TGA and DTA of Composite Fuel and its Components

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Abstract – The composite fuel and its components are studied by TGA and DTA methods: the milled peat residue after extraction of humus substances in an alkaline medium and the corn harvest residues. The temperature range and the rate of dehydration, thermal decomposition of organic and mineral substances, moisture and ash content are determined. Thermal effects of thermal decomposition of organic substances in fuel and components are estimated.

Keywords – composite fuel, peat, extraction, humus substances, corn harvest residues.

Introduction

High prices for fossil fuels and the course for decarbonization encourage the acceleration of production of alternative fuels and peat extraction. In Ukraine, peat reserves are of industrial importance. Geological reserves amount to 2.04 billion tons, which is equivalent to 660 billion m^3 of natural gas [1].

In addition to energy use, peat is widely used as a fertilizer and can be a raw material for the production of physiologically active substances based on humus substances (GS). They are used in crop production, horticulture, animal husbandry and feed production [2, 3]. The need to increase the productivity of agriculture and the use of peat as fuel raises the question of the integrated use of peat.

The IET of NAS of Ukraine proposed a technology according to which a certain part of the peat extracted for energy needs is used for the production of GS extract. And the peat residue after GS extraction is mixed with the original peat and directed to the production of fuel in the technological line of the peat briquette plant.

The use of peat residue as a fuel requires increasing its calorific value and reducing the danger of formation of new phases during combustion, which can be solved by production of composite fuel using components with a higher calorific value and low ash content [4].

The production of composite fuels using peat after extraction of GS from it requires the study of thermal decomposition of both the fuel and its components.

Materials and methods

Samples of milled peat residue (MPR) after extraction of humus substances, corn harvest residues (CHR) and composite fuel from a mixture of MPR and CHR in the ratio (1:1) by mass were subjected to thermal analysis. The extraction was carried out at 70 °C in an alkaline medium using NaOH. Lowland milled peat from the Smolynsky deposit of the Chernihiv region was used. CHR samples were obtained from the corn harvest residues in the village of Sosonka, Vinnytsia region.

The TGA and DTA methods implemented in the modernized derivatograph "Q-1000" ("MOM" company, Hungary) in the range of 21…1003 °C at a heating rate of 7.4 K/min were used in the work. The samples were placed in an open conical platinum crucible without compression. Still air was used as the surrounding medium. Aluminum oxide was used as an inert substance in the reference crucible. The collection and processing of information was carried out using the applied computer program "Derivatograph".

The analysis of thermal decomposition processes was carried out according to the curves of sample mass change (TG) (Fig. 1), differential thermogravimetry (DTG) (Fig. 2) and differential thermal analysis (DTA) (Fig. 3).

Results

As can be seen from Figs. 1–3, the process of thermal decomposition of samples of MPR, CHR and composite fuel has a pronounced staged character. The results of determining the moisture content, the content of organic and mineral substances and the ash content of the samples are presented in the Table.

MPR. Dehydration takes place at the first stage (23…184 °C). The maximum rate of dehydration is observed at 82 °C (Fig. 2). Dehydration is accompanied by an endothermic effect, represented by a peak in the DTA curve (Fig. 3).

The second stage is the thermal decomposition of organic substances. It is accompanied by active gas formation and thermal generation. As noted in [4], treatment of peat with a NaOH solution leads not only to the formation of water-soluble salts of humic acids, but also to qualitative changes in the organic substances remaining in the solid residue. Therefore, the thermal decomposition of organic substances of MPR, in contrast to the organic substances of the original peat, occurs in a wider temperature range and takes place in three stages.

The first stage is 184...324, the second – 324...580 and the third – 580...786 °C (Fig. 2). The average decomposition rate by stages is 0.97, 0.51 and 1.18 % dry matter/min (% DM/min), respectively.
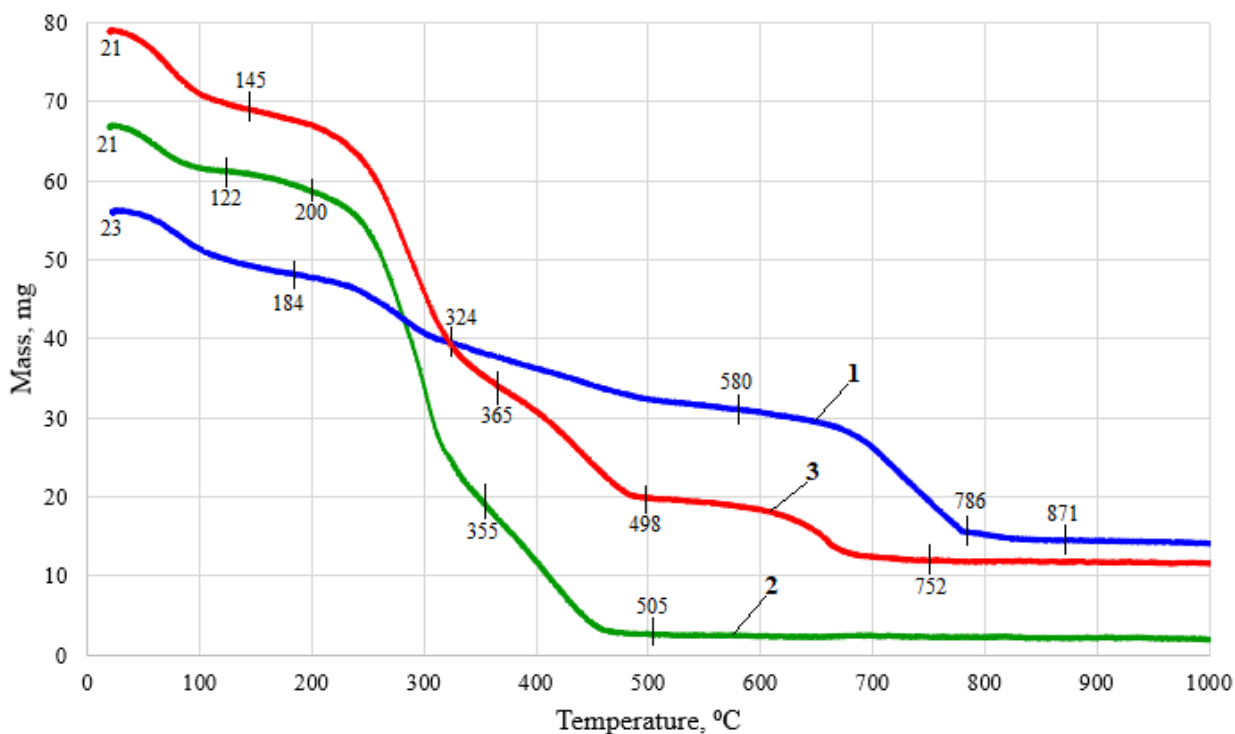

Fig. 1. Combined TG curves: 1 – MPR; 2 – CHR; 3 – composite fuel.

Thermal dissociation of calcium and magnesium carbonates in the composition of dolomite is observed after the completion of decomposition of organic substances in the range of 786...871 °C. It is accompanied by the absorption of heat. The ash content in the studied sample turned out to be quite high (Table 1).
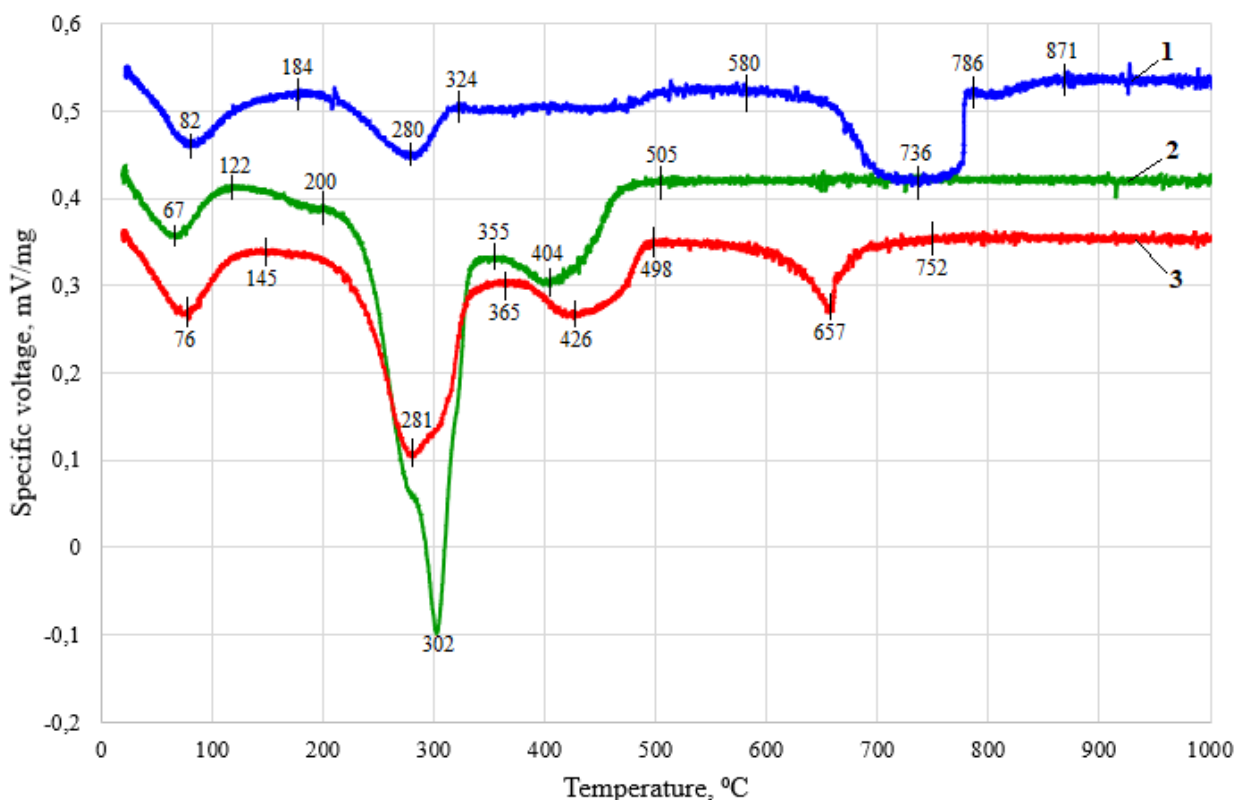
Fig. 2. Combined DTG curves: 1 – MPR; 2 – CHR; 3 – composite fuel.

Table 1

Results of thermal decomposition analysis

Material	Dehydration		Thermal decomposition				Ash content
			Organic substances		Mineral substances		
	range, °C	moisture content, %	range, °C	content, % DM	range, °C	content, % DM	% DM
MPR	23–184	13,93	184–786	67,84	786–1002	2,91	29,25
CHR	21–122	8,23	122–505	95,76	505–1002	0,98	3,26
Composite fuel	21–145	12,55	145–752	82,75	752–1003	0,44	16,81

CHR. The CHR sample has the kinetics of thermal decomposition, which is characteristic of plant raw materials [5]. Complete dehydration occurs in the temperature range of 21…122 °C. The maximum rate of water removal is recorded at 67 °C. Thermal decomposition of organic substances occurs in the range of 122…505 °C and has two pronounced stages (Fig. 2). At the first stage (122…355 °C), the material rapidly degrades, a high rate of decomposition (2.37 % DM/min) with a maximum value at 302 °C and a strong increase in heat generation is observed (Fig. 3). At the second stage (355…505°C), the rate of decomposition of organic substances decreases to 1.21 % DM/min. A further increase in temperature does not cause a change in the mass of the sample (Fig. 1).

Compared with the MPR sample, the CHR sample has a 2.2 times higher intensity of thermal decomposition of organic substances and a 9 times lower ash content.
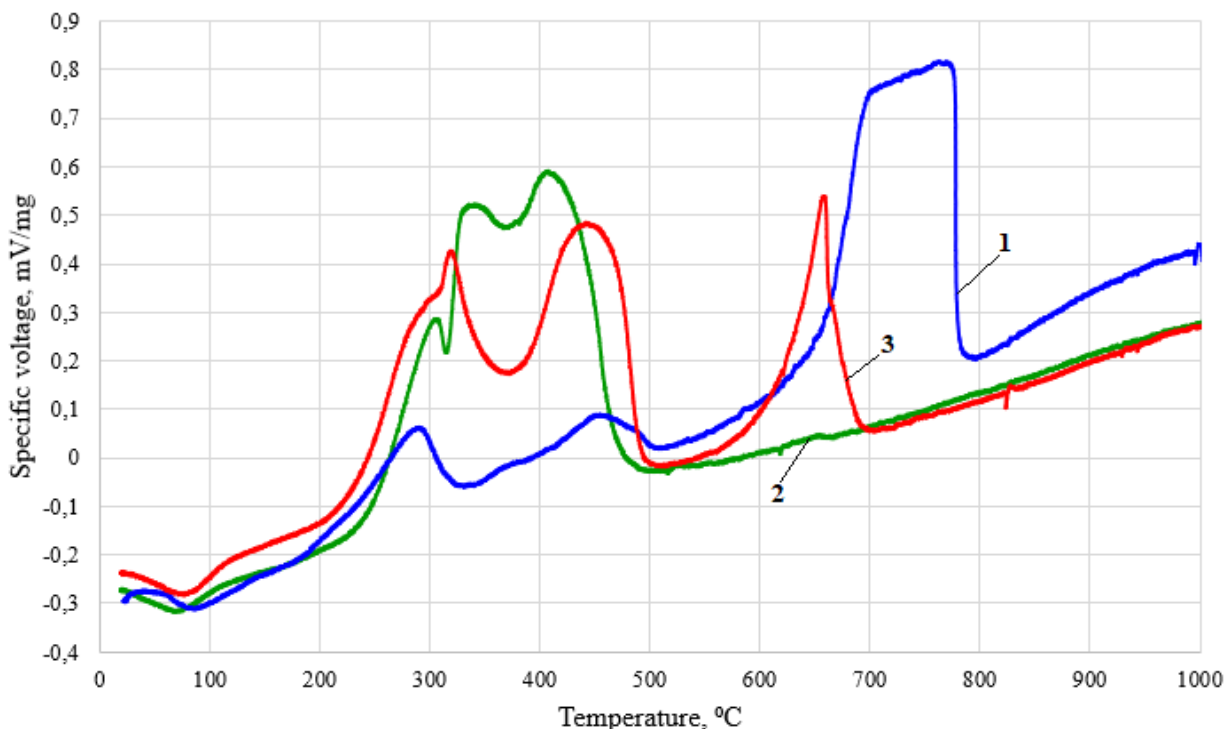
Fig. 3. Combined DTA curves: 1 – MPR; 2 – CHR; 3 – composite fuel.

Composite fuel. Dehydration of the fuel is completed at 145 °C, which is 39 °C earlier than that of the MPR sample and 23 °C higher than that of the CHR sample. The maximum rate of dehydration is recorded at 76 °C (Fig. 2).

The addition of CHR to MPR leads to a narrowing of the decomposition temperature range compared to MPR. Co-decomposition of organic substances of fuel components occurs, as in MPR, in 3 stages: 145…365, 365…498 and 498…752 °C. However, the decomposition kinetics itself has a slightly different intensity. In the fuel at the first, second and third stages, the decomposition rate is 1.77, 1.10 and 0.34 % DM/min, respectively. Compared to MPR, the fuel decomposition rate is 1.8 and 2.1 times higher in the first and second stages, respectively. However, at the third stage, it is 3.5 times lower and is only 0.34 % DM/min.

The intensive decomposition of CHR in the fuel at the first stage changes the conditions for the decomposition of MPR. The heat generated during the decomposition of CHR intensifies the decomposition of MPR. The factual specific power of heat release, which is equivalent to the specific voltage (mV/mg), is higher than the one calculated based on the contributions of individual fuel components (Fig. 3). Probably, high-temperature exothermic reactions between the constituent components take place in the fuel.

According to the technique described in [6], the conditional specific thermal effect (CTE) of the thermal decomposition of organic substances of the composite fuel and its components was determined. CTE of thermal decomposition of organic substances is 918.0 for MPR, 970.0 for CHR, and 1116.0 mV·s/mg DM for composite fuel. As we can see, CTE of thermal decomposition of CHR is 5.7 % higher than the CTE of thermal decomposition of MPR. Unexpectedly, it turned out that CTE of thermal decomposition of composite fuel is 15.0 % higher than the CTE of thermal decomposition of CHR.

This fact confirms the assumption of high-temperature exothermic reactions in the composite fuel between the elementary constituents of the fuel components during simultaneous heating of the MPR and CHR.

Conclusion

The composite fuel and its components are studied by TGA and DTA methods: the milled peat residue after extraction of humus substances and the corn harvest residues.

The temperature range and the rate of dehydration, thermal decomposition of organic and mineral substances, moisture and ash content are determined.

Completion of the thermal decomposition of organic substances of the composite fuel occurs 34 °C lower than the corresponding temperature of the milled peat residue.

The overall average rate of decomposition of organic substances of composite fuel is 20% higher than the rate of decomposition of milled peat residue.

Addition of 50% corn harvest residues to the residue of milled peat allows to obtain a composite fuel with an ash content that is 1.7 times lower than the ash content of the milled peat residue.

The conditional thermal effect of thermal decomposition of organic substances of composite fuel and its components is estimated. It was found that the conditional specific thermal effect of the thermal decomposition of organic substances of the composite fuel is higher than the conditional specific heat effect of the fuel components. It is assumed that the reason for the increase in the specific thermal effect of the thermal decomposition of the composite fuel is the exothermic reactions between the fuel components.

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