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Parameters and methods for evaluation of lignite processing method into biogas

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Abstract: In the article parameters of lignite organic matter conversion into biogas are collated and verified in terms of the process evaluation and control. Possibilities and limitations of usage of the parameters for this type of the process are also indicated. The following parameters were selected: a gas amount and its quality, isotope analysis of the gas produced, measurement of dissolved organic carbon (DOC) in biomass-free liquid media, presence of the VFA (volatile fatty acids) and other possible intermediates of the process in liquid medium, pH, as well as (not discussed in this article) microbiological analyses. On the basis of experiments of Polish lignite biogasification, examples of application of these parameters in laboratory scale for identification of the biodegradation lignite reactions occurrence are presented and discussed. We found that apart from analyses of the biogas produced, the following parameters are also possible to be implemented: DOC, specific surface area of solids measured before and after the process, and the parameters that are normally used for evaluation of rocks' maturity and origin, i.e. *S1*, *S2* and *HI* determined from *Rock-Eval* analysis, as well as GC-MS analysis of *EOM* (Extractable Organic Matter) separated from lignite. For the analyses of the *EOM*'s, relatively high amount of solid is required for measurements, limiting its implementation for continuous operations in practice. It was indicated that measurement of elementary coals' composition, total organic carbon (TOC) in solids or of pH of the liquid are not applicable parameters for verification of the progress of the lignite biogasification process.

Keywords: lignite, biogasification parameters, coals biodegradation

1. Introduction

Lignite/coals biogasification consists of the biochemical, anoxic degradation of its matrix into biogas (CH₄ + CO₂) by the activity of several groups of microorganisms. The microorganisms are able to convert coals' organic matter into simple, water soluble compounds (bioliquefaction), being substrates in the next reactions of the process, i.e. methanogenesis (Zinder et al., 1993; Fakoussa, et al., 1999; Liu, 2012). The process is based on the following biochemical reactions: hydrolysis of lignite organic matter into soluble organic acids (long chain) and other by-products, as well as H₂ and CO₂, then a fermentation of soluble organic acids (long chain) to volatile organic acids and alcohols, and finally, an acetogenesis:

- CH₃(CH₂)₂COO⁻ + 4H₂O → CH₃COO⁻ + 2CO₂ + 6H₂ (by microorganisms producing H₂),
- 2CO₂ + 5H₂ → CH₃COO⁻ + 2H₂O + H⁺ (by microorganisms using H₂: to produce an additional amounts of the acetate),

and the methanogenesis:

- CH₃COO⁻ + H₂O → CH₄ + HCO₃⁻ (ΔG° = -31 kJ/mol), and/or CO₂ + 4H₂ → CH₄ + 2H₂O (ΔG° = -135 kJ/mol) (by microorganisms using acetate and CO₂).

A majority of studies on the biological treatment of different coals was related only to coal bioliquefaction and desulfurisation processes. A new information on coal biodegradation, has been published in literature in recent years (Gao et al., 2012; Jiang et al., 2013; Gupta, 2014), but the experience

in coal biodegradation into biogas is still limited. No standard experimental tools or models of the process exist. The unique parameters usually used for the process control are analyses of the biogas produced, supported by analyses of a microbiological consortium. Information about possible process intermediates is available in the literature, but the data are not systematized.

In response to an increasing interest of the biogasification of low rank coals in recent years, we attempted to determine the parameters, that could be useful for the biogasification reaction control, better prediction of this process efficiency, and in consequence for adjusting of individual parameters to enhance the efficiency and kinetics of the process. The increased efficiency of the reaction, as well as better knowledge on the mechanisms of the process and on tools of the process control may lead to wide range studies and further applications of this process in practice. The anaerobic biogasification process could be applied for *in-situ* methane production from lignite deposits, which are not possible to mined in a traditional way., by appropriate stimulation of autochthonic bacteria present in the lignite matrix, or by injection of the biomass into the seam. It can be also a way to produce a range of valuable process intermediates in on surface bioreactors, of a potential application in different industrials sectors, like in agriculture.

2. Possible parameters of coals/lignite bioconversion

The first group of parameters we selected from literature is related to the characteristics of the feed (coal's), while the second one rather to quantification and identification of intermediates and products of the process.

Type of macerals in coals was shown to impact coals' biodegradation efficiency (Ibister et al., 1993). This was however rarely measured prior to biodegradation, so it is difficult to give some other examples of such dependency, at the moment. Similarly, it was recognized that as coal solubility (in organic solvents) increases, microbial rates decrease (Harding et al. 1993). In the case of this parameter, possible toxic impact of organic solvents that were used by researchers for the solubilisation prior to the biogasification should be considered.

As a standard tool for coals characteristics, the elementary analyses (i.e. the content of C, H, O, N and S) are proposed. For the higher rank coals, the carbon content is higher and the hydrogen and the oxygen content decrease: this proportion is obviously different for lower rank coals Liu, 2012 based on Orem et al, 2003).

The most important aspect, of the biogasification process, is related to mechanism of coals' organic matter decomposition. The organic matter is characterised by a very complex structure, that is more complex as the coals maturity decreases. The characteristics of coals' organic matter compounds depends also on coals' origin, and differs strongly for different types of coals. Lignite for example consists of several distinct compound classes: the hydrophobic bitumen, the alkali soluble humic and fluvic acids and an insoluble residue - the matrix. The heterogeneous character of coals is a major difficulty in the process control because of limited possibility of detection of microbial growth and activity towards "a mixture of thousand components" of the organic matter that are potential candidates for biodegradation (Fakoussa, et al., 1999). Based on studies of an origin of a methane naturally present in coals (i.e. CBM - coal bed methane) it was determined that the bioavailability of the coal components decreases with increasing coal rank (Jones et al, 2008; Strąpoć et al., 2011).

In term of identification of the process intermediates, different experiments on biological decomposition of the complex organic matter into simple compounds (bioliquefaction) and then, on their conversion into the biogas are presented in literature. It was shown that the coal matrix may be degraded to alkanes, long chain fatty acids or aromatic compounds, and then to simple compounds that are precursors of the methanogenesis. At the same time, some of these compounds, like long chain fatty acids, were found to be toxic for methanogens. Several examples of the studies, presenting examples of the intermediates, were given so far, for example by Liu (Liu, 2012) based on previous literature data. The final reactions of the biogasification, i.e. conversion of low-molecular compounds into acetate, CO₂ and H₂, and finally into methane are easier to be controlled, and that is why these reactions are better recognized. It was found that the concentrations of the acetate, oxalate, or formate differed depending on the rank of the coal, and increased with increasing extraction time (Vieth et al., 2008). Also, Harris (Harris et al., 2008) analysed methane production from previously extracted organic matter from lignite

and sub-bituminous coal and showed that the methane production depended on the concentration of extractable organic matter.

Geochemical analyses of coals for a presence of alkaline substances (like ammonia or biogenic amines) were also studied before and during biodegradation, as they were supposed to influence the biodegradation (Fakoussa et al. 1999). Further studies however indicated that these kind of intermediates does not impact the reaction.

As it is widely known that metals ions may also inhibit microbial activity, some authors suggested to focus on analysis of their impact on the process. Depending on how the biodegradation process is conducted, removal of the metals ions could be considered (Ozbayoglu, 2011), prior to biodegradation, if necessary.

For analyses of possible intermediates or changes of the coals' organic matter components, several analytical tools may be applied. Machnikowska (Machnikowska et al., 2002) by using Fourier transform infrared spectroscopy (FTIR) indicated differences in carboxylic phenolic, alcohol and ether compounds in oxidized and biodegraded lignite. Other examples of FTIR implementation are reported by Jiang (Jiang et al., 2013). For the same purpose, ^{13}C -NMR spectroscopy can be also applied (Klein et al., 1999) but it requires the biodegradation products/intermediates to be clearly determined, which is difficult at this stage of the knowledge about the mechanisms of the process. Similar limitation may be determined for electron paramagnetic resonance (EPR). Gas chromatography-mass spectrometry (GC-MS) is a technique commonly used in organic geochemistry and can be used on a sub-milligram scale for studying the structure of macromolecules and for quantification of products: that is why it can be an useful tool for controlling changes of the organic macromolecules over the biosolubilisation process (Klein et al., 1999). This method can be also used for verification of the expected built up of extractable organic matter in fluids during the reaction, as it was observed e.g. by Orem (Orem et al., 2010; Hofrichter et al., 1997).

An interesting approach of analysing of coals' biodegradability, that could be adapted for analysing and controlling of the biogasification process was proposed by Formolo (Formolo et al., 2008) for studies on biological pathways of biogenic methane formation. They identified C31- hopane the most bioresistant compound present in their coal samples from Powder River and San Juan Basin (US). Biodegradation indices were calculated based on loss of the more susceptible compounds relative to the sum of the more resistant compounds. Greater values of the biodegradation index indicated an increase of relative removal of the compound(s) of interest, i.e. greater biodegradation. Biodegradation was evaluated for the following groups of the compounds: nC15–nC19 alkanes, nC20–nC24 alkanes, nC25–nC30 alkanes, three acyclic isoprenoids (norpristane, pristane, phytane), nC18–nC27, alkylcyclohexanes, methyl-naphthalene, di-, tri-, and tetra-methylnaphthalenes, phenanthrene and its derivatives,

The possible organic process intermediates were also measured in liquid media, as an effect of coals organic matter biological dissolution. One of the groups, the researchers were searching for, were humic and fulvic acids. The acids are complex organic compounds of different structures that may be further biodegraded into more simple ones. These acids contribute substantially to global soil fertility and agricultural production (Jiang et al., 2013), and that is why possibility of their recovery from coal via the aerobic and anaerobic biodegradation, have been widely studied, and even commercialised (Arctech company, US). In liquids, they were usually identified with UV method analyses at 450 nm (Gao et al., 2012; Gokcay et al., 2001) or with HPLC (high performance liquid chromatography). Concerning the other group of the intermediates expected in liquids, volatile fatty acids (VFA), like acetic, propionic and n-butyric, valeric and isocaproic acids, as well as alcohols (methanol, ethanol, and iso-propanol) were quantified by Gas Chromatography (GC) (Liu, 2012). Several metabolites, e.g. phthalic or benzoic acids, were also identified in different biodegradation tests, as well as in waters sampled from different coals' seams (Urlich et al., 2008). Therefore, the data didn't represent a comprehensive analysis of hydrocarbon metabolism, which means that is not known whether these compounds are microbiologically cycled and which intermediates they were produced from. Another parameter used to determine organic carbon biological dissolution was a Dissolved Organic Carbon (DOC), in the liquid, as a possible indicator of the presence of the organic compounds released to liquid phase (Liu, 2012).

For the process control also pH measurements were carried out in order to compare its changes before and after the process) (Faison, 1992). Green (Green et al., 2008) did not observed significant changes of pH of the liquid phase during biogasification experiments of a subbituminous Wyodak coal after 26 days of the test. Similar results were obtained by Liu (Liu, 2012) from biogasification tests of coal from Powder River Basin (Wyoming).

In our studies we find measurements of a specific surface area [m^2/g] of coal's as one of the interesting parameters of measurement of the biodegradation progress. This was measured before the process in order to verify a dependency of the amount of methane produced from the reaction surface. The idea of using the specific surface area parameter is based on studies indicating that biodegradation rates of organic solids can be limited by the solid-liquid mass transfer rate when the solid surface area is low (Gilcrease, 1997; Faison, 1992; Scott, 1999). Increasing the coals' surface area by using smaller particle size of the coal, increased significantly methane production rates from coals (Green et al., 2008; Gupta et al., 2014). This shows that methane production rates are mass transfer limited. This dependency was however not the case when coals of higher solubility were tested (Harding et al. 1993). Also, Gockey (Gockey et al., 2001) reported an opposite effect, i.e. slower reaction rates when using smaller particles sizes (or higher surface area) of the feed; the authors explained this fact by an inhibition of the activity of the bacteria by certain intermediates of the process (like acetate). To visualize the surface changes in coal caused by microbial activity a scanning electron microscopy (SEM) was adapted (Klein, et al., 2013). SEM method however does not allow for quantitative analysis of the process, and can be used only to support biogasification results proved by other analytical methods.

Among the parameters, that are used mainly for process control, an amount and a content of the biogas produced is obviously the main one. It is generally analysed by the gas chromatography in order to control of changes of CH_4/CO_2 ratio and impurities' content in the gas. Additionally, the biological origin of methane produced may be also confirmed by isotopic analyses of the gas (Flores, et al., 2008; Urlich et al., 2008; Scott, 1999).

The microbiological analyses like an identification of microorganisms involved in the process are not discussed in this article.

3. Biogasification experiment

In the article a serie of experiments investigating a susceptibility of a Polish lignite to biogasification is presented. The lignite sample used for our work was obtained from one of Polish lignite mines. Before biogasification experiment, the sample was grounded (0.8-0.063 mm). The experiments were carried out in anaerobic conditions, in bottles (Duran® Schott, 250 cm^3). 180 g of lignite in nutrient medium (MgSO_4 0.2 g/dm^3 , CaCl_2 0.02 g/dm^3 , KH_2PO_4 1.0 g/dm^3 , K_2HPO_4 1.0 g/dm^3 , NH_4NO_3 1.0 g/dm^3 , FeCl_3 0.05 g/dm^3 ; pH 7.0), and the microbiological consortium previously isolated from Polish lignite were used. The biogasification experiments were carried out during 35 days, at room temperature.

The total amount of the methane produced from the sample during the experiment was 15,5 – 20,0 cm^3 . The biogas (CO_2+CH_4) didn't contain H_2S or any other impurities.

4. Measurements methods of the selected parameters

- The gas amount was identified and its content was verified with a gas chromatograph AGILENT 7890 A.
- Petrographic analyses were performed with Axioskop microscop from Zeiss, equipped with microphotometer MSP 200. The analyses and reflectance measurements were performed according to the ICCP and International Committee For Coal And Organic Petrology recommendations.
- Elementary analysis of the lignite sample was done in the EA 1108 analyser from Fisons.
- Total organic carbon (TOC) in lignite sample was determined by high-temperature combustion (1350 $^\circ\text{C}$) with detection of the combustion products by the infrared (IR) detector in Leco CR-120 carbon analyser. Also, the TOC was determined by Rock-Eval analysis.
- For the Rock-Eval analysis 50 - 100 mg of lignite sample were used. The method consists in: lignite pyrolysis at 300 to 650 $^\circ\text{C}$, in N_2 atmosphere, and then an oxidation at 300 to 850 $^\circ\text{C}$ in the air. The main parameters identified based on the analysis are S1 (free hydrocarbons (HC) released from lignite during pyrolysis at 300 $^\circ\text{C}$); S2 (HC released from a cracking of a kerogene at 300 - 650 $^\circ\text{C}$), T_{max}

(temperature detected at a maximum of HC generation); pyrolytic carbon, PC (a sum of pyrolytic carbon in compounds released during pyrolysis), TOC (a sum of carbon present in S1, S2, CO and CO₂), and a residual carbon, RC, in products of the oxidation phase.

- Analysis of the components present in a saturated and aromatic hydrocarbons of the extractable organic matter (EOM) with different analytical tools, like with the GC-MS. The organic matter was extracted from 100 g of the lignite in Soxhlet apparatus, with a mixture of dichloromethane and methanol. The extract was purified from aromatic hydrocarbons, asphaltens and resins, by column chromatography. Then in the separated hydrocarbons fractions, selected biomarkers, were identified by GC-MS method.
- Humic acids presence was also determined in solids via their extraction and identification (UV spectrophotometer *Jasko V-530* at $\lambda=254$ nm), based on (Rodrigues at al., 2008).
- Specific surface area was measured with a TriStar II 3020 (Micrometrics) equipment. The measurements were carried out in liquid nitrogen atmosphere. The specific surface area was determined by *Brunauer-Emmett-Teller (BET)* method.
- Dissolved organic carbon (DOC) was measured in liquid phase, after its previous filtration and removal of a fraction of an inorganic carbon (*Hach Lange GmbH* photometer).
- pH of the liquid before and at the end of the experiment.

5. Results and discussion

In the analysed lignite sample, macerals of huminite group dominated (84.38%), including humodetrinite (50.63%) and humotellinite (31.25%), and some humocollinite (2.5%). Content of liptinite group was lower (14.38%) and it contained mainly a sporinite and a resinite. An average reflectance of huminite (ulminite) in this sample was $R_0 = 0.35\%$.

Results of elementary analysis of the lignite sample, measured before and after biogasification are presented in the table 1. They indicate that the carbon content increased due to microorganisms' presence in the system, and in consequence, in the solid phase after the process. Higher H, N or S contents after the process was probably due to the expected increase of saturated HC content (H content), but also by biomass growth and components of the nutrient medium. Similar results were obtained for the measurements of the total organic carbon (TOC). In both cases (tables 1 and 2), TOC and the total carbon (TC) contents increased after biogasification due to biomass growth on solids samples. This means, that the both methods are not suitable for verification of organic carbon degradation during the biogasification process.

Table 1. Results of elementary analysis, as well as TOC, TC (by *Leco CR-120* analyser) and humic acids contents in the Polish lignite sample before and after biogasification (amount of elements in [% w/w])

Lignite sample	N	C	H	S	O	H/C	O/C	TC [% w/w]	TOC [% w/w]	Humic acids content in the lignite sample, [%]
T1 - before	0.40	37.57	3.99	0.45	22.23	1.27	0.44	40.35	36.83	1.60
T1 - after	1.64	42.12	5.53	0.49	33.32	1.58	0.59	43.01	41.46	2.74

Results of parameters determined based on Rock-Eval analyses of the lignite sample, performed before and after biogasification experiment, are presented in the table 2. The S1 parameter after biogasification is higher than before the experiment. It indicates that a reaction of organic matter destruction to produce the HC occurs. As a result, the PC value lowers, as this carbon is being used in the destruction process. In effect, the organic matter become less complex (less "mature") which is also reflected in lower T_{max} value detected after our biogasification experiment. At the beginning of the process, the amount of HC (expressed as the Hydrogen Index, HI) is cumulated in the rock; then, these

HC are used as substrates for further reactions of the biogasification. If so, the value of the HI should decrease; this was reflected in our studies (see the table 2). As for the analysis few milligrams only of the solid are required, it seems that the method could be one of good methods for evaluation of the process kinetics via verification of amounts of simple HC production and their consumption. This idea however requires further investigation.

The increase of hydrocarbons content in lignite sample after biogasification was also confirmed by characteristics of the main components of the organic matter extracted from the samples. After the experiments, a higher percentage of the mass loss was observed for aromatic HC in comparison to the saturated ones (table 3), which by theory should be more susceptible for biodegradation. It may signify that at the moment of the analysis a biodestruction of more complex organic compounds (aromatic hydrocarbons or resins) to the simpler ones occurred and dominated over a biodestruction of the saturated HC into C2 or C1 compounds. Also, some loss of asphaltenes was detected, although other studies indicated that these compounds may partially inhibit biological methane generation (Liu, 2012). This may signify much longer period of time needed for biodegradation of these complex compounds. The amount of extractable organic matter (EOM) after biogasification was about 16% lower than before the process, which also means its partial biodestruction. The method of analysis of the EOM may be also a valuable tool to observe the progress of the biodegradation reaction. A disadvantage of this method is however a relatively high (of the order of 100 g) amount of the coal sample, rather difficult to be withdrawn from the system during experimental studies.

After biogasification also humic acids content increase was observed (table 1), which also signifies conversion of the organic matter structure during the process.

Table 2. Parameters determined based on Rock-Eval analysis of the lignite sample

Lignite sample	T _{max} [°C]	S ₁ [mgHC/g of lignite]	S ₂ [mgHC/g of lignite]	PC [%]	TOC [%]	HI [mgHC/g of TOC]	Total inorganic carbon [%]
T1 - before biogasification	402	4.56	95.58	9.33	33.57	285	1.12
T1 - after biogasification	391	5.08	93.05	9.09	35.71	261	1.16

Table 3. Characteristics of organic matter extracted from the lignite sample (EOM) and its characteristics

Lignite sample	EOM [ppm]	Composition of bitumen fraction [% m/m]				EOM TOC mg/g	HC TOC mg/g	HC HZ
		Hydrocarbons, HC		Heterocompounds				
		Saturated	Aromatic	Resins	Asphaltenes			
T1 - before biogasification	40 646	2.6	4.7	34.9	57.8	121.1	8.8	0.08
T1 - after biogasification	34 273	3.0	4.0	27.2	65.8	96.0	6.7	0.08
% of mass loss after biogasification	15.7	2.7	28.24	34.3	4	-	-	-

After separation of different groups of components of the bitumen, they were analysed with GC-MS method. We decided to identify of typical groups of biomarkers present in the EOM, because based on the literature it was difficult to justify what other kind of the EOM's compounds could be investigated. In the fraction of saturated hydrocarbons a very small increase of low molecular compounds and small changes of higher molecular HC were determined (Fig. 1). In the same samples, some structural changes could be also determined in diterpenoids (D) and norhopanes (N) structures (Fig. 2), although these compounds are known as ones of the most resistant to biodegradation (Formolo et al., 2008).

Among the fraction of the saturated hydrocarbons, in the steranes group, C-29 compounds dominated. Their presence indicates a terrestrial origin of this lignite's the organic matter. After the biogasification experiment, small changes of their structure could be observed, indicating that the

organic matter biodegradation occurs (Fig. 3). Under the same genetic features of the organic matter, an increase of structures of the $\beta\beta$ and S configuration of the compounds was observed. It proves that destruction/formation reactions took place in the system. A presence of the biomarkers in the fraction of the aromatic HC was limited. Some phenantrene and its derivatives and some small amounts of dimethylnaphthalenes and trimethylanphthalenes (Fig. 4.) were detected. Also sulphur compounds were identified in the extract (m/z 198, m/z 212), but their content and character were the same before and after the biogasification process. This confirms that the produced biogas did not contain any sulphur impurities.

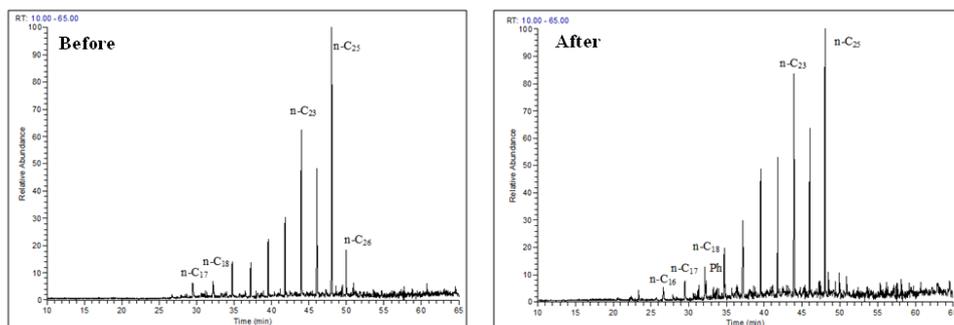


Fig. 1. GC-MS spectra of $n\text{-C}_{17}$ do $n\text{-C}_{26}$ alkanes in bitumen fraction extracted from the Polish lignite sample, before and after biogasification experiments

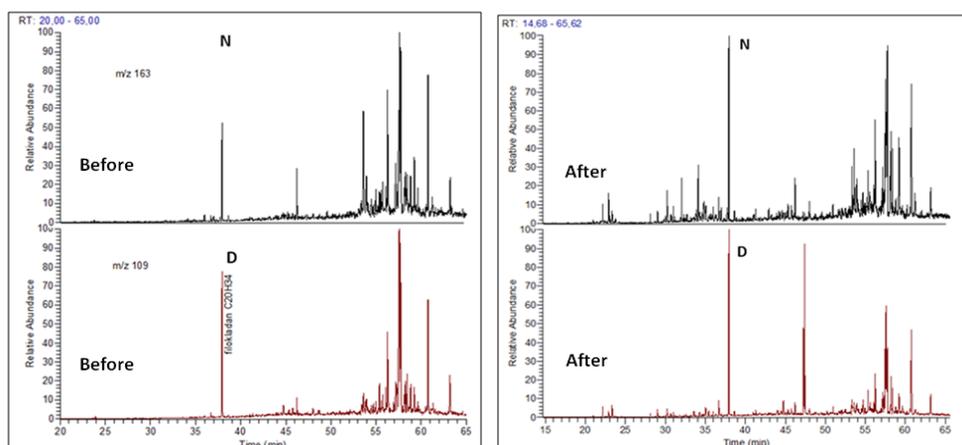


Fig. 2. GC-MS spectra (m/z 163 i m/z 109) of norhopanes (N) and diterpenoids (D), including filokladane C20, in bitumen fraction extracted from the Polish lignite sample, before and after biogasification experiments

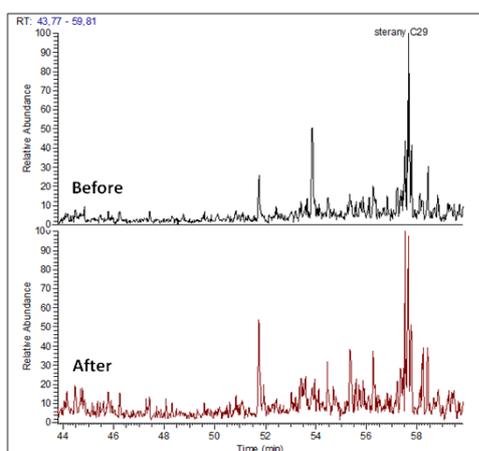


Fig. 3. GC-MS spectra (m/z 217) of steranes fraction, mainly C29, in the tested lignite sample before and after biogasification experiment

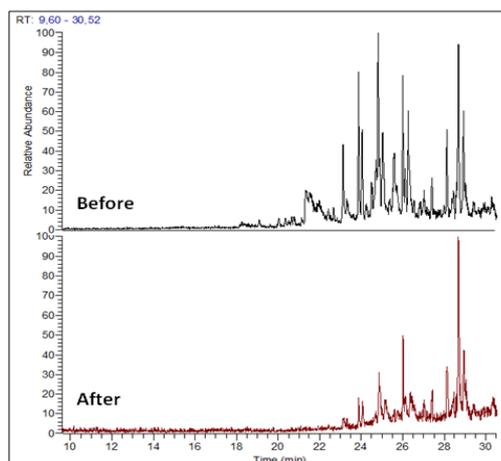


Fig. 4. GC-MS spectra of naphthalene's derivatives in the tested lignite sample before and after biogasification experiment

Also, a specific surface area of the sample before and after the process was measured and compared. It was determined that the surface area was higher after the process (5,384 [m²/g]) compared to the same sample analysed before it (3,608 [m²/g]). It is another approach we proposed in order to indicate a progress of the biogasification. It may be supposed that the increase of the surface area of the lignite is caused by the organic matter loss and its structure changes during the process, similarly like it was proposed for another types of processes related with chemical and biological dissolution of rocks (Levenspiel, 2005; Szubert et al., 2006).

Apart from the indicators of the microbiological activity during the experiment (not presented in this article), a concentration of a dissolved organic carbon (DOC) and pH were also measured in the liquid phase. The increase of the DOC was observed, which was due to the lignite organic matter biological dissolution. After a longer biogasification time, a consumption of these compounds by microorganisms and their conversion into biogas was expected. As the biomass was filtered prior to the DOC measurements, its presence didn't influence the analysis. The pH of the liquid didn't change significantly. It is consistent with the literature data and may indicate that a production of organic acids, which may lower the pH during the process, is immediately followed by activity of other microbial strains, converting them into more simple organic compounds and H₂.

Table 6. pH and DOC concentrations in liquids before and after biogasification of the Polish lignite sample

Lignite sample	pH	DOC [mg/l]
T1 - before biogasification	7.0	237
T1 - after biogasification	6.8	163

6. Conclusions

Apart from the biogas analysis, no standard parameters and methods for control of coals biogasification process exists. Because of a growing interest of this method in recent years, an attempt to determine some of them was undertaken in this study. This was based both on literature data and on results of experiments on biogasification of Polish lignite. It was found that selected parameters of solids (S1, S2, HI, T_{max}) determined based on Rock-Eval, as well as on EOM's analyses (changes of amount of the EOM and its components, changes of the structure of the components) could be good indicators to determine and/or to control a progress of the biogasification. Also changes of the specific surface area and the DOC concentration in liquid phase are suggested as good indicators of the progress of the reaction of the lignite biodegradation. The other ones were found to be useless for biogasification experiments (TOC, TC, basic parameters from the elementary analysis or pH of the liquid).

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