Study of technological modes of formaldehyde-containing solid waste pyrolysis

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Abstract. The technological modes of medium-temperature non-oxidative pyrolysis of formaldehyde-containing solid waste are studied, using the example of particle boards waste. During the study, the moisture content of formaldehyde-containing waste of particle boards and the preheating temperature of the pyrolysis chamber varied in intervals of 5...35 % and 400...700 °C respectively. It is established that the most rational value of the preheating temperature of the pyrolysis chamber is in the interval of 550...600 °C. It was found that temperatures more 600 °C do not lead to a significant decrease in the duration of the pyrolysis process of formaldehyde-containing waste of particle boards, and temperatures less 550 °C lead to a significant increase in the duration of the pyrolysis process. It is shown that the moisture content of the waste of particle boards has a great influence on the duration of the pyrolysis process, when the waste moisture content is more than 15%, the total pyrolysis process time is significantly increased.

1. Introduction

Composite materials with formaldehyde-containing resins are used are widespread in the modern national economy, in particular mechanical engineering, instrumentation and construction. The use of these materials has a number of advantages regarding the manufacturability of manufacturing and processing of products, and also their cost, which in the future will lead to an even greater increase in the production of such materials. At the same time, the volume of solid waste generated in the production and processing of products made of formaldehyde-containing composites inevitably increases. The use of these materials has a number of advantages regarding the manufacturability of manufacturing and processing of products, and also their cost, which in the future will lead to an even greater increase in the production of such materials. Therefore, an actual problem is to develop safe, from an environmental point of view, methods of utilization or processing of these types of waste.

One of the ways to solve this problem is the use of medium-temperature oxidation-free pyrolysis [1-3]. This process represents thermal decomposition of organic compounds without access of the oxidant (oxygen) passing at relatively low temperatures (400...750 °C) compared to the combustion processes. At
the same time, pyrolysis products (both solid and gaseous) after collection can be used in various sectors of the national economy [4-6].

The technology of medium-temperature pyrolysis is known and widely used, but different materials require various technological modes of process. The main parameters determining the velocity of all reactions and the necessary conditions for their current, which can be operated during the pyrolysis process are: temperature in the pyrolysis chamber before loading of waste, decomposition time, moisture content and weight of solid waste.

One of the most common solid waste containing formaldehyde resins is waste from the production of particle boards (chipboards), in which the content of formaldehyde resins can reach 2.5 %. In the pyrolysis process of particle board waste parallel decomposition reactions occur phenol formaldehyde resin and timber components. When pyrolysis of phenol formaldehyde resins is initially destroyed to benzene, which is then destroyed to the simplest alkanes. The process of thermal decomposition of phenol formaldehyde resins begins at a temperature of about 400 °C. At the same time, there is a selection of gas (≈1.3 %), liquid products (≈13.2 %) and coke-ash residue (≈85.5 %). In common case the decomposition of phenol formaldehyde resin is described by the following reaction [7, 8]:

\[
\text{C}_6\text{H}_5\text{(OH)}-\text{CH}_2-\xrightarrow{T} \text{CH}_4+\text{CO}+\text{C}_n\text{H}_m+\text{H}_2.
\]

Pyrolysis of timber produces gaseous products including carbon dioxide ≈45...55% and oxide ≈28...32%, hydrogen ≈1...2 %, methane ≈8...21 % and other hydrocarbons ≈1.5...3.0 %, as well as ash residue consisting mainly of salts of alkaline earth metals [5].

Accurately describe a mechanism of the pyrolysis process is quite difficult, this is due to a fact that pyrolysis is complex of successive and parallel chemical reactions, including many transitions and interactions of some components with others. Depending on a number of carbon atoms in molecule, the number of possible hydrocarbon decay directions also increases [4, 9, 10].

To establish the effect of temperature in the pyrolysis chamber before loading formaldehyde-containing solid waste and their moisture content on the total pyrolysis time, experimental studies were carried out.

2. Research methods

The study was carried out on an experimental thermal decomposition device, shown in figure 1. The device consisted of the following modules: chamber of pyrolysis – 1, afterburning unit of light hydrocarbons – 2, gas distribution system – 3, outgoing gases cooling unit – 4, unit of rough cleaning of outgoing gases – 5 and unit of plasma cleaning of outgoing gases – 6 [1].

Technological process provides for sequential gasification of solid waste without oxygen access in the chamber of pyrolysis, afterburning of coke residue and purification of outgoing gases from harmful substances and dust to the level of maximum permissible concentrations according to environmental standards. Cleaning of gases is carried out by dry, wet methods and using a plasma unit. With the dry cleaning method, large particles of dust and ash contained in gases are eliminated. With the wet cleaning method, smaller solid dust particles (less than 5 μm) are eliminated, which cannot be removed using the dry cleaning method. Using plasma processing gases in the final purification step allows to produce electro filtered gases with the removal of fine particles and destruction of persistent chemical compounds under action of low-temperature plasma [1].

To assess the environmental safety of the pyrolysis process, concentration of harmful substances in the outgoing gas was measured. To assess environmental safety of the pyrolysis process, the concentration of harmful substances in the exhaust gas was measured using an automatic analyzer GANK-4. The ash residue formed after pyrolysis was subjected to biological analysis on Daphnia (Daphnia magna Straus),
freshwater algae (Scenedesmus quadricauda) and changes of intensity of bacterial luminescence (Ecolum test system) to determine hazard class of waste. Sampling and analysis, as well as preparation of the analysis was carried out in according requirements of conventional techniques [1].

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To determine rational modes of the pyrolysis process (time, preheating temperature, decomposition and moisture content) of formaldehyde-containing waste of particle boards were prepared samples with a starting weight of 20 kg and a moisture content of 5...35 % in increments of 5 %. Aim of study was to determine the pyrolysis time of formaldehyde-containing particle boards waste depending on the preheating temperature of the pyrolysis chamber, as well as the moisture content of the waste. In the course of the study, temperature and vacuum were recorded in the pyrolysis chamber, at intervals of 5 minutes.

A series of tests was carried out to estimate the pyrolysis time depending on the initial heating temperature of the pyrolysis chamber. The preheating temperature of the pyrolysis chamber was 400; 500;
550; 600; 650 and 700 °C (maximum temperature is limited by the technical capabilities of the installation), the initial moisture content of the waste was 5%.

3. Results
Graphs of temperature and vacuum changes in the pyrolysis chamber depending on the preheating temperature are shown in figures 2 and 3.

![Graphs of change of temperature (a) and vacuum (b) in the pyrolysis chamber for preheating temperatures 400, 500 and 550°C.](image)

**Figure 2.** Graphs of change of temperature (a) and vacuum (b) in the pyrolysis chamber for preheating temperatures 400, 500 and 550°C.

It is established that the pyrolysis process can be divided into three stages: drying, thermal decomposition and completion of pyrolysis. At the drying stage, the heated waste products are heated, contained in them moisture and light hydrocarbons (alkanes, alkenes) are evaporated. This stage is characterized by a slight drop in temperature in the pyrolysis chamber. When loading the formaldehyde-containing waste of particle boards into the pyrolysis chamber preheated at 650 °C a duration of the drying stage took about 10 minutes.

The thermal decomposition stage is characterized by abundant gas emission and temperature increase in the pyrolysis chamber. At the preheating temperature of the pyrolysis chamber of 650 °C, this stage begins at the 8th minute of the pyrolysis process and ends at the 53rd minute, i.e. the duration of this stage is about 45 minutes.

![Graphs of change of temperature (a) and vacuum (b) in the pyrolysis chamber for preheating temperatures 600, 650 and 700°C.](image)

**Figure 3.** Graphs of change of temperature (a) and vacuum (b) in the pyrolysis chamber for preheating temperatures 600, 650 and 700°C.
The stage of completion of pyrolysis is characterized by a stable decrease in temperature in the pyrolysis chamber, as well as end of gas emission and stabilization of the vacuum.

Total time of the pyrolysis process with sufficient accuracy can be considered as sum of the drying time and the time of thermal decomposition, which is confirmed by the results of biological examination of the ash residue.

It is revealed that one of factors affecting the total time of the pyrolysis process is the initial moisture content of the waste. Figure 4 presents data on the time of the stages of drying and thermal decomposition in the pyrolysis process of formaldehyde-containing waste of particle boards weighing 20 kg at the preheating temperature of the pyrolysis chamber of 650 °C and the initial moisture content of the waste 5...35 %. Analogous data were obtained for other preheating temperatures of the pyrolysis chamber.

From the graph shown in figure 4 it can be seen that with increasing moisture content of waste increases the time of the drying stage, and therefore the total time of pyrolysis process.

4. Discussion

The graphs presented in figures 2 and 3 show that at the preheating temperatures of the pyrolysis chamber from 400 to 550 °C, the total time of pyrolysis process is longer than at higher temperatures, since more time is required for heating and drying the waste.

At the preheating temperatures of the pyrolysis chamber from 650 to 700°C, there is no significant reduction in the pyrolysis time, but the time of preliminary heating of the pyrolysis chamber increases significantly (for the considered experimental installation by about 30%), which negatively affects the technical and economic indicators of the technological process. External heating of the pyrolysis chamber at the experimental device is carried out by diesel burners, so an increase in the preheating temperature of the chamber leads to an increase in the consumption of diesel fuel, especially at an ambient temperature of less than 5 °C.

The temperature drop at the initial stage of pyrolysis (immediately after loading) is due to the absorption of part of the thermal energy of the loaded waste, going to their heating and evaporation of moisture, as well as the temperature difference in the pyrolysis chamber and loading unit. At same time, when the preheating temperature of the pyrolysis chamber increases, a faster decrease in the vacuum is observed (figure 2 (b) and 3 (b)), which can be explained by accelerated evaporation of moisture and light
hydrocarbons from the waste. This is especially noticeable at the preheating temperature of the pyrolysis chamber up to 700 °C.

The increase in temperature in the pyrolysis chamber at the stage of thermal decomposition can be explained by additional heating of the pyrolysis chamber from combustion of light hydrocarbons in the afterburning chamber. At same time, higher the preheating temperature of the pyrolysis chamber, the less influence the heat coming from the afterburning chamber has on temperature fluctuation. This is especially noticeable on temperature change curves in the pyrolysis chamber for preheating temperatures of 400 and 500°C (figure 2 (a)). Approximately from the 25th to the 65th minute, an increase in temperature in the pyrolysis chamber by 40°C relative to the initial value can be observed.

An important factor determining the duration of the pyrolysis process is moisture content of the waste. It is shown that with an increase in the moisture content of the waste, there is an increase in the duration of the drying stage and practically does not change the time of the thermal decomposition stage. When the initial moisture content of particle boards waste is more than 20%, time spent on drying is more than half the duration of thermal decomposition, which negatively affects the technical and economic indicators of the entire process of pyrolysis.

5. Conclusion
The obtained results allow us to draw the following conclusions and recommendations for the implementation of the pyrolysis process of formaldehyde-containing waste:

- the most rational preheating temperature of the pyrolysis chamber is 550...600 °C, at these temperatures the process proceeds stably, predictably, with minimal energy costs for heating the device and maintaining the process;
- to ensure the economic feasibility of pyrolysis, it is recommended to use waste of particle boards with a moisture content of not more than 15%, waste with greater moisture content is recommended to dry beforehand.

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