

# Thermovolumetric investigations of steam gasification of coals and their chars

Stanisław Porada<sup>1,\*</sup>, Grzegorz Czernski<sup>1</sup>, Przemysław Grzywacz<sup>1</sup>, Tadeusz Dziok<sup>1</sup>, and Dorota Makowska<sup>1</sup>

<sup>1</sup> AGH University of Science and Technology, Faculty of Energy and Fuels, Mickiewicza Av. 30, 30-059 Cracow, Poland

**Abstract.** The process of steam gasification of three coals of various rank and three chars obtained from these coals by the *ex-situ* method at 900 °C was compared. In the coal gasification process, the pyrolysis stage plays a very important part, which is connected with its direct impact on the kinetics of gasification of the resulting char. What is more, taking into consideration the impact of pyrolysis conditions on char properties, it should be anticipated that the gasification kinetics of coal and char, formed from it by the *ex situ* method, will be different. In order to examine and compare the process of gasification of coals and chars, an isothermal thermovolumetric method, designed by the authors, was applied. For all the examined samples the measurements were performed at three temperatures, i.e. 850, 900, and 950 °C, and at the pressure of 0.1 MPa. An evaluation of the impact of raw material on the steam gasification of the examined samples was made. The carbon conversion degree and the kinetic parameters of CO and H<sub>2</sub> formation reaction were calculated. It was observed that the course of gasification is different for coals and chars obtained from them and it can be concluded that coals are more reactive than chars. Values of kinetic parameters of carbon monoxide and hydrogen formation calculated for coals and corresponding chars are also different. Due to the observed differences the process of gasification of coals and of chars with steam should not be equated.

## 1 Introduction

Coal gasification is a clean and effective method of coal conversion to a gas which has a very broad range of applications in the synthesis of chemicals, substitutes of petroleum and natural gas as well as in power generation [1-3]. In the era of dwindling resources of primary energy carriers and increasing consumption, a revival of interest in the gasification technology can be observed, which is reflected in the recent rapid growth of the number of coal gasification plants [4] and the number of works devoted to problems of coal gasification [5-10].

In order to further develop and optimise the operation of gasification reactors it is necessary to acquire a thorough knowledge of the process and factors which influence it.

---

\* Corresponding author: porada@agh.edu.pl

One of the fundamental problems is getting to know the impact of the applied raw material on the kinetics of the gasification process. An analysis of the course of gasification reveals that it is a complex process which involves: (1) coal pyrolysis with the formation of char and volatile products of pyrolysis, (2) gasification of the resulting char, and (3) secondary reactions in the gaseous phase. In spite of the fact that the gasification of char, limiting the course of the entire process, is the slowest stage, the coal pyrolysis stage, which directly influences char properties, should not be underestimated. Factors having an effect on the reactivity of char, apart from the properties of the applied coal, include: the final temperature of pyrolysis, the rate of its growth, pressure, and the character of the atmosphere [11-23].

The pyrolysis stage plays a very important part in the gasification process, which is connected with its direct impact on the kinetics of gasification of the resulting char. What is more, taking into consideration the impact of pyrolysis conditions on char properties, it should be anticipated that the gasification kinetics of coal and char, formed from it by the *ex situ* method, will be different.

The aim of the work was to investigate and compare the steam gasification kinetics of selected coals and chars formed from them by the *ex situ* method. In the majority of examinations presented in literature, the measurements concerning gasification are conducted for chars, leaving out the pyrolysis stage, and the authors of the paper apply coals in their works [1,7,9,10].

An isothermal thermovolumetric method, developed by the authors, which consists in an analysis of the composition of the resulting gas, was used for examining the process of steam gasification of coals and chars. Thanks to such an approach, the conditions of measurements better reflect the process of coal gasification occurring in the commercial reactors. The conducted measurements allowed for the determination of kinetic parameters of gaseous products formation. Additionally, the carbon conversion degree was calculated.

## 2 Material and method

### 2.1 Characteristics of samples and conditions of measurements

The object of this study were three Polish coals of different rank and three chars obtained from these coals by the *ex situ* method at 900 °C and under atmospheric pressure. For this purpose a Jenkner type retort was used. Mass sample of coals used amounted to 5 kg. Yield of resulting char was depending on coal type and amounted to from about 2 to 3 kg. The coals selected for the examinations comes from abundant resources and with good prospects of being put to use. For the purposes of examinations, samples were used with the particle size of 0.315-0.5 mm and the mass of 1 g. Table 1 shows the characteristics of the examined samples. The proximate and ultimate analyses were supplemented with the composition of ash, and, additionally, the alkali index, which influences the gasification kinetics [24], was calculated in accordance with the Eq. (1):

$$AI = A^a \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O}{SiO_2 + Al_2O_3} \quad (1)$$

$A^a$  – ash content in sample, %

$Fe_2O_3, CaO, MgO, Na_2O, K_2O, SiO_2, Al_2O_3$  – content of particular oxides in ash, %.

From an analysis of Table 1 it can be inferred that chars are featured by greater contents of carbon and ash and lower contents of hydrogen, sulphur, moisture and volatile matter with respect to initial coals. Despite small differences in ash composition between

coals and chars, greater values of the alkali index (AI) are observed for chars, which is connected with a higher content of ash in them.

For all the samples, the examinations were conducted for three temperatures, i.e. 850, 900 as well as 950 °C, and at the pressure of 0.1 MPa.

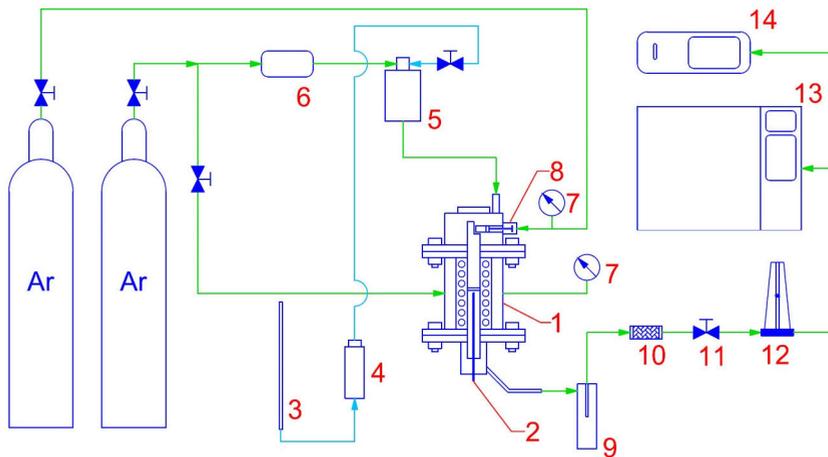
**Table 1.** Characteristics of examined coals and coal chars

Parameter	Bełchatów coal	Bełchatów char	Janina coal	Janina char	Wieczorek coal	Wieczorek char
Proximate analysis (%)						
Moisture - M <sup>a</sup>	19.4	1.6	14.1	2.8	3.3	1.0
Ash - A <sup>a</sup>	19.9	40.8	12.8	15.6	13.0	20.5
Volatile matter - VM <sup>daf</sup>	57.0	0.7	42.1	1.2	38.2	4.9
Fixed Carbon – FC	26,1	57,2	42,3	80,6	51,7	74,7
Ultimate analysis (%)						
C <sup>daf</sup>	67.1	97.5	79.6	98.5	83.8	96.5
H <sup>daf</sup>	5.2	1.1	5.5	1.0	5.8	1.06
S <sub>t</sub> <sup>a</sup>	0.81	1.02	4.00	0.83	1.71	0.83
Ash composition (%)						
SiO <sub>2</sub>	48.5	49.9	45.9	47.1	49.0	61.9
Al <sub>2</sub> O <sub>3</sub>	23.7	22.8	26.1	26.7	17.9	14.7
Fe <sub>2</sub> O <sub>3</sub>	3.9	3.6	10.1	7.5	10.5	8.3
MgO	0.95	0.85	1.56	1.61	2.75	2.05
CaO	11.74	11.69	2.88	3.26	5.69	3.19
K <sub>2</sub> O	0.39	0.28	2.40	3.13	2.26	2.23
Na <sub>2</sub> O	0.17	0.06	2.46	2.76	1.35	1.25
Alkali index AI (-)	4.73	9.25	2.53	3.86	2.83	5.42

## 2.2 Laboratory equipment

The investigations of steam gasification were conducted with the use of unique laboratory equipment which allows for measurements of the kinetics of gasification under isothermal conditions within a broad pressure range. The measuring device consists of three basic systems: a high pressure reactor with a heating system, a system for supplying the reactor with steam, inert gas (argon) and coal as well as a system for collecting and analyzing the resulting gas. The system for supplying the reaction zone with steam and argon consists of a micropump dispensing water, a steam generator, high pressure cylinders with argon and a set of pressure reducing valves, control and release valves, filters, manometers and a flow controller.

Inside the reactor a retort is located with the diameter of 20 mm and with an especially designed quartz grid. After stabilizing the parameters of examinations (temperature, pressure, and flow rates) a piston feeder puts a coal sample with the mass of 1g onto the grid. The resulting gas, after the evolution of water-tar condensate and drying, decompresses and is continuously analysed in respect of the contents of CO, CO<sub>2</sub> and CH<sub>4</sub>. Moreover, the gas is taken into pipettes in order to be analysed in respect of the content of hydrogen with the use of a gas chromatograph equipped with a thermal conductivity detector (TCD). A diagram of the laboratory equipment is presented in Fig. 1.



**Fig. 1.** The laboratory equipment for kinetic examinations of gasification process. 1 - reactor, 2 - thermocouple, 3 - water tank, 4 - water pump, 5 - steam generator, 6 - mass flowmeter, 7- pressure gauge, 8 - sample feeder, 9 - cooler, 10 - filter, 11 - pressure regulator, 12- rotameter, 13 - gas chromatograph, 14 - CO, CO<sub>2</sub> IR analyser

### 2.3 Methodology of evaluation of gasification process

In order to evaluate the gasification process on the basis of changes in the concentration of the analyzed components, their time curves of formation were determined, which enabled the determination of the yields of the products and the composition of the resulting gas. Moreover, for the most important products, i.e. carbon monoxide and hydrogen, the reaction rate constants and the kinetic parameters of their formation reaction were calculated. The work [7] describes the methodology of determining the kinetic parameters in detail. Assuming the first order of reaction, the formation rate of a product can be expressed by Eq. (2):

$$\ln \frac{V_{\infty}}{V_{\infty}-V} = k \cdot t \quad (2)$$

$k$  – constant reaction rate, 1/min,

$V_{\infty}$  – maximal volume of gas product, cm<sup>3</sup>,

$V$  – volume of released gas component at time  $t$ , cm<sup>3</sup>,

$t$  – time, min

On the basis of Eq. (2), the formation rate constants were determined for carbon monoxide and hydrogen at three temperatures (850, 900 and 950 °C), and then, based on the

Arrhenius Equation (3), the values of the activation energy  $E$  and the pre-exponential factor  $A$  were calculated.

$$k = A \times e^{-\frac{E}{RT}} \quad (3)$$

The carbon conversion degree was estimated on the basis of the Eq. (4):

$$X = \frac{(V_{CO} + V_{CO_2} + V_{CH_4}) M_C}{V_{mol} m C^{daf}} \times 100 \% \quad (4)$$

$V_{CO}$ ,  $V_{CO_2}$ ,  $V_{CH_4}$  – volume of released gas component, dm<sup>3</sup>/g,

$M_C$  – molar mass of carbon, g/mole,

$m$  – mass of sample, g,

$C^{daf}$  – dry ash free carbon content in sample, %,

$V_{mol}$  – molar volume of gas at temperature of 273 K and pressure of 101325 Pa, dm<sup>3</sup>/mole.

## 3 Results and discussion

### 3.1 Impact of raw material on gasification process

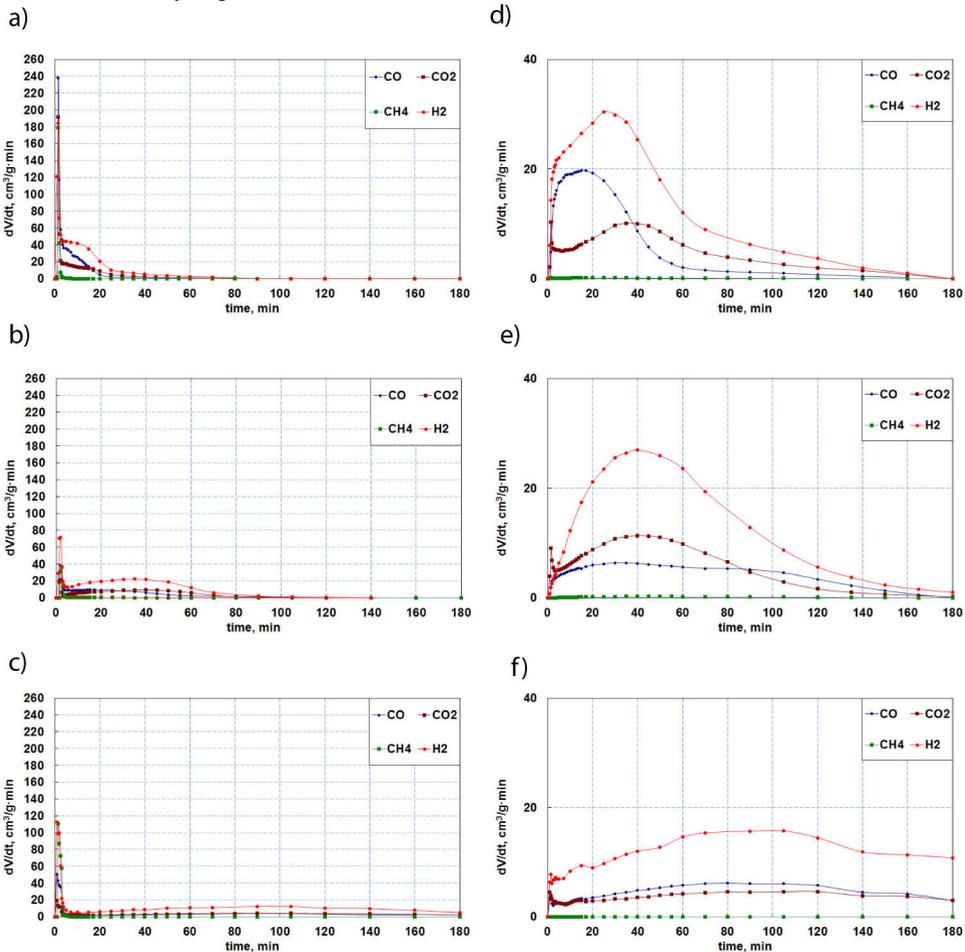
On the basis of the composition of the resulting gas the curves of formation rate of CO, CO<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub> were developed, and are presented in Fig. 2. Generally, in the case of coals at the first stage of the process, considered equivalent to the course of pyrolysis, high rates of evolution of gaseous products are observed. The second stage is the proper gasification of the resulting char which is featured by significantly lower formation rates of the examined gaseous components.

In the case of chars, the shape of the curves is different. At the initial stage of the process, there are no peaks of gaseous products formation rates, which are characteristic for pyrolysis, and, instead, a consistent growth of the formation rates of CO, CO<sub>2</sub> and H<sub>2</sub> is observed, which, after reaching the maximum, slowly decrease. Hydrogen is characterized by the highest formation rate, both in the case of coals and chars. The curves of formation of carbon monoxide and carbon dioxide are diverse and depend on the examined material. Methane is formed only during the first minutes of the gasification of coals, which is connected with the occurring pyrolysis reactions. During the gasification of chars, the formation of methane is not observed.

The shape of the formation curves of gaseous products of gasification constitute a proof of reactivity of the examined material. It can be observed that coals of different rank differ in reactivity, and the highest reactivity is that of the Belchatów brown coal of the lowest rank, while the lowest reactivity is that of the Wieczorek bituminous coal of the highest rank. The obtained results correspond to those reported by other researchers [19-21]. This fact may be attributed to a high content of functional groups rich in oxygen, a big share of transient pores and macropores as well as a high dispersion of the inorganic substance in coals of low rank.

Similarly to coals, chars also differ in reactivity, and the chars obtained from the Belchatów and Janina coals of low rank are more reactive than the char from the Wieczorek coal. A comparison of the gasification rate for coals and chars obtained from them leads to the conclusion that coals are more reactive than chars obtained from them by the *ex situ* method, despite the fact that the alkali index had higher values for chars than for coals. This statement can be attributed to the impact of different conditions of char formation on its

reactivity and the fact that higher values of alkali index for chars are connected with a higher content of ash in them and not with increased share of alkali and alkaline earth metals that catalyse gasification reactions.

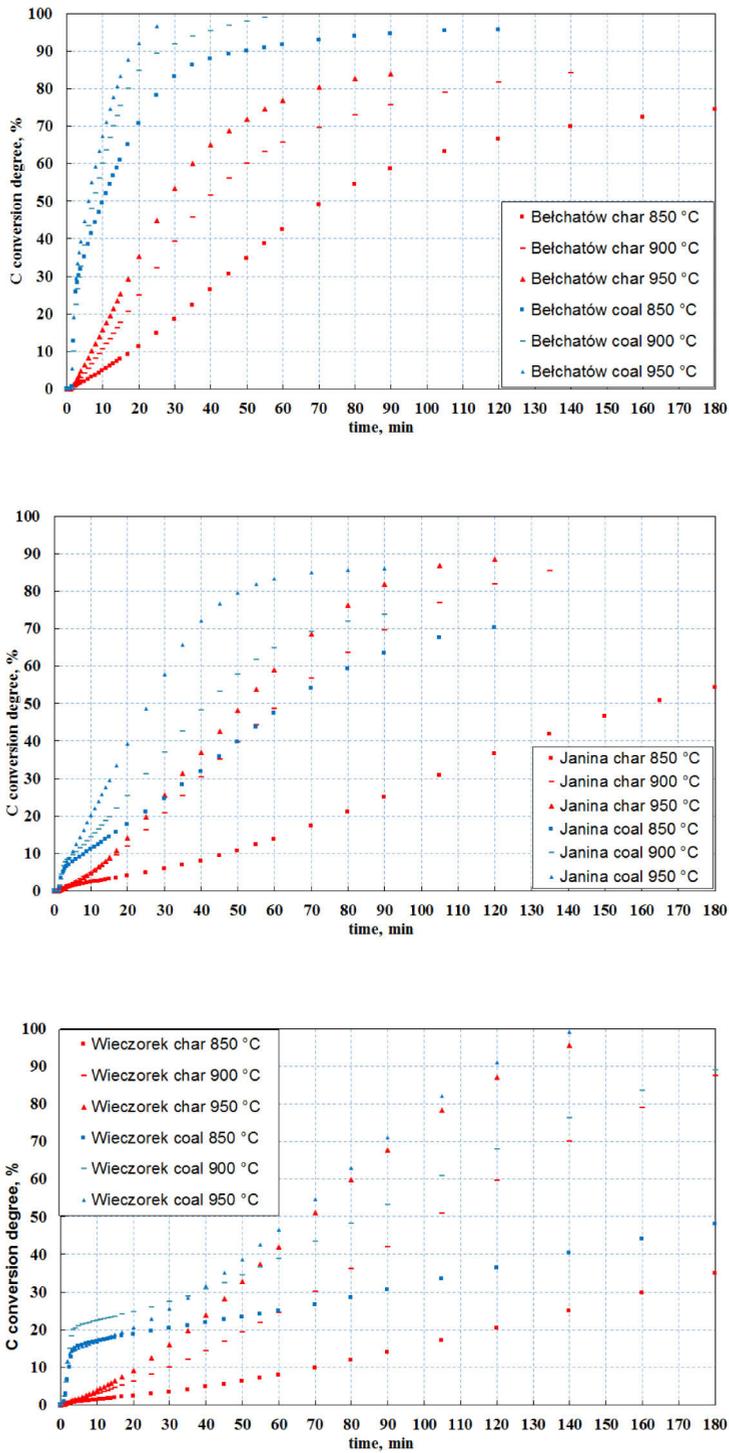


**Fig. 2.** Curves of evolution rate of gaseous products of gasification ( $t = 900\text{ }^{\circ}\text{C}$ ): a) *Belchatów coal*; b) *Janina coal*; c) *Wieczorek coal*; d) *Belchatów char*; e) *Janina char*; f) *Wieczorek char*

### 3.2 Analysis of carbon conversion degrees

An analysis of the curves of the carbon conversion degree for coals and chars makes it possible to notice easily differences in their reactivity, the measure of which is the slope of the curve translating into the time of reaching the maximal conversion degree. Carbon conversion degree curves for all examined samples are shown in Fig. 3.

Analysing the shape of the curves of the conversion degree for coals and chars, certain differences can be observed. Namely, in the case of coals, in contrast with chars, in the first minutes a rapid growth can be noticed of the conversion degree, after which the slope of the curve decreases. This phenomenon is caused by the reactions of coal pyrolysis, occurring in the first minutes, and by a rapid evolution of gaseous products. It can also be stated that coals, especially those of a low rank, are featured by a higher reactivity when compared to chars formed from them by the *ex situ* method.



**Fig. 3.** Comparison of carbon conversion degree curves

### 3.3 Kinetic parameters of gasification process

In order to quantitatively describe the process of gasification, on the basis of the Eq. (2), the formation rate constants of carbon monoxide  $k_{CO}$  and of hydrogen  $k_{H_2}$  were calculated for the three examined temperatures. Next, on the basis of the Eq. (3), kinetic parameters i.e. the activation energy  $E$  and the pre-exponential factor  $A$  of CO and H<sub>2</sub> formation reactions were determined. The results of the calculations are presented in Table 2 and Table 3. Comparing kinetic parameters for coals and for chars it can be seen that they are different. In the case of carbon monoxide, both energy activation and pre-exponential factor values for Belchatów and Janina chars are higher than for corresponding coals. In the case of Wieczorek samples activation energy assumes a slightly lower value for char and its lower reactivity is associated with much lower value of pre-exponential factor. In the case of hydrogen such a clear relationship is not observed which can be explained by a more complex mechanism of its formation.

**Table 2.** Kinetic parameters of carbon monoxide formation reaction

Kinetic parameters of CO formation	Belchatów coal	Janina coal	Wieczorek coal	Belchatów char	Janina char	Wieczorek char
E [kJ/mol]	140	218	269	201	230	254
A [1/min]	2.58E+01	2.73E+04	2.07E+06	5.93E+03	3.50E+04	3.07E+05

**Table 3.** Kinetic parameters of hydrogen formation reaction

Kinetic parameters of H <sub>2</sub> formation	Belchatów coal	Janina coal	Wieczorek coal	Belchatów char	Janina char	Wieczorek char
E [kJ/mol]	133	181	181	106	248	242
A [1/min]	8.95E+00	7.28E+02	2.40E+02	3.25E-01	3.77E+05	9.63E+04

## 4 Conclusions

The process of steam gasification of three coals of different coal ranks and three chars obtained from them by the *ex situ* method at 900 °C was compared. The obtained results of the examinations lead to the following most important conclusions:

- the courses of the gasification process of coals and chars obtained from these coals by the *ex situ* method differ from each other: in the case of coals, in the first minutes, a rapid evolution of gaseous products is observed, which is connected with the pyrolysis of the coal matter; this phenomenon is not observed during the gasification of chars,
- generally, coals are more reactive than chars obtained from them, the reactivity of char decreases along with a growth of the parent coal rank and similarly the reactivity of coals decreases along with the growth of its rank,
- kinetic parameters of formation reactions of the most important products i.e. carbon monoxide and hydrogen calculated for coals and chars are different; generally it can be stated that in case of gasification process both kinetic parameters should be considered i.e. activation energy and pre-exponential and not only activation energy because of their compensation effect on reactions kinetics,

- d) differences in the gasification of coals and chars suggest that conditions in which the char is formed bear on its properties that is why gasification process of coal and the *ex situ* prepared char should not be equated.

This work was prepared as a part of the statutory activity of the Faculty of Energy and Fuels at the AGH University of Science and Technology, No. 11.11.210.213

## References

1. G. Czerski, T. Dziok, A. Strugała, S. Porada, *Przem. Chem.* **93**, 1393–1400 (2014)
2. X. Yujie, Z. Guiyan, Ch. Haisheng, D. Binlin, T. Chunqing, *Int. J. Hydrogen Energy* **37**, 11805–11814 (2012)
3. D. Y. Young, J. L. Seung, Y. Yongseung, *Koeran J. Chem. Eng.* **24**, 350 (2007)
4. C. Higman, State of the Gasification Industry – the Updated Worldwide Gasification Database, Proceedings of Gasification Technologies Conference; 2013 Oct 16; Colorado Springs, USA
5. A. Strugała, G. Czerski, *Przem. Chem.* **91**, 2181–2184 (2012)
6. A. M. Dubinin, E. V. Cherepanova, O. A. Obozhin, *Solid Fuel Chemistry* **49(2)**, 31–33 (2015)
7. S. Porada, G. Czerski, T. Dziok, P. Grzywacz, D. Makowska, *Fuel Process. Technol.* **130**, 282–291 (2015)
8. K. Murakami, M. Sato, N. Tsubouchi, Y. Ohtsuka, K. Sugawara, *Fuel Process. Technol.* **129**, 91–97 (2015)
9. S. Porada, G. Czerski, P. Grzywacz, T. Dziok, D. Makowska, *Przem. Chem.* **93** 2059–2063 (2014)
10. S. Porada, A. Rozwadowski, *Przem. Chem.* **93**, 384–387 (2014)
11. M. J. G. Alonso, A. G. Borrego, D. Alvarez, J. B. Parra, R. Menendez, *J. Anal. Appl. Pyrolysis.* **58–59**, 887–909 (2001)
12. L. Tingting, Z. Lei, D. Li, L. Chun-Zhu, *Fuel* **117**, 1190–1195 (2014)
13. A. Molina, F. Mandragon, *Fuel* **77** 1831–1839 (1998)
14. R. C. Messenbock, D. R. Dugwell, R. Kandiyoti, *Fuel* **78**, 781–793 (1999)
15. C. Li, J. Zhao, Y. Fang, Y. Wang, *Front. Chem. Eng. China.* **4(4)**, 385–393 (2010)
16. S. Kajitani, S. Hara, H. Matsuda, *Fuel* **81**, 539–546 (2002)
17. M. A. Elliott editor. *Chemistry of coal utilization.* John Wiley & Sons Inc; 1981.
18. K. E. Benfell, G. S. Liu, D. G. Roberts, D. J. Harris, J.A. Lucas, J.G. Bailey, T.F. Wall, *P. Combust. Inst.* **28**, 2233–2241(2000)
19. D. P. Ye, J.B. Agnew, D.K. Zhang, *Fuel* **77**, 1209–1219 (1998)
20. C. Z. Li, *Fuel* **86**, 1664–1683 (2007)
21. M.J.G. Alonso, A.G. Borrego, D. Alvarez, R. Menendez, *Fuel* **78**, 1501–1513(1999)
22. Q. Yan, J. Huang, J. Zhao, Ch. Li, L. Xia, Y. Fang, *J. Ther. Anal. Calor.* **116**, 519–527 (2014)
23. J. Tanner, S. Bhattacharya, *Chem. Eng. J.* **285**, 331–340 (2015)
24. M. Sakawa, Y. Sakurai, Y. Hara, *Fuel* **73**, 717–720 (1982)