

# A Novel Method for Birch Outer Bark Quality Control Using Higher Heating Value

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*Abstract. In plywood plants, the bark of a birch tree is a readily accessible and already concentrated feedstock for further processing. It consists of two distinct layers: outer bark and inner bark. Up to 25.7 % of biologically active compounds (betulin, lupeol, betulinic acid) are concentrated in outer bark, with a broad spectrum of applications in the chemical, pharmaceutical, cosmetic and food industries. The inner bark must be separated from outer bark as well as possible because it causes a decrease in the yield and purity of the prepared ethanol extractives. Therefore, it is very important to predict the content of inner bark in the feedstock taken for the extraction process.*

*A novel method for the characterization of feedstock was developed using the higher heating value (HHV) as a reference. The developed method for birch outer bark quality control is very useful in birch outer bark extraction plants. Thus, it would be possible to control the purity of the feedstock and to predict the potential yield of extractives as well as the amount of the solvent to be taken for the extraction process. Pure enough ( $\geq 90$  % of outer bark) feedstock for biologically active extractives production can be obtained by the floating method after 5 h if the HHV is more than 32-33 MJ/kg.*

**Keywords:** Birch bark, feedstock quality, polysaccharides, higher heating value.

## I. INTRODUCTION

Birch wood in the Northern hemisphere is widely used in the furniture, pulp and plywood manufacture. 2 % of veneer blocks' mass is made up of birch outer bark (BOB) [1]. It is readily accessible and already concentrated for further processing. In the concept of the circular bio-economy, it is necessary to upgrade the by-products generated in the processing of forest products. In this context, birch plywood, furniture or pulp plants are well established industrial enterprises that generate known amounts of birch bark residues, which could have considerable value as a feedstock for the production of higher added value products, for example, triterpene rich extractives [2], [3]. Pentacyclic lupane type triterpenes (betulin, lupeol, betulinic acid) are promising starting materials for the synthesis of biologically active compounds with a broad spectrum of medical applications [4]. Additionally, after triterpene extraction, the remaining biomass can still be used for the production of other products from suberin – individual suberic acids for macromolecular materials [5] or as a hydrophobic binder for particleboards [6]. It is known that valuable triterpenes and suberin are concentrated in BOB, up to 27 % [3] and 45 % [2], respectively. Birch inner bark (BIB) has a completely different chemical composition (Table I), especially regarding the

content of carbohydrates and hot water extractives [7], [8].

Table I  
Chemical Composition of Birch Bark Constituents Calculated on the Oven-dry Mass

Value	BOB	BIB	Ref.
Carbohydrates (%)	4.4-10.4	45.2-55.0	[2,7-9]
Ash (%)	0.3-1.0	1.5-2.4	[2,8,9]
Organic solvent extractives (%)	29.1-40.0	9.0-15.8	[2,8,9]
Hot water extractives (%)	0.9	19.3	[8]
Suberin - NaOH soluble extractives (%)	34.5-45.0	25.2-25.5	[2,8,9]
Lignin (%)	2.2-9.0	9.1-18.1	[2,8,9]
HHV (MJ/kg)	34.1	21.1	Table II

The above-mentioned substances may cause a decrease in the yield and triterpenes content in the obtained extractives if BIB and woody admixtures are present in the feedstock. Therefore, it is very important to predict the content of BIB in the feedstock taken for the extraction process.

The main aim of the study was to develop an appropriate and precise BOB quality controlling method. Therefore, two different BIB and BOB analysis methods were used, which could serve on an industrial scale:

1) Easily- and hardly hydrolysable polysaccharides (EHP and HHP) due to the difference of BIB and BOB in carbohydrates;

2) Higher heating value (HHV) because that for BOB is 1.5 times higher and HHV for BIB is similar to that of wood.

## II. MATERIALS AND METHODS

### A. Feedstock

Birch bark, left over at a plywood factory in Latvia, was selected as a representative industrial waste with the relative moisture content 35-40 %. The collected feedstock was dried at room temperature to a moisture content of 4-7 % and milled in a cutting mill SM 100 (Retsch GmbH & Co) to pass the sieve with holes of diameter 2.00 mm.

Milled dry birch bark samples were soaked in deionized water for 48 h by occasional mixing. Birch outer bark, floated to the top of the water surface (BOBF), was collected and used as a reference raw material for the pure BOB sample. To determine the optimal floating time and suitability of the above-mentioned BOB control method based on HHV, a flotation experiment was carried out, in which dry birch bark (200 g) was soaked from 15 min to 48 h by occasional mixing (bark/water hydro modulus 1/5). After flotation, BOBF was dried to a moisture content of 4 % for further operations. The BIB, which sank to the bottom, was collected and dried to a moisture content of 7 % for further operations. For elemental and HHV analysis needs, the samples were additionally ground to the particle size below 0.5 mm directly prior to analyzing.

For EHP and HHP analysis, the collected birch bark was separated from the BIB by hand to prevent the leaching of polysaccharides during the flotation.

### B. Analytical Methods

Moisture and ash content was determined according to EN 14774 and EN 14775 standards, respectively.

Elemental analysis was performed according to EN 15104 on an Elementar Analysensysteme GmbH – vario MACRO CHNS Element Analyzer – an analyzer used for the determination of C, H and N in solid and liquid samples, using a thermal conductivity detector.

The content of EHP was determined by mild hydrolysis of approximately 5.0 g of the sample with 2 % HCl for 3 h. The hydrolyzed sample, after EHP analysis, was further hydrolyzed by 80 % H<sub>2</sub>SO<sub>4</sub> for 5 h and the content of HHP was determined [10].

HHV was determined according to the EN 14918 standard. Measurements were performed on a "Parr" Oxygen Bomb Calorimeter, in which approximately 1.0 g of an oven-dried birch bark sample was completely combusted under a pressurized (3000 kPa) oxygen atmosphere. The rise in temperature of the cylinder allows the calculation of the calorific value when the exact weight of the sample is known.

The net calorific value was calculated on a dry basis (MJ/kg) to compare the samples.

All analyses were performed in triplicate, and their average values did not exceed a 1.0 % variation.

### C. Experimental Procedure

At first separated by hand, milled dry birch outer (BOBH) and inner (BIBH) bark samples were mixed together in five proportions (0, 30, 50, 70 and 100 % of the BIB admixture calculated on the oven-dry mass) for EHP and HHP analysis, and for creation of a calibration curve. When the more precise HHV method was chosen, additional points in the curve were added (10, 20, 40, 60, 80 and 90 % of the BIB admixture), the prepared barks' mixture samples were analyzed and a calibration curve was created.

## III. RESULTS AND DISCUSSION

### A. Easily- and Hardly-hydrolyzable Polysaccharides

As mentioned in the introduction, valuable triterpenes are concentrated in BOB. The purity of BOB depends on the separation methodology, as well as the starting feedstock's composition (admixture of BIB, woody particles). Therefore, it is very important to predict the content of BIB in the feedstock taken for the extraction process.

Because BOB has a very low content (4-10 %) of total sugars (carbohydrates) [2], [8], [9], but BIB has a relatively high content (45-55 %) of carbohydrates [7], [8], our first idea was to use this difference between these two representative parts of birch bark for determining its purity.

Mixed BIBH/BOBH samples in five proportions, as described in the experimental section, were prepared. The content of EHP and HHP was determined. The obtained results are shown in Fig. 1. Both EHP and HHP content logically increases with increasing BIBF proportion in the sample.

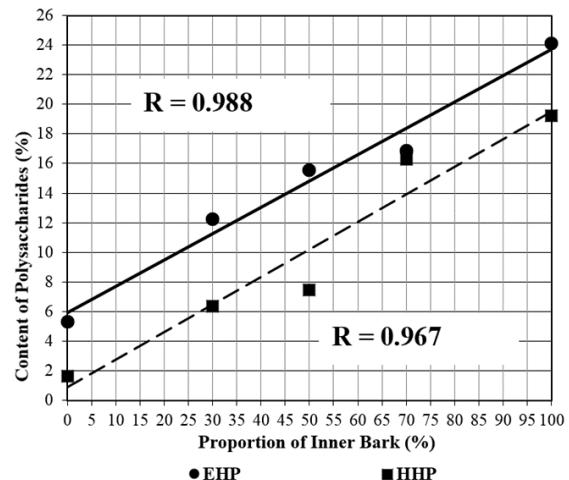


Fig. 1. Calibration curves for the content of easily- and hardly-hydrolyzable polysaccharides in the prepared birch bark mixtures.

It can be concluded that the EHP content shows better correlation ( $R=0.988$ ) than the content of HHP ( $R=0.967$ ), and the method for determining the EHP

content is less time-consuming. Still, the method has some disadvantages, which were observed during the research.

It is very difficult to obtain 100 % pure BOB if separated mechanically – by hand or by winnowing. Fig. 1 shows that the total content of EHP and HHP in pure BOBH is already 6.9 % (5.3 % + 1.6 %), and it is reported in the available literature that the content of carbohydrates can vary in the range of 4.4–10.4 % (Table I), which means that there are some BIB admixtures left after mechanical separation.

It is possible to obtain pure BOB by the floating method, but then it is difficult to calibrate EHP because, during the floating in a water environment, about a half of EHP could be leached off from BIB. Besides, there are also woody particles in the BOB and as we know, the EHP content in the birch wood (up to 28 % [11]) is higher than that in BIB (24.1 %). Of course, it is possible to make some assumptions but it will not improve the obtained results, and the controlling process of the BOB quality will not be precise enough.

#### B. Higher Heating Value and Elemental Composition

The above-mentioned obstacles (leaching of polysaccharides from BIB, non-homogeneous admixture composition) enabled us to find some properties which would not have so many variables depending on the BOB separating methodology. During the routine BOB and BIB analysis, a parameter – HHV – was revealed. It can be seen from Table II that HHV for pure BOB was more than 1.5 times higher than that for BIB calculated on the oven-dry mass. In addition, HHV for birch wood was close to that for BIB. This gave a hope that it would be possible to obtain a more precise calibration curve for controlling the BOB purity.

There are some differences between BOB samples depending on the separation method. The highest HHV was for BOBF – 34.1 MJ/kg; therefore, this was chosen as a reference feedstock for pure BOB in the calibration experiments. BIBH was chosen as a representative of the 100 % admixture because its HHV (21.1 MJ/kg) was almost the same as for birch wood (21.2 MJ/kg). This means that the origin of the admixture – BIB or wood particles – will not affect the HHV.

Table II  
 Higher Heating Value and Ash Content of Birch Log Components  
 Calculated on the Oven-dry Mass

Sample	HHV (MJ/kg)	Ash content (%)
Birch wood (BW)	21.2 ± 0.0	0.4 ± 0.0
Birch bark (BB)	26.0 ± 0.1	1.0 ± 0.0
Inner bark (floating) (BIBF)	21.5 ± 0.0	2.4 ± 0.1
Inner bark (by hand) (BIBH)	21.1 ± 0.1	2.4 ± 0.1
Outer bark (floating) (BOBF)	34.1 ± 0.0	0.5 ± 0.0
Outer bark (by hand) (BOBH)	32.2 ± 0.1	1.0 ± 0.0
Outer bark from log (BOBL)	33.3 ± 0.0	0.3 ± 0.0

Table III  
 Elemental Composition of Birch Log Components

Sample*	C (%)	N (%)	H (%)	O (%)**
<b>BW</b>	48.9 ± 0.1	0.2 ± 0.0	5.0 ± 0.1	46.0 ± 0.2
<b>BB</b>	67.5 ± 0.1	0.5 ± 0.0	6.0 ± 0.1	26.0 ± 0.1
<b>IHF</b>	52.7 ± 0.1	0.5 ± 0.0	5.3 ± 0.3	41.5 ± 0.2
<b>IHB</b>	52.4 ± 0.3	0.5 ± 0.0	5.2 ± 0.2	41.9 ± 0.2
<b>BOBF</b>	71.3 ± 0.1	0.4 ± 0.0	8.5 ± 0.1	19.7 ± 0.1
<b>BOBH</b>	70.4 ± 0.2	0.5 ± 0.0	6.3 ± 0.1	22.9 ± 0.1
<b>BOBL</b>	70.9 ± 0.1	0.4 ± 0.0	7.4 ± 0.1	21.3 ± 0.1

\* Abbreviations are explained in Table II

\*\* By difference

The BIBF obtained after floating has a close enough HHV (21.5 %), but still somewhat higher because of some BOB particles sediment together with the BIB fraction.

BOBL was collected from a birch log before the soaking operation in a plywood factory. This sample showed that, after soaking and floating operations, small amounts of EHP were extracted, which led to an increase in HHV.

The elemental composition shown in Table III testifies the above-mentioned facts. The HHV of BOB is higher than that of BIB because it has a higher content of carbon and hydrogen, as well as a lower content of oxygen due to a lower amount of carbohydrates in the structure.

After the decrease of oxygen, also HHV can be prognosticated because that for BIB samples is approximately 1.5 times higher than for BOB samples.

#### C. Calibration Curve of HHV

In the light of known facts, the calibration curve for the characterization of the feedstock was developed using HHV as a reference to determine the content of the pure BOB (Fig. 2).

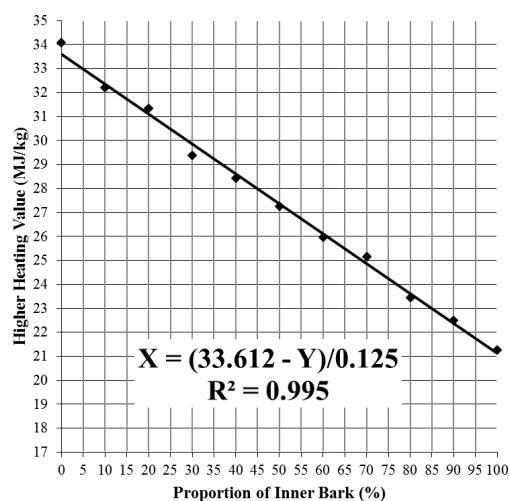


Fig. 2. Calibration curves for the HHV in the prepared birch bark mixtures.

HHV increases with the increase of the BOB proportion in the sample. Such a method turned out to be more accurate ( $R=0.995$ ) and faster (45 min). Obtained equation of the calibration curve allow

calculating the amount of impurities, depending on the calorific values determined experimentally.

#### D. Impact of the Floating Time on HHV

To determine the optimal floating time, an experiment was carried out, in which equal dry birch bark samples were soaked in distilled water and the HHVs were determined as a reference for pure BOBF. Experimental results are shown in Table IV.

Table IV  
Impact of the Floating Time on the Yield and Higher Heating Value of Birch Outer Bark

Floating time (h)	Floating yield (% dry mass)	HHV (MJ/kg)
<b>0 (BB)</b>	100	26.0 ± 0.1
<b>0.25</b>	52.3 ± 0.1	29.4 ± 0.1
<b>1</b>	48.0 ± 0.1	30.8 ± 0.0
<b>3</b>	43.2 ± 0.0	31.3 ± 0.1
<b>5</b>	39.5 ± 0.1	32.2 ± 0.0
<b>12</b>	38.7 ± 0.1	32.5 ± 0.1
<b>24</b>	36.9 ± 0.1	33.5 ± 0.0
<b>48 (BOBF)</b>	35.4 ± 0.1	34.1 ± 0.0

It is obvious that, with increasing floating time, the yield of BOBF decreases while the HHV increases due to the increase of the BOB proportion in the obtained sample. To obtain a sufficiently pure BOBF, the flotation time must be at least 5 h, in which the yield of the floated BOBF is 39.5 % from the dry birch bark. The BOBF obtained by the floating method can be regarded as qualitatively and sufficiently purified from birch inner bark if its combustion heat is above 32-33 MJ/kg (BIB content would be below 10 %).

Therefore, the developed method for the BOB quality control is very useful in BOB extraction plants. Thus, it would be possible to control the purity of the feedstock and to predict the potential yield of extractives as well as the amount of the solvent to be taken for the extraction process.

#### IV. CONCLUSION

If we compare EHP and HHP, then the EHP content shows better correlations ( $R=0.988$ ) than the content of HHP ( $R=0.967$ ), and the method for determination of the EHP content is less time-consuming. Still, the method has some disadvantages – it is very difficult to obtain 100 % pure BOB if separated mechanically – by hand or by winnowing.

The HHV for pure BOB was more than 1.5 times higher than that for BIB. Therefore, the calibration

curve for the characterization of the feedstock was developed using HHV as a reference to determine the content of pure BOB, which was more accurate ( $R=0.9955$ ) and faster (45 min).

Pure enough ( $\geq 90\%$  of BOB) feedstock for triterpene production can be accepted if the HHV is more than 32-33 MJ/kg.

#### V. ACKNOWLEDGMENTS

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#### REFERENCES

- [1] E. Bergelin and B. Holmbom, "Reactions and distribution of birch extractives in kraft pulp oxygen delignification," *J. Wood Chem. Technol.*, vol. 28, pp. 261-269, 2008.
- [2] P. C. R. O. Pinto, A. F. Sousa, A. J. D. Silvestre, C. P. Neto, A. Gandini, Ch. Eckerman and B. Holmbom, "*Quercus suber* and *Betula pendula* outer barks as renewable sources of oleochemicals: A comparative study," *Ind. Crops Prod.*, vol. 29, pp. 126-132, 2009.
- [3] J. Rizhikovs, J. Zandersons, G. Dobele and A. Paze, "Isolation of triterpene-rich extracts from outer birch bark by hot water and alkaline pre-treatment or the appropriate choice of solvents," *Ind. Crops Prod.*, vol. 76, pp. 209-214, 2015.
- [4] S. Alakurtti, T. Mäkelä, S. Koskimies and J. Yli-Kauhaluoma, "Pharmacological properties of the ubiquitous natural product betulin," *Eur. J. Pharm. Sci.*, vol. 29, pp. 1-13, 2006.
- [5] A. Gandini, C. P. Neto and A. J. D. Silvestre, "Suberin: a promising renewable resource for novel macromolecular materials," *Prog. Polym. Sci.*, vol. 31, pp. 878-892, 2006.
- [6] J. Rizikovs, J. Zandersons, A. Paze, A. Tardenaka and B. Spince, "Isolation of subericin acids from extracted outer birch bark depending on the application purposes," *Baltic Forestry*, vol. 20, pp. 98-105, 2014.
- [7] A. J. Mian and T. E. Timell, "Isolation and characterization of a cellulose from the inner bark of white birch (*Betula Papyrifera*)," *Can. J. Chem.*, vol. 38, pp. 1191-1198, 1960.
- [8] D. N. Vedernikov, N. Yu. Shabanova and V. I. Roshchin, "Change in the chemical composition of the crust and inner bark of the *Betula pendula* Roth. birch (Betulaceae) with tree height," *Russ. J. Bioorganic Chem.*, vol. 37, pp. 877-882, 2011.
- [9] A. Karnaouri, U. Rova and P. Christakopoulos, "Effect of different pretreatment methods on birch outer bark: New biorefinery routes," *Molecules*, vol. 21, pp. 427-443, 2016.
- [10] A. V. Obolenskaya, Z. P. Elnitsdkaya and A. A. Leonovich, *Laboratory Works in the Chemistry of Wood and Cellulose* (source is in Russian). Moscow: Ecologya, 1991.
- [11] A. Bredihhin, U. Mæorg and L. Vares, "Evaluation of carbohydrates and lignocellulosic biomass from different wood species as raw material for the synthesis of 5-bromomethylfurfural," *Carbohydr. Res.*, vol. 375, pp. 63-67, 2013.