Investigation of solid organic waste processing by oxidative pyrolysis

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Abstract. A thermal analysis of a mixture of municipal solid waste (MSW) of the average morphological composition and its individual components was carried out in order to develop ways to improve the efficiency of its utilization for energy production in thermal reactors. Experimental studies were performed on a synchronous thermal analyzer NETZSCH STA 449 F3 Jupiter combined with a quadrupole mass spectrometer QMC 403. Based on the results of the experiments, the temperature ranges of the pyrolysis process were determined as well as the rate of decrease of the mass of the sample of solid waste during the drying and oxidative pyrolysis processes, the thermal effects accompanying these processes, as well as the composition and volumes of gases produced during oxidative pyrolysis of solid waste and its components in an atmosphere with oxygen content of 1%, 5%, and 10%. On the basis of experimental data the dependences of the yield of gas on the moisture content of MSW were obtained under different pyrolysis conditions under which a gas of various calorific values was produced.

1. Introduction

One of the focal points of Russia’s energy policy is the use of non-conventional renewable power sources. Such sources include solid organic wastes including municipal solid waste (MSW). Utilization of this feedstock for energy production makes it possible to solve a number of problems, such as production of gaseous fuel, reducing harmful impact on the environment, rehabilitation of land cleared of waste deposit and other.

Solid waste conversion technologies utilize various configurations of pyrolysis plants [1], for example shaft furnaces, in which the pyrolysis process is accompanied by a slight oxygen ingress (oxidative pyrolysis). The method of oxidative pyrolysis with the subsequent burning of pyrolysis gas is universal and does not depend on the fractional composition and phase state of the waste, its moisture and ash content. At the same time, the combustion products of pyrolysis gas are less polluted with ash and soot compared to the direct combustion of solid waste, thus the gas purification is greatly simplified.

To increase the efficiency of solid waste treatment by oxidative pyrolysis this process needs to be experimentally studied in order to assess the influence of a number of parameters (moisture content of...
the feedstock, the solid waste composition, the increase of oxygen content in atmosphere, etc.) on the yield and composition of pyrolysis gases [2,3,4].

Conducting a thermal analysis of a mixture of municipal solid waste with an average morphological composition and its individual components for developing ways to improve the efficiency of its energy use in heat engineering.

2. Materials and methods of research

The following methods of thermal analysis were used to study the process of low-oxidation pyrolysis of solid waste:

- thermogravimetric analysis (TG analysis) [5]. In the course of TG analysis a change in the mass of the sample under study was continuously recorded with a change in its temperature;
- differential scanning calorimetry (DSC). In the course of DSC thermal effects were continuously recorded, which accompanied phase and chemical transformations of the sample during its heating;
- mass spectral analysis of gas mixture (MSA).

Studies of low-oxidation pyrolysis were carried out for samples of a mixture of solid domestic waste of an average morphological composition (43 wt.% paper, 42% food waste, 7.5% textile waste and 7.5% polymer film) [6] and individual components of the mixture in the atmosphere with oxygen content of 1%, 5% and 10%. Experimental studies were performed using a complex of synchronous thermal analysis unit STA 449 F3 Jupiter, a quadrupole mass spectrometer QMS 403 C Aeolos and a pulse thermal analysis unit PulseTA.

The experimental research of low-oxidation pyrolysis was carried out in the following sequence. A sample of municipal solid waste was loaded into a platinum crucible that was placed on the microbalance in the first cell of a differential scanning DSC sensor. A reference sample was placed in the second cell, a crucible without a sample (standard for comparison). A double measuring cell allows to compensate for extraneous effects (processes associated with heat release or heat absorption) on the result of measurement. Heat was supplied from the electric heater of the chamber, inside which the samples were placed. The weight of the sample varied from 3 to 15 mg. The temperature of the test sample was measured by differential thermocouples located on the lower surface of the crucible, which were connected to the secondary instrument. Heating was performed in an atmosphere of inert gas (argon), enriched in oxygen (1%, 5% or 10% by volume) from 20°C to 900°C at a rate of 5°C/min.

In the course of the experiment STA 449 F3 Jupiter continuously recorded the loss of the mass of the solid waste sample during heating of the same (TG curve), the sample temperature and the DSC signal. The ultimate sensitivity of the instrument by mass was 0.1 µg, and 0.001°C by temperature.

The qualitative composition of the pyrolysis products was determined by the quadrupole mass spectrometer QMS 403C Aéolos by finding the partial pressure of the individual components of the gas mixture.

3. The results of experiment and discussion

The results of thermal analysis of a sample of a mixture of municipal solid waste consisting of paper, textile, food waste and polymer film in the process of oxidative pyrolysis in an atmosphere with oxygen content of 1% are shown in Fig.1 as DSC, TG and DTG curves.

The results of the TG analysis (TG curve) demonstrated that the curve of the sample mass change in the course of heating can be divided into several characteristic intervals. The first temperature interval from 20°C to 220°C is characterized by a slight change of the mass of the sample (0.5% to 8%) due to evaporation of physical and inherent moisture from the porous surface of the material. With a further increase in temperature to 320-330°C, a fairly rapid decrease in mass occurs, due to thermal decomposition of the substance and intensive release of volatile compounds. When the temperature reaches 330°C, the mass change curve (line 1 in Fig.1) has a pronounced bending, which indicates a decrease in the rate of escape of volatile compounds. At a temperature of 490°C there is a sharp drop
in a rate of decrease in the mass of the substance, which indicates a slowdown in the thermal decomposition of solid waste. At a temperature of 540°C, the yield of volatile substances ends.

Figure 1. 1- TG curve, 2- DSC curve, 3- DTG curve for solid waste samples in atmosphere with oxygen content of 1%.

The results of the differential scanning calorimetry (line 2 in Fig.1) show that at a temperature up to 220°C endothermic processes occur in the samples under study associated with evaporation of moisture. With further temperature increase, exothermic processes occur in the samples.

The DSC curve (line 2 in Fig.1) has two distinct exothermic peaks at temperatures of 330°C and 470°C. Then the function starts to decrease sharply. This clearly shows that the intensity of exothermic processes decreases.

The results of the differential thermogravimetric analysis (line 3 in Fig.1) show that the maximum loss of the sample mass occurs at temperatures of 330°C and 470°C, which corresponds to the maximum yield of the gas phase during the process of pyrolysis of solid waste.

Similar experiments were performed in the environment with oxygen content of 5% and 10%, which intensified the pyrolysis process. The results of the experiments are shown in Fig.2 and Fig.3 as DSC, TG and DTG curves.

The results of thermal analysis of the process of pyrolysis of a mixture of municipal solid waste (MSW) and its individual components in environment with an oxygen content of 1%, 5% and 10% are shown in Table 1.

| Substance       | Temperature of beginning and end of the process of pyrolysis, °C | Maximum rate of weight loss, %/min. | Thermal effect of pyrolysis, J/g |
|-----------------|---------------------------------------------------------------|------------------------------------|---------------------------------|
| Mixture of MSW  | 225÷540 220÷560 215÷560                                     | 4.27 4.72 5.89                     | 4816 5847 6884                  |
| Paper           | 245÷492 220÷490 245÷488                                      | 6.06 6.3 6.61                      | 4951 5710 6624                  |
| Potatoes        | 225÷540 220÷550 215÷550                                      | 5.29 6 6.75                        | 3672 5084 6696                  |
| Polyethylene    | 340÷540 300÷550 280÷550                                      | 6.67 6.2 5.23                      | 3954 6320 8685                  |
| Textile         | 240÷500 240÷500 240÷490                                      | 10.4 9.5 8.68                      | 4376 5051 5925                  |

Table 1. The results of thermal analysis of MSW and its components.
The qualitative composition of the pyrolysis gas was obtained as a result of processing of signals of the mass spectrometer (the ion current versus temperature dependence) distributed over mass numbers (Fig.2). Fig.2 shows the results of measurements during pyrolysis of MSW in an environment with oxygen content of 1%. Similar experiments were performed for pyrolysis of MSW in an environment with oxygen content of 5% and 10%.

![Figure 2. a) Gases with a large mass spectrometer signal](image)

![Figure 2. b) Gases with a small mass spectrometer signal](image)

Mass spectrum of the gas produced during pyrolysis of solid waste in an atmosphere containing 1% oxygen. (The numbers at the curves denote the mass numbers)

For identification of the pyrolysis gas components we used the data bases of mass spectrometers NIST that contain information about mass spectra of substances.

Analysis of Fig.4 shows that the main components of pyrolysis gas are: H2 (2), CH4 (16), H2O (18), CO (28), CO2 (44). The contribution of other components with mass numbers 12, 13, 14, 15, 17 and 46 to the mass component of the main components was determined by comparison with the results presented in the data bases of mass spectrometers NIST.

Table 2 shows the mass spectrum data of the main components of the gas mixture in the following form: experiment / base value of the NIST mass spectra.
Table 2. Comparison of the experimental date with data base NIST.

| Mass number | 2   | 12  | 13  | 14  | 15  | 16  | 17  | 18  | 28  | 44  | 46  |
|-------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| H₂          | 100 | -   | -   | -   | -   | -   | -   | -   | -   | -   | -   |
| CH₄         | -   | 2.8/3 | 6.8/8 | 17/20 | 80/87 | 100 | -   | -   | -   | -   | -   |
| CO          | -   | 4.5/5 | -   | -   | -   | 0.8/1.1 | -   | -   | 100 | -   | -   |
| H₂O         | -   | 7.9/9 | -   | -   | -   | 0.7/1 | 20/23 | 100 | -   | -   | -   |
| CO₂         | -   | -   | -   | -   | -   | -   | -   | 8.8/9 | -   | 10/13 | 100 | 0.2/0.5 |

The quantitative composition of the pyrolysis gas was determined by the internal standard method [7], following which a signal intensity of compounds under investigation is compared to the signal of a standard substance (calibrating gas), and the method proposed by A.N.Kozlov and A.V.Keiko [8] was used to calculate the mass fractions of the pyrolysis gas components.

In accordance with the above method the amount of substance of i-th component of the pyrolysis gas is determined by formula:

\[ n_i = \frac{S_i}{k_i^0} \]  

where: \( S_i \) is a peak area under the curve of ion current of the i-th component (CO, CH₄, H₂, CO₂, H₂O) of the pyrolysis gas (Fig.3), \( A \cdot s \); \( k_i^0 \) is a calibration factor of the i-th component of the pyrolysis gas.

The peak area under the curve of ion current of the i-th component of the pyrolysis gas:

\[ S_i = \int_{t_i}^{t_f} I_i d\tau \]  

where: \( I \) – ion current, \( A \); \( \tau \) - time, s.

The calibration factor of the i-th component of the pyrolysis gas is calculated by formula [9]:

\[ k_i^0 = \frac{S_i^0 \cdot 10^4 \cdot Rmu \cdot T^o}{P \cdot V^o \cdot x_i^0} \]  

where \( i \) – component (CO, CH₄, H₂, CO₂, H₂O) index; \( S_i^0 \) – peak area under the curve of ion current for calibrating gas, \( A \cdot s \); \( Rmu \) – universal gas constant, J/mole·K; \( V^o \) – calibration gas volume, \( m³ \); \( P^o \) – instrument inlet gas pressure, Pa; \( T^o \) – instrument inlet gas temperature, °C; \( x_i^0 \) – component concentration in the calibration gas, %.

Table 3 shows data on the qualitative and quantitative composition of the gas released during oxidative pyrolysis in the atmosphere with oxygen content of 1%, 5% and 10%.

Table 3. Comparison of the experimental date with data base NIST

| MSW       | Paper   | Potatoes | Textile | Polyethylene |
|-----------|---------|----------|---------|--------------|
| O₂        | 1%      | 5%       | 10%     | 1%           | 5%           | 10%       | 1%      | 5%     | 10%     |
| CH₄       | 22.2    | 18.68    | 11.93   | 20.7         | 16.24        | 11         | 22.94   | 20.45  | 14      | 16.24   | 11.4    | 7.2      | 21.82   | 14.23   | 9.32    |
| CO        | 41.25   | 36.4     | 32.91   | 52.51        | 48.1         | 44.59      | 32.52   | 26.1    | 22.55   | 31.87   | 35.82   | 39.4     | 26.1    | 45.05   | 34.93   |
| H₂O       | 18.9    | 23.12    | 26.66   | 13.84        | 16.96        | 19.64      | 24.34   | 27.91   | 32.34   | 20.58   | 23.29   | 26.98    | 20.28   | 25.67   | 29.75   |
| CO₂       | 17.21   | 21.74    | 28.47   | 12.9         | 18.66        | 24.75      | 22.11   | 25.5    | 31.08   | 20.48   | 27.03   | 29.94    | 12.78   | 20.67   | 30.93   |
| H₂        | 0.14    | 0.06     | 0.03    | 0.05         | 0.04         | 0.02       | 0.04    | 0.04    | 0.03    | 0.04    | 0.03    | 0.07     | 0.03    | 0.01    |

According to the results of the analysis it was found out that the content of other components of the pyrolysis gas does not exceed 0.5%.

Calculation of the calorific value of pyrolysis gas is based on the additivity concept:

\[ Q'_o = \sum_{i=1}^{n} Q_{CH₄} \cdot g_{CH₄} + Q_{CO} \cdot g_{CO} + Q_{H₂} \cdot g_{H₂} \]  

where \( Q_{CH₄}, Q_{CO}, Q_{H₂} \) – lower calorific value of respectively methane, carbon monoxide and hydrogen, J/kg; \( g_{CH₄}, g_{CO}, g_{H₂} \) – mass fractions of methane, carbon monoxide and hydrogen, respectively.
The results of calculation of the calorific value of the combustible gas produced during oxidative pyrolysis in an atmosphere with oxygen content of 1%, 5% and 10% are tabulated below in Table 4.

Table 4. Comparison of the experimental date with data base NIST.

| Oxygen content | Q, MJ/kg |
|----------------|----------|
| 1%             | 16.73    |
| 5%             | 13.74    |
| 10%            | 10.00    |
| MSW            | 16.43    |
| Paper          | 13.87    |
| Potatoes       | 14.22    |
| Textile        | 11.16    |
| Polyethylene   | 12.56    |
|                | 8.30     |

From the analysis of the data in Table 3 and Table 4 one can see that the main combustible components of the pyrolysis gas are carbon monoxide and methane. The percentage of hydrogen in the pyrolysis gas is low (less than 1%).

During the oxidative pyrolysis of solid waste in and atmosphere with oxygen content of 1%, the combustible part of the pyrolysis gas accounts for 66% (by mass), the remaining 34% is ballast. As the oxygen content of the atmosphere increases to 10%, the combustible component decreases to 45%, and the ballast part increases to 55%.

The calorific value of the pyrolysis gas decreases from 16.73 MJ/kg in oxidative pyrolysis when oxygen content in the atmosphere is 1% to 10.00 MJ/kg in oxidative pyrolysis when oxygen content in the atmosphere is 10%.

Using the experimental data, the heat balance calculation of the thermal reactor (shaft furnace) was made and the yield of pyrolysis gas was determined.

The heat balance calculation of the furnace was made for three regimes of oxidative pyrolysis of municipal solid waste with oxygen content of atmosphere of 1%, 5% and 10%.

Fig.3 shows the graphical dependences of the gas yield on the moisture content of the solid waste under various pyrolysis regimes, during which a gas of different calorific value is produced (Table 4).

![Figure 3](image)
It can be seen in the Figure 3 that an increase in oxygen content of the atmosphere contributes to an increase in the yield of the pyrolysis gas. In this case, it becomes possible to increase the initial moisture content of solid waste that is loaded into the reactor. Thus, in the process of pure pyrolysis, the initial moisture content of feedstock should not exceed 42%, but at oxidative pyrolysis in atmosphere with oxygen content of 10% it can reach 53%. In general, in all the regimes under consideration, there is a tendency for a decrease in gas yield with an increase in the moisture content of solid waste.

4. Conclusions

1. The thermal analysis of the process of oxidative pyrolysis of a mixture of municipal solid waste of an average morphological composition and its individual components was carried out for environment with oxygen content of 1%, 5% and 10%, and the data on volatiles yield were obtained as well as data on maximum rate of mass loss and temperature of peak heat release.

2. The composition and volumes of gases produced during the oxidative pyrolysis of a mixture of municipal solid waste of an average morphological composition and its individual components were experimentally.

3. Dependences of the gas yield on the moisture content of the municipal solid waste were determined under various pyrolysis regimes, during which a gas of various calorific value was produced.

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