

Methane rich gasification of wood pellets

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Abstract. In the work there are shown the results of experimental studies on methane rich gasification of pinewood pellets in Bio-CONOX technology. The experiment was carried out on a laboratory scale gasifier (5 kW), which design features allow producing a high quality gas with a high methane content. In the results there was identified the impact of the quantity of Bio-CONOX on the amount of flammable gas compounds (methane, hydrogen and carbon monoxide) in the synthesis gas and the gas calorific value. The additive was added in 10,20,30 and 50% concentrations to the gasifier chamber. It has been shown that increasing the amount of the additive has a positive effect on the calorific value of the synthesis gas (Fig.1,2). Gas with a high content of methane (and high calorific value) was obtained from gasification of biomass with a 50% addition of Bio-CONOX. There was also examined the proportion of blowing air (gasifying medium) for which the properties of obtained syngas were the best.

1 Introduction

The growing demand for heat and electricity, and the specter of depletion of fossil fuels affects the ongoing development of renewable energy. Biomass provides a number of possibilities for energy production, among others, through its gasification. By the term "gasification" are named biomass thermal processings, which lead to obtain the synthesis gas. During gasification the solids are heated in an atmosphere of a gasification medium which can be air, oxygen, steam or a mixture of the ones above [1]. The process has been known for over 200 years, but recent technological development has increased interest in it. The main reason for this state of affairs is the trend of development, thus popularizing the technology of producing energy in diffuse sources that can meet the energy needs of a small scale for local needs. An example of such cogeneration can be a co-gasifier supplied by solid fuels (eg. coal, biomass or fuel from waste RDF) combined with a gas turbine systems or even implementing more efficient gas power associations of circulating steam power plants i.e. IGGC [2,3,4]. In the practical application of cogeneration, small power can successfully provide a source of energy for the industrial plant and for small towns and villages. Such technologies require the implementation of high-performance transformations implemented at every stage of the manufacturing energy process. Specific values of the energy conversion chain is attributed to processes for gas production, as already mentioned above, in gasification of solid fuels there is a great flexibility of feed material selection (almost any type of biomass can be subjected to the process). Widely used in power

generation gasification technologies are characterized by relatively low efficiency of fuel/gas conversion estimated at approx. 60-65% [5]. The efficiency of the gasifier, defined by the quotient of the calorific value of the fuel to the calorific value of obtained in this gasifier syngas, unambiguously determines its progress in technological development. In the literature, much attention was paid to research the technology of gasification of different solid fuels by picking as an aim high efficiency. A first aspect of differentiating known technologies is the difference of used gasifying agent, ie. in the case of air, heating value of the gas produced fluctuates within 4-7·MJ m⁻³ for gasifying wood chips. Relatively better calorific values are achieved when gasification takes place with the use of oxygen or water vapor wherein it is possible to achieve calorie gas order of 10-18 MJ·m⁻³ [6,7]. The few known domestic installations gasifying solid fuels [8-11] are mainly based on the gasification on the fixed grate or circulating fluidized bed. They allow to obtain a gas from wood chips with a low calorific value of approx. 4.5-5.5 MJ·Nm⁻³ and a methane CH₄ content from 1.3 to 5%. It should be emphasized that the high methane content is a significantly associated priority element of the heating value of the synthesis gas obtained which is shown by the VDI computational algorithm used to examine the calorific value of gaseous fuels:

$$W_o = 126 \cdot [\%CO] + 108 \cdot [\%H_2] + 359 \cdot [\%CH_4] + 665 \cdot [\%C_nH_m] \quad (1)$$

Polish gasifier EKOD (containing a fixed grate) allows to obtain a gas having a methane content to 4.4%

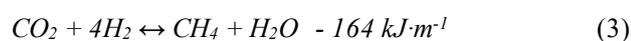
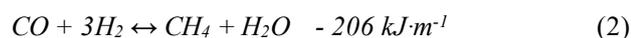
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for the synthesis gas calorific value of $5.65 \text{ MJ}\cdot\text{m}^{-3}$, which limits the industrial use of this constitution [9]. Superior parameter, both in the country [12] and abroad, are obtained with the fluidized bed gasifiers, where the contact gasifying agent/fuel factor is increased and which increases the reaction rate and efficiency of the process. Typical levels of methane in a fluidized bed technology are 5-12%, and the calorific value reaches even $14 \text{ MJ}\cdot\text{m}^{-3}$ [13]. There are also known methods of improving the quality of synthesis gas by the use of catalysts and mineral puffs dosaged directly to the interior of the reaction chamber [14,15,16] in which for example Rapagnano et al. received gas at high hydrogen content of approx. 56% but a very low methane quantity of 2%

Another application of synthesis gas rich in reduction ingredients is attributed to low-emission technologies of combustion in boilers supplied by coal dust i.e. NO_x reduction by the reburning method [17]. An example of the use of such low-carbon technologies in a power unit with a capacity of 600 MWel is the Longannet power station in Scotland, where is achieved a 40-60% reduction in nitrogen oxide emissions [18]. It is worth noting, which indicates the size of the gasifier, that the reburning gas is approx. 20% of the whole chemical energy supplied to the block. Fine reduction properties are achieved during reburning with the use of natural gas of which, as known, the dominant component is CH_4 . For example, Hassan et al. using methane (purity of 99%) reached a 94% reduction of NO_x [19]. In syngas there was not obtained a high methane concentration. The methane content is usually instigated at approx. 0.8-2.5%. In contrast, as indicated by the reports in the literature [20], a high reduction efficiency is obtained by a methane-rich reburning gas. Taking into account the importance of methane in the clean combustion of solid fuels in terms of reduction the emissions of NO_x and as well considering the importance of the efficiency of the process, ie. high calorific value of synthesis gas, this paper presents the results of experimental studies of methane-rich gasification of biomass. High content of CH_4 , and hence high gas calorific value was obtained by the addition to the biomass a fuel preparation so called Bio-CONOX [17,18].

1.1 Methane creating reactions

Methanation is an exothermic process that aims in the methane production from hydrogen and carbon oxides (Eq.2 and Eq.3):



Stoichiometrically, methanation of carbon monoxide releases $206 \text{ kJ}\cdot\text{m}^{-1}$ of energy (heat) and the reaction of carbon dioxide $164 \text{ kJ}\cdot\text{m}^{-1}$. The two reactions are influenced by pressure and temperature, where high pressure favours the methanation processes. In contrast, high temperature limits the methanation processes [21].

Obtained, in the experiment, low temperatures in the fuel zone (of approx. 400°C) contributed to the achievement of a high methane content in the produced syngas. Mostly known in the literature installations which require the methane production are controlling methane production by the conversion of CO and CO_2 but not taking into account the reactions of heavy hydrocarbons cracking. The cracking reactions require the presence of oxygen when hydrocarbons may decompose to inter alia hydrogen (Eq. 4):



As a result of the above mentioned equilibrium, in the stream of the raw gas from gasification, the hydrogen concentration is very high. Hydrocarbons which did not react with oxygen, may be reacted with hydrogen, which is presented in the reactions of hydrocracking (Eq. 5, Eq. 6) [22]:



Reactions 4, 5 and 6 are strongly exothermic and their presents results in a significant increase in the temperature. In the conducted gasification experiment, above the fuel layer, were observed temperatures of approx. 800°C , which taking into account the high purity of the obtained gas, were the result of cracking and hydrocracking reactions.

2 Materials and methods

2.1 Materials

2.1.1 Pellet fuel properties

The used in the experiment biomass were pinewood pellets which were divided to a particle size in the range of 1.25 mm to 3.15 mm. Properties of pellets are given in the table below.

Table 1. Pellet fuel properties

Parameter	Value
Carbon C	50,00 %
Hydrogen H	6,00 %
Oxygen O	43,00 %
Nitrogen N	0,20 %
Humidity	8,84 %
Ash content	<1,50 %
LHV	18,50 $\text{MJ}\cdot\text{kg}^{-1}$

2.1.2 Bio-CONOx fuel properties

Bio-CONOx additive is a methane-forming waste fuel of natural origin. It was used in the gasification process in weight concentrations of 10%, 20%, 30% and 50% of the sample. The table below presents fuel properties and chemical composition of the sorbet.

Table 2. Bio-CONOx fuel properties

Parameter	Value
Carbon C	49,30 %
Hydrogen H	6,96 %
Sulfur S	1,38 %
Chlorine Cl	0,001 %
Oxygen O	35,59 %
Nitrogen N	6,76 %
Humidity	6,60 %
Ash content	6,50 %
LHV	15,70 MJ·kg ⁻¹

Nitrogen contained in the Bio-CONOx affects the autonomous reduction of acidic nitrogen oxides NO_x and it eliminates the need for special installation injecting urea or insufflating ammonia. Low content of chlorine Cl in the preparation is not conducive to the occurrence of high-temperature corrosion of boiler components. Thus, the addition of Bio-CONOx to solid fuels reduces the mass content of Cl in the fuel mixture. Chlorine Cl is often found in biomass fuels in an amount greater than 0.1%, which drastically increases the risk of corrosion. Bio-CONOx has a relatively high proportion of sulfur S, wherein the preferred mass ratio of sulfur to chlorine (S/Cl=2,2) inhibits the formation of low-melting chloride. The fulfillment of the above ratio conditions results in the formation of a protective layer on the elements of the alkali sulfates utility system, thereby heat exchange surfaces are protected against chloride corrosion. It should be stressed that the preparation, if added to the fuel, strongly influences the formation of reducing zones in the gasification process, but the quality of the gas from the gasification of Bio-CONOx alone no longer accepts such a high performance of the process [1, 18].

2.2 Methods

The fuel was task to the tray (shown in Figure 1) and transported by a screw conveyor into the reaction chamber. Gasification occurred in a stream of heated air, blown through the chamber from the bottom and controlled by an inverter and two valves. Airflow was

measured using a flowmeter (Figure 2). Due to the fact that the system does not have a burner, start-up takes place when the auto-ignition temperature is reached. After stabilizing the temperature in the boiler, the gas was sampled from the upper part of the reaction chamber. Sampled gas flown through the filtering system and was subjected to composition analysis by the 3100 Syngas Gas Analyser.

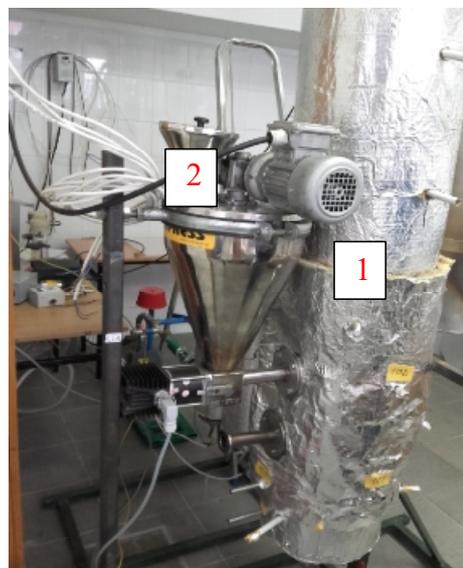


Figure 1. Gasifier (1-gasification chamber, 2-fuel feeder)

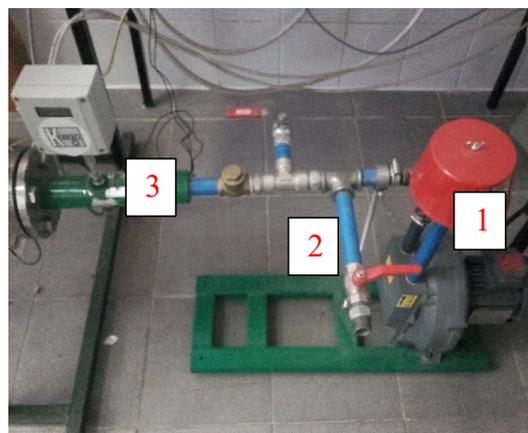


Figure 2. Air intake system (1-blower, 2-flow control valves, 3-flowmeter)

The gasification process was conducted in conditions of a temperature of approx. 720°C and at atmospheric pressure prevailing in the reactor. Efficient fuel flow supplied to the reaction chamber was constant at 0.42 g·s⁻¹. Under these conditions, the average ratio of fuel to air was Air/Fuel = 1.38. There have been changes in the value of the gasifying agent flow: 0.52; 0.55; 0.60; 0.65 g·s⁻¹ and for it the values of the coefficients Air/Fuel were successively 1.23; 1.31; 1.43; 1.55.

3 Results

The table below shows the values of obtained syngas for different concentrations of Bio-CONOx in the fuel mixture.

Table 3. Calorific value of obtained syngas

Bio-CONOx concentration %	Maximum LHV (MJ·m ⁻³)	Average LHV (MJ·m ⁻³)
10	4,30	3,50
20	5,23	4,43
30	5,57	5,12
50	12,04	8,27

Shown in figures 3-6 results of the conditions in which was obtained the methane rich syngas establish the combustible syngas components in dependence of oxygen content in the syngas for various fuel compositions containing Bio-CONOx preparation. Variable gas composition was obtained by various Bio-CONOx additives to the fuel mixture i.e. 10%, 20%, 30% 50%. The most favorable process conditions, where was obtained methane rich gas, are sought by changing the flow of blowing air into the reaction zone of the gasifier. In each case airflows were the same: 0.50; 0.55; 0.60; 0.65 g·s⁻¹. The O₂ content in the past-process gas is a real reflection of the reactivity of the used fuel, which was enriched varying additions of Bio-CONOx. Fig. 3 shows the process conditions of wood pellets gasification without the addition of Bio-CONOx. Also, noteworthy is the high, comparing to conventional gasification technology [12] proportion of CH₄ which reached approx. 8%, where in the case of gasification in a fixed bed was achieved only 0,5-2% of CH₄, in a fluidised bed about 4% CH₄. The high share of CH₄ is achieved by tubular gasifier structures with an intense air purge into the fuel layer. The nature of the gasyfing medium flow, through the gasification bed, is determining not typical temperature distribution in the reaction chamber, i.e.: the temperature in the fuel layer is 370-420°C, the temperature above the fuel layer - 700-850°C. The temperature in the fuel layer favors the methanation processes of CO and CO₂ [17], and temperature conditions above the fuel layer are assisting the processes of tar cracking where one of the products is CH₄ [17]. A similar character of the process in terms of temperature distribution, was examined in the case of gasification of pellets and 10%, 20%, 30% 50% of Bio-CONOx. The test results shown in fig. 4,5,6,7 clearly show the increase in the proportion of CH₄ in the syngas, with an increasing share of the Bio-CONOx. At the same time increasing the participation of the additive, in each case, with the same air stream, causes a change in the reactivity of the bed in relation to the gasifying agent.

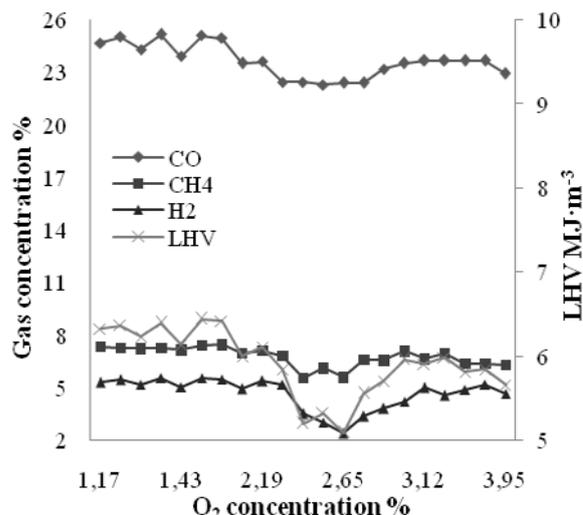


Figure 3. Synthesis gas composition in the amount of oxygen for particulate pellets without any addition

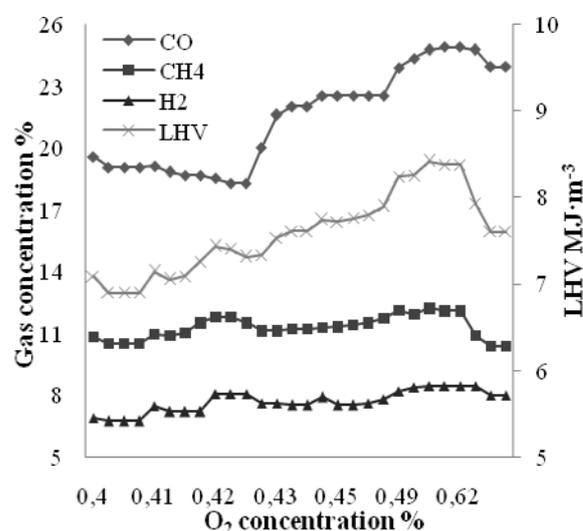


Figure 4. Synthesis gas composition in the amount of oxygen for particulate pellets with a 10% Bio-CONOx addition

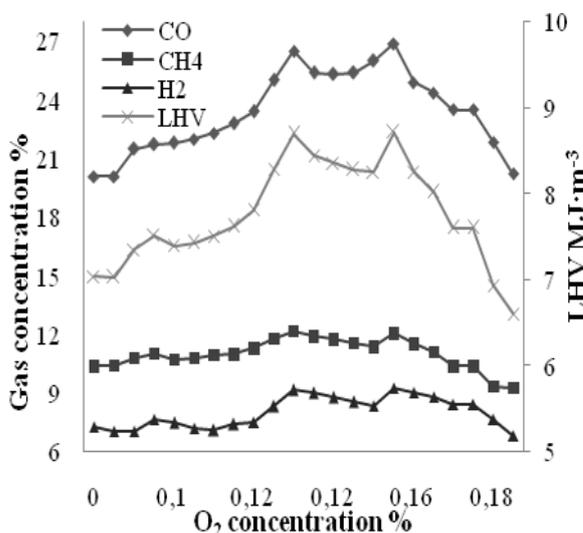


Figure 5. Synthesis gas composition in the amount of oxygen for particulate pellets with a 20% Bio-CONOx addition

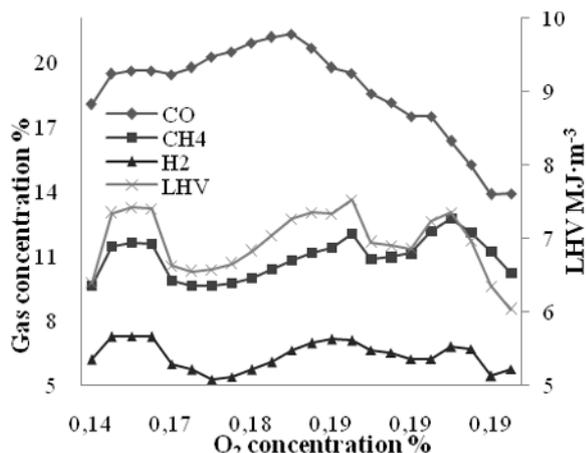


Figure 6. Synthesis gas composition in the amount of oxygen for particulate pellets with a 30% Bio-CONOx addition

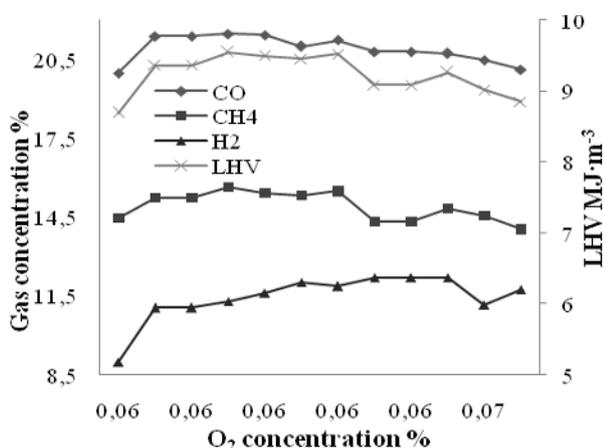


Figure 7. Synthesis gas composition in the amount of oxygen for particulate pellets with a 50% Bio-CONOx addition

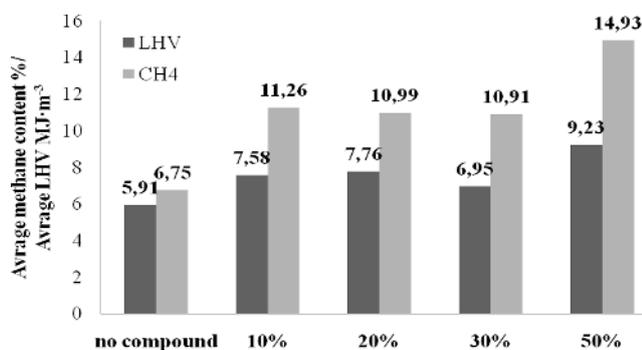


Figure 8. The calorific value of the syngas depending on the content of methane and the amount of Bio-CONOx in the fuel mixture

In the case shown in fig. 3 (without Bio-CONOx) high proportion of O₂ (1.17-3.95%) shows its lower reactivity compared with the other cases (fig. 4,5,6,7), where the part of the preparation increases. Thus, the addition of Bio-CONOx to the pellets resulted in increased reactivity of deposits which affect the activity, among other things, methanation process. The addition of Bio-CONOx in the reaction chamber of the gasifier, easily persisted reducing conditions, which favor the formation of methanogenic components such as CO and H₂. Shares of CO and H₂, in each test

case, did not undergo major changes despite increased CH₄ content. This indicates the methanation process occurring i.e. the hydrogenation of CO.

In the table above and at Fig. 8 are shown the syngas calorific values obtained from the preparation of various concentrations of Bio-CONOx. Calorific value was significantly dependent on the content of CH₄ as shown in fig. 3-8 where the nature of the curve is similar to a curve illustrating the change in the CH₄ content. The best parameters of synthesis gas (the highest calorific value) was obtained in a sample of 50% addition of Bio-CONOx.

Methane-rich gasification process was carried out on a laboratory stand which contained an atmospheric fixed bed reactor with a maximum output of 5 kW, using air as a gasifying agent. Gasified biomass was in the form of crushed pinewood pellets with different amounts of Bio-CONOx addition i.e. 10,20,30 and 50% to the fuel mixture. Specific temperature layers were obtained in the atmospheric conditions process i.e. the temperature in the fuel zone was approx. 400°C, where took place reducing reactions of methanation (hydratation) of CO and CO₂; above the fuel layer the temperature reached 800°C. The high temperature conditions favour the reactions of tar cracking and hydrocracking where the main gas product is methane. In the research process action was taken at increasing the calorific value of syngas by increasing the methane content in the gas mixture. The indicated research show that Bio-CONOx, thanks to its specific chemical structure, favours the methane production while gasification processes i.e. it increases the reactions rate occurring during gasification i.e. hydrogenation and methanation. The average amount of methane occurred from gasifying pinewood pellets was 5,91% and it let to obtain the gas LHV at 6,75 MJ·m⁻³. Increasing the amount of Bio-CONOx resulted in higher syngas methane content and the highest effectiveness of gasification was observed using a 50% supplement of Bio-CONOx (Fig. 7,8) where average CH₄ content was 9,23% and the syngas LHV 14,93 MJ·m⁻³.

In the frame of the experiment was analyzed the stability of the gasification process. The assessment was made by referring to oxygen content in the obtained syngas. Dependence on content of CH₄, H₂, CO, CO₂ from the O₂ content show high reactivity of the used fuels. On the resulting high gas performance primarily has an affect high content of calorific methane (due to the tendency of creating reduction zones), by which it can be used in prosumer power generation eg. to drive Capstone microturbines.

Further studies should be performed to optimize the amount of the additive in the fuel while maintaining high efficiency of the gasification process.

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References

1. S. Poskrobko, J. Łach, D. Król, *Energetyka i Ekologia* (2010).
2. P.N. Pressley, T.N. Aziz a , J.F. DeCarolis, M.A. Barlaza , F.He, F. Li, A. Damgaard, *J. Cl. Pro.*, 70 (2014).
3. I. Hwang , J. Kobayashi, K. Kawamoto, *Waste Manage.*, 34 (2014).
4. C. Cormos, *INT J Hydrogen Energ.*, 35 (2010).
5. M. Asadullah, *Renew. Sust. Energ. Rev.*, 29(2014).
6. A.V. Bridgwater, *Fuel*, 74 (1995).
7. G. Schuster, G. Loffler, K. Weigl, H. Hofbauer, *Bioresource Technol.*, 77 (2001).
8. M. J. Stolarski, S. Szczukowski, J. Tworkowski, M.Krzyzaniak, *Renew. Energ.*, 59 (2013)
9. T. Chmielniak, M. Ścieżko, T. Iluk, K. Matuszek *Przemysł Chemiczny*, 8-9 (2006).
10. M. Ścieżko, A. Sobolewski, P. Billig, Patent PAT.208616. Zgazowarka ze złożem stałym.
11. A.Sobolewski, J.Koowicz, K.Matuszek, T. Iluk, *Polityka Energetyczna*, 14 (2011).
12. Monograph. Instytut Energetyki (2010).
13. S. Heidenreich, P. U. Foscolo *Prog. Energ. Combust.*, 46 (2015).
14. S. Rapagnà, K. Gallucci, M. Di Marcello, P.U. Foscolo, M. Nacken, S. Heidenreich, M. Matt, *Fuel* 97 (2012).
15. J.A. Ruiz, M.C.Jua, M.P.Morales, P.Munoz, M.A.Mendivil, *Renew. Sust. Energ. Rev.*, 18 (2013).
16. P. Chairprasert, T. Vitidsant, *Korean J. Chem. Eng.*, 26 (2009).
17. D. Król, S. Poskrobko, Gaz reurningowy – wysokometanowe zgazowanie preparatu Bio-CONOX.
18. D. Król, *Arch. Gosp. Odpad. Ochr. Środ.*, 2 (2010).
19. M. I. Hassan, T.W. Wu, K. Saito, *Fuel* 108 (2013).
20. M.W. Sackett, S. Nakaparksin, D. Dalrymple, *Advances in Organic Geochemistry* (1966).
21. S.Rönsch, J. Schneider, S.Matthischke, M. Schlüter, M. Götz, J. Lefebvre, P. Prabhakaran, S. Bajohr, *Fuel* 166 (2016).
22. P. Babiński, G. Łabojko, *Polityka energetyczna* 15 (2012).