

Use of CoO/ZnAl₂O₄ Catalysts and Microwaved Assisted in Vanillin Synthesis

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Received: December 2022; Revision: March 2023; Accepted: May 2023; Available online: May 2023

Abstract

Vanillin is a main component in vanilla, which is widely used in the industrial world. Market demand for vanillin extract continues to increase, while the availability of vanilla pods is decreasing. To overcome this problem, research on the synthesis of vanillin continues to be carried out and develops every year. This research aims to examine the conversion level and selectivity of the catalyst as well as microwave radiation efficiency usage in vanillin synthesis. Catalyst CoO/ZnAl₂O₄ was synthesized from CoO and ZnAl₂O₄ using the impregnation method, then analyzed using FTIR, XRD, and SEM-EDX. Vanillin synthesis was conducted in two steps, incorporating microwave usage at 120°C, underwent 30 minutes to be completed then followed by oxidation around 10- and 15-minutes involving nitrobenzene also 1%, 4%, and 7% of catalysts CoO/ZnAl₂O₄. The result showed that during 10 and 15 minutes, the selectivity value and various yield percentages for each time variation and catalyst loading of vanillin had been successfully 100% converted. The best result was obtained using CoO/ZnAl₂O₄ with 4% catalyst loading for 15 minutes. The selectivity value and yield percentages were 67.78% and 7.5%. A one-step vanillin synthesis with conventional reflux could also be a comparison. The reactions were done at 130°C for 2 and 3 hours with 4% catalyst loading.

Keywords: Catalyst CoO/ZnAl₂O₄; eugenol isomerizes; vanillin oxidation; vanillin synthesis

DOI: 10.15408/jkv.v9i1.29727

1. INTRODUCTION

Vanillin synthetic became available for the first time in the 1930s, which was produced from sulfite pulping waste in the paper industry containing ligands. In the early 2000s, vanillin was developed as a result of the synthesis of microorganisms with ferulic acid (Yang et al., 2013), glucose (Ni et al., 2015), eugenol (Birhi et al., 2021), curcumin (Gallage & Møller, 2015), isoeugenol, and vanillyl alcohol (Rahmanivahid et al., 2019) as a starting material with eugenol as the most widely used starting material. The development of vanillin synthesis continues to be updated every year in various matters such as synthesis methods, reactant compositions, heat sources, and the use of catalysts. In the last 10 years, there have been

several studies that have focused their research on the use of catalysts in the synthesis of vanillins, such as metal catalysts, metal oxides, to a combination of several metals and mesopore silica.

Metal catalysts that have been widely used in the benzylic oxidation reaction of aromatic eugenol compounds include cobalt, iron, copper, manganese, and chromium (Franco et al., 2017; Jha & Rode, 2013). These transition metal catalysts are considered cheaper than precious metal catalysts such as Pt, with cobalt catalysts having higher activity and strong in dioxygen activation (Jha & Rode, 2013). However, the direct use of metal Co as a catalyst in the synthesis of vanillin has low selectivity (Franco et al., 2017), so it is

considered necessary to make it a metal oxide-based catalyst. The use of metal oxide catalysts has been shown to have higher effectiveness with a conversion rate of 98% within 2 hours (Jha & Rode, 2013). This result is better than using the metal Co as a catalyst, which gives a conversion rate of 60% for 2 hours (Franco et al., 2017).

The catalyst used in this research is a combination of CoO with ZnAl₂O₄ as catalyst support. CoO is a low-cost, highly effective catalyst (Lu et al., 2012), is magnetic, catalytic, and has high electrochemical properties. ZnAl₂O₄ has good metal dispersion capacity, is inert, has hydrophobic characteristics, has low surface acidity, and has high thermal stability (Eskandari et al., 2020; Peymanfar & Fazlalizadeh, 2020). In previous studies, the use of ZnAl₂O₄ in the synthesis of vanillin resulted in vanillin with excellent effectiveness (Birhi et al., 2021). Currently, there is no research that combines the CoO catalyst with ZnAl₂O₄ support, as well as its use in the synthesis of vanillin. This research will synthesize CoO/ZnAl₂O₄ catalyst using the impregnation method. This method was chosen because the manufacturing process is simple, easy to do, and economical. In addition, CoO and ZnAl₂O₄ used are also catalysts synthesized in this study.

Vanillin synthesis is a reaction that requires a high temperature (130-150 °C) for a long time. Vanillin can be synthesized for 1-24 hours with a conversion rate and selectivity of 72% based on data from previous studies. This is because the inability of heating to reach the optimal temperature will affect the conversion rate of the raw materials used. To overcome this problem, microwave irradiation can be used instead of a heat source. The use of microwave radiation can later shorten the reaction time because heating with microwave radiation occurs without an intermediary, so the optimum temperature will be reached faster, and the reaction will run faster. Garcia-Albar in a recent study in 2021, used microwave heating to synthesize vanillin by involving a metal catalyst to obtain vanillin with a conversion rate of 50-60% from isoeugenol for 30 minutes (García-Albar et al., 2021). In this study, a microwave was used to synthesize vanillin in two stages, where eugenol was first isomerized to produce isoeugenol. Isoeugenol will then be used in an oxidation reaction to produce vanillin, which will involve a CoO/ZnAl₂O₄ catalyst. In addition to the synthesis using two reaction

steps, a CoO catalyst will also be used in the synthesis of vanillin but using a one-pot reaction with reflux heating as a comparison of the catalytic effectiveness of each catalyst in the synthesis of vanillin.

2. MATERIALS AND METHODS

Materials and instrumentation

Eugenol oil was obtained from PT. Javagri Inti Lestari, Indonesia. *n*-hexane, diethyl ether, methanol, sodium hydroxide, aluminum oxide, cobalt chloride dihydrate (CoCl₂·2H₂O), potassium hydroxide (KOH), dimethyl sulfoxide (DMSO), anhydrous sodium sulfate (Na₂SO₄), nitrobenzene, hydrochloric acid (HCl), sodium bisulfite (NaHSO₃), ethylene glycol, sulfuric acid (H₂SO₄), were obtained from Sigma Aldrich Instrumentation applied for analysis. The heat used comes from the Electrolux EMM2308X microwave. The IR Spectra uses KBR pellets with the SHIMADZU brand, IR Spirit-T model, with serial No. A22415801432 AE. Gas Chromatograph – Mass Spectrometry (GCMS) brand SHIMADZU QP2010 SE. X-ray Diffraction (XRD) uses the PANANALYTICAL brand, type Expert Pro. Scanning Electron Microscopy (SEM) FEI brand, Type: Inspect-S50 equipped with EDAX. Calcination using Furnace-6000 brand Barnstead Thermolgne.

Catalyst Synthesis

The CoO catalyst was synthesized by dissolving 3.3 grams of CoCl₂·6H₂O in 30 mL of methanol. The solution is stirred for 60 minutes, add 2 M NaOH to pH 8 then stir again for 2 hours. The precipitate was heated in an oven at 85 °C, then calcined at 500 °C for 30 minutes. On the other hand, CoO/ZnAl₂O₄ was synthesized using the impregnation method, where ZnAl₂O₄ reacted with the previous CoO in a glass beaker with a ratio of 1:1 (% v:w). The mixture was left for 22 hours at room temperature and covered with paraffin plastic. The precipitate was filtered and dried in an oven at 110 °C for six hours. The result was calcined at 800 °C for 7 hours (Angasa *et al.*, 2012), then analyzed by FTIR, XRD, and SEM-EDX.

Vanillin synthesis

One-Step Synthesis (Conventional Heating)

Synthesis of vanillin using a one-step method was carried out using the method used in previous studies (Birhi et al., 2021). This study uses CoO and CoO/ZnAl₂O₄ catalyst

which would be compared with ZnAl₂O₄ catalysts in previous studies. The reaction is carried out using reflux for two and three hours at 130°C.

Two-stage synthesis (Microwave)

In this method, the reaction is carried out two times, isomerization and oxidation involved the use of a microwave. Isomerization was carried out by reacting 5 mL of eugenol and 5 grams of KOH in 15 mL of ethylene glycol. The solution was reacted in the microwave for 30 minutes at 120 °C. The results were diluted and 36% HCl was added to pH 2-3 and filtered. The organic layer was extracted three times with diethyl ether, then evaporated and analyzed using FTIR and GCMS. The isoeugenol from this reaction was reacted with 5 grams of KOH in 7 mL of distilled water and stirred for 5 minutes. The mixture was reacted with 10 mL nitrobenzene, 20 mL DMSO, and CoO/ZnAl₂O₄ catalyst with variations in loading of 1%, 4%, and 7%. The mixture was reacted in the microwave for 10 and 15 minutes at 120 °C. The reaction product is acidified with HCl to form 2 layers. The top layer was extracted with diethyl ether to separate it from water, DMSO, and other oxidizing compounds. Extraction was carried out with 15 mL of 20% NaHSO₃ and 10 mL of H₂SO₄, then heated at 50 °C for 1 hour. The result was extracted again with diethyl ether, then evaporated. The product will crystallize at room temperature, then be purified with *n*-hexane. The synthesis results were tested for solubility in water and alcohol, tested for melting point, and analyzed by FTIR and GCMS

3. RESULTS AND DISCUSSION

Synthesis Catalyst

CoO synthesized was analyzed by FTIR. The results (Figure 1) show that there is strong absorption at wave numbers 584 cm⁻¹ and 668 cm⁻¹ which are vibrations for the Co-O spinel group (Manteghi et al., 2015). Other absorptions are seen at wave numbers 1319 cm⁻¹ for symmetric C-O vibrations, and 1638 cm⁻¹ for asymmetric C-O. FTIR analysis for the CoO/ZnAl₂O catalyst shows absorption for –OH, C=O, Al-O, and Zn-O groups at wave numbers 3457 cm⁻¹, 1635 cm⁻¹, 670 cm⁻¹, and 496 cm⁻¹. The presence of absorption of OH groups may be due to the presence of air which is re-captured by the catalyst when the catalyst is stored before being analyzed by FTIR.

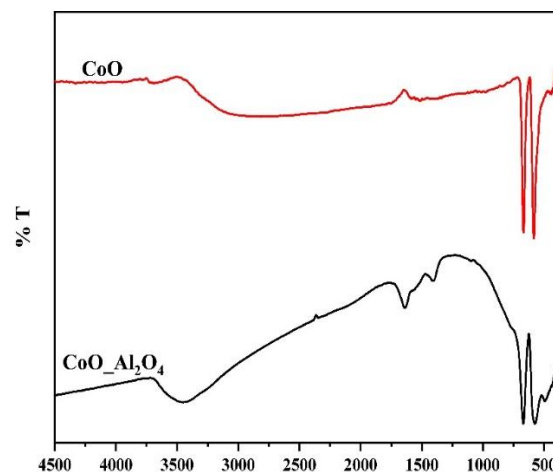


Figure 1. FTIR analysis results of CoO and CoO/ZnAl₂O₄

Further, analysis with XRD did not show any other corner positions other than the corner positions for CoO and ZnAl₂O₄ as described in Table 1. The XRD diffractogram (Figure 2) provides the same corner positions according to JCPDS card no.71–0968 for ZnAl₂O₄ and JCPDS card no.43 –1004 for CoO at corner positions 31.2°, 36.8°, 36.2°, 44.8°, 56.5°, 59.3°, 62.8°, 65.2°, 74.1°, and 77.3°. Analysis using the Rietveld method with Rietica software showed that the CoO/ZnAl₂O₄ was in a nanoparticle size of 18.1 nm, which has a cubic crystal system with space groups *fm3m* for CoO and *fd3m* for ZnAl₂O₄. Results of the surface morphology depiction (Figure 4) with SEM show that the resulting CoO/ZnAl₂O₄ still has an irregular shape with an uneven distribution of particle sizes. The comparison of each element based on EDX analysis is shown in Table 2, with the elemental ratio of Co:O:Zn:Al being 1:12:1:2.

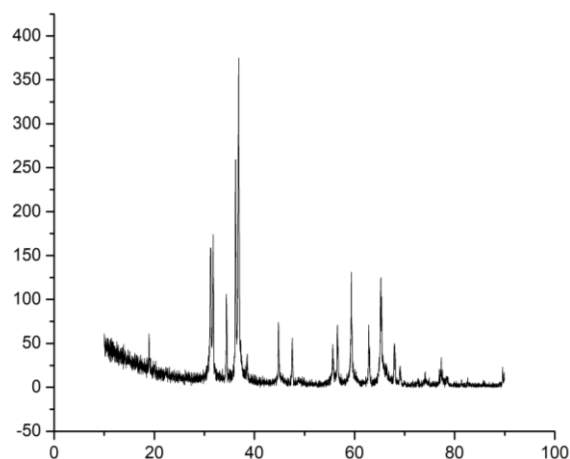


Figure 2. CoO/ZnAl₂O₄ XRD analysis results

Table 1. Comparison of the angular positions of 2θ

| No | Theta positions (°) | | |
|----|--------------------------------------|--|---------------------------------|
| | CoO/ZnAl ₂ O ₄ | JPDS card no. 71 – 0968 for ZnAl ₂ O ₄ | JPDS card no. 43 – 1004 for CoO |
| 1 | 31.2876 | 31.2 | |
| 2 | 36.8477 | 36.9 | |
| 3 | 36.2511 | | 36.4 |
| 4 | 44.8001 | 44.9 | |
| 5 | 56.5981 | 56.8 | |
| 6 | 59.3623 | 59.1 | |
| 7 | 62.8725 | | 61.6 |
| 8 | 65.2334 | 65.1 | |
| 9 | 74.148 | | 73.6 |
| 10 | 77.3221 | | 77.6 |

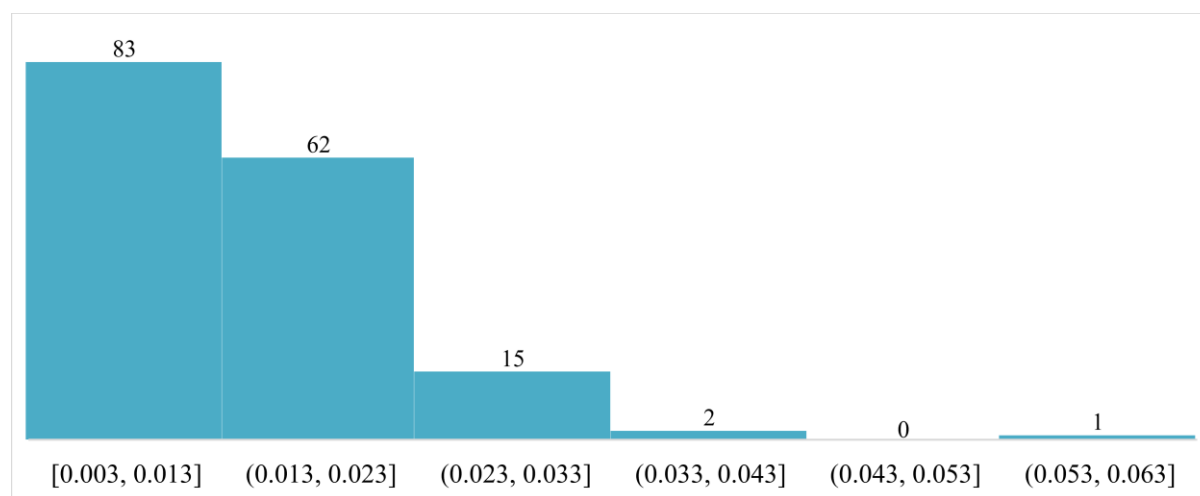


Figure 3. Distribution of CoO/ZnAl₂O₄ granules

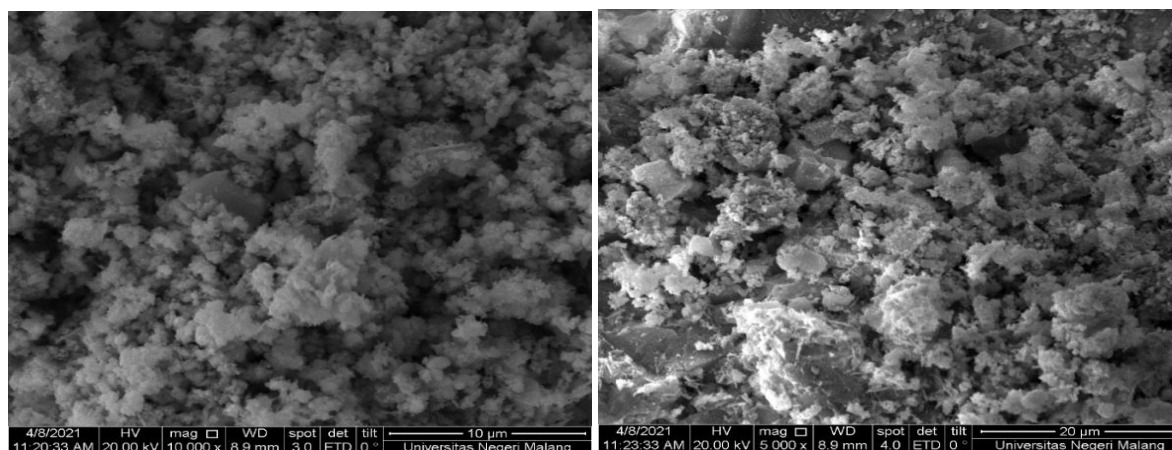


Figure 4. Morphological description of CoO/ZnAl₂O₄ by SEM

Table 2. Elements composition of CoO/ZnAl₂O₄ catalyst

| No | Unsure | Scale 40 | | Scale 41 | |
|----|--------|----------|-------|----------|-------|
| | | % Wt | % At | % Wt | % At |
| 1 | O | 22.40 | 47.96 | 22.14 | 47.38 |
| 2 | Al | 12.67 | 16.09 | 13.32 | 16.91 |
| 3 | Co | 33.60 | 19.53 | 33.14 | 19.26 |
| 4 | Zn | 31.33 | 16.42 | 31.40 | 16.45 |

Vanillin synthesis

One-Step Synthesis (Conventional Heating)

At this stage, the synthesis of vanillin was carried out involving CoO and CoO/ZnAl₂O₄ catalysts. This is intended to compare the effectiveness of the CoO/ZnAl₂O₄ catalyst with its constituent catalysts, then be compared with the results of previous studies using ZnAl₂O₄ catalysts. Catalyst loading is 4% for 2 and 3 hours of reaction using reflux with conventional heating. Reaction with an oil bath at 130 °C will produce *k*-vanillat. This result is acidified with HCl to obtain vanillin products. After adding HCl, the solution was extracted with diethyl ether. The Diethyl ether layer which contains vanillin was separated from the organic layer. The layer is added with sodium bisulfite to form vanillin bisulfite, which will then be converted into vanillin by adding concentrated H₂SO₄ (Figure 5). Diethyl ether was evaporated using a rotary evaporator until the volume of the solution was reduced and it produced vanillin crystal when cooled. The vanillin is purified using hot *n*-hexane for ± 2-3 days until pure vanillin crystals form again. The results of solubility tests in water and alcohol proved that the vanillin product complied with standard vanillin, where the vanillin had good soluble properties in alcohol, but was slightly/insoluble in water.

The GCMS analysis of vanillin can be seen in Table 3. Based on the results, vanillin

has a very good conversion value of 100%. The best value of catalyst activity was found in the CoO/ZnAl₂O₄ catalyst, with the highest percent yield of 3.69% within 3 hours used conventional heating. The yield percentage produced with the CoO/ZnAl₂O₄ catalyst has a better value than in previous studies, where in previous studies the synthesis of vanillin without a catalyst was carried out for 3 hours and obtained a yield percent of only 1.94% (Birhi et al., 2021). The solubility test in water and alcohol gave positive results, where the vanillin crystals produced have good solubility in alcohol and are slightly soluble in water. In addition to the solubility test, the analysis of the melting point found that the resulting vanillin had a melting point that was in accordance with the literature, in the range of 80-83°. In this one-step vanillin synthesis, the catalyst is assumed to work immediately at the beginning of the reaction up to the vanillin formation stage. It has been said that in the one-step synthesis of vanillin, eugenol is directly reacted with nitrobenzene and involves the use of a catalyst. In this reaction, eugenol still undergoes an isomerization reaction as in the two-step synthesis reaction, it is just that the isomerization and oxidation reactions are carried out under the same conditions without any pauses or separations as in the two-step vanillin synthesis reaction.

Table 3. GCMS analysis of vanillin which is formed uses a one-step method

| | CoO | | CoO/ZnAl ₂ O ₄ | |
|--|-----|--------|--------------------------------------|-------|
| | 2 h | 3 h | 2 h | 3 h |
| % yield | 2.7 | 0.8 | 2.7 | 3.69 |
| % conversion | 100 | 100 | 100 | 100 |
| % selectivity | 100 | 39.061 | 100 | 95.12 |
| Side Products | | | | |
| Benzeneacetic acid, alpha.,4-dihydroxy-3-methoxy-, | - | 2.067 | - | - |
| Sulfurous acid, cyclohexyl-methyl heptyl ester | - | - | - | 4.881 |
| 1-Octadecene | - | - | - | - |
| 1-Docosene | - | - | - | - |
| Azoxybenzene | - | 11.791 | - | - |
| 1-Docosene | - | 1.575 | - | - |
| Tetracosane | - | 7.909 | - | - |
| Octadecane | - | 1.537 | - | - |
| Methanesulfanilide | - | - | - | - |
| Phenol, 2-methoxy-4-(1-propenyl)- | - | - | - | - |
| 2H-Pyran-5,6-dicarboxylic acid, 3,4-dimethyl-2- | - | - | - | - |
| Tridecane, 1-iodo- | - | 1.099 | - | - |
| Undecanoic acid, ethyl ester | - | 1.108 | - | - |
| heptadecane | - | 4.339 | - | - |
| 2-methylhexacosane | - | 6.108 | - | - |
| heneicosane | - | 20.847 | - | - |

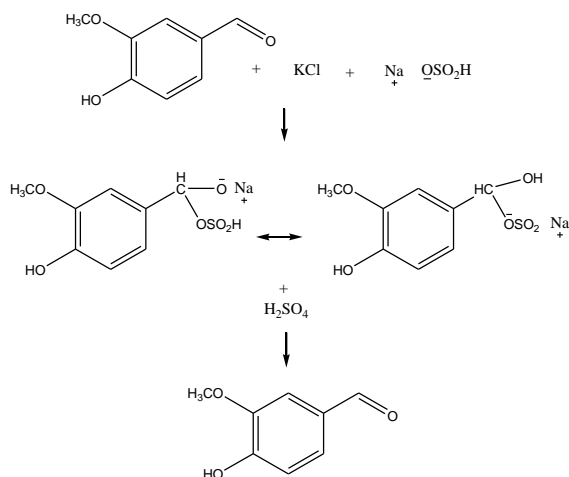


Figure 5. Mechanism of adding sodium bisulfite and releasing SO_2

Two-Stage Synthesis Isomerization

Reaction with the microwave was allowed to run for 30 minutes at 100% power. The use of a relatively short time due to the use of a microwave, which can speed up the achievement of the reaction, because of the heat energy produced being directly absorbed by the material without involving a container as an intermediary. The isoeugenolat ions are acidified to form isoeugenol (**Figure 7**).

Characterization with FTIR for isoeugenol as the isomerization product gives typical absorptions at wavelengths of 785 cm^{-1} and 961 cm^{-1} which are absorptions for *cis*-isoeugenol and *trans*-isoeugenol (**Figure 8b**). This is in accordance with the literature where it is said that the typical absorption of isoeugenol is in the range of wave numbers $962\text{--}964.41\text{ cm}^{-1}$ for *trans*-isoeugenol and 785 cm^{-1} for *cis*-isoeugenol (Mulyono, 2012; Sudarmin, 2014). On the other hand, **Figure 8a** is the result of FTIR analysis for eugenol which gives absorption at wave numbers 3508 cm^{-1} , 1637 cm^{-1} , 1511 cm^{-1} , 1032 cm^{-1} , and 912 cm^{-1} , where each absorption shows the presence of the --OH groups, C=C alkenes, C=C aromatic, C-O methoxy, and C=C-H eugenol groups. With the use of a microwave, the resulting isoeugenol has a very high purity with a conversion rate of 100% based on GCMS analysis. This is because the use of microwaves as a heat source has several advantages, including accelerating reaction rates, providing selective and uniform heating, developing a cleaner synthesis route, and achieving greater reaction repeatability (Soekartawi, 2006; Suratayah, 2006). The presence of 100% isoeugenol is divided into 80.779% for *trans*-isoeugenol, and 19.221% for *cis*-isoeugenol (**Figure 9b**).

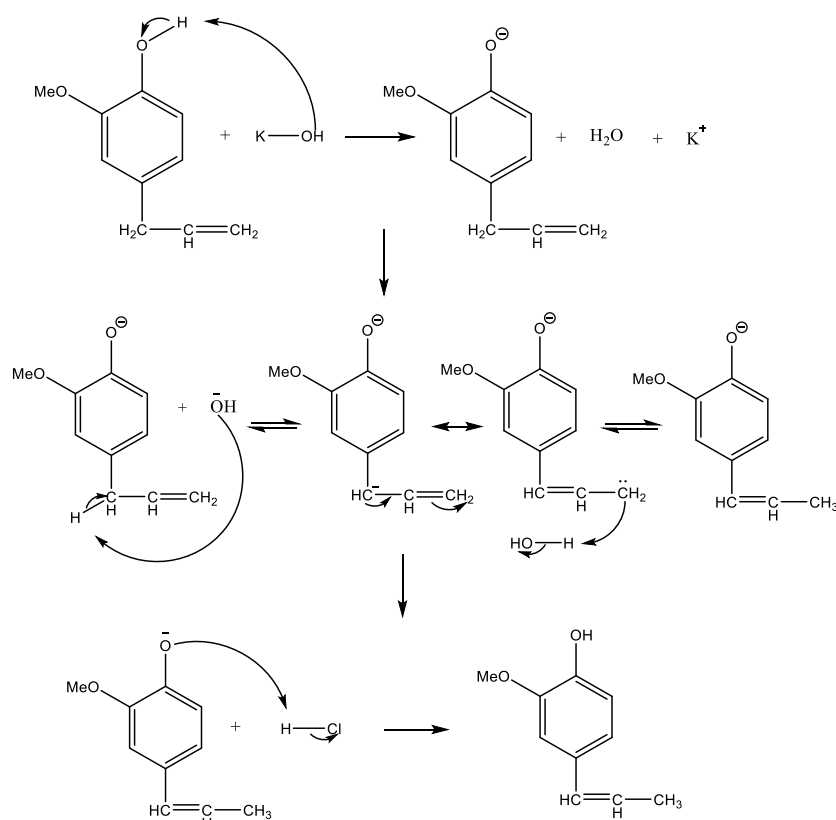


Figure 7. Isomerization mechanism of eugenol to isoeugenol

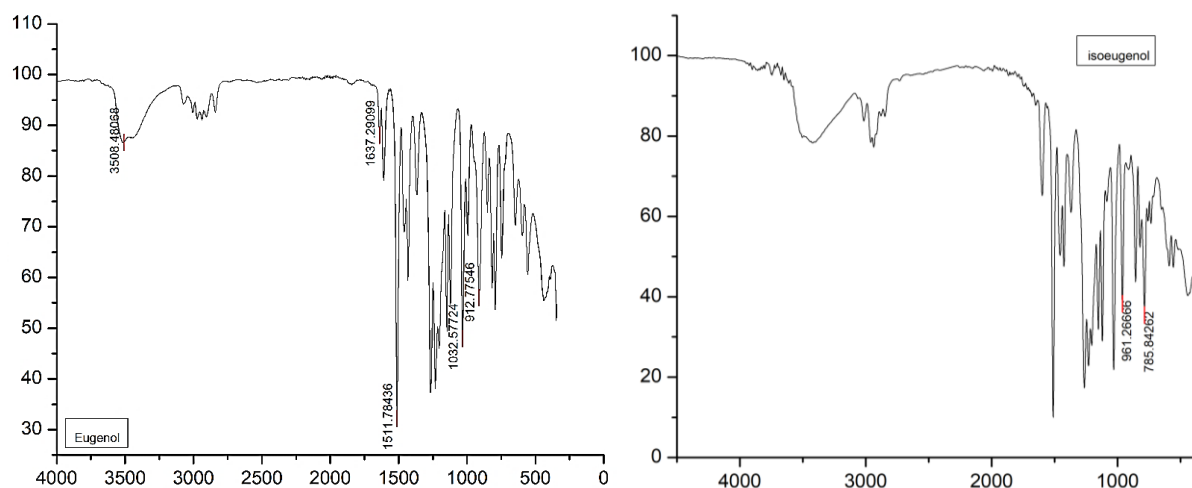
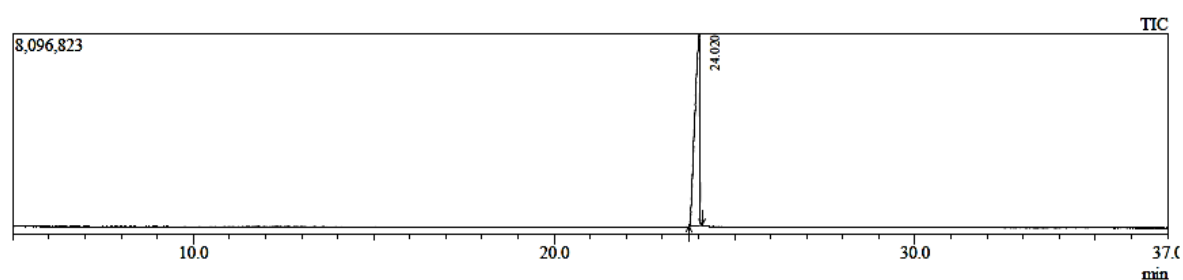
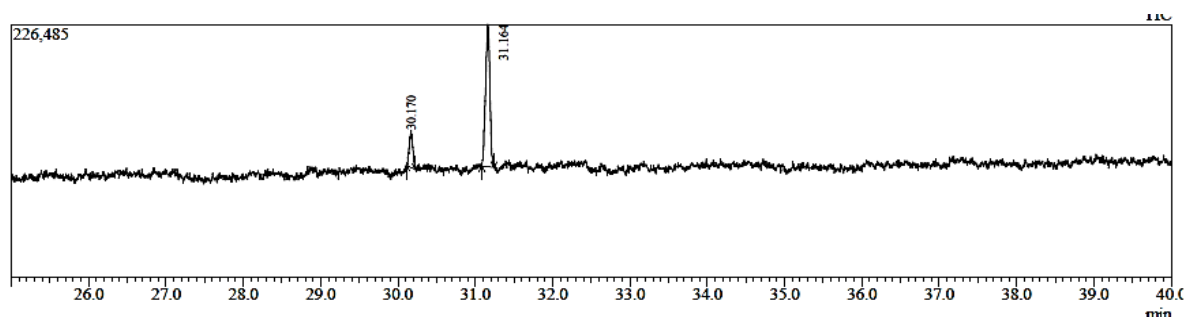


Figure 8. FTIR spectra of eugenol and isoeugenol



| ID# | Name | R.Time | m/z | Area | Height | Conc. |
|-----|---------|--------|--------|----------|---------|-----------|
| 1 | Eugenol | 24.02 | 164.00 | 11481466 | 1280590 | 100.000 % |

(a)



| ID# | Name | R.Time | m/z | Area | Height | Conc. |
|-----|---|--------|--------|-------|--------|----------|
| 1 | Phenol, 2-methoxy-4-(1-propenyl)- | 30.17 | 164.00 | 19698 | 5495 | 19.221 % |
| 2 | Phenol, 2-methoxy-4-(1-propenyl)-, (Z)- | 31.16 | 164.00 | 82781 | 21532 | 80.779 % |

(b)

Figure 9. GCMS results of (a) eugenol and (b) isoeugenol.

Oxidation

Analysis by FTIR (Figure 10 and 11) for oxidized vanillin showed the absorption of hydroxy groups at wave numbers 3180 cm⁻¹ for -OH stretching and 1300-1266 cm⁻¹ for -OH bending. The presence of stretching and bending carbonyl groups was seen at wave numbers of 1668 cm⁻¹ and 631 cm⁻¹, and the weak absorption at 2859-2977 cm⁻¹ was absorption for the -C-H stretching group. In

addition to the three functional groups, it is also seen that there is absorption at a wave number of 1026 cm⁻¹ for stretching vibrations of O-CH₃ and at a wave number of 1430-1591 cm⁻¹ resulting from the C=C double bond in the benzene ring. Analysis with GCMS is briefly described in Table 4. Overall, vanillin produced from isoeugenol has a higher percent yield with an average of 4.16%. Vanillin with the largest yield percentage of 10.5% was produced for 15

minutes using a loading catalyst of 7% CoO/ZnAl₂O₄. In contrast to the percent yield, vanillin with the best selectivity value was obtained for 15 minutes with a catalyst loading of 4%. Judging from the percent yield, conversion value, and selectivity value, the use

of a 4% loading catalyst gives vanillin better results. This is because the increasing mass of the catalyst allows for higher agglomeration so that the pores of the catalyst become closed which results in reduced effectiveness of the catalyst.

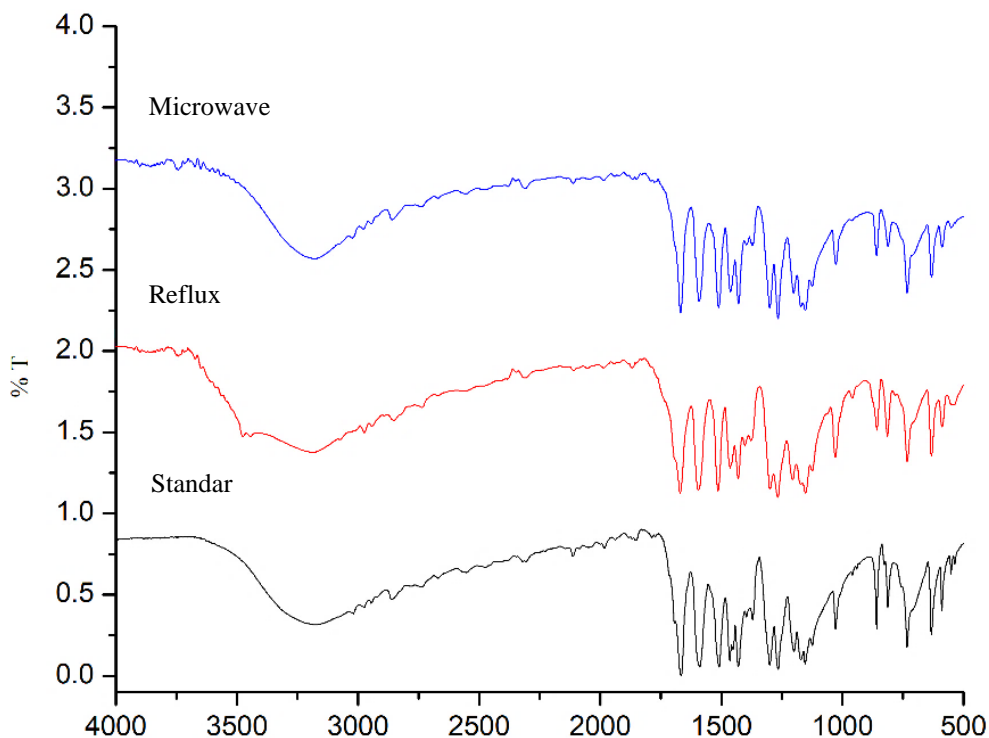


Figure 10. FTIR spectra of vanillin using microwave, reflux, and vanillin standard

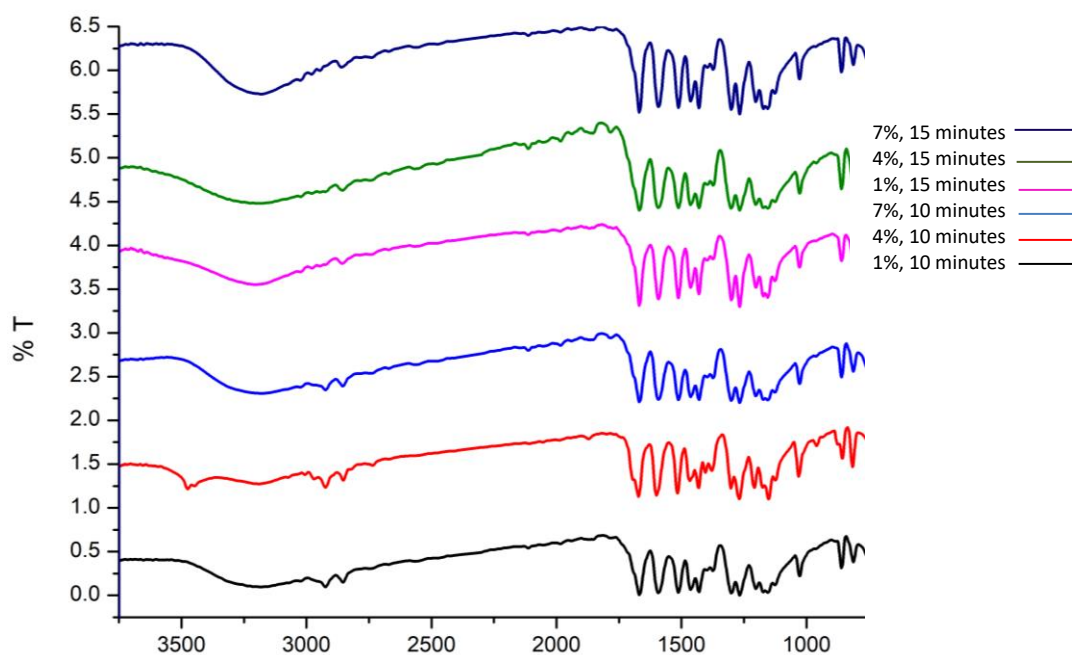


Figure 11. FTIR spectra of vanillin using the two-step method (microwave)

Table 4. GCMS analysis of vanillin using the two-step method

| | 1% | | 4% | | 7% | |
|---|------------|------------|------------|------------|------------|------------|
| | 10 minutes | 15 minutes | 10 minutes | 15 minutes | 10 minutes | 15 minutes |
| % yield | 1.44 | 2.22 | 1.66 | 7.5 | 1.66 | 10.5 |
| % conversion | 100 | 100 | 100 | 100 | 100 | 100 |
| % selectivity | 53.158 | 44.016 | 60.177 | 67.788 | 64.049 | 48.518 |
| Side products (%) | | | | | | |
| Ethyl (p-hydroxyphenyl) carbonate | 34.536 | - | - | - | - | - |
| Sulfurous acid, cyclohexylmethyl heptyl ester | 12.306 | - | - | - | - | - |
| Hexadecane | - | - | 9.96 | - | 4.286 | - |
| 2H-Pyran-5,6-dicarboxylic acid, 3,4-dimethyl- | - | 55.984 | 10.967 | 32.212 | 10.987 | 51.482 |
| Tridecane | - | - | 4.444 | - | 3.031 | - |
| Oxalic acid, cyclohexylmethyl tridecyl ester | - | - | 5.950 | - | 17.647 | - |
| Octadecane | - | - | 4.273 | - | - | - |
| Tetracosane | - | - | 4.229 | - | - | - |

With a very short reaction time of 10 minutes and 15 minutes, vanillin can be produced with an average selectivity level of 56%. These results are quite good when compared to previous studies, where Garcia-Albar used microwave heating in the synthesis of vanillin by involving a metal catalyst to obtain vanillin with a conversion rate of 50-60% from isoeugenol for 30 minutes (García-Albar et al., 2021). In addition to Garcia-Albar, the results obtained in Optimum conditions in this study 4% CoO/ZnAl₂O₄ catalyst for 15 minutes proved to provide a better percent selectivity and conversion than the results obtained by Marquez who received vanillin with a selectivity rate and conversion rate of 65% for 15 minutes (Marquez-Medina et al., 2018a). CoO/ZnAl₂O₄ has a selectivity level which is good because it has several active sites that interact during the reaction. This is because when a metal oxide is combined with a spinel, there will be a rearrangement of chemical bonds on the surface of the host oxide, which in turn can change the electronic properties of the metal oxide. The role of the catalyst is not only able to speed up the reaction time by lowering the activation energy, but the catalyst also makes it easier for the sample in this case eugenol to react with nitrobenzene. Where the mechanism of the oxidation reaction that occurs on the surface of the catalyst is predicted to start when isoeugenol needs to release the H atom in the

hydroxy group to form isoeugenol ions. The O atom in the isoeugenol hydroxy group interacts with Zn²⁺ and Co²⁺ which are positive sites on the CoO/ZnAl₂O₄ catalyst so that the O atom will be more electronegative. At the beginning of this reaction step, there is also an interaction between the H atom attached to the hydroxy group and the O atom in CoO/ZnAl₂O₄ so that the H atom can be easily separated. Furthermore, the catalyst plays a role again at the time of breaking the bond in the formation of an aldehyde group, where the positively charged N atom interacts with the O atom which is a positive side on the CoO/ZnAl₂O₄ catalyst so that the N atom becomes easily attacked by OH⁻ and the double bond moves to the other side of the catalyst. atom O. The source of OH⁻ can come from KOH or H₂O. These two interactions cause isoeugenol with the oxidizing agent to interact more easily.

The side products within 10 minutes are more diverse are 2 to 6 different compounds, while the reaction that is carried out for 15 minutes only produces 1 side product. This is because the isoeugenol which was reacted for 10 minutes had not fully reacted with the catalyst or other reagents. In addition, the nitrobenzene used is a good electrophilic reagent, so when isoeugenol is not fully converted to vanillin, the remaining compounds will react with nitrobenzene to form other compounds.

Table 5. The ratio of vanillin in optimum conditions

| No | Catalyst | Time | Heat source | conversion | % selectivity | |
|----|---|--------|--------------|------------|---------------|---------------|
| | | | | | Vanillin | Side products |
| 1 | Fe/Al-SBA-15 (Franco, De, Balu, Romero, <i>et al.</i> , 2017) | 2 h | Conventional | 90 | 55 | 45 |
| | | | | 69 | 66 | 34 |
| 2 | Nb/Al-SBA-15 (Franco, De, Balu, Romero, <i>et al.</i> , 2017) | 2 h | Conventional | 61 | 63 | 37 |
| | | | | 60 | 32 | 68 |
| 3 | Fe/RGO (Franco, De, Balu, Garcia, <i>et al.</i> , 2017) | 2 h | Conventional | 93 | 50 | 50 |
| | | | | 67 | 74 | 26 |
| 4 | Co/RGO (Franco, De, Balu, Garcia, <i>et al.</i> , 2017) | 1 h | Conventional | 93 | 50 | 50 |
| | | | | 67 | 74 | 26 |
| 5 | FeSBA-15HSO ₃ ^{BM} (Ostovar <i>et al.</i> , 2018) | 1 h | Conventional | 93 | 50 | 50 |
| | | | | 67 | 74 | 26 |
| 6 | CuO/MgAl ₂ O ₄ (Rahmanivahid <i>et al.</i> , 2019) | 2 h | Conventional | 67 | 74 | 26 |
| | | | | 53 | 46 | 54 |
| 7 | CuO/MgFe ₂ O ₄ (Rahmanivahid <i>et al.</i> , 2019) | 5 h | Conventional | 81 | 100 | - |
| | | | | 64 | 100 | - |
| 8 | CuO/MgAl ₂ O ₄ (Rahmanivahid <i>et al.</i> , 2019) | 8 h | Conventional | 81 | 100 | - |
| | | | | 64 | 100 | - |
| 9 | CuO/MgFe ₂ O ₄ (Rahmanivahid <i>et al.</i> , 2019) | 8 h | Conventional | 81 | 100 | - |
| | | | | 64 | 100 | - |
| 10 | Co ₃ O ₄ (Jha & Rode, 2013) | 6 h | Conventional | 80 | 98 | 2 |
| | | | | 100 | 100 | - |
| 11 | *CoO/ZnAl ₂ O ₄ | 2 h | Conventional | 100 | 100 | - |
| | | | | 100 | 95.12 | 4.88 |
| 12 | Cu-MINT (García-Albar <i>et al.</i> , 2021) | 30 min | Microwave | 69 | 66 | 34 |
| | | | | 75 | 65 | 35 |
| 13 | FeMag-160 (Marquez-Medina <i>et al.</i> , 2018b) | 15 min | Microwave | 77 | 64 | 36 |
| | | | | 81 | 57 | 43 |
| 14 | FeMag-170 (Marquez-Medina <i>et al.</i> , 2018b) | 15 min | Microwave | 80 | 56 | 44 |
| | | | | 100 | 60.177 | 39.823 |
| 15 | *4% CoO/ZnAl ₂ O ₄ | 10 min | Microwave | 100 | 60.177 | 39.823 |
| | | | | 100 | 67.788 | 32.22 |

* = Catalyst in this research

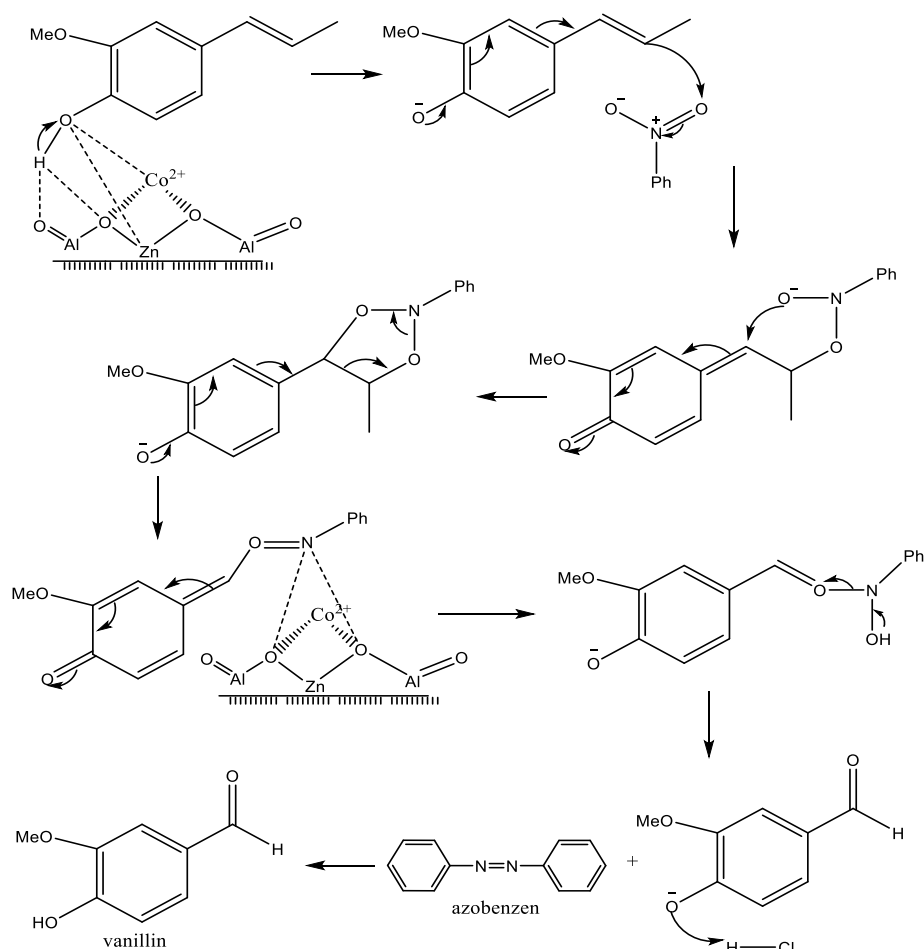


Figure 12. Prediction of vanillin oxidation mechanism reaction using CoO/ZnAl₂O₄ catalyst

The difference in percent conversion and selectivity of vanillin produced in this study and other studies is described in **Table 5**. Compared with vanillin produced in previous studies, vanillin produced in this study has a very good conversion rate of 100% and a high selectivity value of 100 % with a reaction time of 2 hours using a conventional heater, and 67.78% for 15 minutes using a microwave heater. In addition to the conversion and selectivity values, the by-products produced in this study were 0% for the synthesis reaction with conventional heating for 2 hours, and 33.22% using a microwave for 15 minutes. The by-products are 2H-Pyran-5,6-dicarboxylic acid,3,4-dimethyl (**Table 4**).

The vanillin oxidation reaction using CoO/ZnAl₂O₄ catalyst is predicted to occur on the surface of the catalyst as shown in Figure 12. The mechanism reaction starts when isoeugenol needs to release hydrogen on the hydroxy groups to form isoeugenolate ions. The oxygen in the isoeugenol hydroxy group interacts with Zn²⁺ and Co²⁺ which are positive sites on the catalyst so that the oxygen will be

more electronegative. At the beginning of this reaction, there is also an interaction between the hydrogen attached to the hydroxy group and the oxygen in catalyst so that the hydrogen can be easily released. Furthermore, the catalyst plays a role again at the time of breaking the bond in the formation of the aldehyde group, in which the positively charged nitrogen interacts with the oxygen which is the positive site on the CoO/ZnAl₂O₄ catalyst so that the nitrogen becomes easily attacked by OH⁻ and the double bond moves to the other side of the oxygen. The source of OH⁻ can come from KOH or H₂O. These two interactions make it easier for isoeugenol to interact with the oxidizing agent. The isoeugenol used in the oxidation stage is isomerized crude containing cis and trans-isoeugenol without any purification. In its mechanism, both cis and trans isoeugenol undergo oxidation reactions, but the possibility of trans-isoeugenol to undergo oxidation to vanillin is greater. This is due to stereochemical factors such as geometric structure and degree of polarity.

4. CONCLUSIONS

The CoO/ZnAl₂O₄ catalyst was successfully synthesized by combining CoO and ZnAl₂O₄ spinel as catalyst support using the impregnation method based on FTIR, XRD, and SEM-EDX analysis. The CoO/ZnAl₂O₄ catalyst provides high catalytic activity, as seen from the high percentage of selectivity, conversion, and percent yield of vanillin produced in the vanillin synthesis process. Where the resulting selectivity value is higher than other catalysts, with a conversion value of 100%, 48-100% selectivity, and 2.7-10.5% yield percent. In addition, the use of microwaves has also been shown to influence the vanillin synthesis process, where the required time is 10-15 minutes with a conversion rate of 100% and a selectivity of 60% vanillin. The use of a CoO/ZnAl₂O₄ catalyst with the help of a microwave is proven to produce vanillin with high selectivity and in a shorter time compared to previous studies. In the future, it will be necessary to carry out further research on the synthesis of vanillin at different lengths of time and use other oxidizing agents to reduce by-products.

ACKNOWLEDGMENTS

This work is supported by Lembaga Pengelola Dana Pendidikan (LPDP) Indonesia.

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