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Several years ago, the authors recognized the need for a systematic study to obtain quantitative data on the volatile decomposition products (pyrolysis and combustion products) of a wide variety of organic materials.[1] To accomplish this, a standardized method of decomposition, suitable for collection and subsequent analysis of products, is required. A method used earlier in the DBR Fire Research laboratory for the study of combustion products of polymeric materials containing nitrogen [2] is not suitable for subsequent analysis of important components such as hydrogen chloride ($HC\ell$). The problem is attributed to the exposed heating element which comes in contact with the decomposition products. Because of the wide use of halogen compounds to impart fire retardance, halogen acids are produced by many materials. Any standardized method of decomposition, therefore, must not have an exposed heating element.

The purpose of this paper is to describe a new flow method for thermal decomposition that has been developed, and to present experimental results obtained from the combustion (or pyrolysis) of PVC and wood (white pine). The toxicity indices [3] obtained from the decomposition products of the two materials, based on these results, are also presented.

MATERIALS

Specimens were made in the form of pellets from PVC general purpose resin and white pine sawdust.

THERMAL DECOMPOSITION

The experimental setup for the decomposition of PVC is shown in Figure 1. Samples were decomposed in a horizontal quartz tube through which air was metered. The inside diameter of the furnace tube was 57 mm.

The sample was weighed in a quartz boat and moved to the hot zone of the furnace by a magnetic sample insertion device. Glass wool was placed at the outlet end of the furnace tube to trap solid particles, and a heating tape was wound around the same area to prevent condensation of volatile products. The sample weight was varied from 400 mg to 2 g, air was metered at various rates ranging from 500 to 4000 $cm^3 min^{-1}$, and the furnace tube was maintained at temperatures ranging from 400 to 800°C.

Hydrogen chloride was collected in liquid traps containing 2 per cent NaOH and analyzed using a specific ion electrode for chloride ion. The gaseous sample was collected in a plastic bag and analyzed for CO and CO_2 using gas chromatography.

The experimental setup for the decomposition of white pine was similar except that the glass wool filter and the heating tape were not used. Experiments with white pine were conducted in air, nitrogen and mixtures of both. CO and CO_2 were analyzed.

RESULTS AND DISCUSSION

1. Polyvinyl chloride

When PVC is heated to temperatures above 250°C, it decomposes and produces HCℓ. The removal of HCℓ leaves a residue having a polyene structure which breaks down further to yield benzene and other aromatics. When PVC is heated in an oxidizing atmosphere, some of the volatile components burn to produce oxidation products such as CO, CO_2 and H_2O.

Quantitative data on the main decomposition products of PVC are presented as a function of air flow rate (Figure 2) and as a function of sample weight (Figure 3). The yield of HCℓ was approximately equal to the theoretical amount expected from complete conversion of Cℓ atoms to HCℓ. Variation in air flow rate or sample weight had very little influence.

Quantitative data on decomposition products of PVC at different temperatures are presented in Table 1. The variation of temperature from 400 to 800°C had little effect on the HCℓ yield which was again approximately equal to the theoretical amount for complete conversion to HCℓ. The authors believe that the CO_2 results were lower than those actually produced by decomposition of PVC in the oxidizing atmosphere because of absorption of some of this gas in the NaOH trap. Separate experiments for CO_2 determination were not conducted to correct this discrepancy because the difference in results would not make a significant difference to the over-all toxicity due to the combined effect of HCℓ, CO and CO_2.

The quantitative results for CO, CO_2 and HCℓ reported in Table 1 were used to determine the toxicity index (which is a measure of toxicity)[3] from the equation $T = \frac{c}{c_f}\frac{V}{W}$

where T = toxicity index

c = concentration of a gaseous compound

c_f = concentration of the same compound that is fatal to man in 30 minutes

V = volume into which the decomposition products are diffused

W = weight of sample

For convenience in calculation, c is expressed in volume ratio, that is $c = v/V$ where v is the volume of the gaseous compound, then, $T = \frac{v}{c_f W}$.

The toxicity indices for the study are reported in litres per g., and were obtained by using $c_f = 4 \times 10^{-3}$ (i.e., 4000 ppm) for CO [4], 85×10^{-3} for CO_2 [5] and 1×10^{-3} for HCℓ [4].

The toxicity index data for PVC, presented in Table 2, vividly illustrate that the toxicity of the decomposition products was primarily due to the high yield of HCℓ. The additional effect of CO was very small.

2. Wood (White Pine)

When wood is decomposed by heat, a large variety of combustible vapours are produced along with carbon, CO, CO_2 and water vapour. Some pyrolysis products act as irritants to the eyes and respiratory tract. When wood is subjected to flaming combustion, some of these combustible vapours are consumed by the fire. Because large amounts of CO and CO_2 are produced in comparison with other harmful compounds, the toxicity due to CO and CO_2 only were considered in this study.

Quantitative data on CO and CO_2 produced by combustion of white pine are presented as a function of decomposition temperature in Figure 4. Experimental data showing the influence of varying the sample weight and the atmosphere are presented in Table 3. Toxicity index data based on these results are presented in Table 4. In combustion experiments, generation of CO increased with increase in temperature (Figure 4) and was greatest with the larger sample weights. Experiments in nitrogen and mixtures of nitrogen and air gave higher yield of CO than experiments in air.

CONCLUSIONS

1. A standardized method of decomposition for obtaining quantitative data of decomposition products of different materials has been developed.

2. The maximum toxicity index obtained for PVC using the new flow method was about 360 $\ell\ g^{-1}$. The maximum toxicity index for white pine was about 50 $\ell\ g^{-1}$.

3. The higher value for PVC indicates that it has a substantially greater propensity for generating toxic decomposition products than white pine.

ACKNOWLEDGEMENT

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TABLE 1

DECOMPOSITION PRODUCTS OF PVC

Temperature °C	Products, g/g sample			
	CO	CO_2	HCℓ	Residue
400	0.003	trace	0.557	0.22
400	0.003	"	0.576	0.22
500	0.025	0.049	0.563	0.08
500	0.016	0.048	0.554	0.08
600	0.056	0.135	0.554	<0.01
600	0.055	0.139	0.555	<0.01
700	0.063	0.215	0.558	<0.01
700	0.060	0.222	0.561	<0.01
800	0.044	0.299	0.564	<0.01
800	0.042	0.282	0.564	<0.01

Air flow rate = 2,000 $cm^3 min^{-1}$

Sample weight = 800 mg

TABLE 2

TOXICITY INDEX FROM DECOMPOSITION PRODUCTS OF PVC

Temperature, °C	Toxicity Index, ℓ g^{-1}			
	CO	CO_2	HCℓ	SUM
400	0.6	0	342	342
400	0.6	0	341	342
500	5.0	0.3	346	351
500	3.2	0.3	340	344
600	11.2	0.8	340	352
600	11.0	0.8	341	352
700	12.6	1.3	342	355
700	12.0	1.3	344	358
800	8.8	1.8	346	357
800	8.4	1.7	346	356

TABLE 3

DECOMPOSITION PRODUCT OF WHITE PINE

Atmosphere	Sample Weight mg	Products, g/g sample		
		CO	CO_2	Residue
Air	250	0.076	0.744	0
"	250	0.073	0.755	0
"	500	0.146	0.507	0
"	500	0.152	0.507	0
"	800	0.167	0.376	0
"	800	0.166	0.367	0
"	1200	0.185	0.268	<0.01
"	1200	0.181	0.272	<0.01
"	1600	0.171	0.209	<0.01
"	1600	0.160	0.197	<0.01
25% N_2, 75% air	500	0.236	0.432	<0.01
"	500	0.236	0.451	<0.01
50% N_2, 50% air	500	0.213	0.246	0.02
"	500	0.227	0.257	0.03
75% N_2, 25% air	500	0.217	0.110	0.05
"	500	0.248	0.118	0.04
Nitrogen	500	0.226	0.032	0.08
"	500	0.217	0.032	0.08

Temperature = 800°C

Flow rate = 1000 $cm^3 min^{-1}$

TABLE 4

TOXICITY INDEX FROM DECOMPOSITION PRODUCTS OF WHITE PINE

Atmosphere	Sample Weight mg	Toxicity Index, $\ell.g^{-1}$		
		CO	CO_2	SUM
Air	250	15.2	4.5	20
"	250	14.6	4.5	19
"	500	29.2	3.0	32
"	500	30.4	3.0	32
"	800	33.4	2.3	36
"	800	33.2	2.2	35
"	1200	37.0	1.6	39
"	1200	36.2	1.6	38
"	1600	34.2	1.3	36
"	1600	32.0	1.2	33
25%N_2, 75% air	500	47.2	2.6	50
"	500	47.2	2.7	50
50%N_2, 50% air	500	42.6	1.5	44
"	500	45.4	1.5	47
75%N_2, 25% air	500	43.4	0.7	44
"	500	49.6	0.7	50
Nitrogen	500	45.2	0.2	45
"	500	43.4	0.2	44

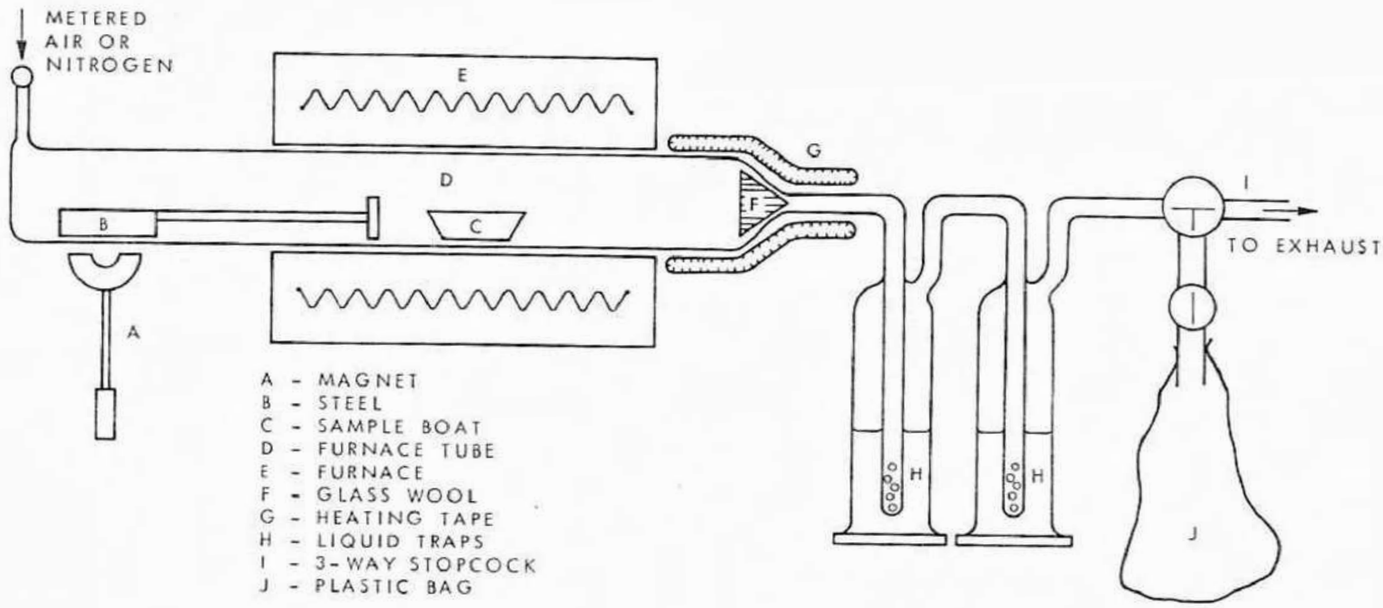

FIGURE 1

THERMAL DECOMPOSITION APPARATUS

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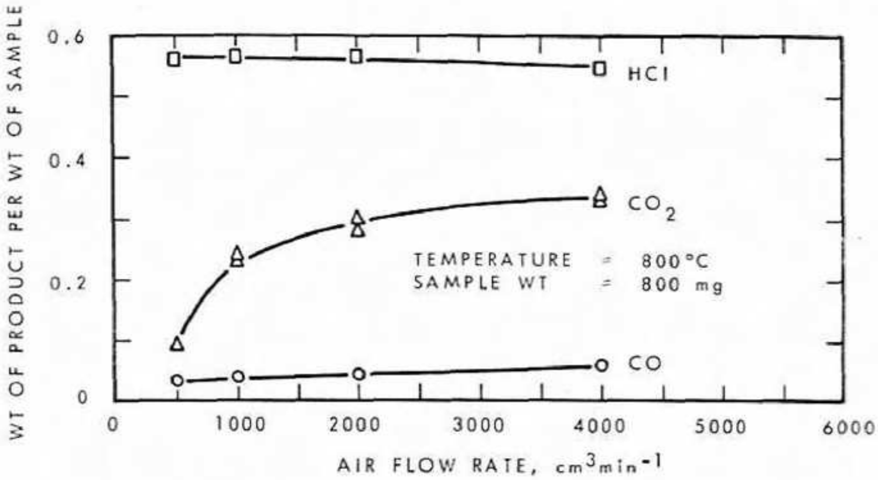

FIGURE 2

DECOMPOSITION PRODUCTS OF PVC VS AIR FLOW

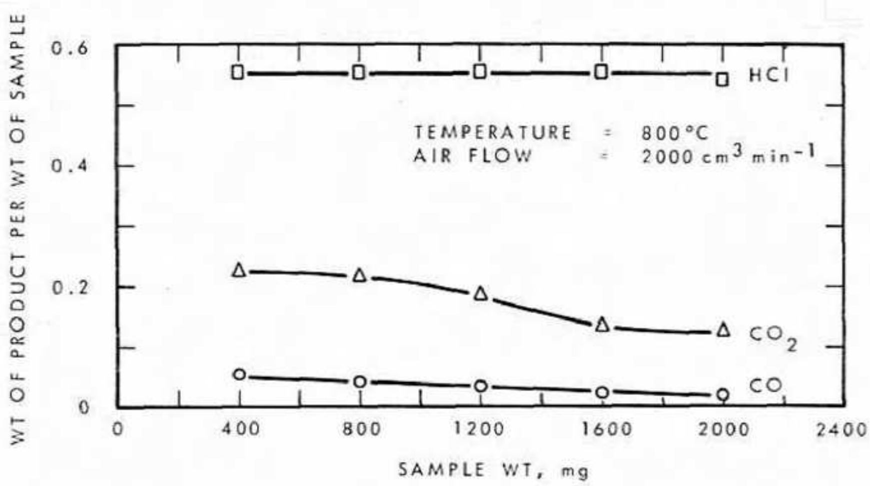

FIGURE 3

DECOMPOSITION PRODUCTS OF PVC VS SAMPLE WEIGHT

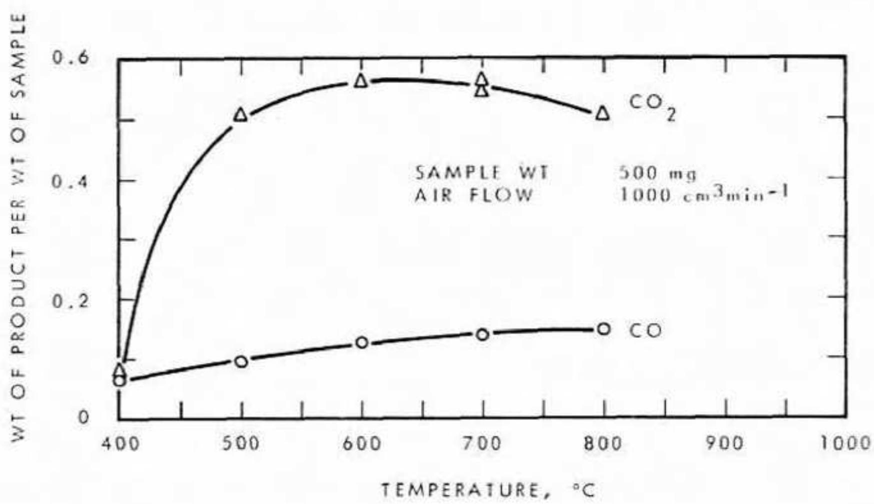

FIGURE 4

DECOMPOSITION PRODUCTS OF WHITE PINE VS TEMPERATURE

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