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EXPERIMENTAL STUDIES OF THERMAL ACTIVITY PROCESSES OF CROPPED SEEDS OF OIL CULTURES

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Abstract

We've conducted experimental studies of thermal activity processes with crushed seeds of oil crops, in particular rapeseed, soybean, sunflower of fractions I) $> 1 < 2$ mm; II) $> 0.45 < 1$ mm; III) $> 0.1 < 0.45$ mm, respectively. The results of experimental studies showed that the ignition/self-ignition temperatures of crushed rapeseed, soybean and sunflower seeds for fractions $> 1 < 2$ mm; $> 0.45 < 1$ mm; $> 0.1 < 0.45$ mm do not change and have a value of $322 \pm 2/345$ °C; $293 \pm 2/415$ °C and $222 \pm 2/365$ °C, respectively. The fraction $> 0.45 < 1$ mm was selected for the study of the thermal stability of oilseeds by thermogravimetric analysis, as it showed the most dangerous temperature values in studies of ignition and self-ignition temperatures. The results of the experimental studies showed that endothermic processes occur in the studied samples of crushed rapeseed, soybean, and sunflower seeds in the temperature range of 20-245 °C, which was accompanied by a loss of sample mass. Intensive destruction of samples, accompanied by a rapid loss of mass, begins at temperatures of 235-245 °C. In the temperature range of 235-459 °C, exothermic oxidation processes occur, which end in the flaming combustion of decomposition products, and at temperatures above 406-459 °C, the carbonized residue of the samples burns, which is accompanied by the appearance of rapid exo-effects. Studies of the effect of dispersion on the thermal stability of crushed oil cultures seeds showed that the degree of samples grinding does not significantly affect the temperature of the onset of thermo-oxidative destruction. However, the processes of flame combustion of pyrolysis products in the sample with a high degree of dispersion proceed more intensively, and the combustion of the carbonized residue of the sample with a higher degree of grinding is accompanied by a greater release of heat.

Key words: thermal stability, self-ignition, ignition, thermogravimetric analysis, destruction, oil cultures, exoeffect, combustion.



Introduction

Taking into account the experience of the oil and fat production enterprises of Ukraine, increased fire safety is achieved by the process of drying and conditioning of the solution, which under certain conditions causes the thermal activity of the raw material (the process of self-heating and (or) self-ignition (smoldering) of the solution [1]. Factors contributing to the self-ignition of seeds and raw materials are: clogging with various impurities, slowing down the flow of raw materials in the dryer shaft, exceeding the temperature set by the technological regulations, etc. It is important that raw materials, finished products, solid combustible materials are susceptible to ignition, as well as, textile materials oiled with vegetable oils and remnants of raw materials on technological lines, which at an ambient temperature of 10-20 °C are capable of releasing such a quantity of heat that after a few hours it can cause their self-ignition and further combustion.

The purpose of the work is to study the peculiarities of the processes of thermal activity of crushed oil cultures seeds, such as rapeseed, soybean, and sunflower.

The object of research is the self-heating and self-ignition processes of crushed oil cultures seeds.

Analysis of publications

The works of L.P. Vogman, V.P. Olshanskyi, Grekov S.P., V.K. Kostenko, O.L. Zavyalova, Alvaro Ramirez, Bei Li, Rafael Font, Yongjun Wang and others are devoted to the study of the processes of self-heating and self-ignition of substances and materials [1-10]. These works aim to research methods of controlling the self-heating process of plant raw materials during their storage. The paper [2] presents the calculation of the self-ignition induction period of deposited combustible dust in the air ducts of ventilation systems and on the supply. The authors established that the places of maximum accumulation of sediments are most often formed on the surfaces of connections and on the bends of pipelines of ventilation systems. The conditions of combustible dust self-ignition depending on the characteristics of the technological process were investigated by calculation-analytical method. In work [6], the ignition temperature and self-ignition temperature of the biomass layer were determined experimentally. Proposed mathematical model allows you to calculate the self-ignition temperature of biomass depending on the technical characteristics of the dryer, atmospheric conditions, mass flow and moisture content. According to these results, the fire-safe operating conditions of the drying process were determined. Alvaro Ramirez and other authors in work [7], using the calculation of the Maciejasz index, thermogravimetric analysis, and the method of differential scanning calorimetry, studied the thermal behavior of agricultural products stored in silos, in particular corn, wheat, barley, lucerne, soy, powdered sugar, and bread flour. R. Font [8] studied the processes of self-heating and self-ignition of almond shells. The paper considers two processes contributing to self-heating – water vapor sorption and chemical oxidation.



Considering the peculiarities of self-heating processes of substances and materials [9-11] and the existing threats of fires due to these processes, the study of oilseeds for their tendency to self-heating and self-ignition is a topical task.

Materials and methods

Experimental studies of the processes of self-heating and self-ignition were carried out with crushed seeds of oil crops – rapeseed, soybean, and sunflower [12].

The selected seeds of oilseeds were ground in an electric coffee grinder and three fractions of each type of seed were sifted using sieves I) $> 1 < 2$ mm; II) $> 0.45 < 1$ mm; III) $> 0.1 < 0.45$ mm. The moisture content of all samples was within 7.5-8.0 %.

Currently, the regulatory document ДСТУ 8829:2019, "Fire-explosive hazard of substances and materials. Nomenclature of indicators and methods of their determination. Classification" is in force in Ukraine, establishing methods for determining indicators of the fire hazard of substances.

Experimental studies of the ignition temperature and self-ignition temperature of rapeseed, soybean and sunflower experimental samples were carried out according to the method [13], on the OTP installation.

The essence of the experimental method of determining the ignition temperature consists in heating a certain mass of a substance at a given rate, periodically igniting the released vapors, and establishing the fact of the presence or absence of ignition at a fixed temperature.

The essence of the self-ignition temperature determining method is to add a certain mass of a substance into a heated volume and evaluate the test results. By changing the test temperature, its minimum value is found at which the self-ignition of the substance occurs.

Also, we've used the method of thermogravimetric analysis of the studied samples, using the Q-1500D derivatograph of the "Paulik - Paulik - Erdei" system with the registration of the analytical signal of mass loss and thermal effects using a computer.

The research was carried out in a dynamic mode with a heating rate of 5 °C/min in an air atmosphere. The weight of the samples was about 100 mg. The thermal stability of the samples research was carried out in the temperature range of 20-800 °C. The reference substance was aluminum oxide. [14, 15].

Results and discussion

At the initial stage, experimental studies were performed to identify the effect of dispersion on the ignition temperature and self-ignition of crushed oilseeds, the results of which are presented in table 1.



Table 1. The effect of dispersion on the ignition and self-ignition temperature of crushed oil cultures seeds of different fractions

| Sample name, dispersion, mm | Ignition temperature, °C | Self-ignition temperature, °C |
|------------------------------------|--------------------------|-------------------------------|
| Rapeseed, fraction $> 0.1 < 0.45$ | 323 ± 2 | 345 |
| Rapeseed, fraction $> 0.45 < 1$ | 322 ± 2 | 350 |
| Rapeseed, fraction $> 1 < 2$ | 320 ± 2 | 350 |
| Soy, fraction $> 0.1 < 0.45$ | 293 ± 2 | 415 |
| Soy, fraction $> 0.45 < 1$ | 293 ± 2 | 420 |
| Soy, fraction $> 1 < 2$ | 293 ± 2 | 420 |
| Sunflower, fraction $> 0.1 < 0.45$ | 221 ± 2 | 365 |
| Sunflower, fraction $> 0.45 < 1$ | 222 ± 2 | 370 |
| Sunflower, fraction $> 1 < 2$ | 222 ± 2 | 370 |

The analysis of experimental studies results shows that the ignition/self-ignition temperatures of crushed rapeseed, soybean and sunflower seeds for fractions $> 1 < 2$ mm; $> 0.45 < 1$ mm; $> 0.1 < 0.45$ mm do not change and have a value of $322 \pm 2/345$ °C; $293 \pm 2/415$ °C and $222 \pm 2/365$ °C, respectively.

The fraction $> 0.45 < 1$ mm was chosen to study the thermal stability of oilseeds by the method of thermogravimetric analysis [16], since it showed the most dangerous temperature indicators in studies of ignition and self-ignition temperatures by this method [13].

Studies of the thermal stability of crushed rape, soybean and sunflower seeds with a dispersion of $> 0.45 < 1$ mm are presented in the form of thermograms in fig. 1-3.

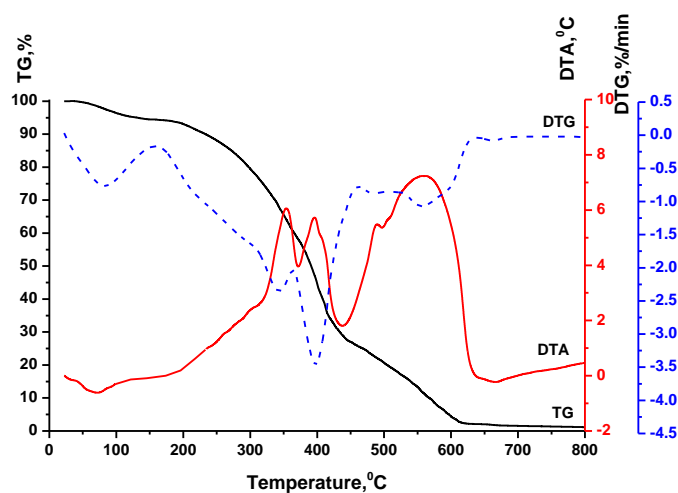


Fig. 1. Thermogram of a crushed sunflower seeds sample



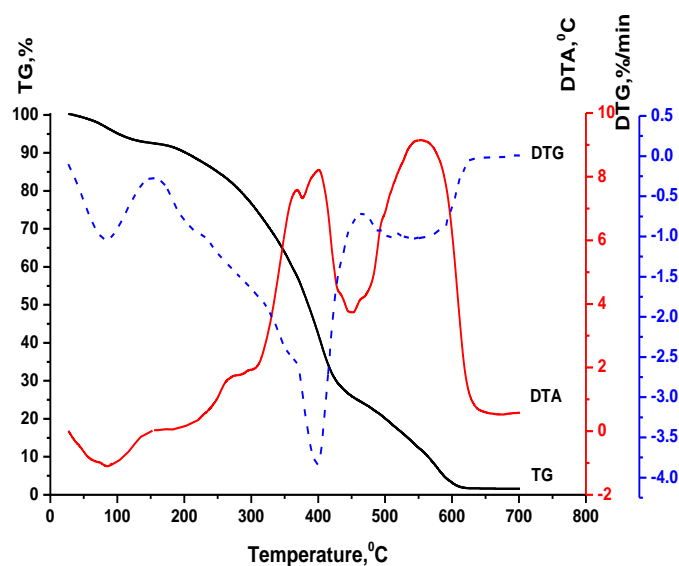


Fig. 2. Thermogram of a crushed rape seeds sample

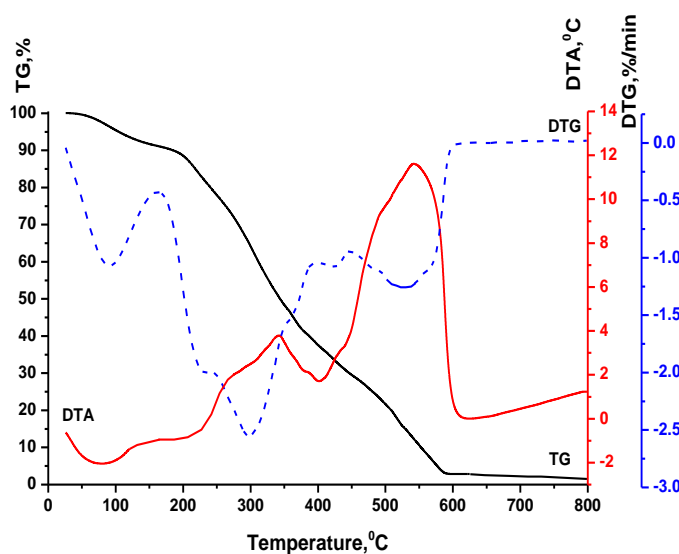


Fig. 3. Thermogram of a crushed soy seeds sample



In all the studied samples, in the temperature range of 20-245 °C, endothermic processes occur, accompanied by the loss of sample mass, which corresponds to the evaporation of unbound water and the release of constitutional water without destruction of the sample material. It should be noted that the soybean sample has the highest content of unbound and constitutional water (21.07 %), which is lost in the temperature range of 20-245 °C. Water loss in sunflower and rapeseed samples occurs in the temperature range of 20-235 °C and is 10.16% in the sunflower sample and 13.16 % in the rapeseed sample.

Intensive destruction of samples, which is accompanied by a rapid loss of mass, begins at temperatures of 235-245 °C. The nature of the extremes on the DTA and DTG curves of the samples is different, which indicates differences in their chemical composition.

A number of complex processes take place in the temperature range of 235-459 °C. In this temperature range, along with the endothermic processes of pyrolysis, exothermic oxidation processes take place, which end with the flaming combustion of decomposition products. This is evidenced by the appearance of the DTA curves, namely, a slight deviation of the curves in the region of exoeffects at temperatures below 300 °C and an intense increase in the height of the peak in the temperature range of 300-459 °C.

At temperatures above 406-459 °C, the carbonized residue of the samples burns, which is accompanied by the appearance of rapid exo-effects on the DTA curves.

Compared to rapeseed and sunflower samples, the soybean sample has higher thermal stability. This is evidenced by a less intense loss of sample mass (42.29 %) in the temperature range of 245-406 °C and the appearance of a less clear exoeffect on the DTA curve with a maximum at a temperature of 345 °C, which accompanies thermo-oxidative and destructive processes in the studied sample.

Should be noted that the rapeseed sample is less heat-resistant than the sunflower sample. The appearance of a noticeable endo-effect at a temperature of 300 °C, which is superimposed by an exo-effect starting at a temperature of 235 °C, indicates the intensity of pyrolysis processes (splitting of volatile products) in this sample. The presence of the fastest exothermic effect on the DTA curve of the rape sample with a maximum at a temperature of 400 °C indicates the most intense flame burning of the sample.

To evaluate the effect of dispersion on self-heating processes, crushed rapeseed was chosen, since it had the fastest exothermic effect.

In fig. 4 and 5 show thermograms of crushed rapeseed samples of different dispersion.



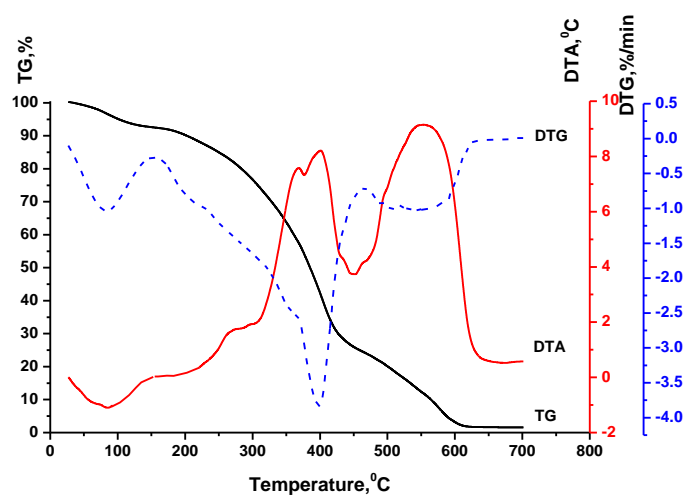


Fig. 4. Thermogram of a crushed rape seed sample, fractions from 0.45 to 1 mm

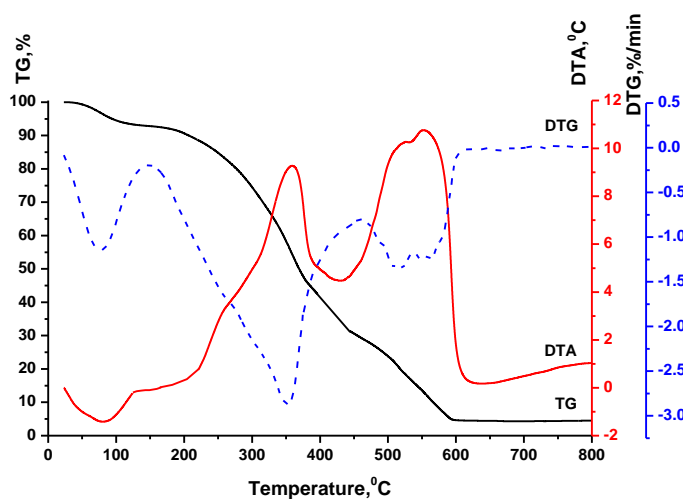


Fig. 5. Thermogram of a crushed rape seed sample, fractions from 0.1 to 0.45 mm

In fig. 6 and 7 presented curves of thermogravimetric and differential thermal analysis of crushed rapeseed with a dispersion of 0.45 to 1 mm and 0.1 to 0.45 mm.



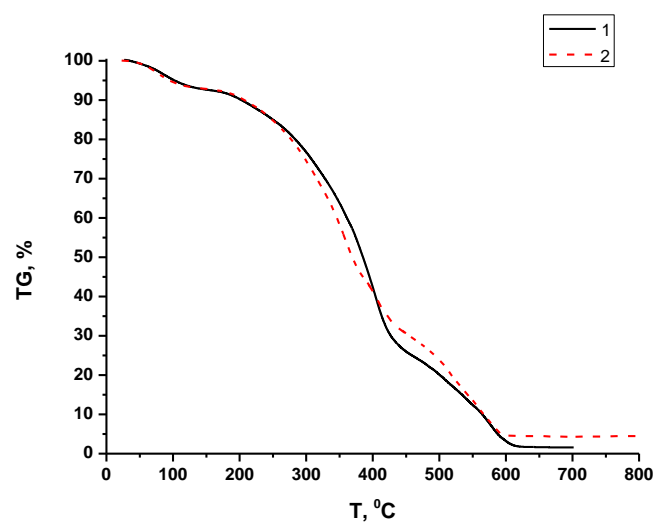


Fig. 6. TG curves of the tested crushed rapeseed samples, fractions:
1 – from 0.45 to 1 mm; 2 – from 0.1 to 0.45 mm

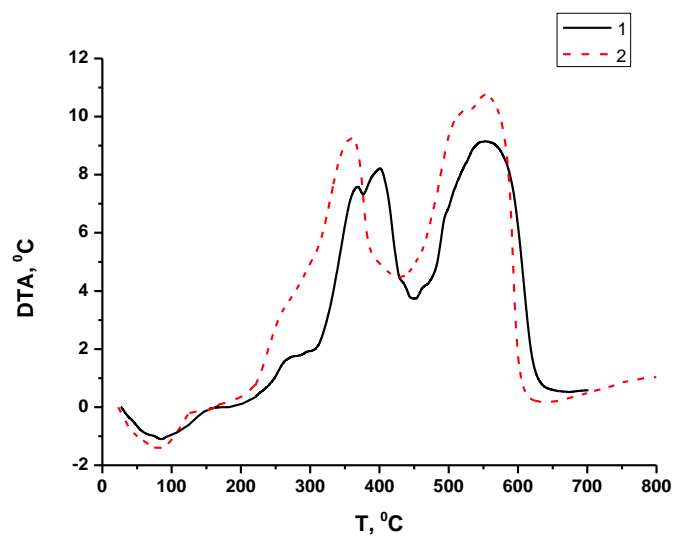


Fig. 7. DTA curves of the tested crushed rapeseed samples, fractions:
1 – from 0.45 to 1 mm; 2 – from 0.1 to 0.45 mm



As can be seen from the given thermograms, the degree of grinding of the samples does not significantly affect the temperature of the onset of their thermo-oxidative destruction. However, the processes of flame combustion of pyrolysis products in a sample with a high degree of dispersion proceed more intensively. This is evidenced by a more intense loss of sample mass in the temperature range of 250-430 °C and the appearance of a higher exothermic effect on the DTA curve, the maximum of which (357 °C) is shifted to the region of lower temperatures compared to the sample with a dispersion of 0.45 to 1 mm (398 °C). Combustion of the carbonized residue of the sample with a higher degree of grinding is accompanied by a greater release of heat compared to the sample with a dispersion of 0.45 to 1 mm. This is evidenced by the faster exoeffect that appears on the DTA curve of this sample at temperatures above 430 °C. This property of the sample with a higher degree of dispersion can be explained by its more developed surface area.

Conclusions

It was established that the ignition temperatures of cropped rapeseed, soybean and sunflower seeds are 322 ± 2 °C; 293 ± 2 °C and 222 ± 2 °C, and the self-ignition temperature of the specified seed is 345 °C; 415 °C and 365 °C, respectively, and do not depend on their dispersion in the range of fractions from 1 to 2 mm; from 0.45 to 1 mm; from 0.1 to 0.45 mm.

According to the results of experimental studies using the method of thermogravimetric analysis, it was found that in the investigated samples of cropped rapeseed, soybean and sunflower seeds, endothermic processes occur in the temperature range of 20-245 °C, which are accompanied by a loss of sample mass. Intensive destruction of samples, which is accompanied by a rapid loss of mass, begins at temperatures of 235-245 °C. In the temperature range of 235-459 °C, exothermic oxidation processes occur, which end in the flaming combustion of decomposition products, and at temperatures above 406-459 °C, the carbonized residue of the samples burns, which is accompanied by the appearance of rapid exo-effects. Studies of the dispersion effect on the thermal stability of cropped oilseeds showed that the degree of grinding of samples does not significantly affect the temperature of the beginning of their thermo-oxidative destruction. However, the processes of flame combustion of pyrolysis products in the sample with a high degree of dispersion proceed more intensively, and the combustion of the carbonized residue of the sample with a higher degree of grinding is accompanied by a greater release of heat.



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