

THE COMBUSTION AND PYROLYSIS OF SOME HALOGENATED ORGANIC COMPOUNDS IN A LABORATORY TUBE FURNACE

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Summary

Experiments on the combustion of polychlorinated biphenyls (PCB) in a 1 metre long tube furnace indicated that PCB containing ca. 40% w/w chlorine or less is essentially completely destroyed within 3 to 4 seconds at 900° to 1,000° C using 100% excess air. Temperatures in excess of 1,000° C are required to destroy PCB containing ca. 60% w/w chlorine and distillation residues arising from PCB manufacture. Domestic waste incinerators operating at 800 to 900° C are unlikely to prove suitable for incinerating waste containing more than trace quantities of PCB. Pyrolysis experiments at 900° C with a nominal residence time of 3.5 seconds gave a 40% to 60% recovery of chlorine as hydrogen chloride from PCB. Under similar pyrolysis conditions quantitative recovery of chlorine from ethylene dichloride 'tars' was achieved.

Some halogenated aromatic compounds, in particular, polychlorinated biphenyls (PCB's) arising as wastes, pose a special disposal problem owing to their toxicity to living organisms through bioaccumulation and their resistance to environmental degradation. Consequently the only recommended disposal route for bulk arisings of PCB wastes is high temperature incineration [1]. American workers have suggested [2] that the incineration of pure PCB requires a temperature of 1,480° C for 1.5 seconds at 2% excess oxygen. This communication describes a laboratory study of the combustion of three PCB's and three wastes arising from PCB manufacture. The high temperature (above 700° C) gas phase pyrolysis of two pure PCB's and two wastes from vinyl chloride manufacture was also investigated. Other workers have described [3] a low temperature (ca. 545° C) gas-liquid pyrolysis process for recovering values from vinyl chloride manufacturing wastes and, in this case, the products were hydrogen chloride (50%), vinyl chloride (20%) and other C₂ halogenated organics (30%). Less than 1% of the recovered chlorine remained as solid residues.

The apparatus used in the laboratory combustion and pyrolysis experiments consisted of a 1 metre long electrically heated silica tube furnace. In the combustion experiments a 25 mm i.d. silica tube was used which had ports let into

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the side to allow gas samples to be withdrawn. In the pyrolysis experiments a 40 mm i.d. silica tube with no ports was used. Materials were admitted to the furnace by means of an atomiser, for liquids, or a long boat driven into the furnace at a constant rate, for solids. Gases leaving the furnace passed firstly through a cold trap and, secondly, through bubblers to collect any combustion products. A probe for withdrawing gas samples from the end of the furnace was fitted during the pyrolysis experiments.

Samples of Arochlor 1342, Pyroclor 5, Arochlor 1260, and PCB manufacturing wastes were donated by Monsanto Co., Newport. The manufacturing wastes consisted of Aroclor 1342 liquid residues which were trapped from a hydrogen chloride stream during the chlorination process, a sludge containing filter aid which was produced during the filtration of the crude PCB product and Aroclor 1342 distillation residues remaining as still bottoms following the purification of Aroclor 1342 by distillation. The composition and calorific values of these wastes were determined along with the calorific values of the three PCB's studied and these results are shown in Table 1. There was a general tendency for calorific value to increase with increasing carbon content but the correlation with decreasing chlorine content was rather poor. The figures for hydrogen chloride recovery from combustion of the manufacturing residues suggest that less than 10% w/w of the chlorine was retained in the ash.

Many waste incinerators operate with ca. 100% excess air, a rather higher figure than suggested by the American recommendations. However, combustion trials with the tube furnace suggested that use of 50% or 200% excess air resulted in substantially more soot formation than 100% excess air which was used in the experiments discussed below. Tests on Aroclor 1342 showed no PCB in the exhaust gases above a detection limit of ca. 50 mg/m³ for the gas temperature range 830 to 920° C and a nominal residence time range of 1.2 to 3.5 seconds. However, at temperatures below ca. 900° C and residence times below 3.5 seconds unburnt organics and carbon monoxide were detected in the exhaust gases. At 910° C with a residence time of 4.5 seconds less than 0.001% w/w of the PCB entering the furnace was trapped from the gas stream leaving the furnace and no organics or carbon monoxide were detected. The Aroclor 1342 liquid residues which were quite similar to Aroclor 1342 in composition and calorific value, also appeared to require similar conditions for incineration.

Less than 0.001% w/w of Pyroclor 5 entering the furnace was trapped from the exhaust gases when a gas temperature of 920° C was used with residence time of 4.5 seconds. However, in this case some 0.1% v/v of carbon monoxide was present in the gas stream after 3.5 seconds. The same degree of destruction of Aroclor 1260 was not achieved until the gases reached 1,050° C for 4.5 seconds. Similar conditions were required to incinerate the sludge containing filter aid.

The Aroclor 1342 distillation residues proved the most difficult to incinerate of all the materials tested. On entry to the furnace this material generated a char which took several minutes to burn down to an ash. At a gas temperature

TABLE 1

Composition and calorific values for some PCB's and their manufacturing residues

Material**	Appearance	Carbon (%)	Hydrogen (%)	Chlorine (%)	Oxygen (%)	Nitrogen (%)	Ash (%)	Calorific* value (kJ/kg)	HCl (%)
Aroclor	Colourless mobile liquid	55.9***	2.7***	41.3***	0	0	0	22.8	40
Pyroclor 5	Colourless mobile liquid	44.1†	1.5†	54.4†	0	0	0	14.7	56
Aroclor 1260	Colourless resin. Mobile at 80° C	39.9††	1.1††	59.0††	0	0	0	15.4	65
Aroclor 1342 Liquid residues	Brown/red mobile liquid	52	2.5	47	0.9	0	0.3	19.5	43
Sludge containing filter aid	Brown/red resin. Mobile at 80° C	35	1.4	47	2.6	0	17	12.5	42
Aroclor 1342 Distillation residues	Brown/red glassy solid. Mobile at 200° C	36	2.0	36	13	0	36	14.8	30

* Determined by ballistic bomb calorimetry, HCl was determined from the product gases, Elemental and gas chromatographic analyses were carried out by Chemical Analysis Group, Environmental and Medical Sciences Division. Calorific values and dissolved chloride were determined by Industrial Chemistry Branch, Chemical Technology Division, Harwell Laboratory.

** Samples of PCB's and manufacturing wastes were donated by Monsanto Co., Newport.

*** Theoretical figures for $C_{12}H_7Cl_3$.

† Theoretical figures for $C_{12}H_9Cl_5$.

†† Theoretical figures for $C_{13}H_4Cl_6$.

of 910° C both organic products and PCB could be detected in the gas stream after ca. 6 seconds. When the temperature was raised to 1,050° C the concentration of PCB in the gas stream fell below the detection limits after 3.5 seconds and, after 4.5 seconds, less than 0.002% w/w of the PCB entering the furnace was trapped from the exhaust gases.

Based on the detection limits of 0.001% w/w of the total PCB entering the furnace and 50 mg/m³ of PCB in the hot gases, complete combustion of PCB's containing 55% w/w chlorine or less may be effected within 5 seconds at 950° C with 100% excess air in the apparatus used. PCB's containing 60% w/w chlorine or more and distillation residues require a gas temperature of over 1,050° C for complete combustion to occur within 5 seconds with 100% excess air. These results suggest that the American recommendation of 1,100° C for 3 seconds may be adequate for PCB's containing less than 55% chlorine. However, this recommendation may not be adequate for more highly chlorinated materials or for distillation residues.

The results of the pyrolysis experiments using nitrogen as the carrier gas are presented in Table 2. The materials studied were Aroclor 1342, Pyroclor 5 and two types of ethylene dichloride 'tars' from vinyl chloride manufacture. The 'EDC lights' fraction were obtained as a mobile colourless liquid comprising ca. 60% ethylene dichloride, 20% chloroform, 12% carbon tetrachloride (all % w/w) and traces of other organic compounds. The 'EDC Heavies' were obtained as a mobile black/brown liquid comprising ca. 52% ethylene dichloride, 22% 1,1,2-trichloroethane, 6% tetrachloroethylene (all % w/w) and traces of other organic compounds. The major product of all the pyrolysis tests was an intractable black tar, which was insoluble in both hexane and toluene, and hydrogen chloride. The addition of 5% air by volume to the nitrogen to act as an initiator for pyrolysis reactions had no significant effect on the experimental results.

TABLE 2

Results of pyrolysis experiments

Material *	Mean furnace** wall temperature (° C)	Nominal gas residence time (sec)	Hydrogen chloride recovery (% w/w)	Soluble organic recovery (% w/w)
Aroclor 1342	900	3.5	47.5	0.3
Aroclor 1342	750	2.0	0.5	0.5
Pyroclor 5	900	3.5	50.5	0.08
Pyroclor 5	750	2.0	21.3	0.60
EDC 'Lights'	900	3.5	100	0.16
EDC 'Lights'	750	2.0	44	0.33
EDC 'Heavies'	900	3.5	100	0.024
EDC 'Heavies'	750	2.0	39.5	0.071

* Samples of EDC 'Lights' and 'Heavies' were donated by BP Chemicals Limited, Baglan Bay.

** Centre line gas temperatures in the furnace were ca. 50° C lower than the furnace wall temperature.

At 750° C with a nominal residence time of 2 seconds only 0.5% w/w of the chlorine in Aroclor 1342 was recovered as hydrogen chloride and only 0.5% w/w of the input PCB was recovered in the form of hexane or xylene soluble organic compounds. The corresponding HCl recovery for Pyroclor 5 was somewhat higher at 21.3% w/w but again little soluble organic material was recovered. At 900° C even less material was recovered as soluble organics but HCl recovery increased to ca. 50% w/w for both Aroclor 1342 and Pyroclor 5. These results suggest that, even at a gas temperature of 700° C over 99% of PCB is converted to an intractable tar which is not dissolved by hexane or toluene.

The pyrolysis of 'EDC tars' also afforded little in the way of hexane or xylene soluble organics. In all cases less than 0.4% w/w of the input material was recovered in this form. However, higher HCl recoveries were found than for PCB's and at 750° C ca. 40% recovery of HCl was obtained, while at 900° C quantitative recovery of HCl was achieved with a 3.5 second residence time. On the basis of these results it would seem that pyrolysis in the gas phase at 700–900° C offers little prospect for the recovery of values from PCB's. However, pyrolysis of 'EDC tars' at 900° C for 3.5 seconds would allow recovery of hydrogen chloride for reuse. The other major pyrolysis product would be a low chlorine content tar which could be incinerated without need for gas treatment to remove HCl from the flue gases. Such a process may provide a practical alternate to fractional distillation, pyrolysis at low temperature to mixed products [3] or exhaustive chlorination to carbon tetrachloride [4,5] provided waste heat is available to effect pyrolysis, perhaps from an incinerator.

Acknowledgement

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