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PLASMA TREATMENT OF SPENT CHEMICAL REAGENTS

Keywords

Plasma treatment, thermal destruction, fluid waste, spent chemicals.

Abstract

The paper has in view the solution of problems concerning the utilization of spent fluid chemical reagents. The Plasma Technology and Environmental Protection Group of the Technical University of Lodz worked out a compact device - PDUCR (Plasma Destructor of Used Chemical Reagents) for safe utilization of spent chemicals. The device will be able do utilize from one to a few kilograms of reagent per hour.

Introduction

With the moment of accession to the European Union, Poland had to adapt its regulations to the community law. According to the Directive 91/156 /EEC, the storage of hazardous wastes is allowed to be temporary in special conditions only until the time of their utilization.

In a chemical analytic laboratory practice, small amounts of diverse reagents, mostly liquid organic substances are used for many purposes such as chromatography. They are the chlorinated solvents, solvents from the group of alcohols, esters, and aliphatic or aromatic hydrocarbons. Annually, a particular analytic laboratory has been using from several to a dozen tones of those reagents, which, since they containing some dirt, must be qualified as the waste. The small daily production rate of those wastes (from several to some tens of kilograms) must be collected and temporary stored before transportation to a place of utilization. The cost of building and exploitation fulfilling the suitable requirements of storage is, in this process is the largest burden financially.

The avoidance of stockpiling and transportation of these waste is the economic challenge in the procedure of the utilization of the used reagents. So far, any device able to utilize those wastes “in situ,” where they are produced, had not been offered. Such a device had to be placed in/or close to the laboratory and may be working in measure of the need (batch mode), in principle, like an office document shredder.

The aim of this paper is to study a stream rate and quantity of organic fluid waste production by an average analytic chemical laboratory, to find out the required conditions of its thermal treatment and to demonstrate a concept of a compact device PDUCR able do utilize from one to a few kilograms of reagent per hour.

1. Quantitative and parametric analysis of the chemical reagents waste stream

The quantitative and parametric analysis has been done through the review of accessible literature and by inquiries of representative laboratories in the range of the following: cosmetic industry, industry of paints and varnishes as well as the chemical and pharmaceutical industry. Selection of those laboratories (356) was done in the areas of advanced technologies where analytical tests are the standard procedures. The more detailed data were collected from research institutes in the way of personal conversations. In this way, information has been collected from 57 institutions. However, the most credible and reliable data were obtained from 27 chemical profile faculties of Polish universities [1]. An estimate for the whole country of the quantity of chemical wastes generated in the university laboratories can reach 100 tones annually in which organic solvents represent 36% (Fig.1).

The collected data affirmed that organic solvents in industry and chemical services are also the most often used compounds (Fig. 2). It seems that the utilization of this group of wastes is the most important goal, and it requires the quickest solution. In the year 2002, the European Union estimated the number of institutions using such reagents at about 400 000, whereas in France alone there was 60 000. However, the small analytical laboratories will be the users' target group. Within this group the capital cost of building a store-house of wastes or the adaptation of existing space, in accordance with the required safety regulations, exceeds the cost of utilization in a few years. Such institutions have to provide storage in special installations with the attention on flammability and toxicity of this group of wastes.

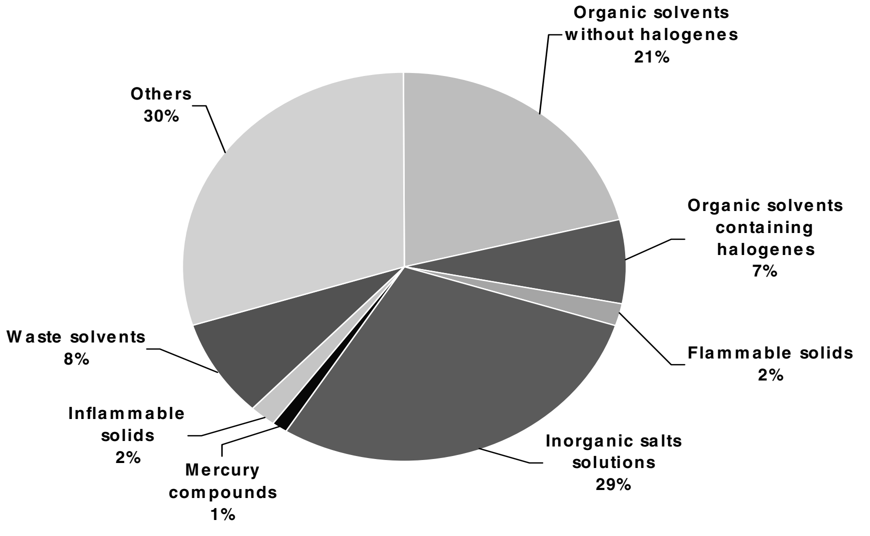

Fig. 1. The percentage ratio of diverse chemical wastes produced by Polish universities

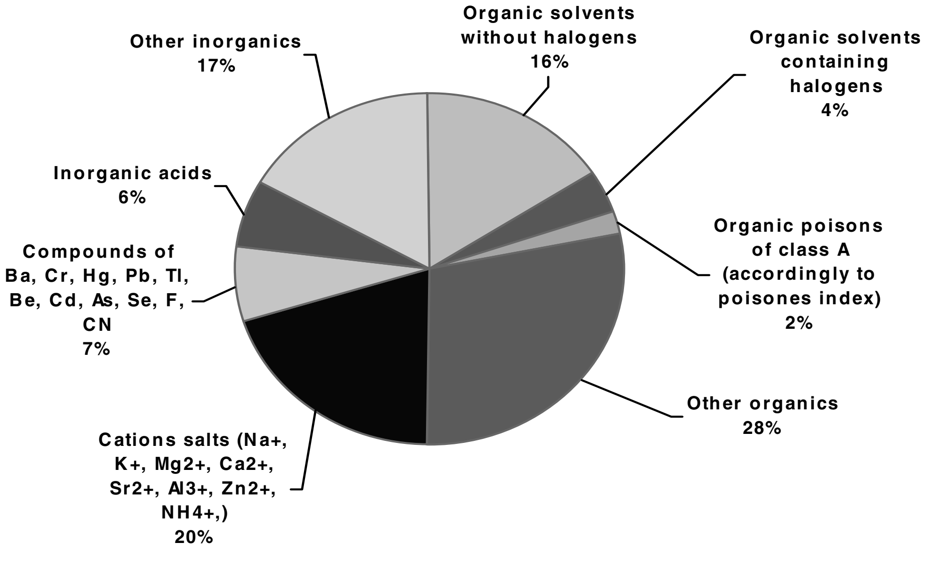

Fig. 2. Quantity of different chemical reagents stored temporary in laboratories

The traditional thermal utilization (incineration) is very difficult, because of the chlorine content in the waste that cause the possible formation of furans and dioxins. With some limitations, it can be done in commercial incinerator plants, but the wasted fluids can not be added to a fuel, i.e. heating a boiler. The most adequate solution is then pyrolytic thermal treatment. It can be successfully performed with the use of thermal plasma, which can be generated in an oxygen free atmosphere.

2. Chemical reagent's thermal destruction

To find the most effective conditions for this waste destruction in the thermal plasma, the thermochemical calculations have been done before the PDUCR designing and employing it in the experiment. A major advantage of plasma processing is that the heat input may be accomplished in an atmosphere of any desired composition and reactivity. In practice, there are only a few variations of chemical strategies available for thermal processing, i.e. pyrolysis, oxidation, reaction with hydrogen and water. To optimize the conditions of the reaction, we have calculated the decomposition of solvents within the range of temperatures from 400 to 2400 K using the CHEMSAGE program based on the minimization of Gibb's free energy [2].

The results of the quantitative and parametric analysis of the chemical reagents waste stream indicated that the organic solvents may be selected as the representative stream of wastes to demonstrate the treatment process in the device - PDUCR. The organic solvents after pyrolytical treatment produce similar gaseous products, mainly hydrogen, carbon monoxide and, if the solvents contain chlorine - hydrochloric acid. Among those we decided to choose, methanol, being a typical solvent used in fluid chromatography and representing, alcohols, ketons and esters.

In Figs. 3 and 4, the results of thermochemical calculations presenting the methanol decomposition are presented.

It can be seen in Fig. 3, a temperature of 1200 K is required to convert the whole volume of the fluid into a gas phase. This is because soot is formed in the temperature range bellow 1200 K. Up to 1200 K the soot is only partially oxidized, but above 1200 K, nearly all soot particles are oxidized to form carbon monoxide. Considering the results shown in Fig. 4, we can notice that the mass ratio of methane and carbon dioxide also decreases and disappears above the threshold point (1200 K). All of this is done due to steam generated from the water self extraction in the alcohol that works as an oxidant.

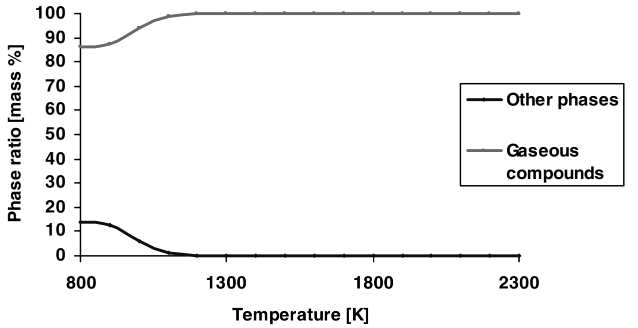

Fig. 3. Phase ratio of methanol during its thermal decomposition

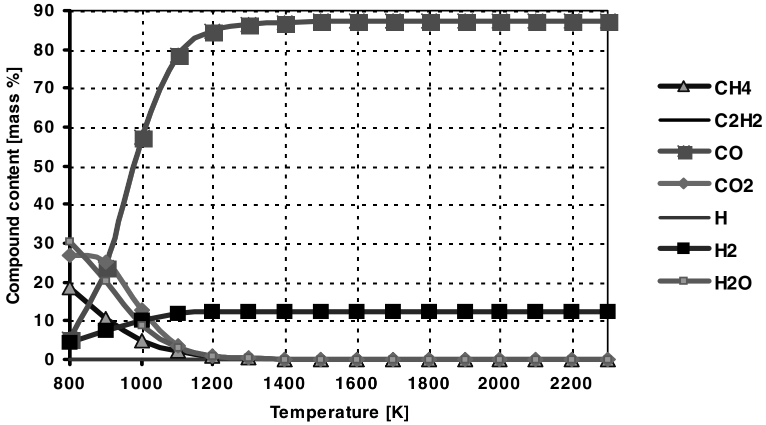

Fig. 4. Thermal decomposition of methanol gaseous fraction

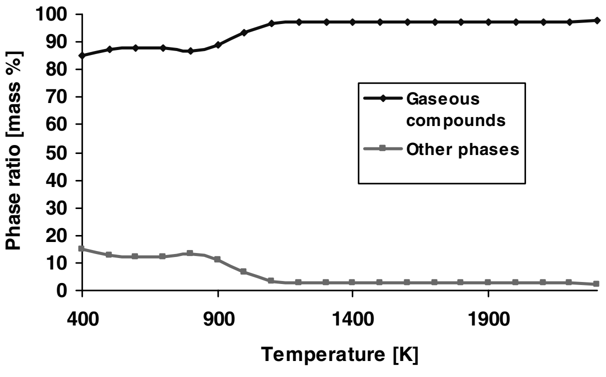

Fig. 5. Phase ratio of methanol (66%) admixed with carbon tetrachloride (34%) during thermal decomposition

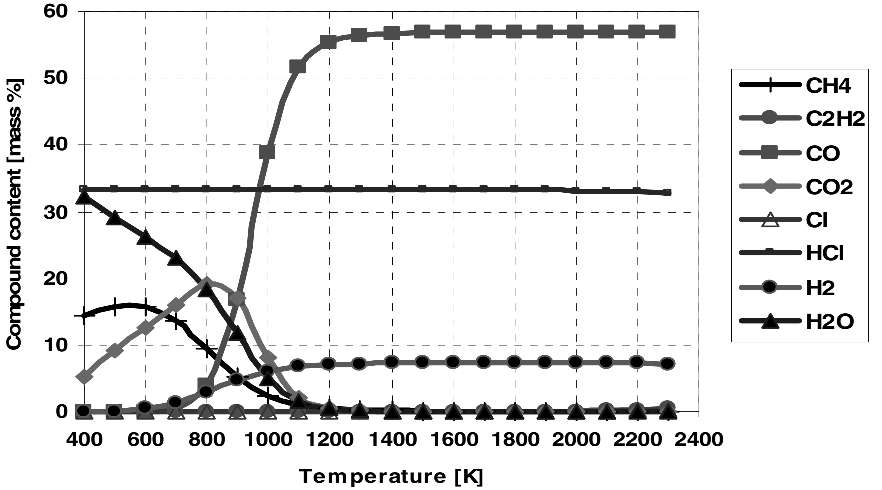

Fig. 6. Thermal decomposition of gaseous fraction of methanol and carbon tetrachloride mix (66%/34%)

However solvents may contain chlorine. We can see in Figs. 1 and 2 that the ratio of solvents with chlorine to the solvents without chlorine amounts to 1/4 for general laboratories (Fig. 2) up to 1/3 for university laboratories. We have assumed in our calculations the worst case in which the admixed solvent amounts 34%, and that it is very rich in chlorine, so we selected carbon tetrachloride.

In Figs. 5 and 6, one can see the phase ratio and thermal decomposition of the gaseous fraction of methanol and carbon tetrachloride mix (66%/34%). In this case, the mixed solvent is so rich in carbon that after the 1200K threshold, the residue of 2.7% weight of soot remains. In such extreme conditions, a little volume of water should be added to avoid sooting which allows keeping the installation clean.

In Fig. 6, the thermal decomposition of gaseous fraction of the methanol and carbon tetrachloride mix (66%/34%) is presented. We can see here that 33% by weight hydrochloride must be converted into salt before hydrogen and carbon monoxide burning.

3. PDUCR (Plasma Destructor of Used Chemical Reagents) concept

In Fig. 7, the compact device PDUCR and required installation are presented. The main part of the device is the plasma reactor (1) equipped with the adjustment actuator (2) and the power and flow control unit (5). The collected wasted solvents must be added into the container (4) feeding the reactor (1). The off gas must be flowing through the compact chlorine absorber and catalytic oxidizer (3) before the fan (6) cools it down, admixing with ambient air.

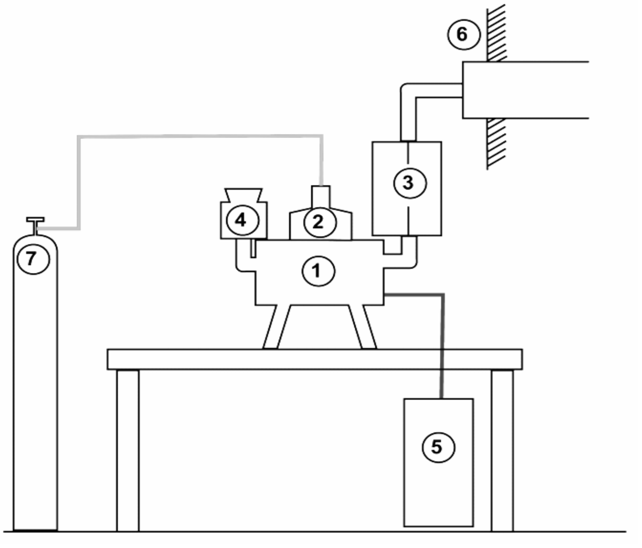

Fig. 7. PDUCR installation (parts numbered described in the text)

The PDUCR will be supplied with the inert gas delivered from the bottle (7) in the slow rate and atmospheric pressure.

Conclusions

The PDUCR is now tested to find out its technical performance. The PDUCR is dedicated for analytic chemical laboratories to make utilization of spent reagents in place of their formation. Such a solution is essential economically, because it allows avoiding stockpiling and transportation of waste before the utilization of spent reagents. The PDUCR is able to utilize those wastes "in situ" where they are produced. It can be placed in/or close to the laboratory and may be work in relation to the need (batch mode) on a similar principle to how an office document shredder is used.

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1. Opracowanie sposobu oraz systemu organizacyjnego gospodarowania substancjami chemicznymi na wydziałach chemicznych i pokrewnych szkół wyższych oraz koncepcji technologicznej neutralizacji oraz utylizacji odpadów z laboratoriów chemicznych. [W:] Informacja o pracach nad systemem zarządzania chemikaliami w polskich uczelniach. Wydział Chemiczny Politechniki Śląskiej, Gliwice, 2000, PCZ 0316 (in Polish).
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Reviewer:
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Plazmowa utylizacja zużytych odczynników chemicznych

Słowa kluczowe

Utylizacja plazmowa, rozkład termiczny, odpady ciekłe, zużyte chemikalia.

Streszczenie

Przedmiotem przedstawionych w artykule badań jest próba rozwiązania problemów związanych z utylizacją zużytych płynnych odczynników chemicznych. Międzywydziałowy zespół badawczy Technologii Plazmowych i Elektrotechnologii Ochrony Środowiska w Politechnice Łódzkiej opracował kompaktowe urządzenie – PUOC (Plazmowy Utylizator Odczynników Chemicznych) dla bezpiecznej utylizacji odczynników chemicznych w miejscu ich powstawania, to znaczy w analitycznych laboratoriach chemicznych. Urządzenie będzie pracowało z wydajnością od jednego do kilku kilogramów odczynnika na godzinę.