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GAS CHROMATOGRAPHY - MASS SPECTROMETRY (GC-MS) IN ORGANIC GEOCHEMICAL INVESTIGATION OF CRUDE OILS FROM KIKINDA AND VELEBIT FIELDS IN SERBIA

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Abstract

In this work two crude oil samples were investigated to present the difference between biodegraded (Velebit) and non-degraded (Kikinda) oil. Two samples are from the Velebit oil–gas field and the Kikinda oil-gas field. These are two of the largest oil and gas deposits in the Serbian part of the Pannonian Basin. In the experimental part of this work, two samples of crude oil were separated by column chromatography. Saturated hydrocarbons were analyzed by gas chromatography-mass spectrometry instruments. Based on the abundance and distribution of biomarkers, it could be conclude that the distribution is typical of oil in both samples, with difference in the distribution of n-alkane. GC-MS chromatogram of n-alkanes and isoprenoids of saturated fraction isolated from Velebit crude oil show the distribution typical of oils altered by biodegradation.

Keywords: Gas Chromatography (GC); Mass Spectrometry (MS); N-Alkanes Biodegradation; Biodegradation.

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1. Introduction

Crude oil and its derivatives, as the key energy-generating substances and raw materials used for production, are very widely used in all domains of work and everyday life. With the advent of oil as a fuel, there was the most intense economic growth and it can be said that the entire modern civilization is based on the utilization of oil.

However, rapid growth and development of civilization in the past two centuries with the mass use of fossil fuels has led to imbalances and distortions of natural processes. In spite of improvements in technology and equipment used for oil drilling, transport and processing by the petroleum industry, oil and oil derivatives represent a significant source of environmental contamination. (Beškoski V., Gojgić-Cvijović G., Jovančičević B., Vrić M., in *Gas Chromatography - Biochemicals, Narcotics and Essential Oils*, B. Salih, Ö. Çelikbıçak, Eds., InTech, Rijeka, Croatia, 2012).

Petroleum and petroleum products are complex mixtures consisting of thousands of compounds that are usually grouped into four fractions: aliphatics, aromatics, nitrogen– oxygen–sulphur (NSO) compounds and asphaltenes. Asphaltenes are generally solvent insoluble and resistant to biodegradation. Aliphatic hydrocarbons consist of normal alkanes (n-alkanes), branched alkanes (isoalkanes) and cyclic alkanes (naphthenes). Isoalkanes, naphthenes and aromatics are much less biodegradable than n-alkanes. The fraction of saturated hydrocarbons is the dominant fraction in most oils as compared to aromatic hydrocarbons and NSO compounds.

When crude oil or petroleum products are accidentally released into the environment, they are immediately subject to a wide variety of weathering process. These weathering processes can include: evaporation, dissolution, microbial degradation, dispersion and water–oil emulsification, photooxidation, adsorption onto suspended. Biomarkers are complex organic compounds composed of carbon, hydrogen and other elements such as oxygen, nitrogen and sulfur. Biomarker compounds are analyzed using gas chromatography and mass spectrometry and they are divided into several basic types of n-alkanes and isoprenoid n-alkane, steranes, diterpanes, triterpanes and their derivatives and aromatic hydrocarbons. (Dougle W. Waples, 1945-*Geochemistry in petroleum exploration*).

In this work two crude oil samples were investigated to present the difference between biodegraded (Velebit) and non-degraded (Kikinda) oil. In the experimental part of this work, two samples of crude oil were separated by column chromatography. Saturated hydrocarbons were collected in the first fraction and eluted by petroleum ether and then, aromatic hydrocarbons with some sulfur were collected in the second fraction and eluted by mixture solvent petroleum ether and benzene (2:1, v:v). Saturated hydrocarbons were analyzed by gas chromatography -mass spectrometry instruments. (Niessen W.M.A. (2001) *Current practise of Gas chromatography-Mass spectrometry*; Copyright by Marcel Dekker, Inc).

2. Materials and Methods

The study aims to analyze the effect of two of the crude oil samples were investigated in this thesis originated from the Velebit oil–gas field and the Kikinda oil-gas field. These are two of the largest oil and gas deposits in the Serbian part of the Pannonian Basin.

The analysis of these two eyes through your device Gas chromatography - Mass spectrometry (GC-MS).

3. Results and Discussions

The crude oils (a sample from the Velebit oil–gas field and a sample from Kikinda oil-gas field) were separated into saturated and aromatic using column chromatography over silica gel. Saturated hydrocarbon fraction was eluted with petroleum ether, aromatic hydrocarbons with mixture of petroleum ether and benzene (2:1, v:v) and the NSO fractions (polar fraction) was determined from the difference to 100%.

Table 1: Mass of sample, adsorbent and solvent.

Sample	Mass of sample (mg)	Mass of SiO ₂ (g)	V petroleum ether (ml)	V petroleum ether/ Benzene (ml)
Kikinda crude oil	30.20	9.06	67.95	113.25
Velebitn Crude oil	34.80	10.44	78.30	130.50

In column chromatography, a glass tube 50 cm in length was held a vertical position and filled with silica gel suspended in solvent (n-hexane) after the addition of a small amount of cotton in the bottom of the column. The amount of 30 mg of crude oil was added to the top of the column (Figure 1). The hydrocarbon solvent (petroleum ether) dissolved the saturated hydrocarbons and carried them slowly along with it down the column. The other more polar compounds of the bitumen remain stationary or move much more slowly than the saturated, which rates of movement depend on the relative affinity of bitumen molecules for the solvent and for the stationary phase (silica gel). Non polar molecules move rapidly because they have little affinity for the highly polar stationary phase.

In contrast, other molecules including aromatic hydrocarbons and polar NSO compounds are held much more by stationary phase and can not be eluted from the column by petroleum ether. Petroleum ether was allowed to pass through the column until the saturated hydrocarbons were eluted and collected in the first fraction. Aromatic hydrocarbons with some sulfur were collected in the second fraction and eluted by mixture solvent petroleum ether and benzene (2:1, v:v) respectively. After solvents of these fractions (saturated hydrocarbons and aromatic hydrocarbons) were removed also with rotary evaporator and then transferred these fractions into small glass tubes.

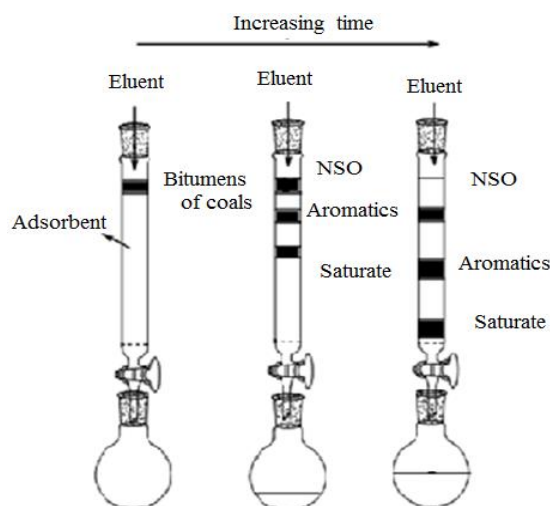


Figure 1: Column-chromatography separation of fractions bitumens of coals.

4. Gas Chromatographic - Mass Spectrometric (GC-MS) Analyses

Saturated hydrocarbons were analyzed by gas chromatography-mass spectrometry (GC-MS). A gas chromatograph Agilent 7890A GC (H5-MS capillary column, 30 m x 0.25 mm, He carrier gas 1.5 cm³/min, FID) coupled to a Agilent 5975C mass selective detector (70 eV) was used. The column was heated from 80 to 310 °C, at a rate of 2 °C/min, and the final temperature of 310 °C was maintained for an additional 25 min. Detailed analyses of the target compounds were conducted using the following ion chromatograms: $m/z = 71$ (*n*-alkanes and isoprenoids), $m/z = 191$ (terpanes) and $m/z = 217$ (steranes). The individual peaks were identified by comparison with the literature data¹² and on the basis of the total mass spectra (library: NIST5a). Biomarker parameters were calculated from GC-MS chromatogram peak areas (software GCMS Data Analysis).



Figure 2: Gas chromatograph Agilent 7890N and a Hewlett-Packard 5972 MSD.

Table 2: Values of group organic geochemical parameters.

Sample	Saturated HC (%)	Aromatic HC (%)	NSO (%)
Kikinda crude oil	48.01	18.87	33.12
Velebit crude oil	47.13	29.02	23.85

5. Specific Organic Geochemical Parameters

Kikinda crud oil: *n*-alkanes are identified in range C₁₂ to C₃₈ with a maximum at *n*-C₁₆ (Figure 3). The CPI value is 1.2, close to 1, which is typical of mature organic matter and an oil distribution. The Pr/*n*-C₁₇ and Phyt/*n*-C₁₈ values is < 1, which can be an indicator of a fair degree of OM maturity. The pristane (Pr) to phytane (Phyt) ratio is widely used as a redox indicator of the depositional environment. Pristane dominates over phytane, which is indicative of organic matter formation in a oxygenous environment. Biomarker parameters (CPI, Pr/Phyt) indicated a mixed origin of the organic matter (Table3).

Velebit crude oil: n-alkanes are identified in range C12 to C38 with a maximum at n-C16 (Figure 3). GC-MS chromatogram (m/z 71) of saturated fraction show the distribution typical of oils altered by biodegradation. The n-alkanes are not most abundant, while pristane (Pr) and phytane (Phy) dominate. The Pr/n-C17 and Ph/n-C18 values is > 1 , which is also an indicator of biodegradation. Phytane dominates over pristane, which is indicative of organic matter formation in a reducing environment (Table 3).

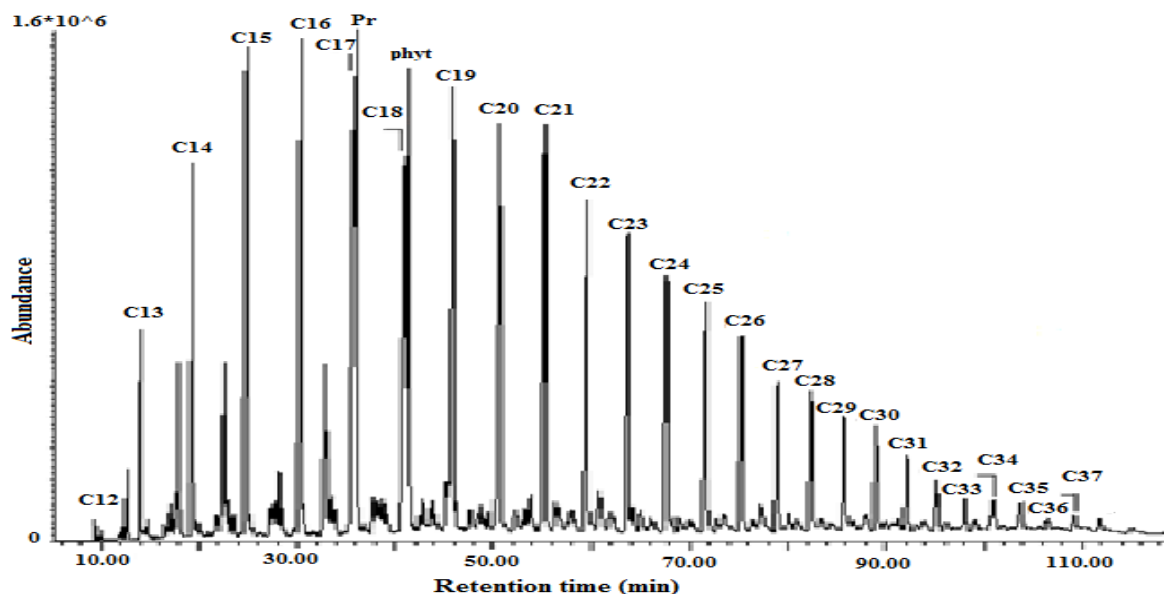


Figure 3: GC-MS chromatogram of n-alkanes and isoprenoids, m/z 71 of saturated fraction isolated from Kikinda crude oil.

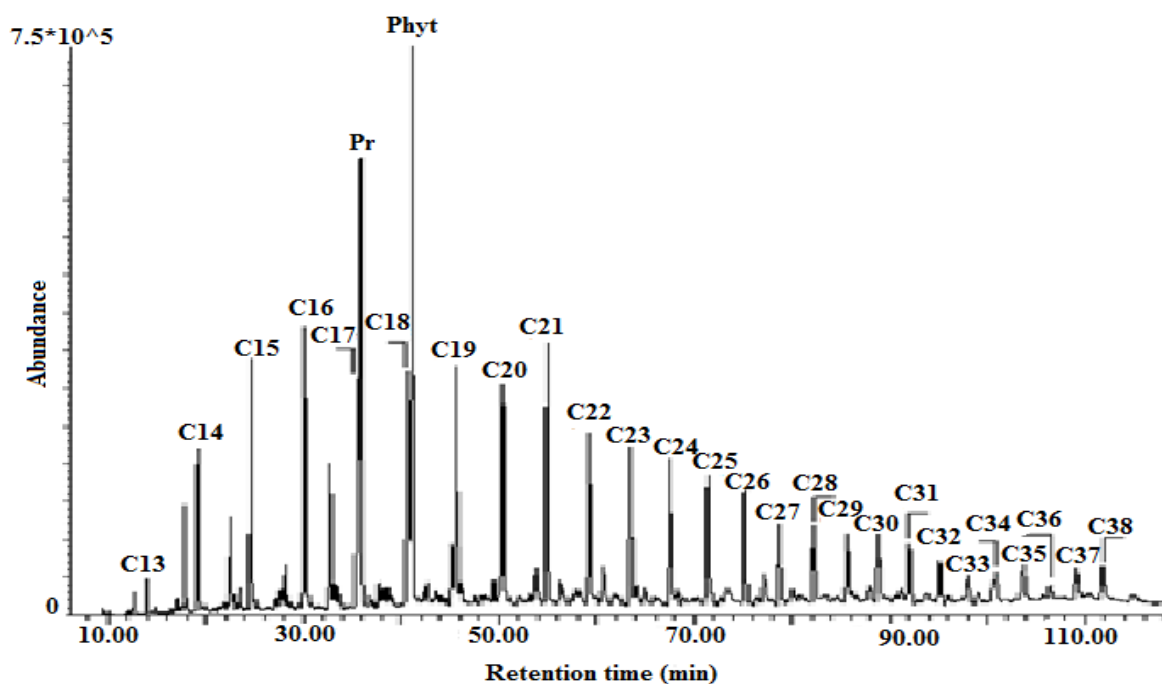


Figure 4: GC-MS chromatogram of n-alkanes and isoprenoids, m/z 71 of saturated fraction isolated from Velebit crude oil.

Table 3: Values of specific organic geochemical parameters calculated from distributions and abundances of n-alkanes and isoprenoides.

Sample	n-alkane range	n-alkane max.	CPI	Pr/Phyt	Pr/n-C ₁₇	Phyt/n-C ₁₈
Kikinda crude oil	C ₁₂ -C ₃₈	C ₁₆	1.2	0.98	0.75	0.74
Velebit crude oil	C ₁₃ -C ₃₈	C ₁₆	1.01	0.78	1.01	1.77

6. Steranes

Kikinda crude oil: sterane distributions is typical of oil, with thermodynamically more stable isomers, 5 α (H)14 α (H)17 α (H)20(S), 5 α (H)14 β (H)17 β (H)20(R), and 5 α (H)14 β (H)17 β (H)20(S) configurations, typical geoisomers, and 13 β (H)17 α (H)- and 13 α (H)17 β (H)-diasteranes (Figure 24). The use of the 14 α (H)17 α (H)20(R) C₂₇-C₂₉ regular steranes in the evaluation of the OM type is based on the observation that C₂₇ steranes originate dominantly from marine plankton, C₂₈ steranes from yeast, fungi, plankton and algae, and C₂₉ steranes from higher plants and brown and green algae. However, this use has limitations, considering that it is known that marine algae produce sterols with 27 to 29 carbons. Based on percent of C₂₇, C₂₈ and C₂₉, we concede that Kikinda crude oil has a mixed origin of the organic matter, dominated by terrestrial organic matter. Values of sterane maturity ratios are in the range typical for crude oils (Table 12).

Velebit crude oil: sterane distributions is typical of oil (Figure 25). As mentioned above, the distribution of 14 α (H),17 α (H),20R C₂₇-C₂₉ regular steranes is use in the evaluation of organic matter type in the depositional environment. The distribution of C₂₇-C₂₉ regular steranes in Velebit crude oil indicating a mixed origin for the oils. Values of sterane maturity ratios show that Velebit crude oil is less mature than Kikinda crude oil (Table 12).

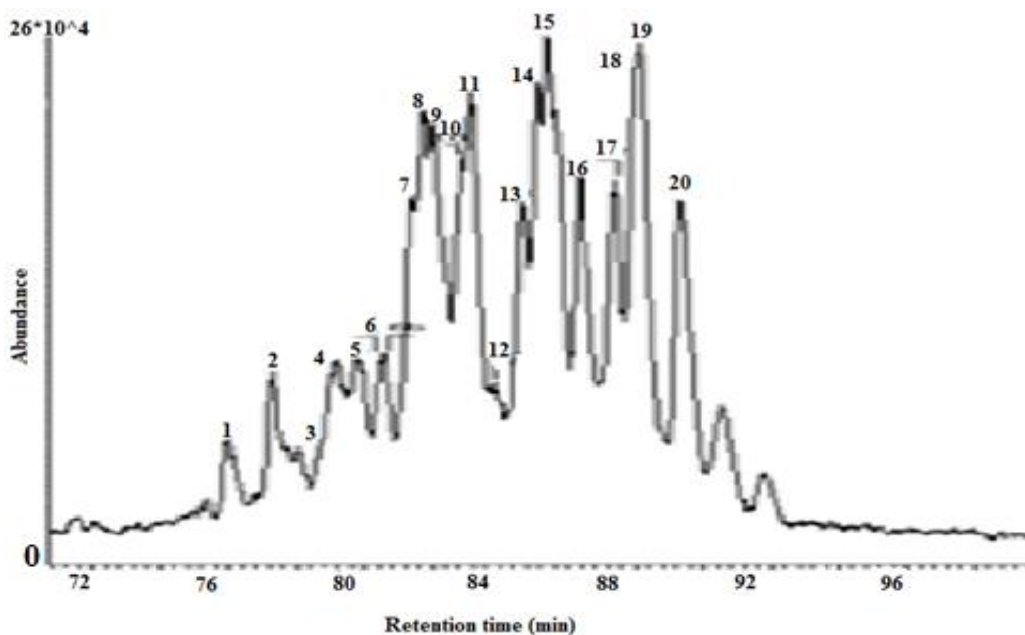


Figure 5: GC-MS chromatogram of steranes m/z 217 of saturated fraction isolated from Kikinda crude oil (Peak identification is shown in Table 4).

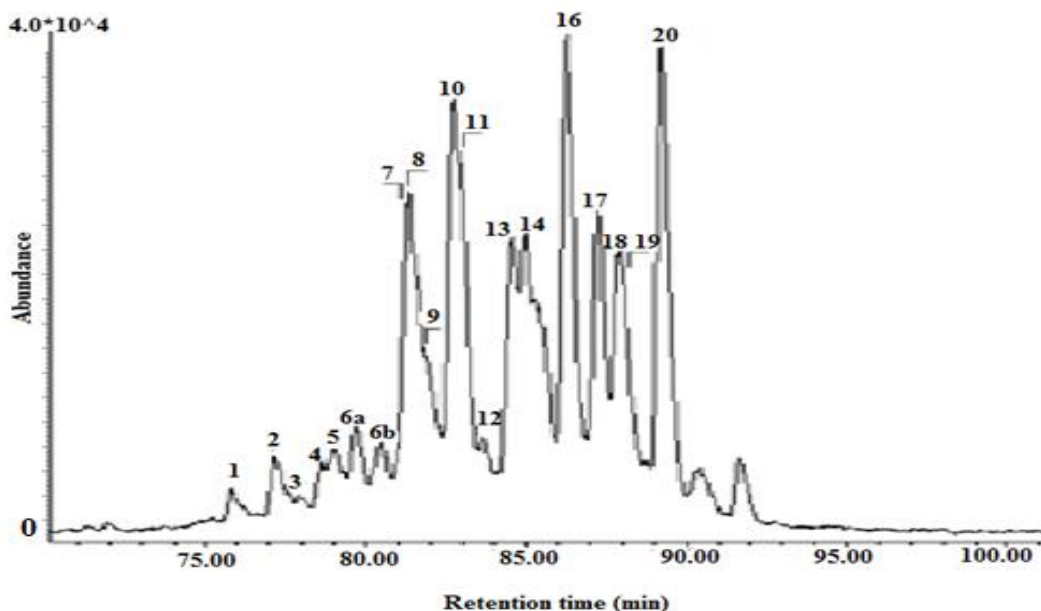


Figure 6: GC-MS chromatogram of steranes, m/z 217 of saturated fraction isolated from Velebit crude oil (Peak identification is shown in Table 4).

Table 4: Identification of the peaks in the chromatogram shown in Figures 24 and 6 (steranes).

Peaks	Compound
1	$C_{27}13\beta(H)17\alpha(H)20(S)$ -diasterane
2	$C_{27}13\beta(H)17\alpha(H)20(R)$ -diasterane
3	$C_{27}13\alpha(H)17\beta(H)20(S)$ -diasterane
4	$C_{27}13\alpha(H)17\beta(H)20(R)$ -diasterane
5a	$C_{28}13\beta(H)17\alpha(H)20(S)24(S)$ -diasterane
5b	$C_{28}13\beta(H)17\alpha(H)20(S)24(R)$ -diasterane
6a	$C_{28}13\beta(H)17\alpha(H)20(R)24(S)$ -diasterane
6b	$C_{28}13\beta(H)17\alpha(H)20(R)24(R)$ -diasterane
7	$C_{28}13\alpha(H)17\beta(H)20(S)$ -diasterane + $C_{27}14\alpha(H)17\alpha(H)20(S)$ -sterane
8	$C_{29}13\beta(H)17\alpha(H)20(S)$ -diasterane + $C_{27}14\beta(H)17\beta(H)20(R)$ -sterane
9	$C_{28}13\alpha(H)17\beta(H)20(R)$ -diasterane + $C_{27}14\beta(H)17\beta(H)20(S)$ -sterane
10	$C_{27}14\alpha(H)17\alpha(H)20(R)$ -sterane
11	$C_{29}13\beta(H)17\alpha(H)20(R)$ -sterane
12	$C_{29}13\alpha(H)17\beta(H)20(S)$ -sterane
13	$C_{28}14\alpha(H)17\alpha(H)20(S)$ -sterane
14	$C_{29}13\alpha(H)17\beta(H)20(R)$ -diasterane + $C_{28}14\beta(H)17\beta(H)20(R)$ -sterane
15	$C_{28}14\beta(H)17\beta(H)20(S)$ -sterane
16	$C_{28}14\alpha(H)17\alpha(H)20(R)$ -sterane
17	$C_{29}14\alpha(H)17\alpha(H)20(S)$ -sterane
18	$C_{29}14\beta(H)17\beta(H)20(R)$ -sterane

Table 5: Values of specific organic geochemical parameters calculated from distributions and abundances of steranes.

Sample	C ₂₉ sterane 20S/(20S+20R)	C ₂₉ sterane-ββ/ ββ + αα	C ₂₇ (%)	C ₂₈ (%)	C ₂₉ (%)
Kikinda	0.65	0.59	29.26	30.48	40.24
Velebit	0.47	0.50	29.29	34.39	36.30

7. Terpanes

Kikinda crude oil: terpane distributions is typical for oils (Figure 7). They are characterized by predominance of thermodynamically more stable isomers with 17α(H)21β(H) and 22(S) configurations, by the presence of typical geoisomers. These compounds have never been reported in biosphere and recent singenetic organic matter. The oils contain of oleanane and gammacerane. Oleanane is an indicator of input from angiosperm land plantsand, gammacerane is an indicator of organic matter deposited under a stratified water column or from an evaporitic and hypersaline environment. Oleanane and % C₂₉ sterane can be indicatore of higher plant contribution (Table 7).

Velebit crud oil: terpane distributions is typical for oils (Figure 8), with characterization which was mentioned above. Values of terpane maturity ratios show that Velebit crude oil is less mature than Kikinda crude oil (Table 7). Because of biodegradation values of biomarker parameters could not be safely used, although steranes and terpanes are very resistant to biodegradation.

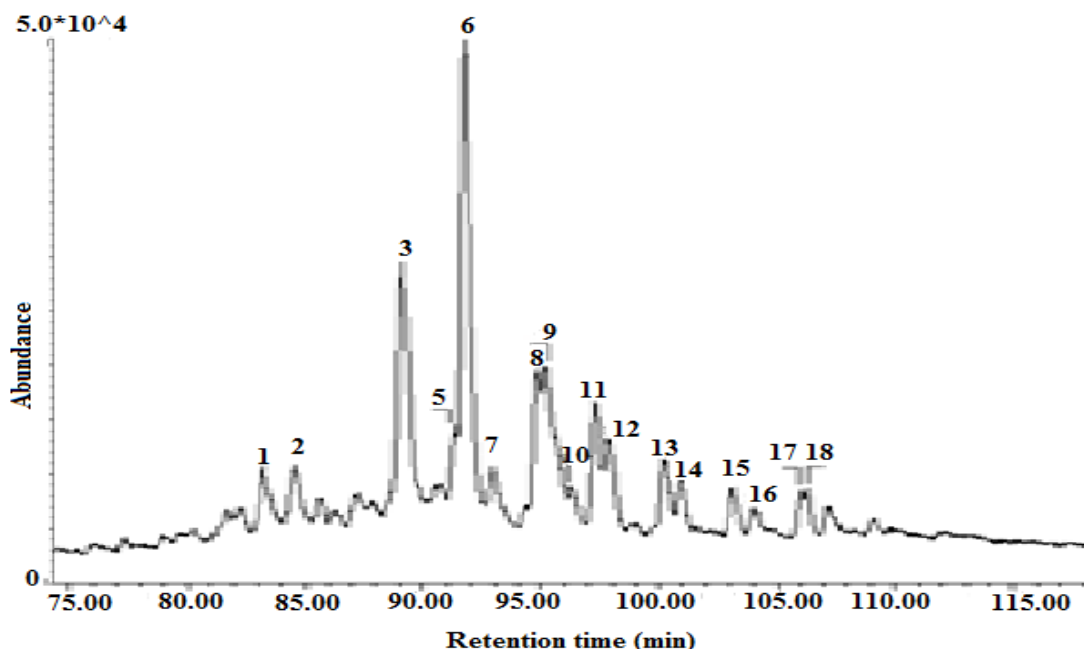


Figure 7: GC-MS chromatogram of terpanes m/z 191 of saturated fraction isolated from Kikinda crude oil (Peak identification is shown in Table 6).

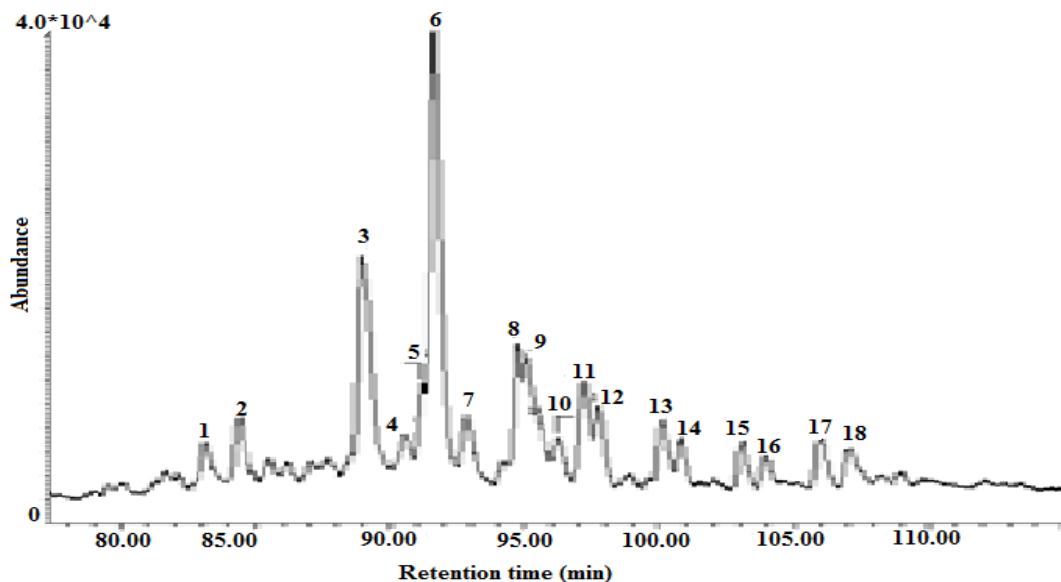


Figure 8: GC-MS chromatogram of terpanes m/z 191 of saturated fraction isolated from Velebit crude oil (Peak identification is shown in Table 6).

Table 6: Identification of the peaks in the chromatograms shown in Figures 7 and 8 (terpanes).

Peaks	Compound
1	C ₂₇ 18α(H),22,29,30-trisnorhopane; T _s
2	C ₂₇ 17α(H),22,29,30-trisnorhopane; T _m
3	C ₂₉ 17α(H)21β(H)-hopane; C ₂₉ H
4	C ₂₉ 17β(H)21α(H)-moretane; C ₂₉ M
5	Oleanan
6	C ₃₀ 17α(H)21β(H)-hopane; C ₃₀ H
7	C ₃₀ 17β(H)21α(H)-moretane; C ₃₀ M
8	C ₃₁ 17α(H)21β(H)22(S)-hopane
9	C ₃₁ 17α(H)21β(H)22(R)-hopane
10	Gamacerane
11	C ₃₂ 17α(H)21β(H)22(S)-hopane
12	C ₃₂ 17α(H)21β(H)22(R)-hopane
13	C ₃₃ 17α(H)21β(H)22(S)-hopane
14	C ₃₃ 17α(H)21β(H)22(R)-hopane
15	C ₃₄ 17α(H)21β(H)22(S)-hopane
16	C ₃₄ 17α(H)21β(H)22(R)-hopane
17	C ₃₅ 17α(H)21β(H)22(S)-hopane
18	C ₃₅ 17α(H)21β(H)22(R)-hopane

Table 7: Values of specific organic geochemical parameters calculated from distributions and abundances of terpanes.

Sample	C ₃₁ hopane-22S/(22S+22)	C ₃₀ moretan/ C ₃₀ hopane	Ts/Tm	Oleana/ C ₃₀ hopane	Gamaceran/ C ₃₀ hopane
Kikinda	0.51	0.09	1.07	0.03	0.05
Velebit	0.55	0.13	0.65	0.067	0.075

8. Conclusion

In this study two crude oil samples were investigated to present the difference between biodegraded (Velebit) and non-degraded (Kikinda) oil. Two samples are from the Velebit oil–gas field and the Kikinda oil-gas field. These are two of the largest oil and gas deposits in the Serbian part of the Pannonian Basin. In the experimental part of this work, two samples of crude oil were separated by column chromatography. Saturated hydrocarbons were analyzed by gas chromatography-mass spectrometry instruments.

The values of group organic geochemical parameters indicate that soluble organic matter in both samples of crude oil is mainly represented by hydrocarbons, which is in accordance to the high maturity of the crude oil, as highly mature organic matter.

Based on the abundance and distribution of biomarkers, it could be conclude that the distribution is typical of oil in both samples, with difference in the distribution of n-alkane. GC-MS chromatogram of n-alkanes and isoprenoids of saturated fraction isolated from Velebit crude oil show the distribution typical of oils altered by biodegradation. The n-alkanes are not the most abundant, while pristane (Pr) and phytane (Phy) dominate. In the distribution of steranes and terpanes, biodegradation was not observed, probably because steranes and terpanes are more resistant to biodegradation. Values of maturity ratios show that Velebit crude oil is less mature than Kikinda crude oil.

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