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Vanillin production from lignin degradation using hydrothermal method over Fe_2O_3/Al_2O_3 catalysts

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Abstract

Vanillin synthesis from lignin degradation using catalytic hydrothermal process over Fe_2O_3/Al_2O_3 catalyst was investigated. The Fe_2O_3/Al_2O_3 catalyst was prepared by wetness impregnation. The prepared catalysts were characterized by using XRD and BET method. The lignin degradation reaction was carried out in a batch high-pressure reactor. The effects of initial pressure, reaction temperature, and catalyst loading on vanillin yield were studied. It was found that an increasing of temperature gave an increasing of vanillin yield. However, the increasing of pressure and a number of catalyst loading showed the decrease of vanillin production due to the oxidation of produced vanillin to another product. The highest vanillin concentration of 8.54 mg/L was obtained at 160 ºC, 2 bars, and 0.5 g of the catalyst.

Keywords: Vanillin, Lignin degradation, Catalyst, Hydrothermal

1. Introduction

Nowadays, vanilla is largely demanded because it can be used in various industries such as a flavoring and coloring agent in foods and pharmaceuticals. The production of vanilla is produced in two ways which are from vanilla pods and chemical processes. Vanilla produced from vanilla pods are not enough to meet demand. The production of vanilla using chemical process become interesting. A product from the chemical process is called vanillin, which is the main element of vanilla.[1] Raw materials used in the chemical process are commonly guaiacol and lignin. Guaiacol is used in the petrochemical industry which is a limited resource [2]. The lignin [3] is a rather more interesting because lignin can be obtained from a renewable source. Thus, the lignin becomes more interesting than guaiacol. The lignin is mainly present in plants such as softwood, hardwood, and herbaceous plants. Since it is the main component of wastewater in pulp mills called black liquor. Previously, the treatment of this type of waste is burning to recover the chemical residues in the recovery boilers. The disadvantage is the destruction of high-value lignin in the recovery process. Borges da Silva et al [4] proposed the production of vanillin from Kraft lignin in black liquor. The production process was to take black liquor into extraction process to bring out the lignin, then took the lignin into vanillin production by lignin oxidation. However, vanillin yield was quite low, it must be improved before applying in the industry.

The important point to improve the yield of vanillin from lignin oxidation is the degradation of lignin. The degradation of lignin are various such as pyrolysis[5], photo-degradation[6] and hydrothermal[7]. From reaction above the most appropriate lignin degradation for vanillin-synthesis is hydrothermal due to the mild operating condition. There were many researchers studied the lignin degradation using a homogeneous catalyst. $Fe^{3+}$and Co^{2+} were used as homogeneous catalysts for degradation of lignin [8-9]. They showed the good catalytic performance and gave some of the vanillins after the reaction, however, the presence of metal ions in the product after the reaction might contaminate in product and yield the toxicity. Sales et al [10] reported the heterogeneous catalyst, supported Palladium on alumina which was a good catalyst for the lignin degradation at the mild condition, however, it was very expensive. The researchers are interested in using the supported Fe on alumina for the synthesis of vanillin at the mild condition. Thus, this research was to study the decomposition of lignin to vanillin using the catalyst Fe_2O_3/Al_2O_3 at the conditions of 100-160 ° C and pressure of 2-10 bars to get a higher yield of vanillin.

2. Materials and methods

2.1 Preparation and characterization of Fe_2O_3/Al_2O_3 catalyst

Catalyst support, alumina, was prepared by the precipitation method. The aluminum nitrates purchased

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from (AR Grade, QRec, New Zealand) was used as a precursor. 100 grams of aluminum nitrate was dissolved in 100-ml of distilled water, then the pH of the solution was adjusted by adding ammonium solution until the gel was formed. The obtained gel was washed and dried at 100 ° C for 12 hours, followed by calcination in a muffle furnace at 600 °C for 4 hours. $Fe(NO_3)$ purchased from (AR Grade, QRec, New Zealand) as a precursor for iron was coated on prepared alumina by wetness impregnation method[11]. The coated sample was dried in an oven at 100 °C for 12 hours and calcined in a muffle furnace at 350 °C for 4 hours.

The phase structures of prepared catalyst and alumina were identified by X-Ray Diffractometer (XRD; Model D8 Discover, Bruker AXS, Germany). The BET surface areas were conducted in an N_2 gas adsorption apparatus at 77 Kelvin (Model ASAP 2010).

2.2 Hydrothermal process

Decomposition of lignin by the hydrothermal process was carried out in a high-pressure reactor. The desired amount of catalyst (0.5 g or 1.5 g) was added into the reactor containing 500-ml of lignin solution with an initial concentration of 500 milligrams per liter. The air was introduced into the reactor until the reactor pressure reached 2 or 10 bars and then began heating the reactor until hit evaluated temperature in the range of 100°C to 160°C. During the reaction, the solution in the reactor was sampling every 15 minutes for 120 minutes.

The concentrations of vanillin in the samples were analyzed by High-Performance Liquid Chromatography (HPLC; e2695, Separation Module, Water, USA) equipped with a SunfireC_{18} column. The carrier phase, a mixture of methanol and 1% citric acid (30:70, V/V), was used at a flow rate of 0.75 mL per minute.

3. Results

3.1 Catalyst characterization

The catalyst was characterized to determine the phase structure of iron in the catalyst with XRD as shown in Figure 1. According to figure 1, the results showed that the phase of iron was Fe_2O_3 [12]. The BET surface area of Fe_2O_3/Al_2O_3 catalyst was 171.71 m^2/g while the BET surface area of support, Al_2O_3, which had a surface area of 256.87 m^2/g.

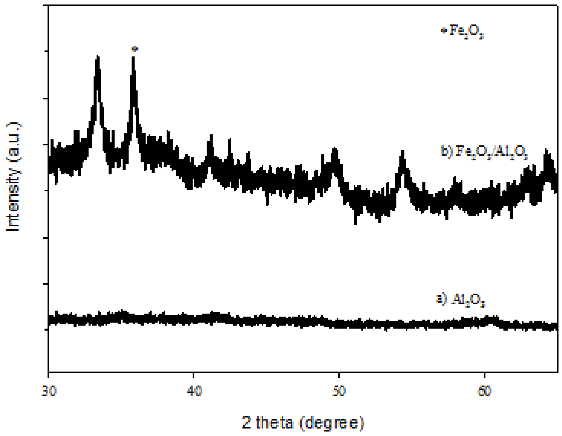

Figure 1 XRD patterns of prepared catalysts; a) Al_2O_3, b) Fe_2O_3/Al_2O_3

3.2 Vanillin synthesis from lignin degradation

The amount of 0.5 and 1.5 g of catalytic was used in lignin degradation test under a pressure of 2 bars at various temperatures. The vanillin concentrations yielded at various temperature and time when using 0.5 g and 1.5 g of catalysts shown in Figure 2 and Figure 3, respectively. It was found that the use of less amount of catalyst (0.5 g) had better trends than 1.5 g of catalyst. It could be explained by the excess of catalyst gave a fast reaction and then this reaction was induced to any by-product. The amount of 0.5 and 1.5 g of catalyst was used in lignin degradation under the pressure of 10 bars, is displayed in Figure 4 and Figure 5, respectively. This experiment has a similar result with a first section. The amount of 0.5 g of catalyst was obtained higher vanillin product than the adding of 1.5 g of catalyst. This cause could be the excess of the catalyst. The both of experiment is indicated to similarly result while the reaction under pressure at 2 bars has an interesting trend due to the operating reaction under pressure at 10 bars was induced to oxidation of vanillin and this cause occurred by-product from vanillin. The reaction at temperature 160 ºC (Figure 2) is shown the trend which it would be increased however the operation at 10 bars (Figure 4) at the same temperature for 60 min was showed the high of vanillin product after that the vanillin product was decreased. Furthermore, the compared of pressure between 2 and 10 bars in the same condition is shown a small different but in a long time, the operation at 10 bars has the low vanillin product due to the excess of oxygen was induced the vanillin to another by-product (Figure 4 and Figure 6).

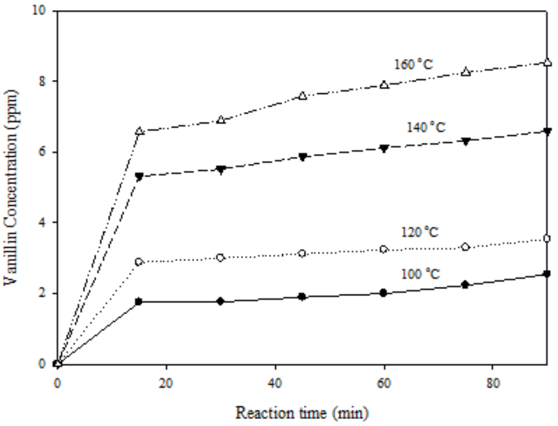

Figure 2 Relationship between vanillin concentration and time at the catalyst loading of 0.5 gram and 2 bars

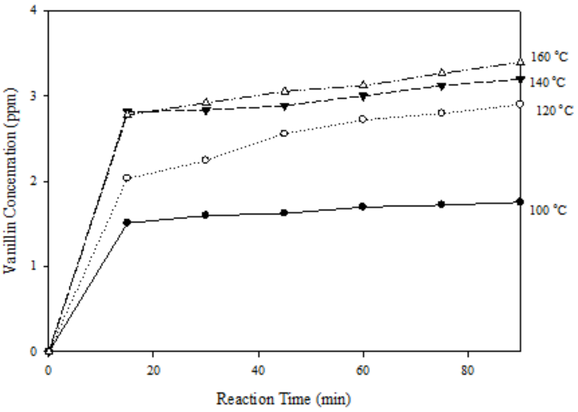

Figure 3 Relationship between vanillin concentration and time at the catalyst loading of 1.5 gram and 2 bars

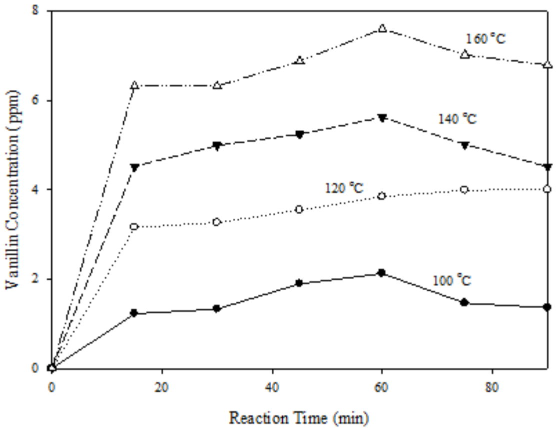

Figure 4 Relationship between vanillin concentration and time at the catalyst loading of 0.5 gram and 10 bars

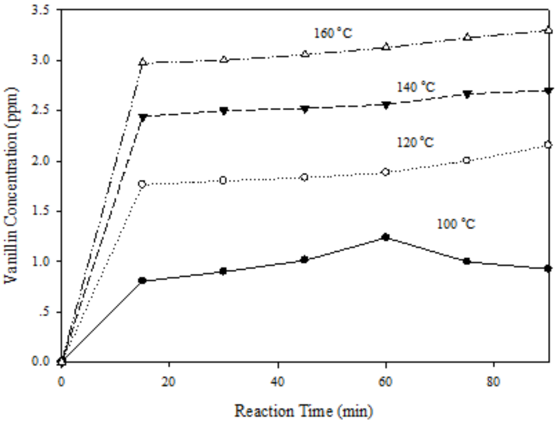

Figure 5 Relationship between vanillin concentration and time at the catalyst loading of 1.5 gram and 10 bars

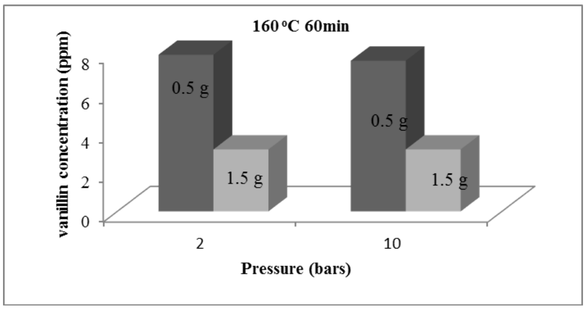

Figure 6 Relationship between vanillin concentration and pressure at 160°C for 60 mins

4. Conclusions

The synthesis of vanillin from lignin by hydrothermal process shows the maximum operating condition with the amount of 0.5 g of catalyst, temperature at 160 ºC, pressure at 5 bars and reaction time for 90 min which this condition was obtained the maximum of vanillin product about 8.54 mg/L and the trend of vanillin product was increasing. Furthermore, the result is indicated the decreasing of vanillin product by the excess of catalyst and the excess of oxygen.

5. Acknowledgements

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