

THE ROLE OF VOLATILE COMPONENTS IN THE PROCESS OF THERMAL DESTRUCTION AND IGNITION OF THE SUNFLOWER HUSK BIOMASS

РОЛЬ ЛЕТКИХ КОМПОНЕНТІВ У ПРОЦЕСІ ТЕРМАЛЬНОЇ ДЕСТРУКЦІЇ ТА ЗАПАЛЮВАННЯ БІОМАСИ ЛУШПИННЯ СОНЯШНИКА

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ABSTRACT

The final composition of volatile components in the process of oxidative pyrolysis depends on the temperature level of the process. The gas output increases with the growth of hydrogen, methane and heavy hydrocarbons concentration in the process of pyrolysis in the range of 200-500°C. In this case, there is a noticeable decrease in undesirable impurities in the output of carbon dioxide and nitrogen in the fuel gas. The obtained data on the dynamics of thermal decomposition of biomass under heating conditions reflect the complex dependence of the yield of total gas individual components both on time and on the temperature of the process. The more volatiles contained in the source fuel, (the other things being equal) the faster the gas mixture ignites, and the more intensely it burns out. The composition and temperature of the gas mixture affects the pressure drop and auto-ignition temperature in the pyrolysis chamber. It was found that the lowest self-ignition temperature of a gas mixture is 490°C. A series of experiments to determine the critical condition for self-ignition at a constant temperature of 490°C and various initial pressures of the mixture (100-300 kPa) was carried out. It was found that the transition from a smooth increase in pressure of 90 kPa to an explosive one (up to 300-400 kPa) depends on the composition and temperature of the gas mixture. Therefore, the composition of the gas and its ignition temperature can be controlled by adjusting the mode of pressure increase in the reactor.

ТЕЗИ

Кінцевий склад летких компонентів у процесі окисного піролізу залежить від температурного рівня процесу. Вихід газу збільшується із зростанням концентрації водню, метану та важких вуглеводнів у процесі піролізу в діапазоні 200-500 °С. При цьому на виході помітно зменшується кількість небажаних домішок вуглекислого газу та азоту в паливному газі. Отримані дані про динаміку термічного розкладання біомаси в умовах нагрівання відображають складну залежність виходу окремих компонентів газової суміші як від часу, так і від температури процесу. Чим більше летких речовин міститься в вихідному паливі, тим (за інших рівних умов) швидше запалюється газова суміш і тим інтенсивніше вона вигорає. Склад і температура газової суміші впливає на перепад тиску і температуру самозаймання в піролізній камері. Встановлено, що найнижча температура самозаймання газової суміші становить 490°C. Була проведена серія експериментів з визначення критичного стану самозаймання при постійній температурі 490°C і різних початкових тисках суміші (100-300 кПа). Встановлено, що перехід від плавного підвищення тиску 90 кПа до вибухового (до 300-400 кПа) залежить від складу та температури газової суміші. Отже, склад газу і температуру його займання можна регулювати, змінюючи режим підвищення тиску в реакторі.

INTRODUCTION

During last decades sunflower has occupied significant sown areas among industrial crops in Ukraine, which are mainly located in agricultural enterprises of the Steppe and Forest-Steppe (Cherednichenko, 2020). It is known that raw sunflower husk has several disadvantages such as low heating value and bulk density, high moisture, and volatile matter contents (Bala-Litwiniak and Zajemska, 2020). Several case studies have shown that for effective use of biomass as energy, feedstock in thermochemical conversion processes requires pretreatment (Zajemska et al., 2017; Isemin et al., 2017; Islamova et al., 2021).

Crop residues biomass can also be processed in torrefaction, gasification and liquefaction processes (Zolotovska et al., 2016; Kaczynska et al., 2019).

The pellets application for heat production allows diminishing the atmospheric burden of greenhouse gases (Kuznetsova, 2012) and creates the conditions for sustainable economic development (Cui et al., 2019). It was shown that in terms of price, sunflower seed husk pellet fuel is 71% cheaper than natural gas and 75% cheaper than coal. Meanwhile, there is still uncertainty in the assessment of the impact of pollutant emissions caused by the burning of biomass on air quality caused by the lack of emission factors that would characterize real combustion (Pastorello et al., 2011; Zajac et al., 2019).

At the same time, biomass contains lower sulfur and ash amount than non-renewable sources, such as fossil fuels, and, therefore, it generates lower NO_x and SO_x emissions (Klason and Bai, 2007; Perea-Moreno et al., 2018). As a rule, sulfur content in the biomass does not exceed 0.2% and only certain biomass fuels reach 0.5-0.7% (for brown coal 0.7-7%) (Demirbas, 2004; Parmar, 2017). Meanwhile, biomass is characterized by a high proportion of volatile parts and high humidity content (Zolotovska et al., 2016). The amount of ash, active carbon and volatile matter contained in sunflower seed husk briquettes is about 2.4%, 22.7% and 72% accordingly (Spirchez et al., 2019). The content of combustible matter (C, S and H) significantly decreases after thermal processing, while the contents of oxygen (O) and volatile matter significantly rise after drying (Matin et al., 2019).

It is known that the high volatility of the biomass material provides numerous advantages associated with a low ignition temperature and retention of ignition over a longer period of time (Sivabalan et al., 2021). An increase in volatile substances led to increase the heating value of the feedstock. The sunflower husk calorific value is 3500-4000 Cal/kg being supplied through burning (Popescu et al., 2013). The thermal reactivity of the sunflower seed husk is extremely higher than that for the other samples (hazelnut shell, rice husk, and olive refuse) under investigated conditions (Haykiri-Acma and Yaman, 2011). The volatilization stage is characterized by the release of volatiles caused by the decomposition of hemicellulose and cellulose and partial decomposition of lignin (Tibola et al., 2022).

This work aims to study the role and composition of volatile components in the process of thermal destruction and ignition of the sunflower seed husk biomass.

MATERIALS AND METHODS

The thermal analysis of sunflower seed husk biomass was carried out using the derivatograph Q-1500D of the "F. Paulik-J. Paulik-L. Erdey" system. Differential mass loss and heating effects were recorded. Samples of biomass were analyzed dynamically at a heating rate of 10°C/min in an air atmosphere. The mass of samples was 100 mg. The reference substance was aluminum oxide. The activation energy of thermo-oxidation destruction samples is determined by the method of Broido (Broido, 1969).

The value of the double logarithm for each temperature was calculated using the dependence:

$$\ln\left(\ln\frac{100}{100-\Delta m}\right) = -\frac{E}{R} \cdot \frac{1}{T} \quad (1)$$

where:

- m is the sample mass, %;
- E – the activation energy, kJ/kmol;
- R – universal gas constant, 8.314 J (mol.K);
- T – temperature, K.

High performance capillary gas chromatography was used to separate hydrocarbons in fuel gas using a flame ionization detector. A glassy highly permeable polymer, polytrimethylpropyne (PTMSP), was chosen as the stationary phase for the separation of hydrocarbon gases. A quartz capillary column with an outer metal protective coating, 10 m long and 0.35 mm in inner diameter, filled with PTMSP was used. The thickness of the adsorption layer was 30 µm. The polymer was dissolved in toluene. The capillary was filled with this solution under pressure. It was removed by heating the column and passing a flow of carrier gas. The following analysis conditions were chosen: column oven temperature - 55°C, evaporator and detector temperatures - 130°C. The carrier gas is nitrogen. The specified flow rate of nitrogen was controlled by a rheometer at a level of 18 cm³/s. The analysis time was 10 min.

The presence of inorganic components of the pyrolysis gas was determined on a gas chromatograph using a conductometric detector. Separation was carried out at a temperature of 45°C on two packed columns.

A column 2 m long and 4 mm in diameter filled with 5A molecular sieves was used to determine H_2 , N_2 , CO , H_2 , O_2 . It is noticed that at higher temperatures their crystal structure is destroyed. The second column of the same size with a polymeric sorbent, a copolymer of styrene and divinylbenzene, was used to determine CO_2 , and H_2S . The carrier gas, grade A helium, was used for both columns. The temperature of the evaporator and the thermostat of the detector is 110°C . Gas samples with a volume of 3 cm^3 were introduced through a sampling probe. The ignition temperature was determined by the method of inlet of a pre-prepared gas mixture into an evacuated (residual pressure no more than 0.4 kPa) heated flask, 200 cm^3 in volume, made of quartz glass. The test equipment is shown in fig.1. The reaction vessel (127 mm long and 127 mm in diameter) was placed in a horizontal steel cylinder of an electric furnace. The stainless-steel cylinder is inserted into the ceramic body. Three Chromel-Alumel thermocouples were used to measure the furnace temperature. The temperature measurement error under static conditions did not exceed $3\text{-}6^\circ\text{C}$ in the range of $220\text{-}490^\circ\text{C}$.

The supplied mixture of gases was prepared in a 3-liter cylinder. The prepared mixture was kept in the cylinder for at least 10 hours before the start of the experiment to complete mixing of the reagents.

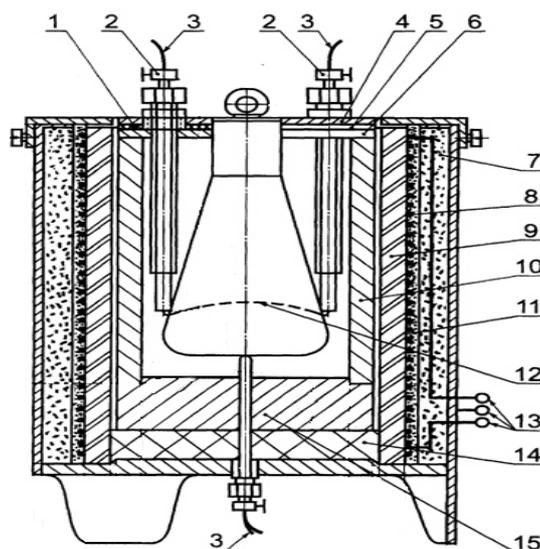


Fig. 1 - Test equipment for determining the ignition temperature of a gas

1 - high-temperature insulation; 2 - clamping sleeves; 3 - thermocouples; 4 - upper part of the cover; 5 - insulating ring; 6 - lower part of the cover; 7 - thermal insulation; 8 - heater; 9 - ceramic tube; 10 - steel cylinder; 11 - high-temperature mastic; 12 - control points; 13 - heater connection for voltage 220 V; 14 - insulating disk; 15 - metal base

The prepared mixture was admitted into the reaction vessel using a 200 cm^3 sealed glass syringe equipped with a three-way valve and connecting tubes (Fig. 2).

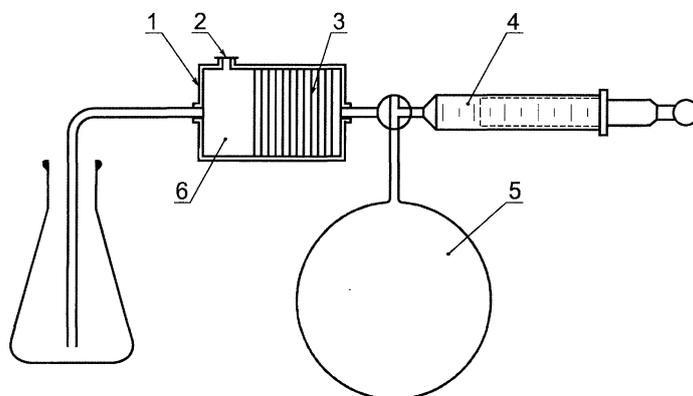


Fig. 2 - Introduction of a gas sample

1 - flame arrester; 2 - safety membrane; 3 - sintered glass plates; 4 - sealed syringe; 5 - tank with gas; 6 - pre-chamber

Eight volumetric gaseous samples ($20\text{-}55\text{ cm}^3$) were taken in the temperature range of $220\text{-}600^\circ\text{C}$ to be tested at various initial pressures of the mixture (from 100 to 400 kPa).

The pressure of the mixture in the reaction vessel after the inlet was determined by the pressure in the dosing tank before the inlet, taking into account the valve opening time (0.07–1 s).

The pressure in the reactor was recorded by a fast inertia inductive pressure sensor. All the results obtained were treated by statistical methods using the StatGraphics Plus5 software package at significance level of 0.95% (p -value < 0.05).

RESULTS

Thermal destruction of sunflower husks begins at a temperature of 29–30°C. The main decomposition of volatile components and evaporation of water occurs in the range of 40–150°C. The process speed is low, on average 5.5%/min. The maximum rate (8.7–8.84%/min) was observed at a temperature of 79–91°C (Fig. 3, curve 3). The weight loss at this stage is small and amounts to 8.3% (Fig. 3, curve 1). The process of volatile components decomposition is accompanied mainly by endothermic reactions with the most pronounced effects in the temperature range of 61–79°C (Fig. 3, curve 2).

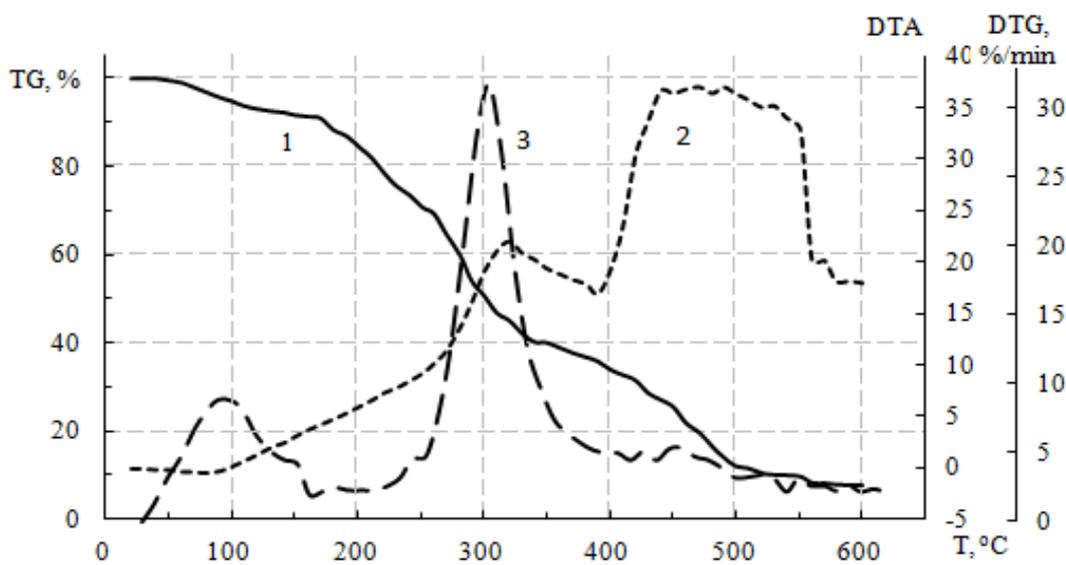


Fig. 3 - Curves of thermogravimetric (1), differential thermal (2) and differential thermogravimetric (3) analysis of sunflower husk

The process of decomposition of the main components of sunflower husk takes place in the temperature range of 151–400°C. The degradation ranges of hemicelluloses (220–320°C) and cellulose (300–380°C) partially overlap. That is why only one peak is observed on the *DTG* curve at a temperature of 300°C (Fig. 3, curve 3). The average speed of the process is 13.7–14.2%/min, the maximum is 31.7%/min. The mass loss at this stage is the largest and amounts to 57.8% (Fig. 3, curve 1). Decomposition reactions of hemicelluloses and cellulose are exothermic with the greatest thermal effects in the temperature range of 280–300°C.

The process of lignin destruction begins at a temperature of 250–280°C. However, the bulk of lignin decomposes in the range of 400–550°C. Typically, the decomposition rate is 3.5–4.0%/min (maximum 5.4%/min). One small peak is observed at a temperature of 430–440°C (Fig. 3, curve 3). The weight loss was 26.3%. Decomposition reactions are exothermic with pronounced thermal effects in the temperature range of 440–500°C (Fig. 3, curve 2). Combustion of sunflower husk ends in the range of 550–600°C. The fireproof residue was 7.6% of the total mass.

According to the activation energy data, the heat resistance of sunflower husks is low (Fig. 4). The activation energy was 33.7 kJ/mol at the initial stage of decomposition. Its value at the stage of destruction of the main components was 32.1 kJ/mol. Low activation energy values are explained by a rather large amount of pentosans (27–28%) and a relatively small amount of cellulose (31–38%) in sunflower husk (Yadav *et al.*, 2016). During the process, pyrolysis produces both solid and liquid products (bio-oils, tars, and water), and a gas mixture composed mainly of CO_2 , CO , H_2 , and CH_4 (Castello *et al.*, 2017; Uddin *et al.*, 2018).

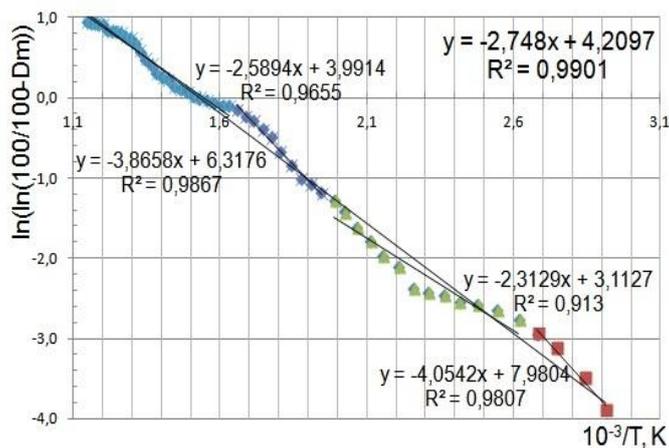


Fig. 4 - Diagram of the process of non-isothermal decomposition of sunflower husk

The results of assessing the release of volatile substances from the particles of sunflower husk biomass are shown in Figures 5 and 6.

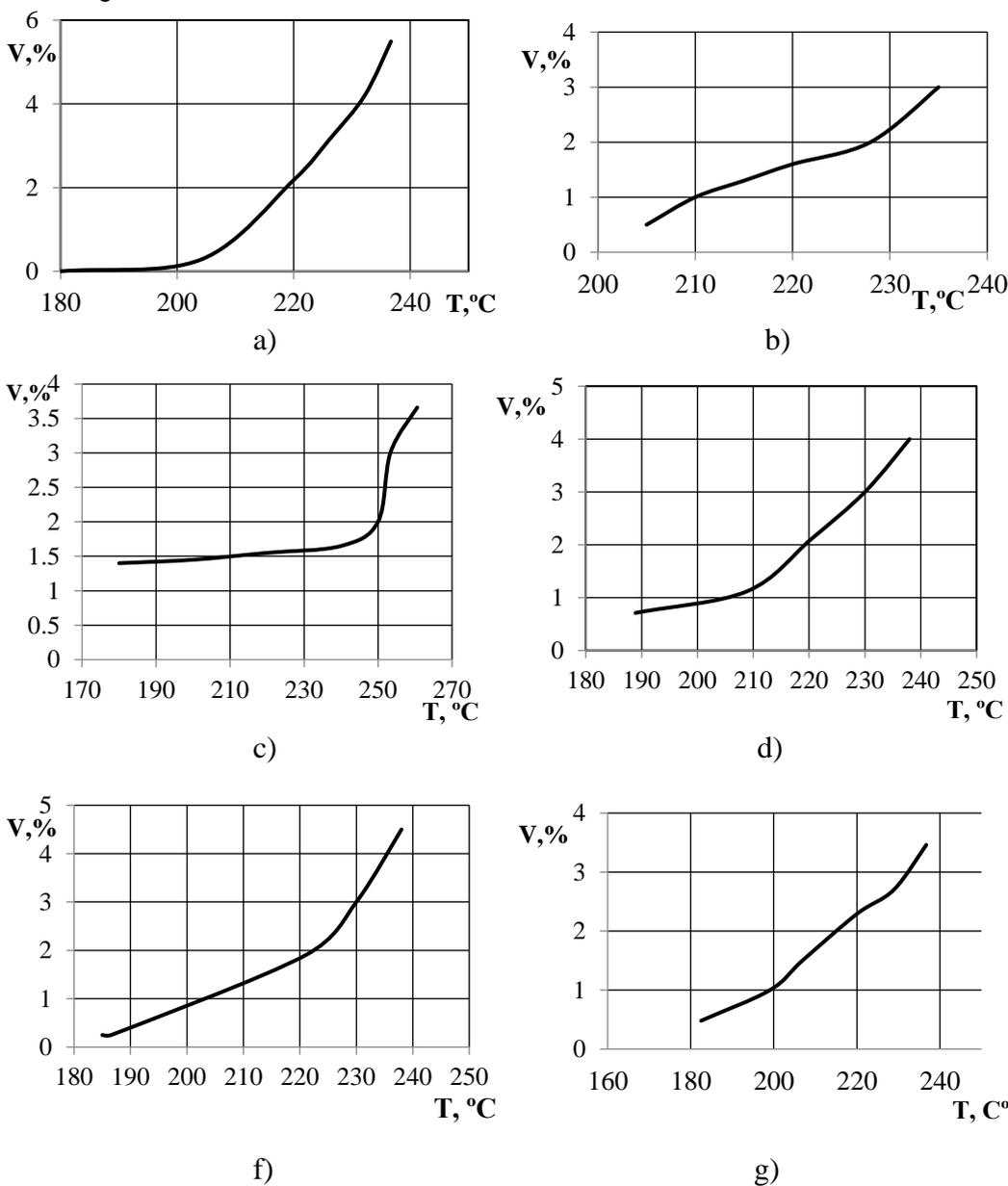


Fig. 5 - Emission of volatiles from sunflower husk biomass

a) hydrogen; b) methane; c) heavy hydrocarbons; c) carbon monoxide; d) carbon dioxide; f) nitrogen

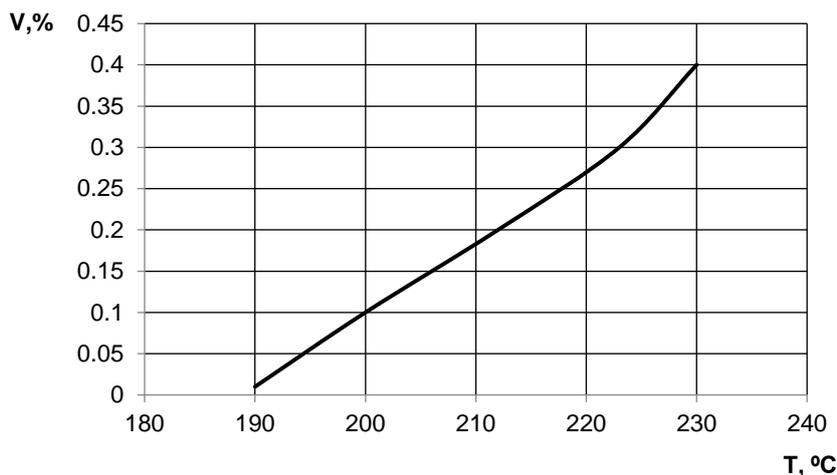


Fig. 6 - Hydrogen sulfide emission from sunflower husk biomass

The growth of gas emission is directly caused by the rise in the pyrolysis temperature in the range of 200-500°C. This is due to an increase in the concentration of hydrogen and methane and to a lesser extent it depends on heavy hydrocarbons. The roots of this effect are associated with a more complete decomposition of biomass particles. The volume of pyrolysis gas increases by 1.04; 1.21; 1.3 and 1.61 times at temperatures of 260, 320, 380 and 420, respectively, compared with the volume of the gas mixture at a temperature of 220°C.

Meanwhile, a noticeable decrease in the yield of carbon dioxide and nitrogen (undesirable impurities in the fuel gas) occurs in the temperature range of 280-500°C. The amount of hydrocarbons in the resulting gas mixture also increases with increasing temperature and reaches a maximum at a temperature of 420°C, exceeding this value corresponding to a temperature of 200°C by 2.1 times. The chemical content of the test gas is shown in Table 1.

Table 1

Chemical content of pyrolysis gas								
Components	H ₂	CH ₄	CO	CO ₂	N ₂	C _n H _m	H ₂ S	A
	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
Concentration	22.70	16.20	20.80	19.12	2.29	15.54	2.65	0.70

It is known that the thermal decomposition of xylan produces furfural, which quickly ignites and causes a sharp increase in temperature and self-heating of biomass (Zaichenko *et al.*, 2020). An ignition risk ranking is estimated using both kinetic parameters and characteristic temperatures (Jones *et al.*, 2015). Some crop residues, olive cake and sunflower husk are predicted to have a high risk of low temperature ignition. The determination of the critical condition for self-ignition was carried out at a constant temperature of 490°C and various initial pressures of the mixture (100-300 kPa). Typical barograms are shown in figure 7. The analysis of thermo-barograms showed that the heating of the gas mixture occurs mainly in the process of puffing. Insufficient heating of the gas to the level of the reactor temperature at the moment of closing the valve was 1-2% and depended both on the pressure and the diameter of the reactor. The completion time of gas heating after closing the valve did not exceed the ignition delay in the entire studied temperature range of 200-600°C (Fig. 8).

The transition from a smooth increase in pressure of 90 kPa to an explosive one (in the range of 300-400 kPa) occurred when the initial pressure of the mixture after the injection into the reactor changed by 1-10%. This transition depends on the chemical content and temperature of the gas mixture. The composition of the gas can be controlled by adjusting the pressure pulsations and the ignition temperature of the gas mixture. The flash point changes with increasing pressure (Fig. 9).

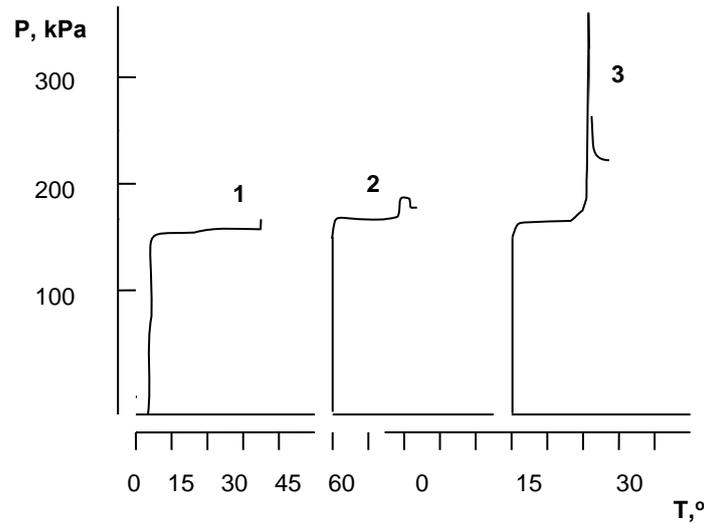


Fig. 7 - Barograms of studies at a temperature of 490°C with O₂ = 42.3%
 1 - no ignition; 2 - degenerate ignition; 3 - self-ignition

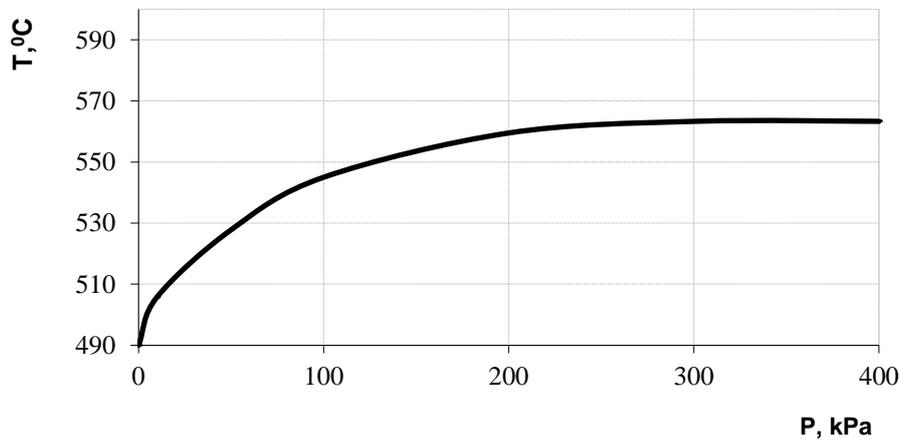


Fig. 8 - Dependence of the autoignition temperature on pressure

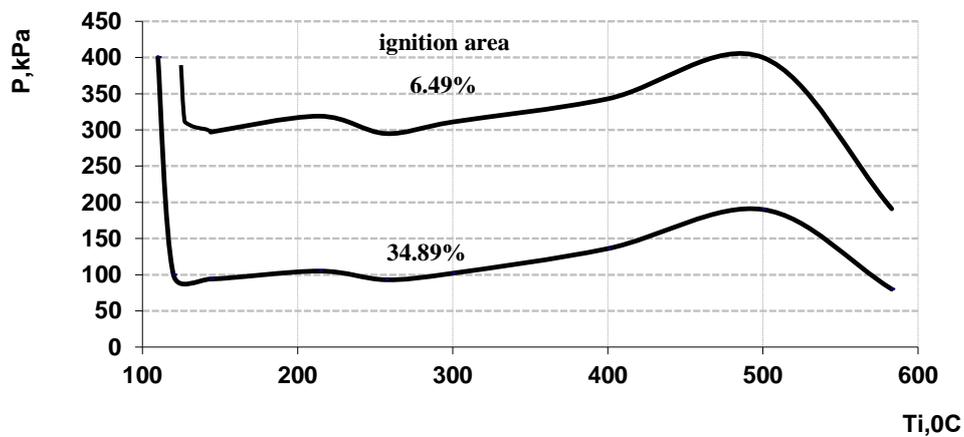


Fig. 9 – The dependence of the autoignition temperature on pressure for a gas mixture with air

A change in pressure from 100 to 200 kPa leads to an increase in the flash point to 300-500°C. As can be seen, the pyrolysis process occurs at varying pressure. Ignition of pyrolysis gas is possible when the limit temperature is reached.

CONCLUSIONS

Decomposition reactions of hemicelluloses and cellulose are exothermic with the greatest thermal effects in the temperature range of 280-300°C. The process of lignin destruction begins at a temperature of 250-280°C. However, the bulk of lignin decomposes in the range of 400-550°C. Combustion of sunflower husk ends in the range of 550-600°C. The fireproof residue was 7.6% of the total mass. The activation energy value at the stage of destruction of the main components was 32.1 kJ/mol. Gas emission increases with an increase in the pyrolysis temperature in the range of 200-500°C due to an increase in the composition of hydrogen, methane and slightly from heavy hydrocarbons. The amount of pyrolysis gas in the gas mixture increases with increasing temperature. The amount of hydrocarbons in the resulting gas mixture also increases with increasing temperature and reaches a maximum at a temperature of 420°C. The analysis of thermo-barograms showed that the heating of the gas mixture occurs mainly in the process of puffing. Insufficient heating of the gas to the level of the reactor temperature at the moment of closing the valve was 1-2% and depended both on the pressure and the diameter of the reactor. The completion time of gas heating after closing the valve did not exceed the ignition delay in the entire studied temperature range of 200-600°C. The composition of the gas can be controlled by adjusting the pressure and the gas mixture temperature of the ignition. A change in pressure from 100 to 200 kPa leads to an increase in the flash point to 300-500°C.

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