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Advances in flame retardancy of asphalt pavement: A review

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A B S T R A C T

Asphalt pavement is widely applied to the surface in high-grade highway tunnels due to its prominent preponderance in road performance. However, asphalt is flammable as the binder material to adhere the aggregates and other additives, resulting that a fire in the semi-closed space of the tunnel can ignite and burn asphalt pavement to generate a large amount of heat and smoke. Therefore, further promoting the advance of flame-retardant asphalt pavement is essential to ensure security in tunnels. We gathered the relevant standards or regulations of diverse nations and test methods concerning flame retardancy of asphalt. Then we reviewed the research status of flame-retardant asphalt mixture, including thermal characteristics of the asphalt and four fractions, the flame retardants applicable to asphalt, and effects on other components. This review demonstrated that establishing universal standards and test methods is a research basis specifically for flame-retardant asphalt pavement. To optimize the flame retardancy of asphalt pavement, it should focus on the synergy with diversified aspects such as asphalt binders, multiple flame retardants, aggregates, mineral powders, fibers, and other additives.

1. Introduction

The pavement surface used in the tunnel, specifically the high-grade highway tunnel, is mainly constructed by cement concrete or asphalt mixture. At the beginning of the 20th century, cement concrete with higher strength, stability, and durability constructed most pavements in tunnels because it is known as white pavement and has a considerable advantage on lighting in the dark tunnel. The guidelines JGT/T D70 [1] enacted by the Ministry of Transport of the People's Republic of China in 2010 stipulated that highway tunnels of different grades can adopt cement concrete pavement, requiring measures to optimize skid resistance and noise reduction. However, cement concrete pavement still frequently induced traffic accidents due to high speed and slippery pavement in tunnels. Hence, in high-grade highway tunnels, cement concrete pavement was gradually replaced by asphalt pavement with better performance in skid resistance and ride comfort. According to the specification JTG3370.1 [2] enacted in 2018, highway tunnels in China suggested pavement structure with an asphalt layer.

Asphalt pavement is paved and compacted by the asphalt mixture that consists of asphalt binders, aggregates, mineral powders, fillers, and other additives. As the binder material to adhere aggregates and other additives, asphalt has received significant attention because it is a flammable material in the air and burns quickly at high temperatures to assist fire propagation [3]. Asphalt is a complex material composed of hydrocarbons and nonhydrocarbons, and its elements mainly include carbon, hydrogen, and small amounts of sulfur, nitrogen, oxygen, and heteroatom. When a fire occurs in the semi-closed space of the tunnel, asphalt can be promptly ignited and generate a large amount of smoke and toxic gas, seriously affecting the rescue and endangering the lives and properties (Fig. 1).The report [4] published by the World Road Association stated that tunnels can pave asphalt

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Abbreviations

ASTM	American Society for Testing and Materials
AASHTO	American Association of State Highway and Transportation
LOI	limiting oxygen index
CONE	cone calorimeter
HRR	heat release rate
THR	total heat release
TTI	time to ignition
EHC	effective heat of combustion
MLR	mass loss rate
TSR	total smoke rate
TG	thermogravimetry
DTG	derivative thermogravimetric analysis
DSC	differential scanning calorimetry
SEM	scanning electron microscope
XRD	X-ray diffraction
TEM	transmission electron microscope
OMMT	organic montmorillonite
ARC	accelerating rate calorimeter
AFM	atomic force microscope
MSD	maximum smoke density
SDR	smoke density rating
FTIR	Fourier transform infrared spectrum
GC	gas chromatography
MS	mass spectrometry
PAHs	polycyclic aromatic hydrocarbons
SPME	solid-phase microextraction
RSM	response surface methodology
FDS	fire dynamics simulator
SARA	saturates, aromatics, resins, asphaltenes
DBDPO	decabromodiphenyl oxide
DBDPE	decabromodiphenyl ethane
ATH	aluminum hydroxide
MH	magnesium hydroxide
HL	hydrated lime
RP	red phosphorus
APP	ammonium polyphosphate
PS	phosphorus slag
EG	expanded graphite
EVMT	expanded vermiculite
MMT	montmorillonite
IFR	intumescent flame retardant
PER	pentaerythritol
MA	melamine
ZB	zinc borate
LDHs	layer double hydroxides
AC	dense-graded asphalt concrete
SMA	stone matrix asphalt
OGFC	open graded friction course
WMA	warm mix asphalt
HMA	hot mix asphalt

pavement when without a significant negative impact on fire safety. The guidelines JGT/T D70 [1] also stipulated that asphalt pavement should be prevented from burning and releasing smoke in the event of a tunnel fire. Additionally, fire is the primary threat to tunnels [5], so the flame retardancy of asphalt pavement must be enhanced to ensure safety.

To present the research results of flame-retardant asphalt or asphalt combustion in the world, we searched the Scopus database

Fig. 1. Fire in tunnels.

(www.scopus.com), as shown in Fig. 2. The flame retardancy of asphalt initiated to be investigated mainly on bituminous paint in the 1970s. Over the past 20 years, there has been a remarkable increase in publications and patents on the flame retardancy of asphalt binder and asphalt mixture used for pavement. China is the nation with the greatest number of articles on flame-retardant asphalt or asphalt combustion, followed by USA, while other nations published fewer articles.

Specializing in the thermal characteristics of asphalt and fractions and exploiting flame retardants suitable for asphalt are the focuses of ameliorating the flame retardancy of asphalt pavement in tunnels. The primary aim of this review is to integrate and summarize the research on thermal characteristics and flame retardants of asphalt binder and asphalt mixture, which can conduce to establish the system of flame-retardant asphalt pavement in tunnels. This review was organized as follows. Section 2 presented the standards promulgated by different nations to restrict the flame retardancy of asphalt and discussed how to improve the specification requirements in the future. Section 3 described conventional and innovative research methods for flame retardancy, thermal characteristics, and gaseous products. Section 4 mainly analyzed the combustion and pyrolysis mechanism of asphalt and fractions and obtained the chemical compositions of gaseous products generated during combustion and pyrolysis. Section 5 introduced diversified flame retardants used for asphalt and the corresponding flame retardancy mechanism. Section 6 concluded how other compositions of asphalt mixture influence flame retardancy. According to this review, we suggested that multi-factor should be comprehensively considered, such as asphalt binder, gradation, aggregate, warm mix asphalt, mineral powder, and fiber, to improve the flame retardancy of asphalt pavement in tunnels.

2. Standards of different nations on the flame retardancy of asphalt

The regulations of building materials enacted by each country strictly required fire protection to ensure security. Regarding asphalt pavement in tunnels, a few nations enacted specialized standards of flame retardancy, but most other nations and regions did not. Instead, they referred to other standards of flame

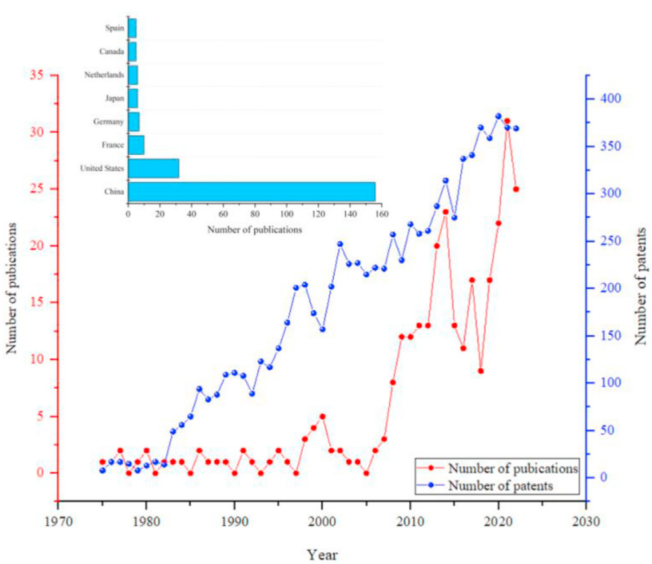

Fig. 2. Evolution of the number of publications and patents on flame-retardant asphalt or asphalt combustion.

retardancy, such as UL-94 that is generally used for plastic or other polymer materials. Since plastic as a typical polymer material is more widely used and shares similarities with asphalt in terms of chemical compositions and inflammability. Standards of some nations was shown in Table 1.

The American Society for Testing and Materials (ASTM) and the American Association of State Highway and Transportation (AASHTO) put out several standards for road petroleum asphalt, such as ASTM D3381/3381M [6], D946/D946M [7], D6373 [8], and AASHTO M320 [9], M226 [10], which have been widely used and referenced worldwide. Albeit some of the standards are outdated or not used in the United States nowadays, some developing countries still adopt some momentous indicators. Among them, the safety indicators of asphalt are flash point and fire point, indicating the possibility of fire and explosion. Flash point and fire point can characterize the safety performance of asphalt in storage and construction, but there are significant limitations in evaluating the sustained combustion performance. UL-94 [11], as a standard published by Underwriter Laboratories, has been most extensively applied to evaluate flame retardancy in polymers, including asphalt. In addition, adopting vertical burning test may assess the ability of materials to extinguish the flame after being ignited. Materials are divided into three levels (V-2, V-1, and V-0 by following up UL-94 standard) through various evaluation index, including burning speed, burning time, anti-dripping, and whether the dripping beads burn.

In Europe, the Building Regulations 2010 Fire safety specified the requirements of building materials and tested fire gradation by adopting the BS 476 norm [12]. Besides, most European Union nations, Singapore, and other nations also recognized and imitated the fire safety norms of Britain, so BS 476 serial norms have been developed into quite important test standards required for building materials in international trade. However, these standards lack effective indicators for the flame retardancy of asphalt, which is very similar to American national standards. According to several European norms of asphalt, such as EN 12591 [13], EN 14023 [14], EN 13924 [15], the safety indicators still are flash point and fire point. For the flame retardancy of asphalt, BS 476 and UL-94 grade are frequently used for classification.

China developed a series of standards for the flame retardancy of road asphalt, aiming to standardize the performance of flame-retardant asphalt. As shown in Table 2, the national standard GB/29051 [16] issued by the standardization administration in 2012 specified the terminology, definition, symbol, classification, and test method of flame-retardant asphalt for road engineering, of which the oxygen index (test to evaluate the difficulty of igniting material) should not be less than 23%. It additionally required the smoke density rating (test to quantify the amount of smoke during combustion) not more than 75 for long tunnels, essential transportation routes, or exceptional engineering with high safety requirements. Combined with the above-mentioned parameters and asphalt's mechanical properties, it formed a complete system on flame-retardant asphalt. National Energy Administration enacted two industry standards of NB/SH/T0820 [17] and NB/SH/T0821 [18] to refine the parameters of the flame-retardant asphalt and modified asphalt for pavement, which were divided into type I (the oxygen index not less than 23%) and type II (the oxygen index not less than 25%). Moreover, JT/T860.3 [19] issued by the Ministry of Communication in 2014 specified the physical properties of asphalt adding flame retardants, including the needle penetration and softening point. Based on national and industry standards, some provinces provided local standards, of which Guangdong Province [20] adopted minimum parameters of the national standard on flame retardancy. The minimum oxygen index of the standard DB22/T2769 [21] provided by Jilin Province in 2017 increased to

Table 1
The standards of major nations on asphalt.

	Asphalt or modified asphalt for pavement	Flame-retardant asphalt for pavement	Indicators of flame retardancy
America	ASTM D3381/3381M ASTM D946/D946M ASTM D6373 AASHTO M320 AASHTO M226	No Refer to UL-94	Burning speed Burning time Anti-dripping whether the dripping beads burn
European Union	EN 12591 EN 13924 EN 14023	No Refer to BS476 or UL 94	Final spread of flame Spread of flame
China	JTG E20 NB/SH/T 0522	GB/29051 NB/SH/T0820 NB/SH/T0821 JT/T860.3	Limiting oxygen index Smoke density rating

Table 2
Combustion requirements for flame-retardant asphalt for pavement in China.

	Oxygen index	Smoke density rating
Requirements	≥23%	≤75

27% compared to the national standard. Except for oxygen index and smoke density rating, standard DB42/T1219 [22] provided by Hubei Province in 2016 requested the particle size, moisture content, heating stability (mass loss), and hydrophilic coefficient of inorganic flame-retardant fillers.

The lack of a standard for flame-retardant asphalt in Japan resulted in referring to plastic standards instead. Based on Japanese industrial standard JISK7201-1 [23], flame-retardant materials were divided into five levels through the Limiting Oxygen Index (≥30%, 30%–27%, 27%–24%, 24%–21%, ≤21%), while it is generally divided into three levels in China (>27%, 27%–22%, <22%). In addition, Australia [24] and Kenya [25] also developed flame-retardant standards depending on national conditions. They were similar to Japan and referred to plastic standards instead.

3. Research and analysis methods for flame retardancy

Multiple approaches have been created to evaluate flame retardancy, including experimental and numerical analysis methods. The experimental methods directly investigate the combustion characteristics and compositions of gaseous products during heating asphalt, and numerical analysis methods applied to simulation can help understand the testing process and explain observed phenomena.

3.1. Research methods of flame retardancy

3.1.1. Flash point and fire point

Flash point is defined as the initial temperature of the flash fire when volatile combustible gas produced by heating asphalt is blended with air to expose fire under the specified conditions. Fire point is the temperature of asphalt that can maintain combustion for more than 5 s. Fire point is generally 10 °C higher than flash point. When the more oils in asphalt, the temperature difference between fire point and flash point is smaller. The comparison among a few international accepted standards on flash point and fire point, including ASTM D92 [26], ISO 2592 [27], and GB/T3536 [28], it is almost consistent that test methods adopt Cleveland open cup.

Based on the previous description, there are significant limitations in evaluating flame retardancy using flash point and fire point. Study [29] showed that flash point and fire point of asphalt had not markedly changed after adding flame retardants, which was different from the results of the limiting oxygen index. Therefore, it is a considerable deviation to evaluate the flame retardancy alone using flash point and fire point.

3.1.2. Limiting oxygen index

Limiting oxygen index (LOI) is defined as the minimum oxygen concentration maintaining the combustion under an oxygen–nitrogen condition. The formula is given as follows.

$$\mathrm{LOI} = \frac{[O_2]}{[O_2] + [N_2]} \times 100\%$$

where O_2 is the oxygen concentration, and N_2 is the nitrogen concentration.

Numerous standards of nations and organizations, such as ASTM D2863 [30], ISO 4589 [31], GB/T2406.1 [32], and NB/SH/T0815 [33], regard LOI as a test to evaluate the difficulty of igniting material. In China, it is usually divided into three levels, including inflammable material (LOI < 21%), combustible material (21% ≤ LOI ≤ 27%), and flame retardant material (LOI > 28%). The test method of LOI is easy to test and operate, but as a small combustion test, it evaluates the flammability of material under the non-fire condition, which induces low precision. Moreover, the LOI test hardly reflects the effects on the formation of the char layer.

3.1.3. Burning test

Vertical tests are applied to evaluate the flammability of material, and the test result is usually divided into three levels (V-2, V-1, V-0). The standards of most nations on the burning test are mainly the same, except for specimen dimensions [34–36]. When the specimen is placed vertically and ignited, flammability grade is estimated by observing the combustion process and recording burning time, burning speed, anti-dripping, and whether the dripping beads burn. Thus, due to human factors and subjectivity, diverse operators and observation techniques may acquire disparate experimental data and results. Especially asphalt still turns into softening, deformation, and heavy droplets during combustion, so the burning test can merely be applied to detect and assay asphalt qualitatively [37].

3.1.4. Cone calorimeter test

Cone calorimeter (CONE), is a fire test tool based on the direct correlation between heat release and oxygen concentration during combustion. Compared with traditional test methods, CONE can objectively evaluate the combustion performance of the material under the simulation of a real fire scene. Based on the principle of oxygen consumption, there is the quantitative relationship between the heat release of burning materials in fire and oxygen consumption, so the combustion environment in CONE is highly analogous to the real combustion environment. CONE obtains diversified data correlated excellently with real fire. Furthermore, CONE not only assays flame retardant mechanism but is also applied for fire modeling research using experimental data, so CONE has become a vital test instrument in flame retardancy and fire science. CONE that can be used for asphalt and asphalt mixture acquires a few parameters, such as Heat Release Rate (HRR), Total Heat Release (THR), Time To Ignition (TTI), Effective Heat of Combustion (EHC), Mass Loss Rate (MLR), Total Smoke Rate (TSR). However, CONE has the drawback of limited ability to measure smoke compositions during combustion [38].

3.1.5. Thermal analysis

Thermogravimetry (TG), is a desirable approach for the correlation between the mass of the substance and the temperature or time at the temperature of process control. By analyzing the TG curve, we can acquire information about the specimen related to the mass, including thermal stability, thermal decomposition, and residues. Derivative thermogravimetric analysis (DTG), derived from the first derivative of the TG curve with the temperature or time, can effectively distinguish a series of cascading thermal reactions that occurred at diverse temperatures, acquiring more information about the velocity of the mass loss, initial and termination reaction. TG and DTG curves that have been widely applied in the field of asphalt combustion and pyrolysis can assay characteristics of thermal stability. There are some differences between TG and the actual fire, and it cannot fully reflect the flame retardancy of the material.

Differential scanning calorimetry (DSC) has been frequently combined with TG and DTG. DSC curve is defined as the relation curve between required heat and temperature in unit time when the temperature difference between the specimen and the reference object is kept to zero, which can analyze endothermic and exothermic reactions during heating specimen. DSC curves with TG and DTG can analyze flame retardant mechanism after adding flame retardants into asphalt, particularly endothermic functions.

3.1.6. Scanning electron microscope

Scanning electron microscope (SEM) is a modern electronic apparatus used in medicine and material. This test can observe the microstructure, morphology, and elemental composition of combustion residues, by which analyzes the combustion characteristics.

Xia [39] utilized SEM to inspect combustion residues' characteristics and revealed the thermal stability of bituminous four fractions. When observing the combustion residues by SEM, it was discovered that asphalt adding flame retardants could form the densified char layer on the surface that hindered the heat transfer and optimized the thermal stability [40].

3.1.7. X-ray diffraction and transmission electron microscope

X-ray diffraction (XRD) and transmission electron microscope (TEM) can directly confirm the microstructure of modified asphalt based on the measurement of interlayer spacing and crystallization parameters. XRD can detect the compatibility of modifiers or nanomaterials and asphalt, but some layered silicates exhibit less apparent base reflections, resulting that these Nanostructures characterized by XRD lack persuasion [41].

By XRD (Fig. 3), Zhang [42] perceived that asphalt molecules were embedded into the interlayer of organic montmorillonite (OMMT) to form the intercalated structure, of which the interlayer height decreased with the raising of OMMT content. Vargas [43] discovered a large number of OMMT embedded into the nanosheets based on TEM images of asphalt modified by OMMT.

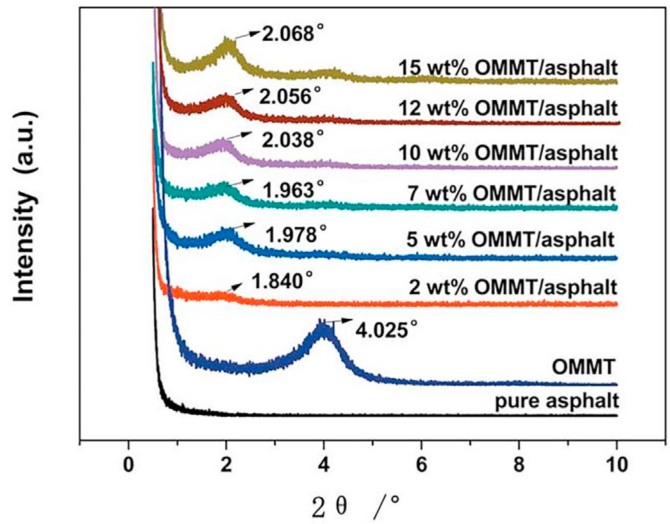

Fig. 3. XRD curves of the OMMT and OMMT-modified asphalts with different contents [42].

3.1.8. Other methods

More and more innovative methods have been created with further research on asphalt combustion. Li [44] directly ignited the Marshall test piece using the gasoline, after which burning time and surface temperature evaluated the flame retardancy, and smoke area calculated by recording smoke images during combustion estimated smoke suppression. Adopting the same recording techniques and evaluation methods as Li, but rutting slabs [45] and loose asphalt mixtures [29] were instead of the Marshall test piece. Ren [46] utilized a flame spraying gun to fire the Marshall test piece, recording the ignition time and combustion temperature to achieve the goals.

As shown in Fig. 4, Chang'an university designed and manufactured a new flame-retardant analyzer [47,48], consisting of a combustion chamber, data acquisition system, and control system. The data acquisition system automatically detected the mass and temperature, obtaining results of the ignition time, sustained combustion temperature, and residual carbon rate. The test results were essentially consistent with LOI and TG—DTG curves. At the "San Pedro de Anes" test center in Spain, a full-scale test (Fig. 5) was conducted in a 600-m-long tunnel to simulate a real fire scenario [49]. Currently, the test methods of flame retardancy tend to simulate the real fire scene or even conduct the test directly in the tunnel to obtain more realistic experimental results.

Accelerating rate calorimeter (ARC) generally measures data about the temperature and pressure during the exothermic reaction to evaluate the safety of chemicals, and its preponderance is capable of maintaining the specimen in the adiabatic environment. Using the ARC test, Zhao [50] studied crude oil's burning property and kinetics. Atomic force microscope (AFM) is a non-destructive imaging tool that can qualitatively and quantitatively analyze bituminous sub-nanometer resolution ratio [51]. ARC and AFM have great potential for application in asphalt research.

3.2. Research methods of asphalt smoke

3.2.1. Smoke density test

Depending on the smoke density generated by materials during combustion, the smoke density test can characterize the performance of smoke suppression through maximum smoke density (MSD) and smoke density rating (SDR). Smoke density has been

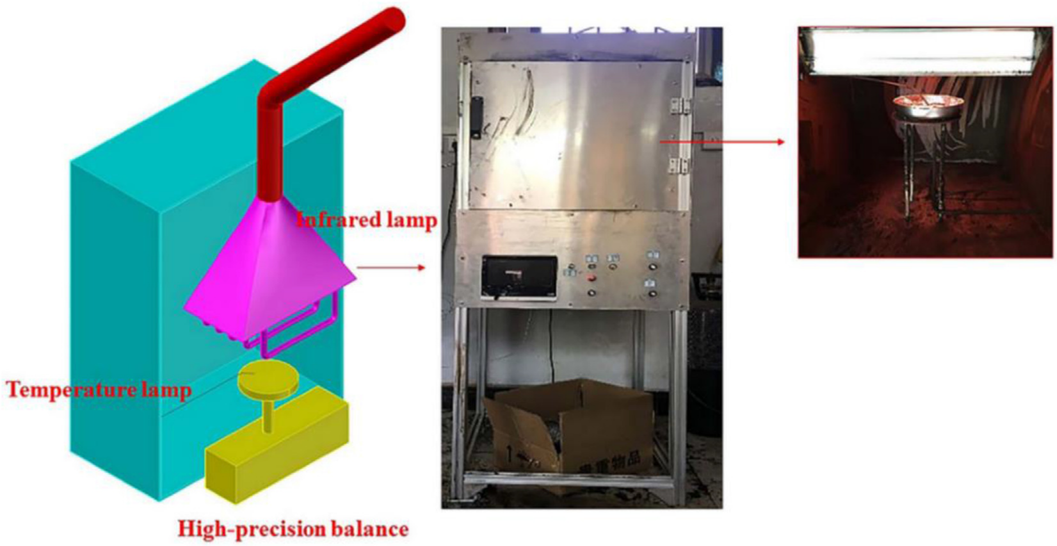

Fig. 4. Flame-retardant analyzer designed by Chang'an university [47].

Fig. 5. Images of a full-scale test in a tunnel [49].

absorbed in the Chinese national standard to restrict the performance of flame-retardant asphalt [16]. However, the smoke density test also has the drawback of considerable fluctuations, despite the same test instrument.

3.2.2. Loss of quality method

The loss of quality method is the mass differences of asphalt between before and after the combustion, which is relatively simple to operate. However, the test results can merely acquire the total concentration of asphalt smoke, but not the specific constitutions and each concentration. Wang [52] found that the mass differences before and after the combustion were probably not the same as the total concentration of asphalt smoke because of the problematic collection of CO_2, CO, and NO_2, etc. In addition, the loss of quality method is not indicative of the disservice of asphalt smoke chiefly composed of noxious gas during combustion.

3.2.3. Fourier transform infrared spectrum

Fourier transform infrared spectrum (FTIR) can qualitatively and quantitatively analyze main gaseous products during combustion through chemical functional groups. With Fourier changes on the interfered infrared light, FTIR shows the chemical bonds and the corresponding wavebands to confirm the dominating constitutions of gaseous products. By FTIR, Xia [39] accurately verified the constitutions and number of gaseous products during the combustion of asphalt fractions.

3.2.4. Gas chromatography/mass spectrometry

When the gas is used as the move phase and the liquid uniformly coated on the carrier or the solid is used as the stationary phase, gas chromatography (GC) can segregate the mixed constituents through continuous distributions of constituents between the gas phase and liquid phase or solid phase. GC is a rapid and efficient method of separation and analysis. Moreover, mass spectrometry (MS) can rapidly identify the gas generated during the thermal reaction by detecting polycyclic aromatic hydrocarbons (PAHs) in asphalt smoke [53]. MS can provide particular identification of unknown compounds with high sensitivity. Therefore, combining GC with MS has been an optimal tool for the separation and detection of complex mixed compounds, which is also applicable for the analysis of gaseous products during asphalt combustion and pyrolysis [54].

Solid-phase microextraction (SPME) can condense the analytes in samples by sorption and desorption. SPME-GC/MS has advantages of operation and high accuracy for component analysis of asphalt smoke during combustion [55,56].

3.2.5. Other methods

Zhu [57] invented a patent for the device detecting asphalt smoke density and sample preparation method on the basis of the smoke density test. This patent ameliorated droplets during heating asphalt and made asphalt burn adequately, to the benefit of differentiation of asphalt smoke. According to the loss of quality test, a simple measuring device was intended to collect asphalt smoke by Huang [58]. A convenient and highly sensitive Surface-enhanced Raman Scattering can detect naphthalene, a volatile substance challenging to identify, which can be used to detect asphalt smoke in the future [59].

3.3. Analysis methods

3.3.1. Kinetics study

Thermal kinetics study usually is based on the thermal analysis technology in physicochemical properties of substances. The activation energy, a kinetics property, is defined as the energy required to transform from the normal state to the reactive state. The higher the activation energy is, the lower the reaction capacity. Asphalt combustion involves complex physical and chemical processes, and its activation energy reflects the relationship between the reaction rate and the temperature. At the microscopic scale, simple kinetics models can decipher the intricate mechanism of the combustion [60], and what are used for the analysis of asphalt are the Kissinger method [61], Friedman method [62], Coats–Redfern method [63], Flynn–Wall–Ozawa method [64]. Other kinetic methods, such as distributed activation energy model, have been widely used in other material fields and should be extended to research of flame-retardant asphalt in the future.

3.3.2. Response surface methodology

Asphalt pavement in the tunnel not only focuses on flame retardancy but also should comprehensively consider pavement performance, such as physical and mechanical properties. Response surface methodology (RSM) can synthesize multiple objectives for analysis and optimization, conquering the problem that orthogonal tests can not accurately determine the optimal values of each factor. RSM can effectively and rapidly optimize the formulation and keep good consistency of test results with an error of less than 5% [65]. Li [66] established a regression model using RSM and better achieved the multi-objective optimization on the all-around performance of asphalt mixtures.

3.3.3. Fire dynamics simulator

Fire dynamics simulator (FDS) is a computational hydrodynamics model depicting smoke movement to calculate the temperature field and the smoke field of the fire, which can evaluate the smoke suppression after asphalt adding the flame retardants. This analysis method evaluates the smoke suppression through the temperature and the distribution of smoke height [67]. Zhao [68] verified that the result of FDS was almost in concordance with the TG–DTG–MS test and that the temperature and smoke height distinctly decreased in the tunnel after adding the flame retardants.

There are already diverse test methods to study the combustion characteristics, flame retardancy, and smoke suppression of asphalt. A variety of parameters, such as LOI, SDR, and CONE, may be synthetically used to limit the performance of flame-retardant asphalt in the standard. The standards may adopt the combination of these straightforward parameters to specify the asphalt pavement.

4. Thermal behavior of asphalt heating

4.1. Process of asphalt heating

Due to a relatively sealed environment in the tunnel, the extremely ascending temperature can rapidly ignite asphalt pavement once a fire occurs. According to Wu [69], when the scale of the fire in the tunnel reached 50 MW calculated by a hydrodynamics simulation, asphalt pavement was bound to burn and the burning range was 160–300 m. After asphalt pavement is ignited with elevated temperature, asphalt pavement undergoes multiple stages (Fig. 6) of combustion, inadequate combustion, pyrolysis, and gasification following continuous consumption of oxygen and incessant generation of gas such as CO_2 and CO, of which multiple reactions may coexist and inadequate combustion is the leading way in the tunnel [70]. This chapter analyzed the thermal behavior of asphalt heating primarily based on the TG test.

4.1.1. Combustion of asphalt

Asphalt shows multi-stage characteristics of the combustion under adequate oxygen content. The combustion of asphalt in the TG test under air atmosphere and 5 °C/min heating conditions is divided into three stages (Fig. 7) of oil release, resin pyrolysis, asphaltene, and char layer combustion, and reactions become increasingly intense [63,70]. Xu [70] found that some unstable weak bonds were broken in the first stage of asphalt combustion and the light components volatilized and burned, producing volatiles with low molecular weight; in the second stage, some of the principal bonds were broken and decomposed into small molecules; in the last stage, the molecular structure of asphalt was rearranged, and hydrogen and methyl group were gradually

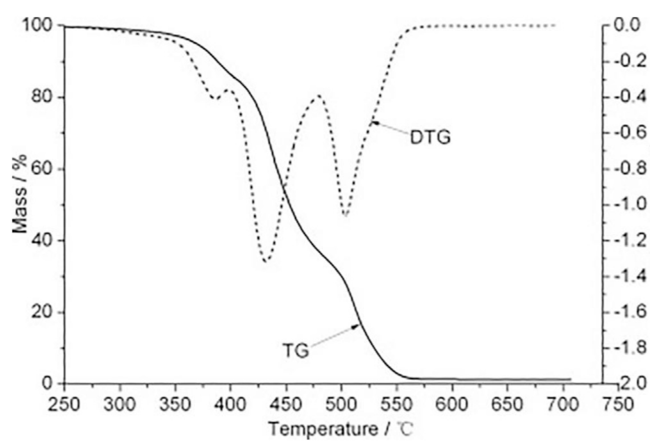

Fig. 7. TG–DTG curves of asphalt binder combustion [70].

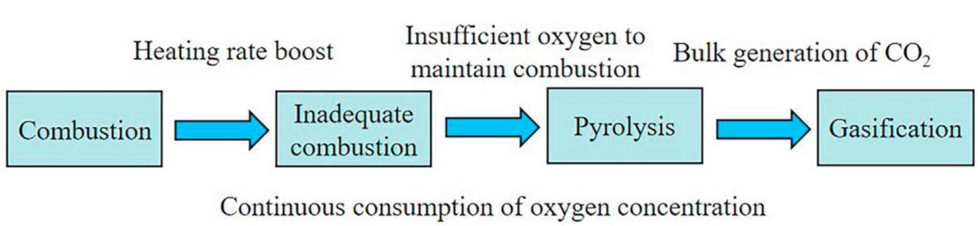

Fig. 6. Fire process of asphalt pavement in tunnel.

removed due to dehydrogenation and polymerization reactions. Furthermore, in the last stage, the char layer formed during the combustion acutely burned and released large heat [71].

When a fire occurs in the tunnel, the heating rate is speedy and the temperature can ascend to 700 °C in just a few minutes. As the heating rate increases, some thermal reactions are gradually delayed following the elevation of inadequate combustion (Fig. 8). Zhu [72] showed that three weight loss peaks gradually overlapped in the first stage of asphalt combustion and the weight loss peak was decreased in the last stage with the elevation of the heating rate, which was also proved by the thermal kinetics study. In addition, the elevation of the heating rate affected that the first stage of asphalt combustion required more activation energy, indicating more difficult reactions. The activation energy in the last stage was lessened, implying more easy reactions. When the heating rate was raised to 120 °C/min using the test platform of fixed bed by Wu [73], burning volatiles of the second stage and burning the char layer of the third stage were merged, differing from the three stages of asphalt combustion with low heating rate. Because the thermal hysteresis produced by the large heating rate would affect the pyrolysis of the inner part of the particles and cause the second stage and third stage reactions to be merged. Hence, inhibiting the heating rate can effectively retard the combustion of asphalt.

As the tunnel fire continues, the oxygen concentration is continuously consumed and descends linearly to the ultimate state [74], resulting in inadequate combustion of asphalt. Based on the results of asphalt combustion with different oxygen concentrations [75], the mass loss and mass loss rate decreased, the carbon residue rate increased, the reaction lagged, and some residues of inadequate combustion were produced with decreasing oxygen concentration. As shown in Fig. 9, under low oxygen concentration, most of the aliphatic groups in the asphalt were transformed into the ether, sulfonic acid, and other compounds, which existed in the form of residues. Insufficient oxygen did not maintain the aerobic combustion of asphalt, and it was estimated that the oxygen concentration required for aerobic combustion was between 12% and 15%.

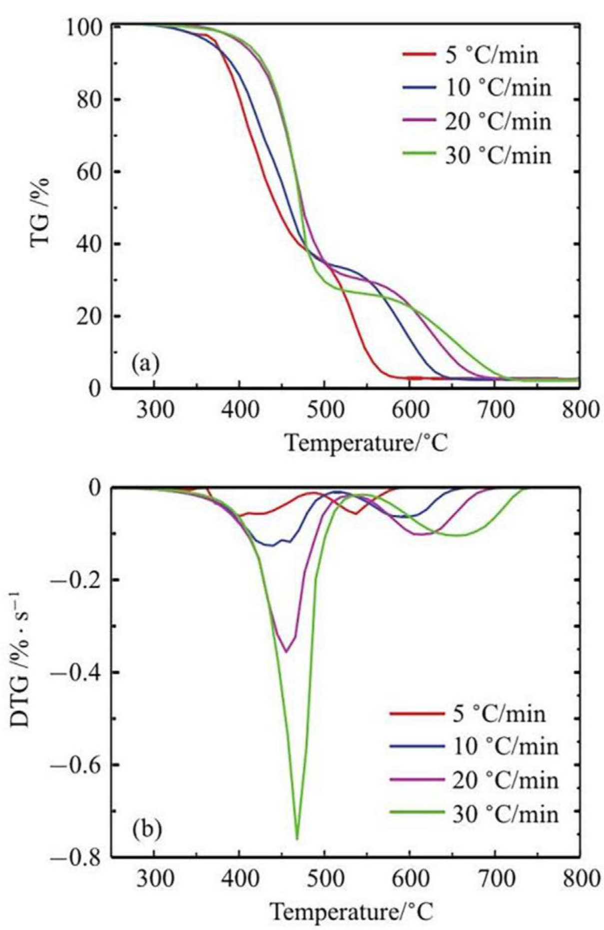

Fig. 8. TG/DTG curves of asphalt combustion at different heating rates [63].

4.1.2. Pyrolysis of asphalt

A fire in the tunnel leads to the upper layer of asphalt pavement burn because of exposure to the air. The intermediate layer and the lower layer of asphalt pavement undergo pyrolysis reactions in the absence of oxygen. With the consumption of the oxygen in the tunnel, it is not adequate to maintain the combustion and then the upper layer of asphalt pavement also undergoes pyrolysis reactions. Differing from the complexity of asphalt combustion in the air due to their component differences, the results of studies on asphalt pyrolysis is generally consistent in different test results due to lack of oxygen content [76–78].

Zhu [79] compared asphalt combustion reaction with pyrolysis reaction using the TG test. The weight loss rate of pyrolysis was proportionally greater than that of combustion in the first stage, in which more light components were directly decomposed by pyrolysis and did not further participate in crosslinking reaction to produce more stable asphaltene analogs. However, the carbon residue rate of asphalt pyrolysis was greater than that of combustion. Pyrolysis reaction that is equivalent to the oxygen concentration of combustion reaction dropping to zero shows the law of similarity with the change of oxygen concentration.

4.1.3. Gasification of asphalt

With the further combustion and pyrolysis of asphalt pavement in the tunnel, prodigious gaseous products are produced, among which CO_2 is the dominant gaseous product in this process (Fig. 10) [70]. The thermal reaction of asphalt enters the next complex stage. At this stage, CO_2 gas as the main gas potentially induces asphalt to undergo the gasification reaction at high temperatures close to 1000 °C.

$$C + CO_2 = 2CO$$

TG test by Zhang [80] showed that the gasification reaction of asphalt in the CO_2 atmosphere was similar to the pyrolysis reaction in the N_2 atmosphere. Gasification of asphalt occurs at higher temperatures than pyrolysis, meaning relatively more complex. Studies on asphalt gasification to now have been relatively few.

4.2. Thermal characteristics of SARA fractions heating

The asphalt is usually segregated into several chemical compositions with similar chemical properties and definite connections to engineering properties. The current specification JTG E20-2011 in China has three fractions separation test and four fractions separation test [81], while ASTM consistently adopts four fractions separation test [82]. Four fractions (Fig. 11) have been wildly applied to analyze the thermal reaction mechanism of asphalt. Asphalt is divided into saturates (alkanes and cycloalkanes), aromatics (aromatic rings), resins (polycyclic hydrocarbon compounds with N, O, and S), and asphaltenes (aromatic hydrocarbon compounds) through the various solubility of four SARA fractions in different solvents. Saturates are the fraction with the simplest molecular structure, while asphaltenes are the most intricate fraction with a considerable number of aromatic structures [83].

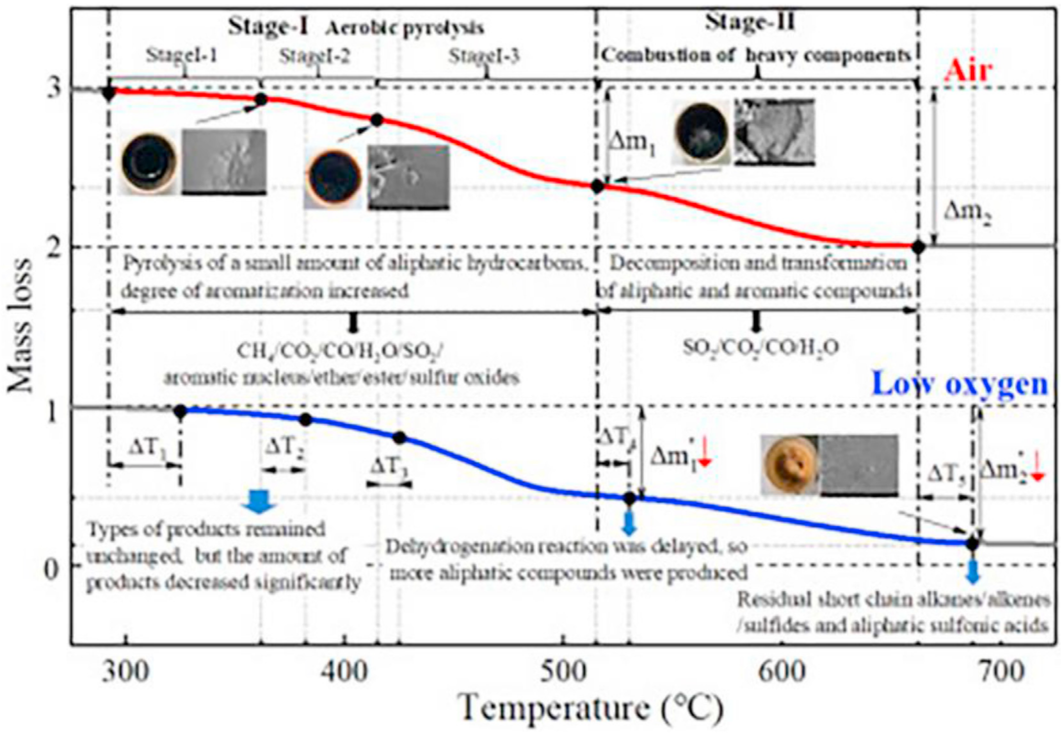

Fig. 9. Combustion mechanism of the asphalt binder at air and low oxygen concentration [75].

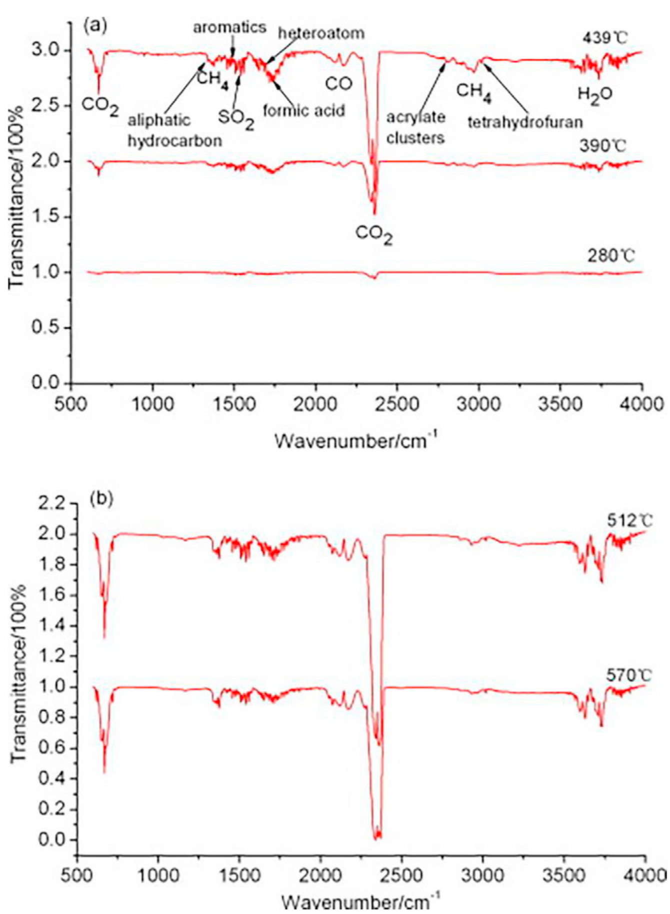

Fig. 10. FTIR spectra of volatile products at representative temperature during asphalt combustion [70].

Contents of aromatics and resins in asphalt are generally greater than saturates and asphaltenes. The molecular structures of four fractions are given in Fig. 11.

4.2.1. Combustion/pyrolysis of SARA fractions

Four fractions of asphalt have different combustion characteristics and reaction temperatures commonly divided into two stages of light components volatilization and char layer combustion. Depending on studies of Xia [84,85], the mass loss of saturates and aromatics was mainly in the first stage, and that of resins and asphaltenes had little difference in both stages. As shown in Fig. 12, except for saturates and aromatics which had a small number of endothermic reactions, resins and asphaltenes merely had exothermic reactions with only one exothermic peak. Among them, resins were the heavier part of asphalt and released more heat during the combustion [86].

Combustion of SARA four fractions exhibit a remarkable resemblance to asphalt with diverse heating rates. Ascending the heating rate, the combustion of SARA lags, and the required reaction heat is lessened [88]. Depending on studies by Zhao [89,90], different heating rates did not affect the ultimate mass loss of four fractions but only the burning speed. The results calculated by the activation energy showed that the combustion of saturates and aromatics became more complicated, and resins and asphaltenes became more ease with ascending temperature. Yang [91] found that saturates had minimum initial decomposition temperature and carbon residue rate, the highest weight loss rate, which is crucial to determine the ignition characteristics of asphalt. Moreover, due to the prime weight loss of asphalt combustion provided by aromatics and resins, inhibiting the thermal decomposition of aromatics and resins are highly critical to control the combustion and suppress smoke.

Pyrolysis of SARA four fractions resembled combustion, with two stages of saturates and aromatics and only one stage of resins and asphaltenes. There were endothermic and exothermic

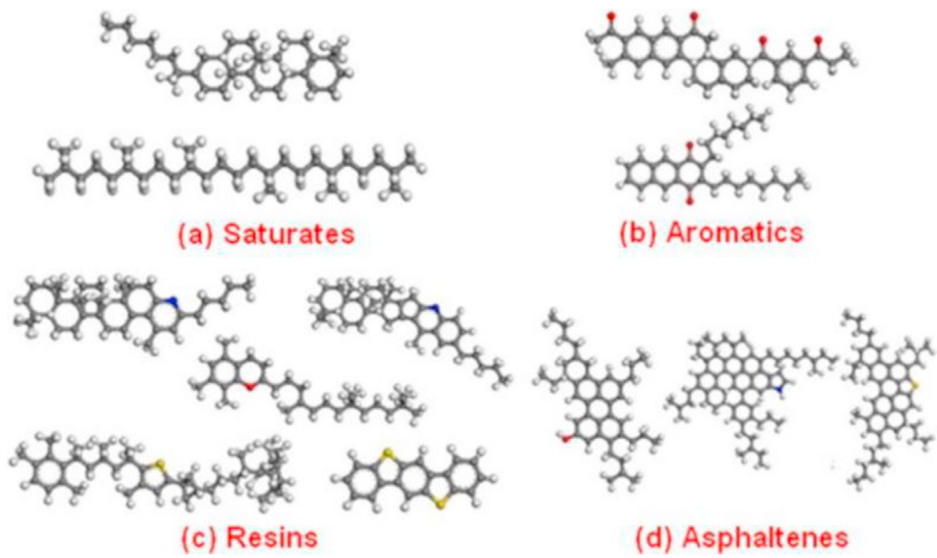

Fig. 11. Molecular structures of SARA fractions [84].

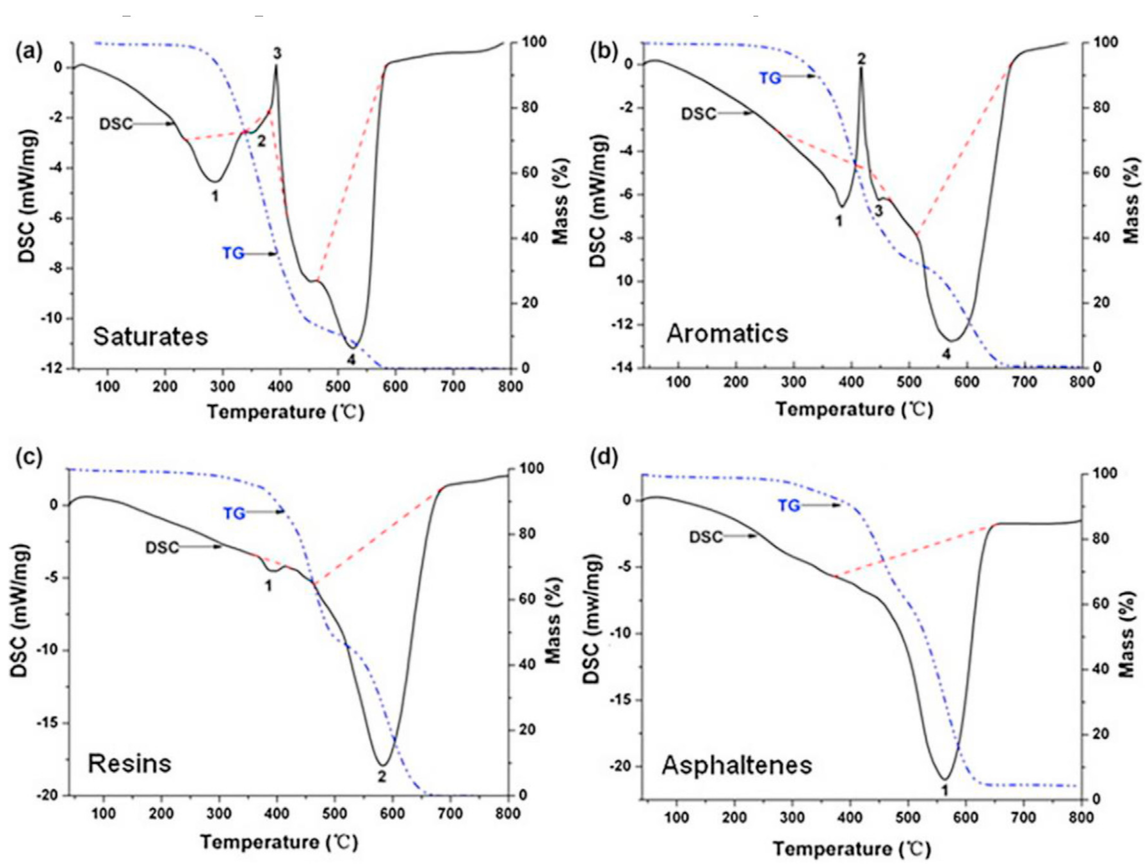

Fig. 12. DSC test results of SARA fractions in asphalt combustion [87].

reactions in the pyrolysis of SARA, but exothermic reactions were dominant [92]. Thermal stability elevated from saturates to asphaltenes [93].

4.2.2. Residues of SARA fractions heating

Residues of SARA four fractions have diverse microstructures and morphology. After observing combustion residues, Shi [87,94] showed that char layer had better integrity and the content of S gradually increased from saturates to asphaltenes (Fig. 13), of which C, O, and heteroatom were present in all four fractions. Elena Alvarez [62] found that asphaltenes were the dominating constituents to form the char layer, followed by aromatics and resins with a similar carbon residue rate, while saturates were almost completely volatilized.

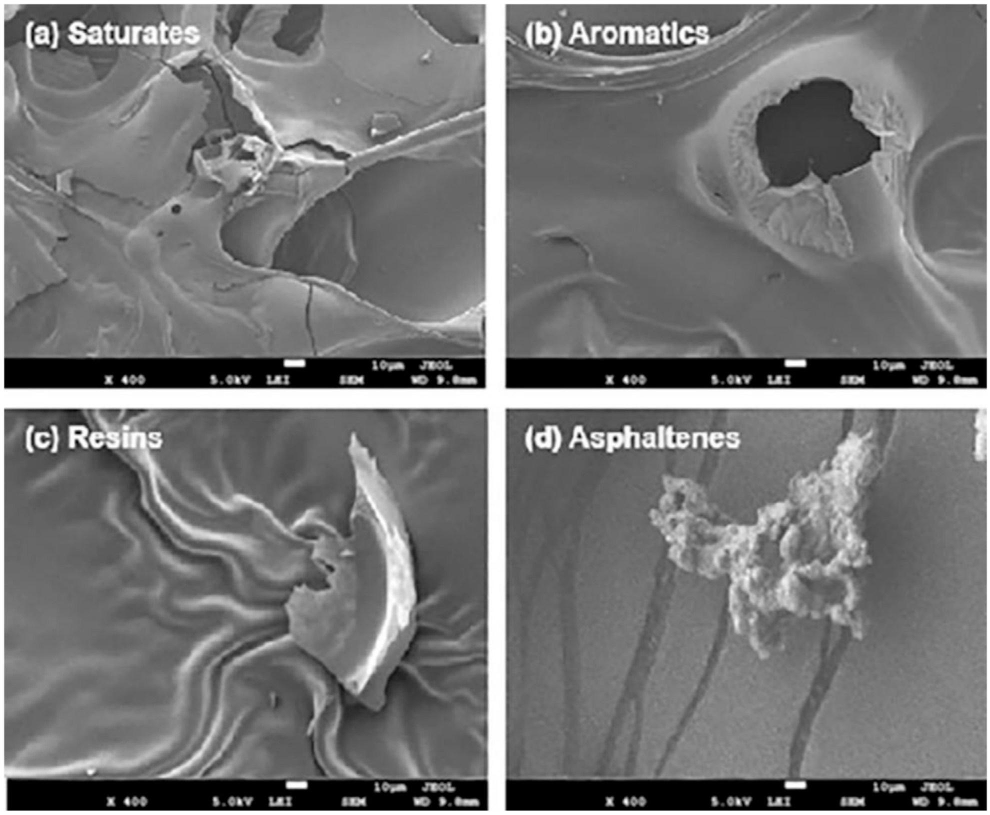

Fig. 13. SEM images of combustion residues of each SARA fraction [94].

4.3. Constituents of gaseous products

The main gaseous products of asphalt and four fractions are H_2O and CO_2, and the other gaseous products are almost toxic gas. Zhao [89], Xia [85,95] and Shi [87,94] all detected gaseous products of SARA fractions in each combustion stage through the MS and FTIR test, as shown in Table 3. Gaseous products of saturates and aromatics were similar, and yields of CO and CO_2 in the second stage were significantly greater than in the first stage. Apart from ordinary H_2O and CO_2, the volatiles released by resins and asphaltenes during the combustion were SO_2 [96]. To summarize, gaseous products of asphalt combustion mainly include alkanes, olefins, alkynes, esters, aromatic hydrocarbon, and a small number of organic sulfur compounds.

The heating rate and the oxygen concentration do not affect the types of gaseous products but only the number. As the oxygen concentration decreases, the number of gaseous products such as CO_2, H_2O, and SO_2 all decrease, especially the significant reduction in CO_2 [75]. When increase of the heating rate or lack of the oxygen concentration, the number of CO is significantly elevated. Since the deficiency of oxygen induces more inadequate combustion of asphalt, large molecules fail to participate in the reaction and remain in the original asphalt. Likewise, inadequate combustion can be observed more easily with a higher heating rate, which is consistent with the results of the DTG curve [63,72].

5. Flame retardants of asphalt

Due to the inflammability of asphalt, in-depth research on flame-retardant asphalt is the inevitable outcome caused by the exploration of asphalt pavement in the tunnel. Asphalt with flame retardants can effectively decrease thermal decomposition rate, adjourn ignition time, and enhance carbon residue rate [40]. The flame retardants may be divided into two categories of additive and reactive based on diverse surface activity properties, while they are customarily categorized and analyzed by element type, including halogen, phosphorus, boron, metal hydroxide, nanomaterial [97].

5.1. Flame retardant mechanisms of asphalt

The flame retardants can inhibit or discontinue thermal decomposition through condensed phase, free radical, cooling, and gas phase mechanisms [98]. Condensed phase mechanism can strengthen the char layer on the asphalt surface to impede heat transfer and form the physical barrier between the air and flammable gas produced during the combustion. According to free radical mechanism, fine particles generated by heating flame retardants can facilitate the mutual combination of the free radicals that include a large amount of dissociative •OH and H• during asphalt combustion, which can discontinue the chain reaction. When heating flame retardants undergo dehydration and endothermic reaction, cooling mechanism can reduce the temperature of the asphalt surface and hold back thermal decomposition. Gas phase mechanism refers that a great deal of nonflammable gas generated by flame retardants dilutes the concentration of combustible gas and oxygen to interrupt combustion. The combustion of asphalt after adding flame retardants is sophisticated progress involving many factors, so flame retardants generally have a synergistic effect through multiple flame-retardant mechanisms.

5.2. Flame retardants of asphalt

5.2.1. Brominated flame retardant

Halogen flame retardants generally are classified as iodine, fluorine, bromine, and chlorine, of which iodine has the optimal flame retardancy, followed by bromine [99]. However, iodine is so

Table 3
Gaseous products of four fractions combustion.

Components	Peak 1	Peak 2	References
Saturate	H_2O, CO_2, CO, C_2H_4O, ethers alkene, acetone, butane, ketone	CO_2, C_2H_4O, esters, ketones	[85,95]
Aromatic	H_2O, CO_2, CO, SO_2, C_3H_5, methanol, ethers, alkenes, acetone	H_2O,CO_2, CO, SO_2, methanol, C_5H_6, diacetylene	[85,89,95]
Resin	H_2O, CO_2, C, SO_2, C_3H_5, methanol, ethers, alkenes, acetone	CO_2, C, SO_2, methanol, C_5H_6, diacetylene	[87,94]
Asphaltene	H_2O, CO_2, C, C_3H_5, C_3H_6	CO_2, C, SO_2, methanol, C_5H_6, formic acid	[87,89,94]

active that brominated flame retardant is the most widely used. Due to the low bond energy of C—Br in brominated flame retardant, HBr gas that is easily thermally decomposed into can react with the free radical HO generated by asphalt, thus halting the chain reaction to stop the combustion [100].

Brominated flame retardant cooperated with Sb_2O_3 can form a classical bromine-antimony flame retardant system [101]. Sb_2O_3 reacts with bromides to produce $SbBr_3$ that are heavier than air and stay on the surface of burning asphalt, which forms the flow barrier to hold back the free radicals, such as •OH and H• [102]. Decabromodiphenyl oxide (DBDPO), as a typical brominated flame retardant, combined with Sb_2O_3 significantly elevates the LOI of asphalt with a modest dosage [103—106], while still improving the high-temperature and anti-aging performance but reducing low-temperature performance [107,108]. However, DBDPO was prohibited by the EU because of deleterious effects on the environment and the body. Decabromodiphenyl ethane (DBDPE) is a highly efficient and environmentally friendly flame retardant whose heat and light resistance are better than DBDPO. Compared to phosphorous and Metal hydroxide flame retardants, DBDPE has a greater influence on the flame retardancy of asphalt [109]. Likewise, in combination with Sb_2O_3 in asphalt (Fig. 14), DBDPE can substantially improve flame retardancy compared to use alone [110,111], consistency, and high-temperature performance but reduce the plasticity and low-temperature cracking resistance [112]. Hence, brominated flame retardants with preeminent synergy can efficiently ameliorate the flame retardancy of asphalt, but there is generally a negative impact on the low-temperature performance.

5.2.2. Metal hydroxide flame retardant

As the inorganic fillers, metal hydroxide flame retardants release crystal water and absorb large amounts of the combustion heat after thermal decomposition, decreasing the temperature of the asphalt surface. Furthermore, metal oxide generated by dehydration can further the formation of the char layer to impede combustion [113]. Currently, aluminum hydroxide (ATH), magnesium hydroxide (MH), and hydrated lime (HL) are the most widely used inorganic hydroxide flame retardants in asphalt.

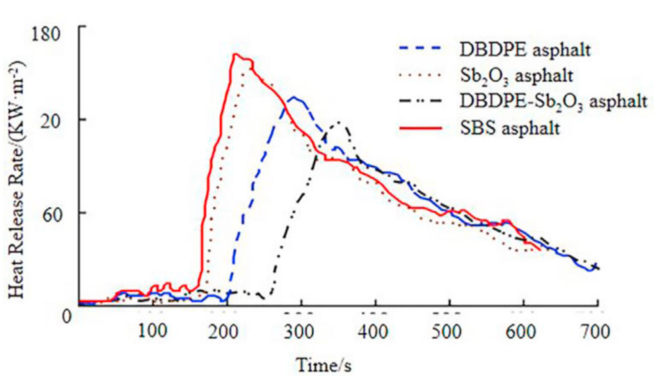

Fig. 14. Heat release rate for different flame-retardant asphalt [112].

ATH reveals the thermal decomposition temperature of 300 °C that is lower than the ignition temperature of asphalt, and weakens the reactive intensity of asphalt by absorbing heat, producing water and forming alumina char layer [114,115]. However, asphalt with massive ATH, whose dosage is close to 30%, can observably affect flame retardancy [116] but reduce economic efficiency and mechanical properties such as low-temperature performance, water stability, and moisture resistance [117]. Hence, ATH individually used for asphalt is inefficient and needs to cooperate with other flame retardants. Huang [118] studied the effect on ATH particle size in asphalt, and the results showed that the larger the particle size, the better the flame retardancy. ATH, whose particle size was 45 μm, had the best effect on the LOI of asphalt, reaching 28.5, which was a nonflammable material.

The thermal decomposition temperature of MH is approximately 350 °C, higher than ATH. The flame retardant mechanism of MH is very similar to ATH, but compared to alumina, magnesium oxide that is alkaline can rapidly neutralize with prodigious acidic combustion products to decrease the content of gaseous products [119]. Based on the TG test by Xu [120—122], asphalt adding MH with large dosages could significantly adjourn and decrease the maximum weight loss rate and increase the final residual carbon rate. Besides, MH also improved the Marshall stabilization of asphalt and reduced the loss of Marshall stabilization, differing from ATH that there were no apparent effects on low-temperature performance and moisture resistance. As shown in Fig. 15, Ren [123] discovered that LOI increased with the decrease of MH particle size, and these results were opposite to ATH. With further reducing MH particle size, it did not improve LOI because MH was too fine that it clumped in the asphalt, resulting in poor flame retardancy.

HL, also known as $Ca(OH)_2$, is decomposed above 350 °C, which is higher than ATH and MH [124]. Compared with ATH and MH, the flame retardant mechanism of HL is the stronger condensed phase and the weaker gas phase [125], which causes less effect on

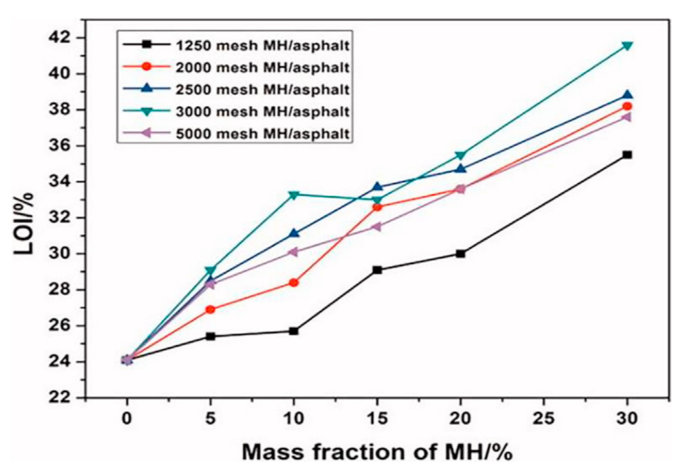

Fig. 15. LOI curves of MH-filled flame-retardant asphalt with different particle size [123].

adjourning the ignition time but shows more preponderance in inhibiting the combustion and heat release rate [126]. As shown in Fig. 16, $CaCO_3$ produced by carbonation of HL, an inert barrier layer, can inhibit asphalt combustion. Through CONE, Wu [126] and Zhu [127] obtained that HL had the preferable performance of smoke suppression to MH with the same dosage, significantly reducing smoke release rate, total smoke release, and generation amount of CO and SO_2.

Metal hydroxides with low efficiency on the flame retardancy of asphalt universally need massive dosages to exert the functions, which reduces economic efficiency and mechanical properties. Therefore, metal hydroxides have been gradually used in synergies with other flame retardants, particularly nanomaterials, taking full advantage of non-toxic and smoke suppression. Interestingly, since ATH, MH, and HL reacted at different temperatures, three metal hydroxides had good synergistic effects with each other [128,129].

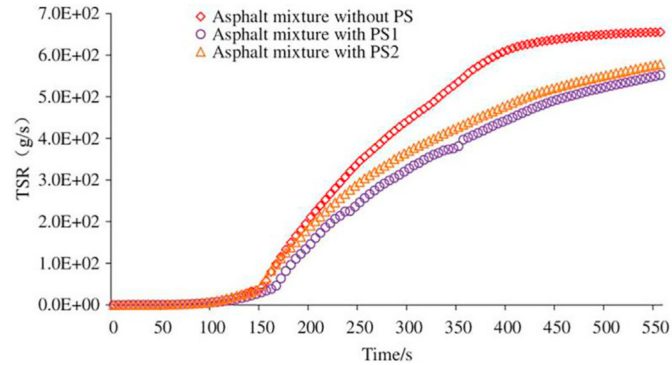

Fig. 17. Impact of PS on THR of asphalt [136].

5.2.3. Phosphorous-containing flame retardant

Phosphorous-containing flame retardants are classified as inorganic flame retardants and organic flame retardants based on the properties and compositions, of which inorganic flame retardants mainly include red phosphorus (RP), ammonium polyphosphate (APP), phosphorus slag (PS), and organic flame retardants have phosphate ester, phosphonate, phosphine oxide, phosphite.

Inorganic phosphorus, such as RP, generate PO and PO_2 free radicals by heat to consume the HO and H free radicals produced by asphalt to hold back the combustion and form the phosphoric acid and metaphosphoric acid to strengthen the char layer [130]. As shown in Fig. 17, after adding two different types of PS, the THR of asphalt was effectively reduced, indicating that PS can improve the smoke suppression of asphalt combustion. However, inorganic phosphorus flame retardants need to be compounded or modified on account of low efficiency and negative impact on the mechanical properties of asphalt [131], which increases the use cost. Organic phosphorus flame retardants with better flame retardancy than inorganic phosphorus have more noticeable effects in asphalt [132,133], which can adjourn the ignition time [134]. However, organic phosphorus flame retardants that mainly are oil components have bad compatibility with asphalt and also cause severe environmental pollution detected by many nations in the atmosphere, water, soil, and sediment [135].

In consequence, APP is one of the most widely used phosphorous-containing flame retardant in asphalt and has good synergy with nanomaterials [137,138], such as expanded vermiculite (EVMT) [139], montmorillonite (MMT) [140], for which nanomaterials can strengthen the char layer formed by phosphorous-containing flame retardants.

5.2.4. Intumescent flame retardant

Intumescent flame retardant (IFR) systems generally consist of APP as an acid source, pentaerythritol (PER) as a carbon source, and melamine (MA) as a gas source [141,142]. At high temperatures, APP decomposes into ammonia gas, polyphosphoric acid, a dehydrating agent to dewater and carbonize asphalt. The polyphosphoric acid undergoes an esterification reaction with PER, which can intensify the char layer through further dehydration into carbon. Ammonia gas generated by MA decomposition foam the char layer, achieving enormously efficient flame retardancy through heat isolation, oxygen barrier, and smoke suppressing.

IFR also has the drawbacks of uneven dispersion and poor compatibility, so the introductions of the compatibility agent and synergistic agent enhance the interfacial adhesion. Dispersing IFR in asphalt with $scCO_2$ [143], graphite nanoplatelets [144], and expanded graphite (EG) [145] (Fig. 18) is a very effective method to provide better flame retardancy and mechanical properties.

5.2.5. Boron-containing flame retardant

Boron-containing flame retardants are used as additives for polymers because of their low toxicity and molecular diversity [146]. Zinc borate (ZB), as a typical boron-containing flame retardant, has been extensively applied in the field of flame-retardant asphalt. ZB alone in asphalt has low efficiency of flame

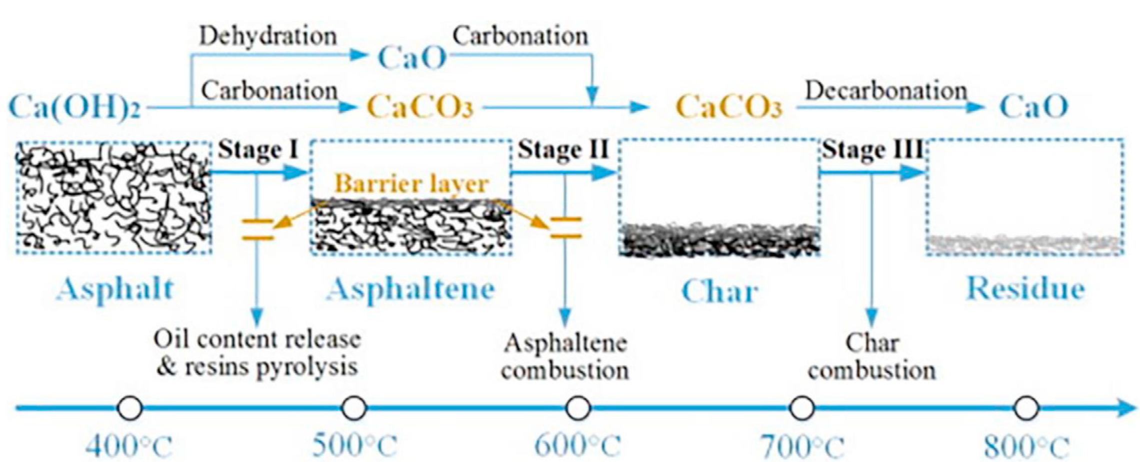

Fig. 16. Combustion process of asphalt with HL [126].

retardancy [146] but shows good synergistic effects with IFR systems [147], metal hydroxides [148,149], and EG 150]. ZB improves the compactness of the char layer through condensed phase mechanism [151], inducing better smoke suppression than flame retardancy in asphalt. Furthermore, ZB can provide asphalt with well high-temperature, low-temperature, and anti-aging performance [152] but soften the asphalt.

5.2.6. Nanomaterial based flame retardant

Nanomaterial is a material with one or more components in nanometer size or molecular level dispersed in another component base. Due to the large specific surface area, high diffusivity, and volume effect, nanomaterial used in flame-retardant asphalt can enhance flame retardancy. In addition, as the modifier for asphalt, nanomaterials can improve the water damage resistance and rutting resistance of asphalt mixtures [153]. The flame retardant mechanism of nanomaterial mainly is to hold back the contact between small combustible molecules generated by thermal decomposition and oxygen, hindering the heat transfer [154], which contributes to decreasing the peak heat release rate [155]. Moreover, nanomaterials can promote the formation of the char layer to defend the asphalt base and isolate oxygen [156,157].

As a typical type of nanomaterial, the layered silicate can form the phase separated structure, intercalated structure, and exfoliated structure in asphalt. The phase separated structure is that the layered silicate is dispersed in the base, and its layered structure does not change due to poor compatibility between asphalt and the layered silicate [158]. When asphalt is inserted into the interlayer of the layered silicate, the intercalated structure magnifies the interlayer spacing and each layer is arranged with regularity. The layered silicate that is exfoliated to disperse in asphalt forms the exfoliated structure uniformly. Uniform dispersion of nanomaterial in asphalt is a primary factor that enhances flame retardancy and mechanical property [159,160]. Regardless of whether the microstructure of asphalt with nanomaterial is an intercalated or exfoliated structure, it can improve flame retardancy and smoke suppression during combustion [161].

MMT, a typical nanomaterial, with highly fine aqueous aluminates is the layered mineral. OMMT with good compatibility is uniformly dispersed into the asphalt base to form the intercalated structure [162,163]. It can add a shielded char layer with a reduction in heat and smoke release (Fig. 19), since OMMT collapse by heat and push into the asphalt surface to create a compact surface barrier [164,165]. In addition, asphalt with OMMT can improve the

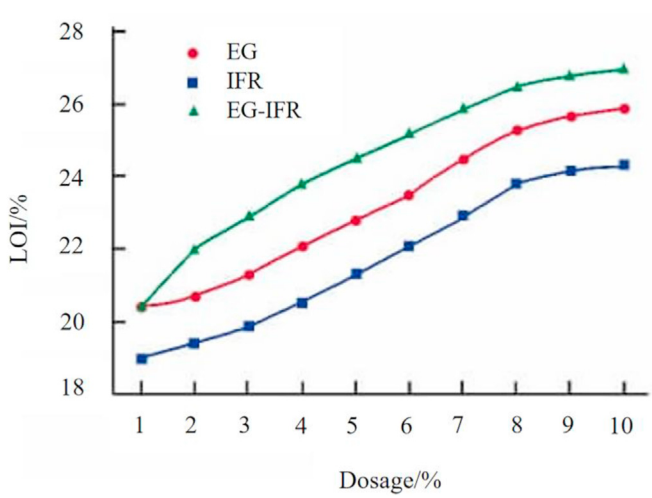

Fig. 18. LOI of EG, IFR or EG-IFR under different dosages [145].

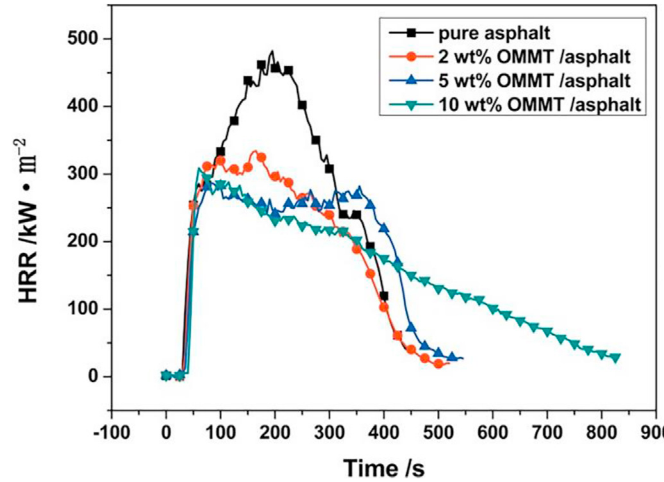

Fig. 19. HRR curves for asphalt and OMMT-modified asphalts with different contents [42].

medium-temperature cracking resistance and have little effect on the fatigue cracking performance, but there is a negative effect on the low-temperature cracking resistance [166].

Hydrotalcite, a layer double hydroxide (LDH), is a novel flame-retardant additive for asphalt [167], including a sheet structure with an average diameter of 1–2 μm and a thickness of approximately 50 nm (Fig. 20). LDHs were previously applied for inhibiting volatile organic compounds when asphalt pavement was paved [168–170], because LDHs effectively restrain the volatilization rate of small molecules, but not larger ones. Besides, the layered structure of LDHs can retard the heat exchange and flame propagation, while the metal oxides generated by thermal decomposition promote the formation of barriers [171]. However, the elevation of the flame retardancy, such as LOI, by LDHs is limited [172,173], so LDHs are generally used along with other flame retardants to play a synergistic role in asphalt.

Except for OMMT and LDHs, other nanomaterials, such as EVMT [174] and halloysite nanotubes [175,176], have been used for flame-retardant asphalt. Alone nanomaterial has minimal improvement in the flame retardancy of asphalt even at large dosages (Fig. 21) but does not negatively affect the mechanical properties [177,178]. Unlike nanomaterials, metal hydroxide flame retardants with low efficiency require high dosages improve the flame retardancy of asphalt but reduce mechanical properties (Fig. 21). As shown in Fig. 22, many studies found that hydroxides and nanomaterials have an excellent synergistic effect [179,180]. The combined use of ATH and nanomaterials, such as sepiolite [181], MMT [182], OMMT [183,184], EG [185], and EVMT [186], can significantly improve LOI and smoke suppression of asphalt even at small dosages because the exfoliated silicates enhance the compactness of the alumina char layer.

As a promising flame-retardant material, nanomaterial has some preponderance over traditional flame retardants, including the all-around performance, friendly environment, and good synergy, but needs to resolve the defects of poor compatibility with asphalt.

Xia [187–189] prepared a composite flame retardant that each corresponding flame retardant with various working temperatures was formulated based on various reaction temperatures of SARA four fractions. As the temperature rose during asphalt combustion, each flame retardant was successively decomposed to inhibit the multi-stage reactions, decreasing the number of gaseous products. The flame retardancy of this composite flame retardant was

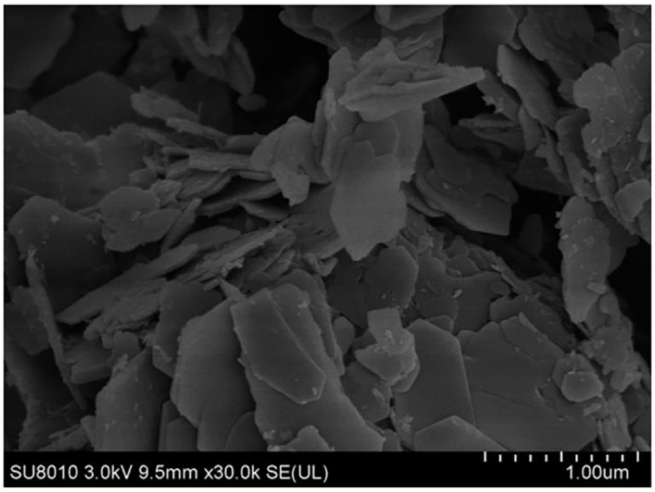

Fig. 20. SEM image f LDHs [172].

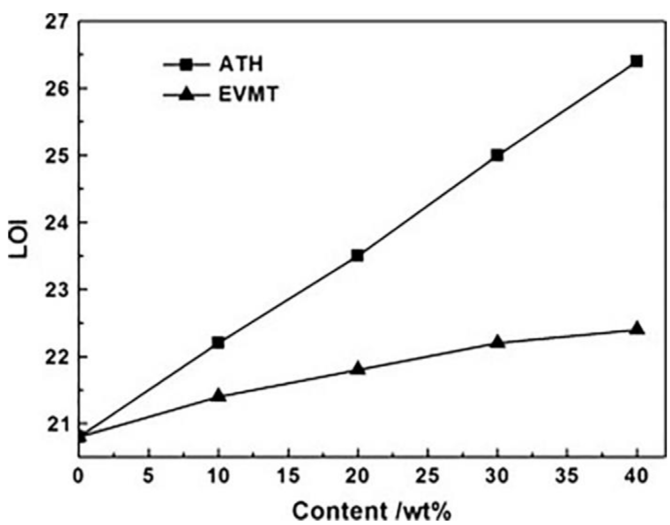

Fig. 21. Effect of single ATH and EVMT on LOI of asphalt [186].

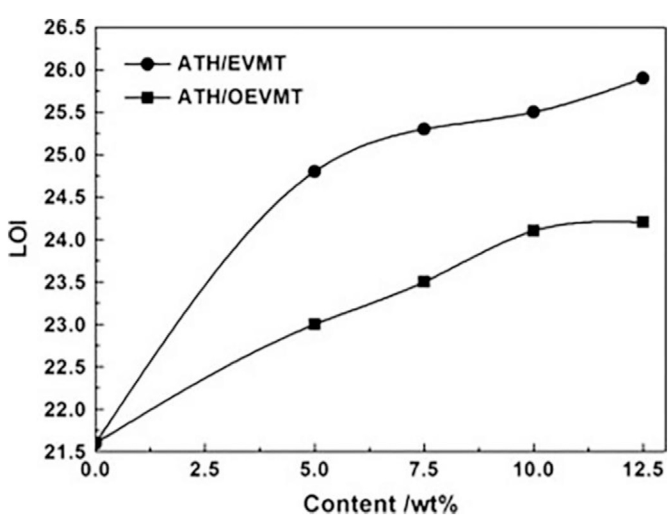

Fig. 22. Effect of mixed flame retardant on LOI of asphalt under the same ATH content (10 wt%) [186].

remarkable. The proportions of EG, ATH, MH, HL, and MRP are 3:2:12:11:1. Compared to each flame retardant with the same dosage, composite flame retardant suppressed bituminous thermal decomposition, and lowered the release amount of volatiles and heat at high temperature. It revealed a considerable inspiration for future research on flame-retardant asphalt, which prepared different flame retardants to match different reaction stages. The combination of disparate flame retardants promotes the effects on flame retardancy of asphalt because of the introduction of some synergists, as summarized in Table 4.

6. Flame-retardant asphalt mixture

As shown in Fig. 23, asphalt mixture is a composite material used for asphalt pavement, mainly composed of asphalt binder, coarse aggregate, fine aggregate, mineral powder according to a certain gradation, and in some cases, warm mix agent, polymer additive, and wood cellulose. Hence, not only should the flame retardancy of asphalt mixture investigate asphalt binder, but also other factors, such as the gradation, warm mix agent, aggregate, mineral powder, and fiber.

6.1. Open graded friction course

The gradation of asphalt mixture used in the surface course of asphalt pavement mainly has the Dense-graded Asphalt Concrete (AC), Stone Matrix Asphalt (SMA), and Open Graded Friction Course (OGFC), as shown in Table 5, among which OGFC with air voids of 18–25% is widely paved in tunnels due to outstanding performance of skid resistance and noise reduction [191,192]. Asphalt pavement with higher air voids can improve its heat conditions and reduce the temperature of the pavement in comparison to AC [193–195]. Furthermore, when fuel leakage occurs in the tunnel, OGFC can decrease combustible materials by infiltrating fuel into the drainage surface via the voids, thus achieving the objective of discontinuing the combustion [196,197]. Ding [198,199] showed that OGFC distinctly excelled AC and SMA in terms of the escaped fuel, burning time, and temperature. Accordingly, air voids play a critical role in the combustion characteristics of asphalt mixture, and can rapidly evacuate combustible liquids from the surface of asphalt pavement [200].

Nonetheless, OGFC as the gradation of the pavement in the tunnel has its defects. Firstly, considering that voids are easily blocked for long-term use of OGFC pavement, fuel cannot be infiltrated in a short period to be ignited. Secondly, escaped fuel in the voids undergoes inadequate combustion or pyrolysis reaction to generate more smoke due to oxygen deficiency. Hence, there are some limitations on the OGFC asphalt mixture in dealing with the fire in tunnels.

6.2. Warm mix asphalt

Warm Mix Asphalt (WMA) is a sustainable paving technology that can effectively decrease the construction temperature compared to Hot Mix Asphalt (HMA), and not damage the engineering properties of materials. Owing to relatively closed space in tunnels, traditional paving technology that generates asphalt smoke at higher construction temperatures is harmful to the health of constructors, WMA is generally used for paving asphalt pavement in tunnels. Warm mixing agents are generally Evotherm made in the United States and Sasobit made in Germany. As an organic additive with the wax component, Sasobit decreases the flame retardancy of asphalt [201–203], while Evotherm is a chemical additive. Therefore, warm mixing agents should be used

Table 4
Types of flame retardants in asphalt.

Types	Representation	Synergist	References
Brominated flame retardant	Decabromodiphenyl oxide	Sb_2O_3	[102–104]
	Decabromodiphenyl ethane		[41,110–112]
Metal hydroxide flame retardant	Aluminum hydroxide	Nanomaterials	[177,178,181–186]
Phosphorous-containing flame retardant	Ammonium polyphosphate	Nanomaterials	[137–140]
Intumescent flame retardant	Ammonium polyphosphate/pentaerythritol/melamine	Nanomaterials	[143–145,190]
Boron-containing flame retardant	Zinc borate	Metal hydroxides	[148,149,152]
Nanomaterial based flame retardant	Layered silicate	Metal hydroxides	[160,176]
		Phosphorous	[187–189]
	Hydrotalcite	Metal hydroxides	[173]
		Phosphorous	[167]

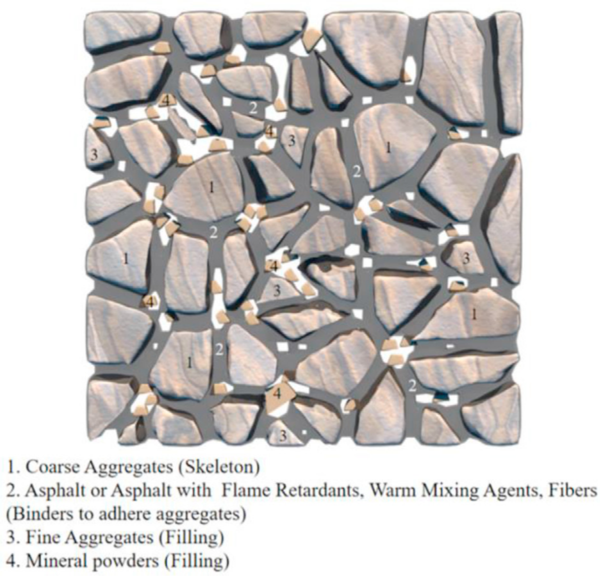

Fig. 23. Composition of asphalt mixture.

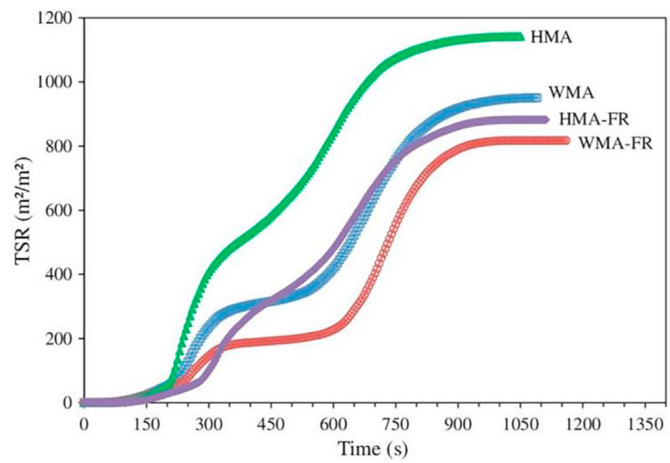

Fig. 24. TSR of different asphalt mixtures [29].

in combination with flame retardants to weaken the negative effects on flame retardancy.

As shown in Fig. 24, Li found that asphalt with Sasobit warm mixing agents had less smoke than HMA whether adding flame retardants. Wan [204] developed Evotherm for the surface modification of ATH, so those warm mix particles and flame-retardant particles were uniformly dispersed in asphalt, significantly weakening the agglomeration, whose LOI approximately reached 28. Several studies [205–207] found a common problem that WMA with flame retardants could dramatically improve high-temperature performance and flame retardancy but harmed low-temperature performance. Hence, it is a future research direction to intensify the dispersion of warm mixing agents and flame retardants in asphalt and weaken the effect on low-temperature performance.

6.3. Type of aggregate

The aggregates subdivided into coarse and fine aggregate in asphalt mixture respectively play the skeleton and the filling role. Some types of aggregates are routinely used in highway engineering, such as limestone, basalt, diabase, granite, gneiss, and sandstone. Asphalt mixture prepared from diverse aggregates unfolded disparate combustion characteristics in CONE [208]. As shown in Table 6, Asphalt mixture prepared from steel slag increased in ignition time and reduced in combustion duration and maximum temperature compared to basalt [46] because of the high specific heat capacity and low thermal conductivity of steel slag. Aggregates processed by organic silicon resin could significantly further the heat resistance, high-temperature performance, and water stability of asphalt mixtures [209]. Asphalt mixture with waste glass aggregates had higher heat resistance [210], because waste glass aggregates were nonmetal materials that could not be burned and decomposed.

Table 5
Common gradations of asphalt mixture in the surface course in China.

	Dense-graded		Open-graded	Nominal maximum grain size (mm)	Maximum grain size (mm)
	Continuous graded	Gap graded	Open graded friction course		
Coarse graded	AC-25	–	–	26.5	31.5
Medium graded	AC-20	SMA-20	–	19.0	26.5
	AC-16	SMA-16	OGFC-16	16.0	19.0
Fine graded	AC-13	SMA-13	OGFC-13	13.2	16.0
	AC-10	SMA-10	OGFC-10	9.5	13.2
Sand graded	AC-5	–	–	4.75	9.5

Table 6
Combustion parameters of asphalt mixtures with different aggregates.

Type of aggregates	Ignition time	Combustion duration	Maximum temperature	References
Basalt	30	490	335	[46]
Steel slag	40	450	315	

In general, research on flame retardancy of asphalt mixture primarily focuses on asphalt binder and additives, but aggregates that are the largest components of asphalt mixture have a non-negligible impact. In the future, some aggregates with good heat resistance may be selected to ameliorate flame retardancy of asphalt mixture without affecting other mechanical properties.

6.4. Mineral filler

Mineral filler whose particle size is less than 0.075 mm mainly plays a filling role in asphalt mixture and is usually developed from substances with hydrophobicity, such as limestone. As shown in Fig. 25, mineral powder can improve the LOI of asphalt whether adding flame retardants. In addition, replacing partial aggregates with mineral powders can increase the flame retardancy of asphalt mixture at the cost of the loss of partial mechanical properties, but its flame-retardant efficiency is far less than that of conventional flame retardants [211]. Because frequently-used mineral powders such as limestone, whose main component is $CaCO_3$, are decomposed only at high temperatures [212–214].

According to the exploration of Zhang [215], a mineral powder with alkalinity and strong hydrophobicity, as a substitute for limestone mineral filler in asphalt mixture, enhanced the flame retardancy with better economy. Hu [216] yet found that alkaline fillers did not affect the high-temperature performance and water stability of asphalt mixture compared to limestone mineral filler because the adhesion of alkaline filler to asphalt was preferable to that of limestone. Hence, more alkaline mineral fillers may be used in tunnels for better flame retardancy of asphalt mixture.

6.5. Fiber

Fiber is generally added to asphalt mixture to increase the physical and mechanical properties. However, traditional wood fibers and polymer fibers are flammable. Qin [217,218] showed that a Miber III mineral fiber with the main reaction stage at 400 °C–500 °C had the synergistic effects with flame retardants to both increase the decomposition temperature and reduce the total decomposition rate and heat release, which was better than both wood and basalt fibers (Fig. 26).

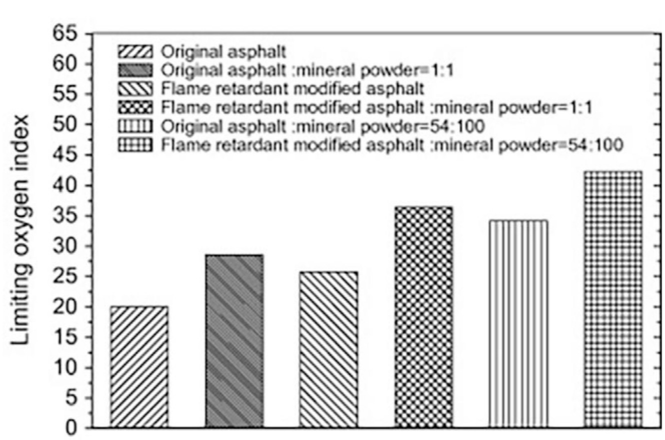

Fig. 25. LOI test of asphalt with flame retardant or mineral powder [211].

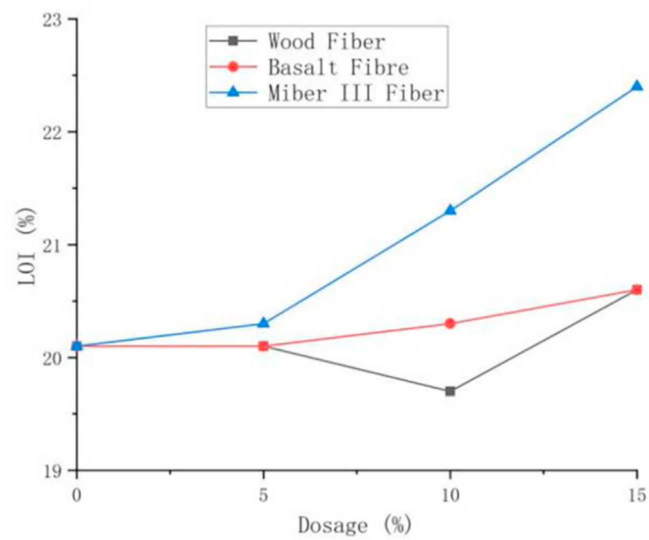

Fig. 26. LOI test result of asphalt with three kinds of fiber [218].

Based on overall consideration, it is a new notion that non-combustible fibers substitute traditional fibers in tunnels to optimize the physical and mechanical properties of the asphalt mixture without damage to flame retardancy.

7. Conclusion, challenge and prospect

7.1. Conclusion

This article mainly reviewed the current progress of flame retardancy on asphalt pavement. Asphalt, as the binder material of asphalt mixture, is very flammable, so asphalt pavement can be effortlessly ignited and propagated in the event of a fire in the tunnel, producing heat and toxic gas to endanger people and property.

i) Most nations and regions have not yet set specialized standards for the flame-retardant asphalt pavement but instead refer to plastics or other polymers, even directly evaluating the flame retardancy by flash point and fire point.
ii) There are already diverse test methods to study the combustion characteristics, flame retardancy, and smoke suppression of asphalt. Comprehensibly adopting multiple methods can obtain the flame-retardant parameters, and the standards may adopt the combination of these straightforward parameters to specify the asphalt pavement.
iii) The combustion and pyrolysis mechanism of asphalt and its SARA fractions have been extensively studied to help understand the properties of asphalt materials. The saturates and aromatics, particularly saturates, are crucial to flame-retardant design because of easy thermal decomposition in the initial combustion stage. The critical factors in the design

of smoke suppression are aromatics and resins with the largest weight loss and asphaltenes that can generate noxious gas during combustion.

iv) Flame retardants, functional additives that impart flame-retardant properties to flammable materials, are commonly added to asphalt to achieve the purpose of flame retardancy and smoke suppression, but some harm the environment or the physical and mechanical properties. Nanomaterials have a good synergistic effect with other flame retardants, hardly damaging properties of asphalt, which are promising materials.

v) Except for asphalt and flame retardants, the asphalt mixture is composed of coarse and fine aggregate, mineral powder, fiber, and other additives based on a certain gradation, and all components have a non-negligible effect on flame retardancy. Therefore, contribution of each component to the flame retardancy should be concerned.

7.2. Challenge and prospect

In order to develop environmentally friendly and high-performance flame-retardant asphalt pavement, researchers have taken a lot of effort in this work. Despite the significant advance in the field of flame-retardant asphalt pavement in recent years and possessing high academic insights and application potential, several challenges remain.

i) It is an urgent need for some nations and regions to perfect the standards of flame-retardant asphalt pavement, further standardizing the test methods and establishing the correlation between flame-retardant indicators and mechanical parameters.

ii) Current research on the combustion and pyrolysis of asphalt is based on the TG test, which is still somewhat different from the real fire scenario and may exist a bias in understanding the combustion behavior of asphalt material.

iii) Compatibility between flame retardant and asphalt has been the main problem in the preparation of flame-retardant asphalt. Some flame retardants with high lipophilicity show poor compatibility with asphalt, easily forming unstable agglomeration that affects the mutual dispersion. Non-uniform dispersion of flame retardants and asphalt has a serious negative on flame retardancy and physical and mechanical properties.

iv) Due to the low efficiency of some flame retardants in asphalt, it usually requires larger dosages to achieve a satisfactory effect, but the mechanical properties of composite asphalt and economic efficiency are affected. The balance between flame retardancy and mechanical properties is a challenge to be solved for flame-retardant asphalt.

v) There have been relatively few studies on other components of asphalt mixture, which is not the hotspot and attention compared to asphalt binder. However, asphalt pavement is paved by the asphalt mixture that consists of a few components with quite different properties, so the amelioration of flame retardancy should not be limited to asphalt binder and the influence of other components should not be ignored.

Although the development of flame-retardant asphalt pavement still faces many challenges to date, as a relatively new research field, the existing results of the research are positive and encouraging. The evolution of more excellent technologies for flame-retardant asphalt pavement can improve the safety of people and property in the event of a fire, which has a high application value. The following aspects could be considered for promoting further research:

First of all, it is urgent to establish a set of universal standards and test methods for asphalt pavement and provide a basis for the evaluation of flame retardancy. Moreover, except for the heating rate and oxygen concentration, influences of environmental factors in the tunnel such as ventilation rate, humidity, and maximum combustion temperature on the combustion behavior of asphalt pavement can be further explored in the future. Under the premise of ensuring safety, the flame-retardant asphalt pavement test can also be used in the actual tunnel, approaching the real fire scenario.

Secondly, it is very important to develop new technology to optimize the compatibility and dispersion of flame retardants in asphalt in order to balance the properties of flame retardancy and mechanical performance. It includes to developing high-efficiency, environmentally friendly, and energy-saving flame retardants to improve the flame retardancy of asphalt without losing physical and mechanical properties, notably exploiting and utilizing nanomaterials with good prospects that have efficient synergy with other flame retardants.

Finally, it would be wise to consider to solve the flammability of asphalt mixture as a whole, since asphalt mixture is a complex construction material comprising multiple substances with disparate physical properties. Therefore, it will be very promising to have a comprehensive study on all components such as asphalt binder, flame retardant, gradation, aggregate, mineral powder, fiber, and other additives, etc.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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