m<sup>3</sup> is not exceeded by most legal emissions.

Since the metallurgy industry and power plants are responsible for most of the emission to justify the estimates a series of measurements were made in 2005 (Table 4).

Technology, Measuring location	Production, combusted material (t)	PCDD/PCDF (g)
Household combustion FKF RT.,Hulladékhasznosító Mű, Bp.	279 000 (waste combusted)	
Thermal power station (braun coal), Vértesi Erőmű, Oroszlány	1 432 000	0.02
Thermal power station (biomass), Pécsi Erőmű	3 350 000 (chipping)	0.002
Thermal power station (biomass), Kazincbarcikai Erőmű	354 500 (chipping)	0.014
Thermal power station (biomass), Bakonyi Erőmű, Ajka	135 000 (chipping)	0.005
Iron and steel industry – cast iron Rába Futómű, Győr	14 660	0.0015
Iron and steel industry - cast iron Mohácsi Vasöntöde	1 902	0.0001

<b>Iron and steel industry, sinter, Dunaferr Dunaújváros</b>	1 000 000	1.46
<b>Iron and steel industry, sinter, BÉM, Sajókeresztúr</b>	21 000	1.69
<b>Primer aluminum production, MAL, Inota</b>	533 000	1.05
<b>Other metallurgy secondary aluminum production MAL, Ajka</b>	10 440	2.27
<b>Secondary zinc production Sátoraljaújhely</b>	231	0.0001
<b>Electro steel production, DAM 2000 Kft., Diósgyőr</b>	1 100	0.0003
<b>Secondary copper production</b>	5 500	0.015
<b>Tested location total</b>		<b>6.528</b>

Figure 4

Dioxin emission values of representatives of high temperature technologies in Hungary, 2005 [20]

It is remarkable, that no dioxin could be measured at the garbage combustion plants in Budapest.

The dioxin emissions levels are decreasing, similar to the world trends in Hungary. The 103 g-TEQ measured in the atmosphere fits into the European average. The dioxin pollution coming from the industry gradually decreased due to the fact, that many factories closed or decreased its production.

The domestic sources are responsible for most of the emissions (25%), while in Hungary it is responsible for a smaller portion (12%). The primary reason is that most of the households changed to natural gas and its dioxin emission coefficient is practically zero. On the other hand it can be expected that after the gas prices are raised the ratio of mixed and fossil burning will increase.

The emissions is around 3g/year from power plants, including biomass burning, which is 3 percent of the total emission [20]. The reason for the good results from the environmental aspect is that in power plants to reduce the regular pollutants (SO<sub>2</sub>, NO<sub>x</sub>, 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 (BAT), the filters and electrostatic precipitator, the use of semidry or moist exhaust gas cleaners [11].

Further decrease can be achieved using the following methods [21]:

- Limiting household, illegal garbage burning.  
 The polluted waste wood should only be combusted in furnaces with proper gas cleaners.
- Further improvement of furnace technology.

## 7 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, as it is illustrated by Tables 2 and 3.

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 [11]. The treatment of plants with pesticide can also be a source of dioxin since they can be precursors [13].

However the untreated plants are also significant sources which were examined in case of forest fires, wasteland burning and household heating [23, 24].

In case of household wood burning 0.35 – 2.4 µgTEQ/ton is the rate of emission. Data from Germany show (15 g/TEQ/year) that it is bigger than the one of the coal and oil furnaces (5 g/TEQ/year) [24]. Examining smaller furnaces the emission rate is 0.0020 ng I-TEQ/m<sup>3</sup> for oil and gas furnaces while it is 0.014 - 0.076 ng I-TEQ/m<sup>3</sup> for furnaces burning wood [24, 25].

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 Figure 6 [26, 27].

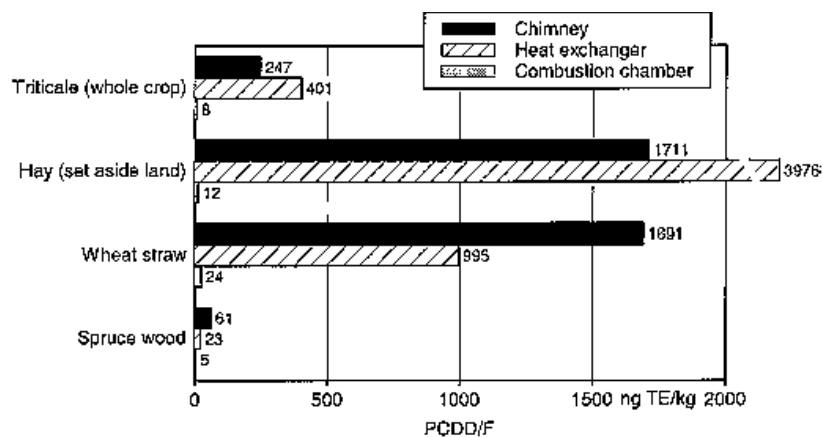


Figure 6  
 Dioxin concentration in ash and chimney soot, combusting different kind of plants [31]

If untreated biomass is burnt, the following causes the formation of dioxin [23]:

- 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 [32].

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.

In the future, dioxin emissions can be effectively reduced by using appropriately designed furnaces as it was started in the USA in 1990 [29].

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 significant dioxin emission [20, 25].

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.

## 8 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
- Briquette
- 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<sub>2</sub>) 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 [2, 11]. 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.

## 9 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.

## 10 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 (>100 µm) 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<sub>2</sub>) is introduced in some way to the area belonging to the De Novo synthesis.

## 11 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 [30]. 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 [18].

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 claim they can measure dioxin, but only 3 has the required high resolution GC/MS device to provide uncountable analysis results.

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