

THE EFFECT OF SMALL AMOUNT OF CATALYSTS ON STEAM GASIFICATION PROCESS

Katarzyna Zubek^{a,b*}, Grzegorz Czerski^a, Stanisław Porada^a

^aAGH University of Science and Technology

^bE164 – Institute of Chemical Technologies and Analytics

INTRODUCTION

Gasification is a clean and effective process of gas generation that may be used to produce power and chemicals or converted into synthetic fuel ^[1]. Because of these advantages numerous works are conducted in order to improve gasification technology, including addition of catalysts. However, in order to use catalyst on an industrial scale, beyond the high catalytic activity it should be characterized by the low price. These conditions are met by catalysts based on alkali and alkaline earth metals that have gained the greatest popularity ^[2]. However, the manner in which catalyst affects the process depends on many factors, such as type of fuel subjected to gasification, process conditions, type and amount of catalysts etc. ^[3]. Therefore, there is a necessity to analyse the kinetics of catalytic coal gasification in order to determine their impact on the process. This is important step providing information needed to design gasifiers. The complexity of the gasification intensified by the addition of catalyst makes that kinetics of this process is still a current issue which requires further research. Because of that, the aim of this study was to analyse the kinetics of gasification of 'Janina' coal with small amount of cations of sodium, calcium and potassium and compare the results with those obtained from non-catalytic gasification process.

EXPERIMENT

Bituminous coal from the Polish mine 'Janina' was selected as feedstock for the research. Ions of sodium, potassium and calcium, introduced by wet impregnation method were used as catalysts. Obtained samples of coal contained small amount (1% wt) of the corresponding metal. Isothermal measurements of the gasification process were carried out at 800 °C, 900 °C, 950 °C and 1000 °C under elevated pressure of 1 MPa. Weight of the sample fed into the reaction zone was 1 g, steam flow was 0.3 g/min, while the argon flow (carrier gas) was 20 dm³/min. In the resulting gas the content of CO was continuously controlled by automatic analyser. In addition, the content of H₂ was analysed using gas chromatographs equipped with thermal conductivity detector (TCD). Based on the concentrations of the main components of the resulting gas (CO and H₂) the yields of these gases were determined and kinetics parameters of CO and H₂ formation reaction were calculated. For this purpose the Grain Model (GM) was used, described by equation 1.

$$\frac{dX}{dt} = k_{GM}(1 - X)^{\frac{2}{3}} \quad (1)$$

where:

k- kinetic rate constant

X- degree of conversion

RESULTS AND DISCUSSION

The results have shown that the yields of the hydrogen were much higher than CO but this difference decreased with increasing temperature of the process. This effect resulted from the

increasing amount of CO at higher temperatures. The addition of any catalysts increased the yields of both H₂ and CO compared to non-catalytic process, however, only at lower temperatures.

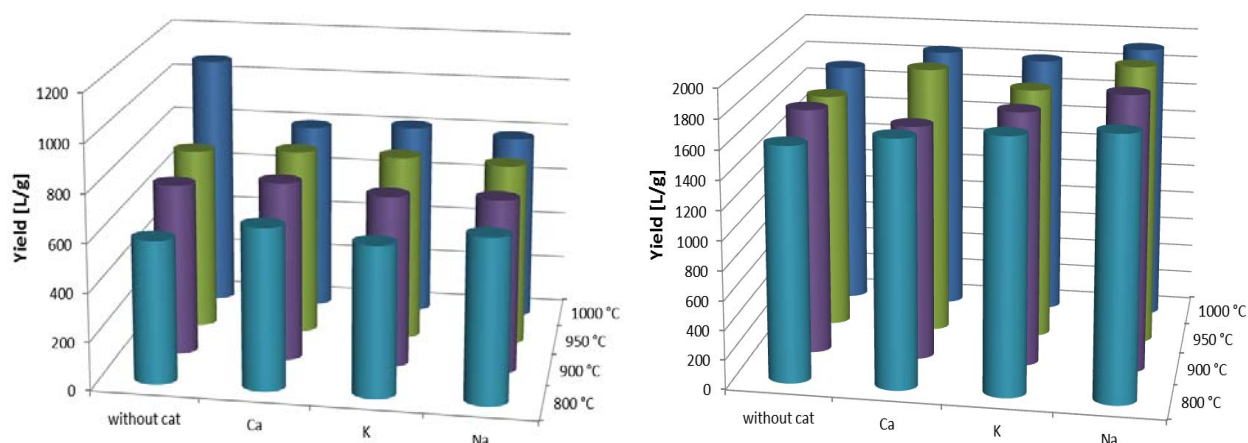


Figure 1 Yield of CO (a) and H₂ (b) from steam gasification process at various temperatures and with/without addition of various catalysts

Activation energies of CO and H₂ formation during non-catalytic coal gasification were the highest and simultaneously very similar. The addition of catalysts caused their significant reduction in a various way. The values of activation energy of CO formation were irrespective of the catalyst used and ranged between 52.1 and 55.2 kJ/mol. In case of E_a of H₂ formation differences were bigger - from 46.9 (Na) to 56.8 (Ca). The results confirmed the catalytic activity of alkali and alkaline-earth metals in the gasification process.

'Janina' coal	CO		H ₂	
	A [1/min]	E _a [kJ/mol]	A [1/min]	E _a [kJ/mol]
without catalyst:				
with addition of:	57.9	80.3	20.2	72.4
➤ Na ⁺	2.8	52.1	1.4	46.9
➤ K ⁺	6.7	55.2	5.0	56.3
➤ Ca ²⁺	3.0	53.1	4.0	56.8

Table 1 Kinetics parameters (activation energy E_a and pre-exponential factor A) of CO and H₂ formation reactions

CONCLUSION

The obtained results have proven that even small amount of properly selected catalyst can improve the gasification process, thus increasing the chances of wider industrial use. Further work will involve examination of 'Janina' coal gasification process with various (greater) amount of catalysts based on alkali and alkaline earth metals.

REFERENCES

1. E. Mostafavi, N. Mahinpey, M. Rahman, M.H. Sedghkarder, R. Gupta, High-purity hydrogen production from ash-free coal by catalytic steam gasification integrated with dry-sorption CO₂ capture, *Fuel*, **178**, 272–282 (2016).
2. L. Zhang, S. Kudo, N. Catalytic effects of Na and Ca from inexpensive materials on in-situ steam gasification of char from rapid pyrolysis of low rank coal in a drop-tube reactor, *Fuel Process Technol*, **113**, 1-7 (2013).
3. F. Kapteijn, G. Abbel, J. A. Moulijn, CO₂ gasification of carbon catalyzed by alkali metals: reactivity and mechanism, *Fuel* **63**, 1036-1042 (1984).