Thermochimica Acta, 103 (1986) 231–237
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

COMBUSTION EXPERIMENTS OF POLYSTYRENE BY USE OF A MODIFIED BAYER–ICI–SHELL APPARATUS

W. KLUSMEIER, K.-H. OHRBACH and A. KETTRUP *

University-GH Paderborn, FB 13, Applied Chemistry, P.O. Box 1621,
4790 Paderborn (Federal Republic of Germany)

(Received 24 October 1985)

ABSTRACT

The combustion of polystyrene by use of a quartz tube modified Bayer–ICI–Shell apparatus yields, beside the main component styrene, a lot of other products known as biological hazards like benzene, naphthalene and biphenyl. The experiments have been performed in air atmosphere. According to DIN 4102, technical polystyrene mainly used in the building industry has been burnt and the composition of the resulting combustion products has been compared with that produced from the Bayer–ICI–Shell (BIS) experiments. The fire gases adsorbed on charcoal XAD 4 and XAD 2 have been desorbed in carbon disulfide as a solvent.

It is concluded that a combination of XAD 4 and charcoal is the most efficient adsorbent. In addition, a method for quantitative determination of fire gas containing decomposition products is discussed.

INTRODUCTION

A great number of test specifications and testing methods exists to classify the combustibility of raw materials [1] but only a few are concerned with the problems of fire gases. Perhaps this is due to the exceptional complexity in this field of research which is at its initial stage of a systematic examination with regard to theoretical and practical foundations. The assessment of people's risks from toxic fire gases and the development of suitable testing procedures has been described elsewhere [2]. A report on the importance and the difficulties of elaborating testing rules is given by Punderson [3].

Nowadays, several biological testing methods in fire gas analytics can be distinguished, first the investigations in the NBS chamber (Japanese decree no. 1231) and secondly the German DIN 53436 [4–6]. Regarding the complete analysis Wooley was one of the first who investigated the degrada-

---

* To whom correspondence should be addressed.

0040-6031/86/$03.50

tion behaviour of polyvinyl chloride, polyurethane (soft, hard) and polyethylenes [7,8]. We have taken up the experiments of Wooley by carrying out a practice relevant thermal decomposition of raw materials in air atmosphere, followed by gas chromatographic identification of the released gases. The fire performance of poly(1-methyltetramethylene) and poly(1-hexamethylene) has been proved successfully [9].

In our current studies dealing with the identification of the decomposition products of polystyrene the work done by Lichtenstein has been taken into consideration [10].

EXPERIMENTAL

We have used technical grade polystyrene glassy as sample material of 0.1 mm diameter for the combustion experiments in the BIS apparatus, while the samples used in the experiments according to DIN 4102 had a size of 5 × 5 × 0.5 cm differing from the above mentioned specification.

The modified BIS combustion apparatus (see Fig. 1) consists of a tube furnace (2) bearing especially strong filament windings at the ends (produced by Heraeus), a quartz tube (3), quartz boat (8), one or two flow meters (1), a water cooled adsorption tube (4), a needle valve and a rotary pump (7).

The maximum weight of sample was 100 mg, the diameter of the quartz tube has been reduced from 20 mm diameter in the centre of the tube to allow enhanced rates of air flow in front of the sample, avoiding a back flash of the combustion products. Before performing the combustion experiments the air flow rate is measured and set to this value as constant by use of the needle valve in the range from 100 to 400 cm^3 min^{-1}.

The combustion according to DIN 4102 has been carried out applying edging flame action, time of flame application has been 15 s and the mode of combustion equal to DIN 4102, see Fig. 2. The combustion products were sucked off above the sample, separated from soot to avoid plugging of the

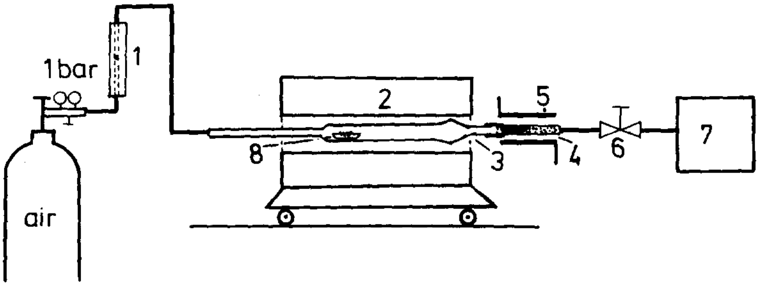

Fig. 1. Modified BIS combustion apparatus.

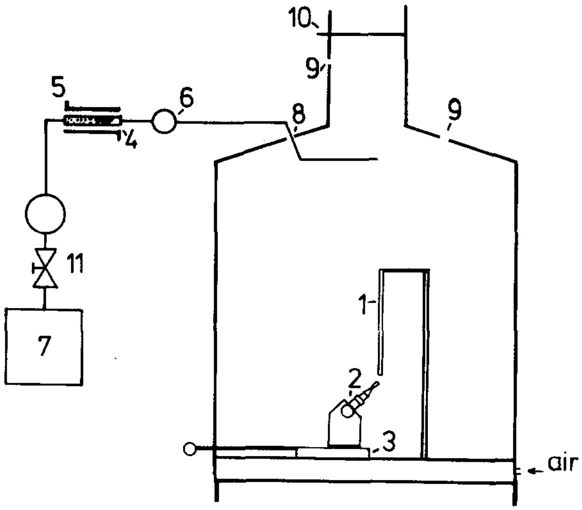

Fig. 2. Self constructed combustion apparatus: (1) sample material, (2) miniature gas burner, (3) motion mechanism of the miniature gas burner, (4) charcoal tube, (5) soot filter (micro glass), (6) water cooling, (7) rotary pump, (8) and (9) installation place for additional charcoal tubes and, (10) closing cover of the furnace.

adsorption tubes. Residual decomposition products on the soot filter could not be detected. A gas meter and a needle valve to regulate the air flow rate are installed after the adsorption tubes.

Adsorption of gases

The enrichment procedure of organic compounds from air using charcoal tubes followed by desorption has been described in detail in earlier studies [11–13]. The Supelchem LOT 121 charcoal tubes have been used in our investigations. During the current experiments self prepared tubes filled with XAD 4, e.g., XAD 2 have been mounted in front of the charcoal tubes yielding higher desorption efficiency for polyaromatic compounds like phenanthrene and naphthalene in comparison to charcoal.

XAD 4 and XAD 2 have been purified by 8 h soxhlet extraction with *n*-hexane, e.g., methanol and then vacuum dried at 100°C. The separation of the combustion products has been performed by means of a DANI 3900 gas chromatograph equipped with a 50 m fused silica column (OV 101).

Experimental procedure using the BIS apparatus

The quartz tube is charged with the quartz boat containing the sample material, then the desired decomposition temperature is selected and the preheated furnace placed around the sample for 10 min. After finishing the oxidative decomposition the used adsorbent is put into a septum bottle and

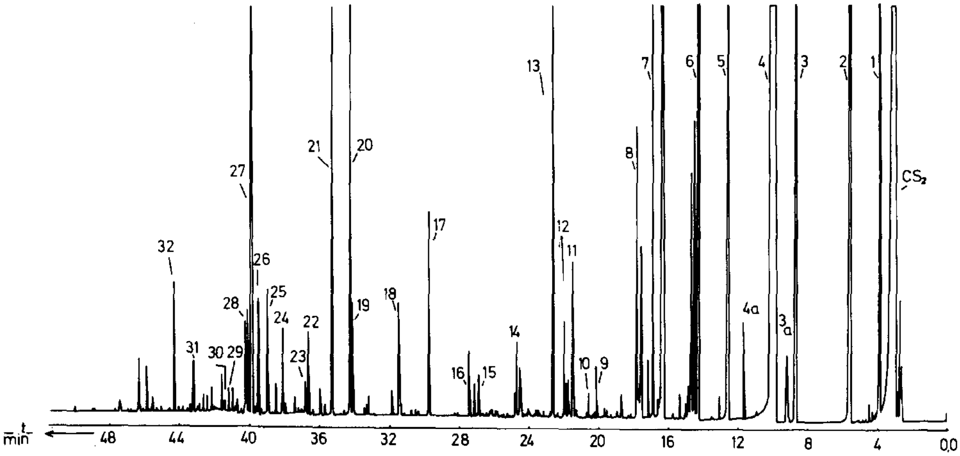

Fig. 3. Chromatogram of polystyrene combustion in a BIS apparatus at a temperature of 800°C, air flow rate 200 cm^3 min^{-1}.

treated with carbon disulfide. The application of different adsorbents one after the other needs carbon disulfide treatment of each sample.

The quantitative evaluation has been carried out using the method of the internal standard (iso-octane). The recovery rates have been determined by injecting a defined volume of a standard dissolved in carbon disulfide into the quartz boat.

Experimental procedure according to DIN 4102

The sampling during the combustion according to DIN 4102 has been analogous to that applied in the BIS apparatus. A volume of 200 cm^3 were sucked off from the combustion chamber applying a pumping rate of 1 dm^3 min^{-1}. The other experimental parameters have been set as constant.

RESULTS AND DISCUSSION

By comparing the retention times of polystyrene decomposition products several compounds could be identified, see Fig. 3. Gas chromatographic conditions: 60°C, 4 min holding time, 5°C min^{-1} heating rate, 250°C final temperature, divisor 10 cm^3 min^{-1}, 1.6 bar preliminary pressure. The compounds listed below correspond with the peak numbers indicated in Fig. 3.
(1) Benzene, (2) toluene, (3) ethylbenzene, (3a) *m*-, *p*-xylene, (4) styrene, (5) isopropylbenzene, (6) alpha-methylstyrene, (7) indene, (8), (9) divinylbenzene, (11) naphthalene, (15) 1-methylnaphthalene, (16) 2-methylnaphthalene,

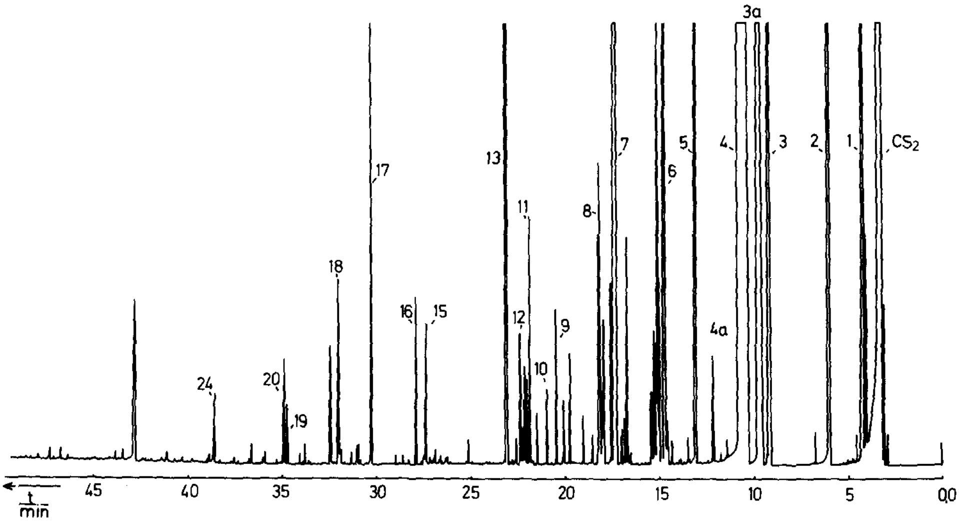

Fig. 4. Chromatogram of polystyrene combustion products obtained for *m* combustion according to DIN 4102.

(17) biphenyl, (18) diphenylmethane, (19) 1,1-diphenylethane, (20) 1,2-diphenylethane, (21) 1,2-diphenylpropane, (29) phenanthrene, (30) anthracene.

According to DIN 4102, all compounds listed above could be detected employing the same gas chromatographic conditions, see Fig. 4.

A comparison of both chromatograms shows the appearance of nearly all decomposition products only yielding small differences regarding the intensities of the fragments especially of higher condensed aromatic compounds. Quantitative information about the formation of degradation components related to the polystyrene weighed sample is only possible by performing the experiments in the BIS apparatus.

A series of compounds has been determined quantitatively after the estimation of their recovery rates and desorption rates in carbon disulfide as solvent. These experiments led to the results that some compounds show acceptable adsorption properties on charcoal but extremely bad desorption like phenanthrene and anthracene in contrast to benzene and toluene. On the other hand, XAD 4 has yielded good adsorption in the cases of naphthalene, biphenyl, anthracene and phenanthrene but the results were modest regarding the adsorption of toluene and benzene. For this reason the adsorbents have been combined with each other, by first passing the decomposition products through XAD 4, e.g., XAD 2 and then through charcoal resulting in higher yields of all degradation components. To determine accurately the loss of the identified components from combustion of polystyrene in the BIS apparatus in correlation with the adsorbent, their recovery and their transport rates have been estimated. All experiments have been

TABLE 1

Average values of the transport rates applying different adsorbents

Compound	XAD 4/charcoal (%)	XAD 2/charcoal (%)	Charcoal (%)
Benzene	93	90	90
Toluene	95	89	91
Ethylbenzene	87	87	87
Styrene	82	79	85
Naphthalene	73	70	55
1-Methylnaphthalene	65	61	48
2-Methylnaphthalene	67	63	52
Biphenyl	66	66	53
Diphenylmethane	66	66	52
Phenanthrene	39	43	2
Anthracene	33	32	1

performed five times by injecting 10, 25, 50, 75 μl into the BIS apparatus at temperatures of 600°C and 200 cm^3 min^{-1} air flow.

The results obtained by combination of XAD 4 and charcoal yielding an optimum adsorption of the decomposition products of polystyrene are listed in Table 1

Table 2 shows the percentage distribution of the combustion products of polystyrene at different temperatures.

Varying the experimental conditions, e.g., the temperature, increases the influences on the yield of low molecular compounds like benzene, toluene and several cracking products.

TABLE 2

Percentage distribution of polystyrene combustion products (polystyrene weighed sample 30 mg, applied temperatures 400, 600, 800, 1000°C, air flow rate 200 cm^3 min^{-1}. The data shown in Table 1 are average values taken from five measurements)

Compound (%)	400°C	600°C	800°C	1000°C
Benzene	0.18	0.42	3.55	4.30
Toluene	0.25	0.87	2.49	4.50
Ethylbenzene	0.10	0.06	0.46	1.00
Styrene	51.41	64.12	47.66	54.20
Indene	0.03	0.13	1.57	1.90
Naphthalene	0.03	0.08	0.98	1.28
1-Methylnaphthalene	–	–	0.06	0.10
2-Methylnaphthalene	0.03	0.02	0.10	0.15
Biphenyl	0.03	0.05	0.33	0.42
Diphenylmethane	–	0.03	0.11	0.19
Phenanthrene	0.10	0.03	0.24	0.38
Anthracene	0.03	0.04	1.17	2.02
Relative standard deviation 10%				

REFERENCES

1 J. Troitzsch, Brandverhalten von Kunststoffen, Carl Hanser Verlag, München, 1982.
2 ISO Technical Report 6543, 1979.
3 J.O. Punderson, Fire and Materials, 5 (1981) 1, 41.
4 B. Kimmerle and E.H. Prager, Kautsch., Gummi Kunstst., 5 (1980) 354
5 H.Th. Hofmann and H. Sand, Kunststoff Rundsch., 21 (1974) 10, 413.
6 DIN 53436, Erzeugung Thermischer Zersetzungsprodukte von Werkstoffen unter Luftzufuhr and ihre Toxische Prüfung.
7 W.D. Wooley and P.J. Fardell, Fire Safety J., 5 (1982) 29.
8 W.D. Wooley, Fire Safety J., 5 (1982) 186.
9 W. Klusmeier and K.-H. Ohrbach, J. Polym. Degradation Stability, 13 (1985) 121.
10 N. Lichtenstein, Dissertation, Bochum, 1979.
11 L. Weber and U. Knecht, Fresenius' Z. Anal. Chem., 321 (1985) 544.
12 VDI Richtlinien 3482, Blatt 4, 1980.
13 K. Grob and G. Grob, J. Chromatogr., 62 (1971).