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Fire-Retarding Asphalt Pavement for Urban Road Tunnels: A State-of-the-Art Review and Beyond

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Abstract. With the rapid urbanization and development of metropolises, urban road tunnels have been constructed at an increasing rate, significantly alleviating urban traffic pressure, and improving urban resilience. Fire hazards have become a major threat to modern road tunnels due to the growing popularity of electric vehicles and high-density transportation of goods, particularly flammable materials. Asphalt pavements, as an essential component of road tunnels, may release harmful effluences and smoke under high temperatures, exacerbating the fire and adding risk to life safety. It is hence critical to investigate fire-retarding asphalt materials and their potential use in urban road tunnels pavements. This paper provides a comprehensive review of fire-retarding asphalt pavements for urban road tunnel pavements. The review covers tunnel fire generation mechanisms, evaluation methods, flame retardants for asphalt pavements, and recent developments in flame retardant technologies. By investigating these aspects, this paper aims to better understand the flammability of asphalt mix-

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tures and asphalt pavements in urban road tunnels, promote the research of flame-retardant technology, and ultimately reduce the damage and loss caused by asphalt road tunnel fire accidents. Additionally, this study identifies the limitations of current research and provides an outlook for future research to contribute to the resilience of urban road tunnel structures and the longer service life of asphalt pavement in semi-closed road tunnels.

Keywords: Urban road tunnels, Fire-retarding asphalt pavement, Urban resilience, Tunnel fires

Abbreviations

| | |
|------|---|
| ATH | Alumina trihydrate |
| APP | Ammonium polyphosphate |
| BSG | Bulk specific gravity |
| CAHC | Ca–Al hydrotalcite |
| CRP | Coated red phosphorus |
| CNTs | Carbon nanotubes |
| CC | Calcium carbonate |
| CH | Calcium hydroxide |
| CCA | Cone calorimeter apparatus |
| DGM | Dense graded mixture |
| EG | Expandable graphite |
| EV | Expanded vermiculite |
| FR | Flame retardant |
| FTIR | Fourier transform infrared spectroscopy |
| GM | Grouted macadam |
| GC | Gas chromatography |
| HMA | Hot mix asphalt |
| HL | Hydrated lime |
| LOI | Limited oxygen index |
| LS | Limestone modified binder |
| LDH | Layered double hydroxide |
| MS | Mass spectrometry |
| MH | Magnesium hydroxide |
| OMMT | Organic-modified montmorillonite |
| OGM | Open graded mixture |
| PA | Porous asphalt |
| RSR | Rate of smoke release |
| SARA | Saturates, aromatics, resins, and asphaltenes |
| SBS | Styrene–butadiene–styrene |
| TGA | Thermogravimetric analysis |
| VOCs | Volatile organic compounds |
| WMA | Warm mix asphalt |

1. Introduction

The rapid development of metropolises and urbanization has created numerous challenges for contemporary cities, including a shortage of land resources, traffic congestion, and high-density buildings [1–3]. In some international mega-cities like Shanghai and New Delhi, these problems are particularly acute, as the urban construction area is projected to expand much more quickly (276% by 2030) than population growth (66% by 2030) [4]. These issues exacerbate the trade-off

between population growth and land resources and contribute to increased carbon emissions. As a result, there is a need to explore alternative living spaces and resources. One approach to alleviate urban traffic pressure, resolve long-term traffic congestion problems, and improve urban resilience is to develop underground transportation space, such as constructing urban road tunnels [5, 6]. Asphalt pavement is an essential component of urban road tunnels, particularly in China, where asphalt pavement constitutes 90% of the total pavement structures, and in the USA, where over 94% of pavements are surfaced with asphalt or bituminous mixtures [7–10]. Asphalt pavement is favored for its good skid resistance, low noise, and ease of rehabilitation and maintenance compared to cement concrete pavement [11]. However, as urban road tunnels increase in length, burial depth, and diameter, asphalt pavement's flammable nature presents a potential safety risk during a fire accident [12–15].

Asphalt is a complex hydrocarbon mixture that is flammable, and its volatile content increases with temperature due to its combustible nature [16, 17]. As shown in Figure 1 [18, 19], the sharp temperature rise in the tunnel fire can cause pyrolysis and burning of asphalt, producing toxic volatile substances and fumes that hinder evacuation and rescue processes [20]. The fire in the road tunnel creates a complex environment involving chemical reactions, turbulence, and radiation that are influenced by various parameters such as geometry, tunnel slope, ventilation velocity, sidewall restriction, and passing air pressure [21, 22]. Additionally, the toxic fumes distributed throughout the tunnel can be more harmful than the fire itself [23–25]. As shown in Figure 2, exposure to complex volatile organic compounds (VOCs) will cause headaches, nausea, vomiting, fatigue and other serious symptoms in body health [26]. The aforementioned facts necessity the need to understand the pyrolysis of asphalt, the combustion behavior of bituminous mixtures, and the release of hazardous fumes. Therefore, research on the measurement, emission characteristics, and control methods of emissions generated from asphalt pavements in urban road tunnels during a fire is currently receiving significant attention.

Road tunnel fires are low-probability but high-consequence incidents [18, 27–30]. To minimize the impact of fire accidents in road tunnels, fire-retarding or fire-proof asphalt pavement has been investigated since the 1950s [31]. The fire-retarding mechanisms typically fall into three categories: free radical, physical covering, and thermal barrier mechanisms. Researchers have also explored various flame-retardant additives for road asphalt pavement [11, 32]. However, evaluating the effectiveness of these materials for urban road tunnels is challenging due to the unique semi-closed environment. Therefore, there is an urgent need to develop safe and effective fire-retarding asphalt materials, evaluation methods, and standards for road tunnel fire safety. Despite the importance of this topic, limited research is available to provide a comprehensive review and systematic summary.

To fill the research gap, this paper aims to enhance our understanding of the flammability of asphalt mixtures and asphalt pavement in urban road tunnels, and to promote the development of flame-retardant technology for road tunnel asphalt pavement. By doing so, the damage and loss caused by asphalt road tunnel fires can be minimized. The paper provides a comprehensive and detailed review of



Figure 1. Major tunnel fire [18, 19].

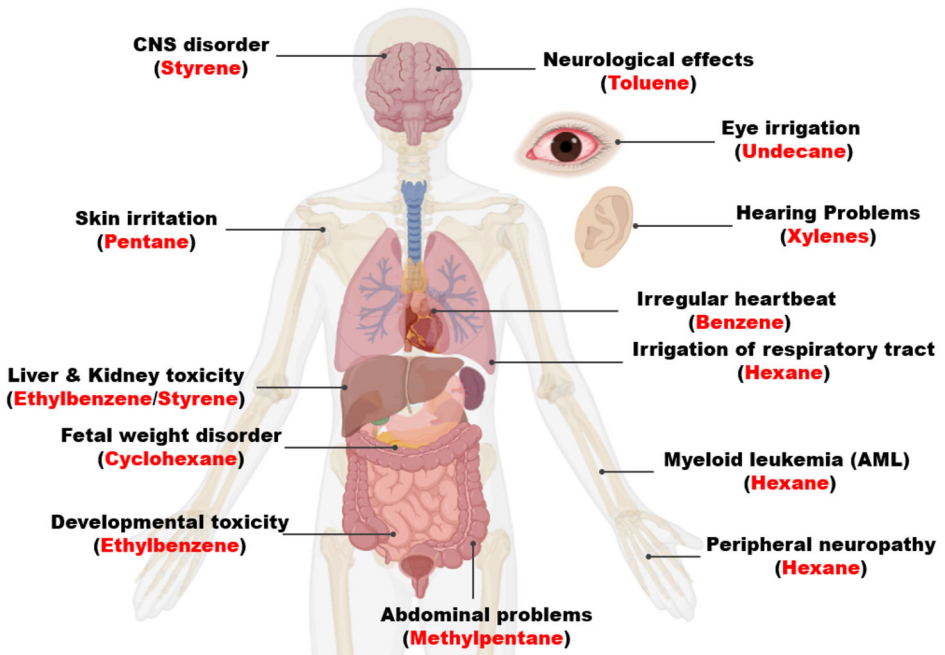


Figure 2. Major impacts of VOCs on human body health.

fire-retardant asphalt pavement for urban road tunnels, covering various topics. Firstly, the paper presents a brief introduction to the mechanism and combustion behaviors of urban road tunnel fires, setting the stage for a review of existing measures to improve the fire resistance of asphalt pavement. The paper then delves into various evaluation methods of flame retardancy, as well as a thorough discussion of the existing development of fire-retardant technology for urban road tunnel asphalt pavement. Additionally, the paper explores the feasibility of using nanotechnology to enhance the fire retardancy of road tunnel asphalt pavement. Finally, the paper concludes with a summary of current research limitations and recommendations for future research directions. To provide an overview of the topics covered, Figure 3 presents a clear framework for this comprehensive review.

2. Urban Road Tunnel Fire

2.1. Mechanisms of Road Tunnel Fire

Road tunnel fires are primarily caused by vehicle combustion resulting from collisions and rollovers (e.g. rear-end and side-impact collisions) as well as spontaneous combustion [15]. Studies have shown that asphalt mixtures are less prone to burning due to their high proportion of inert aggregates [33, 34]. As shown in Figure 4, the combustion process in a road tunnel primarily involves the burning of solid and liquid materials. The leakage of liquid fuels such as gasoline, diesel, and lubricating oil can cause fires to spread to nearby vehicles, becoming uncontrollable. Moreover, burning fuel that spreads on the ground may ignite bituminous pavement. Table 1 provides a summary of critical road tunnel fire accidents and their causes in China over the past two decades.

2.2. Characteristics of Road Tunnel Fires

The semi-enclosed environment of a road tunnel can lead to the accumulation of smoke and heat, which can cause heavy smoke, low visibility, and high temperatures. These factors can greatly impede escape and rescue efforts [18, 40]. The typical characteristics of a road tunnel fire can be summarized as follows:

- (1) Road tunnel fires occur randomly in terms of time and location.
- (2) Low visibility is expected due to the fast generation of smoke and fumes in the enclosed space of a road tunnel.
- (3) Rescue efforts can be extremely challenging due to the large amount of harmful and poisonous smoke and fumes generated by the fire, which can spread rapidly. Furthermore, firefighting equipment may have difficulty reaching the accurate location of the fire, and the flames can easily spread from vehicle to vehicle due to fiery air flows, making firefighting efforts even more challenging.

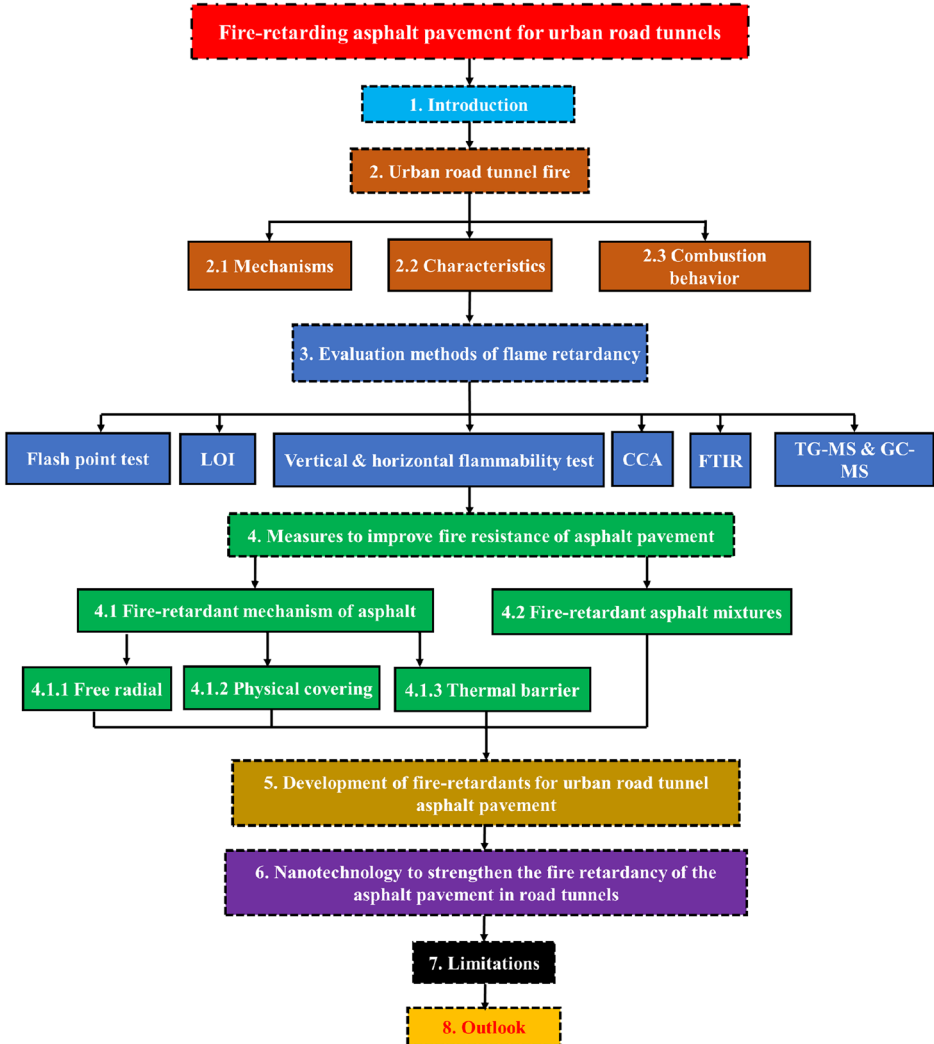


Figure 3. The overall framework of this paper.

2.3. Combustion Behavior of Road Tunnel Asphalt Pavement

As previously mentioned, the leakage of liquid fuels can exacerbate the fire by heating and igniting the asphalt pavement. Figure 5 depicts the development of asphalt pavement burning in the urban road tunnel fire. The high temperature near the fire location initiates pyrolysis reactions in asphalt, resulting in the production of a large amount of flammable and toxic gas products. The combustion of flammable gases produces heat, which intensifies the burning of asphalt and leads to the release of additional heat and toxic fumes [41, 42]. Furthermore, the negative impact on the ecological environment and human health resulting from

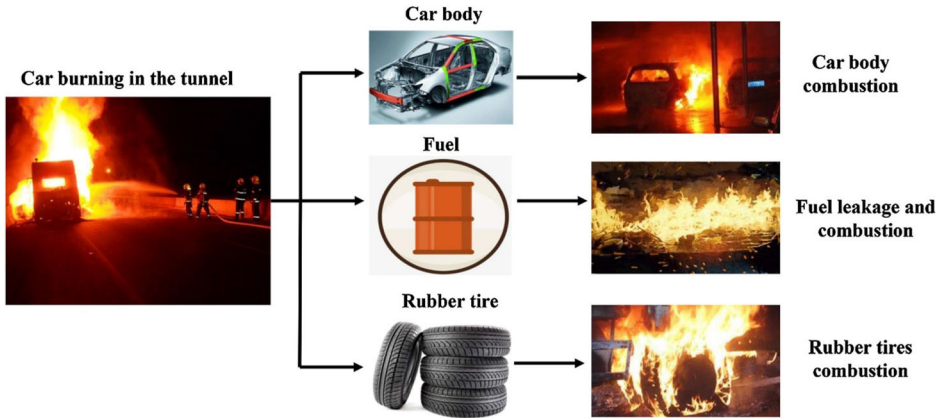


Figure 4. Combustion of a vehicle in a road tunnel [19].

**Table 1
Typical Road Tunnel Fire Accidents in China**

| Year | Location | Tunnel | Possible causes | Damage | | | References |
|------|-----------|-----------------------|---|--------|---------|--------|------------|
| | | | | Driver | Vehicle | Tunnel | |
| 2001 | Liaoning | Madaoling | Motor fire | √ | √ | | [35] |
| 2002 | Zhejiang | Maoliling | Motor fire | √ | √ | | [36] |
| 2003 | Anhui | Shidaoshan | Spontaneous combustion of carried goods | | √ | √ | [36] |
| 2004 | Zhejiang | Niuguantou | Spontaneous combustion of carried goods | | | √ | [35] |
| 2005 | Fujian | Feiluanling | Brake failure, wheels on fire | √ | √ | | [37] |
| 2006 | Guangdong | Wenquan | Tires fire | | √ | √ | [36] |
| 2007 | Chongqing | University city | Spontaneous combustion of vehicle | √ | √ | √ | [35, 36] |
| 2008 | Guangdong | Dabaoshan | Collisions | √ | √ | √ | [36] |
| 2009 | Shanxi | Qinling zhong-nanshan | Spontaneous combustion of carried goods | | √ | | [35] |
| 2010 | Zhejiang | Daxiling | Tires fire | √ | √ | √ | [36] |
| 2011 | Gansu | Xinqidaoliang | Collisions | √ | √ | √ | [35] |
| 2012 | Gansu | Taohuagou | Collisions | √ | √ | √ | [35] |
| 2013 | Fujian | Liushililiang | Collisions | √ | √ | √ | [37] |
| 2014 | Shanxi | Yanhou | Collisions | √ | √ | √ | [36] |
| 2015 | Zhejiang | Fenghuangshan | Collisions | √ | √ | √ | [37] |
| 2017 | Shanxi | Qinling No.1 | Collisions | √ | √ | √ | [38] |
| 2019 | Zhejiang | Maoliling | Tires fire | √ | √ | √ | [39] |

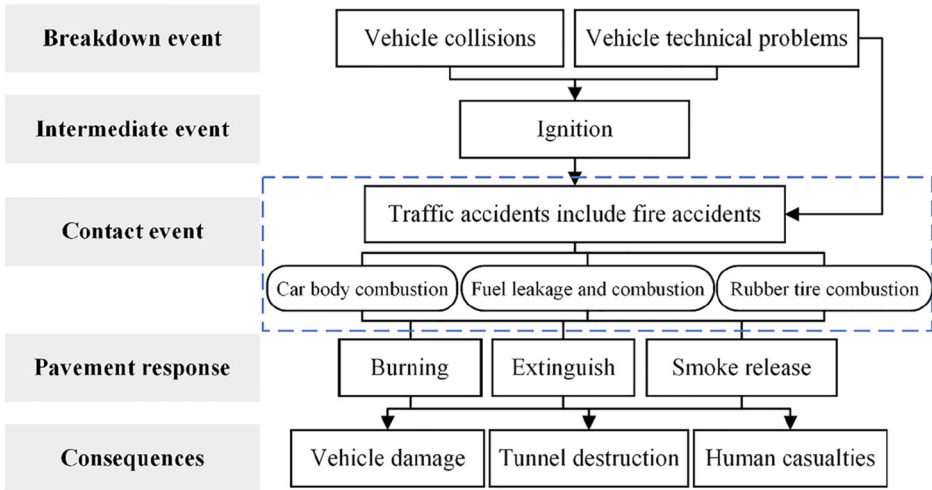


Figure 5. Main process of asphalt pavement burning in a road tunnel fire [43].

the fume toxicity can impede the escape of trapped individuals and make rescue operations more challenging, as depicted in Figure 6.

During a road tunnel fire accident, heated and ignited asphalt pavement induces volatile substances and smoky particles (fumes), as shown in Figure 7 [50, 51]. Volatile substances are semi-volatile vapor-phase compounds, while asphalt fumes are aerosol-phase particles. When asphalt is heated, heating asphalt leads to the release of a range of volatile substances, including inorganic gases, suspended particles, VOCs, and condensed vapors. Additionally, asphalt fumes and similar emissions (such as smoke, gas, VOCs, aerosols, and mists resulting from their condensation after volatilization) can be highly odorous and potentially harmful. Asphalt VOC is comprised of a mixture of alkanes, sulfur hydrocarbons, polycyclic aromatic hydrocarbons, benzopyrene, anthracene, naphthalene, acridine, pyridine, and phenols.

3. Evaluation Methods for Flame Retardancy of Asphalt Materials

The investigation into evaluation methods for measuring flame retardancy in asphalt materials is crucial to ensure their suitability and accuracy, thereby enhancing the safety of road tunnels. Currently, there are two main categories of evaluation methods for assessing asphalt flame retardancy: equipment-based methods, including the flash point test, oxygen test, cone calorimeter (CCA), mass spectrometry (MS), and analytical methods such as Fourier transform infrared spectroscopy (FTIR), gas chromatography (GC), and thermogravimetric analysis (TGA) [52]. This section aims to provide a comprehensive overview of testing

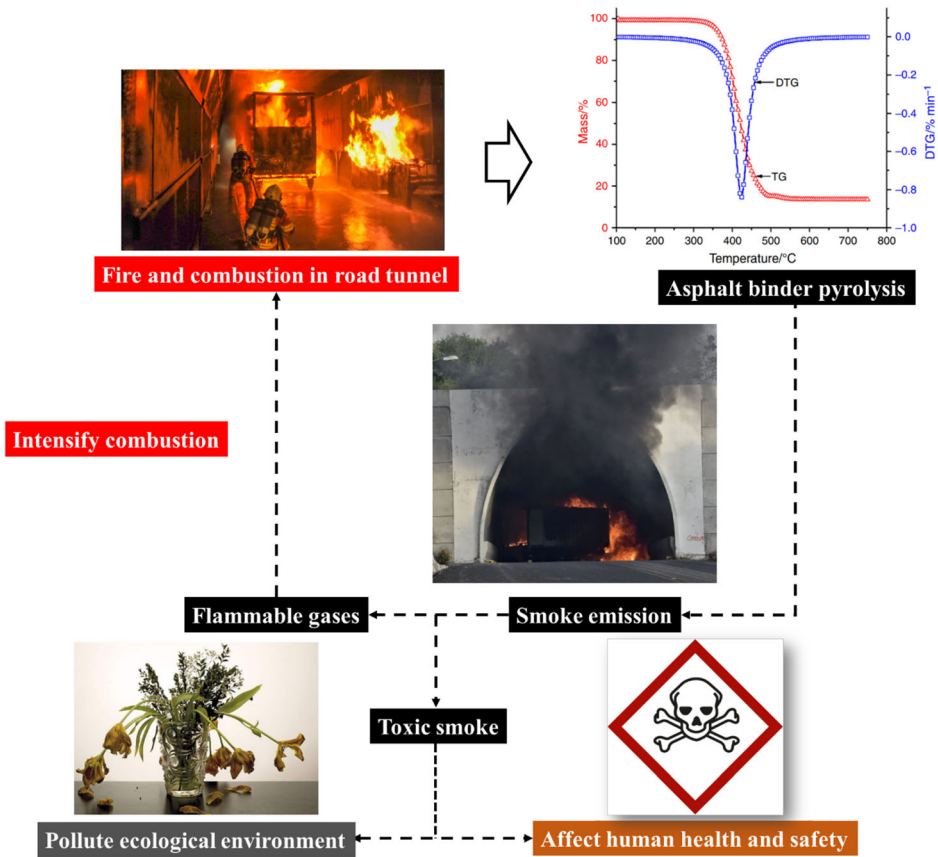


Figure 6. Effect of asphalt pavement burning [44–49].

methods for fire-retarding asphalt materials, offering a reference and guideline for future experimental programs.

3.1. Flash Point Test

The flash point test measures the temperature at which asphalt continues to burn for more than 5 s, according to the JTG E20-2011 (Chinese Standard). A higher flash point indicates better flame retardancy. This test is typically used to assess the safety of asphalt during storage, delivery, and pavement construction.

3.2. Oxygen Test

The oxygen test, conducted according to the ASTM D-2863 standard, is used to evaluate the burning capacity of asphalt. The Limited Oxygen Index (LOI) is used to assess the effectiveness of flame retardants and the intrinsic flammability of the source materials. The LOI (see Equation 3-1) indicates the minimum oxygen con-

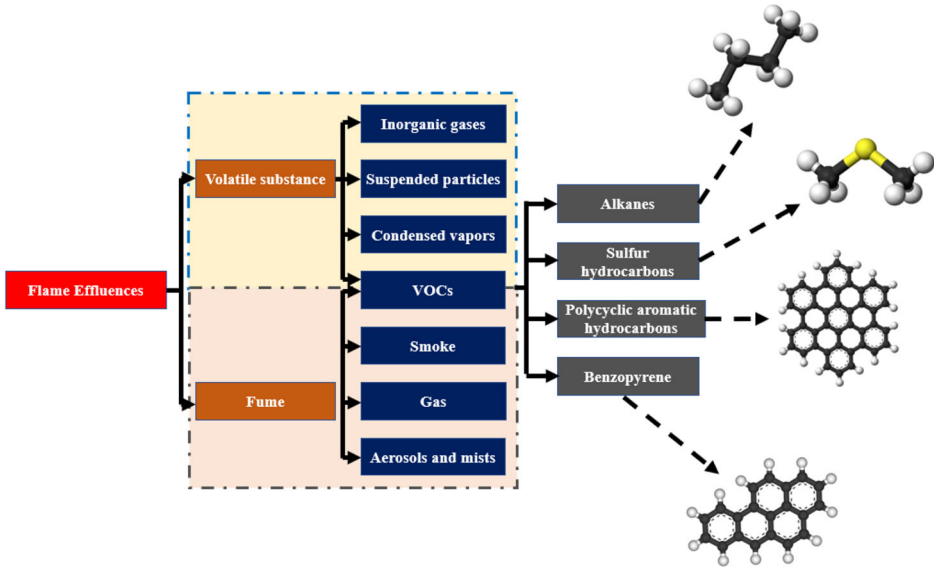


Figure 7. Emission classification of asphalt under fire.

centration required for burning, based on the volume of oxygen and nitrogen at critical oxygen concentration.

$$LOI = \frac{[O]}{([O] + [N])} \tag{3 - 1}$$

where [O] represents the volume of oxygen at critical oxygen concentration and [N] represents the volume of nitrogen at critical oxygen concentration.

The sample size used in the oxygen test is typically 100 mm 10 mm 6 mm, as shown in Figure 8. The LOI value indicates the minimum concentration of oxygen required for burning, with higher values indicating better intrinsic fire resistance. Materials with an LOI value lower than 22% are considered flammable, while those with an LOI value above 27% are considered flame-retardant. For materials falling within the intermediate LOI range of 22%–27%, such as this modified asphalt, combustion is difficult to achieve [53].

3.3. Vertical and Horizontal Flammability Test

The UL 94 standard includes both vertical and horizontal flammability tests to measure the self-extinguishing time of asphalt specimens in each orientation. These tests evaluate the burning and afterglow times, as well as the dripping of the burning specimen. Table 2 provides the evaluation criteria for assessing asphalt’s performance under fire conditions in a road tunnel. There are three classifications for flammability, known as V-0, V-1, and V-2. The V-0 rating indicates that the flame must extinguish within 10 s and there should be no dripping during

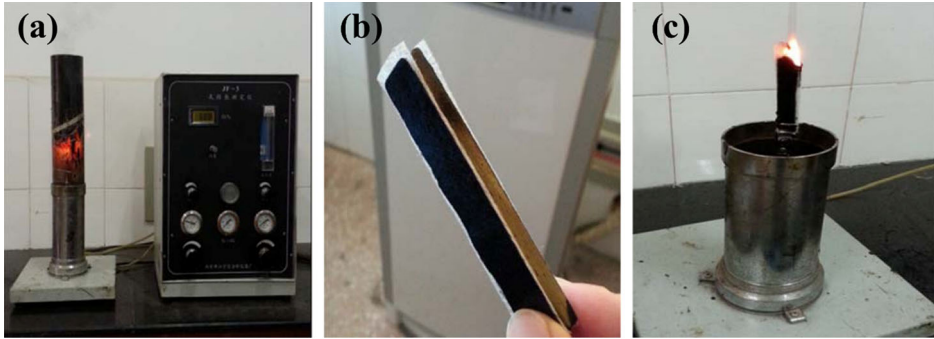


Figure 8. Oxygen test: (a) oxygen index apparatus; (b) standard sample; (c) burning sample [17].

Table 2 Evaluation Criteria for the Asphalt Under a Road Tunnel Fire [54–56]

| Test criteria | V-0 | V-1 | V-2 |
|---|-----|------|------|
| Burning time of each test specimen (s) (After first and second flame applications) | ≤10 | ≤30 | ≤30 |
| Total burning time (s) (10 flame applications) | ≤50 | ≤250 | ≤250 |
| Burning and afterglow times after the second flame application (s) | ≤30 | ≤60 | ≤60 |
| Dripping of burning specimens (Ignition of cotton batting) | No | No | Yes |
| Combustion up to holding clamp (Specimens completely burned) | No | No | No |

the test. The V-1 rating requires that the flame extinguishes within 30 s, with no dripping allowed. The V-2 rating permits dripping during the test, but the flame must extinguish within 10 s. These ratings are used to assess the flammability of materials and are commonly referenced in safety standards and regulations.

3.4. Cone Calorimeter Apparatus (CCA)

The cone calorimeter (CCA) is a bench-scale apparatus for combustion testing based on the principle of oxygen consumption and is a modified form of a truncated cone heater. The CCA test is conducted according to ASTM E-1354 Standard [57–59], as shown in Figure 9. The standard specimen size for CCA testing is 10 10 5 cm³. The asphalt specimen is wrapped in aluminum foil, leaving only the top surface exposed. The top surface is then ignited with a spark igniter, causing the specimen to pyrolyze and release volatile substances [60]. To evaluate the combustion behavior of asphalt, the heat release rate (HRR) is analyzed under various thermal radiation conditions, which is influenced by the concentration of oxygen required for combustion. In addition to HRR, the Cone Calorimeter Apparatus

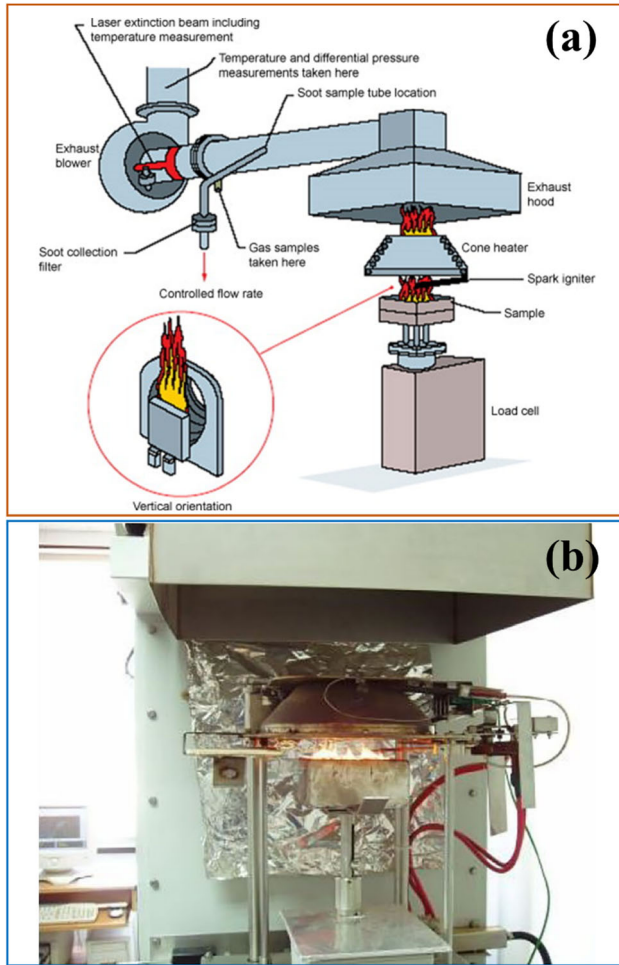


Figure 9. Cone calorimeter: (a) schematic review; (b) physical device [61, 62].

(CCA) test provides valuable data on smoke parameters such as specific extinction area (SEA), smoke production rate (SPR), total smoke production (TSP), and the volume of carbon monoxide (CO) and carbon dioxide (CO₂) emitted during combustion [50, 51]. The CCA test can be used to simulate the combustion of asphalt in an enclosed environment, making it a suitable method for evaluating the behavior of asphalt during a road tunnel fire.

Compared to traditional methods such as the flash point test and oxygen test, the CCA test has several advantages, particularly when it comes to evaluating the behavior of asphalt during a road tunnel fire. The CCA test can provide a more comprehensive set of evaluation indicators all at once, as well as a more practical simulation of the road tunnel fire scenario. Furthermore, the quantitative results

obtained from the CCA test can be used for further analysis and applied to theoretical models, providing a more nuanced understanding of the behavior of asphalt during a fire.

3.5. Fourier Transform Infrared Spectroscopy (FTIR)

Given the complex and rapidly changing chemical reactions and concentrations of fire effluences induced by asphalt during a road tunnel fire, it is critical to use a highly sensitive and accurate test method to analyze their composition. FTIR gas analysis can effectively address these issues by detecting the components of fire effluences and their concentration changes. Moreover, FTIR can capture spectral information of previously unknown components, providing valuable insights into their toxicity. Previous studies have used FTIR to analyze burning asphalt, and Table 3 summarizes the parameters of FTIR tests.

Many researchers have recently used FTIR to investigate flame-retardant asphalt [72–75]. However, there have been limited studies using FTIR to analyze the toxicity of road tunnel pavement during burning. Nowadays, FTIR coupled with DSC curves is a popular technique used to study the main representative volatiles such as CO, CO₂, SO₂, and CH₄. The concentration of these compounds can be calculated based on the absorption peak area corresponding to the temperature of the maximum exothermic peak. In addition, TG-FTIR analysis is a widely used method to study the thermal decomposition of asphalt materials, as illustrated in Figure 10. The sample is heated uniformly under controlled conditions, and TGA records the mass loss of the sample, which provides information about the composition of volatiles and inert fillers. The evolved gases are analyzed using FTIR spectroscopy in a beam-conforming flow cell, where the FTIR molecular fingerprinting detects different components. By collecting and processing the FTIR spectra, TG coupled with FTIR spectroscopy can identify gases released during sample decomposition, such as volatile compounds, solvents, and polymers [76]. To evaluate the volatile releasing characteristics, TG/derivative TG (DTG)-FTIR can be used. This technique allows for the real-time measurement of various gas compounds released during the pyrolysis process by detecting the characteristic absorption peaks of functional groups in the evolving gaseous volatiles. In addition, it enables the identification and quantification of volatile compounds released during the thermal degradation of materials. TG-FTIR has proven to be a useful tool in the analysis of thermal degradation of materials and gas evolution, as reported by previous studies [77, 78]. Furthermore, studies have shown the usefulness of TG-FTIR analysis in determining the weight loss of pyrolysis behavior and species of various gas compounds [67, 69, 77].

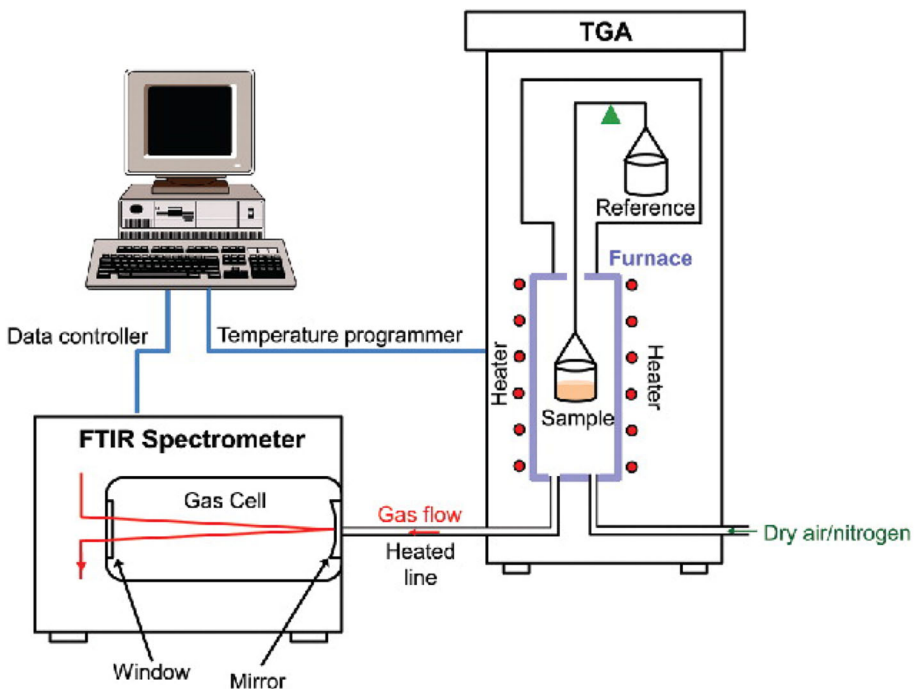
3.6. TG-MS and GC-MS Methods

Asphalt emissions can be quantified using either gravimetric or gas chromatography methods. TG-MS, a technique that has been used since the 1990s, allows for the investigation of thermal decomposition components and combustion behavior of polymer materials [80–83]. The combination of different analytical methods can facilitate the analysis of thermal compositions and concentrations of fire effluences

Table 3
Parameters of the FTIR Test

| Model | Heating rate (C/min) | Temperature range (C) | Carrier flow rate (mL/min) | Resolution (cm ⁻¹) | References |
|------------------|----------------------|-----------------------|----------------------------|--------------------------------|------------|
| Vector 22 type | 5 | AT-750 | 100 | 4 | [63–65] |
| STA 409 | 10 | AT-1000 | 50 | 8 | [66] |
| IZ10 | 10 | AT-800 | 40 | 4 | [67, 68] |
| Bruker Tensor 27 | 10 | AT-800 | 100 | 4 | [69] |
| Nexus 670 | 10 | 50–850 | 90 | 4 | [70] |
| Perkin-Elmer | 10 | 40–700 | 50 | 4 | [71] |

AT Ambient temperature

**Figure 10. Typical TG-FTIR analysis system [79].**

released during the burning of asphalt and asphalt mixtures in road tunnels. The typical TG-MS analysis system is shown in Figure 11, and it can calculate the mass change of testing materials during thermal decomposition and combustion while measuring the volatiles released during the heating process [84–86].

Pyrolysis GC-MS analysis is another effective method to characterize the VOC emissions from burning asphalt. The typical GC-MS analysis system, as shown in

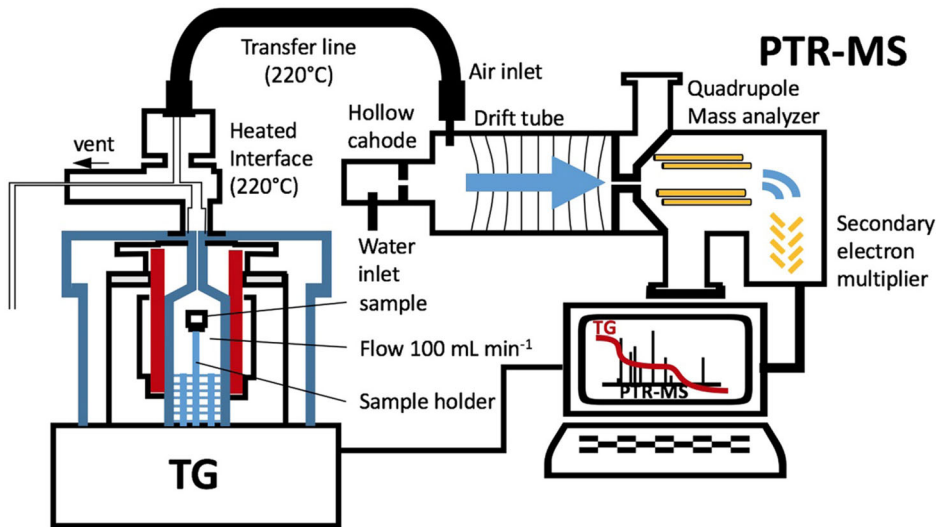


Figure 11. Typical TG-MS analysis system [87].

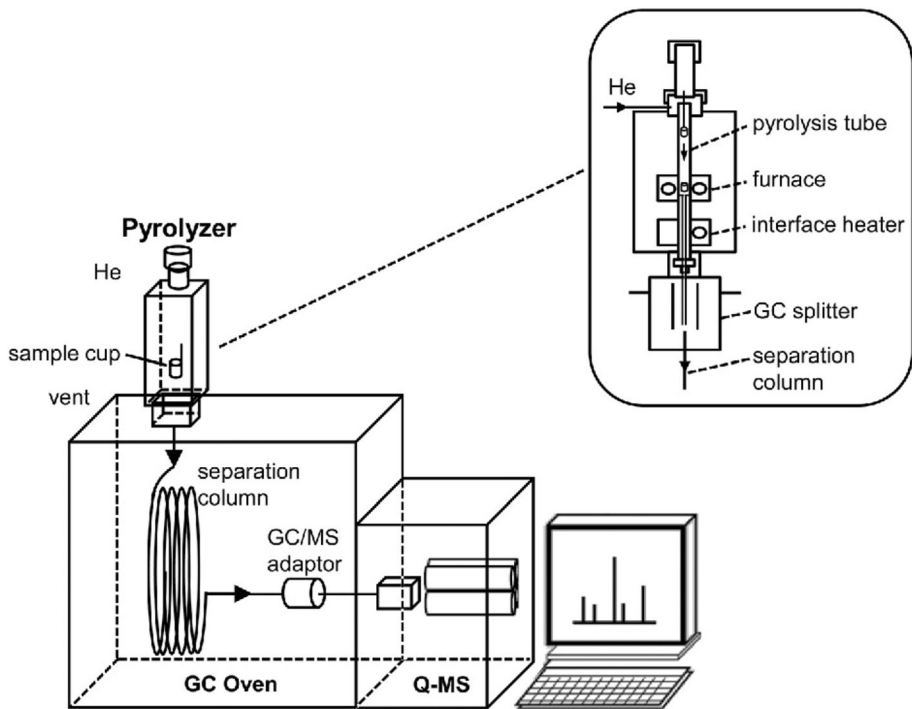


Figure 12. Typical pyrolysis GC-MS analysis system [79].

Figure 12, can provide both quantitative and qualitative identification of VOCs present in asphalt [88].

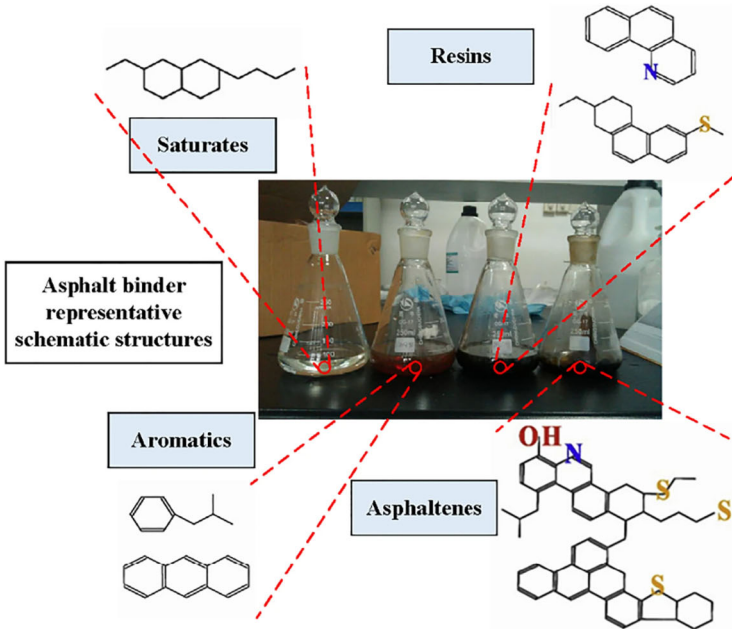
This section emphasizes the significance of investigating evaluation methods for measuring the flame retardancy of asphalt materials. The importance lies in ensuring that these methods are suitable and accurate, as their results directly impact the safety of road tunnels. Given the potential risks associated with fires in tunnels, it becomes essential to have reliable techniques that can effectively assess the flame-retardant properties of asphalt materials. This section also highlights the two main categories of evaluation methods currently used for this purpose—equipment methods and analytical methods. By providing a comprehensive overview of these testing methods, the paragraph aims to offer a reference and guideline for future experimental programs in this field. In summary, this section underlines the importance of determining suitable and accurate evaluation methods to enhance the safety of road tunnels, specifically by evaluating the flame retardancy of asphalt materials.

4. Measures to Improve the Fire Resistance of Asphalt Pavement

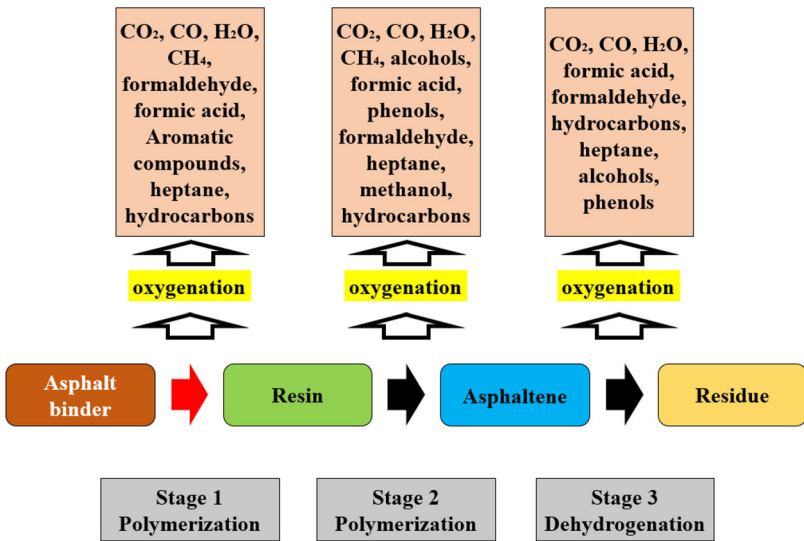
Existing literature has identified three critical categories of methods to enhance the fire resistance of asphalt pavement in urban road tunnels, by (1) strengthening the fire resistance of the asphalt source, (2) implementing measures to control the source (asphalt in this study) of tunnel fires, and (3) selecting suitable asphalt mixture types.

4.1. Fire-Retardant Mechanism of Asphalt

Mitigating losses and saving lives after a tunnel fire requires reducing the rate of asphalt combustion and the resulting effluences [89, 90]. Asphalt is a highly complex substance composed mainly of Saturates, Aromatics, Resins, and Asphaltenes (SARA), as illustrated in Figure 13a. The combustion of asphalt binder produces numerous combustible gases, and the volatiles released during each burning stage of the SARA fraction consist of different gaseous products and hydrocarbon compounds. Consequently, the fire effluences released from each SARA fraction differ. Nonetheless, CO₂ and H₂O typically constitute the two primary products of SARA fractions in various combustion sections, as demonstrated in Figure 13b. Due to the complex interplay between endothermic volatilization and exothermic reaction, the morphologies of the burning residues of the SARA fractions are diverse, as illustrated in Figure 13c. Saturates, aromatics, and resins are primarily composed of carbon, oxygen, and a few heteroatoms, while asphaltenes contain less carbon and more oxygen and heteroatoms. The sulfur content of asphalt increases from asphaltenes to saturates [91], emphasizing the importance of studying the fire-retardant mechanism of asphalt. Popular current flame-retarding mechanisms include the free radical mechanism, physical covering mechanism, and thermal barrier mechanism [63, 92, 93].



(a)



(b)

Figure 13. (a) Molecular structure of asphalt binder representative schematic structures-SARA [84, 88, 94]; (b) Possible combustion reaction process of asphalt binder [84, 91]; (c) SEM images of asphalt binder components after combustion [94].

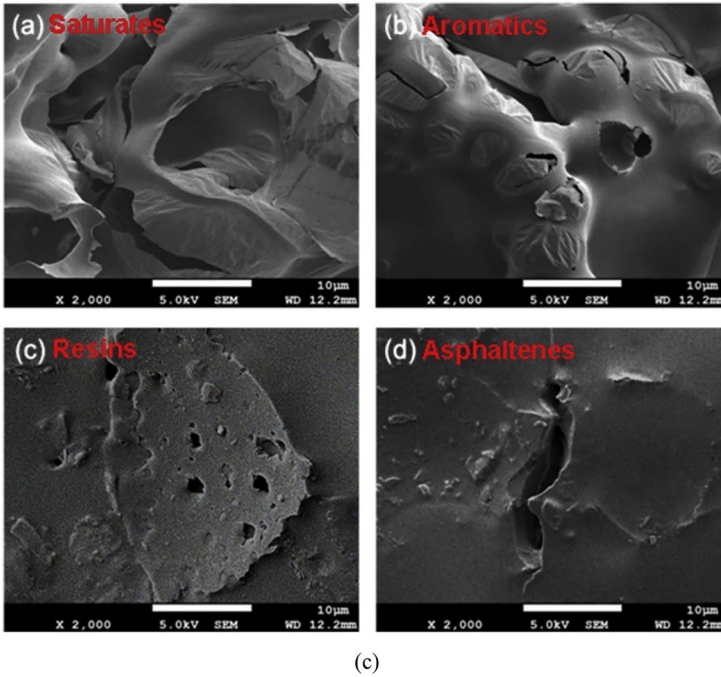


Figure 13. continued.

4.2. Measures to Control the Source (Asphalt in This Study) of Tunnel Fires

4.2.1. *Free Radical Mechanism* The free radical mechanism for flame retardation is based on the chain reaction theory of combustion, which requires the presence of free radicals to sustain the combustion process [93]. Materials containing halogens can interrupt the gas-phase combustion zone by capturing free radicals in the combustion reaction, inhibiting the flame from spreading and lowering its density in the combustion zone. This action eventually leads to slowing down the combustion reaction until it comes to a halt. The mechanism relies on a series of chain reactions that happen in the flame, as shown in the following formulas:



At elevated temperatures, the halogen-containing material breaks down and liberates HX (where X represents halogen), which interacts with the free radicals in the fire according to the following equations:



4.2.2. Physical Covering Mechanism The physical covering mechanism aims to insulate the contact between asphalt and oxygen and can be accomplished by utilizing gas-phase and solid-phase fire retardant materials. Gas-phase fire retardants create non-combustible gases such as CO₂, NH₃, HCl, and HBr upon heating, which decreases the concentration of combustible gases and oxygen in the combustion zone [95]. Additionally, organic halogen compounds release HX, which is heavier than air, when heated. This forms a protective layer that reduces the burning rate of the material. Conversely, solid-phase fire retardants produce a non-combustible carbonized film or glassy foam when heated. This film or foam covers the surface of the flammable asphalt and blocks the contact between oxygen and combustibles. It also prevents the escape of combustible gases, achieving flame retardancy [96].

4.2.3. Thermal Barrier Mechanism Additives can help reduce the impact of tunnel fires by absorbing some of the heat generated during combustion. This results in lower temperatures on the asphalt surface, less flammable gases, and fewer toxic emissions. For instance, Mg(OH)₂, Al(OH)₃, and layered double hydroxide (LDH) can be heated to a specific temperature and decomposed to produce water, which is an endothermic reaction that can absorb heat and slow down the rate of temperature rise. These mechanisms aim to achieve flame retardancy.

The free radical mechanism and physical covering mechanism can work together to prevent combustion during the early stages. Halogen-containing materials can capture free radicals, and solid-phase fire retardants can produce a non-combustible film or foam to block oxygen's contact with flammable asphalt. As combustion progresses, the thermal barrier mechanism becomes more effective in slowing down the process. Therefore, the three mechanisms can work synergistically to achieve flame retardancy [97, 98].

4.3. Fire-Retardant Asphalt Mixtures

The behavior of volatiles in bituminous mixtures after exposure to fire is influenced by various factors [99]. Table 4 presents the characteristics of typical asphalt mixtures, where hot mix asphalt (HMA) is found to have the worst performance in terms of gas emissions under fire, while grouted macadam (GM) shows better performance compared to HMA [32]. This is mainly due to the higher content of asphalt in HMA, which undergoes incomplete combustion, resulting in a larger amount of CO. In contrast, GM burns without a flame and produces less CO due to the relatively lower content of asphalt and the influence of the cement mortar coating. There is little difference in fire effluence production between open-graded and dense-graded mixtures [51]. In addition, the asphalt mixture plays a significant role in controlling smoke emissions during fire, as observed by Bonati et al. [50, 51]. Figure 14 displays the RSR curves of open-graded and dense-graded asphalt mixtures, revealing that the former exhibits a later and higher peak compared to the latter. The open structure of open-graded mixtures allows for fuel leakage and can contribute to fire propagation. However, Tao [100] proposes a different viewpoint, suggesting that open-graded friction course (OGFC) asphalt can aid in flame retardancy due to its high air void content that provides an escape route for flammable liquids and greases, reducing economic and personnel losses. Similarly, the GM or Combi-layer, which is an open bituminous mixture filled with cement mortar (with a void content of 30%), is utilized on tunnel pavement to prevent fire. By enveloping the aggregates with asphalt, the cement mortar limits the contact of the asphalt with fire, thereby increasing the material's thermal inertia [32, 101]. Apart from HMA, warm mix asphalt (WMA) has gained popularity in recent years due to its lower compaction temperature than traditional hot mix asphalt (HMA). According to research by Xiao et al. [56] WMA is considered a promising pavement surface material for road tunnels. Furthermore, studies by Li et al. [17] have shown that WMA produces significantly less CO₂ and CO under fire conditions compared to HMA. The addition of flame retardant and warm mixing agents in WMA has also been shown to have a synergistic effect on reducing smoke production. These findings highlight the potential benefits of using WMA in tunnel construction to improve safety and reduce environmental impact.

5. Development of Fire-Retardants for Urban Road Tunnel Asphalt Pavement

5.1. Development of Asphalt Fire Retardants

To enhance the ability of bituminous pavements in road tunnels to resist fires, one of the most frequently utilized methods is the addition of flame-retardant additives to asphalt binders or mixtures. This approach is preferred due to the high cost of producing fire-resistant materials with high thermal oxygen stability [19, 44]. Flame retardants can be divided into two primary types: additive and reactive flame retardants. Additive flame retardants can be inorganic, halogenated,

Table 4
Characteristics of Typical Asphalt Mixtures

| References | Aggregate grading | Asphalt content (%) | Air voids (%) | BSG (g/cm ³) |
|------------|-------------------|-----------------------|-----------------------|------------------------------------|
| [51] | Dense and open | 5.5 | DGM: 3.0; OGM: 2.4 | DGM: 2.285; OGM: 1.422 |
| [99] | Dense and open | 4.734 | 6.9 | 2.480 |
| [32] | GM and HMA | 5.5 | | |
| [102, 103] | AC-HMA | 4.9 | 5.7 | 2.510 |
| [104] | Dense and open | DGM: 5.5; OGM: 4.0 | DGM: 5.2–9.7; | DGM: 2.165–2.285; OGM: 1.384–1.422 |
| [105] | PA-13 | 3.9 | 23.5 | |
| [106] | AC-13 | 4.7 | 4 | |

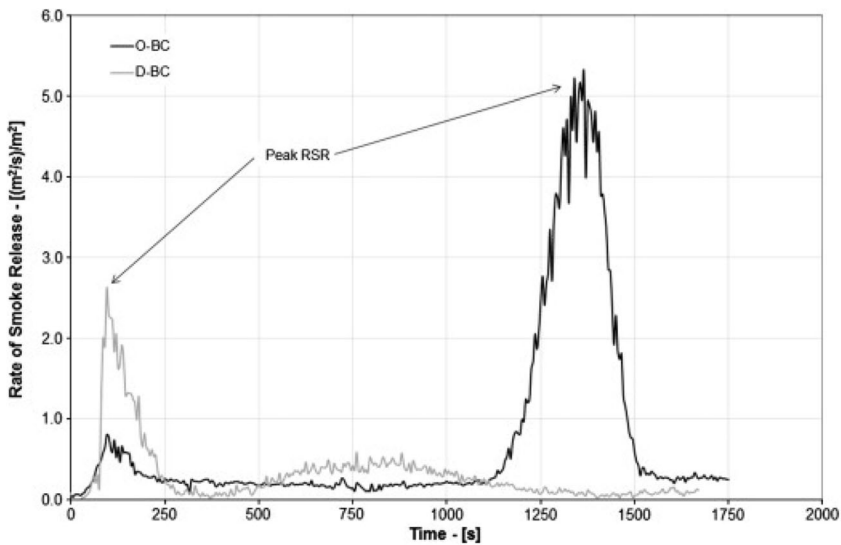


Figure 14. Typical RSR curves of the open-graded and dense-graded mixes [104].

phosphorus-based, or nitrogen-based, while reactive flame retardants include organophosphorus monomers containing reactive functional groups and organic halides [104]. Table 5 summarizes the main classifications of flame retardants. By adding an appropriate amount of flame retardants, the flammability of asphalt pavements in road tunnels can be reduced, and the spread of fire can be slowed down, thereby minimizing the production of smoke. Flame-retardant asphalt materials were first introduced in the 1950s, and significant advancements in

Table 5
Main Classifications of Flame Retardants (FR)

| Classification | Mechanism | Phase of action | Comments | References |
|----------------|---|----------------------------|---|----------------|
| Halogen FR | Substitute highly reactive free radicals, which are responsible for the propagation of flames, with more stable substances, such as anions of chlorine and bromine | Gas phase | While flame retardants can have a good effect on reducing the risk of fire, they often produce highly toxic and corrosive volatile compounds that are rich in incomplete combustion products and emit significant smoke. Additionally, the technology used to mix flame retardants can be complex and expensive, making it unsuitable for producing asphalt binders | [20, 109, 110] |
| Phosphorus FR | A char layer that contains phosphorus is generated to impede combustion | Condensed phase | This is a highly efficient and environmentally friendly flame retardant that is smokeless, low in toxicity, and produces no pollution. However, it releases significant amounts of black smoke and toxic substances when exposed to fire | [56, 100] |
| Antimony FR | The efficient elimination of hydrogen halide free radicals and related reaction products can facilitate the formation of a compact char layer, thereby minimizing the emission of smoke | Gas phase | While they exhibit good flame stability and long-lasting flame-retardant performance without generating corrosive gases, they can be toxic and have poor flame retardant effects when used alone | [111, 112] |
| Zinc borate | N/A | Liquid and condensed phase | Although this approach offers several benefits, including low smoke, low toxicity, and the absence of corrosive gas generation, its compatibility with asphalt is poor | [92] |

Table 5
continued

| Classification | Mechanism | Phase of action | Comments | References |
|---------------------|---|-------------------------|---|--------------------|
| MH & ATH | The flame retardant can create a surface layer that acts as an inert barrier, thereby restricting the absorption of oxygen and limiting the release of flammable byproducts during combustion | Condensed and gas phase | While they exhibit excellent flame retardant, smoke suppression performance, and thermal stability, adding large amounts can negatively impact the physical and mechanical properties of asphalt. Furthermore, their compatibility with asphalt is poor | [66, 70, 104] |
| CC | Form an inert dense layer on the asphalt surface | Condensed and gas phase | N/A | [70, 113] |
| LDHs | N/A | Condensed phase | While LDHs are abundant and easy to prepare, their addition to asphalt can improve its physical and mechanical properties but has a limited flame retardant effect | [66, 89, 104, 114] |
| Nanomaterials FR | An efficient and dense layer of carbon quickly formed at the interface | Condensed phase | While flame retardants can enhance the physical and mechanical characteristics of asphalt materials, their flame-retardant properties alone are inadequate, and they must be used in conjunction with other flame retardants | [56, 62, 94, 115] |

N/A Not applicable

flame-retardant technology for bituminous pavements were made in Europe and the United States during the 1980s [85, 107, 108]. Figure 15 illustrates the development of asphalt fire retardants.

Road tunnel fires can cause significant casualties, with toxic smoke and effluences from burning asphalt pavements being the main culprits. As a result, the primary goal of using flame-retardant pavement in urban road tunnels is to limit smoke generation from burning asphalt materials and minimize the amount of combustion effluences produced by burning asphalt pavements. The preparation parameters for flame-retarding asphalt are detailed in Table 6.

In the past, halogenated flame retardants were commonly used to enhance the fire resistance of asphalt materials. However, their incomplete combustion often

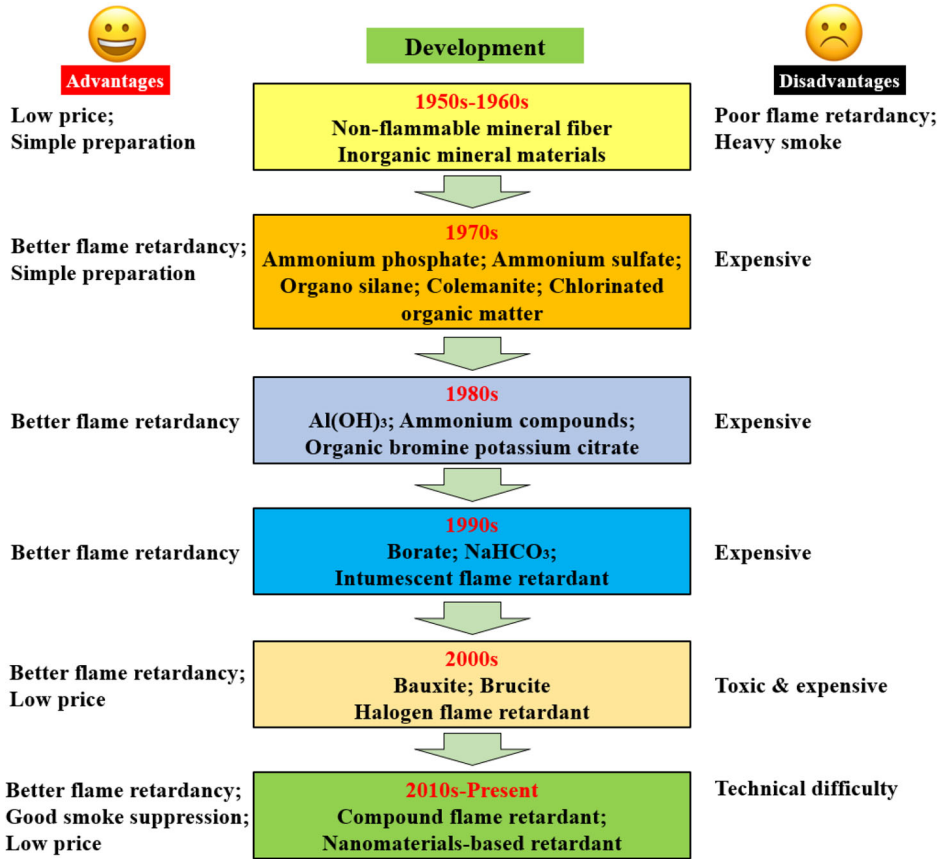


Figure 15. Development of asphalt flame retardants [19].

led to increased amounts of CO and smoke, which made them unsuitable for use [117]. Nowadays, the focus is on fire safety and environmental protection, which has led to a shift towards non-toxic and environmentally friendly flame retardants. In China, the majority of flame retardants used for asphalt materials are still low-efficiency and toxic products. However, research and development of green flame retardants for urban tunnel asphalt pavements is gaining momentum. Inorganic halogen-free flame retardants, such as smoke-reducing fillers, are becoming popular [99]. Specifically, for asphalt pavements in urban road tunnels, the emphasis is on resource-rich, cost-efficient, green, and highly thermally stable products.

5.2. Current Development of Fire Retarding Asphalt Materials

The current research status of asphalt flame-retardant technology in urban road tunnels involves ongoing efforts to develop and improve flame-retarding additives for asphalt pavements. Researchers are exploring various chemical compounds and nanomaterials to enhance the flame resistance of road tunnel asphalt pave-

Table 6
Preparation Parameters of Flame Retarding Asphalt Materials

| Asphalt type | Retardant type | Temperature (□) | Shearing speed (r/min) | Time (min) | References |
|--------------|--------------------|-----------------|------------------------|------------|------------|
| Ssangyong-70 | OMMT, ATH | 150 ± 5 | 4000–1000 | 60–10 | [66] |
| SBS | ATH, LDHs | 165 ± 5 | 3000–500 | 60–15 | [116] |
| PG-64–22 | LDHs | 160 ± 5 | 1000–5000-500 | 15–30-15 | [114] |
| SK 70 | HL, LS, MH | 160 ± 5 | 5000–500 | 30–15 | [70] |
| SBS modified | Compound FR | 140–150 | 1500–2000 | 20 | [17] |
| SBS | EG, MH, CH, APP | 170 ± 5 | 1600–4000 | 5–10 | [31] |
| SBS | CAHC, APP, CRP, EV | 170–180 | 1500–5500-1000 | 10–25-15 | [5] |
| SBS | OMMT, ATH | 180–200 | 5000 | 45 | [71] |
| SBS | MH | 170 ± 5 | 3000–5000-500 | 15–30-15 | [63, 65] |

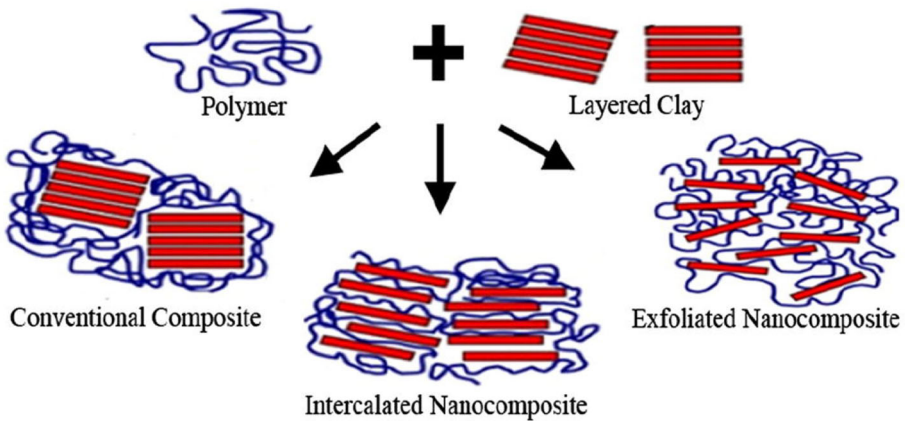


Figure 16. Microstructure type of nano-clay modified asphalt materials of different structures [129, 130].

ments. Recently, a polymer flame retardant called brucite, which is halogen-free, has been used to improve the fire resistance of asphalt materials. Brucite is highly effective at suppressing smoke and has excellent thermal stability [118]. Alumina trihydrate (ATH) coupled with LDH has also shown great potential as a fire retardant for asphalt materials. According to experimental results, the combination of ATH and LDH has significantly reduced fire effluences and the release of aldehydes, CO, and methane [116, 119, 120]. Organic-modified montmorillonite (OMMT), which is the primary component of layered silicates, has also been applied to asphalt materials due to its superior ability to control flame effluences and fire retardancy, as demonstrated in Figure 16 [121–127]. Yang et al. [128] con-

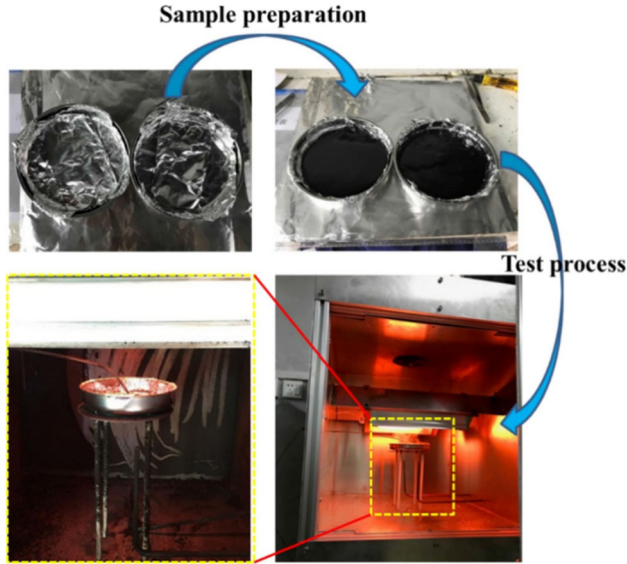


Figure 17. Flame retardant performance test for ATH/OMMT modified asphalt materials [128].

Table 7 Properties of Commonly Used Flame Retardants for Asphalt Pavement

| FR type | Dosage in asphalt (wt. %) | Specific gravity (g/cm ³) | Median particle size (μm) | PH | References |
|--------------------|---------------------------|---------------------------------------|--|-----------------------|------------|
| ATH, MH, CC | 4.0 & 5.5 | ATH: 2.42; MH: 2.36; CC: 2.71 | ATH: 1.1; MH: 0.9; CC: 3.2 | ATH: 9; MH: 10; CC: 9 | [104] |
| ATH, CH, CC | 20, 4, & 2 | ATH: 2.39; CH: 2.30; CC: 2.70 | N/A | N/A | [119] |
| HL, CC & MH | 40 | HL: 2.24; CC: 2.71; MH: 2.36 | HL: 7.4; CC: 41.8; MH: 21.3 | HL: 12; CC: 9; MH: 10 | [70, 113] |
| OMMT & ATH | 3 & 10 | N/A | OMMT: 300 mesh; ATH: <15 | ATH: 9.52 | [71] |
| CAHC, APP, CRP, EV | 8 | N/A | CAHC: 0.6; APP: 1.7; CRP: 7.5; EV: 7.4 | N/A | [94] |
| MH | N/A | 2.36 | 2.2–3.0 | 10.2 | [63, 65] |

ducted LOI and SEM tests to investigate the flame retardancy and mechanism of the ATH/OMMT composite asphalt mixture, as shown in Figure 17. The results indicate that the combination of ATH and OMMT improves the strength and compactness of the composite-modified asphalt carbon layer and enhances its

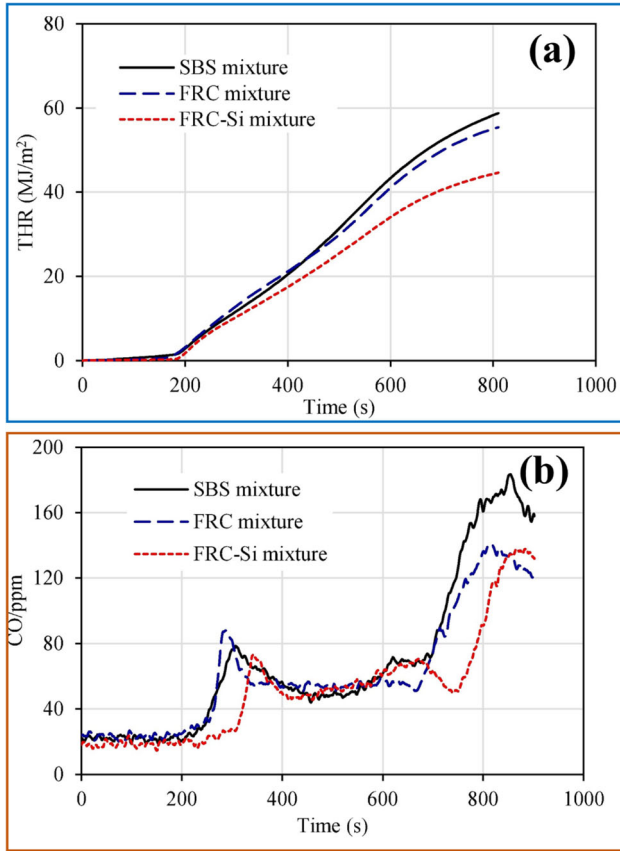


Figure 18. Total (a) heat release rate (b) carbon monoxide curves of BS, FRC, and FRC-Si mixtures [132].

flame-retardant performance due to the favorable synergistic effect between OMMT and ATH. [66]. Nanoclays have also been validated for their ability to reduce VOC emissions [104].

Tables 5 and 7 compare the flame retardant ability of different compositions and properties, suggesting that there is variability in the effectiveness of various flame retardants [131]. In a study conducted by Sheng et al. [132], four flame retardant components, namely, expandable graphite (EG), magnesium hydroxide (MH), calcium hydroxide (CH), and ammonium polyphosphate (APP), were evaluated for their potential as flame retardants for asphalt pavements in tunnels. The results indicated that a flame-retardant composite with a silane coupling agent (FRC-Si) could effectively reduce the amount of heat and carbon monoxide released during combustion, as well as delay the release of CO, indicating that it has the potential to be used as a flame retardant in asphalt pavements, as shown in Figure 18. Nan and Yu [60] found that LK had good fire effluence suppression ability and reduced the release of CO and CO₂ during the combustion of modified

asphalt. Zhu et al. [70, 114] compared the smoke emission suppression ability of LS, HL, and MH-modified asphalt materials and found that MH exhibited the best flame-retardant ability, forming a barrier layer that protected the asphalt. However, in the later stages of combustion, the MH-based protection layer was destroyed, and an intensified flame occurred, leading to increasing RSR values. HL, on the other hand, contributed to forming an inert layer of CaCO_3 on the asphalt, which delayed its burning and inhibited smoke emissions. The inert layer also isolated the heat transfer from asphalt to the external environment, thereby slowing down and reducing smoke release during asphalt burning. To improve the fire resistance of asphalt pavement during a fire accident in urban road tunnels, metal hydroxides have been used as fire retardants. Camino et al. [133] and Wilkie et al. [134] found that the carbon generated from the breakdown of polymers can be deposited on an oxide formed through the decomposition of metal hydroxides. This process prevents the release of smoke by causing the carbon to evaporate as CO_2 .

Flame retardants play a critical role in suppressing combustion and reducing the amount of smoke generated during fire incidents. In the future, the development of flame retardants for asphalt pavement in urban road tunnels should focus on the following aspects:

- (i) High efficiency in controlling asphalt combustion to prevent or minimize the spread of flames;
- (ii) Stable thermal performance and good temperature compatibility with asphalt and mixtures to ensure the effectiveness of the flame retardants during extreme temperatures;
- (iii) Long service life and no harmful effluences released to minimize the environmental impact;
- (iv) High-cost efficiency and environmentally friendly to ensure sustainability and affordability.

By developing flame retardants that meet these requirements, the fire safety of urban road tunnels can be significantly improved, protecting both human lives and the environment.

6. Nanotechnology to Strengthen the Fire Retardancy of the Asphalt Pavement in Road Tunnels

The microstructures of asphalt pavement materials, particularly at the micron and nano scales, are crucial to the overall performance of asphalt pavements [135–140]. To meet the demands of increasing traffic and rapid urbanization, nanomaterials with a dispersed phase size of less than 100 nm in at least one dimension have been employed to improve the fire resistance of asphalt pavement. Previous studies have classified these nanomaterials into three categories based on their dimensions: zero-dimensional, one-dimensional, and two-dimensional [56, 141–143]. Table 8 provides an overview of the typical nanomaterials used to

Table 8
Typical Nanomaterials for Asphalt Retarding Improvement

| Type | Definition | Nanomaterials |
|------------------|--|---|
| Zero-dimensional | All three dimensions meet the nanometer scale | Nano calcium, nano mesoporous silica hollow spheres |
| One-dimensional | Two dimensions meet the requirements for the nano-meter size | Carbon nanotubes (CNTs) |
| Two-dimensional | One dimension meets the requirements of nanometer size | Layered nanoclays |

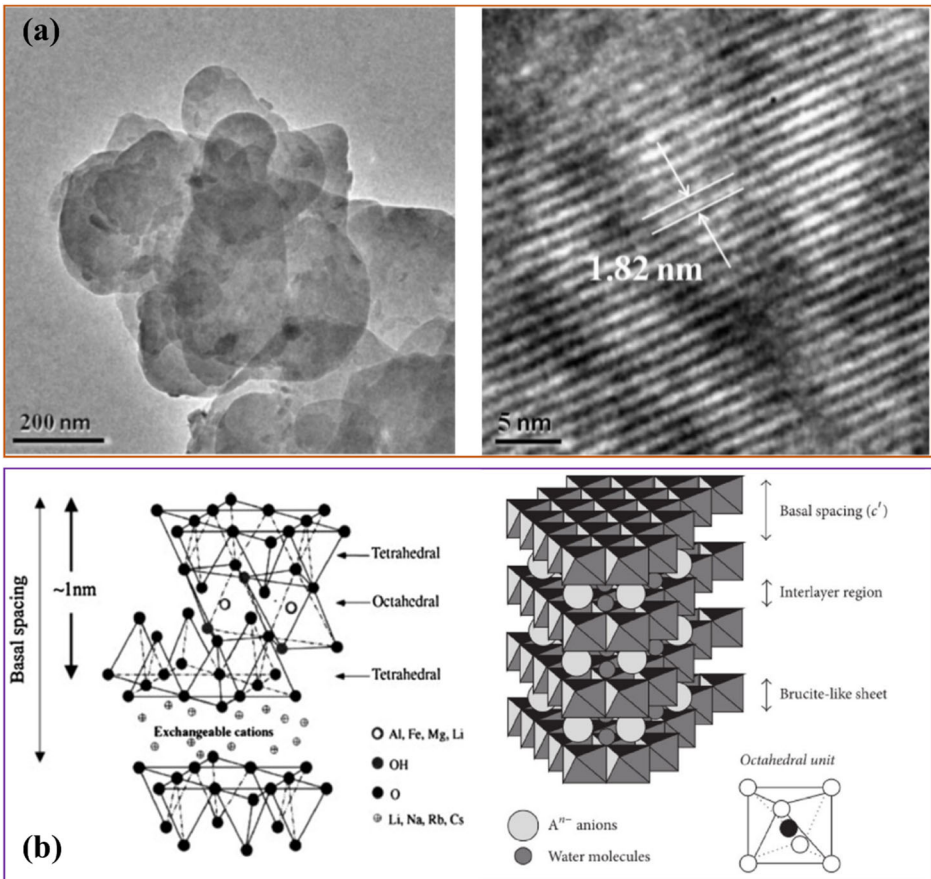


Figure 19. (a) TEM and high-resolution TEM images of the LDH [146]; (b) Crystal structure of OMMT and LDH [130, 147].

enhance flame retardancy and suppress the smoke release of asphalt materials in asphalt pavements.

The use of zero-dimensional nanomaterials in fire retarding asphalt pavement can be effective due to their small size and large specific surface area, which allows for a good adsorption effect on smoke molecules and light components, leading to fume suppression. For instance, Cui et al. [144] found that the addition of 6 wt% nano calcium carbonate to SBS-modified asphalt binder could achieve a fume suppression effect of 32%. One-dimensional materials, such as CNTs, have also been investigated for their ability to suppress asphalt fumes, with Calooyak et al. [145] reporting an inhibitory effect of over 60%.

In addition, layered nanoclays have been used to improve the fire resistance of asphalt materials. These can be categorized as cationic and anionic types, with OMMT being the most commonly used cationic nanoclay due to its compatibility with asphalt binders. Anionic nanoclays, such as LDHs, have also shown promise for improving the fire resistance of asphalt materials, as shown in Figure 19.

Layered nanoclay can form three different phased structures when combined with bituminous materials: conventional separation composite phase, intercalation composite phase, and exfoliation composite phase, as shown in Figure 19. In the conventional separation composite phase, the compatibility between the asphalt binder and nanoclay is poor, leading to the segregation of the modified asphalt materials. As a result, the nanoclay has little contribution to the performance of the modified asphalt materials during this stage. However, during intercalated and exfoliated stages, the compatibility between the asphalt binder and nanoclay is significantly improved, leading to improved flame resistance of asphalt materials. Previous studies have found intercalated and exfoliated composite structures in organic-modified montmorillonite (OMMT) [148, 149]. Intercalation composites offer interlayer spacing that allows for the lighter components of asphalt materials to occupy while preventing the entry of heavier components such as asphaltene into the matrix. By forming a stripping layer-net structure, the thermal stability of bituminous mixtures can be enhanced, limiting the thermal movement of lighter components and reducing smoke generation. In addition, Kong et al. [150] discovered that OMMT (Organically Modified Montmorillonite) can capture free radicals such as $H\cdot$ and $OH\cdot$ during the pyrolysis process of asphalt materials, thereby preventing the decomposition of chain ends and effectively suppressing the release of VOCs in asphalt fumes.

Studies indicate that the use of nanomaterials can effectively inhibit the emission of asphalt fumes through space restriction, adsorption, and catalytic oxidation mechanisms. However, incorporating nanomaterials into asphalt materials may result in decreased low-temperature performance. Additionally, there are significant challenges related to ensuring the compatibility between asphalt binder and nanomaterials, as well as achieving proper dispersion of the nanomaterials within the asphalt [151].

7. Limitations of Research at the Current Stage

This paper provides a thorough review of the flame retarding asphalt materials and asphalt pavements in urban road tunnels, including the tunnel fire-generation mechanisms, evaluation methods, flame retardants for asphalt pavements, and recent developments in flame retardant technologies. However, several limitations of the research at the current stage need to be addressed:

- (1) While different evaluation indexes for asphalt pavement during urban road tunnel fire have been presented in this study, the effective relationships and correlations among different test methods for the fire of asphalt pavements have not been established. Therefore, future studies should focus on developing a comprehensive assessment system that consists of more test parameters to provide a more efficient evaluation experimental framework.
- (2) Existing measures to control and reduce the fire effluences of asphalt pavements mainly include controlling from the asphalt source, asphalt mixtures, and tunnel fire source. However, a fire retarding asphalt pavement design guideline in the urban road tunnels has not been studied yet. Establishing an asphalt pavement design guideline is crucial to improving the fire resilience of road tunnels.
- (3) Burning asphalt pavements produce complex fumes that contain harmful components, which can threaten human health and damage the ecological environment, particularly in semi-closed road tunnels. However, the specific components of VOCs induced from burned asphalt pavement during a road tunnel fire have not been identified yet.
- (4) The compatibility between different fire retardants and asphalt materials has not been thoroughly investigated, which hinders the effects of fire retardants on the asphalt pavements in the road tunnels. Furthermore, some additive fire retardants can impair the performance of asphalt pavements. Therefore, balancing the properties of fire retardants and bituminous materials during the construction stage is necessary to ensure the best combination of engineering performance and flame retardants.

8. Outlook

To further promote research on flame-retarding road tunnel asphalt pavements and reduce their risks to the environment and human health, future research can be carried out in the following areas:

- (1) Currently, the relationship between indoor and field tests regarding asphalt fumes is not yet fully understood, and future research should aim to address this gap. One approach could be to integrate indoor test data on asphalt mixtures with field test results in semi-closed environments like tunnels. This could help establish the connection between the two methods from mathematical, organic chemistry, and toxicology perspectives, thus improving fire retarding asphalt research. Additionally, there is a need to develop consistent and

appropriate testing standards to guide the construction of low-fume asphalt pavements.

- (2) More research is needed to investigate the underlying mechanisms of flame retardancy in road tunnel asphalt pavements, which can help optimize the design and formulation of flame-retarding additives. Research can focus on understanding how these additives interact with the asphalt binder and aggregate, and how they inhibit flame spread and reduce smoke generation. In order to address the issue of asphalt fume emissions at their source, it is important to develop cost-effective and eco-friendly flame retardants and fume suppressants, while maintaining the required road and working performance.
- (3) It is crucial to assess the potential environmental impacts associated with the use of flame-retardant additives in road tunnel asphalt pavements. Research can focus on evaluating the leaching behavior of additives into the surrounding environment and their potential effects on air and water quality.
- (4) It is essential to study and provide design guidelines and a series of construction standards for urban road tunnels with asphalt pavement. This approach will ensure that more potential dangers are considered during the design and construction stages, lowering the risk of road tunnel fires, strengthening the resilience of road tunnel structures, and increasing the service life of asphalt pavement. In addition, collaboration with international organizations and experts can help develop standardized testing methods, guidelines, and regulations for flame-retardant road tunnel asphalt pavements. This can ensure consistency and compatibility in assessing and implementing flame-retardant technologies worldwide.
- (5) Research should also consider the economic viability of using flame-retardant additives in road tunnel asphalt pavements. Cost-effectiveness analyses can help determine the feasibility of implementing flame-retardant technologies and identify potential barriers to their widespread adoption.

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Declarations

Conflict of 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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