

# Polycyclic Aromatic Hydrocarbons (PAHs) in Soot Produced by Combustion of Polystyrene, Polypropylene, and Wood

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## SYNOPSIS

The smoke and soot produced by the combustion of plastics or wood in a domestic stove or fireplace contain many poisonous compounds, including the polycyclic aromatic hydrocarbons (PAHs), many of which are carcinogenic. PAHs were selected as the subject of our study to gain a better sense of the hazards of burning plastics. Small samples of polystyrene, polypropylene, and wood underwent combustion in a tubular oven at 700°C; in addition, polystyrene and wood were combusted at room temperature. After their extraction and purification, the PAHs were analyzed by gas chromatography and mass spectrometry. Conditions in the hot oven promoted soot production, whereas combustion at room temperature led to somewhat more complete combustion. The PAH profiles of the examined materials resembled each other to some extent, though the original chemical structure of the polymeric materials varied a great deal. However, clear differences between the materials could be detected from the soot extracts, the soot of polystyrene being especially rich in compounds containing remnants of the polymer structure. Carcinogenic activity caused by the PAHs can be assumed to be of the same order of magnitude as soot from the combustion of wood.

## INTRODUCTION

A certain amount of plastics are burned in domestic stoves and fireplaces, though this is known to cause some pollution. In such cases the black smoke and specific odors produced may reveal the presence of plastics. The odor from burning plastics is so specific that it has even been utilized to identify plastics in simple burning tests. For instance, the burning of PVC will produce hydrogen chloride, which has a typical acid odor. Polyamides and polyurethanes contain nitrogen in their chemical structure, and their burning at low temperatures will produce various noxious nitrogen compounds, and, even at high temperatures, nitrogen oxides and hydrogen cyanide. In addition, because of their poor burning and a strong soot forming tendency, it is inadvisable to

burn the plastics mentioned above in domestic stoves.

On the other hand, polymers and corresponding plastics which are made up of only three elements (carbon, hydrogen, and oxygen) are potentially good fuels. In principle, they can be combusted to form carbon dioxide and water, though in practice the combustion is not complete. The most important of this latter type of plastics are polyethylene, polystyrene, and polypropylene. In fact, the burning of polyethylene is rather harmless. As a fuel it can be, because of its chemical structure, compared to stearine. The burning of polystyrene is problematic because it produces quite a lot of smoke and soot. The burning of polypropylene lies between the two others.

Soot is harmful not only as dirt but because it contains poisonous compounds, especially PAHs. Residential fireplaces are one of the major sources of PAHs. BaP is one of the five ring PAHs known to have high carcinogenic activity. Its emission from residential fireplaces in the United States was es-

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**Table I Production of Soot, Phenanthrene, and BaP<sup>a</sup>**

Material	Soot (mass %) <sup>b</sup>	Phenanthrene (mg/g) <sup>b</sup>	BaP (mg/g) <sup>b</sup>
Polypropylene	4.6	0.35	0.07
Polystyrene	33.3	4.0	0.27
Wood	3.3	0.18	0.03

<sup>a</sup> Combustion in the oven at 700°C.<sup>b</sup> All measures are relative to the amount of the combusted sample.**Table II Production of Soot, Phenanthrene, and BaP<sup>a</sup>**

Material	Soot (mass %) <sup>b</sup>	Phenanthrene (mg/g) <sup>b</sup>	BaP (mg/g) <sup>b</sup>
Polystyrene	17.0	0.04	0.006
Wood	3.9	0.03	0.003

<sup>a</sup> Combustion at room temperature.<sup>b</sup> All measures are relative to the amount of the combusted sample.

estimated to be 77 metric tons in the year 1985.<sup>1</sup> The occurrence of PAHs in the environment has been intensively studied. For instance, the *Handbook of Polycyclic Aromatic Hydrocarbons*<sup>2</sup> gives a survey of sources of PAHs and their analytical methods. However, it does not review the combusted products of synthetic polymers.

In fact, it has been difficult to find a general overview of the compounds produced by the combustion of polymers. One reason for that is the very high dependence of the products on the conditions of combustion. Another reason is that the methods used to study the field are rather heterogeneous. Cullis and Hirschler<sup>3</sup> have given a good review of the combustion process of polymers which can explain these problems.

A few papers are available concerning the PAH production of burning plastics. Morikawa analyzed the soot and BaP production of several polymers. He used a tubular oven, similar to the one used in our work, to burn polymers at different temperatures.<sup>4</sup> The BaP content of the soot produced was determined by gas chromatography. Klusmeier et al., in their experiments, found about 50% styrene and many of polystyrene's other pyrolysis products in their combustion experiments made in a modified Bayer-ICI-Shell apparatus.<sup>5</sup> Hawley-Fedder et al. have analyzed products obtained during the combustion of polymers under simulated incinerator conditions.<sup>6</sup> Temperatures used by Hawley-Fedder were 800–950°C. Polystyrene appeared to be a significant source of PAHs. Their experiments also showed that the majority of PAHs were associated with particulate matter. It has also been reported elsewhere that the major part of the toxic smoke components do not occur freely in combustion samples, but are up to 90% associated with aerosol particles in the respirable range.<sup>7</sup> On the other hand, Keränen et al. found most of their PAHs in the gas

**Table III Content of the Reference PAH Mixture**

1. Naphthalene	19. Fluoranthene
2. 2-Methylnaphthalene	20. Pyrene
3. 1-Methylnaphthalene	21. Benzo[a]fluorene
4. Biphenyl <sup>a</sup>	22. Benzo[b]fluorene
5. Acenaphthylene	23. Cyclopenta[cd]pyrene <sup>a</sup>
6. Acenaphthene	24. Benzo[a]anthracene
7. 3-Methylbiphenyl	25. Chrysene + triphenylene
8. Dibenzofuran	26. Benzo[b]fluoranthene
9. Fluorene	27. Benzo[k]fluoranthene
10. <i>Trans</i> -stilbene <sup>a</sup>	28. Benzo[e]pyrene
11. Dibenzothiophene	29. Benzo[a]pyrene
12. Phenanthrene	30. Perylene
13. Anthracene	31. 1,3,5-Triphenylbenzene
14. Carbazole	32. 3-Methylcolanthrene
15. 2-Methylanthracene	33. Benzo(a,h)anthracene
16. 1-Methylphenanthrene	34. Picene
17. 2-Phenylnaphthalene	35. Benzo[ghi]perylene
18. 3,6-Dimethylphenanthrene	

<sup>a</sup> Compound identified without reference by retention index and mass spectrum.

phase when analyzing flue gases from the furnace of a boiler of a one-family house.<sup>8</sup> The difference in results has probably been caused by different sampling strategies. In the last mentioned work, 5–20% of the fuel was plastic, which was added to firewood. PAH production generally decreased when only 5% of the fuel was hydrocarbon polymers, but increased rapidly when higher loads of polymers were used.

Our own combustion experiments were performed under two quite different conditions. First in an oven at 700°C and second at room temperature. Only polystyrene and, as reference, wood were combusted at room temperature. The aim of this work is to compare the PAH productions from polystyrene and polypropylene to that of wood to gain a better sense of the hazards of burning plastics.

## EXPERIMENTAL

### Apparatus

The gas chromatographic (GC) analyses were performed by means of a Dani 6800 gas chromatograph equipped with a fused silica capillary column. Column length was 25 m, i.d. 0.20 mm, phase SE54 and phase thickness 0.15  $\mu\text{m}$ . A programmable temperature vaporizer injector and a flame ionization detector (FID) were used. Gas chromatograms were produced by a Hewlett Packard 3392A integrator and further treated by an Apple IIe microcomputer. Samples were combusted using two methods. First, in an oven made of a quartz tube having an inner diameter of 10 mm, and in a regulated stream of dry air. The quartz tube was heated to 700°C in a laboratory oven, which made it possible to regulate the temperature at the point where the samples were located to within an accuracy of 5°C. Second, wood and polystyrene samples were combusted at room temperature using an oxygen index apparatus.<sup>9</sup> The soot was collected, in both cases, in glass fiber Cambridge filters similar to those used in tobacco smoke standard tests.<sup>10</sup> GC-mass spectrometric (GC-MS) analyses were performed by means of a Hewlett Packard 5890 GC and Hewlett Packard 5970A quadrupole mass analyzer combined with a Hewlett Packard 9825 personal computer. Experimental conditions included a scan speed of 600 amu/s, an ionization energy of 70 eV, a photomultiplier voltage of 1600 V, a vacuum of  $10^{-10}$  torr, and an injector temperature of 280°C. The column was of the same type as described above but 15 m in length.

### Materials

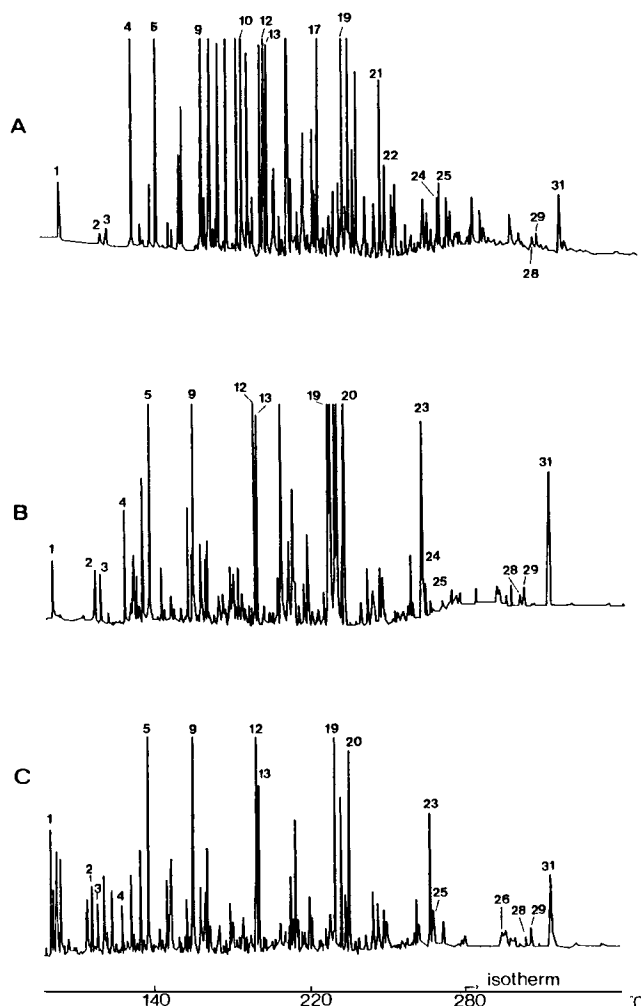
Despite being commercial, the materials examined were reasonably pure polymers: Polypropylene (PP)

ICI Propathene GW 521, and polystyrene (PS) Stymer PS-S. The reference material was birch of the type used as firewood. All the solvents used were of a chromatographic grade.

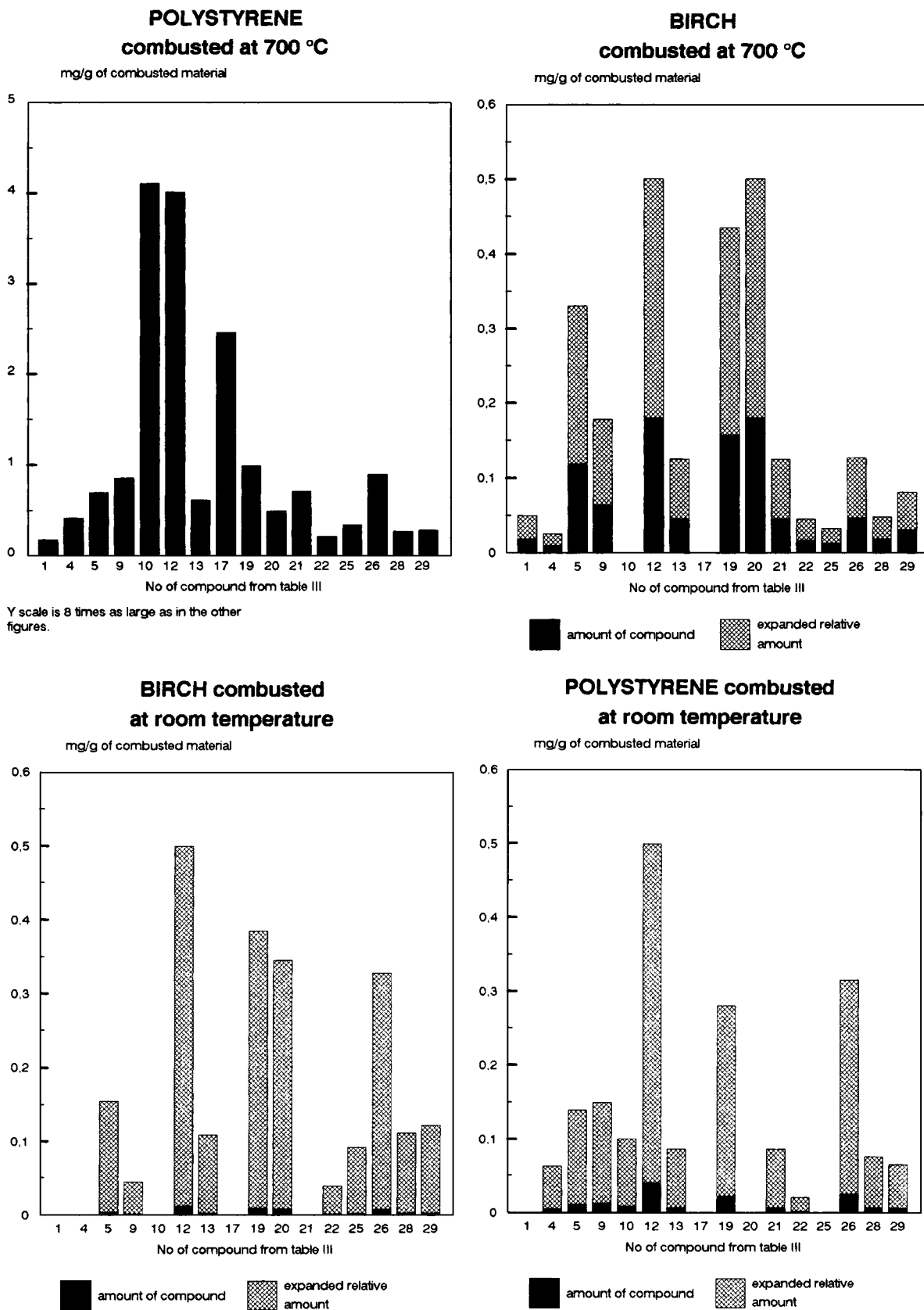
### The Combustion Experiments

The combustion in the oven: Samples of about 50 mg were subjected to a sudden temperature of 700°C. Air flow through the oven was 1 L/min. The soot was collected in a filter which had been conditioned in the air stream to a constant weight. Soot production was determined by gravimetry.

The combustion at room temperature: These experiments were done in the O.I. apparatus. Samples were 100  $\times$  6  $\times$  3 mm of shape. They were ignited by a small propane flame and allowed to burn for a



**Figure 1** Chromatograms of a soot extract of (A) polypropylene, (B) polystyrene, and (C) wood, combusted in the oven at 700°C.



**Figure 2** Comparison of the relative amounts of PAHs and several other aromatic compounds in the soot.

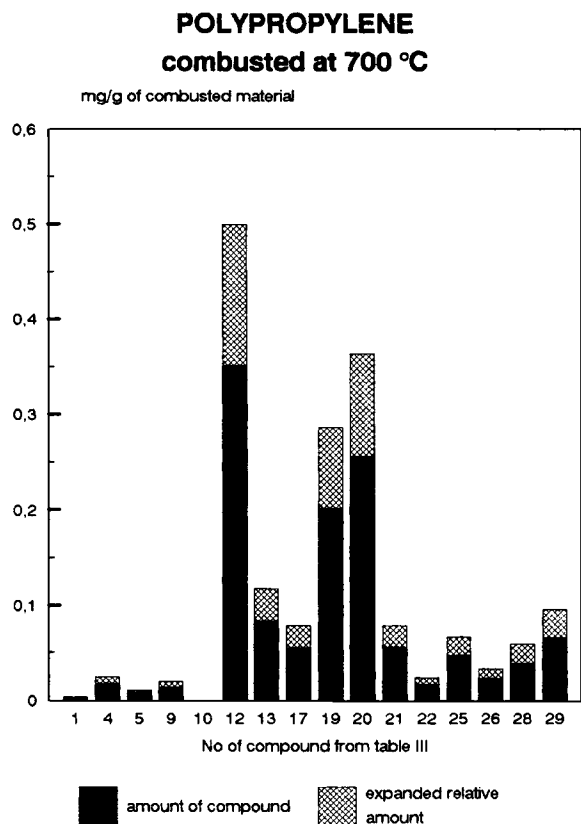


Figure 2 (Continued)

while in a upward stream of dry air. PS samples were ignited from the top, but wood samples had to be ignited from the bottom to get them to burn. To gain a qualitative result, soot was trapped in a filter from a determined part of the flow by means of a sample collecting bump.

Both of the two environments mentioned above led to a considerable formation of smoke. A fundamental difference between the conditions was due to the difference in the temperature of the surroundings. At 700°C each sample got immediately fire. The flame so formed was rich of fuel because of the rapid thermal degradation at 700°C. The formation of smoke was further promoted by the air stream which swept the flame to a lower temperature. The drop in the temperature was from 700 to 25°C between the positions of sample and filter. The situation resembled a moment in practice when a high load of fuel is added into a hot furnace. In the other conditions, combustion at the room temperature, only the energy necessary for an ignition was brought from outside, and the heat needed for the continuous flame was produced by the combustion itself.

### Sample Preparation for GC and GC-MS Analysis

The filters were ultrasonically extracted twice using 20 mL of 50% acetone hexane solution. An internal standard, 1,3,5-triphenylbenzene (TPB), was added before extraction. The sample was carefully evaporated to dryness and dissolved in 2 mL of hexane. The hydrocarbons were applied to a small alumina column and eluted with hexane and then with ethanol and finally with methanol to confirm that aromatics up to picene were separated. The hexane eluent contained nonpolar aliphatic hydrocarbons. The ethanol portion was concentrated to 2 mL and used as a sample in the GC and GC-MS examinations.

### Treatment of the Results

Identification of the compounds was based on PAH retention indexes,<sup>11</sup> separate runs with a GC-MS system, and comparisons to the results achieved with a standard PAH mixture. Determination of the quantities was based on TPB, the internal standard.

## RESULTS AND DISCUSSION

The soot production of the combusted materials as well as the amount of two of the PAHs analyzed from the soot are presented in Tables I and II. Phenanthrene was the most abundant of the PAHs. BaP has been included in the tables because it is widely used as an indicator of carcinogenic activity. Under both conditions, polystyrene produced the most soot and PAHs. Combustion at the ambient temperature led to a more complete combustion of polystyrene and, interestingly, clearly decreased the amount of PAHs in the soot. A reference mixture of 32 compounds was used in the identification of PAHs. Its composition is presented in Table III.

Comparison of the chromatograms (Fig. 1) shows that the compounds extracted from soot are characteristic of combusted materials. In our experiments the soot produced by polystyrene contained the greatest variety of compounds. A comparison of PAH emissions (Fig. 2), when based on the identified compounds (of Table III), shows most differences in the amount but not in the quality of the PAHs. The amount of the PAHs is usually approximately consistent with the soot production. It must be noted that all of the analyzed compounds are not actually PAHs, but also include some other aromatics like stilbene and biphenyl. These additive

compounds and some phenyl-substituted PAHs are characteristic of polystyrene's soot. This indicates a clear effect from the polymer's structure on the products of its combustion.

In conclusion, it can be said that, qualitatively, the soots contained mostly the same PAHs and even their relative amounts resembled each other. Thus, a reduction of the amount of soot produced is essential to reducing PAH production. It is not possible to say anything final about the virulence of a complicated mixture like soot, but on the basis of the analyzed PAHs, the carcinogenic activity of the soot of polystyrene can be assumed to be of the same order of magnitude as that of wood. Some additional virulence may, however, be caused by the added compounds typical especially of the soot of polystyrene.

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