Characterization of Asphaltene from Kazakhstan Crude Oils

By

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ORIGINALITY STATEMENT

I, Madina Bakhytzhanova, hereby declare that this submission is my own work and to the best of my knowledge it contains no materials previously published or written by another person, or substantial proportions of material which have been accepted for the award of any other degree or diploma at Nazarbayev University or any other educational institution, except where due acknowledgement is made in the thesis.

Any contribution made to the research by others, with whom I have worked at NU or elsewhere is explicitly acknowledged in the thesis.

I also declare that the intellectual content of this thesis is the product of my own work, except to the extent that assistance from others in the project's design and conception or in style, presentation and linguistic expression is acknowledged.

Signed on 15.04.2020

NOMENCLATURE

f_a	Aromaticity factor
n	Average number of carbon per alkyl side chain
La	Diameter of aromatic unit
FTIR	Fourier Transform Infrared
C NMR	Carbon Nuclear Magnetic Resonance
H NMR	Proton Nuclear Magnetic Resonance
TGA	Thermogravimetric analysis
SEM	Scanning Electron Microscopy
EDS	Energy Dispersive Spectroscopy
DTG	Derivative thermogravimetry
SARA	Saturates Aromatics Resins Asphaltenes
TLC-FID	Thin layer chromatography with flame ionization detection
AI	Aromaticity index
DBE	Double-Bond Equivalent
GPC	Gel permeation chromatography
Mn	Number average molecular weight
Mw	Molecular weight
VPO	Vapor Pressure Osmometry
PAH	Polycyclic aromatic hydrocarbons
Φ	Shape factor
R^2	Determination coefficient
XRD	X-Ray Diffraction
C_{ar}	Aromatic carbons
C_{al}	Aliphatic carbons

ABSTRACT

Despite availability of an extensive literature on characteristics of asphaltene molecules and their ability to aggregate, it remains still a very active research area owing to complex molecular structure and thermodynamic behavior of asphaltenes. Characteristics and properties of asphaltenes vary greatly depending on the origin of the oils by molecular weight, aromaticity, and elemental composition, and functional groups. Similar research is not yet reported in the literature for asphaltenes extracted from crude oils in Kazakhstan. There are several petroleum deposits in the West of Kazakhstan characterized by problem of asphaltene deposition in the process of oil production and transportation via pipelines. In this research work, first asphaltenes were extracted from three crude oils originated from West Kazakhstan using *n*-heptane and the IP-143 method. Then, the asphaltenes were characterized by using various methods including CHNS/O analysis to obtain elemental content of asphaltenes, TGA analysis to determination kinetic behavior of asphaltenes under thermal destruction, scanning electron microscopy to study the surface morphology of the asphaltenes. Additionally, three spectral analyses methods namely the Fourier Transform Infrared, Carbon and Proton NMR, and RAMAN spectroscopy were used to investigate the average molecular parameters: aromaticity factor f_a, the number of carbons per alkyl side chain (n), and diameter of aromatic unit L_a. According to the results obtained from this study, the aromaticity factor (f_a), which shows the stability of asphaltenes, is higher for the light oil sample. The high value of this parameter shows more tendency to asphaltene aggregation. However, the absence of OH functional group in lighter oil sample compensates the high value of f_a, and equalizes the crude oil's stability. Also, the average number of carbons per alkyl side chain (n), varies on the range of 9 to 18 in all asphaltene samples tested. Diameter of the aromatic unit (L_a) in all three asphaltenes showed ranges from 1.36 to 1.94nm which is in a good agreement with other research works reported in the literature. Spectral analysis illustrated the presence of the main functional groups such as alcohols, aliphatic, aromatic, carbonyls, methylene, and methyl in the Kazakhstani asphaltenes. Additionally, thermogravimetric analysis revealed the temperature ranges of decomposition of soft and hard asphaltenes. The morphology of asphaltenes indicated that asphaltenes are characterized by both an irregular surface consisting of micro particles with a diameter of 4-15µm, and a smooth plain surface. The insights obtained from conducting this research will help the future research in development of proper asphaltene deposition inhibitors from major Kazakhstani crude oils.

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1. INTRODUCTION

In this chapter, first a background information is provided on the issue of asphaltene disposition worldwide and in the Republic of Kazakhstan and characteristics of asphaltene molecules. Then, the statement of problem is presented to justify the need for this research on characterization of asphaltene samples extracted from some West Kazakhstani crude oils. In the consequent sections, the industrial relevance of the current research along with the research objectives and research methodology are presented. In the final section of this chapter, the organization and structure of this thesis is described to ease the navigation throughout this report for the readers.

1.1 Background

The problem of flow assurance during oil production and mitigation of asphaltene deposition is one of the most significant concerns for the researchers nowadays. Precipitation of asphaltene particles from the oil system can cause enormous problems at various stages of production, refining or transportation. This may be due to fact that the separation of solid fractions from the liquid phase may block the pore spaces of the reservoirs, plug the bottom-hole zone of the wells, or settle on the walls of the tubing and line pipes. Asphaltene deposition can create problems associated with their precipitation and subsequent sticking, and consequently lead to blockage of the pipeline, wells, surface equipment, and pore space in reservoir formations.

Intensive production of light oils will ultimately lead to depletion of reserves of such reservoirs. This in turn will inevitably lead to increased production and use of heavy oils and heavy oil residues accumulating significant amounts of non-hydrocarbon high molecular weight heteroatomic compounds - resins and asphaltenes, containing condensed aromatic structures. These compounds complicate the production of oil, preventing the easy oil recovery.

The disposition of oil toward precipitation of asphaltenes does not depend only on the amount of asphaltenes contained in it. For instance, the Mata-Acema oil field in Venezuela has serious problems related to asphaltenes deposition, although their asphaltenes content varies between 0.4%–9.8%. Another example is the Boscan oil field which does not have any issues with asphaltenes deposition; while, the asphaltene content in oil is very high ~ 17.2%. One more confirmation to this, is the Hassi-Messaoud field in Algeria, literally in the first two weeks of production, the wells lost up to 25% of the initial pressure due to problems with asphaltenes, which contained only about 0.062% in the oil (Civan, 2016).

Considering the above mentioned issues, the number of researches done on various aspects of asphaltene precipitation and deposition and related topics is increasing every year (Figure 1-1) which shows the evermore increase in importance of this research topic for both academic and the petroleum industry. The molecular nature of asphaltenes is studied by many scientists around the world. Spectral and analytical analyzes characterize asphaltenes, which vary greatly depending on the origin of the oils by molecular weight, aromaticity, and elemental composition, and functional groups. The choice of a method of controlling asphaltene deposition should be based on experimental results and technical-economic assessment. To prevent the formation of solid precipitation in the wells, it is advisable to conduct laboratory studies to determine their composition and to select dissolving agent of deposits, as well as for determination of effective and economically attractive asphaltene inhibitors. Undoubtedly, there is no worth to propose chemical additives and measures against unless the appropriate properties about characteristics of Kazakhstani asphaltenes are not known. Hence, the presence of problematic oil reservoirs with asphaltene deposition issue in Kazakhstan crude oil suggests the need for conducting high quality research work on characterization of asphaltenes extracted from major crude oils in the country. Such studies are needed to further our understanding of the molecular structure and other properties of asphaltenes in Kazakhstan in order to better understand their behavior towards deposition during oil production.

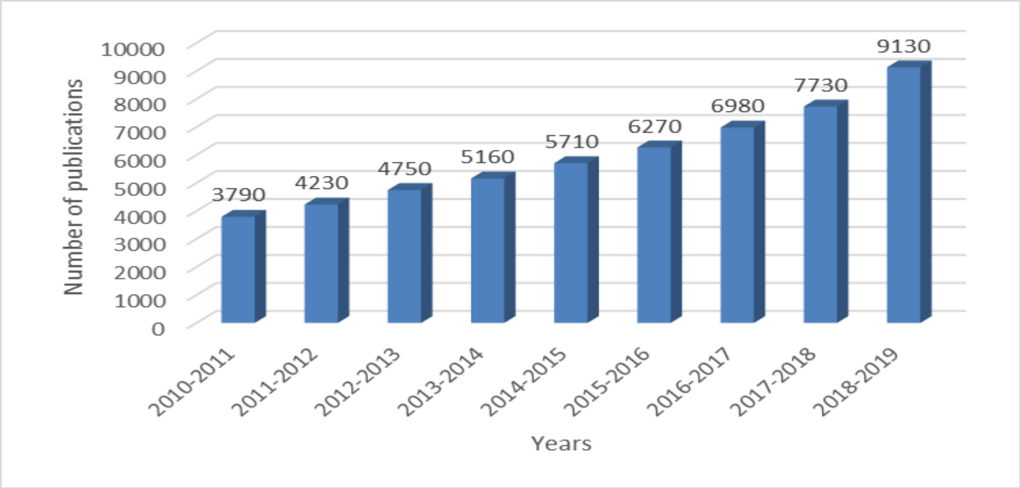


Figure 1-1. The number of annual publications related to asphaltene subject within 2010-2019 years (Source: Google Scholar)

1.1 Problem statement

Asphaltenes are characterized by their extremely rich set of chemical and molecular structures. Despite availability of an extensive literature (Figure 1-1) on the study of asphaltene structure and their ability to aggregate, this remains still a very active research area owing to complex molecular structure and thermodynamic behavior of asphaltenes. A large body of research has been reported on precipitation, aggregation, and deposition of asphaltene flocs for the purpose of forecasting, modeling, and controlling asphaltenes' deposition in the oil industry. As can be judged from the statistics of Google Scholar, an interest in the problem of asphaltenes does not subside over the years, but on the contrary is one of the most acute problems in the whole world, which may be caused by changes and related difficulties in the oil production process. The number of publications related to this topic is growing annually, starting from the data in 2010 till 2019 (Figure 1-1).

Several studies related to characterization of the asphaltene are reported for asphaltenes obtained from Colombia, Mexico, Italy, Turkish, Algeria, and other countries and there is a lack of high quality research and publications on characteristics of asphaltenes from Kazakhstan in the literature (Poveda-Jaramillo et al., 2016; Ancheyta et al., 2002; Calemma et al., 1994; Yasar et al., 2009; Larbi et al., 2015). The molecular structural properties of asphaltenes and their disposition for aggregation largely depend on the geological origin and physicochemical environment (Vukovic et al., 2019; Cruz et al., 2017; Yudin et al., 1998). These studies confirm that asphaltene molecules are unique in their nature and characteristics. This issues combined with the fact that there is extremely low knowledge of asphaltenes characteristics and behavior originated from Kazakhstan and the insufficient number of high quality research papers related to characteristics of asphaltenes makes this topic of worthy of a through and comprehensive research work. Hence, owing to uniqueness and complexity of asphaltene molecules, their characterization before doing any research on development of asphaltene deposition inhibitors for Kazakhstani oil fields is inevitable. This is the major motivation behind this research work.

1.2 Relevance to the industry

There are several petroleum deposits in the West of Kazakhstan characterized by the problem of deposition of asphaltene in the process of oil production and transportation. In modern Kazakhstan, this issue has not been studied properly yet. Since the collapse of the Soviet Union, the domestic oil industry was aimed at producing easily recoverable oil. For this reason, today the country is facing challenges in way of oil production from problematic reservoirs and there is a lack of adequate knowledge and technology in addition to insufficient number of scientific and engineers on the topic of asphaltene and related flow assurance issues in Kazakhstan.

As an example, according to the reservoir development plan of Kariman oil field, the oil production suffers difficulties from asphaltene deposition. Thus, in different years, well cleanout frequency (intervals) varied in average from 8.25 days in 2014 to 12.75 days in 2017. During this period of time various measures to control asphaltene deposits including scrubbing and hot oil treatments were tried. On average, 2-3 days per moths was dedicated to such treatments (The technological scheme of the development of the North Kariman field, 2017). But these measures are not preventive and asphaltene deposition remains to be the problem that has to be solved on a daily basis because deposition of asphaltene can eventually shut down the wells causing loss of oil production in addition to additional financial costs for repairing the wells. The consequences of asphaltene deposition described above represents a serious challenge for the petroleum sector in Kazakhstan from the viewpoints of technical, technological, and economic.

1.3 Research objectives

The primary objective of this research work was to extract and characterize 3 asphaltene samples from 3 West Kazakhstani crude oils using various analytical methods such as spectral chromatography, and thermal destruction approaches. The research objectives aimed at during the course of this study were:

- Characterizing the asphaltenes extracted from Kazakhstan crude oil using different methods including:
    - Spectral analysis: FTIR, C and H NMR, Raman
    - CHNS/O, TGA, SEM
- Determination of the average molecular parameters such as aromaticity factor (f_a), the average number of carbons per alkyl side chain (n), diameter of the aromatic unit L_a;
- Studying functional groups of asphaltene components;
- Conducting thermal destruction of the chemical components;
- Studying the morphology and size of microparticles in the composition of the asphaltenes.

1.4 Research methodology

The achievement of this goal involves the implementation of empirical research and laboratory works. All known and utilized empirical research methods give only averaged characteristics to asphaltenes, which are in reality complex compositions consisting of aromatic molecules interconnected by alkyl chains and containing heteroatoms. The molecules included in the composition of asphaltenes are characterized by various properties, such as aromaticity (f_a), the average number of carbon per alkyl side chain (n), diameter of aromatic unit, (L_a), functional groups, elemental and metal compositions (Mullins and Sheu, 2013). In fact, any of the analytical methods that can individually characterize one of the properties of asphaltenes is important, but no less essential is the incorporation of all the results and combining them into one comprehensive understanding.

During this research the crude oil properties API gravity and viscosity were investigated in order to observe the relation of asphaltene content with the main crude oil characteristics. The average molecular parameters: , n, and La were aimed to be measured by spectral analysis such as, carbon NMR, proton NMR, and Raman spectroscopy, respectively. Further, the functional groups that are responsible for the characteristic chemical reactions of asphaltene molecules were studied by FTIR spectroscopy. Additionally, thermal decomposition of asphaltenes was performed by TGA analysis, which enabled the observation of the kinetic behavior of asphaltenes. Finally, SEM analysis was applied to investigate the surface morphology of asphaltenes.

1.4 Thesis organization

This thesis consists of the following six chapters: introduction, literature review, project plan, methodology (The description of the experimental and the analytical methods used), results and discussion, and finally conclusions and recommendations. Chapter 1 provides background information about relevance of the asphaltene characterization to tackle the asphaltene disposition problem and flow assurance issues in the oil field followed by industrial relevance of the research topic, problem statement, and research objectives and also gives a brief coverage to the methodologies used, and organization of the thesis. Chapter 2 contains a literature review with more detailed information on asphaltenes, their properties, and well-known approaches for asphaltene characterization. The organization and time management plans in order to complete the project on time are presented in Chapter 3. It also contains information about the project risks, Chapter 4 is the methodology part where the information on the experimental and analytical methods and procedures are presented in detail. In Chapter 5, the results obtained from the experimental and analytical work performed are presented, as well as, discussion of the results obtained. Finally, the conclusions and some recommendations future/further research based on the conduced research works are provided in Chapter 6.

2. LITERATURE REVIEW

This literature review highlights the genesis of asphaltenes, reveals its most important properties, which cause the aggregation of molecules at different stages of production in the oil industry. It describes various techniques of studying the properties of asphaltenes, as well as their extraction methods from crude oil. In addition, this chapter contains information on various studies by scientists around the world who are linked by one passion for the research of asphaltenes.

2.1 Asphaltene classification

The term “asphaltene” was firstly introduced by French chemist Jean-Baptiste Boussingault in 1837. At the present time, asphaltenes are most often called as components of oil, insoluble in n-alkanes (most often, in normal pentane, and normal heptane), but completely soluble in aromatic solvents, such as toluene, benzene, or xylene. The separation of asphaltenes from oil and petroleum products is based on this property, and n-alkanes usually are used to precipitate asphaltenes from crude oil. Despite the fact that the discovery and the first acquaintance with asphaltenes were more than a hundred years ago, the chemical composition and molecular structure still have their vagueness (Vargas and Tavakkoli, 2018).

Heteroatom content of the crude oil consist of two main components: resins and asphaltenes. The molecules of those compounds apart from organogenic elements contain carbon, hydrogen, oxygen, nitrogen, and sulfur, they also concentrate almost the whole amount of metals from which consists of the oil (Ni, V, Fe, Co, Al, Mo, Mn, etc).

Total content of high molecular weight heteroatomic components in the crude oil can vary in wide range from trace amount till 40% and above. Some of the heavy oil by their resinous-asphaltenic content become very close to natural bitumen.

Classification of the crude oil by the composition of resinous-asphaltenic content is given in the Table 2-1.

Table 2-1 Content of resins and asphaltenes in oil obtained on the territory of Kazakhstan and Russia, (Sergienko et al., 1979)

Oil	Specific weight	Crude oil		Resinous-asphaltenic content	
		Resin, %	Asphaltene, %	Resin, %	Asphaltene, %
Dossor	0.892	2.0	0.0	100	0.0
Zhetybai	0.860	15.5	2.7	85.0	15.0
Uzen	0.867	17.0	2.6	87.0	13.0
Romashkinskaya	0.867	10.6	3.8	74.0	26.0

As can be seen, the asphaltene content in the crude oil ranges from 1% to 4-5%, and in resinous-asphaltenic content asphaltene amount in average 15-30% depending on the origin of oil.

2.2 Asphaltene extraction methods

In recent years the SARA method has been used in laboratory to determine the group analysis of crude oil. This method is based on the separation of oil on saturate, aromatics, resins and asphaltenes compounds by their solubility and polarity. This method allows to describe the oil system and its components; describe the change in the content of asphaltenes as the pressure drops; determine the number of dropped asphaltenes, install upper and lower boundary of the deposition of asphaltenes (Strausz et al., 2008). Another advantage of this method is the direct release of asphaltenes from crude oil, which allows to further explore with using mass spectroscopy, molecular diffusion methods. The advantage of the SARA method is also its simplicity and applicability in many laboratories. The methodology for the separation of oil into composite groups looks according to the Figure 2-1.

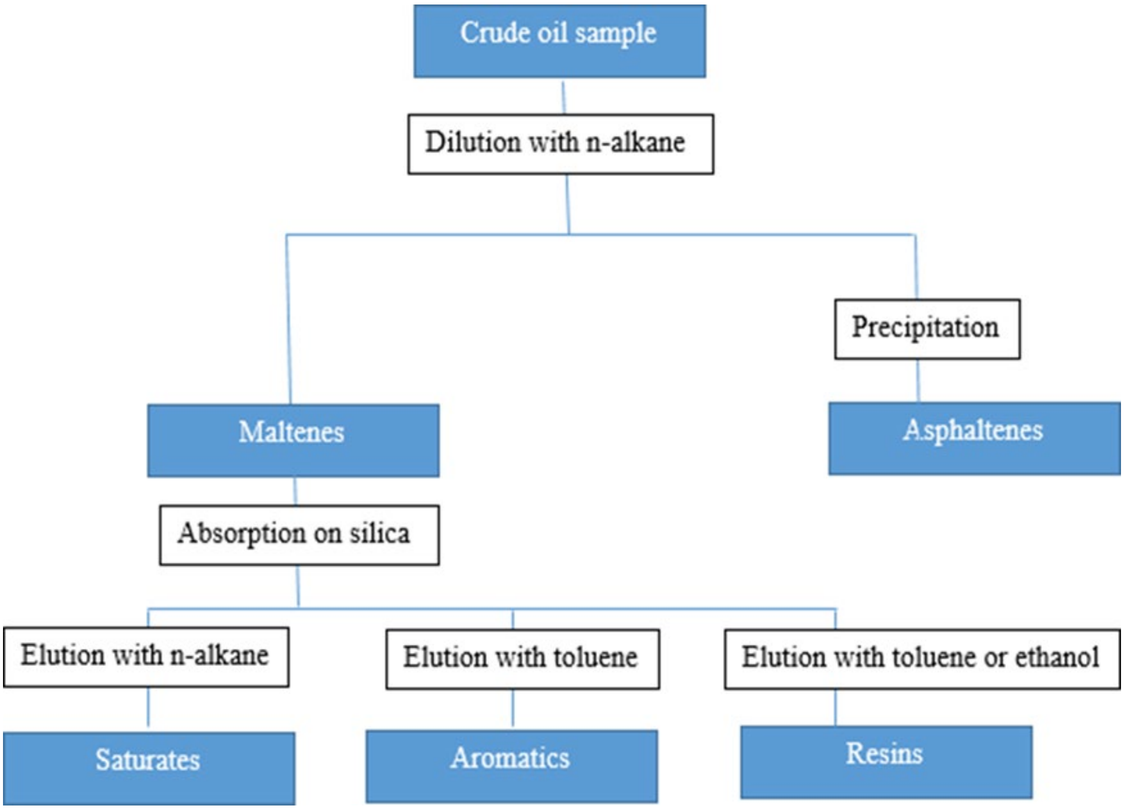


Figure 2-1. Separation of crude to saturates, aromatics, resins and asphaltenes as per SARA method (From Vargas and Tavakkoli, 2018)

Nowadays there are three general methods for separating fractions into Saturates, Aromatics, Resins and Asphaltenes: automated high-pressure liquid chromatography (HPLC), introduced by two scientists Suatoni J.C and Swab R.E. in 1975, which is based on the polarity and solubility; clay-gel adsorption technique, using clay and silica gel; and the third one is the thin layer chromatography with flame ionization detection (TLC-FID) or Iatroscan, which was developed by Suzuki in 1972 (Tavakkoli et al., 2017; Fan et al., 2002).

Asphaltenes can be removed from crude oil using conventional IP-143 technology (ASTM D6560 standard) (Vargas and Tavakkoli 2018). The essence of this technique is to separate the sample product in an amount of 5-10 grams. During this method, a test sample of crude oil is mixed with n-heptane in a ratio of 40:1, and then heated under reflux. After heating, the mixture of *n*-alkane with oil sample is left plugged for a while in a dark place. The asphaltenes are then precipitated and separated from the maltenes using the filter paper. Further, the contents of the filter paper are placed in a Soxhlet apparatus (Figure 2-2) and refluxed with heptane. Wax-free asphaltene residues are separated from the inorganic material by hot toluene. At the very end, the extracting agent is evaporated from the mixture and the asphaltene mass is weighed (ASTM D 6560, 2012).

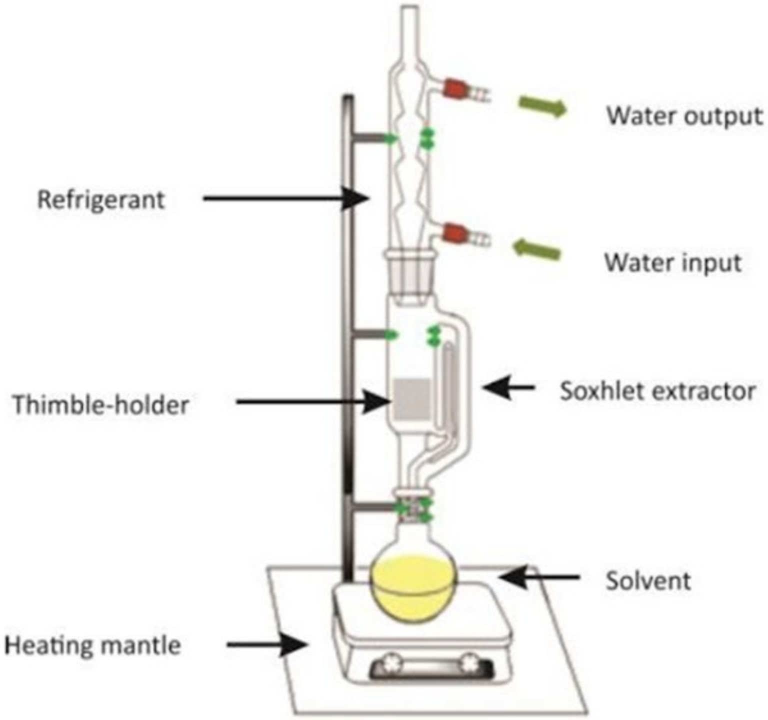


Figure 2-2. Soxhlet apparatus. (Reprinted from Guntero et el., 2017)

Ancheyta et al. (2002) have used different solvent/oil ratios in order to find appropriate volume of n-alkane to precipitate asphaltenes. They have added in oil samples two types of solvents such as n-pentane and refinery solvent, which was a cheaper alternative. And the following volume of precipitant were taken for the experiment: 3.4% mol, 25.9% mol, 30.5% mol, 40.9% mol. As can be seen from Figure 2-3, the precipitated asphaltene amount stabilized and showed constant trend at the solvent to oil ratio 40:1.

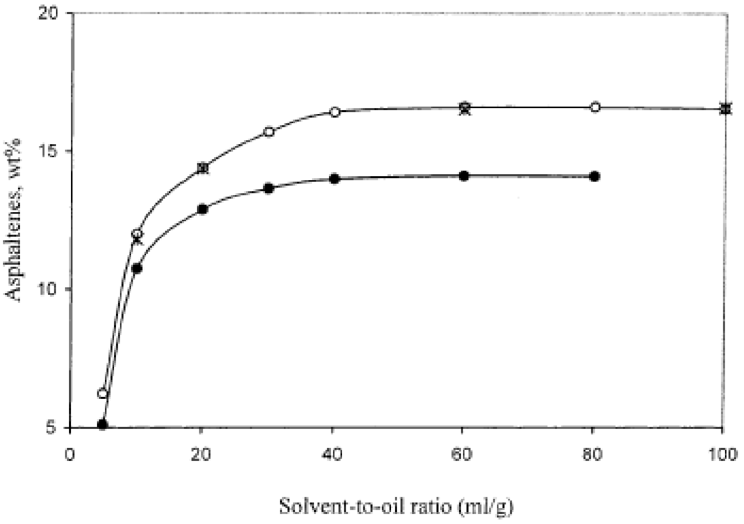


Figure 2-3. The effect of precipitant to oil ratio on asphaltene precipitation amount. (O) Refinery solvent and (●) n- C5. (/) Repetitions. (From Ancheyta et al., 2002)

2.3 Chemical properties of asphaltene

2.3.1 Elemental composition

Speight and Moschopedis in 1981 used several oil samples taken from different parts of the Earth and determined the composition of asphaltenes according to the Table 2-2. As can be seen, the carbon content in asphaltenes varies from 79.5% to 84.2%, hydrogen 7-8%, and these values are the highest among other high molecular weight oil components. An amount of sulfur in asphaltene is in the range of 5.0 -9.8 %, nitrogen 0.8 -1.6%, and oxygen 1.1 -4.6%. As the authors further indicate in their work, according to the percentages of H and C in the content of crude oil, their H/C ratio almost always remains unchanged, approximately in the region of 1.15±0.5%, despite the presence of other heteroatoms and metals, such as Ni, V, Na, Ca, Fe, etc. In this regard, there is a general opinion that the H/C ratio is dependent not only from the nature of oil, but also theon the used hydrocarbon solvents. Asphatenes extracted by n-heptane has less H/C ratio comparing to asphaltenes obtained by n-pentane, which in turn shows higher aromaticity in heptane solvent. However, as can be seen from the Table 2-2, the composition of nitrogen is almost unaltered, but amount of oxygen and sulfur is significantly differentiating in oil samples.

Table 2-2. Elemental composition of asphaltenes taken from oil samples originated in different parts of the Earth (From Speight and Moschopedis, 1981)

		Composition (%)					Atomic Ratios			
Source	Precipitating medium	C	H	N	O	S	H/C	N/C	O/C	S/C
Kuwait	n-pentane	82.4	7.9	0.9	1.4	7.4	1.14	0.009	0.014	0.034
	n-heptane	82.0	7.3	1.0	1.9	7.8	1.07	0.010	0.017	0.036
Iraq	n-pentane	81.7	7.9	0.8	1.1	8.5	1.16	0.008	0.010	0.039
	n-heptane	80.7	7.1	0.9	1.5	9.8	1.06	0.010	0.014	0.046
Iran	n-pentane	83.8	7.5	1.4	2.3	5.0	1.07	0.014	0.021	0.022
	n-heptane	84.2	7.0	1.6	1.4	5.8	1.00	0.016	0.012	0.026
Canada	n-pentane	79.5	8.0	1.2	3.8	7.5	1.21	0.013	0.036	0.035
	n-heptane	78.4	7.6	1.4	4.6	8.0	1.16	0.015	0.044	0.038

Elemental analysis of asphaltenes was carried out by Ancheyta et al. 2002 using three different types of crudes - Maya, Isthmus, Olmeca distinguishing with each other by their density, 21.3°API, 33.1°API and 38.7°API respectively. During the experiments the effect of two solvents, n-pentane and n-heptane on the characteristics of asphaltenes was studied. The carbon content nearly was not changed in both solvents during the test. The values of hydrogen were being increased slightly in n-C5, reducing the density of the crudes. The O, N and S contents was higher in n-C7 as the crude became less dense. The ratio of different elements to carbon has changed in accordance to their values in both solvents. As the experimental results showed, the H/C ratio was greater in normal pentane, which means that aromaticity factor is greater in normal heptane.

The results of elemental analysis can be used to study the aromaticity of asphaltenes, and defined as the ratio of aromatic carbones to the total amount of aliphatic and aromatic carbones, or unbonded carbon to total hydrogen C/H. It is considered, that the smaller the value of this parameter, the more stable asphaltenes in crude oil (Vargas and Tavakkoli, 2016). The aromaticity factor can be calculated from Dickinson mathematical statement (Dickinson, 1980):

$$f_a = \frac{C\ aromatic}{C\ aromatic + C\ aliphatic} \tag{1}$$

The ratio of C/H can be measured using another tools, such as Nuclear magnetic resonance (NMR) spectroscopy and Fourier-transform infrared spectroscopy (FTIR). C NMR and H NMR can be recognized as the most regularly used approaches for measuring the aromaticity. The spectrum of signals obtained at proton NMR is divided into groups according to aromatic (6.5-9.5 ppm) and aliphatic hydrogen (0.5-4.5ppm) peaks. The aliphatic hydrogen group has been divided further into γ, β and α signals. The same approach is applicable for carbon NMR spectroscopy. In the case of the C NMR technique, the spectrum of aromatic carbons group places in the range of 90-180 ppm, and aliphatic carbons are in the diapason of 0 to 70 ppm (Fergoug and Bouhadda, 2014).

FTIR is another technique which helps to measure asphaltene properties. In order to find out the composition of asphaltenes, it is enough to resort to infrared spectrum. FTIR spectrum of asphaltenes is divided to different regions: aliphatic, aromatic and polar. Each compound has its own areas of peak, according to which aromatic section is located in the range 750-860 cm^{-1} for the C-H bond, and C=C stretching aromatic bond is placed around 1600 cm^{-1}. C-H aliphatic stretching bond is placed in the range of 2922 – 2852 cm^{-1}, and aliphatic bending C-H bond is in 1458-1375 cm^{-1}. The ratio of aromaticity factor is defined as ratio C=C aromatic bonds to aliphatic C-H bonds (Wu and Kessler 2015; Vargas and Tavakkoli 2018).

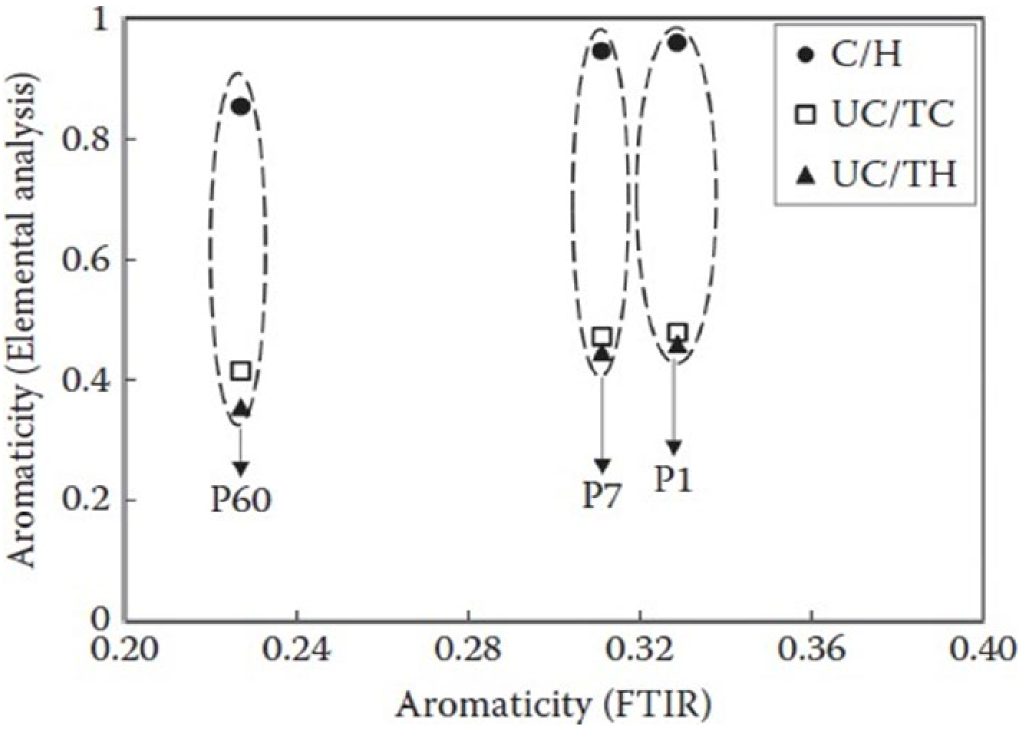


Figure 2-4. Correlation of aromaticity obtained from elemental analysis and FTIR spectroscopy. (Reprinted from Vargas and Tavakkoli, 2018)

The correlation of aromaticity according to the results of studies using the methods of FTIR and elemental analysis is given by the Figure 2-4. As can be shown, three crude oil samples (P1, P7, and P60) show good consistency in terms of the outcome of aromaticity research. The largest amount of aromatic compounds is represented by sample P1, while P60 and P7 contains more aliphatic group. Moreover, P1 has the highest degree of aromaticity, whereas P60, on the contrary, has the least value.

In addition, according to investigations of Koch and Dittmar (2006), aromaticity index can be determined using the following mathematical statement:

$$AI = \frac{DBE_{AI}}{C_{AI}} = \frac{1 + C - O - N - 1/2H}{C - O - S - N - P} \tag{2}$$

When DBE_{AI} and C_{AI} are less or equal to 0, AI will be equivalent to 0.

DBE (Double-Bond Equivalent) in this case reflects the degree of unsaturation of double bonds in molecule. The prefix AI presents the characterization to double bonds that do not act in formation of aromatic rings (Koch and Dittmar, 2006).

2.3.2 Metals in asphaltene content

Asphaltene-resin components contain the largest number of metals that are a part of high molecular compounds, and the most abundant elements are nickel and vanadium. It is believed that vanadium and nickel are more concentrated in asphaltenes, and their content dictate an amount of these metals in oil. In support of the said words, the Table 2-3 is presented that shows the concentration of the Ni and V metals. It has also been proven that the nickel in asphaltenes increases proportionally to the vanadium content, which is exist in the form of VO^{2+}.

Table 2-3. Metals content in resins and asphaltenes from different origins. (From Ramírez-Corredores, 2017)

Origin of crude oil	Resins		Asphaltenes	
	Ni, ppm	V, ppm	Ni, ppm	V, ppm
Maya	44	242	286	1602
Arabian Heavy	30	81	170	594
Beta	124	147	429	749
Kern River	149	75	492	361
Boscan	160	1595	375	4410
Hondo	105	198	474	979
Heavy Maya	21	77	202	1141
Cerro Negro	26	110	360	1600
Wilmongton	32	17	430	360
Prudhoe Bay	4	10	96	250
Furrial			164	845

As can be clearly seen from the Table 2.3, in almost all oil samples, vanadium prevails in the amount of asphaltene fraction. It is proved that 40-90% of vanadium and 25-75% of total nickel are found in asphaltenes. This fact may explain the trend, where with the increase of these metals the molecular mass of asphaltenes also increases (Yakubov et al., 2016).

2.3.3 Molecular weight of asphaltenes

The matter of the molecular weight of asphaltene is the subject of debate and heated discussions, due to the fact that asphaltene molecules have the property to self-associate, thereby creating nanoaggregates and difficulties in measurements. In their structure, asphaltene molecules can contain asphaltenes that are active in interaction between molecules and have the tendency to build chains; as well as passive resin molecules, which by their properties usually complete the chains.

Researcher Boduszynski devoted one of his early works to determination of the molecular weight of heavy oil fractions. Using the method of mass spectroscopy, he determined that their molecular weight does not exceed 2000 g/mole, and the average value is approximately 800-850

(Boduszynski, 1987). More recent works of scientists have established the molecular weight of asphaltenes ranging from 300 – 1400 g/mole, with averaged value 750 g/mole. This number is valid for asphaltene molecules with 4-10 aromatic rings (Akbarzadeh et al. 2007) and was confirmed by Groenzin and Mullins 1999, 2000 under fluorescence depolarization techniques. Nevertheless, according to investigations it can be said, that in many ways, the molecular weight of asphaltenes mainly depends on their origins, type of solvents and the temperature at which laboratory tests were carried out.

There are numerous methods for determining molecular weight, the well-recognized approach among them is GPC (gel permeation chromatography) analysis. This technique can be used to calculate the distribution of molecular weight, as well as to find its average value. The GPC determines the number average molecular weight Mn, and the weight average molecular weight Mw. Their ratio, which is called the polydispersity index – D, shows the measure of the spread of molecular weight values. If the index is equal to 1, it means that the molecular weight of all particles is identical and dispersion is absent, the higher the value of this indicator, the more extensive the molecular weight of the composition (Leon et al. 2010).

Octylated asphaltenes fractionated from Hamaca crude oil also were studied for molecular weight by group of researchers. They have used gel permeation chromatography technique to obtain Mn, Mw values. As stated in their results, the number average molecular weight Mn and the weight average molecular weight Mw were 2250 and 6000, respectively. The outcome of Mn presented good consistency with vapor pressure osmometry (VPO) analysis performed for the same type of crude oil previously (Acevedo et al., 1998).

2.4 Aggregation of asphaltenes

The determination of asphaltenes as a class of substances, distinguished by their solubility characteristics and not by chemical properties, made them difficult to study compared to lighter components — saturated hydrocarbons and aromatic compounds, which have a strictly defined chemical structure. The heavy components of the oil — asphaltenes and resins were often considered together as a single residue and were not considered worthy of further study.

Yen (1967) proposed a structural model that takes into account the presence of various chemical components in asphaltenes, such as polycyclic aromatic hydrocarbons (hereinafter - PAHs), their compounds, saturated hydrocarbons (alkanes), and oil porphyrins. However, the proposed model could not properly describe the molecular and colloidal properties of asphaltenes. Recent advances in analytical chemistry have allowed to identificate many chemical compounds contained in petroleum and asphaltenes, and led to modify Yena model or the Yen-Mullins model as shown by Figure 2-5 (Mullins, 2010).

Figure 2-5. Adapted Yen-Mullins model. (Reprinted from Mullins, 2010)

On the left - the asphaltene molecule contains a single core in the form of a polycyclic aromatic hydrocarbons (PAHs) with peripheral alkane chains. In the center - molecules of asphaltenes form nanoaggregates containing in average 6 molecules and a single unordered set of PAH with peripheral alkane. On the right - nano-aggregates of asphaltenes that form clusters, combining an average of 8 pieces.

With regard to asphaltene molecule structure, in recent years there are two basic models of asphaltene molecules - “continent” and “archipelago” (Hasanvand et al., 2018). Figure 2-6 shows a model of the “continent” type asphaltenes molecule, which is represented by a powerful condensed system comprising six to eight aromatic naphthenic rings and heterocycles in the center and short side chains along the periphery. Another type of asphaltene molecules structure is represented on Figure 2-7. According to the publications of Strausz et al., 2008, the asphaltene molecule consists of small clusters (condensed 3-4 aromatic and naphthenic rings), which are connected by aliphatic, sulfide, ether, and ester bridges.

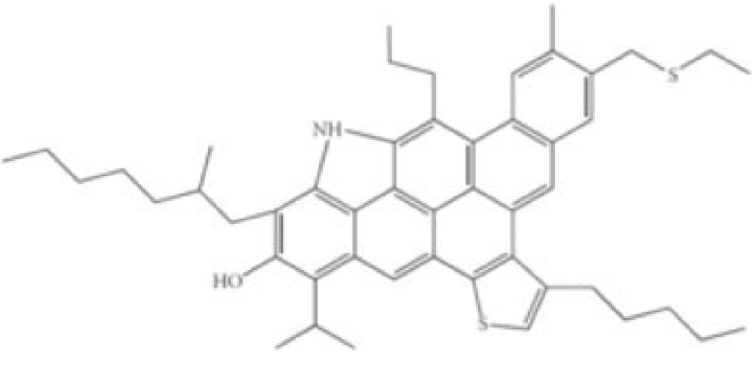


Figure 2-6. Continent model of asphaltene structure. (Reprinted from Hasanvand et al., 2018)

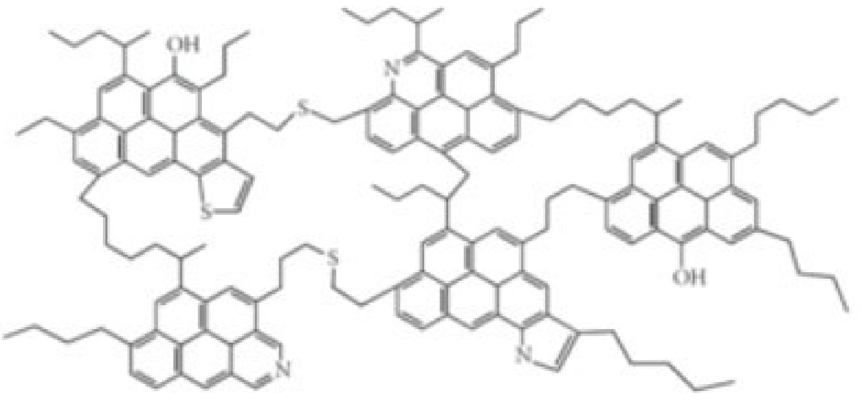


Figure 2-7. Archipelago model of asphaltene structure. (Reprinted from Hasanvand et al., 2018)

2.5 Determination of structural parameters of asphaltenes

2.5.1 Spectral studies of asphaltenes

The structural analysis of various petroleum high molecular weight compound has been demonstrated by many authors using the NMR spectroscopy method. The application of this method allowed to establish generally the structure of the asphaltenes. Also, the use of already known data about the structure of compound as a reference, was able to determine the presence of structural groups and give more information about aromaticity.

Larbi et al., (2015) investigated thoroughly the structure and properties of stable and unstable asphaltenes from Algerian oil based on H NMR spectroscopy. Asphaltenes were obtained from crude oil by precipitation in n-heptane at a ratio of 40: 1. During scientific research, such parameters as aromaticity factor, alkyl side chain, and aromatic sheet were determined. According to the results, unstable asphaltene sample showed higher shape factor (Φ=0.55 vs Φ=0.35), lower aromaticity (f_a = 0.43 vs. f_a = 0.53), and greater number of alkyl side chain (Larbi et el., 2015).

The molecular structures of asphaltenes from crude and upgraded bio-oil were described by Chinese scientists leaded by Xu et al. (2014) using NMR spectroscopy. During upgrading, the bio- oil was exposed to a pressure of 2-6 MPa and high temperatures surrounded by CO. A decrease in the molecular weight of asphaltenes, as well as an increase of aromatic rings were observed after upgrading of bio-oil. The basic structural parameters were calculated in order to compare both obtained aphaltenes. As a result of NMR spectroscopy, the aromaticity parameter expanded after upgrading.

Among the spectral research methods Fourier Transform Infrared (FTIR) spectroscopy is widely used. This technique can easily solve the problems of qualitative and quantitative analysis of matter, and can give the information about the structure of molecules. Another advantage is that FTIR analysis requires small amount of samples in any state aggregation.

In addition to molecular structure characterization, FTIR was applied in non-trivial investigations. Specifically, Fourier transform spectroscopy was also used to determine asphaltenes in 50 different oil samples collected from worldwide (Wilt et al., 1998). Partial least-square regression model was applied for 42 crude oils in order to predict the presence of asphaltene. The proposed model was tested by 8 randomly selected oil samples. Determination coefficient R^2 of the model was equal to 0.95 with standard error of 0.92 wt. %. This method showed comparably rapid test results and does not need solvents for asphaltene precipitation.

As illustrated on the Figure 2-8, the absence of distinctive for asphaltenes peaks can be clearly seen on the deasphalted oil spectra. For instance, these areas were found at peaks 1306 cm^{-1}, 1302 cm^{-1}, 868 cm^{-1}, and 752 cm^{-1}. It should be emphasized, that both crude oils have belonged to different geological origins with various asphaltene amount (1.6 and 8.5 wt. %).

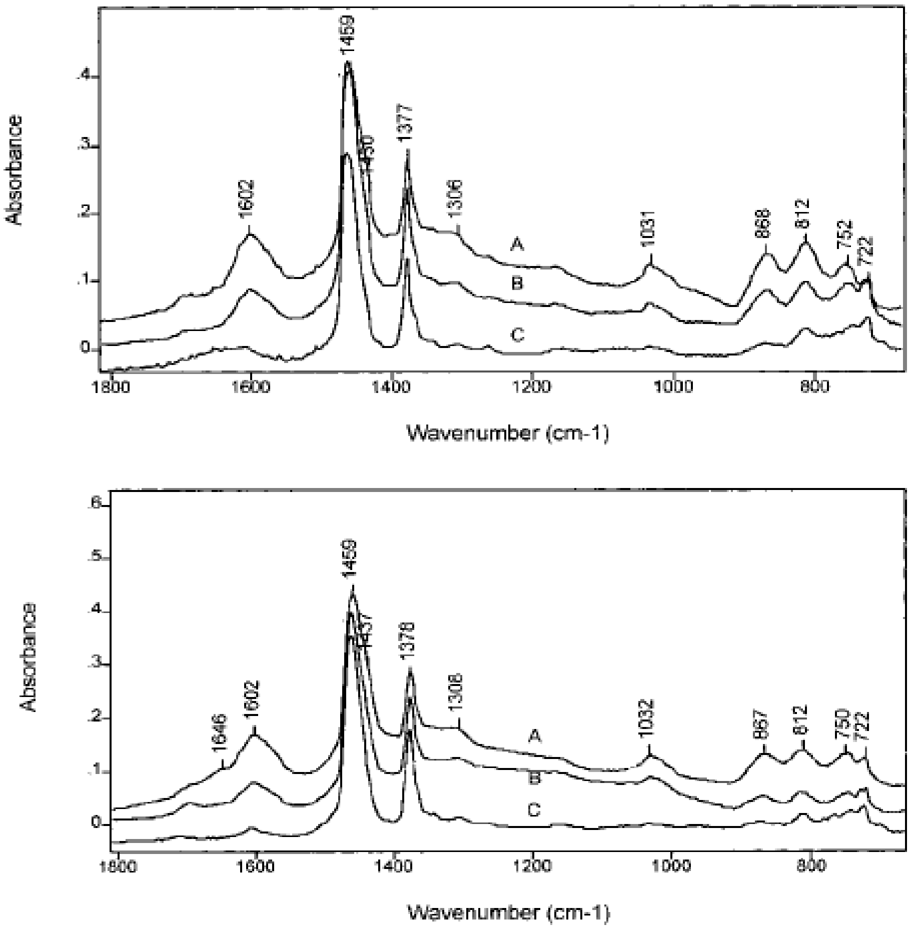


Figure 2-8. FTIR spectra for CTX (upper) and EIC (lower) crude oil samples with different asphaltene wt %. A – 100% asphaltene; B – 50% asphaltene and 50% deasphalted oil; C – 100% deasphalted oil. (From Wilt et al., 1998)

Supplementary and mutually complementary to the FTIR analysis method which is applied to describe the molecular structure of materials is Raman spectroscopy. This method is non- destructive, since there is no need for preliminary preparation, for example, dissolving or pressing the solids, thereby changing the physical and chemical structures of the sample. This research approach is based on irradiating the sample with monochromatic light, which is usually a laser. As a result of the analysis, it is possible to identify chemical components (determine the nature of the substance) or to study intramolecular interactions by observing the position and intensity of the bands in the Raman spectrum.

Three samples of asphaltenes from the Algerian Hassi-Messaoud oil field were examined by Raman and XRD laboratory analyzes under the guidance of Bouhadda and co-workers (2007). Based on the bands (G and D1) obtained throughout Raman scattering many researchers proposed their mathematical correlations with the aim of calculating the number of aromatic rings in the compounds. In the investigations of the Algerian asphaltenes scientists utilized Gaussian and Lorentzian functions for this purpose. As a consequence, they suggested that asphaltene aggregation consist of 8 molecules, which was confirmed by Raman and XRD experimental approaches (Bouhadda et al., 2007).

Practically the same results were observed by Abdallah and Yang in 2012 through the use of Raman spectroscopy. Specifically, they have calculated 7-8 aromatic rings from seven various asphaltene samples collected from different geological origins. The peaks of G and D1 bands obtained as a result of spectroscopy showed good agreement with the investigations of Tunistra and Koenig. In addition to this, Abdallah and Yang determined the diameters of aromatic sheets. As they stated, the average size of La varies between 1.52nm and 1.88nm. In general, based upon the results that showed good consistency with other performed studies, this parameter does not depend on the origin of the oil (Abdallah and Yang, 2012).

2.5.2 Analysis of asphaltenes by thermal methods

Thermogravimetric analysis (TGA) is used to determine mass loss of various samples against time and temperature. TGA is widely employed to ascertain the temperature of polymers' degradation and rate of decomposition over time. This kind of research is useful for studying the stability of asphaltenes under high temperature.

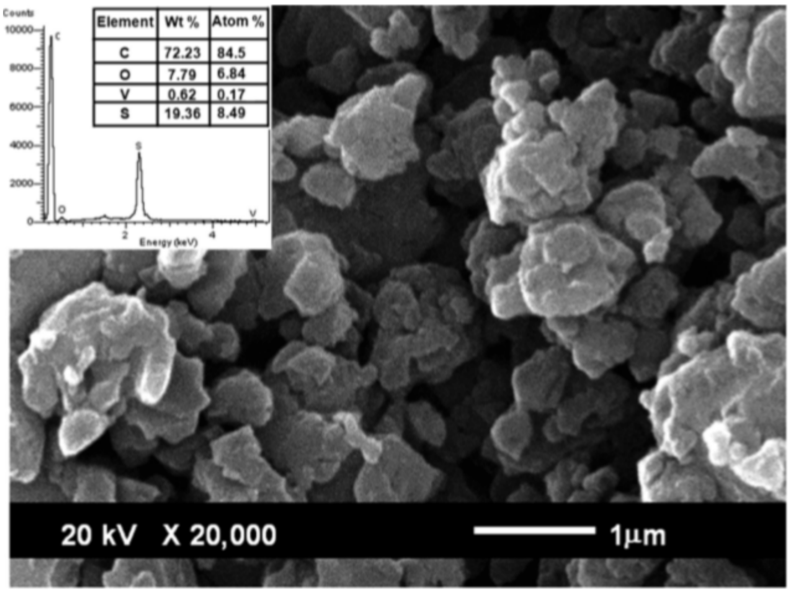
In the late 80s of the last century, group of scientists headed by Moschopedis studied the behavior of Athabasca asphaltenes under thermal conditions. Asphaltene portion derived from the aforementioned bitumen was exposed to high temperatures from 200°C until 600°C, at the same time obtained during the test gaseous fraction was further explored by gas chromatography for the compositional analysis. Researchers have witnessed methane, ethane, and carbon dioxide at temperatures below 300°C. They assumed that at temperatures below 350°C the groups from peripheral positions are destroyed, then with increasing the temperature decomposition of heavier compounds takes place (Moschopedis and Speight, 1977).

Canadian asphaltenes derived from Cold-Lake bitumen was investigated in nitrogen surrounding under high temperature by thermogravimetric analysis. Experimental tests were performed at 20- 845°C temperature range with flow rates of 50 ml/min and 120 ml/min. According to the results, the greatest weight loss for both flow rates was observed after 12 min at the temperature around 480-500°C. In addition to this, it was stated that changes in the flow rate of nitrogen did not make an influence on asphaltene decomposition (Khulbe et al.,1984).

2.5.3 Microstructural investigations of asphaltenes

The study of the microstructure of the asphaltenes has been ongoing for a long time. Morphological features of the asphaltenes obtained from Maya crude oil samples were investigated with the help of electron microscopy. An influence of different solvents on hydroprocessed and purified asphaltenes were analyzed by transmission and scanning electron microscopies. As the results showed, the changes observed from SEM analysis can be characterized by temperature of hydroprocessing process and solubility properties of asphaltene in different solvent combinations. In the most cases the surfaces of asphaltenes were porous or smooth with microparticles (Trejo et al., 2009).

Asphaltenes originated from the same oil field was analyzed later by another group of scientists. Arenas-Alatorre et al. (2016) described Maya asphaltenes with the aim to determine the size of agglomerations and particles in it. In their research they utilized different tools such as scanning and transmission electron microscopies with high resolution and low vacuum. In addition to imaging tests, energy dispersive spectroscopy (EDS), and FTIR were performed. Electron microscopy results presented that the size of agglomerates varied from 1 to 150 nm.



Element	Wt %	Atom %
C	72.23	84.5
O	7.79	6.84
V	0.62	0.17
S	19.36	8.49

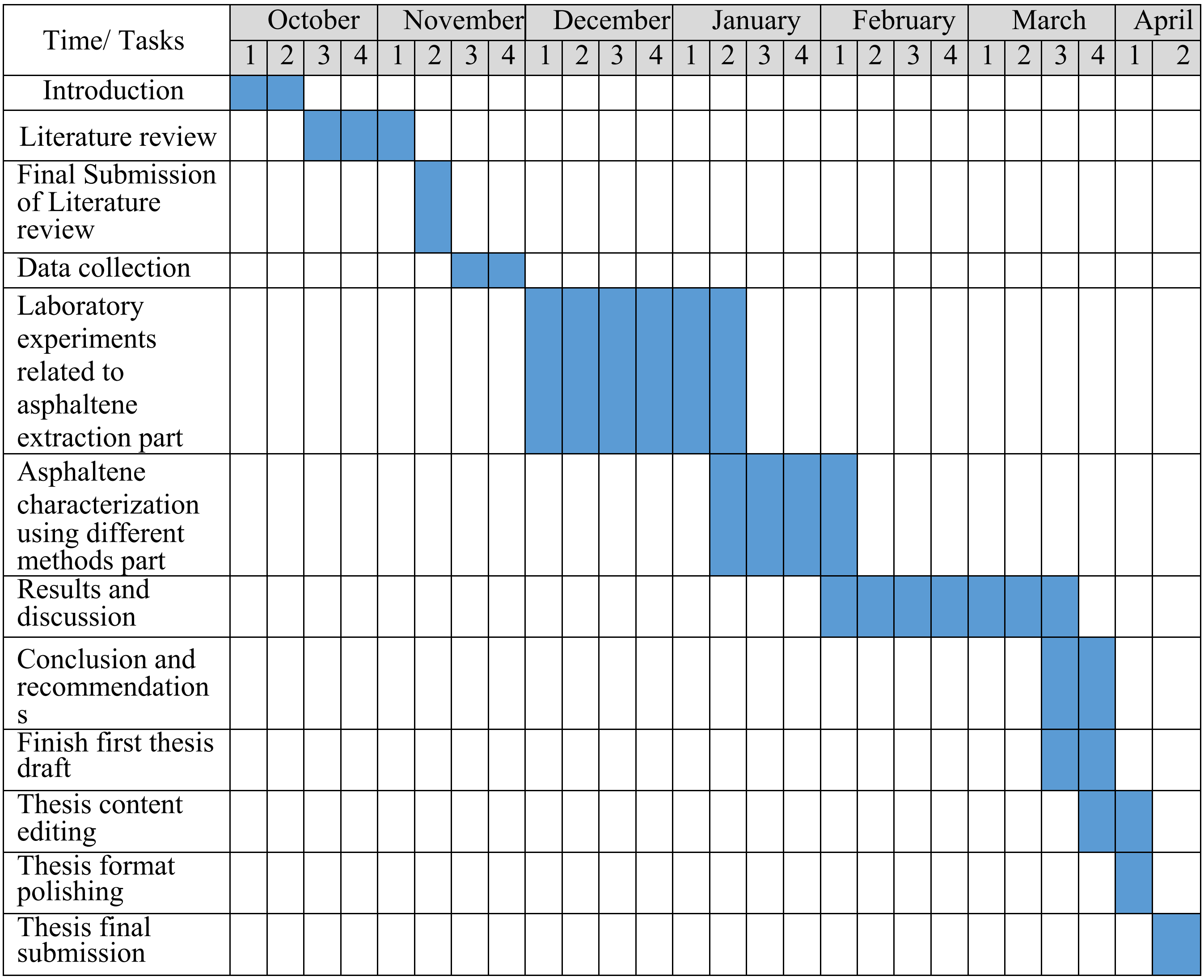
Figure 2-9. Image obtained from SEM and elemental analysis performed using EDS. (From Arenas-Alatorre et al., 2016)

As per Figure 2-9, the elemental content of the sample was determined by EDS and the morphology was observed by SEM. According to the results, asphaltenes have predominantly consisted of carbon, over 70%. The structure of the asphaltenes was entirely rough with many microparticles.

3. PROJECT PLAN

3.1 Project schedule

Below Gantt Chart is presented. It was developed to ensure that the project will be delivered on time.



Time/ Tasks	October				November				December				January				February				March				April	
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2
Introduction	■	■																								
Literature review			■	■	■																					
Final Submission of Literature review						■																				
Data collection							■	■																		
Laboratory experiments related to asphaltene extraction part									■	■	■	■	■	■												
Asphaltene characterization using different methods part														■	■	■	■									
Results and discussion																	■	■	■	■	■	■	■			
Conclusion and recommendations																							■	■		
Finish first thesis draft																							■	■		
Thesis content editing																								■	■	
Thesis format polishing																									■	
Thesis final submission																										■

Figure 3-1. Thesis schedule

3.2 Resource requirements

The necessary resources for project completion are identified and listed.

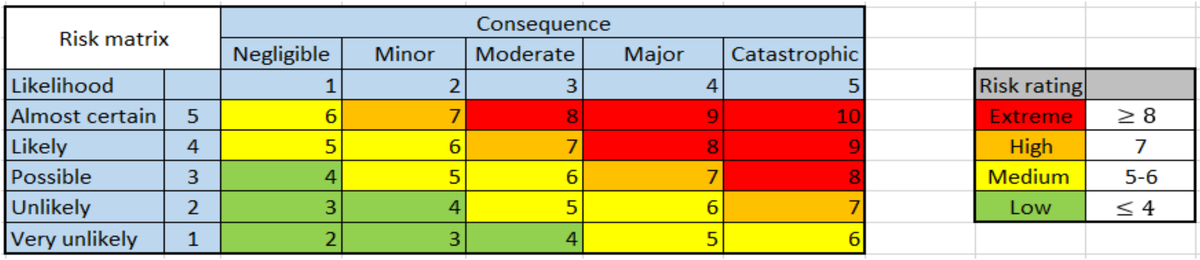
Table 3-1. Required resources

Device/material	Function
Laptop or PC	My own laptop or PC from computer lab is used to conduct the research
Crude oil samples	To perform laboratory tests
Soxhlet extractor	To perform extraction of asphaltenes
CHNS/O Elemental Analyzer	To determine elemental content of the samples
NMR spectrometer	To perform NMR analysis
FTIR spectrometer	To perform FTIR analysis
RAMAN spectrometer	To perform RAMAN analysis
Simultaneous Thermal Analyzer	To perform thermogravimetric analysis of asphaltenes
Sputter coater	For preparation samples to SEM analysis
Scanning Electron Microscope	To perform characterization of asphaltenes morphology
Printer	To print out articles or papers
Access to internet	To download essential materials related to my thesis

3.3 Risk management

Risk is a measure of probability of not achieving expected outcome, and it can be avoided or mitigated through well thought out planning. Risk mitigation plan was developed for this thesis to identify the possible risks and the ways of avoiding or controlling them. One of the common risk assessment tool is WRAC analysis that uses a 5x5 likelihood-consequence matrix. Table 3-2 illustrates the risk rating from low to extreme cases. Risk ranking matrix

Table 3-2. Risk ranking matrix



Risk matrix		Consequence				
		Negligible	Minor	Moderate	Major	Catastrophic
Likelihood		1	2	3	4	5
Almost certain	5	6	7	8	9	10
Likely	4	5	6	7	8	9
Possible	3	4	5	6	7	8
Unlikely	2	3	4	5	6	7
Very unlikely	1	2	3	4	5	6

Risk rating	
Extreme	≥ 8
High	7
Medium	5-6
Low	≤ 4

3.3.1 Physical hazards

Physical hazard is a factor that can harm a person’s mental or physical condition without the need for physical contact. The possible physical hazards that can occur during the thesis work and the ways to avoiding them are given in Table 3-3.

Table 3-3. Physical hazards

Physical Hazard	Description	Risk rating	Risk Control
Eye-strain	Fatigue of the eyes due to prolonged presence in front of the computer screen	7 High	Regular exercise for eyes, regular breaks during using the computer
Injury during experimental analysis in the laboratory	Mangle from lifting heavy weights	5 Medium	Conducting laboratory experiments supervision and use of personal protective equipment
High stress	Irritation from the overwork	5 Medium	Good study/relax balance, proper time management
Illness	Disease from mild colds to flu	5 Medium	Maintain immunity of the body, dress warmly at cold conditions, stay away from sick people

3.3.2 Project hazard

Project hazards are the factors that can affect to the provision of the thesis on time due to unexpected situations as shown in Table 3-4.

Table 3-4. Project hazards

Project hazard	Description	Risk level / rating	Risk control
Sudden computer crash	Accidental fall to the floor	3 Low	Obligatory carrying in a bag
Thesis related documents loss	Sudden failure of the hard drive, computer crash due to viruses, not saving the thesis files	5 Medium	Use cloud services like google drive, do not forget to save, installation of anti-virus software
Change of thesis supervisor	Supervisor may be unable to continue student supervision due to some circumstances	5 Medium	Advice with co-supervisor or another professor competent in student’s thesis topic
Inaccessibility of laboratory equipment	Access to laboratory equipment in order to perform appropriate analysis	7 High	Use accessible laboratory equipment, find another reliable sources.
Non-receipt of crude oil samples	Non-receipt of crude oil samples	5 Medium	Work with another reliable oil samples

4. METHODOLOGY

In this section, the methodology and experimental and analytical tools, methods, and the procedures sued for the purpose of this research work are described. A summary of the techniques used is presented in Figure 4-1. First, laboratory tests performed to understand the main crude oil properties such as API gravity and viscosity. Then, the IP-143 method was used to extract the asphaltenes from three crude oil samples obtained from West Kazakhstan. Further, asphaltenes were characterized by using various methods such as CHNS/O analysis to obtain elemental content of asphaltenes, TGA analysis to determination kinetic behavior of asphaltenes under thermal destruction, scanning electron microscopy to study the surface morphology of the asphaltenes. Additionally, three spectral analyses methods namely the Fourier Transform Infrared, Carbon and Proton NMR, RAMAN spectroscopies were used to investigate the average molecular parameters: aromaticity factor (f_a), the number of carbons per alkyl side chain (n), and diameter of aromatic unit (La).

Table 4-1. Methodology

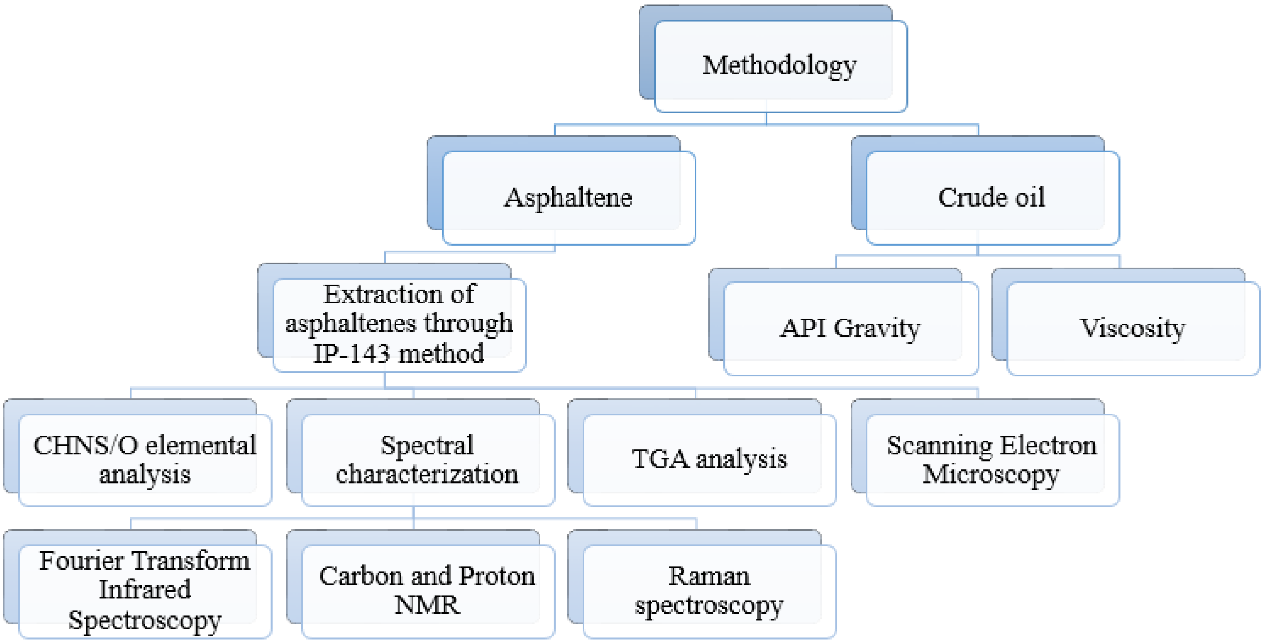


Figure 4-1. Methodology

4.1 Property measurements of crude oil samples

4.1.1 API Gravity

The API gravity was measured using the SVM 3001 Viscometer manufactured by Anton Paar Company which allowed to determine density. The properties were measured at temperatures from

80°C to 40°C with an interval of 10 degrees. In some cases, when the properties of the oil did not allow to perform measurements due to the high viscosity, tests were carried out at the lowest possible temperature (from 50°C to 80°C). Due to the technical capabilities of the equipment, the API gravity was automatically extrapolated to the temperature of 15°C or 60°F according to the API standard ASTM D6822, which states that the values should be determined at standard conditions. This made it possible to classify oil by categories. Considering that the oil samples were too viscous, all oil samples were preheated to measure density and stirred prior analysis. In order to avoid the occasion of bubbles, the samples were degassed by an ultrasonic bath for about 30 minutes.

4.1.2 Viscosity

The rheological behavior of the oils was analyzed using an Anton Paar MCR 302 Rheometer. The viscosity of oil was not measured directly, since at the ambient condition high viscous fluid lead to its stucking in equipment due to low temperature, thereby inability of providing the viscosity readings. During this measurement, the effect of shear rate and shear stress on the viscosity of oils was studied. All tests were carried out at a constant room temperature of 25°C according to API MPMS (2004) requirements. To determine the general trend, the values of shear rates started from 0 to 400 1/s.

4.2 Asphaltene extraction

Three oil samples from the West Kazakhstan region were tested to determine the characteristics of asphaltenes. Separation of asphaltenes from oil samples was carried out on the basis of ASTM 6560 - IP-143 standard. The technological scheme of the whole process is shown on Figure 4-2.

Since we were dealing with highly viscous oil, the samples required preliminary preparation before the experiment. Oil samples were heated at a temperature of 70°C, then they were stirred for 30 minutes with 1000 rpm. For the experiment we used oil weighing 10 g, and n-heptane in a weight ratio of 40:1 as a solvent. In the course of experiments, with the aim of asphaltene precipitation n-heptane with a purity of 99% from Sigma-Aldrich company was used. Furthermore, for the purpose of asphaltene dissolution toluene with the purity 99% manufactured by Sigma-Aldrich was utilized. An Erlenmeyer flask was used to dissolve the mixture, which was then directed to boil for 60 minutes under reflux in order to avoid escaping of light crude oil components. Further, the flask with the contents was removed, cooled and left tightly plugged for asphaltene precipitation in a dark place for 24 hours.

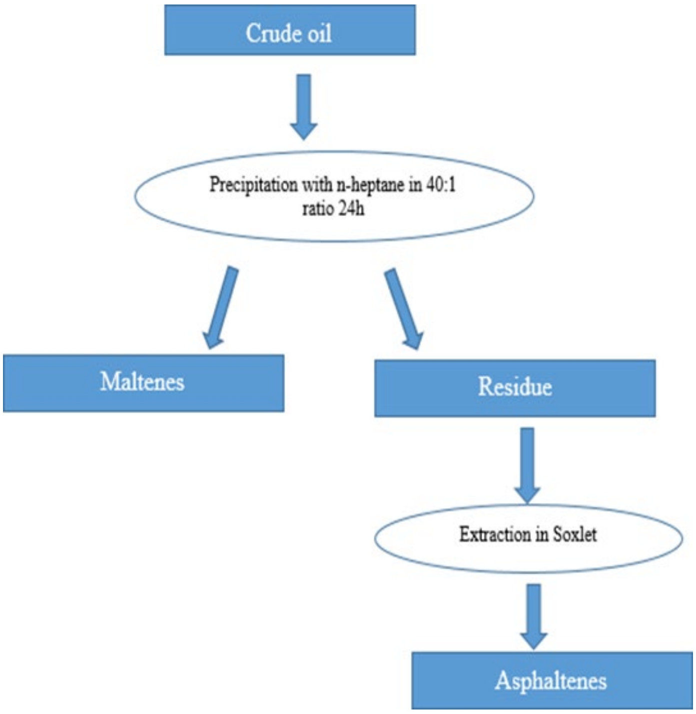


Figure 4-2. Scheme of asphaltene extraction from crude oil sample

On the next day, the filter paper Whatman Grade 597, with pore size of 4-7 μm (medium fast filter paper) was used to separate the asphaltene precipitate from the maltene fraction. The filter paper was placed in a funnel where liquid was then decanted. The contents of the flask were subsequently rinsed with hot heptane until it became completely colorless.

Thereafter, the filter with asphaltene content was placed into an extractor of Soxhlet for co-precipitation of resins and paraffins. New amount of *n*-heptane was poured into the flask and boiled under the Soxhlet extractor during 1 hour at the temperature 105°C. The condensation rate was set to approximately 2-4 drops per second. Additionally, the temperature of the condenser coolant (in our case, the water was used) was set at 15°C. After extraction with n-heptane, the flask is replaced by toluene with a volume not exceeding 60 ml. The toluene is heated under the Soxhlet apparatus at temperature 111°C with the speed of condensation 2-4 drops per second until the whole asphaltenes dissolve in toluene.

Afterwards, the contents of the flask were transferred to a beaker for further evaporation under water bath. The entire evaporation process was carried out under the hood in accordance with the safety instructions. Then the asphaltenes were dried in an oven at a temperature of 110°C for 30 minutes, after which they were cooled for 1 hour.

Figure 4-3. Filtration of asphaltenes

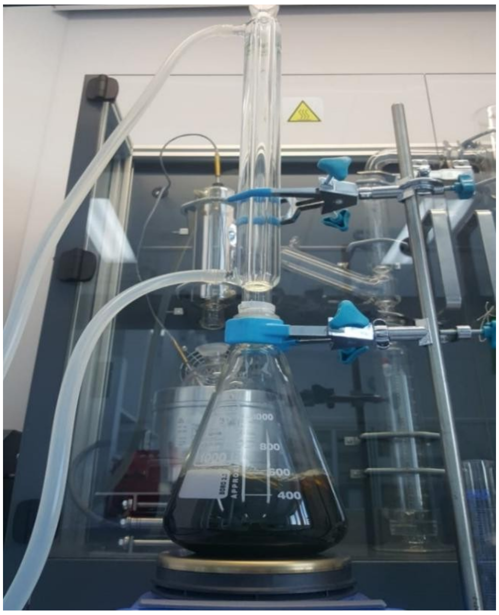


Figure 4-4. Boiling the mixture of crude oil and n-heptane under the reflux

At the end, the asphaltene content was determined by the following formula:

$$\text{Asphaltene (wt \%)} = \frac{Weight\ of\ dried\ asphaltene}{Weight\ of\ crude\ oil\ sample} * 100 \quad (3)$$

4.3 Asphaltene characterization methods

4.3.1 Elemental analysis

Elemental analysis was performed in order to measure elemental content of asphaltene samples. It was carried out using a Vario Micro CHNS/O elemental analyzer. This equipment is fully automatic and is designed for the simultaneous quantitative analysis of elements such as carbon, hydrogen, nitrogen, sulfur, and oxygen, depending on the options. The elemental content test was performed under the following environment: the temperature - 23°C, pressure 95.5kPa, and humidity – 70%. The weight of samples varied between 2.75 – 4.39 mg. Each sample tested 3 times during 15 minutes. It should be emphasized, that the indicated oxygen content may have some inaccuracies because it was calculated based on the difference of mass balance.

4.3.2 Raman spectroscopy

The Raman spectroscopy technique is aimed to measure the molecular parameter – diameter of aromatic unit. The principle of the Raman spectroscopy technique is based on monochromatic light that is emitted by a laser. It is believed that, the frequency of the incident and scattered beam from the sample have the same value. This process is also widely known as Rayleigh light scattering. However, a certain number of photons of scattered radiation have shifted frequencies in comparison with the frequency of the initial radiation. This change or shift in the frequency is known as the Raman Effect.

Laboratory tests of Raman spectroscopy were performed using the LabRAM HR Evolution spectrometer manufactured by HORIBA company. The excitation of the samples was carried out by a solid state 532 nm laser utilizing a 10x zoom objective. An optical microscope was mounted to the Raman spectrometer, which essentially facilitated the operational procedures. Since, in such equipment the exciting laser is focused in a small area near the focus of the microscope objective. Thus, it provided localization of measurements with the possibility of connecting spectra to a specific point on the surface of the asphaltene samples. The spectral accumulation time varied from 20sec to 30 sec depending on the type of measurements, because some samples of asphaltenes scattered the light poorly. The spectrum was recorded in the ranges of 800–2000 cm^{-1} and 800– 4000 cm^{-1}. Processing of the received data was carried out using the LabSpec 6 software from the Horiba Company.

4.3.3 FTIR spectroscopy

As well as Raman spectroscopy FTIR analysis provides observations about the structure of the material or its characteristics. If Raman spectroscopy is based on the study of scattered light, Fourier spectroscopy is based on the absorption of the light. Both Raman and FTIR spectroscopy give a spectral characteristic of molecular vibrations. Using the Fourier spectrometer, the optical spectra of the studied object are obtained in two stages. At the first stage, the photodetector registers the "interferogram". In the second stage, the mathematical processing of the interferogram is performed. As a result, the spectral composition of the radiation which is also known as the spectrum is received. The main part of the Fourier spectrometer is the interferometer Michelson. The process of recording interferograms is demonstrated further. Its principal optical scheme is shown in Figure 4-5.

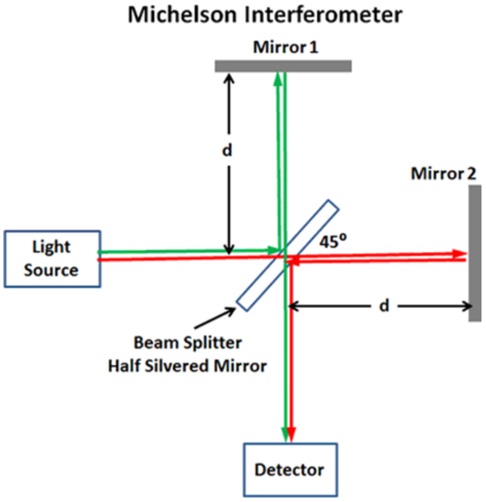


Figure 4-5. Principal scheme of Michelson interferometer. (From mpoweruk.com)

The light source directs a beam (green line) which hits a translucent mirror, so-called a beam splitter, which makes an angle of 45° with the beam. Part of the beam is reflected from the beam splitter, the other part passes through it (red line). The green line reflects from the Mirror 1, then again falls on the beam splitter and, passing through it, and falls on the photodetector. A similar way applies to the red light passing through the beam splitter. It is reflected from the flat Mirror 2, and partially reflected from the beam splitter, also hits the photodetector. Thus, two waves get on the photodetector, resulting from the separation of the initial light beam. If the coherence conditions are met, the photodetector will record the result of their interference.

In our study Fourier Transform Infrared analysis was performed on a Nicolet iS10 FT-IR spectrometer manufactured by Thermo Scientific Company. Spectra of the FTIR analysis was recorded in the range from 500 till 4000 cm^{-1}. Processing of the data was conducted using Omnic software, which represents the spectrum of the samples as the results.

4.3.4 1H and 13C NMR Spectroscopy

The Nuclear Magnetic Resonance was performed in order to measure aromaticity factor and the number of carbons per alkyl side chain. The NMR technique is based on the use of the magnetic properties of atomic nuclei. Protons and neutrons behaves as small bar magnets. This property of magnetic nuclei is called nuclear spin. Due to the quantum properties, the spin can accept only strictly defined values, which are integer or half-integer numbers and Planck's constant. The nuclei of the H and C atoms have the nuclear spins equal to +½ and -½, and the materials which contain these atoms can be studied using NMR spectroscopy.

To register NMR spectra, the sample is placed in a strong magnetic field: the stronger the field, the higher the sensitivity and spectral resolution. In such a case, in accordance with the laws of quantum mechanics, the magnetic nuclei with spin 1/2 will be in one of two states: the spin directed along or opposite to the direction of the external magnetic field. When the sample is in the magnetic field, their spin energy levels are split and an energy transition from one level to another becomes possible. This transition is the physical basis of nuclear magnetic resonance spectroscopy, which is based on the absorption of electromagnetic radiation from the nuclei of the sample placed in the magnetic field. Graphically, it is presented as a spectrum of the dependence of absorption on the frequency of electromagnetic radiation.

In our research, NMR spectroscopy was recorded on the equipment JNM-ECA 500 produced by Jeol company. Samples of asphaltenes were previously dissolved in deuterated chloroform (CDCl3). The accumulation of signals for proton spectra was carried out for 15 minutes with the frequency of 500 MHz. While carbon spectroscopy was carried out with accumulation for 4 hours with the frequency of 125 MHz. The recording was performed in 5 mm standard ampoules at the room temperature 20°C. The whole experimental data obtained by nuclear magnetic resonance was processed using the MestReNova software package.

4.3.5 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is based on the continuous recording of variation in the mass of the samples depending on the temperature change. The change in the temperature of the medium is set by the user, and in our case we heated samples of asphaltenes at a constant speed of 2°C per minute under nitrogen environment. This heating rate was chosen, since at higher rates the asphaltene samples were not able to reach the programmed temperature. As a consequence, the measurement results might be questioned.

Thermogravimetric analysis was performed on Simultaneous Thermal Analyzer (STA) 6000 equipment from Perkin Elmer Company. The analyzed asphaltene sample was originally placed in a crucible where it was weighed. The initial weight of the samples ranged from 3.5 mg to 21.97 mg. Then, the crucible was heated by an electric heater. The experiment has started with an initial temperature of 30° C which required 1 minute to achieve stability throughout the analyzed sample. Over time and a change in temperature, the weight of the asphaltene samples was measured. Testing was completed at a temperature of 880°C. Heating was carried out at the rate of 2°C/min in an inert atmosphere using nitrogen. Finally, graphically depicted measurement results give a thermogravimetric curve.

4.3.6 Scanning electron microscopy

Scanning Electron Microscopy was aimed to investigate the surface morphology of asphaltenes and measure the sizes of microparticles in the content of them. Asphaltenes samples were put to the analysis on a scanning electron microscope (SEM). Microscope JSM-IT200 was utilized for these purposes. However, before sending the samples to SEM analysis, the asphaltenes underwent through the preparation procedure. The samples due to their poor electrical conductivity were sprayed by gold with a thin layer of 2 nm on a sputtering machine to obtain better images at high magnifications. Samples were sticked to the SEM holder using double-sided carbon tape. Then loaded sequentially into the microscope chamber.

The secondary electron detector (SED) in high vacuum mode (HighVac) was used to perform an analysis of asphaltene samples. We individually selected the values of the accelerating voltage and current for each asphaltene sample at which they behaved stably and allowed to capture the highest quality image. Electronic images of samples in quantities of up to 10 pcs were obtained at different magnifications from a minimum of 500x to a maximum of 5000x. During the shooting some (low conductivity) samples, the maximum magnification was taken according to their physical possibilities/limitations. Additionally, the images were used to measure the sizes of typical morphological features where they existed.

Elemental analysis of the samples was carried out on a JEOL spectrometer integrated into the EDS microscope at an accelerating voltage of 25 kV in high vacuum mode. The distribution maps of the elements were taken in order to determine the chemical compositions of the samples. EDS mapping reports include an electronic image, local map elements, as well as the total spectrum of the map with the percentage of each element.

5. RESULTS AND DISCUSSION

This chapter includes the results and discussion parts obtained during investigation of characteristics of the asphaltene fractions from the three Kazakhstani crude oil samples. In the first sub-section, the results from determining crude oil properties such as API gravity and viscosity are presented and discussed. Then, the results of asphaltene extraction and the relationship between the asphaltene content and the API gravity are presented. In the third sub-section, the results obtained from laboratory studies for characterization of the extracted asphaltenes using various analytical methods are presented and discussed. To cap this chapter, finally, a discussion of the results with description of the benefits of using different methods used for the purpose of this research work is provided followed with a comparison between the results obtained in this research work with the findings of other scientists on asphaltenes characterization parameters reported in the literature.

5.1 Crude oil properties

5.1.1 API gravity

Results from API gravity measurements obtained from SVM 3001 Viscometer are presented in the Table 5-1. According to a Study Group of the World Petroleum Congress (Martinez, A. R., et al. 1987) the crude oil was classified into different categories by API Gravity: Extra Heavy oil – (API gravity less than 10°); Heavy oil - (10-22.3°); Medium oil - (22.3° - 31.1°); Light oil – (API Gravity is greater than 31.1°). Taking into account this classification, the crude oil samples originated from West Kazakhstan region can be also classified as follow. As can be seen from the Table 5-1, the values of API gravity for samples #2 and #3 are almost the same, 31.088° and 31.152°, respectively. Nevertheless, considering the strong categorization proposed by World Petroleum Congress, the degassed oil samples #1 and #2 can be attributed to medium oils, and the less dense oil sample #3 can be characterized as light oil.

Table 5-1. Classification of crude oil by API gravity

	Sample #1	Sample #2	Sample #3
API Gravity @15°C, °	28.205	31.088	31.152
Oil classification by API Gravity	Medium oil	Medium oil	Light oil

5.1.2 Rheological behavior of crude oil

The rheological properties of the oils obtained in the course of this study are shown in Figure 5-1, which illustrates the dependence of viscosity and shear rate under constant room temperature of 25°C. As follows from the graph, the three crude oils have the behavior of non-Newtonian fluids, since, with an increase of shear rate, the viscosity of the samples decreases gradually. In general, the entire oil samples show a similar trend. However, the samples from the 2nd and the 3rd sources demonstrate distinctive correspondence, because in the same values of the shear rate they show approximately the same data points of viscosity. The rheological behavior of oil #1 is slightly different from the previous two samples since at minimum shear rates the viscosity reaches the values over 80000 cp. The relatively high viscosity can be explained by presence of asphaltene nano-aggregates in the content of the oil.

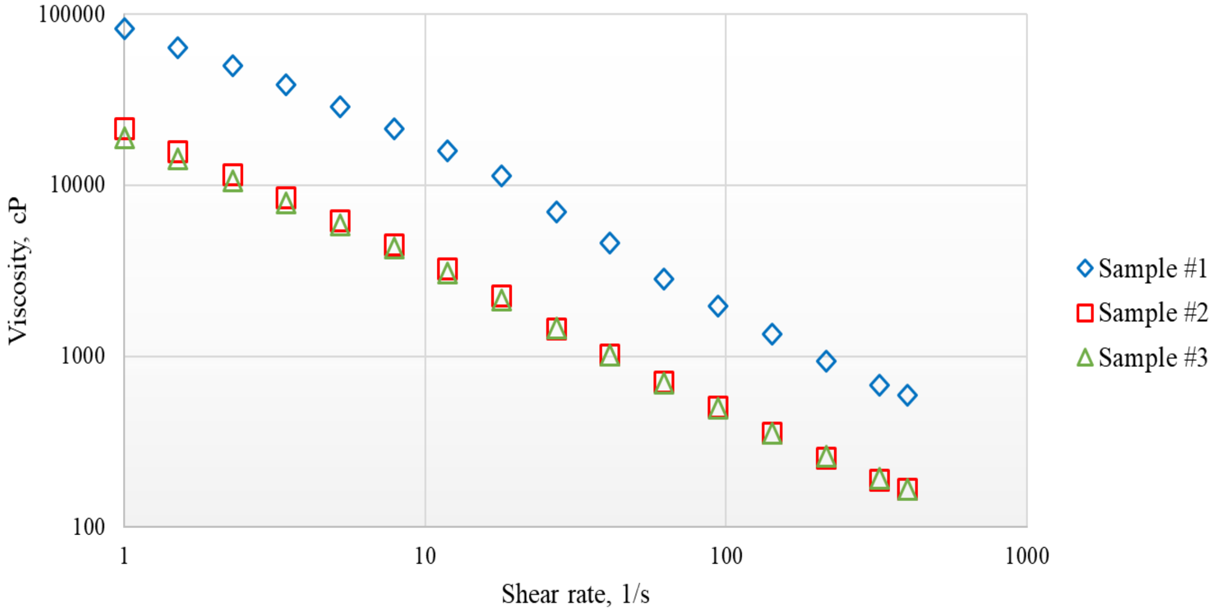


Figure 5-1. Dependence of viscosity on the shear rate for three crude oil samples

5.2 Asphaltene extraction results

In the course of experiments, the asphaltene content in all three oils was obtained using the IP-143 technique. As a consequence of separation asphaltene fraction from the oils using n-heptane, the following outcome was obtained: from sample #1 – 0.625 wt % asphaltenes, from the sample #2 – 0.402 wt %, and the sample #3 – 0.202 wt%.

As can be observed from Figure 5-2, the amount of obtained asphaltenes varied depending on the properties of the oil. This pattern is consistent with statements of other researchers (Speight, 1999; Evdokimov, 2005), where they report about the strong correlation between density (API gravity) of oil and asphaltenes. A large number of empirical tests found that low API gravity can indicate a high asphaltene content.

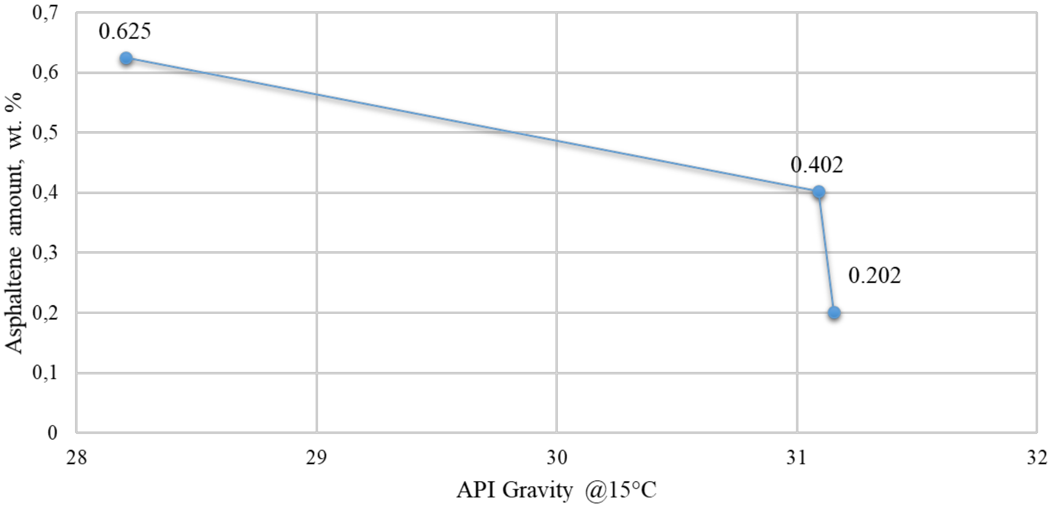


Figure 5-2. The amount of asphaltenes depending on the API gravity of oil

5.3 Results of asphaltenes characterization

Results from elemental analysis of three asphaltene samples collected from West part of Kazakhstan and extracted by n-heptane are given in the Table 5-2. As can be seen from the Table 5-2, the amount of carbon increases from the left to the right (74.57wt % to 81.32 wt %). The oxygen content, on the contrary, decreases in the same direction (from 13.99% to 7.9%). It should be noted that the amount of oxygen may be somewhat inaccurate, as it was calculated by the difference of elemental content. The ratio of N/C, O/C, and S/C was calculated from a knowledge of the weight percent and atomic weights of these elements. As an example, the element ratio of H/C was calculated as follow:

$$\frac{H}{C} = \frac{Weight\ Percent\ of\ H /\ Atomic\ weight\ of\ H}{Weight\ Percent\ of\ C /\ Atomic\ weight\ of\ C} \tag{4}$$

The large value of the N/C, O/C or S/C indicates that these non-carbon atoms predominate in the amount of the heterocyclic compound. Consequently, for instance, oxygen heteroatoms are most widespread in the sample #1, nitrogen is most prevalent in the sample #3, and sulfur heteroatoms are approximately equal in both samples #1 and #3. As can be seen from the Table 5-2, asphaltenes from light crude oil has higher aromaticity compare to medium oil samples. The same results were obtained by Ancheyta et al. (2002), when asphaltenes of Maya heavy oil had higher H/C content than Olmeca light crude oil asphaltenes.

Table 5-2. Elemental content of asphaltene samples

Elements	Sample #1	Sample #2	Sample #3
Carbon (wt %)	74.57	78.91	81.32
Hydrogen (wt %)	10.46	10.78	9.41
Sulfur (wt %)	0.42	0.27	0.45
Nitrogen (wt %)	0.56	0.55	0.92
Oxygen (by difference) (wt %)	13.99	9.49	7.9
H/C (atomic ratio)	1.683	1.639	1.389
N/C (atomic ratio)	0.013	0.012	0.019
O/C (atomic ratio)	0.141	0.090	0.073
S/C (atomic ratio)	0.002	0.001	0.002

5.3.1 FTIR analysis

The spectral research methods are widely used in order to identify the structural features of asphaltenes and diagnose the functional groups. The FTIR spectroscopy data of the asphaltene samples indicate the presence of complex structures containing aliphatic and aromatic hydrocarbon fragments, as well as oxygen-containing functional groups.

In the FTIR spectrum of the asphaltenes from Figures 5-3 to Figures 5-5, absorption bands are observed approximately at 1600 cm^{-1}, due to stretching vibrations of the C = C bonds of aromatic rings. A faint signal of aromatic C-H stretch is seen in the range of 3000-3100 cm^{-1}. The C-H out of plane aromatic bands are assigned in average to 740 cm^{-1} and 870 cm^{-1}, 960 cm^{-1}. The infrared spectra of the asphaltenes show absorption bands at approximately 1460 cm^{-1} and 1370 cm^{-1}, characteristic of bending vibrations of C-H bonds of methylene and methyl groups, respectively. Bands of various intensities also appear at peaks of 1720 cm^{-1} (stretching vibrations of the C = O bond in the carboxylic groups of acids). In addition, the presence of a weak hydrogen bonds (O–H and C-H) in the region of 3000 to 3700 cm^{-1} shows low content of these functional groups, which are essential in the aggregation of asphaltenes by hydrogen bonds (Calemma, V. et al., 1995). Absorption bands in the region of 2900 – 3000 cm^{-1} are due to stretching vibrations of the aliphatic C – H bonds. Furthermore, peaks observed in the region of “fingerprint” at approximately absorption bands of 1120 cm^{-1}and 1270 cm^{-1} belong to C-O bond stretching. The comparative table of functional groups (Table 5-3) are presented further.

Table 5-3. Comparison of FTIR peaks for asphaltene samples

Sample 1	Sample 2	Sample 3	
Wavenumber, (cm^{-1})	Wavenumber, (cm^{-1})	Wavenumber, (cm^{-1})	Vibrational response
3400			O-H stretching
2954.46	2956.48	2955.68	Aliphatic C-H stretching
2848.58	2921.69	2918.75	
	2855.01	2849.69	
1729.36	1724.77	1725.43	Carbonyl C=O stretching
1600	1599.73	1599.74	Aromatic C=C stretching
	1580.04	1580.01	
1462.28	1459.9	1461.68	Methylene C-H bending
1377.54	1378.59	1378.18	Methyl C-H bending
1269.87	1267.68	1268.00	C-O bond stretching
1121.01	1119.7	1119.77	
1071.18	1070.42	1070.5	Sulfoxide S=O stretching
1039.72	1039.2	1039.21	
870	867.88	868.61	
740.59	740.71	740.71	Aromatic C-H out of plane bending
729.78			
719.46			
	704.37	704.29	C-H bending
	651.4	651.60	
	576.47	576.94	

As follows from the FTIR spectra, the regions assigned to the aromatic functional group are more pronounced in the asphaltene samples # 2 and #3, while this spectrum in the sample #1 is shallow. However, the OH group, which is characteristic in the signal spectrum from 3100 cm^{-1} to 3700 cm- ^{1}, and is involved in the aggregation of asphaltenes, is noticeable in samples #1.

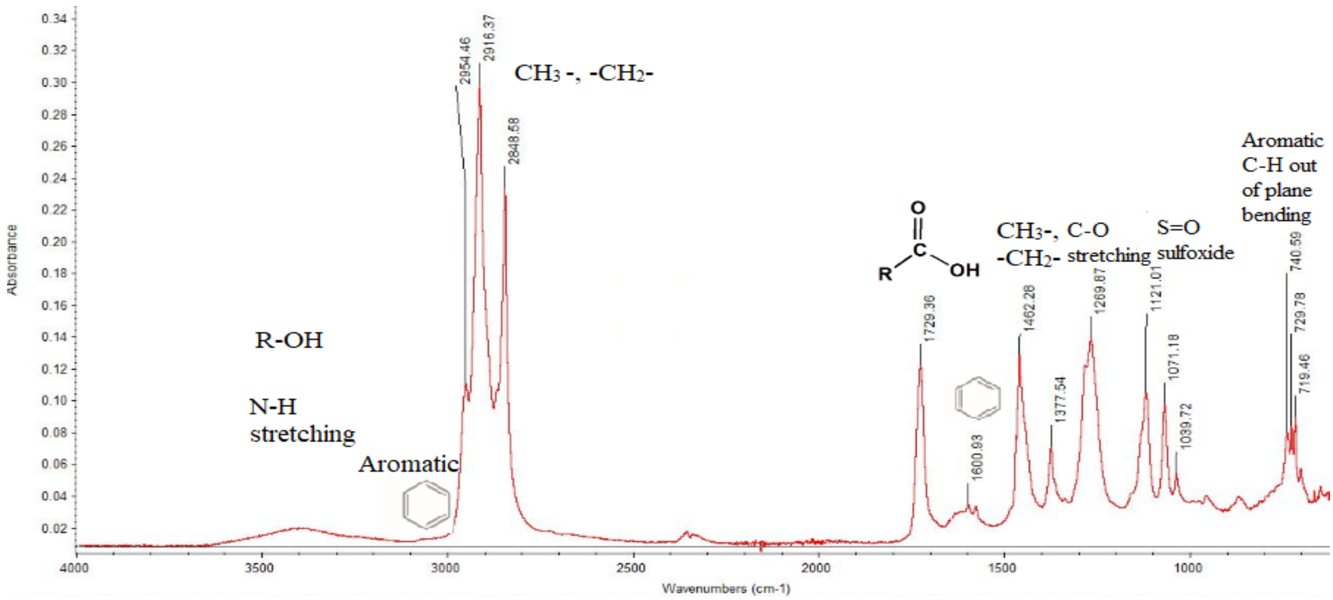


Figure 5-3. FTIR spectrum of asphaltenes sample #1

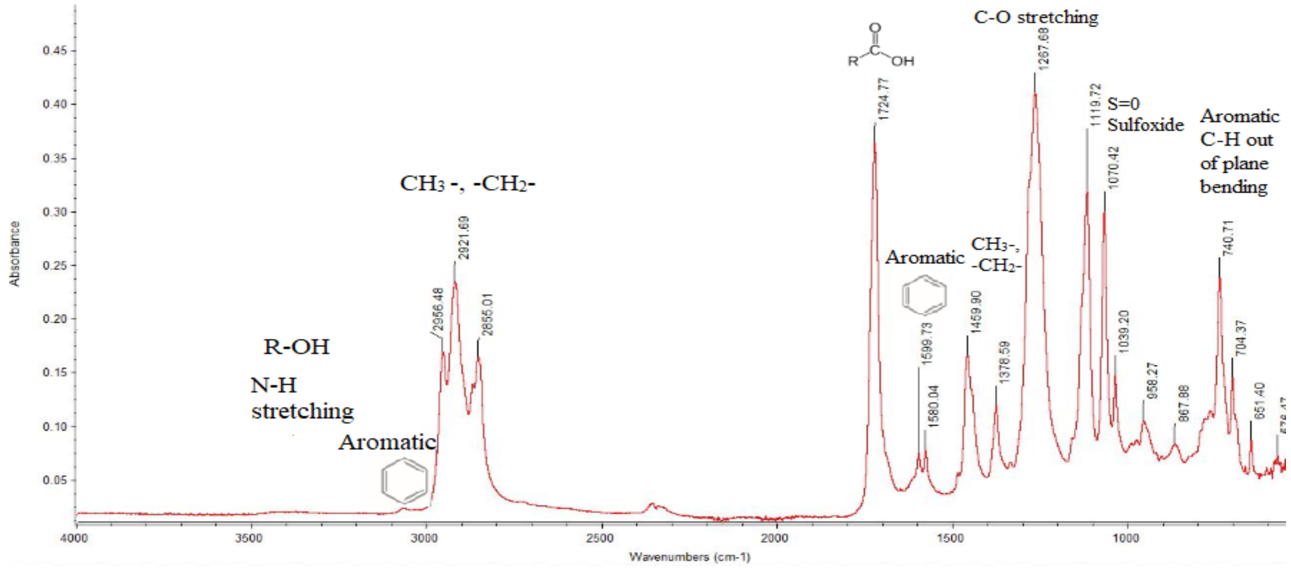


Figure 5-4. FTIR spectrum of asphaltenes sample #2

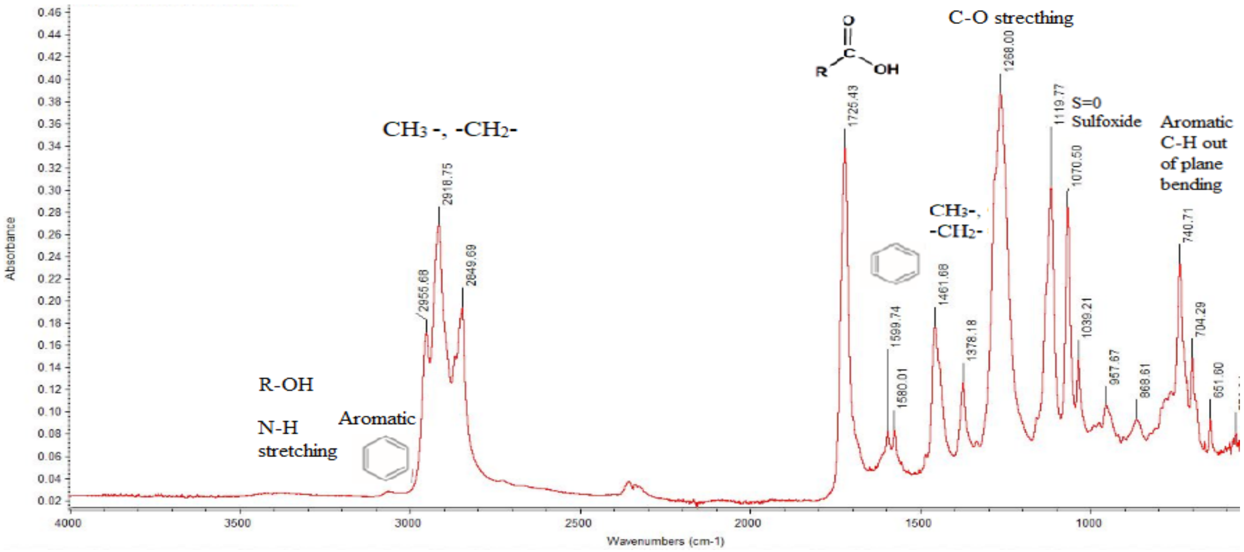


Figure 5-5. FTIR spectrum of asphaltenes sample #3

5.3.2 1H and 13C NMR

Based on the analysis of 1H NMR spectra, the structural-group composition of the components forming asphaltenes can be estimated. The use of nuclear magnetic resonance for the structural analysis of organic compounds made it possible to accumulate the large database on the position of signals of various structural groups on the scale of chemical shifts. This makes it possible to sensibly carry out the assignment of various structural units not only for individual compounds but also for complex organic mixtures, such as asphaltenes.

The proton nuclear magnetic resonance spectrum can be divided into 4 regions. These areas are proportional to the number of protons giving these signals. The separation of the regions is carried out according to the values of the integration of area in the spectrum. Region in 6.0-9.0 ppm corresponds to the position of the aromatic protons signals (Har); region in 0.1-1.0 ppm (Hγ) - signals of methyl groups (CH3) protons, that more distant from aromatic rings; region in 1.0-2.0 ppm (Hβ) - signals of methylene, methane, and methyl (CH2, CH, CH3,) protons in β-position to the aromatic nucleus; region in 2.0-4.5ppm (Hα) - proton signals of CH, CH2, and CH3-groups located in the α-position to the aromatic nucleus. The main separation of functional groups according to the NMR spectrum signals are given in the Table 5-4.

With the help of Dickinson’s equation, the number of carbon per alkyl side chain can be determined:

$$n_{carbon} = \frac{H\alpha + H_{\beta} + H\gamma}{H\alpha} \tag{5}$$

Table 5-4. Structural assignation of the integrated area of H and C NMR by Poveda-Jaramillo, Juan-Carlos, et al. (2016); Mullins, O. C., and Sheu, E. Y. (2013)

Region, ppm	Structure	Integrated area		
		Sample #1	Sample #2	Sample #3
Proton NMR				
9.0-12.0	Aldehydic and carboxylic Hydrogens	0.02	0.19	0.06
7.2-9.0	Aromatic hydrogens in poliaromatic rings	0.14	1.12	0.21
6.0-7.2	Aromatic hydrogens in monoaromatic rings	0.03	0.19	0.04
4.5-6.0	Olefinic hydrogens	0.01	0.14	0.03
2.0-4.5	CH, CH_2, CH_3 type naphthenic and paraffinic hydrogens in α positions to aromatics	0.24	1.85	0.40
1.5-2.0	CH_2, naphthenic hydrogens in β positions to aromatics	0.37	2.19	0.45
1.0-1.5	Paraffinic hydrogens in β positions to aromatics, CH_2, CH_3 groups	2.48	7.31	1.81
0.1-1.0	Paraffinic hydrogens in γ positions to aromatics, CH_3 groups	1.46	5.44	1.28
Carbon NMR				
100 – 170	Aromatic carbons	0.11	0.39	0.28
10-65	Aliphatic carbons	1.00	1.00	1.00

Results obtained by the Dickinson's equation for all three asphaltene fractions are presented in the Table 5-5. Additionally, integrated areas related to α, β, and γ positions of protons on the H NMR spectrums are illustrated on the Figures 5-6, 5-7, and 5-8. Integrations were performed 3 times, and the average values were taken.

No less informative are the results of the spectroscopy of carbon nuclear magnetic resonance. As of now, many years of research have made it possible to create a description not only for H NMR spectra, but also for C NMR. The C NMR spectra also allows to get information about the proportion of aromatic, primary, secondary and other types of carbon atoms.

Additionally, using the integrated data from the spectrum in the regions of aromatic and aliphatic carbons, there is the possibility to estimate aromaticity factor (f_a):

$$f_a = \frac{C_{ar}}{C_{ar} + C_{al}} \tag{6}$$

Where C_{ar} is the integrated area related to aromatic carbons, and C_{al} is the integrated area of aliphatic carbons. Here, it should be mentioned that in the course of the experiment since the concentration of asphaltenes in the deuterated chloroform solvent was low, the signals on the C NMR spectrum were not sufficiently pronounced. Thus, the obtained integration regions may have inaccuracies due to experimental errors. As per H NMR, the spectrum of carbon NMR spectroscopy was integrated 3 times and the average results were chosen. The spectrums of asphaltenes obtained from carbon NMR are presented by Figures 5-9, 5-10, and 5-11.

The results, which represent the average molecular parameters of asphaltenes obtained using proton and carbon NMR spectroscopy are indicated in Table 5-5

Table 5-5. Average molecular parameters obtained by H and C NMR spectroscopy

Parameter	Sample #1	Sample #2	Sample #3
The number of carbons per alkyl side chain, n	18.96	9.08	9.85
Aromaticity factor, f_a	0.1	0.28	0.22

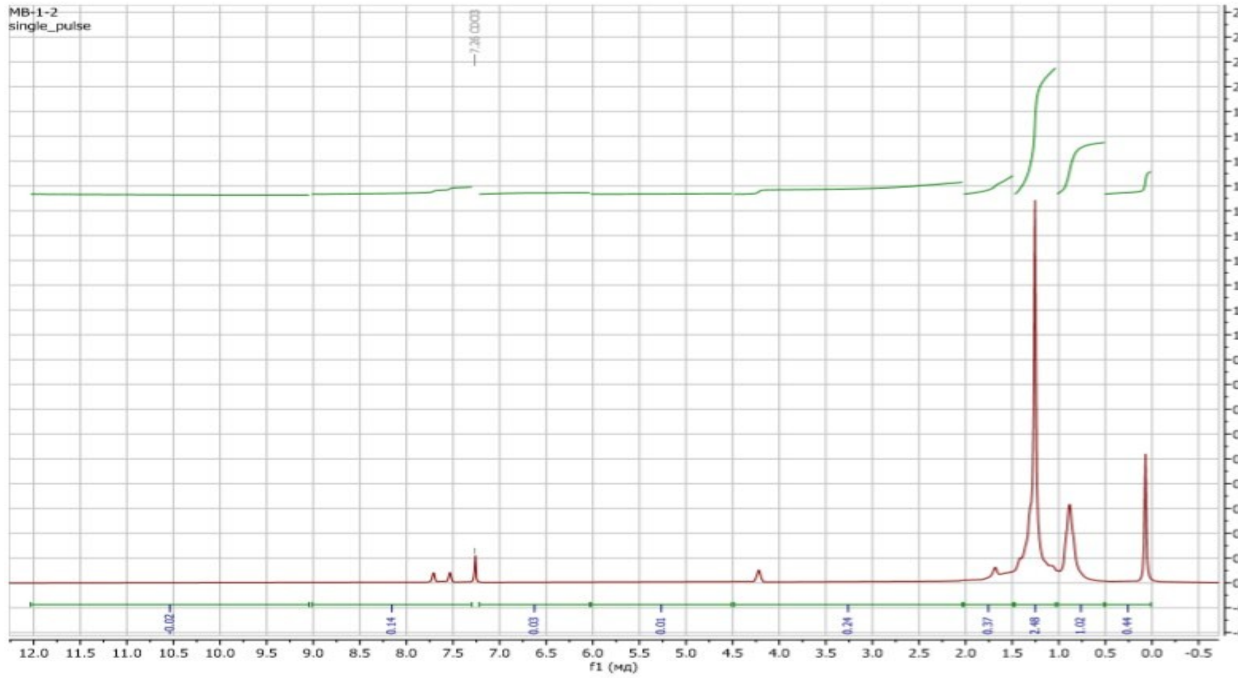


Figure 5-6. Proton NMR spectrum for asphaltene sample #1

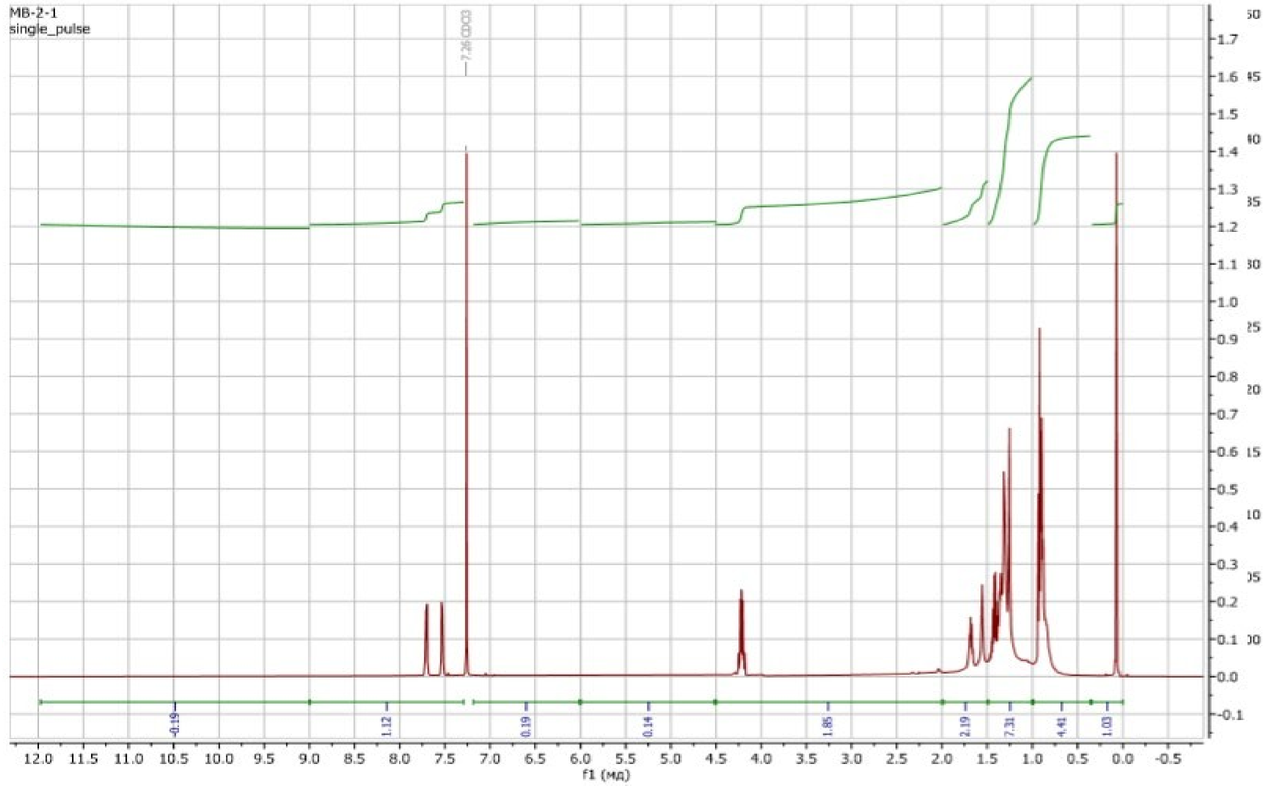


Figure 5-7. Proton NMR spectrum for asphaltene sample #2

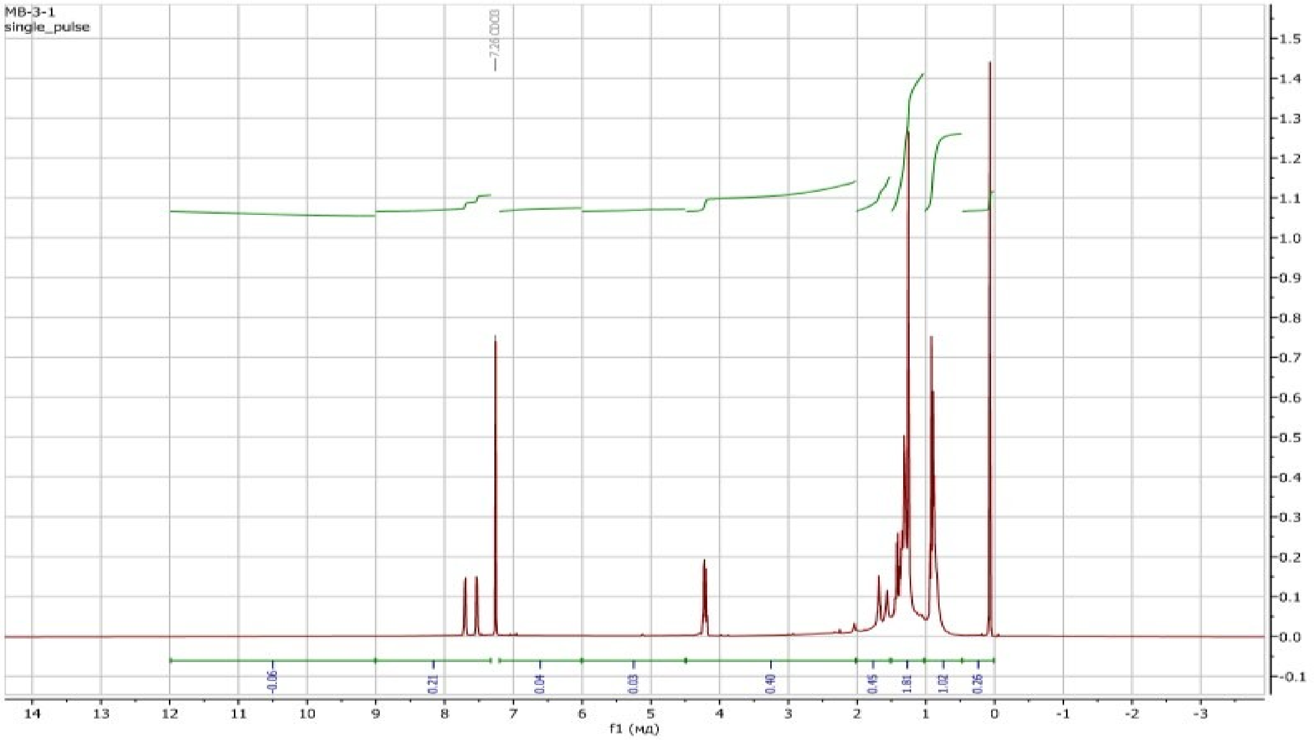


Figure 5-8. Proton NMR spectrum for asphaltene sample #3

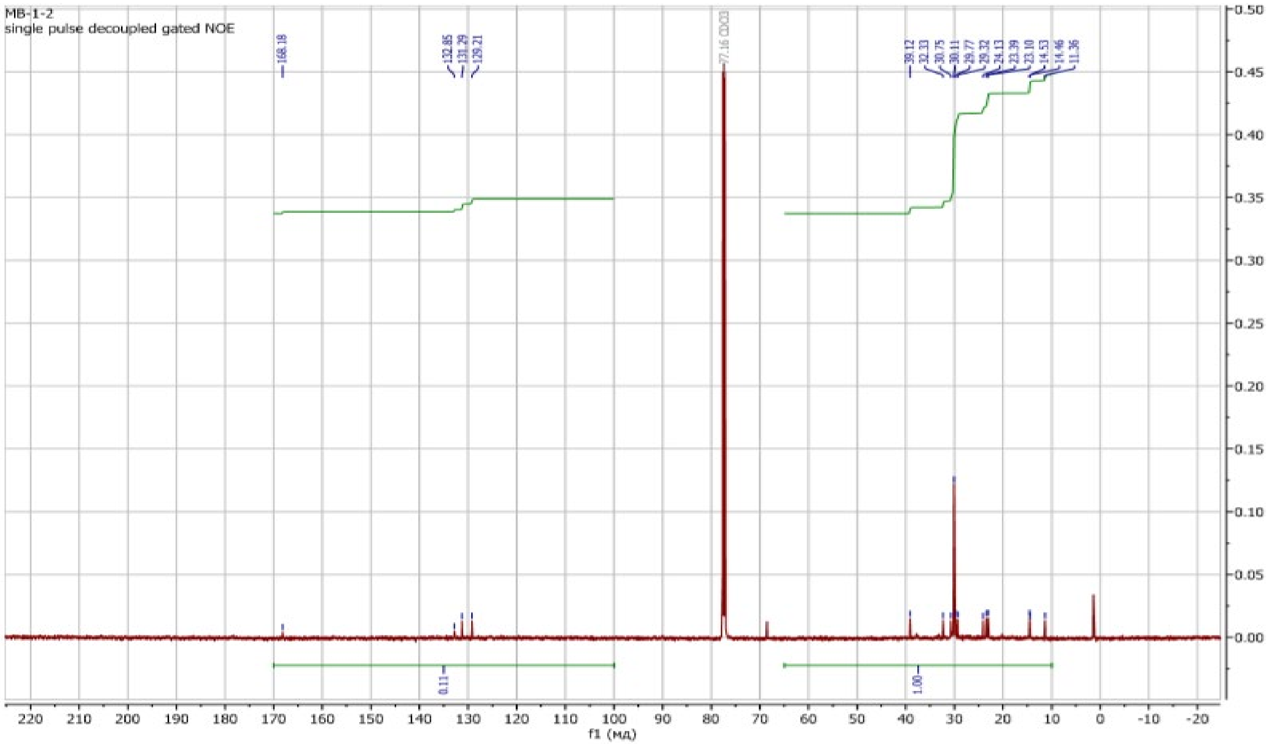


Figure 5-9. Carbon NMR spectrum for asphaltene sample #1

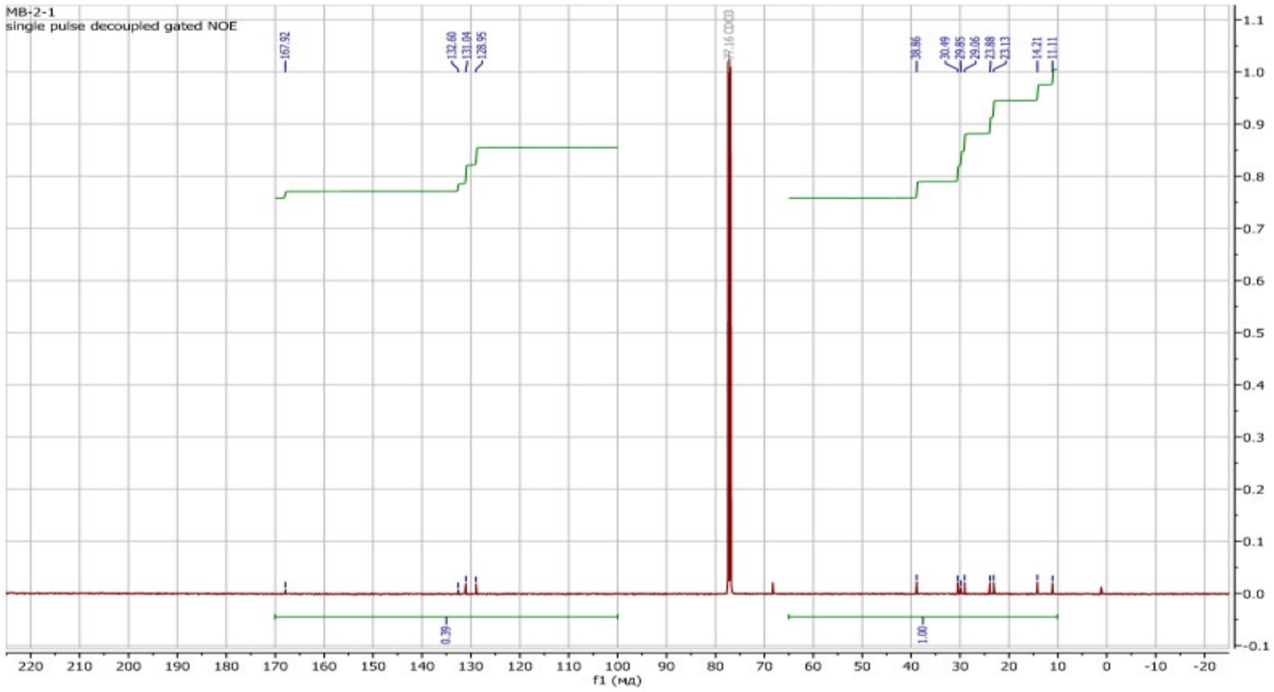


Figure 5-10. Carbon NMR spectrum for asphaltene sample #2

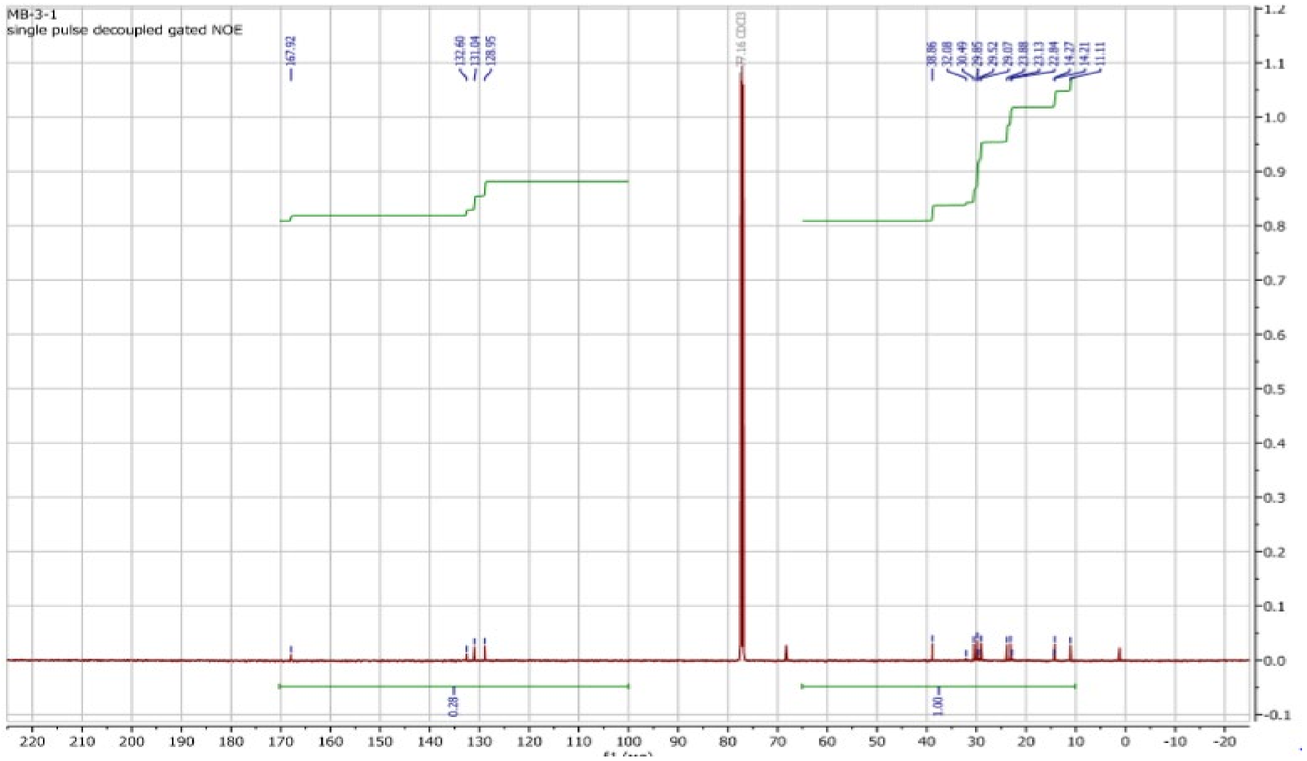


Figure 5-11. Carbon NMR spectrum for asphaltene sample #3

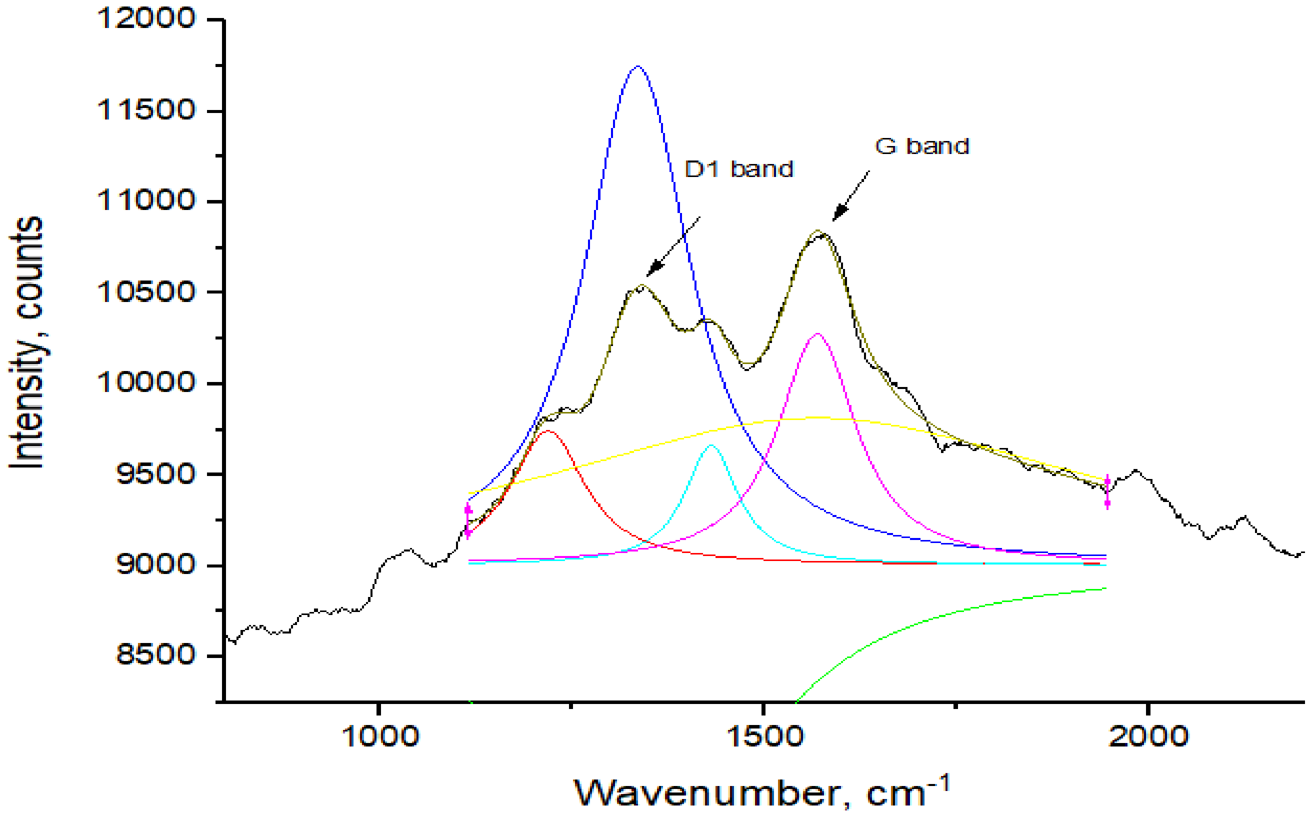
5.3.3 *Raman spectroscopy*

Further structural study of asphaltenes properties was carried out by the Raman spectroscopy method. The quantitative characteristics of the Raman spectra of asphaltene samples were calculated by processing the spectra using different functions in the “Origin” program. The Raman spectrum is characterized by two peaks in different frequencies: D1 band in the region of 1350cm^{-1} and G band at 1580 cm^{-1}. G type band vibrations are formed by carbon atoms in sp^2 states when there are carbon atoms with double bonds, also these vibrations are associated with aromatic carbon rings. The intensity of the D1 band is strictly related to the proportion of aromatic carbon rings. If aromatic clusters are small, then the position of the maximum shifts to the region of higher frequencies. For this reason, Raman spectroscopy allows to measure the average diameter of aromatic layer (*La*).

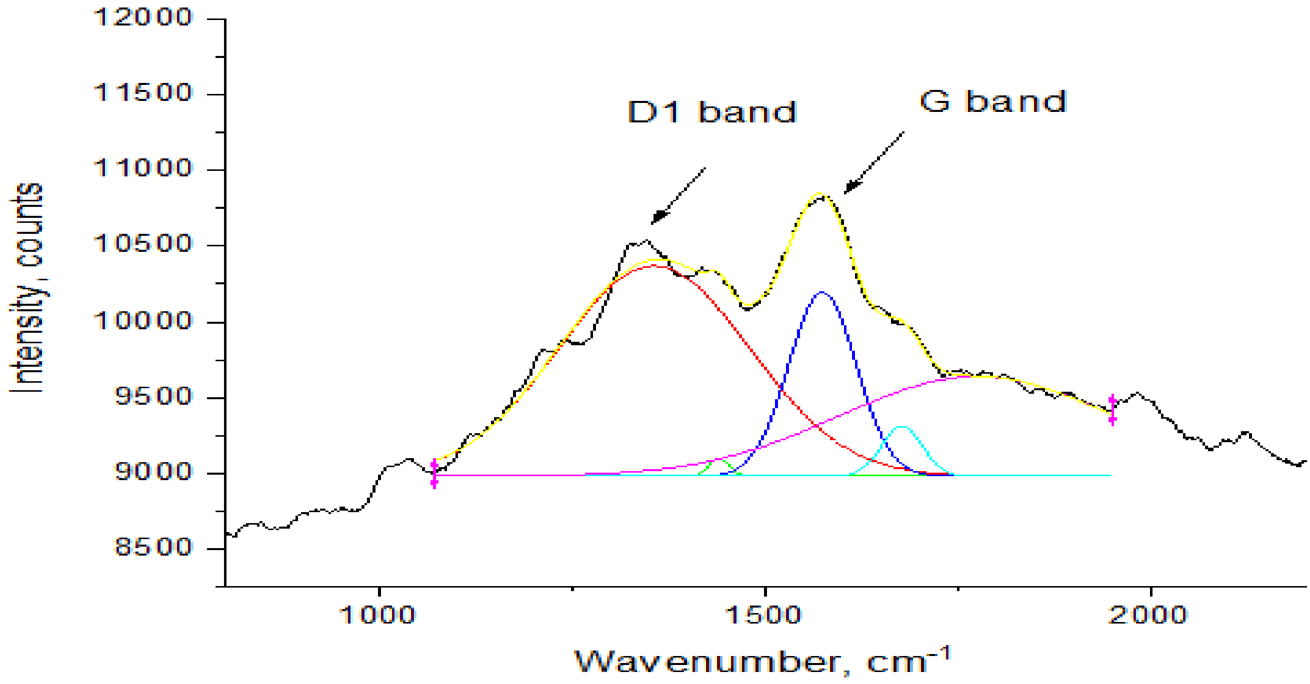
With the aim of analyzing the Raman spectrum, the Gauss and Lorentz functions were used. In order to fit the general profile from three to six peaks were used for the fitting. The molecular properties of asphaltenes (average diameter of aromatic unit) were calculated by the mathematical expression proposed by and Tuinstra and Koenig (1970):

$$\mathrm{La\ (diameter, nm)} = 4.4\frac{\mathrm{I_G}}{\mathrm{I_{D1}}} \tag{7}$$

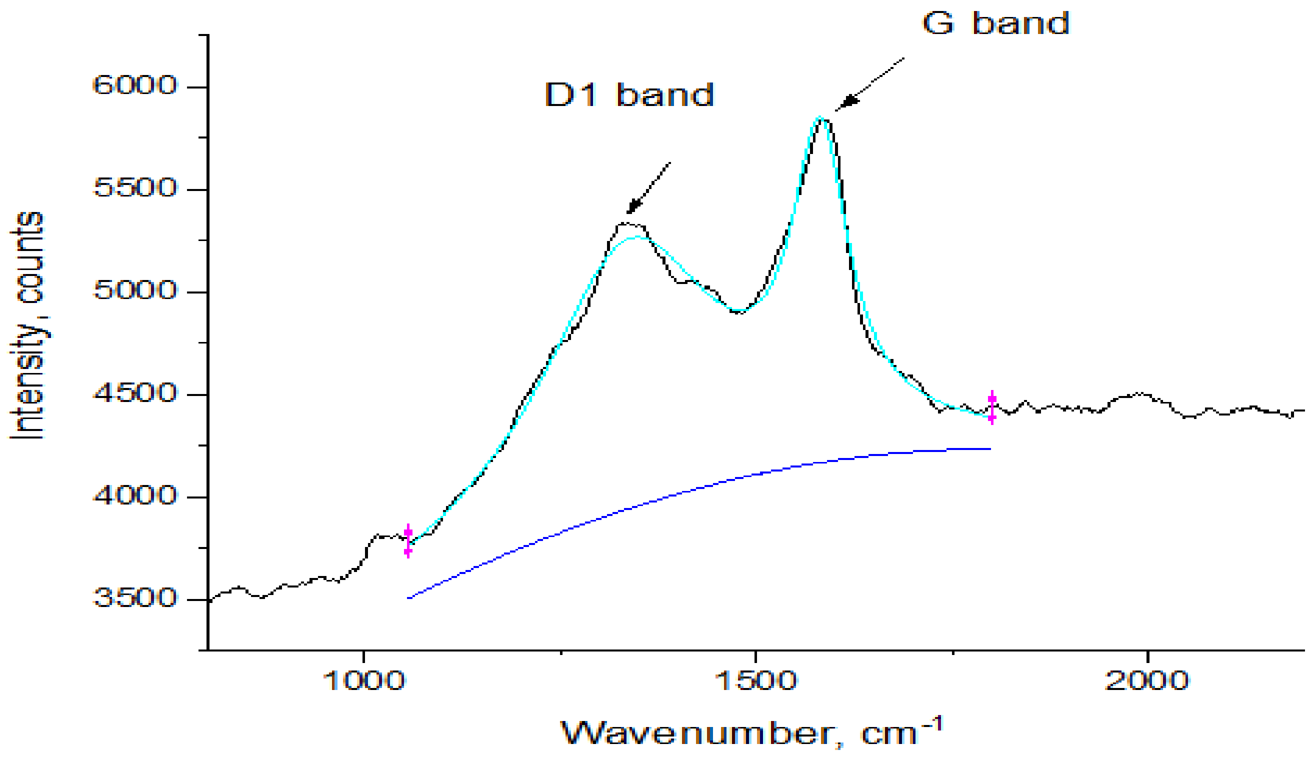
Where, $\mathrm{I_{D1}}$ – integrated intensity of peak D1, $\mathrm{I_G}$ – integrated intensity of G band.


12000
11500
11000
10500
10000
9500
9000
8500
Intensity, counts
1000
1500
2000
Wavenumber, cm^{-1}
D1 band
G band

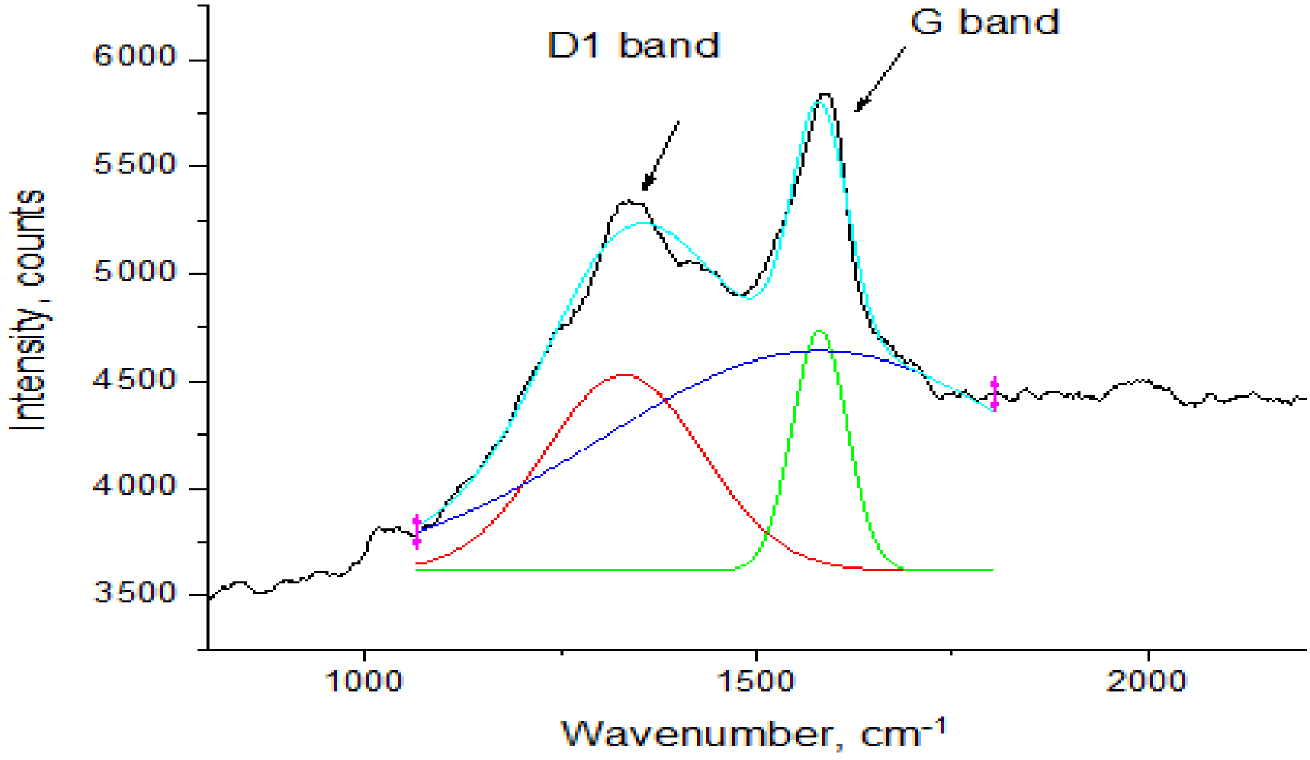
a)


12000
11500
11000
10500
10000
9500
9000
8500
Intensity, counts
1000
1500
2000
Wavenumber, cm^{-1}
D1 band
G band

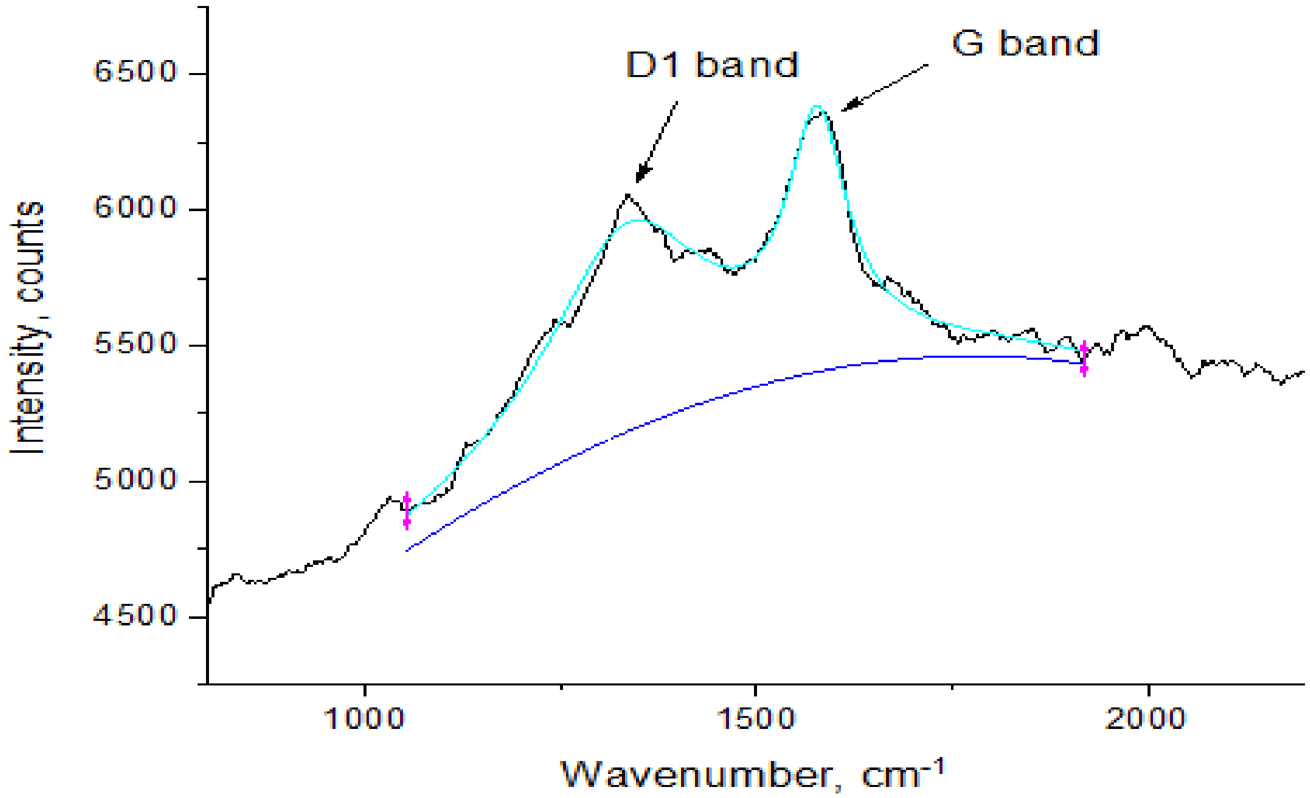
b)


G band
D1 band
6000
5500
5000
4500
4000
3500
Intensity, counts
1000
1500
2000
Wavenumber, cm^{-1}

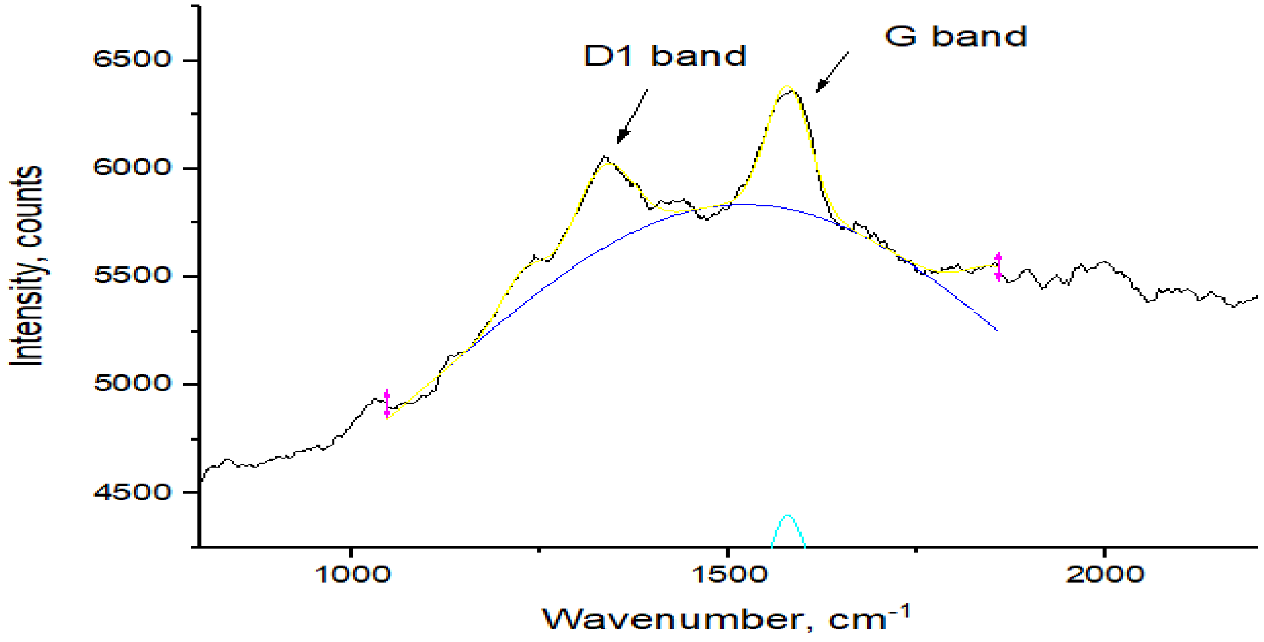
c)


D1 band
G band
6000
5500
5000
4500
4000
3500
Intensity, counts
1000
1500
2000
Wavenumber, cm^{-1}

d)



e)



f)

Figure 5-12. RAMAN spectrum for asphaltenes fitted by different functions: a) Sample #1 by Lorentz function; b) Sample #1 by Gauss function; c) Sample #2 by Lorentz function; d) Sample #2 by Gauss function; e) Sample #3 by Lorentz function; f) Sample #3

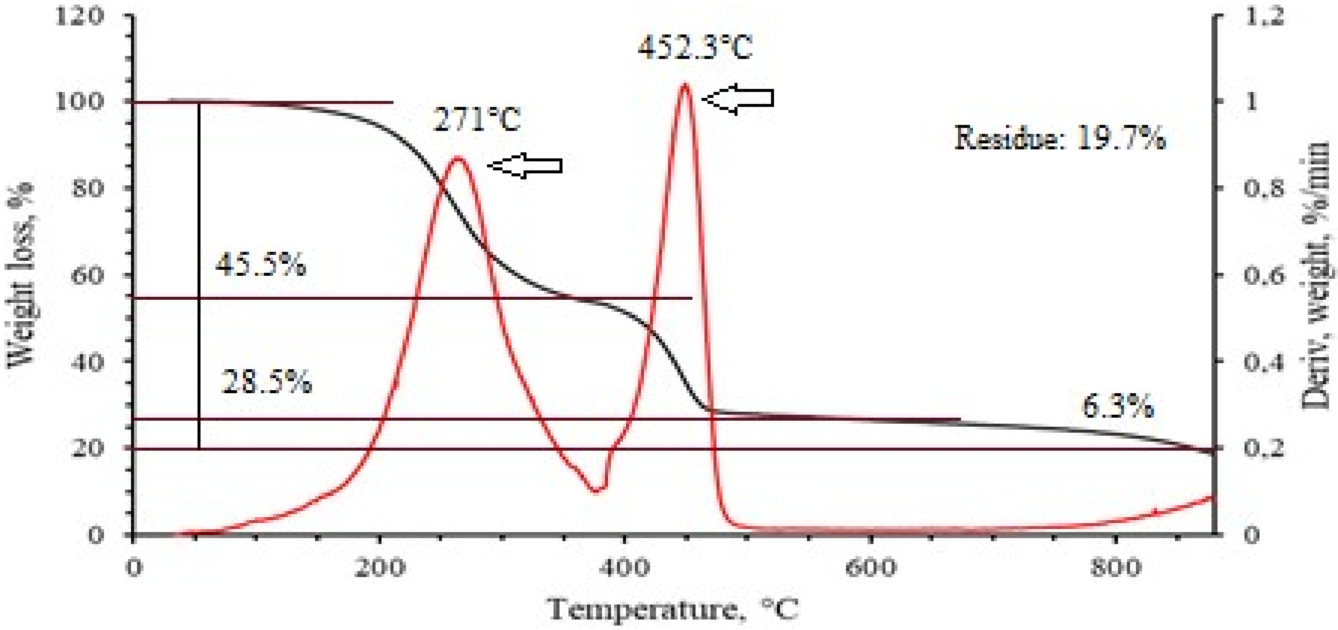
The integration of the intensities of D1 and G bands in the Gauss and Lorentz functions processed in the Origin software are presented on the Figure 5-12. Analysis of Raman is presented in Table 5-6. The table contains the results of the average diameter of aromatic layer and the coefficient of determination R^2. The value of *La* varied in the range of 1.36-1.94 for the Gauss and 1.5-1.78 for Lorentz functions. The obtained sizes of aromatic units are similar to those published in different works (Abdallah and Yang, 2012; Bouhadda et al., 2007).

Table 5-6. Analysis of Raman spectrum

	Lorentz function				Gauss function			
Asphaltene sample	Position of band (cm^{-1})	Integrated intensity	La (nm)	R^2	Position of band (cm^{-1})	Integrated intensity	La (nm)	R^2
#1	1335 (D1) 1568 (G)	731957.63 249489.38	1.5	0.99	1356 (D1) 1574 (G)	432485.97 133988.22	1.36	0.98
#2	1337 (D1) 1581 (G)	543555.11 189306.08	1.53	0.99	1330 (D1) 1580 (G)	229850.14 98004.67	1.88	0.99
#3	1334 (D1) 1577 (G)	290888.09 117795.95	1.78	0.99	1322 (D1) 1575 (G)	214168.86 53295.73	1.94	0.98

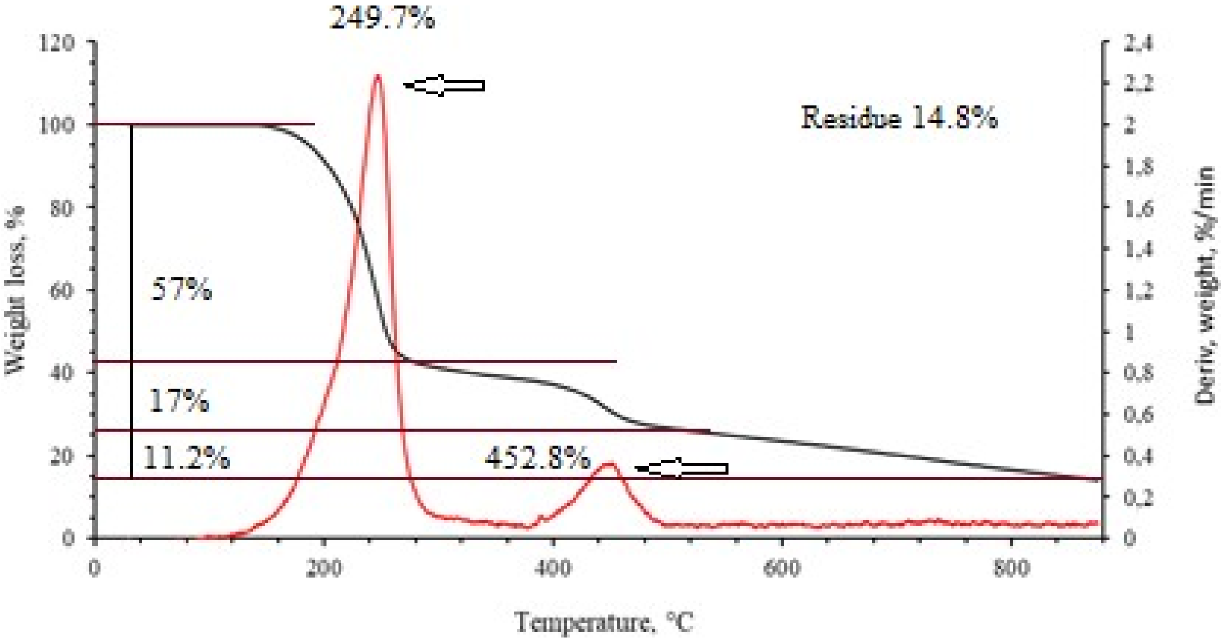
5.3.4 Thermogravimetric analysis results

Thermogravimetric tests were carried out in the temperature range from 30°C to 880°C with a heating rate of 2°C/min. The Figure 5-13 indicates the results of the thermogravimetric analysis for all samples of asphaltenes. According to the graph, the profile of thermal degradation for samples 2 and 3 is almost similar to each other and in many respects differs from the behavior of asphaltenes # 1. As the graph shows, the thermal reactions with a decrease in molecular weight for asphaltenes began at temperature about of 150°C. Significant weight loss can be observed at temperatures from 200 to 300, when more than 50% of the total weight of samples # 2 and 3 burned out. Maximum weight loss is observed at a temperature of 480°C for all three asphaltene samples.



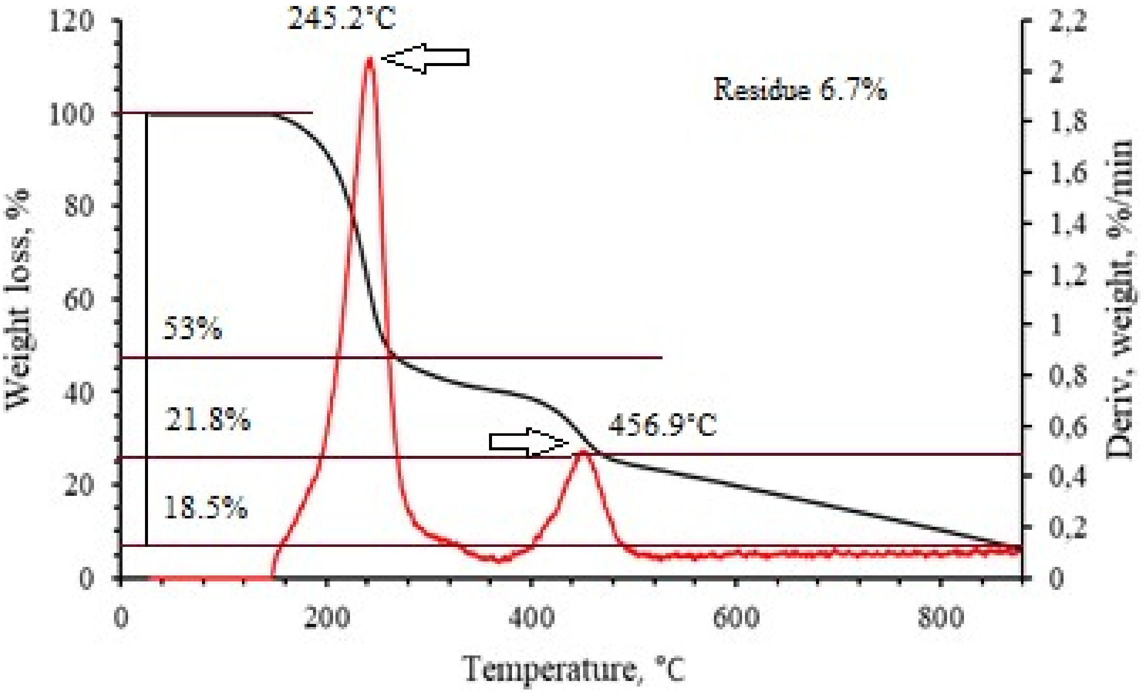
452.3°C
271°C
Residue: 19.7%
45.5%
28.5%
6.3%
Weight loss, %
Deriv, weight, %/min
Temperature, °C
0
20
40
60
80
100
120
0
200
400
600
800
0
0,2
0,4
0,6
0,8
1
1.2

a)



249.7%
Residue 14.8%
57%
17%
11.2%
452.8%
Weight loss, %
Deriv, weight, %/min
Temperature, °C
0
20
40
60
80
100
120
0
200
400
600
800
0
0,2
0,4
0,6
0,8
1
1,2
1,4
1,6
1,8
2
2,2
2,4

b)



c)

Figure 5-13. TGA and DTG curves of thermogravimetric analysis for asphaltenes. a) Sample #1, b) Sample #2, c) Sample #3

5.3.5 *Scanning electron microscopy*

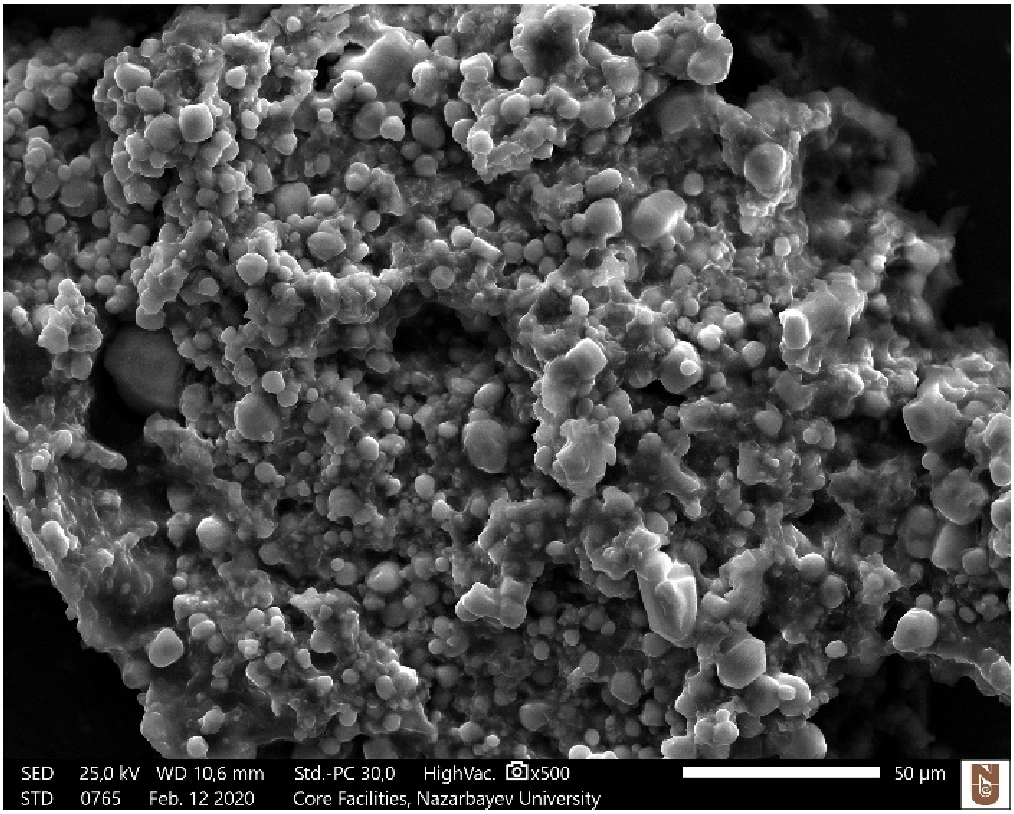
An analysis of the morphology and chemical composition of samples of asphaltenes obtained by n-heptane was carried out by scanning electron microscopy. The asphaltenes of the studied oils differ in the elemental composition received using the EDS and the variety of morphological features of their surface. Thus, the surface structure of asphaltenes is characterized by a certain inhomogeneity of granulometric size composition and a variety of shapes of their constituent particles. At the same time, it is noteworthy to mention the similarity in the surface morphology of some asphaltenes.

Figure 5-14 shows the results of scanning samples of asphaltenes from oil #1 at different magnifications. As can be seen from the images, the surface morphology of asphaltenes is characterized by agglomerates of various sizes and irregular shapes. Following from the Figure 5-14, the sizes of these microparticles, which were able to be measured with the magnification of x1000 can vary from 4µm to 15µm.

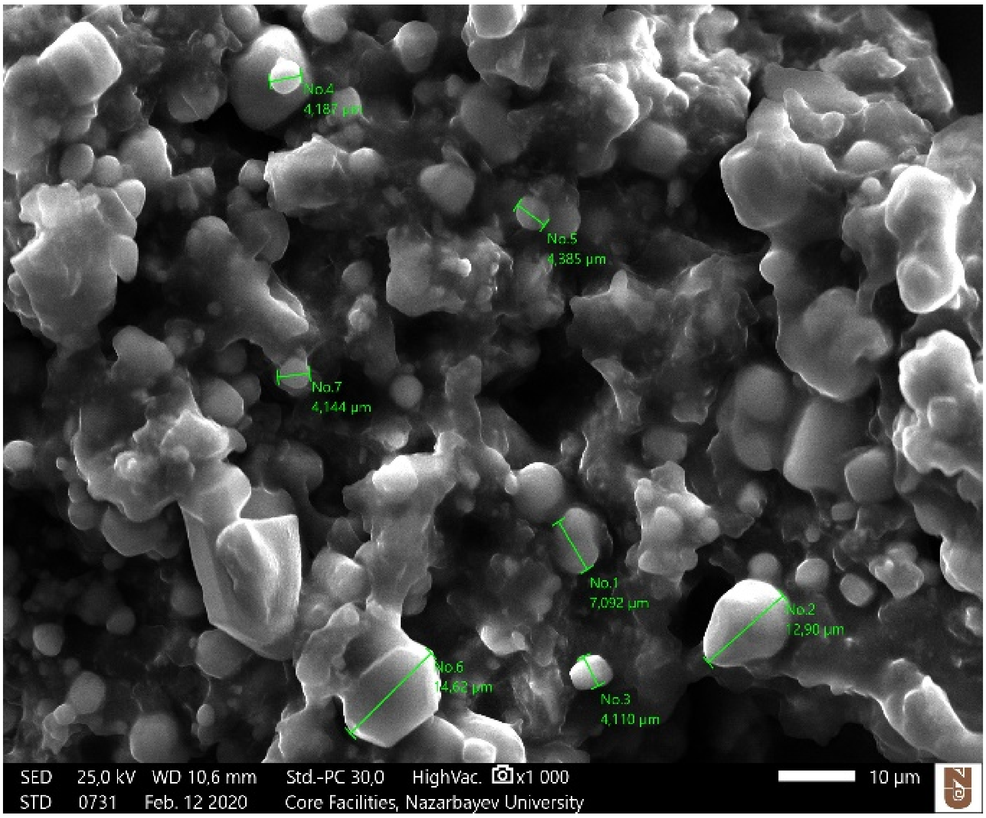
According to the Table 5-7, elemental content of asphaltene sample #1 is mainly consisted from carbon around 73%, oxygen, chlorine and nitrogen, 11.5%, 8.1% and 4.63%, respectively. The measurements received with the help of the EDS are somewhat different from those obtained with the CHNS/O analysis. In addition to these elements, a small amount of Si, K, Ca, Fe are also present in the composition of asphaltenes. Map of local elements obtained from asphaltene sample #1 by EDS analysis is presented on the Figure 5-17

The results of the study of the asphaltene obtained from crude sample #2 showed the presence of a smooth surface, with the inclusion of some particles contrasting with the surface, as can be seen in Figure 5-15. In addition, among particles of oil asphaltenes # 2, whitish point inclusions similar to crystal-like formations are observed. According to EDS analysis, the elemental composition of this sample is mainly represented by carbon, oxygen, sodium, magnesium, sulfur, chlorine. The entire results of elemental analysis are presented in Table 5-7, which also shows the presence of other inorganic material. The EDS analysis of local elements for asphaltene sample #2 is shown on the Figure 5-18.

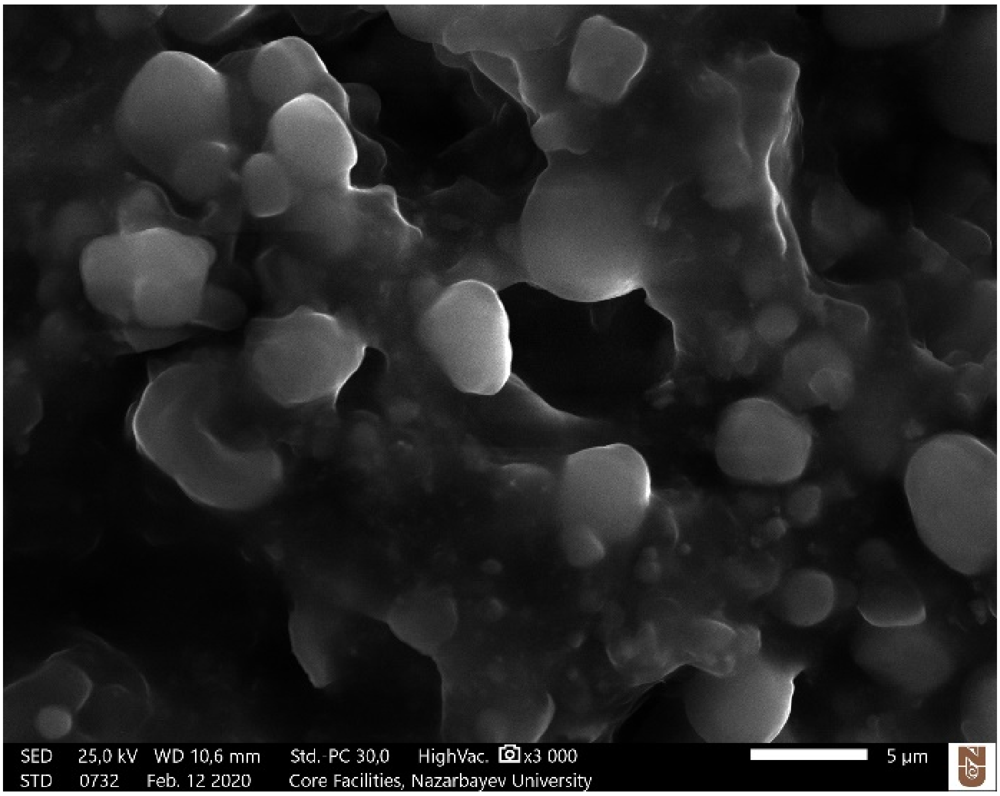
Morphological features of asphaltenes #3 are also similar to the previous sample of oil asphaltenes # 2. It may be observed in Figure 5-16, that the surface of the asphaltenes is also pretty smooth and plain. On the surface, the presence of small particles can be seen. In comparison with sample # 2, the number and size of microparticles are noticeably smaller. According to the elemental analysis of the EDS in the Table 5-7, the composition of asphaltenes predominantly consists of carbon – 80.52%, oxygen – 14.73%, chlorine – 1.75%, sodium – 1.22%, considerably less in the composition of such inorganic elements as Mg, Al, Si, S, Ca, and Cu. The presence of these elements are shown on local map by Figure 5-19.



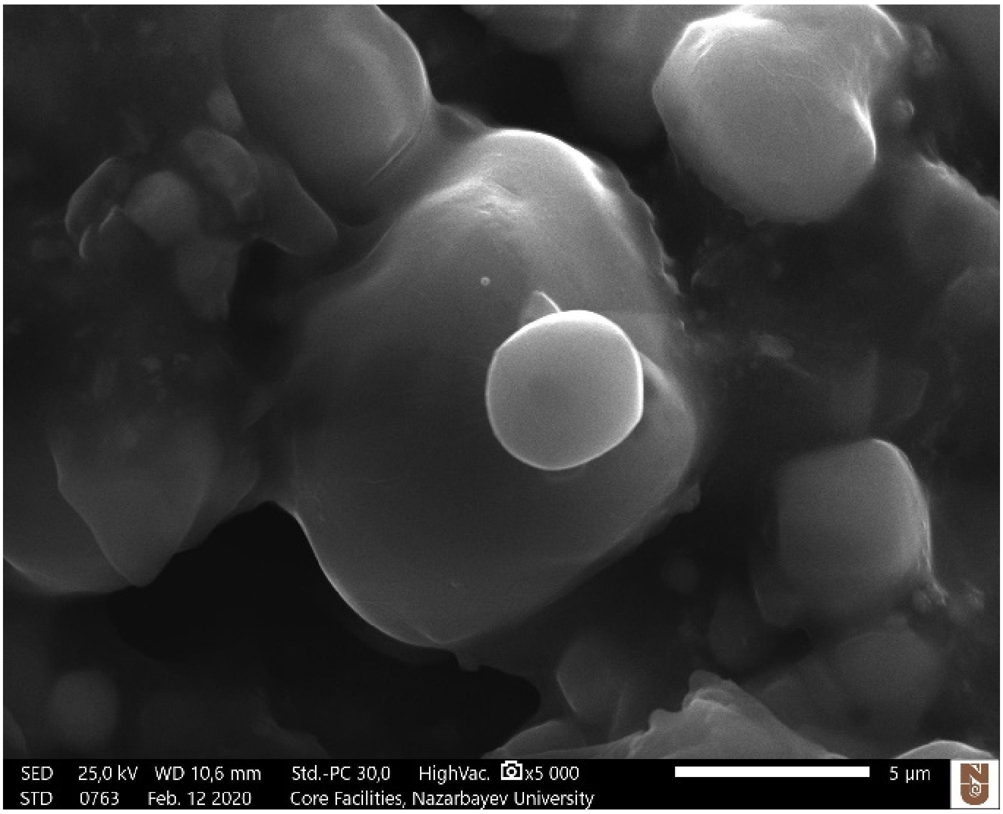
Scanning at magnification x100



Scanning at magnification x1000

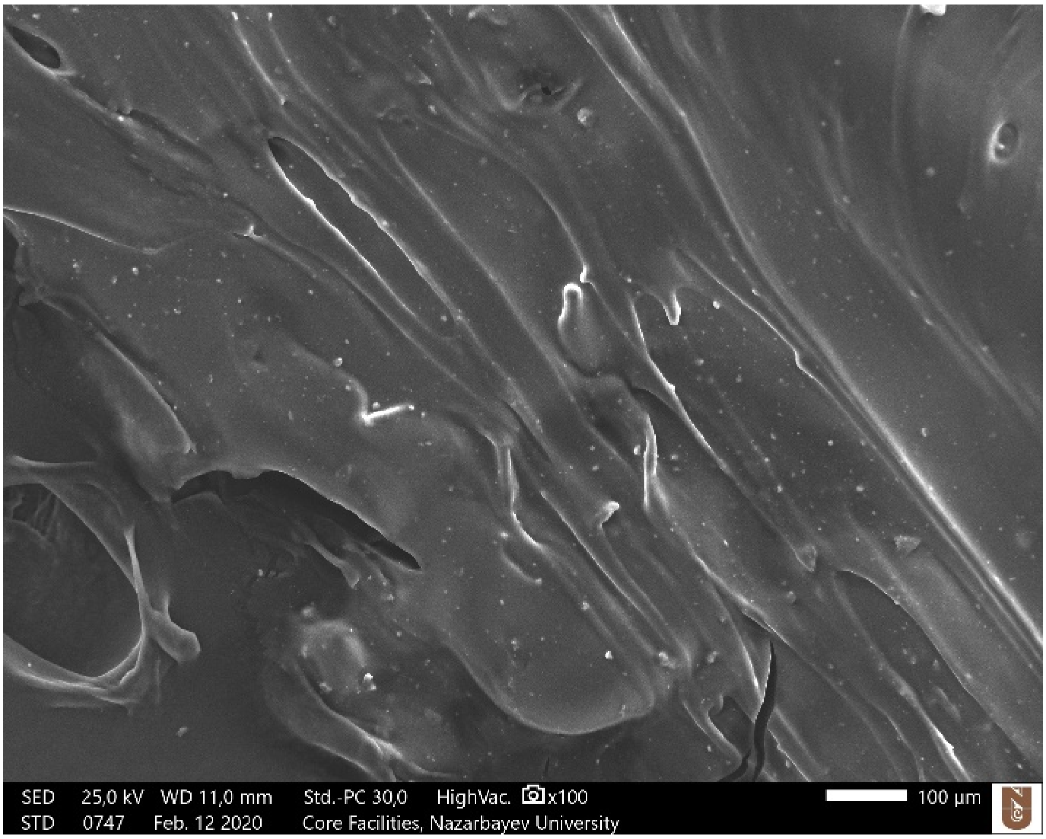


Scanning at magnification x3000

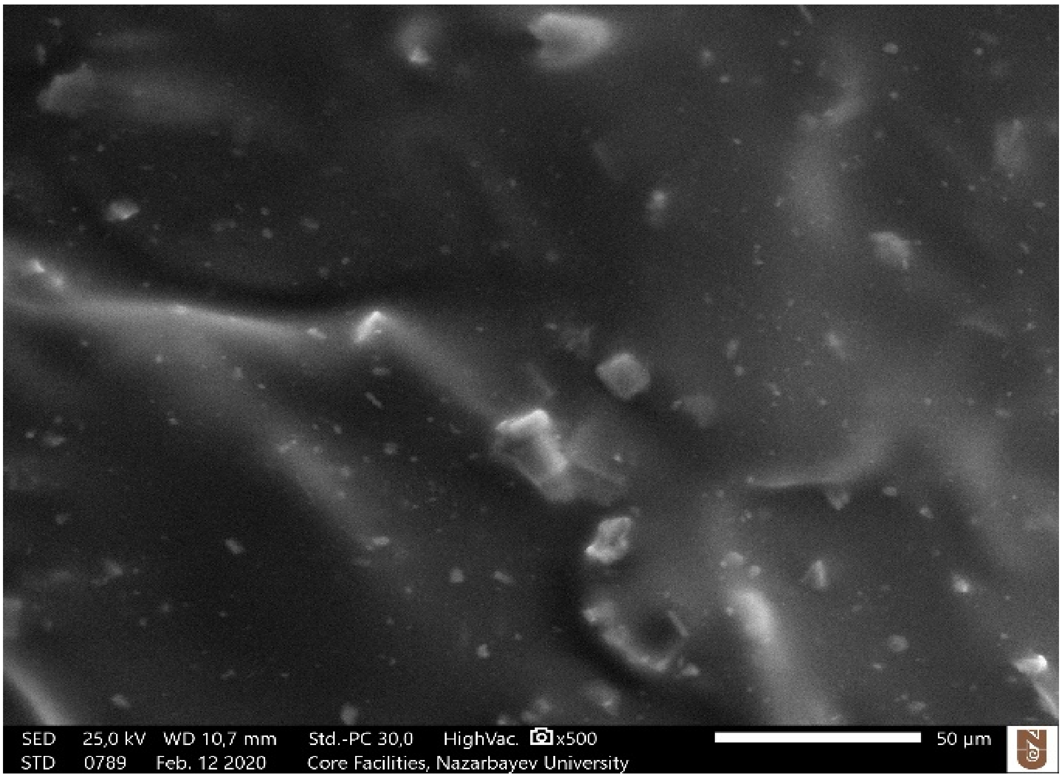


Scanning at magnification x5000

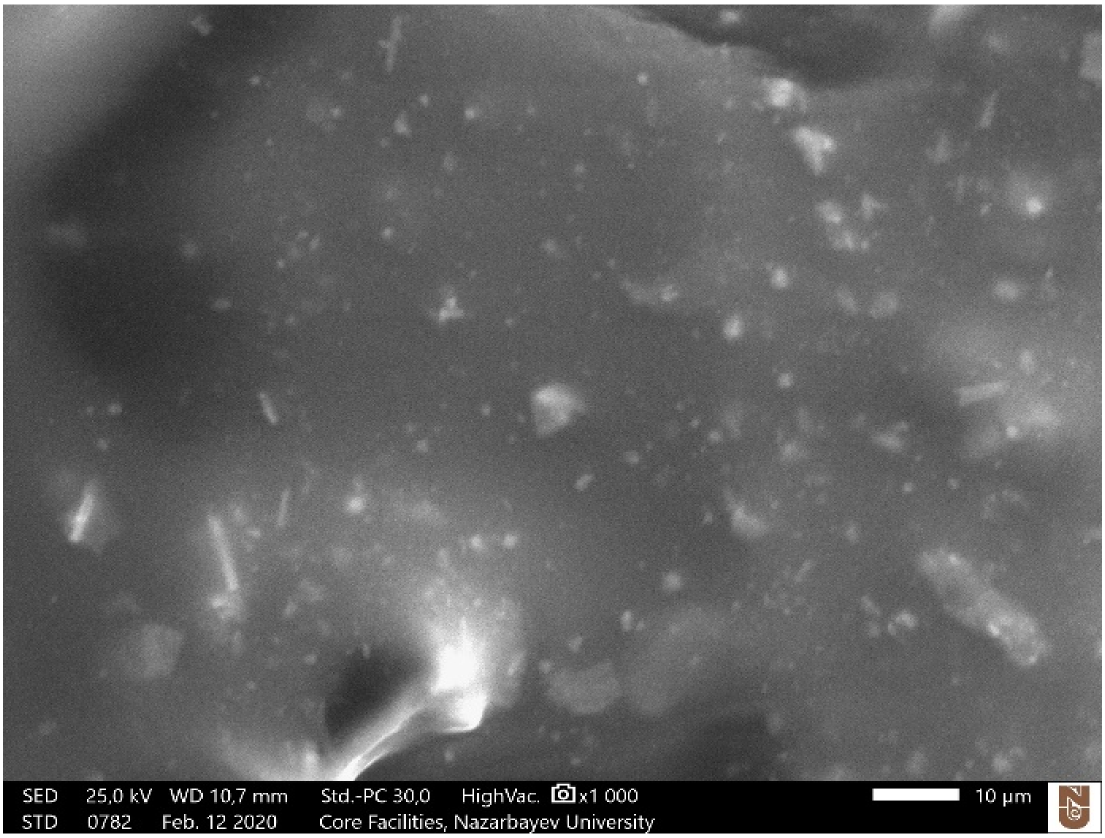
Figure 5-14. SEM analysis of Sample #1 with various magnifications



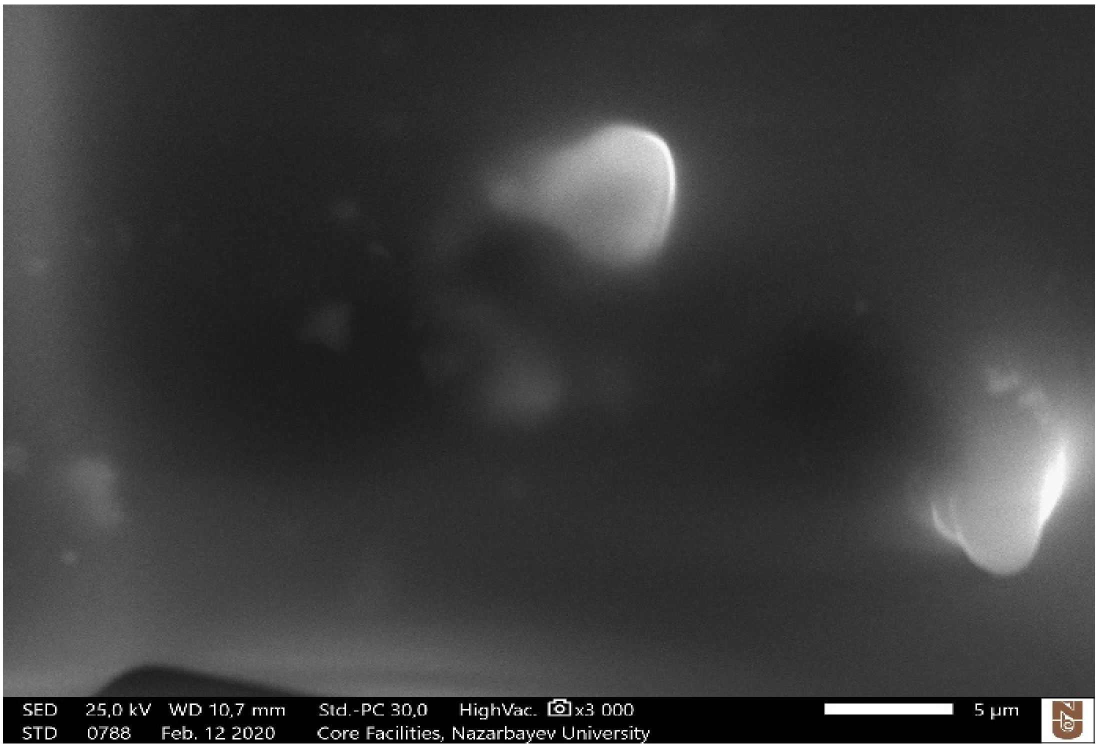
Scanning at magnification x100



Scanning at magnification x500

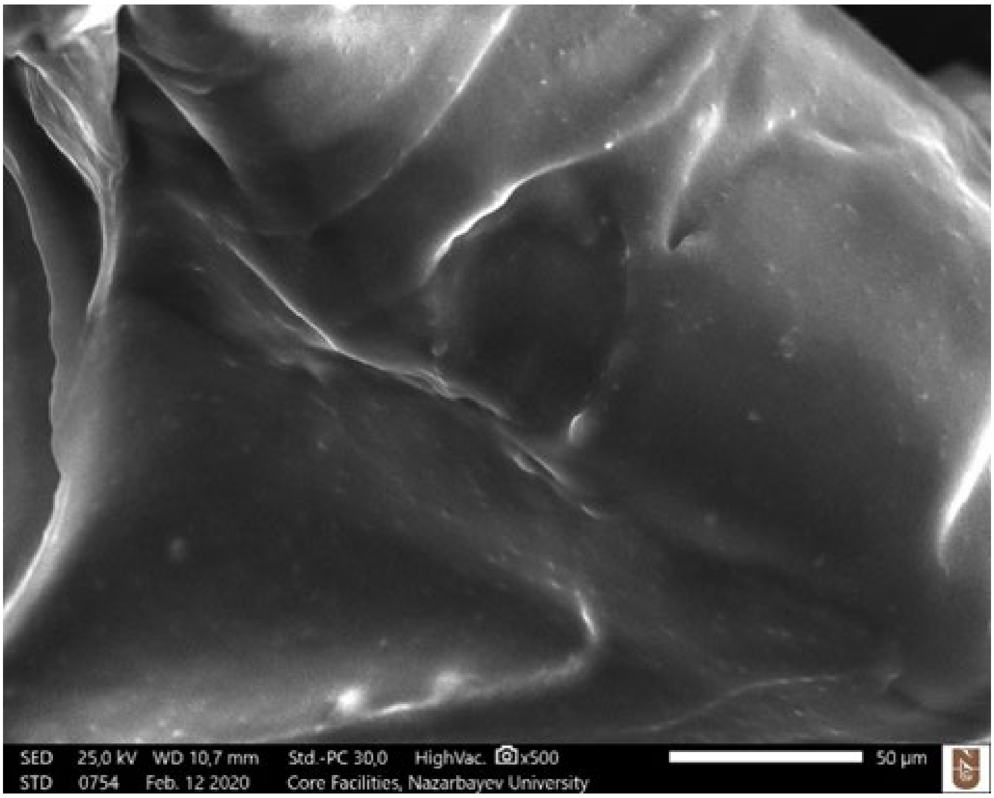


Scanning at magnification x1000

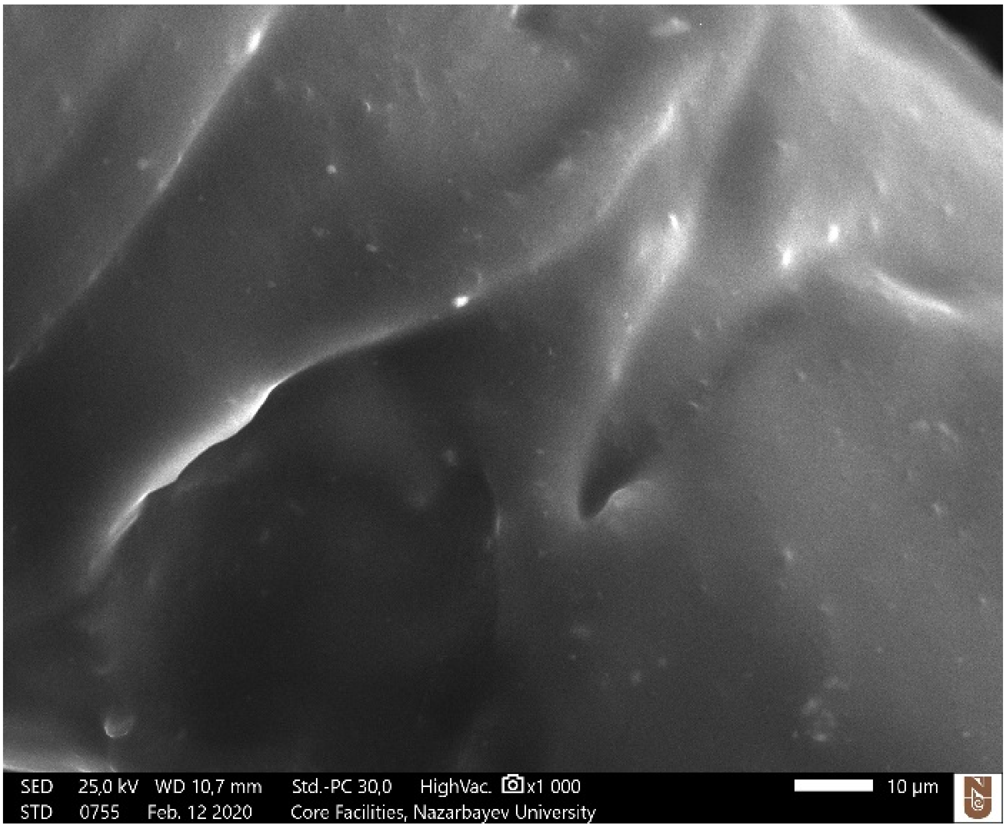


Scanning at magnification x3000

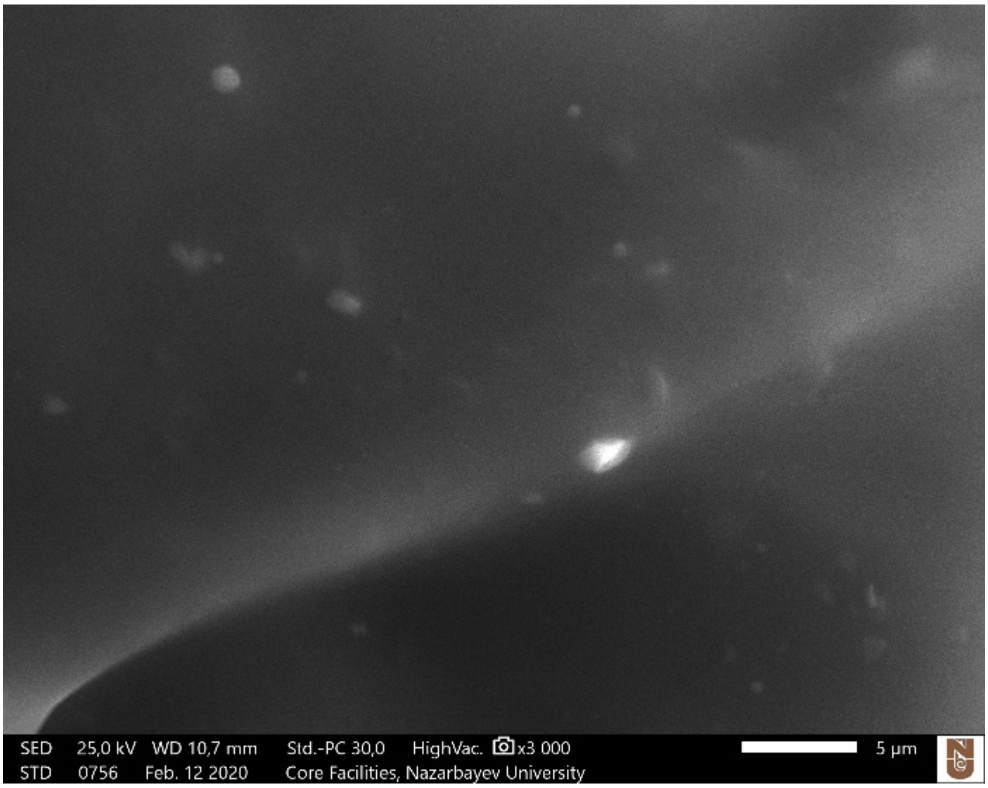
Figure 5-15. SEM analysis of Sample #2 with various magnifications



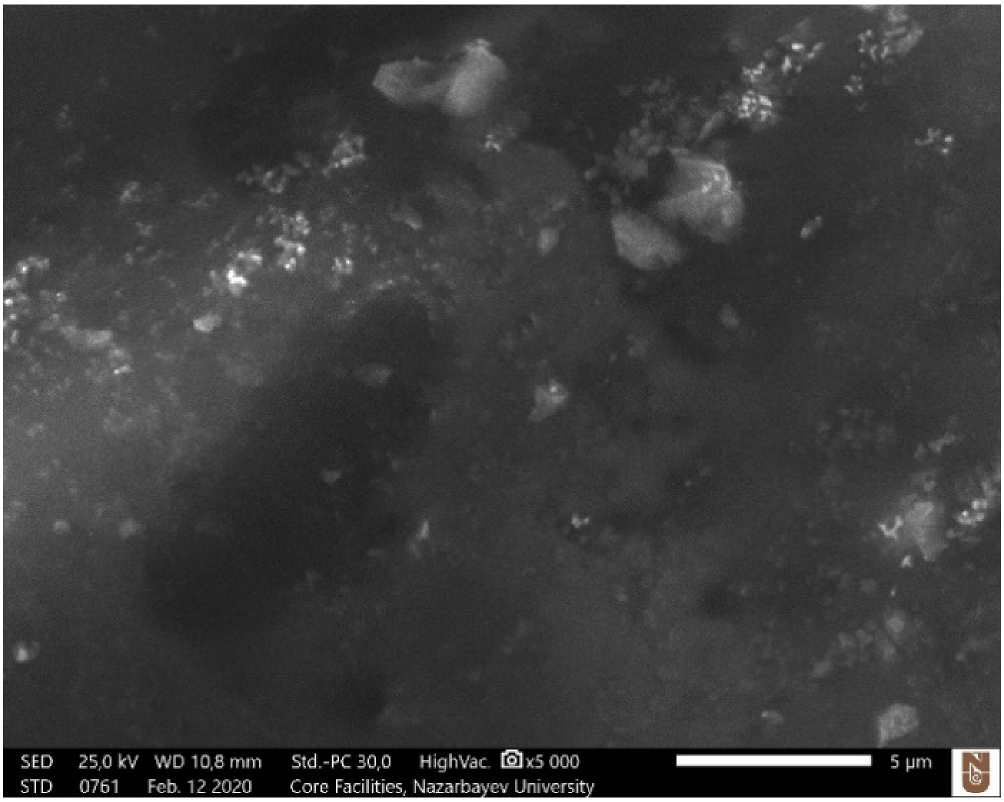
Scanning at magnification x500



Scanning at magnification x1000



Scanning at magnification x3000



Scanning at magnification x5000

Figure 5-16. SEM analysis of Sample #3 with various magnifications

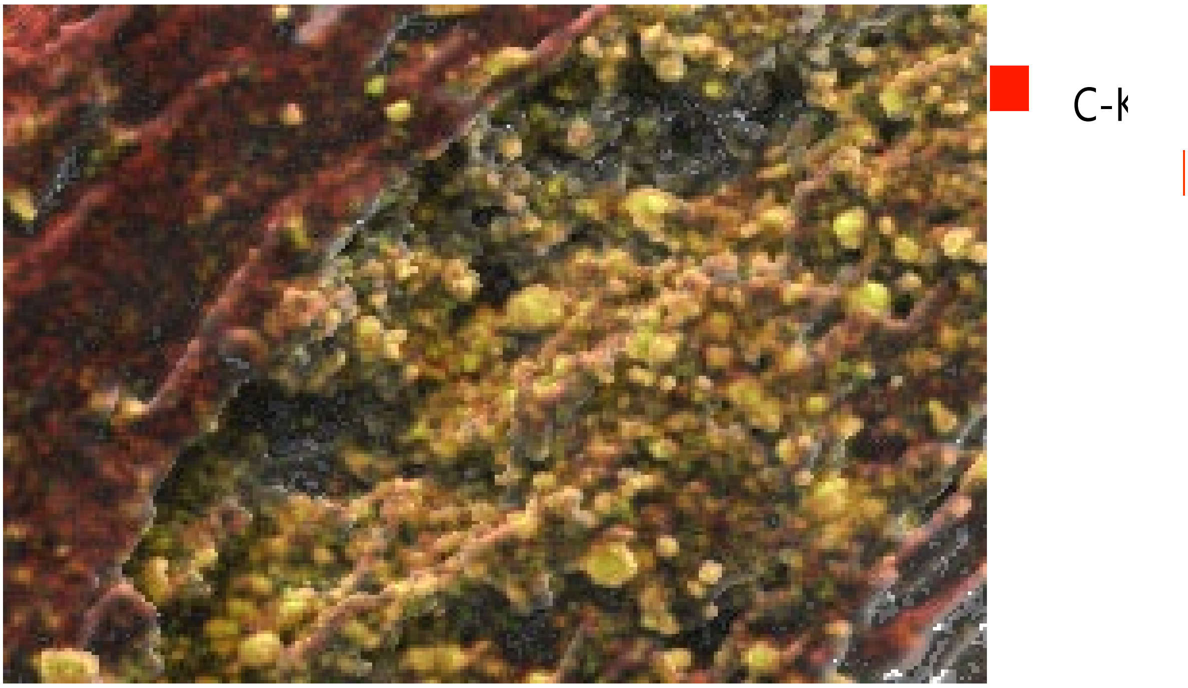


Figure 5-17. Map of local elements by EDS analysis for asphaltene sample #1

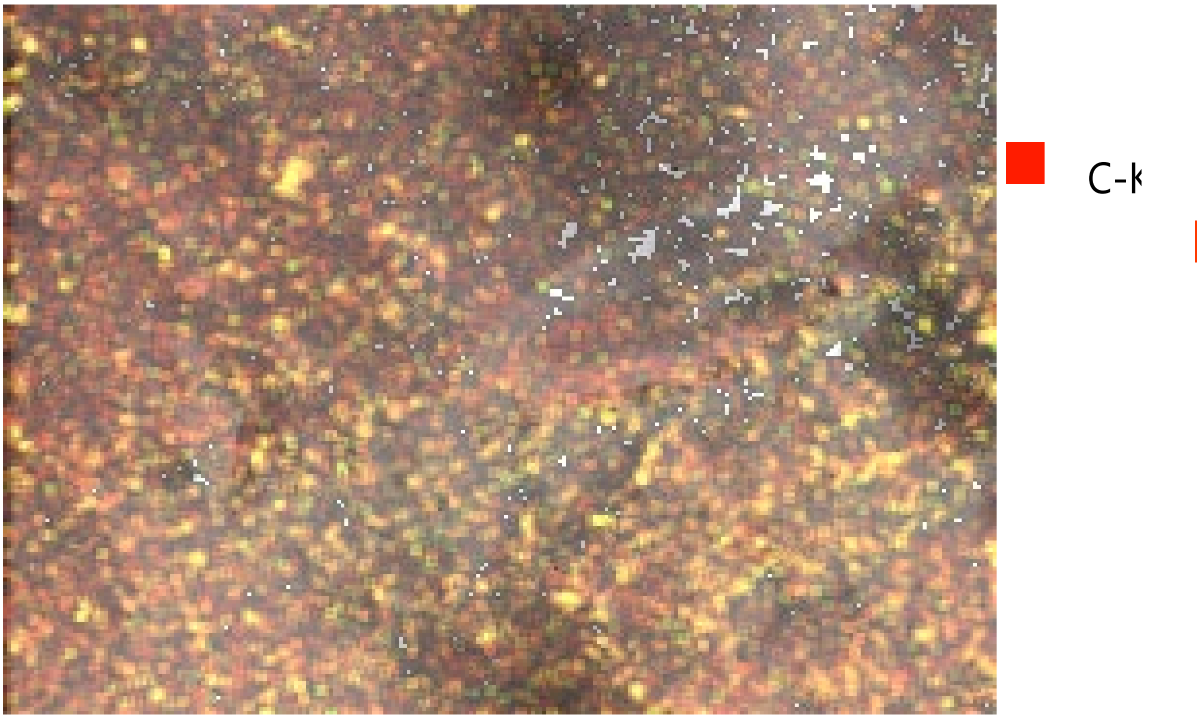


Figure 5-18. Map of local elements by EDS analysis for asphaltene sample #2

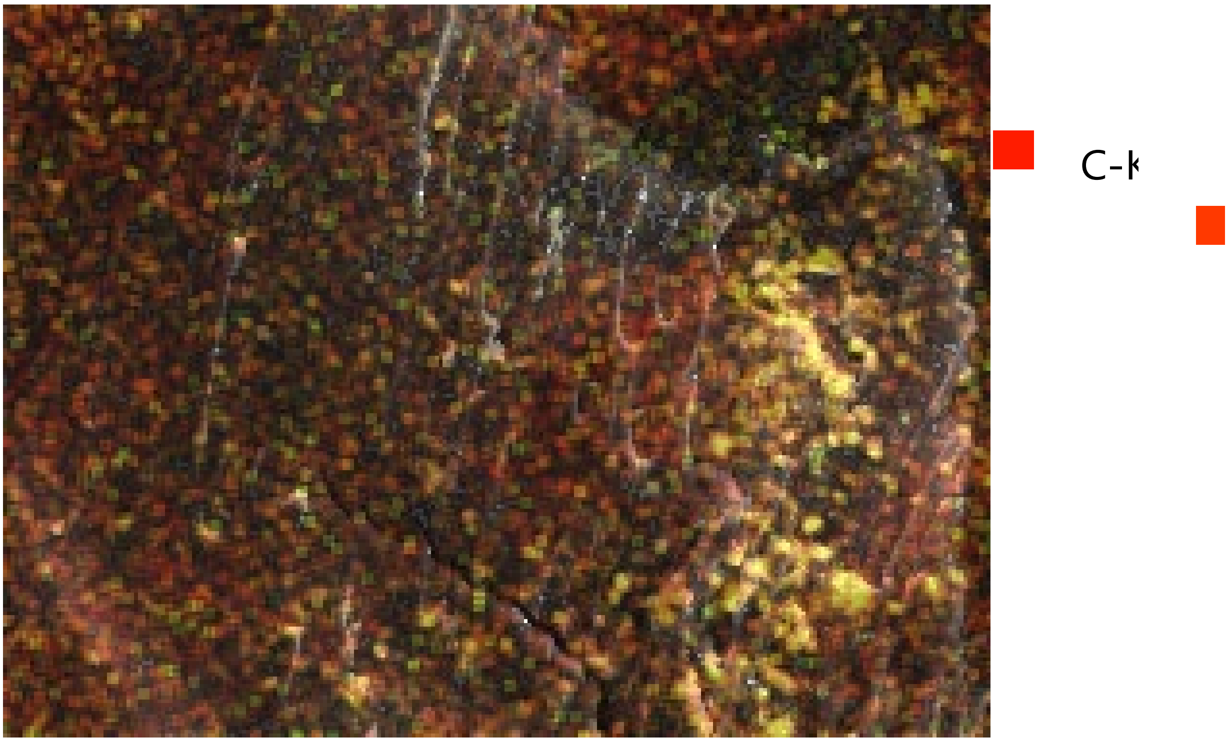


Figure 5-19. Map of local elements by EDS analysis for asphaltene sample #3

Table 5-7. Elemental content of asphaltene samples obtained by EDS analysis

	Sample 1		Sample 2		Sample 3	
Element	Mass%	Atom%	Mass%	Atom%	Mass%	Atom%
C	72.85±0.11	83.24±0.13	81.26±0.12	86.84±0.13	80.52±0.13	86.22±0.14
O	11.54±0.09	9.90±0.08	13.83±0.14	11.10±0.11	14.73±0.16	11.84±0.13
Na	4.63±0.03	2.76±0.02	1.47±0.03	0.82±0.01	1.22±0.03	0.68±0.02
Si	0.26±0.01	0.13±0.00			0.11±0.01	0.05±0.00
Cl	8.09±0.03	3.13±0.01	2.01±0.02	0.73±0.01	1.75±0.02	0.64±0.01
K	0.43±0.01	0.15±0.00	0.12±0.01	0.04±0.00		
Ca	1.49±0.02	0.51±0.01	0.26±0.01	0.08±0.00	0.48±0.02	0.16±0.01
Fe	0.70±0.02	0.17±0.00				
S			0.49±0.01	0.20±0.00	0.31±0.01	0.12±0.00
Mg			0.24±0.01	0.13±0.01	0.24±0.01	0.13±0.01
Cu			0.31±0.02	0.06±0.00	0.52±0.03	0.11±0.01
Al					0.12±0.01	0.06±0.01
Total	100	100	100	100	100	100

5.4 Discussion

As a result of scientific work, we separated asphaltene fractions from three Kazakhstan crude oil samples. It was observed, that the denser the oil, the more asphaltenes are contained in the oil. So, for example, for oil with API gravity of 28.2 the content of asphaltenes was 0.625 wt. %; for API gravity 31.1 - 0.402 wt.% of asphaltenes, and finally for API gravity 31.2 - 0.202 wt. % of asphaltenes. This trend is quite reasonably and was traced among other scientists (Speight, 1999; Evdokimov, 2005).

Also, as a result of the study, molecular parameters such as aromaticity factor f_a, the average number of carbons per alkyl side chain (n), and diameter of aromatic unit L_a were determined. As mentioned earlier, the high aromaticity indicates a greater tendency for asphaltenes to aggregate and precipitate. In the case of our three oil samples, the low aromaticity factor has the asphaltene sample #1, with the value of 0.1, which is not typical for oils with high content of asphaltenes. Here it is necessary to mention the presence of OH functional group which is predominantly present in asphaltenes #1, but extremely smaller in asphaltenes #2 and #3. This OH group is responsible for the aggregation of asphaltenes, which explains their high content in crude oil #1 (Calemma, V., et al.,1995).

As presented in the rows 1and 2 of the Table 5-8, Sample #1 has a lower f_a value but a higher n value, compared to Sample #2 and Sample #3. This seems consistent with the H/C atomic ratios of the three samples, in which the H/C atomic ratio of Sample #1 was roughly higher than that of the other two samples.

Table 5-8. Summary of the average molecular parameters

Parameter	Sample #1	Sample #2	Sample #3
The number of carbons per alkyl side chain, n	18.96	9.08	9.85
Aromaticity factor, f_a	0.1	0.28	0.22
Diameter of aromatic unit, L_a, (nm)	1.36 – 1.5	1.53 – 1.88	1.78-1.94

Based on the obtained the number of carbons per alkyl chain (n), aromaticity factor f_a and diameter of aromatic unit (L_a) the properties of crude oil and asphaltenes can be compared with Mexican oil (Maya, Isthmus and Olmeca). In the course of research authors also observed higher aromaticity factor for light Olmeca crude oil and lower for heavy Maya. Additionally, the same trend of the results for the number of carbons per alkyl chain were noticed (Ancheyta, J., et al., 2002). Moreover, another asphaltene sample originated from Colombia have similar values of aromaticity factor analyzed by XRD technique (Poveda-Jaramillo, J. C., 2016). This information can be helpful in selection of appropriate chemical inhibitors.

6. CONCLUSIONS AND RECOMMENDATIONS

In this research work, first asphaltenes were extracted from three crude oils originated from West Kazakhstan by *n*-heptane and using the IP-143 method. Then, the asphaltenes were characterized by using various methods including CHNS/O analysis to obtain elemental content of asphaltenes, TGA analysis to determination kinetic behavior of asphaltenes under thermal destruction, scanning electron microscopy to study the surface morphology of the asphaltenes. Additionally, three spectral analyses methods namely the Fourier Transform Infrared, Carbon and Proton NMR, and RAMAN spectroscopy were used to investigate the average molecular parameters: aromaticity factor f_a, the number of carbons per alkyl side chain (n), and diameter of aromatic unit L_a. The following 6 conclusions based on the results of this modelling and simulations study can be drawn:

1. The crude oils originated from the West Kazakhstan region can be classified as medium, with the API gravity of 28.2 and 31.09, had asphaltene content 0.625 wt.% and 0.402 wt.%, respectively. The light crude oil with API gravity of 31.15 had less amount of asphaltenes ~ 0.202 wt.%.
2. Sulfur and oxygen atoms participate in the structure of the studied asphaltenes both in peripheral substituents in the form of functional groups (-OH, -SH) and in the form of connecting bridges made of carbon atoms (-C-O-C-; -C-S-C-). These results are confirmed by the elemental composition and EDS analysis conducted in this research.
3. A complex of modern physicochemical methods of analysis for the first time carried out a detailed study of the chemical composition of asphaltenes of West Kazakhstan origin. Based on spectroscopy data, it was determined that the main fragments bound via ether and sulfide bridges are aromatic, aliphatic, and heterorganic compounds.
4. With the aid of NMR spectroscopy, the molecular parameters, parameters such as aromaticity factor and average number of carbons per alkyl side chain were determined. The aromaticity factor for three asphaltene samples namely sample #1, sample#2, and sample#3 were determined to be 0.1, 0.28, and 0.22, respectively. In addition, the calculated average diameter of the aromatic layer varies between 1.5-1.78 nm and 1.36-1.94 nm according to the Lorentz and Gauss functions, respectively.
5. Based on the results obtained from TGA analysis, at heat treatment temperatures

of 200- 300°C the reactions of the soft asphaltenes destruction is predominate. At temperatures of 370-480°C, the other reactions prevail. The degradation of hard asphaltenes and coke formation also increases at the later temperature range.

6. The characteristic structure of asphaltenes which determined by SEM showed irregular agglomerates with cavities formed by localized spherical particles on the surface. SEM results showed that asphaltenes consist of flakes and each of which makes up irregular micelles of about from 4μm to 15μm in diameter. It was also found that in addition to flakes having a different structure, smooth surfaces are also characteristic of the studied asphaltenes.

The question of the true values of the mass of the molecules of asphaltenes or their molecular weight, is fundamental scientific importance for understanding the most important physical properties of the most complex in chemical composition and the highest molecular weight molecules of non-hydrocarbon components of oil. The knowledge of the true values of their molecular weights can help to solve the question of the chemical structure and physical structure of these solid amorphous oil components. For this reason, it is recommended that scientific work be supplemented with missing information on molecular weight for a more complete picture of the structure of the studied asphaltenes.

Additionally, the structure of asphaltenes could be assembled together on the basis of the obtained results and the results from future studies on molecular weight of the compound. Thereby, presented in the form of a hypothetical molecular structure of asphaltenes.

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