



Dynamic evolution of emitted volatiles from thermal decomposed bituminous materials



Tao Xu^{a,*}, Huaquan Shi^a, Hao Wang^b, Xiaoming Huang^c

^a School of Civil Engineering, Nanjing Forestry University, Nanjing 210037, China

^b Department of Civil and Environmental Engineering, Rutgers, The State University of New Jersey, NJ 08854, USA

^c School of Transportation, Southeast University, Nanjing 210096, China

HIGHLIGHTS

- The pyrolysis behavior of bituminous materials in nitrogen was investigated.
- The dynamic evolution of volatiles evolved from bitumen pyrolysis were characterized.
- The overall releasing evolutions of each main pyrolysis products were analyzed.
- The pyrolyzed regularity of flammable volatiles was discussed at flash and fire points.
- The microscopic pyrolysis mechanism of bitumen materials was further studied.

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ABSTRACT

Bituminous material is widely utilized in building waterproof, pavement engineering, etc. However, when the fire happens, hazardous fumes are released due to bitumen decomposition, affecting adversely the environment and human health. The thermal decomposition behavior of bitumen is the first step of its conversion process, such as combustion, and carbonization. To better understand the bitumen conversion when exposed to fire, the decomposition characteristics of bitumen was investigated and the dynamic evolution of gaseous products was characterized in this study. The results from thermogravimetry (TG) indicate that the decomposition of bitumen shows a single-step decomposition mechanism. The spectrum profiles from Fourier transform infrared spectroscopy (FTIR) further characterizes the decomposition mechanism and the overall evolution of volatiles from bitumen at flash and fire points. The evolved volatiles include carbon dioxide (CO₂), carbon monoxide (CO), methane (CH₄), water (H₂O), nitrogen dioxide (NO₂), sulfur dioxide (SO₂), hydrocarbon, methanol, formic acid, phenols, aromatic compounds, etc. The vapor pressure is a main factor to determine the concentration and hazards of gaseous products during bitumen decomposition. It was found that the evolution of each gaseous product was concentrated from 60 min to 110 min and each volatile was emitted from different chemical compositions of bitumen at various temperature ranges.

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1. Introduction

Bitumen is composed of saturated hydrocarbons to poly-nuclear aromatics, including aliphatic, aromatic and naphthenic hydrocarbons, saturates, resins, asphaltenes, etc. [1]. It has been widely used as the waterproof of buildings, binder of pavement engineering, thermal-protective coating of cold storage, antiputrefactiva of wood, antirust agent pipeline, etc. [2,3]. However, when a fire

happens, a great deal of fumes is released because of bitumen decomposition, including inorganic gases, volatile organic compounds as well as the aerosols and mists resulting from their condensation after volatilization [4]. These hazardous fumes adversely affect the environment and human health, and prevent the trapped personnel from escaping from the fire site, and hamper the rescuing work of firemen [5]. According to statistics, eighty-five percent of deaths in a fire are due to inhaling toxic fumes [6].

As a result of environmental and safety issues, it is important to study the releasing evolution of gaseous products from bitumen material at the high temperature [7]. Since the pyrolysis is the first step of bitumen conversion process, such as combustion, hydro-treatment, carbonization and gasification, it is necessary to know

* Corresponding author. Address: School of Civil Engineering, Nanjing Forestry University, 159 Longpan Road, Nanjing 210037, Jiangsu, China. Tel.: +86 25 8542 7747; fax: +86 25 8379 5184.

E-mail address: seuxt@163.com (T. Xu).

the pyrolysis characteristics of bitumen for better understanding its conversion process [8]. Little research has been conducted on the decomposition behavior of bitumen in nitrogen (N_2) and the characteristics of evolved volatiles, although we have studied the effects of smoke suppressant on the volatile release during the combustion process of bitumen in air [9].

Recently, there is an increasing attention on the decomposition or thermal decomposition of bitumen materials. Spadaro et al. [10] studied the thermal properties of linear low density polyethylene modified bitumen to find a substitute for styrene butadiene styrene (SBS) triblock copolymers in polymer-modified bitumen. Mothe et al. [11] investigated the degradation behavior of three different bitumen samples, and calculated the kinetics parameters to study the decomposition mechanism. Siddiqui [12] analyzed the mean molecular weight distribution of residue and asphaltene after decomposition reactions. Sun [13] investigated the composition, structure, and thermal behavior of Xinjiang asphaltite and evaluated its potential for bitumen modification.

Additionally, several key temperatures need to be studied during bitumen decomposition, such as flash point and fire point, because these temperatures indicate the time when the potential hazard from bitumen happens [4]. The flash point for a liquid is the lowest temperature at which the application of the test flame causes the vapors of the test specimen to ignite [14]. The fire point is one measure of the tendency of the bitumen to ignite and sustain burning for a minimum of 5 s [14]. The flash and fire points are the important physical properties that are usually used as criteria to characterize fire and explosion risk for liquid flammable materials [15]. They can indicate the possible presence of volatile or flammable materials in a relatively nonvolatile or non-flammable material [16]. However, few studies investigated the components of volatiles evaporated at flash and fire points.

The thermo-gravimetry (TG) is often used together with Fourier transform infrared spectroscopy (FTIR) to analyze the evolved gas compositions and the decomposition mechanism of polymeric materials [17]. Granada et al. [18] proposed a novel method to quantify the main light gaseous products from the decomposition of several biomasses using the tandem technique. Tao et al. [19] discussed the decomposition characteristics and gas evolution of mixtures of several wastes considering various heating rates, particle sizes and final temperatures. Huang and Wang [20] studied the effect of calcium carbonate ($CaCO_3$) on the thermal degradation of ethylene–butylacrylate (EBA) copolymer via the TG analysis. Although thermal chemical analysis gives a deep insight into the evolution of thermal decomposition reactions, few researchers have utilized it to investigate the decomposition mechanism of bitumen and the releasing evolution of gaseous products.

In this study, the thermal decomposition behavior of bitumen was investigated using the non-isothermal TG in N_2 . The gaseous products evolved from the bitumen decomposition were characterized using the FTIR. The pyrolyzed regularity of bitumen volatiles was analyzed at specific temperatures such as flash point, and fire point. The dynamic evolution of each main volatile and the thermal decomposition mechanism of bitumen were also discussed. This work may provide a complete characterization of microscopic decomposition mechanism for bitumen, and assess potential hazards from bitumen burning to which humans could be exposed when the fire happens.

2. Experimental

2.1. Raw material

Bitumen was obtained from Shell Bitumen Co., Ltd. in Guangdong province, China, with penetration of 72 dmm (ASTM D5-61), ductility of 36.5 cm at 5 °C (ASTM D113-86), softening point of 75.5 °C (ASTM D36-26), viscosity of 2.6 Pa s at 135 °C (ASTM D4402), flash point of 323 °C (ASTM D92) and fire point of

358 °C (ASTM D92). The elemental analysis of a bitumen sample was conducted. The element contents (wt%) of C, H, N, S and others are 86.59%, 10.56%, 0.83%, 0.44%, 1.58%, respectively. It can be seen that the bitumen is mainly composed of carbon and hydrogen elements.

2.2. Experimental method

The TG–FTIR analyses were conducted using a thermal analyzer system (TGA-92 type, SETARAM Co., Ltd., France), coupled with an infrared spectrometer (Vector22 type, Bruker Optics Inc., Germany.) equipped with an IR gas cell. In order to reduce the possibility of gases condensation along the transfer line, the transfer line consisted of a Teflon tube of 800 mm in length (4 mm in inner diameter) and was heated at a constant temperature of 230 °C. FTIR measurements were performed with a detector in a specifically developed low-volume gas cell with a 123 mm path length at a constant temperature of 230 °C. In the present work, the input gas was high purified nitrogen (N_2), and the gas flux is 100 ml/min. Samples were heated in TG equipment and pyrolyzed from room temperature to 710 °C at a heating rate of 5 °C/min. The mass loss of sample was recorded. Meanwhile, the volatile products were directly introduced into the gas cell for FTIR during the decomposition, and the changes of the products with the temperature rising were monitored by the spectrometer. The spectra were collected at a resolution of 4 cm^{-1} . The spectra data (baseline calibration and integral) were processed using the software OPUS 6.0 (Bruker Company, Germany).

The spectral intensity was calculated by Eq. (1):

$$\text{Transmittance (\%)} = (I/I_0) \times 100\% \quad (1)$$

where I_0 is incident light intensity and I is transmitted light intensity.

3. Results and discussion

3.1. Thermal decomposition behavior of bitumen

The decomposition behavior of bitumen was studied using TG experiments in N_2 . The TG and differential TG (DTG) curves of the bitumen are shown in Fig. 1.

From Fig. 1, it is noted that the bitumen decomposition process is in one main stage. When the sample was heated from room temperature to 300 °C, a small mass loss of 1.4% was observed. This is due to the evaporation of moisture and other low molecular weight compounds [8]. It indicates that there are few chemical or physical reactions below 300 °C [8], showing no noticeable changes on the TG–DTG curves.

Subsequently, the main temperature stage of bitumen decomposition is from 300 to 500 °C with a mass loss of 88.9%. It is attributed to the volatilization of bitumen components such as saturates, aromatics, light hydrocarbons, and the decompositions of asphaltene. [21]. This suggests that the bitumen has been subjected to a major mass loss stage. Especially, as the testing temperature was increased to around 323 °C, i.e. the flash point of bitumen, a few of flammable volatiles began to release, leading to the flash above the bitumen specimen when ignited [14]. As the bitumen

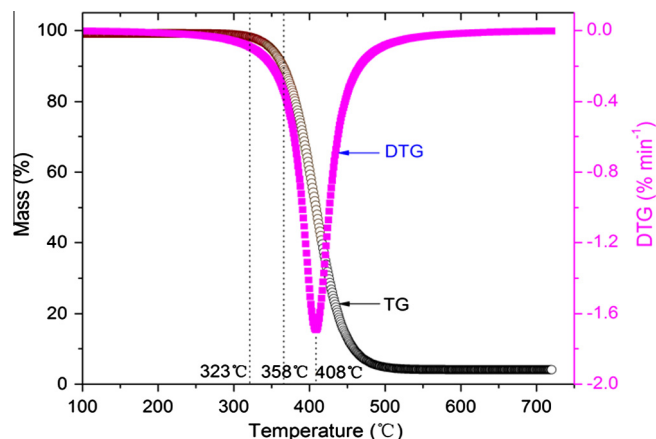


Fig. 1. TG–DTG curves of bitumen decomposition.

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