Catalytic depolymerization of lignin from wood waste biomass over natural sourced ZSM-5 catalysts

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Abstract. Lignin isolated from wood waste biomass, contains 61.07 % of lignin, was converted to vanillin using ZSM-5 catalysts. Prior to use, wood waste biomass was delignified to enrich its lignin contents followed by added 10 % H2SO4 to isolate the lignin such as solid black material. Three types of ZSM-5 catalysts i.e. hierarchical ZSM-5, NiO/hierarchical ZSM-5 and CuO/hierarchical ZSM-5 zeolites were used as catalysts in this study. Hierarchical ZSM-5 zeolite was prepared through TPAOH template synthesis methods followed by PDDAM as secondary template. Silicate and aluminate source based on a natural source to form hierarchical ZSM-5 zeolite. Hierarchical ZSM-5 zeolite is modified with NiO and CuO by using impregnation method with Ni nitrate and Cu nitrate solution followed by calcination at 550 °C. The characterization of catalysts employed FTIR, XRD, and SEM-EDX. The reaction was carried out in 200 mL-batch reactor at 100 °C, 150 °C, 200 °C, 250 °C and 300 °C in the presence of ethanol and water (v/v) for 30 min. CuO/hierarchical ZSM-5 zeolite gave the highest % yield of vanillin as product (4.68 %) followed by NiO/hierarchical ZSM-5 zeolite (3.82 %) for the variation of temperature, compared to other ZSM-5 catalysts.

Keywords: Zeolite, ZSM-5, lignin conversion, heterogeneous catalysts, biomass

1. Introduction
The human population worldwide is continued to grow at a high rate, that implicates, the percentage of global energy used to be increased rapidly. Biomass and CO2 are the alternatives for common sources energy form such as fossil feedstocks. Utilization of biomass could increase the energy supply in the future, reducing the CO emissions of fossil feedstock, and providing source of platform chemicals[1].

Lignocellulose biomass is mainly contained with cellulose (31–42 %), hemicellulose (10–25 %), and lignin (15–33 %) [2]. Cellulose contained in lignocellulosic biomass can be used as the raw material for producing levulinic acid [3]. The development of optimizing the use of cellulose from biomass is growing rapidly. To obtain cellulose from lignocellulosic biomass, delignification pretreatment, a process of separating lignin and cellulose was carried out. Lignin is quite dominant in lignocellulosic biomass, similar to the amount of cellulose but is still rarely used optimally.

Lignin in lignocellulose could be converted into more useful or value-added chemical products using zeolites as catalysts. Lignin undergoes several reactions such as oxidative catalysis, pyrolysis, hydrogenation or depolimeration which produces several compounds such as vanillin, syringol, 4-ethyl guaicol, 4-ethyl phenol, guaiacol, phenol, and phenol compounds [4]. For instance, vanillin, one of
phenolic compounds which contains different functional groups, including aldehyde, hydroxyl, and ether, is the most widely used flavoring agents in the world [5].

Increasing the lignin conversion in lignocellulosic biomass requires optimization. The catalyst in lignin depolymerization must increase the conversion and suppress char formation. One of the industrial heterogeneous catalysts often used is zeolite because of its alkaline nature, having active sites, and also having porosity. Zeolites, such as ZSM-5, are ideally used as catalysts because of their uniform pore size, large surface area, and the typical structure and selectivity of their reactions [6].

Wannmolee et al. reported the degradation of lignin into monomeric phenols using homogeneous catalyst (i.e. sulfuric acid) and heterogeneous catalyst (i.e. H-Y zeolite) for the degradation of lignin produced phenol 0.68 % and vanillin 0.22 % [4]. Milovanovic et al. have identified the variations of metal oxides as catalysts supported by natural ZSM-5 in lignin conversion reactions to produce phenolic products with the best liquid phase yield of 34.8 % for NiO/ZSM-5 catalysts and the best phase yields gas by 17.6 % for the CuO/ZSM-5 catalyst [7]. Furthermore, Mullen et al. reported the overall conversion of dominant content in lignocellulosic biomass using H-ZSM-5 and K-ZSM-5 as catalysts for maximum yield of around 13 % for phenols [8]. Wang et al. investigated the effect of particle on the catalytic activity of H-ZSM-5 zeolite in conversion of lignin to phenols in the supercritical ethanol-water gave 6 % yield of phenols [9]. On the other hand, in this study, the hierarchical ZSM-5 using silicate and aluminate natural source from natural Bayat zeolite with ludox as silica synthetic source was prepared [10].

This study focused on the synthesis of natural sourced ZSM-5 zeolite and prepared the other catalysts. The three types of catalysts were used, including hierarchical ZSM-5, NiO/ZSM-5, CuO/ZSM-5. It is aimed to compare the activity and selectivity of each heterogeneous catalyst in catalytic depolymerization of lignin. To the best of our knowledge, the utilization of wood waste biomass as lignin source in the production of phenolic compound such as vanillin using heterogeneous catalyst from natural sourced ZSM-5 is rarely reported.

2. Materials and method

2.1. Materials
Natural zeolite applied in this research was received Bayat Klaten, Central Java, Indonesia. Indonesian kaolin from Belitung island was supplied by PT. Aneka Kaoline Utama (Belitung Island, Indonesia). Sodium hydroxide (pellet, 99 %), hydrogen peroxide (30 %), nitric acid, acetic glacial acid, hydrochloric acid, sodium acetate trihydrate, trisodium citrate dihydrate, sodium bicarbonate, Ni(NO3)2.6H2O, Cu(NO3)2.3H2O, ethanol and methanol were procured from Merck (Germany). Sodium aluminate (99 %), tetrapropylammonium hydroxide (TPAOH, 1 M), and polydialydimethyl ammonium chloride acrylamide (PDD-AM, 10 %) were obtained from Sigma Aldrich, US. Phosphoric acid (97 %) was procured from PT. Smart Lab Indonesia. Distilled water was used in the preparation of each solution.

2.2. Synthesis of hierarchical ZSM-5 zeolite based on natural source
Natural zeolite and natural Belitung kaolin were sieved to the size of about 100 μm and were treated using the activation, purification, fragmentation and calcination processes [10, 11]. Synthesis of hierarchical ZSM-5 zeolite based on natural source was conducted using natural Bayat zeolite and natural Belitung kaolin as its silicate and aluminate source. Bayat natural zeolite and natural Belitung kaolin were mixed with H2O, stirred overnight. Furthermore, TPAOH was slowly added into the reaction mixture under vigorous stirring at 100 °C. Then, the mixture pH solution was adjusted to ±11 for 3 h. Afterward, certain amount of cationic PDD-AM was slowly added into the reaction mixture at room temperature and stirred for 48 h. After stirring, the mixture was transferred into an autoclave for further crystallization at 170 °C for 144 h. The product was washed with H2O and filtered and calcinated at 550 °C for 5 h and characterized using XRD, FTIR, SEM, EDS and SAA instruments.
2.3. Preparation of hierarchical NiO/ZSM-5 zeolite and CuO/ZSM-5 zeolite

Hierarchical NiO/ZSM-5 zeolite was prepared using wet impregnation method with Ni²⁺ solution (from nickel nitrate hexahydrate) for 24 h at 25 °C into a calcined hierarchical ZSM-5 zeolite. The mixture was dried at 110 °C for 5 h followed by calcination at 550 °C. Hierarchical CuO/ZSM-5 zeolite was prepared using wet impregnation method with Cu²⁺ solution (from copper(II) nitrate trihydrate) and similar preparation steps with that for NiO/ZSM-5 zeolite.

2.4. Pre-treatment of wood waste biomass and Lignin isolation

Wood waste biomass was subjected to the delignification pre-treatment. Delignification was carried out by refluxing the biomass with 10 % NaOH solution (1:25, m/v) at 150 °C for 90 min while stirring. The lignin content was determined before and after pre-treatment using the procedure outlined in our previous study [3]. After that, the suspension was filtered and the black filtrate (black liquor) was obtained. Then, to the black liquor, 10 % H₂SO₄ was added until the precipitate was formed. After that, the precipitate was filtered and washed with distilled water until neutral, then the precipitate was dried.

2.5. Catalytic depolymerization lignin from wood biomass

Lignin depolymerization reaction was carried out by using a stainless steel batch reactor with a capacity of 200 mL containing pressure and temperature in an autoclave reactor. The 0.25 gram of lignin was dissolved in a solvent of water and ethanol (50:50, v/v) mixture, then it was transferred into the reactor along with a certain amount of catalyst. The reactor was flowed with N₂ gas and filled with 2 atm at room temperature. Initially, the mixture was stirred at 100 rpm until reached the desired condition at variation temperature 100–300 °C, then the stirring speed is increased at the desired time. After the reaction completed, the reactor was cooled. After that, the reaction mixture was filtered and then the obtained filtrate was analyzed using High Performance Liquid Chromatography (HPLC).

3. Results and discussion

3.1. Characterization of raw materials

3.1.1. XRD patterns. Raw natural Bayat zeolite diffraction pattern shown in figure 1a shows that there is a peak at 2θ of 9°, 22° and 25°. Fragmentation process aims to destroy the zeolite frame structure. It damages the Si-O-Si and Si-O-Al bonds into Si and Al active and tetrahedral structures XRD pattern of both raw and fragmented natural Bayat zeolite are similar to the pattern reported by Krisnandi et al. [12]. XRD patterns of raw natural Belitung kaolin in figure 1a shows that the structure of raw kaolin was still intact after pretreatment, then, it was changed in the pattern of extracted silica, leaving some high intensity peaks around 2θ 15–35°, indicating an amorphous structure. XRD patterns of kaolin before and after pretreatment are similar to the pattern reported by Krisnandi et al. [11].

3.1.2. FTIR spectra. Figure 1b presents the raw and after pretreated materials’ spectra. Both natural Bayat zeolite and kaolin showed two peaks between 3800 cm⁻¹ and 3600 cm⁻¹, typically for stretching hydroxyl groups structure such as -Si-OH and -Al-OH. It was typical of phyllosilicate alumina silicates [13]. The two materials also have 1650–1600 cm⁻¹ band, which are attributed to the adsorbed water molecule bending vibration (H-O-H). A group of bands at1120–1020 cm⁻¹ related to T-O asymmetric stretching vibration groups, and in 920-925 cm⁻¹, attributed to T-OH groups, were observed. This result shows disruptive of-Al-O-Si-in kaolin was transformed in the extracted silica, indicating the aluminum removal. The opposite occurs in the fragmented natural bayat zeolite, -Si-OH group at 3700–3490 cm⁻¹ was reduced, indicating the reduced amount of silica.
3.2. Catalyst characterization

3.2.1. XRD patterns. ZSM-5 was synthesized from natural sourced fragmented zeolite of natural Bayat zeolite and extracted silica from kaolin. XRD analysis was conducted to confirm the structure of the as-synthesized ZSM-5 zeolite. Its diffraction pattern (figure 2a) has typical peaks of standard ZSM-5, there are two sharp peaks between \(2\theta = 7–10^\circ\) and three peaks between \(2\theta = 22–25^\circ\) [14]. For NiO characteristic of \(2\theta\), there are two peaks between 35–40° and one peak between 47–50° (JCPDS Card No.47-1049) [15]. CuO has a typical pattern of two sharp peaks at \(2\theta = 35–40^\circ\) and one peak at 47–50° (JCPDS Card No.01-089-2529) [16]. In general, all samples indicated that the preparation of all catalysts was successful.

3.2.2. FTIR spectra. Figure 2b shows the FTIR spectra of as-synthesized ZSM-5 and its derivatives. In the ZSM-5 FTIR spectra before calcination, peak at the wave number 2950–2850 cm\(^{-1}\) and

![Figure 1](image1.png)

**Figure 1.** (a) XRD pattern and (b) FTIR spectra of raw natural Bayat zeolite, fragmented natural Bayat zeolite, raw kaolin and extracted silica from kaolin.

![Figure 2](image2.png)

**Figure 2.** (a) XRD pattern and (b) FTIR spectra of catalysts.
1450–1350 cm⁻¹ are the vibration and absorption band of C-H bend vibration [17]. This absorption band was from a TPAOH as primary template used in the synthesis of ZSM-5 and it was removed by the calcination process to form pores. ZSM-5 after calcination indicated the loss of organic template as the intensity of C-H vibration and C-H bending band absorption decreased. In this case, modification of both NiO and CuO to hierarchical ZSM-5 zeolite did not cause any damage to the structure of the ZSM-5 zeolite.

The FTIR spectra shows the main functional groups of the zeolite from vibration of OH stretching at around 3300 cm⁻¹, OH bending vibration at 1600 cm⁻¹, T-O-T (T = Si/Al) bending and stretching asymmetry vibration at 1300–750 cm⁻¹ and double five-ring vibration at 550 cm⁻¹ which are the infrared characters of ZSM-5 [14].

3.2.3. Scanning electron microscopy. SEM characterization provided morphology information of the catalysts. Figure 3 clearly shows the surface morphology and crystal size of the calcined ZSM-5. Natural sourced ZSM-5 zeolite synthesized using TPAOH template has a coffin-like morphology and has hexagonal crystal geometry [18].

3.2.4. EDX analysis. The composition of the as-synthesized hierarchical ZSM-5, NiO/ZSM-5 and CuO/ZSM-5 were determined with EDX analysis, shown in table 1. It shows that the Si/Al ratio of the hierarchical ZSM-5 zeolite was 18.15. The elemental analysis of NiO/ZSM-5 and CuO/ZSM-5 shown in table 1 gave the mass percent of nickel and copper around 10 %, which are close to the desired amount in this work (c.a. 10 %).

3.3. Catalytic Depolymerization of lignin to phenolic compound

Lignin was isolated from raw wood waste biomass. Before isolation, the raw biomass contained 26.48 % of lignin and after isolation process, the lignin content was increased to 61.07 % (from its black liquor). In this study, vanillin was chosen as the produced of phenolic compound that was analyzed. It has some functional groups including aldehyde, hydroxyl, and ether due to the phenolic compound functional group in it [19]. Figure 4 shows that the optimal temperature to produce the highest

### Table 1. Catalysts variations of hierarchical ZSM-5 and its modification.

| Material       | Si  | Al  | Cu  | Ni  | Si/Al mol ratio |
|----------------|-----|-----|-----|-----|-----------------|
| ZSM-5          | 48.01 | 2.82 | -   | -   | 16.36           |
| NiO/ZSM-5      | 40.08 | 2.43 | -   | 9.84 | 15.84           |
| CuO/ZSM-5      | 36.55 | 2.49 | 11.03 | -   | 14.10           |

![Figure 3. SEM images of (a) ZSM-5, (b) NiO/ZSM-5 and (c) CuO/ZSM-5.](image-url)
Figure 4. Percent yield of product catalytic reaction of depolimerization lignin to vanillin with temperature and catalysts variation.

vanillin yield is 200 °C. It is suggested that the catalyst used was started to actively depolymerize lignin at 200 °C [4]. However, at temperature above 200 °C the percent yield of vanillin decreased. It may be due to vanillin was degraded or oxidized further to produce other products [20].

Furthermore, figure 4 shows that the reaction without the presence of catalyst shows a lower % yield compared to the reaction with catalysts. This is because the presence of a catalyst will lower the activation energy, causing the reaction to take place faster and the optimal yield of vanillin. In this work, each type of catalyst give a different percentage yield of vanillin, depends on the elements contained in each catalyst. In addition, several studies on the vanillin conversion turned out to provide the optimal results with ZSM-5 catalysts [7] and Cu catalysts [21] followed by Ni catalysts [22], then two of the composite study here gave the highest product yield. Followed by NiO/ZSM-5 catalysts and ZSM-5 catalysts without impregnation. This supports the elemental analysis using EDS characterization that CuO/ZSM-5 has the smallest Si/Al ratio, thereby increasing its acidity, will give the greater % yield from lignin depolymerization.

4. Conclusion
Phenolic compounds such as vanillin can be obtained from lignin derived from lignocellulose biomass through the heterogeneous catalytic depolymerization reactions. The lignin depolymerization reaction can take place at a temperature of 200 °C in the presence of hierarchical ZSM-5 zeolite catalysts variation and its modification with Ni or Cu. The highest percent yield of vanillin is given by CuO/ZSM-5 followed by NiO/ZSM-5 and ZSM-5.

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