PYROLYSIS TEMPERATURE EFFECT ON GASEOUS HYDROCARBONS ISOTOPE COMPOSITION ON THE EXAMPLE OF GEOLOGICAL SAMPLES (PY-GC-IRMS)

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Introduction

Pyrolysis is a process of thermochemical decomposition in an anaerobic atmosphere. Parameters of pyrolysis (temperature, time) have large impact on the obtained products (quantity, type, proportions). Apparatuses allowing to perform a pyrolysis process under defined conditions are pyrolyzers. The pyrolyzers can be combined with various devices such as mass spectrometers, gas chromatographs, and isotopic mass spectrometers. The GC-IRMS sets allow to obtain $\delta^{13}C$ values of individual compounds from the mixture without the necessity of physical separation. The combination of the on-line GC-IRMS set with the pyrolyzer allows to determine the isotopic composition of the pyrolysis product (the individual chemical compounds of the pyrolysis product) [1].

Methodology

Py-GC-IRMS sets enable the pyrolysis of many different types of geological samples. The work presents the results of analyses of pyrolysis products - gaseous hydrocarbons. The compounds obtained are: methane, ethene, ethane, propylene, propane, 1-butene, n-butane and carbon di-oxide. The Py-GC-IRMS set used is a Thermo Scientific Delta V Advantage mass spectrometer with a Trace GC Ultra chromatograph (HP-PLOT / Q capillary column, 30 m) and Pyroprobe 6150 pyrolyzer. Details of methodology and its partial validation are described in "Pyrolysis Py-GC-IRMS – partial validation…". During reproducibility test values of relative standard deviations are below five percent for each compound [1].

Results

Analyses were performed for: Silurian shale sample, Menilite beds sample (rock and kerogen) and for hard and brown coal. All types of samples were pyrolysed at temperatures of: 600°C, 700°C, 800°C, 900°C and 1000°C. Pyrolysis at 500°C for the Silurian shale sample K-1 does not allow for the generation of products, therefore, for next samples, this temperature was not used. Part of results are shown in table 1. Values of $\delta^{13}C$ for each compound and each temperature, excluding 600°C, does not vary significantly, which is rather surprising. Similar situation exists for the rest of samples, excluding rock sample from Menilite beds. For all samples the trend is maintained that at higher temperature the value of $\delta^{13}C$ is also higher.

The ratio between unsaturated and saturated hydrocarbons varies and as the temperature rises unsaturated predominate. However, this does not affect the isotopic composition and the individual pairs have similar $\delta^{13}C$ values for the K-1 shale and the Menilite shale (both rock and kerogen). However, for hard coal saturated compounds assume values higher than the corresponding unsaturated compounds. For brown coal the situation is reversed.

In addition, the results of pyrolysis in 1000°C for all geological samples are summarized in one graph (correlation curves) in figure 1. The results of both shale samples (two rocks and kerogen) are similar. The difference that occurs is the greater amount of carbon dioxide and its isotopic composition for the K-1 sample. Both coals samples differ from shales and from each other. Particularly noticeable are the differences for pairs of saturated and unsaturated hydrocarbons, whereas for shale and kerogen samples, these differences are negligible.

Table 1 *Carbon isotopic composition of pyrolysis products generated in different temperatures from Silurian shale sample [‰]*

	Pyrolysis in 500°C	Pyrolysis in 600°C	Pyrolysis in 700°C	Pyrolysis in 800°C	Pyrolysis in 900°C	Pyrolysis in 1000°C
CO_2	-19,28	-14,16	-13,80	-13,92	-8,34	-8,43
Methane		-37,13	-32,86	-32,93	-32,48	-31,16
Ethene		-33,20	-30,19	-30,41	-29,41	-29,01
Ethane		-33,38	-30,27	-30,30	-30,04	-28,95
Propylene	-30,99	-30,66	-29,01	-28,94	-27,59	-27,03
Propane		-31,13	-29,23	-28,69	-28,16	-26,17
1-Butene		-27,82	-28,23	-28,73	-25,98	-25,47
n-Butane	-31,00	-29,52	-27,28	-27,44	-25,93	-25,75

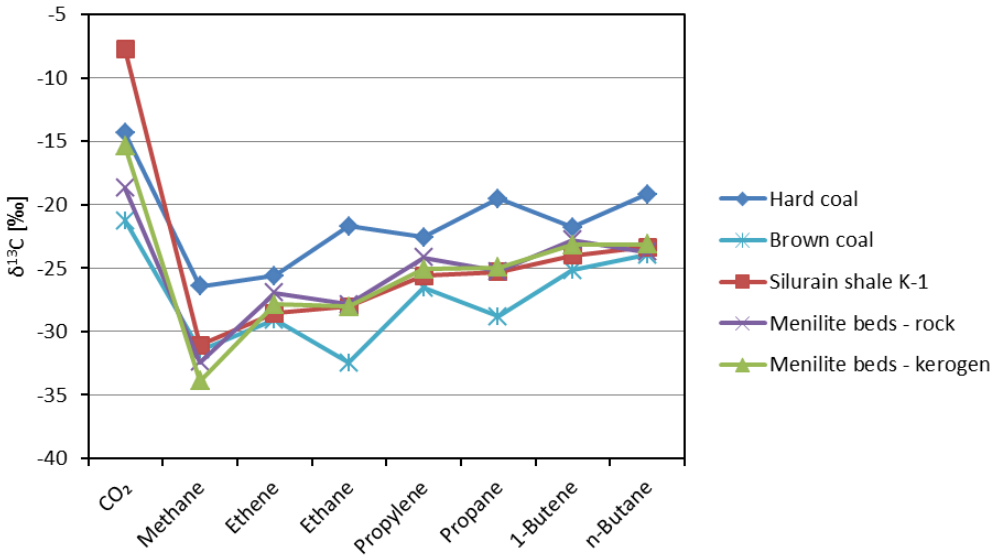

Figure 1 *Carbon isotopic composition of pyrolysis products of various samples [‰].*

References

Janiga M., Kania M. Pyrolysis Py-GC-IRMS – partial validation of "on-line" carbon isotope composition determination, 2019, submitted to Nafta-Gaz

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