1. Introduction
Crude oil is the fundamental energy source of the world economy. In earlier times, the process of oil refining was much more simple compared to the present days when refining requires more complex production technologies. Crude oil can be refined in a variety of ways depending on the type of crude oil. Since bitumen is the end-product of refining, the chemical composition differs with each production process. This causes a problem that bitumen, meeting the limit values set by the standard to bitumen properties, are of different chemical composition and microstructure what significantly affects the properties of asphalt mixtures.

Asphalt pavement performance is related to different operation properties which become the main object of today's scientific research. Under unfavorable climatic conditions of Lithuania, where asphalt pavement temperature may rise to +60 °C and in winter may drop to −30 °C, asphalt pavements become not resistant to such temperature variations. The most frequent problem, related to road pavement structure, is rutting. Analysis of bitumen constitution, determination of the relationship between chemical and mechanical properties of bitumen and identification of the recommended values for its fractional composition, ensure that bitumen and at the same time asphalt pavement is resistant to rutting.

The knowledge of crude oil and processing are essential because of established percentage of each bitumen component, which has a high influence to bitumen performance. For instance, asphaltenes are responsible for the presence of structure in bitumen and for their non-Newtonian behavior. They impact on the strength, stiffness and colloidal structure of bitumen. Resins provide adhesion, plasticity and ductility. Saturates and aromatics are responsible for viscosity and fluidity of the bitumen (Allen et al. 2014; Leiva-Villacorta et al. 2013; Nahar et al. 2014; Oyekunle 2007).

Bitumen is an organic material, which can be described as a colloidal system consisting of high molecular weight asphaltene micelles dispersed in a lower molecular weight maltenes (resins, aromatics and saturates). Over the years many...
different techniques were used to determine bitumen chemical composition. Relationship between bitumen chemical composition and asphalt pavement performance, different proposals for the structure of bitumen have been published over the last 100 years. Scientists are still trying to figure out the most reliable test method for the determination of bitumen chemical composition and influence to bitumen physical, mechanical properties and whole asphalt pavement performance (Redelius, Soenen 2014; Wang et al. 2015).

This paper will give an explanation of how the chemistry of bitumen influence physical, mechanical properties and asphalt pavement resistant to rutting.

2. Analysis of research works investigating the effect of bitumen aging on asphalt pavement performance

Bitumen constitution is defined by the chemical composition and structure depending on the type of crude oil and conditions of production technology. Bitumen constitution is described by elemental composition, structural elements, fractional composition and molecular structure. The chemical composition, the structure and the properties of bitumen differ significantly since in the process of bitumen production, depending on the market situation and demand for petroleum products, crude oil may be refined by using different techniques. Bitumen is the end-product of refining, thus its chemical composition differs throughout the production time.

When bitumen is exposed to air it hardens. The increased stiffness is due to increased interactions between molecules. Oxidative aging causes asphalt hardening, which leads to pavement embrittlement and the development of distresses such as cracks or fractures (Lu, Isacsson 2000; Yang et al. 2003; Petersen 2009). Significant progress has been made on understanding the fundamental physical-chemical process of asphalt oxidation (Petersen 2009; Redelius, Soenen 2015; Wang et al. 2015; Yut, Zofka 2014).

Bitumen is a substance made of organic compounds of various hydrocarbons of high molecular weight containing the fragments of aromatic hydrocarbons and remaining functional groups in which carbon, hydrogen and the other heteroatoms (sulphur, nitrogen, oxygen) are found. Also, bitumen contains a small amount of metals: vanadium, nickel, iron, magnesium and calcium in a form of inorganic salts, oxides or complexes with organic compounds (Corbett, Urban 2005; Jones 1992; Lesueur 2009; Petersen 1984).

The fractional composition of bitumen is made of the fractions of organic compounds: asphaltenes, resins, aromatic hydrocarbons and saturated hydrocarbons (Fig. 1).

Bitumen is a colloidal system consisting of maltenes (resins, aromatics, saturates) and asphaltenes (Nellensteyn 1924). The most important components of a colloidal system of bitumen are asphaltenes the quantity and the interaction with the resins, aromatics and saturates of which influence the rheological properties of bitumen (Barre et al. 1997). In order to determine the interaction between bitumen fractional composition and its physical and mechanical properties, the Gaestel Index \((I_c)\) is used. The Gaestel Index indicates a colloidal stability of bitumen and is calculated as follows:

\[
I_c = \frac{\text{Saturates + Asphaltenes}}{\text{Resins + Aromatics}}
\]

Road bitumen is colloidal stable when the Colloidal Instability Index \(I_c\) varies from 0.5 to 2.2. When \(I_c > 0.5\) bitumen is distinguished for hardness, when \(I_c < 0.22\) bitumen is distinguished for softness. For polymer-modified bitumens when \(I_c > 0.28\) the inappropriate selection of polymer or its amount in bitumen is anticipated (Table 1) (Gaestel, Smadja 1971; Oliver 2012).

Fig. 2 describes the relationship between the Gaestel index \((I_c)\) and five bitumens from different producers. There is an optimal range of the \(I_c\) values beyond which the colloidal stability decreases. The index is therefore very helpful in comparing the stability of binder samples. Colloidal stability of bitumen shows an increasing trend with an increased level of asphaltenes.

Bitumen comprises a wide variety of molecules with different size and nature, polar and non-polar molecules. This rich chemistry at a molecular level may result in different intermolecular associations leading to bitumen properties. The basic scheme of the constitution of bitumen is shown in Fig. 3.

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**Table 1. Requirements to the Colloidal Instability Index** (Gaestel, Smadja 1971)

| \(I_c\) | 0.5–2.2 | \(I_c > 0.5\) | \(I_c < 0.22\) | \(I_c > 0.28\) (only PMB) |
|---|---|---|---|---|
| State of bitumen | Colloidal system is stable | Bitumen becomes harder | Bitumen becomes softer | Inconsistency of bitumen and polymer |

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**Fig. 2.** Bitumen colloidal stability
Fig. 3. A basic scheme of the constitution of bitumen

Fig. 4. A scheme of experimental research
3. Experimental research on the determination of the change in bitumen constitution and mechanical properties

Seeking to determine the change in the properties of bitumen of different producers and different type of crude oil before and after short-term aging, experimental research was carried out in the laboratory. During experimental research, bitumens 50/70, 70/100 and PMB 45/80-55 of five different producers were selected and tested in the laboratory (Fig. 4).

The aim of this experimental study was to determine the effect of bitumen constitution on its mechanical properties and asphalt pavement resistance to rutting under the influence of short-term aging.

In the course of experiment, the penetration and softening point of bitumens, produced by different producers, were determined in order to check the grade of bitumens. The dynamic and kinematic viscosity was identified, also the bitumen resistance to hardening under the influence of heat and air, the Fraass breaking point, adhesion properties, chemical composition, structure and mechanical properties of bitumens.

During the experiment, evaluation of the service properties of bitumen were determined. The relationship between the chemical composition and mechanical properties of bitumen was developed. Also the changes in bitumen properties under the influence of short-term aging was determined.

Bitumen, contained in the asphalt layers of road pavement structure, is continuously affected by atmospheric and other environmental factors, therefore over time its properties inevitably change, i.e., bitumen starts to age. Aging is related to the mass loss and oxidation of bitumen components during asphalt mixing, transportation and laying (short-term aging), also to the gradually increasing oxidation during the operation of asphalt pavement structure (long-term aging). Oxidation of thioether to the sulfoxide during a short-term aging is presented in Fig. 5.

Infrared (IR) spectroscopy was applied to determine the functional groups in the organic molecule. Infrared spectrum at the appropriate wave length gave as an information about visible functional groups in bitumen such as sulfoxide, carbonyl groups, aromaticity. The analysis of bitumen functional groups showed the changes in sulfoxide and carbonyl content before and after short term aging.

The highest changes in sulfoxide content is recognized in bitumen from producer C (Venezuelan crude oil), which can be due to the manufacturing processing (Fig. 6).

Investigation of the elemental composition of bitumen using Organic Elemental Analyzer showed a content of sulphur, nitrogen, oxygen, carbon and hydrogen in bitumen. Having made a pyrolysis and having identified a real content of oxygen, it was possible to determine whether the compounds containing sulphur belong to organic or inorganic compounds. This determines a content of metals in bitumen and bitumen resistance to oxidation.

Having written the proton nuclear magnetic resonance spectrum 1H NMR, it was determined that polymer-modified bitumen contains unsaturated hydrocarbons and this has been proven by the response obtained in 1H NMR spectrum. It was also determined that the largest amount of aromatic hydrocarbons and the most changed aromatics was contained in bitumen produced by the producer C, since during refining process no additional techniques were used to extract bitumen. The largest branchiness of molecular structure was defined in bitumen from producers A and B (uncycled crude oil) which worsens interaction between the rings of aromatic hydrocarbons. Therefore, when modifying bitumen, the best option is to select bitumen with the lowest branchiness, for example bitumen from producers D and E. The proton nuclear magnetic resonance spectrum of bitumen 50/70 is given in Fig. 7.

Analysis of the fractional composition of bitumen before and after short-term aging has determined that bitumen of the producer C (Venezuelan crude oil), having the largest content of aromatic hydrocarbons, is distinguished for the lowest penetration, the lowest softening point and the best adhesion with crushed dolomite. Bitumen of the producer E (Russian crude oil) contains the largest amount of asphaltenes, the lowest amount of aromatic and saturated hydrocarbons, therefore it is distinguished.
for the largest dynamic viscosity and softening point, and for the lowest breaking point. Bitumen of the producer A (Russian crude oil) contains the largest amount of saturated hydrocarbons and a certain amount of paraffins which negatively affect bitumen properties (Fig. 8). According to experimental research and other long term scientists’ studies, some of the countries have their own requirements of bitumen fractional composition. Recommended bitumen fractional composition from the experimental research is presented in this Fig. 9.

Bitumen structure is made of various polar and non-polar fragments which interacting in-between form the certain structures called Sol, Gel and Sol-Gel. In nature, water micelle is polar and non-polar fragments encapsulate inside the micelle, whereas polar fragments – locate outside (Fig. 10). Talking about bitumen it is the contrary, bitumen is non-polar. However, asphaltenes are polar and non-polar, so polar fragments are concentrated in the center, while the non-polar – outside. In Gel type structure polar asphaltene part interacts with other polar asphaltenes and non-polar asphaltene part interacts with resins which are non-polar. In the sol-type structures asphaltenes do not react with each other, that is breaks asphaltene interaction and non-polar fragments remain only asphaltenes surrounded by resins (Fig. 11).

Analysis of bitumen photographs with an electronic scanning microscope (SEM) has identified that a larger aggregate size and a lower micelle density is represented by Venezuelan crude oil. Whereas, in bitumen of Russian crude oil, molecular aggregates are smaller but the density of micelles is higher. When using polymers, asphaltenes connect into a wider network and help to maintain a solid structure (Fig. 12). In places where asphaltenes non-polar molecules have better interaction with resins non-polar molecules, the resins are removed much more slowly due to a stronger interaction with asphaltenes, therefore, a lattice structure can be seen (of Gel type). At high temperatures, the interaction between asphaltenes and resins breaks and the microstructure becomes of Sol type.

Bitumen properties make large effect on the quality of asphalt mixture and on the performance of asphalt pavement structure. To determine rheological properties of bitumen the Dynamic Shear Rheometer (DSR) is used which simulates a shear effect of vehicle driving at a certain speed. The DSR is used to determine rheological properties

![Fig. 8. The change in the fractional composition of bitumen 50/70 produced by different producers before and after short-term aging](image)

![Fig. 9. Recommended bitumen fractional composition from the experimental research](image)

![Fig. 10. Micelle in the nature](image)

![Fig. 11. Distribution of micelles in the structures of type Sol and Gel and comparison with a micelle existing in nature](image)

![Fig. 12. Bitumen structure before short-term aging: a – bitumen of the producer B (Russian crude oil); b – bitumen of the producer C (Venezuelan crude oil); c – polymer-modified bitumen of the producer E (Russian crude oil)](image)
of bitumen at medium to high temperatures based on the Complex Shear Modulus $G^*$ and the phase angle $\delta$. The highest average bitumen stiffness at 20 °C temperature was defined in bitumen of the producer C (3808 kPa) since heavy naphthenic crude oil was used in bitumen production. The lowest average bitumen stiffness at a certain temperature was defined in bitumen of the producer E (2147 kPa) since bitumen of this producer is extracted from medium heavy paraffinic – naphthenic crude oil. The largest change in bitumen stiffness before and after short-term aging was represented by bitumen of the producers A and E, the lowest – in bitumen of the producer C. The change in bitumen stiffness was influenced by the type of refining and the type of crude oil. Bitumen extracted from Venezuelan crude oil (naphthenic) already in the very beginning of extraction was distinguished for its higher stiffness compared to bitumens of other producers. Stiffness of bitumens of other producers, extracted from Russian crude oil with a certain amount of paraffin, is lower. The Complex Shear Modulus of bitumen 50/70 of one of the producers before and after short-term aging is given in Fig. 13.

4. Evaluation of the effect of bitumen properties on asphalt pavement performance

The chapter determines bitumen resistance to rutting based on bitumen classification of the United States of America, i.e., requirements of Performance Grade Bitumen Specifications – PG. Statistical evaluation of the relationship between chemical composition and mechanical properties of bitumen was conducted.

The aim of experimental research – to evaluate bitumen resistance to short-term aging and rutting, based on the requirements of Performance Grade Bitumen Specifications and the relationship between chemical and mechanical properties of bitumen.

Since tests were performed at the relatively low temperatures, in order to determine bitumen performance at critically high temperatures, the extrapolation of temperatures was carried out. In order to establish master curves the Sigmoidal model was used (Formula 2):

$$\log \left( \frac{G_{\text{min}}}{G_{\text{max}}} \right) + \left( G_{\text{max}} - \log (G_{\text{min}}) \right) \left( 1 - \frac{1}{\left( 1 + \frac{10^{10 \log(\omega)}}{\beta} \right)^{\gamma}} \right)$$

Based on Christensen, Anderson and Marasteanu (CAM) model (Marasteanu, Anderson 1999) the phase angle was calculated at each temperature under consideration (Formula 3).

$$\delta(\omega) = \frac{90}{1 + \left( \frac{\omega}{\omega_0} \right)^{\nu}}$$

Having calculated the values of bitumen resistance to rutting $\left( \frac{G^*}{\sin \delta} \right)$ before and after short-term aging (RTFOT) at the temperatures: 52 °C, 58 °C, 64 °C, 70 °C, 76 °C and 82 °C, with the help of extrapolation method the temperatures were determined where:

- $\left( \frac{G^*}{\sin \delta} \right) = 1$ (before RTFOT);
- $\left( \frac{G^*}{\sin \delta} \right) = 2.2$ (after RTFOT).

Having determined the values of critical temperature of resistance to rutting of bitumen 50/70, produced by different producers before and after short-term aging and the highest PG temperature, it was obtained that according to PG requirements, the highest bitumen softening point is 64 °C for all bitumens except for the bitumen from producer C (58 °C). This means that bitumens of above producers are the most resistant to rutting and the highest critical temperature at which ruts can occur is 64 °C and 58 °C, respectively. After short-term aging, the softening point according to PG requirements did not change for bitumens of the producers C, D and E, whereas, the softening point of bitumens of the producers A and B fell down from 64 °C to 58 °C. Determination of the resistance to rutting temperatures according to PG requirements for bitumen 50/70 produced by one of the producers is presented in Fig. 14.

5. Conclusions

1. Bitumen, as the end-product of oil refinery, depends on the type of crude and the refining technology. The most bitumen is extracted from naphthenic type crude containing a large amount of asphaltenes, sulfur, and a small amount of paraffin. Using paraffin or aromatic type crude, which contains paraffin, requires additional bitumen production processes to ensure the necessary physical and mechanical characteristics of bitumen.
2. A high asphaltene and aromatic hydrocarbon count reduces bitumen penetration and increases bitumen hardness. Thermal movement of aromatic hydrocarbons leads to a lower softening point. Bitumen fluidity is conditioned by an aromatic hydrocarbons influenced by resins at a certain temperature. A larger amount of asphaltene and paraffin weakens the adhesion characteristics; however, a larger amount of the aromatic hydrocarbons and resins increases it. The largest effect on bitumen chemical composition is represented by elements: carbon, oxygen, and sulfur, influence the structure of asphaltene the most.

3. According Supperpave Performance Grading the highest critical temperature of all bitumen tested is +64 °C, except producer C (Venezuelan crude oil) where the bitumen temperature is only +58 °C. After a short-term aging process (RTFOT), the critical bitumen temperature did not change for producers D and E (Russian crude oil), whereas for the rest of the producers (A, B, and C) the critical bitumen temperature did fall down to +58 °C. Even short term aging has a significant influence on bitumen performance.

4. Heavy metals in bitumen are environmentally harmful and have a negative impact on bitumen aging, i.e. reduce asphaltene in the structure. Sulfur in the organic compounds increases sensitivity to oxidation. The carbon shows a significant amount of condensed aromatic systems, which results in a larger amount of asphaltene. A high amount of asphaltene (>25%) leads to more viscous bitumen performance (so called Gel type).

5. Statistical analysis proved that the fractional composition is independent from bitumen type e.g. 50/70 and 70/100. No correlation between the complex shear modulus and fractional composition was found. Short-term aging influences the complex shear modulus as well as the resins and aromatic hydrocarbons. Distributions of these indices before and after short-term aging differ (the p-value is equal to 0.007; 0.028, and 0.022, respectively). Distributions of asphaltene and saturated hydrocarbons before and after short-term aging do not differ (the p-value is equal to 0.575 and 0.285, respectively).

6. Based on the experimental research results, the fractional composition of bitumen should be as follows: asphaltene (17–30%), resins (40–52%), aromatic hydrocarbons (22–30%), saturated hydrocarbons (6–8%). A bitumen colloidal instability index \( I_c \) is recommended as the asphalt pavement performance indicator during road operation. Bitumen is colloidal stable when the \( I_c \) varies from 0.5 to 2.2. When \( I_c \) is greater than 0.5, bitumen is too hard, whereas for \( I_c \) less than 0.22 bitumen is too soft.

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