

The Variation of Catalyst and Carrier Gas on Anisole Deoxygenation Reaction

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Abstract. This research aims to determine the best catalyst and carrier gas in anisole deoxygenation reaction. The reaction was carried out over a flow system with a variation of catalyst CoMo A (CoMo/USY reduction), CoMo B (CoMo/USY oxidation-reduction), and CoMo C (CoMo/ZAA oxidation-reduction). In addition, variation of carrier gas nitrogen and hydrogen was investigated. The result was analyzed using Gas Chromatography-Mass Spectroscopy (GC-MS). The deoxygenation anisole result showed that CoMo A catalyst with hydrogen as the carrier gas has the highest total product yield (50.72 %), intermediate product yield (38.49 % in phenol and 6.99 % in benzaldehyde), and deoxygenation yield (5.24 %). The CoMo C catalyst exhibited the most selective deoxygenation product. The nitrogen carrier gas with the CoMo C catalyst has the best selectivity of benzene product (93.92 %).

1. Introduction

Bio-oil is an alternative fuel produced from biomass pyrolysis and has the potential to replace conventional fuels. Bio-oil has the advantage of being environmentally friendly when compared to conventional fuels because when combusted, bio-oil produces less pollution than fossil fuels. Bio-oil produces emissions of NO_x and SO_x lower than fossil fuels[1].

Bio-oil contains phenolic compounds (phenol, catechol, guaiacol, syringol, and their derivatives) which are came from the decomposition of lignin fractions of biomass. The major functional groups of lignin derived phenolics are hydroxyl (–OH) and methoxyl (–OCH₃) [2]. Anisole or methoxybenzene has a methoxy group (one of the major functional groups of lignin phenolics) to be used as a bio-oil model compound [3].

Bio oil has many undesirable characteristics such as high viscosity, low stability, high water content, high acidity, and corrosiveness. Those characters caused due to a high of molecular weight and oxygen content. So it cannot be used directly as engine fuel. High oxygen content of bio-oil also causes a low heating value being, which is only half value heating of fossil fuels [4], therefore it is necessary to upgrading bio-oil. Current, bio-oil upgrading techniques include deoxygenation [1].

The process of deoxygenation reaction needs the catalyst to accelerate of the reaction and optimize the product obtained. [5] Reported the product of anisole hydrodeoxygenation reaction with thermal treatment (without catalyst) obtained a lower yield of 0.31% than using a Mo-Co/ USY catalyst of 1.07 %. In the process of deoxygenation reaction, the catalyst serves to absorb the reactant molecule, so reactant reactions occur on the surface of the catalyst and produce the desired product. Different catalyst characters will result in different catalytic activities [2,4,3,6–11]. High temperature (250–400



°C) and high pressure (3–5 MPa) hydrotreating of bio-oil over sulfide CoMo catalyst can effectively reduce the oxygen content of phenolics in the bio-oil [2]. Reference [10] investigates anisole deoxygenation using Pt/Al₂O₃ catalyst. The result showed that the total deoxygenation product is 93.6 %. [12] reported the deoxygenation reaction using CoMo/Al₂O₃ catalyst obtained a total product yield of 96.8 %. This indicates that the CoMo/Al₂O₃ catalyst has a higher yield than Pt/ Al₂O₃. The effect of CoMo catalysts supported on various materials such as activated carbon, γ -Al₂O₃, HZSM-5, MCM-41, and SBA-15 has been studied by [4]. Among all the supported CoMo catalysts, CoMo/MCM-41 has the best catalytic activity. The size of medium pore diameter (66 Å) leads to a more effective and stable reaction in CoMo catalyst. Based on the studied, in this work used metal Co and Mo with variations catalyst support and methods that have synthesized by some researchers. The catalysts used include CoMo/USY reduction (CoMo A) [13], CoMo/USY oxidation-reduction (CoMo B) [14], and CoMo / ZAA oxidation-reduction (CoMo C) [15]. In the process of testing, the catalyst is formed into pellets to be easily separated from other products.

The catalytic activity may use a flow system [2] and a batch system [9]. The catalytic reaction using the flow system requires a carrier gas to assist the diffusion of the reactant to the catalyst surface. According to [16] the carrier gas also has an effect on the selectivity and stability of the catalyst, as well as being able to as reactants in the formation of the product [1]. [17] found that an increase in H₂ carrier gas pressure could improve the stability of the HZSM-5 catalyst for cracking n-heptane at 270 °C. In addition, [3] reported anisol conversion using H₂ carrier gas is better than using He carrier gas in the same reaction. This is influenced by better catalyst stabilization if the reaction uses H₂ carrier gas compared to He gas. [18] found that higher benzene selectivity was observed when using N₂ compared with H₂ as carrier gas.

2. Experimental

2.1. Materials

The supported material that used in this research was NH₄-USY which was purchased from Tosoh Inc (Japan), and natural zeolite obtained from Klaten, Indonesia. Other materials were ammonium heptamolybdate and cobalt nitrate hexahydrate purchased from Merck (Germany). Anisole as model compound (methyl phenyl ether, Merck) had a minimum purity of 99%. Nitrogen and hydrogen gas purchase from PT. Samator Surabaya.

2.2. Methods

Three types of catalysts were prepared. The preparation of the CoMo A catalyst follows [13], the CoMo B catalyst preparation was carried out by [14], and the CoMo C catalyst preparation was carried out by [15].

The deoxygenation catalytic was carried out by drying the catalyst at 110 °C for 3 hours. The catalyst samples are inserted into reactor, then further thermocouple in furnace heated with temperature 350 °C. After a temperature of 100 °C, anisole is included in feed reactor. Then the thermocouple on anisole was turned on at 160 °C and the carrier gas was set at 5 mL/ min. The deoxygenation reaction is carried out for around 1 h. The product is identified using GC-MS to know the type and quantity of the product.

3. Result and Discussions

3.1. Total Product Yield

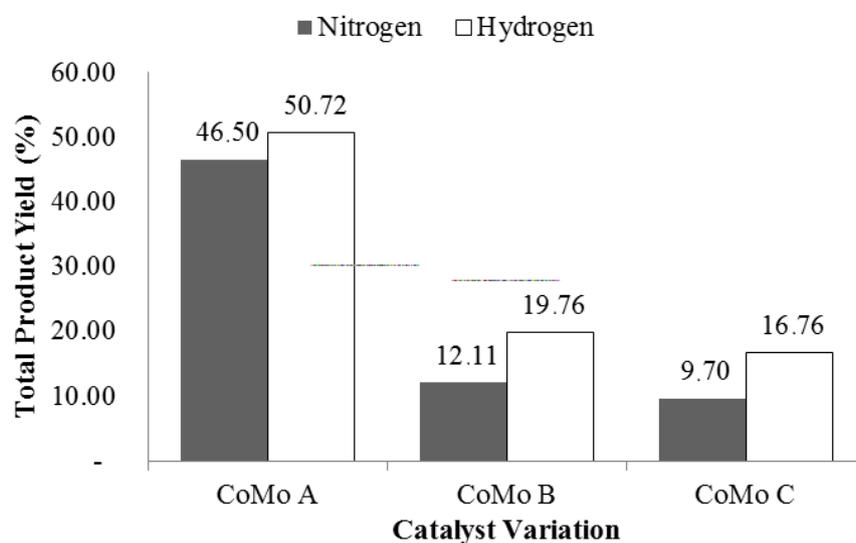
Catalysts with different components (metal and support) will have different catalyst characteristics and different catalyst activity as well [8]. The catalyst character that influences the catalytic activity can be investigated from the acidity, surface area, the metal contents, and the average pore radius shown in Table 1. Catalytic activity using a flow system requires a carrier gas to react with the surface of the catalyst. The type of carrier gas can affect the deoxygenation process of anisole from its properties.

Table 1. Characteristics of CoMo catalysts [13–15]

Catalyst	Weight (%)		Total acidity (mmol/g)	Specific surface area (m ² /g)	Average pore radius (Å)
	Co	Mo			
CoMo A	0.49	0.69	11.21	497.00	16.23
CoMo B	0.764	0.244	8.61	362.55	19.07
CoMo C	0.229	0.148	0.31	25.48	15.19

Based on figure 1, it can be seen that the highest total product yield is anisole deoxygenation with CoMo A catalyst. The high catalytic performance of CoMo A is estimated because it has the highest acidity compared to other catalysts. The order of total acidity values is among CoMo A > CoMo B > CoMo C (see table 1). This trend is similar to the yield of the total product obtained. The higher acidity value of a catalyst indicates the more acidic sites that contributes to anisole hydrogenolysis [19]. This is according to the research that reported by [8]. [8] says that the higher acidity of the catalyst can increase catalyst activity.

The hydrogen as carrier gas has a higher total product yield than the nitrogen carrier gas in each catalyst, as shown in figure 1. The nitrogen carrier gas has an inert property, so it does not react to the catalytic process and acts only as a carrier gas [18]. The inert property caused by the covalent bonds originating from the three lone pairs electrons in the N₂ molecule. Unlike nitrogen gas, hydrogen gas may react which causes hydrogen not only acts as a carrier gas but also takes a part in hydrogenation and hydrogenolysis reactions to produce deoxygenation products.

**Figure 1.** Total product yield on catalyst and carrier gas variations

3.2. Intermediate Product Yield

The yield of intermediate products in this study was represented by the largest intermediate product of phenol and benzaldehyde. [20] also stated in his research that the conversion of anisole over zeolites produces intermediate products such as benzaldehyde and phenol. The CoMo A catalyst has the highest intermediate product yield compared to the other catalysts, as shown in figure 2. This is influenced by Co and Mo metals on the catalyst. The Mo metal is present on the CoMo A catalyst is thought to be a CoMoO₄ particle so it is possible to bind the low oxygen, whereas the Co metal that support on the catalyst is not much (see table 1). Consequently, the available hydrogen (both in the

reactant and carrier gas) can't be split and reacts for the hydrogenolysis process, so the reaction stops at the formation of intermediate products. Therefore, at the end of the reaction there are more intermediate products obtained. [19].

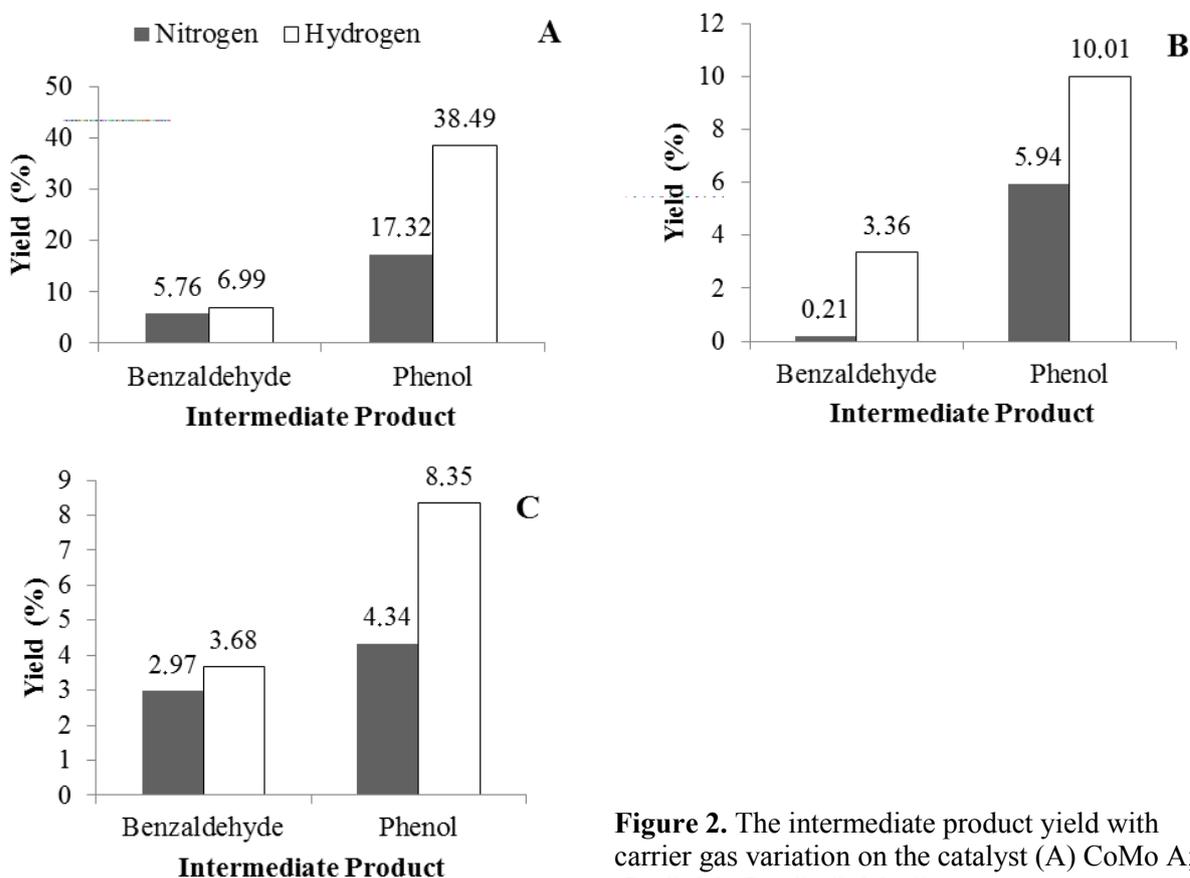


Figure 2. The intermediate product yield with carrier gas variation on the catalyst (A) CoMo A; (B) CoMo B; (C) CoMo C

The catalytic test using three different catalysts produces the highest intermediate product with hydrogen as a carrier gas in both benzaldehyde and phenol products. The use of a hydrogen carrier gas should be capable of providing hydrogen which can be broken down by Co metal and acting as a reactant to the hydrogenolysis reaction. The phenol product should be lower than the benzene product. Excessively low hydrogen flow rates result in high phenol yields.

3.3. Deoxygenation Product Yield

The yield of the anisole deoxygenation product is shown in figure 3. Deoxygenation thermally produces a lower deoxygenation product than catalytic deoxygenation. This case proves that the use of catalysts can improve deoxygenation products. The catalyst can increase the rate of reaction by lowering the activation energy through a different reaction mechanism. So that the reaction can run faster and obtain better results. The CoMo A catalyst has the highest total deoxygenation product yield than any other catalyst. The high value of deoxygenation product yield can be influenced by the large surface area of the catalyst and the amount of Mo metal contain on each catalyst. The order of the surface area and the amount of Mo metal contain are: CoMo A > CoMo B > CoMo C (see table 1). This trend is similar to the yield of anisole deoxygenation product obtained. Large surface area indicates that active site dispersion in the catalyst is increasing [21].

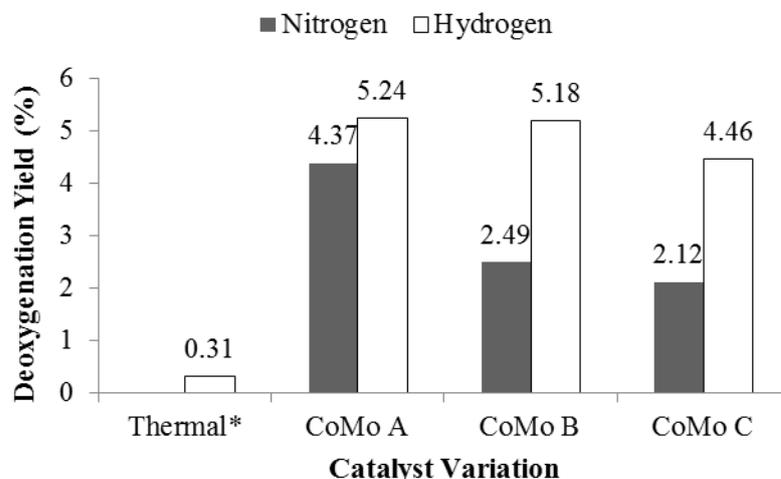


Figure 3. The yield of deoxygenation product by variation of carrier gas on thermal treatment [5] and variation of catalyst

The catalytic test using hydrogen carrier gas results the highest deoxygenation product yield for each catalyst. The hydrogen carrier gas in the catalytic test not only acts as a carrier gas but may also act as a reactant. Metal Co in catalyst can break down hydrogen gas into free hydrogen, then react to form deoxygenation product. In contrast to hydrogen, nitrogen can not participate in the deoxygenation process of anisole and only pure acts as a carrier gas. In the deoxygenation with N₂ carrier gas, hydrogen that plays a role in the hydrogenation reaction is only provided by the support. The other hand, hydrogen supplied by the support are limited in number. so, its deoxygenation product yield is low.

3.4. Selectivity Deoxygenation Product

Figure 4 shows the selectivity of the anisole deoxygenation product using CoMo A, CoMo B, and CoMo C catalysts with hydrogen and nitrogen carrier gas. The CoMo C catalyst produces only two oxygen-free products benzene and toluene. This suggests that CoMo C catalyst is the most selective because it is able to inhibit the formation of the other products. It is possible because of the CoMo C catalyst has the smallest catalyst pore (15.19 Å) when compared with catalyst CoMo A and CoMo B. In a small pore radius, the interaction between the reactants and the catalyst is more effective and selective [22].

The selectivity of benzene products was higher when using nitrogen as carrier gas on CoMo A (75.55%) and CoMo C (93.92%) catalyst. However, hydrogen carrier gas has the highest selectivity of benzene product of 76% on CoMo B catalyst. This difference is cannot be explained.

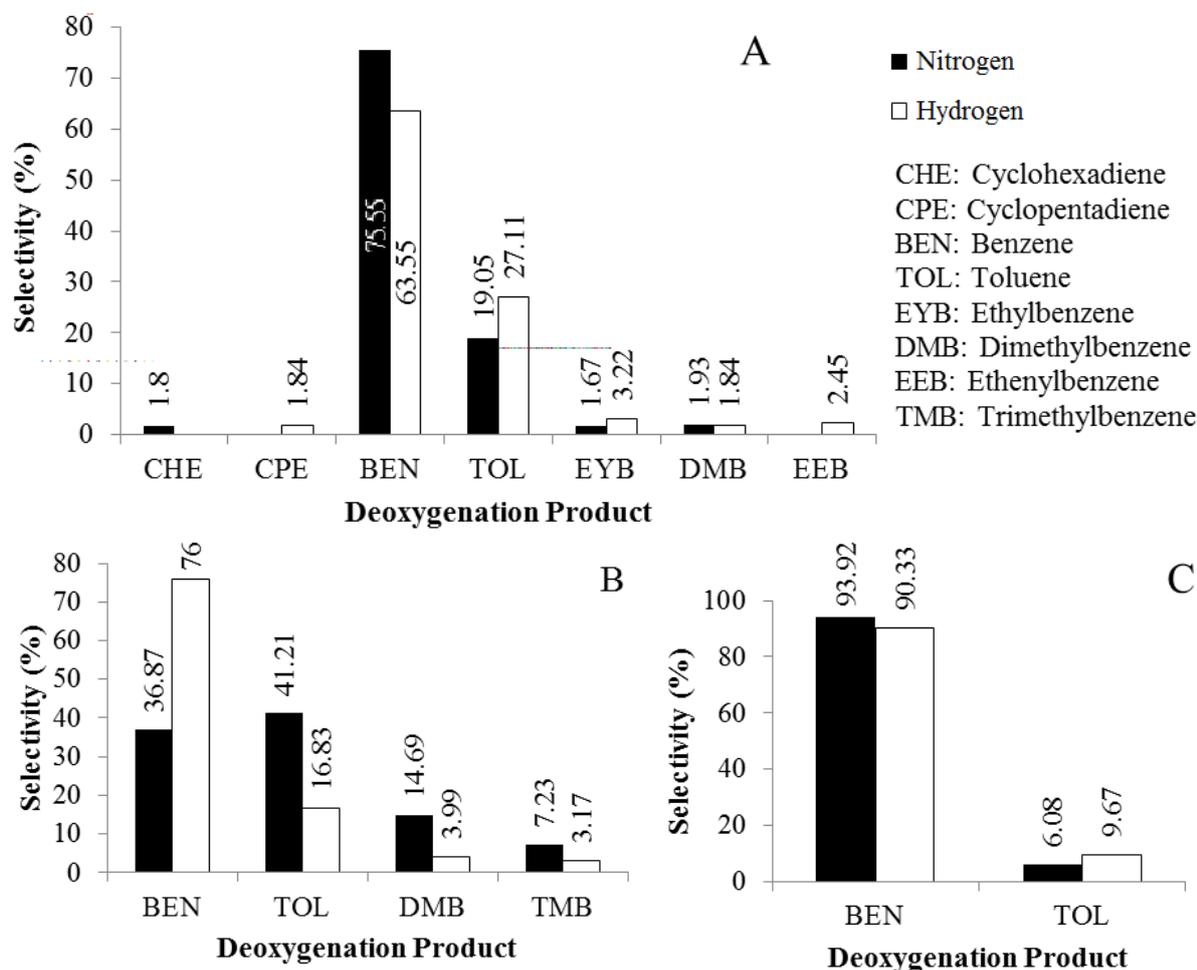


Figure 4. Selectivity of anisole deoxygenation product with CoMo A (A), CoMo B (B), and CoMo C (C) catalysts.

4. Conclusion

The CoMo A catalyst with hydrogen carrier gas has better activity. This is indicated by the result of the highest total product yield and deoxygenation product yield of 50.72 % and 5.24 %, respectively. In addition, anisole hydrodeoxygenation by using CoMo A catalyst and hydrogen carrier gas also has highest intermediate product yield of 38.49 % in phenol and 6.99% in benzaldehyde. The highest selectivity of benzene product is anisole deoxygenation by using a CoMo C catalyst and nitrogen carrier gas, i.e 93.92%.

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