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ABSTRACT OF PhD DISSERTATION

Origin of natural gas in the Zechstein Main Dolomite strata in selected areas of the Polish Permian Basin: stable isotope and hydrous pyrolysis studies

The origin of natural gas associated and non-associated with oil accumulated in the Zechstein Main Dolomite (Ca₂) Basin in the south-western part of the Polish Permian Basin was determined by means of analytical and experimental methods of petroleum geochemistry including molecular and stable carbon (in CH₄, C₂H₆, C₃H₈, *n*-C₄H₁₀, *i*-C₄H₁₀, *n*-C₅H₁₂, *i*-C₅H₁₂ and CO₂), hydrogen (in CH₄, C₂H₆, C₃H₈) and nitrogen (in N₂) isotope compositions of natural gas, molecular and stable carbon (in CH₄, C₂H₆, C₃H₈, *n*-C₄H₁₀, *i*-C₄H₁₀, *n*-C₅H₁₂, *i*-C₅H₁₂, and CO₂) and hydrogen (in CH₄, C₂H₆, C₃H₈) isotope compositions of gases generated during hydrous pyrolysis (HP) experiments. The research comprises eleven natural gas samples collected from Buk, Jarocin, Kije, Mozów S, Ołobok, Połęcko, Radoszyn, Retno, Tarchały and Wysocko Małe E petroleum deposits and four gas samples generated during HP experiments.

HP is an experimental method simulating natural processes of oil and natural gas generation and expulsion during deep burial from a source rock. It involves heating of a rock sample in the presence of water. The HP experiments were performed at 300 and 355°C for 72 h, which are considered to represent early and late oil generation stages, respectively. HP experiments were performed at the Laboratory of Petroleum and Environmental Geochemistry of the AGH University of Science and Technology in Kraków, the third in the world and first in Europe laboratory equipped with this type of installation.

Gases generated from Ca₂ source rocks during HP experiments are used to identify natural thermogenic gas and also for tracking of changes in molecular and isotope compositions of natural gases at different maturity of organic matter resulting from different temperatures of HP experiments.

The study attempts for the first time in Europe to determine the origin of natural gas by the use of stable hydrogen composition of ethane and propane in natural gases and gases generated during HP experiments and to assess if these data provide additional information on the type and maturity of a source rock.

The type and maturity of source organic matter is determined based on the results of Rock-Eval pyrolysis of Ca2 carbonate source rocks, stable carbon isotope and elemental compositions of kerogen isolated from Ca2 source rocks as well as results of measuring of random reflectance of composites prepared for HP experiments.

In the study area two independent genetic groups of hydrocarbon gases have been distinguished. The first genetic group comprises natural gases of either microbial and thermogenic origin or of only thermogenic origin. The lack of microbial components in some of natural gases indicates that during microbial phase of hydrocarbon generation the traps within the Ca2 carbonates had not been formed and sealed yet. The occurrence of microbial components in the rest of analysed natural gases reveals that accumulation of natural gas of the Ca2 reservoir has a cumulative character. At first, microbial gases had been generated and then thermogenic gases were produced from Type II kerogen during the entire range of oil window. The second genetic group comprises thermogenic hydrocarbon gases not genetically related to dispersed organic matter of the Ca2 strata, which had originated from Type III kerogen of high maturity from presumably Pennsylvanian strata and migrated through local fault zones to the Ca2 reservoir.

$\delta^{13}\text{C}$ values of CH_4 , C_2H_6 and C_3H_8 generated during HP experiments from two different types of kerogen plotted against the reciprocal of their carbon number show concave and convex trends evidencing that non-linear orders cannot be indicative for multiple thermogenic gas generation regardless of the kerogen type. Similarly, stable hydrogen isotope composition of CH_4 , C_2H_6 and C_3H_8 of gases generated during HP experiments plotted versus the reciprocal of their hydrogen number showing concave trend reveal that non-linear orders of $\delta^2\text{H}$ values in relation to the reciprocal hydrogen number of alkane gases also cannot be indicative of a simple generation process.

Results of stable carbon isotope composition of hydrocarbon gases generated during HP experiments indicate that the carbon isotopic signature of original kerogen has a major effect on $\delta^{13}\text{C}$ values of hydrocarbon gases which it generates. The thermal maturity of organic matter during HP experiments at 330 and 355°C is reflected by the increase of $\delta^2\text{H}$ of CH_4 with no significant changes in $\delta^2\text{H}$ of C_2H_6 and C_3H_8 suggesting that only $\delta^2\text{H}$ values of methane reflect the maturity of a source organic matter. Likewise, no dependency on kerogen type in $\delta^2\text{H}$ values of C_2H_6 and C_3H_8 with different HP temperatures have been noticed. $\delta^2\text{H}$ values of C_2H_6 and C_3H_8 have not provided neither information on hydrocarbon genetic type nor data about mixing processes between genetic components of hydrocarbon gases.

Two genetic groups of CO_2 occur in the study area. The first genetic group comprises CO_2 generated within Ca2 carbonates during thermal decarboxylation of kerogen and this genetic group may contain CO_2 originated from microbial sulphate reduction (MSR) and/or thermochemical sulphate reduction (TSR) processes. The second

genetic group of CO₂ comprises natural gases with CO₂ genetically not related to the Ca₂ carbonates that was generated from thermal decomposition of possibly the Zechstein Limestone carbonates.

The occurrence of H₂S in most of analysed natural gases is closely related to the presence of CO₂ and these two non-hydrocarbon components are considered to be of common origin connected to MSR and TSR processes.

N₂ concentration and stable nitrogen isotope composition reveal that molecular nitrogen in analysed natural gases was generated mainly during thermal decomposition of organic matter.