STUDY OF ALKYLBENZENES AND NAPHTHALENES OF THE ASHALCHINSKOYE OIL FIELD BY GC-MS

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Abstract. In this article, the composition of alkylbenzenes and naphthalenes of Ashalchinskoye oil was studied using gas chromatographic mass spectrometry (GC-MS). The work included identification and quantitative assessment of alkylbenzenes and naphthalenes both in the initial state and after aquathermolysis with various additives. It was found that thermal and chemical effects lead to changes in the composition of alkylbenzenes, indicating complex processes of decomposition and transformation of hydrocarbons. The results demonstrate the importance of using GC-MS to study the composition of oil and its transformations during aquathermolysis.

Keywords: Alkylbenzenes, Naphthalenes, Ashalchinskoye oil field, Gas chromatography–mass spectrometry (GC-MS), Hydrocarbon composition, Aromatic hydrocarbons, Structural analysis, Molecular composition.

Аннотация: В данной статье исследован состав алкилбензолов и нафталинов нефти Ашальчинского месторождения с использованием газовой хромато-масс-спектрометрии (ГХ–МС). Работа включала идентификацию и количественную оценку алкилбензолов и нафталинов как в исходном состоянии, так и после акватермолиза с различными добавками.

ISSN 3030-3907

Установлено, что термические и химические воздействия приводят к изменениям в составе алкилбензолов, что указывает на сложные процессы разложения и трансформации углеводородов. Полученные результаты демонстрируют важность применения метода ГХ–МС для изучения состава нефти и её преобразований в ходе акватермолиза.

Ключевые слова: Алкилбензолы, Нафталины, Ашальчинское нефтяное месторождение, Газовая хромато-масс-спектрометрия (ГХ–МС), Углеводородный состав, Ароматические углеводороды, Структурный анализ, Молекулярный состав.

Annotatsiya: Ushbu maqolada Ashalchinskoye neft koni neftining alkilbenzenlar va naftalenlar tarkibi gaz xromatografik mass-spektrometriya (GC–MS) usuli yordamida o‘rganildi. Ishda alkilbenzenlar va naftalenlarning dastlabki holatda hamda turli qo‘shimchalar bilan akvatermolizdan so‘ng aniqlanishi va miqdoriy baholanishi amalga oshirildi. Aniqlanishicha, issiqlik va kimyoviy ta’sirlar alkilbenzenlar tarkibida o‘zgarishlarni keltirib chiqaradi, bu esa uglevodorodlarning parchalanish va o‘zgarish jarayonlarining murakkabligini ko‘rsatadi. Olingan natijalar GC–MS usulining neft tarkibini va uning akvatermoliz jarayonidagi o‘zgarishlarini o‘rganishda muhim ahamиятга ega ekanligini ko‘rsatadi.

Kalit so‘zlar: Alkilbenzenlar, Naftalenlar, Ashalchinskoye neft koni, Gaz xromatografik mass-spektrometriya (GC–MS), Uglevodorod tarkibi, Aromatik uglevodorodlar, Tuzilma tahlili, Molekulyar tarkib.

INTRODUCTION

The study of the composition of oil and its refined products is one of the key tasks in petrochemistry and geochemistry. Alkylbenzenes, which are aromatic hydrocarbons, play a significant role in understanding the mechanisms of formation, processing and behavior of oil under various conditions. Determining their composition and concentration allows us to assess the quality of oil, its age and processing conditions [1, 7].

Gas chromatography combined with mass spectrometry (GC-MS) is a highly sensitive and accurate method of analysis that provides a detailed study of complex hydrocarbon mixtures in oil. The use of this method allows not only to determine the component composition of oil, but also to record changes occurring under the influence of geochemical and thermal processes such as aquathermolysis, etc. [8, 24].

The purpose of this study is a comprehensive study of the composition of alkylbenzenes and naphthalenes of Ashalchin oil using the GC-MS method.

Materials and methods

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The study used oil samples extracted at the Ashalchinskoye field. The objects of study were both the original oil samples and oil subjected to aquathermolysis with the addition of various reagents used as a catalyst. Carrying out aquathermolysis made it possible to simulate the conditions of the thermal effect of reagents on oil in order to study changes in the composition of hydrocarbons, including alkylbenzenes.

To isolate saturated hydrocarbons containing alkylbenzene compounds, the oil was preliminarily subjected to fractional distillation. The process of separating the components was carried out on a Chromatec-Crystal 5000 gas chromatograph. A CR-5ms capillary column with a length of 30 meters, an internal diameter of 0.25 mm and a stationary phase layer thickness of 0.25 μm was used, which ensured high resolution. Helium was used as a carrier gas, which ensured high accuracy and stability of the analysis. Chromatography was carried out using the linear temperature programming mode, which included several stages. The analysis process included sequential heating with carefully controlled parameters. The initial stage was carried out at a temperature of 100 °C, after which the first heating range ensured a rapid temperature increase at a rate of 125 °C per minute in the range from 100 °C to 150 °C. In the second range from 150 °C to 310 °C, the heating rate decreased to 3 °C per minute, which contributed to a more accurate separation of the components. After reaching 310 °C, the temperature was maintained in the isothermal mode for 8 minutes to complete the separation process. A mass spectrometric detector with an ionization energy of 70 eV was used to identify the components, which contributed to the formation of fragment ions characteristic of organic compounds. The ion source operated at a temperature of 270 °C to prevent condensation of the compounds and ensure their stable ionization. Mass scanning was performed in the range from 50 to 500 Da with a frequency of 0.2 scans per second, which ensured high time resolution and accuracy of analysis of complex mixtures. These parameters made it possible to achieve accurate separation, reliable detection and correct identification of hydrocarbons contained in oil samples, as well as determination of their structure and composition. The chromatogram of the studied sample is shown in Fig. 1.

ISSN 3030-3907

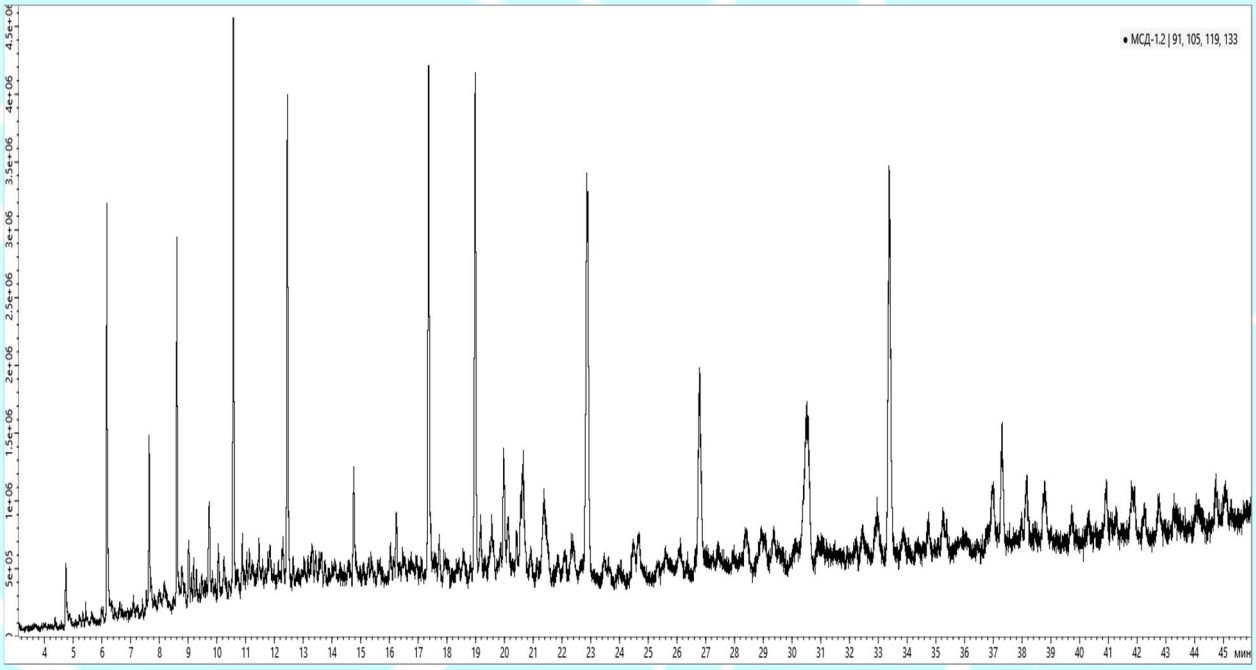


FIGURE 1. Chromatograms of the alkylbenzene fraction of oil Identification of alkylbenzenes was performed based on NIST library data and literature sources. The relative content of each identified alkylbenzene was calculated as the ratio of its concentration to the total concentration of all identified compounds in the sample.

Result And Discussion

As a result of the conducted studies by the method of gas chromatography-mass spectrometry (GC-MS), the composition of alkylbenzenes in oil of the Ashalchinskoye field was studied in detail, both in the original sample and after aquathermolysis with various additives. The analysis showed that the oil of the Ashalchinskoye field contains a wide range of alkylbenzenes, among which methylbenzenes (toluene), ethylbenzenes, propylbenzenes and other alkyl-substituted benzenes predominate. In the original oil sample, methylbenzenes had the highest concentration, which may indicate a high degree of biochemical decomposition of organic matter at the stage of oil formation. Fig. 2 shows data on the content of alkylbenzenes of different carbon chains (C10-C18 and C19-C25) in oil of the Ashalchinskoye field under various processing conditions.

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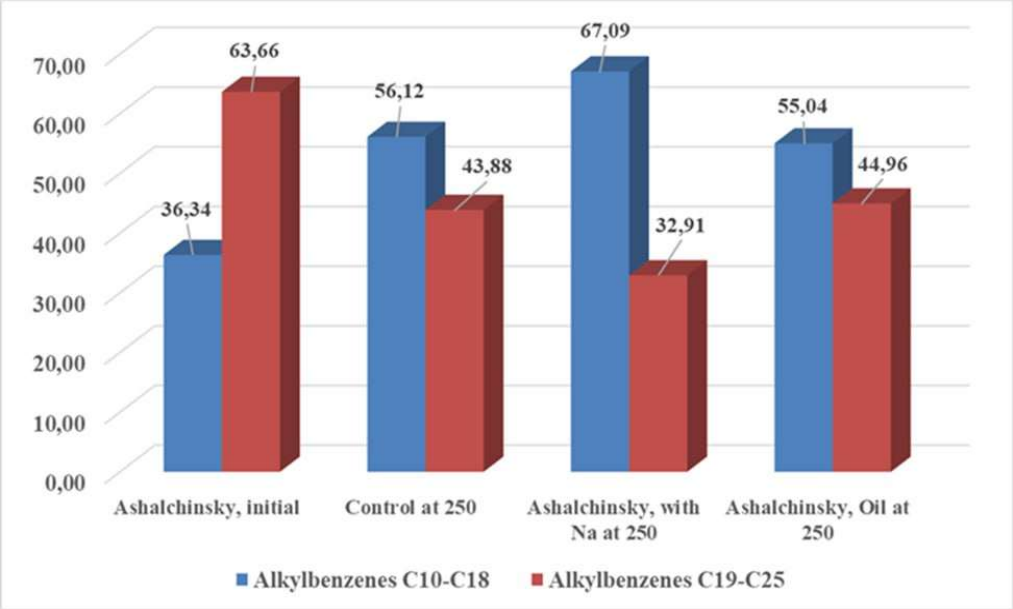


FIGURE 2. Mass fraction of alkylbenzenes C10-C18 and C19-C25 The content of C10-C18 alkyl benzenes in the original oil is 36.34%. This is the base value for comparison with the results after heat treatment. After heat treatment without additives (control at 250 °C), the content of C10-C18 alkyl benzenes increases to 56.12%.

This significant increase indicates thermal decomposition of larger hydrocarbons (C19-C25) to lighter alkyl benzenes. With the addition of sodium, the content of C10-C18 alkyl benzenes increases even more to 67.09%. This indicates that sodium helps catalyze the thermal decomposition of heavy hydrocarbons, increasing the yield of lighter alkyl benzenes. The addition of oil results in a C10-C18 alkyl benzene content of 55.04%, which is slightly less than in the control sample.

The content of alkylbenzenes C19-C25 in the original high-viscosity oil is 63.66%. After heat treatment without additives, the content of C19-C25 alkyl benzenes decreases to 43.88%. The decrease in the concentration of these heavy alkyl benzenes confirms the decomposition of larger molecules during heating, which correlates with the increase in the content of C10-C18 alkyl benzenes. With the addition of sodium, the content of C19-C25 alkyl benzenes decreases further to 32.91%. This confirms that sodium enhances the thermal decomposition of heavy hydrocarbons, promoting the formation of lighter fractions. With the addition of oil, the content of C19-C25 alkyl benzenes is 44.96%, which is higher than with the addition of sodium, but still lower than that of the original oil. This shows that the oil is not as effective in promoting the decomposition of heavy hydrocarbons compared to sodium. The composition and content of naphthalene hydrocarbons were also analyzed. Fig. 3 shows the data on the content of naphthalene hydrocarbons (C12H12, C13H14, C14H16, etc.) for different experimental conditions: Original oil from the Ashalchinskoye field (blue line). Control samples

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at 250°C (red line). Samples with the addition of sodium at 250°C (green line). Samples with oil at 250°C (purple line). The relative content of naphthalene hydrocarbons C12H12, C13H14 and C14H16 is shown as histograms in Fig. 4.

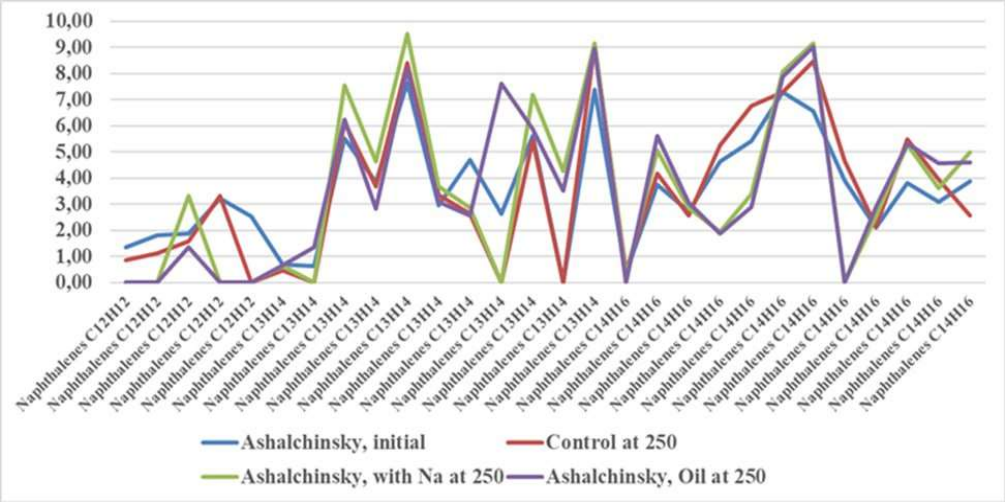


FIGURE 3. Chromatograms of naphthalene hydrocarbons after aquathermolysis

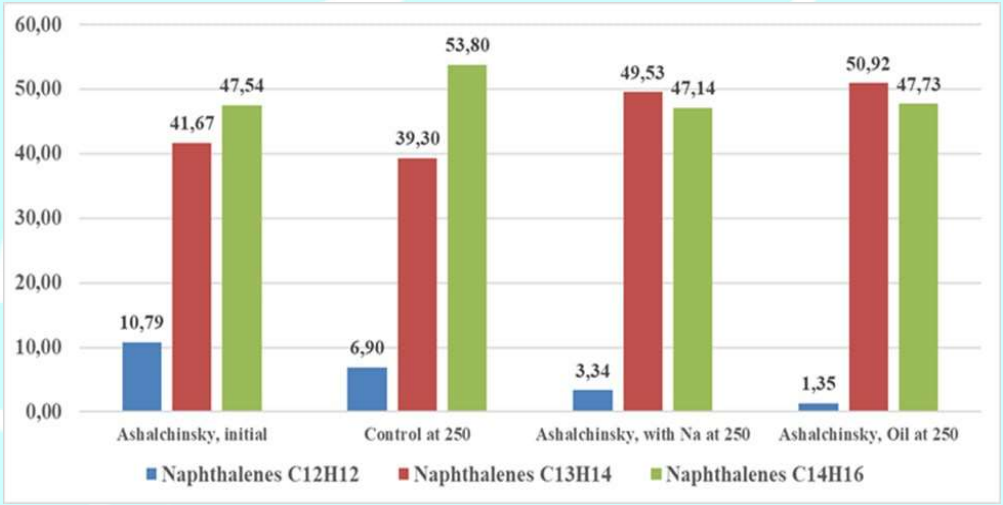


FIGURE 4. Relative content of naphthalene hydrocarbons

It is evident from Fig. 4 that the initial sample ("Ashalchinis") has a low content of naphthalenes C12H12 (10.79%) and a significant predominance of hydrocarbons C13H14 (41.67%) and C14H16 (47.54%), which indicates a high content of heavy naphthalenes. In the control sample, processed at 250°C without a catalyst, the content of C12H12 decreases to 6.90%, and the proportion of C13H14 and C14H16 increases to 39.30% and 53.80%, respectively, which indicates a redistribution of fractions under the influence of temperature. With the addition of sodium ("Ashalchi with Na at 250°C"), the content of C12H12 decreases to 3.34%, which is the minimum value among all the samples, and the proportions of C13H14 and C14H16 are 49.53% and 47.14%, which reflects the destruction of light components and the formation of heavier fractions. In the sample with the addition of oil ("Ashalchi oil at 250°C"), the content of C12H12 reaches a minimum value (1.35%), while C13H14 and C14H16 are distributed

ISSN 3030-3907

almost uniformly (50.92% and 47.73%), which may be due to the catalytic effect of oil, which promotes the redistribution of heavy components.

General conclusions show that heat treatment of high-viscosity oil at 250°C without catalysts leads to an increase in the proportion of heavy naphthalenes (C14H16), which is associated with the thermal effect on hydrocarbon fractions. Addition of sodium or oil leads to a significant decrease in the content of light naphthalenes (C12H12), which indicates increased destruction of light components. At the same time, when using catalysts (Na or oil), a stable proportion of heavy naphthalenes is observed, which may be associated with redistribution or stabilization of processes under aquathermolysis conditions. The results obtained confirm the high efficiency of catalysts in processing heavy oil and controlled conversion of naphthalene hydrocarbons, which makes this approach promising for improving oil quality.

Thus, heat treatment at 250 °C promotes the redistribution of hydrocarbon fractions, reducing the content of heavier alkylbenzenes (C19–C25) and naphthalenes (C12–C16) with an increase in the proportion of lighter hydrocarbons (C10–C18). Addition of sodium photoemulsion significantly increases the efficiency of thermal decomposition of heavy hydrocarbons, providing an increased yield of light alkylbenzenes compared to control samples. Aromatic hydrocarbons (alkylbenzenes) play a key role in optimizing the composition and properties of the resulting gasoline. Due to their high resistance to detonation, they increase the octane number of gasoline, which is especially important for stable engine operation under increased loads.

The high energy value of alkylbenzenes makes them a valuable fuel component capable of increasing the calorific value of gasoline. In addition, their use helps to reduce the content of sulfur-containing compounds in fuel, which reduces sulfur dioxide (SO_2) emissions and increases the stability of fuel mixtures due to their dissolving properties. On the other hand, excess alkylbenzenes can lead to increased emissions of polycyclic aromatic hydrocarbons (PAH), which requires compliance with strict environmental standards.

Low-molecular alkylbenzenes, such as toluene, additionally contribute to improving the evaporation of gasoline due to their low boiling point, facilitating engine starting at low temperatures. Thus, alkylbenzenes are important components that improve fuel quality. However, their use must be balanced with environmental requirements.

CONCLUSION

In the course of the study, using the method of gas chromatography-mass spectrometry (GC-MS), the composition of alkylbenzenes and naphthalenes of Ashalchin oil was analyzed in detail both in the initial state and after

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aquathermolysis with various catalysts. Thermal treatment at a temperature of 250°C led to the redistribution of hydrocarbon fractions, a decrease in the content of heavy alkylbenzenes (C19-C25) and naphthalenes (C12-C16) with a simultaneous increase in the proportion of light hydrocarbons (C10-C18). The addition of sodium significantly increased the efficiency of decomposition of heavy hydrocarbons, ensuring a high yield of light alkylbenzenes.

Analysis of the composition of naphthalene hydrocarbons showed that the use of sodium or oil leads to the destruction of light naphthalenes (C12H12) and the redistribution of heavy fractions. The obtained data confirm that the addition of catalysts enhances the processes of thermal decomposition of heavy hydrocarbons, which makes the aquathermolysis method promising for processing high-viscosity oil.

The results of the study emphasize the importance of the GC-MS method for analyzing complex hydrocarbon mixtures and studying changes in their composition under thermal and chemical influences.

Acknowledgments

The authors affirms absence of conflicts of interest, ensuring transparency and integrity in the research.

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ISSN 3030-3907