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mgr inż. Anna Kisiela

Title of the PhD dissertation

THERMAL CONVERSION OF HIGH CARBONACEOUS WASTES

Supervisor: **prof. zw. dr hab. inż. Wiesław Rybak**

Auxiliary supervisor: **dr hab. inż. Wojciech Moroń**

Abstract

The fuel and energy industry belongs to the sector of the economy with the most harmful impact on the natural environment. The processing of raw materials is accompanied by formation of high carbonaceous wastes, including: unburned carbon separated from fly ash, coke from gasification process or coke from oil refining process. Interest in the development of thermal conversion methods of high carbonaceous wastes is dictated mainly by the global increase in electricity demand, the need to improve the efficiency of existing power units and regulations limiting the possibility of their storage. As a consequence of insufficient knowledge about physicochemical properties and ambiguous legal status of high carbonaceous wastes, their definition, recycling concepts and ways of disposal are missing.

With a view to, that unburned carbon separated from fly ash is the most commonly occurring high carbonaceous waste in the Polish industry, for the sake of this work, it was considered to be a representative of the analysed wastes category. Although, among the methods of thermal conversion practised so far, the returning of unburned carbon to the combustion chamber is mainly developed, in the presented work special attention was paid to its gasification and use as an adsorbent/ catalyst for the flue gasses purification. Consideration of adsorption and catalytic reduction as a thermal conversion methods seems justified, for the sake of fact, that these processes like combustion or gasification include heat and mass transfer as a results of heterogeneous reactions occurring on the border between solid and gas phase and homogeneous reactions in the gas phase.

The main aim of this work is to establish properties of high carbonaceous wastes for the purpose of developing their definition and directions of thermal conversion. The scientific goal is an attempt to explain mechanisms of: isothermal gasification of unburned carbon, adsorption of sulphur dioxide and catalytic reduction of nitric oxide in the presence of this material. As part of the research, assessment of the impact of the raw material nature and the process of its combustion in the energy boiler on crystal structure of the carbonaceous matter and determination of the role of the porous structure and the chemical nature of surface on the rates processes were taken.

The thesis postulates that high carbonaceous wastes can be valuable products, that find application in the fuel and energy industry and their structure is significantly conditioned by the raw material nature and physicochemical changes occurring during its heating.

The subject of this work are fractions of unburned carbon, separated from fly ash from pulverized boilers in a heat and power plants at Janikowo and Belchatow. As a reference materials were used samples of petroleum cokes and commercially available activated cokes. To a limited extent, coal and brown coal, which are source fuels, were also investigated. The research was carried out with the use of advanced laboratory facilities, applying techniques of: low temperature sorption of C_6H_6/ N_2/ CO_2, mercury porosimetry, X-ray powder diffraction (XRD), X-ray microanalysis of chemical composition (SEM-EDS), enlarged chemical elemental analysis (ICP-OES), titration and electrochemical analysis, thermogravimetric analysis (TGA), infrared spectroscopy (FTIR),

differential scanning calorimetry (DSC), temperature-programmed desorption of NH_3/ CO_2 (TPD), and research stand for SO_2 adsorption and NO catalytic reduction testing.

Based on the performed tests, it was found that in the case of unburned carbons from brown coal fly ash, conditions prevailing in the energy boiler, lead to the formation of graphite-like structures separated by an amorphous phase, development of the porous structure and formation of acidic and neutral functional groups on their surface. Analysis of the gasification reactivity in CO_2, leads to the conclusion that this property depends on parameters of the porous structure (especially micro- and mesopores), as well as the chemical nature of unburned carbons surface (carbonyl, carboxylic and phenolic groups), wherein these relationships were observed only at temperatures up to 1050 °C. The study of the sulphur dioxide adsorption process reveals that it is associated with the porosity of the bed and the presence of carbon-oxygen groups (phenolic and/ or carbonyl groups). Analysis of the catalytic process of NO reduction proves, that it is controlled by two consecutive stages, including the reaction of ammonia with a phenolic group and the reaction on nitric oxide with a carbonyl group.

The conducted research leads to the conclusion that analysed high carbonaceous wastes have valuable physicochemical properties, enabling their development using chosen thermal conversion methods. Samples of unburned carbons from brown coal fly ash seem particularly interesting, because their characteristic predestine them for development for the purpose of adsorption/ catalytic purification of flue gasses. On the other hand, in the light of the obtained information, in the case of an unburned carbon from coal fly ash, the optimal conversion direction seems to be its gasification. It is worth stressing, that the analyses included in this work allowed to formulate the definition of high carbonaceous wastes, which can contribute to classify these materials as products rather than wastes.

Anna Kisiela