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## UTILIZATION OF ENDS FROM PVC PRODUCTION WITH APPLICATION OF Fe-Cr CATALYST - DIOXINS HAZARD

### UTYLIZACJA ODPADU Z PRODUKCJI PCW Z UDZIAŁEM KATALIZATORA Fe-Cr W ASPEKCIE ZAGROŻENIA DIOKSYNAMI

**Abstract:** The subject of the investigation was the model solution containing 50 g/dm<sup>3</sup> waste light ends from PVC production, dissolved in the ethanol-water (1:1) mixture. The main components of light ends were as follows: trichloromethane, tetrachloromethane, and chloroderivatives of ethane. Granular ferric-chromic catalyst (TZC 3/1) was used in the investigation. The temperature range applied in experiments was 400-600°C and the contact time was 0.27 s. Gaseous products of the reaction were analysed in order to determine among others concentration of chlorine, formaldehyde, oxygen, carbon monoxide and dioxins. The content of total organic carbon (TOC), chloride ions and formaldehyde was determined in a condensate. Oxidation of the mixture proceeded in the all temperature range with high efficiency in regard to initial TOC value of the solution. The concentration of dioxins in the combustion gases obtained in the process carried out in temperature 450°C amounted to 0.021-0.027 ng TEQ/m<sup>3</sup>, and was significantly lower than the admissible value of 0.1 ng TEQ/m<sup>3</sup>. Congeners of polychlorinated dibenzofuranes (PCDFs) predominated in the combustion gases. Tested catalyst did not undergo deactivation during 150 h substrate oxidation.

**Keywords:** ferric-chromic catalysts, liquid chloroorganic wastes, thermocatalytic oxidation, dioxins

## Introduction

Chloroorganic compounds, components of useful preparations as well as wastes and industrial wastewater, can be transferred to the aqueous environment and soil. These substances are resistant to biodegradation and are toxic to aqueous organisms of plants and animals [1-3]. Waste chloroorganic compounds generated in three states of matter during polyvinyl chloride production, are utilized by combustion in the temperature of about 1350°C, at reaction time of about 2.5 s and with rapid combustion gases cooling. This process, for example carried out in Anwil S.A. in Włocławek, consists in total oxidation of organics and conversion of chlorine contained in organics into dry hydrogen chloride or commercial hydrochloric acid [4-6]. The application of proper catalysts enables a decrease

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in a temperature of total oxidation of chloroorganic compounds to the range of 300-600°C. Moreover, this usually enables a decrease in process costs [7-13]. The first aim of our investigations was to determine an effect of a temperature on catalytic oxidation efficiency of a mixture containing chloroorganic wastes, ethanol and water. The second aim was to determine the content of *polychlorinated dibenzo-p-dioxins* and *dibenzofuranes* (PCDD/Fs) in the combustion gases [11, 14], characterized by *toxic equivalent quality* (TEQ). These compounds are highly toxic, mutagenic and carcinogenic, especially congener - 2,3,7,8-tetrachlorodibenzo-p-dioxin with *toxic equivalent factor* (TEF) of 1 [14-23]. The admissible value of TEQ for combustion gases sample from waste incinerating plant in Poland and Europe is 0.1 ng TEQ/m<sup>3</sup> [24].

## Experimental

A model solution containing 50 g/dm<sup>3</sup> waste light ends from PVC production was the object of the investigation. Its main components were as follows: trichloromethane, tetrachloromethane, chloroethanes and chloroethenes [25] dissolved in ethanol-water mixture (1:1). Air and substrate flow rate was 300 dm<sup>3</sup>/h and 16 g/h, respectively. The contact time ( $\tau_k$ ) was 0.27 s. The temperature range applied in experiments was 400-600°C. Granular ferric-chromic catalyst (TZC 3/1) was obtained from Fertilizer Research Institute in Pulawy and applied in the investigations, which were carried out in an apparatus presented in previous papers [11, 14]. Gaseous products of the reaction were analysed in order to determine among others concentration of chlorine, formaldehyde, oxygen, carbon monoxide and PCDD/Fs. The content of *total organic carbon* (TOC), chloride ions and formaldehyde was determined in a condensate. Analysis of combustion gases in order to determine the content of PCDD/Fs was carried out according to the standard EN-1948-3-2006 in Laboratory of Environment Protection in the Institute of Biopolymers and Chemical Fibers in Lodz. PCDD/Fs content was determined with the application of high performance gas chromatography coupled with mass spectrometry [26].

## Results and discussion

Selected results of the experiments are presented in Figures 1-4 and Tables 1-2.

Figure 1 presents a dependence of TOC values and chloride ions concentrations in a condensate on temperature of reaction furnace in the oxidation of the substrate solution, with the application of TZC 3/1 catalyst. These parameters varied with the increase in temperature in the range from 400 to 600°C, probably due to methodology of the investigation. TOC value was in the range from 3.433 to 8.307 mg C/dm<sup>3</sup> and chloride ions concentration varied from 25.21 to 29.42 g/dm<sup>3</sup>. Hydrogen chloride, carbon dioxide and water vapour were the final products of the solution oxidation with the application of the catalyst. The intermediate (mostly reactive) products were as follows: formaldehyde, chlorine, carbon monoxide and dioxins. Gaseous chlorine, except for hydrogen chloride, was formed during chloroorganic compounds oxidation. Figure 2 presents a dependence of chlorine concentration in combustion gases on the temperature changed in the above-mentioned range during the oxidation of the mixture containing the wastes. The maximal concentration of chlorine (43.9 mg/m<sup>3</sup>) was achieved in the temperature of 500°C.

Table 1 presents average concentrations of products obtained in the substrate oxidation with the application of catalyst in the optimal temperature of 450°C in the process carried

out for 50 hours. The conversion of liquid products of the reaction, calculated as a change in TOC value of the oxidized solution (initial value of 192 000 mgC/dm<sup>3</sup>) was very high and exceeded 99.99%. The condensate and combustion gases contained trace amounts of products of non-complete oxidation of the initial mixture, *ie*, carbon monoxide and formaldehyde.

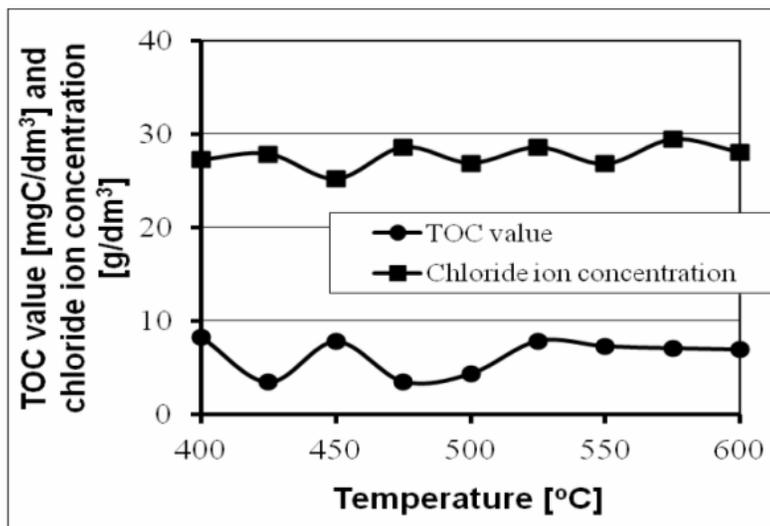


Fig. 1. A dependence of TOC value and chloride ion concentration in the condensate obtained during substrate oxidation on process temperature range 400-600°C [25]

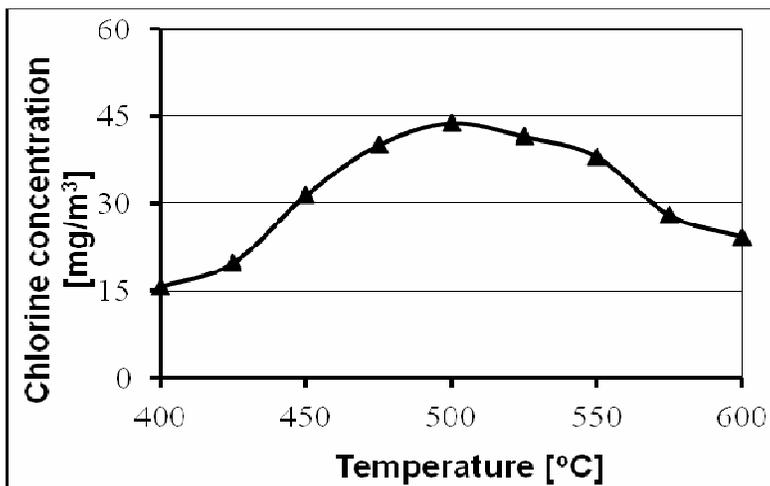


Fig. 2. A dependence of chlorine concentration in the combustion gases obtained during substrate oxidation on process temperature range 400-600°C [25]

Table 1

Analysis results of condensate and combustion gases from the oxidation process lasting 50 h in the presence of TZC 3/1 catalyst of 450°C [25]

Reaction products	Average value of parameter
TOC [mgC/dm <sup>3</sup> ]	6.637
X <sub>TOC</sub> [%], X <sub>TOC</sub> - TOC decrease	≥ 99.99 (min.)
Formaldehyde in condensate [mg/dm <sup>3</sup> ]	0.61
Chloride ions in condensate [g/dm <sup>3</sup> ]	28.89
Formaldehyde in combustion gases [mg/m <sup>3</sup> ]	0-0.31 (value range)
Chlorine in combustion gases [mg/m <sup>3</sup> ]	32.34
Hydrogen chloride in combustion gases [mg/m <sup>3</sup> ]	≤ 18 (max.)
Carbon monoxide [ppm]	1
Oxygen [%]	18.58
Carbon dioxide [%]	1.73

Table 2

PCDD/Fs content in combustion gases sample of 10 m<sup>3</sup> volume obtained in the catalytic oxidation of waste and solution (50 g/dm<sup>3</sup>) in the mixture of ethanol-water (1:1), from PVC production with the application of TZC 3/1;  $\tau_k = 0.27$  s,  $T = 450^\circ\text{C}$

Congeners	Mass/toxic equivalent quality of congeners in combustion gases sample with 10 m <sup>3</sup> volume	
	[ng]	[ng TEQ]
2378-TCDD	< 0.03	< 0.030
12378-P <sub>5</sub> CDD	< 0.03	< 0.015
123478-H <sub>6</sub> CDD	< 0.03	< 0.003
123678-H <sub>6</sub> CDD	< 0.03	< 0.003
123789-H <sub>6</sub> CDD	< 0.03	< 0.003
1234678-H <sub>7</sub> CDD	< 0.06	< 0.0006
OCDD	4.06	0.0024
2378-TCDF	0.20	0.200
12378-P <sub>5</sub> CDF	0.11	0.0055
23478-P <sub>5</sub> CDF	0.10	0.050
123478-H <sub>6</sub> CDF	0.38	0.0380
123678-H <sub>6</sub> CDF	0.16	0.016
123789-H <sub>6</sub> CDF	0.22	0.022
234678-H <sub>6</sub> CDF	<0.03	<0.003
1234678-H <sub>7</sub> CDF	4.78	0.048
1234789-H <sub>7</sub> CDF	< 0.06	< 0.0006
OCDF	7.77	0.0077
<b>Total</b>		<b>0.210-0.267*</b>
<b>Concentration of PCDD/Fs, ngTEQ/m<sup>3</sup></b>		<b>0.021-0.027*</b>

< means that the content of a determined substance in the sample is lower than the detection limit.

Detection limit for the following substances: TCDD/TCDF, P<sub>5</sub>CDD/P<sub>5</sub>CDF and H<sub>6</sub>CDD/H<sub>6</sub>CDF totals 0.03 ng and for H<sub>7</sub>CDD/H<sub>7</sub>CDF and OCDD/OCDF - 0.06 ng.

The line „Total” contains:

- sum of congeners content, which amounts in the samples were higher than the detection limit,
- sum of all congeners content (labelled as \*) assuming that the content of not detected congeners equals the detection limit.

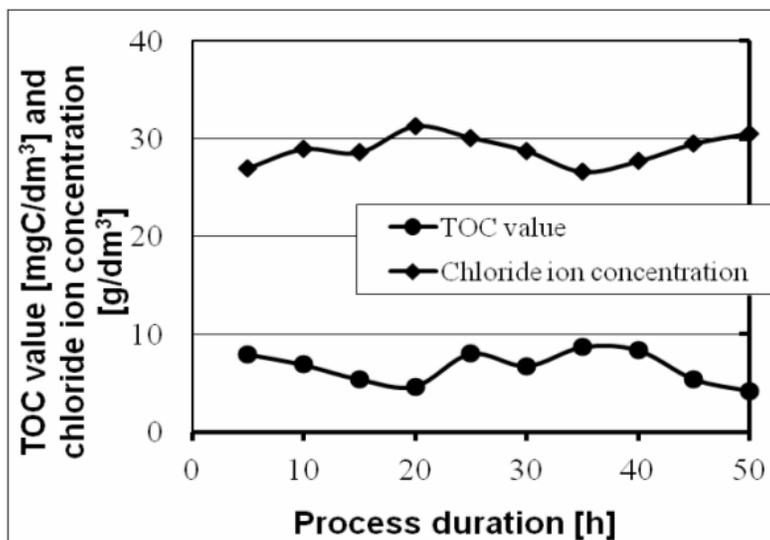


Fig. 3. A dependence of TOC value and chloride ions concentration in the condensate obtained during the substrate oxidation in the temperature of 450°C on the process duration

Figure 3 presents dependence of TOC value and chloride ions concentration in the condensate obtained during the substrate oxidation in the temperature of 450°C on the process duration (50 h). A dependence of chlorine concentration in the combustion gases for the same time of the oxidation with the application of TZC 3/1 catalyst, is shown in Figure 4. Curves presenting concentration of TOC, chloride ions and chlorine have similar values in this time range. This fact proves the lack of catalyst deactivation during the substrate oxidation lasting 50 h in the temperature of 450°C.

All investigations concerning the catalyst activity were carried out during about 150 hours and included experiments lasting 8 to 10 hours per day. After these experiments, the catalysts had the activity comparable with the initial activity in the substrate oxidation. Thus, the deactivation was not stated.

Combustion gases sampled during the reaction carried out in the temperature of 450°C were analysed in order to determine total content of dioxins (PCDD/Fs). Toxic equivalent quality (TEQ) was calculated taking into consideration contents of PCDD/Fs congeners with chlorine atom connected with carbon atoms located in 2, 3, 7 and 8 position. These congeners are especially toxic and have to be analysed according to law regulations [24, 26]. The middle column in Table 2 contains congeners masses and the right column contains calculated values of TEQ in combustion gases sample with volume of 10 m<sup>3</sup>. The presence of two PCDDs congeners and eight congeners of PCDFs was found. The value of toxic equivalent quality (TEQ) expressed in ngTEQ/m<sup>3</sup> was calculated in two forms. The first one was the sum of toxicity equivalent quality calculated for these congeners which contents exceeded the lowest limit of PCDD/Fs detection. Calculations of the second one took into consideration also these congeners which concentrations did not exceed the lowest limit of detection. Determined congeners occurred in trace amounts and their toxicity

equivalent quality in the combustion gases sample was significantly lower than the admissible value of  $0.1 \text{ ngTEQ/m}^3$  and was in the range from  $0.021$  to  $0.027 \text{ ng TEQ/m}^3$ .

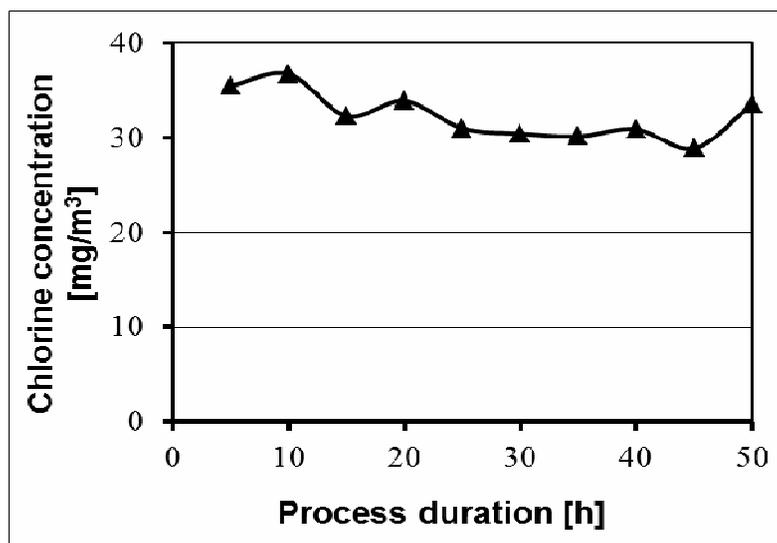


Fig. 4. A dependence of chlorine concentration in the combustion gases obtained during 50 h the substrate oxidation in the temperature of  $450^{\circ}\text{C}$  on the process duration

## Conclusions

1. Oxidation of the chloroorganic wastes at the concentration of  $50 \text{ g/dm}^3$  in the ethanol-water (1:1) mixture proceeded with the application of the TZC 3/1 catalyst in the temperature range of  $400\text{-}600^{\circ}\text{C}$  with the efficiency of 99.99% in relation to initial TOC value in the solutions.
2. Carbon dioxide, water vapour, and hydrochloric acid were the final products of the chloroorganic compounds oxidation. Formaldehyde, carbon monoxide, chlorine and dioxins were the intermediate products in this process.
3. The catalyst did not undergo deactivation during 150 h substrate oxidation.
4. It was found that the content of PCDD/Fs in the process of the substrate oxidation in the temperature of  $450^{\circ}\text{C}$  was  $0.021\text{-}0.027 \text{ ng TEQ/m}^3$ , and did not exceed the admissible value of  $0.1 \text{ ng TEQ/m}^3$ .
5. Congeners of polychlorinated dibenzofuranes (PCDFs) predominated in the combustion gases.
6. Results of the investigations show that the application of the TZC 3/1 catalyst makes possible a decrease in the reaction temperature from about  $1350^{\circ}\text{C}$  (applied in industry) to the range of  $400\text{-}600^{\circ}\text{C}$ . The contact time was 0.27 s.

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## UTYLIZACJA ODPADU Z PRODUKCJI PCW Z UDZIAŁEM KATALIZATORA Fe-Cr W ASPEKCIE ZAGROŻENIA DIOKSYNAMI

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**Abstrakt:** Przedmiot badań stanowił roztwór modelowy zawierający 50 g/dm<sup>3</sup> frakcji lekkiej odpadów z produkcji PCW w mieszaninie etanol-woda (1:1). Głównymi składnikami odpadu były: trichlorometan, tetrachlorometan i chloropochodne etanu. Natężenie przepływu powietrza wynosiło 300 dm<sup>3</sup>/h, substratu 16 g/h, a czas kontaktu 0,27 s. Zakres temperatury doświadczeń wynosił 400-600°C. Stosowano ziarnisty katalizator żelazowo-chromowy TZC 3/1. W gazowych produktach reakcji oznaczano m.in. stężenie chloru, formaldehydu, tlenu i tlenku węgla, natomiast w kondensacie zawartość ogólnego węgla organicznego (OWO), jonów chlorkowych, formaldehydu i dioksyn. Utlenienie substratu zachodziło w zakresie temperatury 400-600°C bardzo wydajnie względem początkowego OWO tych roztworów. Stężenie PCDD/Fs w spalinach w procesie realizowanym w temperaturze 450°C wynosiło 0,021-0,027 ngTEQ/m<sup>3</sup> i było znacznie mniejsze od wartości dopuszczalnej 0,1 ngTEQ/m<sup>3</sup>. W spalinach dominowały kongenery polichlorowanych dibenzofuranów (PCDFs). Badany katalizator nie uległ dezaktywacji w okresie 150 h utleniania substratu.

**Słowa kluczowe:** katalizatory żelazowo-chromowe, ciekłe odpady chloroorganiczne, utlenianie termokatalityczne, dioksyiny