

MOLECULAR AND ISOTOPIC COMPOSITIONS, ORIGIN AND BIODEGRADATION OF NATURAL GAS IN THE EASTERN PART OF THE POLISH OUTER CARPATHIANS

Maciej J. Kotarba

AGH University of Science and Technology, Krakow, Poland

Introduction

Origin and influence of secondary biodegradation of natural gases occurring within the Lower Cretaceous-Miocene sandstone reservoirs of the eastern part of the Polish Outer Carpathians in area between Sanok and Polish-Ukrainian state border based on molecular and stable C, H and N isotope (12 , 13 C in CH₄, C₂H₆, C₃H₈, *n*C₄H₁₀, *i*C₄H₁₀, *n*C₅H₁₂, *i*C₅H₁₂ and CO₂, 1 , 2 H in CH₄, C₂H₆ and C₃H₈, and 14 , 15 N in N₂) analyses are determined and explained.

Geological outline, petroleum occurrence and source rock

The Outer Carpathians, one of the largest petroleum provinces of Central Europe, is a fold-thrust belt of Late Jurassic-Late Miocene age rocks, up to 6 km in stratigraphic thickness. They consist the major nappes (tectonic units) named from south to north as the Magura, Dukla, Silesian, Sub-Silesian, Skole and Zgólbice. The study area covers the eastern part of the Polish Outer Carpathians. Dukla, Silesian, Sub-Silesian and Skole units occur in this area. Both oil and gas are currently produced in the study area. The Oligocene Menilite Shales have the best hydrocarbon potential of formations within the Dukla, Silesian and Skole units (e.g., Kotarba et al., 2007).

Samples and Methods

Natural gas samples from the Lower Cretaceous-Miocene sandstone reservoirs, twenty one samples from Czarna, Dwernik, Grabownica, Jurowce-Srogów, Rudawka Rymanowska, Strachocina, Turze Pole, Wetlina, Zabłotce-Sanok and Zatwarnica petroleum deposits of the Silesian Unit, and eleven samples from Łodyna, Tyrawa Solna and Wańkowa petroleum deposits, Kuźmina uneconomic accumulation, and Wara seep of the Skole Unit (Fig. 1) were collected.

Molecular compositions of natural gases (CH₄, C₂H₆, C₃H₈, *i*-C₄H₁₀, *n*-C₄H₁₀, C₅H₁₂, C₆H₁₄, C₇H₁₆, unsaturated hydrocarbons, CO₂, O₂, H₂, N₂, He, Ar) were analysed in a set of columns on Hewlett Packard 5890 Series II, Hewlett Packard 6890 Series and Chrom 5 gas chromatographs equipped with flame ionization (FID) and thermal conductivity (TCD) detectors. The stable C, H and N isotope analyses were completed on a Finnigan Delta Plus and a Thermo Scientific Delta V Plus mass spectrometers. Methane, ethane, propane, butanes, pentanes and carbon dioxide for C isotopes were separated chromatographically. Analytical precision is estimated as $\pm 0.2\%$. Methane, ethane and propane for H isotopes were separated chromatographically. Analytical precision is estimated to be $\pm 3\%$ for methane and $\pm 5\%$ for ethane and propane. Molecular nitrogen was separated chromatographically. Analytical precision is estimated to be $\pm 0.4\%$.

Results

The analysed natural gases in the study area are variable both in their molecular and isotopic compositions. The molecular composition, gas indices and stable isotope ratios vary within the following ranges: CH₄ from 38.3 to 98.6 %, C₂H₆ from 0.05 to 18.1 %, C₃H₈ from 0.02 to 16.6 %, *i*C₄H₁₀ from 0.004 to 5.1 %, *n*C₄H₁₀ from 0.002 to 5.2 %, *i*C₅H₁₂ from 0.003 to 1.76 %, *n*C₅H₁₂ from 0.005 to 1.73 %, N₂ from 0.12 to 22.1 %, CO₂ from 0.01 to 20.9 %, hydrocarbon index [$C_{HC} = CH_4 / (C_2H_6 + C_3H_8)$] from 2 to 1412, carbon dioxide/methane index {CDMI = $(CO_2 / [CO_2 + CH_4]) \cdot 100$ (%) } from 0.02 to 35.3 %, $\delta^{13}C(CH_4)$ from -56.0 to -34.8% , $\delta^{13}C(C_2H_6)$ from -33.8 to -24.0% , $\delta^{13}C(C_3H_8)$ from -33.2 to -22.6% , $\delta^{13}C(iC_4H_{10})$

from -30.6 to -24.7% , $\delta^{13}\text{C}(nC_4H_{10})$ from -29.8 to -24.6% , $\delta^{13}\text{C}(iC_5H_{12})$ from -28.6 to -23.7% , $\delta^{13}\text{C}(nC_5H_{12})$ from -27.7 to -24.2% , $\delta^2\text{H}(\text{CH}_4)$ from -231 to -153% , $\delta^2\text{H}(\text{C}_2\text{H}_6)$ from -198 to -127% , $\delta^2\text{H}(\text{C}_3\text{H}_8)$ from -161 to -115% , $\delta^{13}\text{C}(\text{CO}_2)$ from -22.1 to 12.0% and $\delta^{15}\text{N}(\text{N}_2)$ from -5.1 to 1.8% . The gases are wet and contain hexanes from 0.00 to 1.34% .

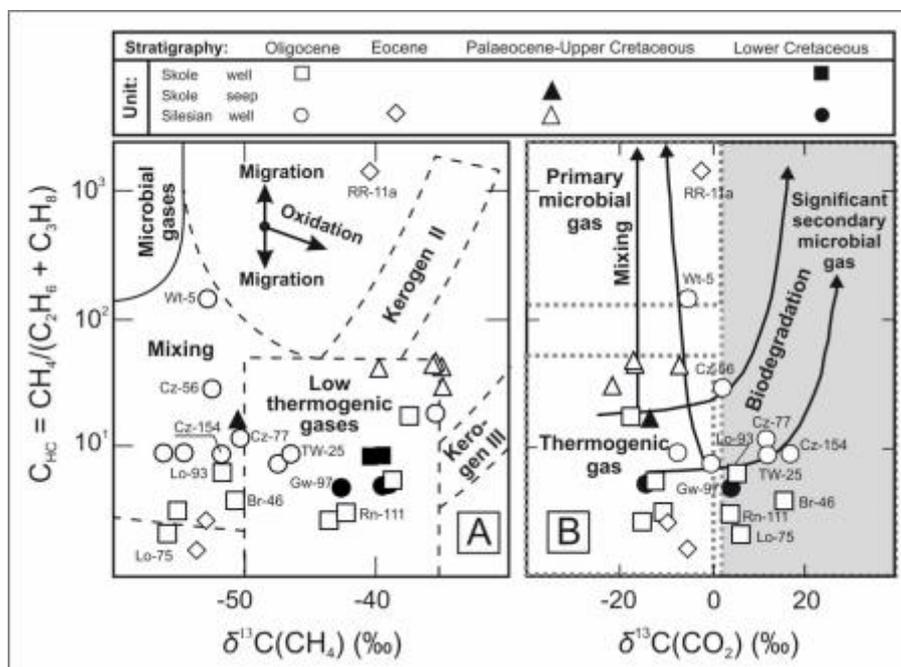


Figure 1 Hydrocarbon index (CHC) versus (A) $\delta^{13}\text{C}(\text{CH}_4)$ and (B) $\delta^{13}\text{C}(\text{CO}_2)$ for analysed natural gases. Compositional fields from (A) Whiticar (1994) and (B) Milkov (2010).

Conclusions

Mentioned above results of molecular and isotopic analyses of natural gases accumulated in Silesian and Skole units of the eastern part of the Polish Outer Carpathians reveal: (i) gaseous hydrocarbons are generally related to thermogenic (thermocatalytic) processes; (ii) 13 of 32 analysed gases also occur genetically component of microbial (bacterial) methane (Fig. 1A), which proves that petroleum traps had already been formed and sealed before the initial microbial processes affecting the organic matter of the Oligocene Menilite Shales; (iii) thermogenic gases were generated during low-temperature, and occasionally during high-temperature stages at a maturity level of 0.8 to 1.8% in vitrinite reflectance scale assuming type II and mixed type II/III kerogen of the Oligocene Menilite Shales; (iv) thermogenic gaseous hydrocarbons were generated from a single source irrespectively of kerogen type; (v) 9 of 32 analysed gases underwent the secondary biodegradation (Fig. 1B); (vi) carbon dioxide was generated during both thermogenic and microbial processes; (vii) molecular nitrogen was generated most probably during thermal transformation of organic matter (thermogenic nitrogen), and partly has a component release from NH_4 -rich illites.

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References

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