Thermochemistry and Kinetics of Plasma Waste Destruction

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Abstract

The arc plasma waste conversion process, PLASCON™, developed by CSIRO and SRL Plasma, has been studied using a combination of thermochemistry, chemical kinetics, and chemical analysis. The mixing temperatures of the waste with the plasma have been determined by free energy minimisation techniques. At a given mixing temperature, the rate of destruction will then depend on the rates of the relevant thermal decomposition reactions. The initial decomposition reaction for the destruction of the chlorofluorocarbon CCl_2F_2 should be $CCl_2F_2 \Rightarrow CClF_2 + Cl$. CF_2 and F radicals may be generated in further thermal reactions and recombination of radicals in the reaction tube of the device yields CF_4 and $CClF_3$, which have been observed in the offgases from the process. In comparison with incinerators the reaction time in plasmas in much less, but this is offset by the higher temperatures available in the argon arc plasma.

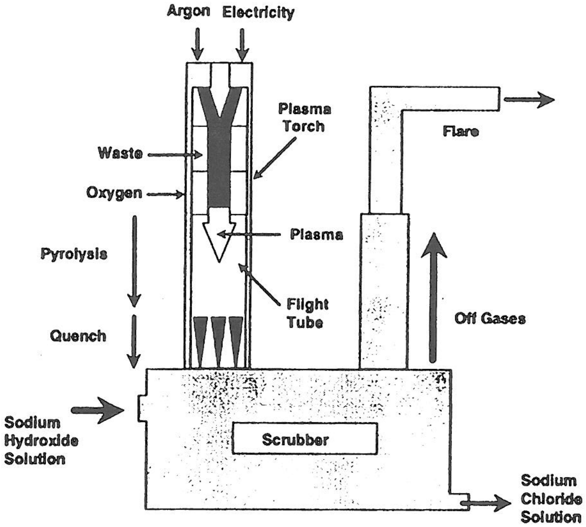
Introduction

The PLASCON device, of which a schematic is shown in Figure 1, has been used to destroy liquid and gaseous organochlorine wastes [1]. A 50 or 150 kW argon arc plasma torch is employed and the waste substance is injected into the plasma, along with oxygen gas, at the injection manifold. The gaseous mixture flows along a reaction tube to a water spray quench, thence into an alkaline scrubber which removes the halogens released by the process. The offgas from the scrubber is vented and may be analysed on line by means of a Varian Saturn II GC/MS. If necessary, samples of the scrubber liquor may be taken for analysis of residuals of liquid organochlorines such as chlorophenols. Destruction performance in the apparatus may be rated in Destruction or Removal Efficiency (DRE), as with incinerators. We also define our performance in terms of a residual, where

Residual = (quantity of waste emitted/quantity of waste injected) x 10^6.

On this measure, a DRE of 99.9999% equals a residual of 1.

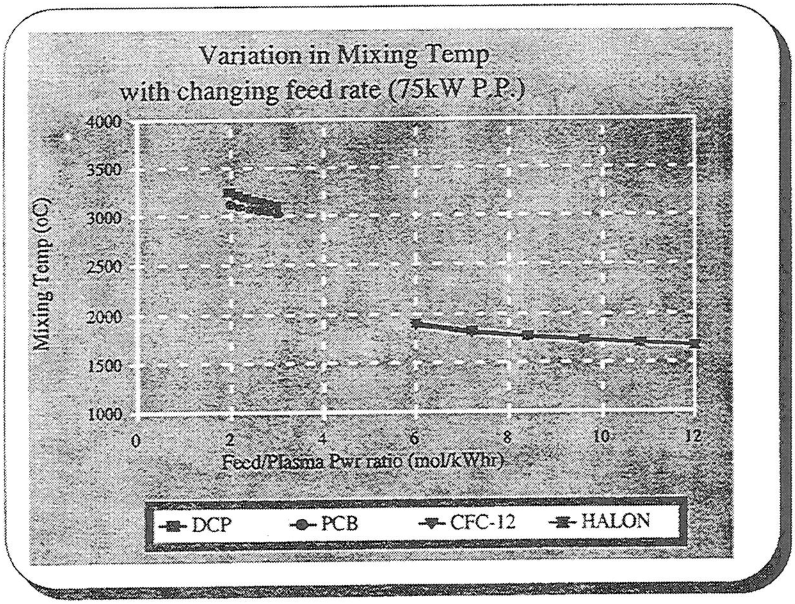
Figure 1. Schematic of Plascon apparatus



Taylor and Dellinger [2] have set out a qualitative stability ranking for organochlorine substances in incinerators which relies on a 2-zone model of incinerator operation. It is postulated that complete destruction occurs in the flame zone of the incinerator, where temperatures of 1200°C and residence times of several seconds are expected. The performance of the incinerator is then dependent on the thermal or pyrolysis zone surrounding the flame where temperatures are lower and reaction rates less. Incinerator performance may then be optimised by maximising both the proportion and the residence time of the waste which goes through the flame zone.

If a similar approach were to be made to the problem of analysing the performance of plasma destruction, it would be necessary, first of all , to determine the temperatures which prevail during a waste destruction operation, then to estimate the extent of the destruction reactions during the residence times of milliseconds which are thought to prevail in this type of apparatus. It is the purpose of this paper to present, first a thermochemical analysis of the plascon operation, and then a chemical kinetic approach which uses temperatures from the thermochemical equilibrium analysis. Finally the analytical results of real experiments on chlorofluorocarbon (CFC) destruction are compared with the theoretical estimates.

Figure 2. Calculated mixing temperatures of waste and plasma in Plascon



Methods

For the determination of mixing temperatures from the flows of argon, oxygen, and waste, and the available plasma power, we use the CSIRO Thermochemistry System of Turnbull and Wadsley [3] which determines equilibrium in a defined chemical system by means of the free energy minimisation algorithm of Ericsson [4]. The system calculates the adiabatic temperature rise at equilibrium for the specified mixture at the input plasma power and determines the equilibrium composition at the mixing temperature. Chemical kinetic schemes are simulated by means of the Larkin kinetic program of Deuflhard and Nowak [5].

Thermochemical Analysis

Typical mixing temperatures for the liquid organochlorines dichlorophenol (DCP) and polychlorinated biphenyl (PCB), and the gaseous ozone depleting substances (ODS) CFC12 and Halon are shown in Figure 2. The feed to plasma power axis is normalised in units of mol/kWh so that the results reflect conditions in both 50 and 150 kW Plascons. Practical feed rates for the DCP and PCB are 2-3 mol/kWh, giving 99.9999% destruction. These are associated with Plascon mixing temperatures of 3000°C or more. By contrast, the feed rates for the ODS are substantially higher (6 mol/kWh and above) because the DRE target set by the Montreal Protocol is 99.99%. These feed rates and destruction levels are associated with mixing temperatures of about 2000°C.

Chemical Kinetics

Any thermal decomposition scheme for the plasma destruction of the substances considered in Figure 2 must begin with the dissociation of a carbon - chlorine bond. Arrhenius rate parameters for the appropriate dissociations are given in Table 1.

Table 1. Decomposition reactions in Plascon

Reaction	*A* (s^{-1})	E_a ($kJ\ mol^{-1}$)	*Source*
$C_6ClH_5 \Rightarrow C_6H_5 + Cl$	3×10^{15}	399.6	(a)
$CBrClF_2 \Rightarrow CClF_2 + Br$	1×10^{13}	251.04	(b)
$CCl_2F_2 \Rightarrow CClF_2 + Cl$	1×10^{13}	340.0	(b)

(a) E.R. Ritter et al., J. Phys. Chem. 1990, 94, 2493.
(b) W. Tsang, J. Phys Chem. 1986, 90, 414.

The rate coefficient for the dissociation of chlorobenzene is the basic parameter for all the liquid organochlorines such as DCP and PCB. Because of the complexity of these molecules, it is not a rewarding exercise to draw up comprehensive reaction schemes. We may infer from the data for chlorobenzene that destruction of the original molecule will proceed rapidly to well beyond 99.9999% at the mixing temperatures shown in Figure 2, on the timescale of a millisecond. More is known of the rates of decomposition of the CFCs and halons, and the relative simplicity of these molecules (methane derivatives with only 5 atoms) lends itself to a more comprehensive kinetic approach. The inference of the data in Table 1 is that the substances will be destroyed to the required level in less than a millisecond at the mixing temperature, but what of the possible complications of recombination as the mixture flows along the reaction tube of the Plascon? Possible reactions are given in Table 2.

Table 2. Recombination to CX_4 where X = F, Cl

Reaction	*Reference*
$CCl_2F_2 \Rightarrow CClF_2 + Cl$	
$CClF_2 \Rightarrow CF_2 + Cl$	
$CF_2 + O \Rightarrow CO + 2F$	(Ryan and Plumb, Plasma Chem. Plasma Proc, 1984, 4, 271)
$CF_2 + F + M \Rightarrow CF_3 + M$	(Modica and Sillers, J. Chem. Phys., 1968, 48,3283.)
$CF_3 + F + M \Rightarrow CF_4 + M$	"
$CF_3 + Cl + M \Rightarrow CClF_3 + M$	

The problem may be illustrated by taking an actual experimental example from our work and doing the necessary thermochemical and kinetic calculations to compare with the observed analytical outcome of the destruction. Table 3 gives data from an experiment on CFC12 (CCl_2F_2) for which the input mixture was, Ar, 45 litres/min, O_2 30 litres/min, CF_2Cl_2 140 g/min (1.158 mol/min), with plasma power 11.3 kW and reaction tube power 9.3 kW. The feed to plasma power ratio was 6.03 mol/kWh.

Table 3. Mixing and quench temperatures (T_m and Tq), equilibrium and offgas analysis for CFC destruction in Plascon.

Calculated Equilibrium concentrations

Species		CCl_2F_2	$CClF_3$	CCl_3F	CF_4
		(mole fraction			)
T_m	(1835°C)	5×10^{-10}	7×10^{-6}	1×10^{-13}	7×10^{-3}
T_q	(1321°C)	1×10^{-10}	3×10^{-6}	6×10^{-15}	6×10^{-2}

GC/MS Residual CCl_2F_2 0.5; $CClF_3$ 62

In this case the thermochemical analysis has been taken one step beyond the mixing temperature to estimate the temperature and equilibrium at the quench from the reaction tube heat flow data . It is evident that at the feed rates used, the observed residual is an order of magnitude higher than the theoretical residual calculated from equilibrium data. Why? One explanation would be similar to the 2-zone effect described by Taylor and Dellinger for incinerators: there is a cooler boundary layer in the reaction tube of the Plascon where the destruction will be substantially less than in the centre of the reaction tube. A further question may be asked of these results: why is the composition of the residual different from the input waste composition? This is an important finding for CFC destruction, as $CClF_3$ (CFC13) has been given the same ozone depleting potential as CCl_2F_2 .These queries may be answered in part by a simulation of the kinetic scheme describing the overall reaction of CFC12 with oxygen in the plasma.

The chemical kinetic scheme which describes the decomposition of CFC12 in the Plascon contains over 150 reactions and space does not permit us to reproduce it in detail here. The critical reactions describing the decomposition and the recombination are given in Table 2 . The result of simulation of the reaction scheme for an assumed linear temperature gradient between mixing and quench of 100 K/msec is shown in Figure 3. This however represents a very simple picture of the Plascon. In reality, temperature will vary thoughout the apparatus in a three-dimensional, axially symmetrical pattern. For example, if a molecule of CFC12 experiences a very rapid decrease in temperature from T_m, which would occur if a proportion of the waste moved off-axis from the injection manifold towards the walls of the apparatus, substantially more CFC13 is predicted by the simulation, as shown in Figure 4. The practical outcome given in Table 3 is presumably due to the sum of many such time-temperature paths through the apparatus. Comparison of Figure 3 with Figure 4 shows how the performance of Plascon depends on holding the majority of the waste in the higher temperature zone on the millisecond timescale. Millisecond reaction times at the temperatures more appropriate to incinerators (1500 K maximum in the flame) are insufficient to destroy the ODS to less than the level required by the Montreal Protocol.

Figure3. Simulation of CFC13 production from CFC12, on the axis of Plascon

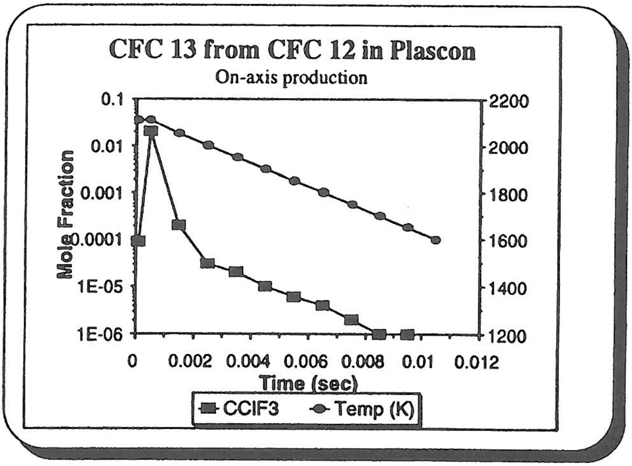
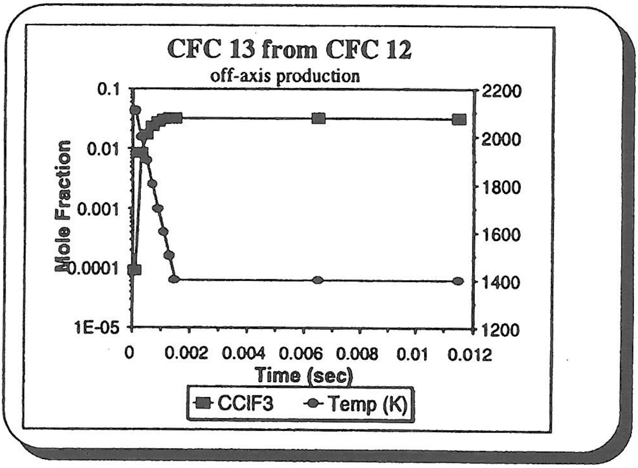


Figure 4. Simulation of $CClF_3$ production off-axis in Plascon



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