Synthesis 1-Propanol from Propanoic Acid

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Abstract—Synthesis of 1-propanol from propanoic acid had been done. Polypropylene was synthesized via two steps. They are; esterification of propanoic acid and methanol in the presence of sulfuric acid catalyst with mole ratio of 1:1 to produce methyl propanoate, and reduction of methyl propanoate with natrium using ethylene glycol as solvent to yield 1-propanol. Structural characterization of methyl propanoate and 1-propanol was done by means of IR, and GC-MS spectrometers. The results show that esterification of propanoic acid with methanol produced methyl propanoate in 75% yield and reduction of methyl propanoate produced 1-propanol in yield of 31%.

Keywords: propanoic acid, 1-propanol, esterification and reduction

I. INTRODUCTION

Because of good combination of chemical and physical properties along with low cost, excellent processibility, polyolefins are widely used in our modern life [1-3]. Low isotactic polypropylene is a problem in polypropylene industry. Now, it has more attention and is widely used as adhesives, sealants and coatings, additives for building to grade high way [4-5]. It has been reported that the atactic polypropylene could be synthesized with some metalloocene compound [6-7], although metalloocene catalytic system needs a great quantity of expensive methylaluminoxane (MAO) as cocatalyst and the existing equipment and technological process also must be changed if using metalloocene catalytic system. Therefore much effort has been put on the development and research to produce polypropylene (PP).

Polypropylene can theoretically be obtained from 1-propanol using acid catalyst. Thus, the transformation of propanoic acid into 1-propanol can be seen as an indirect attempt to produce polypropylene.

In the paper, 1-propanol is synthesized. The esterification reaction and external electron donor in reduction reaction are studied in detail.

II. MATERIALS AND CHARACTERIZATION

The main materials used are: propanoic acid (100%), ethanol, H₂SO₄ (98%), natrium bicarbonate (NaHCO₃), natrium sulfate anhydrous (Na₂SO₄), natrium (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).

III. METHODS

A. Methyl propanoate synthesis

45 mL (0.6 mol) propanoic acid, 25 mL (0.6 mol) methanol and 2 mL sulfuric acid 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 10 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, and IR Yield : 34 g (0.4 mol)
B. 1-propanol synthesis

7 mL (0.07 mol) methyl propanoate was added in a 100 mL three neck flask with 3.30 grams (0.14 mol) of natrium. The mixture was stirred with a magnetic stirrer and heated with an oil bath. After the natrium melting, we added ethylene glycol 15 mL (0.24 mol). (Added as soon without removing the reflux system). The mixture was refluxed for 1 h. The product was distilled at temperature of 90-100 °C. The product was weighed, and analyzed by GC-MS and IR. Yield : 1.9 g (0.032 mol)

IV. RESULTS AND DISCUSSION

A. Methyl propanoate synthesis

An esterification reaction is a reaction of alcohols and carboxylic acids catalyzed by strong acid to produce an ester. The mol ratio of propanoic acid and methanol using H$_2$SO$_4$ as a catalyst in this paper is 1:1. Synthesis is done with the addition of the reactants and then refluxed for 14 h [8]. Reaction mechanisms of the esterification is in Figure 1

![Figure 1. Mechanism of esterification reaction](image)

The esterification reaction of propanoic acid and methanol with sulfuric acid catalyst will produce methyl propanoate. The results of GC analysis of the product is compared with chromatograms of the esterification reaction that have been added by propanoic acid and methanol in Figure 2.
FIGURE 2. CHROMATOGRAM (A) METHYL PROPAANOATE PRODUCT (B) SPIKING PROPAANOATE ACID TO METHYL PROPAANOATE PRODUCT, AND (C) SPIKING METHANOL ON METHYL PROPAANOATE PRODUCT

Based on Figure 3 (a), the peak at a retention time (t_R) 3.908 minutes with a percentage of 97% is expected to be the product, methyl propanoate. The new peak have appeared at retention time (t_R) 6.025 minutes after spiking with propanoic acid and the first peak at a retention time (t_R) 2,809 minutes have increased the percentage from 2.7% to 31% after spiking with methanol. Thus, it is estimated that there is still a little methanol in the product.

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

FIGURE 3. INFRARED SPECTRUM OF METHYL PROPAANOATE

At 3471 cm⁻¹ region showed a vibration range of hydroxyl (OH) methanol remaining in fractions of methyl propanoate. Uptake was observed for a residual alcohol resulting in the vibration 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 indicates that the vibration range -C - O - C- ester.

Absorption at wave numbers 2954 and 2846 cm⁻¹ is a stretch vibration absorption Csp³ - H in the alkyl group. Uptake in the area in 1443 and 1358 cm⁻¹ indicate the presence of C - H vibration bends methylene group (-CH₂-) and vibration of C - H bend a methyl group (-CH₃)
<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Functional group</th>
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<tbody>
<tr>
<td>3471</td>
<td>−OH alcohol</td>
</tr>
<tr>
<td>1080</td>
<td>−C−O alcohol</td>
</tr>
<tr>
<td>1743</td>
<td>−C=O carbonyl</td>
</tr>
<tr>
<td>1203</td>
<td>−C−O−C−</td>
</tr>
<tr>
<td>2954 and 2846</td>
<td>Csp³-H</td>
</tr>
<tr>
<td>1443</td>
<td>−CH₂−</td>
</tr>
<tr>
<td>1358</td>
<td>−CH₃</td>
</tr>
</tbody>
</table>

**B. 1-propanol synthesis**

The reduction reaction in methyl propanoate is produced methanol and propanol. GC analysis of the 1-propanol fraction of the reaction product from reduction in methyl propanoate (Figure 4) showed a major peak which is estimated from propanol 74.55% at a retention time (tR) 2,368 minutes.

**FIGURE 4. CHROMATOGRAM OF 1-PROPANOL PRODUCT**

From the results of the GC, it present of several peaks. It can be seen the main peak (peak 3) is 1-propanol, other components that appear on the chromatogram is a residual reactant. MS analysis results of 1-propanol are shown in Figure 5.

**FIGURE 5. MASS SPECTRUM OF 1-PROPANOL PRODUCT**

The mass spectrum of Figure 5. shows that result is similar to 1-propanol. Analysis the mass spectrum of 1-propanol product is as follows:

| m/z  | 33  | 41  | 42  | 59  |

1-propanol has one functional group that is hydroxyl (-OH), the fragmentation is derived from one kind of ion molecule that is the loss of one of the lone pairs of electrons (n) on the oxygen atom. Molecular ion at m/z 60 corresponding to the molecular weight of the 1-propanol looks small. This indicates that the compound is not stable so the fragmentation produces a peak at m/z 59. The peak at m/z 59 is the base peak that comes from the release of the group H. The peak at m/z 42 and 41 is another peak caused loss of H₂O molecules (BM 18) from the molecular ion peak and essentially it is the hallmark of alcohol. Fragment at m/z 33 is a fragment CH₃H₂O⁺ that produced by the loss of C₂H₂ (M⁺-27). The pattern of fragmentation that occurs in an estimated reduction reaction results as in Figure 6. The
mechanism of reduction reaction in methyl propanoate using metal sodium in ethylene glycol solvent is written in Figure 7.

Reduction of methyl propanoate is written on the mechanism marked the acceptance of electrons from the sodium metal. Electrons formed by dissolving metallic sodium in ethylene glycol. When ethylene glycol become a solution, it will turn into a metal cation and can provide electrons. Methyl propanoate which will be reduced accept an electron, and turn it into a radical anion. In the presence of protons, undergo radical anion protonation into another radical form which then will receive another electron to form the alcohol in this case methanol and propanol.

V. CONCLUSION

Analysis by GC and IR shows that the propanoic acid could be esterification with methanol (1:1) using sulfuric acid catalyst produced methyl propanoate as a main component with a purity of 97%. From the results of this research can be ascertained that the sodium metal can reduce methyl propanoate into methanol and 1-propanol. 1-propanol product obtained has a purity of 75% aof the results.

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REFERENCES