POTENTIAL CORROSION CHALLENGES IN THE EXTRACTION OF HYDROGEN AND METHANE BY PYROLYSIS OF CARBONACEOUS RAW MATERIALS

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This article is devoted to the adaptation of research results on the extraction of combustible gases from carbonaceous raw materials by pyrolysis, paying special attention to the identification and quantification of the formation of corrosive gases, as well as the need to develop effective corrosion protection measures. The goal of this study is to provide further information about composition of the gas phase formed during the pyrolysis of carbonaceous raw materials, emphasizing the importance of integrating anti-corrosion measures into the processes of hydrogen and methane production from coal wastes.

Keywords: carbonaceous raw materials, combustible gases, pyrolysis, hydrogen, methane, corrosive gases

Introduction. In modern world, which is striving for decarbonization and increased energy security, hydrogen is emerging as a key energy carrier of the future [1]. Its unique properties – high energy density, environmental friendliness during combustion (only water is produced), and the possibility of using it in power engineering and road transport – make it a priority in the global energy strategy [2]. In addition to the usual production of hydrogen from natural gas, some technologies have been developed for its extraction from carbonaceous raw materials [3]. This will not only solve the problem of its processing, but will also contribute to energy security and decarbonization of the national economy.

Despite the technological advantages of thermochemical processing of carbonaceous raw materials, this process is accompanied by significant release of corrosively inactive gases (methane) and extremely aggressive corrosive gases, which pose significant threats to the integrity and safety of industrial equipment operation [4].

Among these products, carbon dioxide (CO_2) and hydrogen sulfide (H_2S) stand out in particular. These gases pose a serious threat to the integrity and durability of process equipment, causing various types of corrosion, which leads to significant economic losses, increased risks of accidents and environmental pollution.

Carbon dioxide is one of the main products of the thermochemical destruction of carbonaceous raw materials. Although CO_2 itself is not aggressive, in the presence of moisture it forms carbonic acid H_2CO_3. This acid lowers the pH of the solution, leading to the so-called “carbonic acid corrosion”. It is characterized by uniform dissolution of the metal or the formation of local corrosion centers, especially in places of moisture condensation. At high temperatures, which are characteristic of pyrolysis, CO_2 can also interact with metals, forming carbonates, which changes the protective properties of oxide films.

H_2S is a much more dangerous corrosive agent, especially for carbon and low-alloy steels. Its presence in the gas phase, even in small concentrations, can lead to "acid corrosion" or "sulfur corrosion". The interaction of H_2S with metals leads to the formation of iron sulfides, which can form unstable, peeling films or, conversely, create dense protective layers, depending on the conditions. However, the main danger of H_2S lies in its ability to cause [5]:

- Hydrogen Embrittlement: atomic hydrogen, generated by corrosion reactions on the surface of a metal, penetrates into its crystal lattice, causing a decrease in ductility and an increase in brittleness.
- Sulfide Stress Cracking: the combined action of hydrogen sulfide, tensile stresses, and hydrogen embrittlement leads to sudden brittle failure of the metal without noticeable deformation; this is especially critical for pipelines and pressure vessels.

Depending on the specific composition of the coal waste, the pyrolysis gas may also contain other corrosive impurities, such as chlorides, ammonia, as well as various organic compounds that can form aggressive acids when interacting with water.

Methods. A binary mixture of coal and rock in certain ratios with different fractional composition was taken as a solid carbonaceous raw material. Sapropelite and waste from coal enrichment (sludge) of the Chervonogradska mine of the Lviv-Volyn basin were selected as the coal and rock components of the raw material, respectively. Laboratory studies on the pyrolysis of a mixture of sludge and coal (67% sludge to 33% coal) at a final temperature of 750°C revealed a significant dependence of the composition of gas products on the technological parameters of pyrolysis. The gas phase analysis presented in the table below demonstrates the content of key components that determine corrosion activity, as well as combustible gases (H_2 and CH_4).

Results and discussion. The gas phase analysis, shown in the Fig. 1, demonstrates the amount of hydrogen and methane, when heated to a temperature of 750°C during 20, 25, 40 minutes and held for 20 minutes.

During the thermal treatment of carbonaceous raw materials at a temperature of 750°C, it was found that the total yield of combustible gases significantly depends on both the duration of heating and the size of the fraction.

The analysis of Fig. 1a showed that for a fixed time of 20 min and held for 20 min, the yield of combustible gases increases with increasing fraction size: from 69.2% (0.1 mm) to 71.7% (1.5 mm), which is 10-11% more than under other time conditions of heating the research material.

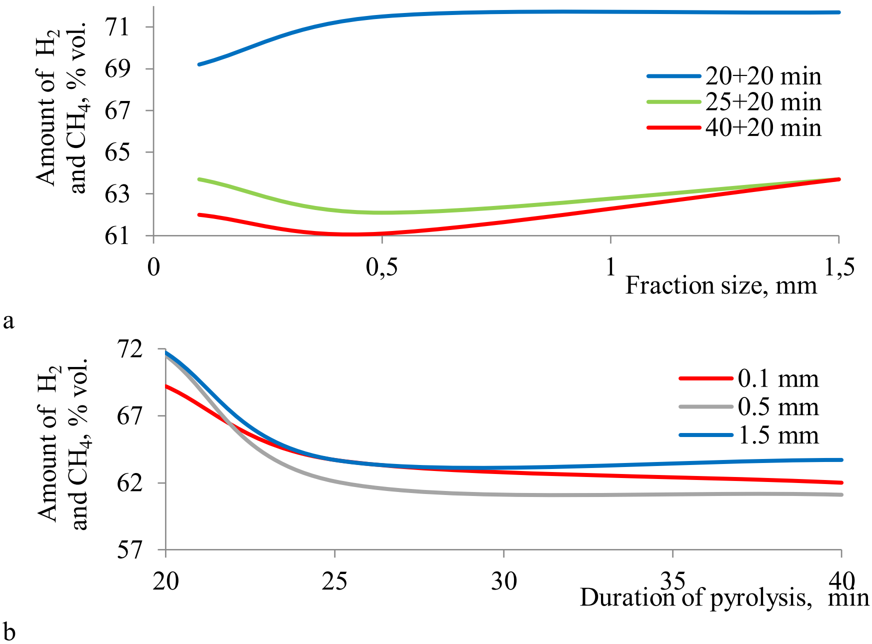

Fig. 1. Dependence of methane and hydrogen yield on fractional size (a) and pyrolysis time (b).

The highest yield was observed at 20-minute heating regardless of the fraction size, after which it gradually decreased. For example, for the 0.1 mm fraction, the yield decreased from 69.2% (at 20 min) to 62.0% (at 40 min), and for the 0.5 mm fraction – from 71.5% to 61.1%, respectively. The smallest decrease was recorded in the 1.5 mm fraction, where after a decrease to 63.7% at 25 min, no further changes were observed. Thus, the optimal conditions for maximum extraction of combustible components are heating for 20 minutes using larger raw material fractions.

According to the previously presented studies, let's consider the yield of corrosive gases, namely CO_2 and H_2S (Table 1). Analysis of pyrolysis of carbonaceous raw materials at a temperature of 750°C revealed clear dependences of CO_2 and H_2S yield on fraction size and duration.

Table 1. Impact of fraction size and duration of pyrolysis on CO_2 yield

Duration of pyrolysis, min	20	25	40	20	25	40	20	25	40
Fraction size, mm	0.1	0.1	0.1	0.5	0.5	0.5	1.5	1.5	1.5
Amount of CO_2 and H_2S, % vol.	9.2	8.0	8.6	8.8	8.5	8.4	8.0	9.8	9.8

For the fine fraction (0.1 mm), the corrosive gases output initially decreased (from 9.2% to 8.0% at 20–25 minutes), then increased slightly (8.6% at

40 minutes), indicating more complex decarboxylation processes. The medium fraction (0.5 mm) showed a gradual decrease in corrosive gases (from 8.8% to 8.4%) with increasing time, which may indicate a more complete release or stabilization. For the coarse fraction (1.5 mm), the corrosive gases output increased significantly from 8.0% to 9.8% between 20 and 25 minutes, remaining stable thereafter. This highlights the need for longer heating for larger particles.

Conclusions. Laboratory studies have confirmed the technical feasibility of efficiently extraction hydrogen and methane from carbonaceous raw material (sludge-coal) by pyrolysis at 750°C. It was found that both the fraction size and duration of pyrolysis have a significant impact on the total hydrogen and methane yield and the quantitative composition of the gaseous products, in particular the carbon dioxide content. Even under our conditions for obtaining combustible gases, the CO_2 and H_2S concentration remains high (8.0%–8.8%). This emphasizes the need for mandatory gas purification from CO_2 to prevent carbonic acid corrosion, sulfide stress corrosion cracking and hydrogen cracking in subsequent processing and transportation stages, especially in the presence of moisture.

Thus, the desire for maximum combustible gas yield does not exclude, but rather emphasizes the urgent need for effective corrosion protection measures. High CO_2 concentrations and the likely formation of H_2S require the integration of gas cleaning systems and the selection of corrosion-resistant materials at all technological stages. For the successful industrial implementation of the technology of obtaining combustible gases from carbonaceous raw materials by pyrolysis, it is necessary to develop and integrate comprehensive corrosion protection measures. This will ensure the durability of the equipment, operational safety and cost-effectiveness of the process.

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