

# Organic geochemistry, its meaning in the process of hydrocarbon exploration and demonstration of its application on samples from Žutica – 1 zapad well

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PROFESSIONAL PAPER

**Organic geochemistry is scientific discipline used in the process of exploration and production of hydrocarbons. Geochemical results provide determination of source rocks, evaluation of their productivity, efficiency of expulsion, and migration phenomena. At the same time this research provides also genetic characterization of hydrocarbons in reservoirs, their comparison and detection of their alteration. Organic geochemistry is applied to development and production engineering while geochemical results usually complement geological and geophysical research. Geochemical research methods in this paper are demonstrated through the example of source rocks examination from Žutica-1 zapad well. This example describes the concept of organic geochemistry, its methods and how they fit into the hydrocarbons exploration process. After testing of source rocks, comparison of bitumen extracted from rock samples and oil from the Žutica oil field was conducted. The conclusion of this paper explains the differences in molecular content between the bitumen and oil and also offers guidelines for further geological and geophysical research, where these results should be incorporated.**

Key words: Organic geochemistry, source rock, reservoir, bitumen, petroleum, Žutica oil field

## 1. Introduction

Petroleum geochemistry is based on application of chemical principles during generation, migration, accumulation and hydrocarbon alterations and the implementation of such knowledge to the processes of research and production. Organic geochemistry studies hydrocarbon accumulation and content, its subsurface movement and its alteration impacted by temperature and pressure. This research is incorporated in other geological and geophysical methods to increase the probability and decrease the risk of hydrocarbon commercial discoveries. For nearly 150 years it has been known that the precursor of hydrocarbons is organic matter deposited in sedimentary basins. The main supplies of organic matter are phytoplankton, zooplankton, bacteria and terrestrial plants.<sup>10,7</sup> All organisms basically consist of the same chemical ingredients, such as proteins, carbohydrates, lipids and lignin. Protein and carbohydrates are unstable and they decompose through microbiological processes. Hydrogen rich, lipids, which are the main petroleum precursor, are very important. Lignin components are constituents of higher terrestrial plants, and are mostly sources of gas hydrocarbons.

Organic matter is deposited in aquatic environment together with mineral particles. Depending on oxygen content in water column, i.e. depositional environment, organic matter is completely decomposed or there is a possibility of its preservation. Then follow the processes of preserved organic matter change which undergo through the phases of diagenesis, catagenesis and metagenesis. Diagenesis is the initial kerogen forming

phase which occurs within biological and chemical processes. Catagenesis and metagenesis are thermal phases, where kerogen molecules crack and form hydrocarbons due to high temperature (Barić, 1996). All organic matter alteration processes mentioned above take place in fine grained sediments called source rocks. The results of geochemical research of source rocks from Žutica -1 zapad well, are presented in the paper. The results were compared with the present data on determined source rocks in Sava Depression.

General properties of source, reservoir rocks and hydrocarbons in Sava Depression are presented in papers written by Barić et al.<sup>3,4,5,6</sup> Source rocks in Sava Depression were determined in the north-western and central part of Gojlo area. In the north-western part of Sava Depression, the source rocks are marly sandstones, lime marls and clay marls of Badenian and Pannonian age, situated between 1 600 to 3 000 m. These rocks contain increased concentrations of organic matter (average TOC is 1.4%). High hydrogen indices (300 up to 600 mgHC/g C<sub>org</sub>), and high content of amorphous kerogen are indicators of petroleum source rocks. Source rocks in Gojlo oil field contain high quantity of resinite and sporinite macerals, terrestrial lipid, confirmed by high negative values of isotopic carbon in kerogen ( $\delta^{13}\text{C}$  -28.1‰). This facies type is the source of high paraffin oil. Source rocks maturity varies between 0.6 and 0.8% R<sub>0</sub>, and early phase of hydrocarbon generation is estimated which had begun during Miocene – Pliocene age, at the depths between 2 100 and 2 200 m. Differences in thickness and depth of source rocks as well as fragmentation caused by

tectonic activity impacted different migration pathways and hydrocarbon accumulation.<sup>5</sup> Source rocks are characterized by small lithology, stratigraphy and organic facies variety which is the cause of minor differences of hydrocarbon properties within reservoir rocks.

Reservoir rocks in Sava Depression are characterized by lithology and stratigraphical variety. Production intervals at the depths between 370 to 2 300 meters are Paleozoic igneous and metamorphic rocks, and Pannonian and Pontian coarse clastic sediments. API gravity of oils and condensates varies between 16.9 and 60.6 °API, and sulfur content changes from 0.0 to 1.0%. Content of resins and asphaltenes in some oils is high and reaches up to 18.0%. The carbon isotope composition varies between  $\delta^{13}\text{C}$ -22.8 to -26.0 ‰ and is an indicator of certain varieties of original organic matter, sedimentary facies conditions and post accumulation alterations of certain oils.<sup>6</sup>

Most of oils chromatographic profiles from Sava Depression show relatively regular molecular distributions.

Oil from Jamarica and Lipovljani oil fields in central part of Sava Depression are characterized by long chain molecular structure (up to  $\text{C}_{40}$ ), which is reflected in high concentrations of paraffin, reaching up to 16%. These high paraffin oil originates from source rocks with increased content of terrestrial lipid components, identified in Gojlo area. Small number of oils in Sava Depression is altered due to post generative processes: biodegradation, water rinsing and evaporate fractionation. Microbiological degradation of oil is particularly expressed in shallow Paleozoic reservoir rocks contaminated with bacteria rich surface water. Biodegradation activity caused partial oil alteration in Bunjani and Kozarice fields and complete alteration was registered in the oil from Križ field. The primary paraffin – aromatic oil content from Križ field was altered into naphthenic – aromatic content that caused alteration of basic and specific parameters. In north-western part of Sava Depression, an important field is Okoli oil field. Shallower reservoir rocks are saturated with light condensate 60.6°



Fig. 1. Index map of north-western part of Sava Depression  
Sl. 1. Položajna karta sjeverozapadnog dijela Savske depresije

API (736 kg/m<sup>3</sup>) while in deeper reservoirs there is partly altered oil 30.8°API (871 kg/m<sup>3</sup>). Registered differences in hydrocarbon types can not be assigned to different levels of source rock thermal maturity; the condensate is a result of evaporative fractionation of light hydrocarbons from deeper reservoir. Separated hydrocarbons which migrated into shallow sediments, were trapped on impermeable barriers, and were retrograde condensed in new traps.<sup>5</sup>

## 2. Geological Setting

Žutica oil field is situated in north-western part of Sava Depression, approximately 30 kilometres south-east from Zagreb (Figure 1.) There is a large number of small oil and oil-gas accumulations (Ivanić, Žutica, Okoli, Stružec fields etc.) (Barić, 1979).

Geochemical analyses were carried out on sediment samples from the Žutica –1 zapad well. Žutica –1 zapad exploration well is located at north-western margin of Žutica structure. The well reached the depth of 2 906.5 m. Quaternary and Neogene sediments were recognized, from Lonja to the upper part of Prečec Formation. Lonja Formation was determined up to the depth of 914 m, and it is bounded by  $\alpha'$  log marker and the surface. These sequences stratigraphically belong to Quaternary and Levantian – Dacian stage (Pliocene). Sands, gravel and clay, sandy and gravel clay with coal intercalations appear in this interval. Široko polje Formation is defined in interval from 917.0 to 1 557.0 m. Formation is bounded by  $\alpha'$  and R $\phi$  log markers while deposits stratigraphically relate to the Upper Pontian and top part to Lower Pontian age. In the upper part of formation clay with gravel sand and with coal intercalations appears. These deposits in deeper parts are transformed into marly clay and clay marl, and at the bottom into mica sandstone. Kloštar Ivanić Formation of Lower Pontian age appears in the interval from 1 557.0 to 2 037.0 m. Formation is bounded by R $\phi$  and Z' markers while sandstones in alteration with marls occur too. Ivanić Grad Formation in interval from 2 037.0 to 2 524.0 m, belongs to Upper Pannonian age and is situated between log markers Z' and Rs5. The sediments are sandstones in alteration with marls. Prkos Formation is situated between 2 524.0 and 2 670.0 m, Rs5 and Rs7 log markers, and corresponds to Lower Pannonian. These deposits are marls enriched with organic matter. Prečec Formation was drilled at the depth of more than 2 670.0 m, and bounded by Rs7 and Tg. This sedimentary interval is of Badenian age and it consists of marls that are gradually transformed into sandy marls, below 2 820.7 m.

## 3. Geochemical Testing Methods for Sediments and Hydrocarbons from Žutica -1 zapad Well and for Oil from Žutica Field

The samples from five core intervals were chosen for geochemical testing. All samples belong to Prkos and Prečec Formation and they originated from the depth range from 2 542 to 2 906 m. This sedimentary complex consists of dark compact marls which in deeper parts change into sandy marls. Pelitic sediments are interest-

ing from geochemical point of view, but all sediments have not been analyzed as cuttings from mud were not preserved. Along with the sediments, oil and bitumen were tested as well, and the results were compared with representative oil sample from Žutica field.

Following analyses and testing methods were performed:

- macroscopic sediments description and hydrocarbon quality tests under fluorescent light
- total organic carbon determination
- determination of source rock properties by Rock-Eval pyrolysis
- optical examination of organic matter
- mathematical modeling
- determination of soluble organic matter, bitumen
- characterization of main group of compounds in bitumen and oil
- gas – chromatographic analyses of bitumen and oil

### 3.1 Macroscopic Sediments Description and Hydrocarbon Quality Tests under Fluorescent Light and Preparation of Chosen Samples

Macroscopic sediments determination showed the presence of dark-grey to black compact marls. After chloroform treating and UV light examination, light-yellow to gold-yellow fluorescence appeared in all samples. The samples taken for further analyses were rinsed with water to remove the mud residues. The samples were dried, pulverized and screened to granulation of 0.5 mm. Such prepared samples were used for further analyses.

### 3.2 Determination of Total Organic Carbon Content

The organic matter content in the rock is expressed as total organic carbon (TOC). This simple and fast analysis is the initial parameter in estimation of the potential source rocks. Examinations of the amount of total organic carbon, on numerous rock samples, of different geological age, showed that the samples from oil bearing regions

Table 1. Organic matter content (TOC) in cores, Žutica –1 zapad well (Leco analyzer)

CORE INTERVAL (m)		TOC (%)
2 542.0 - 2 545.5	I	0.51
	II	1.69
2 577.2 - 2 579.4	I	1.63
	II	0.94
2 731.0 - 2 734.0	I	2.35
	II	2.96
	III	1.56
2 820.7 – 2 823.6	I	1.06
	II	1.14
2 904.5 – 2 906.5	I	0.67
	II	0.57

contain up to three times larger amount of organic matter than samples from other regions (Ronov, 1958). For determining the organic matter quantity approximately one gram of rock sample is sufficient, but if rock is enriched with organic matter, smaller quantities would be enough. The removal of inorganic components containing carbon is implemented in the initial phase while the quantity of organic matter is determined by burning the sample in oxygen current at a temperature of 1 200 °C. Organic matter in the sample is oxidized to CO and CO<sub>2</sub> and the resulting carbon dioxide is proportional to the content of organic matter in the rocks. Results of testing showed that all samples contain increased amount of organic matter, which indicates possible source rocks.

Eleven samples from five intervals were prepared according to the described procedure. TOC measuring was performed using Leco analyzer. TOC values in samples were between 0.51 to 2.96%, average TOC was 1.37% (Table 1). Particularly high concentrations of organic matter (1.56 to 2.96%) contained samples from 2731.0-2734.0 m interval. The results show that all samples contain increased amount of organic matter, which is an indicator of possible source rocks.

The rocks enriched with organic matter were identified at various locations in the northwestern part of Sava Depression. Marly limestones, calcareous and sandy marls of Prkos and Prečec Formations, of Lower Pannonian to Badenian age, at depths from 1 600 to 3 000 m contain increased amount of organic matter. The average content of organic matter is 1.4%, which is in conformity with sediments testing in Žutica-1 zapad well.

### 3.3 Determination of Source Rocks Properties by Rock-Eval Pyrolysis

Rock-Eval pyrolysis was used for source rock hydrocarbon potential determination. As hydrocarbon generation

depended on temperature and geological time, pyrolysis process is performed at much higher temperatures than those of subsurface, what compensates much shorter geological period. Pulverized rock sample is gradually heated in inert atmosphere to the temperature of 550 °C. During the warming, at a temperature of about 250 °C free hydrocarbons release from rock, which is detected as the value of S<sub>1</sub>. Further warming, at the temperature interval between 420 and 460 °C causes cracking of kerogen molecules and release of newly formed hydrocarbons (value S<sub>2</sub>). The value of S<sub>2</sub> is the most important indicator of the ability of the rock to generate hydrocarbons. At the end, rock releases carbon dioxide (S<sub>3</sub> value). Values S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub> are expressed as milligram of hydrocarbons per gram of rock (mg HC/g rock).

Rock-Eval pyrolysis parameters were measured on all samples with TOC higher than 0.5%. The results (Table 2, Figure 2) show that the samples have higher values of residual potential (S<sub>2</sub>). Particularly, high potentials were registered in rock samples from intervals from 2 542.0 to 2 545.5 m, 2 577.2 – 2 579.4 m and 2 731.0 – 2 734.0 m, that belong to marls of Prkos and upper part of Prečec formation. Residual potential in several samples reaches a value of 14.93 mgHC/g rock. According to the existing classification, these sediments represent good to very good source rocks. Rock samples from deeper part of Prečec Formation are sandy marls, containing less content of the organic matter, and generation potential is reduced. Good generation potential of Prkos Formation sediments is the result of enhanced concentration of organic matter and favorable, hydrogen rich lipid kerogen. From the values of hydrogen and oxygen indexes (Table 2) in modified Van Krevelen diagram (Figure 3), kerogen type II was estimated, while mixed type II and III is present in samples from deeper formations. Determined types of organic facies are considered as good petroleum hydrocarbon sources.

Table 2. Results of Rock-Eval pyrolysis of samples from the core, Žutica -1 zapad

Core interval (m)	C <sub>org</sub> (%)	S <sub>1</sub> mg HC g st	S <sub>2</sub> mg HC g st	S <sub>3</sub> mg CO <sub>2</sub> g st	Tmax (°C)	PI	S <sub>2</sub> S <sub>3</sub>	HI mg HC g C <sub>org</sub>	OI mg CO <sub>2</sub> g C <sub>org</sub>	Ekst. (ppm)
2 542.0 – 2 545.5 I	0.31	0.20	1.48	0.26	439	0.12	5.69	477	84	766
II	1.51	0.73	8.62	0.42	436	0.08	20.52	571	28	
2 577.2 – 2 579.4 I	1.42	0.56	7.04	0.35	437	0.07	20.11	496	25	
II	0.72	0.36	3.44	0.29	438	0.09	11.86	478	40	
2 731.0 – 2 734.0 I	2.46	3.35	9.87	0.45	434	0.25	21.93	401	18	7 980
I (E)	1.83	0.18	6.47	0.47	437	0.03	13.77	354	26	
II	3.17	3.26	14.93	0.41	434	0.18	36.41	471	13	
II (E)	2.38	0.20	10.27	0.44	438	0.02	23.34	432	18	9 560
III	1.61	1.20	6.18	0.39	437	0.16	15.85	384	24	
III (E)	1.34	0.15	4.73	0.38	438	0.03	12.45	353	28	
2 820.7 – 2 823.6 I	0.99	0.70	2.67	0.41	442	0.21	6.51	270	41	
II	0.98	0.76	2.80	0.48	441	0.21	5.83	286	49	2 120
2 904.5 – 2 906.5 I	0.55	0.54	1.23	0.35	443	0.31	3.51	224	64	
II	0.43	0.41	0.96	0.24	442	0.30	4.00	223	56	

(E) – extracted sample

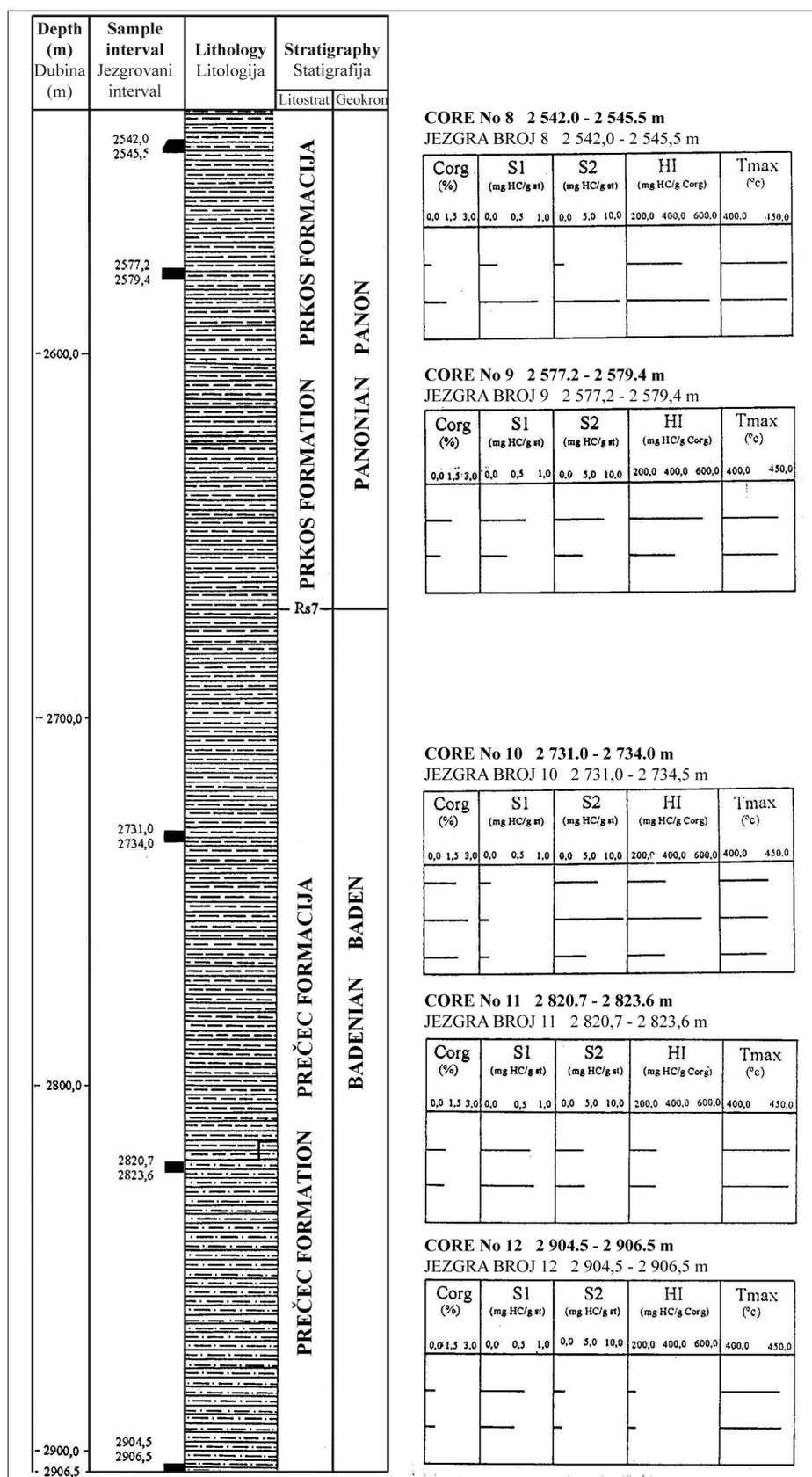


Fig. 2. Rock-Eval parameters in the core, Žutica – 1 zapad  
Sl. 2. Prikaz Rock Eval parametara u mehaničkim jezgrama, Žutica – 1 zapad

T<sub>max</sub> values of tested sediments show regular maturity increase with depth (436 to 443 °C) (Figure 4). Source rocks maturity of oil window was estimated from maturity profiles. Hydrocarbon generation possibilities are significant, S<sub>1</sub> value is high, which indicates increased quantity of free, thermo vaporized hydrocarbons. Only core samples were examined, but uniform lithostratigraphic characteristics of sediments within interval from 2 542 to 2 906 m imply that this sedimentary complex represents mature source rocks and generated hydrocarbons which migrated and saturated reservoir rocks in the Oil field Žutica.

Source rocks characteristics tested in Sava Depression showed similar results. Hydrogen indices between 250 and 600 mg HC/gTOC imply hydrogen rich kerogen, type II, which is a source of petroleum hydrocarbons in this area. Hydrocarbon potential of source rocks is not equable but varies in broad range. The main causes are different conditions in depositional environment (oxic – anoxic) which influenced quantity and quality of deposited organic matter. Measured and calculated values of source rocks maturity show regular increase of maturity with depth. Based on maturity profiles, oil window in Sava Depression starts at the depth of 2 200 m, which corresponds to geothermal gradients of this area (4-5 °C /100 m). The research showed that identified source rocks in Sava Depression were in mature catagenetic phase of hydrocarbon generation.

### 3.4 Optical Examination of Organic Matter

Methods of optical microscopy were also used in determining the type and maturity of organic matter. Results of this research are in accordance with the results of previous chemical and physical determinations. Optical examination of maceral composition of kerogen, enabled further detailed characterization.

**Table 3. Marcceral content and degree of maturation**

INTERVAL (m)	MACERAL CONTENT (vol. %)				DEGREE OF MATURATION		
	Amorfno	liptiniti	vitriniti	inertiniti	%Ro*	TAI	FC
2 542 - 2 545 IIm	100	Tr Ld,Di	-	-	0.62	2+	Y(L) YO(A)
2 577 - 2 579 Im	90	10 Ld,Di	-	-	0.64	2+	Y(L) YO(A)
2 731 - 2 734 IIm	100	Tr Ld,Di	-	-	0.73	2+-3-	Y(L) Y-B(A)
2 820 - 2 823 Im	100	Tr	-	-	0.83	3-	O(L) B(A)
2 904 - 2 906 Im	100	-	-	-	1.10	3	NF(A)

\* conversion TAI to Ro

ACRONYMS:

Tr traces

Di dinoflagelata

Ld liptodetrinite

L liptinite

A amorphous

Y yellow

YO yellow-orange

O orange

OB orange-brown

B brown

NF no fluorescence

CONVERSION:

TAI - %Ro

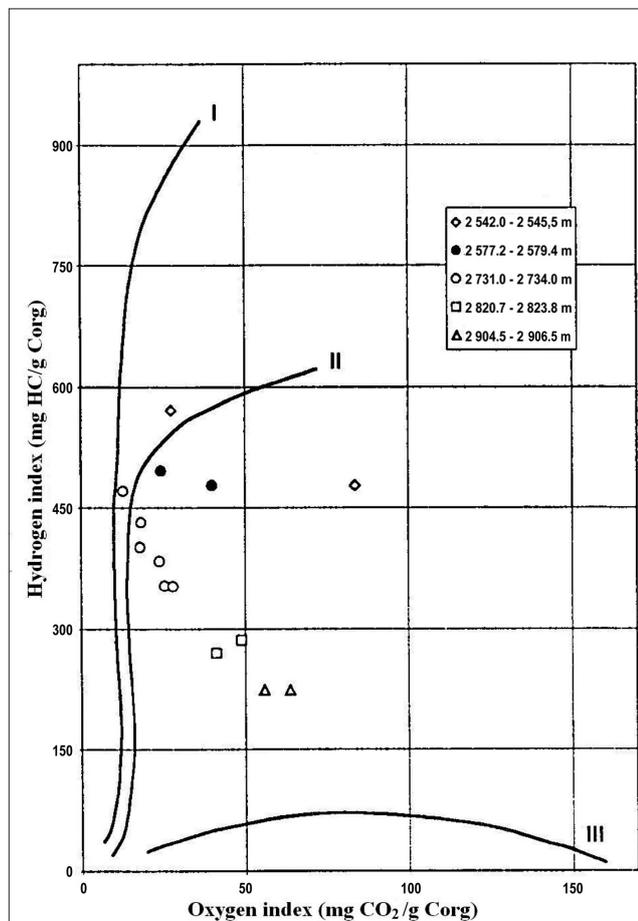
2- 0.35 - 0.45

2 0.45 - 0.55

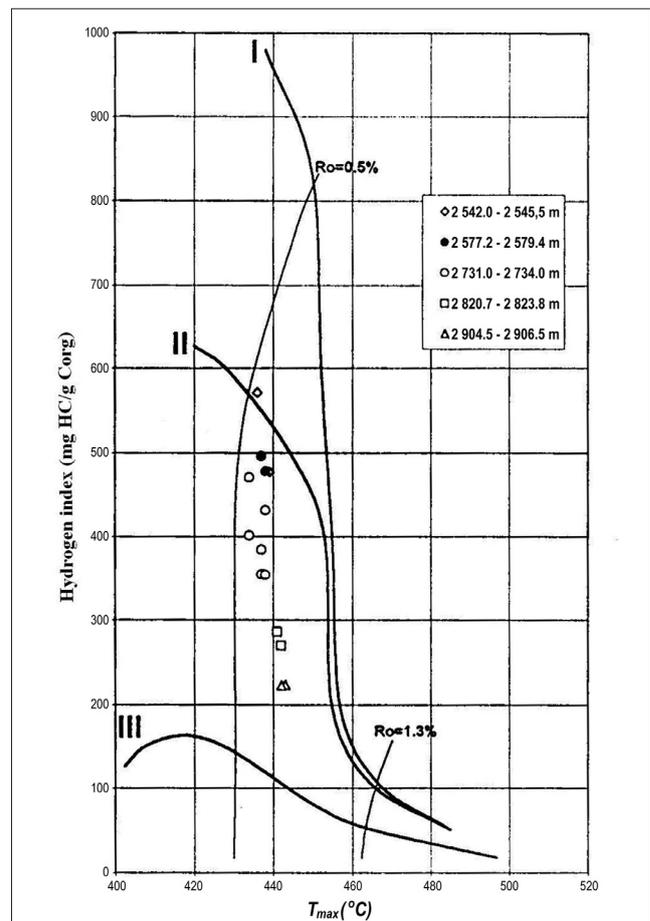
2+ 0.55 - 0.70

3- 0.70 - 0.95

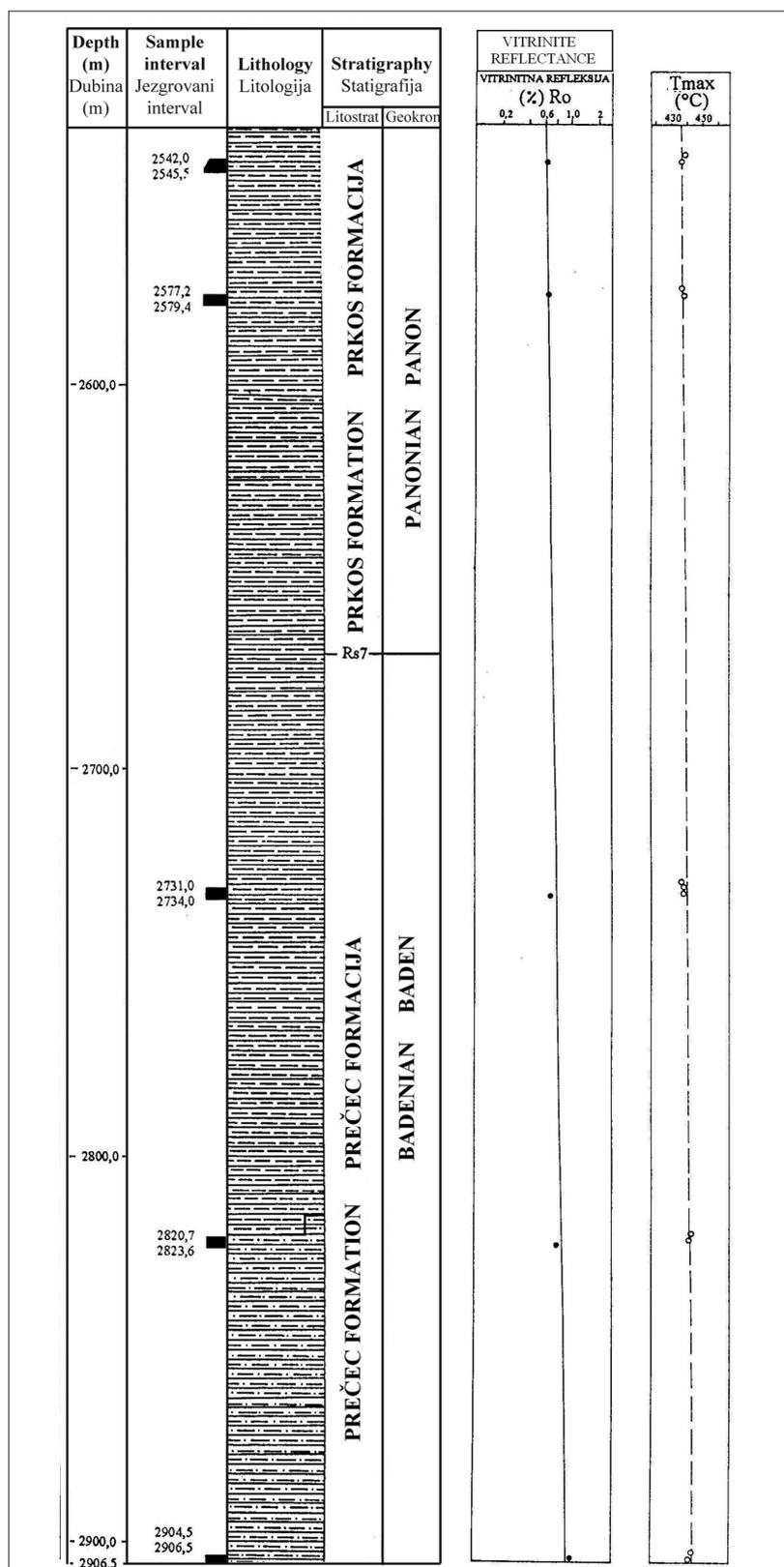
3 0.95 - 1.25

**Fig. 3. Kerogen types in samples from source rocks, Žutica - 1 zapad**

Sl. 3. Tipovi kerogena u uzorcima matičnih stijena, Žutica - 1 zapad

**Fig. 4. Types and maturity of kerogen in samples from source rocks, Žutica - 1 zapad**

Sl. 4. Tipovi i zrelost kerogena u uzorcima matičnih stijena, Žutica - 1 zapad



**Fig. 5. Maturity profiles of source rocks, Žutica-1 zapad, obtained from  $R_0$  and  $T_{max}$  values**  
 Sl. 5. Profili zrelosti matičnih stijena, Žutica-1 zapad, konstruirani iz  $R_0$  i  $T_{max}$  vrijednosti

Isolated kerogen samples were examined in transmitted light and amorphous kerogen was defined as predominant compound (90-100%) (Table 3). Content of liptinite maceral is low, and terrestrial vitrinite has not been found in any sample. Amorphous kerogen visible on microscopic photographs (Figure 6, 7 and 8) indicates hydrogen rich kerogen, which originated from Marine algae, lipid-cell bacteria, as well as from plant wax and resins. Beside amorphous kerogen, the presence of black framboids pyrite was also recognized on the photographs. The presence of pyrite is usual characteristic of anoxic environments which enabled good precursor preservation. Amorphous kerogen is considered as good precursor of petroleum hydrocarbons.

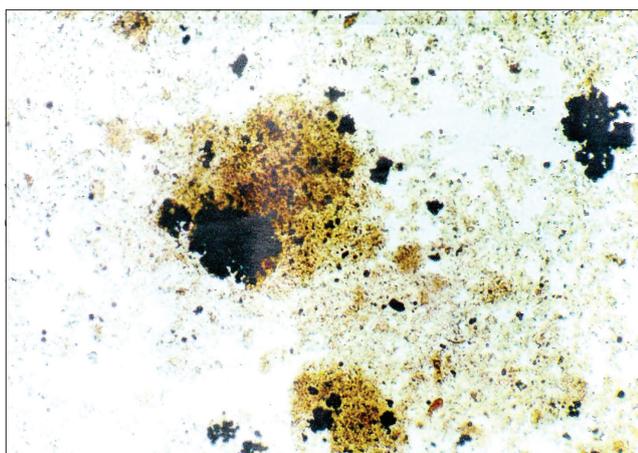
Maturity of organic matter was estimated from the palinomorph color in transmitted and fluorescent light. The color in transmitted light was expressed in numerical values as Thermal Alteration Index (TAI). The Staplin's (1969) scale with values between 1 and 4 was used for color description.

TAI values of tested kerogene varied between 2+ to 3 and they changed with depth. (Table 3). Fluorescence color also changed from yellow-orange, yellow-brown and brown to no fluorescence at the depth of 2 906 m, which is the result of relatively high thermal alteration degree.

Organic matter maturity profile was made by conversion of TAI value into vitrinite reflection ( $R_0\%$ ) (Table 3). Maturity profile (Figure 9) shows a regular growth of maturity with depth, which corresponded to the maturity profile of pyrolytic maturation parameter  $T_{max}$ . It is possible to conclude that the sediments from interval 2 542 to 2 904 m are in mature phase of thermal alteration, respectively, it corresponds to oil window. The estimated depth of sediments entry from Žutica -1 zapad well to oil window, with the use of vitrinite reflection of 0.6%  $R_0$ , is at the depth of 2 250 m when the generation of hydrocarbons begins, which relates to source rocks maturity in Sava Depression.

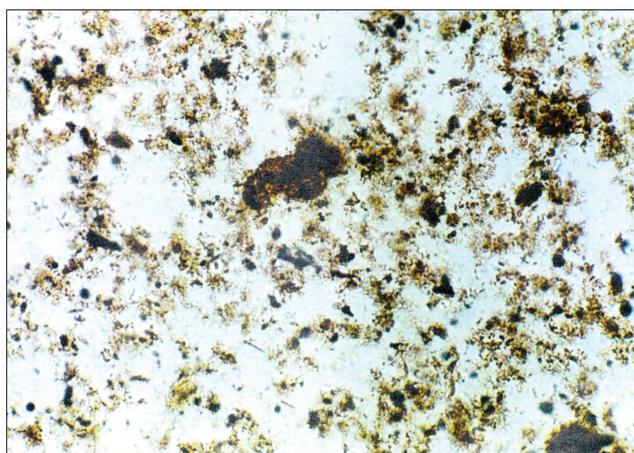
### 3.5 Mathematical Modeling

New trends in hydrocarbon exploration are directed toward quantitative basin modeling, i.e. estimation of hydrocarbon quantities in new, undiscovered areas, but they can also be applied to old areas with lot of measurement data. Modeling is a continuation of existing exploration concepts and provides answers to the question of where, why, when and how the hydrocarbons were generated and accumulated in a particular



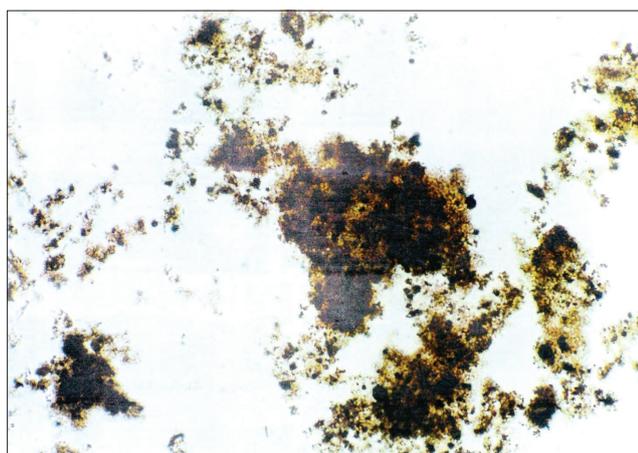
**Fig. 6. Amorphous organic matter and framboids of pyrite (black) in transmitted light, Žutica - 1 zapad, 2 577-2 579 m, (magnification 225x)**

Sl. 6. Amorfna organska tvar i nakupine pirita (crno), Žutica - 1 zapad, 2 577 - 2 579 m, u prolaznom svijetlu (225x)



**Fig. 8. Amorphous organic matter in transmitted light, Žutica - 1 zapad, 2 820- 823 m, (magnification 225 x).**

Sl. 8. Amorfna organska tvar, Žutica - 1 zapad, 2820-2823 m, u prolaznom svijetlu (225 x).



**Fig. 7. Amorphous organic matter in transmitted light, Žutica - 1 zapad, 2 731-2 734 II, (magnification 225x).**

Sl. 7. Amorfna organska tvar, Žutica - 1 zapad, 2 731-2 734 II, u prolaznom svijetlu (225x).

area. First mathematical model in hydrocarbon study dates from early 70's of last century. Lopatin (1971) introduced a model prediction of maturity of organic matter as a function of time and temperature, so called time - temperature index (TTI). Elaboration of model uses the Arrhenius chemical - kinetic theory that implies exponential dependence of chemical reaction velocity and temperature:

$$k = A \exp^{Ea/RT}$$

$k$	reaction-rate constant
$A$	pre-exponential factor
$Ea$	Activation energy
$R$	Universal gas constant
$T$	Temperature (K)

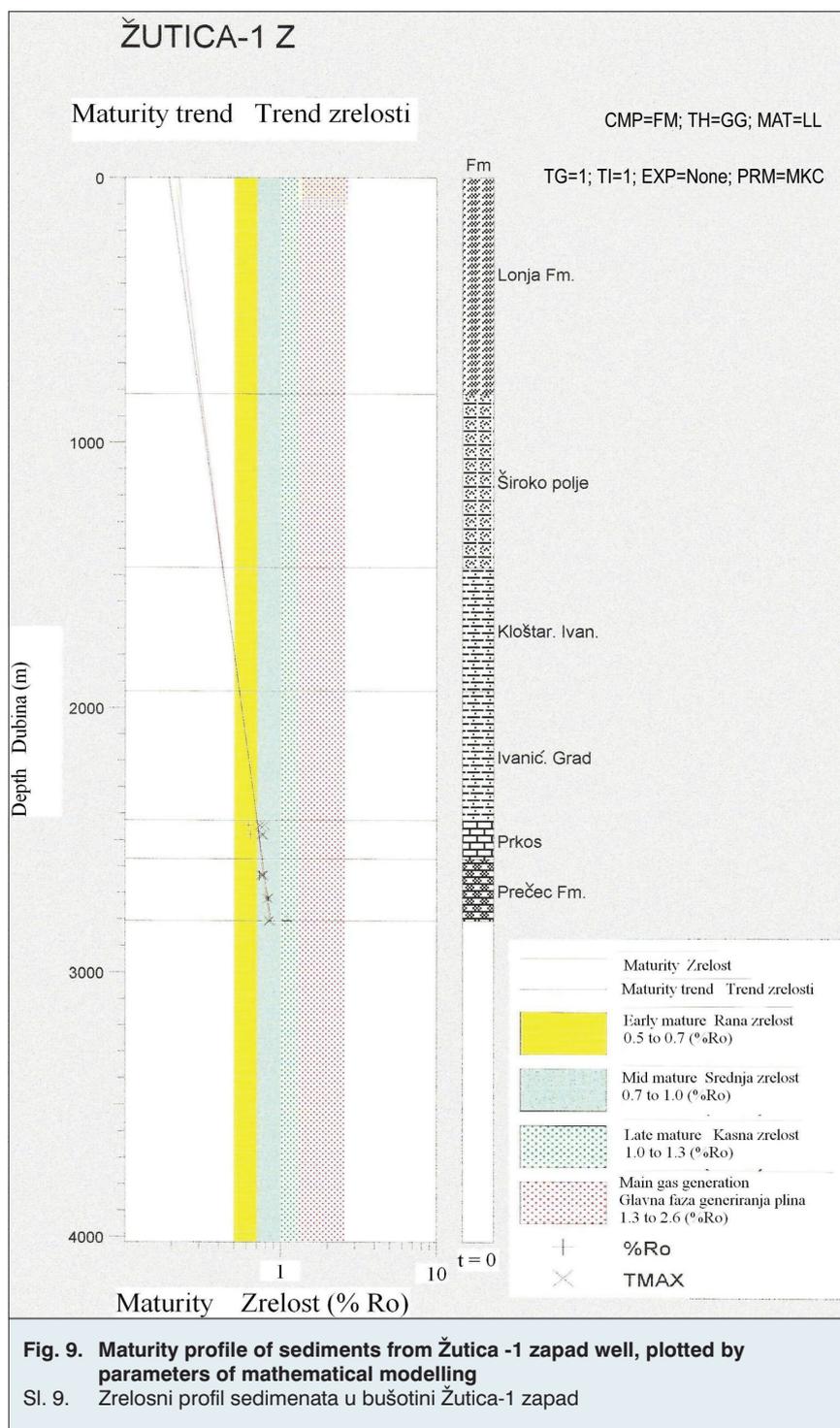
i.e. increase of temperature for every 10 °C, doubles the velocity of chemical reaction. Lopatin method and new models are based on reconstruction of deposition and tectonic relations in certain geological formation. Deposition depth, geological age and geothermal gradient give the relationships, important for thermodynamic properties evaluation of sedimentary rocks.

Exploration Department of INA-Naftaplin has BasinMod® software with maturity model and geological model options. Stratigraphic - time data that enable plot of burial history curves are of great importance in geological model. The input in modeling consists of data on stratigraphy, lithology, thickness of deposits and their deposition time. At the same time, software offers list of options about lithological, physical and thermal rock properties. After geological and maturity modeling, these models are compared. Very important parameter is geothermal gradient, since it enables plot of isotherm and together with burial history curves, they define time and temperature intervals within sediments.

The maturity profile obtained through numerical and measured values, with geothermal gradient of 4.2 °C/100 m displays regular increase maturity with depth (Figure 10). Sediments in Žutica -1 zapad well, reach early maturity stage (0.5%  $R_o$ ), i.e. oil window starts at 1 888.9 m, and middle maturity (0.7%  $R_o$ ) on 2 510.5 m. From history burial plots (Figure 11) it is possible to estimate that Prečec formation source rocks of Badenian age, reached early hydrocarbon generation during Upper Miocene, between 5.71 and 5.30 million years. Source rocks of Prkos formation, of Lower Pannonian age, were situated in early oil window between 5.30 and 4.54 million years (Upper Miocene - Pliocene).

### 3.6 Determination of Soluble Organic Matter, Bitumen

Quantitative determination of soluble organic matter, bitumen, in the samples of rock has been carried by extraction with organic solvents. Pulverized rock sample of 50 g is treated with chloroform in Soxhlet apparatus during



8 to 24 hours. After treatment, the solvent was extracted by vacuum distillation and bitumen quantity recalculated due to quantity of treated rock. Content of hydrocarbons tested samples varied between 766 and 9 560 ppm (Table 2.), a maximum concentration of bitumen contained samples from the core, interval 2 731-2 734 m. High concentrations of hydrocarbons in this interval are the result of very good generation potential and matu-

rity of the source rocks are in the stage of the generation of hydrocarbons.

### 3.7 Characterization of main group of compounds in bitumen and oil

The main groups of compounds in bitumen and oil are saturated and aromatic hydrocarbons, resins (NSO – compounds) and asphaltenes (Table 4). Their ratio is an important parameter in evaluating the origin and maturity of hydrocarbons, allowing assessment of the length of migration flows, but also in determining alteration and degradation of hydrocarbons in the reservoir.

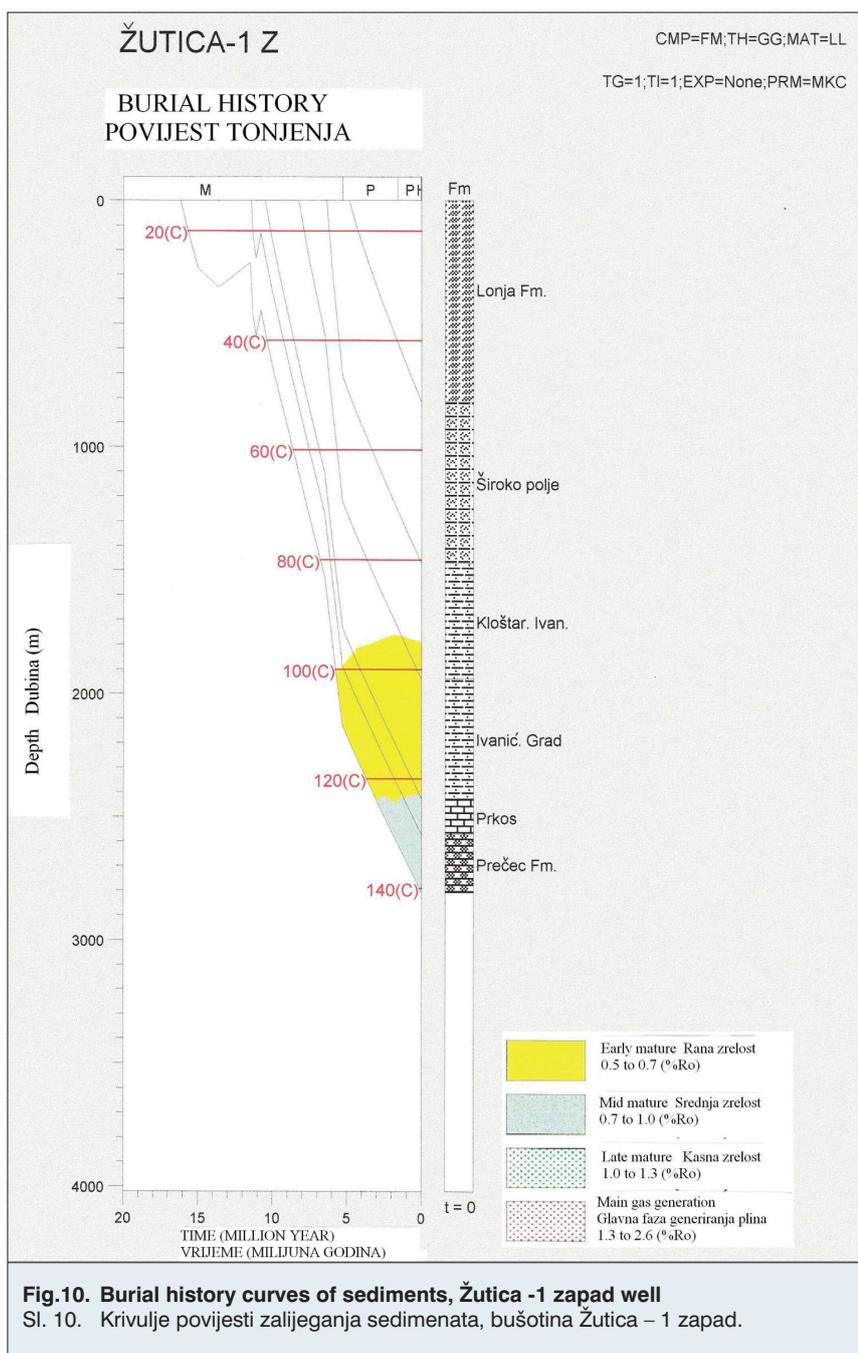
The separation of components groups is carried out by chromatography to the column, which is based on the principle of different absorption capacity of main group compounds and their separation by using different organic solvents. In the first stage the asphaltenes separate, aliphatic and aromatic hydrocarbons and resins are quantitatively transferred to the column with adsorbent. Considering the polarity, related chemical constituents have been eluted by organic solvents: n-hexane, benzene and mixture of benzene and methanol. Organic solvent was removed from separated compounds, and weight.

The results of determining the group composition of bitumen show mutual resemblance. (Table 4). Hydrocarbon concentration reaches about 64%, however, share of non-hydrocarbon components, resins and asphaltenes is high. Relationship between bitumen components separated from source rocks is usual property of bitumen, because primary migration process did not start. Correlation with the sample of Žutica<sup>4</sup> oil in which the proportion of resin and asphaltenes is significantly smaller compared to bitumen. It is well known that concentrations of saturated and aromatic hydrocarbons increase during migration. High-molecular-weight components characterized by high adsorption pos-

sibilities on mineral matrix and limited mobility fall behind source rocks.<sup>10</sup>

### 3.8 Gas – Chromatographic Analyses of Bitumen and Oil

Gas chromatography technique was used for molecular characteristic determination of bitumen and oil. This technique identifies molecules in fraction of saturated



hydrocarbons. Analyses were performed on gas chromatograph Perkin Elmer with capillary column.

Bitumen from Žutica – 1 zapad well and oil from Žutica field were undergoing gas chromatographic analysis. Results showed smaller differences in length of hydrocarbon chain molecule, content of n-alkanes, iso-alkanes and molecule ratios of Pr/C<sub>17</sub>, Ph/C<sub>18</sub> and Pr/Ph. These differences can be seen from gas chromatograms (Figure 9). Differences in molecular distribution are result of differences of their precursors. Molecular distribution of bitumen from 2 820 to 2 823 m interval with increased content of isoprenoids is indicator of enhanced content of terrigenous components (Barić, 1993). Hydrocarbon

distribution corresponds to determined type of organic facies. There is no correspondence between gas chromatography profiles of bitumen and oil from Žutica field. The greatest similarity of oil from Žutica field was detected in bitumen extracted from cores in 2 731-2 734 m interval. Results indicate that oil from Žutica field is the mixture of hydrocarbons generated in nearby source rocks, which show smaller differences in type and maturity of precursors. Alteration of hydrocarbon chemical compounds occurs during migration process and additional alterations are the result of hydrocarbons mixing in reservoir rocks.

#### 4. CONCLUSION

Sediments of Prkos and Prečec Formation, of Lower Pannonian and Badenian age, from the interval 2 522.4 to 2 906.5 m, sampled from Žutica – 1 zapad well, were geochemically tested. Core samples from the 2 542.0 – 2 545.5 m interval and 2 577.0 - 2 579.4 m are highly compact, dark grey to black marls with increased content of carbonaceous compounds. Deeper, the content of sand component in marls increases, which is reflected on decreased quantity of organic matter, organic facies alteration and lower generative potential.

Sediments showed increased quantities of organic matter, and maximum value of TOC (3.17%) was registered in core interval 2 731.0 – 2 734.0 m. Rock Eval pyrolysis confirmed the existence of source rocks, with changeable generation potential which varies between 1.37 to 14.93 mg HC/g rock. Differences in sediment hydrocarbon generation possibilities are result of changes in sedimentation environment. Organic facies determined from pyrolytic parameters, hydrogen and oxygen indices and optical examination showed presence of predominantly hydrogen rich,

lipid kerogen, type II. In sediments at the depths below 2 820.7 m kerogen type slightly changes, as terrigenous components increase and kerogen presents mixture of kerogen type II and III, but with lower generation capacity. Examined sediments are good source rocks and hydrogen rich kerogen is the source of petroleum hydrocarbons.

Maturity of organic matter was determined through pyrolytic ( $T_{max}$ ) and optical (TAI) parameters. Maturity profiles show regular increase in maturity with depth and determined source rocks reached oil window, catagenetic stage of thermal alteration. Sediments from Žutica – 1 zapad well reached oil window phase at 2 250

**Table 4. Results of main group compounds in bitumen from Žutica-1 zapad well and Žutica oil**

Interval (m)	Extract (ppm)	alkanes (%)	aromates (%)	resins (%)	asphaltenes (%)
2 542 - 2 545	722	45.8	18.2	27.8	8.2
2 731 - 2 734	7 980	45.3	18.0	26.5	10.2
Žutica oil	-	60.5	25.7	12.2	1.6

**Table 5. Gas chromatographic data of bitumen Žutica – 1 zapad well and Žutica oil**

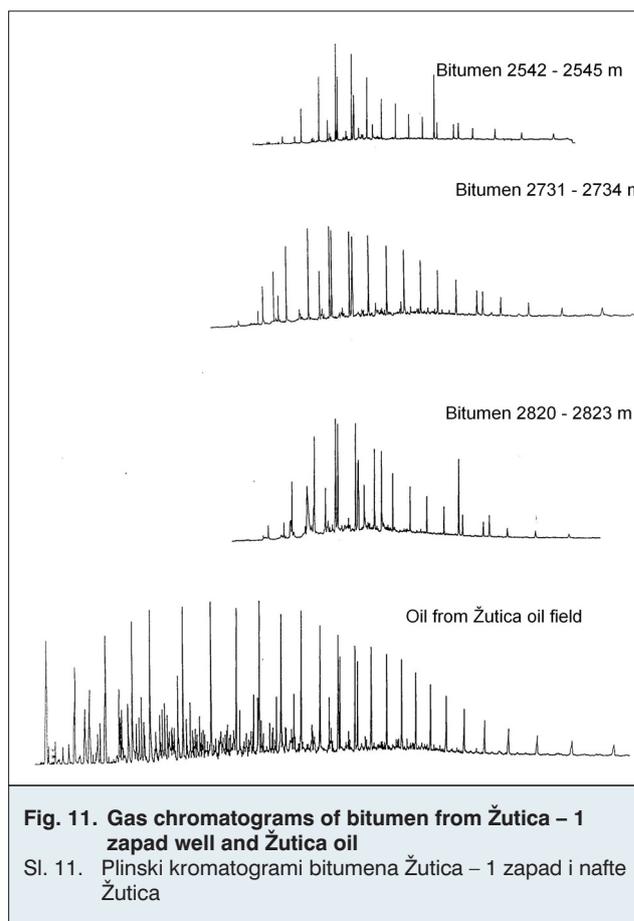
	Sample interval (m)			
	2 542 - 2 545	2 731 - 2 734	2820 - 2823	Žutica
bitumen and oil				
n-alkanes (%)	80.43	77.14	74.79	60.29
iso-alkanes (%)	19.58	22.85	25.21	39.71
Pr/C <sub>17</sub>	0.64	0.54	1.35	0.82
Ph/C <sub>18</sub>	0.92	0.94	1.06	0.86
Ph/Pr	0.89	0.61	1.54	1.07
HC range	C <sub>14</sub> -C <sub>32</sub>	C <sub>13</sub> -C <sub>33</sub>	C <sub>14</sub> -C <sub>33</sub>	C <sub>6</sub> -C <sub>33</sub>

m. Favourable type and maturity of organic matter reflected with increased quantity of hydrocarbons, bitumen. Extracted bitumen, compared with oil from Žutica field, characterized increased content of high molecular resins and asphaltenes and decreased content of alkane and aromatic components. Differences are the result of adsorption of resins and asphaltene compounds and decreased migration possibilities. Bitumen molecular properties show differences too, as a result of differences in type and precursor maturity. Correlation of basic and molecular properties of bitumen and oil from the oil field Žutica showed differences, which is possible to explain by chemical hydrocarbon alteration during migration processes from neighboring precursors, which are of various types and maturity of organic facies and by hydrocarbon mixing processes in the reservoir.

This paper presents sediment complex in hydrocarbon generation stage. Together with geological and geophysical methods it is possible to confirm regional distribution of these source rocks which enable determination of sediments volume characteristics as well as estimation of their real generating properties.

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**Fig. 11. Gas chromatograms of bitumen from Žutica – 1 zapad well and Žutica oil**

Sl. 11. Plinski kromatogrami bitumena Žutica – 1 zapad i nafte Žutica

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