

Catalytic hydrotreating of 2,4'-DDT and 4,4'-DDT

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Abstract

The results of catalytic hydrotreating of a commercial mixture of 2,4'-DDT and 4,4'-DDT are reported. Experimental runs were carried out in a batch reactor (300 cm³) at constant hydrogen pressure ($P_{H_2} = 20$ bar) and temperature. Temperature levels 150, 180, 200 and 230 °C were tested. A commercial sulphide Ni–Mo catalyst was adopted. The reacting medium was hexadecane. The kinetic constant and reaction order of the destruction reaction of 2,4'-DDT and 4,4'-DDT have been evaluated at temperature of 180, 200 and 230 °C. Destruction and removal efficiency (DRE) at $T = 230$ °C has been calculated.

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1. Introduction

Catalytic hydrotreating has been studied for the treatment of a large class of liquid toxic wastes including chlorophenols [1], chlorobenzenes [2,3], chlorofluorocarbons [4], and PCBs [5,6]. Few studies are concerned with other classes of chlorinated compounds: insecticides, pesticides, PCDDs and PCDFs [6].

Obsolete pesticides are pesticides that can no longer be used including organochlorine compounds such as DDT, dieldrin and lindane (HCH), whose production has been banned for public health and/or environmental reasons. Stocks of obsolete pesticides are mostly present in developing countries. Their quantities in individual countries range from a few to several thousands tons. The Food and Agriculture Organization of the United Nations (FAO) conducted an inventory of obsolete pesticide stocks in Africa and in the Near East [7]. The results indicated that more than 100,000 tonnes of obsolete pesticides were stocked in developing countries.

Obsolete pesticides are usually disposed by storage, burial in landfills, and/or burning in combustion systems (e.g., dedicated incinerators, industrial boilers or cement kilns). Actually, combustion systems accomplish a high degree

of destruction, but the environmental impact of incinerators has created a strong public opposition to incineration. This factor, as well as, the increasing infrastructural needs, particularly those associated with the management of air emissions and of other residues, has encouraged the development of different destruction technologies, as gas-phase chemical reduction, solvated electron process, and catalytic hydrotreating.

In this paper the experimental results of hydrotreating of a standard mixture of DDT promoted by a commercial Ni–Mo catalyst are reported. Objective of the paper is to determine the experimental conditions which could be used to hydrogenate DDT, and the destruction efficiency of the process.

2. Experimental section

A standard mixture (neat material) of 2,4'-DDT and 4,4'-DDT (Ultra Scientific Inc.) of technical purity (95–99%) was adopted. The main component of the mixture is 4,4'-DDT, while 2,4'-DDT is present at lower concentration (about 10 wt.%). Before loading into the reactor the DDT standard mixture was dissolved in *n*-hexane.

Reaction runs were carried out in a stirred batch reactor (300 ml capacity) with magnetic stirring. To minimize the catalytic effect of the reactor wall a glass liner was fitted into the reactor. An external loader was connected to the

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headspace of the reactor through a globe valve. Pure hexadecane (the reaction medium) was loaded in the reactor, and the headspace was purged with nitrogen. The reactor was then heated to the reaction temperature. When the set temperature was reached, the *n*-hexane solution of DDT (about 1 cm³) was loaded in the external loader with some additional hexadecane, and the catalyst. The loader was then pressurized with hydrogen at the set pressure value. The globe valve was opened, and the reacting solution was instantaneously injected into the reactor. This was time $t = 0$ for the reaction. The process was carried out at constant pressure and temperature. During the run samples of liquid phase were withdrawn and then analysed by GC-ECD.

GC-ECD analyses were carried out with an HP6890 GC-ECD equipped with a J&W DB-35MS capillary column (30 m, 35% phenyl-methylpolysiloxane, 0.32 mm i.d., 0.25 μm thickness). The quantitative evaluation of DDT in the samples was carried out using hexachloroethane as internal standard.

A commercial catalyst Ni–Mo/γ-Al₂O₃ was adopted (BASF M821PS). Sulphidation was done by the catalyst manufacturer company. Principal characteristics of the catalyst are: NiO 4.0 wt.%, MoO₃ 19.5 wt.%; specific surface 160 m²/g; porosity 0.47 ml/g. Catalyst was stored in sealed box before use. After a process of grinding and sieving, only the fraction between 74 and 105 μm was used in order to minimize intraparticle resistances. It is reported that for HDCI of trichlorobenzene [3] the sulphidation treatment of Ni–Mo catalyst increases the value of the kinetic constant of the single HDCI reactions for a factor in the range 1.38–47.4 at $T = 350$ °C.

The temperature levels 150, 180, 200 and 230 °C were investigated. The other operating conditions are $P_{H_2} = 20$ bar; agitator speed = 800 rpm; hexadecane loaded (W_{hex}) = 120 g; catalyst (W_{cat}) = 0.5 g; DDT (W_{DDT}) = 0.01 g.

3. Results and discussion

The consumption of 2,4'-DDT and 4,4'-DDT during the reaction runs is reported in Fig. 1. Results of the run at $T = 150$ °C are not reported because at this temperature the reaction rate was much lower with respect to that observed in runs carried out at higher temperature (180–230 °C). At $T = 150$ °C the catalyst is not active. In fact, a run carried out at $T = 150$ °C in the absence of catalyst ($W_{cat} = 0$) and in the presence of nitrogen at $P_{N_2} = 20$ bar (blank run) showed a consumption rate of both DDT species similar to that obtained, at the same temperature, in the presence of catalyst and hydrogen.

The hydrotreating process of chlorinated organic compounds promoted by Ni–Mo catalyst takes place through a network of hydrodechlorination steps. The complexity of the network depends on the number of chlorine atoms present on the reacting molecule. Each hydrodechlorination step determines the substitution of a chlorine atom. Single hy-

drodechlorination reactions are generally well modeled by a first order kinetic equation, at low reactant concentration [2]. But the overall reaction of polychlorinated molecules is not necessary first order [8,9]. In this case, even if reactant concentration is low (83 ppm as sum of 2,4'-DDT and 4,4'-DDT), the fitting of experimental data in Fig. 1, assuming a first order kinetic, was poor for reaction time $t > 20$ min. Therefore, it was assumed as kinetic equation a power law of order n

$$\frac{dC_{DDT}}{dt} = -k \left(\frac{W_{cat}}{W_{sol}} \right) \times C_{DDT}^n \quad (1)$$

where C_{DDT} is the concentration [ppm] of alternatively 2,4'-DDT or 4,4'-DDT; k is the kinetic constant of the destruction rate [ppm¹⁻ⁿ g_{sol}⁻¹ g_{cat}⁻¹ min⁻¹]; W_{cat} is the mass of catalyst loaded [g]; W_{sol} is the mass of solution [g] (it is $W_{sol} \cong$ mass of hexadecane loaded W_{hex}); and n is the reaction order.

The integration of Eq. (1) gives the following equation:

$$C_{DDT} = \left((C_{DDT}^0)^{1-n} - k \left(\frac{W_{cat}}{W_{sol}} \right) (1-n)t \right)^{1/1-n} \quad (2)$$

where C_{DDT}^0 is the concentration at time $t = 0$. The values of the kinetic constant k and of the reaction order n obtained by the regression of experimental data with Eq. (2) are reported in Table 1 for runs at $T = 180$ °C. The corresponding fitting curves are reported in Fig. 1. Values of the reaction order

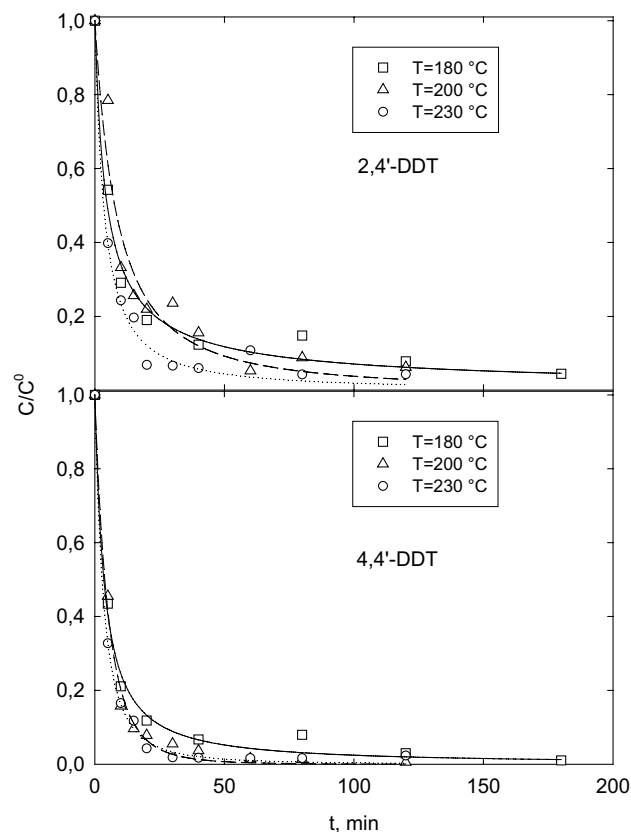


Fig. 1. Experimental data and fitted curves.

Table 1
Results of kinetic analysis: kinetic constant and reaction order

T (°C)	2,4'-DDT		4,4'-DDT	
	k [ppm ¹⁻ⁿ g _{sol} g _{cat} ⁻¹ min ⁻¹]	n	k [ppm ¹⁻ⁿ g _{sol} g _{cat} ⁻¹ min ⁻¹]	n
180	5.76	2.32	2.64	1.86
200	13.92	1.65	21.12	1.24
230	38.4	1.8	21.84	1.49

n reported in Table 1 are quite constant for runs carried out at higher temperature ($T = 200$ – 230 °C). As a matter of fact, reaction order is $n = 1.65$ – 1.8 for 2,4'-DDT and $n = 1.24$ – 1.49 for 4,4'-DDT. While higher values ($n = 2.32$ for 2,4'-DDT and $n = 1.86$ for 4,4'-DDT) were obtained at $T = 180$ °C.

The observed different reaction order could be attributed to the presence of a different destruction process. Blank runs were carried out at temperature 180, 200 and 230 °C with the aim to verify the contribution of other processes responsible of DDT consumption (thermal destruction, catalytic effect of reactor wall, etc.). In fact, results of blank run carried out at $T = 180$ °C show that other processes gave a significant contribution to consumption of both DDT molecules. At higher temperature the catalytic process becomes predominant and other effects are less relevant. Moreover, the presence of the catalyst at $T = 200$ and 230 °C is necessary to achieve a complete dechlorination of DDT.

The destruction and removal efficiency (DRE) defined as:

$$\text{DRE} = 1 - \frac{C_{\text{DDT}}}{C_{\text{DDT}}^0} \quad (3)$$

has been evaluated for both 2,4'-DDT and 4,4'-DDT using Eq. (2) with the values of k and n reported in Table 1. For practical application the temperature level $T = 230$ °C is

of major interest. Therefore, DRE for both 2,4'-DDT and 4,4'-DDT was evaluated at $T = 230$ °C and is reported as function of the operating parameter $(W_{\text{cat}}/W_{\text{sol}})t$ in Fig. 2. The curves in Fig. 2 show that high DRE values can be attained at mild operating conditions. However, 4,4'-DDT reacts more rapidly than 2,4'-DDT. This finding is in agreement with the observations reported in the literature. As a matter of fact, in the case of catalytic hydrotreating with Ni–Mo catalysts of PCBs [10,11] and chlorophenols [12,13] *ortho*-substituted chlorine atoms are less labile than *meta*- and *para*-substituted ones and the corresponding consumption reactions are slower.

To compare the destruction rate of DDT with those of other classes of chlorinated compounds, the experimental data reported in Fig. 1 were regressed assuming a first order kinetics. As reported before, in the case of DDT, if first order kinetic is assumed, the fitting of experimental data is poor but only for reaction time $t > 20$ min. Since hydrotreating of chlorinated compounds is generally carried out at temperature higher than those adopted in this paper (i.e., $T = 250$ °C) it is not easy to make a direct comparison. Moreover, only experimental data obtained with the same, or at least similar, catalyst formulation can be compared. The authors reported values of the kinetic constant at $T = 230$ °C for the hydrotreating of 1,2,3-trichlorobenzene

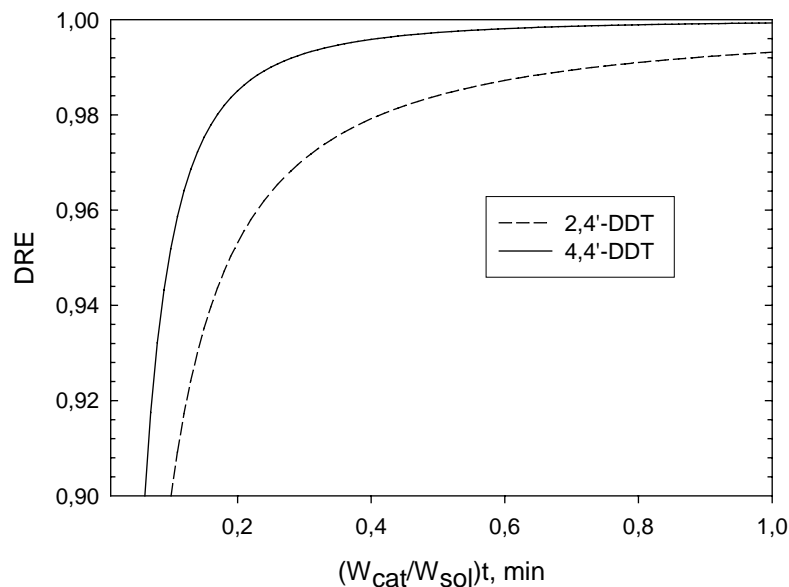


Fig. 2. Destruction and removal efficiency (DRE) of HCl process of DDT ($T = 230$ °C).

and of a PCB dielectric oil. The operating conditions were the same as those reported in this paper and a similar catalyst was adopted. For 1,2,3-trichlorobenzene [3] it is reported $k = 0.96$ [$\text{g}_{\text{sol}} \text{g}_{\text{cat}}^{-1} \text{min}^{-1}$] and for a PCB dielectric oil $k = 0.21$ [$\text{g}_{\text{sol}} \text{g}_{\text{cat}}^{-1} \text{min}^{-1}$] [8]. At $T = 230$ °C, assuming first order reaction, the value of the kinetic constant for DDT is: 34.9 [$\text{g}_{\text{sol}} \text{g}_{\text{cat}}^{-1} \text{min}^{-1}$] for 2,4'-DDT and 46.7 [$\text{g}_{\text{sol}} \text{g}_{\text{cat}}^{-1} \text{min}^{-1}$] for 4,4'-DDT. Therefore, the reaction of DDT is significantly faster than that of both chlorobenzenes and PCBs. As a consequence the hydrotreating process of wastes containing DDT would be easier than that of wastes containing chlorobenzenes and/or PCBs.

The GC-ECD analyses carried out on the liquid samples withdrawn during the reaction runs did not indicate the presence of other chlorinated compounds during the reaction process. Specific GC-FID and GC-MS analyses were then carried out on the same samples to detect the presence of not chlorinated reaction intermediates or products. Also in this case products of DDT decomposition were not detected in significant amounts. The conclusion may be that only very light compounds are formed. However, the identification of the reaction network and then of the reaction mechanism would require further experimental work.

4. Conclusion

The results reported show that catalytic hydrotreating promoted by Ni–Mo catalysts can be proposed as a process for the detoxification of DDT wastes. Catalytic hydrotreating of DDT is easier to perform with respect to other toxic chlorinated compounds. In fact, at the same operating conditions, the destruction rate of DDT by catalytic hydrotreating is significantly higher than that of chlorobenzenes and PCBs. At reaction temperature 200 °C = $T = 230$ °C best fitting of

experimental data was obtained assuming reaction order $n = 1.65$ – 1.8 for 2,4'-DDT and $n = 1.24$ – 1.49 for 4,4'-DDT.

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