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8 ___ INDUSTRIAL CHEMICAL ENGINEERING [ICE] KSIDEJ A.

[Type your address] ? [Type your phone number] ? [Type your e - mail address] Synthesis of !-Terpineol from Turpentine by Hydration in a Batch Reactor Herti Utami*1,2 , Arief Budiman 2, Sutijan 2, Roto 3, Wahyudi Budi Sediawan 2 1Ph.D student in Chemical Engineering Department, Gadjah Mada University, Yogyakarta, Indonesia 1Chemical Engineering Department, Lampung University, Bandar Lampung, Indonesia 2Chemical Engineering Department, Gadjah Mada University, Yogyakarta, Indonesia 3Chemistry Department, Gadjah Mada University, Yogyakarta, Indonesia Tel: +6285868476390 Email address: hertie19@hotmail.com Abstract Turpentine is natural essential oil obtained by distillation of the raw oleoresin collected from pine trees, in which !-pinene is the main component of most turpentine oils. Turpentine from Indonesia contains 65-85 % !-pinene , 1% camphene, 1-3% "-pinene, 10-18 % 3-carene and limonene 1-3%.

When treated with water in the presence of acid catalyst, !-pinene is hydrated to !-terpineol which can be used as perfume, repellent of insect, antifungal and disinfectant. This work presents the result of !-terpineol synthesis by hydration of turpentine. The study investigates that the effect of catalyst (sulfuric acid, chloro acetic acid), temperature (60, 70, 80, 90 oC), the mol ratio of chloro acetic acid to !-pinene (0.8/1; 1.6/1; 2.4/1; 3.2/1; 4/1), and stirring rate (264, 546, 954 rpm).

It suggested that the best condition for the hydration of turpentine was achieved at temperature of 80 oC, reaction time of 240 min, mol ratio of chloro acetic acid catalyst to !-pinene of 2.4/1 and the stirring rate of 546 rpm. The conversion of hydration of turpentine to !-terpineol was obtained to be 54.13%. Keyword: Turpentine, !-Pinene, Hydration, !-Terpineol Introduction Turpentine is the volatile portion of the oleoresinous material contained in conifers.

Trees of the genus Pinus are the source of nearly all turpentines produced on a large scale. Industrially turpentine is classified into four types which are gum, steam-distilled wood, sulfated wood, and destructively distilled wood. Gum turpentine is obtained by distillation of the oleoresin (called gum) from wounds or scars from living pine trees [11].

The chemical composition of turpentine depends on a variety of factors such as method of isolation, the species of tree from which it is obtained, geographical location of the tree and in the case of wood turpentine, age of the dead wood and type of the tree fragment processes. In general, turpentine contains four major classes of components which are hydrocarbon, terpene alcohols, ethers, and sesquiterpenes [11].

!-Pinene (C10 H16) is the main component of most turpentine oils. Turpentine from Indonesia contains 65-85 % !-pinene, 1% camphene, 1-3% "-pinene, 10-18 % 3-carene and limonene 1-3% [5]. !-Pinene and "-pinene are the key compounds for the fine chemical synthesis and the important intermediates in pharmaceutical industry and perfumery [4].

The acid-catalyzed hydration and isomerization of !- pinene yields a complex mixture of monoterpenes, alcohols, and hydrocarbons. The main products are !-terpineol, limonene, and terpinolene . Minor amounts of camphene, ! and #-terpinene, ! and "-fenchol, isoborneol, borneol, #-terpineol, and 1,8-terpine are also formed [7].

!-Terpineol (C 10 H18 O) is the most important of the monocyclic monoterpene alcohols. Terpineol can be used as perfume, repellent of insect, antifungal and disinfectant [1]. The hydration of terpene via acid catalysis is an important method for alcohol synthesis, and has several applications in the perfume and pharmaceutical industries.

!-Terpineol, 4- terpineol and terpineol hydrate are, from commercial viewpoints, the most interesting derivative of !-pinene. !-Terpineol exhibits antimicrobial activity and is used for wound healing and insect bites [3]. The synthesis of alcohols from !-pinene in the presence of different catalyst has been well studied.

Hydration of pure !-pinene using acid zeolites as catalyst, aqueous solutions of acetone and dilute acid solutions has been studied by several workers [1,9,10]. Vital et al. (2001) investigated the hydration of !-pinene over the catalyst of polydimethylsiloxane (PDMS) membranes loaded with USY zeolite. The main reaction product is !-terpineol, while being simultaneously formed are a number of minor products, mainly terpenic hydrocarbon [10].

The hydration/isomerization of !-pinene at 56 oC catalyzed by zeolite H-beta is fast and leads mainly to monocyclic terpenes and alcohols with !-terpineol as the main product (up to 48%). The selectivity toward the commercially interesting bicyclic products (such as borneol and camphene) is about 26%, which is significantly better than that observed when 2SO 4 is used as catalyst.

The reaction rate increases with increasing Si/Al ratio, which is possibly due to the increase of hydrophobicity of the zeolite; the selectivities are, however, not significantly affected [9]. Avila et al. (2010) reported the use of solid acid catalyst. The catalyst was prepared by impregnating trichloroacetic acid (TCA) on different supports such as silica, titania and zirconia (TCA/SiO 2, TCA/TiO 2, and TCA/ZrO 2.nH 2O, respectively). The TCA/TiO 2 catalyst converted !-pinene into hydrocarbon, while the TCA/ZrO 2.nH 2O catalyst was active and selective for producing alcohols, with a conversion of 57% and a selectivity of 75% of total alcohols, and showed 57% selectivity for -terpineol. The TCA/SiO 2 sample did not show catalytic activity due to the elimination of the trichloroacetic acid during the preparation step of the catalyst [3].

Arias et al. (2000) reported the hydration of turpentine oil using dealuminated faujasite as catalyst. The main product was the monocyclic alcohol, !-terpineol (44%) while the non alcoholic isomerization co- product was only 24% [2]. Aguirre et al. (2005) used hydrochloride acid, acetate acid, chloro acetic acid and oxalic acid as catalyst for the hydration of !-pinene.

Choro acetic acid was found as good catalyst for the production of terpineol from pinene.The highest selectivity was 95.5% with the conversion of 10%, whereas the higher conversion was 99% with selectivity of 69%, after 4 h of reaction at 70 oC [1]. Pakdel et al. (2001) used sulphate acid as catalyst to synthesize terpineol from turpentine, in the presence of excess acetone as solubility promoter.

They reported 67% of selectivity to terpineol although the conversion was not reported [8]. However the use of natural essential oils such as turpentine is rare. In this work, the !- terpineol synthesis directly from turpentine is presented. The choice for !-terpineol synthesis directly from turpentine oil is to by-pass the previous distillation stage of turpentine.

Material Turpentine was purchased from PT. Perhutani, Semarang, Indonesia (the content of !-pinene is 67.47 % (w/w)). Sulfuric acid (98% (w/w) purity) and chloro acetic acid were supplied by Merck. Experiments were conducted using the following apparatus : the batch reactor (three neck flask), condenser, thermometer, heating mantle, vials, pippetes and other glass wares. Experimental A 0.25 mol of !-pinene (turpentine) sample was poured into a three neck flask (pyrex 500 ml) equipped with condenser (pyrex), thermometer, stirrer and was warmed up to the desired temperature. In the other glasses, 0.6 mol of aquadest (the mol ratio aquadest to !-pinene : 2.4/1) and the catalyst (the catalyst concentration : 6 mol/L) were warmed up to the desired temperature.

Once the desired temperature was reached, the aquadest and the catalyst was loaded into the flask. The mixture was stirred and the reaction time was started to be calculated. The temperature was kept constant during the process. A sample was taken at every 60 min time interval during the hydration and was kept in a small vial. Then, the samples were analyzed using a Gas Chromatograph (GC).

The analysis was performed in a Hewlett-Packard model 5890 gas chromatograph. The separation was performed using HP-5 capillary column and Flame Ionization Detector with helium as a carrier gas. The GC oven temperature was set at initial temperature of 80oC, held for 5 minutes, increased at a rate of 5oC/min to 115 oC and then increased to 280 oC at a rate of 20 oC/min. The injector and detector temperatures were set at 280 oC respectively.

Results and Discussion Effect of Catalyst In this research two catalysts were used; sulfuric acid and chloro acetic acid. The relation between conversion and reaction time for each catalyst are shown in Fig. 1. The influence of catalyst was examined at mol ratio of chloro acetic acid catalyst to !-pinene of 2.4/1 and the reaction temperature of 80 oC.

For the sulfuric acid, the range of conversion is 4.5%-7.3%. The highest conversion is obtained 7.3%. These values were obtained with the reaction time of 420 min. For the chloro acetic acid, the range of conversion is 33.07% - 54.13%. The highest conversion is 54 .13%. These values were obtained with the reaction time of 240 min and the reaction was almost at equilibrium. Fig.

1: Effect of catalyst on conversion of !- pinene to !-terpineol In this study, chloro acetic acid was better than sulfuric acid as catalyst. The hydration reaction of !-pinene using acid catalyst is schematically shown in Fig. 2: + H 2 O H + OH alpha pinene terpineol Fig 2: The hydration reaction of !-pinene !-Pinene in the presence of acid catalyst is attacked by proton to form a carbocation.

The acid transfers a proton to double bond of the alkene, forming an intermediary carbocation that reacts with water to form a protonated alcohol generates the neutral product and the recovery of the catalyst [1]. Chloro acetic acid is miscible with pinene and also soluble in water, due to this two factors, this catalyst, besides the formation of the proton to form the carbocation, favors the transfer of OH - to organic phase [1] and as a result, hydration conversion is higher than sulfuric acid catalyst.

Effect of Reaction Temperature The influence of temperature was examined at mol ratio of chloro acetic acid catalyst to !- pinene of 2.4/1.The reaction temperature was adjusted to 60, 70, 80, 90 oC. The effect of temperature on conversion of !-pinene to !- terpineol is shown in Fig. 3. The conversion has a tendency to increase by the increase of the reaction temperature.

It is not surprising, since considering the kinetics aspect, the higher temperature leads to the higher reaction rate constant, giving the higher reaction rate and conversion. Fig. 3: Effect of temperature on conversion of !- pinene to !-terpineol Generally, the rising on the temperature of 10 oC enhances the reaction rate of 2-5 times [12].

However the study revealed that the conversion decreased after 240 min (at the temperature of 80 oC) and after 180 min (at the temperature of 90oC). Pakdel (2001) presented the GC/MS analyses indicated the formation of a number of compounds when heating time was greater than 4 h. In addition, a few of those compounds, such as !- and "-terpinene, #-terpineol, and 1,8- terpine were formed in large amounts at a longer heating time [7].

From this study, when the conversion decreased the GC/MS analyses indicated the formation of 1,8-terpine hydrate. Effect of Catalyst Amount Fig 4. shows the conversion of !-pinene to !- terpineol at various catalyst amount (chloro acetic acid). Fig.4: Conversion of !-pinene to !-terpineol at various catalyst amount The effect of catalyst loading on the conversion was studied at the various mol ratio of catalyst to !-pinene (0.8/1; 1.6/1; 2.4/1; 3.2/1; 4/1). The batch reactor was run at the temperature of 80 oC.

Chloro acetic acid as catalyst decreases the activation energy of chemical reactions and increases the reaction rate. Catalyst works to promote a chemical reaction rate by providing an alternate reaction pathway with a lower activation energy. However, for the reversible reaction, catalyst cannot displace the equilibrium, but it reduces the time consumed for reaching the reaction equilibrium and enhances the reaction rate. In this study, the higher mol ratio of catalyst to -pinene will increase the conversion of !-pinene to !-terpineol.

However, the mol ratio of catalyst to !-pinene of 1.6/1 has given better result than that of 0.8/1. The best condition was achieved at mol ratio of chloro acetic acid catalyst to !-pinene of 4/1, but in this condition need more catalyst. The conversion decreased after 240 min at the higher mol ratio catalyst to !-pinene (2.4/1; 3.2/1; 4/1).

The decrease of the conversion maybe caused formation of several by products. Effect of the Stirring Rate The influence of the stirring rate was examined at mol ratio of chloro acetic acid catalyst to !- pinene of 2.4/1 and at the reaction temperature of 80 oC.The effect of stirring rate is shown in Fig. 5. Fig.

5: Conversion of !-pinene to !-terpineol at various stirring rate of hydration The general effect of agitation is to increase the degree of turbulence in a fluid medium, to reduce the thickness of streamline boundary films, and so diminish the resistance to processes of heat or mass transfer by convection [6]. In heterogeneous liquid phase reactions, the reaction mixture should be stirred to increase the contact between the aqueous and oil phase and to reduce the liquid film thickness. The stirring rate between 264-546 rpm increased the conversion.

It showed that the contact between the aqueous (water) and oil phase (turpentine) was good enough. The stirring rate at higher than 546 rpm did not give a significant effect on the conversion. Fig. 5 clearly shows that the optimal stirring rate is 546 rpm. Conclusion Study of hydration turpentine to !-terpineol has been conducted.

Chloro acetic acid was better than sulfuric acid as catalyst for production of !- terpineol from turpentine. It suggested that the best condition for the hydration of turpentine was achieved at temperature of 80 oC, the reaction time of 240 min, mol ratio of chloro acetic acid catalyst to !-pinene of 2.4/1 and the stirring rate of 546 rpm. The conversion of hydration of turpentine to !-terpineol was obtained to be 54.13%.

Acknowledgment The authors acknowledge Directorate General of Higher Education Indonesia (DIKTI) through Doctoral Grant (2009) for funding support of this research. References 1) Aguirre, M.R, De la Torre-Sa´enz,L., Flores, W.A., Robau-Sa´nchez, A., and Elgue´zabal, A., “Synthesis of Terpineol from !-Pinene by Homogeneous Acid Catalysis”, Catalysis Today. 310-314 (2005) 107-108. 2) Arias, D., Guillen, Y., Lopez, C.M.,

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