CATALYTIC DESTRUCTION OF DIOXINS ON V2O5-WO3/Al2O3-TiO2 CATALYST. EFFECT OF TEMPERATURE AND CATALYST LOADING

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Introduction

Incineration of such non-homogeneous material as wastes, no matter if these are municipal, industrial and hospital wastes or sewage sludge, is a source of emissions to the atmosphere of very many chemical substances, often including toxic, carcinogenic and other substances. One of the key arguments against building waste incineration plants is the emission of dioxins from waste incineration process to the atmosphere.

Methods for the reduction of dioxin emission from technological processes can be roughly divided into two groups – primary methods and secondary methods. The primary methods include intervention in the technological process and providing such process conditions that the amount of generated dioxins be as small as possible[1]. Among secondary methods for the reduction of dioxin emissions the most important are as follows:

- Adsorption on activated carbon (on a solid bed or a stream method),

- Catalytic decomposition of dioxins on a catalyst,

- Filtration-catalytic method[2],

- Absorption-adsorption method[3].

Catalytic degradation is the most important method for the reduction of PCDD/Fs emissions from incineration processes. The method has been known since the end of the 1980s[4], but it is still a subject of extensive studies.

Due to significant technical problems with obtaining a stable air stream containing trace (several ng/m^3) concentrations of PCDD/Fs, many researchers carried out their studies using other chloroorganic compounds, e.g. o-dichlorobenzene, trichloroethylene, tetrachloroethylene, etc. The best PCFDD/Fs "simulator" is considered to be o-dichlorobenzene, which has a chemical structure similar to that of the half molecule of tetrachlorodibenzo-p-dioxin.

In the previous work[5], investigations on 1,2-dichlorobenzene destruction on a V_2O_5-WO_3/Al_2O_3-TiO_2 catalyst were carried out.

Methods and Materials

Studies on the catalytic dioxin decomposition were carried out in a specially constructed semi-commercial apparatus, whose most important element was a catalytic reactor with a monolithic catalyst in the form of 150 ´ 150 ´ 100 mm cubes. The apparatus was described in detail in the previous work[5]. A catalyst was made from cordierite with an active layer composed of Al_2O_3 – 64% wt., TiO_2 – 26% wt., V_2O_5 – 6.6% wt. and WO_3 – 3.4% wt. A schematic diagram of the experimental set-up is shown in Fig. 1.

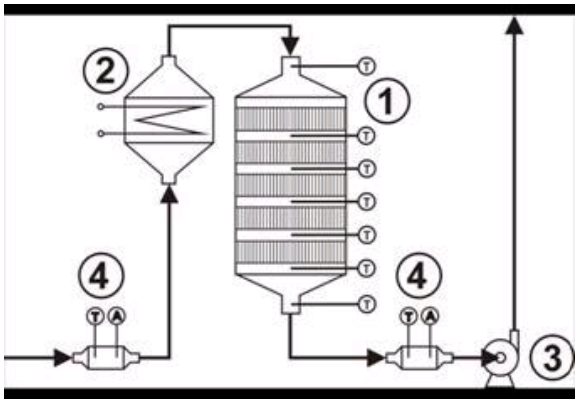

Figure 1. Schematic diagram of the experimental set-up. (1) catalytic reactor, (2) electric heater, (3) fan, (4) point of temperature, pressure, flow rate and concentration control

During the primary tests[5] (with 1,2-dichlorobenzene) no influence of mass transfer processes in the gas phase was reported.

Research on the catalytic decomposition of dioxins was carried out in the installation described above which was connected to a real incineration plant for hazardous wastes of the capacity about 3500 Mg/year, equipped with a rotary kiln. Investigations were performed on real flue gases using the above presented catalyst. The installation was connected behind the incineration chamber, heat exchanger and flue gas removal system (fabric filters). In that place ,the concentration of PCDD/Fs was usually ca. 150-450 ng per m^3. The aim of investigations was to determine the effect of temperature and catalyst load (GHSV) on dioxin decomposition efficiency.

Dioxin concentration in flue gases was determined according to EN-1948 standard. The concentration of 17 PCDD/Fs congeners in flue gases at the inlet and outlet from the catalytic reactor was identified, and then the toxicity index TEQ was determined according to the methodology recommended by WHO.

Results and Discussion

The effect of process temperature on the degree of PCDD/Fs decomposition is illustrated in Fig. 2, while the impact of catalyst loading (GHSV) in Fig. 3.

Very high efficiency of PCDD/Fs decomposition, reaching even 97.5% in the best-efficiency run, was obtained at the temperature of ca. 260ºC and catalyst loading of about 3500 1/h. Not much worse results (90-95%) were attained for the catalyst loading equal to 5900 1/h.

Figure 4 shows profiles of PCDD/Fs congeners at the reactor inlet and outlet, and Figure 5 illustrates the degree of decomposition of particular PCDD/Fs congeners in the best-efficiency run.

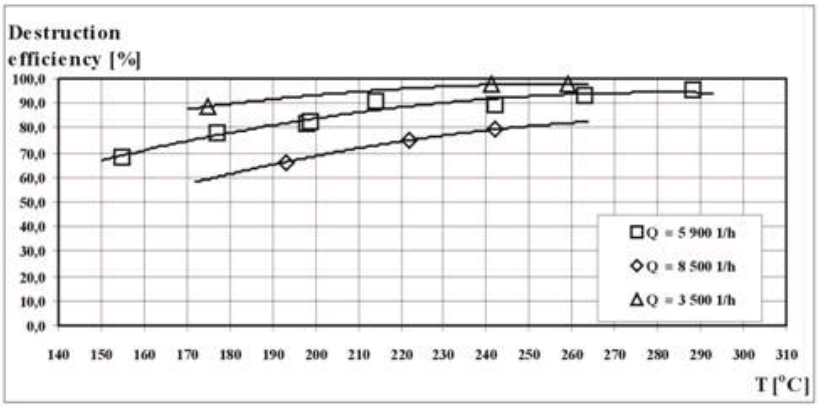

Figure 2. Effect of temperature on PCDD/Fs decomposition efficiency at various catalyst loading (Q [1/h]).

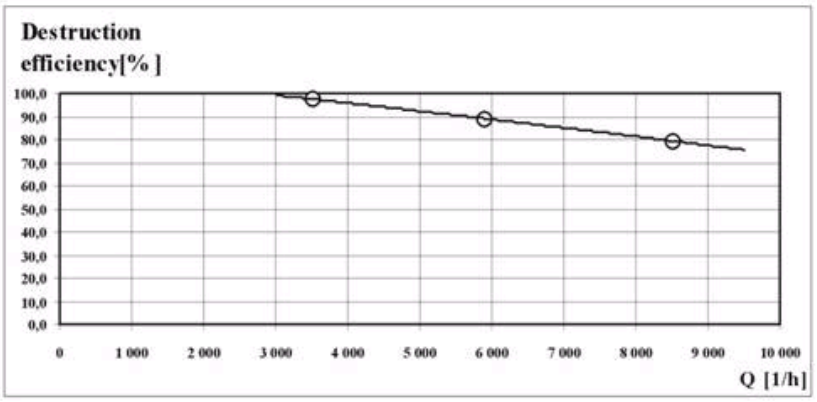

Figure 3. Effect of catalyst loading on PCDD/Fs decomposition efficiency at various temperatures.

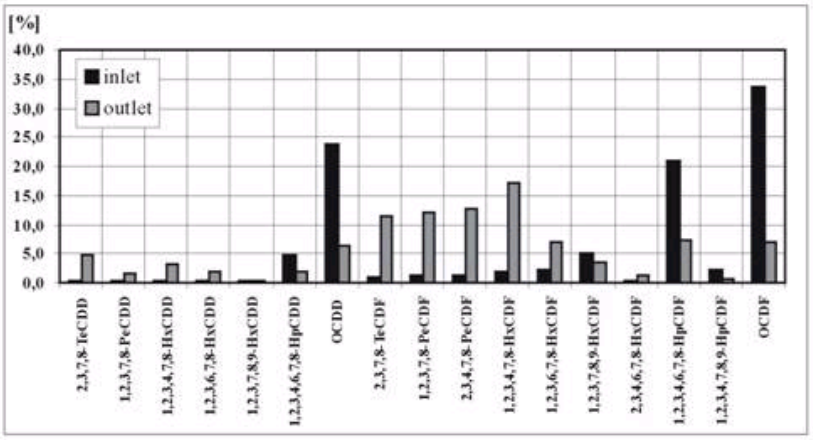

Figure 4. Congeners pattern at the inlet and outlet of reactor in the best-efficiency run.

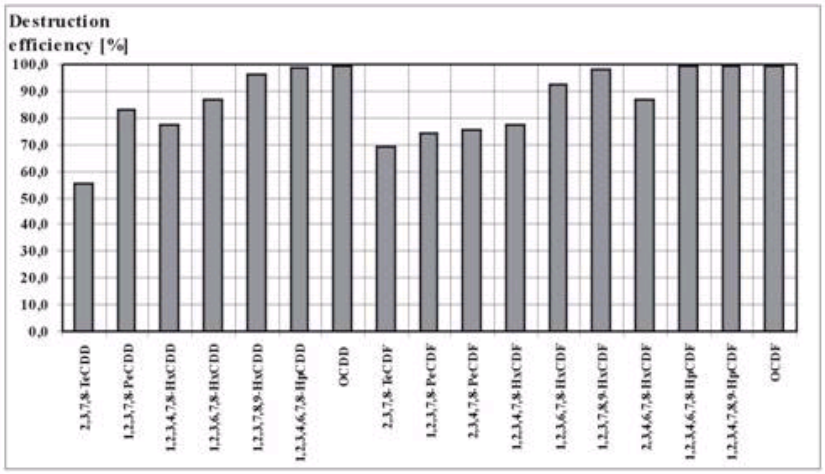

Figure 5. PCDD/Fs destruction efficiency for each congener in the best-efficiency run.

When analysing results of studies for particular congeners, it can be found that the highest efficiency is obtained for these PCDD/Fs congeners which contain the most chlorine atoms in a molecule. This is not in agreement with the

observations made by Weber[6] who found that most easily are decomposed (removal of chlorine atoms and oxygenation) the PCDD/s congeners with the lowest number of chlorine atoms in a molecule. However, Weber performed his research in model conditions, and subjected to decomposition a specified PCDD/Fs congener. In our study, investigations covered real flue gases from a hazardous waste incineration plant that contained all PCDD/Fs congeners. Assuming, after Weber, that congeners with a smaller number of chlorine atoms are decomposed most easily and that the reaction of removal of chlorine atoms from PCDD/Fs is a consecutive reaction (chlorine atoms are detached subsequently from a dioxin molecule), it becomes evident that we will observe a loss of dioxins with the biggest number of chlorine atoms, while in the case of a smaller number of chlorine atoms there will be two opposite processes – loss of a given congener due to decomposition, on the one hand, and on the other hand, an increase of the amount of this congener due to decomposition of molecules with a bigger number of chlorine atoms.

Acknowledgements

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References

1. Wielgosiński G. (2003) *Energy Policy (Polityka Energetyczna)* 6: 131-140.

2. W.L. Gore Associates (2001) - "Remedia®" leaflet.

3. Götaverken Miljö (2003) - "ADIOX®" leaflet.

4. Hagenmeier H. (1989) *VDI Berichte* 730: 239.

5. Wielgosiński G., Grochowalski A., Machej T., Paj ąk T., Ćwiąkalski W. (2004) *Organohalogen Compounds* 66: 1082-1086.

6. Weber R., Sakurai T., Hagenmeier H. (1999) *Appl. Catal. B* 20: 249-256.