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Influence of aluminosilicate materials on the peat low-temperature pyrolysis and gas formation

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ABSTRACT

The influence of natural and synthetic aluminosilicates on the peat low-temperature pyrolysis has been studied. The use of these aluminosilicates as catalysts resulted in the increase of the conversion to gaseous and liquid products by a factor of 1.3–1.5 compared with a non-catalytic process. The use of these catalysts also contributed to the increase of the amount of gaseous products and heat capacity of the gas due to the increase of the gaseous hydrocarbon content. The highest heat of combustion (23.88 MJ/m^3) was achieved with bentonite clay at 460 °C and concentration of 30 wt.%.

1. Introduction

The methods of energy recovery from renewable biogenic raw materials are of great importance due to limited amounts of natural energy resources, such as oil and gas. Peat is one of the biomass renewable resources. The peat reserves are about 4000 mln m^3 worldwide [1]. Its abundance makes its appealing as a renewable energy resource. The typical methods of obtaining energy from peat are thermochemical conversion technologies, e.g. pyrolysis, gasification and combustion [2–4].

Pyrolysis is one of the effective methods of biomass processing into combustible gases, oils and solid carbon-containing residues (sorbents) [5–10]. This paper reports peat low-temperature pyrolysis in the presence of such catalytic systems as natural aluminosilicates and synthetic zeolites.

The choice of a suitable catalyst is of crucial importance for the pyrolysis process because it allows one to operate at lower temperatures and can provide higher selectivity towards the desired products, avoiding any post-process purification, thus enhancing the benefit of the process and making it economically favourable [11–18].

The introduction of the catalysts into the reaction system results in the considerable decrease of the activation energy and allows obtaining more hydrocarbons (target products) at the same temperature as for non-catalytic processes [19,20]. Depending on the conditions of the pyrolysis, the gas of the desired combustion heat (3–30 mJ/m^3) and composition can be obtained [21].

In many industrially developed countries novel catalytic materials for organic raw material pyrolysis and gasification are being actively developed. The examples are zeolite HZSM-5 [22], zeolite catalyst DC-11 [23], aluminum silicate materials MCM-41 [24], Al-MCM-41, Al-SBA-15 [25–27], silica, Al_2O_3, γ-Fe_2O_3, Fe_3O_4, α-FeOOH [28], clays [29], Ni/Al [30], boric and orthophosphoric acids [31], zinc chloride [32], KNO_3–B_2O_3/Al_2O_3 [33], Co/MgO [34], Pd–Pt–La/Al_2O_3 [35].

Here we report the catalytic influence of natural aluminosilicates and synthetic zeolites on the peat pyrolysis. We demonstrate the increase of the conversion into gaseous and liquid products by a factor of 1.3–1.5 compared with a non-catalytic process and the increase of the amount of gaseous products.

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2. Experimental

The samples of eriophorum-sphagnum peat with the degree of decomposition of 30% and ash content of 5% were used as the substrates of low-temperature catalytic pyrolysis. These peat samples had the following elemental composition (wt.%): C—53.96; H—5.96; O—40.79; N—0.79 that agrees well with the brutto formula of the compound $C_{79}H_{105}O_{45}N$. The oxide content of the cinder in the peat raw material samples (in wt.% of a dry substrate) are the following: SiO_2 (0.26–3.2), CaO (0.13–2.79), Fe_2O_3 (0–0.85), P_2O_5 (0.02–0.15), Al_2O_3 (0.04–0.57), and SO_3 (0.04–0.05).

Both aluminosilicate materials of natural origin (kaoline, bentonite, cambrian clays and clay mergel) and synthetic zeolites (H-Beta-25-IE, H-Beta-150-IE, H-Y-12-IE, H-ZSM-5-IE and H-Mord-20-IE purchased from "Zeolyst International" (USA)) were used as the catalysts for peat pyrolysis. It is important to mention that the zeolite catalysts were modified with Fe using repeated ion-exchange (the iron precursor is ferric nitrate) as was described elsewhere [36].

The catalytic action of natural aluminosilicates and synthetic zeolites were estimated depending on (i) the conversion of the initial raw material into liquid and gaseous products; (ii) the increase of the volume of the gaseous products; (iii) the hydrocarbon concentration in the gaseous mixture; and (iv) the heat capacity of the obtained gaseous mixture.

Physicochemical analysis of catalytic materials was carried out via X-ray fluorescence spectroscopy (XRF) (SPECROSCAN MAX), nitrogen physicosorption (Beckman Coulter^{TM} SA 3100^{TM}) and CD_3CN adsorption followed by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. DRIFT spectra were recorded at ambient temperature with a Nicolet 460 Protégé spectrometer equipped with a diffuse reflectance attachment. Two hundred scans of the samples were collected from 400 to 6000 cm^{-1} with a 4 cm^{-1} resolution.

In order to analyze the composition (hydrocarbons, CO, CO_2, H_2) and to estimate the heat capacity of the gaseous mixture, the state-of-the-art analytic complex including a gas chromatograph and a specially developed analyzer of the specific heat of combustion on the base of flame-temperature detector, was used.

3. Results and discussion

3.1. Study of the structure and composition of catalytic materials

Acidic properties of the catalytic systems drastically influence the process of biomass thermal processing [37,10]. Thus, in the Laboratory of Development and Investigation of Polyfunctional Catalysts (Institute of Organic Chemistry by N.D. Zelinsky, Moscow, Russia) the investigation of acidity of natural aluminosilicates and zeolites were performed by the team of Prof. L.M. Kustov as described elsewhere [38]. The following systems were studied: Fe-H-MORD-20-IE, Fe-H-ZSM-5-IE, H-MORD-20-IE and bentonite clay.

Bentonite clay was found to have fewer amounts of acid sites with lower strength in comparison to the zeolites; hence the optimal loading of this clay catalyst was higher: 30 wt.% versus 2 wt.% for zeolites (Fig. 1).

The results of XRF are given in Table 1. The data presented show that all the samples contain small amount of iron (the experimental error is ±0.002 wt.%). It is noteworthy that the concentration of iron in cambrian clay is double compared to that of bentonite and clay mergel and much higher than that in kaoline clay. Among the zeolite samples Fe-H-Mord-20-IE was found to have the highest iron content. Besides, in all the clay samples the traces of Ag, Mn and Ti were also detected (not shown in the table). It was proposed that iron is responsible for the catalytic activity of the aluminosilicates and zeolites studied.

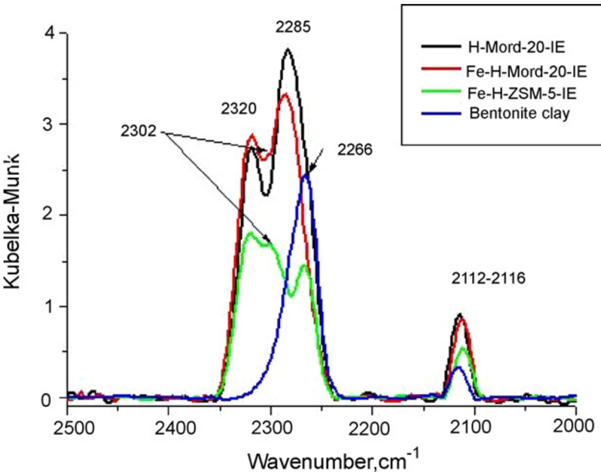

Fig. 1. DRIFT spectra of adsorbed CD_3CN.

Table 1
Iron content of the catalytic.

Catalytic material	Iron content, wt.%
Bentonite clay	2.5
Kaoline clay	0.3
Cambrian clay	4.3
Clay mergel	2.2
Fe-H-ZSM-5-IE	0.2
Fe-H-Mord-20-IE	2.7
Fe-H-Beta-25-IE	2.3
Fe-H-Y-12-IE	Not found
Fe-H-Beta-150-IE	1.1

The accessibility of catalytic sites for the reaction compounds also influences the efficiency of the catalysts along with the presence of catalytically active elements. The data of nitrogen physicosorption on determination of specific surface area is presented in Table 2. As can be seen from Table 2 the specific surface area of all the zeolites studied is much higher than that of clays. The bentonite clay has the highest specific surface area among the clay materials while – Fe-H-Y-12-IE – among zeolites.

The results of pore volume distribution for natural aluminosilicates are presented in Table 3. The majority of the samples are mesoporous, and only kaoline and cambrian clays have also micropores.

3.2. Study of the peat conversion by catalytic pyrolysis

The important characteristic describing the pyrolysis is the conversion of peat compounds. The experimental data (see Table 4) allow us to conclude that the highest peat conversion is achieved in the presence of kaoline and bentonite clays and zeolites

Table 2
Specific surface area of the samples by BET method.

Aluminosilicate material	Specific surface area, m^2/g
Kaoline clay	9
Bentonite clay	59
Cambrian clay	30
Clay mergel	20
Fe-H-ZSM-5-IE	461
Fe-H-Mord-20-IE	758
Fe-H-Beta-25-IE	784
Fe-H-Y-12-IE	1035
Fe-H-Beta-150-IE	779

Table 3
Pore volume distribution from BJT method.

Pore diameter, nm	Bentonite clay		Kaoline clay		Cambrian clay		Clay mergel	
	Pore volume, ml/g	%	Pore volume, ml/g	%	Pore volume, ml/g	%	Pore volume, ml/g	%
Under 6	0	0	0.00271	16.40	0.0105	21.35	0	0
8–6	0	0	0.00166	10.06	0.0046	9.35	0	0
8–10	0	0	0.00133	8.06	0.00361	7.34	0	0
10–12	0.00201	0.11	0.00134	8.10	0.0034	6.92	0.00116	0.12
12–16	0.00968	0.51	0.00161	9.77	0.00413	8.40	0.00504	0.53
16–20	0.01396	0.73	0.00144	8.73	0.00366	7.45	0.01027	1.08
20–80	1.89008	98.65	0.00512	31.00	0.01455	29.60	0.69005	72.48
Above 80	0.00020	0.01	0.00130	7.89	0.00471	9.58	0.24558	25.79
Sum total	1.91593	100	0.01651	100	0.04916	100	0.95210	100

Table 4
Composition of the products of the catalytic peat pyrolysis (catalyst loading 2 wt.%).

Catalytic material	Gas, wt.%	Liquid fraction, wt.%	Solid residue, wt%
Bentonite clay	24.37	30.36	45.27
Fe-H-ZSM-5-IE	23.88	27.36	48.76
Fe-H-MORD-20-IE	23.34	28.01	48.65
Kaoline clay	23.15	27.59	49.26
Cambrian clay	22.16	29.24	48.6
Fe-H-Beta-25-IE	21.56	29.68	48.76
Fe-H-Y-12 IE	21.18	24.63	54.19
Clay mergel	21.00	29.00	50.00
Fe-H-Beta-150 IE	20.89	24.31	54.80
Non-catalytic process	16.70	20.73	62.57

Fe-H-ZSM-5-IE and Fe-H-Mord-20-IE. Fig. 2 shows the kinetics of the accumulation of gaseous mixture depending on the type of catalytic material and for the non-catalytic process. The use of these catalytic materials was found to result in about 1.3–1.5-fold increase of the peat conversion into gaseous and liquid products compared to the non-catalytic process.

It is important to mention that all the experiments were conducted at predetermined optimal conditions: temperature of 460 °C and catalyst loading of 2 wt.% for zeolites and 30 wt.% for clays. Significant difference in percentage of the optimal amount of catalytic materials between aluminosilicates and zeolites is likely due to the different structures of these materials.

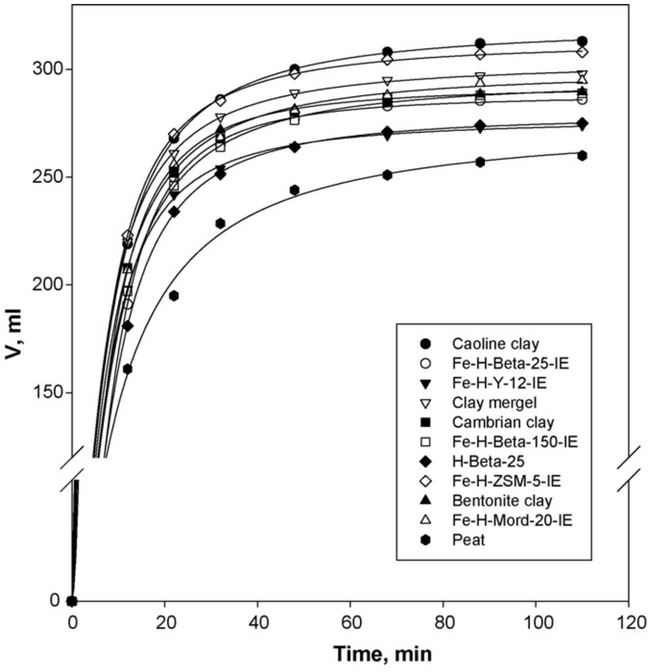

Fig. 2. Kinetics of the gaseous mixture accumulation.

3.3. Study of the change of the amount of hydrocarbons in the gaseous mixture

The use of natural aluminosilicates and synthetic zeolites was found to result in a considerable increase (in about 1.3–2 times) of the hydrocarbon amount in the gaseous mixture (see Fig. 3).

We suggest that the increase of the volume of gaseous mixture as well as combustible hydrocarbons can be explained both by the influence of catalytic centers and the property of aluminosilicate materials to serve as heat-transfer agents. The natural aluminosilicates, when present in significant amounts in the reaction mixture, are known to act as heat-carriers (in addition to catalytic function), considerably increasing the heat conductivity of the mixture, thus promoting more uniform heating [39,40].

The highest amount of gaseous hydrocarbons in the presence of zeolite Fe-H-ZSM-5-IE is in agreement with the literature data describing H-ZSM as the most optimal zeolite for pyrolysis processes [14,41].

The increase of the concentration of lower hydrocarbons (methane, ethane, ethylene and propane) in the presence of catalytic materials is likely due to the fact that the aluminosilicates and zeolites studied have the properties of solid acids [42,43]. Their hydroxyl groups can interact with hydrocarbons of paraffin series forming carbonium ions as a result of peat thermal destruction. Carbonium ions $C_nH_{2n+1}^+$ are unstable and can easily transform into olefin molecules with a shorter carbon chain and a new carbonium ion. Such an ion easily subtracts hydro-

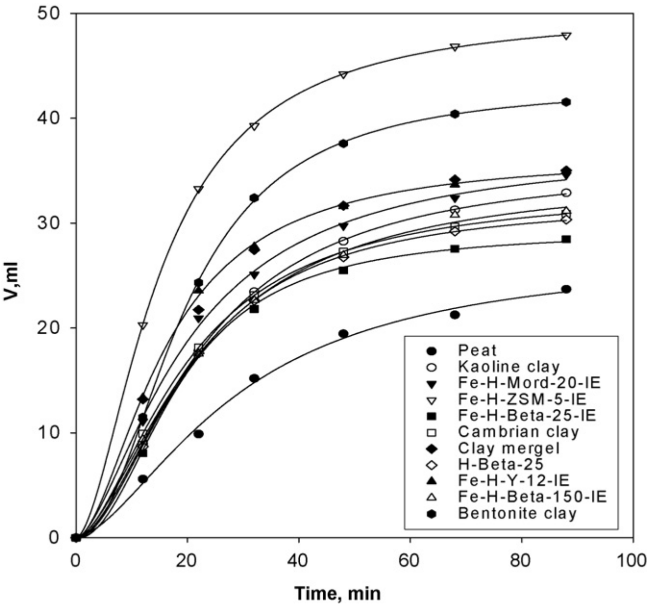

Fig. 3. Kinetics of the accumulation of gaseous hydrocarbons.

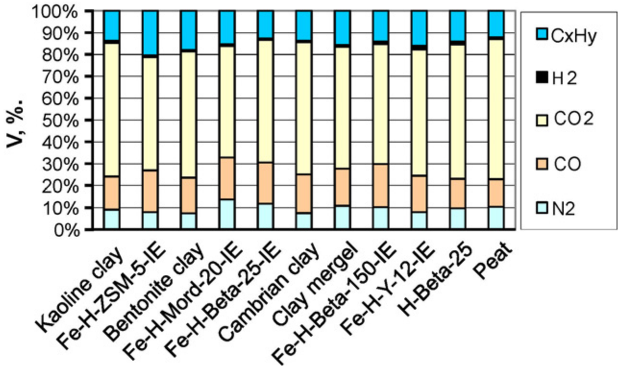

Fig. 4. The composition of the gaseous mixtures for different catalytic materials.

gen in a form of a hydride ion from the initial neutral molecules. As a result of this reaction the hydrocarbon with a short chain is formed and carbonium ion is regenerated. Thus, the change of the mechanism from the chain-radical to the ion and chain takes place.

3.4. Study of the change of pyrolysis gaseous mixture composition

The gaseous mixture obtained in peat pyrolysis was found to consist of carbon monoxide, carbon dioxide, saturated and unsaturated hydrocarbons and hydrogen (Fig. 4).

Carbon dioxide is formed mostly as a result of thermal decomposition of humic acids of peat. CO_2 is incombustible part of the gaseous mixture, thus, its concentration should be decreased in the combustible gaseous mixture obtained. It was experimentally revealed that in the presence of such catalysts as Fe-H-Mord-20-IE, Fe-H-ZSM-5-IE, Fe-H-Beta-150-IE and clay mergel the amount of CO_2 evolved is 51–52 vol.% of the total amount of gases, which is by a factor of 1.1–1.2 lower in comparison with the non-catalytic process (Fig. 5).

The amount of such components of the gaseous mixture as carbon monoxide and hydrogen also depends on the type of the catalyst (Figs. 6 and 7). The highest amount of carbon monoxide is evolved in the presence of Fe-H-Mord-20-IE, Fe-H-ZSM-5-IE, Fe-H-Beta-150-IE, as well as cambrian and bentonite clays. It comprises 18.9–19.5 vol.%, which is by a factor of 1.4–1.7 higher than that of non-catalytic process. Hydrogen content was found to be extremely low compared to other gaseous components: only 0.2–1.6 vol.%.

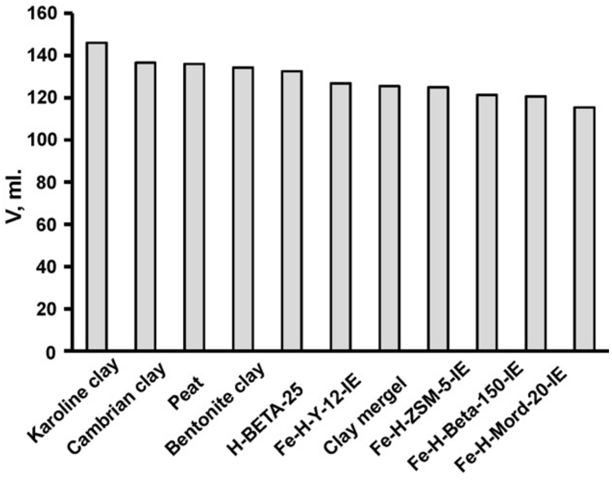

Fig. 5. The volume of CO_2 obtained during the peat pyrolysis.

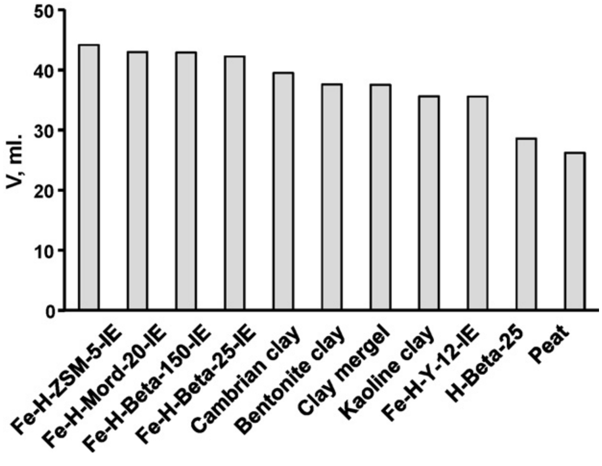

Fig. 6. The volume of CO obtained during the peat pyrolysis.

CO is known to be formed as a result of lignine thermal cracking [44,45]. The presence of Fe_2O_3 (e.g. in bentonite clay) [46] contributes to the formation of activated carbon which reduces high-molecular phenols into hydrocarbons resulting in the formation of carbon monoxide. Hydrogen is mainly formed as a result of lignine thermal decomposition [44] and also of also cracking, i.e. aromatic hydrocarbon condensation.

3.5. Study of the heat capacity of the combustible gases

The heat capacity of the gaseous mixture directly depends on its composition and the amount of combustible components. The above data show that combustible gases obtained in the presence of such catalytic materials as bentonite clay, Fe-H-Mord-20-IE and Fe-H-ZSM-5-IE have the best composition from the point of view of their heat capacity value. The heat of combustion of the gaseous mixture (Fig. 8) in the presence of these materials increases by a factor of 2.6–2.8 in comparison with that of the non-catalytic process.

Eventually the bentonite clay was found to be the most effective catalytic material for peat pyrolysis in contrast to zeolites taking into consideration its availability and low price. Thus the following studies were performed using bentonite clay.

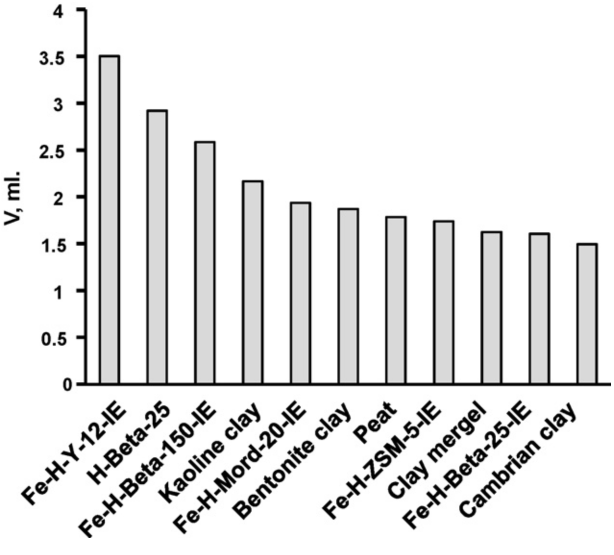

Fig. 7. The volume of H_2 obtained during the peat pyrolysis.

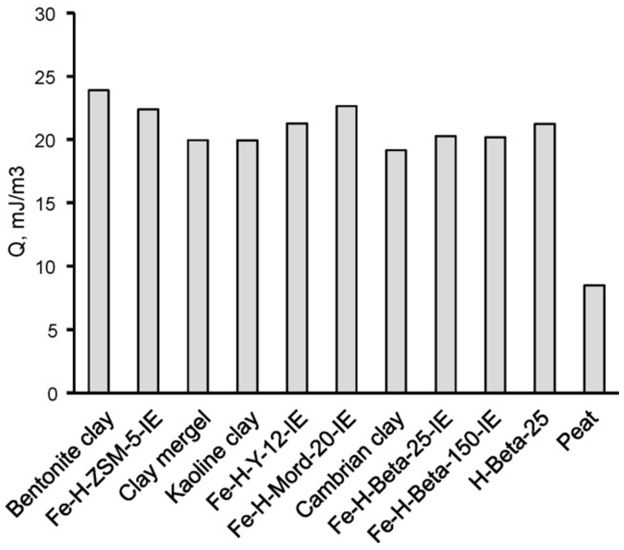

Fig. 8. The heat of combustion of the gaseous mixture obtained during the peat pyrolysis.

3.6. *Influence of the bentonite clay concentration*

The catalyst concentration is an important parameter, which influences the rate of a chemical reaction. The increase of the bentonite clay concentration was found to result in the increase of the volume of the gaseous mixture, the amounts of hydrocarbons, carbon dioxide and hydrogen, while the amount of carbon monoxide decreases with the increase of the catalyst concentration.

This fact allows us to propose a hypothesis of the exothermal reaction of carbon monoxide with water, as a result of which carbon dioxide and hydrogen are formed:

$$CO + H_2O = CO_2 + H_2 + 10,410\,\text{kcal}$$

It was also revealed that the increase of the catalyst concentration results in the increase of the heat of combustion of the gaseous mixture (Fig. 9) due to the appropriate increase of the amount of hydrocarbons.

Thus, the experimental data presented allow us to conclude that the most effective concentration of bentonite clay is 30 wt.% of peat.

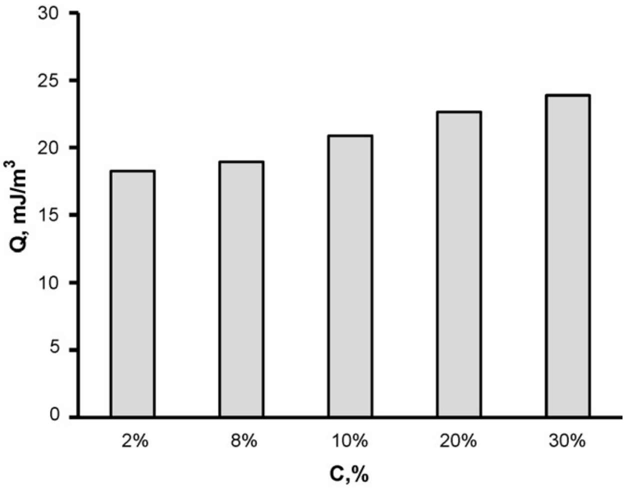

Fig. 9. The influence of the bentonite clay concentration on the heat of combustion of the gaseous mixture obtained.

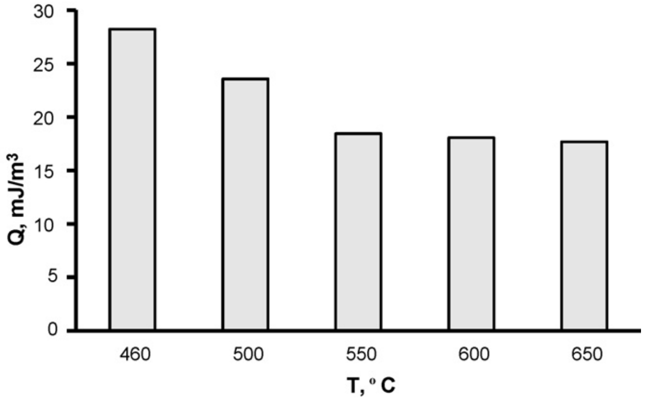

Fig. 10. The influence of the temperature on the heat of combustion of the gaseous mixture in the presence of 30 wt.% of bentonite clay.

3.7. *Influence of the temperature on the peat pyrolysis in the presence of bentonite clay*

Temperature noticeably influences the process of peat pyrolysis. The experiments were conducted in the temperature range from 410 to 600 °C. The increase of the temperature was found to result in the increase of the overall amount of pyrolysis gas, which is likely explained by the highest degree of the peat decomposition. The volume of gaseous mixture obtained at 500, 550 and 600 °C increases by a factor of 1.04, 1.21, and 1.3, respectively, in comparison to the experimental data at 460 °C.

The amount of CO_2 decreases with the temperature increase. This fact can be explained by the acceleration of the following reaction:

$$CO_2 + C = 2CO.$$

The influence of the temperature on the heat of combustion of the gas mixture was also investigated (see Fig. 10). The experimental data show that the increase of the temperature results in the decrease of the heat of combustion of obtained gaseous mixture. The maximal value of the heat of combustion corresponds to the temperature of 460 °C. At this temperature the highest quantity of hydrocarbons with high heat capacity is formed, whereas at the higher temperatures the pyrolysis gas contains mostly methane as well as hydrogen and carbon monoxide that decreases the heat capacity of the gaseous mixture.

From the data obtained during the temperature variation it was found that the value of apparent activation energy for the catalytic process in the presence of bentonite clay is almost a half compared to that of non-catalytic process, while the value of the pre-exponential coefficient (k_0) is higher by several orders of magnitude (Table 5).

The decrease of the apparent activation energy is likely due to the change of the mechanism of the hydrocarbon formation, while the increase of the pre-exponential coefficient corresponds to the increase of the number of the reaction centers [47,48].

Table 5
Parameters of the Arrhenius equation.

Parameters	Methane	Ethane	Ethylene	Propane
Catalytic pyrolysis				
E_a, kJ/mol	38	37	38	22
k_0	7×10^6	2×10^9	5×10^4	9×10^8
Non-catalytic pyrolysis				
E_a, kJ/mol	85	69	51	41
k_0	1×10^2	6×10^4	90	3×10^3

4. Conclusion

We studied the influence of both natural aluminosilicates and zeolites on the peat pyrolysis. Natural aluminosilicates have fewer amounts of acid sites of lower strength than zeolites. Specific surface area of aluminosilicates is also lower. Thus, at the same loading of zeolites and aluminosilicates, the latter reveal less activity in the process of peat pyrolysis.

The use of the above catalytic materials was found to result in the increase of the yield of gaseous and liquid products by a factor of 1.3–1.5 in comparison with that of the non-catalytic process.

The main components of the gas mixture are the lower hydrocarbon gases (methane, ethane, ethylene and propane), carbon monoxide, carbon dioxide and hydrogen.

The application of synthetic zeolites and natural clays as the catalysts allowed us to increase the heat of combustion of the resulting gaseous mixture and the rate of the pyrolysis as well as to decrease the temperature of the peat pyrolysis from 700 °C (average temperature of the non-catalytic pyrolysis) to 460 °C. The highest heat of combustion (23.88 MJ/m^3) was shown to be reached while using bentonite clay at 460 °C and concentration of 30 wt.%.

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