

Influence of ZSM-5 Zeolite on the Composition and Properties of Gaseous and Liquid Products of Fast Pyrolysis of Flax Processing Waste

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In the work, the influence of the initial characteristics of feedstock on the yield, composition, and properties of fast pyrolysis products was studied. Samples of the original flax shive and its cellulose residue obtained as a result of alkaline hydrolysis were chosen as the raw materials for the investigation of fast pyrolysis to obtain useful products – phenyl propane derivatives (guaiacyl- and syringyl propanols, propenes, and propane). The use of preliminary chemical processing of plant raw materials is aimed at maximizing the use of the initial potential of raw materials, as well as reducing energy costs and improving the quality of pyrolysis products. The paper discusses the dependence of the composition and properties of fast pyrolysis products on the process conditions – temperature, retention time of the raw material in the heating zone, and the diameter of the particle of the feedstock. The optimal conditions for fast pyrolysis for flax processing waste are temperature 700 °C, particle size 0.25 -1 mm, and particle residence time in the heating zone of 4.4 s. The results of a study of the process of fast pyrolysis of flax processing waste in the presence of a ZSM-5 catalyst are also presented. The presence of ZSM-5 zeolite increases the content of ethylene, hydrogen, and carbon dioxide, which is probably associated with the cracking of volatile products passing through the catalyst heated to high temperatures. The composition of liquid products of fast pyrolysis obtained using a thermocatalytic purification stage on the synthetic zeolite ZSM-5 was significantly reduced in the number of chemicals compared to the compositions of liquid products of fast pyrolysis obtained without a purification stage.

1. Introduction

At present, environmental and economic problems associated with the use of solid fossil fuels are beginning to become more and more widespread and force us to look for new ways of development in the field of energy production. Due to the limited nature of fossil fuels, technologies for obtaining energy from various types of plant biomass are promising and are undergoing fast development. Such technologies help to eliminate the dependence of energy consumers on energy supplies. An increase in the share of biomass as a fuel for energy generation leads to a decrease in CO₂ emission that inevitably arises from the use of traditional fossil fuels.

Flax production in the Tver region reaches 6 kt/y, with up to 70 % (wt.) being a production waste - a flax shive (lignified parts of the flax, mainly in the form of small straws, remaining after the flax scutching stage). Usually, flax shive forms huge dumps or is undergone to be burned in a furnace for heating factories. In the northwestern region of the Russian Federation, there are large constantly replenished stocks of flax shive, which today, for various reasons, is practically not processed. Plant biomass waste can be converted into valuable products and biofuels using various thermal, physicochemical, and biological processes. For the production of these products, it is possible to use raw materials of plant origin as one of the alternative ways to obtain various hydrocarbons.

Fast pyrolysis, according to many researchers, is one of the most effective methods for processing plant waste feedstock. It has such advantages as low tar content in volatile products, the possibility of creating

autonomous mobile power plants with a closed cycle operating in a continuous mode, and the possibility of controlling the conversion to target products by controlling the retention time of feedstock in the heating zone. The necessity of fine purification of fast pyrolysis gas from tars is a disadvantage of this method. In addition, high oxygen content in the resulting liquid products of fast pyrolysis leads to its high acidity, aggregative instability, and immiscibility with hydrocarbon fuels (Bhoi et al, 2020).

According to the authors, the most effective approach to increase the efficiency of pyrolysis processes is a strategy that includes two stages of processing plant materials. The first stage is associated with chemical processing, which is aimed at obtaining valuable chemical products - furfural, vanillin, and syringaldehyde, as well as phenylpropane derivatives (guaiacyl and syringyl propanols, propene, and propane). At the second stage, it is supposed to use fast pyrolysis with the stage of thermal catalytic tar removal (Lugovoy et al, 2021). The problem of increasing the efficiency of the pyrolysis process, as well as the quality of the final products obtained, is mainly solved through the use of catalysis (Ratnasari et al, 2020). The problem of coking and extraction of expensive zeolite catalysts directly introduced into the composition of the feedstock is particularly acute. The highest interest is to technological schemes in which the catalyst is taken out of direct contact with the raw material. One of the promising methods for processing and improving the quality of liquid fractions obtained during the thermal processing of biomass is the method of catalytic gas cracking. Catalytic cracking provides deoxygenation processes by simultaneous dehydration, decarboxylation, and decarbonylation occurring in the presence of zeolite catalysts (Liang et al, 2021). In the catalytic gas cracking method, synthetic zeolites are used to convert oxidized organic compounds into hydrocarbons. Zeolite cracking removes oxygen from oxygen-containing organic compounds in the form of carbon dioxide. Modernization and change in the chemical composition of the zeolite can affect the properties of liquid fractions and gaseous products of thermal processing of biomass (Mati et al, 2021).

The mesoporous structure of the synthetic industrial zeolite makes it an effective catalyst for the thermal degradation of tars. The use of this catalyst in thermal degradation processes is most often found in modern publications (Bhoi et al, 2020). The experimental study of the effect of zeolite ZSM-5 on deoxygenation processes in the framework of the process of fast pyrolysis of flax processing waste is of scientific and practical interest. According to the authors, this stage of the study is important for the further development of cheaper catalytic systems based on natural aluminosilicates impregnated with active metal-containing phases. This study will allow the solution of the problem of processing flax waste with the maximum economic effect.

2. Experimental part

2.1 Materials

Samples of flax shive and flax cellulose residue were selected as raw materials for the pyrolysis process. Flax shive samples of the Republican Scientific Subsidiary Unitary Enterprise "Institute of Flax" of the Republic of Belarus were selected for research. A sample of zeolite ZSM-5 with a specific surface area of 560 m²/g and Si/Al ratio of 25 manufactured by Sorbis Group (China) was used in the study.

2.2 Analysis methods

The study of the composition and properties of gaseous products of non-catalytic fast pyrolysis was carried out for samples of flax shive and cellulose residue of flax shive at a temperature of 700 °C, the residence time of raw materials in the heating zone 4.4 s and a fraction size of 0.25-1 mm. The analysis of gaseous products was carried out by gas chromatography. Analysis of gaseous products of fast pyrolysis included determination of the content of C₁-C₄ hydrocarbons, carbon oxides, and hydrogen, as well as express analysis of the lower volumetric heat of combustion of gaseous products. The analysis of gaseous products of pyrolysis was carried out using the gas chromatography method, and using an analytical complex based on «Kristalluks 4000M» and «Gasokhrom 2000» gas chromatographs. Chromatographic separation and determination of hydrocarbon components were carried out on a «Kristalluks 4000M» chromatograph with a packed column filled with silica gel with a particle size of about 0.25 mm in a nitrogen flow at a temperature of 40 °C. Chromatographic determination of the content of carbon oxides and hydrogen in the composition of gaseous pyrolysis products was carried out using a «Gasokhrom 2000» chromatograph with a packed column filled with AG-5 grade activated carbon at a temperature of 40 °C.

The composition of samples of liquid pyrolysis products was determined by gas chromatography-mass spectrometry. The study of the liquid pyrolysis products of flax shive samples and the cellulose residue of the shive obtained at a temperature of 700 °C was carried out using a GCMS-QP2010S gas chromatography-mass spectrometer (SHIMADZU, Japan). High-purity helium was used as a carrier gas on an HP-1MS capillary column (d = 0.25 mm, l = 30 m). The temperature analysis program was the following: the initial

column temperature is maintained at 50 °C for 1 min, then the temperature is gradually increased to 280 °C at a rate of 2 °C/min.

2.3 Pyrolysis procedure

To study the processes of fast pyrolysis with the stage of catalytic deoxygenation of volatile products, a semi-batch laboratory setup was used. The feedstock was loaded into the loading device in an amount from 10 to 20 g. The raw material was fed by a screw feeder to the heating zone of the fast pyrolysis reactor. The fast pyrolysis reactor was heated by a coil of an induction furnace. The residence time of the feedstock in the heating zone was controlled by the speed of rotation of the screw using a frequency controller in the range of 1 to 20 seconds. Further, the solid carbon residue formed in the process was poured into an unloading device, and the volatile pyrolysis products passed through the stage of catalytic deoxygenation. The temperature of the catalytic purification stage was maintained by a separate furnace controlled by a temperature controller and a contact thermocouple. The temperature of the catalyst inside the stage of thermal catalytic purification was in the range of 350 to 750 °C.

3. Results and discussion

The results of preliminary experiments showed that an increase in the residence time of raw materials in the heating zone leads to a significant increase in tars that are formed as a result of secondary processes. A decrease in the retention time of raw materials in the heating zone leads to difficulty in heat transfer. As a result, a low conversion of raw materials was observed. Experiments on fast pyrolysis of flax shive were carried out in a higher temperature range from 500 to 700 °C with a residence time of the feedstock in the heating zone up to 2 to 20 s.

Figure 1 presents the results on the study of temperature influence on the pyrolysis (flax shive fraction size 1-2 mm, the residence time of the raw material in the heating zone 4.4 s). From the data presented in Figure 1, it can be seen that an increase in the temperature of the fast pyrolysis reactor leads to a decrease in the mass of the solid carbon-containing residue.

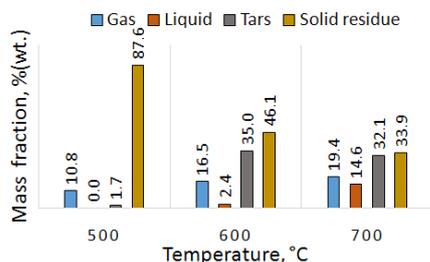


Figure 1: Dependence of the mass fraction of products of fast pyrolysis of flax shive on the process temperature

It should be noted, that the decrease in the mass of the solid residue occurs most intensively in the range from 500 to 600 °C, while the masses of gaseous and liquid products increase with increasing temperature. The maximum amount of tars formed during the fast pyrolysis of flax shive corresponds to a temperature of 600 °C. At a temperature of 500 °C, a smaller amount of tars is formed, which can be explained by a lower conversion of raw materials at a given temperature and a low rate of secondary reactions between the carbon residue and volatile pyrolysis products.

At a temperature of 700 °C, the amount of tars slightly decreases compared to a temperature of 600 °C. This can be explained by a deeper course of thermal destruction processes with the formation of a larger number of products with a relatively low molecular weight - liquid and gaseous substances.

The effect of particle size distribution on the yield of fast pyrolysis products is shown in Figure 2. An increase in the particle size of the feedstock in fast pyrolysis led to a decrease in the mass fraction of gaseous substances and tars, as well as to an increase in the mass fractions of liquid products and solid carbon residues. An increase in the mass of solid carbon residues of fast pyrolysis is probably associated with complicated processes of mass and heat transfer with an increase in the particle diameter of the processed raw material. It should also be noted that the degree of maturity of the resulting coal residues decreases with an increase in the particle size of the feedstock. The optimum feedstock particle size was found to be a fraction from 0.25 to 1 mm. This particle size distribution allows the high yields of gaseous and liquid products of fast pyrolysis to be obtained.

The influence of the heating time of the raw material is one of the most important characteristics of the fast pyrolysis process, since the heating time of the feedstock determines the conversion of the raw material into final products, and affects their composition and properties.

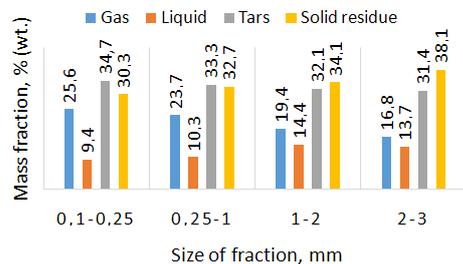


Figure 2: Dependence of the conversion of flax shive on the time spent in the heated zone ($T = 700\text{ }^{\circ}\text{C}$, the heating time of the raw material 4.4 s)

On the one hand, there is a need to strive to reduce the residence time of the raw material in the heated zone, since this reduces the level of secondary processes and, consequently, reduces the yield of tars. On the other hand, high conversion of the feedstock with short heating times is achievable only at sufficiently high temperatures and a small particle size of the feedstock, which entails additional structural difficulties and economic costs.

According to Figure 3a, an increase in the residence time of flax shive particles in the heated zone led to an increase in conversion to gaseous, liquid, and tar products.

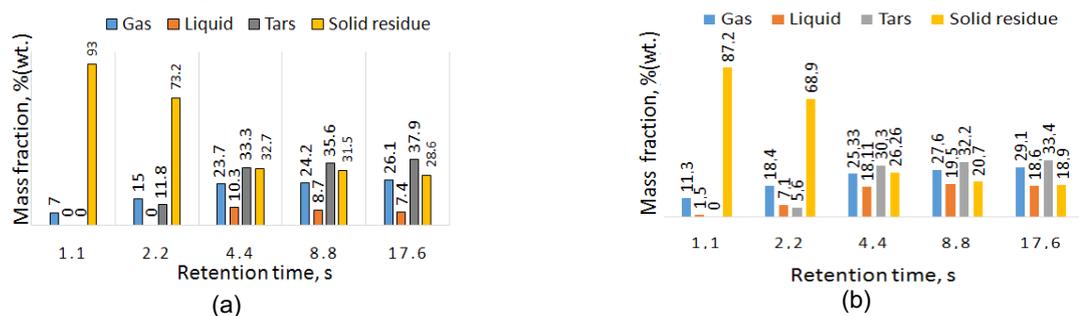


Figure 3: Dependence of the conversion of flax shive (a) and cellulose residue of flax shive (b) on the time the raw material is in the heated zone ($T = 700\text{ }^{\circ}\text{C}$, fraction size 0.25-1 mm)

Significant decrease in the mass of the solid carbon-containing residue is observed in the range from 2.2 to 4.4 s. With a further increase in the residence time of the raw material in the heated zone, the mass of the solid residue decreases to a lesser extent. It should be noted that with an increase in the residence time of the flax shive in the heating zone from 4.4 to 17.6 s, a significant increase in total tars from 33.3 to 37.9 % by weight was observed in the process of fast pyrolysis. For cases of using flax cellulose residue as a raw material for fast pyrolysis (Figure 3b), lower yields of solid carbon residues and tars, as well as higher yields of gaseous and liquid products in the studied range of the residence time of the raw material in the heated zone was obtained. This pattern can be explained by the fact that cellulose is less heat-resistant compared to the original shive in which the content of lignin is significantly higher. The lower content of lignin in the cellulose residue of the flax shive can lead to a lower yield of the solid carbon residue of fast pyrolysis. In accordance with the data presented in Figure 4, the composition of the gaseous products of the rapid pyrolysis of flax is characterized by a high content of C_1 - C_4 hydrocarbons and lower concentrations of carbon monoxide and dioxide. The data on the composition of gaseous products of fast pyrolysis is indirectly confirmed by the obtained experimental values of the lowest volumetric heat of combustion of gaseous products, which were 14.3 MJ/m^3 and 11.4 MJ/m^3 for flax shive and cellulose residue of the shive. Chromato-mass spectrometric study of gaseous products made it possible to determine the presence of low molecular weight aldehydes, ketones, alcohols, acids, and other products in the gaseous products of fast pyrolysis of plant biomass. The influence of the stage of thermocatalytic purification on the volume and heat of combustion of gaseous products in the process of rapid pyrolysis is presented in Table 1.

Table 1: Influence of the stage of thermocatalytic cleaning on the volume and heat of combustion of gaseous products in the process of fast pyrolysis of flax shive

Parameter	-	750 °C	350 °C	450 °C	550 °C	650 °C	700 °C	750 °C
		non-cat						
V gas, l	1.10	1.19	1.21	1.23	1.26	1.28	1.29	1.30
Q, MJ/m ³	12.1	11.7	16.5	16.7	17.5	17.8	18.2	18.1

An increase in the temperature of the thermocatalytic purification led to an increase in the volume of gaseous products. For comparison, data are added to the table using a furnace heated to 750 °C without using a catalyst. Zeolite ZSM-5 also increased the content of ethylene, hydrogen, and carbon dioxide. This is probably associated with the cracking of volatile products passing through the bed of the catalyst heated to high temperatures. The optimum temperature for obtaining large volumes of combustible gases with high calorific values is 700 °C. This temperature contributes to a significant decrease in the content of tars in the composition of gaseous products from 0.6 % to 0.16 %.

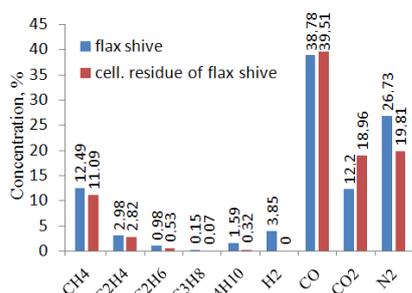


Figure 4: Composition of gaseous products of fast pyrolysis depending on the type of raw materials under study ($t = 700\text{ }^{\circ}\text{C}$; 4.4 s; diameter of raw material particles 0.25-1 mm)

The heat of combustion of gaseous products when using synthetic zeolite ZSM-5 increases in the range from 350 to 700 °C and then practically does not change when the temperature rises to 750 °C. This is due to the fact that with an increase in temperature, an increase in the concentration of methane and a decrease in the concentration of hydrocarbons C₂-C₄ are observed. The effect of the catalyst on the composition of liquid products of fast pyrolysis of the studied samples of flax shive and cellulose residue of the shive is shown in Figures 5a and 5b, where 1 - acetone; 2 - vinyl acetate; 3 - acetic acid; 4 - 2-butenal; 5 - 2-oxopropanal; 6 - acetylpropionyl; 7 - hydroxyl acetaldehyde; 8 - not recognized; 9 - 1-hydroxy-2-butanone; 10 - furfural; 11 - 3,4-dihydro-2-pyran; 12 - 3-methylcyclopentanone; 13 - 3,4-dihydroxy-3-cyclobutene-1,2-dione; 14 - 1,2-dioxocyclohexane; 15 - guaiacol; 16 - 2-methoxy-p-cresol; 17 - 4-vinyl guaiacol; 18 - 2,6-dimethoxy phenol; 19 - isovanillin; 20 - 2-methoxy-4-propenylphenol; 21 - acetovanillone; 22 - vanillyl methyl ketone; 23 - dodecanoic acid; 24 - 4-ethylguaiacol

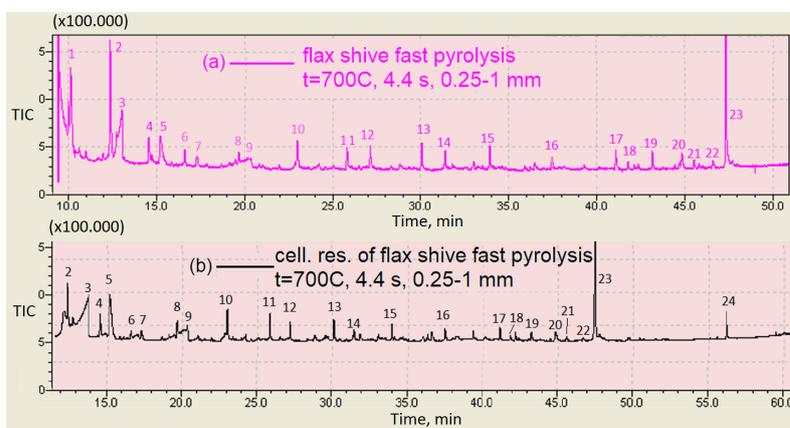


Figure 5: Composition of liquid products of rapid pyrolysis of flax shive (a) and cellulose residue of flax shive (b)

The data were obtained by analyzing liquid products in the presence of an additional thermocatalytic stage of purification of volatile products in the presence of synthetic zeolite ZSM-5. According to experimental data, the composition of liquid products of fast pyrolysis obtained using a thermocatalytic purification stage using synthetic zeolite ZSM-5 was significantly reduced in the number of chemicals compared to the compositions of liquid products of fast pyrolysis obtained without a thermocatalytic purification stage. The composition of liquid products of fast pyrolysis obtained using the stage of thermocatalytic purification (see Figure 6) is characterized mainly by low molecular weight ketones and ethers, as well as heterocyclic and aromatic substances, which are products of thermal destruction of the main components of plant biomass.

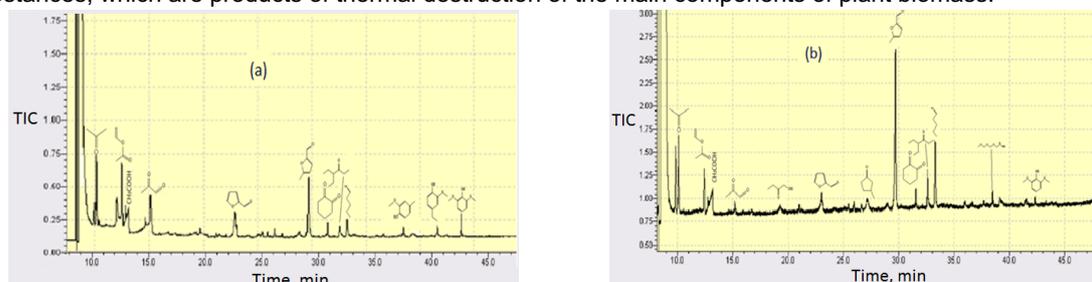


Figure 6: Composition of liquid products of fast pyrolysis in the presence of a thermocatalytic purification stage: a - flax shive; b - cellulose residue of flax shive

As a result, the use of a zeolite made it possible to improve the gaseous and liquid products of fast pyrolysis of the studied samples of plant biomass waste.

4. Conclusion

The optimal conditions for fast pyrolysis of flax processing waste were found to be temperature 700 °C, particle size 0.25 -1 mm, and particle residence time in the heating zone 4.4 s. The stage of catalytic purification with ZSM-5 zeolite affected the composition of gaseous and liquid products of fast pyrolysis of flax processing waste. The heat of combustion of gaseous products when using synthetic zeolite ZSM-5 increases in the range from 350 to 700 °C and then practically does not change when the temperature rises to 750 °C. This is due to the fact that an increase in temperature led to an increase in the concentration of methane and a decrease in the concentration of hydrocarbons C₂-C₄. In presence of zeolite ZSM-5, the content of ethylene, hydrogen, and carbon dioxide also increased, which is probably associated with the cracking of volatile products passing through the bed of the catalyst heated to high temperatures. The optimum temperature for the thermal catalytic purification stage is 700 °C. The composition of liquid products of fast pyrolysis when using ZSM-5 was presented by the reduced number of chemicals compared to the composition of liquid products of fast pyrolysis obtained without a thermal catalytic purification stage. It is characterized mainly by low molecular weight ketones and ethers, as well as heterocyclic and aromatic substances, which are products of thermal destruction of the main components of plant biomass. The use of a two-stage scheme for processing plant biomass waste can significantly increase the prospects for the processing process for energy purposes.

Acknowledgments

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