Low-waste production of pectin from beet pulp

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Abstract. The aim of the research work is to develop a method for processing beet pulp – a waste of sugar production. The study proposes a method for extracting pectin from beet pulp with a solution of weak citric acid. Characteristics of beet pulp such as total acidity, pH value, total sugar, carbon, nitrogen, volatile matter, hydrogen, fixed carbon, ash content have been determined. The pectin was extracted. To achieve the highest yield of pectin, the extraction conditions are optimized. The physical and chemical characteristics of the obtained pectin have been determined: the degree of esterification, color parameters, the methoxyl component, water activity, identification of pectin using infrared spectroscopy with Fourier transform. The torrefaction of pectin extraction waste to obtain biofuel was carried out. A feature of the proposed method is its low waste, since the waste of sugar production is used as a raw material, and weak and cheap citric acid is used as an extractant. The obtained pectin (the output of pectin was 21 ... 29%) can be used in the food industry (as a stabilizer, gelling agent, thickener).

1 Introduction

Many countries around the world are growing sugar beets at present (Figure 1).

Fig. 1. Global sugar beet production 2018.

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According to the latest data from the Food and Agriculture Organization of the United Nations [1], the largest production volumes in 2018 were recorded in the Russian Federation (42.065.957 tons), France (39.579.925 tons), the USA (30.068.647 tons) and Germany (26.191.400 tons).

In the Russian Federation, in particular, in the Republic of Bashkortostan, the yield of sugar beet is growing every year, and at the same time, the amount of waste from its processing – beet pulp – is growing.

Fresh pulp is used for the needs of animal husbandry within a radius of 100 km from the sugar factory. Its delivery to consumers over a longer distance becomes economically unprofitable due to the high cost of transportation. In addition, fresh beet pulp is fed to farm animals within 1-2 days after production, or it is preserved in special pulp pits or in polyethylene "sleeves", as the pulp deteriorates rapidly due to the development of putrid microflora, the beginning of butyric fermentation and mold [2].

However, according to the Framework Directive 2008/98/EC (WFD2008) on waste [3], waste processing aimed at obtaining a new useful product, bioenergy and/or biofuels can be an interesting alternative to the disposal of such waste, as it will not only reduce environmental impact of the waste but also help to reap economic and social benefits [4].

In particular, beet pulp can be used as a raw material for obtaining a valuable product – pectin. This technology is not yet perfected. In this regard, scientists from different countries are looking for approaches, methods and tools to improve the processing of beet pulp in order to obtain pectin [5-11].

Most of the investigated methods of obtaining pectin from beet pulp are not «green technologies», as the production waste is generated. Therefore, low-waste production of pectin from beet pulp is an important and urgent topic.

The purpose of this paper is to study an environmentally friendly and low-waste method of processing beet pulp.

The specific aims of the paper are as follows:

- to study of the physical and chemical properties of pectin synthesized from beet waste;
- to undertake a comparative analysis of the studied properties of beet pectin with the properties of commercial citrus pectin;
- to examine a biofuel production from pectin extraction waste.

2 Materials and methods

In previous works [12, 13], the results of determining the physical and chemical properties of beet pulp are presented in detail. The method for extracting pectin, which makes it possible to obtain pectin with a yield of 21 ... 29% is presented. Figure 2 shows a block diagram of the developed method for obtaining pectin.

This article presents the results of determining the physical and chemical properties of the obtained beet pectin, a comparison of these properties with the properties of citrus pectin, as well as the results of torrefaction of pectin extraction waste. Torrefaction is a new thermal processing of biomass into a high-energy fuel by heating it in an inert atmosphere to temperatures ranging from 200 to 300 °C.

Determination of physical and chemical characteristics of two samples of beet pectin and commercial citrus pectin was carried out to compare the results.

Water activity measured with testo 650.

Beet and citrus pectin color parameters (L^* , a^* and b^*) were measured using a CR-300 Chroma meter. The «L» value for each scale means the level of light or darkness respectively; the "a" value means redness or green; the "b" value means yellowness or blue.

Fig. 2. Block diagram of the developed method for producing pectin from beet pulp.

The esterification degree (DE) and the number of methoxyl groups (DM) were determined titrimetrically according to the method of Concha et al. [14]. Dried beet pectin after the third extraction (50 mg) was transferred into a 250 ml flask, moistened with 2 ml of 95% ethanol solution and dissolved in 20 ml of bidistilled water. The solution was heated for 25 minutes at 40 °C on an electromagnetic stirrer in order to completely dissolve the pectin in water. After complete dissolution, the mixture was titrated with a NaOH solution with a normality of 0.09322, with the addition of 5 drops of phenolphthalein indicator, the first volume of titrant (V_1) was noted. 30 ml NaOH solution with a normality of 0.09322 was added with stirring, the solution was left stirring for 30 minutes to de-esterify the pectin. 31 ml of HCl with a normality of 0.0783 was added until the pink color disappears with shaking. Three drops of phenolphthalein was added, titrated with NaOH solution until a faint pink color appeared, retaining after shaking (end point). This titration volume was recorded as the saponification titer (end titer, V_2).

Each ml of sodium hydroxide used in the titration is equivalent to 3.1 mg of methoxyl. The esterification degree of pectin, in percent, is calculated as follows:

$$DE = \frac{V_1}{V_1 + V_2} \cdot 100\% \quad (1)$$

The percentage of methoxyl groups (DM) in pectin is calculated using the following equation:

$$DM = \frac{V_2 \cdot N_{NaOH} \cdot MW_{OCH_3}}{m_{pectin}} \cdot 100\% \quad (2)$$

where N_{NaOH} – NaOH solution normality, mol/L;
 MW_{OCH_3} – molecular mass of methoxyl (31 g/mol);
 m_{pectin} – initial mass of pectin, g.

Fourier-transform infrared (FTIR) spectroscopic characterization of pectin samples was performed using a Thermo Nicolet Nexus spectrometer. FTIR spectra were obtained using discs containing about 10 wt%. finely ground samples. For each sample, from 4000 to 400 cm^{-1} , 32 scans were performed with a resolution of 4 cm^{-1} . The background spectrum was recorded before each spectrum.

A schematic representation of a fixed bed plant used for torrefaction experiments is shown in Figure 3.

The torrefaction reactor consists of a quartz tube surrounded by an electric heating tape.

The reactor temperature was controlled by an electronic PID temperature controller that reads the bed temperature using a thermocouple inserted in the center of the reactor.

Fig. 3. Diagram of the developed experimental torrefaction plant with a fixed bed.

The nitrogen supply unit consists of a flow meter with a flow rate range of 0.15-1.5 N L/min. A cooling horizontal glass tube trap was used to condense the vapor of the precipitates. Approximately 3 g of air-dried biomass particles from 1 to 2 mm are charged into the reactor and mixed uniformly with 28 g of 400-600 μm aluminium oxide granules to provide better temperature control throughout the packed bed and prevent localized hot spots in the reactor, due to the greater thermal inertia and higher thermal conductivity of aluminum oxide granules in comparison with the particles of beet pulp. After removing air from the system by passing nitrogen through the bed at a rate of 1.5 N L/min for 10 minutes, the reactor is heated to the desired torrefaction temperature (i.e. 200, 250 and 300).

After a predetermined time (i.e., 30 minutes), the bed temperature decreases as quickly as possible, turning off the electric heater and blowing cold compressed air onto the surface of the reactor. At the end of the reaction, the system is left to cool down to room temperature, and the solid and liquid products are removed and weighed.

The amount of biomass burned is calculated by subtracting the initial mass of the alumina particles from the total mass of the layer. The weight of non-condensable gaseous products is calculated from the difference.

$$MY_{\text{SOLID}} (\%, \text{ar}) = \frac{m_{\text{torrefied solid}}}{m_{\text{SBP feedstock}}} \quad (3)$$

$$MY_{\text{LIQUID}} (\%, \text{ar}) = \frac{m_{\text{condensable}}}{m_{\text{SBP feedstock}}} \quad (4)$$

$$MY_{\text{GAS}} (\%) = 100 - MY_{\text{SOLID}} (\%) - MY_{\text{LIQUID}} (\%) \quad (5)$$

$$I_{\text{ED}} (-, \text{db}) = \frac{LHV_{\text{torrefied solid}}}{LHV_{\text{SBP feedstock}}} \bigg|_{\text{db}} \quad (6)$$

$$EY_{\text{SOLID}} (\%, \text{db}) = MY_{\text{SOLID}} (\%, \text{db}) \times I_{\text{ED}} (-, \text{db}) \quad (7)$$

where $m_{\text{torrefied solid}}$ – mass of torrefied solid products, g;

$m_{\text{condensable}}$ – mass of liquid products, g;

$M_{\text{SBP feedstock}}$ - the mass of the feedstock - beet pulp, g;

MY_{SOLID} – mass yield of solid products, %;

MY_{LIQUID} – mass yield of liquid, %;

MY_{GAS} – mass output of the gas component, %;

I_{ED} – energy densification index;

EY_{SOLID} – energy yield, %.

Torrefaction was carried out at three different temperatures (i.e. 200, 250 and 300 ° C) for 30 minutes. The mass yields of solid (MY_{SOLID}), liquid (MY_{LIQUID}) and gaseous (MY_{GAS}) products are estimated based on the results obtained using equations (3-5). The Energy Densification Index (I_{ED}) and the Energy Yield (EY) of the burnt solids were also estimated on a dry basis using equations (6-7).

3 Results and discussion

The paper presents the results of determining the characteristics of pectin obtained in the course of two extractions with the highest yield of pectin (pectin I and pectin II), as well as for comparison of the results, similar characteristics of commercial citrus pectin were determined.

Determination of the physical and chemical characteristics of two beet pectin samples and commercial citrus pectin is carried out in this work.

The water activity of beet pectin was 0.601 at 20.8°C. This means that beet pectin is not microbiologically stable because the activity value is above 0.6.

The results of measuring the color parameters of two beet pectin samples and citrus pectin are presented in Table 1. These pectins are characterized by redness and yellowness. Beet pectin (I) is darker than beet pectin (II) and citrus pectin, so the L value is lower.

The DE and DM results for the two beet pectin samples and citrus pectin are shown in Table 1. These results show that beet and citrus pectin are low esterified.

Table 1. Color parameters, DE and DM pectin.

Type of pectin	Color parameters			DE, %	DM, %
	L	a	b		
Pectin (I)	86.69±3.68	+0.2±0.48	+15.68±4.29	27.73±0.39	4.05±0.00
Pectin (II)	63.39±6.31	+3.66±1.25	+24.88±2.08	14.51±0.91	4.12±0.29
Citrus pectin	83.68±0.88	+0.61±0.08	+14.91±0.20	26.79±0.00	4.08±0.03

FTIR is a method of analyzing chemical and structural changes that occur in biomass components (i.e. hemicellulose, cellulose, lignin, etc.) due to various treatments. In this work, in particular, FTIR spectroscopy was used to obtain information on possible chemical and/or structural changes occurring in pectin.

Fig. 4. IR spectra of beet pectin (I) and (II). Spectra have been split for easy comparison.

It was found that in both pectin samples the same absorption bands are observed in the region of functional groups of the FTIR spectra (Figure 4), which extends from 4000 to 1800 cm⁻¹, namely: a) A broad absorption band at about 3400 cm⁻¹, corresponding vibration of hydrogen bonds of OH groups of galacturonic acid; b) Narrow C-H absorption band at approximately 2900 cm⁻¹, corresponding to O-CH₃ from galacturonic acid methyl esters. The range from 1800 cm⁻¹ to 650 cm⁻¹ shows that the FTIR spectra of both pectin samples show characteristic pectin absorption bands.

Table 2. Chemical composition of dried pectin, % obtained by two different extraction methods with citric acid.

Elemental analysis (%)	Pectin (I)	Pectin (II)	Citrus pectin
C	38.24	37.11	37.13
H	5.6	5.51	5.69
N	0.29	0.37	0
O	55.87	57.01	57.18

The result is consistent with the elemental analysis results: the presence of a small amount of nitrogen in both samples of pectin (Table 2). The very small 1540 cm^{-1} band also confirmed the presence of a small amount of protein amide in the extracted beet pulp pectin samples.

Torrefaction is the optimal process for the production of high quality solid fuel from beet pulp [15]. The heating value increased 1.4 times for biomass treated at $300\text{ }^{\circ}\text{C}$ in 30 minutes, varying from 17.2 to 24.5 MJ/kg . O/C ratio decreased by 59%. It has been experimentally established that pectin extraction waste PE-SBP is a more suitable material for torrefaction than the original beet pulp Raw-SBP, due to the lower ash content.

Table 3 and Table 4 show the main results of fixed bed torrefaction tests performed on samples of PE-SBP and Raw-SBP, where VM is the amount of volatiles, FC is the amount of bound carbon, C, H, N, O is the amount of carbon, hydrogen, nitrogen, oxygen, respectively, LHV and HHV - lower and higher heating value, respectively.

Table 3. Experimental conditions and results of torrefaction.

Biomass	Temperature (°C)	Period (min)	MY _{SOLID}	MY _{LIQUID}	MY _{GAS}	I _{ED}	EY _{SOLID} (%)
			(wt%)				
Raw-SBP	200	30	69.50	8.01	22.49	1.19	83.23
	250	30	49.07	16.57	34.35	1.29	63.31
	300	30	44.46	16.43	39.11	1.40	61.19
PE-SBP	200	30	66.30	16.11	17.59	1.12	77.73
	250	30	48.06	16.96	34.98	1.31	66.10
	300	30	31.81	15.82	52.38	1.57	52.57

Table 4. Chemical composition and heating value of solid torrefaction products.

Solid product	Ash content (wt%)	Technical analysis (wt%)		Elemental analysis (wt%)				Heating value (MJ/kg)	
		VM	FC	C	H	N	O	LHV	HHV
Raw-SBP – 200	4.28	76.15	23.85	53.67	6.26	2.36	37.71	21.14	19.83
Raw-SBP – 250	4.83	63.75	36.26	58.61	5.92	2.38	33.10	22.71	21.48
Raw-SBP – 300	6.68	60.59	39.40	64.67	5.67	2.78	26.89	24.53	23.37
PE-SBP – 200	3.72	72.46	27.55	52.85	5.92	1.92	39.32	20.45	19.21
PE-SBP – 250	5.06	60.39	39.61	62.15	5.53	2.10	30.22	23.69	22.54
PE-SBP – 300	7.40	40.06	59.95	75.80	4.91	2.62	16.67	28.07	27.08

Thus, the waste from pectin extraction (PE-SBP) can be used to obtain high quality solid biofuels.

4 Conclusions

This paper presents the results of determining the physical and chemical properties of the obtained pectin from beet pulp – a waste of sugar production. The color parameters of two beet pectin samples and citrus pectin were measured: these pectins are characterized by redness and yellowness. The results of determining the esterification degree and the methoxyl component show that beet and citrus pectin are low methoxylated.

The results of pectin extraction waste torrefaction are presented: the potential possibility of converting this type of raw material into high-quality biofuel with a higher heating value comparable to the heating value of peat, wood, coal (20 ... 23 MJ/kg) has been established.

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