

## Investigating Pt/Pumice catalyst for efficient 3-methyl-1-butanol conversion

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**Abstract:** The objective of this study was to obtain a modified Pt/pumice catalyst to support the conversion reaction of 3-methyl-1-butanol under specific reaction conditions. To achieve this objective, the first step involved preparing modified pumice catalyst pellets by impregnating them with Pt metal followed by activation at a temperature of 500 °C. The second step involved characterizing the Pt/pumice catalyst, including the surface distribution of Pt metal using SEM. The third step involved conducting the catalyst activity test against 3-methyl-1-butanol in a reactor (furnace) at temperatures ranging from 400 to 500°C with a flow system for the feed. The fourth step involved analyzing the conversion results using GC-MS chromatograms. The research results showed that the Si/Al ratio in the modified Pt/Pumice catalyst using a PtCl<sub>4</sub> solution with a concentration of 0.0321 M for impregnation was 4:1, compared to 4.8:1 for Pt/Zeolite and 3.2:1 for Pt/ABP. The modified catalyst activity test for 3-methyl-1-butanol showed the following conversion results: Pt/Pumice 27.63%, Pt/Zeolite 23.85%, Pt/Black Pumice 14.81%, and for platinum catalyst, the conversion was 22.35%. These results indicated that the highest conversion was observed in the treated sample A-3 under the reaction condition of 450°C. The conversion products analyzed using GC-MS showed the presence of three molecules: 3-methylbutanal, 2-methylbutanal, and anhydrous isobutanoate.

**Keywords:** Modified Pt/pumice catalyst; conversion activity test; 3-methyl-1-butanol

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### INTRODUCTION

The availability of petroleum fuels in Indonesia has been decreasing recently and global fuel prices have been soaring, indicating an energy crisis due to limited availability of conventional energy sources. Alternative energy sources are necessary to address this issue. One of the efforts being made is the conversion of fuel oil into alternative fuel. Fuel is a by-product of sugarcane factories, with its major component being 3-methyl-1-butanol, or isoamyl alcohol. To facilitate the desired conversion reaction, the Pt/pumice catalyst was modified. There are several studies related to alternative energy sources in Indonesia, including biodiesel production from *Jatropha* oil using natural zeolite catalyst klinoptilolite, the analysis of dimethyl ether (DME)

characteristics as a liquid petroleum gas (LPG) fuel substitution for household stove, and the role of fiscal policy to increase energy security. The potential of bioethanol as a substitute for petroleum in Indonesia has also been studied, with lessons drawn from Brazil's bioethanol industry, which has been successful due to massive research and development, effective and strong long-term government commitment, and subsidies for ethanol producers.

Another reason was that 3-methyl-1-butanol was one of the components of fuel produced by sugar factories like the one in Tolangohula Sugar Factory, Gorontalo Province. This isoamyl alcohol was a waste product of sugarcane processing in the factory. The abundance of fuel content every year inspired the author to convert it into an

alternative fuel source through conversion reactions assisted by heterogeneous catalysts such as pumice supported with platinum (Pt).

Pumice was commonly found as fragments ejected during volcanic eruptions, ranging in size from gravel to large chunks. Pumice could also be produced by heating obsidian, causing gases to escape. The required temperature to convert obsidian into pumice was typically around 880°C [1]. The specific gravity of obsidian, originally 2.36, decreased to 0.416 after the treatment, allowing it to float in water. Pumice possessed hydraulic properties and appeared as white-gray to yellowish-red in color. It had a vesicular texture with varying sizes of interconnected or non-interconnected pores and a scoriaceous structure with oriented pores. Sometimes, these pores were filled with zeolite or calcite. The rock was resistant to frost, and it was not highly hygroscopic. It had low thermal conductivity and compressive strength ranging from 30-20 kg/cm<sup>2</sup>. The main composition was amorphous silicate minerals. Other types of rocks with similar physical structures and origins as pumice included pumiceite, volcanic tuff, and scoria. Minerals found in pumice included feldspar, quartz, obsidian, cristobalite, and tridymite [1]. Another unique characteristic of pumice was its ability to chemically filter, making it intriguing to study when modified with specific metals such as platinum (Pt).

The pore properties of pumice and the modified acid active sites were expected to influence the catalyst's performance in the conversion reaction of 3-methyl-1-butanol. Babu, Murthy, and Krishnan (1997) reported that the conversion of 3-methyl-1-butanol using an acid catalyst (reaction dependent on acid centers) HZSM-5 was 87.5%. Priatmoko and Yahya (2014) converted 3-methyl-1-butanol using a Pt/zeolite catalyst (0.5% Pt) with a yield of 19.3% at 400°C. The products of 3-methyl-1-butanol conversion using Pt/zeolite catalyst, through mass spectrometry analysis, were 3-methyl-1-butene, acetone, 2-methyl-2-butene, and 3-methylbutanal. Paputungan and Triyono (2000) studied the Pt/zeolite catalyst (0.25% Pt) in the conversion of 3-methyl-1-butanol, resulting in an 11.31% conversion yield. Several factors that influenced the low conversion yield of 3-methyl-1-butanol conversion included the metal content (Pt), metal adsorption properties on the carrier surface, and reaction conditions.

The suboptimal performance of the catalyst in supporting the conversion reaction of 3-

methyl-1-butanol was an interesting problem to be investigated. Among them were the contributions of pore types and sizes produced during catalyst modification, as well as the optimization of reaction temperature for the occurrence of the reaction. Paputungan (2003) reported the characterization results of the active rock catalyst from Gorontalo, including pore size properties, namely micropores at 23.98%, mesopores at 31.39%, and macropores at 44.63%, with acidity properties ranging from 3.116 to 3.5. Furthermore, [6] reported the characterization results of the naturally active rock catalyst from Gorontalo, supported with Pd metal, with acidity properties of 0.2935 and surface area of 425 m<sup>2</sup>/g. From the various reports above, there was still no adequate data regarding the pore characteristics of the catalyst for maximum adsorption of feed (reactant) within the catalyst. Ideally, the catalyst's pore area should be > 600 m<sup>2</sup>/g, and there should be numerous active sites on its surface to support conversion reactions at high temperatures. This study aimed to create a Pt/pumice modified catalyst to support the conversion reaction of 3-methyl-1-butanol. To achieve this goal, the following steps were conducted: (1) determining the mineral composition of pumice, including Fe, Mn, Cr, Ca, Mg, and Cu, as the research sample, (2) creating a modified pumice catalyst with Pt metal to produce Pt/pumice catalyst with pore properties, crystal structure, and Pt metal distribution that better supported the conversion reaction, and (3) testing the activity of the Pt/pumice catalyst in the conversion reaction of 3-methyl-1-butanol at temperatures of 400-500°C.

## MATERIALS AND METHODS

The pumice was initially analyzed for the content of metals such as Mg, Ca, Cr, Mn, Al, and Fe using the microplasma instrument, MP-AES 4100. Subsequently, the pumice was modified with Pt as a catalyst through a series of steps involving the production of pumice pellets and the modification of the pumice catalyst with Pt metal. The production of Pumice pellets involved several steps. First, the Pumice was finely ground to 80 mesh size. Then, 1% of either dextrin or gum Arabic was added to the ground Pumice and thoroughly mixed. The mixture was slightly moistened with water, using aquades, and prepared for pellet formation using a pelletizer with a cylinder hole diameter of 0.5 cm. A relatively constant pressure of approximately 2 kN was

applied to create the pellets. The Pumice pellets were then dried for 24 hours and subjected to calcination in a furnace at 500°C for 4 hours (first catalyst activation).

In the application of metal impregnation of Pt into Pumice pellets, the process involved several interesting steps. First, a solution was prepared by dissolving 1 gram of solid PtCl<sub>4</sub> in aquades until the solution reached a volume of 100 mL. Second, the active Pumice pellets were immersed in the PtCl<sub>4</sub> solution for 24 hours. After immersion, the pellets were dried at room temperature and then further dried in an oven at around 200°C. The third step involved the calcinations of the Pt/Pumice pellets at a temperature of 500°C in a furnace. The catalyst formed from the platinum and pumice mixture was characterized using SEM. Subsequently, the modified Pt/Pumice

catalyst's activity towards 3-methyl-1-butanol was tested and characterized using GC-MS. These steps provided interesting insights into the development and characterization of Pt/Pumice catalysts and their potential in the conversion reaction of 3-methyl-1-butanol.

## RESULTS AND DISCUSSION

### Content of metal and non-metal of Buol pumice

As a preliminary stage in this research, the composition of the content of the original pumice (PB) from Buol Toli-Toli has been tested. The measurement results using the MP-AES 4100 instrument obtained the metal composition in pumice as shown in the following Table 1.

**Tabel 1.** Metal Content of Buol Pumice (BP)

Sampel	Concentrations (ppm)						
	Ba	Al	Fe	Cu	K	Sr	Mn
BP	5.07	904	20.29	13.78	13.28	45.82	14.32

Buol Pumice (BP) had significantly higher aluminum content, 904 ppm, compared to other metals. Pumice has high aluminum content because it is formed through a geological process that involves volcanic eruptions. When magma erupts and cools into foamy lava, dissolved gases like water vapor and carbon dioxide are released, while the aluminum in the magma is carried along. As the foamy lava cools and hardens into pumice, aluminum becomes part of its mineral composition, especially in the form of aluminum silicate. The aluminum content in pumice can vary depending on its volcanic source, but an understanding of this geological origin helps explain why pumice has a high aluminum content [7]. Pumice is formed through a geological process involving volcanic eruptions [8]. When magma erupts and cools into frothy lava, dissolved gases like water vapor and carbon dioxide are released, while aluminum elements present in the magma are carried along. As the frothy lava cools and solidifies into pumice, aluminum becomes part of its mineral composition, primarily in the form of aluminum silicate. The aluminum content in pumice can vary depending on its volcanic source, but understanding its geological origin helps explain why it has a high aluminum content. Pumice is a volcanic origin rock formed during

explosive eruptions. It has a highly porous structure which is formed by dissolved gases precipitated during the cooling as the lava hurtles through the air [9].

Pumice Buol (BB) has a significantly higher concentration of Al compared to other metals, with a value of 904 ppm [10]. Pumice is a type of volcanic rock that can be found in large deposits in Indonesia, including in the Kali Sambong river in Malang [11], [12]. Several studies have been conducted to evaluate the characteristics of pumice and its potential applications. One study analyzed the metal content in pumice from Gorontalo City and Buol, and found that the levels of Si in Gorontalo and Buol pumices increased with immersion in HNO<sub>3</sub>, while the Al content decreased [10]. Another study evaluated the permeability and resistance characteristics of pumice and other volcanic materials, and found that pumice has a low density and a high permeability coefficient due to its large cavities. A third study investigated the physical and ineralogical characteristics of piroclastic material from Gunung Kelud, including pumice, and found that it can be classified as fine sand based on AASHTO and USCS classifications. The study also found that the specific gravity and porosity of the material were similar to those of sand in general. The table above only showed the metal content because the MP-

AES 4100 instrument could only test for metal content, while semi-metals such as silicon could not be measured. Therefore, the silicon content and other elements of this pumice were measured using SEM, as shown in Table 2.

### Activated Buol Pumice (ABP)

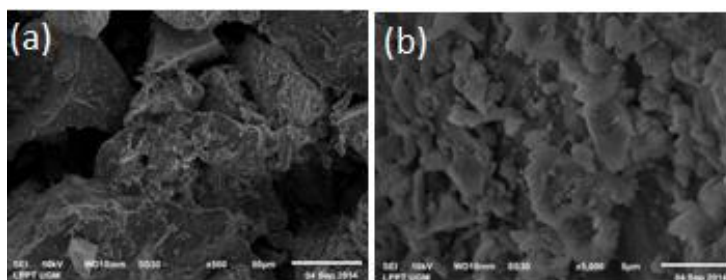
As preliminary information, it was noted that Buol Toli-Toli pumice originated from Buol, which provided further guidance for the subsequent process, namely activation by immersing the pumice in a strong acid solution. However, a difficulty arose due to the high silicon content (21.99-23.66% by mass) (Table 2), which increased during the acid immersion. Nevertheless, the Si/Al ratio was remarkably high, indicating that this pumice was highly suitable for conversion catalysts, which operated at high temperatures to break substrate bonds and form new compounds.

**Table 2.** Chemical Composition of ABP based on SEM Analysis

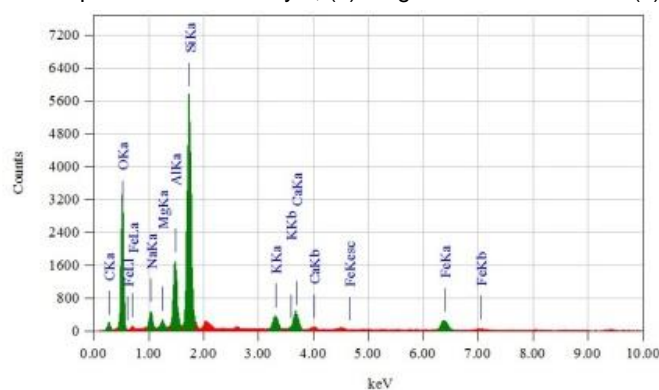
Elements	ABP (%massa)
C	17.06
O	38.53
Na	2.77
Al	6.78
Si	24.62
K	1.53
Ca	3.21
Fe	4.66

The distribution of particles in ABP catalyst and Cu/Pumice was analyzed using the Scanning Electron Microscopy (SEM) instrument. This instrument had the advantage of depicting the catalyst's surface profile, allowing us to determine the average particle size, particle shape, and the percentage of particles within a certain range of diameters. This information was crucial because when the particle size was in the nanometer range, the properties of the particles were influenced by their size and size distribution. The active Pumice (BA) catalyst, at a magnification of 5000x, exhibited an uneven surface. The distribution of particles was non-uniform, forming polydisperse particles. The surface profile of the active BA catalyst was shown in Figure 1.

In Figure 1, the particles in the ABP catalyst were generally observed to be irregular but contained pores. These particles had a micrometer-scale size and an average horizontal orientation. To accurately determine their size, applications such as Paint, MS Excel, and OriginLab could be used. With these applications, the average particle size, cross-sectional area, and particle diameter could be calculated. The comparison of the percentage of metal oxide mass ratio formed in the active BA catalyst was shown in Figure 2.



**Figure 1.** Surface profile of ABP catalyst; (a) magnification of 500 and (b) 5000 times



**Figure 2** Comparison of the mass percentage ratio of metal oxides in ABP catalyst

In Figure 2, the ratio of silicon and aluminium metals was observed to be higher, at 24.62% and 6.78% mass, respectively, but it still contained 17.06% mass of carbon. It was expected that the addition of Pt metal as the active center would reduce the carbon concentration in this catalyst, as it could decrease the selectivity and activity of the catalyst. The mass percentage comparison in the catalyst indicated that this catalyst had good intensity but still required other metal doping such as Pt to improve its catalytic activity capabilities [13]–[17].

### Test of Pt/ABP Catalyst

As part of the Pt/ABP catalyst testing, the conversion analysis results of Pt/ABP catalyst towards 3-methyl-1-butanol at various concentrations and temperatures, as well as towards the standard and comparator, were tested. The gas chromatography analysis results revealed the conversion results of 3-methyl-1-butanol, as shown in the following Table 3.

**Table 3.** Conversion data of isoamyl alcohol with catalyst at 450°C

Code	Catalyst (gram)	3-methyl-1-butanol (mL)	Reaction Time (minute)	Conversions (%)
S-1	0	9	-	-
S-2	0	9	9	2.67
A-1	3 Pt/ABP	9	8	16.74
A-2	3 Pt/ ABP	6	6	24.89
A-3	3 Pt/ ABP	3	4-5	27.63
B-1	2 Pt/ ABP	9	9	13.03
B-2	2 Pt/ ABP	6	7	19.83
B-3	2 Pt/ ABP	3	7	24.11
C-1	1 Pt/ ABP	9	7	6.88
C-2	1 Pt/ ABP	6	5,5	12.66
C-3	1 Pt/ ABP	3	4	19.424
D-1	3 Pt/ ABP	6	4	5.51
D-2	3 Pt/ ABP	6	4	7.21
D-3	3 Pt/ ABP	6	4	14.4
Z-1	3 Pt/Zeolit	9	8	22.748
Z-2	3 Pt/Zeolit	6	6	23.19
Z-3	3 Pt/Zeolit	3	4	23.85

Based on the table, it can be inferred that the conversion of isoamyl alcohol ranged as follows: sample A-3 had a conversion of 27.63%, sample B-3 had a conversion of 24.11%, and sample C-3 had a conversion of 19.42% using the Pt/ABP catalyst. The conversion of 3-methyl-1-butanol with the Pt/Zeolite catalyst was 23.85% for sample Z-3. Based on the gas chromatography analysis, the highest conversion observed was 27.63%. Upon examining the chromatogram data, it was found that at peak number 5 with a retention time of 3.001 minutes, the product

concentration reached 14.83%. This was presumed to be the olefin product, while the remaining 8.92% consisted of hydrogenolysis products (around 3 peaks) and other compounds closely related to olefin products. Further insights into the prediction of compound components in the product were obtained through GC-MS analysis. The analysis of the GC-MS chromatogram results revealed the presence of three additional products alongside the original compound, namely 3-methylbutanal, 2-methylbutanal, and butanoic acid as shown in Figures 3, 4, and 5.

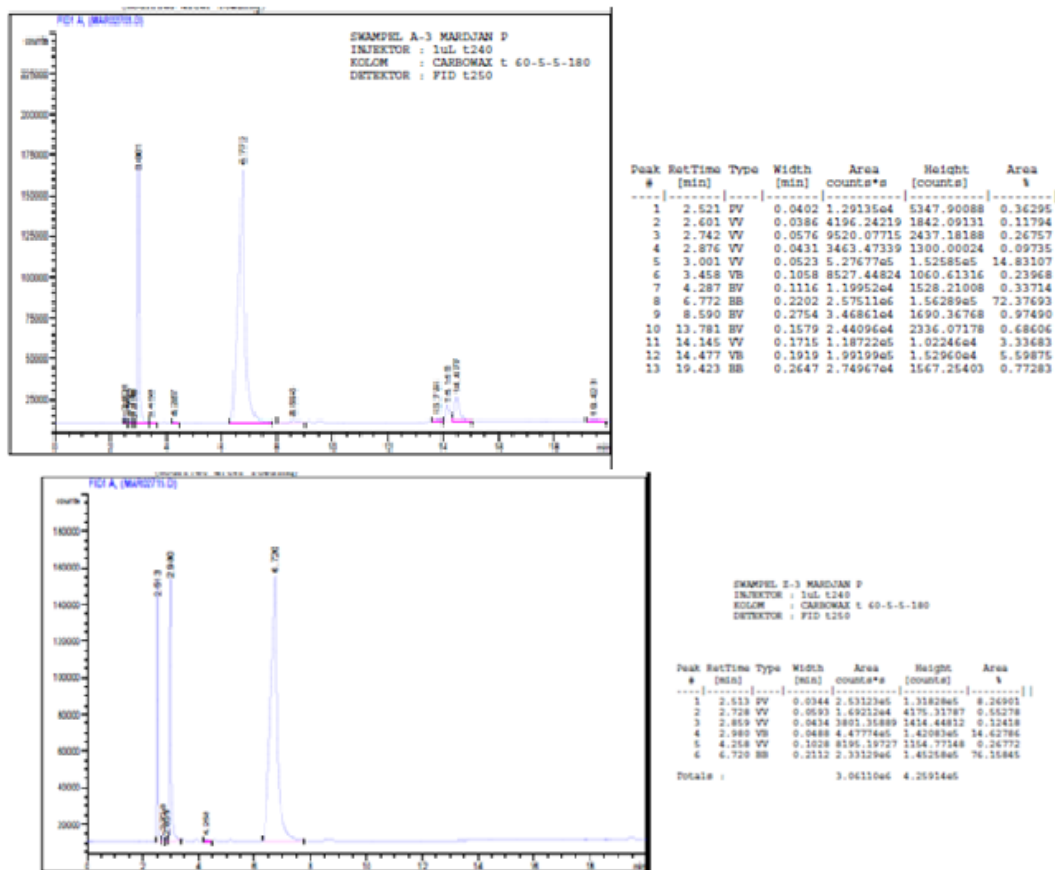


Figure 3. GC chromatogram of conversion of 3-methyl-1-butanol with Pt/ABP (A-3) and Pt/Zeolite (Z-3)

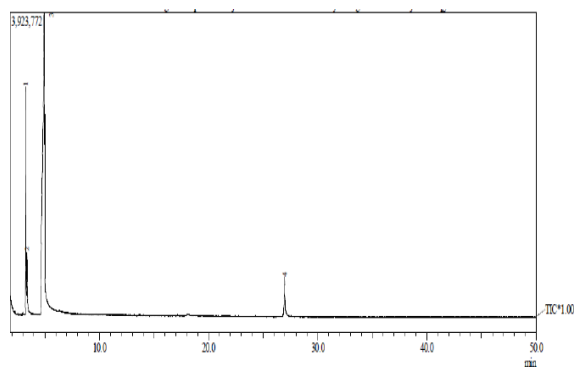


Figure 4. GC-MS Chromatogram of Sample A-3

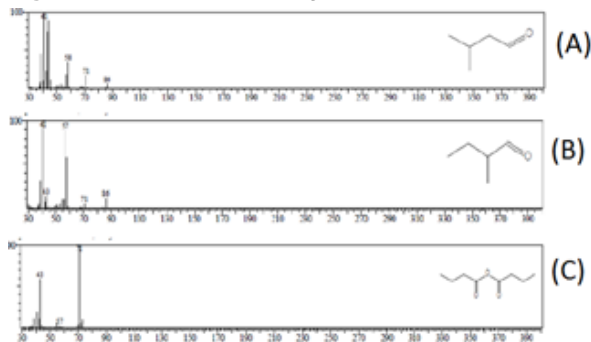


Figure 5. (A) 3-methylbutanal, (B) 2-methylbutanal, and (C) butanoic acid.

The 3-methyl-1-butanol conversion product uses Pt/ABP catalyst, the results of the GC-MS chromatogram analysis are as shown in Figure 4.

Activated pumice was a type of pumice that has been treated to enhance its catalytic properties [18]. Pumice is a volcanic rock characterized by its highly porous structure, which provides a large surface area for catalytic reactions. When pumice is activated, its surface is modified to increase its reactivity and efficiency as a catalyst [19]. In the context of converting 3-methyl-1-butanol, activated pumice can play a role as a catalyst in various reaction pathways. One possible conversion involves the dehydration of 3-methyl-1-butanol to form an alkene, such as 3-methyl-1-butene [20]. The presence of activated pumice as a catalyst provides several benefits. First, the porous structure of the pumice increases the surface area available for the reactant molecules to come into contact with the catalyst, facilitating the reaction. The large surface area also allows for more active sites on the catalyst, which can enhance the catalytic activity.

Additionally, the activated pumice catalyst can provide an alternative reaction pathway with lower energy barriers. This can lead to increased reaction rates and improved selectivity towards the desired product, such as 3-methyl-1-butene, while minimizing the formation of unwanted byproducts. The specific conditions for the conversion of 3-methyl-1-butanol using activated pumice as a catalyst would depend on the reaction mechanism and the desired outcome. Factors such as temperature, pressure, and the presence of other reactants or solvents can influence the reaction. Therefore, it is important to consider the specific requirements and experimental conditions when using activated pumice as a catalyst in this conversion.

## CONCLUSION

The Pt/Modified pumice catalyst was capable of converting 3-methyl-1-butanol up to 27.63% under the temperature condition of 450°C in a fixed-bed reactor system with a passing feed. When compared to the Pt/Zeolite catalyst, its conversion was 28.85%, and for the Pt/BPH catalyst, it was 14.81%. The Pumice, which originated from Raja Island in Buol Toli-Toli Regency, contained metal compositions such as As, Fe, Ba, Mn, Cr, Cu, K, and Zn, as well as relatively high amounts of semi-metals Al and Si. The results of the Pt/Modified Pumice modification and the distribution of Pt metal showed a Si/Al ratio of 4:1 for the Pt/Modified Pumice catalyst. It was important to note the reaction conditions at temperatures around 500°C to 570°C, as observed in sample B-3, where incomplete combustion occurred inside the reactor (resulting in a high amount of carbon in the reactor). This fact indicated that under such conditions, many conversion products in the form of hydrocarbon compounds were formed but did not immediately condense and instead burned at that temperature.

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