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Pyrolytical Processing of Flax Shive and it Derivatives

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The article presents the results on the thermal processing of the samples of flax production - flax shive and the cellulose residue of flax shive. Experimental data on the conversion of selected samples of flax production waste obtained on a laboratory installation of slow pyrolysis in a temperature range of 500-750 ℃ are presented. The composition of gaseous pyrolysis products has been studied in detail and the main content of methane, hydrogen, and carbon oxides in the course of the process have been determined. Data on the composition of liquid products of pyrolysis of selected samples of plant biomass using the method of gas chromatography-mass spectrometry are presented. As part of the work, elemental analysis of samples of solid carbon-containing residues for the studied samples of flax and cellulose residue was carried out, and an analysis was carried out by the method of low-temperature adsorption of nitrogen.

1. Introduction

The problems of processing plant biomass waste for energy production have not yet been fully resolved, which is associated with a wide variety of biomass composition (Domínguez et al, 2007). Difficulties in processing biomass are also determined by differences in the physicochemical characteristics of the biomass of different origins. The main sources of biomass are timber, herbaceous, and bog plants. The composition of plant biomass can vary significantly depending on the parts of the plant (bark, roots, and branches), the storage conditions of the biomass, and the method of its collection. These factors determine the initial moisture content, ash content, and, as a consequence, the heating value of the raw material. It is possible to increase the efficiency of the fields of the agro-industrial complex producing various crops by involving waste in the production of energy obtained from millions of tons of secondary biomass (Huang et al, 2008).

Flax seed 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 (Nikitin, 2017; Marshall et al, 2007).

Currently, 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 (Marculescu, 2011; Lewandowski et al, 2011; 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 (Bosmans et al, 2010). At the first stage, it is planned to carry out chemical processing of raw materials by hydrolysis or methanolysis to obtain valuable chemical products - furfural, vanillin, and syringaldehyde, as well as phenylpropane derivatives (guaiacyl and syringyl propanols, propene, and propane) (Ross et al, 2010). At the second stage of processing, thermal treatment of solid residues of chemical treatment of plant biomass is carried out, which is aimed at obtaining gaseous and liquid energy carriers and solid carbon sorbents (Mohabeer, 2018; Klasson et al, 2009).

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. In this paper, the results of a study of the process of pyrolysis of the initial flax shive and the cellulose residue of the flax shive obtained at the stage of chemical processing are

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presented. Comparison of the results of pyrolysis of the selected samples will make it possible to conclude 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 extraction of lignin from a flax shive sample (ethanolysis) was performed in the Institute of Chemistry and Chemical Technology of the Siberian Branch of the Russian Academy of Sciences. The ethanolysis 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 1000 mL of a 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, the heat of combustion, specific area, and pore size distribution) were carried out. The study of the air-equilibrium moisture content of flax shive samples and the cellulose residue of flax shive was carried out in accordance with GOST R 54186-2010 (Solid biofuels. Determination of moisture content by drying. Part 1. Total moisture. Standard method).

The analysis of ash content was carried out by calcination of 1 g of the samples placed in porcelain crucibles for 4.5 hours at a temperature of 575 °C in a muffle furnace. The temperature range for ashing processes has been selected to determine the total ash content (including fly ash) (Obolenskaya et al., 1991).

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 ABK-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 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^{TM} SA 3100^{TM} instrument (Coulter Corporation, USA) and a specimen preparation instrument: Becman Coulter^{TM} SA-Prep^{TM} (Coulter Corporation, USA). Further, the study of the pyrolysis process was carried out in the temperature range from 450 to 750 ºC. A detailed study of the kinetics of the formation of pyrolysis gases and their calorific value has been carried out.

The gaseous product analysis was performed by the gas chromatography method. The analysis of the fast pyrolysis gaseous products consisted of C_1-C_4 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 the optimization of the process (at t = 600 ℃), 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 ºC, 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. The analysis of solid carbon pyrolysis residues obtained at a pyrolysis temperature of 600 ºC was carried out using the methods of elemental analysis (CHNO) and low-temperature nitrogen adsorption (see earlier).

2.3 Pyrolysis procedure

The study of the pyrolysis process was carried out in the temperature range from 450 to 750 ºC on a laboratory setup with a steel batch reactor (see Figure 1) 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 (1) 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 (3), which is measured using a contact thermocouple installed in the electric oven (2). During pyrolysis, volatile products are formed, which pass through the nozzle (4) into a water trap (6). Liquid products are condensed in the water trap, and gaseous products accumulate in the eudiometer (7). The volume of gaseous products was measured by the displaced volume of water measured by the cylinder. Gas samples are taken from the sampler (5). 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, respectively. The experiment time for slow pyrolysis was 56 minutes.

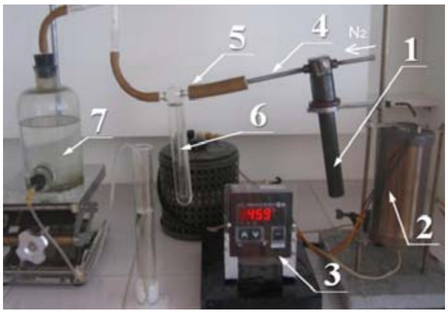

Figure 1: Laboratory setup for slow pyrolysis

3. Results and discussion

Moisture and ash content of the samples selected for analysis — the initial flax and cellulose-containing residue — taking the following values of 4.5 %, 2.7 % and 4.1, 0.9 %, respectively. According to the experimental data obtained, the cellulose residue of flax shive has significantly lower ash content, which is probably due to the dissolution of some ash components during the extraction of ethanol-lignin. Also, during interaction with alcohol, extractives are retrievable from plant biomass; this is the basis for the methods for determining extractives (Wilén et al, 1996). After the extraction of ethanol-lignin, the hydrolysis residue of the flax shive has a slightly lower calorific value of 16.83 MJ/kg, compared to the initial heat value of the flax shive, which is 17.25 MJ/kg.

The content of carbon and hydrogen in the hydrolysis residue after the extraction of ethanol-lignin from the flax increased from 47.9 to 50.6 % (wt.), and from 4.7 to 6.1 % (wt.), respectively. Based on the obtained data of elemental analysis, it can be concluded that the hydrolysis residue of flax is a more perspective raw material from the point of view of pyrolytic processing into gaseous and liquid energy carriers.

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 larger proportion of pores with sizes from 20 to 80 nm and more, as compared to the initial shive flax which, most likely, indicates that during the extraction of ethanol-lignin, large pores are formed due to the destruction of the initial microporous structure of the flax shive. The experimental data on the specific pore volume and specific surface area for flax and cellulose (hydrolysis) residue have similar values and are 0.0097 and 0.0116 mL/g; 9.6 and 9.5 m^2/g, respectively.

The study of the effect of temperature on the processing process in the range of 500-750 ºC on a laboratory installation of slow pyrolysis was carried out on samples of flax and cellulose residue. The data on the conversion of flax shive and cellulose residue from flax shive is shown in Figure 2.

In the studied temperature range, with an increase in the reactor temperature, the mass of the solid carbon-containing residue decreased and the mass of gaseous products increased. It should be noted that the yields of gaseous and solid products of pyrolysis of flax shive exceeded the corresponding values for a sample of cellulose residue from flax shive. 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 hive 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 ºC for both samples under study. Thus, the optimal temperature for reaching the maximum amount of gaseous and liquid energy carriers is 600 ºC. The dependence of the concentration of the main gaseous products (methane, carbon oxides, hydrogen) for the samples under study is shown in Figure 3.

When analyzing the data presented in Figure 3, it can be concluded that in the case of using the initial flax shive as a raw material for pyrolysis, the relationship of the carbon monoxide concentration on the processing time is similar to the analogous dependence obtained for the sample of the cellulose residue of the flax shive. The relationship on the concentration of carbon dioxide differs quite significantlyfor using samples. In the case of the flax shive sample, the dependence of the carbon dioxide concentration has a more pronounced extreme character (the maximum concentration corresponds to 8 minutes of the experiment and is 30.98 %), while for the cellulose residue of the shive, the maximum concentration is reached at 10 minutes and is 24.47 % (vol.).

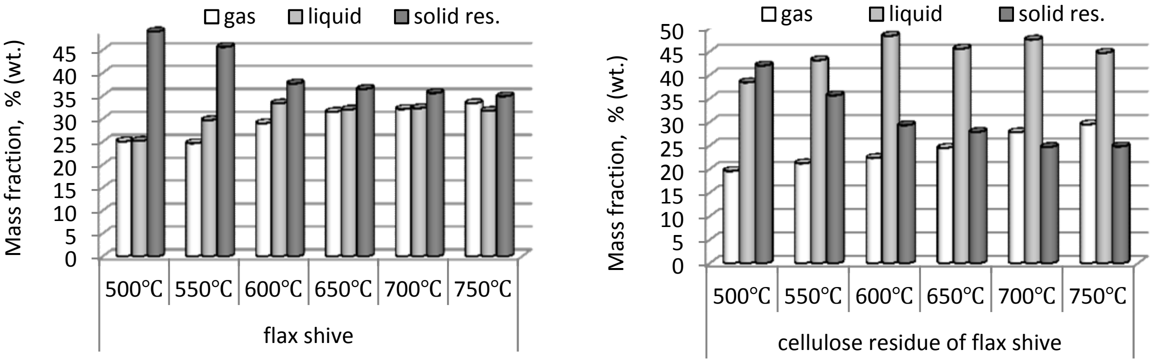

Figure 2: Dependences of the conversion of the studied samples of biomass in the process of pyrolysis

The dependence of the methane concentration for the two samples under study is also slightly different. A slower increase in methane concentration is observed for the flax shive sample, which is associated with high yields of carbon monoxide and especially carbon dioxide. It should be noted, that after 25 min from the beginning of the experiment methane concentration came to a constant value, and took rather close values for both samples. The relationship between time and H_2 concentration are also quite similar for both samples, since, during the experiment, the hydrogen concentration increased with time, which corresponds to the processes of deep destruction of the raw material and the accompanying dehydrogenation reactions (Demirbas, 2007). The maximum concentrations of hydrogen in a mixture of gaseous pyrolysis products correspond to flax shive (34.5 %), which is associated with a higher concentration of lignin in its composition (Augustine, 2015).

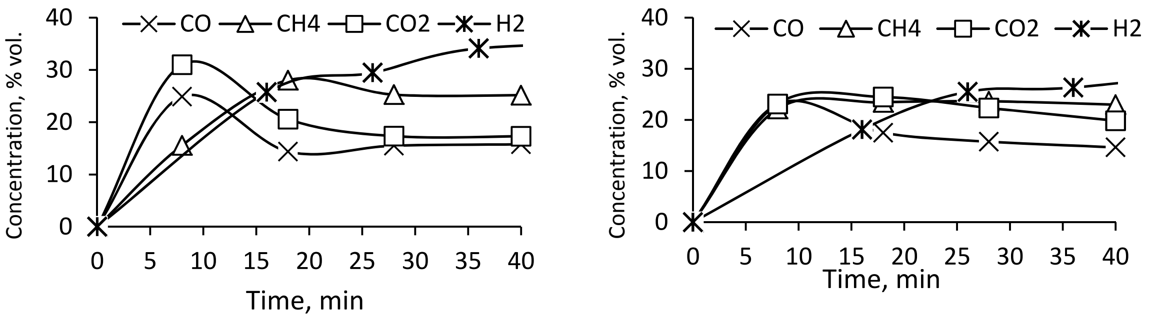

Figure 3: Dependences of the concentration of methane, carbon oxides, and hydrogen for the samples under study: (a) - flax shives, (b) - cellulose residue from the shive(t = 600 °C, fraction size 1-2 mm)

According to the data, the composition of liquid products for the studied samples of the shive and the cellulose residue of the shive is in many respects similar (see Figures 4, 5), but it should be noted that 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 (for example, acetic acid). Mohabeer (2018) also indicates a high content of organic acids in liquid pyrolysis products of flax shive. The composition of liquid products includes phenolic compounds - cresols, xylenols, pyrocatechol, pyrogallol, and their methyl esters, alcohols, acids, esters, carbonyl compounds, and low-volatile hydroxy acids, lactones, sugar anhydrides, polyhydric phenols, furan compounds. It is very important to consider that the liquid pyrolysis products of the cellulose residue of the shive have a narrower molecular weight distribution, which is preferable when obtaining liquid pyrolysis derivatives of lower acidity and a higher quality.

As part of the work, elemental analysis of samples of solid carbon-containing residues for the studied samples of flax and cellulose residue was carried out by the method of low-temperature adsorption of nitrogen (see Table 1). 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 carbon-containing residues. Experimental data by low-temperature adsorption of nitrogen indicate that the obtained carbon residue of pyrolysis of the hydrolysis residue of flax shive has a similar pore size distribution in comparison with the solid carbon-containing residue of pyrolysis of flax shive. Klasson et al, (2009) indicates the potential for obtaining activated carbons from flax fire after the stage of activation of the pyrolysis carbon residue.

Table 1: Characteristics of solid carbon-containing residues for the studied samples

	Carbon residues from pyrolysis	
Content, %	Flax shive	Cellulose residue shive
C	65.9	76.6
H	6.7	5.9
O	12.6	12.8
N	0.8	0.7
Pore size distribution, %		
< 6 nm	29.28	29.22
6-8 nm	14.05	14.13
8-10 nm	7.28	7.68
10-12 nm	8.20	8.09
12-16 nm	8.06	8.42
16-20 nm	7.39	7.54
20-80 nm	20.25	20.08
> 80 nm	5.48	4.84
Specific pore volume, ml/g	0.0253	0.0312
	S,m^2/g	
t-Plot	23.1	29.5
coeff. correlations	0.99909	0.99935

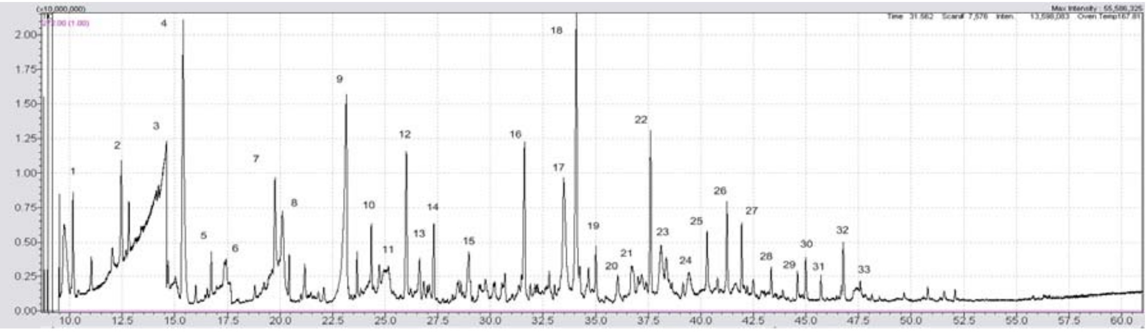

Figure 4: Chromatogram of liquid pyrolysis products of flax shive (t = 600 ℃, fraction size 1-2 mm)
(1) – aceton, (2) – acetic acid ethenyl ester, (3) – acetic acid, (4) – 2-oxopropanal, (5) – 2,3-pentadione, (6) – hydroxy acetaldehyde, (7) – not recognized, (8) – 1-hydroxy-2-butanone, (9) – 2-furancarboxaldehyde, (10) – ethyl 2-oxopropionate, (11) – fufruryl alcohol, (12) – 3,4-dihydro-2-pyran, (13) – 4-vinyl-4,5-dihydro-3H-pyrazole, (14) – 3-methylcyclopentanone, (15) – 5-methyl-2-furfural, (16) – 1,2-dioxocyclohexane, (17) – pentanal, (18) – o methoxyphenol, (19) – 2 - nonen, (20) – 4-ethyl-3-hexanone, (21) – 1-methylhexyl hydroperoxide, (22) – 2-methoxy-p-cresol, (23) – heptyl hydroperoxide, (24) – 3-hydroxy-6-methylpyridazine, (25) –methoxy-4-ethylphenol, (26) – 4-hydroxy-3-methoxystyrene, (27) – 1,3-dimethoxy-2-hydroxybenzene, (28) – hydroxy-4-methoxybenzaldehyde, (29) – 1,2,4-trimethoxybenzene, (30) – 2-methoxy-4-propenyl-phenol, (31) – 4'-hydroxy-3'-methoxy- acetophenone, (32) – vanillyl methyl ketone, (33) – 2-methylbutyl acetate.

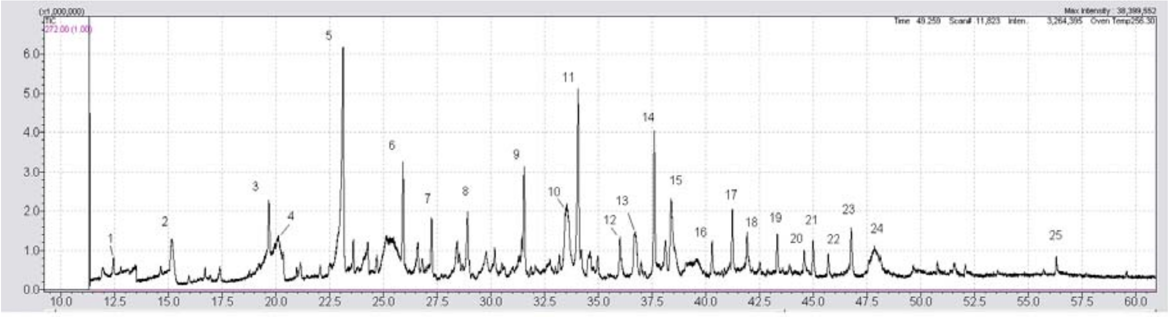

Figure 5: Chromatogram of liquid pyrolysis products of the cellulose residue of flax shive (t = 600 ℃, fraction size 1-2 mm); (1) – acetic acid ethenyl ester, (2) – 2-propanone, 1-hydroxy- acetol, (3) – not recognized, (4) – 1-hydroxy-2-butanone, (5) – 2-furancarboxaldehyde, (6) – 3,4-dihydro-2-pyran, (7) – 3-methylcyclopentanone, (8) – 5-methyl-2-furfural, (9) – 1,2-dioxocyclohexane, (10) – pentanal, (11) – o-methoxyphenol, (12) – 4-ethyl-3-hexanone, (13) – 1-Methylhexyl hydroperoxide, (14) – 2-methoxy-p-cresol, (15) –heptyl hydroperoxide, (16) – 2-Methoxy-4-ethylphenol, (17) - 4-hydroxy-3-methoxystyrene, (18) – 1,3-dimethoxy-2-hydroxybenzene, (19) – 3-hydroxy-4-methoxybenzaldehyde, (20) – 1,2,4-trimethoxybenzene, (21) – 2-methoxy-4-propenyl-phenol, (22) – 4'-hydroxy-3'-methoxy- acetophenone, (23) – vanillyl methyl ketone, (24) – 2-Methylbutyl acetate, (25) – tridecanoic acid

The experimental data on the specific pore volume and specific surface area for the carbon-containing pyrolysis residue of flax shive have lower values (23.1 m^2/g) than the corresponding carbon-containing residue of pyrolysis of the cellulose residue of the shive (29.5 m^2/g), which confirms the correctness of the chosen strategy complex processing of flax shives.

4. Conclusion

According to the experimental data, the optimal pyrolysis temperature, which allows reaching the maximum amount of gaseous and liquid energy carriers, is 600 ℃. In the case of the flax shive, a large mass of gaseous products was formed, while during the pyrolysis of the cellulose residue of the shive, liquid products. The dependence of the mass of the liquid fraction on the process temperature has an extreme nature for the selected types of biomass samples. Liquid pyrolysis products of the cellulose residue of the shive have a narrower molecular weight distribution, which is more preferable when obtaining liquid pyrolysis derivatives of 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 carbon-containing residues. Thus, it can be concluded that the cellulosic residue of flax shive as a raw material has many advantages in the pyrolysis process in comparison with the initial flax shive. Consequently, an integrated approach is potentially more efficient in the process of processing flax waste.

Acknowledgments

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