Alkane Influence of Combustion Products in Polyethylene and Gasoline

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Abstract

To study the influence of fire residues between gasoline and polymeric materials, it discussed the types and characteristics of Polyethylene (PE) combustion produce on different stages, according to its pyrolytic process after burning, and then compared with combustion residues of gasoline. The results shown that the combustion produces of PE on different burning stages were mainly contained C\textsubscript{10}~C\textsubscript{16} linear alkenes, which were different from gasoline on the characteristics and distribution. Though it would be interference with gasoline on composition in material evidence identification, but also can be distinguished by careful analysis.

1. Introduction

In recent years, Arson cases are raising sharply in the criminal cases, which could be a great danger and damage to our society\cite{1}. Gasoline is a commonly used accelerant in arson cases, whether it contains accelerant in combustion residue on the scene of fire will play an important role in detection and confirmation for arson cases\cite{2-4}. With the commonly and increasingly used of polymer materials in architectural decoration, furniture and others, they are deep into industrial and agricultural production, national defense, scientific research and human daily life. These materials are belong to flammable or combustible materials, which will release high heat when they are burning, even speed up the development and spread of fire, and also, it will produce some gas and a large number of small molecules with pyrolysis and combustion, which will be disturbance for the accelerant detection of material evidence. So in recent years, the fire behavior of polymer materials has gradually become a new research field.

The paper mainly studied the types and characteristics of small molecules which generated from different decompose combustion process of Polyethylene material, and then compared with gasoline burning residues for suppressing interference of them.

2. Experiment

2.1. Instrument and sample

(1) Experimental apparatus
7890A/5975C Gas Chromatography-Mass Spectrometer, made in Agilent, STA409PC Thermal Analyzer, NETZSCH

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2.2. Experimental conditions

100um PDMS Extraction head, HP—5 MS column (30m×250um×0.25um); Temperature program is: 50℃ (3min) → 5℃/min 250℃ (5min) → 5℃/min 300℃ (15min); Carrier gas is helium, flow velocity is lmL/min, split ratio is 10; Injector temperature 250℃; Ion source temperature 230℃; Quadpole mass spectrometer temperature 150℃; EI ion source (70eV); Full-scan, amount range from50 u to 550u; Transmission lines temperature 280℃; NIST Spectrum library.

Put 100 g Polyethylene material in constant temperature furnace for heating, according to the thermal analysis selected heating temperature, heating time is 30min.

3. Results and Discussion

3.1. Thermal analysis results

Thermal analysis can directly give the thermal decomposition stage of materials. Fig.1 is the thermal gravimetric results of Polyethylene. It showed that the quality change was began from 340.5 ℃. Its thermal decomposition process can be simply divided into three stages. The first weightlessness stage was beginning from 340.5 ℃, weight sharply fell, and its weightlessness rate was 45.32%.And then weight loss began to slow when the temperature rose to 360 ℃; when the temperature is higher than 390 ℃, the second weightlessness stage began, the long chain of polymers began to fracture in this stage, and began to lose some small molecular chain. Until 460 ℃, the third weightlessness stage began, the carbon residue of decomposition give off a lot of heat after burning. After then the quality was no longer drop when the temperature rose to 510 ℃.So, according to the three thermal decomposition stages of Polyethylene, we selected a temperature at each stage, they were 350 ℃, 400 ℃ and 480 ℃, And then studied the types and characteristics of products on different stages, which to find out the interference of gasoline residues.

![Fig.1. Thermo gravimetric analysis curve of Polyethylene](image)

3.2. Analysis of Polyethylene residues on different burning stages

The molecular structure of Polyethylene can be simplified for \( \overset{\text{CH2}}{\text{CH}_2} \text{CH}_2 \), materially was high molecular alkyl chains, its molecular structure only contained elements of C, H, and even \( --\text{C}--\text{C}--\) structure was flexible chain, there was no polar groups exist. Because of the regular chain and good flexibility, which made the molecular chain could be folded repeatedly and regular stacked to form crystallization, and burning easily. But after burning decomposition, macromolecular chains of Polyethylene began to transfer to free radicals, its results were that make Polyethylene macromolecular generate long branches chains and short branched chains of \( \text{C}_2 \sim \text{C}_4 \). Because the Polyethylene structure only contained C and H, so in extracting ion, we just need to detect whether it contained alkenes, olefins, cyclane and cyclenes. As shown in fig.2 was TIC map of Polyethylene residues by 350 ℃, we extracted the characteristic ion of alkenes for \( \text{m/z}=57, 71, 85 \), we found the composition of residues contained \( \text{C}_{10} \sim \text{C}_{16} \), and the peakedness of \( \text{C}_{12} \) and \( \text{C}_{14} \) were highest, \( \text{C}_{16} \) took second place, while the peakedness of \( \text{C}_{13} \) and \( \text{C}_{15} \) were only 10000. Compared with chromatographic graphs of burning residue by 400 ℃ on fig. 4 and fig.5, the main composition were still alkenes of \( \text{C}_{12} \sim \text{C}_{16} \), just the relative peakedness reduced, as the highest
of C12 and C14 were 340,000, which shown Polyethylene macromolecular chains broken down, with the rising of temperature, some low molecular compounds disappeared, while the number of macromolecular compounds also reduced, these reduced parts were broken into small molecules, and then disappeared. When the temperature continued to rise to 480 °C, the residues of Polyethylene completely burning analysis diagram as shown in fig. 6 and fig. 7, which macromolecule carbon chain compounds continued to reduce, we only detected C12, C14 and C15, but the relative peakedness dropped to about 4000, that shown most macromolecular chains broken to generate some small molecules, while these small molecules were also disappeared with the rising of temperature. So when Polyethylene were burning after fire, its composition of the residues were only linear alkanes of C10–C16, and as the temperature increases, the relative peakedness of alkanes will gradually reduce, and finally there were no much left. The process of Polyethylene decomposition and chains transfer can use the following equations to interpretation[5].

Experiments shown, in Polyethylene macromolecule, there were 20 ~ 30 ethyl or short chain branched butyl, and 4 to 10 long chain branches on every 1000 carbon atoms. This, it is easy to see in the burning products of Polyethylene, the formation products can contain inordinately straight or branched alkanes due to the large molecules transfer or intramolecular transfer and even branching.

Fig.2. TIC Chromatogram of PE residue after 350°C burning
Fig.3. Extracted Ion Chromatograms of PE residue after 350°C burning (m/z=57,71,85)
3.3. Analysis of gasoline residues

Gasoline is mainly composed of C$_4$~C$_{12}$ alkanes, its boiling point is 40~200 °C, which nature stability, heat large and difficult to oxidation, and even contains long alkanes and benzologue, etc. Lead-free petrol, most used at present, contains aromatics, olefins, oxygen compounds and isomerization alkanes, even benzene. Through the mass spectrometry detection of gasoline residues after burning, we detected C$_7$~C$_{16}$ alkanes, cyclanes, aromatic hydrocarbons and unsaturated hydrocarbon more than 80 organic matters in it. Fig.8 was TIC chromatogram of gasoline residues. We extracted the alkanes composition for comparison, as shown in fig.9, we can see that the compositions of gasoline after burning mainly contain C$_{10}$~C$_{16}$ linear alkanes, normal distribution presented, and in all contents, the highest was C$_{11}$, and the lowest was C$_{13}$. 

Fig.4. TIC Chromatogram of PE residue after 400°C burning  
Fig.5. Extracted Ion Chromatograms of PE residue after 400°C burning (m/z=57, 71, 85)

Fig.6. TIC Chromatogram of PE residue after 480°C burning  
Fig.7. Extracted Ion Chromatograms of PE residue after 480°C burning (m/z=57, 71, 85)

Fig.8. TIC Chromatogram of gasoline residues  
Fig.9. Extracted Ion Chromatograms of gasoline residues (m/z=57, 71, 85)
4. Conclusion

By the GC/MS analysis, the combustion products of Polyethylene on different stages only contained linear alkanes, and these alkanes were certain difference from gasoline residues in the characteristics and distribution. These can give technical supports for laboratory testers to eliminate interference in the detection of gasoline of fire residues.

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