Catalytic conversion of citronellal to citronellol over skeletal Ni catalyst

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Abstract. Catalytic conversion of citronellal to citronellol was performed via hydrogenation over skeletal Ni catalyst. The reaction parameters applied include variation of reactant-catalyst ratio, reaction temperature, pressure, and time. Citronellal 78% obtained from the fractionation of citronella oil was used as the reactant. The reaction was carried out using reactant-catalyst ratio of 1:5 % and 1:10 % at temperatures of 100 °C, 150 °C and 200 °C and pressure of 10 bar, 15 bar and 20 bar for 1 and 3 hours. Results show that the optimum reaction condition was at 100 °C with reactant-catalyst ratio of 1:10 % under pressure of 20 bar for 1 hour giving 100 % conversion of citronellal, 51.78 % yield of citronellol and 40.39 % selectivity.

1. Introduction

Indonesia is a country rich in biodiversity with various types of plants that can be used as raw materials for essential oils, such as citronella [1]. Essential oils are exported to the United States and Europe, while in reality only a few essential oils are further and processed into raw materials that can be directly used as the final product [2]. There are at least eleven chemical components of citronella oil that can be identified by gas chromatography and mass spectrometry analysis [3]. Citronellal is one of the main components in citronella oil, which can be converted catalytically into citronellol via hydrogenation reaction.

Almost all chemical manufacturing process in industries used catalysts for producing a particular product. Catalysts widely used in hydrogenation reactions are mostly transition metals since they have an empty d orbital’s that can bind in coordination with other species, one of which is the Ni metal [4]. The effects of external parameters such as temperature, atmosphere (especially the partial pressure of steam), the surface area of the carrier, and particle size have also previously been considered [5]. One popular catalysts used for a hydrogenation reaction is Skeletal Ni.

Research on the catalytic conversion of citronellal to citronellol has been reported previously via hydrogenation using Ni/zeolite-beta catalyst generating yield of 43.91% citronellol [6]. Nie et al. [7] used a Ni/MCM-41 catalyst which showed 49% selectivity towards citronellol, and Milone et al. [8] applied a Ru/C catalyst resulting in 40% citronellol. However, the conversion of citronellal to citronellol over Skeletal Ni catalyst hydrogenation has not yet to be investigated. This study aims to evaluate the catalytic conversion of citronellal to citronellol via hydrogenation over Skeletal Ni catalyst in various reaction conditions.

2. Experimental

2.1. Materials
The catalyst that used for this study is Skeletal Ni catalyst, which purchased from Tokyo Chemical Industry. Citronellal with purity of 78% was obtained from PT. Graha Atsiri Indonesia.

2.2. Methods

2.2.1. Determination of optimum temperature. Catalytic conversion of citronellal to citronellol was conducted using Skeletal Ni catalyst via a hydrogenation process. Variations in reaction temperatures applied were 100 °C, 150 °C and 200 °C [9]. 1 g of citronellal and 10 wt.% Ni skeletal catalysts were inserted into the reactor and H₂ gas was flowed with a constant pressure of 20 bar and stirred for 3 hours. The product was analysed using a Gas Chromatography-Mass Spectroscopy (GC-MS) Agilent 19091S, column HP-5MS, 30 m x 250 μm, 0.25 μm. The sample was filtered prior to insert in the auto sampler of GC-MS with condition parameters as follows: The initial for column temperatur is 65 °C and then raised up to 300 °C with temperature rate about 3 °C/min, the carrier gas that used in this parameter is Helium gas with volumetric rate about 0.6 μL/min while the injector temperature was kept as constant at 300 °C. The optimum temperature obtained was then used for further experiments in determining the optimum reaction pressure.

2.2.2. Determination of optimum pressure. Determination of optimum reaction pressure was performed using conditions optimum temperature. 1 gram of citronellal and 10 wt.% Ni skeletal catalysts were inserted into the reactor and H₂ gas was flowed with pressure variations of 10, 15 and 20 bar [10] for 3 hours. The product was analysed using GCMS technique as follows: The sample was filtered prior to insert in the auto sampler of GC-MS with condition parameters as follows: The initial for column temperatur is 65 °C and then raised up to 300 °C with temperature rate about 3 °C/min, the carrier gas that used in this parameter is Helium gas with volumetric rate about 0.6 μL/min while the injector temperature was kept as constant at 300 °C. The reaction pressure that produced high yields of citronellol was then used for further experiments in determining the optimum catalyst-reactant ratio.

2.2.3. Determination of optimum catalyst-reactant ratio. Determination of optimum catalyst-reactant ratio was conducted using the optimum reaction temperature and pressure. 1 g of citronellal and 10 wt.% Ni skeletal catalysts were inserted into the reactor and H₂ gas was flowed with a constant pressure of 20 bar for 3 hours with variation of catalyst-reactant ratio of 1:5 % and 1:10 %. The product was analysed using a GCMS technique as follows: the sample was filtered prior to insert in the auto sampler of GC-MS with condition parameters as follows: The initial for column temperatur is 65 °C and then raised up to 300 °C with temperature rate about 3 °C/min, the carrier gas that used in this parameter is Helium gas with volumetric rate about 0.6 μL/min while the injector temperature was kept as constant at 300 °C. The catalyst-reactant ratio producing high yields of citronellol was then used for further experiments in determining the optimum reaction time.

2.2.4. Determination of optimum reaction time. Determination of optimum reaction time was conducted using optimum reaction temperature, pressure, and catalyst-reactant ratio. 1 g of citronellal and 10 wt.% Ni skeletal catalysts were inserted into the reactor and H₂ gas was flowed with optimum reaction pressure, time of 1 hour [11] and 3 hours [6]. The product was analysed using a GCMS technique as follows; the sample was filtered prior to insert in the auto sampler of GC-MS with condition parameters as follows: the initial for column temperatur is 65 °C and then raised up to 300 °C with temperature rate about 3 °C/min, the carrier gas that used in this parameter is Helium gas with volumetric rate about 0.6 μL/min while the injector temperature was kept as constant at 300 °C. The conversion of citronellal was calculated as follow:

\[
X_{\text{citronellal}} = \frac{\text{initial citronellal concentration} - \text{final citronellal concentration}}{\text{initial citronellal concentration}} \times 100\% \quad (1)
\]

The yield of citronellal derivatives were calculated as follow:

\[
Y_{\text{citronellol}} = \frac{\text{citronellol product concentration}}{\text{initial citronellal concentration}} \times 100\% \quad (2)
\]

The selectivity of citronellol product was calculated as follow:

\[
S_{\text{citronellol}} = \frac{\text{citronellol concentration}}{\text{total of products concentration}} \times 100\% \quad (3)
\]
### Table 1. Catalytic conversion of citronellal to citronellol using skeletal Ni catalyst in various reaction temperatures.

| Temperature (°C) | Conversion (%) | Citronellol Yield (%) | Selectivity (%) | Isopulegol Yield (%) | Menthol Yield (%) | 3,7-dimethyl-1-octanol Yield (%) |
|------------------|----------------|------------------------|-----------------|-----------------------|-------------------|----------------------------------|
| 100              | 97.14          | 32.63                  | 24.72           | 0.00                  | 2.75              | 77.52                            |
| 150              | 99.88          | 0.74                   | 0.58            | 0.00                  | 3.49              | 97.23                            |
| 200              | 99.81          | 0.32                   | 0.25            | 0.00                  | 4.80              | 85.60                            |

Note: operating conditions of citronellal (78% purity, 1 g), catalyst-reactant ratio (1: 10), 20 bar, 3 hours

### Figure 1. Reaction scheme of the hydrogenation of citronellal [18].

### 3. Results and discussion

#### 3.1. Catalytic testing

##### 3.1.1. Determination of optimum temperature. As mentioned in previous reports, the hydrogenation rates usually increase with increasing temperatures in the hydrogenation of cyclohexenone [12] and citral [13]. Therefore, in order to reduce a carbonyl group, heat and pressure are usually required [14]. The results of GCMS analysis of the reaction products can be seen in the table 1.

The Skeletal Ni catalyst used in the hydrogenation reaction produces various citronella derivatives of citronellol, 3,7-dimethyl-1-octanol, isopulegol and menthol in different yields. Based on table 1, citronellol were mostly produced at 100 °C, whereas at a temperature of 150 °C and 200 °C only 0.74% and 0.32% yield of citronellol were obtained, respectively. The selectivity decreases with increasing temperature. This result was in accordance with those reported by Vijayalakshmi and Subbarao [15], which states that Skeletal Ni catalysts are used for the hydrogenation reaction of aldehydes and ketones at temperature around 100 °C. Several studies have also shown that Ni-based catalysts can reduce ketone or aldehyde groups into alcoholic groups at 100 °C. Malyala et al. [16] conducted a hydrogenation reaction of acetophenone to unsaturated alcohols with Ni/H-Y catalyst and Keane [17] conducted a hydrogenation reaction of benzaldehyde into unsaturated alcohols with the catalyst Ni/SiO.

The hydrogenation reaction of citronellal generally obtained its derivate compounds i.e citronellol, isopulegol, menthol and 3,7-dimethyl-1-octanol as reaction mechanism follow figure 1.

At temperature of 150 °C and 200 °C, the hydrogenation reaction produces the most compound of 3,7-dimethyl-1-octanol. This is caused by high heating can lead to continuous hydrogenation reaction resulting in the formation of by products [19]. The compound 3,7-dimethyl-1-octanol was formed due to the hydrogenation of alkenes group present in citronellol as can be seen in the figure 2.


Table 2. Catalytic conversion of citronellal to citronellol using skeletal Ni catalyst in various reaction pressures.

| Pressure (Bar) | Conversion (%) | Citronellol Yield (%) | Selectivity (%) | Isopulegol Yield (%) | Menthol Yield (%) | 3,7 dimethyl-1-octanol Yield (%) |
|---------------|----------------|-----------------------|-----------------|----------------------|-------------------|----------------------------------|
| 10            | 98.28          | 24.62                 | 18.87           | 0.00                 | 3.27              | 75.40                            |
| 15            | 99.58          | 3.48                  | 2.7             | 0.00                 | 3.48              | 91.72                            |
| 20            | 97.14          | 32.63                 | 24.72           | 0.00                 | 2.75              | 77.52                            |

Note: operating conditions of citronellal (78 % purity, 1 g), 100 °C, catalyst-reactant ratio (1: 10), 3 hours

Figure 2. The hydrogenation of citronellol to 3,7-dimethyl-1-octanol [14].

Figure 3. Cyclization of citronellal [7].

Citronellal can also undergo isomerization into an unsaturated cyclic product of the isopulegol. Furthermore, the Isopulegol compound was hydrogenated into saturated alcohol product i.e. menthol [7]. The cyclization reaction can be seen in the figure 3.

3.1.2. Determination of optimum pressure. The optimum temperature of 100 °C was then used to determine the optimum pressure of the reaction. Based on the GCMS results, catalyst pressure variations show different yields of citronellol as in table 2.

The reacted citronellal in all reaction pressures were converted more than 97 %. The highest citronellol yield of 32.63 % was obtained at 20 bar with selectivity of 18.87 %. At a pressure of 10 bar 24.62 % yield citronellol was obtained. However, at a pressure of 15 bar only 2.70 % of citronellol was produced giving a high yield of 3,7-dimethyl octanol of 91.72 %.

3.1.3. Determination of catalyst-reactant ratio. The optimum pressure of 20 bar was then used in subsequent reactions with various catalyst-reactant ratio. The results of GCMS analysis of the reaction products can be seen in table 3. Table 3 showed that in higher catalyst-reactant ratios, greater yields of citronellol was obtained. At a ratio of 1:5, 14.79 % yields of citronellol was produced with selectivity of 11.26 %. While at a ratio of 1:10 %, the yield of citronellol was 32.63 % with selectivity of 24.72 %.

3.1.4. Determination of optimum reaction time. Catalyst-reactant ratio of 1:10 was then used to determine the optimum reaction time. Based on the GCMS results, variations in reaction time show different yields of citronellol as in table 4. Table 4 showed that reaction time greatly affect the yield and selectivity of citronellol. At reaction time of 1 hour, higher yield of 51.78 % citronellol (40.39 % selectivity) was obtained compared with 3 hours which gave 32.63 % yield (24.72 % selectivity). This
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**Table 3.** Catalytic conversion of citronellal to citronellol using skeletal Ni catalyst in various catalyst-reactant ratios.

| Ratio (%) | Conversion (%) | Citronellol Yield (%) | Selectivity (%) | Yield Isopulegol (%) | Yield Menthol (%) | Yield 3,7 dimethyl-1-octanol (%) |
|-----------|----------------|-----------------------|-----------------|----------------------|-------------------|----------------------------------|
| 1:5       | 97.63          | 14.79                 | 11.26           | 0.16                 | 3.30              | 85.59                            |
| 1:10      | 97.14          | 32.63                 | 24.72           | 0.00                 | 2.75              | 77.52                            |

Note: operating conditions of citronellal (78 % purity, 1 g), 100 °C, 20 bar, 3 hours

**Table 4.** Catalytic conversion of citronellal to citronellol using Ni skeletal catalyst HCl in various reaction time.

| Time (hour) | Conversion (%) | Citronellol Yield (%) | Selectivity (%) | Yield Isopulegol (%) | Yield Menthol (%) | Yield 3,7 dimethyl-1-octanol (%) |
|-------------|----------------|-----------------------|-----------------|----------------------|-------------------|----------------------------------|
| 1           | 100            | 51.78                 | 40.39           | 0.00                 | 0.00              | 18.54                            |
| 3           | 97.14          | 32.63                 | 24.72           | 0.00                 | 2.75              | 77.52                            |

Note: operating conditions of citronellal (78 % purity, 1 g), 100 °C, 20 bar, catalyst-reactant ratio (1:10)

suggests that it only takes an hour for the Skeletal Ni catalyst to reduce the carbonyl bond of the citronellal compound to citronellol. Nie et al. [7] succeeded in the hydrogenation of citronellal compounds using 15 % Ni/MCM-41 catalyst yielding 49 % citronellol for 5 hours and after 22 hours of selectivity decreased to 0.7 %. This shows that skeletal Ni catalyst is excellent in the hydrogenation of carbonyl bonds in a relatively short time.

### 4. Conclusions

Skeletal Ni catalyst can reduce citronellal to citronellol via hydrogenation under optimum reaction conditions of 100 °C, catalyst-reactant ratio of 1:10 with a pressure of 20 bar for 3 hours. At this optimum condition, 100 % conversion of citronellol giving 51.78 % citronellol (40.39 % selectivity).

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