Microwave-Assisted Cationic Polymerization of Turpentine: Change in Infrared and Ultraviolet Spectra

Muhamad Farid¹, Bambang Soegijono¹ᵃ, Zainal Alim Mas’ud² dan Surya Herlambang⁴

¹ Department of Physics, Faculty of Mathematics and Natural Science, University of Indonesia, Depok 16424, Indonesia
² Department of Chemistry, Faculty of Mathematics and Natural Science, Bogor Agricultural University, Bogor 16680, Indonesia
⁴Email: bambangsg11@yahoo.com

Abstract. Indonesia is a turpentine producer country. So far, only one factory is carrying out turpentine fractionation to increase its selling price. Chemical conversion is necessary to produce more valuable derivatives of this renewable biomass-based material. In this experiment, turpentine as the raw material and the four products: α-pinene, β-pinene, limonene, and δ-carene were reacted successively with sulfuric acid, hydrochloric acid, nitric acid, and ethereal boron trifluoride, respectively. The reaction products were further irradiated using a commercial microwave oven. The raw material composition, functional group, and ultraviolet absorption were analyzed using a gas chromatograph, Fourier transform infrared spectrophotometer, and UV-Vis spectrophotometer, respectively. Half of the reaction products were neutralized with sodium bicarbonate whether or not it irradiated. All products which viscous colored liquid was examined on their ultraviolet and infrared spectrum. The turpentine reacted with sulfuric acid and boron trifluoride ethereal produced a brownish viscous liquid, but did not react with hydrochloric acid and nitric acid. The reaction products with sulfuric acid and boron trifluoride ethereal and microwave irradiation processes showed some shifts on the infrared spectra, particularly in C=C band due to the polymerization and C=C reforming reaction. The products also demonstrate the presence of OH group in the infrared spectra.

1. Introduction

Indonesia produces about 12000 tons of turpentine [1] and is the second largest producer in the world after China [2]. The main components of turpentine are mono and bicyclic monoterpenes (C₁₀H₁₆; Mr 136.2) as α-pinene, β-pinene, δ-carene, and limonene [3]. However, since 2014, Perum Perhutani began to produce turpentine derivatives such as α-pinene, β-pinene, δ-carene, and δ-limonene to increase the value of the products [4].

Based on the turpentine functional group, the transformation is due to a reaction of the unsaturated C=C bond. The transformation includes isomerization, hydration [5], condensation, hydrogenation, cyclization, oxidation [6,7], hydroformylation, rearrangement, ring contraction/enlargement [6], as well as epoxidation [6]. In addition, the C=C group may also undergo polymerization reactions. The cationic polymerization was facilitated by the presence of acid [8]. Cationic polymerization of α-pinene [9-14], β-pinene [15-19], α- and β-pinene [20], α-, β-pinene and limonene [21], limonene [22-24] have been
studied, but not for δ-carene. Microwave technique has been used in facilitating the synthesis process, including polymer synthesis [25-33] and has never been used for turpentine and their derivatives.

In this paper, we employed four acidic agents (H$_2$SO$_4$, HCl, HNO$_3$, and boron trifluoride ethereal) as a catalyst for microwave- assisted cationic polymerization of turpentine, α-pinene, β-pinene, δ-carene, and δ-limonene. The resulted products were analyzed by ultraviolet and Fourier transform infrared spectrophotometry and compared with the raw material.

2. Material and methods

2.1 Materials

The raw materials, namely turpentine, α-pinene, β-pinene, δ-carene, and δ-limonene were provided by Perhutani Pine Chemical Industry (PPCI), Pemalang. All raw materials were directly used without purification. Analytical grade purchased from Merck: hexane, H$_2$SO$_4$ 95%-97% (d=1.84), HCl 32% (d=1.16), HNO$_3$ 65% (d=1.39), and NaHCO$_3$. Boron trifluoride ethyl ether complex (BF$_3$.C$_4$H$_{10}$O) was acquired from TCI.

2.2 Instrumentation

Turpentine as the raw material was analyzed for its composition using Shimadzu GCMS QP-2010. Ultraviolet spectra were taken using Shimadzu Pharmaspec UV-1700. The infrared spectra were observed using PerkinElmer Spectro One on a demountable liquid cell module. The reactions were carried out in 100 ml Erlenmeyer inserted in threaded PTFE reactors (workshop made, ØID = 60 mm ID, ØOD = 100 mm, h = 85 mm) (Fig. 1). The microwave oven used was Samsung MG23H3185PK (230 V, 50 Hz, 2450 MHz; input 1400 W output 800 W).

![Figure 1. PTFE Reactor.](image)

2.3 Instrumentation

Turpentine as the raw material was analyzed for its composition using Shimadzu GCMS QP-2010. Ultraviolet spectra were taken using Shimadzu Pharmaspec UV-1700. The infrared spectra were observed using PerkinElmer Spectro One on a demountable liquid cell module.

2.4 Method

The amount of raw material uses and time of reaction we use, are based on our initial study in the lab. Reaction with HCl and HNO$_3$: 60 g of the raw material in 100 mL Erlenmeyer was reacted with 3 g of reagent and stirred for 1 h.

Reaction with H$_2$SO$_4$: 60 g of the raw material in 100 mL Erlenmeyer was reacted with 3 g of reagent and stirred in an ice bath for 30 min. we using ice bath because the addition of H$_2$SO$_4$ into turpentine is exothermic and it’s is can cause the raw material spurt out. The stirring was continued without the ice bath for 30 min because after the several minutes of stirred the temperature did not increase anymore.

Reaction with BF$_3$-ethereal: 15 g raw material in a 100 mL Erlenmeyer was stirred in an ice bath for 20 min, and carefully reacted dropwise with 0.75 g of BF$_3$-ethereal. Stirring was continued in the ice bath for 20 min and continued for 40 min without the ice bath. This experiment was repeated 4 times, and all products were mixed.

The polymerization process divided into 2 parts ("A" and "B"). The "A" parts were divided into 2 portions ("A$_1$" and "A$_2$"). The "A$_1$" portions were stored directly in vials, while the "A$_2$" portions were
neutralized with NaHCO$_3$. The "B" parts were irradiated with the microwaves under 800W of power for 10 min. The irradiated products were divided into 2 portions ("B$_1$" and "B$_2$"). The "B$_1$" portions were stored into vials, while the "B$_2$" portions were neutralized first with NaHCO$_3$. The products showing thick brownish liquid were picked up for observation using ultraviolet and infrared spectrophotometers.

3. Result and discussion

3.1 Turpentine composition
The GCMS analytical results showed that turpentine was composed of 81.6% α-pinene, 10.94% δ-carene, 2.92% β-pinene, and 0.93% δ-limonene. Since α-pinene is the main component of turpentine, it is expected that the reaction behavior is analogous to α-pinene.

3.2 Effect of microwave irradiation on raw materials
Microwave irradiation treatments against turpentine, α-pinene, β-pinene, δ-carene, and δ-limonene do not visually change the color and the viscosity. However, all UV spectra pattern differ, showing an increase in absorption. The pattern change of the turpentine UV spectrum is not like that of the α-pinene. The IR spectrum intensity of C=C band, $\nu = 1600$–$1680$ cm$^{-1}$ [34] do not change due to irradiation. The pattern of IR spectrum change is random and cannot be generalized.

3.3 The reaction products of the raw material and the acid and the effects of microwave irradiation
Formation of polymers was characterized by the appearance of thick brownish red liquid and the reaction underwent exothermically. H$_2$SO$_4$ (Fig. 2(b) before and 2(c) after irradiation), HCl (Fig. 2(d), before and Fig. 2(e) after irradiation) and HNO$_3$ (Fig. 2(f) before and Fig. 2(g) after irradiation) reagents do not produce the desired product with all the raw materials, and BF$_3$-ethereal reagents (Fig. 2(h) before and (i) after irradiation) produced thick brownish-colored liquid; all reactions with all raw materials were exothermic.

3.4 Infrared spectra changes caused by treatments
IR spectra changes due to H$_2$SO$_4$ and BF$_3$-ethereal treatments, microwave irradiation, and neutralization are shown in Fig. 3. The H$_2$SO$_4$ and BF$_3$-ethereal treatments increase the transmittance (\%T) (decrease the absorbance) in the range of $\nu = 1600$–$1680$ cm$^{-1}$, due to the transformation of the C=C bond to the C–C bond as the consequence of polymerization. However, the microwave irradiation treatment decreases the transmittance in the same range, presumably due to the re-forming of C=C bonds. Surprisingly, the appearance of absorption around 3500 cm$^{-1}$ wavenumber is strong and wide and unchanged due to the irradiation and the neutralization. This band corresponds to the OH group.

Figure 2. Visual change of turpentine during reaction and microwave irradiation.
3.5 Ultraviolet spectra changes caused by treatments

UV spectra changes due to \( \text{H}_2\text{SO}_4 \) and BF\(_3\)-etheral treatment, microwave irradiation, and neutralization are shown in Fig. 4. The \( \text{H}_2\text{SO}_4 \) treatments increase UV absorbance (except that for δ-carene). Microwave irradiation treatment varies, decreasing the absorbance (α-pinene, β-pinene, δ-limonene) and increasing (turpentine and δ-carene). Neutralization processes increase the absorbance.

The BF\(_3\)-etheral treatments increased the UV absorbance (except for β-pinene). The effect of microwave irradiation treatment varies, decreasing the absorbance (α-pinene, and δ-limonene) and increasing (turpentine, β-pinene, δ-carene). Neutralization increases the absorbance only for δ-limonene. It is interesting since this treatment changes the color from dark to light without changing the viscosity.

---

**Figure 3.** Changes in infrared spectrum of turpentine, α-pinene, β-pinene, δ-carene and limonene without catalyst (b) and with acid catalysts BF\(_3\)-etheral (c), HCl (d), HNO\(_3\) (e), \( \text{H}_2\text{SO}_4 \) (f) towards control (a).
Figure 4. Changes in ultraviolet spectrum of turpentine, α-pinene, β-pinene, δ-carene and limonene without catalyst (b) and with acid catalysts BF₃-etheral (c), HCl (d), HNO₃ (f), H₂SO₄ (h), and acid catalyst neutralization HCl (e) and HNO₃ (g) towards control (a).

4. Conclusions
Turpentine, α-pinene, β-pinene, limonene, and δ-carene react with sulfuric acid and ethereal boron trifluoride to produce polymers which visually forming viscous liquids and reduced intensity of C=C infrared absorption bands. In addition to polymer formation, these reactions also produce hydroxyl groups.

5. References
[1] Perum Perhutani 2015 Statistik Perum Perhutani Tahun 2010–2014
[2] Ukkonen K 2015 A Pine Chemicals-Global view
[3] Gscheidmeier M and Fleig H Turpentines 2012 In B Elvers (Eds) Ullmann’s Encyclopedia of Industrial Chemistry, Vol 37 Wiley-VCH Verlag GmbH & Co KGaA, Weinheim
[4] Perum Perhutani 2015 Profil Perum Perhutani
[5] Robert W J and Day A R 1950 J. Am. Chem. Soc. 72 1226–1230
[6] Monteiro J L F and Veloso C O 2004 Topics Catal. 27 169–180
[7] Schwab W Fuchs C and Huang F C 2013 Eur. J. Lipid Sci. Technol. 115 3–8
[8] Faust R and Shaffe T D 1997 Cationic Polymerization-Fundamentals and Applications ACS Symp. Ser. 665 226
[9] Higashimura T, Lu J, Kamigaito M, and Sawamoto M 1992 Makromol. Chem. 193 2311–2321
[10] Higashimura T, Lu J, Kamigaito M, and Sawamoto M 1993 Makromol. Chem. 194 3441–3453
[11] Higashimura T, Lu J, Kamigaito M, and Sawamoto M 1993 Makromol. Chem. 194 3455–3465
[12] Shiwei L, Congxia X, Shitao Y, and Fusheng L 2009 Catal. Commun. 10 986–988
[13] Zuguang L, Taishun Z, Wei Z, Hualong Z, and Xinnan A 2011 React. Kinet. Mech. Cat 104 125–137
[14] Shiwei L, Lin Z, Shitao Y, Congxia X, Fusheng L, Zhanqian S 2013 Biomass and Bioenergy, 57 238–242
[15] Pietila H, Sivola A, and Sheffer H 1970 J Polymer Sci Part A: Polymer Chem. 8 727–737
[16] Martinez F 1984 J Polymer Sci Part A: Polymer Chem. 22 673–677
[17] Jian L, Kamigaito M, Sawamoto M, Hicashimura T, and Yun-Xiang D 1996 J. Appl. Polymer Sci. 61 1011–1016
[18] Kukhta NA, Vasilenko IV and Kostju SV 2011 Green Chem 13 2362–2364
[19] Karasawa Y, Kimura M, Kanazawa A, Kanaoka S and Aoshima S 2014 Polymer J. 47 1–6
[20] Corma A, Iborra S, and Velty A 2007 Chem. Rev. 107 2411–2502
[21] Lu J, Liang H, Zhang R and Deng YX 1998 Acta Polymerica Sinica 68 698–703
[22] Norström E 2011 Terpenes as renewable monomers for biobased-materials KTH Chemical Science and Engineering Thesis p 125
[23] Firdaus M 2013 Terpenes as Renewable Resources for Organic and Macromolecular Chemistry. Karlsruher Institut für Technologie Dissertation p 193
[24] Zhang Y J 2014 Copolymerization of Limonene Department of Chemical Engineering Faculty of Engineering University of Ottawa Thesis p 91
[25] Zong L, Zhou S, Sgriccia N, Hawley M C and Kempel L C 2003 J. Microw. Power Electromagn. Energy 38 49–74
[26] Wiesbrock F, Hoogenboom R and Schubert U S 2004 Macromol. Rapid Commun. 25 1739–1764
[27] Evalueserve 2005 Developments in Microwave Chemistry Royal Society of Chemistry Burlington House London p 52
[28] Koopmans C, Iannelli M, Kerep P, Klink M, Schmitz S, Sinnwell S and Ritter H 2006 Tetrahedron 62 4709–4714
[29] Hoogenboom R and Schubert U S 2007 Macromol. Rapid Commun. 28 368–386
[30] Sinnwell S and Ritter H 2007 Aust. J. Chem. 60 729–743
[31] Mallakpour S and Rafiee Z 2008 Iranian Polym. J. 17 907–935
[32] Sosnik A, Gotelli G and Abraham G A 2011 Prog. Polym. Sci. 36 1050–1078
[33] Mishra A, Vats T and Clark J H 2016 Microwave-Assisted Polymerization The Royal Society of Chemistry Milton Road Cambridge p 183
[34] Pavia D L, Lampman G M, Kriz G S, and Vyvyan J R 2009 Introduction to Spectroscopy (4th ed) Belmont: Brooks/Cole, Cengage Learning