Quality of organic matter of the Lublin Formation in the Lublin Coal Basin (Poland)

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Abstract. Lublin Formation (upper Westphalian A and Westphalian B) is composed mainly of mudstones and claystones. It is the most important part of the coal-bearing Carboniferous series of the Lublin Coal Basin (LCB). The paper presents geochemical data such as total organic carbon (TOC), Rock-eval pyrolysis data, as well as vitrinite reflectance and petrographic composition of organic matter in the Westphalian claystones from the central part of the Lublin Coal Basin. Investigation of organic matter has been used to determine the source rock characteristics and petroleum generative potential. The TOC contents of the analysed samples range from 0.38 to 12.95 % indicating their different petroleum generative potential. The results of Rock-eval pyrolysis indicate that most of the samples contain type III kerogen. Tmax range of 421-438°C suggesting low degree of thermal maturation, which can be described as the initial phase of oil generation.

1. Introduction
The Lublin Coal Basin (LCB) is located in south-east Poland. The most important part of the coal-bearing Carboniferous series of LCB is the Lublin Formation containing the main multi-seam coal deposits [1]. Lublin Formation (upper Westphalian A and Westphalian B) is built mainly of mudstones and claystones interbedded with sandstones interlayers. The lowest part of this formation (Westphalian A) belongs to the paralic series which ends the highest marine faunal horizon Dunbarella [2]. Above this level are continental sediments (Westphalian B) belonging to the limnic series [1]. Lublin region from a petroleum point of view belongs to the Upper Palaeozoic Basin located in the border zone of the East European. A few hydrocarbon deposits in upper Carboniferous of the Lublin region have been reported (i.e. Stężyca gas–oil field, Świdnik - oil field) [3]. A detailed study of the organic matter of the Carboniferous of the discussed area were presented in many papers [e.g.4, 5, 6, 7, 8, 9, 10, 11].

Study of organic matter of the Westphalian claystones from the central part of Lublin Coal Basin have been carried out for the purpose of quantity and quality of organic matter and thermal maturity level as well as to determine the source rock characteristics and petroleum generative potentials.

2. Geological setting
The Lublin Coal Basin (LCB) is located in southeast Poland, in the Lublin Province, and is conterminous with the Lviv-Volhynia Coal Basin located in Ukraine (figure 1). It is situated in the contact zone of two great geological units: the Precambrian East European Platform and the Early Palaeozoic West European Platform. The LCB takes the form of an extended province stretching along a line from southeast to northwest, 20 to 40 km wide and 180 km long [1].
The basement for the Carboniferous sediments is made up of Proterozoic crystalline rocks and Early and Late Paleozoic deposits (including upper parts of the Devonian system). The Carboniferous strata, which lie inconsistently on the older substrate, are represented by Visean to Westphalian B deposits. The Visean Namurian A (the Huczwa and Terebin Formations), and Namurian B,C and lower Westphalian A (the Dęblin Formation and the lower part of the Lublin Formation) deposits compose the paralic series. Above this (the upper part of the Lublin Formation), there are only lacustrine and fluvial sediments. The top of the Carboniferous deposits is of an erosive nature. The overlying sediments consist of a sequence of Permo-Mesozoic and Cenozoic rocks. The thickness of the overburden varies from 350 m near Włodawa to over 1200 m to the west of Lublin [1, 12].

![Geological map of the Lublin Coal Basin](image)

**Figure 1.** Geological map of the Lublin Coal Basin (Zdanowski 1999 [12], amended). Explanations: K- mining area Lublin K 9, C- mining area Lublin K 6-7, S- mining area Lublin K 8, Q – mining area Lublin K 4-5; 1, 2, 3, 4 – boreholes.

### 3. Sampling and methods

The research material was provided by core samples from the boreholes 1, 2, 3 and 4 located in mining areas K-4-5, K-6-7, K-8, K-9 in the central part of Lublin Coal Basin (figure 1, figure 2). This study utilises data for 20 samples (grey claystones) taken from the Lublin Formation (Westphalian A and B). 11 samples represent limnic series (Westphalian) B whereas 9 represent the upper part of the paralic series - *Dunbarella* marine marker horizon (Westphalian A). Samples were selected based on their dark color and the relatively high total carbon content (TOT/C) found in earlier geochemical researches.
Figure 2. Sampling location within the simplified Carboniferous profiles of the analysed boreholes (LCB).

Researches included TOC and Rock-Eval analysis as well as the petrographic examinations of the organic matter for all selected samples.

Rock-Eval pyrolytic analysis using Rock-Eval 6 analyser were carried out at the Institute of Geology and Geochemistry of the Oil and Gas Institute - National Research Institute in Cracow.

Rock-Eval pyrolysis was done to identify and calculate the following parameters:

- $S_1$ [mg HC/g rock] - free hydrocarbons present in the sample evolved at 300°C;
- $S_2$ [mg HC/g rock] - hydrocarbons evolved between 300 and 650°C;
- $S_3$ [mg CO$_2$/g rock] - CO$_2$ yield during thermal breakdown of kerogen (organic CO$_2$);
- MIN C – the mineral carbon content (%);
- RC – residual organic carbon content (%);
- TOC - total organic carbon (%);
- PC - pyrolyzable carbon corresponding to carbon content of hydrocarbons volatilized and pyrolyzed during the analysis (%);
- $T_{\text{max}}$ the temperature at which the maximum release of hydrocarbons from cracking of kerogen occurs during pyrolysis (top of $S_2$ peak);
- Production Index (PI) - defined as the ratio ($S_1/(S_1+S_2)$);
- Hydrogen Index (HI) the $S_2$/TOC ratio of (mg HC/g TOC);
- Oxygen index (OI) - the $S_3$/TOC ratio (mg CO$_2$/ g TOC).

Petrographic analysis of dispersed organic matter were performed on polished cut samples at the Department of Applied Geology of the Silesian University of Technology.
Microscopic examinations were carried out using a Zeiss optical light microscope equipped with a microphotometer MSP 200. They included mean vitrinite reflectance measurements and petrographic composition of organic matter.

4. Results and discussion

The geochemical data such as total organic carbon (TOC), Rock-eval pyrolysis data, as well as vitrinite reflectance and petrographic composition of organic matter are presented and discussed for the Westphalian claystones from the central part of the Lublin Coal Basin. Investigation of organic matter has been used to determine the source rock characteristics and petroleum generative potentials.

Table 1 illustrates the values of total organic carbon and Rock–Eval pyrolysis for the samples of claystones of the Lublin Formation.

Identification of the kerogen type is an important factor in evaluating source rock potential and has important influence on the nature of the hydrocarbon products. Cross plot of Rock-Eval Tmax versus hydrogen index (HI) data shows the range in thermal maturity as well as hydrocarbon generative (kerogen) types of samples. The results indicate that the most of the samples contain type III kerogen composed of terrestrial organic matter and they are mainly gas prone [14]. The results for samples 1, 2, 3, 17 suggest the presence of oil-prone type II kerogen, typical for marine sediments (figure 3). The similar results were obtained by Botor et al. (2002) for organic matter in the Lower and Upper Carboniferous sediments of the Lublin Trough [4].

Table 1. Geochemical results of Rock-Eval and Total Organic Carbon analyses.

| Number of sample | Tmax (°C) | S1 (mg HC/g rock) | S2 (mg HC/g rock) | S3 (mg CO2/g rock) | PI (%) | PC (%) | RC (%) | TOC (%) | HI (mg HC/g TOC) | OI (mg CO2/g TOC) | MINC (%) |
|-----------------|----------|-------------------|-------------------|-------------------|--------|--------|--------|---------|-----------------|------------------|---------|
| 12              | 434      | 0.02              | 1.14              | 0.25              | 0.02   | 0.11   | 1.33   | 1.44    | 79              | 17               | 0.13    |
| 11              | 431      | 0.04              | 1.28              | 0.46              | 0.03   | 0.15   | 1.38   | 1.53    | 84              | 30               | 0.33    |
| 10              | 432      | 0.03              | 0.67              | 0.63              | 0.04   | 0.2    | 0.86   | 1.06    | 63              | 59               | 4.26    |
| 17              | 432      | 0.05              | 13.57             | 0.3               | 0.00   | 1.15   | 6.33   | 7.48    | 181             | 4                | 0.07    |
| 16              | 432      | 0.06              | 1.19              | 0.33              | 0.05   | 0.14   | 1.2    | 1.34    | 89              | 25               | 0.34    |
| 15              | 432      | 0.03              | 1.15              | 0.52              | 0.03   | 0.17   | 1.29   | 1.46    | 79              | 36               | 1.11    |
Table 2. Classification of the organic matter quantity and source rock petroleum potential from Baskin (1997) [14].

| TOC (%) | S2   |
|---------|------|
| Poor    | 0-0.5| 0-1  |
| Fair    | 0.5-1| 1-5  |
| Good    | 1-2  | 5-10 |
| Very good | 2-4 | 10-20 |
| Excellent | >4  | >20  |

Tmax, which is a pyrolysis parameter commonly used to monitor the level of maturity ranges between 421 and 438°C (table 1) suggesting low degree of thermal maturation, which can be described as the initial phase of oil generation.

The maturity of organic matter can also be expressed by its Production index (PI), which is defined as the ratio of the amount of hydrocarbons generated in the total amount of the organic matter [16]. The PI value of most analysed samples from the Lublin Formation is less than 0.1 indicating immature organic matter that has generated little or no petroleum. The results obtained by Gola et al. (2013) for the bituminous coals and clastic rocks of the upper Westphalian B from the Bogdanka mine suggest that the Carboniferous deposits attained relatively low levels of thermal maturity, at the end of the microbial processes/initial phase of the oil window [11].

Kerogen types can also be distinguished by plotting the HI versus OI generated from the Rock-Eval pyrolysis on a modified Van Krevelen diagram [15, 16].

The amount of oxygen and hydrogen present in kerogen defines the kerogen type as I, II, or III and if the rock will be oil or gas prone. The hydrogen index (HI) versus oxygen index (OI) plot of the samples from the Lublin Formation suggests the presence kerogen type III (gas prone) or mixed type III and II (gas and oil prone) (figure 4).
Figure 3. Kerogen types based on HI and thermal maturity estimated from $T_{\text{max}}$. 
Other indication that is extensively used to determine source rock petroleum potential is parameter $S_2$ (mg HC/g rock) using to estimate the remaining hydrocarbon generating potential of the sample [14, 17, 18]. The $S_2$ values of the analysed range from 0.10 to 40.51 (mg HC/g rock). Four samples (samples 1, 2, 3, 17) have shown $S_2$ values > 10 (mg HC/g rock) which suggests very good to excellent generative potential.

Plot of $S_2$ versus total organic carbon content (TOC wt%) shows that samples with an increased TOC content are also characterized by high values of the $S_2$ parameter (figure 5).

**Figure 4.** Kerogen types based on H/I/OI plotted on Van Krevelen diagram.
**Figure 5.** Plot of $S_2$ versus total organic carbon content (TOC wt%) indicating source rock potential.

**Table 3.** The vitrinite reflectance of the organic matter from the Lublin Formation.

| Number of sample | $R_0$ [ % ] | Standard deviation | $R_{\text{max}}$ [ % ] | $R_{\text{min}}$ [ % ] | n  |
|------------------|--------------|---------------------|------------------------|------------------------|----|
| 12               | 0.64         | 0.10                | 0.89                   | 0.43                   | 49 |
| 11               | 0.54         | 0.11                | 0.77                   | 0.39                   | 73 |
| 10               | 0.57         | 0.07                | 0.73                   | 0.41                   | 50 |
| 17               | 0.69         | 0.07                | 0.79                   | 0.5                    | 46 |
| 16               | 0.66         | 0.07                | 0.8                    | 0.52                   | 50 |
| 15               | 0.67         | 0.15                | 0.95                   | 0.43                   | 69 |
| 14               | 0.63         | 0.08                | 0.75                   | 0.44                   | 53 |
| 13               | 0.65         | 0.07                | 0.79                   | 0.45                   | 70 |
| 19               | no data      | no data             | no data                | no data                | 0  |
| 18               | 0.65         | 0.07                | 0.77                   | 0.48                   | 45 |
| 20               | 0.60         | 0.09                | 0.78                   | 0.44                   | 61 |
| 4                | 0.59         | 0.11                | 0.83                   | 0.38                   | 50 |
| 3                | 0.49         | 0.07                | 0.68                   | 0.38                   | 55 |
| 2                | 0.53         | 0.08                | 0.68                   | 0.31                   | 50 |
| 1                | 0.56         | 0.04                | 0.65                   | 0.47                   | 52 |
| 7                | 0.66         | 0.06                | 0.77                   | 0.51                   | 35 |
| 6                | 0.62         | 0.06                | 0.76                   | 0.5                    | 48 |
| 5                | no data      | no data             | no data                | no data                | 0  |
| 9                | 0.65         | 0.06                | 0.78                   | 0.49                   | 55 |
| 8                | no data      | no data             | no data                | no data                | 0  |
The most common method used for determining the stage of thermal maturation, apart from the Rock-Eval pyrolytic analysis, is vitrinite reflectance measurement ($R_v$) [16]. The mean vitrinite reflectance of the analysed samples ranges from 0.49 to 0.69 % indicating immature to mature samples. The results of vitrinite reflectance measurements correspond well with the values of the pyrolysis parameter $T_{max}$.

Analysis of the petrographic composition of the organic matter have shown that the dominant group of macerals is vitrinite. The vitrinite content in the analysed samples reaches 70%. Liptinite group macerals occur in variable amounts (20-50%). The proportion of inertinite group does not exceed 30%. The petrographic composition of organic matter in most samples is typical of type III kerogen [14]. Three samples from the paralic series are characterized by high content of liptinite, which may indicate the kerogen type II. The results of petrographic research correlate very well with the classification of organic matter made on the basis of geochemical data from the Rock-eval pyrolysis.

5. Conclusions

Rock-Eval pyrolysis data, as well as vitrinite reflectance and petrographic composition of organic matter from the Lublin Formation of the Lublin Coal Basin has been used to quantity and quality of organic matter and determine the source rock characteristics and petroleum generative potentials.

The TOC contents of the analysed samples range from 0.38 to 12.95 % suggesting their different petroleum generative potential. $T_{max}$ range of 421-438°C suggests low degree of thermal maturation, which can be described as the initial phase of oil generation.

The results from the Rock-Eval pyrolysis of the organic matter from the Lublin Formation of the Lublin Coal Basin indicated that the most of the samples contained gas-prone type III kerogen composed of terrestrial organic matter. The results for three samples of from upper part of the paralic series and one from the limnic series suggest the presence of oil-prone type II kerogen typical for marine sediments as well as very good to excellent generative potential. The results of the petrographic research correlate very well with the classification of organic matter made on the basis of geochemical data from the Rock-Eval pyrolysis.

6. References

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