CARBON STABLE ISOTOPE COMPOSITION OF INDIVIDUAL HYDROCARBONS (CSIA) FOR SHALE FORMATION EVALUATION

Abstract

The relationship between the change of carbon isotopic composition of gaseous hydrocarbons in natural gas and the increase of source rock organic matter thermal maturity are especially important in the petroleum geochemistry. The thermal maturity evaluation and interpretation based on the chemical and isotopic compositions is commonly performed for natural gases conventional reservoirs, shales, coals, seeps and other geological habitats. The carbon isotopic composition of individual hydrocarbons in gas samples provided by the compound specific isotope analysis (CSIA) can be used for interpretation and correlation purposes. On the basis of the $\delta^{13}C$ value of methane, ethane and propane, the estimation of thermal transformation degree of the source rock (from which the gas was generated) can be made.

In this dissertation, organic geochemistry methods (chemical and isotopic composition of gas and pyrolysis indices) are used for the shale petroleum system evaluation and to find the values of parameters determining the sweet spot. The case study of five exploration wells located in the north of Poland is presented and discussed. Wells are situated in the area of three concessions (Wejherowo , Kartuzy-Szemud and Stara Kiszewa) located in Pomorskie Voivodship.

The work presents results of chemical/isotopic composition analyses of natural gases and geochemical Rock-Eval analyses from five wells exploring the Silurian and the Ordovician shale formations. The statistical analyses were conducted with the use of the following: descriptive, correlation and liner regression. Using all the results as one statistical population, Pearson's linear correlation coefficients of the gas isotopic composition with the pyrolytic and molecular indices were calculated. Surprisingly, there are no high correlations between the pyrolytic indices and the isotopic composition or the chemical indices. Moderate correlations are between maturity of the source organic matter (Tmax) and the isotopic composition of carbon in methane ($r = 0.63$).

The results of carbon isotope analyses clearly differentiate samples from each well, only L-1 and O-2 wells natural gases are quite similar. Methane, ethane and propane $\delta^{13}C$ values are progressively higher in sequence L-1, O-2, K-1, B-1 and W-1. The thermal maturity of the source organic matter was assessed using Tang's mathematical model including the share of biogenic methane. The thermal maturity corresponds mainly to the range from 0.9% (L-1 and O-2) to 1.5% (B-1 and W-1) vitrinite reflectance. Natural gas compositions shows mixing with the biogenic gas (below approximately 25%).

A noticeable drift of methane towards negative values in all wells samples confirmed mixing with biogenic gas (with the use of the natural gas plot - Chung plot). Values of the isotopic composition of ethane and propane were also skewed (especially in W-1 and B-1; a little less in O-2 and K-1 wells). This confirmed the occurrence of secondary cracking.

The inversion of the isotopic composition of carbon in methane, ethane and propane (the roll-over effect) does not occur in analysed gases. Usage of the diagram ($\delta^{13}C$-C_3 - $\delta^{13}C$-C_2) vs ($\delta^{13}C$-C_2 - $\delta^{13}C$-C_1) is considered to be the best way of presenting of the isotopic data. For all samples, the difference between ethane and methane ($\delta^{13}C$-C_2 - $\delta^{13}C$-C_1) is constantly decreasing with an increase of thermal maturity. The propane and ethane difference ($\delta^{13}C$-C_3 - $\delta^{13}C$-C_2) is increasing at lower thermal maturities (to approximately 1,5% VRo), and decreasing with higher values of maturity. This suggests presence of the secondary cracking, resulting in the sweet spot occurrence.

Using the hydrocarbon composition, molecular indices were calculated (C_1/C_{2+3}, C_2/C_3, i-C_4/n-C_4 and i-C_5/n-C_5). These indices are a valuable source of information about natural gas, whose complete composition analyses can be affected by the manner of taking a sample and the type of well. Similarly to the isotopic composition the samples plot progressively in sequence L-1 and O-2, K-1, B-1 and W-1.

The main aim of this work was to establish the values of chemical and isotopic composition parameters determining sweet spots. Using the composition of gases from W-1 well (the highest thermal maturity of the source organic matter) and the Barnett reference data, approximate values at which prospective levels can be expected were defined.

Janiga Maud