

Refining of Crude Sulfate Turpentine Obtained from a Kraft Pulp Mill: A Pilot Scale Treatment

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Crude sulfate turpentine (CST), a by-product of the kraft process, has commercial value that depends on the removal of sulfur compounds. The current study investigates desulfurization of CST using basic process steps for a paper mill at a pilot scale treatment. In another aspect, the sulfurous compounds in CST were removed by passing to the aqueous phase with terpin hydrate production, followed by α -terpineol conversion with citric acid catalysis. The goal was to design an environmentally friendly, low-cost, zero waste process and thereby refine the CST or byproducts to a quality that can produce chemical raw materials. Refining processes included hypochlorite oxidation, air oxidation, washing with water, and distillation. The sulfur content was decreased to 170, 106, and 29 ppm from respectively by 1260 ppm initial sulphur content of CST. The chlorine amount, due to treatment with hypochlorite oxidation, did not decrease with refining processes, even in distilled fraction. By obtaining α -terpineol from terpin hydrate, the sulfur compounds were completely removed. According to the GS-MS analysis results, distilled sulfate turpentine (DST) as the final product of the refining process of the CST sample increased the ratio with pinenes. On the other hand, with two reaction steps by obtaining terpin hydrate from CST and then α -terpineol, pinenes were converted to α -terpineol.

Keywords: Sulfate turpentine; Sulfur removal; CST refining; Terpin hydrate; α -terpineol

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INTRODUCTION

During kraft processing, the lignocellulosic structure is digested, and crude sulfate turpentine is obtained as a by-product of delignification. In addition to carbon dioxide (CO₂), sulfur dioxide (SO₂), and nitrogen oxides (NO_x) as primary emissions to air during pulp production, small amounts of total reduced sulfur (TRS) are released. These malodorous compounds and primary emissions need to be eliminated immediately due to the risk of environmental pollution. While several studies have examined the composition of reaction products, others have focused on certain products for their odor properties (Valkanias and Iconomou 1963; Williams and Whittaker 1971). The toxic sulfur compounds (dimethyl sulfide, dimethyl disulfide, dimethyl sulfoxide, hydrogen sulfide, methyl mercaptan) are consequences of the reaction of wood components and chemical substances such as NaOH and Na₂S, known as components of white liquor (Drew and Pylant Jr. 1966; Cheremisnoff and Rosenfeld 2010; Ilichev *et al.* 2014). Effective control of the treatment and combustion process will reduce sulfurous emissions released into the atmosphere.

Crude sulfate turpentine (CST) and its distilled fractions usually contain high concentrations (5000 ppm and above) of sulfur compounds (Jennings 1939; Lloyd and

Bruce 1994; Leonardos *et al.* 1969; Ilichev *et al.* 2014; Rehman *et al.* 2016). These compounds are transported to the distillate fraction of turpentine and adversely affect the reactions of fractions (Hamby *et al.* 1972). Besides, these sulfur compounds, which affect the catalysts, can hurt the yield of the final product, the quality, and industrial convenience of the components (Ilichev *et al.* 2014; Izmet'ev *et al.* 2019). The reaction of the sulfurous components are deleterious to rather than 'fraction of the turpentine include' α -pinene, β -pinene, phellandrene, myrcene, camphene, carene, limonene, *etc.* Moreover, they can poison catalysts and affect yields of resultant products as chemical raw material (Hamby *et al.* 1972; Izmet'ev *et al.* 2019). For turpentine to have commercial value, these sulfurous compounds, typically known as organic sulfides and mercaptans, should be reduced or removed from CST before they enter the contents of the ingredients such as perfume, fragrance formulations (Koppenhoefer *et al.* 1994), cleaning products, chemical raw material, polymer production, cosmetic products (Buisman and Lange 2016; Izmet'ev *et al.* 2019; Sinhmar and Gogate 2020), or blends with biodiesel production (Dubey and Gupta 2018; Aguas *et al.* 2020; Ballesteros *et al.* 2020). Among the advantages of the processes to be developed in this study, it is aimed to desulfurize CST and distillate fractions in practical, economical, and environmentally friendly ways by chlorinating organic components in tolerable ratios.

The odor problems arising from manufacturing operations of kraft processing, the odor thresholds of the sulfurous odorant chemicals (Leonardos *et al.* 1969), and final sulphur content (Collins and Brunswick 1946; Prochazka and Foy 1958; Lloyd and Bruce 1994; Hwang *et al.* 1994; Wang *et al.* 2011; Tyurmina *et al.* 2017; Sinhmar and Gogate 2020) are of vital importance (Rehman *et al.* 2016). They need to be controlled to represent the effect of chemical purity represented in Table 1. The limitation of 'S' compounds is desired to reduce the sulfur concentration preferably less than 5 ppm with ultra-deep desulfurization (Sinhmar and Gogate 2020) for fragrance, flavor, varnishes, *etc.*, and for final products acceptability. An application level of 10 ppm has been judged to be acceptable in the manufacture of flotation oil disinfectants and detergents. Since the aim of the study was to separate the sulfur components from the CST in the simplest and most economical way possible, a sulfur content of 10 ppm was targeted as 'Maximum Acceptable Concentrations' in Table 1.

Table 1. Possible Contaminant of Sulfide Compounds that Need to be Removed

'S' Compounds	Boiling Point (°C)	Odor Threshold in Air (ppm)	Maximum Acceptable Concentrations (ppm)
Hydrogen sulfide (H ₂ S)	-61.8	0.0040	10
Methyl mercaptan (MeSH)	5.8	0.0021	10
Dimethyl sulfide (Me ₂ S)	38	0.0010	-
Dimethyl disulfide (MeSSMe)	118	-	-

Hydrodesulfurization (a general term used for refined petroleum products) is defined as a catalytic chemical process commonly used to remove sulfur compounds from organic substances. A typical hydrodesulfurization reaction occurs in a fixed bed reactor at absolute pressures of 30 to 130 atmospheres, temperatures ranging from 300 to 400 °C, generally in the presence of catalysts. Hydrodesulphurization with various catalysts such as cobalt molybdenum (CoMo) for removal of heteroatoms including S, O, and N has been

adapted for the terpenic hydrocarbon process (Topsøe *et al.* 1996; Knuutila 2013; Kazakov *et al.* 2020; Wiecka *et al.* 2020). The dehydrogenation process could be used for removing sulfur compounds to avoid the additional treatment of sulfate turpentine in the case of achieving selective formation of cymene (Linnekoski *et al.* 2014). CST was desulfurized by processing with an aqueous sodium hypochlorite solution stabilized with varying sodium hydroxide ratio (Ghinet and Orza 1967; Foran 1995). With the desulfurization process, the solution pH reaches the range of 11 to 12, and desulfurization resulted in significant chlorination of unsaturated organic compounds. Effective sulfurization can be achieved by factors such as the temperature of the dispersion, efficiency of the agitator type, velocity, *etc.* In some trials, NaClO, CST, and NaOH solution with nonylphenol compounds that are precursors to the commercially important non-ionic surfactants were added to make the dispersion more effective and increase the efficiency.

Organic sulfur compounds can act as hydrogen acceptors and receive hydrogenolysis, disproportionation and reduction, as shown in Eqs. 1 through 3 (Linnekoski *et al.* 2014).



Turpentine is a mixture of unsaturated, bicyclic terpene hydrocarbons, monoterpene hydrocarbons, and also contains monocyclic dipentene (Gscheidmeier and Fleig 1996; Anonymous 2002). The varying percentage of these components mainly depends on the treatment process and the origin of the tree (Drew and Pylant Jr. 1966). There are even differences in chemical composition between sulfate turpentines produced in summer and winter seasons (Miller 1970; Ucar *et al.* 2000).

A method has been developed to describe the practical maximum efficiency of desulfurization with an aqueous solution of the alkaline earth divalent ions as Na, K, Ca, Mg. The sequential process before distillation during the recovery of the distillate components results in increased economy and less environmental pollution compared with the previously proposed cleaning processes for CST and its distillate fractions (Vital *et al.* 1992; Pakdel *et al.* 2001). In addition, the purification of crude sulfate turpentine, terpin hydrate and α -terpineol were obtained. In contrast, the common approach for synthesis of α -terpineol from CST (Pakdel *et al.* 2001) was employed. Thus, α -terpineol transition was made from terpin hydrate in this study. In addition, with the refining process, high purity sulfate turpentine and its derivatives were obtained with high efficiency and low energy consumption. Besides, high-efficiency α -terpineol was obtained by hydration reaction with the help of acid catalysts. In the second stage, terpin hydrate production from CST was carried out in a simple reaction step on acid catalyst. Thus, the sulfide compounds remained in the aqueous phase and an additional by-product terpin hydrate was obtained. Then, α -terpineol was synthesized from terpin hydrate. Thus, the disadvantages of producing α -terpineol directly from CST were eliminated and α -terpineol from CST without refining process were compared. Sulfurous compounds remained in the aqueous phase during terpin hydrate production, and it was aimed to increase the efficiency of the conversion of α -terpineol. Thus, the sulfur content is completely removed, and two different valuable by-products were obtained. Among the advantages of the processes to be developed in this study, it is aimed to desulfurize CST and distillate fractions in practical, economical, and environmentally friendly ways by chlorinating organic components in tolerable ratios.

Crude rosin contains monohydrate remaining after the separation of terpene hydrocarbons and alcohols by distillation, which can be separated from the medium by steam distillation. Monohydrate is most easily obtained artificially by the reaction of dilute H_2SO_4 with α -pinene. During acid hydration of sulfur compounds, malodor is eliminated by passing into aqueous form.

Terpin hydrate is easily converted into the α -terpineol by partial dehydration (Sell 2006; Surburg and Panten 2016). Terpin hydrate and α -terpineol, which are obtained as a result of hydration of α -pinene that is present in the turpentine after the refining of sulfate turpentine, are the most demanded turpentine derivatives (Ávila *et al.* 2010; Prakoso *et al.* 2020). Crude sulfate turpentine refiners primarily separate the purified turpentine into its main components, α - and β -pinene (Packer *et al.* 1998; Pakdel *et al.* 2001; Naoum *et al.* 2019). Subsequently, α -pinene can be converted into α -terpineol by hydrating under various conditions (Santos and Morgado, 2005) or from crude sulfate turpentine to α -terpineol (Pakdel *et al.* 2001), α -terpineol is produced in the presence of various catalysts, and the α -terpineol obtained after the purification process is compared in terms of sulfur content (Pakdel *et al.* 2001). α -Terpineol conversion is called sweetening and shows similarities with the refining process of CST with terpin hydrate extraction; a product may obtain directly from crude sulfate turpentine without the need for refining (Pakdel *et al.* 2001).

In the current study, desulfurization stages of CST, a by-product of kraft mill, with an economical and efficient method were investigated. Terpin hydrate production from CST and α -terpineol from terpin hydrate, and sulfur components that could be completely eliminated with that method, were also examined in this respect. Thus, in addition to the removal of sulfur, α -terpineol and terpin hydrate products can be obtained in the kraft mill.

EXPERIMENTAL

Materials

Crude sulfate turpentine (CST) samples were obtained from OYKA paper mill in Turkey. Commercial sodium hypochlorite with an active pH was 12 and additionally, sodium hydroxide, H_2SO_4 , citric acid, nonylphenols (NP-10) were selected in the experiments. Sodium hypochlorite is preferred as an economical reagent for oxidation process.

Method

Crude sulfate turpentine was kept in a 5-ton stock tank, and the basic analyses were performed according to ASTM D889-13 (2017) and ASTM D233-13(2017). The sequential stage of sulfur removal from CST is shown in Fig. 1. As a following stage, the distillation process was operated with a pilot extractor. Samples from each of the four stages of refining CST and α -terpineol sulfur and chlorine content were analyzed by High Definition Energy Dispersive X-Ray Fluorescence (HDXRF). The test was conducted directly without any further preparation. GC-MS analyzes of CST, DST (Distilled Sulphate Turpentine), and α -terpineol were conducted at central laboratory at Istanbul University-Cerrahpasa. Analyses were carried out by capillary column. The temperature program was 2.00 min at 80 °C, 10 °C/min to 240 °C, 20 °C/min to 280 °C, and 10.0 min at 280 °C. The column flow was 1.1 mL/min.

Oxidation Process with Hypochlorite

Sodium hypochlorite solution with 15% chlorine content and 10% NaOH was prepared in the pH range 12 to 13. The hypochlorite solution and crude sulfate turpentine were mixed in a 1:1 to 1:0.5 v/v ratio, and 0.1 to 0.2% nonylphenol was added the dispersion with a vigorous mechanical agitator at 30 °C. NP-10 was used as an emulsifier and allowed the emulsion to be broken, with separation of the aqueous phases in 4 h time.

With the oxidation process with sodium hypochlorite, the impurities of the sulfurous organic compounds, which are responsible for the malodor and coloration besides causing corrosion of equipment's and pipeline in the final product of CST (Sinhmar and Gogate 2020), were converted to a water-soluble form. At the end of the period, the dispersed mixture was taken from the container and kept in a separation funnel until the two phases were separated entirely. NP-10 remained in the chlorine phase with aqueous residue. After removing the aqueous phase, the upper phase was washed several times by rinsing with warm distilled water until the pH was neutral and the impurities were removed.

Air Oxidation

The sample was modified by air oxidation by passing oxygen for 3 to 4 h with an air oxidation stage, and the sulfur and chlorine content was controlled by High-Definition X-Ray Fluorescence (HDXRF; XOS, New York, USA).

Distillation

The distillation process aimed to completely remove residual sulfur and chlorine. The deodorized turpentine at an early stage was distilled in a pilot extractor (Fig. 2). Various impurities were separated from the refined product, which was initially heated to 130 °C until distillate and water stream ended completely. The remained sample was heated up to 180 °C with a controlled elevated temperature system. The distilled sample was collected in a 5-ton stock tank and labelled DST (Distillated Sulphate Turpentine).

Terpin Hydrate Production

25% H₂SO₄ solution and CST were mixed in a 4:1 w/w ratio, then 0.1% NP-10 was added the dispersion at the acid-proof vigorous mechanical agitator at a constant temperature of 30 °C. NP 10 was selected as an emulsifier to provide turpentine emulsion in H₂SO₄ apart from previous studies acetone, toluene sulfonic acid used as emulators. Hence, during acid hydration of sulfur compounds, malodor is eliminated by passing into aqueous form easily.

The reaction was ended after 25 hours at constant temperature. The crystals were separated from the aqueous phase by centrifugation. The filtered crystals were washed in 10% sodium carbonate solution, the acidic parts were removed and neutralized, and then the sample was dried and weighed.

α-Terpineol Production

α-Terpineol was obtained in the presence of citric acid catalyts. A citric acid solution with a pH of 2.8 was prepared 20% aqueous solution and 2:1 w/w ratio terpin-hydrate was added. The mixture heated and stirred at 15 hours in a reflux at atmospheric pressure in the pilot extractor (Fig. 2).

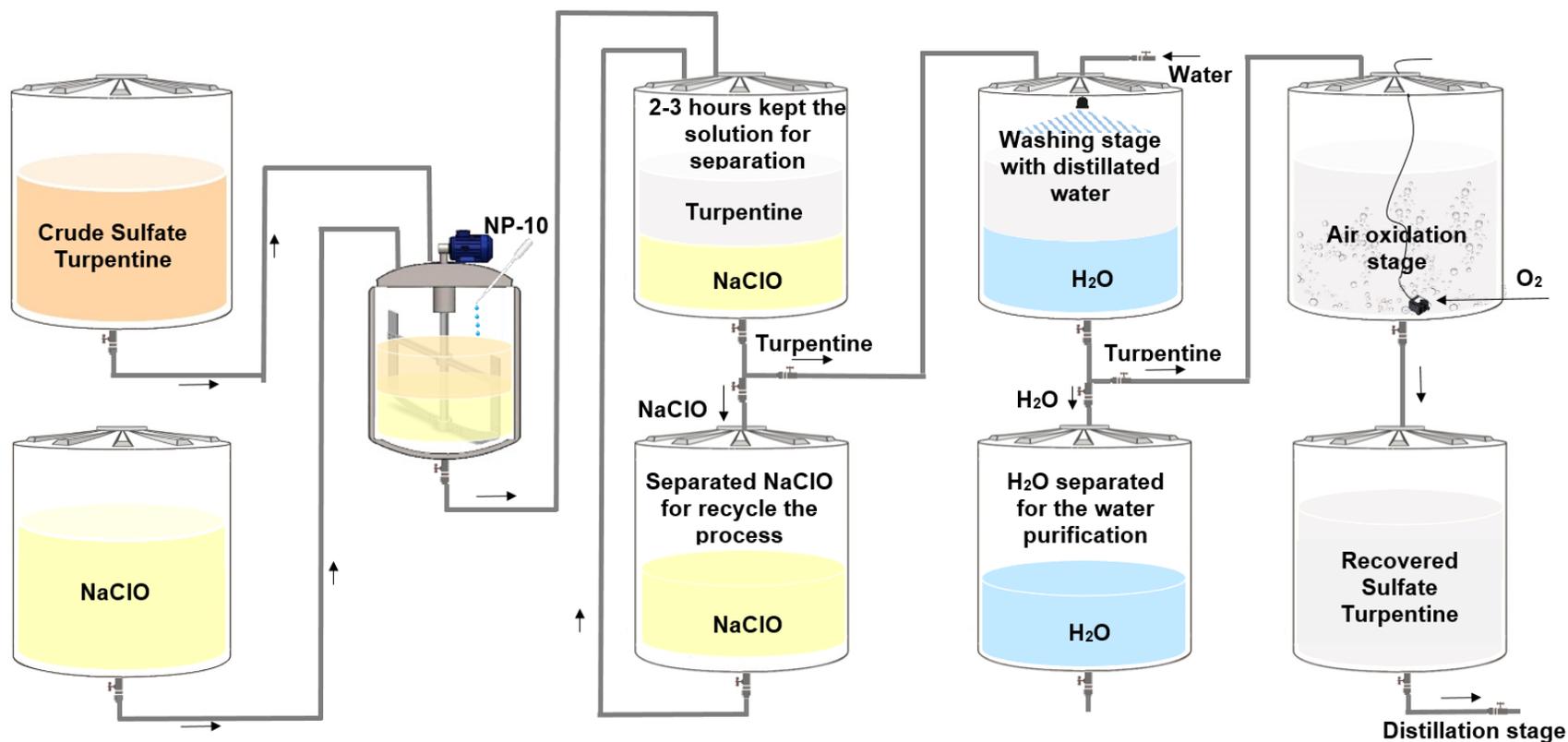


Fig. 1. Sulphur removing stages from CST

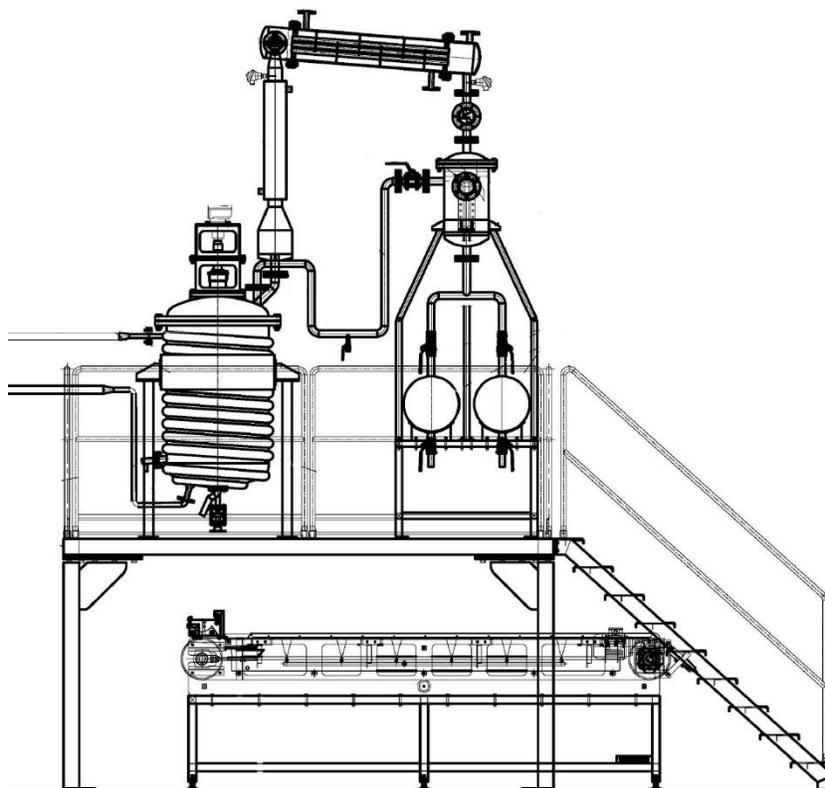


Fig. 2. Pilot extractor for distillation process of turpentine and α -terpineol production

Samples from each of the four stages of refining CST and α -terpineol sulfur and chlorine content were analyzed by High Definition Energy Dispersive X-Ray Fluorescence (HDXRF).

RESULTS AND DISCUSSION

Sulfur and Chlorine Content

The sulfur and chlorine content were determined by HDXRF, as shown in Table 2, which refers to sulphur contents after treatments. Compared to the CST, the sulphur content of the chlorinated CST was reduced from 1260 to 170 ppm. Washing with water reduced the sulphur amount by 110 ppm, and air oxidation was reduced 110 ppm. The distillation process reduced the sulphur content by 29 ppm. The α -terpineol product had no sulphur content.

Table 2. Sulfur and Chlorine Content of Each Stage of Samples

Material	CST	Chlorinated CST	Water Wash	Air Oxidation	Distillation
Sulfur (ppm)	1260	170	110	106	29
Chlorine (ppm)	-	4839	2905	2165	121

Various studies on removal of sulfur compounds such as dimethyl disulfide, dimethyl disulfide, methyl mercaptan, *etc.* found in the CST were compared to the results of the current study. Hydrodesulphurization based on cobalt molybdenum catalyst reduced initial sulphur content from 501 ppm to 55 ppm (Lloyd and Bruce 1994). H₂O₂ oxidation and rectification process reduced the sulphur content from 20,000 ppm to 3000 ppm and 70 ppm respectively (Tyurmina *et al.* 2017). Various refining steps of CST as batch distillation, N₂ stripping, sodium hypochlorite treatment, and water wash, respectively, reduced the sulphur content of final products to 1147 ppm, 552 ppm, 26 ppm, and less than 10 ppm (Hamby *et al.* 1972). Peracetic acid oxidation process and activated carbon adsorption treatment reduced sulphur content from 38.5 ppm to less than 5 ppm (Sinhmar and Gogate 2020). Quantitative comparison is based on the degree of desulfurization, as the concentration of oxidant (chlorine in current study) and sulfur initiated from the CST used in this process cannot be compared directly all previous studies. However, there is a similarity in the literature that multiple oxidation steps are more effective than a single step oxidation for removing sulfur compounds. Air oxidation led to a decrease of 500 ppm in chlorine content without significant change in sulfur removal.

Chemical Content of CST and α -Terpineol with GC-MS

The composition of the CST is shown in Table 3. Methyl mercaptan, allyl methyl sulfide, dimethyl disulfide, and dimethyl trisulfide were not detected in GC-MS analysis because of low boiling points of the sulphur components. The composition of CST was similar to the literature, but the amount of pinenes in CST was 70% quantity and final products of refining process DST was 80% (Table 3). The regional location of the kraft mill, the source of pine species, and the supply season of CST may have the reason for the compositional variance.

Table 3. GC-MS Results of CST and DST

Retention Time (min)	Quantity (%)		Library/ID
	CST	DST	
3.28	69.93	78.39	α -pinene
3.86	6.89	6.36	β -pinene
4.22	3.38	3.35	Delta 3-carene
4.49	2.40	3.42	D-limonene
5.30	2.22	0.36	α -terpinolene
5.84	0.33	0.59	D-Fenchyl alcohol
6.20	0.33	0.80	Isopinocarveol
6.64	0.74	0.51	Borneol
6.73	0.51	0.10	1-4-Terpineol
6.95	2.47	1.25	α -terpineol
10.01	4.54	1.12	α -Murolene
10.91	1.44	0.21	α -Cubebene

Compounds of α -terpineol fractions are given in Table 4 based on GC-MS analysis. The α -pinene was converted to the terpin hydrate crystal, then α -terpineol was produced. The amount of α -pinene in CST (Table 3) was 63.93% initially, and pinenes were transformed to α -terpineol. The main products in the α -terpineol, as well as residual monocyclic monoterpenes, remained (Table 4).

Table 4. GC-MS Results of the Experiment of α -Terpineol Conversion from Terpin Hydrate

Retention Time (min)	Quantity (%)	Library/ID
3.50	3.80	α -Fenchene
4.22	1.99	Delta 3-Carene
4.31	3.34	Isocineole
4.54	2.51	D-Limonene
4.76	0.22	β -Phellandrene
4.90	17.19	Γ -terpineol
5.35	51.45	α -Terpinolene
5.84	1.01	D-Fenchyl alcohol
6.11	8.55	Terpinene-1-ol
6.29	2.09	β -terpineol
6.56	11.13	Isobornyl acetate
6.79	0.42	1-4-Terpineol
7.01	4.39	β -Fenchyl alcohol
8.68	0.07	Terpin Hydrate
10.79	0.11	Γ -Cadinene

Terpineol formation 16 h after hydration was investigated by GC/MS analyzes (Table 4). The α -pinene and β -pinene were all transformed to α -terpineol. A significant amount of α -terpineol, which was found in small amounts in turpentine, was formed as a result of the hydration reaction of α -terpineol.

CONCLUSIONS

1. Results related to refining of crude sulfate turpentine (CST) products were obtained with various process steps from a pilot extractor operation. The refining stages of the CST product were compared with the derivatives products concerning sulphur content. In all cases the greatest increase was achieved by a chlorination process. However, even at constant levels of chlorination, the chlorine content of the product was affected. Even after distillation of the last stage of the process, traces of sulfur and chlorine remained in the product.
2. The purification of sulfate turpentine and the recovery of sulfurous compounds were achieved. This contributed to the closure of the process cycle deficit by producing a sulfate turpentine product. Such a product currently is not industrially produced in Turkey. Progress also was achieved in the direction of zero waste, as well as the avoidance of environmental pollution and malodorous compounds (total reduced sulfur, TRS) obtained as by products.
3. The conversion of terpene as α -terpineol was investigated. The main purpose of the study at this stage is to optimize the reaction efficiency by developing an efficient hydration reaction with a short reaction time for the production of α -terpineol from CST.

- Besides, terpin hydrate production also can be considered as an alternative to refining process. Thus, while the amount of sulfur was reduced by α -terpineol conversion, an alternative byproduct was obtained at the same time. Consequently, a kraft mill could remove the amount of sulfur by obtaining alternative byproducts.

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