

Biomass waste thermal processing in the presence of iron subgroup metals compounds

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Abstract— In this work the results of the investigation of thermal destruction of biomass waste, using flax shive as an example in the presence of iron subgroup metals oxides, nitrates and chlorides are presented. Metal chlorides have the highest influence on the flax shive thermodestruction. In the paper the thermogravimetric study of biomass waste thermodestruction process is presented. The results of kinetic modeling are also shown on the base of thermogravimetric analysis both of the samples of flax shive and flax shive with addition of 10% (wt.) nickel chloride at different heating rate. The data on kinetic modeling show that in the presence of NiCl₂ the apparent activation energy of one of the stages of thermal destruction decreased by 38±3 kJ/mol.

Keywords— thermal destruction, pyrolysis, thermogravimetry, biomass wastes, iron subgroup metals, kinetic parameters.

I. INTRODUCTION

IN the last few decades the idea of using various types of biomass for energy production is of great interest to the research teams worldwide. The current interest is mostly determined by the limit of traditional fuel sources, the increase of CO₂ emission to the atmosphere, etc.

The problems of biomass processing for energy production still have no solution on a full scale that is connected with the variety of biomass composition [1, 2]. The difficulties of biomass processing are also determined by the differences in physical chemical characteristics of biomass of different origin. The primary biomass sources are wood, vestures and marsh plants. The raw material composition can change depending on the parts of plants (bark, roots, and branches, stock), storage conditions and biomass harvesting methods. These factors can affect the initial humidity, ash content and as the result heat-generation.

The effectiveness of the branches of agricultural industry producing various plant crops can be increased due to the energy obtained from millions of tons of secondary biomass [3]. For example, an amount of straw obtained after the

treatment of cereal crops is 1.3 times more than the corn mass. The total amount of carbon-containing phytogenic waste accounted more than 110 million tons of the total cereal crops mass in the Russian Federation in 2014 [4]. Thus such big volume of biomass waste makes the problems of biomass processing to energy topical.

The same problem is observed in the field of processing of plants cultivated for plant fiber production. According to the data [4] the flax production in Russia in 2013 amounted up to 39 thousand tons. The major part of the flax is cultivated now in Siberia, the Volga region and South regions of Russia. The world leader in flax production is Canada where 350 thousand tons of flax is reaped annually.

The flax shive is the lignified parts of the flax stem mainly in the form of small straws which remain after the flax scutching. In the north-western region of the Russian Federation there is big constantly renewed supply of flax shive which is not used now [5].

The biomass waste processing is rather complex because of the physical-chemical characteristics of this type of raw material: low temperature of ash melting, high ash content etc., so their conversion is an important applied problem [6, 7].

To process the plant biomass into energy different methods such as combustion, gasification, pyrolysis, bioconversion etc are used. Among the existing ways of biomass conversion, thermal methods conducted in the inert medium for the obtaining of heat, electricity, liquid fuels and solid carbon-containing sorbents are of the great interest [8-10].

Among the technological solutions aimed at the production of maximum amount of valuable products from plant biomass waste the techniques based on pyrolysis are the most effective. These methods allow obtaining gaseous and liquid fuels and solid sorbents which yield depends both on lignin concentration of the raw material and process conditions. Fast pyrolysis allows obtaining the maximal yield of valuable products from agricultural waste [11-12].

The major advantages of fast pyrolysis are high controllability of the process, high yield of gaseous products, low possibility of secondary processes decreasing fuel quality and closed circuit processing lowering the ecological risks [13, 14].

The properties of carbon-containing phytogenic source have great influence on pyrolysis products yield, their composition and physical chemical characteristics. Hence until now no data

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has been obtained to choose the optimal conditions of biomass thermal destruction process.

From the scientific point of view the search of the compounds which allow controlling the thermodestruction process of cellulosic material and decreasing the initial thermodestruction temperature is of practical interest. The iron subgroup metals compounds [15-17] have rather high activity in the pyrolysis process of various types of organogenic raw material. For this reason, oxides, nitrates and chlorides of metals of iron subgroup were chosen for the study of thermal destruction of flax shive.

II. EXPERIMENTAL

THE flax shive obtained after flax scutching was used as the raw material for the thermal destruction process. The flax shive samples were crushed with an electric mill and the fraction with drop size in the range of 0.045-0.1 mm was chosen. The initial humidity of flax shive was 5.48% and the ash content was 4.16%.

To study the influence of iron subgroup metals oxides, nitrates and chlorides on flax shive thermodestruction process the samples with 10% content of mineral compounds were prepared by trituration.

The study of flax shive pyrolysis process kinetics was carried out using thermoscales TG 209 F1 (NETZSCH) with different heating rate (5, 10, 15, 20°C/min). The samples mass used in the thermogravimetric analysis was about 5 mg.

The analysis conditions were the following: sample heating from 30 up to 600°C with heating rate 5, 10, 15 or 20°C/min and further holding up for 30 min at 600°C. The analyses were carried out in argon at a gas rate of 20 mL/min.

Mathematical handling of the pyrolysis experimental data was done by «NETZSCH Thermokinetics 3.1» software using both differential Freedman method and integral Ozawa-Flynn-Wall method [18] based on the principal of isoconversion when the reaction rate at a definite degree of conversion is the function only of temperature (1):

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot f(\alpha) \quad (1)$$

A – pre-exponential factor, E – activation energy, R – gas constant, T – temperature.

The method of non-linear regression [19, 20] was used to compute the kinetic model of the destruction process. The regression value was calculated by quintic Runge-Kutta method using internal formula of Prince-Dormand. Statistical comparison of different models was done using F-test.

In this work the reactants produced by «AquaChem» (Kazan, Russia) were used. Fe₂O₃, CoO, NiO, Fe(NO₃)₃*9H₂O, Co(NO₃)₂*4H₂O, Ni(NO₃)₂*4H₂O, FeCl₂*4H₂O, CoCl₂*2H₂O, NiCl₂*2H₂O were chosen for the investigation.

To estimate the influence of the components under study on

the weight loss of the sample, thermogravimetric analysis of pure mineral compounds were carried out. For the further comparison the flax shive samples without additives were analyzed. Obtained TG and DTG curves for pure compounds were compared with the same curves for the mixture of flax shive and mineral reagents.

III. RESULTS AND DISCUSSION

IRON subgroup metal oxides influence

According to experimental thermogravimetric study the investigated metal oxides do not undergo any changes in above-noted temperature range.

In Figs. 1 and 2 TG and DTG curves for both pure flax shive and samples with the addition of 10% (wt.) iron, cobalt and nickel oxides are shown.

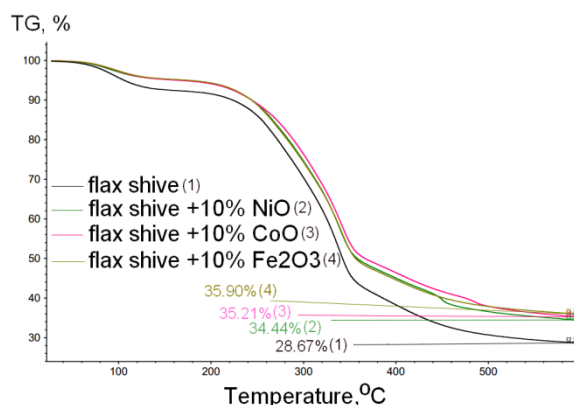


Fig. 1 thermogravimetric curves of pure flax shive and samples contained 10% (wt.) iron subgroup metal oxides

As it can be seen from the data in Figs. 1 and 2 the addition of iron subgroup metal oxides to the flax shive did not affect the shape of the curves obtained by TG and DTG. The TG curves analysis shows that the samples of flax shive with iron subgroup metal oxides content have lower initial humidity and a higher mass of solid non-volatile residues. This fact can be explained by the decrease in the weight content of the flax shive and by the higher thermal stability of the used oxides in the studied temperature range.

In Fig. 2 the DTG curves of pure flax shive and the samples with 10% (wt.) of iron subgroup metal oxides are presented. Peak 1 shown in Fig. 2 corresponds to the initial moisture loss of all the studied samples.

According to the researchers data [23] the flax shive consists of cellulose (45-58%), lignin (21- 29%) and hemicelluloses (23-26%).

The degradation of the plant biomass components takes place as follows: at first the hemicelluloses decompose in a temperature range from 200 up to 320°C, then the destruction of cellulose occurs in the range of 280-400°C and finally the thermal destruction of lignin takes place (from 260 up to 500°C).

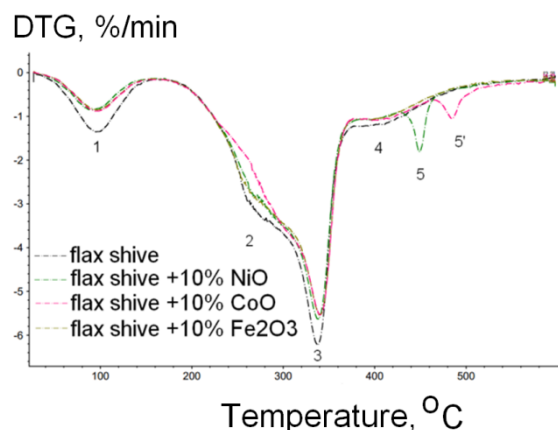


Fig. 2 differential thermogravimetric curves of the pure flax shive and of the samples containing 10% (wt.) iron subgroup metal oxides (description below)

Peak 2 (Fig. 2) corresponds to the maximal rate of hemicelluloses destruction. It is noteworthy that in case of adding cobalt oxide to the flax shive this peak is not observed.

The destruction rate of flax shive cellulose is almost similar for all the studied metal oxides and is slightly lower than the rate of the pure flax shive thermodestruction (peak 3, Fig. 2). It can be explained by the lower mass of flax shive of the samples.

Peak 4 corresponds to lignin intensive destruction; peak location and intensiveness have equal values for all the samples. It means that the studied oxides do not influence the destruction of this component of the flax shive.

The differences in the amount of solid residue for the samples with iron subgroup metal oxides can be explained by the differences in the reduction potentials of the studied metal oxides. Thus in Fig. 2 weight loss peaks (5 and 5' respectively) which correspond to the reduction of nickel and cobalt oxides used as an addition to flax shive samples are shown. There is no such a peak in the case of iron oxide added to the flax shive. This fact can be explained by a higher reduction potential of iron which reduces at higher temperature beyond the studied temperature range [24].

Iron subgroup metal nitrates influence

In the work the study of the influence of iron subgroup metal nitrates on the flax shive thermodestruction was carried out. Thermogravimetric analysis results of individual metal nitrates are shown in Figs. 3 and 4.

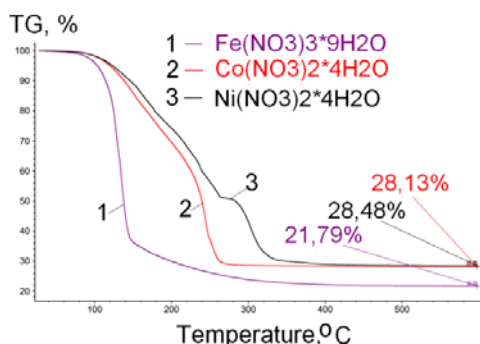


Fig. 3 thermogravimetric curves of iron subgroup metal nitrates decomposition in temperature range 50-600°C.

The metal nitrates residual masses calculation based on the data presented in Figs. 3-4 showed that hexaqua iron subgroup metal nitrates completely decompose to the corresponding metal oxides.

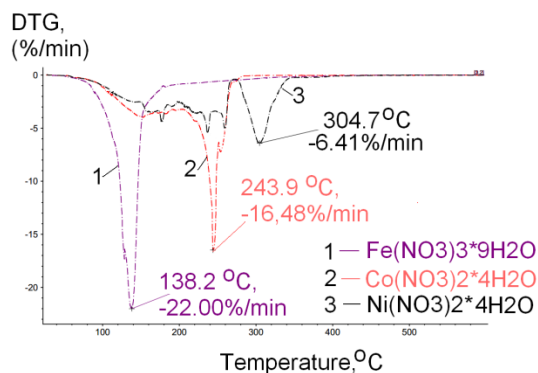


Fig. 4 differential thermogravimetric curves of individual metal nitrates in a temperature range 50-600°C.

According to Fig. 4 thermostability of iron subgroup metal nitrates decreases from nickel to iron. The influence of the studied nitrates on flax shive thermodestruction process is shown in Figs. 5-6.

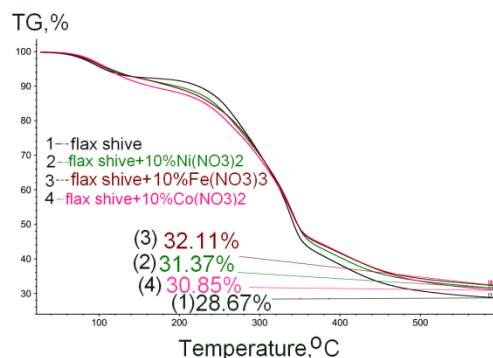


Fig. 5 TG curves of flax shive with iron subgroup metal nitrates addition

According to the data presented in Figs. 5 and 6 it can be concluded that metal nitrates have no significant influence on flax shive thermodestruction process. The conclusion was made basing on the comparative analysis of TG and DTG curves shape obtained for both pure flax shive and the samples containing 10% (wt.) iron subgroup metal nitrates.

The calculated weights of thermodestruction solid residue agree well with the experimental value that proves negligible influence of the studied nitrates on flax shive thermodestruction.

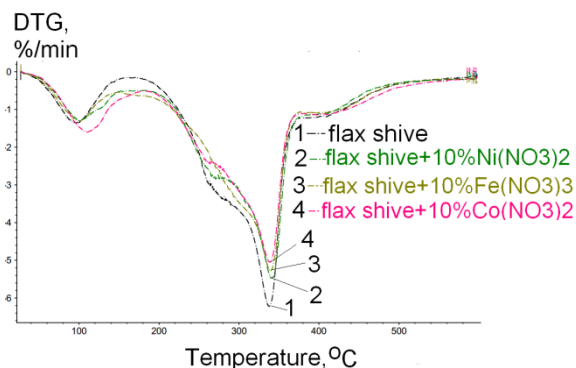


Fig. 6 DTG curves of flax shive samples with iron subgroup metal nitrates addition

According to Figs. 5 and 6 DTG curves shape does not practically change when iron subgroup metal nitrates are introduced into the flax shive that also proves low activity of the studied nitrates in the flax shive thermal decomposition.

Iron subgroup metal chlorides influence

To estimate the influence of iron subgroup metal chlorides on the flax shive thermodestruction process, thermogravimetric analysis of the individual mineral compounds was done (Fig. 7-8).

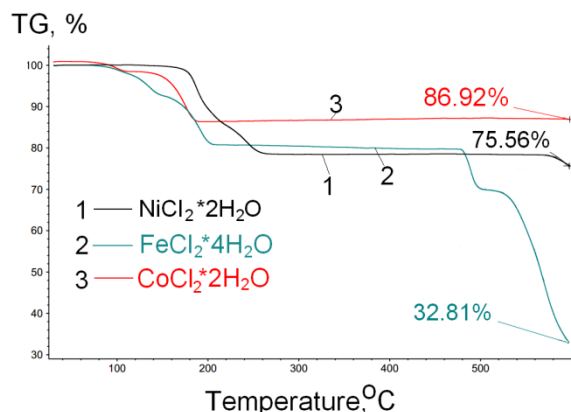
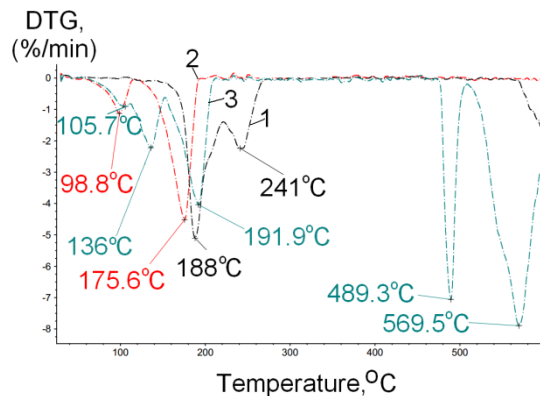


Fig. 7 TG curves of thermal decomposition of iron subgroup metal chlorides in a temperature range 50-600 °C

As Fig. 7 shows all the studied metal chlorides are thermally stable around up to 500 °C. The weight loss of the investigated chlorides in a temperature range from 100 to 200 °C corresponds to combined water evaporation. At a temperature above 500 °C the decomposition of metal chlorides takes place that is proved by the significant weight loss of the samples. According to the thermal stability the studied metal chlorides can be ranged in descending order: $\text{CoCl}_2 > \text{NiCl}_2 > \text{FeCl}_2$.



1 — $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ 2 — $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ 3 — $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$
Fig. 8 DTG curves of thermal decomposition of iron subgroup metal chlorides in a temperature range 50-600 °C

The influence of iron subgroup metal chlorides on the flax shive thermal destruction process is shown in Figs. 9-10. Basing on the data presented in Figs. 9-10 it can be noted that iron subgroup metal chlorides contribute to the acceleration of the sample weight loss processes in a temperature range from 200 up to 320 °C.

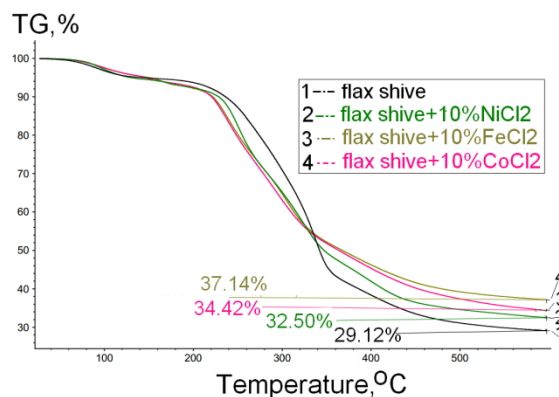


Fig. 9 data of TG analysis of flax shive samples with 10% (wt.) addition of iron subgroup metal chlorides

As it is shown in Fig. 10, the use of iron subgroup metal chlorides results in the decrease in hemicelluloses destruction temperature by 30 - 40 °C compared to the flax shive without any additives. Lower destruction temperature of hemicelluloses can be explained by its partial decomposition in the presence of metal chlorides that leads to the decrease in hemicelluloses molecular weight and thermostability. The lowest destruction temperature of hemicellulosic component corresponds to the presence of iron and cobalt chlorides as an additive to flax shive samples (Fig. 10).

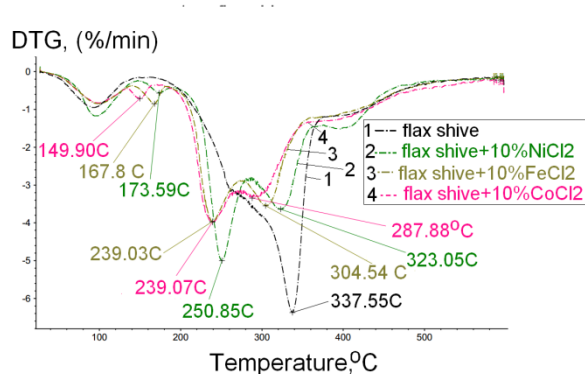


Fig. 10 DTG curves of pure flax shive and the samples with the addition of iron subgroup metal chlorides

A higher destruction temperature was observed while using nickel chloride but it is important to note the higher rate of the sample weight loss in comparison with the use of iron and cobalt chlorides

According to the influence on cellulose destruction temperature the studied metal chlorides can be ranged as follows: $\text{CoCl}_2 > \text{FeCl}_2 > \text{NiCl}_2$. Besides in spite of the decrease in the temperature of the flax shive cellulosic compound decomposition the use of iron subgroup metal chlorides led to the slight decrease in the destruction rate mainly due to the decrease in hemicelluloses decomposition temperature.

According to the curves presented on Fig. 10 it also can be noted the negligible decrease of destruction temperature of lignin which is a compound of flax shive while using both nickel and cobalt chloride. In the case of use of nickel chloride also the increase of lignin destruction rate was observed.

Kinetic modeling of flax shive pyrolysis process

The singular dynamic measurement using thermogravimetry method does not allow statistically estimating the reaction type and kinetic parameters although it contains all the necessary information. For this reason thermogravimetric analysis of the flax shive was carried out at different heating rates – 5, 10, 15 and 20°C/min.

The flax shive pyrolysis process is a complex multistage process. The analysis of differential curves of the weight loss (Fig. 10) of the pure flax shive and of the sample with the addition of nickel chloride shows that a non-catalytic process includes at least 3 stages whereas a catalytic process has 4 stages. So to simplify the process modeling the temperature range characterized by the samples highest weight loss ($\sim 230\div 360$ °C) was chosen.

$$\frac{\log d\alpha}{dt} = f\left(\frac{1}{T}\right)$$

Using Ozawa-Flynn-Wall method function graphs were plotted (Fig. 12 a, b).

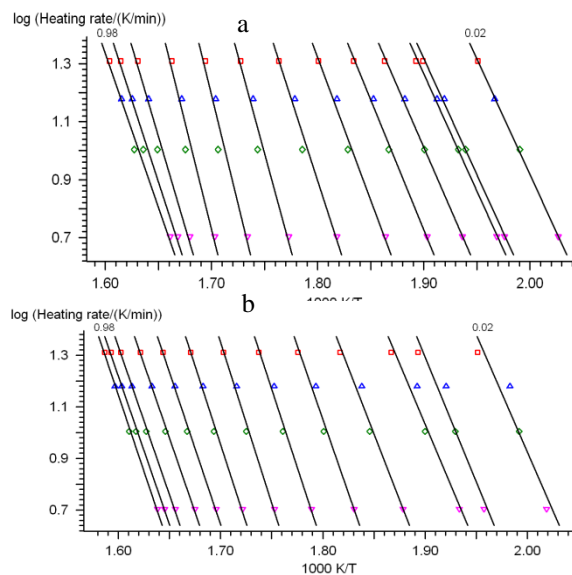


Fig. 12 – Samples weight loss curves in the coordinates of $\log(d\alpha/dt)-1000/T$ obtained using Ozawa-Flynn-Wall method: a – flax shive (non catalytic); b – flax shive + NiCl_2 10%.

According to the data obtained, for both catalytic and non-catalytic processes the incline change of the lines directly-proportional to activation energy is observed with the increase of the conversion degree that indicates the existence of more than one destruction stage in the temperature range studied.

In the case of a multistage process the information can be obtained only for initial step using Friedman method. The analysis of the dependences of the destruction rate logarithm on the reciprocal temperature plotted by Friedman method (Fig. 13 a, b) shows that non-catalytic pyrolysis initiation can be complicated by the diffusion processes. It can be concluded because the lines joining the experimental dots in the range $0.02 \leq \alpha \leq 0.1$ have lower angle of slope towards abscissa than isoconversion lines. In the case of catalytic process the angle of slope is congruent therefore the initial process can be described by the n-order reactions.

The values of the activation energy and pre-exponential factor calculated by both Friedman and Ozawa-Flynn-Wall methods have high convergence. According to the dependences of kinetic parameters obtained from Arrhenius equation on the partial weight loss (Fig. 14 a, b), both catalytic and non-catalytic flax shive decomposition has two stages since there are the activation energy maxima at $\alpha = 0.5$ for non-catalytic and $\alpha = 0.75$ for catalytic processes.

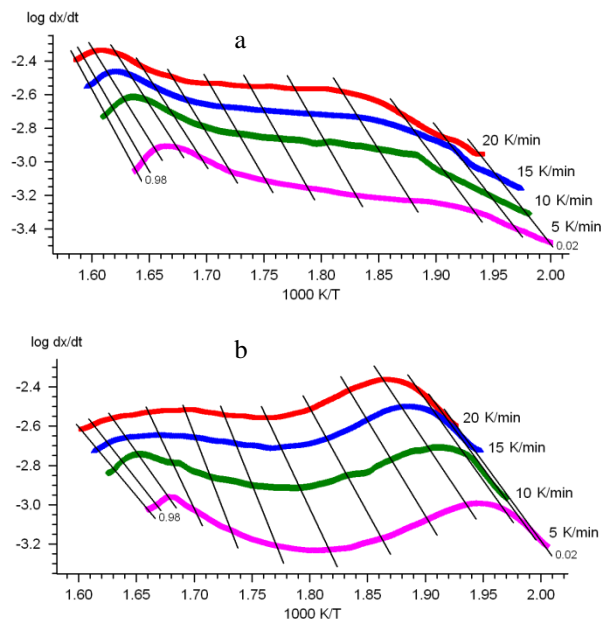


Fig. 13 samples weight loss rate curves in the coordinates $\log(dx/dt)-1000/T$ obtained using Friedman method: a – flax shive (non catalytic); b – flax shive + NiCl_2 10%

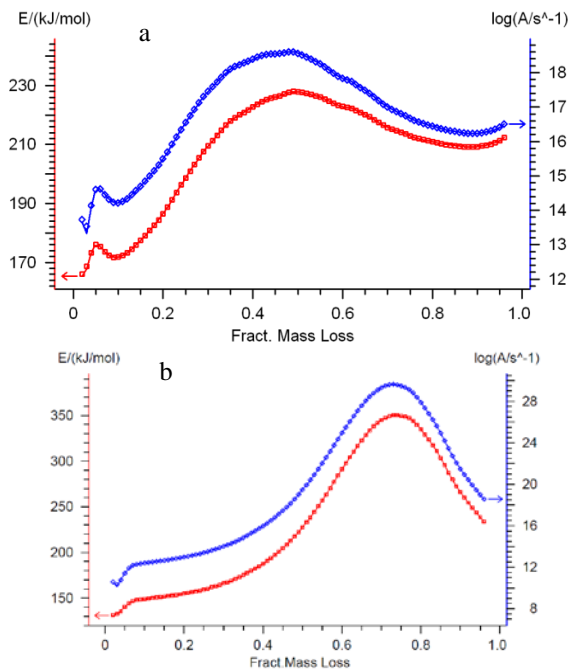


Fig. 14 activation energy and pre-exponential factor dependence on the sample partial weight loss obtained by Ozawa-Flynn-Wall method: a – flax shive (non catalytic); b – flax shive + NiCl_2 10%

Taking into account the kinetic parameters several models were tested. The statistical analysis of these models on the base of F-test shows that there is one kinetic model for both catalytic and non-catalytic flax shive destruction processes description which meets the condition $F_{\text{exp}} \leq F_{\text{crit}}$ with significance level 95%. According to the model the flax shive pyrolysis process consists of two parallel competitive stages

(Fig. 15 a, b). One of the stages can be presented as topochemical process described by Avrami-Erofeev equation. The calculated kinetic parameters of thermodestruction processes of both flax shive and flax shive with 10% (wt.) nickel chloride addition are presented in Table 1.

Table 1. Activation energies (E), common logarithm frequency factors ($\lg A$) for the models of both flax shive non catalytic and catalytic pyrolysis

Parameter		Step 1	Step 2
E_a , kJ/mol	non catalytic	193	213
	NiCl_2 10%	200	175
$\lg A$, c^{-1}	non catalytic	14.2	17.7
	NiCl_2 10%	15.3	15.5

The presented data show that the first stage of thermodestruction of the pure flax shive and of the sample with nickel chloride addition is almost equal within the experimental error $\pm 3\text{kJ/mol}$. The second stage has lower activation energy in the presence of nickel chloride.

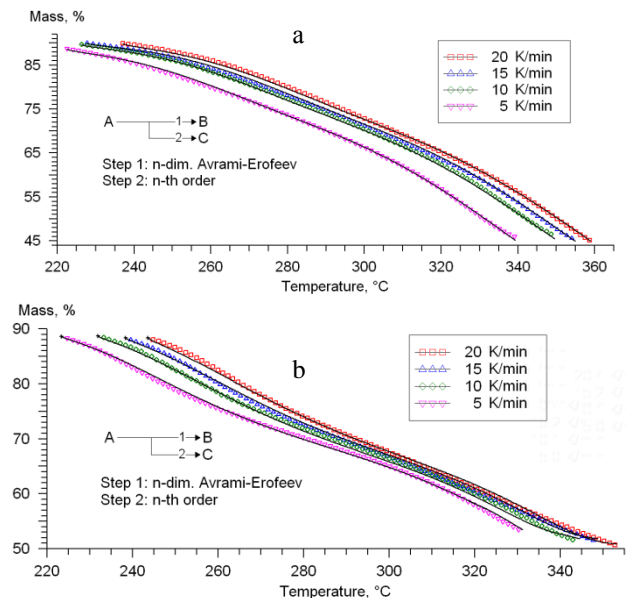


Fig. 15 – Curves of the flax shive sample weight loss at a different heating rate K/min: 5, 10, 15, 20; a – flax shive (non catalytic); b – flax shive + NiCl_2 10%. Line: computed; symbol: experimental.

The flax shive pyrolysis is a complex process consisting of numerous chemical reactions and depending on the chemical composition of raw material, reaction medium, catalyst presence and temperature. So the kinetic models obtained are formal and it is difficult to describe the flax shive pyrolysis process chemistry.

IV. CONCLUSION

BASING on the results of the investigation it can be concluded:

- 1) According to the activity in the flax shive thermodestruction processes the compounds of iron subgroup metals can be ranged as follows: oxides < nitrates < chlorides;
- 2) The flax shive samples containing iron subgroup metal chlorides showed lower thermal stability;
- 3) Iron subgroup metal chlorides lead to the decrease in thermal stability of all the flax shive components (hemicelluloses, cellulose and lignin);
- 4) Among metal chlorides studied nickel chloride with the content of 10% (wt.) has the highest activity;

The use of nickel chloride (10% wt.) results in the decrease of the activation energy of one of the stages of the flax shive thermodestruction process by 38 ± 3 kJ/mol

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