

Synthesis 1,1-Dibutoxybutane from Single Reagent of *n*-Butanol Using Cr/Activated Carbon Catalyst

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Received: April 8, 2019

Accepted: May 16, 2019

DOI: 10.22146/ijc.44829

Abstract: Synthesis of 1,1-dibutoxybutane from the single reagent of *n*-butanol using Cr/Activated Carbon (Cr/AC) as a catalyst has been done. The aims of this research were to evaluate the effect of temperature, amount of catalyst, and alcohol flow rate towards the yield of 1,1-dibutoxybutane. Activated carbon (AC) was prepared by activating coconut shell carbon at 650 °C in the atmosphere of H₂ at a flow rate of 15 mL/min for 4 h. The product was washed using acetone in a Soxhlet for 15 rounds, washed 3 times by 1.0 M HCl, and finally, it was sieved at 60–80 mesh. Metal content was analyzed using atomic absorption spectrophotometry (AAS) for Na, Ca, and Fe. The AC was impregnated with Cr(VI) solution and reduced with H₂ at 650 °C. The acidity of Cr/AC catalyst was determined by the adsorption of ammonia vapor. Optimization of *n*-butanol conversion to 1,1-dibutoxybutane using Cr/AC catalyst was conducted in an oven using variations of temperature of 450, 500, and 550 °C, catalyst amount of 5, 10, and 15 g, under an alcohol flow rate of 0.10, 0.50, and 0.90 mL/min. The conversions of 1,1-dibutoxybutane were analyzed by GC-MS and ¹H-NMR. The results showed that after washing by acetone and 1.0 M HCl, the content of metals in the AC was significantly decreased. The AC and Cr/AC showed acidity of 2.49 and 8.27 mmol/g, respectively. The highest product of 1,1-dibutoxybutane (53.42%) was achieved at 450 °C using 5 g catalyst of Cr/AC under the alcohol flow rate of 0.10 mL/min.

Keywords: *n*-butanol; 1,1-dibutoxybutane; Cr/AC; catalyst

■ INTRODUCTION

The increase in the number of vehicles and industries causes the consumption of fuel oil has raised. This condition has caused the use of the fossil fuel to increase, and the world stock of this material is running low, and this condition will cause an energy crisis as it happened in 2008 [1].

In 2010, Europe consumed 12% energy from a renewable source, and 21% from electricity, wherein 2005, the consumption from renewable source had just reached 6.38% and 13.97% from electricity [2]. In Indonesia, the consumption of subsidizing petroleum oil in 2011 reached 41.79×10^3 million Liter. To overcome the crisis due to the rare of the oil in the future, a lot of researchers have

studied the use of new materials of fatty animal [3-5] and vegetable oil [6-8], biomass, dissociated rubbish, roots, and fruits, as the source of bio-diesel and ethanol [9-10].

The cetane number is a measure of the quality of diesel fuel and can be increased by the addition of fuel additives. Primary alcohol and ether are known as a fuel additive, which has a burning temperature lower than diesel oil. These compounds can have a lower machine knock and lower unnecessary gas emission as carbon monoxide [11-14].

Fuel additives as a booster of ether compound could be produced from alcohol. In this case, Nord and Haupt [15] showed that the utilization of acetal such as 1,1-dietoxyethane as diesel fuel additive decreased

particulate matter emission and smoke, and lower burning temperature [16-18].

Acetal or diether could be produced from alcohol and aldehyde using an acid catalyst, as shown by Capelletti et al. [19] and Kaufhold and El-Chawawi [20]. It can be produced from a single reagent of ethanol using Cu/SiO₂ and H-Y-Zeolite as the catalyst [21] and from the conversion of butanol into dibutyl ether [22]. In addition, alcohol with C atoms more than 4 is non-hygroscopic and noncorrosive; hence, it was proposed to replace ethanol with *n*-butanol [23-25]. Research work of Falah and Triyono [26] reported that when the contact time between catalyst and feed is longer, and the temperature is higher, the diether compound as a product could be used as booster diesel oil. The catalytic reaction using Cu on activated carbon (AC) or the other metals for the conversion of alcohol to the diether is cheap because this reaction occurs in the gas phase; hence, it will not easily deactivate the catalyst.

The reaction between alcohols using a Cr/AC catalyst at high temperature (400–550 °C) is rarely discussed. The utilization of Cr/AC catalysts could convert the alcohol into H₂ and aldehyde, or react with another alcohol to produce ether and H₂O. Based on the above consideration, we undertook the evaluation of conversion of alcohol (*n*-butanol) to diether (1,1-dibutoxybutane) using the Cr/AC catalyst under variation of temperatures (450–550 °C) and a new route of 1,1-dibutoxybutane formation as a better fuel additive will be discussed.

■ EXPERIMENTAL SECTION

Materials

The chemical used in the experiment were purchased from Merck in p.a. quality. i.e., *n*-butanol, AgNO₃, HNO₃ 65%, HCl 37%, H₂O₂ 20%, CrO₃, NaCl, Ca(OH)₂, FeCl₃·6H₂O, acetone, and ammonia. Coconut shell, glass-wool, pH paper, aquabidest were also needed. H₂ and N₂ gases were from Surya Indotim Imex with a purity of 99.999%, while CO₂ was from Samator with a purity of 99.999%.

Instrumentation

The catalyst was prepared using 40–60 and 60–80 mesh sievers, Soxhlet extractor, electric oven, and Mettler electric balance (model AT200). The metals were determined using atomic absorption spectrophotometer (AAS Perkin Elmer Model 3110). Products of Hydrogenation were characterized by FTIR (Shimadzu Prestige 21), GC-MS (Shimadzu QP2010S) using HP-5MSUI column, GC148 (Shimadzu) using CBP1 column and FID detector, ¹H-NMR (JEOL JNM ECZ-500R).

Procedure

Synthesis of activated carbon and metal content analysis

The coconut shell was ground and sieved using 40–60 mesh siever. Then, it was activated at 650 °C for 4 h, while CO₂ gas flowed at 20 mL/min. The carbon was then put in a Soxhlet and extracted using acetone for 15 rounds, followed by drying in an open-air. Then it dipped 3 times in 1.0 M HCl solution for each 24 h. Finally, the carbon was sieved again using 60–80 siever.

Further, 0.20 g of the activated carbon was destructed in 100 mL round bottle by adding 10.0 mL of HNO₃ 65% and then refluxed for 1 h at 130 °C. As much as 1.0 mL of this solution was inserted into 50 mL volumetric flask, and 4 mL of 20% H₂O₂ was added. Finally, the solution was diluted until 50 mL. This solution was used for analyses of Na, Ca, and Fe using FES and AAS. This procedure was also used for the carbon after washing with 0.1 M HCl 1, 2, and 3 times.

Preparation of Cr/AC catalyst

Four grams of CrO₃ was put into 500 mL beaker glass, and 50 mL aquabidest was added. After all, CrO₃ was dissolved, 100 g of activated carbon was added. After 24 h, while it was stirred, the mixture was heated at 90 °C until all water evaporated, and then the temperature was increased to 110 °C for 3 h (until the mass was constant). Further, the obtained solid was reduced at 650 °C for 4 h by flowing H₂ at 15 mL/min. Before and after impregnated with Cr, the carbon was analyzed using FTIR.

Determination of catalyst acidity

Empty crucible porcelain was heated at 110 °C for 1 h, and then it was used as samples holder of (0.2 g) dry sample of activated carbon or (0.30 g) of the Cr/AC catalyst. The porcelain was placed in a desiccator, and then 20 mL ammonia was inserted. After 24 h, the ammonia was evaporated for 30 min. The acidity of the activated carbon (or the catalyst) was calculated as follow:

$$\text{Acidity} = \frac{W_3 - W_2}{(W_2 - W_1)M} \times 1000 \frac{\text{mmol}}{\text{g}}$$

where M is the molecular weight of ammonia (17.03 g/mol), W_1 and W_2 are the weight of empty crucibles, and crucible contains activated carbon (or the catalyst). W_3 is the weight of crucible after adsorbed ammonia.

Conversion of n-butanol to 1,1-dibutoxybutane

Five grams of Cr/AC catalyst was inserted into a reactor, where the lower part of this reactor was already closed by glass-wool, and then this reactor was inserted into an electric tube furnace. The upper part of this reactor was connected with Liebig cooler, and the lower part was connected with three necks bottles. The other necks bottle was used to insert a sample of n-butanol at a flow rate of 0.10 mL/min and insert H_2 gas at a flow rate of 15 mL/min, and this bottle was heated at 130 °C. The temperature of the electric furnace was varied at 450, 500, and 550 °C; the flow rate of n-butanol was varied at 0.10, 0.50, and 0.90 mL/min, while the amount of the catalyst was varied at 5, 10, and 15 g. The products were analyzed using GC-MS, FTIR, and 1H -NMR.

RESULTS AND DISCUSSION

Activated carbon from coconut shell is an excellent material for catalyst support because it has an abundance of micro-pore, low ash content, and low reactivity. The carbon is inert and stable in acid or base condition, and it

can be prepared in particle form; hence, this material is very good to be used as a support of a catalyst.

Determination of Na, Ca and Fe on the Carbon

As support of catalyst, activated carbon has to have a large surface area. This condition could be reached using a small particle, but it must not cause a gas flow to stop while it is used in the reaction system. Hence, the carbon particle used in this work was 60–80 mesh.

Table 1 showed the metal content in carbon after washing with acetone and HCl solution. It is shown that around 50% of metals could be washed out in this work, whereas metals ion was replaced by hydrogen ion, which then disappeared when heated. Hence, the content of the metals decreased in this work.

The Acidity of AC and Cr/AC Catalyst

From 3 experiments, it was known that the AC and Cr/AC catalyst acidity were 2.49 and 8.27 mmol/g, respectively. This data showed that the impregnation of Cr metal onto the AC significantly increased the acidity of AC.

Catalytic Conversion of 1,1-Dibutoxybutane from n-Butanol

Table 2 and Fig 1-4 showed the result of analyses using GC-MS, where the compound at a retention time (R_t) 16.29 min was predicted as 1,1-dibutoxybutane, at R_t of 2.98 min was n-butanol, and at R_t of 3.60 min was n-butanol. Table 2 also showed that the highest product of 1,1-dibutoxybutane was 53.42%. This product resulted at a temperature of 450 °C, the mass of catalyst 5 g, and the flow rate of n-butanol 0.10 mL/min, with the rest of n-butanol 25.46% and a total of other product was 16.60%.

In analyzing the conversion of n-butanol to 1,1-dibutoxybutane, the FTIR spectra of the reagent and

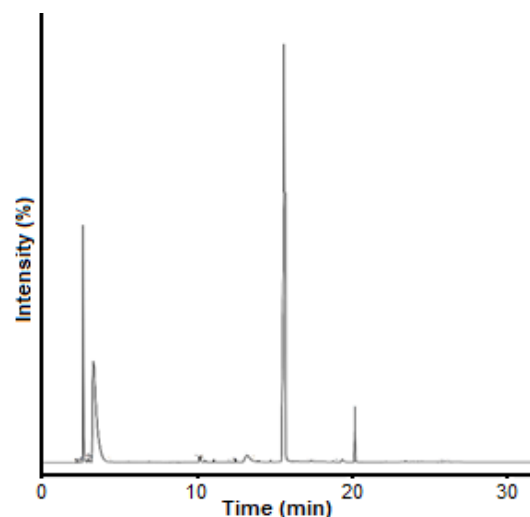
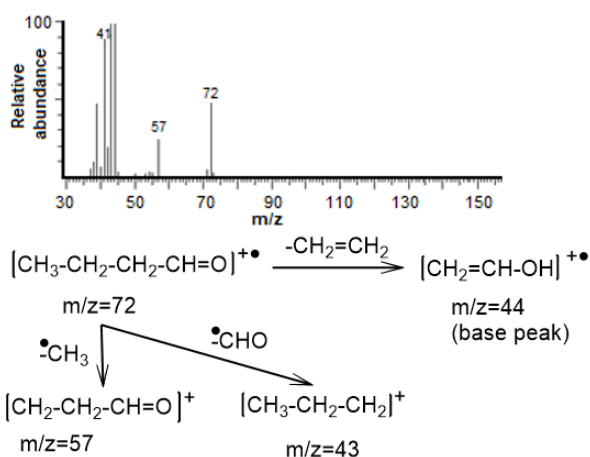
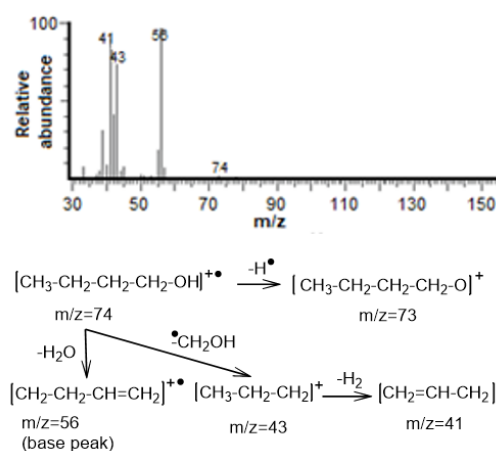
Table 1. Metals content in the activated carbon after washing

Liquid washing	Metal content in the carbon (ppm)		
	Na	Ca	Fe
Acetone	1.846	3.980	2.396
0.10 M HCl (the first)	1.022	3.205	1.316
0.10 M HCl (the second)	0.802	2.827	1.146
0.10 M HCl (the third)	0.692	2.569	1.052

Table 2. Result of conversion of *n*-butanol to 1,1-dibutoxybutane

Temperature (°C)	Weight of catalyst (g)	Flow rate of <i>n</i> -butanol (mL/min)	Product (% area GC)		
			<i>n</i> -butanol	1,1-dibutoxybutane	Other
450	5	0.10	25.46	53.42	16.60
450	10	0.50	79.43	9.21	1.08
450	15	0.90	92.74	6.43	0.81
500	5	0.10	95.61	0.39	3.81
500	10	0.50	33.40	47.74	13.58
500	15	0.90	62.45	33.32	3.27
550	5	0.10	58.45	29.55	10.45
550	10	0.50	89.31	2.03	8.39
550	15	0.90	78.75	9.46	11.35

product are showed in Fig. 5(a) and 5(b). Spectra of *n*-butanol (Fig. 5(a)) showed absorption with strong intensity at 3348 cm⁻¹ due to the existence of -OH group. This peak was significantly reduced in the product (Fig. 5(b)) because OH group has been converted into C-O-C of diether and C=O of aldehyde (butanal). The high peaks at 2932 and 2832 cm⁻¹ were consistent due to these peaks related to the bond of C-H, which were not converted to the other bond. From Fig. 5(b), could be seen a strong peak at 1720 cm⁻¹ whereas in Fig. 5(a), this peak did not appear. This peak is related to the formation of C=O bond of butanal as a side product. Another fact is that fingerprint at 1057 cm⁻¹ from C-O alcohol changed to a broad peak at 1000–1150 cm⁻¹ of C-O ether. These facts showed that most alcohols had been converted into 1,1-dibutoxybutane, and a small part has changed into an aldehyde.

**Fig 1.** Chromatogram of *n*-butanol conversion product at 450 °C, using 5 g catalyst of Cr/AC, a flow rate of the alcohol 0.10 mL/min and flow rate of H₂ 15 mL/min**Fig 2.** Mass spectra and fragmentation of the first peak at R_t of 2.98 min**Fig 3.** Mass spectra and fragmentation of the second peak at R_t of 3.60 min

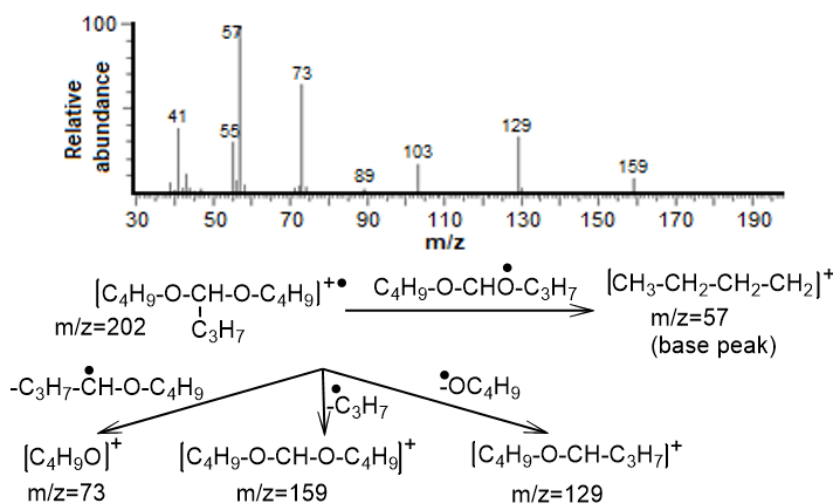


Fig 4. Mass spectra and fragmentation of the third peak at R_t of 16.29 min

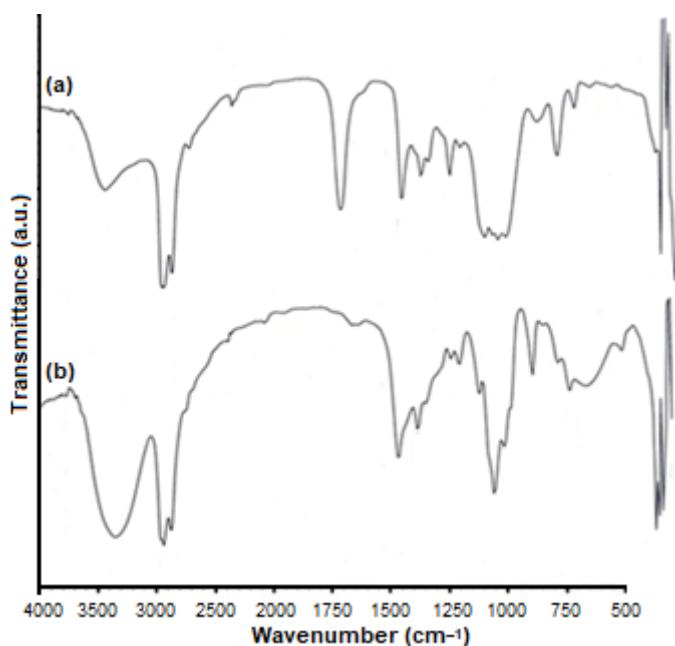


Fig 5. FTIR spectra of (a) *n*-butanol (b) *n*-butanol dehydration product using 5 g Cr/AC catalyst, temperature 450 °C, and flow rate of the alcohol 0.10 mL/min

Analyses of GC-MS and FTIR are supported by 1H -NMR, where this spectra showed the existence of proton from 1,1-dibutoxybutane as the main product and butanal as a side product, while the *n*-butanol as a starting material was present in a small amount (Fig. 6).

The existence of 1,1-dibutoxybutane was clearly indicated from the signal of proton **l** appeared as a triplet

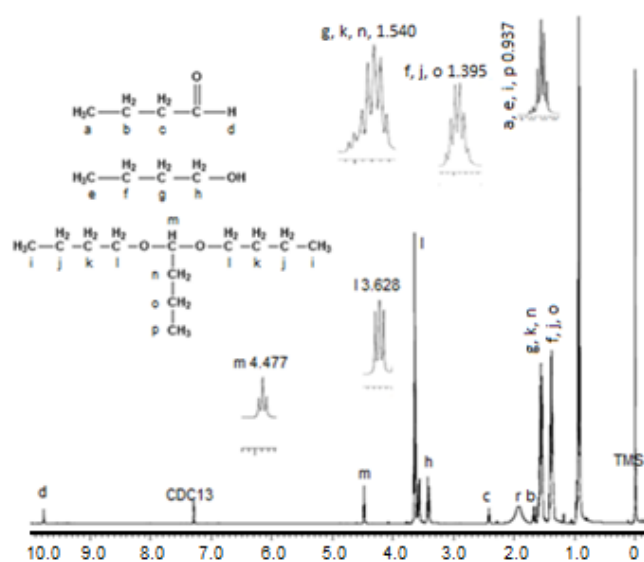


Fig 6. 1H -NMR spectra of *n*-butanol conversion product

at a chemical shift of 3.628 ppm from $(CH_2-O)_2-CH-$, and signal of proton **m** as a triplet from $(R-CH_2-CH_2-O)_2-CH-$ appeared at 4.447 ppm. In addition, the CH_2 of the propyl group was detected at a chemical shift of 1.540 ppm overlap with other CH_2 .

The side product of *n*-butanol could be proved from the presence of a singlet peak **d** at 9.766 ppm, which belongs to the CH aldehyde and signal **c** at 2.419 ppm for the CH_2 next to a carbonyl group. Furthermore, the starting material of *n*-butanol was appeared as a broad signal **r** at 1.900 and signal **h** at 3.420 ppm for the presence

of OH and CH₂-O, respectively.

■ CONCLUSION

Preparation of activated carbon by washing with acetone and 1.0 M HCl consecutively, could significantly decrease the ions of Na, Ca, and Fe in the activated carbon. Impregnation of activated carbon with Cr metal could increase its acidity from 2.49 to 8.27 mmol/g. The GC-MS and ¹H-NMR analysis showed that dehydration of *n*-butanol at 450 °C using 5.0 g catalysts of Cr/AC and 0.10 mL/min of the alcohol could produce 1,1-dibutoxybutane in 53.42%.

■ ACKNOWLEDGMENTS

The authors thank the Indonesian Directorate General of Higher Education, who already supported this research under the contract no. 1969/UN1/DITLIT/DIT-LIT/LT/2018.

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