

Studies of catalytic coal gasification with steam

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One of the promising processes, belonging to the so-called clean coal technologies, is catalytic coal gasification. The addition of a catalyst results in an increased process rate, in which synthesis gas is obtained. Therefore, the subject of this research was catalytic gasification of low-ranking coal which, due to a high reactivity, meets the requirements for fuels used in the gasification process. Potassium and calcium cations in an amount of 0.85, 1.7 and 3.4% by weight were used as catalytically active substances. Isothermal measurements were performed at 900°C under a pressure of 2 MPa using steam as a gasifying agent. On the basis of kinetic curves, the performance of main gasification products as well as carbon conversion degree were determined. The performed measurements allowed the determination of the type and amount of catalyst that ensure the most efficient gasification process of the coal 'Piaś' in an atmosphere of steam.

Keywords: gasification, catalyst, coal, thermovolumetry.

INTRODUCTION

The process of catalytic steam gasification is widely perceived as an effective way to convert a variety of solid fuels such as coal or biomass to synthesis gas, natural synthetic gas or hydrogen¹. The use of catalysts may increase the carbon conversion degree as well as shorten the process time, which, from an economic point of view, is highly advantageous. Moreover, an important feature of catalysts is their selectivity, which enables controlling the process in order to obtain gas that meets the requirements for further use. Selectivity of catalysts was used, among others, by Li et al.², who employed potassium carbonate to obtain a synthesis gas enriched in methane. The same catalyst was applied by Sharma et al.³ in order to increase the amount of hydrogen in the resulting gas, which also was successful. These results demonstrate complexity of the gasification process showing that the type of catalyst is only one of many factors influencing the process. An important role is played by the type of fuel used, its synergy with a catalyst, the concentration of catalytic components, degree of their dispersion as well as process parameters^{4–7}. Therefore, catalytic coal gasification is an attractive subject of many studies. In 1867 first official reports emerged concerning the effectiveness of catalysts based on alkali and alkaline earth metals in this process⁵. Since then a number of studies have confirmed this hypothesis^{8–10}, imposing the conclusion that these are the most effective and also the cheapest catalysts for the gasification process. Otto et al.¹¹ confirmed also the catalytic effect of precious metals like platinum, ruthenium, rhodium and palladium, the addition of which significantly increased the rate of the gasification reaction; however, their use is associated with high costs of preparing catalysts. The use of transition metals as catalysts in the gasification process¹² is associated with the problem of violent deactivation. At a high temperature, required to achieve a significant coal conversion, catalysts based on transition metals undergo deactivation, which was often observed while using nickel catalysts^{13, 14}. The way a catalyst affects the course of the gasification reaction depends on many factors, i.e. the properties of the catalyst, which are derived from their composition and the method of

preparation as well as its quantity and dispersion, which depend on the method of combining the catalyst with a feedstock subjected to gasification. The addition of a catalyst to coal is generally carried out in two ways, i) by physically mixing coal with the catalyst or ii) by coal impregnation using a catalytically active substance¹⁵. The most common method is the physical mixing of the fuel with the catalyst; then, the obtained mixture is fed to the gasification reactor. The unique advantage of this method is its simplicity and short time of execution as well as certainty that the amount of catalyst is exactly the same as the adopted one. Consequently, physical mixing is a commonly used method, particularly in the case of catalysts based on the alkali and alkaline earth metals^{16–19}. Another, equally common method is wet impregnation^{20, 21}, that provides a good contact between coal and the catalyst, as confirmed by Spiro et al.^{22, 23}. Moreover, Hung et al. found that adding a catalyst to coal by the physical mixing method requires higher temperatures during the gasification process to enable the action of the catalytically active substance, than in the case of the wet impregnation²⁴. In the literature cases can also be found where incipient wetness impregnation²⁵ or, ion exchange²⁶ were used for the application of a catalyst to the feedstock for the gasification process. However, due to the greater workload and time expenditure, these are not commonly used methods. An important factor is also the quantity of the catalyst used, which may vary within different limits depending on the process conditions as well as the quality of coal and the catalyst. The amount of the catalyst used in coal gasification with steam, which is widely reported in the literature, is 10 wt%, suggesting that increasing this amount further is unfounded, since it does not lead to a significant improvement of the process, generating higher costs at the same time^{27, 28}.

Previous studies show that the gasification process, as a very complex one, is susceptible to the influence of a large number of factors such as i) the type of coal and the catalyst used, ii) the concentration and dispersion degree of the catalyst, which depends on application way, or iii) process conditions. All these parameters can be monitored and controlled in order to achieve the best results in a given case. The aim of this study was to determine the effect of potassium and calcium cations

on the gasification of the low-ranking coal from the mine 'Piast' in an atmosphere of steam, under isothermal conditions of 900°C and at the pressure of 2 MPa. The temperature 900°C was chosen in order to examine the effect of catalytic additives on the coal gasification, which task is to accelerate the rate of the process at low temperatures.

MATERIAL AND METHODOLOGY

Characteristic of material

The subject of this study was the low-ranking coal from the mine 'Piast'. The main factor determining the course of the gasification process is the reactivity of the feedstock, dependent on the coal rank. A lower coal rank has a beneficial effect on the gasification process and, therefore, the coal from the 'Piast' mine was selected as a feedstock for research. However, a very important factor was also the size of operative resources offered by the mine 'Piast' that guarantees a decades-long operation. The characteristics of the coal samples are summarized in Table 1.

Table 1. Characteristics of coal

Parameter	Value, [%]
Proximate analysis	
Moisture – M^{ad}	5.7
Ash – A^{ad}	8.8
Volatile matter – VM^{daf}	39.6
Fixed carbon ^{ad}	51.6
Ultimate analysis	
Carbon – C^{daf}	78.9
Hydrogen – H^{daf}	5.08
Sulfur – S^{daf}	1.02
Oxygen* – O^{daf}	13.99
Nitrogen – N^{daf}	1.01

ad – air dry basis; daf – dry ash free basis; *calculated by difference.

The samples for research were prepared via physical mixing of coal with nitrates of potassium or calcium, in a suitable weight ratio. The weight percentages of the introduced cations were 0.75, 1.7, and 3.4; then the whole mixture was ground to ensure a uniform dispersion of the catalyst. Samples prepared in this way were placed in the dispensing system of the installation.

Methodology of examinations

A description of laboratory equipment, with the use of which the measurements of coal gasification were conducted, was shown repeatedly in earlier publications^{29, 30}. A schematic diagram of this installation is shown in Figure 1. The basic systems of the installation are i) a high pressure reactor with a heating system, ii) a system for feeding the reactor with the gasifying agent – steam, inert gas – argon and coal, as well as iii) a system for collection and analysis of gas formed in the gasification process. After stabilization of the adopted parameters, the valve that supplies compressed argon to the coal feeder is opened, resulting in the introduction of the tested sample into the reactor. The obtained gas, after cooling and drying, was analyzed continuously in respect of the content of methane, carbon mono- and dioxide, using an automatic analyzer. For a comprehensive analysis of the resulting gas, samples were taken at

specified time intervals during the measurement, and then analyzed in respect of hydrogen content using a gas chromatograph.

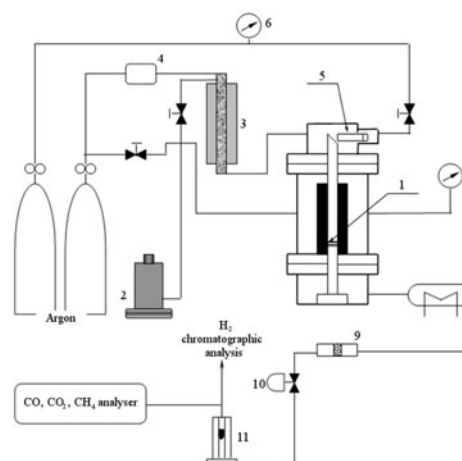


Figure 1. The laboratory equipment for kinetic measurements of coal gasification: 1 – reactor, 2 – water pump, 3 – steam generator, 4 – mass flowmeter, 5 – coal feeder, 6 – pressure gauge, 7 – condenser, 8 – tar separator, 9 – gas filter, 10 – backpressure regulator, 11 – rotameter²⁹

RESULTS AND DISCUSSION

Figures 2 and 3 show the effect of addition of various amounts of potassium and calcium on the formation rate of main components of the obtained gas i.e. carbon monoxide, hydrogen and carbon dioxide as a function of time. During measurements the amount of methane formed in the process was also recorded, but it was negligible and there was no apparent effect of any of the tested catalysts on the rate of its formation.

Changes in the formation rate of CO, H₂ and CO₂, due to the addition of various amounts of potassium, are shown in Figure 2a, 2b and 2c. The addition of only 0.8 wt% of potassium significantly increased the formation rate of all the presented components during the entire process, thus confirming the catalytic activity of this metal in the gasification process. With an increase in the amount of potassium nitrate added, a marked growth in the formation rate of hydrogen and carbon monoxide was observed, both at the initial stage of the process, associated with pyrolysis reaction, as well as during the gasification of char which has been formed at the pyrolysis stage. Thus, the greatest formation rate of the two primary components of syngas – carbon monoxide and hydrogen, was observed with the addition of 3.4 wt% of potassium.

In the case of carbon dioxide, a clear influence of increasing the amount of the catalytic substance on the formation rate was not observed as shown in Figure 2c. The addition of 1.7 wt% of potassium increased the formation rate of CO₂ at the pyrolysis stage; however, during char gasification, which is a fundamental part of the process, this rate was not improved. Increasing the amount of potassium further to 3.4 wt% not only did not improve the formation rate of carbon dioxide, but also resulted in a slight decrease in comparison with the addition of 1.7 wt%.

The addition of the catalysts also had an impact on the duration of the process – regardless of the amount of potassium added, time needed to complete gasification process was significantly reduced.

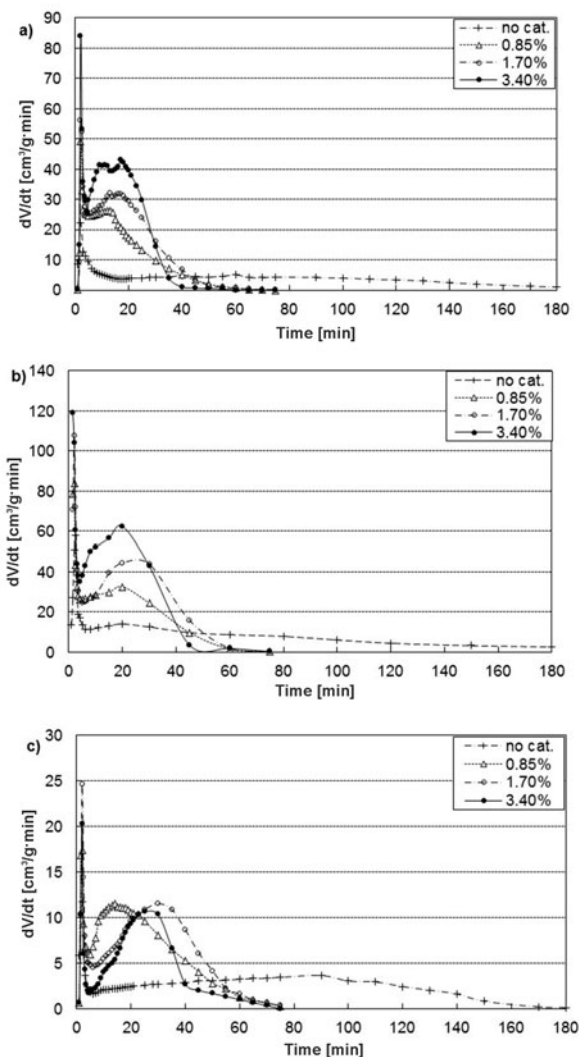


Figure 2. The effect of addition of various amounts of potassium on the formation rate of a) CO; b) H₂; c) CO₂ during gasification of the coal 'Piast'

The effect of various amounts of the second tested catalyst, i.e. calcium, on the coal gasification process is shown in Figure 3. As in the case of potassium, here also a small addition of the catalyst increased the rate of formation of all the gaseous products during the process, when compared with gasification without the addition of the catalytically active substance. It was also observed that increasing the amount of catalyst used in the process to 1.7 wt% caused a growth of the formation rate of carbon mono- and dioxide as well as hydrogen, both at the initial pyrolysis stage and at the subsequent stage of char gasification. The results obtained during the gasification of coal with 3.4 wt% of calcium showed that the use of this amount of the catalyst is unfounded, since it does not affect the process in a positive way. Moreover, the formation rate of hydrogen and carbon dioxide at the initial stage of the process was lower than in the case of using 0.85 wt% of the catalyst. The rate at which carbon monoxide was formed during pyrolysis was similar to the rate observed during the gasification of coal containing 1.7 wt% of calcium. It should also

be noted that the curves of the carbon monoxide and hydrogen formation during the gasification of coal containing 3.4 wt% of calcium were slightly different from the curves obtained in the other measurements – after the pyrolysis stage, a renewed increase in the formation rate of gaseous products, which is characteristic for the char gasification process, did not appear.

An analysis of the presented results enabled drawing conclusions that the impact of a catalytic substance on the gasification process depends not only on its type, but also on its amount. The amount of Ca, at which the formation rate of gaseous products was greatest, was located in the range between 1.7 and 3.4 wt%. The addition of calcium catalyst also greatly contributed to shorten the process time, although not as much as the addition of potassium.

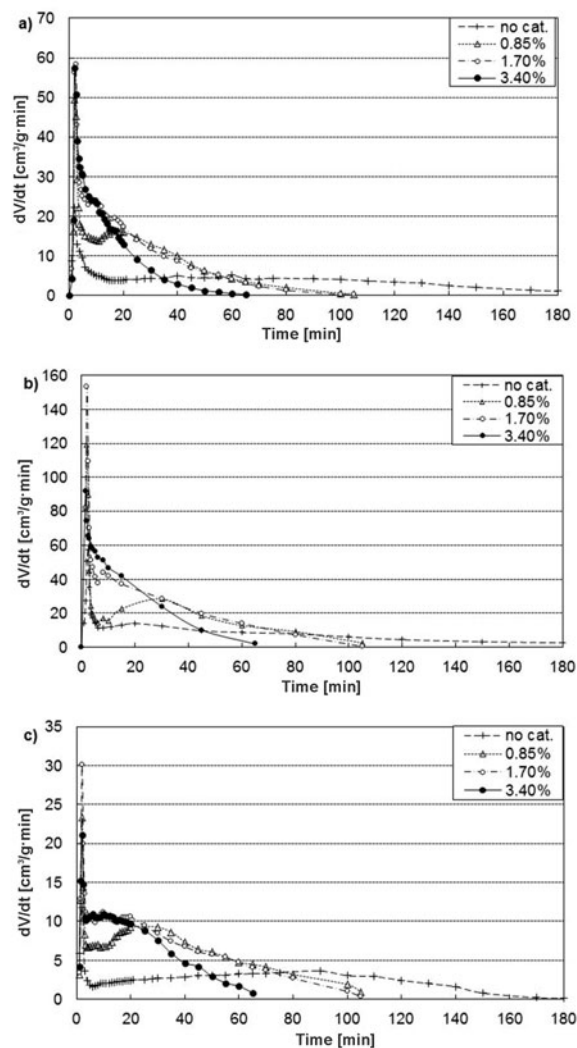


Figure 3. The effect of addition of various amounts of calcium on the formation rate of a) CO; b) H₂; c) CO₂ during gasification of the coal 'Piast'

The increase in the rate of gasification process, caused by the addition of a catalytic additives, has been the subject of numerous investigations^{31, 32, 33}. Four reaction mechanisms, including oxygen transfer mechanism, electrochemical mechanism, free radical mechanism and intermediate mechanism were proposed^{34, 35}. Among them, oxygen transfer mechanism is a generally postulated and it seems to describe the catalytic gasification process in the most accurate way^{36, 37, 38}. In such a mechanism oxygen is extracted from the reactant gas – H₂O by the

catalyst, which then transferred it to the carbon active sites through the catalytically active alkali and alkaline earth species, followed by the liberation of CO from the active carbon-oxygen complexes (by breaking the neighboring C-C bonds)^{34, 37}. The last step is considered as rate-limiting³⁷. The principal embodiment of such a process is a redox mechanism in which the catalyst is alternately reduced by the carbon and oxidized by the gaseous reactant³⁴.

The conclusions drawn on the basis of changes in formation rate of gaseous products were confirmed by the results of the determined yields of particular gases in the gasification process, as shown in Figure 4.

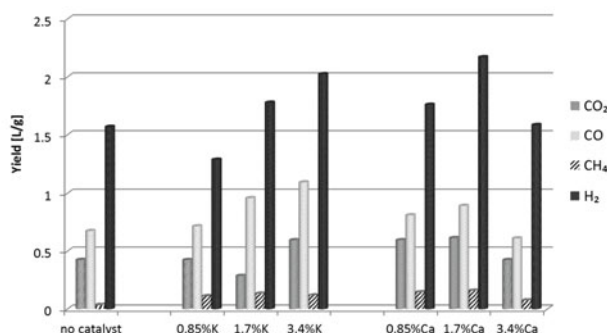


Figure 4. The yields of gaseous components in the gasification process of the coal 'Piast' with different amounts of potassium or calcium

As a result of coal gasification gas was obtained wherein hydrogen and carbon monoxide were the main components, and the amount of hydrogen was almost three times greater than that of carbon monoxide. The addition of 0.85 wt% of potassium significantly increased the share of the resulting CO, but also reduced the amount of hydrogen; thus, conclusion may be drawn that this amount of the catalyst is not sufficient for an efficient process. A further growth of potassium content led to a considerable increase in the share of hydrogen and carbon monoxide in the resulting gas, while the best results were achieved through mixing 3.4% by weight of potassium with coal. In the case of calcium, an increased yield of gaseous products was observed even at the smallest amount of the catalyst – 0.85 wt%. Both the share of carbon monoxide and that of hydrogen were higher than in the reaction without the catalyst. A growth of the calcium content to 1.7 wt% had a positive impact on the process, leading to a continuous increase in the share of both analyzed gases. The syngas obtained in this process was characterized by the highest yields of hydrogen and carbon monoxide among all the measurements with calcium cations as the catalyst substance. The addition of 3.4 wt% of Ca resulted in syngas with a composition almost identical to the case of gasification without the catalyst. Thus, increasing the amount of calcium up to that level is pointless.

It is also worth noting that conclusions can be drawn concerning the selectivity of both catalysts. The addition of potassium resulted in obtaining gas in which the hydrogen content was nearly twice as high as that of carbon monoxide, regardless of the amount of the catalyst. In the measurements using calcium it was observed, however, that the H₂/CO ratio exceeded the value

of 2, and this value increased along with the amount of the catalyst. Depending on the desired composition of final gas, a different catalyst can be used. If the main objective is to obtain a synthesis gas with the highest content of carbon monoxide, the potassium should be used as a catalyst. In the case, however, where the aim is to significantly increase the amount of hydrogen in the post-reaction gas, calcium catalysts seem to be the better option.

The next step was to calculate the carbon conversion degree in the catalytic gasification for all amounts of the catalysts. Figure 5 shows the effect of the addition of potassium on this parameter. It can be seen that potassium content significantly increased the carbon conversion degree to gaseous products, wherein increasing the amount of the catalyst caused also a growth of the conversion degree, reaching the value of 79% for the smallest amount of the catalyst used, to almost 96% with the application of 3.4 wt% of potassium. Very important is also the time in which a specific degree of conversion was achieved. The process of coal gasification without a catalyst lasted 180 minutes, and the carbon conversion degree achieved 71%. The addition of any quantity of potassium shortened the duration of this process almost two and a half times – the time of the catalytic gasification of coal amounted to about 76 minutes.

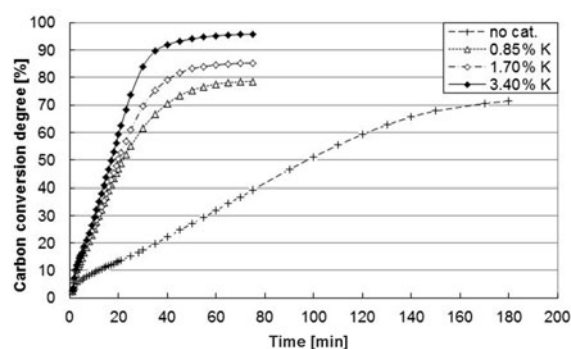


Figure 5. The carbon conversion degree during the catalytic gasification of the coal 'Piast' with various amounts of potassium as the catalyst

The carbon conversion degrees achieved during the coal gasification with the addition of calcium are much more varied than the results achieved during the gasification with the addition of potassium. The results shown in Figure 6 indicate that the addition of 0.85 wt% of Ca resulted in shortening the process time to 105 minutes, at which time the carbon conversion degree to gaseous products reached 97%. Doubling the amount of the catalyst further shortened the process time, while increasing the conversion degree – during 80 minutes, nearly 100% of the element C has been converted. As previously mentioned, further increasing the amount of catalyst used, taking into account the yields of the various gaseous products, was unfounded. Similar conclusions were drawn by analyzing the maximum carbon conversion degree achieved by the gasification of the coal 'Piast' with the addition of 3.4 wt% of calcium. The obtained carbon conversion degree was 70% and was comparable to the value achieved during coal gasification without a catalyst. However, the time needed to reach the conversion degree of 70% was almost three times shorter in the case of

catalytic gasification. Such a significant reduction of the gasification time is tantamount to a lower cost of the process. However, in order for such actions to be justified, the gains arising from the reduction of the process time must be sufficiently greater than the expenditure related to the use of a catalyst.

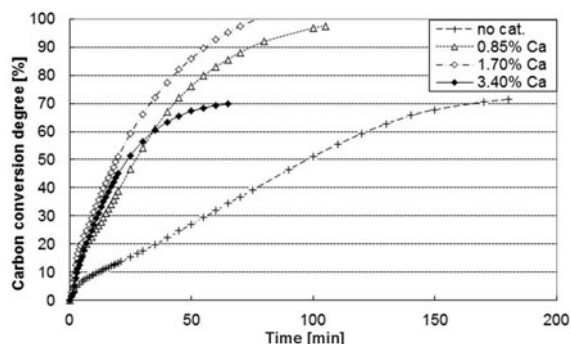


Figure 6. The carbon conversion degree during the catalytic gasification of the coal 'Piast' with various amounts of calcium as the catalyst

CONCLUSION

Catalytic gasification is a process which is likely to become an effective alternative to conventional methods of coal combustion, which is why in this study the effect of calcium and potassium addition on the process was assessed. The obtained results confirmed the catalytic activity of both studied alkali metals which accelerated the formation rate of carbon monoxide and hydrogen during the process, resulting in their increased yields in the post-reaction gas. The factor determining the impact of the catalysts on the yields of gas components was their quantity. The addition of 0.85 wt% of potassium was not sufficient to improve the process, only a greater amount of this catalyst resulted in an increased yield of carbon monoxide and hydrogen. In the case of calcium, an improvement was found in the presence of 0.85 wt% of catalyst. It was also observed that increasing the amount of calcium to 3.4 wt% was unfounded, since it did not improve the process and the yields of gas components were comparable with the yields in the post-reaction gas from gasification without a catalyst. The analysis of the results also made it possible to determine the selectivity of the catalyst – it was found that calcium gasification led to a significant increase in the content of hydrogen in the resulting gas, and potassium allowed for an increase in the share of carbon monoxide in the synthesis gas. Moreover, it was also found that the catalytic additives greatly improved the carbon conversion degree while reducing the process time even more than two and a half times, which was observed in the case of potassium as the catalyst. The catalytic gasification of the 'Piast' coal is, therefore, more economical, and both potassium and sodium may be successfully used as the catalysts.

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LITERATURE CITED

- Ding, L., Zhou, Z., Guo, Q., Huo, W. & Yo, G. (2015). Catalytic effects of Na_2CO_3 additive on coal pyrolysis and gasification. *Fuel* 142, 134–144. DOI: 10.1016/j.fuel.2014.11.010.
- Li, W.W., Li, K.Z., Qu, X., Zhang, R. & Bi, J.C. (2014). Simulation of catalytic coal gasification in a pressurized jetting fluidized bed: Effects of operating conditions. *Fuel Proc. Technol.* 126, 504–512. DOI: 10.1016/j.fuproc.2014.06.006.
- Sharma, A., Takanohashi, T., Morishita, K., Takarada, T. & Saito, I. (2008). Low temperature catalytic steam gasification of HyperCoal to produce H_2 and synthesis gas. *Fuel* 87(4–5), 491–497. DOI: 10.1016/j.fuel.2007.04.015.
- Namkung, H., Yuan, X., Lee, G., Kim, D., Kang, T.J. & Kim, H.T. (2014). Reaction characteristics through catalytic steam gasification with ultra clean coal char and coal. *J. Energy Inst.* 87(3), 253–262. DOI: 10.1016/j.joei.2014.03.003.
- Tang, J. & Wang, J. (2016). Catalytic steam gasification of coal char with alkali carbonates: A study on their synergic effects with calcium hydroxide. *Fuel Proc. Technol.* 142, 34–41. DOI: 10.1016/j.fuproc.2015.09.020.
- Qi, X., Guo, X., Xue, L. & Zheng, C. (2014). Effect of iron on Shenfu coal char structure and its influence on gasification reactivity. *J. Anal. Appl. Pyrol.* 110, 401–407. DOI: 10.1016/j.jaap.2014.10.011.
- Parthasarathy, P. & Narayanan, K.S. (2014). Hydrogen production from steam gasification of biomass: Influence of process parameters on hydrogen yield – A review. *Renew Energ.* 66, 570–579. DOI: 10.1016/j.renene.2013.12.025.
- McKee, D.W. (1979). Catalysis of the graphite-water vapor reaction by alkaline earth salts. *Carbon* 17(5), 419–425. DOI: 10.1016/0008-6223(79)90058-7.
- Lang, R.J. (1989). Anion effects in alkali-catalysed steam gasification. *Fuel* 65(10), 1324–1329. DOI: 10.1016/0016-2361(86)90097-9.
- Wang, J., Yao, Y., Cao, J. & Jiang, M. (2010). Enhanced catalysis of K_2CO_3 for steam gasification of coal char by using $\text{Ca}(\text{OH})_2$ in char preparation. *Fuel* 89(2), 310–317. DOI: 10.1016/j.fuel.2009.09.001.
- Otto, K. & Shelef, M. (1977). Catalytic steam gasification of graphite: effects of intercalated and externally added Ru, Rh, Pd and Pt. *Carbon* 15(5), 317–325. DOI: 10.1016/0008-6223(77)90038-0.
- Hung, X., Zhang, F., Fan, M. & Wang, Y. (2015). Chapter 7 – Catalytic Coal Gasification. *Sus. Catal. Proc.* 179–199. DOI: 10.1016/B978-0-444-59567-6.00007-8.
- Ratchahat, S., Kodama, S., Tanthapanichakoon, W. & Sekiguchi, H. (2015). CO_2 gasification of biomass wastes enhanced by $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst in molten eutectic carbonate salt. *Int. J. Hydrogen Energ.* 40(35), 11809–11822. DOI: 10.1016/j.ijhydene.2015.06.059.
- Lee, I.G., Nowacka, A., Yuan, C.H., Park, S.J. & Yang, J.B. (2015). Hydrogen production by supercritical water gasification of valine over Ni/activated charcoal catalyst modified with Y, Pt, and Pd. *Int. J. Hydrogen Energ.* 40(36), 12078–12087. DOI: 10.1016/j.ijhydene.2015.07.112.
- Kopyscinski, J., Rahman, R., Gupta, R., Mims, C. & Hill, J. (2014). K_2CO_3 catalyzed CO_2 gasification of ash-free coal. Interactions of the catalyst with carbon in N_2 and CO_2 atmosphere. *Fuel* 117(Part B), 1181–1189. DOI: 10.1016/j.fuel.2013.07.030.
- Kim, Y.K., Park, J.I., Jung, D., Miyawaki, J., Yoon, S.H. & Mochida, I. (2014). Low-temperature catalytic conversion of lignite: 1. Steam gasification using potassium carbonate supported on perovskite oxide. *J. Ind. Eng. Chem.* 20(1), 216–221. DOI: 10.1016/j.jiec.2013.04.004.
- Waheed, Q., Wu, C. & Williams, P. (2015). Hydrogen production from high temperature steam catalytic gasification of bio-char. *J. Energy Inst.* 89(2), 222–230. DOI: 10.1016/j.joei.2015.02.001.

18. Supramono, D., Tristantini, D., Rahayu, A., Suwignjo, R. & Chendra, D. (2014). Syngas Production from Lignite Coal Using K_2CO_3 Catalytic Steam Gasification with Controlled Heating Rate in Pyrolysis Step. *Procedia Chem.* 9, 202–209. DOI: 10.1016/j.proche.2014.05.024.
19. Mazumber, J. & Lasa, H. (2014). Fluidizable $Ni/La_2O_3-\gamma Al_2O_3$ catalyst for steam gasification of a cellulosic biomass surrogate. *Appl. Catal. B.* 160–161, 67–79. DOI: 10.1016/j.apcatb.2014.04.042.
20. Marchand, D.J., Schneider, E., Williams, B.P., Joo, Y.L., Kim, J., Kim, G.T. & Kim, S.H. (2015). Physical and chemical changes of coal during catalytic fluidized bed gasification. *Fuel Proc. Technol.* 130, 292–298. DOI: 10.1016/j.fuproc.2014.10.039.
21. Lu, T., Li, K.Z., Zhang, R. & Bi, J.C. (2015). Addition of ash to prevent agglomeration during catalytic coal gasification in a pressurized fluidized bed. *Fuel Proc. Technol.* 134, 414–423. DOI: 10.1016/j.fuproc.2015.02.024.
22. Spiro, C.L., McKee, D.W., Kosky, P.G. & Lamby, E.J. (1983). Catalytic CO_2 -gasification of graphite versus coal char. *Fuel* 62(2), 180–184. DOI: 10.1016/0016-2361(83)90194-1.
23. Spiro, C.L., McKee, D.W., Kosky, P.G. & Lamby, E.J. (1984). Observation of alkali catalyst particles during gasification of carbonaceous materials in CO_2 and steam. *Fuel* 63(5), 686–691. DOI: 10.1016/0016-2361(84)90167-4.
24. Huhn, F., Klein, J. & Jüntgen, H. (1983). Investigations on the alkali catalysed steam gasification of coal: kinetics and interactions of alkali catalyst with carbon. *Fuel* 62(2), 196–199. DOI: 10.1016/0016-2361(83)90197-7.
25. Liu, Z.-l. & Zhu, H.-h. (1986). Steam gasification of coal char using alkali and alkaline-earth metal catalysts. *Fuel* 65(10), 1334–1338. DOI: 10.1016/0016-2361(86)90099-2.
26. Phuhiran, C., Takarada, T. & Chaiklangmuang, S. (2014). Hydrogen-rich gas from catalytic steam gasification of eucalyptus using nickel-loaded Thai brown coal char catalyst. *Int. J. Hydrogen Energ.* 39(8), 2649–2656. DOI: 10.1016/j.ijhydene.2013.12.155.
27. Wu, X., Tang, J. & Wang, J. (2016). A new active site/intermediate kinetic model for K_2CO_3 -catalyzed steam gasification of ash-free coal char. *Fuel* 165, 59–67. DOI: 10.1016/j.fuel.2015.10.034.
28. Namkung, H., Yuan, X., Lee, G., Kim, D., Kang, T.J. & Kim, H.T. (2014). Reaction characteristics through catalytic steam gasification with ultra clean coal char and coal. *J Energy Inst.* 87(3), 253–262. DOI: 10.1016/j.joei.2014.03.003.
29. Porada, S., Czerski, G., Dziok, T., Grzywacz, P. & Makowska, D. (2015). Kinetics of steam gasification of bituminous coals in terms of their use for underground coal gasification. *Fuel Proc. Technol.* 130, 282–291. DOI: 10.1016/j.fuproc.2014.10.015.
30. Porada, S. & Rozwadowski, A. (2014). Kinetic study of steam gasification of bituminous coal at elevated pressures. *Przem Chem.* 93(3), 384–387. DOI: 10.12916/przemchem.2014.384.
31. Saber, J.M., Falconer, J.L. & Brown, L.F. (1986). Interaction of potassium carbonate with surface oxides of carbon. *Fuel* 65, 1356–1359. DOI: 10.1016/0016-2361(86)90103-1.
32. Saber, J.M., Kester, K.B., Falconer, J.L. & Brown, L.F. (1988). A mechanism for sodium oxide catalyzed CO_2 gasification of carbon. *J Catal.* 109, 329–346. DOI: 10.1016/0021-9517(88)90216-3.
33. Matsukata, M., Fujikawa, T., Kikuchi, E. & Morita, Y. (1988). Interaction between potassium carbonate and carbon substrate at subgasification temperature. Migration of potassium into the carbon matrix. *Energ Fuel* 2, 750–756. DOI: 10.1021/ef00012a006.
34. Wood, B.J. & Sancier, K.M. (1984). The mechanism of catalytic gasification of coal char: a critical review. *Catal Rev.* 26, 233–79. DOI: 10.1080/01614948408078065.
35. Wang, J., Jiang, M., Yao, Y., Zhang, Y. & Cao, J. (2009). Steam gasification of coal char catalyzed by K_2CO_3 for enhanced production of hydrogen without formation of methane. *Fuel* 88, 1572–1579. DOI: 10.1016/j.fuel.2008.12.017.
36. McKee, D.W. (1983). Mechanisms of the alkali metal catalysed gasification of carbon. *Fuel* 62, 170–175. DOI: 10.1016/0016-2361(83)90192-8.
37. Chen, S.G. & Yang, R.T. (1997). Unified mechanism of alkali and alkaline earth catalyzed gasification reactions of carbon by CO_2 and H_2O . *Energ Fuel* 11, 421–427. DOI: 10.1021/ef960099o.
38. Wang, J., Sakanishi, K. & Saito, I. (2005). High-Yield Hydrogen Production by Steam Gasification of HyperCoal (Ash-Free Coal Extract) with Potassium Carbonate: Comparison with Raw Coal. *Energ Fuel* 19, 2114–2120. DOI: 10.1021/ef040089k.