



Determination of optimal temperature and amount of catalysts based on alkali and alkaline earth metals for steam gasification process of bituminous coal



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ABSTRACT

The subject of this study was to analyze the influence of catalysts addition on the kinetics of 'Janina' coal gasification with steam. Thermovolumetric, isothermal measurements were performed at 800 °C, 900 °C, 950 °C, and 1000 °C at a pressure of 1 MPa. Samples of coal, and then coal with various amounts (1, 3 or 5 wt%) of calcium, potassium, and sodium cations were gasified. Based on the obtained results, the formation rates of main gaseous products as well as their yields and percentage share in the resulting gas were determined. Moreover, the influence of the amount of catalyst and operating temperature on the half times and rate constants of CO and H₂ formation reactions, as well as their kinetic parameters (the activation energy E_a and/or the pre-exponential factor A), were specified based on the isoconversional method, the grain model and the random pore model. The obtained results confirmed the positive effect of catalysts addition as well as increasing their amount but only to a certain level and at the temperature range of 800–900 °C. The optimum amount of catalyst for Na⁺ was 3 wt% and for K⁺ and Ca²⁺ it decreased along with an increase in temperature. Moreover, selectivity of the catalysts towards specific gas components was observed (Na⁺ resulted in a high H₂ content; K⁺ in a high CO content). In addition, the values of kinetic parameters (E_a and A) were reduced along with the increase in the amount of catalysts. However, while analyzing the catalytic gasification one should also take into account other parameters defining the process (half times and rate constants of gasification reactions at specific temperatures).

1. Introduction

Increasingly stringent carbon dioxide emission regulations result in the fact that traditional coal combustion methods are no longer viable because the CO₂ emission exceeds the expected regulatory levels [1]. As an alternative, the coal-based technologies can be used, in which the fuel is converted to gas in the gasification process. These technologies allow for achieving a higher efficiency and, consequently, remarkably reduce the CO₂ emissions when compared to conventional coal-fired solutions [2,3]. The production of gas from coal is a major step in the power generation process; however, the obtained gas may also be used to produce chemicals and liquid fuels [4,5]. The wide range of gas applications justifies the interest in analyzing various ways of improving the gasification process, including the use of catalysts [6–9]. The catalytic gasification is an attractive field of research because it allows for gasifying low reactivity coals at a low temperature and with a high thermal efficiency [10–12]. These benefits are particularly significant in the case of fluidized bed reactors since they operate at relatively low temperatures. Thus, the high reaction rate is essential to

ensure favorable efficiency of the process. Most of the low-rank coals contain components that may influence the rate of the gasification process. These e.g. alkali and alkaline earth metallic (AAEM) species, such as Na, K and Ca as well as a variety of oxygen-containing groups like phenolic and carboxyl groups [13]. The oxygen-containing groups are characterized by ion exchange functionality. Due to this property they dispersed the AAEM species to atomic scales [14] which may catalyze the gasification reaction [15–19]. However, as it is accepted that the activity of AAEM catalysts increases with increasing loading [13], the number of catalytically active species contained in the raw coal may not be sufficient. What is more, some components in the ash react with and deactivate AAEM species [20] (e.g. alumina and silica species in the ash react with potassium and form potassium aluminosilicates that are not catalytically active [21]). To avoid this phenomenon coal is subjected to the enrichment process (removal of mineral matter). However, this operation is energy-intensive. Therefore, increasing the number of active species by catalyst addition may be a more efficient solution. Numerous studies on the catalytic gasification of coal chars with inherent or loaded catalytic species have been carried

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out [22–26]. Research confirmed that the addition of a catalyst allows for obtaining a gas with the desired composition (e.g. a hydrogen-rich gas [27]) as well as improves the rate of the gasification reaction. Nevertheless, the activity of the catalysts levels off or starts to decline at a certain loading. A growth of catalyst concentration tends to cause an increase in the size of catalytic particles through coalescence (sintering) and/or agglomeration. As a result, the activity of the catalysts is decreased. [28,29]. This phenomenon was also confirmed by Cazorla-Amorós et al. [30], who found that a higher calcium content caused easier the coarsening of the catalyst particles. Moreover, Zhang et al. proved that the sample with a higher content of the catalyst was more active at 900 °C, but less active at 1000 °C, than the sample with a lower content of Ca [13]. This observation leads to the conclusion that temperature is a key parameter that causes the decrease in specific activity of the catalyst. The determination of the optimal operating temperature and amount of the catalyst is, therefore, an important issue while planning the process. A precise knowledge of the process kinetics, including kinetic parameters, is, in turn, essential for understanding and modelling gasification on an industrial scale. As proven, the kinetic parameters obtained from different kinetic models may vary, even when the specific coal was gasified under the same conditions [31,32]. Therefore, analysis of the gasification kinetics is necessary to determine the most appropriate model describing the process. Due to the above statements, this work was aimed at analyzing the kinetics of the ‘Janina’ coal gasification process without and with the addition of 1, 3 and 5 wt % of Na, K and Ca cations. The AAEM species were introduced by the wet impregnation method. In contrast to the commonly used approach, in this work samples of coal were subjected to gasification instead of chars prepared in a separate process (ex-situ). In this way, the pyrolysis stage, which has a substantial impact on the properties of char and its reactivity, was taken into account [33–35]. Porada et al. confirmed that the in-situ formed chars, whether derived from lignite or bituminous coal, are more reactive than ex-situ prepared chars (the examinations concerned also the “Janina” coal) [34,36]. Thus, an analysis of the kinetics of the gasification process based on chars formed directly in the reactor is a more reliable approach. The isothermal measurements were performed with the use of unique thermovolumetric equipment. The gasification process was evaluated based on methodology developed by the authors which enables: i) the determination of formation rates and yields of the main gaseous products; ii) the designation of composition of the resulting gas; iii) the calculation of kinetic parameters of the gasification reactions. Moreover, this methodology allows for assessing both effectiveness and selectivity of the catalysts used in the steam gasification process. Based on the results of the measurements, kinetic curves of the gasification products formation (CO, H₂, CO₂, and CH₄) were developed. Further analysis was conducted with respect to the main components of the resulting gas – carbon monoxide and hydrogen. The various amounts of the tested catalysts as well as the operating temperatures were analyzed to select the best process conditions based on the half times and rate constants of the CO and H₂ formation reactions. Finally, the kinetic parameters of the formation reactions of the individual products (CO and H₂) were calculated based on the iso-converional method, the random pore model and the grain model.

2. Material and methodology

2.1. Characteristic of material

Bituminous coal from the Polish mine ‘Janina’, which can be used for the gasification process in fluidized bed reactors, was selected as a feedstock for the research. The results of the proximate and ultimate analyses as well as the composition of ash from the ‘Janina’ coal are summarized in Table 1.

The main components of ash, i.e. SiO₂ and Al₂O₃ inhibit the gasification reactions [37–39]; however, there were also oxides of alkali and alkaline earth metals that catalyze the process. To increase the

Table 1
Characteristic of ‘Janina’ coal and ash composition.

Parameter	Value
Proximate analysis (wt%)	
Moisture - M ^{ad}	8.7
Ash - A ^{ad}	14.0
Volatile Matter - VM ^{daf}	46.1
Fixed Carbon - FC	41.7
Ultimate analysis (wt%)	
Carbon - C ^{daf}	77.8
Hydrogen - H ^{daf}	3.9
Sulfur - S ^{daf}	1.3
Nitrogen - N ^{daf}	1.1
Oxygen - O ^{daf}	15.9
Ash composition (wt%)	
SiO ₂	59.4
Al ₂ O ₃	23.3
Fe ₂ O ₃	8.2
MgO	1.2
CaO	2.2
K ₂ O	2.9
Na ₂ O	2.8

* calculated by difference, ^{daf}-dry and ash free state, ^{ad} – air dried state, ^t- total.

number of catalytically active species contained in the raw coal, the cations of sodium, potassium, and calcium in an amount of 1, 3 or 5 wt % were introduced by the wet impregnation method. The addition of catalysts enabled a comparison of the initially performed non-catalytic coal gasification measurements in an atmosphere of steam with catalytic gasification.

2.2. Methodology of measurement

A detailed description of the laboratory equipment, with the use of which the measurements were carried out was presented in previous publications [40–42], and its schematic diagram is shown in Fig. 1.

1 – reactor, 2 – water pump, 3 – steam generator, 4– mass flow-meter, 5 – coal feeder, 6 – manometer, 7 – cooler, 8– condensate tank, 9 – filter, 10 – pressure regulator, 11– rotameter.

The equipment consists of several basic systems: a high pressure reactor with a heating system, a system for feeding the reactor with the gasifying agent – steam, carrier gas – argon and coal, a system for collecting and purifying the resulting gas and the gas analysis system. A quartz retort equipped with a grate is placed inside the reactor. After stabilizing the conditions of the measurement, coal a sample is introduced onto the grate by the piston feeder. The movement of the piston is caused by opening the inlet valve of the pipe supplying the gas into the chamber of the feeder. The heating of the retort with the sample is carried out by means of an electric oven. The pressure casing of the quartz reactor is composed of a heat-resistant steel blanket, the ends of which are closed with lids equipped with pipes supplying steam and argon as well as pipes carrying away the resulting gas. Mineral wool fitted inside the casing forms the insulation of the oven. The temperature of the coal sample is measured by a sensor of the thermocouple type K which additionally sends impulses to the controller-programmer maintaining the required temperature of the sample. The system for feeding steam and argon to the reaction zone is composed of a micro pump dosing water, a steam generator, compressed gas cylinders with argon and a set of the pressure reducing valves, control/release valves, filters, a pressure gauge and a flow rate regulator. The resulting gas flows to the condenser where water and tar condensate are separated and, subsequently, thoroughly cleaned and dried on the filter. After decompression, the contents of carbon monoxide, carbon dioxide and methane are continuously measured by an analyzer operating on the principle of infrared radiation adsorption. In addition, the content of hydrogen is analyzed with the use of gas chromatographs equipped

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