

# Integrated extraction-catalytic processing of mechanically activated pine bark

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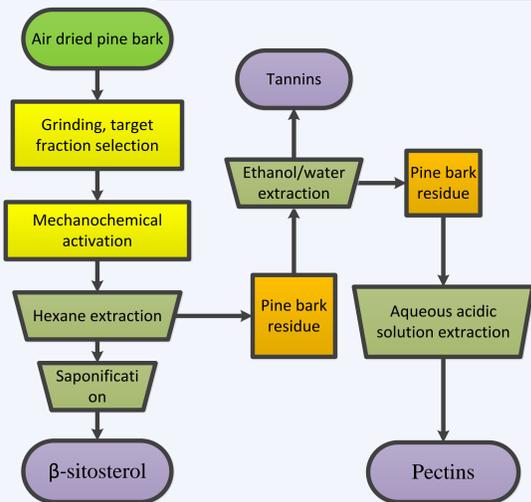
## Introduction

The aim of the project is to develop the fundamental scientific foundations of a new environmentally friendly integrated extraction-catalytic technology of pine bark-wood waste processing into a range of chemical products with high added value.

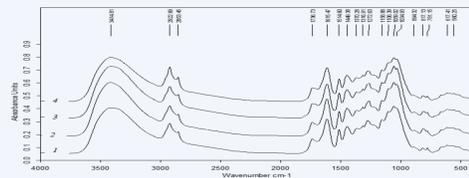
### The novelty of the project idea is:

- firstly, in using an integrated approach to solve the problem of pine bark-wood waste processing, based on the integration of extraction methods for extracting the most valuable organic substances and catalytic methods to obtain chemical products with high added value from the main lignocellulosic biomass components - lignin and polysaccharides;
- secondly, in using new catalytic methods of reductive fractionation into phenols and holocellulose with presence of Ru and Ni catalysts during the processing of bark and bark-wood waste lignocellulosic component.

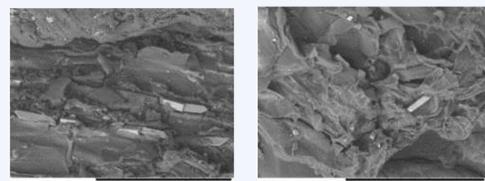
## Mechanical activation, extraction



- Grinding was carried out on RM-120 - a rotary knife mill with a sieve diameter of 3 mm.
- Fractionation was carried out on a GR-30 vibrating screen and a fraction of the bark with a size of 1 + 3 mm was sorted out.
- Mechanochemical activation of pine bark was carried out by processing in drum or planetary mills (MCA), as well as by the method of explosive autohydrolysis (VAG).



IR spectra of pine bark before (1) and after explosive autohydrolysis at different pressures (2 - 4): explosive autohydrolysis temperature 120 °C, time 30 s. 2 - pressure 1.0 MPa; 3 - 1.5 MPa; 4 - 2.0 MPa.

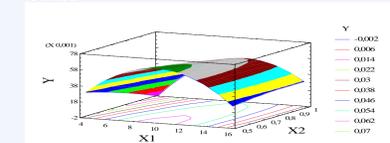


Micrographs of pine bark before (a) and after explosive autohydrolysis at a pressure of 1.0 MPa. VAG conditions: temperature 120 °C, time 30 s. Magnification - 500 times..

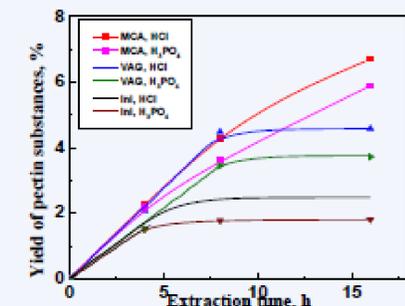
The yield of  $\beta$ -sitosterol as a result of saponification with sodium hydroxide alcoholic solutions for samples of pine bark.

Sample	Weight, g	Hexane extraction time, h	The concentration of an caustic soda alcoholic solution, n	$\beta$ -sitosterol yield, mg	$\beta$ -sitosterol yield, %*
Ini	12,96	4	0,5	1,137	0,009
Ini	12,96	4	1,0	1,036	0,034
Ini	12,96	8	0,5	4,377	0,011
Ini	12,96	8	1,0	1,384	0,011
Ini	12,96	16	0,5	3,264	0,025
Ini	12,96	16	1,0	2,316	0,018
VAG	12,97	4	0,5	3,037	0,023
VAG	12,97	4	1,0	0,842	0,006
VAG	12,97	8	0,5	10,068	0,078
VAG	12,97	8	1,0	4,938	0,038
VAG	12,97	16	0,5	2,319	0,018
VAG	12,97	16	1,0	4,689	0,036
MCA	11,02	4	0,5	1,462	0,013
MCA	11,02	4	1,0	1,352	0,012
MCA	11,02	8	0,5	3,924	0,036
MCA	11,02	8	1,0	2,364	0,021
MCA	11,02	16	0,5	2,124	0,019
MCA	11,02	16	1,0	0,542	0,004

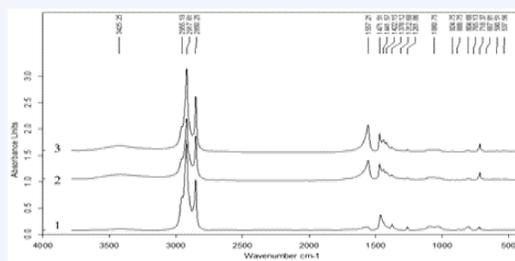
- The mathematical model of the variable factors X1, X2 influence on the output parameter Y displayed graphically in the form of a response surface



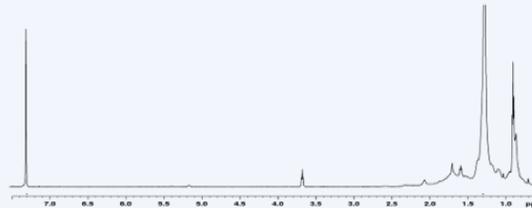
- The maximum predicted value of the  $\beta$ -sitosterol yield is 0.071 for the initial sample of pine bark in the studied area of the factor space, according to the calculated mathematical model (2), at the point corresponding to the following values of the variable factors: extraction time is 9.8 hours, the concentration of the saponification solution NaOH 0.5 N.



Graphs of the influence of the extraction time on extractive pectin substances yield.

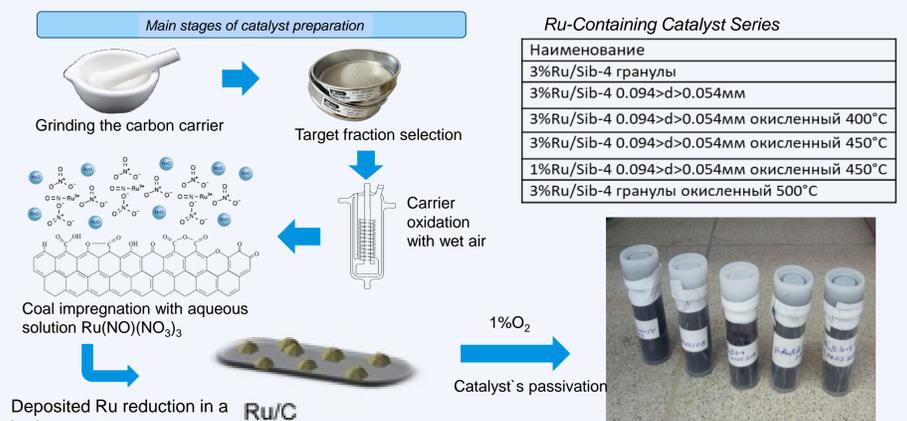


IR spectrum of  $\beta$ -sitosterol isolated from the original pine bark (1) and its activation products (2, 3): 2 - activation by explosive autohydrolysis under the following conditions: 120 °C, time 30 s, water vapor pressure 1.0 MPa; 3 - activation in a drum mill for 1 hour.



<sup>1</sup>H NMR spectrum of  $\beta$ -sitosterol isolated from pine bark after its activation by VAG

## Preparation and examination of catalysts



Ru-Containing Catalyst Series	
Наименование	3%Ru/Sib-4 гранулы
	3%Ru/Sib-4 0.094>d>0.054мм
	3%Ru/Sib-4 0.094>d>0.054мм окисленный 400°C
	3%Ru/Sib-4 0.094>d>0.054мм окисленный 450°C
	1%Ru/Sib-4 0.094>d>0.054мм окисленный 450°C
	3%Ru/Sib-4 гранулы окисленный 500°C



Textural characteristics of carbon supports and Ru catalysts (3% Ru) based on them

Носитель	Удельная поверхность (S <sub>БЕТ</sub> ) m <sup>2</sup> /g		Объем пор (V <sub>пор</sub> ), cm <sup>3</sup> /g		Средний размер пор <d пор>, нм	
	носитель	кат.	носитель	кат.	носитель	кат.
Sib-4	375	321	0,55	0,43	5,8	5,4
Sib-4-Гр	364	273	0,51	0,32	5,6	4,7
Sib-4-Ох-400	332	300	0,42	0,37	5,0	5,0
Sib-4-Ох-450	380	341	0,53	0,50	5,6	5,8
Sib-4-Ох-500Гр	287	233	0,37	0,28	5,1	4,8

Serensen-de Bruyne method (pH<sub>тис</sub>), for determination of the catalyst acid properties

Support	pH <sub>тис</sub>	
	Support	3% cat.
Sib-4-Гр	7,66	8,05
Sib-4	7,59	8,01
Sib-4-Ох-400	6,88	7,12
Sib-4-Ох-450	5,33	6,89/6,06*
Sib-4-Ох-500Гр	3,44	6,44

\*1%Ru/Sib-ox-450

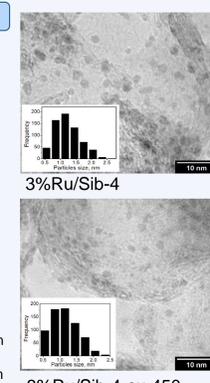
- An increase in the acidity of the support leads to a Ru dispersion increase, which can be explained by an increase in the number of acid sites responsible for the Ru distribution..

### TEM studies of catalysts

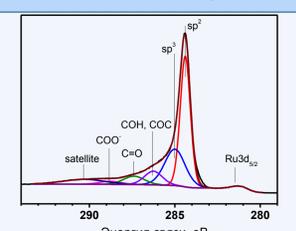
Catalyst	Размеры частиц Ru, нм <sup>1</sup>				D <sub>Ru</sub>
	d <sub>min</sub>	d <sub>max</sub>	<d>	<d <sub>c</sub> >	
1%Ru/Sib-4-ox-450 <sup>2</sup>	0.52	1.79	1.06	1.27	1.03
3%Ru/Sib-4-ox-450 <sup>2</sup>	0.52	2.37	1.13	1.39	0.94
3%Ru/Sib-4-ox-400 <sup>2</sup>	0.66	3.00	1.19	1.40	0.94
3%Ru/Sib-4 <sup>2</sup>	0.60	2.73	1.22	1.48	0.88
3%Sib-4-ox-500-гранулы <sup>3</sup>	0.69	3.14	1.30	1.53	0.85
3%Ru/Sib-4-гранулы <sup>3</sup>	0.76	3.46	1.42	1.71	0.77

<sup>1</sup>d<sub>min</sub>, d<sub>max</sub> - minimum and maximum particle diameter; <d> =  $\sum d/N$  - average particle size; <d<sub>c</sub>> =  $\sum d^3 / \sum d^2$  - weighted average size per unit surface. D<sub>Ru</sub> - dispersion of ruthenium.

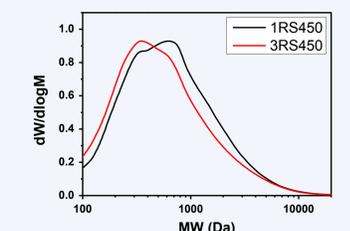
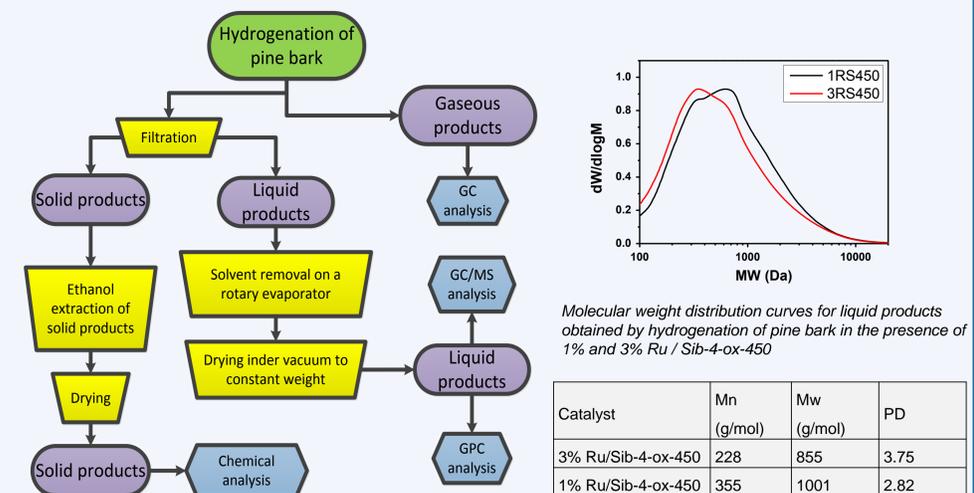
<sup>2</sup> Fractional composition: 56-94 micron; <sup>3</sup> 1.0 - 1.6 mm



### XPS studies of catalysts



## Tests of Ru-containing catalysts



Molecular weight distribution curves for liquid products obtained by hydrogenation of pine bark in the presence of 1% and 3% Ru / Sib-4-ox-450

Catalyst	Mn (g/mol)	Mw (g/mol)	PD
3% Ru/Sib-4-ox-450	228	855	3.75
1% Ru/Sib-4-ox-450	355	1001	2.82

Степень превращения, выход жидких продуктов и состав газообразных продуктов гидрирования коры сосны в среде этанола

Catalyst	Conversion degree, wt. %	Solid products yield, wt. %	Liquid products yield, wt. %	Gaseous products yield, wt. %	CO, wt. %	CO <sub>2</sub> , wt. %	CH <sub>4</sub> , wt. %
w/o	34.8	65.2	17.8	8.9	9.0	48.3	42.7
3% Ru/Sib-4-ox-450	44.0	56.0	18.0	19.4	40.7	32.5	26.8
1% Ru/Sib-4-ox-450	55.6	44.4	29.0	17.0	41.2	34.1	24.7

## Conclusion

- The physical and chemical properties of pine bark products activated with processes of explosive autohydrolysis and mechanical mills grinding were studied. Obtained data showed these impacts to lead to a noticeable decrease in the average particle size of the crust and the destruction of the structure of the polymers included in its composition.
- The effect of the two least destructive methods of activation (explosive autohydrolysis at 1 MPa at 120 °C and mechanical activation in a drum mill for 1 hour) on the yields and physicochemical extractives of pine bark (resinous and pectin substances,  $\beta$ -sitosterol) was studied. Extraction products were studied by IR and <sup>1</sup>H NMR spectroscopy, GLC-MS.
- It was shown that the pine bark activation could significantly increase the extraction rate and yields for all of the target products. Experimental optimization of the extraction processes was carried out to explore the best target substances extraction conditions. For resinous substances and  $\beta$ -sitosterol: activation by explosive autohydrolysis, alkali concentration 0.5 N. For pectin substances: activation by explosive autohydrolysis, using hydrochloric acid.
- Basing on CM Sibunit-4, a series of catalysts was prepared with different acidity, granule size, and content of the active component (1 and 3% Ru). It was found that as the temperature of the support oxidative treatment increases, surface oxygen-containing functional groups are formed, which are responsible for the improved distribution of Ru.
- In the process of noncatalytic pine bark hydrogenation, the lignin conversion degree is 34.8 wt%, the yield of liquid products is 17.8 wt%, and the yield of solid product is 65.2 wt%. The degree of crust conversion with presence of the best catalysts 1 wt% Ru / C increases to 44-56 wt%, the yield of liquid products - up to 29 wt%, and the yield of solid product decreases to 44.2 wt%. The yield of gaseous products more than doubles.
- The presence of a catalyst in the reaction medium intensifies the hydrodeoxygenation process; a decrease in the average molecular weight towards the predominant formation of monomers and dimers is also observed.
- GC-MS liquid products analysis showed that the main products were propylguaiaacol and ethylguaiaacol with maximum yields of 36.0 and 14.7 wt. %, respectively.
- This work was conducted within the framework of the by RFBR Grant No. 19-43-240011 r\_a for Institute of Chemistry and Chemical Technology SB RAS using the equipment of Krasnoyarsk Regional Research Equipment Centre of SB RAS