Product Comparison for Slow and Fast Pyrolysis of Flax Shive

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Abstract

In the current work, a comparison of the composition and properties of products obtained by the slow and fast pyrolysis of flax shive is presented to evaluate the influence of the process mode on the thermal decomposition of agricultural waste. The thermogravimetric studies were carried out to estimate the temperature range of the decomposition of the feedstock main component (cellulose, hemicelluloses, and lignin) and to choose the pyrolysis temperature. It was found that the slow pyrolysis was found to provide the higher conversion depth of the feedstock resulting in the formation of gaseous and liquid products with higher calorific values (9.65 MJ/m³, and 16.51 MJ/kg respectively). Moreover, the solid residue of the slow pyrolysis was characterized by the higher surface area and narrow pore size distribution in comparison with that obtained by the fast process.

1. Introduction

Environmental problems related to the use of fossil fuels as well as the diminishing of oil reserves result in the focus on alternative energy sources. As one of such alternatives, biomass is considered to be a carbon-neutral, eco-friendly, renewable, and low-cost feedstock for the production of fuels and chemicals. There are a lot of studies on biomass processing including thermal, electrochemical, and biochemical methods. However, thermal conversion remains the major approach for the conversion of this renewable source [1, 2]. Among thermal methods, pyrolysis is one of the most suitable for the production of value-added products (i.e. combustible gas, bio-oil, and bio-char) [3–7].

The pyrolysis product yield and composition strongly depend on the process conditions, catalyst presence, reactor type, feedstock pretreatment, and the heating mode [8–10]. Two main technologies can be applied for the successful conversion of biomass to valuable compounds. The first one is the slow pyrolysis which consists of the slow heating (5-10°C/min) of feedstock with a high retention time in the heating zone. The second one is fast pyrolysis which includes fast heating (100-120°C/min) of biomass [11–13]. According to the literature data, slow pyrolysis mainly results in the formation of non-condensable gases and char [14, 15], while the fast one allows a high yield of bio-oil to be produced [6, 16].

The comparison of the products for fast and slow pyrolysis of biomass was presented in numerous studies [6, 17–20]. Here we report the results of the studies of thermal decomposition of the agricultural wastes by these two approaches. This work is focused on the yield, composition, and properties of gaseous, liquid, and solid products obtained by slow and fast pyrolysis of the secondary product of flax processing – flax shive. The composition and properties of this waste are close to wood pulp. Besides, flax shive is a low-cost and prospective material that can be used for energy production.

2. Experimental

2.1 Initial Feedstock

Flax shive collected from the Torzhok district of Tver region was purchased from the Federal Research Center of Bast-Fiber Crop and used as received. The characteristics of the initial feedstock were estimated according to the standard procedures. The total humidity of the flax shive was determined by the thermogravimetric method described in [21]. Ash content in the flax shive was determined according to the procedure described in [22]. The lower calorific value of the flax shive was determined using the bomb adiabatic calorimeter ABK-1 (Retech, Russia) according to [23]. Studies of the flax shive composition were performed according to the methods described in [24].

According to the experiments, the following feedstock properties and composition were obtained (see Table 1).

Table 1
Composition and characteristics of flax shive
used for pyrolysis

Characteristics	Value
Component composition, % (wt.)	15.2
Hemicelluloses	38.1
Cellulose	27.7
Lignin	9.9
Extractives	
Elemental composition, % (wt.)	46.9
C	5.7
H	0.6
N	37.5
O	0.1
S	
Humidity, % (wt.)	3.8
Ash content, % (wt.)	4.2
Lower calorific value, MJ/kg	17.3

2.2 Thermogravimetric analysis

To estimate the thermal stability of the flax shive and choose the temperature range for pyrolysis, the thermogravimetric analysis was performed using TG 209 F1 NETZSCH (Netzch Group, Germany). The sample heating was carried out at the constant heating rate (10°C/min) in the inert atmosphere (argon, 99.9%, AGA, Russia). The temperature range of 50 – 600°C was chosen for the analysis. Flax shive samples were preliminary milled and the fraction with the particle size below 0.25 mm was taken. The

mathematical modeling of the thermograms was performed using NETZSCH Thermokinetics 3.1 (Netzsch Group, Germany).

2.3 Slow pyrolysis procedure

The slow pyrolysis of flax shive was carried out in a batch reactor included in the experimental setup presented in Figure 1.

A sample of the flax shive with the weight of 3 g was loaded into the reactor (1) and purged with nitrogen using a valve (2). The reactor was heated up to the experimental temperature using an electric furnace (6) equipped with the heat controller (7) with a patch thermocouple. The experimental setup is equipped with a sampler (3) for gas sampling and water trap (4) for the separation of liquid pyrolysis products. 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 are collected in a eudiometer (5). The slow pyrolysis of flax shive was performed at a temperature of 600 °C. The duration of the experiment was 96 min.

2.4 Fast pyrolysis procedure

The fast pyrolysis of flax shive was carried out in a screw-type laboratory set up [25] presented in Figure 2.

A sample of feedstock with a weight of 20 g was loaded into the loading device (1) with an electric low-speed mixer which prevents the formation of bridging and ensures a uniform supply of flax shive particles to the screw feeder. The rate of rotation of the screw feeder is controlled by a device connected with the gear motor (4). The rotational rate of the screw feeder determines the residence time of the feedstock in the heated zone. The screw feeder is located inside the tubular pyrolysis reactor (2), which is heated using an induction furnace (3). The heating zone length is 10 cm. After the heating zone, the reaction mixture passes the discharge hopper (5). Volatile products are collected in a flask (6) connected to a reflux condenser (7). Gaseous products are separated in a water trap (8), collected in a eudiometer (9).

The results of the preliminary experiments showed that the increase in feedstock residence time in a heating zone led to a significant increase in the resin yield. The decrease in the feedstock residence time, in contrast, led to the heat transfer limitation that results in a low degree of conversion. Based on the literature data [26] and the preliminary experiments, the fast pyrolysis process was carried out at a temperature range of 600 °C. The feedstock residence time in the heating zone of the reactor was 4.4 sec.

3. Results And Discussion

3.1 Flax shive thermal analysis

The data of thermogravimetric analysis of flax shive and the thermogram deconvolution obtained using NETZSCH Thermokinetics 3.1 tool are presented in Figure 3a and b respectively. The weight loose peak observed at a temperature range of 80 – 140 °C (peak 1 in Figure 3b) indicates the dehydration of the feedstock and corresponds to the data obtained at the moisture content estimation (see Table 1). A wide peak in a temperature range of 210 – 450 °C can be correlated with the thermal decomposition of the main biomass components – hemicelluloses, cellulose, and lignin [27].

Peak 2 (temperature range of 170 – 430 °C) corresponds to the decomposition of hemicelluloses of flax shive. Peak 3 (temperature range of 280 – 360 °C) indicates the decomposition of cellulose. Peak 4 (temperature range of 280 – 560 °C) correlates with the decomposition of lignin from the flax shive. The determined ranges of the flax shive component decomposition are well correlated with the literature data [6, 17, 28, 29].

To confirm the DTG modeling adequacy, the differential scanning calorimetric analysis was performed using NETZSCH DSC Q200 in a temperature range of 50 - 600 °C with a heating rate of 10 °C/min. The data obtained is presented in Fig. 4.

As it can be seen, endothermal effects with different intensities are observed at all temperatures studied. Peak 1 corresponds to the evaporation of water from the sample. As the humidity of the initial feedstock was quite high, the peak area seems to be high. Peak 2 can correspond to the summarized effects of the removal and decomposition of low-boiling compounds (i.e. extractives). Then, the endothermal effects of the decomposition of main flax shive components (hemicelluloses, cellulose, and lignin) can be observed. Peak 3 can correspond to the endothermal effects of the destruction of the thermal stable components of the lignin network.

During thermogravimetric analysis, a mass-spectrometry study of the volatile product of flax shive thermal decomposition was also performed in the mass range of 1-300 a.m.u. (see Fig. 5). The analysis was carried out using the mass-spectrometer device Aelos CSM 403 P (Netzch Group, Germany).

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3.2 Pyrolysis product analysis

To compare the process mode on the yield of pyrolysis product the estimation of product weights was carried out. The results obtained are presented in Fig. 6. Slow pyrolysis provides a higher yield of gaseous and liquid products in comparison with the values obtained in the fast process. This can be explained by the increase in the feedstock conversion degree while increasing its residence time in the heating zone. Moreover, tar formation was not observed in the slow pyrolysis due to the behavior of the side reactions

of tar decomposition. Interestingly to note, that the fast pyrolysis of flax shive is characterized by the relatively low yield of the liquid products in comparison with the literature data for biomass fast pyrolysis [6, 16]. It can be connected with the high ash and char content which can catalyze the side cracking reactions as well as with the high humidity of the feedstock resulting in the behavior of syn-gas formation [30, 31]. However, this characteristic can be concerned as positive for the use of the products in a gas-diesel cycle.

To estimate the influence of pyrolysis mode, a comparison of the composition of products was done. Table 2 presents the data on the composition and properties of gaseous products obtained by fast and slow pyrolysis. The analysis was performed by the gaseous chromatography method using the analytical complex based on the Crystallux 4000M chromatograph [32].

Table 2
Composition and properties of gaseous products of flax shive
slow and fast pyrolysis (process temperature 600 °C)

Value	Slow pyrolysis	Fast pyrolysis
V _{gas} , mL/g of feedstock	182	157
CH ₄ , vol. %.	14.43	6.07
C ₂ H ₄ , vol. %.	0.53	1.17
C ₂ H ₆ , vol. %.	1.10	0.62
C ₃ H ₈ , vol. %.	0.20	0.14
C ₄ H ₁₀ , vol. %.	0.25	0.78
H ₂ , vol. %.	6.93	5.49
CO, vol. %.	18.76	18.10
CO ₂ , vol. %.	12.74	3.50
N ₂ , vol. %.	40.53	63.90
Tars, vol. %.	4.53	0.23
Lower calorific value, kJ/L	9.65	7.05

According to the data obtained, the volume of gaseous products produced by slow pyrolysis per unit of the feedstock weight was higher than that obtained in fast pyrolysis. This can be explained by the higher residence time in the heating zone and, hence, by the higher degree of thermal decomposition [18]. The compositions of the gaseous products of slow and fast pyrolysis are close in terms of carbon monoxide

and hydrogen concentration [33]. Slow pyrolysis results in the formation of a higher amount of methane (by 2.38 times), ethane (by 1.77 times), and propane (by 1.42 times). However, taking into account the low value of the total hydrocarbon concentration in pyrolysis gases, such difference does not strongly affect the calorific value. It should be noted that slow pyrolysis produces by 3.64 times higher yield of CO₂ in comparison with a fast one. Meanwhile, the concentration of ethylene in gaseous products was found to be higher for the fast pyrolysis process (by 2.2 times); that can correspond to the decrease in the rate of secondary thermal decomposition processes.

The analysis of the liquid phase of the pyrolysis products obtained at 600°C was performed using GCMS-QP2010S (SHIMADZU, Japan) according to the procedure described elsewhere [34]. The summarized results are presented in Fig. 7.

It is noteworthy that the liquid products contain a high amount of low-weight carbonylic and carboxylic compounds (i.e. acetic acid and acetates, acetone, etc.) which can be corresponded to the products of extractives and cellulose decomposition [35]. Furanes and pyranes obtained are the products of hemicelluloses and cellulose decomposition [35–40]. Phenols are formed during the destruction of lignin and hemicelluloses [31, 41, 42]. The composition of liquid products in both pyrolysis modes seems to be close to each other. However, fast pyrolysis results in the formation of a higher amount of carboxylic and carbonyl compounds as well as the furanes. It can be explained by the lower conversion of the feedstock and the decrease in the degree of lignin decomposition. Moreover, fast pyrolysis showed the formation of tars which can be the result of secondary processes such as aldol condensation.

To evaluate the physical properties of the liquid pyrolysis product the measurements of pH, density, viscosity, and calorific value were carried out [43]. The pyrolysis liquid properties are presented in Table 3. It is well seen that liquid obtained by the fast pyrolysis is characterized by the higher pH value and density as well as the lower calorific value. This can be attributed to the increase in the concentration of acidic components in the product obtained.

Table 3
– Physical properties of liquid pyrolysis products (process temperature 600 °C)

Parameter	Slow pyrolysis	Fast pyrolysis
pH	3.02	2.81
Density at 30°C, g/cm ³	1.10	1.15
Viscosity at 40°C, cSt(mm ² /s)	27.9	28.2
Lower calorific value, MJ/kg	16.51	14.87

Properties of the bio-char strongly depend on the process conditions such as temperature and heating time [19]. As carbon pyrolysis product is used as a sorption material, its porosity plays an important role. The solid residue obtained by the slow and fast pyrolysis at 600°C was analyzed by elemental analysis and low-temperature nitrogen physisorption. The analysis results are presented in Table 4.

Table 4
– Elemental composition and porosity of carbon residue obtained by slow and fast pyrolysis (process temperature 600 °C)

Parameter	Slow pyrolysis	Fast pyrolysis
Elemental composition		
Concentration, wt. %	65.9	64.8
C	6.7	6.9
H	12.6	13.5
O	0.8	0.9
N	14.0	13.9
Other elements		
Pore size distribution, %		
< 6 nm	29.28	20.48
6-8 nm	14.05	15.18
8-10 nm	7.28	9.32
10-12 nm	8.20	9.61
12-16 nm	8.06	8.92
16-20 nm	7.39	6.59
20-80 nm	20.25	26.62
>80 nm	5.48	3.28
Pore volume, cm ³ /g	0.025	0.019
Specific surface area, m ² /g	1.7	1.1
Langmuir model	2.9	2.3
BET model		

Data of the elemental analysis show that for slow pyrolysis carbon content in the solid residue was higher, while the oxygen and hydrogen content were observed to be lower in comparison with the fast one. This can indicate the higher decomposition degree of the initial feedstock in the slow pyrolysis process. Moreover, as it was shown in [19], the surface of the solid residue obtained by fast pyrolysis is characterized by the higher concentration of hydroxyl groups.

The porous structure of the solid residues seems to be mesoporous for both process modes. However, the biochar obtained by the slow pyrolysis process is characterized by the higher specific surface area and narrow pore size distribution, while the carbon residue obtained by the fast pyrolysis shows wide pore size distribution. This is in the accordance with the literature data [20]. In slow pyrolysis, the cell structure of the initial feedstock does not practically change which leads to the retaining in the bio-char morphology. In fast pyrolysis, in contrast, the internal overpressure leads to the formation of internal cavities and the coalescence of small pores [44, 45].

4. Conclusions

This work was focused on the comparison of the yield, composition, and properties of gaseous, liquid, and solid products obtained by slow and fast pyrolysis of flax shive. Based on the results obtained, the following conclusions can be done:

- (1) the slow pyrolysis process is characterized by the higher yield of gaseous and liquid products, and, hence, the lower yield of solid residue due to the higher depth of the feedstock conversion;
- (2) the composition of gaseous products obtained by the slow and fast pyrolysis seems to be close regarding syn-gas. However, the formation of a larger amount of light hydrocarbons was observed in a slow pyrolysis mode. This resulted in the higher calorific value of gases in comparison with those obtained in the fast process;
- (3) liquid product composition was found to be compatible for slow and fast pyrolysis. However, fast pyrolysis liquid is characterized by the higher pH value, density, and viscosity due to the higher concentration of acidic compounds;
- (4) elemental composition of the biochar obtained by fast pyrolysis is characterized by the higher oxygen content, lower surface area, and wide pore size distribution due to the coalescence of small pores and internal cavities formation.

Declarations

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Figures

Figure 1

Scheme of the laboratory set up for slow pyrolysis

Figure 2

Scheme of the laboratory set up for fast pyrolysis

Figure 3

Flax shive thermogram in a temperature range of 30-600 °C (a) and DTG deconvolution (b)

Figure 4

DCS curves of the flax shive

Figure 5

Mass spectrometric study of volatile products of flax shive thermal decomposition

Figure 6

Product distribution for slow and fast pyrolysis of flax shive

(process temperature 600 °C)

Figure 7

Liquid product composition for slow and fast pyrolysis (process temperature 600 °C)