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# Product distribution from catalytic conversion of biomass over $B_2O_3/\gamma-Al_2O_3$ catalyst

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**Abstract.** The catalytic conversion of biomass has been studied by using a conventional fixed-bed reactor. The mixed catalyst is prepared by impregnation method followed by calcination of the catalyst. The  $B_2O_3/\gamma-Al_2O_3$  catalyst composition used in the biomass catalytic conversion process is varied to study the effect on its product distribution. In addition, catalyst variations were performed to test the catalytic effect in producing the target products, so that the optimum catalyst composition to maximize the target products is known. The catalyst composition of  $B_2O_3$  in the mixed catalyst used was 0%, 5%, 10%, 20%, and 25% wt. The use of  $B_2O_3/\gamma-Al_2O_3$  mixed catalyst can convert the small oxygenate compounds produced at the thermal decomposition step of biomass into aromatic hydrocarbon compounds. In addition, other groups of compounds were also observed with different product distributions where the differences were affected by the composition of the mixed catalyst used. Experimental results show that addition of  $B_2O_3$  content up to 20% wt gives the highest catalytic effect with the main product being aromatic hydrocarbons. The decrease in catalytic effect occurs with the addition of 25% wt  $B_2O_3$  content.

## 1. Introduction

In the future, many see the potential of biomass as an alternative to fossil fuels that can produce similar petroleum products. Various hydrocarbon compounds can be produced from biomass through biological, biochemical, and thermochemical processes [1]. Pyrolysis technology is one of the most promising thermochemical routes in biomass conversion to meet interest in the production of bio-fuels and chemicals [2]. Biomass pyrolysis will produce products consisting of bio-oil, char, and gas. Bio-oil is a product of biomass pyrolysis which has great potential to be utilized. However, the bio-oils are of poor quality. They are thermally unstable, degrade with time, acidic, have a low heating value, and are not compatible with existing petroleum-derived oils [3]. Bio-oils must be catalytically upgraded if they are to be used as a conventional liquid transportation fuel [4].

The catalytic conversion of biomass is one of the proven ways that can be used to improve the quality of bio-oil. Basically, this process involves the biomass thermal decomposition stage as occurs in conventional pyrolysis process, but with the presence of catalyst. Catalyst addition to this process led the biomass pyrolysis vapor consisting of small oxygenate compounds enter the pores of the catalyst in which they are converted to  $CO_2$ ,  $CO$ , water, coke, and aromatic hydrocarbon compounds. The conversion of catalytic biomass into aromatic compounds has been successfully performed using zeolite catalysts [5,6]. Introduction of zeolite catalysts into the pyrolysis process can convert



oxygenated compounds generated from pyrolysis into aromatics [7]. The zeolite catalyst has an advantage in performing a shape-selective reaction where the operating conditions and proper selection of the catalyst can maximize the production of aromatic hydrocarbons. However, zeolite catalyst is relatively expensive.

Therefore, in this work to convert biomass into aromatic hydrocarbon compounds mixed catalyst of  $B_2O_3/\gamma-Al_2O_3$  are used which is readily available and more cost-effective. The  $B_2O_3/\gamma-Al_2O_3$  catalyst system is an interesting catalyst and is rarely being researched.  $B_2O_3$  is an acidic solid while  $\gamma-Al_2O_3$  is a solid that can act as an ionic conductor.  $B_2O_3$  has a small particle size as  $\gamma-Al_2O_3$  has a large enough surface area ( $\pm 250 \text{ m}^2/\text{g}$ ), so that the solid particles  $B_2O_3$  can be well dispersed on the solid surface  $\gamma-Al_2O_3$ . Sato [8] reported that the addition of  $B_2O_3$  may form a  $BO_4$  specimen which can add the amount of bronsted acid to the catalyst that plays a role in the formation of aromatic hydrocarbon compounds. Five variations of  $B_2O_3$  addition in  $B_2O_3/\gamma-Al_2O_3$  mixed catalyst used in this work were 0%, 5%, 10%, 20%, and 25% wt. The composition of the catalytic conversion product of biomass will be analyzed to determine the effect of  $B_2O_3$  percentage in the mixed catalyst on the catalytic effect in forming the target product.

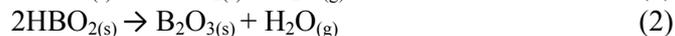
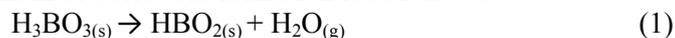
## 2. Experimental

### 2.1. Materials

The type of biomass used as a feed in this experiment is a corncob. Corn cobs must be grounded to a particle size of 1-3 mm by a grinding machine. Corncob is then dried by oven at  $60^\circ\text{C}$  for 5 hours to reduce its water content to  $<10\%$  of total mass. For a typical run, 1 gram of corn cob and 3 gram of catalyst-quartz sand mixture was used.

The catalyst material used is a solid containing boron oxide and  $\gamma-Al_2O_3$ . Boron oxide is obtained from boric acid ( $H_3BO_3$ ) which acts as the precursor of the oxide. Boric acid will decompose into water vapor and metaboric acid ( $HBO_2$ ) at a temperature of  $170^\circ\text{C}$ . Further heating at  $300^\circ\text{C}$  will decompose  $HBO_2$  into water vapor and microcrystalline boron oxide ( $B_2O_3$ ) solids.

The reaction mechanism of boric acid formation is as follows:

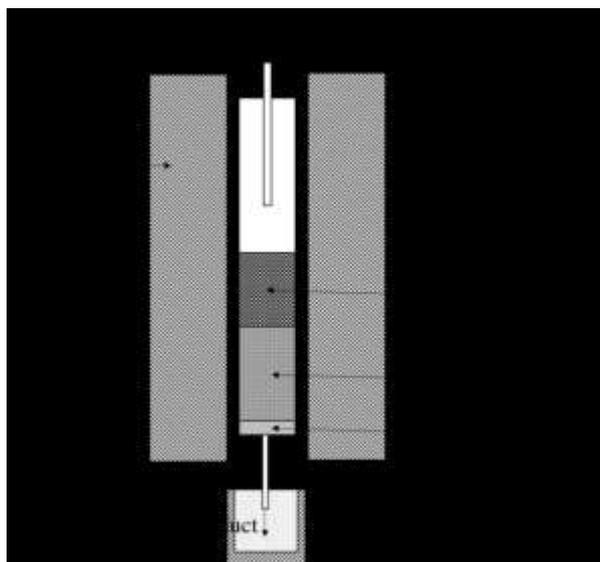


The catalyst used in each catalytic conversion process with different composition variations is as much as 1 gram. The catalyst used cannot be excessive so as not to cover the flow of  $N_2$  gas which will cause the blockage of flow in the tube. However, if the amount of catalyst used is too small it will cause the catalytic conversion process to be less than optimal.

The preparation of the catalyst is carried out by the impregnation method which steps can be described as follows: preparing the boric acid solution by dissolving the solids into the deionized water maintained at  $75^\circ\text{C}$  to completely dissolved solids. The solution is used to impregnate the  $\gamma-Al_2O_3$  solid by adding  $\gamma-Al_2O_3$  solids to the boric acid solution. While stirred and maintained at  $75^\circ\text{C}$  so that the water solvent was all evaporated and dried, a solid was obtained which was a mixture of borate solid acid-  $\gamma-Al_2O_3$ . To obtain a mixture of  $B_2O_3/\gamma-Al_2O_3$ , the solids were calcined under atmospheric conditions respectively at a temperature of  $300^\circ\text{C}$  and  $600^\circ\text{C}$  for 2 hours each.

### 2.2. Methods

The biomass catalytic conversion was performed in a stainless-steel reactor tube. The tube reactor has a length of 300 mm and a diameter of 12 mm. The effluent gas product of biomass catalytic conversion was at the bottom end of the reactor tube. This open-ended tube was successively placed from the bottom with some quartz wool, a mixture of 3 grams of quartz catalyst sand, and 1 gram of corn cobs. Quartz sand was mixed with active catalyst to help uniform heat in all parts of the catalyst. Biomass feeds are placed over a mixture of sand-quartz catalysts as fixed beds. Therefore, the non-catalytic fast pyrolysis took place first and then the primary product vapors were upgraded when they passed through the catalyst layer.



**Figure 1.** Schematic diagram of experimental apparatus for biomass catalytic conversion

Biomass catalytic conversion was performed at 500°C and 1 atm pressure. N<sub>2</sub> gas with a flow rate of 30 ml/min was used as an inert pyrolysis gas. The N<sub>2</sub> gas will remove the air present in the reactor tube before the catalytic conversion reaction takes place. N<sub>2</sub> gas will also force the pyrolysis gas vapor to move downward and enter the pores of the catalyst in which they are upgraded. Schematic diagram of experimental apparatus for biomass catalytic conversion was shown in Figure 1.

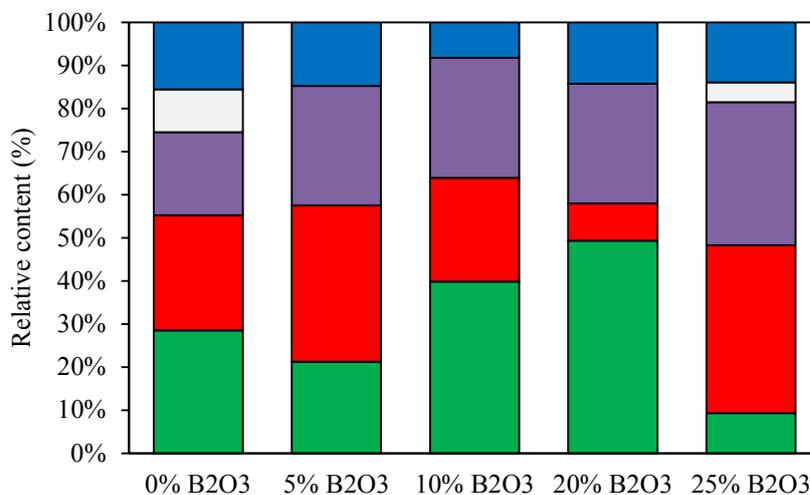
The gas product from catalytic conversion was captured by a system called cold gas absorption. Cold gas absorption is a system in which there is a container containing a solution of ethanol pro analyst and is provided with a cooling jacket to cool the solution. The gas product was streamed into the cold gas absorption system and will be in direct contact with the cold ethanol pro analyst solution so that it undergoes quenching. The product gas was then dissolved together with the solvent. The chemical compositions of the products were analyzed, and their relative contents were determined and discussed

### 3. Results and Discussion

Pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and its mixtures with 5%, 10%, 20%, and 25% B<sub>2</sub>O<sub>3</sub> additions were used as bed materials for catalytic conversion of corncobs. Figure 2 shows the product distribution resulting from catalytic conversion of corncobs comprising groups of compounds such as aromatics, acids, furans, phenols, and others. The result shows that the addition of B<sub>2</sub>O<sub>3</sub> to the catalyst mixture caused the aromatic percentage of the product to increase to its maximum value as the percentage of B<sub>2</sub>O<sub>3</sub> increased from 0% to 20%. On the use of 20% B<sub>2</sub>O<sub>3</sub>, relative aromatic content was obtained with a value of 49.32%, increased from 28.46% with pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a catalyst. When the percentage of B<sub>2</sub>O<sub>3</sub> in the mixed catalyst exceeded 20%, the relative aromatic content decreased as shown in the study where a relative aromatic content of 9.27% was obtained with 25% B<sub>2</sub>O<sub>3</sub> as catalyst.

Pyrolysis of corncobs without the use of a catalyst will produce large molecules of oxygenates. These oxygenates cannot enter the micro-pores of the B<sub>2</sub>O<sub>3</sub> catalyst in which pyrolysis vapor upgrading occurs. As these oxygenates are unable to enter the catalyst micro-pores, this oxygenate molecule undergoes polymerization and forms a large molecule that we know as coke on the surface of the catalyst. It causes the catalyst to be deactivated due to the formation of coke that cover the catalyst surface and block the entrances of the catalyst pores.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is a mesoporous catalyst which has strong cracking characteristic and can convert the large-molecule oxygenates into small-molecule oxygenates [9]. The combination of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub> catalysts will make pyrolysis vapors containing

a lot of large molecules of oxygenate being converted into small molecules of oxygenate first and then enter the micropores of  $B_2O_3$  catalyst to be converted into aromatics.

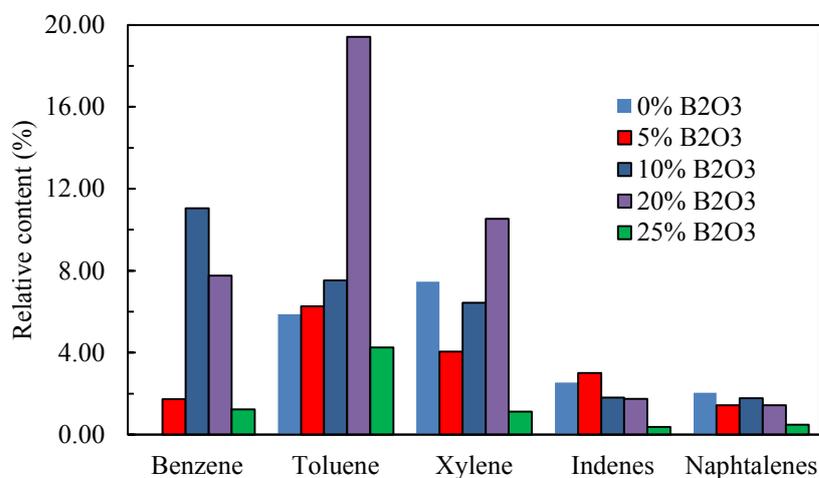


**Figure 2.** Product distribution from catalytic conversion of biomass over five different composition of  $B_2O_3/\gamma-Al_2O_3$  catalyst: 0%  $B_2O_3$ , 5%  $B_2O_3$ , 10%  $B_2O_3$ , 20%  $B_2O_3$ , and 25%  $B_2O_3$ . Key—Aromatics: green, acids: red, furans: purple, phenols: white, and others: blue.

Figure 2 also shows that different percentages of  $B_2O_3$  in the catalyst mixtures will result in difference of aromatic composition in the product. Experimental result show that  $B_2O_3$  is a type of catalyst that can convert small molecules of oxygenate to aromatic hydrocarbon compounds in which the percentage of aromatic hydrocarbons increases with the addition of  $B_2O_3$  percentages in the catalyst mixtures. However, this increase reaches its maximum value with a 20%  $B_2O_3$  catalyst and begins to decrease as the catalyst adds past 20%. So, it can be said that 20%  $B_2O_3$  in  $B_2O_3/\gamma-Al_2O_3$  catalyst mixture is the best catalyst system to convert biomass to aromatic hydrocarbon.

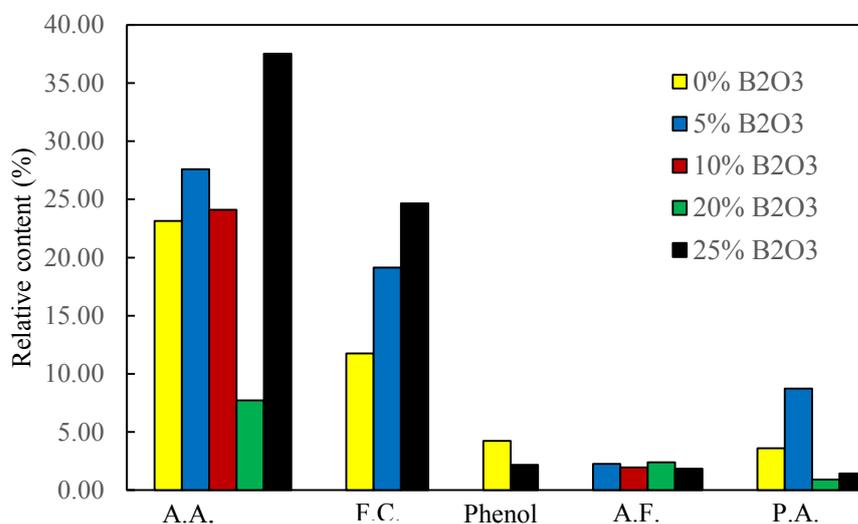
The addition of  $B_2O_3$  should increase the catalytic effect of the catalyst mixtures in converting biomass to aromatic, since the amount of bronsted acid sites will also increase linearly. However, the results of the research showed a decrease in the percentage of aromatic products with the addition of  $B_2O_3$  percentage above 20%. The addition of  $B_2O_3$  can lead to the formation of a layer that covers  $\gamma-Al_2O_3$  which causes the surface area of  $\gamma-Al_2O_3$  to decrease further. The reduced surface area of the catalyst causes the less contact area between  $\gamma-Al_2O_3$  and pyrolysis vapors. This leads to the ability of  $\gamma-Al_2O_3$  in cracking large molecules of oxygenate into smaller ones to decrease so that fewer oxygenate molecules can be converted to aromatic by  $B_2O_3$ .

Figure 3 shows the effect of the percentage of  $B_2O_3$  on the catalyst mixtures used in the catalytic conversion of corncob to the distribution of aromatic products present in the product. Benzene does not form on pure  $\gamma-Al_2O_3$  catalyst and reaches its maximum value at 5%  $B_2O_3$  and then decreases with the addition of  $B_2O_3$ . The addition of  $B_2O_3$  increases toluene production and reached its maximum value at 20%  $B_2O_3$  where toluene was a major component in the aromatic group. Xylene increased with the addition of  $B_2O_3$  in the range of 5-20%. The content of indene and naphthalene in the product was reduced by the addition of  $\gamma-Al_2O_3$ . It can be inferred from the experimental results that  $B_2O_3$  catalyst mixtures were selective on the formation of benzene, toluene and xylene compounds in which there were only small amounts of indene and naphthalene (less than 4%). Monocyclic aromatic reactions with oxygenate fragments produce naphthalene, indene, and their derivatives [10]. Naphthalene is a type of polycyclic aromatic hydrocarbons (PAHs) whose relative contents are worth noting because PAHs were a potent toxin and had a high carcinogenicity. However, the resulting PAHs in catalytic biomass catalysts with  $B_2O_3/\gamma-Al_2O_3$  catalysts were much lower than in the ZSM-5 catalyst [11].



**Figure 3.** Relative content of aromatics from catalytic conversion of biomass over five different composition of B<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst: 0% B<sub>2</sub>O<sub>3</sub>, 5% B<sub>2</sub>O<sub>3</sub>, 10% B<sub>2</sub>O<sub>3</sub>, 20% B<sub>2</sub>O<sub>3</sub>, and 25% B<sub>2</sub>O<sub>3</sub>.

The effect of B<sub>2</sub>O<sub>3</sub> percentage on catalytic conversion of biomass to relative content from oxygenated species is shown in figure 4. The experimental results show that relative content in most oxygenated species is decreasing with the addition of B<sub>2</sub>O<sub>3</sub> percentage. Biomass pyrolysis will produce vapour containing thermally stable oxygenate molecules such as phenols, furans, ketones, acids, aldehydes and others. Thermally stable molecular oxygenate is an intermediate in the production of aromatic.



**Figure 4.** Relative content of oxygenated species from catalytic conversion of biomass over five different composition of B<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst: 0% B<sub>2</sub>O<sub>3</sub>, 5% B<sub>2</sub>O<sub>3</sub>, 10% B<sub>2</sub>O<sub>3</sub>, 20% B<sub>2</sub>O<sub>3</sub>, and 25% B<sub>2</sub>O<sub>3</sub>.

The results showed that increasing percentage of B<sub>2</sub>O<sub>3</sub> in the catalyst mixtures could remove more organic oxygenate compounds in upgraded pyrolysis vapour. These oxygenate molecules were converted to hydrocarbons in the B<sub>2</sub>O<sub>3</sub> micro-pores and remove the oxygen as water, CO and CO<sub>2</sub> through deoxygenation reactions. The 20% percentage of B<sub>2</sub>O<sub>3</sub> can dramatically decrease the oxygenate content such as acetic acid and propionate acid and remove furancarboxaldehyde and

phenol. It has been previously discussed that the 20% percentage of  $B_2O_3$  in the catalyst mixtures is the best catalyst system that provides maximum aromatic production, so most of the oxygenate molecules have been converted to aromatic while relative content of oxygenated organic compounds decreased.

#### 4. Conclusions

The catalytic conversion of corncobs with pure  $\gamma-Al_2O_3$  catalyst and its mixtures with the addition of  $B_2O_3$  was performed on a fixed bed catalytic reactor. The  $\gamma-Al_2O_3$  and  $B_2O_3$  catalyst mixtures can be used to produce aromatic hydrocarbon compounds. The maximum aromatic yield of 49.32% can be obtained with 20%  $B_2O_3$ /80%  $\gamma-Al_2O_3$ . The addition of  $B_2O_3$  to the catalyst mixture  $B_2O_3/\gamma-Al_2O_3$  can increase the selectivity of the formation of aromatic compounds such as benzene, toluene, and xylene which reaches its maximum value at 20%  $B_2O_3$ .

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