

# CHEMISTRY AND TECHNOLOGY OF WOOD PROCESSING

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## PREPARATION OF PINE FLOTATION OIL BY HYDRATION WITH $\alpha$ -PINENE

The hydration of  $\alpha$ -pinene of gum turpentine and separately pinene fractions in the organic acids media for the purpose of obtaining terpene alcohols, which are widely used as flotation reagent for mineral processing in mining production were studied. The best results are obtained among the organic acids when 70% formic acid is used. The  $\alpha$ -pinene hydration process in the acid medium is exothermic, and it is necessary to maintain a constant temperature of 65°C to reduce the rate of side reactions.

The main component of turpentine, resulting in the formation of  $\alpha$ -terpineol is  $\alpha$ -pinene; 3-carene, terpinolene, and limonene contents do not practically change in the reaction mixture, which testify their stability in 70% formic acid media.

The maximum content of terpene alcohols (60,1%) was obtained when using  $\alpha$ -pinene fraction at a ratio of  $\alpha$ -pinene and 70% formic acid 1.0 : 1.1 for 3 hours. Increase of the duration of hydration reaction leads to the decrease in the content of terpineol in the reaction mixture due to the secondary isomerization processes.

**Key words:** hydration, turpentine, pinene, formic acid, terpene alcohols, terpineol, flotation oil.

**Introduction.** The increasing need of many industries in the wood chemical industry production requires the development of new and highly important products based on wood extractives, such as rosin and turpentine. It is possible to obtain a wide range of valuable chemical products for medicine, agriculture, pharmaceutical, perfumery and cosmetics, mining and other industries.

Of particular interest is the processing of turpentine, which is the only major source of terpenes – a valuable raw material for the synthesis of a variety of substances. Products of chemical processing of turpentine are well-known, such as synthetic camphor, technical camphene and their polychlorine derivatives (insecticides), oxyterpene resins, polyterpenes, synthetic fragrances and flotation reagents, (synthetic pine oil), and others.

At present, in the Republic of Belarus 90–95% of such valuable raw material as turpentine is used in its natural form as a solvent and only a small portion is processed into secondary products.

One of the promising directions of gum turpentine processing into secondary products is obtaining of pine oil, which is used as a flotation reagent for mineral processing in mining production.

Flotation is one of the methods of mineral processing. It is based on the difference in the physicochemical properties of fine solids (minerals), resulting in different surface wettability (preferably water) and varying abilities to adhere to the interface, usually liquid – gas.

Pine flotation oil is a mixture of terpene alcohols. In case of air blowing stable foam is formed, when minor quantities of oil are added into the slurry (a mixture of crushed ore with water). This is due to the oil main surfactant component – terpene alcohols – which create conditions for the selective extraction of minerals from the slurry. Pine oil advantages: the formed foam is bulky, small-bubble and degradable. Pine oil shows its effectiveness when potassium ores are enriched by sylvinitic flotation. Thus, the concentrate output is 26–28%, the amount of sylvinitic (KCl) being 78–82%.

Terpene alcohols have different applications. They have a pleasant flowery odour:  $\alpha$ -terpineol – the smell of lilacs,  $\beta$ -terpineol – the smell of hyacinth,  $\gamma$ -terpineol – the smell of roses. Consequently, they are widely used as flavoring agents for soaps and synthetic detergents.

Esters of terpineols and acetic acid, in the form of an isomeric mixture, are used for the preparation of perfume compositions and flavoring agents.

Annually more than 40,000 tons of terpineol are produced in the world. However, there is no production of terpene alcohols in the Republic of Belarus, though there is a rich source of raw materials for their production here.

The aim of the research is to study the dynamics and optimize  $\alpha$ -pinene hydration regime in the presence of organic acids with the highest possible yield of terpineol.

**Main part.** The objects of research are gum turpentine and  $\alpha$ -pinene – the main component of turpentine.

From the literature it is known that the most promising method of producing terpene alcohols is  $\alpha$ -pinene hydration in organic acids, such as formic. It is based on the ability of  $\alpha$ -pinene to add water to form monovalent alcohols [1].

Transformation mechanism of  $\alpha$ - and  $\beta$ -pinenes in terpene alcohols proceeds with the opening of the four-membered pinene ring in the presence of acids (Fig. 1). In the presence of a proton  $\alpha$ -pinene (or  $\beta$ -pinene) molecule forms a carbonium ion, which is isomerized followed by conversion of carbonium ions formed into unsaturated terpene hydrocarbons or unsaturated terpene alcohols [2].

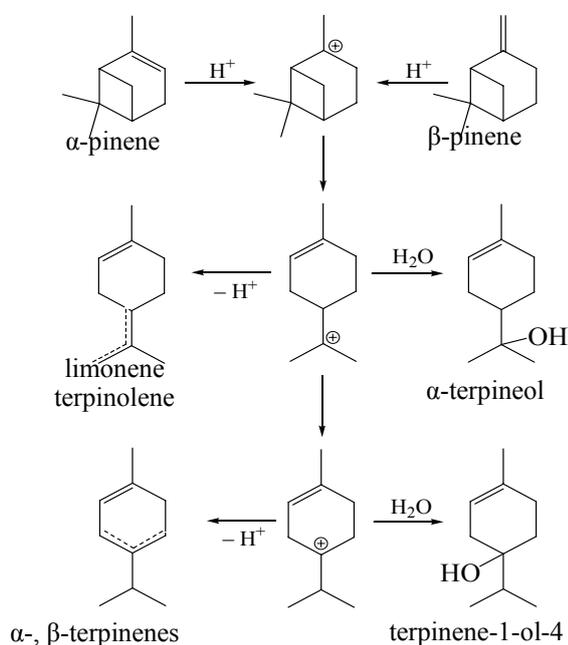
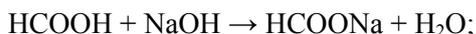
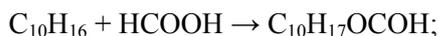


Fig. 1. Pinenes isomerization mechanism

In practice, the process of obtaining terpene alcohols by hydration comprises the following steps:  $\alpha$ -pinene hydration and esterification, neutralization of excess acid, terpenilformiate saponification, terpineol rectification, if there is a need. The following equations represent terpene alcohols preparation [3]:



Preliminary studies have shown that the best results of  $\alpha$ -pinene hydration are obtained using 70% formic acid. Therefore further hydration of turpentine and  $\alpha$ -pinene was carried out in the presence of 70% formic acid, their ratios being different.

The process of obtaining terpene alcohols was carried out in three stages.

**Stage 1.** 100 cm<sup>3</sup> of turpentine were placed in a three-necked flask equipped with a mechanical stirrer, a contact thermometer with temperature controller and an addition funnel. The flask contents were heated to 40°C, and the calculated amount of formic acid was dropped slowly from the addition funnel into the flask. A spontaneous increase in temperature up to 70°C was observed because the reaction is exothermic. After the reaction mass has reached constant temperature (65°C), one hour later it was sampled to monitor the hydration. Qualitative and quantitative analysis of selected samples was performed by gas-liquid chromatography.

The reaction mixture was being heated for 4–5 hours while maintaining constant temperature conditions at 65°C.

When the upper “oily” layer reached density of 0.890–0.900 g/cm<sup>3</sup>, the hydration reaction was considered to be complete.

**Stage 2.** The contents of the reaction flask were transferred to a separation funnel for settling out. The lower aqueous layer was poured out and the upper layer was neutralized with 17.5% concentrated aqueous sodium hydroxide and heated for 10–15 minutes. After neutralization the lower aqueous layer was poured out, and the upper “oily” layer was washed several times with distilled water until the wash water became neutral.

**Stage 3.** Following neutralization the resulting organic portion was saponified. Terpenilformiate contained therein was saponified with 40% sodium hydroxide aqueous solution. For this purpose, a certain amount of sodium hydroxide, calculated by chromatographic analysis, was added to the resulting organic mass and heated for 60 minutes at the mixture boiling temperature. On cooling, the mixture was poured into a separation funnel and washed several times with distilled water until neutral wash water.

Tables 1–3 show the results of turpentine hydration with various quantities of 70% formic acid.

Analyzing the data obtained, it can be noted that the main component of turpentine, which leads to the formation of  $\alpha$ -terpineol is  $\alpha$ -pinene, the content of which is reduced almost twice in an hour after hydration. After completing hydration,  $\alpha$ -pinene content in the reaction mixture was from 2.84 to 6.01%.

3-Carene concentration in the reaction mixture virtually unchanged throughout the process. This suggests that under these conditions there is no disclosure by acids of a 3-membered ring (with subsequent isomerization) in 3-carene, which could lead to the formation of terpene alcohols.

Regarding other terpene hydrocarbons (turpentine components) such as limonene and terpinolene,

their content in the reaction medium, although slightly, but increased with increasing duration of the hydration process.

5 hours later limonene content in the reaction mixture was increased to 10.22% and that of terpinolene to 15.24%. This suggests that in addition to  $\alpha$ -pinene hydration there occur secondary processes caused by acidic isomerization of terpene hydrocarbons.

Since the purpose of our research was to obtain terpene alcohols, we may note the following.

After 3 hours of synthesis  $\alpha$ -terpineol content in the reaction mixture increased and reached its maximum of 21.74% (Table 3). After 4 hours of synthesis  $\alpha$ -terpineol content was 21.40% (Table 2). Subsequently, the content of  $\alpha$ -terpineol was reduced in all experiments with the increase of the process time. It is associated with an increased rate of secondary isomerization processes in the presence of  $\alpha$ -terpineol.

As mentioned above, along with the formation of terpene alcohols, esterification reaction may proceed in the reaction mixture leading to ester formation (terpenilformiate) which, after subsequent alkaline saponification, results in the formation of terpene alcohols. This increases terpeneol yield. According to chromatographic analysis, maximum terpenilformiate content (5.60%) was observed after 3 h of heating the reaction mixture, after which its content decreased. Thus it is possible to obtain the maximum yield of terpeneol after 3 h of heating the reaction mixture at a temperature of 65°C at a ratio of  $\alpha$ -pinene (turpentine) and 70% formic acid 1.0 : 1.3.

Turpentine hydration process is conducted under similar conditions in the presence of 70% acetic acid. Studies have shown that this reaction doesn't virtually proceed in this acid. Only 2.5% of terpene alcohols were detected in the reaction mixture after 3 hours of hydration.

Table 1

**Composition of the reaction mixture at a ratio of  $\alpha$ -pinene (turpentine) and 70% formic acid 1.0 : 0.9**

Component name	Process time, h					Isomerizate composition after saponification
	0	1	2	3	4	
	Content, %					
$\alpha$ -Pinene	59.86	28.80	18.60	13.21	12.34	11.84
3-Carene	27.06	27.32	30.35	28.40	28.02	28.72
Limonene	4.40	5.32	17.21	9.20	8.39	8.39
Terpinolene	2.23	7.90	11.22	12.22	12.00	12.21
$\alpha$ -Terpineol	–	12.70	13.43	18.53	18.15	23.60
Terpenilformiate	–	4.90	3.64	4.53	4.05	–

Table 2

**Composition of the reaction mixture at a ratio of  $\alpha$ -pinene (turpentine) and 70% formic acid 1.0 : 1.0**

Component name	Process time, h						Isomerizate composition after saponification
	0	1	2	3	4	5	
	Content, %						
$\alpha$ -Pinene	59.86	36.61	21.35	11.86	10.09	6.01	10.65
3-Carene	27.06	30.44	32.03	31.63	29.97	31.27	27.99
Limonene	4.40	6.45	7.52	9.22	7.53	9.22	8.76
Terpinolene	2.23	5.17	7.93	8.73	10.19	13.70	12.89
$\alpha$ -Terpineol	–	10.01	14.72	18.00	21.40	13.12	19.5
Terpenilformiate	–	2.57	4.06	5.90	4.50	3.59	–

Table 3

**Composition of the reaction mixture at a ratio of  $\alpha$ -pinene (turpentine) and 70% formic acid 1.0 : 1.3**

Component name	Process time, h						Isomerizate composition after saponification
	0	1	2	3	4	5	
	Content, %						
$\alpha$ -Pinene	59.86	32.60	20.32	5.82	6.41	2.84	2.27
3-Carene	27.06	29.34	30.39	30.45	29.58	31.94	30.86
Limonene	4.40	6.50	7.18	8.52	10.47	10.22	8.46
Terpinolene	2.23	7.79	2.67	11.21	14.82	15.24	15.83
$\alpha$ -Terpineol	–	8.44	19.54	21.74	16.72	13.62	22.14
Terpenilformiate	–	5.73	6.60	5.60	3.44	4.16	–

Besides,  $\alpha$ -pinene hydration process has been studied in the presence of 70% formic acid under the same conditions. Chromatographic analysis of the data showed that the maximum content of the resulting terpene alcohols (53.13%) was observed after 3 hours synthesis at the ratio of  $\alpha$ -pinene and 70% formic acid 1.0 : 1.1 (Fig. 2).

After saponification, the reaction mixture gave a product containing 60.1% of terpene alcohols. Longer hydration reduces terpineol content in the isomerisation mixture.

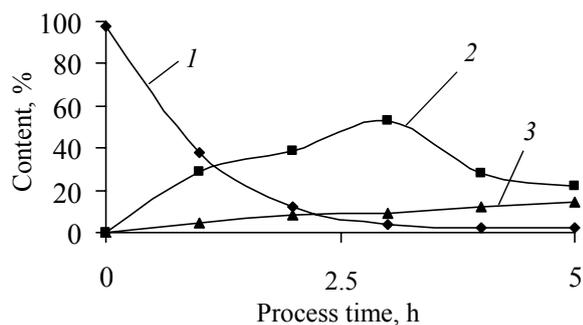


Fig. 2. Dynamics of  $\alpha$ -terpineol accumulation:  
1 –  $\alpha$ -pinene; 2 –  $\alpha$ -terpineol; 3 – limonene

It should be noted that after 48 hours,  $\alpha$ -terpineol crystals precipitated in isomerizate containing after saponification 60.1% of terpene alcohols. This is due to the fact that terpene alcohols ( $\alpha$ -,  $\beta$ -,  $\gamma$ -terpineols) are crystalline materials. They are readily soluble in terpene hydrocar-

bons. If their concentration is high enough, they may form a saturated solution in terpene hydrocarbons from which subsequently  $\alpha$ -terpineol needles can grow.

**Conclusion.** The  $\alpha$ -pinene hydration of gum turpentine and separately of its pinene fraction in organic acids media have been studied. It is found that the maximum yield of terpene alcohols is reached in 70% formic acid during 3 hours at 65°C and amounts to 27.4% (in case of turpentine hydration) and to 60.1% (in case of  $\alpha$ -pinene fraction). Further increase in the duration of the process leads to a decrease in terpene alcohols yield and increases the by-products yield. The optimal ratio of reactants in the hydration of gum turpentine  $\alpha$ -pinene and separately its  $\alpha$ -pinene fraction to 70% formic acid is 1.0 : 1.3 and 1.0 : 1.1, respectively.

For the manufacture of commercial flotation oil, the main component of which are terpene alcohols, the hydration product of gum turpentine containing terpene alcohols and a considerable amount of unreacted and isomerized terpenes, must be subjected to rectification. To reduce the risk of occurrence of undesired side reactions, rectification should be carried out under vacuum. While carrying out hydration of  $\alpha$ -pinene fraction in order to obtain terpene alcohols as flotation reagents, it is not necessarily to subject the hydration product to distillation rectification as terpineol content in the final product corresponds to requirements for flotation oil.

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