

# Influence of the Pyrolysis Mode of Flax Shive on Product Composition

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Flax shive is a highly lignified nonfibrous plant parts obtained from the scutching of straw flax to produce fibers. It is one of the multi-tonnage agricultural wastes. The use of the flax shive as a source for the valuable products is a promising way to solve the problem of the waste processing. This work is devoted to the study of composition and properties of the products of slow and fast pyrolysis of the flax shive. It was found that the slow pyrolysis results in a higher degree of the feedstock decomposition as well as in a higher yield of valuable gases and liquids. The gaseous product yield was found to be over 35 wt. % for the slow pyrolysis, and about 25 wt. % for the fast pyrolysis. For the gaseous products, methane concentration was found to be twice lower for the fast pyrolysis in comparison with the slow one. This decreases the calorific value of gases and leads to the low feasibility of the process. Interestingly, the fast pyrolysis resulted only 20 wt. % of liquids, while for the slow one, a twice increase (ca. 40 wt. %) of liquid yield was obtained. The liquid obtained in a fast mode contained the higher number of carboxylic acids and furanes, while the product obtained in a slow pyrolysis was characterised by the higher concentration of phenols, aldehydes and hydrocarbons increasing its further application. The solid residue obtained by the slow pyrolysis was found to have a higher porosity in comparison with the sample obtained by the fast mode. As the solid residue can be used as an adsorbent, the porosity is a critical parameter to choice the proper mode for flax shive thermal processing.

## 1. Introduction

Biomass is considered an alternative to fossil energy source (Chuah et al., 2022). Biomass is carbon-neutral (Munir et al., 2023), eco-friendly (Guedes do Nascimento et al., 2023), renewable (Chuah et al., 2021), and low-cost feedstock (Bokhari et al., 2016). Regarding the use of biomass, lignocellulosic waste can be prospective for the production of fuels and chemicals (Lugovoy et al., 2021). The flax shive is a waste obtained during flax processing. It is formed in large number annually in the Russian Federation. In the Tver region, over 6 kt/y of flax shive can be produced. The processing of such waste is of great interest. Agricultural wastes are used for the production of fertilizers or in animal farming. However, its use is below 1 wt. %. The remaining quantity of waste is left in the fields and can harm the environment (Kazachenko et al., 2021).

Biomass processing includes thermal, thermochemical, electrochemical, and biochemical methods (Seferlis et al., 2021). Thermal conversion is one of the main approaches used to convert renewable feedstock into valuable products (Brown, 2019) and fuels (Kazachenko et al., 2020). Pyrolysis is one of the widely used processes for the production of combustible gas (Dai et al., 2020), bio-oil (Liu et al., 2014), and bio-char (Chen et al., 2018). The pyrolysis conditions (Akhtar and Saidina, 2012), feedstock pretreatment (Zhou et al., 2021), reactor type, catalysts (Mortensen et al., 2011), and heating mode strongly affect the yield of products as well as its composition and properties. For the conversion of biomass to valuable compounds, fast and slow pyrolysis techniques can be applied (Isahak et al., 2012). Slow pyrolysis involves the slow heating of feedstock with a heating rate of 5-10 °C/min. This type of process is characterized by the biomass retention time in the heating zone from several min to h (French and Czernik, 2010). The fast pyrolysis assumes the feedstock heating with

the rate of 100-120 °C/min. In this case, the biomass retention time counts up to 10 s (Mettler et al., 2012). In this paper, for the first time, the comparison of the yield, composition, and properties of gaseous, liquid, and solid products obtained by slow and fast pyrolysis of flax shive is reported.

## 2. Experimental

### 2.1 Materials

Flax shive was purchased from the Federal Research Center of Bast-Fiber Crop in the Tver region. The feedstock composition was studied according to the standard procedures (Augustine et al., 2015) and was estimated as the following: humidity – 3.8 wt. %, cellulose content – 38.1 wt. %, lignin content – 27.7 wt. %, hemicelluloses content – 15.2 wt. %, extractives – 9.9 wt. %, ash content – 4.2 wt. %. The elemental composition of the flax shive was calculated to be: C – 46.9 wt. %, H – 5.7 wt. %, N – 0.6 wt. %, O – 37.5 wt. %, S – 0.1 wt. %.

### 2.2 Pyrolysis procedures

The slow pyrolysis of the flax shive was carried out in a batch reactor included in the experimental setup presented in Figure 1. 3 g of a sample of the flax shive was loaded into the reactor and purged with nitrogen. After the hermetizing, the reactor was put into the furnace and preliminary heated up to the process temperature. The pyrolysis of flax shive was performed at a temperature of 600 °C for 96 min. The pyrolysis temperature and duration were chosen based on the previous studies (Lugovoy et al., 2021). The weights of solid and liquid products were determined as the difference between the mass of the reactor and liquid trap before and after the experiment. The gaseous products were collected and measured using an eudiometer.

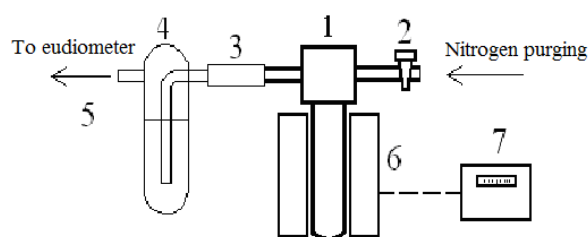


Figure 1: Scheme of the laboratory set up for slow pyrolysis: (1) reactor, (2) valve, (3) gas sampler, (4) water trap, (5) eudiometer, (5) electric furnace, (7) heating controller

The fast pyrolysis of flax shive was carried out in a screw-type laboratory setup (Lugovoy et al., 2021) presented in Figure 2.

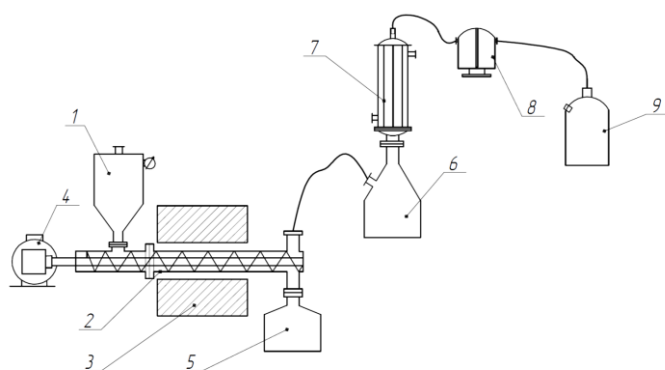


Figure 2: Scheme of the laboratory setup for fast pyrolysis: (1) loading device, (2) tubular pyrolysis reactor, (3) induction furnace, (4) screw feeder with the gear motor, (5) discharge hopper, (6) flask, (7) reflux condenser, (8) water trap, (9) eudiometer

A sample of 20 g flax shive was loaded into the loading device and then fed into the heated reactor using a screw feeder. The rotation rate of the feeder determined the feedstock residence time in the heating zone of the

reactor. The fast pyrolysis process was carried out at a temperature of 600 °C, and the feedstock residence time in the heating zone of the reactor was 4.4 s. The weights of solid and liquid products were determined gravimetrically. The gaseous products were collected and measured using an eudiometer.

The composition of pyrolysis gases was determined by gaseous chromatography using the analytical complex based on the Crystallux 4000M chromatograph. The liquid phase was analyzed using a gas chromatograph GC-2010 and mass-spectrometer GCMS-QP2010S (SHIMADZU, Japan). The study of the pyrolysis solid residue porosity and surface area was carried out using Beckman Coulter SA 3100 analyzer (Coulter Corporation, USA). The elemental composition of solid residue was estimated using a Zeiss Jena VRA-30 spectrometer (Carl Zeiss Industrielle Messtechnik GmbH, Germany).

### 3. Results and discussion

Figure 3 presents the proportion of the products obtained by the fast and slow pyrolysis of the flax shive. Figure 4 shows the composition of the pyrolysis gases depending on the process mode. From Figure 3, it is seen that the slow pyrolysis results in a higher yield of both gaseous and liquid products. Despite the fast pyrolysis provides high liquid yield according to the literature (Mohan et al., 2006), for the flax shive processing, it was found to be lower because of the high ash content catalyzing the side cracking (Zhu et al., 2021) and dehydration (Mu et al., 2013) reactions. The volume of gaseous products obtained by slow pyrolysis was found to be higher in comparison to the fast-mode process. It is known that the higher residence time in the heating zone leads to a higher degree of thermal decomposition of the feedstock (Al Arni, 2018). This correlates well with the results obtained. Slow pyrolysis also results in a higher yield of methane, ethane, and propane leading to an increase in the calorific value of gases (Figure 4).

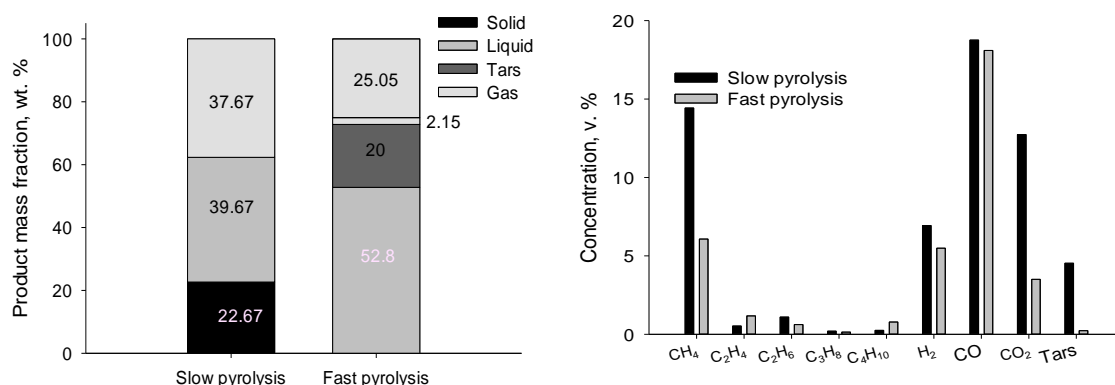


Figure 3: Yields of the flax shive pyrolysis products    Figure 4: Composition of pyrolysis gases

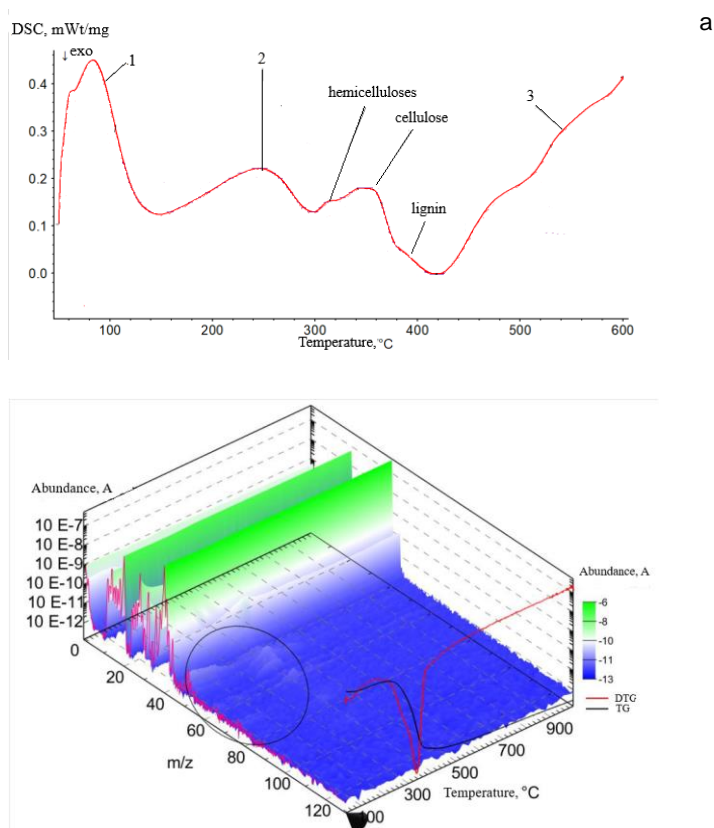
The composition of the liquid products is presented in Table 1. The liquid pyrolysis products obtained by both modes contain a high amount of low-weight carbonylic and carboxylic compounds (acetic acid and acetates, acetone). These compounds are formed from extractives and cellulose (Mettler et al., 2012). Furanes are the main products of hemicelluloses' thermal decomposition (Zhou et al., 2018). Phenols are mainly formed from lignin (Patwardhan et al., 2011). According to Table 1, the fast pyrolysis results in the formation of a higher amount of carboxylic and carbonyl compounds as well as the furanes because of the low feedstock residence time. This results in the prevalence decomposition of cellulose and hemicelluloses as these compounds decompose easily in comparison to lignin (Aziz et al., 2023). For the slow pyrolysis, the higher residence time of the feedstock leads to a higher degree of lignin decomposition, increasing phenol yield. High concentration of carboxylic acids and phenols leads to low pH values for both liquids. For the slow pyrolysis, the higher concentration of hydrocarbons (benzene, naphthalene, toluene) can also be observed, resulting in the lower density and viscosity of the products.

The composition of gaseous and liquid products is in the accordance to those obtained during the thermogravimetric analysis. The analysis was performed using TG 209 F1 NETZSCH (Netzsch Group, Germany) equipped by the mass-spectrometer device Aelos CSM 403 P (Netzsch Group, Germany). Thermal decomposition of flax shive samples results in the formation of a wide range of volatile products including both gaseous and liquid compounds with a molecular weight from 40 to 90 a.m.u. The product formation is

characterized by a wide temperature range corresponding to the temperatures of decomposition of main flax shive components (Figure 5).

*Table 1: Composition and fuel properties of pyrolysis liquid*

	Value	
	Slow pyrolysis	Fast pyrolysis
Aldehydes, wt. %	21.3	19.8
Carboxylic acids, wt. %	32.0	37.5
Furanes, wt. %	14.3	22.2
Oxygenated cyclic, wt. %	8.1	3.8
Phenols, wt. %	21.8	12.5
Hydrocarbons, wt. %	3.2	1.2
pH value	3.02	2.81
Viscosity at 40 °C, cSt(mm <sup>2</sup> /s)	27.9	28.2
Density at 30 °C, g/cm <sup>3</sup>	1.10	1.15



*Figure 5: DCS curves of the flax shive (a) and mass spectrometric study of volatile products of flax shive thermal decomposition (b)*

Concentration of the elements in the carbonaceous residue and its specific surface area are summarized in Table 2. Figure 6 shows the pore size distribution for the solid residue obtained. Solid residue yield for the slow pyrolysis was lower compared to that obtained in the fast pyrolysis. The concentration of carbon was higher, and oxygen and hydrogen concentration was lower in that case (see Table 2). This can be explained by the higher degree of the flax shive decomposition because of the higher residence time in the reactor heating zone. The porous structure of the solid residue can be attributed to the mesoporous in both cases. The carbonaceous residue obtained by the slow process has a higher specific surface area and narrow pore size distribution. For the carbon residue obtained by the fast pyrolysis, a wide pore size distribution can be observed (Figure 6). It can be explained by the deformation of the cell structure of the initial feedstock due to internal overpressure (Kurosaki et al., 2003).

Table 2: Elemental composition and properties of solid residue

	Value	
	Slow pyrolysis	Fast pyrolysis
C, wt. %	65.9	64.8
H, wt. %	6.7	6.9
O, wt. %	12.6	13.5
N, wt. %	0.8	0.9
Other, wt. %	14.0	13.9
Pore volume, cm <sup>3</sup> /g	0.025	0.019
Specific surface area, m <sup>2</sup> /g	2.9	2.3

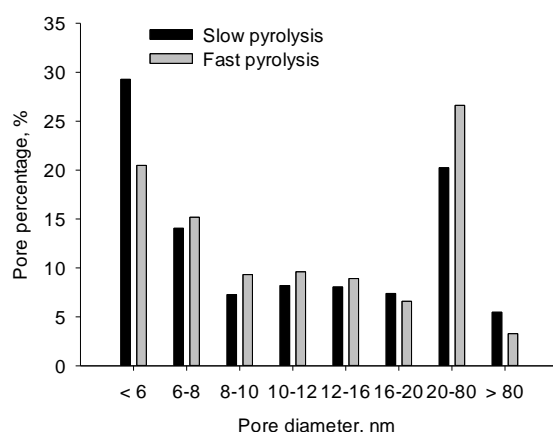


Figure 6: Pore size distribution for pyrolysis solid residue

#### 4. Conclusions

The comparison of the pyrolysis products obtained by the slow and fast thermal decomposition of flax shive was carried out in this work. Slow pyrolysis was found to be the most effective for flax shive processing into valuable products in comparison with the fast-mode process. The yield of pyrolysis gases and liquids was found to be 1.48 and 2 times higher for the slow pyrolysis. The slow pyrolysis provides a higher depth of the flax shive decomposition because of the higher feedstock residence time in the heating zone of the reactor. The data obtained in this study will be the basis for future investigations on the kinetics and mechanisms of flax shive pyrolysis. The presented work supplements the existing data on flax shive pyrolysis, allowing the further development of effective technology for the processing of agricultural waste.

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