Synthesis propanol by esterification and reduction reaction

Salmahaminati¹ and Jumina²
¹Chemistry Departement, Faculty of Mathematics and Natural Sciences, Islamic University of Indonesia, Yogyakarta, 55581, INDONESIA
²Chemistry Departement, Faculty of Mathematics and Natural Sciences, Gadjah Mada University, Yogyakarta, 55281, INDONESIA

E-mail: salmahaminati@uii.ac.id

Abstract. Synthesis of propanol from propanoic acid had been done. Propanol was synthesized via two steps. They are; esterification of propanoic acid and methanol in the presence of the sulfuric acid catalyst with the mole ratio of 4:3 to produce methyl propanoate, and reduction of methyl propanoate with sodium using ethylene glycol as the solvent to yield propanol. Structural characterizations of methyl propanoate and propanol were done using IR, ¹H-NMR, and GC spectrometers. The results show that esterification of propanoic acid with methanol produced methyl propanoate in 75% yield. Reduction of methyl propanoate using ethylene glycol as a solvent produced propanol in yield of 77%.

1. Introduction

Diesel fuel from plant oils such as rapeseed, soybean, and palm could be producing by enhancing technology. It has largely centered on transesterification of oils with methanol to produce fatty acid methyl esters [1]. Life cycle assessments (LCAs) were published by comparing biodiesel to conventional petroleum diesel [2].

Biodiesel as a substitute for petroleum diesel helps reduce GHG emissions; there are quality issues associated with its widespread use [3,4]. Even though it has been documented that the methyl esters have many desirable fuel qualities such as good cetane number and lubricity, the amount of biodiesel added to a petroleum diesel blend is most often limited to 5% or less due to poor storage stability, marginal cold flow properties, excessive solvency and engine compatibility issues [5-8]. Furthermore to these quality issues, an overall energy balance that includes the life cycle of the raw materials used in biodiesel production indicates that petroleum-derived diesel is still more energy efficient [9].

In this paper, propanol is synthesized. The discussion of this study proposes that substituting propanol for petroleum fuel will reduce in both fossil fuel consumption as well as green house gas emissions. The esterification reaction and external electron donor in reduction reaction are studied in detail.

2. Materials and Characterization

The materials used are: propanoic acid (100%), ethanol, H₂SO₄ (98%), sodium bicarbonate (NaHCO₃), sodium sulfate anhydrous (Na₂SO₄), sodium (Na), ethylene glycol, HCl (36%). For characterization,
we used Infrared spectrometer (IR, Shimadzu Prestige-21), Gas Chromatography (GC-Hewlett Packard 5890 series II) and Gas Chromatography-Mass Spectrometer (GC-MS, Shimadzu QP-2010S).

3. Methods

Methyl propanoate synthesis
Propanoic acid 50 mL (0.67 mole), methanol 20 mL (0.5 mole) and two mL sulfuric acids were added in the reflux system. The mixture was refluxed and stirred with a magnetic stirrer for 14 h. The product was distilled at a temperature of 70-80 °C. Then, it was extracted with ten mL of 10% NaHCO₃. The bottom layer was separated, and the top layer is dried with anhydrous Na₂SO₄. The product was weighed and analyzed by GC, IR and ¹H-NMR Yield: 33 g (0.4 mole)

Propanol synthesis
Methyl propanoate 5 mL (0.045 mol) was added in a 100 mL three neck flask with 10 g (0.45 mol) of natrium. The mixture is stirred with a magnetic stirrer and heated with an oil bath. After sodium melting, we added ethylene glycol as a solvent. (Added as soon without removing the reflux system). The mixture was refluxed for one hour. The product was distilled at the temperature of 90-100 °C. The product was weighed and analyzed by GC. Yield: 2.2 g (0.035 mol).

4. Results and Discussion

Synthesis of methyl propanoate
An esterification is a reaction of alcohols, carboxylic acids and catalyzed by strong acid to produce an ester. The mol ratio of propanoic acid and methanol using H₂SO₄ as a catalyst in this paper is 4:3. The synthesis was done with the addition of the reactants and refluxed for 14 h [10]. Reaction mechanisms of the esterification are in Figure 1 [11].

![Mechanism reaction of esterification](image)

Figure 1. Mechanism reaction of esterification

The esterification reaction of propanoic acid and methanol with the sulfuric acid catalyst will produce methyl propanoate. The results of GC analysis product compared with chromatograms of the esterification results that have been added by spiking of propanoic acid and methanol. The chromatograms are presented in Figure 2.
Figure 2. Chromatogram (a) methyl propanoate product, (b) spiking propanoic acid on the methyl propanoate product, and (c) spiking methanol on the methyl propanoate product.

Based on Figure 2 (a), the peak at a retention time ($t_R$) 3.852 minutes with a percentage of 99% is expected to be the product, methyl propanoate. The peak has appeared at the retention time ($t_R$) 6.071 minutes after spiking with propanoic acid (b) and the peak at a retention time ($t_R$) 2,812 minutes has increased after spiking with methanol (c). Thus, it estimated that there is still a little methanol and propanoic acid in the product.

The results of analysis using IR spectrometer provides a spectrum in Figure 3, and the data analysis is in Table 1.
Figure 3. Infrared spectrum of methyl propanoate

At 3448 cm\(^{-1}\) region shows a vibration range of hydroxyl (OH) methanol remaining in the fractions of methyl propanoate. Uptake observe for a residual alcohol resulting in the range of the C-O at 1080 cm\(^{-1}\) region. Uptake sharply with strong intensity in the area of 1743 cm\(^{-1}\) is the vibration of the carbonyl group (-C = O) ester and reinforced by their absorption at 1203 cm\(^{-1}\) that indicates the range -C-O-C- ester. Absorption at wave numbers 2978 and 2854 cm\(^{-1}\) is the stretching of absorption Csp\(^3\)-H in the alkyl group. Uptake in the area in 1357 and 1435 cm\(^{-1}\) are indicated the presence of C-H vibration of the bends methylene group (-CH\(_2\)) and vibration of C-H bend a methyl group (-CH\(_3\))

Table 1. Infrared spectrum data of methyl propanoate

| Wavenumber (cm\(^{-1}\)) | Functional group          |
|--------------------------|---------------------------|
| 3448                     | -OH alcohol               |
| 1080                     | -C=O alcohol              |
| 1743                     | -C=O carbonyl             |
| 1203                     | -C-O-C-                   |
| 2854 and 2978            | Csp\(^3\)-H               |
| 1435                     | -CH\(_2\)-                |
| 1357                     | -CH\(_3\)                 |
Analysis product using $^1$H-NMR spectrometer, Figure 4, shows the four areas that describe the chemical shift of four protons with different chemical environments. A chemical shift of 4.80 to 4.60 ppm is a singlet appearance, equivalent to one hydrogen atom of the first proton from the -OH in methanol remaining in the fractions of methyl propanoate. Singlet appearance is caused by the influence of an electronegative of O atom. Chemical shift area B (δ 3.70 to 3.40 ppm, triplet, 3H) estimated from proton on C3 (-OCH$_3$). Chemical shift area C (δ 2.40 to 2.00 ppm, quartet, 2H) estimated from proton ester -CH$_2$-C=O, equivalent to three H atoms, is estimated from the three protons at C1. Chemical shift area D (1.30 to 1.10 ppm, triplet, 3H) estimated from the group -CH$_3$ protons at C1, triplet appearance, equivalent to 2 H atom, is estimated from the two protons at C2.

According to the analysis by GC, IR and $^1$H-NMR spectrometers, it shows that the propanoic acid could be esterification with methanol (4:3) using concentrated sulfuric acid catalyst to produce methyl propanoate as a main component with 75 % percent of the results.

**Biopropanol synthesis; reduction of methyl propanoate with Na in ethylene glycol**

The reduction reaction of methyl propanoate would produce methanol and propanol. The GC analysis products from the reduction of methyl propanoate are shown in Figure 5.
Based on Figure 5 (a), the peak at a retention time \( t_R \) 3.578 minutes is expected to be the product, propanol because it has increased after spiking with 1-propanol (b) but it estimated that there is still an impurity on the products because we found two peaks at a retention time 2.936 and 3.085 minutes. From this results, it shows that the sodium metal could reduce methyl propanoate to be methanol and propanol.

5. Conclusion

Analysis by GC, IR and \(^1\)H-NMR spectrometers shows that the propanoic acid could be esterification with methanol (4:3) using sulfuric acid catalyst to produce methyl propanoate as a main component with a yield of 75 %. From these results, it can be ascertained that the sodium metal can reduce methyl propanoate into methanol and 1-propanol. 1-propanol product obtained has a yield of 77% of the results.

6. References

[1] Radich A 2004 Biodiesel Performance Costs, and Use Energy Information Administration http://www.eia.doe.gov/oiaf/analysispaper/biodiesel/
[2] Hill J, Nelson E, Tilman D, Polasky S, Tiffany D 2006 Environmental, economic and energetic costs and benefits of biodiesel and ethanol biofuels Proceedings of the National Academy of Sciences. 103 11206
[3] Kalnes T, Marker T, Shonnard DR 2007 *International Journal of Chemical Reactor Engineering* **5** 1542

[4] Edgar L, Yijun L, Dora E, Kaewta S, David AB, and James GG *Ind. Eng. Chem. Res.* **2005** 44 5353

[5] Kinast JA, Tyson KS 2003 *Production of biodiesel from multiple feedstocks and properties of biodiesel and biodiesel/diesel blend Final report*, NREL: Golden, CO

[6] Ma FR, Hanna MA, Biodiesel production: a review *Bioresour. Technol.* 1999 **70** 1

[7] Haas MJ, The interplay between feedstock quality and esterification technology in biodiesel production *Lipid Technol.* 2004 **16** 7

[8] Talley P, Biodiesel Render 2004 (Sept)

[9] Edwards R, Mahieu V, Griesemann J, Larivé J, and Rickeard DJ 2004 Well-to-Wheels Analysis of Future Automotive Fuels and Powertrains in the European Context *SAE Technical Paper* 1 1924

[10] Smith PWG, Furnish BS, Hannaford AJ and Tatchell AR 1989 *Vogel’s Textbook of practical organic chemistry* John Wiley and Sons New York

[11] Salmahaminati, Jumina 2016 3rd *International Conference on Research Implementation, and Education of Mathematics and Science* C-89 ISBN 978-602-73159-1-4