DIOXINS – THE UNCONTROLLED TOXIC CONTENT OF EXHAUST GASES FROM IC ENGINES.

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Abstract
It is found that the chemical composition of exhaust gases emitted by IC reciprocating engines includes not only such harmful toxic substances as NOx, CH, PM and CO but also dioxins. Dioxins are characterized by incredibly destructive impact on human health. In the paper a short profile of dioxins, terms of dioxin formation and measures for their reduction are presented. Some experimental data concerning dioxin emission from the road transport is also involved.

1. INTRODUCTION.

Combustion processes are the main sources of the dioxin emission to the ambient air (see Fig.1.) [4], [9].

Taking the emission percentage of several sources into consideration as the reasonable factor, the road transport is seemed to be not as significant as other sources of dioxins but the road transport sources of dioxins are widespread and they are placed inside human living surroundings, especially in highly urban area. Norms of natural environmental protection in highly industrialized countries include limits of the dioxin emission into ambient air. Dioxins are thought to be the most carcinogenic substances. They have not only allergic features but also they can damage DNA code and have destructive impact on pregnancy. Due to dioxin impact on humans, analysis of transport sources of dioxins should be taken into investigation. It is very probable, that the trace concentration of dioxins (a few ppm) can be more destructive than the NOx or even PAH (polycyclic aromatic hydrocarbons) emission from the IC engine. Moreover, it is worth of noticing that the small dioxin dose does not bring immediate effect on our health. They destroy living creatures by their long-term negative influence on organic tissue as a result of their accumulation feature in the adipose tissue. Up-to-date limits of the dioxin emission from IC engines are not mentioned but it seems it is only a matter of time. The Californian EPA regulations, which are considered to be the strongest in the world, include dioxins (PCDD, PCDF and PCB) on their lists as toxic components of exhaust gases from the IC engine.
2. BRIEF PROFILE OF DIOXINS

When some atoms of hydrogen are replaced by chlorine in the polycyclic aromatic compounds (see Fig.2.) then PCDDs (polychlorinated dibenzo-p-dioxins) or PCDFs (polychlorinated dibenzofurans) can be formed. Using informal language we often called them dioxins.

![Dioxin structures](image)

**Fig.2.** a) 2,3,7,8-Tetrachloro-dibenzo-p-dioxin, b) 2,3,4,7,8-Pentachloro-dibenzofuran.

Dioxins are the chloro-organic polycyclic compounds. They are characterised by extremely high thermal stability (up to 1000 degrees of Centigrade), high resistance for both oxidation and biodegradation. Their half-life is in the range from 10 to 30 years, what seems to be quite a long time in comparison with human life as regards the dioxins accumulation feature in the human adipose tissue. It is observed that long exposure to the UV radiation can rapidly shorten the half-life of dioxins.

Moreover, it is noteworthy that not only chlorine can substitute hydrogen in these compounds but fluorine and bromine can do it as well. In that case we can distinguish:

- PFDD/PFDF (poly-fluorinated dibenzodioxins/furans)
- PCFDD/PCFDF (poly-chlorinated-fluorinated dibenzodioxins/furans)
- PBDD/PBDF (polybrominated dibenzodioxins,furans)
- PCBDD/PCBDF (polychlorinated-brominated dibenzodioxins,furans).

Although, there is a huge number of isomers of the dioxins and furans, the 2,3,7,8-TetraChloroDibenzo-p-Dioxin (T4CDD), the 1,2,3,7,8-PentaChloroDibenzo-p-Dioxin (P5CDD) and the 2,3,4,7,8-PentaChloroDibenzoFuran (P5CDF) are considered to be the most toxic substances.

To evaluate the total toxicity of PCDDs and PCDFs, the so-called I-TEQ (International Toxic Equivalent) indicator was established. The I-TEQ (often appearing as TEQ) informs about the total concentration of dioxins using units of mass. Its value shows the toxicity of some the most harmful PCDD/Fs recalculated to the T4CDD by multiplying their mass ($m_i$) by their importance factors ($T_i$) (see equation 1).

$$ I - TEQ = \sum_i m_i \cdot T_i $$

Where: for 2,3,7,8-T4CDD; $T_i=1$, 1,2,3,7,8-P5CDD; $T_i=1$, 2,3,4,7,8-P5CDF; $T_i=0.5$

H6CDD; $T_i=0.1$; H6CDF; $T_i=0.1$ 

H7CDD; $T_i=0.01$; H7CDF; $T_i=0.01$ 

O8CDD; $T_i=0.0001$; O8CDF; $T_i=0.0001$

I-TEQ is presented in pg, ng or μg per kg or Nm$^3$, however, in literature we could find other units of I-TEQ e.g. fmol-, pmol/m$^3$, ppt, ppb, ppm.
It is found that PCBs (PolyChlorinated Biphenyls) are sometimes measured as dioxins. WHO admits that the TDI (tolerable daily intake) dose for humans cannot exceed 10 pg of the I-TEQ per 1 kg of human body, even though it is not confirmed that such a limit is harmless.

In 1994 the European Union established the 94/67/EC resolution, in which we can find 0.1 ng I-TEQ/Nm$^3$ limit of the dioxin emission from combustion processes in stationary plants (particularly waste incinerators and metallurgical industry). In Poland the adequate legislation act is prepared. It will also include limit of the dioxin emission at maximum value 0.1 ng I-TEQ/Nm$^3$ of exhaust gases.

3. TERMS OF DIOXIN FORMATION.

Mechanisms of the PCDD/Fs formation are still not well recognised. Frankly saying, experimental databases concerning the dioxin emission from combustion processes are not extensive enough to conduct the correct verification of theoretical modelling. It is obvious that for the dioxin formation chlorine is needed as the substrate. From this point of view, appearance of precursors such as PCBs (polychlorinated biphenyls) and chlorinated cyclic hydrocarbons (particularly chlorinated benzenes) as substrates are seen as favourable environment for creating dioxins.

During combustion dioxins can be formed in the following processes [3], [4]:

- Dioxins can be created as products of oxidation of the precursors. Chemical reactions are the most probable in temperature range from 300 to 800 degrees of Centigrade. It is proved that 10 g of PCDFs and 1 g of PCDDs can be obtained after burning 1 kg of PCBs.
- Dioxins can be formed as a result of de novo synthesis, which takes place in the plasma zone or in the flame zone where atoms of carbon, hydrogen, chlorine and oxygen react with each other.
- Dioxin formation is possible on surface-active PM particles. Especially, particles of soot with accompanying HCL, CO$_2$ and H$_2$O provide good terms for dioxins formation. The reactions take place intensively during cooling exhaust gases when temperature of the gases drops to 300-400 degrees of Centigrade [4],[10] (Fig. 3.).

![Fig. 3. Partial pressure of PCDDs formation vs temperature (supported on data from [10]).](image)

In the Fig. 4 we can see the PCDDs formation at change of hydrogen content of fuel. It is found that intensity of the dioxin formation rapidly goes down during combusting fuels with the hydrogen percentage content higher than 7%. On the basis of that analytic relationship we could conclude that dioxin emission is greater for fuels with higher C/H ratio.
Chlorine can be delivered to the combustion process as the content of:
- fuel,
- lubricating oil,
- air.
It is noticed that the trace concentration of chlorine is sufficient enough for dioxin formation. Chlorine concentration of 0.001% can lead to the dioxin creation at amount of 100 ng I-TEQ/Nm³ in favourable circumstances.
The average concentration of chlorine in gasoline is about a few mg per 1kg; in diesel oil – nearly 1 mg/kg [1].

4. EXPERIMENTAL INVESTIGATION.

Although importance of the road transport in global dioxins production is insignificant, it should be considered as the dangerous and regarded source of dioxins due to its specific distribution of toxic components.
Due to elimination of the leaded gasoline from the market, the average dioxin emission from SI engines is about 4 times lower than the dioxin emission from diesel engines, even though it is found, that the percentage content of the most toxic congener T4CDD is higher in the emission from a gasoline engine [8]. In this context the I-TEQ factor for dioxin emission from gasoline engines is about 2.5 times lower than from diesel ones.
Investigation of the dioxin emission caused by the road transport in Germany shows the emission of PCDD/Fs from light duty diesel vehicles at level 0.024 ng I-TEQ per 1L of fuel (0.0024 ng I-TEQ/km). It was assumed the engine fuel consumption equalled 10 km/L of fuel. The dioxin emission from diesel trucks was in the range from 0.070 to 0.081 ng I-TEQ/L. It was reported, that passenger diesel cars emitted 0.048 ng I-TEQ/L. Similar measures conducted in the USA [5] present that the dioxin emission from trucks in highways is equalled 0.0151 ng I-TEQ/km. It is almost 4 times lower in comparison with the emission in city terms of road traffic (0.0499 ng I-TEQ/km). The fuel consumption was assumed as 5.5 km/L.
Additionally, it was found that the T4CDD, H7CDD and OCDD are dominated in the PCDDs composition. However, in the PCDFs composition, the MCDF and DCDF (Mono-chlorodibenzofuran, Di-chlorodibenzofuran) are the dominants. It is also stated that the PCDF emission has greater influence on the I-TEQ because of its greater amount. The results were confirmed by Marklund and others [1], [5], [8]. Furthermore, they examined influence of type of the lubricating oil on the dioxin emission from combustion processes in the IC engine. On the basis of research, which they carried out, it was found that higher emission of dioxins (8.2±11 pg
I-TEQ/m³ of exhaust) was observed after applying a synthetic oil (chlorine content - 50mg/kg) to IC engine. When a mineral oil (chlorine content - 40mg/kg) was used than the PCDD/Fs emission dropped a bit into the range between 2.4÷4.1 pg I-TEQ/m³ [1]. They also obtained similar proportion during analysis of the PCBs emission of exhaust gases from a gasoline SI engine.

5. MEASURES FOR REDUCING DIOXIN EMISSION.

As long as precise mechanisms of the dioxin formation are unknown, we cannot be able to proceed to do any optimization of combustion processes in IC engine for achieving successive reduction in the dioxin emission.

It is unquestionable fact, that the emission of dioxins is correlated with the amount of chlorine. Hence, at first the measures for chlorine limitation in combustion processes should be performed. The fuel composition is the most important within that point of view. The elimination of chlorine from fuel additives, especially for gasoline, should be performed. De novo synthesis is highly affected by the PCBs precursors, so the precursors formation should be limited in the fuel composition. Moreover, the amount of aromatic hydrocarbons (benzene) ought to be reduced.

Similar conclusions can be obtained during making chemical analysis of the lubricating oil composition, which can include up to 50mg chlorine per 1kg. Adding inhibitors or adsorbents for removing precursors from exhaust gases before they are cooled to 400 degrees of Centigrade is the following measure for potential investigation.

Sulphur dioxide SO₂ is the chemical component, which is characterized by the satisfied inhibition feature for the dioxin formation during cooling them. It strongly slows down formation of PCDD/Fs by bonding molecular chlorine according to the Griffin and Lindbauer scheme [7]:

\[
\text{SO}_2 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_3 + 2\text{HCl}
\]

It is observed that the oxygen deficit comes to formation of dioxins during fuel combustion. Incomplete combustion can be estimated by measuring the CO concentration in exhaust gases. For this reason the CO concentration in exhaust gases can be used as the reliable factor for the dioxin emission.

6. CONCLUSIONS.

PCDD/Fs formation is concerned with chlorine presence in substrates and their incomplete combustion. Improper operation and the incorrect excess air number lead to creating soot particles in the CI engine. The dioxin content of exhaust gases from large scale engines (heavy duty) is higher than from light duty ones because of greater number of soot particles, which create favourable conditions for the dioxin formation. Although the influence of oxygen on dioxin formation is not recognised, it is proved that oxygen concentration in combustion zone significantly contributes to both de novo synthesis and the CO content in exhaust gases. From this point of view the CO content is seen as a satisfied indicator for the PCDD/Fs concentration in exhaust gases. Measuring dioxin emission and intensive theoretical research on the field of mechanisms of PCDD/Fs formation should be carried out due to keeping the total PCDD/Fs at minimum and finally to eliminating them from our life.
REFERENCES:


