

## Slow Pyrolysis of Flax Production Waste

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The slow pyrolysis of flax shive and the cellulose residue of flax shive obtained by ethanolysis was studied in this work. Investigation of temperature effect on physical properties of pyrolysis products in the range of 500–750 °C on a laboratory slow pyrolysis unit was presented in this manuscript. The experimental obtained data of initial properties of investigation samples, thermal stability of samples, heat effects of pyrolysis process, chemical composition and physical properties of liquid and gaseous pyrolysis products are presented.

### 1. Introduction

The study of the pyrolysis process attracts of great interest of science because this method requires the lowest capital costs among the many options for industrial execution of existing thermal methods. An important aspect of pyrolysis is that all products obtained in the process can be used to reduce the energy consumption of the process itself (French et al., 2010).

In particular, pyrolysis gas can be used for heating a reactor or drying raw materials in case of high initial moisture content of raw materials, as well as for generating electrical energy. The resulting solid carbon-containing residue can be used as composites that improve the properties of soils, as carbon sorbents, or as coal in the smelting of metals or flux in the production of silicon. Currently, modern methods of processing plant waste into valuable chemical products have great practical interest, however, it should be noted that thermal transformations of chemical processing products and the possibility of combining chemical and thermal stages of processing when creating an integrated technology for processing plant waste have also of scientific interest (Yao Lu et al., 2011).

The development of technologies aimed at using biomass waste to obtain the greatest practical effect is carried out by numerous working groups using various methods and approaches (Hua et al., 2019).

The most justified strategy, according to the authors, is the processing technology, which includes several sequential stages and allows the maximum use of the initial potential of plant biomass. This technology can include two groups of biomass processing methods - chemical and thermal processing methods. At the first stage, it is planned to carry out chemical processing of raw materials by hydrolysis or methanolysis in order to obtain valuable chemical products - furfural, vanillin and syringaldehyde, as well as phenylpropane derivatives (guaiaacyl and syringyl propanols, propenes and propane). At the second stage of processing, thermal treatment of solid residues of chemical treatment of plant biomass is carried out, which is aimed to obtaining gaseous and liquid energy carriers and solid carbon sorbents.

The processing strategy described above should allow obtaining the maximum possible amount of chemical valuable substances, as well as increasing the efficiency of the thermal stage due to a more homogeneous composition of the pyrolyzed raw materials.

Flax shive is a lignified part of the flax stem, which predominantly looks like small straws that remain after flax fluttering. In the northwestern region of the Russian Federation, there are large constantly renewable stocks of flax shive, which are currently not used (Lugovoy et al., 2019).

In this article, the authors present the results of a study of pyrolysis process of the initial flax shive and the cellulose residue of the flax shive obtained at the stage of chemical processing. Comparison of the results of pyrolysis of the selected samples will make it possible to conclude about the advisability of applying an integrated approach to the processing of plant biomass waste of this type.

## 2. Experimental

### 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. The team of the Institute of Chemistry and Chemical Technology of the Siberian Branch of the Russian Academy of Sciences performed the extraction of lignin from a flax shive sample (ethanolysis), which was carried out in an autoclave with a capacity of 2.5 liters at 185 °C for 3 hours, heating the flax shive pulp (100 g) in 1,000 ml of water-ethanol mixture (40/60 % vol.). As a result, samples of the solid residue of flax shive ethanolysis were obtained - cellulose remains of the shive synthesized under optimized conditions for chemical processing of flax shive.

### 2.2 Methods of the analysis

Investigations of the initial characteristics of the selected biomass samples (humidity, ash content, elemental composition, heat of combustion, specific area and pore size distribution) were carried out. The calorific value of the samples was determined in accordance with GOST 147-2013 (ISO 1928-2009 Solid mineral fuel. Determination of the highest heat of combustion and calculation of the lowest heat of combustion). The measurement process was carried out using an ABC-1 adiabatic bomb calorimeter.

In this work, the elemental analysis of the samples was carried out for the content of carbon, hydrogen, nitrogen and oxygen (CHNO). Samples with air-equilibrium humidity were selected for analysis. Carbon and hydrogen were determined according to the accelerated method of GOST 2408.1, and the determination of nitrogen was carried out in accordance with GOST 28743. The data on the sulfur content in the flax shive were taken from scientific and technical literature. The oxygen content was calculated from the difference between the known components based on the analytical state of the sample.

The analysis of the specific surface area of the selected samples and the pore size distribution of these samples was performed by the method of low-temperature nitrogen adsorption using a Becman Coulter<sup>tm</sup> SA 3100<sup>tm</sup> instrument (Coulter corporation, Miami, Florida) and a specimen preparation instrument: Becman Coulter<sup>tm</sup> SA-prept<sup>m</sup> (Coulter corporation, Miami, Florida).

The study of the thermal stability of the samples was carried out on a NETZSCH TG IRIS 209 F1 thermogravimetric analyzer. The samples placed in corundum crucibles were heated at a constant rate (10 °C / min) in an inert argon atmosphere in the temperature range 50 – 1,000 °C. For thermogravimetric analysis, the samples were crushed and then a fraction with a particle size of less than 0.25 mm was taken.

During the thermogravimetric study of the samples, a mass spectrometric study of volatile products of thermal destruction was also carried out in the mass range of 1-300 amu and in the stated temperature range. The analysis was carried out using an Aelos CSM 403 P mass spectrometric attachment to a NETZSCH TG IRIS thermal analyzer. Differential scanning calorimetry analysis of flax shive samples and cellulose residue from flax shive was performed on a NETZSCH DSC Q200 instrument in the temperature range 50-600 °C at a heating rate of 10 °C / min in argon.

Further, the study of the pyrolysis process was carried out in the temperature range from 450 to 750 °C. A detailed study of the kinetics of the formation of pyrolysis gases and their calorific value has been carried out.

The gaseous products analysis was performed by the gas chromatography method. The analysis of the slow pyrolysis gaseous products consisted of C<sub>1</sub>-C<sub>4</sub> 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".

As a result of optimization of the process (at t = 600 °C), samples of liquid products and solid carbon-containing residues of pyrolysis of flax shive and hydrolysis residue of flax shive were obtained. 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 600 °C, was carried out using a GCMS-QP2010S gas chromatography-mass spectrometer (SHIMADZU, Japan). High-purity helium was used as a carrier gas using an HP-1MS capillary column (d = 0.25mm, l = 30m). Temperature analysis program: the initial column temperature of 50 °C is maintained for 1 min, then the temperature is gradually raised to 280 °C at a rate of 2 °C/min.

### 2.3 Pyrolysis procedure

The study of the pyrolysis process was carried out in the temperature range from 450 to 750 °C on a laboratory setup with a steel batch reactor for two selected types - samples of flax shive and cellulose residue of flax. The laboratory setup for slow pyrolysis consists of a cylindrical steel reactor into which a sample weighing 3 g is immersed. The system is sealed and purged with two liters of nitrogen. The required temperature is set on the

automatic thermostat, which is measured using a contact thermocouple installed in the electric oven. During pyrolysis, volatile products are formed, which pass through the nozzle into a water trap. Liquid products are condensed in the water trap, and gaseous products accumulate in the eudiometer. The volume of gaseous products was measured by the displaced volume of water measured by the cylinder. Gas samples are taken from the sampler. The masses of solid and liquid products were determined gravimetrically from the difference between the masses of the reactor and the liquid trap before and after the experiment. The experiment time for slow pyrolysis was 56 minutes.

### 3. Results and discussion

Studies of the initial characteristics of the samples showed that the cellulosic residue of flax shive has a significantly lower ash content, which is probably due to the dissolution of some ash components during the extraction of ethanol-lignin (see Table 1). After ethanol-lignin extraction, the hydrolysis residue of the flax shive has a slightly lower calorific value of 16.83 kJ / g, which is lower than that of the original flax shive -17.25 kJ /g. The content of carbon and hydrogen in the hydrolysis residue after extraction of ethanol-lignin from the flax shive increased from 47.9 to 50.6 wt % and from 4.7 to 6.1 wt %. Based on the obtained elemental analysis data, it can be concluded that the hydrolysis residue of flax is a more valuable raw material from the point of view of pyrolytic processing into gaseous and liquid energy carriers, since it contains a smaller amount of ballast elements (oxygen, nitrogen).

*Table 1: Initial characteristics of the test samples*

Parameter	Flax shive	Cellulose residue of flax shive
Moisture content, %	4.5	2.7
Ash content, %	4.11	0.94
Calorific value, kJ / g	17.25	16.83
Content, %		
C	47.9	50.6
H	4.7	6.1
O	46.7	42.9
N	0.6	0.4
S*	0.07*	-
Pore size distribution, %		
< 6 nm	30.8	24.62
6-8 nm	14.31	12.13
8-10 nm	7.73	6.52
10-12 nm	8.13	6.84
12-16 nm	7.74	7.29
16-20 nm	7.23	7.03
20-80 nm	19.23	25.38
> 80 nm	4.83	10.19

Experimental data obtained by studying the samples by low-temperature nitrogen adsorption indicate that the obtained hydrolysis residue of flax shive has a smaller proportion of pores with sizes less than 6 nm and a greater proportion of pores with sizes from 20 to 80 nm and more than 80 nm in comparison with the original shive. Flax shive, which most likely indicates that during the extraction of ethanol lignin from flax shive, large pores are formed due to the destruction of the initial microporous structure. Experimental data on the specific pore volume and specific surface area for flax and cellulose residue have similar values and are 0.0097 and 0.0116 mL / g; 9.6 and 9.5 m<sup>2</sup> / g.

The content of the main components of plant biomass was determined thermogravimetrically using the NETZSCH program "Peak Separation" (version 2010.09). For this purpose, the main stages of thermal destruction of agricultural waste of plant origin were determined using standard substances - cellulose, hemicellulose and lignin and taking into account the content of moisture, ash and extractive substances. As can be seen from the data obtained, after ethanolysis of flax shive, the lignin content decreased from 27.4 % to 16.7 wt. %.

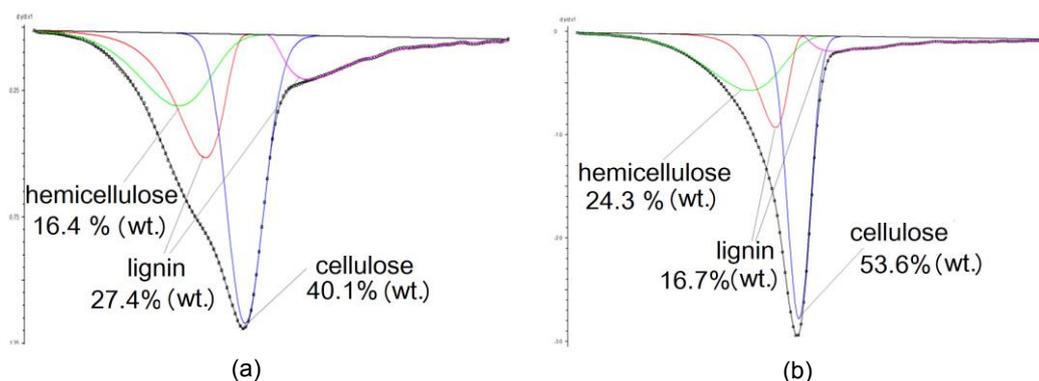


Figure 1: Separation of the peaks associated with the weight loss effects of the main components of flax shive (a) and the cellulose residue of flax shive (b) using the program "Peak Separation" (NETZSCH)

The content of hemicellulose and cellulose increased from 16.4 to 24.3 wt. % and from 40.1 to 53.6 wt. %. Lower values of the mass of solid carbon residues in the case of the cellulose residue of the flax shive are associated with a decrease in the content of lignin in its composition. According to the ability to form a carbon residue, the main components of plant biomass can be arranged in the following order in ascending order: cellulose → hemicellulose → lignin. The rate of formation of volatiles in the case of the cellulose residue of the flax shive exceeded the maximum destruction rate of the flax shive by 1.75 times, which is associated with an increase in the concentration of cellulose in its composition.

According to the data obtained (see Figure 2), a sample of the cellulose residue of flax shive is distinguished by a narrower thermal region of the formation of volatile products compared to that of flax shive, which is also apparently associated with an increase in the proportion of cellulose in its composition. According to the data of thermogravimetric analysis of the samples, the yield of volatile products of the flax shive and the cellulose residue of the shive in the temperature range 50-500 °C is 68.13 and 77.77 wt. %. Higher yields of volatiles in the case of a sample of the cellulose residue of the flax shive indicate the advisability of using this type of raw material for pyrolytic treatment in order to obtain gaseous and liquid energy carriers.

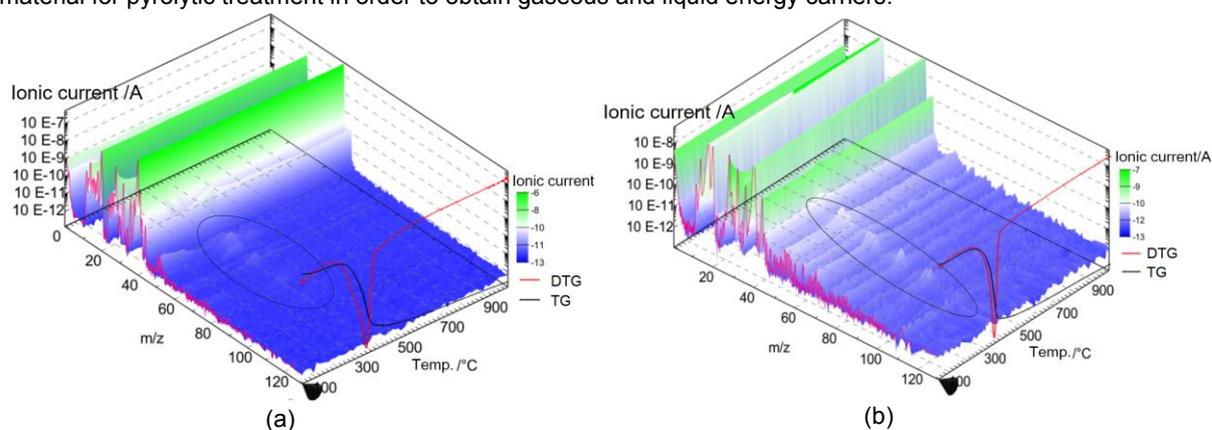


Figure 2: Data of mass spectrometric study of a sample of flax shive (a) and cellulose residue (b) in the temperature range 50-1,000 °C

As can be seen from the data presented in Figure 3, in the entire temperature range during the pyrolysis of the samples under study, endothermic effects of various intensities and widths of the temperature range are observed. The number 1 denotes the endothermic effects corresponding to the evaporation of moisture from the sample. Number 2 shows the total effects associated with heating the sample and the removal and destruction of low-boiling substances (extractives and, possibly, solvent residues after ethanolysis in the case of a cellulose residue). It should be noted that peak 2 in the sample of the cellulose residue of the flax shive is significantly larger in area than the peak of the original flax shive, which is possibly due to the fact that ethanol was included in the residual lignin during extraction. This is followed by the endothermic effects of thermal destruction of hemicelluloses, lignin 1, cellulose, and lignin 2.

It should be noted that in the case of the cellulose residue, only the endothermic effect of thermal destruction of cellulose is clearly visible, which is explained by its high content in this sample. Number 3 is followed by endothermic effects associated with the destruction of the most thermally stable lignin residues.

Note that the area corresponding to these effects is smaller in the sample of the cellulose residue due to the lower content of the latter. In the investigated temperature range of slow pyrolysis carried out on a laboratory setup with an increase in the reactor temperature, a decrease in the mass of the solid carbon-containing residue and an increase in the mass of gaseous products. The yields of gaseous and solid products of pyrolysis of the flax shive exceeded the corresponding values for the sample of the cellulose residue of the flax shive. One of the main characteristics of gaseous pyrolysis products, of course, is the lower volumetric heat of combustion. The time dependences of the heat of combustion of gaseous pyrolysis products for the samples under study are shown in Figure 4.

As can be seen from the data presented in Figure 4, the highest values of the heats of combustion of gaseous products were observed for the flax sample, which is explained by the high content of C<sub>1</sub>-C<sub>4</sub> hydrocarbons and tars in the composition of the pyrolysis gas. These products are most likely formed by thermodestruction of lignin. The content of which is higher in flax shive samples, see above. Nevertheless, it should be noted the similarity of the dependences for the studied samples, as well as the fact that the mass of the liquid fraction for the sample of the cellulose residue of flax shive significantly exceeded the mass of liquid products obtained during pyrolysis of the shive of flax, allows us to conclude that the cellulose residue of the shive of flax in some parameters surpasses the original shive of flax and, therefore, is a more promising raw material for pyrolytic processing into gaseous and liquid fuels.

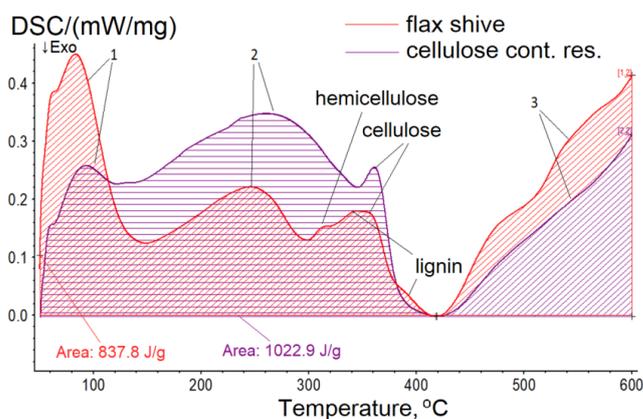


Figure 3: Data obtained by the method of differential scanning calorimetry of the studied samples

The mass of the liquid pyrolysis fraction in the case of the cellulose residue of the shive significantly exceeded the mass of the liquid pyrolysis products of the flax shive in the entire investigated temperature range. It should also be noted that the dependence of the mass of the liquid fraction on the process temperature is extreme. The highest yield of the liquid fraction corresponded to a pyrolysis temperature of 600 °C for both samples under study. The optimal temperature for reaching the maximum amount of gaseous and liquid energy carriers is 600 °C (Lugovoy et al., 2021).

According to the data obtained, the composition of liquid products for the studied samples of the shive and the cellulose residue of the shive is in many respects similar, but the composition of the liquid pyrolysis products of the shive of flax contains a greater number of low-molecular compounds, which, possibly, can be formed during the thermal destruction of extractives and lignin (Lugovoy et al., 2021). The composition of liquid products includes phenolic compounds - cresols, xlenols, pyrocatechol, pyrogallol, and their methyl esters, alcohols, acids, esters, carbonyl compounds, and low-volatile hydroxy acids, lactones, sugar anhydrides, polyhydric phenols, furan compounds (Mohabeer et al., 2019).

The liquid pyrolysis products of the cellulose residue of the shive have a low molecular weight distribution, which is more preferable when obtaining liquid pyrolysis derivatives of a higher quality.

The data of elemental analysis of carbon-containing pyrolysis residues show that in the case of the cellulose residue of the shive, the carbon content is significantly higher (more by 10.7 %), and the hydrogen content is lower by 1.2 %, which indicates a greater "maturity" of the obtained coal residues. Experimental data obtained through the study of samples by low-temperature nitrogen adsorption indicate that the obtained carbon residue of pyrolysis of hydrolysis residue of flax shive has a similar pore size distribution compared to the solid carbon-

containing residue of flax pyrolysis. Experimental data on the specific pore volume and specific surface area for the carbon-containing pyrolysis residue of flax shive have lower values than the corresponding carbon-containing residue of pyrolysis of the cellulose residue of the shive, which confirms the correctness of the chosen strategy for the complex processing of flax shive.

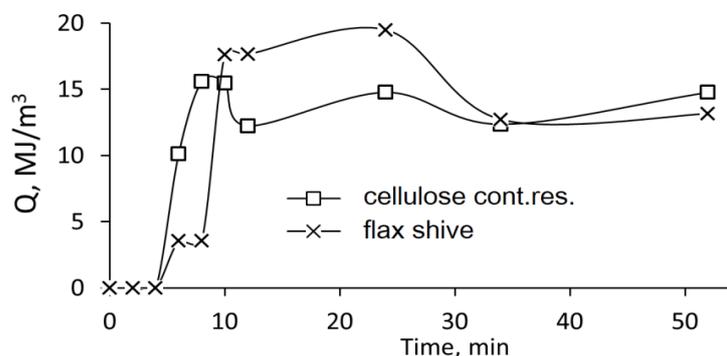


Figure 4: Dependence of the lowest volumetric calorific value on the pyrolysis time for the samples under study

#### 4. Conclusion

The value of the cellulose residues of flax shive as a raw material for pyrolysis is slightly higher than that of the initial flax shive, since the content of ballast elements (O, N) in such residues is significantly lower. The rate of destruction of cellulose residues from ethanolysis of the flax shive is 1.75 times higher than the rate of destruction of the original shive. The amount of volatile products in the case of the original shive and the cellulose residues of the flax shive were 68.13 wt. % and 77.77 wt. %, which also speaks in favor of the fact that the cellulose residues can be more efficiently processed using pyrolysis. The quantity and quality of the resulting liquid in the case of using as a raw material for pyrolysis, the cellulose residues of the flax shive are significantly higher compared to the original flax shive, which suggests that of the prospects of using the processing technology based on the use of the initial chemical and subsequent thermal stages.

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