Historical and geochemical outlines of the oil occurrence and production near Miková village; Flysch Belt, NE Slovakia

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Abstract: Petroleum geological field research since the 2nd half of the 19th century has revealed the presence of hydrocarbons in the Western Carpathian Flysch Belt, especially in the Galicia area of the former Austro-Hungarian Empire. Historical prospecting and exploration in this part of the Flysch belt are well documented, and revival in hydrocarbon exploration interest at the end of the 20th century led to drilling the new Alexander 1 well which supplied a non-commercial methane inflow and only traces of crude oil in form of impregnations. The chemical and isotopic composition of this methane carbon indicates methane associated with oil generation conditions. Oil is genetically related most probably to Upper Eocene to Oligocene source rocks, mainly Krosno-Menilite beds, activated after Oligocene period by thrusting of Flysch formations. The geochemical characteristics are based on low temperature extraction of oil impregnation from the Alexander 1/1065 m well core and on hexane oil extract from the oil-water emulsion at a depth of 390 m in this well.

Key words: ancient oil production, recent prospecting, geochemical features of oil and gas, Flysch Belt, NE Slovakia

1. INTRODUCTION

The oil deposits near Turzovka in the Čadca district and near Miková in the Švidník district are the earliest produced deposits in the Slovak part of the Western Carpathians. The Turzovka deposit was discovered in 1901 and the final small amounts of oil there were produced soon after World War II, while the Miková deposit was discovered in the 2nd half of the 19th century and production continued until 1951.

Miková village is in the Stropkov District in north-eastern Slovakia, and it is one of the oldest oil prospecting areas in the Western Carpathians (Fig. 1). Surface oil there led to excavations around the seepage and prospect drilling survived until 1944 despite World War interruptions. A total of 18 wells ranging in depth from 50 to 1368.9 m were drilled, and these were named Miková-I to XV, M1, Matej-V and H-I (Fig. 1). Oil was discovered in Miková-I to VI, X to XIII, XV and Matej-V wells. Miková-VII, VIII, IX, XIV, Habura-I, Kamjana-I, and Miková-1 wells contained only oil indices but numerous methane gas inflows. However, methane was not exploited at that time, and the Alexander oil mining plant closed in 1953. According to various sources, approximately 600 metric tons was produced during mining and several methane gas inflows have been documented (e.g., Andrusov, 1937).

Surface rock samples from the wider Miková area and well cuttings from the Alexander-1 well were studied using routine geochemical methods (Milička, 1997, 1999). N-pentane extract from well core AX1/1065 m and n-hexane extract from oil-water emulsion at 390 m depth in the AX1 well were studied using gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). Chemical and isotopic composition of natural gases was studied in Miková-VIII and Alexander1 wells and in Vyšný Komárnik seepage (Milička, 1997).

2. BRIEF HISTORICAL OVERVIEW OF EXPLORATION AND PRODUCTION

The oil resources of the former Austro-Hungarian Empire in the 19th century were essentially in Galicia, which now forms part of Poland and Ukraine. This motivated oil prospecting in the close north-eastern region of Slovakia in the 2nd half of the 19th century. The first documents describing oil presence on the slopes of Kamjana ridge between Miková and Habura villages come from Paul (1869) and Oculus (1883) ex Plička & Liškutinová (1958). Both authors referred to the occurrence of “oil spots” on the water surface in two old shafts near Miková village. Andrusov (1937) reported oil manifestations in manually dug wells, and Bilek (1936) provided written information about oil and gas and the character of water formation at the Alexander oil mining plant.

Prior to 1911, oil was produced from shafts dug by various commercial enterprises, where individual shafts produced between 50 and 100 kg of oil per week. In 1911, the Comte Sztaray de Nagymihály supervised two manually excavated wells at a depth of 50 m with a daily production of approximately 100 kg. These wells became the foundation for the future oil mining fields named “Alexander” and “Magdaléna”. In 1914, the
Comte Sztramay’s company established the 580 m deep K1 well near Kamjana which penetrated oil and gas bearing horizons. However, drilling there was interrupted by World War I.

After 1919, the French company “Société anonyme des pétroles de Miková” bought the Miková oil terrains and in 1921 it established the first well in the Miková series – this Miková-I well was up to 280 m deep with an initial daily production of 4 tons of oil but this output gradually decreased. The company initiated two positive and three negative wells. In 1922–23, the 187 m deep H1 well was drilled near Habura village. This offered gas at 78–90 and 128 m, and oil traces were found at 114 m depth. Three barrels of dense oil were subsequently recovered at 132 m depth (Matějka & Kodym, 1936).

From 1924, the Bank of Zemplín in the town of Michalovce became the new owner of the Miková oil terrains, but it did not drill any new wells. The following ownerships then ensued: (1) in 1927–1929, the oil fields belonged to the “Industrial and commercial Company” from Michalovce; (2) in 1929–1932 the Roth brothers owned it; (3) in 1932–1942 it reverted to the “Industrial and commercial Company” which drilled four positive wells and one negative well at a maximum depth of 70 m; (4) in 1942, the J. Rutgers Company drilled the Matej-V well which reached a depth of 1368.9 m in 1944 and became the second most yielding well in the oil field. Thereafter, only the non-productive Miková-XV well was drilled in 1944, and finally (5) after World War II, the Miková oil mining plant was taken over by the Czechoslovak Oil Enterprise. On September 14th 1951 was the plant closed because it was not more economically efficient and it passed into liquidation in 1953 (Menčík & Plička, 1958).

With the revival of interest in oil exploration, the SPP-VVNP Oil Company drilled in 1998 the new Alexander-1 well and discovered a non-commercial methane gas inflow at 1380 m depth. No commercial quantities of oil were found; further details of the drilling were published by Vitáloš (2004). The localization of old wells in the surrounds of Miková village and the most recent Alexander-1 well are depicted in Fig. 1, while the historical process of manual oil production is shown in Fig. 2 and preserved tubing remnants of an old well in the Miková well series appears in Fig. 3.

In addition to the mining in the Miková and Habura village vicinities, past drilling also occurred around the Slovak northwestern villages of Krivá Ofka, Vyšná Radvaň, Hrabovce n.L.,
Rokytovec, Sukov, Vyšný Komárnik, Veľká Driečna, Čertižné, and Regetovka.

3. PETROLEUM-GEOLOGICAL OUTLINE OF THE MIKOVÁ SURROUNDS

The eastern Slovakian section of the Flysch Belt has a quite complicated geological structure, with clear vertical division into three etages (Pereszlényi et al., 1999).

The deep structural etage is formed by the Northern European Platform with Paleozoic and Mesozoic sediments. This was recognized beneath the Flysch nappes in neighbouring Poland. Although there is little information about it in Slovakian territory, it is considered that this most likely reaches beneath the front of the Magura nappe at a depth of approximately 8 km. The middle etage is formed by the Obidowa-Slopnice unit penetrated by the Zboj-1, Smilno-1, and Zborov-1 deep boreholes ranging from 3000 to 3700 m (e.g., Ďurkovič et al. 1982, Leško et al. 1987, Koráb et al., 1991).

This unit spreads throughout the entire area with a marked elevation structure. It formed the dominant oil and gas bearing unit in this region, with the detected intensive water inflows indicating a regional reservoir sealed by overlying low permeable rocks of the Magura and Dukla nappes.

The upper structural etage is formed on the surface by the Magura nappe, Miková-Snina zone, and the Dukla nappe (Leško et al. 1960). This etage is characterized by fold-and-thrust structure and strike slip faulting (Koráb & Ďurkovič, 1978). A favourable indication for hydrocarbon exploration here was the presence

Fig. 2. Oil exploration at the beginning of the 20th century in the Miková prospecting area (photo by Andrusov, 1937).

Fig. 3. Armature remnants from an old well of the Miková well series drilled in 1911–1943. (Photo by the first author; July 2010).
of numerous oil-, gas- and solid bitumen surface occurrences bound to the Magura nappe, the Dukla nappe over-thrust zone, and the Miková–Snina zone. These occurrences presented opportunities for oil prospecting in the first half of the last century and the largest discovered oil deposit was in the Miková area where oil was produced until 1952. Previously, small Miková oil deposits were noted lying in front of the Magura to Dukla nappe thrust zone (Fig. 1). In this section, the Dukla nappe is formed by the Cergow and Menilite beds of the Upper Eocene to Lower Oligocene age of the so-called Medzilaborec Syncline and Miková–Snina zone. The geological profile from Upper Cretaceous to Upper Eocene is known in this zone, and two different evolutions of Eocene Flysch beds have been distinguished here (Koráb & Ŏrkovič, 1978). The first is characterized by variegated Flysch – Submenilite beds, while the second Flysch type comprises greywacke and quartz sandstones alternating with grey to black claystones of conchoidal fracture. The Papín beds were lithologically and faunistically documented in the Upper Eocene (Koráb & Ŏrkovič, 1978).

The Magura nappe consists here of Zlín and Beloveža beds of the Rača Unit and it lies mainly in the south-western part of the studied area.

The pelitic sediments of all three structural etages are potential source rocks in this area. Although the largest hydrocarbon portion was generated in original sedimentary basins and numerous accumulations were most likely destroyed during tectonic events, there still remains great hydrocarbon potential from the large volume of these source rocks.
The best kerogen type contains the youngest sediments— the Menilite and Cergow beds (Milička, 1997). Hydrocarbon generation was activated only during tectonic events after Oligocene (Pereszlényi et al., 1997).

The sandstones present in almost all formations are potential reservoir rocks. Although these usually have low primary porosity, from an oil-geological point of view the sandstones gain sufficient secondary porosity during tectonic events (Pereszlényi et al., 1997).

Geological exploration of this region is rather low; mainly the reflection seismic survey is deficient in the region. The study area is crossed only by one reflection seismic profile 107/88, 89 which is evaluated in detail in Behrmann et al. (2000). Further geological information is contained in results published from

Fig. 4. Aliphatic-, triterpane- (m/z 191) and sterane (m/z 217) distributions of low temperature n-pentane extract from the Alexander-1/1065 m well core.
the Zboj-1, Zborov-1, and Smilno-1 deep boreholes (Ďurkovič et al., 1982, Leško et al., 1987; Wunder, 1991).

The geological architecture and oil-geological relationships in the Miková area have previously been characterized by many authors; especially by Andrusov (1937), Bílek (1936), Budaj et al. (1961), Čepk (1933), Kettner (1937), Koráb & Leško (1977), Matějka & Kodym (1936, 1937, 1949), Menčík et al. (1967), Koráb (1973, 1983) and Koráb & Řurkovič (1978).

4. ANALYSES OF EXTRACTS

No oil samples for analysis from the “historical oil fields” in Miková actually exist. There is only archival documentation of the physical-chemical properties of oils from the old Miková-II, IV, XI and XII wells (Fig. 1; Tab. 1).

Oil as an individual phase was also not available in the most recent Alexander-1 well and therefore the low-temperature n-pentane extract from the AX-1/1,065 m well core was analysed. The relative high amount of free hydrocarbons released by Rock-Eval pyrolysis. An additional sample defining the distribution of the aliphatic oil fraction was available in the n-hexane extract from a water-oil emulsion. This “oil” sample was taken before- and after swabbing at a depth of 390 m in the Alexander-1 well.

Oil extracted from the AX1/390m emulsion and the rock extract from AX 1065 m were analysed at the Brno laboratories of the Czech Geological Survey. The aliphatic fractions of both samples were analysed using the GC-MS method. Chromatograms of the aliphatic fractions and mass fragmentograms m/z 191 and 217 are presented in Figs. 4 and 5.

5. ANALYSES OF NATURAL GAS

Natural gas from the depth of 1,380 m in Alexander-1 well was transferred from drill-tubing into a vacuum sample-tube. Surface gas seepage from the old Miková-VIII well was sampled into special glass tubes filled with a hypersaline solution. The inflowing gas removed the saline solution avoiding dissolution of particular gas components in water and also air “pollution” of the sample. In addition, natural gas seepage samples were collected from a small depression on a grassy slope in the Vyšný Komárnik locality. Since both these latter gas samples were seepages, their precise accumulation depth is unknown.

All three sampled gases were analyzed using GC-TCD, FID gas chromatography and C1 to C7 hydrocarbons were analyzed using capillary gas chromatography. The chemical composition of the natural gas was analyzed in the Brno laboratory of CGS Prague, and the isotopic composition was analyzed in CGS Prague laboratories by the method of Buzek & Michaliček (1989). The analytical results of both chemical and isotopic composition are presented in Tab. 1.

6. GEOCHEMICAL CHARACTERISTIC OF OIL AND EXTRACTS

As previously mentioned, no oil exists for analysis from the ancient Miková oil mining fields and therefore only extracts were analyzed.

These extracts consisted of (1) low temperature n-pentane from the well core rich in free hydrocarbons released by Rock-Eval pyrolysis (S1 = 0.45 mg HC/g rock; Milička 1999a). The n-alkane distribution (Fig. 4) is, however, influenced by the extraction methodology so that the chromatogram portrays extractable bitumen rather than actual oil; and (2) a hexane extract
of hydrocarbons from the water-oil emulsion at 390 m depth in the Alexander-1 well, following swabbing (Fig. 5). This latter extract is expected to provide the most precise indication on the composition of the aliphatic oil fraction.

Because of the absence of oil on Slovakian territory, the Bôbrka oil in Franek well, 60 km inside the neighbouring Poland area, which is geologically comparable with the Slovakian area, was previously studied (Milička, 1999a,b). The geochemical characteristics of oil from Bôbrka were in detail studied within the set of 35 Polish oils and extracts by ten Haven et al. (1993). The basic geochemical characteristics of this oil, including the ratio of aliphatic-, aromatic fractions and NSO compounds, the pristane to phytane ratio, the presence of oleanane and the distribution of C27, C28, C29 αααα20R steranes is comparable with the findings in Poland. Due to biodegradation, it is not possible to evaluate the n-alkane distribution of the Bôbrka oil, but its sterane distribution is comparable with that found in extracts from the Krosno-Menilite shales in the wider area of Miková;
7. GEOCHEMICAL CHARACTERISTICS OF THE NATURAL GAS

The chemical and isotopic analysis of the following three natural gases were evaluated: (1) The natural gas seeping from the old Miková-VIII. Regarding hydrocarbon gas composition, this predominantly consisted of methane at 88.7 vol. % CH₄, and a relatively high content of the higher hydrocarbons; 1.19 % ethane, 1.18 % propane, and the total amount of butanes to heptanes was 2.31 vol. %. The proportion of individual gases is influenced by low air pollution (O₂ = 0.64; N₂ = 2.99; and CO₂ = 2.97 vol. %).

(2) The second gas was sampled directly from drill-tubing into a vacuum sample-tube and this gives the most accurate indication of the actual gas component distribution. Its composition shows a slightly increased amount of higher HC gases compared to the Miková-VIII gas composition.

(3) Methane gas from the Vyšný Komárník locality emanates within the wider Miková area and it is the relatively “driest” gas. Here, the methane content is the absolute highest, and it also exceeds the total of all the higher hydrocarbons; as shown in parameters C₇, and C₆/C₅ in Tab. 2.

Genetically are all these three gases related. Their chemical composition, the methane to higher hydrocarbons and the carbon isotope composition indicate the accompanying methane gases related to the oil generation stage.

Chemical composition of the gases from AX-1/1380 m well and from the seepage in Vyšný Komárník are well comparable with the methane gas from Korňa-1 well situated in the Magura nappe of the NW Flysch part (Milička & Macek, 2012). Chemical composition of the gas from the old Miková-VIII well is comparable with composition of gas seepage near Korňa village (NW Slovakia); both gas samples are slightly influenced by air pollution due to sampling technique.

The methane carbon isotopic composition indicate, however, clear to a more thermal mature gas of all analyzed methane gases from the NW part of the Flysch zone around the Turzovka town area (δ¹³C PDB = -35 to -37 ‰) being associated with the final stages of condensate generation.

8. CONCLUSIONS

Natural gases and extracts from the bitumen rich well core AX-1/1065 m and from the oil-water emulsion AX-1/390 m were studied using GC and GC-MS methods. The results were compared with potential source rock extracts, with Polish Bóbrika oil and AX-1/1065 m n-pentane extract.

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