Preparation of Ni/Bentonite Acid-Activated using Dragon Fruit Peel Extract (*Hylocereus polyrhizus*) As a Reductor for One Pot Synthesis of Menthol

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Abstract

Ni/Bentonite is acid-activated has been synthesized using dragon fruit peel extract (Hylocereus polyrhizus) as a reductor through an impregnation method. This research aims to characterize Ni/Bentonite acid-activated using dragon fruit peel extract as a reductor based on FTIR and XRD instruments and to analyze the product obtained in one pot synthesis of menthol from citronellal using Ni/Bentonite acid-activated catalyst. Preparation of Ni/Bentonite acid-activated catalyst was carried out using a wet impregnation method with dragon fruit peel extract as a natural reductor. The successful synthesis of Ni/Bentonite acid-activated was confirmed by FTIR spectrum identification, showing absorptions at wavelengths of 1049.28 cm^{-1} and 694.37 cm^{-1}, indicating Si-O groups in the bentonite, and XRD diffractogram indicating the presence of Ni at diffraction peaks of $2\theta = 40.5°$ and $2\theta = 47.74°$. The catalyst was able to convert menthol by 0.77% through one pot synthesis without using H_2 sources such as potassium formate.

Keywords: dragon fruit peel extract; impregnation; menthol; Ni/Bentonite; one pot synthesis.

INTRODUCTION

Menthol is a compound obtained from *Mentha piperita L* leaf extract or laboratory synthesis (Cantanhede et al., 2021). Menthol is used to provide aroma and flavor in commercial products within the food, beverage, and cosmetic industries (Adilina et al., 2015), as well as in toothpaste, cigarettes, and pharmaceuticals (Trasarti et al., 2013). The global use of menthol is estimated to reach 32,000 tons annually (Su et al., 2019). The high demand for menthol drives researchers to develop methods to increase menthol production through laboratory synthesis (Lothe et al., 2021). One approach is the synthesis of menthol from citronellal using a one pot system (Virtanen et al., 2009).

Synthesis of menthol from citronellal can be carried out using a one pot system with two sequential reactions. These reactions involve the cyclization of citronellal to isopulegol, catalyzed by acid, followed by the hydrogenation of isopulegol to menthol, catalyzed by metal (Sulaswatty et al., 2019). This reaction uses heterogeneous catalysts, which involve metal impregnation onto porous materials with acidic sites, allowing both cyclization and hydrogenation reactions to occur in one container.

Heterogeneous catalysts can be reused multiple times and are easy to separate at the end of the reaction due to their distinct phase from the reactants (Adilina et al., 2015). Several heterogeneous catalysts that have been developed include Ni/ɤ-Al$_2$O$_3$ (Iftitah et al., 2011), Ni/ZrS (Cortes et al., 2011), Zr-Pillar Montmorillonite (Fatimah et al., 2014), Ni/Natural Zeolite (Adilina et al., 2015), and Ru(Bpy)$_3$-Saponite (Fatimah et al., 2019). These catalysts can produce menthol from citronellal with high yields, achieving 100% menthol with Ni/ZrS catalyst (Cortes et al., 2011).

Heterogeneous catalysts can be made by impregnating metal catalysts into porous materials with acidic sites. Bentonite is one such porous material with surface acidity related to Bronsted and Lewis acids. Additionally, bentonite has a large surface area that can be used to distribute metals (Trisunaryanti, 2018). Nickel metal is a metal catalyst that can be evenly dispersed throughout the pore system of bentonite and can function as an active site in the catalyst due to the incomplete electron filling in the d-orbital, making it effective in accepting electron pairs from reactants to achieve a reaction (Trisunaryanti, 2018).

Previous research has required high-pressure H$_2$ gas as a hydrogen source, both in catalyst preparation and in one pot synthesis. The use of high-pressure H$_2$ gas can

easily explode if exposed to oxygen. Therefore, hydrogen sources can be replaced with more environmentally friendly compounds.

H₂ gas, functioning as a reductor, can be substituted with natural reductors such as plant extracts. Secondary metabolites found in plants can act as reductors, particularly phenolic compounds in flavonoids that serve as natural reductors. One plant that contains secondary metabolites such as flavonoids, tannins, and alkaloids is dragon fruit peel (Putri et al., 2018). Thus, dragon fruit peel extract can be used as a natural reductor, as demonstrated by Rahmawita & Ulianas (2021). In their research, NiFe₂SO₄ nanoparticles were synthesized using dragon fruit peel extract as a reductor. Dragon fruit peel extract contains antioxidants such as vitamin C, flavonoids, tannins, alkaloids, steroids, and saponins, which have potential as natural reductors and stabilizers (Noor et al., 2016).

Given the information above, the development of a one pot synthesis menthol from citronellal using Ni/Bentonite acid-activated catalysts is necessary. In this research, preparation of Ni/Bentonite catalysts is carried out using an impregnation method. The reduction process will use dragon fruit peel extract mixed with Ni(NO₃)₂·6H₂O and acid-activated bentonite. The reduction process will also be conducted using H₂ gas to compare the characteristics of the catalysts produced with two different hydrogen sources. Similarly, in the one pot synthesis of menthol, potassium formate will be used as an alternative hydrogen source to H₂ gas.

METHODS

Preparation of Ni/Bentonite Acid-Activated Catalyst
Bentonite Acid-Activated
1 kg of natural bentonite is washed with distilled water, dried, then ground and sieved using a 140 mesh sieve. Activation is performed by refluxing 25 grams of natural bentonite with 250 mL of 2 M HCl for 3 hours at 90°C. The refluxed product is filtered and neutralized to pH 7 using distilled water, then dried in an oven at 50°C for 15 hours. The dried activated bentonite is then ground and sieved using a 140 mesh sieve. It is subsequently tested using FTIR and XRD.

Dragon Fruit Peel Extract
Three grams of dragon fruit peel simplicia are boiled with 600 mL of distilled water for 5 minutes at a temperature of 50-60°C, then filtered using a Buchner funnel to obtain dragon fruit peel aqueous extract.

Ni/Bentonite Acid-Activated Catalyst
Ni/Bentonite Acid-activated catalyst is prepared using two different reduction methods. For the first method, 2.4758 grams of Ni(NO₃)₂·6H₂O is dissolved in 10 mL of

distilled water and mixed with 10 grams of acid-activated bentonite. The mixture is stirred at 60°C until the solution evaporates. The resulting precipitate is separated from the filtrate using filter paper, then dried in an oven at 110°C for 4 hours. The obtained catalyst is calcined for 3 hours at 400°C with a flow of N₂ gas. The catalyst is then tested using FTIR and XRD. In the second method, a similar process is carried out, but the dragon fruit peel extract as the reductor is replaced with H₂ gas. After calcination with N₂, the catalyst is reduced with H₂ gas at 400°C for 3 hours.

One Pot Synthesis of Menthol from Citronellal Catalyzed by Ni/Bentonite Acid-Activated
0.5 grams of Ni/Bentonite acid-activated catalyst is placed into a three-necked flask, followed by the addition of 10 mL of citronellal and 30 mL of isopropanol. The solution is stirred with a magnetic stirrer while being heated, then 6 mL of potassium formate is added dropwise once the reaction temperature reaches 80°C. The reaction is allowed to proceed for 5 hours at this temperature. The reaction mixture is separated from the solvent using an evaporator at 60°C for approximately 2 hours. The sample is then tested using FTIR and GC-MS. The one-pot system reaction is performed with variations of catalysts: acid-activated Ni/Bentonite with dragon fruit peel extract as the reductor, acid-activated Ni/Bentonite with H₂ gas as the reductor, and acid-activated Ni/Bentonite with dragon fruit peel extract without potassium formate.

RESULTS AND DISCUSSION
Activation of Natural Bentonite with 2 M HCl
The activation of natural bentonite is performed using a reflux method with HCl solvent. The resulting bentonite is characterized using FTIR and XRD. FTIR characterization aims to identify the functional groups present in natural bentonite and bentonite acid-activated. The FTIR spectra show that there are no significant changes between natural bentonite and bentonite acid-activated; however, some absorption peaks have shifted in wavenumber. The shift occurs at 3425.58 cm⁻¹ to 3433.29 cm⁻¹, indicating stretching vibrations of OH from H₂O. The peak at 1033.85 cm⁻¹ shifts to 1042.56 cm⁻¹, indicating bending vibrations of Si-O. The high intensity at this absorption peak indicates a high content of montmorillonite in the bentonite (Mahmudha & Nugraha, 2016). A decrease in intensity is observed at the wavenumber 918.12 cm⁻¹ in acid-activated bentonite, which represents bending vibrations of OH groups in Al-OH-Al. This decrease is due to acid dealumination in the bentonite framework, which involves the removal of Al³⁺ from the octahedral layers (Hidayat & Nugraha, 2018).
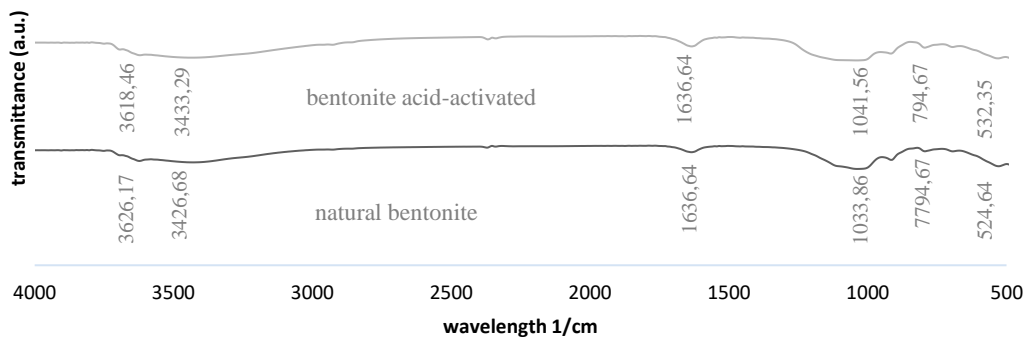
Figure 1. FTIR spectra of natural bentonite and bentonite acid-activated.

XRD Characterization aims to determine the types of minerals in natural bentonite and bentonite acid-activated, as well as the diffraction patterns at 2θ values and the basal spacing of the crystal lattice (Mahmudha & Nugraha, 2016). The XRD diffractogram of natural bentonite in figure 2 shows peaks at 2θ = 5.42° with a basal spacing (d) of 16.3055 Å and 2θ = 19.70° with a basal spacing (d) of 4.5066 Å. These peaks indicate the presence of montmorillonite mineral according to JCPDS No. 13-10135, with d001 = 15.000 Å and d100 = 4.5000 Å. The peak at 2θ = 21.84° with d = 4.0696 Å, according to JCPDS No. 11-0695, indicates the presence of cristobalite mineral, with d101 = 4.05 Å. Peaks at 2θ = 20.72° with d = 4.2870 Å and 2θ = 26.50° with d = 3.3636 Å indicate the presence of quartz mineral, consistent with JCPDS No. 05-0490, with d100 = 4.2600 Å and d101 = 3.3430 Å. The peak at 2θ = 35.48° with d = 2.5302 Å indicates the presence of illite mineral, according to JCPDS No. with d131 = 2.5500 Å.

The XRD diffractogram of bentonite acid-activated shows peaks at 2θ = 5.37° with d = 16.4555 Å and 2θ = 19.68° with d = 4.5111 Å, indicating the presence of montmorillonite mineral. The shift in 2θ values and the basal spacing (d) becomes more pronounced after activation with HCl. The activation process causes the removal of Al from the octahedral layers and replacement with H+ groups, leading to the expansion of the basal spacing in montmorillonite's silicate layers (Mahmudha & Nugraha, 2016). The removal of Al can enhance Si-O-Si bonding, leading to increased quartz intensity (Hidayat & Nugraha, 2018), as evidenced by the increased peaks at 2θ = 9.72° with d = 9.0997 Å and 2θ = 27.90° with d = 3.3636 Å, consistent with JCPDS No. 05-0490, with d002 = 10.300 Å and d101 = 3.3430 Å.

The crystallinity of bentonite is influenced by the Si/Al ratio. Good crystallinity is characterized by a high Si/Al ratio (Wijaya et al., 2016). The Si/Al ratio can be improved through activation with acid. The increase in the Si/Al ratio is evidenced by the XRD diffractogram of H-Bentonite, showing an enhanced absorption peak at 2θ = 9.72°, indicating the presence of quartz mineral.
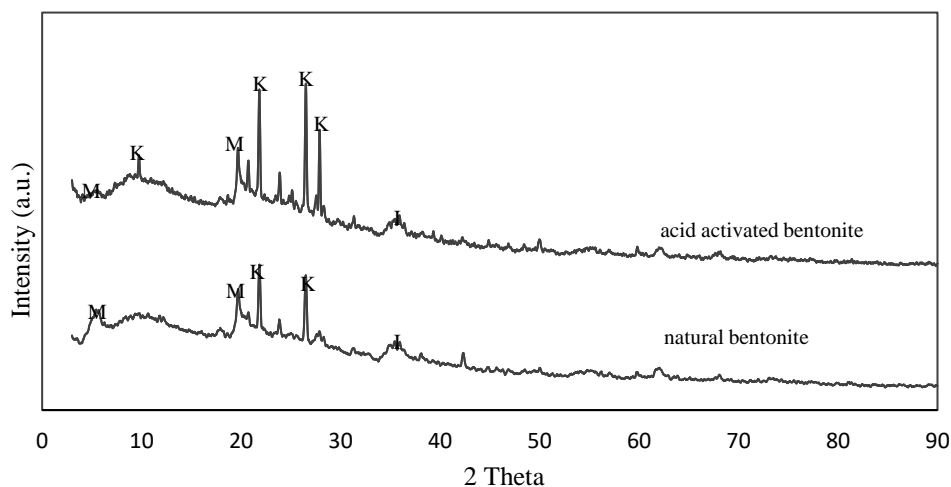

Figure 2. Diffractogram of natural bentonite and bentonite acid-activated.

Preparation of Ni/Bentonit Acid-Activated Catalyst Using Dragon Fruit Peel Extract as a Reductor
The dragon fruit peel extract as a nickel reductor was obtained using a decoction method with distilled water as the solvent (Setiawan et al., 2015). The high flavonoid content in dragon fruit peel can serve as a hydrogen source in the form of –OH groups bound to secondary carbon atoms, which can reduce Ni ions to metallic Ni, while the compounds with –OH groups themselves will undergo oxidation (Muhaini et al., 2014). A comparison was made between the use of this natural reductor and H_2 to evaluate the characterization of the acid-activated Ni/Bentonite catalyst reduced with dragon fruit peel extract. FTIR characterization indicates that the spectra for both types of reducers show no significant changes.
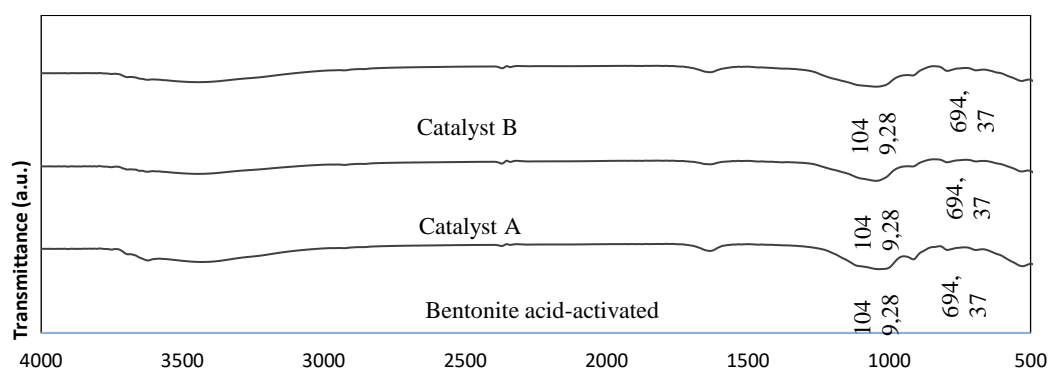

Figure 3. FTIR Spectra of bentonite acid-activated, catalyst A (Ni/Bentonite acid-activated with H_2 reductor), and catalyst B (Ni/Bentonite acid-activated with dragon fruit peel extract reduction).

XRD characterization shows that the mineral structure of bentonite acid-activated remains stable after calcination and reduction. The XRD diffractogram for Catalyst A shows a peak at $2\theta = 19.60°$ with d = 4.5293 Å, indicating the presence of montmorillonite mineral. The increase in basal spacing is due to the impregnation process, which enlarges the space between layers and forms a better pore system. The increase in basal spacing is also a result of the incorporation of nickel metal into the interlayer space of the bentonite structure (Fatimah et al., 2014). Similarly, shifts in 2θ and increases in basal spacing occur at $2\theta = 20.64°$ (d = 4.3034 Å) and $2\theta = 27.52°$ (d = 3.2412 Å). The decrease in peak intensity at $2\theta = 9.72°$ and $2\theta = 27.90°$ is due to a reduction in surface area, pore volume, and changes in pore size distribution in bentonite, likely caused by nickel metal covering its surface (Al Anshori & Muchalal, 2009).

The XRD diffractogram for Catalyst B, reduced using dragon fruit peel extract, shows peaks almost identical to Catalyst A, which was reduced with H_2. This indicates that the dragon fruit peel extract has successfully acted as a bioreductor in reducing nickel metal. The presence of nickel (Ni) is identified at peaks $2\theta = 40.57°$ and $2\theta = 48.25°$ for Catalyst A. For Catalyst B, nickel (Ni) is identified at $2\theta = 40.5°$ and $2\theta = 47.74°$. These results are consistent with JCPDS and the findings of Rahayu et al., (2013). In their research, peaks at $2\theta = 40.570°$ and $2\theta = 48.295°$ correspond to the absorption of Ni metal. The presence of NiO is detected at $2\theta = 62.15°$ for Catalyst A and $2\theta = 62.02°$ for Catalyst B. These peaks match with JCPDS No. 47-1049, where NiO appears at $2\theta = 37.2°$, 43.27°, and 62.87°. This is also observed in the research conducted by Jiang et al. (2018), where the NiO diffraction peak was detected at $2\theta = 62.8°$ for Ni/Bentonite. The appearance of the NiO absorption peak indicates that nickel in the form of oxide is not fully reduced to Ni, as NiO is a relatively stable oxide.
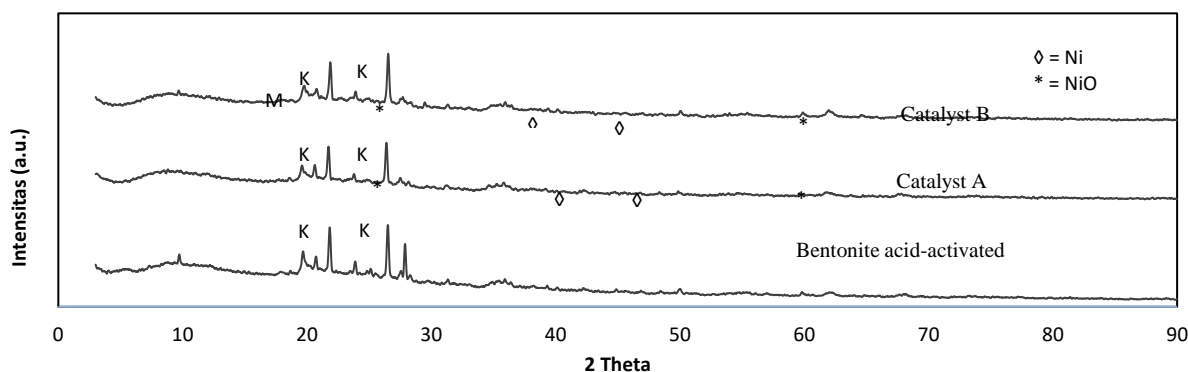

Figure 4. XRD diffractogram of bentonite acid-activated, catalyst A (Ni/Bentonite acid-activated with H_2 reduction), and catalyst B (Ni/Bentonite acid-activated with dragon fruit peek extract redactor).

One-Pot Synthesis of Menthol from Citronellal

The one-pot synthesis of menthol from citronellal, which is predominant in lemongrass oil. Based on GC-MS analysis, citronellal constitutes 57.07% with a retention time of 17.371 minutes. FTIR analysis was conducted to identify the functional groups in lemongrass oil. According to the FTIR spectrum of lemongrass oil, the absorption bands at wavelengths 2916.37 cm⁻¹ to 2862.36 cm⁻¹ correspond to the stretching vibration of aliphatic C-H groups. The wavelength 2715.77 cm⁻¹ represents the stretching vibration of C-H aldehyde, and the aldehyde group in citronellal is also absorbed at 1728.22 cm⁻¹. The presence of the C=C group is identified at 1635.64 cm⁻¹, while the wavelength at 1728.11 cm⁻¹ indicates the presence of C=O or carbonyl groups (Wijayanti, 2015). The wavelength 1450.47 cm⁻¹ shows the –CH₂– group, while the CH₃ group is identified at 1381.03 cm⁻¹. The wavelength 1026.13 cm⁻¹ indicates the stretching vibration of C-O from CH₂OH. These wavelengths suggest that lemongrass oil contains other compounds besides citronellal, such as citronellol and geraniol, which have CH₂OH linkages.
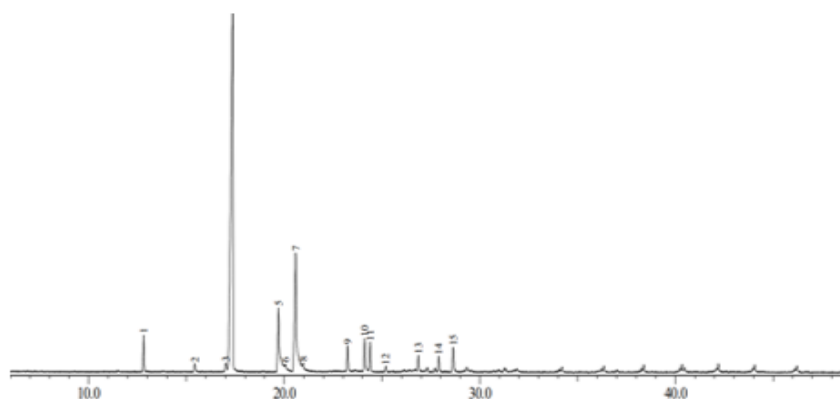

Figure 5. Chromatogram of lemongrass oil.

Table 1. Compounds in lemongrass oil as determined by GC-MS.

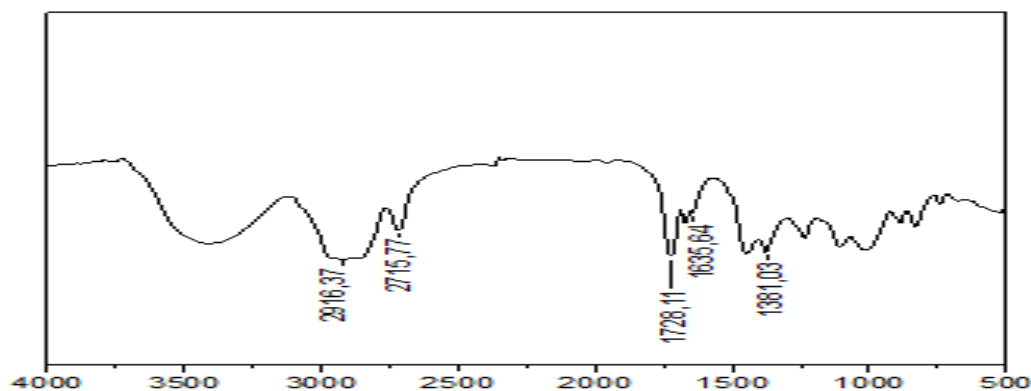| Compounds	R.Time (Minutes)	Area (%)
Citronellal	17,371	57,02 %
Geraniol	20,593	17,15 %
Citronellol	19,715	8,40 %
Limonene	12,817	2,44 %
Citral	20,075	0,43 %
Citral	20,973	0,68 %
11-Tetradecen-1-ol-asetat	23,241	1,89 %
Other compounds		11,99 %
Total		100 %

Figure 6. FTIR spectrum of lemongrass oil.

The one-pot synthesis reaction involves a catalyst, citronellal as the reactant, isopropanol as the solvent, and potassium formate as the hydrogen donor. Potassium formate is used as a hydrogen donor because it decomposes into formic acid and potassium, leaving no other residues at the end of the reaction. Hydrogen

transfer reactions are optimized by using isopropanol as the solvent, which accelerates the hydrogen transfer. The synthesis of menthol from citronellal involves two stages of reaction. The first stage is the cyclization of citronellal to isopulegol, followed by the hydrogenation of isopulegol to menthol. Below is the conversion of menthol from citronellal:
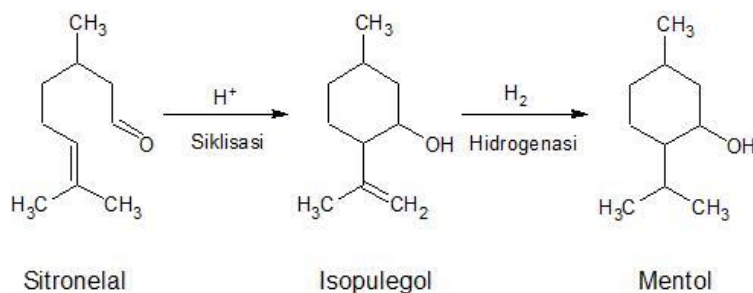

Figure 7. Menthol reaction from citronellal.

Characterization of Reaction Products

The results of the one pot synthesis reaction of menthol were characterized using FTIR to identify the functional groups of the compounds produced from the reaction. The one pot synthesis for citronellal was carried out with three reaction variations. Reaction 1 used catalyst A with the addition of potassium formate. Reaction 2 used catalyst B with the addition of potassium formate. Reaction 3 used catalyst B without potassium formate.
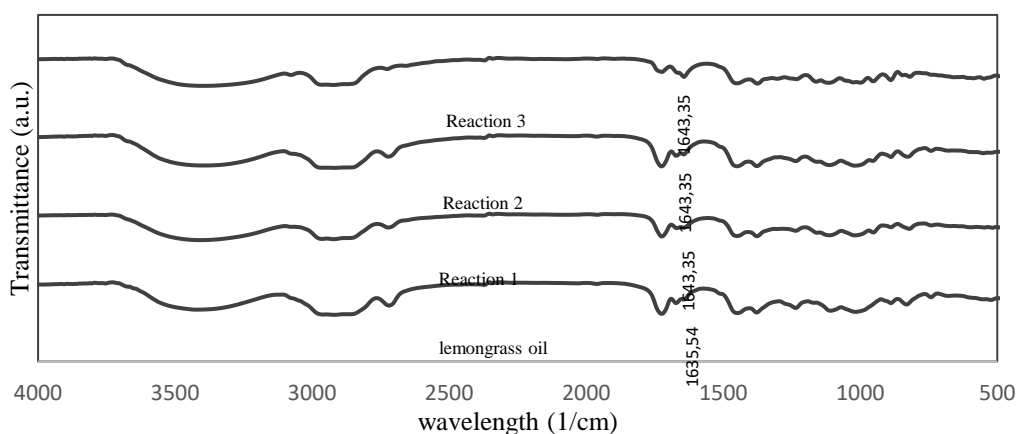

Figure 8. FTIR spectrum of one pot synthesis for citronellal reaction products.

The FTIR spectra of the three reaction products show absorption peaks similar to those of lemongrass oil. The presence of aldehyde groups is identified at a wavenumber of 1728.22 cm^{-1} in both the FTIR spectrum of lemongrass oil and the FTIR spectra of the three reaction products. The wavenumber 1635.64 cm^{-1} in the lemongrass oil spectrum indicates the presence of C=C groups, whereas in the reaction products, this peak shifts to 1643.35 cm^{-1}. The C-O group in menthol is identified at a wavenumber of 1026.13 cm^{-1}. However, this wavenumber is also present in the lemongrass oil spectrum, making it inconclusive whether menthol has been formed in the reaction based solely on the FTIR results. The FTIR does not provide definitive evidence that menthol has been successfully formed during the reaction, as the spectral wavenumber differences between reactants and products are not significant. Nevertheless, the third reaction product has a different FTIR spectrum compared to both the lemongrass oil and the spectra of the other reaction products. Therefore, further analysis using GC-MS was conducted on the third reaction product.
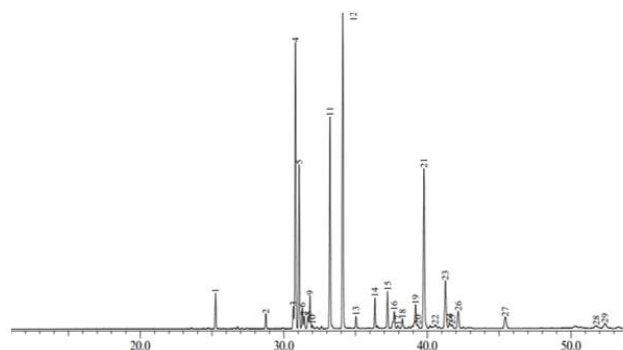

Figure 9. Chromatogram of the third reaction product.

Based on the chromatogram of the third reaction product, citronellal is still detected with a retention time of 30.708 minutes at 1.30%. There is a difference in the retention time of citronellal in the third reaction product compared to citronellal in lemongrass oil, where citronellal appears at a retention time of 17.371 minutes with a concentration of 57.02%. The retention time difference between citronellal in the two samples is 13.337 minutes. This difference in retention time is used to determine changes in peak area percentage and retention time in the lemongrass oil sample and the third reaction product. The retention time difference is consistent with citronellol and geraniol, which are also present in lemongrass oil. Menthol is a new compound produced from the reaction, as there is no corresponding retention time in lemongrass oil based on the retention time reduction in the third reaction product and the observed retention time difference.
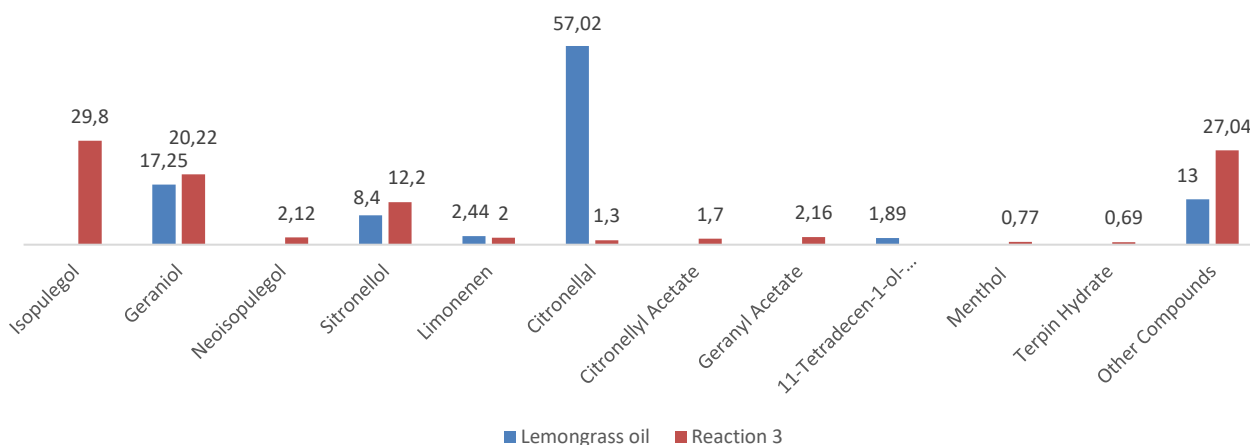

Figure 10. Comparison of compound contents in lemongrass oil and the third reaction product.

From the data above, it can be observed that the reaction can convert citronellal into isopulegol, although not completely, as citronellal is still present at 1.30%. Isopulegol will then react with hydrogen with the help of Ni/Bentonite acid-activated catalyst to produce menthol. The hydrogenation of isopulegol to menthol has occurred without the use of formic acid as an H_2 source. This process involves a reduction reaction utilizing the oxidation effect of other compounds (Muhaini, Syukri, & Syukri, 2014). Based on the GC-MS results, it is identified that the compound undergoing oxidation is limonene, which is converted to terpin hydrate. The reaction occurring is as follows:
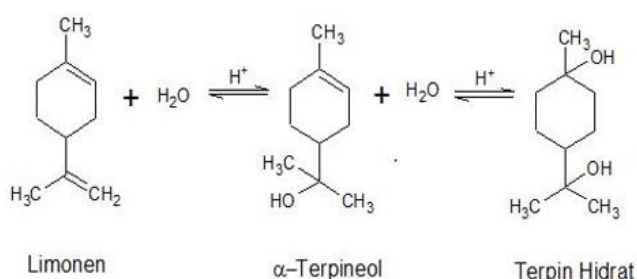

Figure 11. Oxidation conversion reaction of limonene to terpin hydrate

The conversion reaction of limonene to terpin hydrate is an oxidation reaction involving electron release. In the study by Duarte, et al., (1983), this reaction showed a current density of around 1.1 V – 1.3 V. The electrons released from this process react with H_2O to form H_2 as shown in the following equation:

$$2\,\bar{e} + 2H2O \rightarrow 2OH- + H2$$
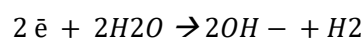
The hydrogen formed from this process can reduce the double bonds in isopulegol to produce menthol.
The reactions occurring in the one pot synthesis for menthol from citronellal are greatly influenced by the amount of metal in the catalyst, as well as the dosage of the catalyst and formic acid relative to citronellal (Fatimah et al., 2019). The presence of H_2 is crucial for reducing the double bonds in isopulegol. Additionally, high catalyst activity and selectivity are essential for achieving a high yield. The formation of unwanted compounds in this reaction is due to the catalyst's lack of selectivity in producing menthol.

CONCLUSIONS

The Ni/Bentonite acid-activated catalyst with dragon fruit peel extract reducer has been successfully formed, as demonstrated by the functional group characteristics using FTIR and XRD, indicating the presence of Ni and NiO in the bentonite. This catalyst can convert citronellal to menthol in a one pot synthesis with a yield of 0.77%, without the addition of an H2 source such as potassium formate.

Competing Interests: The authors declare that there are no competing interests.

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