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UTILIZATION OF LIGHT ENDS OF CHLOROORGANIC WASTES FROM PVC PRODUCTION WITH APPLICATION OF FERRIC-CHROMIC CATALYST

UTYLIZACJA FRAKCJI LEKKIEJ ODPADÓW CHLOROORGANICZNYCH Z PRODUKCJI PVC Z UDZIAŁEM KATALIZATORA ŻELAZOWO-CHROMOWEGO

Abstract: The subject of the investigation was the model solution containing 50 g/dm^3 waste light ends from PVC production dissolved in the ethanol-water (1:1) mixture. Granular ferric-chromic catalyst (TZC 3/1) was used in the investigation. The temperature range applied in experiments was 400÷600ºC 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 in the solution. The concentration of dioxins in the combustion gases obtained in the process carried out in temperature 450ºC amounted to 0.027 ngTEQ/m^3, and was significantly lower than the admissible value of 0.1 ngTEQ/m^3.

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

Waste chloroorganic compounds generated in three states of matter during polyvinyl chloride production, are utilized by combustion in the temperature of about 1350ºC. This process, for example carried out in Anwil S.A. in Wloclawek, consists in total oxidation of organics and conversion of chlorine contained in organics into dry hydrogen chloride or commercial hydrochloric acid [1, 2]. The application of proper catalysts enables a decrease in a temperature of total oxidation of chloroorganic compounds to the range of 300÷600ºC. Moreover, this usually enables a decrease in process costs [3-6]. 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, characterized by *toxic equivalent quality* (TEQ). These compounds are highly toxic, mutagenic and cancerogenic, especially congener - *2,3,7,8-tetrachlorodibenzo-p-dioxin* with *toxic equivalent factor* (TEF) of 1 [7-11]. The admissible value of TEQ for combustion gases sample from waste incinerating plant in Poland and Europe is 0.1 ng TEQ/m^3 [12].

Experimental

A model solution containing 50 g/dm^3 waste light ends from industrial PVC production was the object of the investigation. Its main components were as follows: trichloromethane, tetrachloromethane, chloroethanes and chloroethenes (Table 1) dissolved

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in ethanol-water mixture (1:1). Air and substrate flow rate was 300 dm^3/h and 16 g/h, respectively. The temperature range applied in experiments was 400÷600ºC. Granular ferric-chromic catalyst (TZC 3/1) containing 42.27% Fe, 5.40% Cr and 1.78% Cu was obtained from Fertilizer Research Institute in Pulawy. It was applied in the investigations, which were carried out in an apparatus presented in the paper [5]. 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 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 [13].

Table 1

Average composition of light ends of chloroorganic wastes from PVC production [% w/w]

Components of the light ends	**[% w/w]**
Ethylene	0.1918
Chloromethane	0.0386
Vinyl Chloride	0.3301
Chloroethane	2.0408
Vinylidene Chloride	0.8461
Trans-1,2-dichloroethene	0.8058
1,1-dichloroethane	6.1695
Chloroprene	0.0075
Cis-dichloroethene	1.3788
Trichloromethane	72.735
1,2-dichloroethane	1.6667
2-chloroethanol	0.0095
Benzene	0.0001
Tetrachloromethane	10.7792
Trichloroethene	0.0020
1,1,1-trichloroacetaldehyde	0.0001
1,1,2-trichloroethane	0.0001
Tetrachloroethene	0.0002
Other light ends	2.9936
Other heavy ends	0.0045

Results and discussion

Selected results of the experiments are presented in Figures 1, 2 and Table 2.

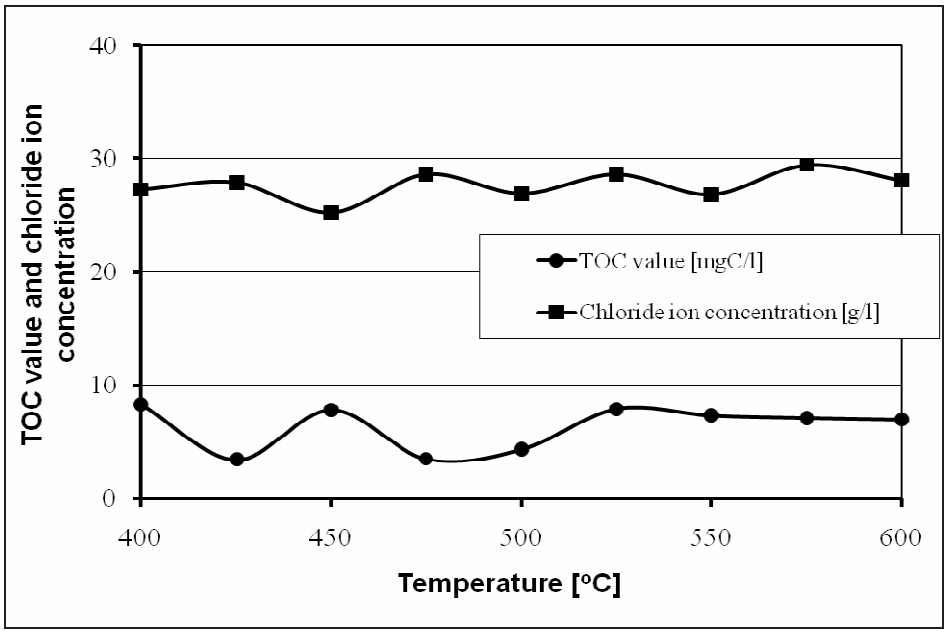

Fig. 1. A dependence of TOC value and chloride ion concentration in the condensate obtained during substrate oxidation on process temperature in the range of 400÷600ºC

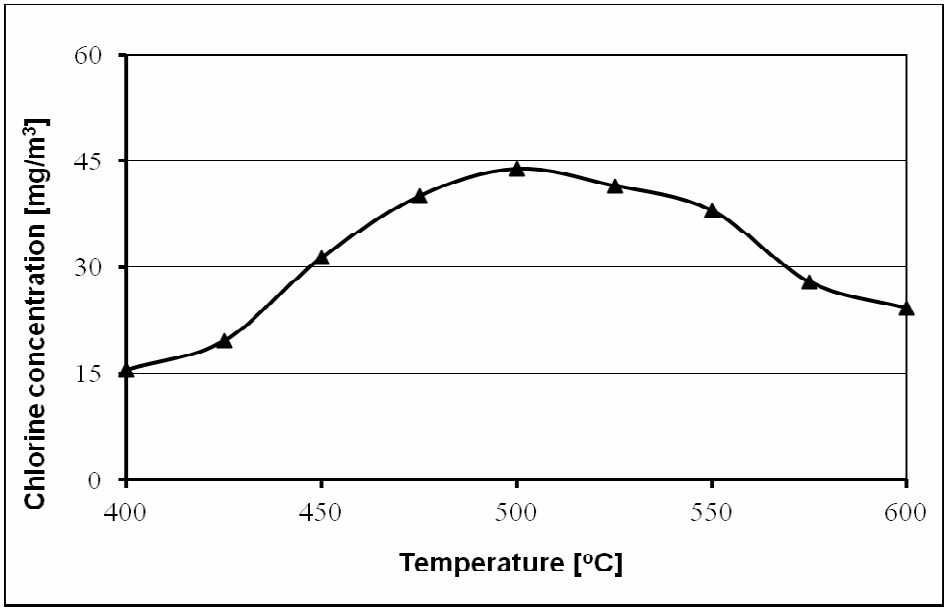

Fig. 2. A dependence of chlorine concentration in the combustion gases obtained during substrate oxidation on process temperature in the range of 400÷600ºC

Table 2
Analysis results of condensate and combustion gases from the oxidation process lasting 50 h in the presence of TZC 3/1 catalyst and in the process temperature of 450ºC

Reaction products	Average value of parameter
TOC [mgC/dm^3]	6.637
X_{TOC} [%] X_{TOC} - TOC decrease	≥ 99.99 (min.)
Formaldehyde in condensate [mg/dm^3]	0.61
Chloride ions in condensate [g/dm^3]	28.89
Formaldehyde in combustion gases [mg/m^3]	0÷0.31 (value range)
Chlorine in combustion gases [mg/m^3]	32.34
Hydrogen chloride in combustion gases [mg/m^3]	≤ 18 (max.)
Carbon monoxide [ppm]	1
Oxygen [%]	18.58
Carbon dioxide [%]	1.73
TEQ of PCDD/Fs in combustion gases [ng TEQ/m^3]	≤ 0.027 (one analysis)

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 600ºC, probably due to methodology of the investigation. TOC value was in the range from 3.433 to 8.307 mg C/dm^3 and chloride ions concentration varied from 25.21 to 29.42 g/dm^3. Hydrogen chloride, carbon dioxide and water vapour were the final products of the solution oxidation with the application of the catalyst. The final (mostly reactive) products were as follows: formaldehyde, chlorine, carbon monoxide and dioxins. 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^3) was achieved in the temperature of 500ºC.

Table 2 presents average concentrations of products obtained in the substrate oxidation with the application of catalyst in the optimal temperature of 450ºC 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 mg C/dm^3) 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. Combustion gases sampled during the reaction carried out in the temperature of 450ºC were analysed in order to determine total content of dioxins (PCDD/Fs) which was presented as toxic equivalent quality (TEQ). The obtained result of 0.027 ng TEQ/m^3 was significantly lower than the admissible value of 0.1 ng TEQ/m^3 [12].

Conclusions

Oxidation of the chloroorganic wastes at the concentration of 50 g/dm^3 in the ethanol-water (1:1) mixture proceeded in the temperature range of 400÷600ºC with the efficiency of 99.99% in regard to initial TOC value in these solutions. Water vapour, carbon dioxide and hydrochloric acid were the final products of the substrates oxidation. The intermediate products in the substrates oxidation were as follows: components including formaldehyde responsible for total organic carbon content in the condensate, as

well as formaldehyde, chlorine and carbon monoxide present in the combustion gases. The concentration of PCDD/Fs in the combustion gases obtained in the process carried out in the optimal temperature, ie 450ºC, amounted to 0.027 ng TEQ/m^3 and was significantly lower than the admissible value of 0.1 ng TEQ/m^3.

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Abstrakt: Przedmiot badań stanowił roztwór modelowy 50 g/dm^3 frakcji lekkiej odpadów z produkcji PVC w mieszaninie etanol-woda (1:1). Stosowano ziarnisty katalizator żelazowo-chromowy TZC 3/1. Zakres temperatury doświadczeń wynosił 400÷600ºC, a czas kontaktu 0,27 s. W gazowych produktach reakcji oznaczano m.in. stężenie chloru, formaldehydu, tlenu i tlenku węgla oraz dioksyn, natomiast w kondensacie zawartość ogólnego węgla organicznego (OWO), jonów chlorkowych, formaldehydu. Utlenienie badanej mieszaniny zachodziło bardzo wydajnie w całym zakresie temperatury doświadczeń względem początkowego OWO tego roztworu. Stężenie PCDD/Fs w spalinach w procesie realizowanym w temperaturze 450ºC wynosiło 0,027 ng TEQ/m^3 i było znacznie niższe od wartości dopuszczalnej 0,1 ng TEQ/m^3.

Słowa kluczowe: katalizatory żelazowo-chromowe, ciekłe odpady chloroorganiczne, utlenianie termokatalityczne, etanol, dioksyny