

Pyrolysis of Agricultural Waste in the Presence of Fe-Subgroup Metal-Containing Catalysts

Yury V. Lugovoy, Kirill V. Chalov, Yury Yu. Kositsov, Esther M. Sulman*, Mikhail G. Sulman

Tver State Technical University, A.Nikitinstr. 22, Tver, 170026, Russian Federation
 sulman@online.tver.ru

In this work, the results of the investigation of catalytic activity of iron subgroup metal-containing catalysts in the process of pyrolysis of flax shive are presented. The influence of iron subgroup metals oxides, nitrates, and chlorides on flax shive pyrolysis process the samples with 10 % content of mineral compounds was investigated by thermogravimetric analysis. The natural and synthetic zeolite materials (ZSM-5) were used as metal-containing catalysts in the pyrolysis process of flax shive. The resulting catalyst – ZSM-Bentonite clay + 2 % (wt.) Co had the highest catalytic activity, which was to accelerate the process of pyrolysis and to increase the content of gaseous hydrocarbons C₁-C₄ at the composition of the pyrolysis gas. In the presence of ZSM-bentonite clay + 2 % (wt.) Co the concentration of hydrocarbons C₁-C₄ was increased compared to the non-catalytic pyrolysis process.

1. Introduction

Year after year, the problem of biomass processing is becoming more urgent due to the competitive struggle for conventional energy sources (Balat et al., 2009). Some of the types of biomass wastes such as flax shive in actual fact are not utilized and pollute the environment (Shabalina and Kapko, 2016). For example, there is a big resupplied stock of flax shive in the north-west region of the Russian Federation over 6,000 t (Nikitin, 2011). 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 (Yanik et al., 2007). It is noteworthy that the complexity and variability of the composition of one type of biomass do not allow the problems of effective complex processing of biomass to be solved (Huber et al., 2006). There are many effective methods which attracted the attention of numerous scientific groups. To process the plant biomass into energy, different methods such as combustion, gasification, pyrolysis, bioconversion, etc. are used (Brown et al., 2017). The flax shive is the lignified parts of the flax stem mainly in the form of small straws which remain after the flax scorching. In as much as a flax shive contain a high content of lignin, it can be used as high-quality carbon materials (Rosse et al., 2010). From this point of view, the pyrolysis is the most effective method of processing flax shive because it is possible to produce a large amount of fixed carbon (Marshall et al., 2007). The use of catalysts is the permissive way to increase the efficiency of pyrolysis, as well as the yield and quality of the final products. The catalyst in the pyrolysis process affects both the reaction rate and selectivity to the desired products and can serve as the heat supplier that leads to the decrease in the process temperature (Antonakou, 2014). For this reason, the search for pyrolysis catalysts causes a significant interest all over the world (Huber et al., 2006). Nowadays, there are numerous studies on the pyrolysis catalysts. Numerous studies are devoted to the application of alkali and alkaline-earth metal oxides (Serio et al., 2017). The alkaline-earth metal carbonates also showed good catalytic efficiency in the pyrolysis of lignocelluloses materials (Quek et al., 2013). However, alkali metals, particularly K, are able to promote char formation and increase the yield of low-molecular products (Chen et al., 2017). For this reason, the researchers are focused on the use of transition metals such as zink chloride (Lu et al., 2011), nickel salts (Mishra et al., 2014), and copper salts (Aguado et al., 2014). The main disadvantages of the transition metals in pyrolysis are the increase in the carbonaceous solid residues and increase in hydrogen formation (Nzihou et al., 2019). The

last works in the field of thermal destruction were carrying out the process in the presence of zeolites (Mishra et al., 2014), zeolites modified with transition metals (Fabbi et al., 2007), Red Mud and ReUS-Y catalysts (Brebu et al., 2014).

However, the application of zeolites is mainly reported for the individual compounds of biomass. There is practically no data for the use of aluminosilicates for the pyrolysis of natural feedstock. For this reason, in this work a preliminary study of process thermal destruction of flax shive in the presence of aluminosilicates containing iron subgroup metal oxides by thermogravimetric analysis was conducted. This study represents a practical benefit because it can lead to an increase in the efficiency of the pyrolysis of biomass, which in general will bring closer to the decision to use the agricultural waste of plant origin for energy production.

2. Experimental

2.1 Materials

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 ± 0.1 %, and the ash content was 4.16 ± 0.1 %. To study the influence of iron subgroup metals oxides, nitrates and chlorides on flax shive thermal destruction process, the samples with 10 ± 0.1 % content of mineral compounds were prepared by trituration.

Natural aluminosilicate materials (bentonite clay), synthetic zeolite (ZSM-5 «Zeolyst International» USA) and mixed samples (bentonite clay - ZSM-5 in mass ratio 1:1) with various containing of an iron subgroup of metals were used as the catalysts of flax shive pyrolysis. The catalyst was prepared by the method of aqueous impregnation with the use of chlorides of the respective metals ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$). The concentration of catalysts in the feedstock was varied from 2 to 10 ± 0.1 % wt. The concentration of iron subgroup metals in chosen for investigation catalysts was about $1-10 \pm 0.2$ % wt.

2.2 Methods of the analysis

The study of flax shive pyrolysis process kinetics was carried out using thermoscales TG 209 F1 (NETZSCH) with the 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.

After completion of the experiment, the following parameters were determined: solid residue weight according to the change of the reactor weight; liquid fraction weight according to water trap and sampler weight; gas weight according to the difference of the initial sample, liquid, and solid residue weight. The standard deviation for the pyrolysis products is ± 0.5 % (wt.) from weight measurements. The gaseous products analysis was performed by the gas chromatography method. The analysis of the fast pyrolysis gaseous products consisted of C₁-C₄ hydrocarbon, carbon oxides, and hydrogen content definition, as well as the express analysis of the lower specific heat value. The chromatographic analysis of the gaseous products was performed on the base of chromatograph "Kristallux" 4000M and modified chromatograph "Gasochrom 2000".

2.3 Pyrolysis procedure

The study of the flax shive catalytic pyrolysis involving the choice of the most active metal-containing aluminosilicate catalyst was conducted using the laboratory setup shown in Figure 1.

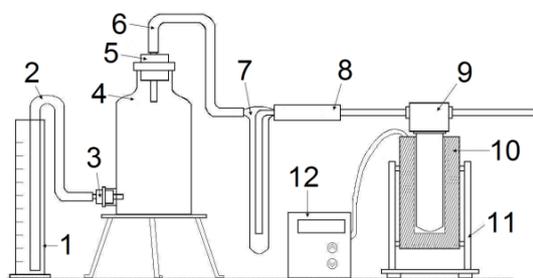


Figure 1: The experimental setup for the pyrolysis experiments: 1 - measuring cylinder, 2 and 6 connecting tubes, 3 and 5 – corks, 4 – eudiometer, 7 – water trap, 8 – sampler, 9 – reactor, 10 - electric furnace, 11 – furnace tripod, 12 – electronic temperature controller

The experimental pyrolysis reactor consists of a metal fixed-bed reactor heated by the electric furnace, a gas sampler, a water trap for collecting liquids, and a eudiometer for collecting gas. The reactor is equipped with an outlet for inert-gas purging. Before the tests, the flax shive feed was placed into the fixed bed reactor. Then the system had been purged by a low flow of nitrogen for 5 min. After that the heating was carried out, the temperature was ranged from 400 °C to 600 °C (400, 500, 550, 600 °C). The duration of the test was an hour, and each test was repeated at least two times.

3. Results and discussion

3.1 Thermogravimetric analysis

3.1.1 The effect of metal oxides of the iron subgroup

According to the reference data (Buranov et al., 2010) and the thermogravimetric studies performed in this work, the investigated metal oxides do not undergo any changes in the temperature range under study. Figure 2 shows TG (a) and DTG (b) curves for clean bonfires, and flax bonfires with 10 % wt. content of iron oxide, cobalt, and nickel.

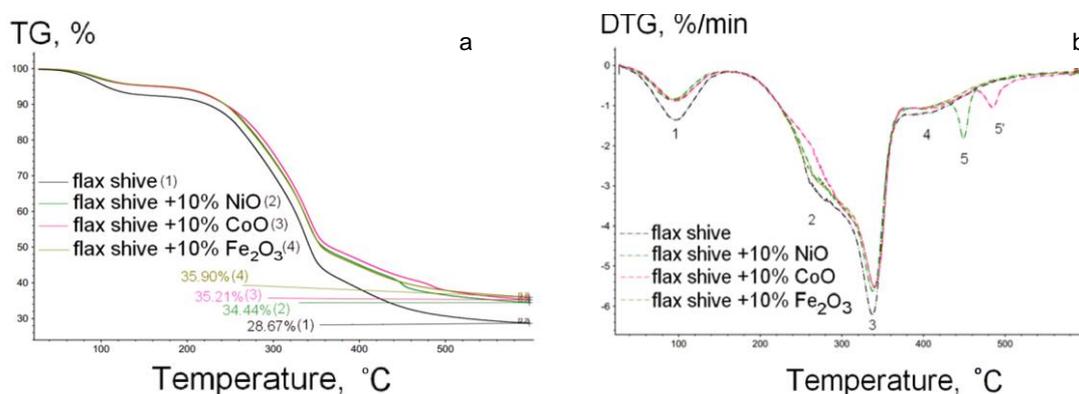


Figure 2: TG (a) and DTG (b) curves for a sample of flax shive and flax shive with the addition of 10% (wt.) of the iron subgroup metal oxides

As can be seen from the data presented in Figure 2, the shape of the TG and DTG curves with the addition of oxides of metals of the iron subgroup did not undergo significant changes compared with the sample of bonfires without additives. An analysis of the TG curves shows that the samples of fires with the addition of metal oxides of the iron subgroup have lower initial moisture content and slightly larger values of the mass of the solid residue. This can be explained by a decrease in the mass fraction of fires in the sample, as well as by the fact that the oxides used have thermal stability in the range of the temperatures studied.

Figure 2b shows the DTG curves of the sample of pure flax shives and samples of flax shive with 10 % wt. content of metal oxides of the iron subgroup. Peak 1, indicated in Figure 2b, corresponds to the loss of the initial moisture contained in all samples studied flax shives. According to (Buranov et al., 2010), flax shives consists of cellulose (45-58 %), lignin (21-29 %) and hemicelluloses (23-26 %). The decomposition of the components of the plant biomass occurs in the following order: hemicelluloses initially destruction in the temperature range from 200 to 320 °C, then cellulose is destructed in the interval from 280 to 400 °C and the thermal destruction of lignin occurs last (260 - 500 °C). Peak 2 corresponds to the maximum rate of thermal destruction of hemicellulose. It should be noted that when using cobalt oxide in additive to the flax shive, this peak is almost completely absent, in contrast to the use of nickel and iron oxides. The rate of cellulose destruction contained in flaxshives when using various metal oxides of the iron subgroup is practically the same for all oxides studied and slightly lower than the thermal decomposition rate of flax shives without additives (see peak 3, Figure 2b). This can be explained by the lower content of flax shives in these samples, which are subject to intense thermal destruction. Peak 4 corresponds to intensive destruction of lignin, the position and intensity of the peak take on similar values for all samples, which indicates the absence of the influence of the oxides understudy on the destruction of this component of flax shives. Differences in the solid residue values of flax shives samples, obtained using the metal oxides of the iron subgroup, can be explained by the different reduction potential of the metal oxides used. For example, in Figure 2b for flax shives samples using nickel and cobalt oxides on the DTG curves, peaks of mass loss are clearly visible (5 and 5'), which most likely correspond to the reduction processes of these oxides. For a sample of flax shives with the addition of iron oxide, such a peak is not

observed, which can be explained by a higher potential for reducing iron, which can be reduced at higher temperatures beyond the temperature range under study.

3.1.2 Effect of metal nitrates of the iron subgroup

In this paper, a study was conducted of the effect of nitrates of metals of the iron subgroup on the thermal decomposition process of flax shives. As shown by the calculation of residual masses of metal nitrate samples, made on the basis of the experimental data, the hexahydride nitrates of metals of the iron subgroup completely decompose to the corresponding metal oxides. The calculated masses of the solid residues of thermal destruction, taking into account the measurement error, completely coincide with the experimental value, which indicates an insignificant effect of the studied metal nitrates on the thermal decomposition process of flax shives (see Figure 3).

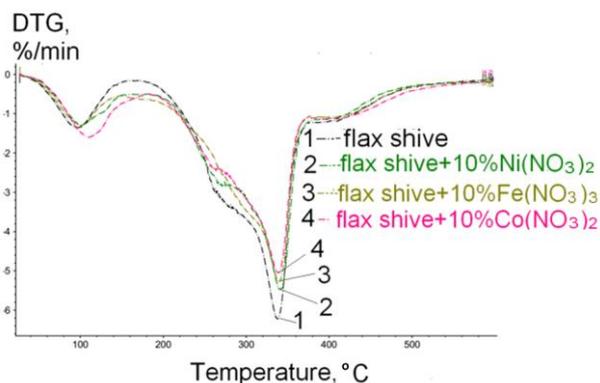


Figure 3: DTG curves of samples of flax shives with the addition of nitrates of metals of the iron subgroup

According to the activity in the flax shive thermodestruction processes the compounds of iron subgroup metals can be ranged as follows: oxides < nitrates < 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 (see Figure 4). 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. Thus further study with using the laboratory setup was carried out for catalytic pyrolysis flax shive in presence of silica-alumina catalysts impregnated by water solution of the cobalt chloride.

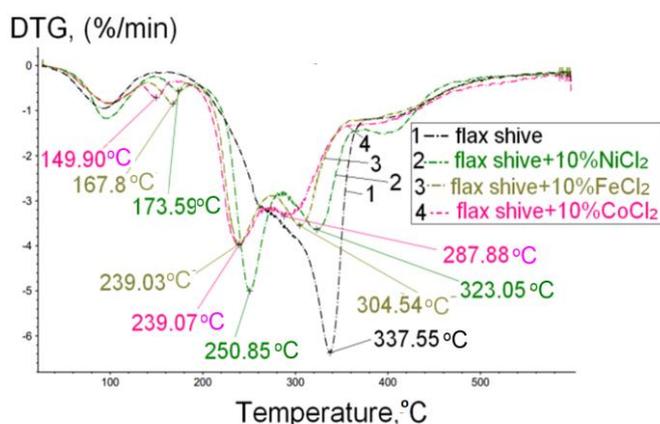


Figure 4: DTG curves of pure flax shive and the samples with the addition of iron subgroup metal chlorides

3.2 Catalytic pyrolysis in a laboratory setup

The temperature range of the process is one of the major parameter determinative the mass distribution of the pyrolysis products. The increase in temperature leads to an increase of gaseous and liquid products mass.

However, while the temperature is increasing the cost of the process is also increasing, that leads to the increase of prime cost of the final product. The optimal temperature of the process is 550 °C (see Figure 5), at this temperature the mass (m) ratio of the pyrolysis products is optimal from the point of view of industrial and economical use. Further experiments were carried out at this temperature.

The introduction of aluminosilicate catalysts was not practically significant effect on the mass distribution of pyrolysis products flax shive. When using selected catalysts significantly changed the properties of pyrolysis gases.

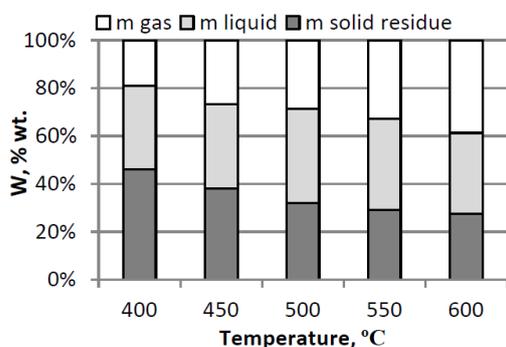


Figure 5: Influence of temperature on conversion of flax shive

When using the studied catalysts, the rate of gas formation was significantly higher compared to non-catalytic pyrolysis process, and time the formation of gaseous products has declined on 15 min. The content of cobalt in the catalyst was varied from 2 - 10 % by weight. The greatest influence on the composition and properties of pyrolysis gas provided to the catalyst with 2 % (wt.) content cobalt. According to Figure 6, in the presence of this catalyst increased the content of gaseous hydrocarbons in the composition of the pyrolysis gas.

Application of all of the studied catalysts results in the decrease of hydrogen concentration, which also affected the increase of the lower volumetric heat of combustion of gaseous pyrolysis products.

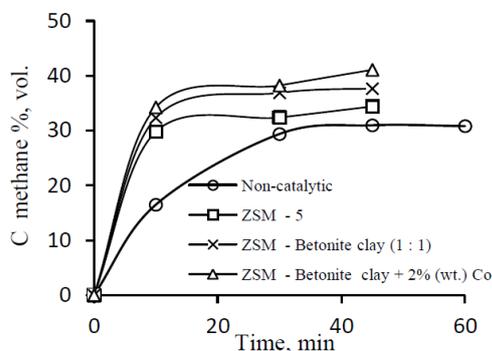


Figure 6: Dependence of methane concentration of time process ($T = 550$ °C)

As can be seen from the presented data, the highest influence on the composition of the gaseous products of flax shive pyrolysis showed ZSM-Bentonite clay + 2 % (wt.) Co. In its presence, the concentration of hydrocarbons C_1-C_4 was increased by 1.3-1.7 times compared to non-catalytic pyrolysis process. Optimal maintenance of ZSM-Bentonite clay+2 % (wt.) Co in raw materials was determined in the course of processing of the received experimental data, which amounted to 5 % wt.

4. Conclusion

The use of synthetic zeolite catalyst ZSM-5 had high activity, but its uses in pure form limit its high cost. Use of supplements of bentonite clay was aimed at reducing the cost of the catalytic system, and the impregnation of cobalt in the composition of the aluminosilicate matrix was intended to increase the catalytic activity.

The resulting catalyst – ZSM-Bentonite clay + 2 % (wt.) Co has the highest catalytic activity which was to accelerate the process of pyrolysis and to increase the content of gaseous hydrocarbons C₁–C₄ at the composition of the pyrolysis gas. In the result, we can draw the following conclusions:

1. The optimal temperature of flax shive pyrolysis process is about 550 °C;
2. According to the influence on cellulose destruction temperature, the studied metal chlorides can be ranged as follows: CoCl₂ > FeCl₂ > NiCl₂;
3. The optimal metal content in the catalyst to 2 % (wt.);
4. Optimal maintenance of ZSM-Bentonite clay + 2 % (wt.) Co in flax shive to 5 % (wt.);
5. In the presence of ZSM-Bentonite clay + 2 % (wt.) Co the concentration of hydrocarbons C₁–C₄ were increased 1.3-1.7 times compared to non-catalytic pyrolysis process.

As a prospective for future studies, the investigations on the influence of other transition metals incorporated to the chosen aluminosilicates as well as the influence of their concentrations on the flax shive pyrolysis process can be proposed. Moreover, the studies on the gaseous and liquid product composition of catalytic pyrolysis process must be also done.

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