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# Quantification of physicochemical properties, activation energy, and temperature susceptibility of foamed asphalt binders

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## HIGHLIGHTS

- The paper presents evaluations on the asphalt binders foamed using ethanol and $NaHCO_3$.
- The activation energy, thermal cracking and possibility of chemical reactions were assessed.
- No evidence of chemical reaction was found in the foamed asphalt binders.
- Foaming agents lower the activation energy based on the analyzed data.
- Higher levels of foaming agents increased the resistance to thermal cracking.

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## ABSTRACT

Applications of foamed binder have been spurred by the increased focus on sustainable construction approach and stringent environmental laws. This study was initiated to evaluate the performance of foamed asphalt binder produced using a combination of physical and chemical foaming agents, known as ethanol and sodium bicarbonate ($NaHCO_3$), respectively. This paper presents the properties of foamed asphalt binder assessed using Fourier transform infra-red (FTIR) spectroscopy, asphalt binder cracking device (ABCD), and activation energy analysis. The FTIR test was conducted to evaluate the possibility of any chemical reaction taken place, as well as to characterize the effects of oxidation on the chemical functional groups present in foamed asphalt binders. The ABCD test was carried out to evaluate the thermal cracking temperatures of prepared binders. The activation energy of each binder type was analyzed based on the viscosity test results and Arrhenius equation to estimate the energy required to overcome the intermolecular forces between the molecules in the asphalt binder to initiate flow. The FTIR results reveal that ethanol alone is unreactive with the binder, where most of the functional groups have shown comparable change ratios. This indicates that there are no chemical reactions that occurred in the foamed asphalt binders, either with the addition of ethanol or various combinations of ethanol and $NaHCO_3$. The application of foaming agents definitely lowers the activation energy to overcome the intermolecular forces between the molecules in the asphalt binder to allow flow to occur. The foamed binders were found to have a comparable or better low temperature characteristic as compared to the control binder. A higher dosage of foaming agents proportionally increased the resistance to thermal cracking of asphalt binders. Overall, the use of foaming technique and newly proposed foaming agents has shown great potential to produce eco-friendly pavement material.



## 1. Introduction

Production of asphalt mixture through foaming techniques has become increasingly popular due to its benefits to the environment and as a practical solution to meet stringent environmental regulations in flexible pavement construction. Various types of asphalt foaming units are commercially available to support the application of this method, for instance, WAM-Foam® [1], Low Energy Asphalt (LEA) [2–4], Low Emission Asphalt (LEA2) [5], Gencor® Green Machine Ultrafoam GX® system [6], Aquablack™ WMA [7], Double Barrel® Green System [8], Accu-Shear™ [9] and so on.

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The applicability of the foaming process in bituminous materials was discovered at Iowa State University in 1950s, and the foamed asphalt binder was used as a binding material for different types of soils to enhance its properties. The materials were then used as alternatives to moderate the shortage of good quality aggregates for road construction [10,11]. Hansen and Newcomb [12] reported that the asphaltic mixture production in the United States using the foaming technique became the most popular method in 2011. Based on the survey conducted by the National Asphalt Pavement Association (NAPA), this is mainly due to the emergence of a variety of mechanical foaming units, which instigates about 83%, 92%, and 95% of the warm mix productions in 2009, 2010, and 2011, respectively [12,13]. This resulted in increments of warm mix asphalt usage in 2011 by 67% and 300% compared to 2009 and 2010, correspondingly [13]. Toward its application, numerous methods have been proposed to evaluate the quality of foamed binders. Earlier, Saleh [14] evaluated the quality of foamed binders through the measurement of its viscosity using the Brookfield viscometer during the first 60s. However, it was hard to achieve a good repeatability of viscosity measurements due to the nature of the foamed binder being highly unsteady and non-Newtonian [15]. Meanwhile, Kutay and Ozturk [16] used X-ray Micro-tomography to assess the bubble size distribution in cryogenically frozen samples. The results indicated that the dissipation of moisture in the foamed binder was affected by the performance grade of the asphalt binder and the foaming process that was used.

Fourier Transform Infra-red (FTIR) spectrometry has been used for the identification and quantification of functional groups present in asphalt binders [17]. The absorption of different types of bonds at various wave numbers enabled the identification of the asphalt binder's chemical functionalities [18]. In general, the peak height and peak area in an FTIR spectrum can be used to assess the relative concentration of a specific bond [19]. Based on previous studies, a quantitative oxidation analysis, based on relative peak areas and the changes in the relative peak areas, can give a quantitative assessment of chemical changes. Peak area calculations often provide less variation by eliminating the effects of the thickness of the specimen [20,21].

Namutebi et al. [22] used FTIR to evaluate the effects of foaming on the chemistry of bitumen. Two similar grade asphalt binders from different sources were used. FTIR analysis was performed on the asphalt specimens before and after foaming. Evaluations on the carbonyls and sulfoxides in the compounds were also performed to investigate the effects of aging on the chemical composition of binders. The Carbonyl Index ($I_{C=O}$), Aromatic Index ($I_{C=C}$), and Sulfoxide Index ($I_{S=O}$) are typically used to characterize the oxidation level of asphalt binders [19,23,24]. The study performed by Namutebi et al. [22] showed that the foaming process did not change the chemical compounds in the asphalt binder foamed using water.

Rotational viscosity testing is typically used to characterize the mixing and compaction of asphalt mixtures, as recommended in the Superpave protocol. But, it can also be used to estimate the activation energy of an asphalt binder, which is related to the thermal susceptibility of asphalt binders [25,26]. This principle was clearly discussed by Haider et al. [27], where in a state below ideal conditions, the layers of fluid molecules slide over each other as the fluid flows; however, the existence of intermolecular forces resists the motion of the fluid, which may result in inconsistent distributions of the particles in the mixture. This is due to the asphalt binder not being sufficiently fluid prior to its use in the mixing process and the coating of aggregate particles. The activation energy can be defined as the force required to overcome the intermolecular forces of attraction between the molecules in the asphalt binder to allow flow to occur [27–29]. Generally, a higher activation energy designates that greater force is required for the asphalt binder to flow, which indicates less susceptibility to temperature. This parameter was also used to predict the relative effort to compact asphalt mixtures [28,29]. Different asphalt sources, polymer types, and aging conditions have various impacts on activation energy [28]. Jamshidi et al. [30] mentioned that a higher activation energy indicates that a higher temperature or more energy is required to transform the binder into the liquid state, so that it is fluid enough for mixing with aggregate particles.

The resistance to thermal cracking is also an important parameter in evaluating the capacity of the asphalt mixture to resist low temperature cracking at freezing temperatures, especially in cold regions. Recently, a researcher team at Ohio University developed the Asphalt Binder Cracking Device (ABCD) test to accurately evaluate the thermal cracking of asphalt binders [31,32]. The ABCD was developed to provide a highly repeatable testing procedure to evaluate the performance of an asphalt binder at low temperatures [32]. This device was voluntarily tested in 31 laboratories, including 18 State and Federal Government laboratories, a Superpave Center, a Canadian Province Ministry of Transportation, five universities, and six private laboratories [31]. The ABCD incorporates different coefficients of thermal expansion and contraction of asphalt binders and metals to determine the thermal cracking that would be experienced by asphalt binders at freezing temperature. Based on the validation with the performance in the field, the ABCD cracking temperatures are highly correlated with the performance of all test sections studied [32].

This study was conducted to adapt the idea of using a combination of physical and chemical foaming agents from the polymer industry, and to introduce the idea in the asphalt pavement industry. In order to understand the effects of these newly proposed foaming agents on the pavement composite, it is essential to conduct the assessment at every material phase. In this investigation, all of the specified tests were utilized to quantify the chemical and temperature susceptibility performance of foamed binders. The foamed asphalt binders were prepared using ethanol, $NaHCO_3$, and various combinations of ethanol and $NaHCO_3$ at 100 °C. All of the foamed binders were prepared using manual injection and stirring, and then evaluated at three different aging conditions (unaged, RTFO-aged and PAV-aged) depending on the purpose of each test. The assessment was conducted as part of a continuous effort to improve the adaptability, applicability, and its performance, based on previous studies carried out at this institution [33–43].

## 2. Materials

### 2.1. Samples preparation for chemical reaction analysis

To evaluate the possibility of chemical changes during the foaming process of the asphalt binder, samples were prepared by blending the asphalt binder with the foaming agents in a simple reactor as shown Fig. 1. Prior to having a similar aging condition, all four beakers, each with a specific composition (Table 1), were placed in the same water bath and continuously heated at 100 °C for two hours using a hot plate. All of the blends were then allowed to dry overnight at room temperature to remove excess ethanol. Samples were then tested using FTIR Spectroscopy.

### 2.2. Samples preparation for property characterization

The foamed asphalt binders were prepared using ethanol, $NaHCO_3$, and various combinations of ethanol and $NaHCO_3$ at 100 °C. All of the foamed binders were prepared via manual injection and a stirring as shown in Fig. 2. Asphalt binder PG58-28 was used in the preparation of all of the foamed asphalt binders. Table 2 shows the samples of the foamed asphalt binders involved in this evaluation and their designations. During the preparation of the foamed asphalt binders (which incorporated a combination of foaming agents), the preheated binder was formerly foamed using ethanol followed by the addition of sodium bicarbonate ($NaHCO_3$) powder. In order to evaluate the effect of aging on the chemical functional groups in the foamed binders, the samples were subjected to three different aging conditions: unaged, RTFO-